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Study The Adsorption Of Cadmium Cd(II) Ions In Aqueous – Mineral Acids By Resinex™ K-8.

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ABSTRACT

The purpose of this work is to investigate the possibility of using aqueous solutions containing some inorganic acids such as Phosphoric, Sulphoric, Nitric and Hydrochloric acid .Elimination of cadmium Cd(II) ions based on the data of uptake values when adsorbed on Resinex™K-8 strong cation exchange resin in the H^+ form, it is used in this study under different conditions. The results obtained indicates the amount of cadmium Cd(II) ions adsorbed on the adsorbent increases with increasing it's initial concentrations, and the adsorption of Cd(II) 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. Also the amount of metal ions adsorbed on the surface of cation exchange resin (Resinex™ K-8) increases at low dilute solutions of acidic medium but the amount of cadmium Cd(II) ions adsorbed on anion exchange resin increases at high concentrations of acidic media.

Key words: Resinex™ K-8, Kinetics Modeling, Temperature, Thermodynamics.

Introduction

Cadmium (Cd) and Cadmium compounds as compared to other heavy metals are relatively water soluble therefore mobile in soil and tends to bioaccumulate. Adsorption studies have been carried out on a newly synthesized tin(IV) phosphate (SnP), a non-fibrous ion exchanger, for alkaline earths and heavy metal ions in different acidic media. Effect of anionic (SDS, SDBS), cationic (CTAB, DPC) and nonionic (TX-100) surfactants has also been studied on its adsorption behavior (Varshney *et al*, 2007).

Selective adsorption toward Pb(II), Cd(II) and Zn(II) ions. ZrPSadsorption toward all the three metals is dependent upon solution pH due to the ion-exchange nature. As compared to another inorganic exchanger zirconium phosphate [$Zr(HPO_4)_2$, denoted ZrP], ZrPS exhibits highly selective adsorption toward these toxic metals from the background of calcium ions at great levels (Zhanga *et al*, 2009).

A novel composite adsorbent silica gel microspheres encapsulated with 5-sulfosalicylic acid functionalized polystyrene (SG-PS-azo-SSA) has been used to investigate the adsorption of Mn(II), Fe(III), Co(II), Ni(II), Zn(II), Cd(II), Hg(II), Pd(II), Cu(II), Ag(I) and Au(III) from aqueous solutions. The research results revealed that SG-PS-azo-SSA has the better adsorption capacity for Cu(II), Ag(I) and Au(III)(Yin *et al*, 2009).

The applicability of the microporoustitanosilicate ETS-4 (Engelhard Titanium Silicates No. 4) to uptake Cd^{2+} from aqueous solution, in order to evaluate its potential as ion exchanger material.The equilibrium data at pH 6 were accurately represented by the Langmuir-Freundlich isotherm under the experimental conditions studied(Barreiraa *et al*, 2009).

The Cd(II)adsorption studies on silica synthesized by sol-gel method has been investigated. The adsorption of Cd^{2+} ions is found to increase with increasing concentration and temperature of electrolyte solution. The Langmuir model is used to interpret adsorption of cadmium (Cd) ions on the solid surface. The adsorption of Cd^{2+} ion is found to increase with the increase in surface area of the solid(Waseem *et al*, 2011).

The adsorption of Pb(II) and Cd(II) were found to be maximum at pH in the range of 5.0-6.0. The adsorption kinetics of both metal ions followed the pseudo-second-order model. Equilibrium data were best fitted with the Langmuir isotherm model, and the maximum adsorption capacities of Pb(II) and Cd(II) were determined to be 520.83 and 238.61mgg^{-1}, respectively. Moreover, more than 80% of Pb(II) and 85% of Cd(II) adsorbed onto TNs can be desorbed with 0.1MHCl after 3 h. Thus, TNs were considered to be effective and promising materials for the removal of both Pb(II) and Cd(II) from wastewater (Xionga *et al*, 2011).

Various adsorbents are available for the removal of heavy and toxic metals, silica-based materials have been the most popular. Recently, there has been considerable interest for the modification of organic moieties and mesostructured materials to enable their use as efficient adsorbent for metal removal(Jeong *et al*, 2011).

The melamine-based dendrimer amines (MDA) used in the study the adsorption of Pb(II), Cu(II) and Cd(II) ions onto SBA-15, NH2-SBA-15 and MDA-SBA-15 from a single metal aqueous solution for the effect of contact time, adsorbent dose, solution pH and concentration of metal ions in batch systems. The equilibrium

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data were analyzed using the Langmuir and Freundlich isotherm by nonlinear regression analysis(Shahbazia *et al*, 2011).

Furthermore, they also show high selectivity in the removal of highly toxic heavy metal ion Cd(II) than less toxic ions Zn(II) and Ni(II). This study highlights that titanatenanoflowers are potential adsorbents for efficient removal of toxic metal ions. The adsorption mechanism was also discussed. It is found that the equilibrium data fitted well with the Langmuir model, while the adsorption kinetics followed the preudo-second-order model (Huang *et al*, 2012).

The process of adsorption of cadmium (Cd) from aqueous solutions using Na-zeolitic tuff, Fe-zeolitic tuff and carbonaceous material from pyrolyzed sewage sludge treated with HCl was investigated. The cadmium (Cd) removal efficiency was studied as a function of contact time, adsorbateconcentration, pH and adsorbent dose. The results showed that removal of cadmium was best described by the LangmuireFreundlich isotherm(Segura *et al*, 2012).

Expermintal:

Rate of adsorption process were determined by the limited Batch technique. Series of adsorption experiments was established at constant temperature a known amount (1.0 g) of strongly acidic cation exchange resin in the H-form of Resinex^{TM}K-8 of gel type structure supported from JacobI (Swedish company)was added into each bottle. Solutions (50 ml) of Cd(II) ions at constant ionic strength (0.005M) were thermostated at the required temperature (19°C) in 250 ml wide-mouth propylene test bottles with screw closure caps using a finn pipette (accurate to ±0.03).

A weighed amount of the adsorbent (0.5 gm) was added for each solution. The bottles were thoroughly shaken. After appropriate intervals, 5, 15, 25, 45, 65, 95 and 155 min., the contents of each bottle separately were filtered and the metal ion concentration in the liquid phase were determined.

Standard 0.01 M EDTA solution, Eriochrome Black T, as indicator, ammonium chloride solution, ammonia solution approximately (pH = 10), $CdCl_2$ solution. All reagents were of Analar grade or BDH products.

The metal ion solution (1.0 ml) was transferred into 250 ml. Erlenmeyer flask and then diluted to 100 ml with distilled water, 2.0 ml of buffer solution (pH=10) was added, followed by indicator, the solution acquires a red colour. Titrate with standard EDTA 0.01 M until there is a sharp change of colour from red to blue.

The concentration of Cd(II) before and after equilibrium was calculated by using the Cd(II) factor. { 1 cm^3 of 0.01 M EDTA = 1.1241 mg Cd(II) }

The amount of metal ion adsorbed per unit mass of the adsorbent q_e (mg\g) was evaluated by using the following mass balance equation: $q_e = \frac{C_0 - C_e}{m} V$

Where C_0 and C_e are the concentrations (mg l^{-1}) in the solution at time (t = 0) and at equilibrium time (t), V is the volume of solution treated adsorbate (l) and m is the weight of the adsorbent (g). The percent removal of metal ion was calculated by the following equation: $\text{Removal}\,(\%) = \frac{C_0 - C_e}{C_0} \times 100$

Results And Discussions

In order to investigate the effect of acidity solution on the metal ions uptake on Resinex^{TM} K-8 strong acid cation exchange resin, series of experiments were carried out at 19°C using 1.0g cation exchange resin, and at a constant concentration, 8 mmol/L of M^{+2} (M^{+2}=Cd(II) ions in aqueous solution with alter initial acidity values from 0.1 to 1.5 M.

The equilibrium uptake of Cd(II) ions on Resinex from different acidic media was carried out. The effect of acids type including H_3PO_4, H_2SO_4, HNO_3 and HCl at acid concentration ranging from 0.1 to 1.5 M on the uptake of these toxic metal ions are presented in (Fig. 1).

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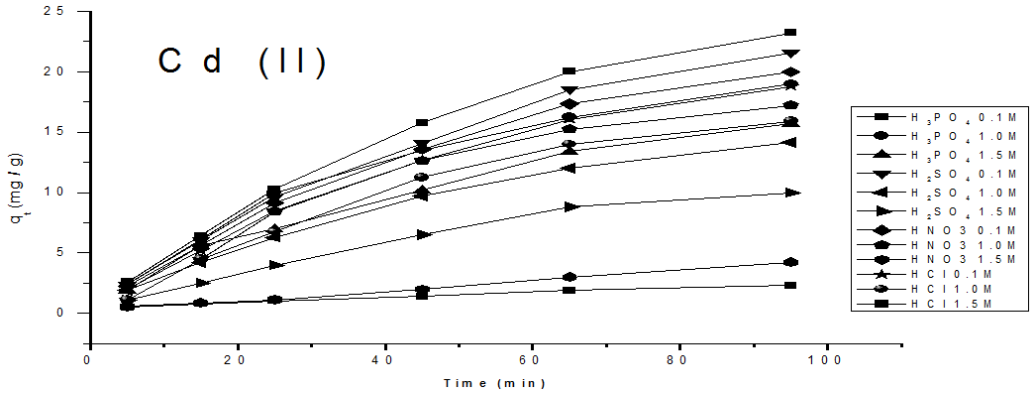

Fig. 1: Effect of different concentra tions of some in organic acids on the adsorption of cd (II) ions (8mm ol/l).

The acidity of the aqueous solution is one of the main variable parameters in the adsorption process. It may affect the ionization degree of the adsorbate and the surface property of the adsorbent (Vu *et al*, 2012).

As shown in (Fig. 1) the removal efficiency of cadmium metal ionsCd(II) by the cation exchange resin increased when the acidity was decreased. The adsorption of Cd(II) ions on the surface of cation exchanger can probably be explained by an ion-exchange mechanism based on surface complex formation model, which is facilitated by the dissociation of different functional groups present in cation exchanger particles resulting in the formation of metal complex (Ren *et al*, 2012).

As the results (Fig.1), at acidity ranging from 0.1 to 1.5 M, cadmium Cd(II) adsorption capacity decreases sharply from 23.22 to 15.71, 21.58 to 10, 20 to 4.22 and 18.79 to 2.3 mg/g with the acidity elevation from 0.1 to 1.0 M H_3PO_4, H_2SO_4, HNO_3 and HCl. However, at further higher acid molarities (1.0 M) unfavorable conditions are found to exist for adsorption.

At high acidity, due to high positive charge density (H^+) on the surface sites, electrostatic repulsion between Cd^{+2} and H^+ ion will be high during uptake of metal ions resulting in lower removal efficiency. With decreasing acidity, electrostatic repulsion decreases due to reduction of positive charge density of proton on the adsorption sites thus resulting in an enhancement of cadmium uptake (Khalid *et al*, 2005).

(A)- Studies Of The Adsorption Processes:

The relationships between the amount of Cd(II) adsorbed on Resinex^{TM} K-8 (strong acid cation exchange resin) and their equilibrium concentration solution were described by the adsorption isotherms (Figs. 2. a, b, c and d&3. a, b, c and d&4. a, b, c and d &5. a, b, c and d). The adsorption data of the metal complexes $[M(IOA)]^{n+}$ on these cation exchanger were analyzed according to the Langmuir, Freundlich, Temkin and Dubinin-Radushkevich (D-R) models.

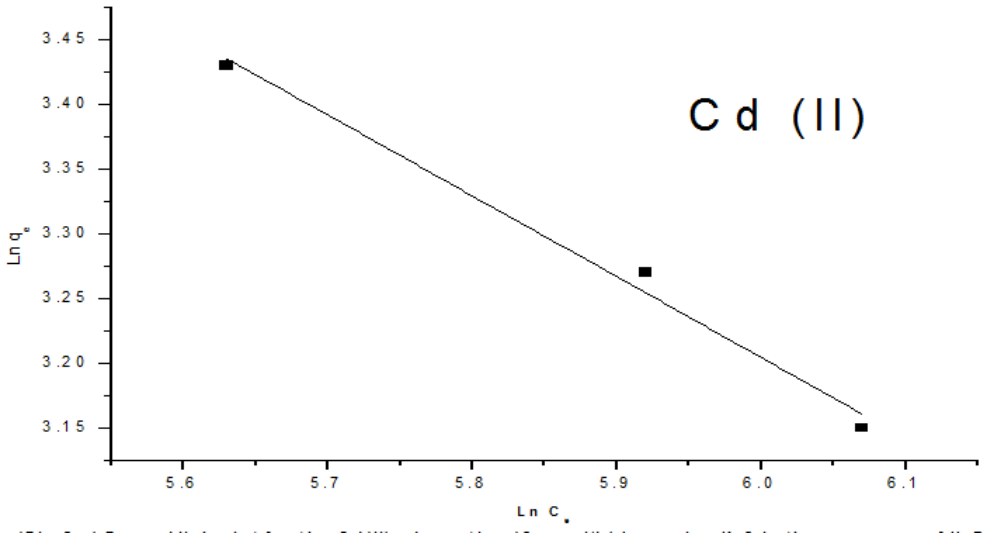

Fig. 2a: Freundilch plot for the Cd (II) adsorption (8mm ol/L) by resinx K-8 in the presence of H_3 PO_4 0.1M

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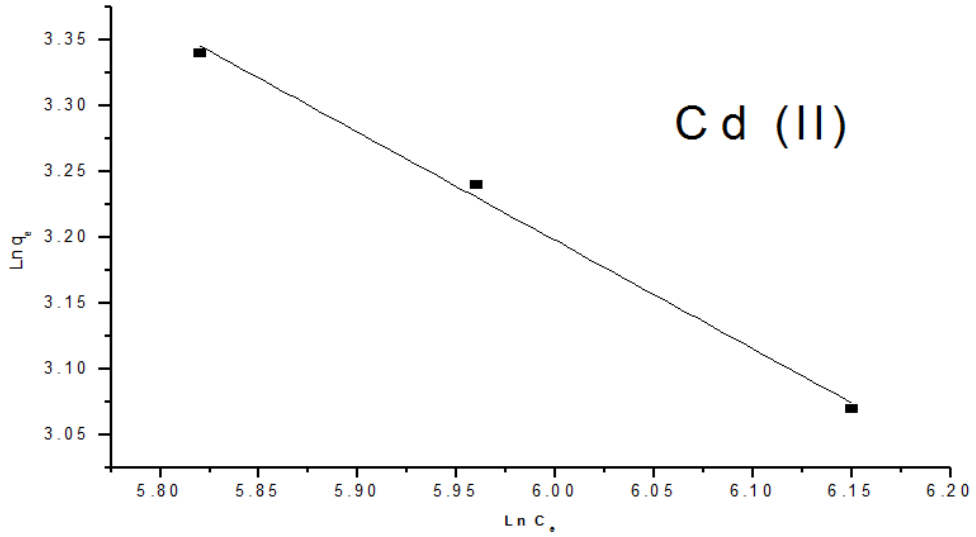

Fig. 2b: Freundlich plot for the Cd (II) adsorption (8mm ol/L) by resinx K-8 in the presence of $H_2 SO_4$ 0.1M

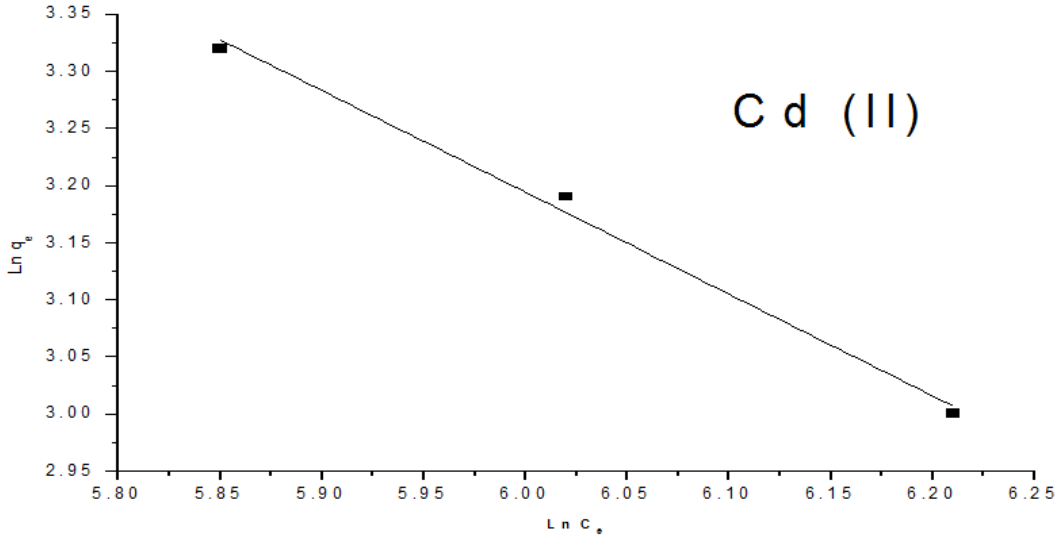

Fig. 2c: Freundlich plot for the Cd (II) adsorption (8mm ol/L) by resinx K-8 in the presence of HN_3 0.1M

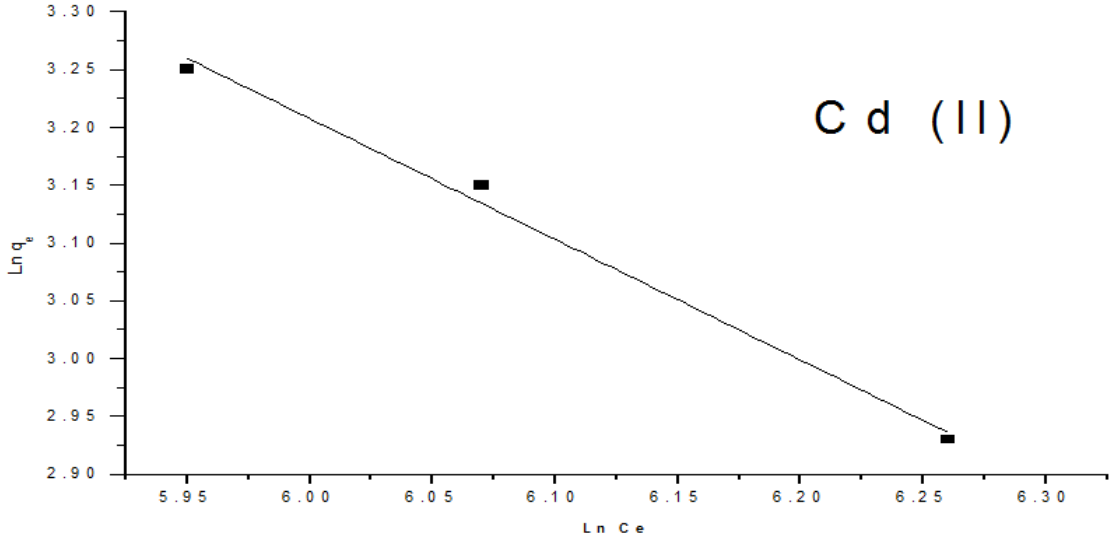

Fig. 2c: Freundlich plot for the Cd (II) adsorption (8mm ol/L) by resinx K-8 in the presence of HCI 0.1M

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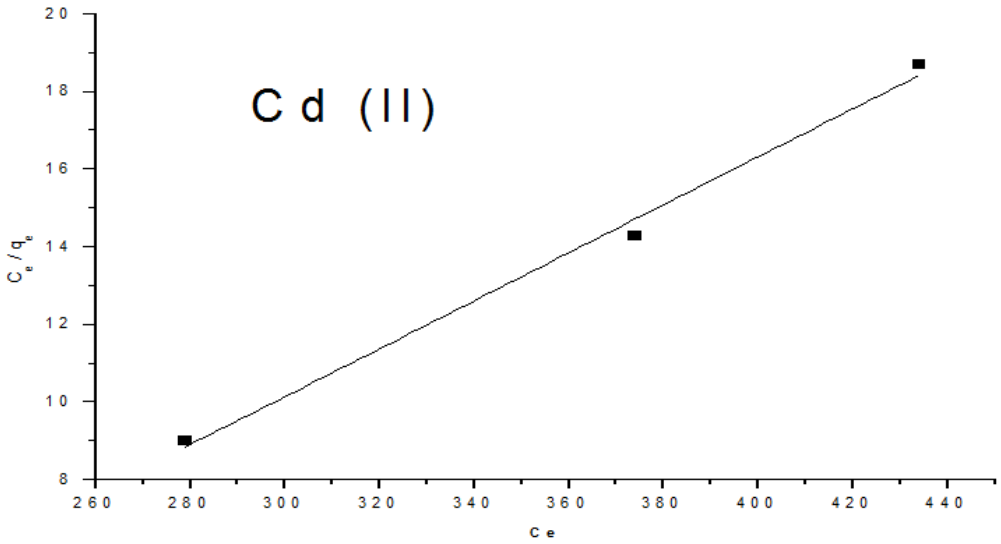

Fig. 3a: Langmiur plot for the Cd (II) adsorption (8mm ol/L) by resinx K-8 in the presence of H_3 PO_4 0.1M

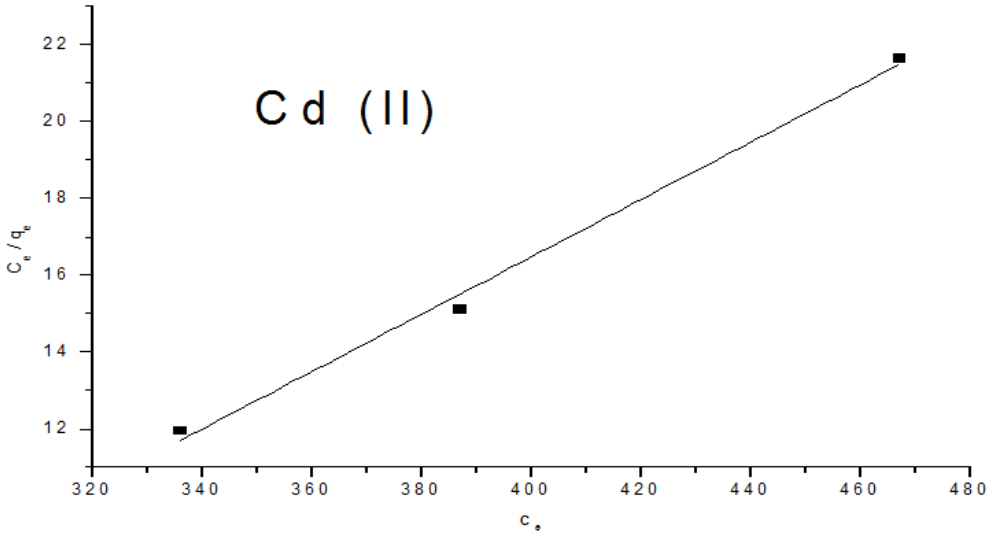

Fig. 3b: Langmiur plot for the Cd (II) adsorption (8mm ol/L) by resinx K-8 in the presence of H_2 SO_4 0.1M

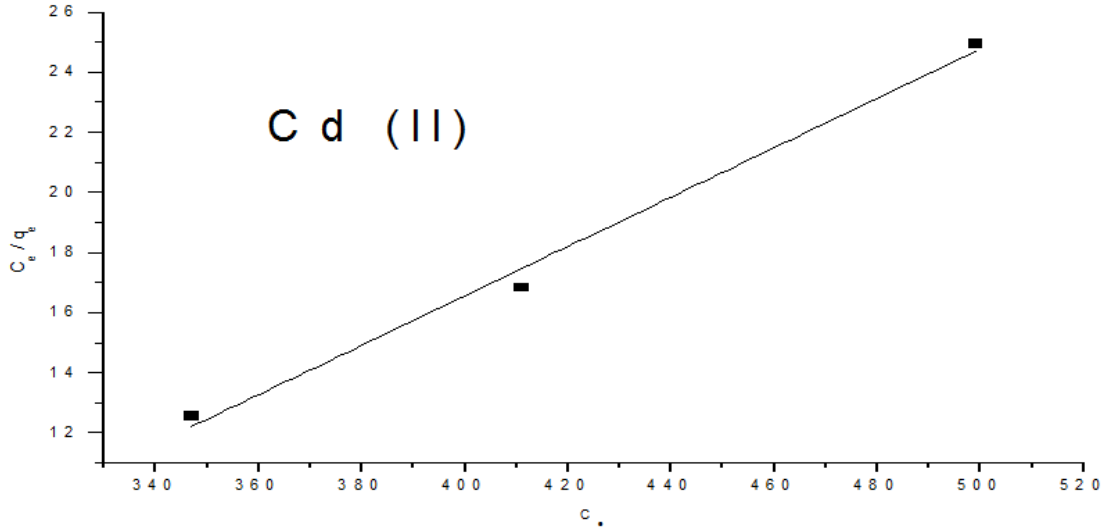

Fig. 3c: Langmiur plot for the Cd (II) adsorption (8mm ol/L) by resinx K-8 in the presence of HNO_3 0.1M

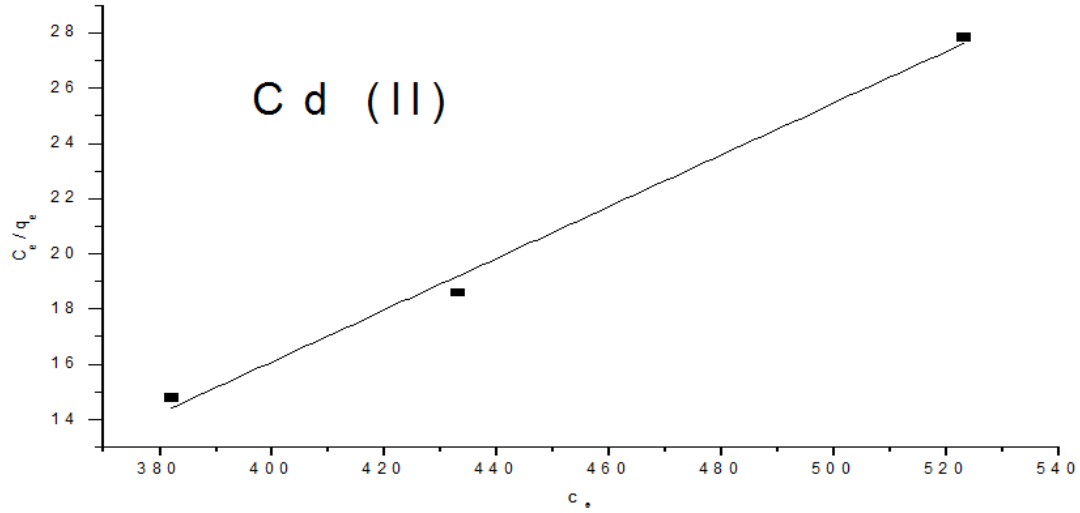

Fig. 3d: Langmiur plot for the Cd (II) adsorption (8mm ol/L) by resinx K-8 in the presence of HCI 0.1M

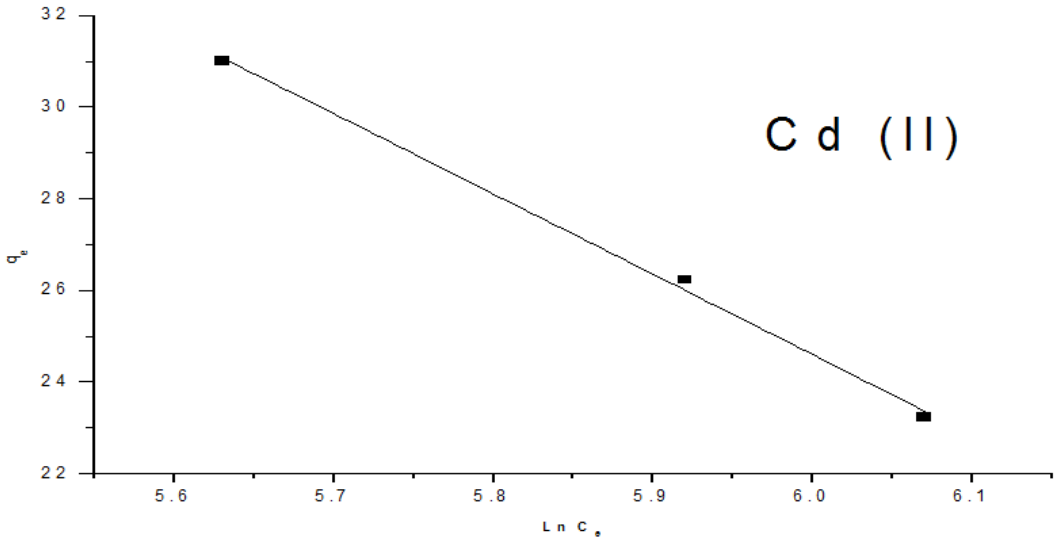

Fig. 4a: Temkin plot for the Cd (II) adsorption (8mm ol/L) by resinx K-8 in the presence of H_3 PO_4 0.1M

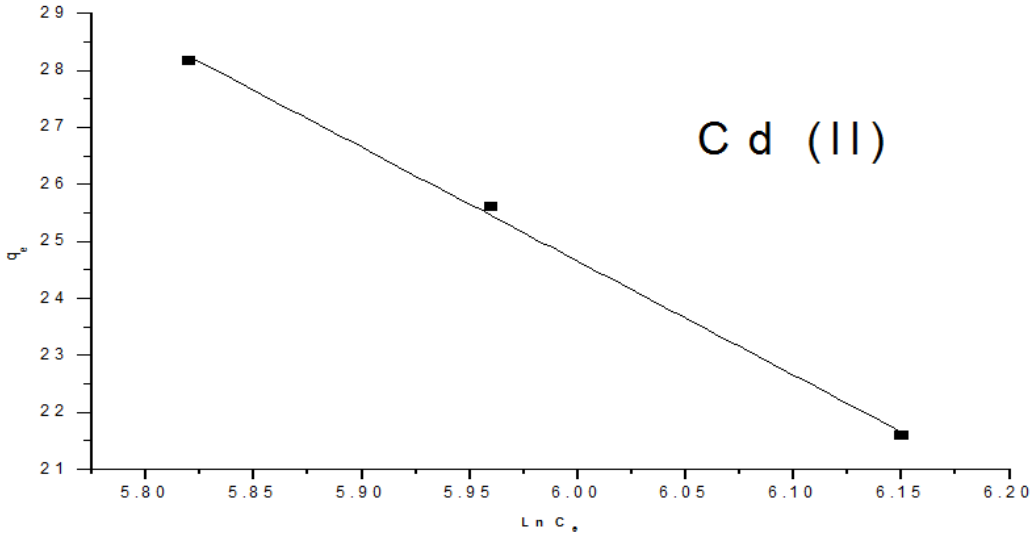

Fig. 4b: Temkin plot for the Cd (II) adsorption (8mm ol/L) by resinx K-8 in the presence of H_2 SO_4 0.1M

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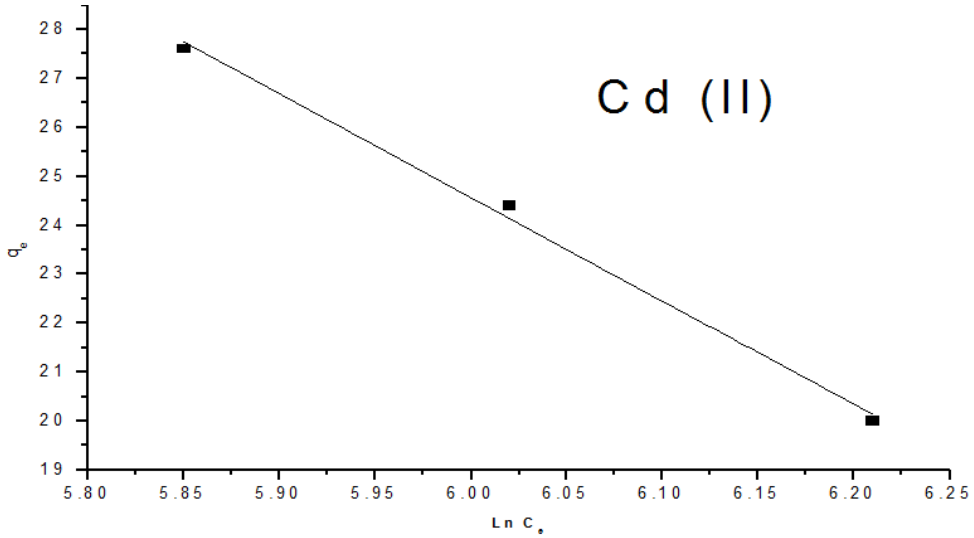

Fig. 4c: Temkin plot for the Cd (II) adsorption (8mm ol/L) by resinx K-8 in the presence of HN_3 0.1M

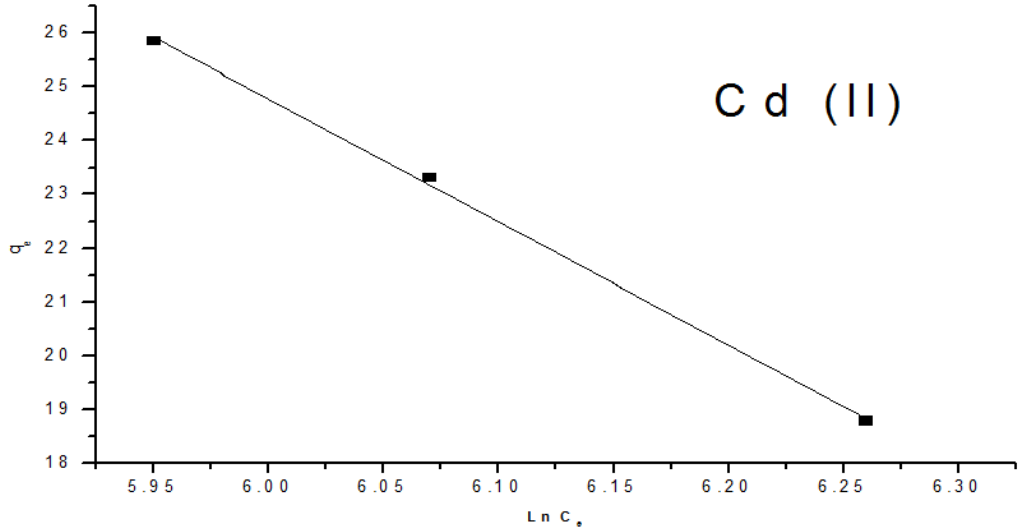

Fig. 4d: Temkin plot for the Cd (II) adsorption (8mm ol/L) by resinx K-8 in the presence of HCI 0.1M

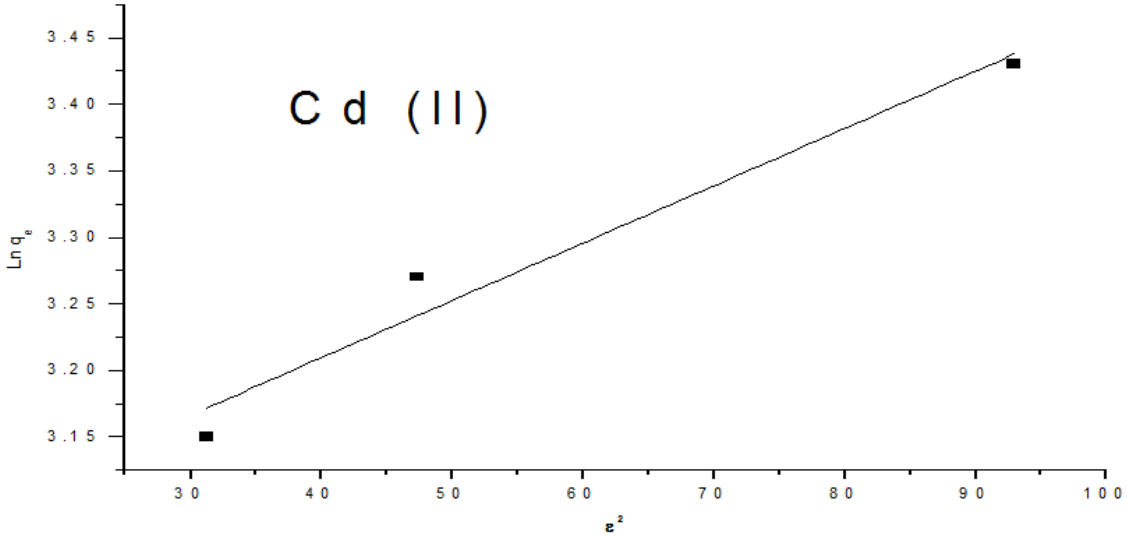

Fig. 5a: D-R plot for the Cd (II) adsorption (8mm ol/L) by resinx K-8 in the presence of $H_3 PO_4$ 0.1M

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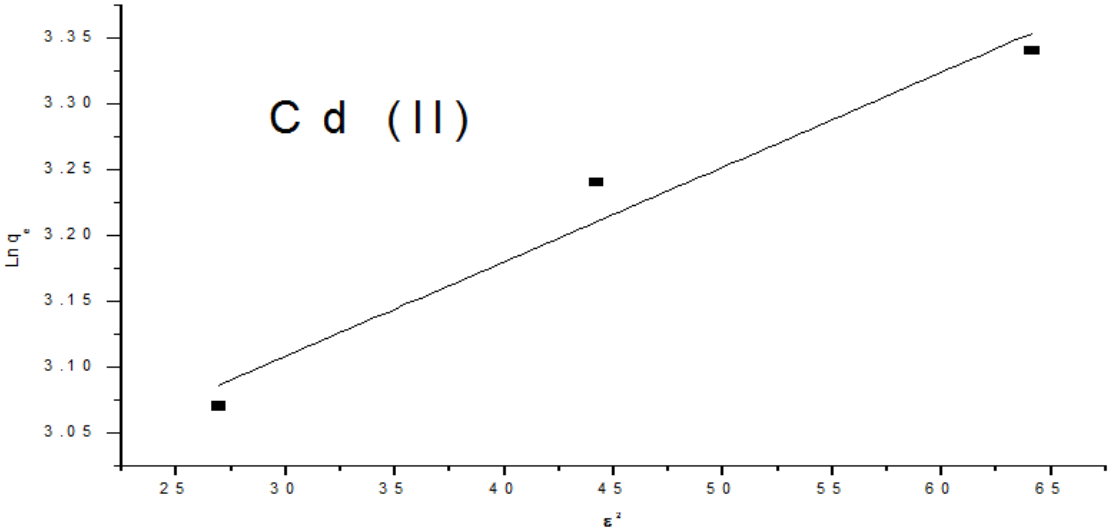

Fig. 5b: D-R plot for the Cd (II) adsorption (8mm ol/L) by resinx K-8 in the presence of H_2 SO_4 0.1M

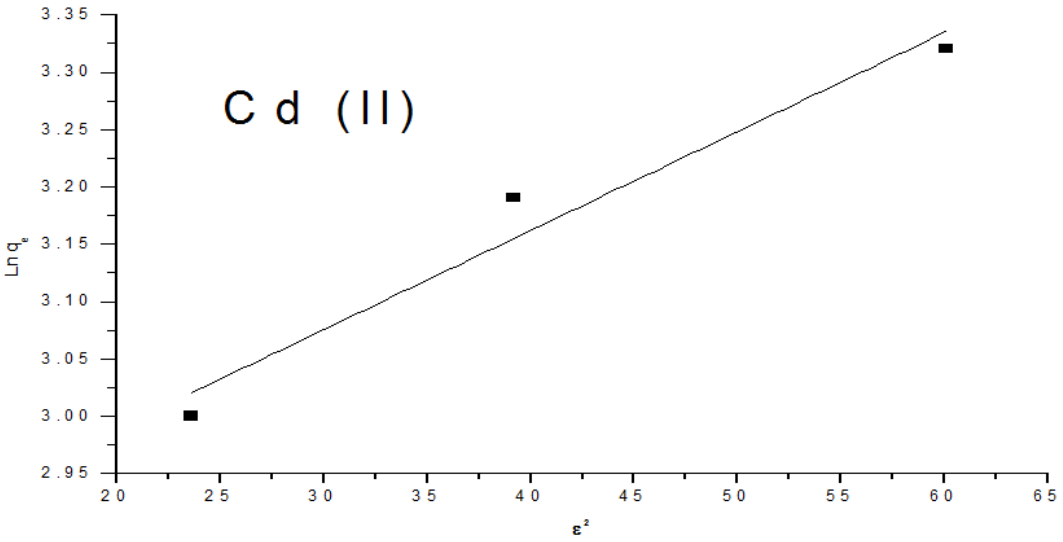

Fig. 5c: D-R plot for the Cd (II) adsorption (8mm ol/L) by resinx K-8 in the presence of HNO_3 0.1M

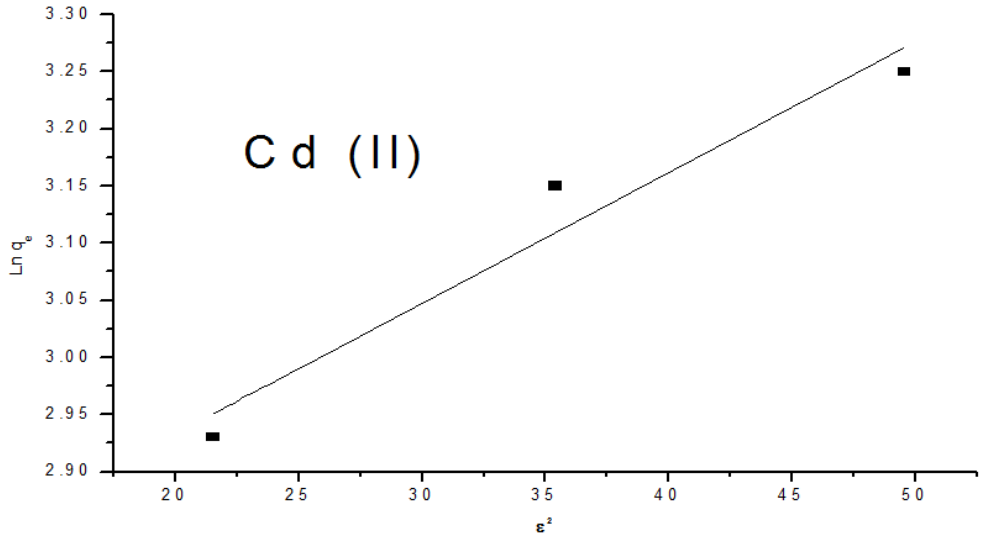

Fig. 5d: D-R plot for the Cd (II) adsorption (8mm ol/L) by resinx K-8 in the presence of HCI 0.1M

In the case of Freundlich isotherm (Fig. 2. a, b, c and d), the higher values of the K_F indicate the higher affinity of the cation exchanger for the metal complexes. The values of n are inbetween zero and one indicating favourable adsorption. The parameter K_F related to the adsorption density is higher in the case of adsorption on Resinex^{TM}K-8. The R^2 values in the case of Freundlich isotherm ranged from 0.980 to 0.992.

Based on Langmuir model (Fig. 3. a, b, c and d) for $[M(IOA)]^{n+}$ complexes adsorption on Resinex^{TM} K-8 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 Cd-phosphate, Cd-sulfate, Cd-nitrate and Cd-chloride media are as follows; 0.119, 0.025, 0.061 and 0.047, respectively.

The high values of K_L were obtained for the Resinex^{TM} K-8 (strong acid cation exchange resin),Generally, these values follows the order: Cd-phosphate > Cd -sulfate > Cd -nitrate > Cd -chloride media. This trend is consistent with the results presented earlier. 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.

The Temkin and Pyzhev isotherm for Cd(II) is shown in (Fig. 4. a, b, c and d), b_T related to heat of adsorption. Values lower than eight indicate weak interaction between metal and the adsorbent. However, lower value of B_T for Cd(II) indicates presence of relatively weaker cohesive forces in between the adsorbent and cadmium ions. Process, as indicated by B_T values can be expressed as physical adsorption (Fritzand Pietrzyk, 1961).

In the present study, Dubinin-Radushkevich (D-R) isotherm constants, monolayer capacity (X_m) and adsorption energy (β) are represented in (Fig. 5. a, b, c and d). The magnitude of β is used to determine the type of adsorption mechanism. When one mole of ions is transferred to the adsorbent surface, its value was higher than 8.0 kJ/mol which indicates chemical adsorption. However, at lower 8 KJ/mol the adsorption processes are physical in nature(Aksuand Karabbayir, 2008).

(B)- Kinetics Modeling On Adsorption:

In order to characterize the adsorption kinetics of the studied Resinex^{TM}K-8 (strong acid cation exchange resin), adsorption experiments were carried out with single metal ionCd(II) in inorganic acid solutions(phosphoric, sulfuric, nitric and hydrochloric acid). According to the above presented assumption of complexation conditions, the cation exchange process of Cd(II) complexes in the Cd(II)–inorganic acid systems on Resinex^{TM} K-8 strong acid cation exchange resin.The pseudo first-order and the pseudo second-order kinetic models (Figs. 6. a, b, c and d& 7. a, b, c and d) it was also found in (Tables 9 and 10) that the values of k_1 were greater than k_2 values of the adsorption of $[Cd(IOA)]^{n+}$ on the cation exchanger. The values of correlation coefficients (R^2) for the adsorption were equal to 0.998, 0.999, 0.999 and 0.998 for the pseudo first-order kinetic model and 0.995, 0.998, 0.998 and 0.995 for the pseudo second-order kinetic model, respectively.

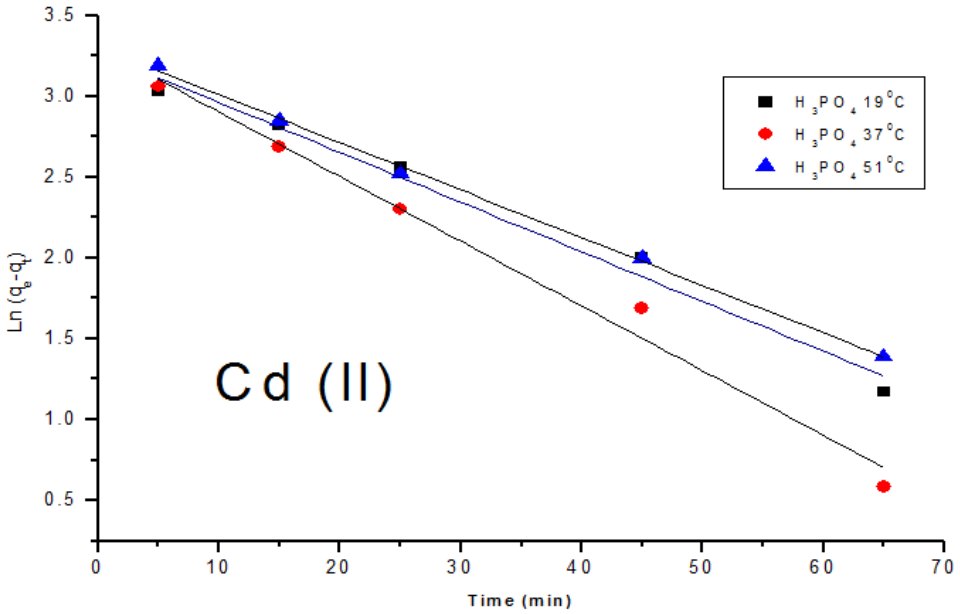

Fig. 6a: Pseudo first order plot for the Cd (II) adsorption (8mm ol/ L) by resinx K-8 in the presence of H_3 PO_4 0.1M

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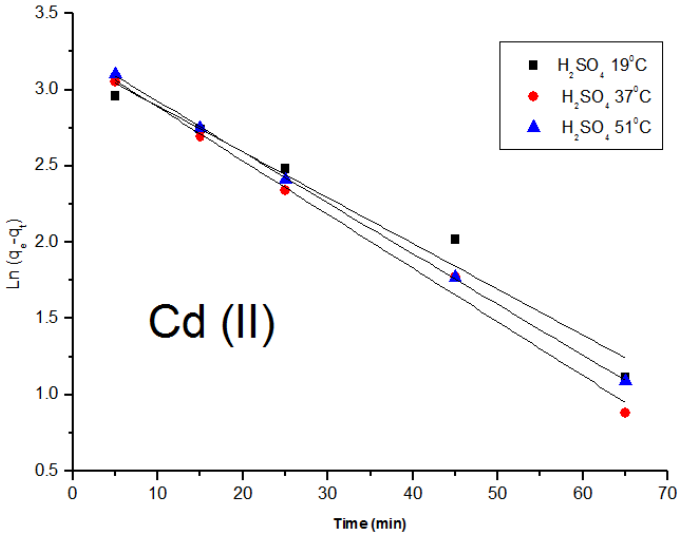

Fig. 6b: Pseudo first order plot for the Cd (II) adsorption (8mm ol/ L) by resinx K-8 in the presence of $H_2 SO_4$ 0.1M

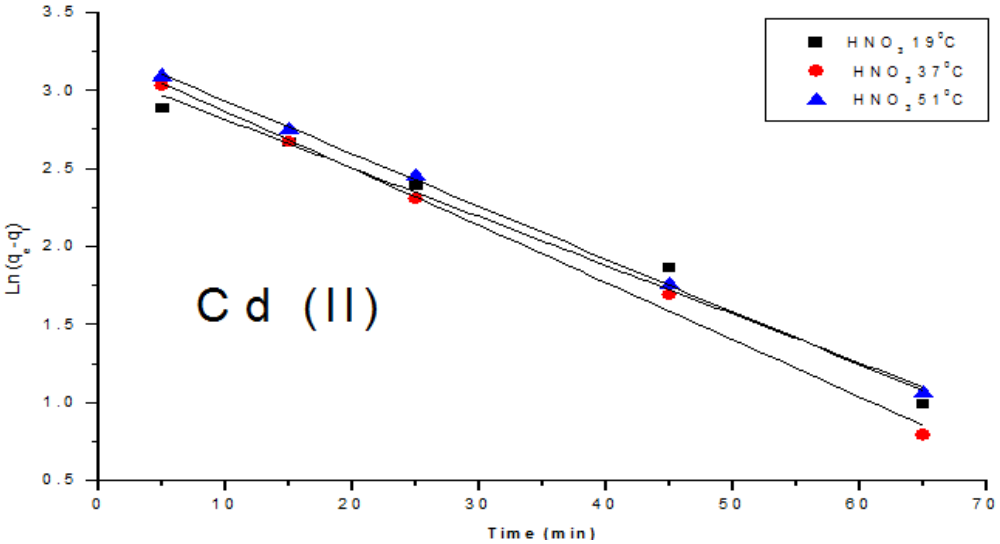

Fig. 6c: Pseudo first order plot for the Cd (II) adsorption (8mm ol/ L) by resinx K-8 in the presence of HNO_3 0.1M

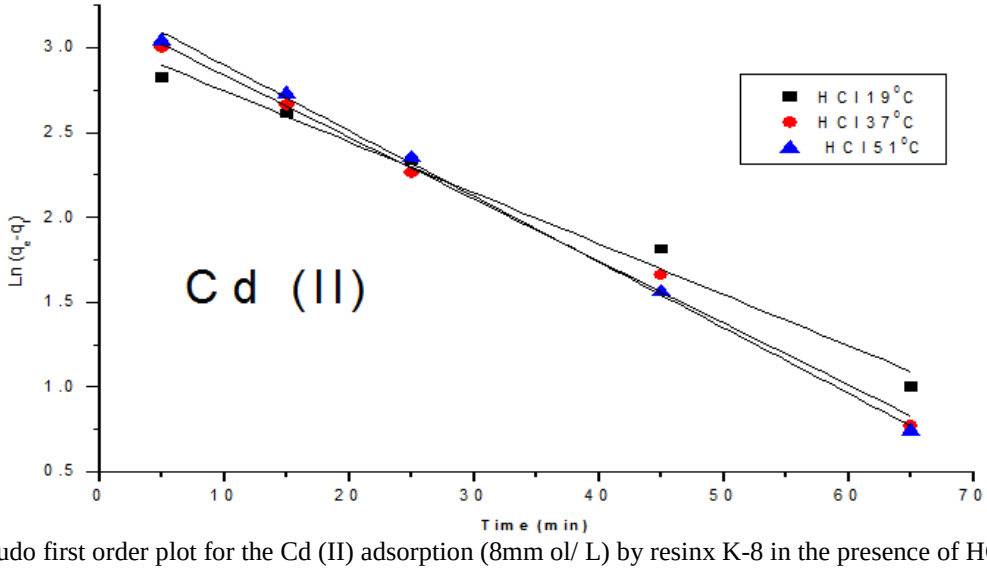

Fig. 6d: Pseudo first order plot for the Cd (II) adsorption (8mm ol/ L) by resinx K-8 in the presence of HCI 0.1M

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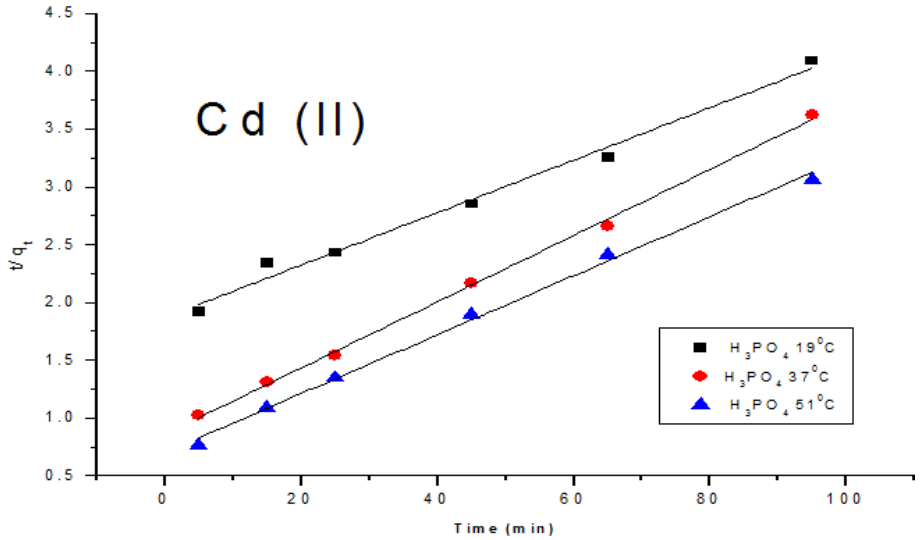

Fig. 7a: Pseudo second order plot for the Cd (II) adsorption (8mm ol/ L) by resinx K-8 in the presence of H_3PO_4 0.1M

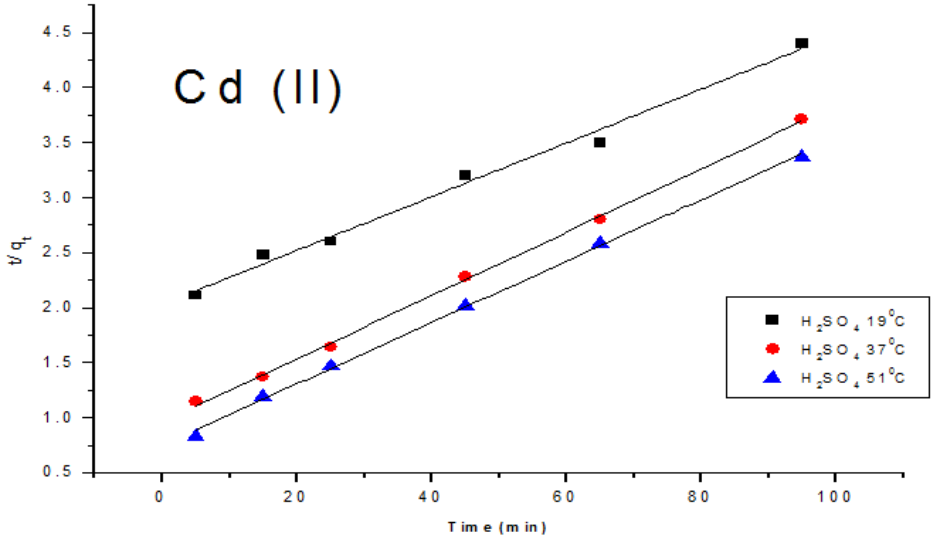

Fig. 7b: Pseudo second order plot for the Cd (II) adsorption (8mm ol/ L) by resinx K-8 in the presence of H_2SO_4 0.1M

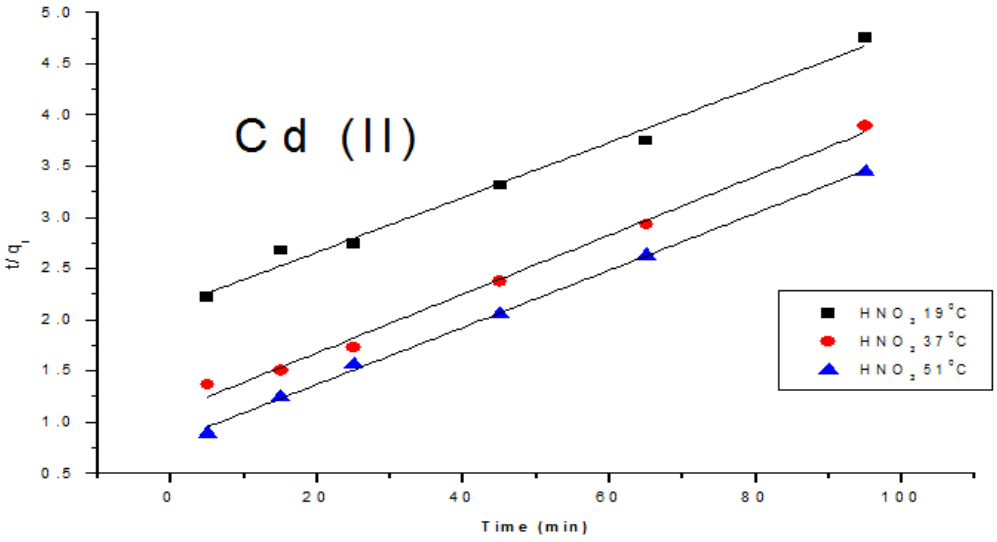

Fig. 7c: Pseudo second order plot for the Cd (II) adsorption (8mm ol/ L) by resinx K-8 in the presence of H_2SO_4 0.1M

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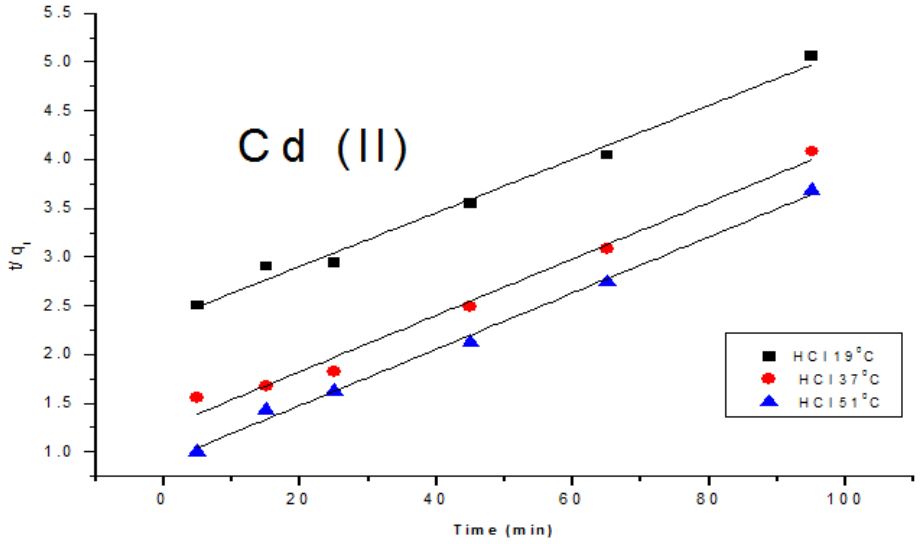

Fig. 7c: Pseudo second order plot for the Cd (II) adsorption (8mm ol/ L) by resinx K-8 in the presence of HCI 0.1M

Consequently, the pseudo first-order equation was selected as the most adequate to the model adsorption of Cd(II) complexes with inorganic acids. As follows from the literature data other researchers also proposed the pseudo first-order kinetic model for describing the adsorption of toxic metal ions on the ion exchangers(Aksuand Karabbayir, 2008) and (Saraswat *et al*, 1979).

As follows from the obtained plots (Fig.8. a, b, c and d) there are three different regions before the equilibriumthe diffusion through the solution to the external surface of ion exchanger, the intraparticle diffusion and the stage to the final equilibrium where intraparticle diffusion starts to slow down. In the presented research the k_{id} values were determined by the slopes of the straight-line portion of plots.

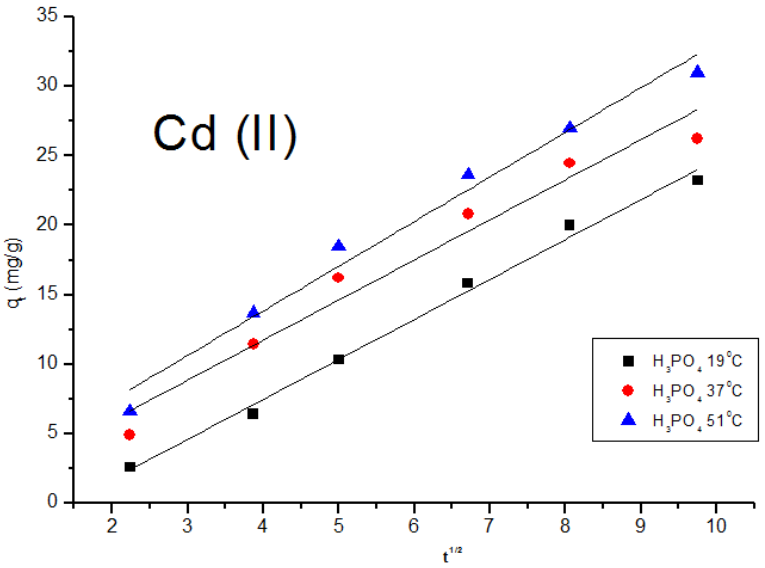

Fig. 8a: Weber plot for the Cd (II) adsorption (8mm ol/ L) by resinx K-8 in the presence of H_3 PO_4 0.1M

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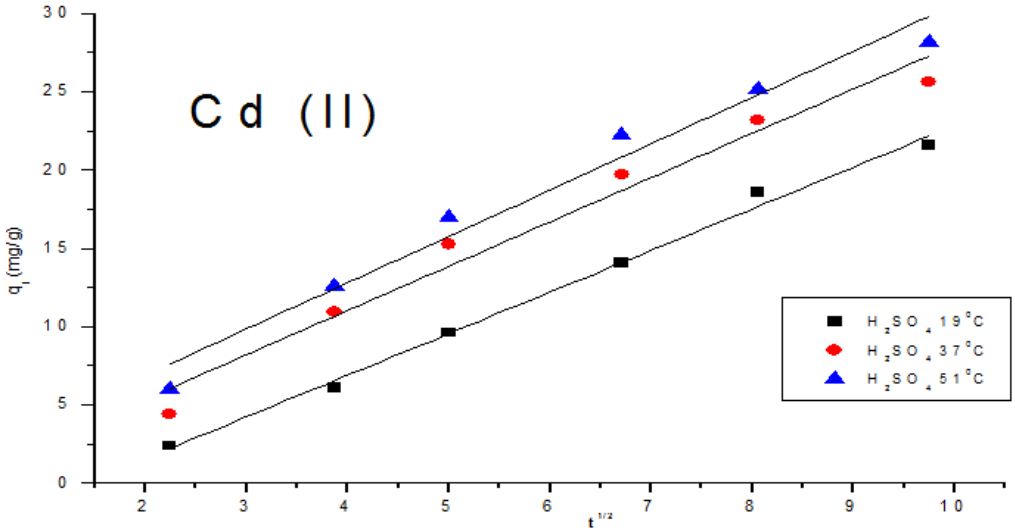

Fig. 8b: Weber plot for the Cd (II) adsorption (8mm ol/ L) by resinx K-8 in the presence of H_2 PO_4 0.1M at different tem pretures

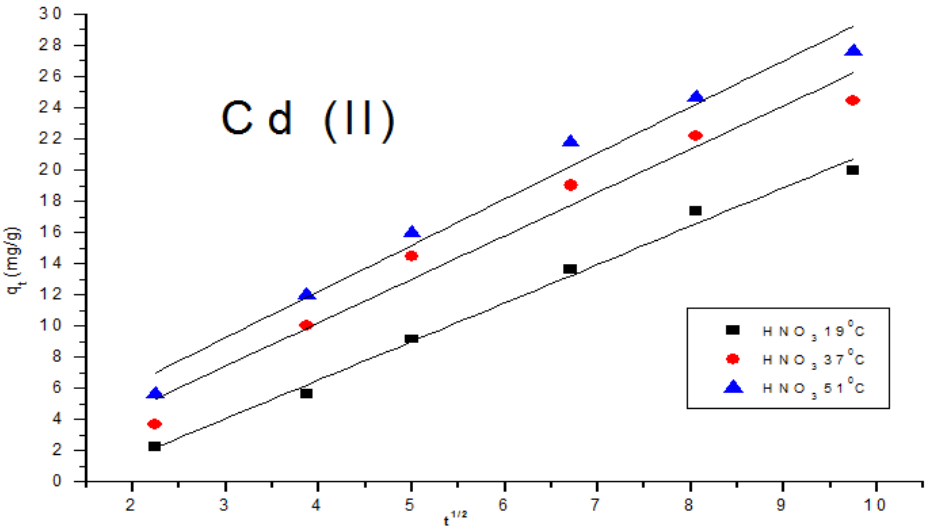

Fig. 8c: Weber plot for the Cd (II) adsorption (8mm ol/ L) by resinx K-8 in the presence of HNO_3 0.1M at different tem pretures

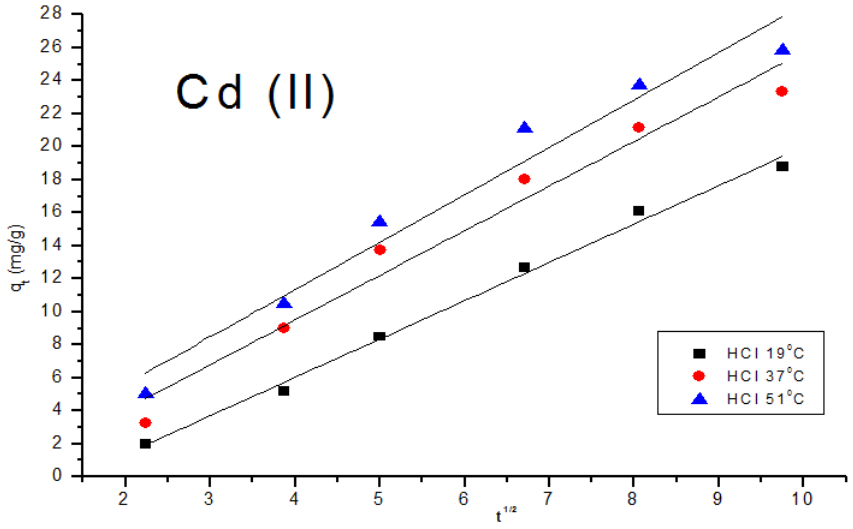

Fig. 8d: Weber plot for the Cd (II) adsorption (8mm ol/ L) by resinx K-8 in the presence of HCl 0.1M at different tem pretures

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.

(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 $[Cd(IOA)]^{n+}$complexes adsorption (Fig. 9) can be calculated. The increase in adsorption capacity of the above-mentioned cation exchangers may be attributed to the enlargement of pore size or activation of the adsorbent surfaces (Fig.9). The values of *qe/ce* (K_D) are also high at all temperatures and increase with the increase of temperature showing endothermic process.

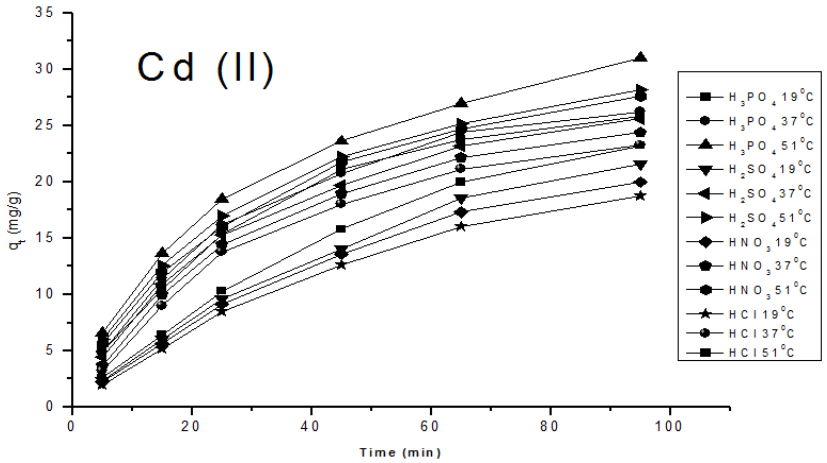

Fig. 9: Effect of different tem pretures on the adsorption of Cd (II) 8mm ol/L in the presence of some inorganic acids.

The negativeGibbs free energy change(ΔG) values indicated that the adsorption of Cd(II) complexes on the studied cation exchanger 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. 10). The enthalpychanges(ΔH) for the cation exchanger were 20.19, 16.39, 18.71 and 17.34 kJ/mol in presence of phosphoric, sulfuric, nitric and hydrochloric acid, respectively. These values suggest that physical adsorption is predominant as in the case of chemical adsorption the enthalpy changes (ΔH) values are reported to be in the range 200–400 kJ/mol. The positive value indicates the endothermic nature of the adsorption process. The positive values of the entropy change (ΔS) show the affinity for $[Cd(IOA)]^{n+}$complexes with the cation exchange resin.

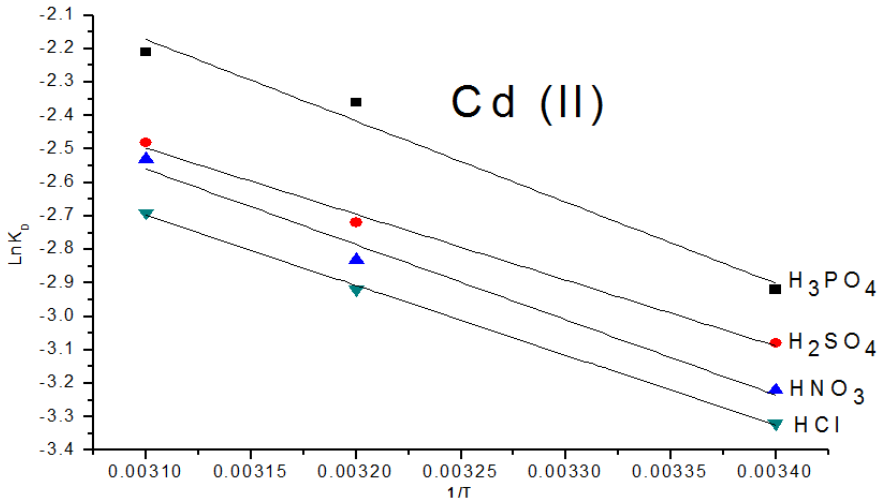

Fig. 10: Van't Hoff plot for the Cd (II) adsorption (8mm ol/ L) by resinx K-8 in the presence of inorganic acids 0.1M at different tem pretures.

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