

## Adsorption mechanisms of divalent metal-organic complexes of Mn(II), Co(II) and Ni(II) onto Resinex<sup>TM</sup>K-8 resin from aqueous-Alcoholic solution

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### ABSTRACT

This study examined the adsorption of divalent metal ions as manganese Mn(II), cobalt Co(II) and nickel Ni(II) from aqueous-Alcoholic solution on the strong cation exchange resin RESINEX<sup>TM</sup>K-8. Equilibrium adsorption tests of aqueous – Alcohols as Ethanol, Ethylene Glycol and Glycerol in percentage (25%) at different temperatures (25, 35 and 45 °C) were measured and analysed by fitting the experimental adsorption with isotherm models as Langmuir, Freundlich and Temkin. The uptake of Mn(II), Co(II) and Ni(II) based on the stability and formation quotient constants of these metal complexes were used in examining the roles of steric hindrance in the adsorption of divalent metal complexes on RESINEX<sup>TM</sup>K-8. The mechanism of adsorption of these complexes suggests the size and the nature of the type of metal complexes have a significant influence on the metal uptake. The data obtained indicated that steric hindrance was not only the dominant factor governing the adsorption of these divalent metal ions. The kinetic data were analyzed using first-order, pseudo-second order and Weber-Morris kinetic models. The results indicated that adsorption fitted well with the first-order for Mn(II) and pseudo-second order kinetic model Co(II) and Ni(II). Activation energy (Ea) was determined as well as the thermodynamic parameters ( $\Delta H$ ,  $\Delta S$  and  $\Delta G$ ) at different temperatures (25, 35 and 45 °C). Also Gibbs free energy analysis shows that Mn(II) adsorption was non-spontaneous while Co(II) and Ni(II) shows opposite trend. However, from the positive values of enthalpy ( $\Delta H$ ) for Mn(II), Co(II) and Ni(II) removal, we can conclude that these metals exhibited endothermic properties.

**Key words:** Resinex<sup>TM</sup> K-8, Alcohols, Thermodynamic, Kinetic, Temperature

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### Introduction

Metal recovery from solution is typically achieved by techniques including chemical precipitation (Calzadot *et al.*, 2005) solvent extraction and adsorption (Yadav *et al.*, 2014, Virolainen *et al.*, 2014, Yengui and Riedel, 2014, Katrina and Boyer, 2013 and Wanga *et al.*, 2014). Adsorption is conducted using adsorbents including activated carbon (Yadav *et al.*, 2014) and ion-exchange resins (Virolainen *et al.*, 2014).

Adsorption using chelating resins has found wide use in industry, in particular for divalent metal ion adsorption (Yengui and Riedel, 2014). Chelating resins are specially oriented ionic and non-ionic groups that are capable of exhibiting high adsorption selectivities and operating capacities. It is therefore not unusual to find that chelating resins have greater success in recovering metals from complex solutions in comparison to cation-exchange resins (Katrina and Boyer, 2013). Commercial chelating resins, for example Dowex M4195, Amberlite IRC748, Ionac SR-5 and Purolite S930, have been used to recover nickel Ni (II) and cobalt Co(II) successfully from sulfate solutions (Wanga *et al.*, 2014).

Organic solvents such as alcohols, find a wide range of applications in pharmaceutical industries, food industries and paint formulations (Grodowska and Parczewski, 2010). For instance, methanol, ethanol, isopropanol and 2-butanol are used as the extractants in the production of medicine, antibiotics and as components in food additives and food processing. In addition, these liquids are used as fuel additives, antifreeze agents, solvents for gums, chemical intermediates, solvents in chemical industries and denitrification agents in wastewater treatment (Pohl and Prusisz, 2010). The presence of trace metals in pharmaceutical products, fuel, food and paint is undesirable. In pharmaceutical products, metal ions have an ability to decompose the material of interest or catalyze the degradation of the active pharmaceutical ingredient. The decomposition may lead to potential toxic effects (Hussain *et al.*, 2011, Fliszar *et al.*, 2006 and Wassel *et al.*, 2014).

In addition, since some alcohols are used as fuel additives, they may be responsible for the decomposition and poor performance of the fuel, leading to corrosion of vehicle parts and formation of precipitates (Chaves *et al.*, 2008). Furthermore, monitoring toxic elements is also important, since they are released into the atmosphere by the fuel combustion, thus causing air pollution. Therefore, it is crucial to investigate the levels of trace metals in alcohols because their presence in these products has negative health effects and most metal impurities are detrimental to catalytic processes used in the industry. Many metals occur naturally in fossil materials and as a result, they can be present in petroleum based products. The presence of the metals in alcohols can also be due

to their incorporation during the production process, by contact with refinement or distillation equipment, storage and transport. Metal concentrations in organic solvents are generally in trace levels, therefore sensitive and fast techniques with low detection limits are required (Santos *et al.*, 2011, Samiey and Toosi, 2010, Wassel *et al.*, 2014 and Qin *et al.*, 2004).

Thus, the present study is focused on manganese Mn(II), cobalt Co(II) and nickel Ni(II) adsorption on strong cation exchange resin **RESINEX™K-8** in aqueous-Ethanol[CH<sub>3</sub>-CH<sub>2</sub>OH], Ethylene glycol [(HO)CH<sub>2</sub>-CH<sub>2</sub>(OH)] and Glycerol [(HO)CH<sub>2</sub>-CH(OH)CH<sub>2</sub>(OH)] solution and the role of steric hindrance in the adsorption of metals was examined.

## Materials and Methods

### Materials:

All the materials and chemicals (Aldrich, USA) were used as received with analytical grade. Stock solutions of manganese Mn(II), cobalt Co(II) and nickel Ni(II) were prepared by dissolving its chloride (AR Grade) in distilled water. The stock solution was diluted with distilled water to obtain the desired concentrations. Strong cation exchange of **RESINEX™K-8** used in this work from Jacobi Swedish Company. Prior to use, the resin was converted to the hydrogen (H<sup>+</sup>) form by washing it in 1.0 M HCl followed by further washing in deionised water. The resin regeneration procedures follow the recommendations provided by the manufacturers. The resin-H was dried and kept at room temperature in a desiccators until it was used (Wassel *et al.*, 2014).

The adsorption capacity in mg/g of the adsorbent ( $q_e$ ) and the metal ion adsorption percentage (Ad%) were obtained by Eqs. (1) and (2),

$$q_e = \frac{(C_0 - C_e)V/1000}{W} \quad (1)$$

$$\text{Ads\%} = \frac{(C_0 - C_e) \times 100}{C_0} \quad (2)$$

where ( $C_0$ ) and ( $C_e$ ) are the initial and final divalent metal ion concentrations (mg/l), respectively, (V) is the volume of metal-Alcoholic solutions (Ethanol, Ethylene Glycol and Glycerol) (L) and W is the weight of adsorbent used (g). The data of isotherms were obtained after an equilibrium time of (24 h). After the equilibrium time, the concentrations were determined.

### Batch adsorption studies:

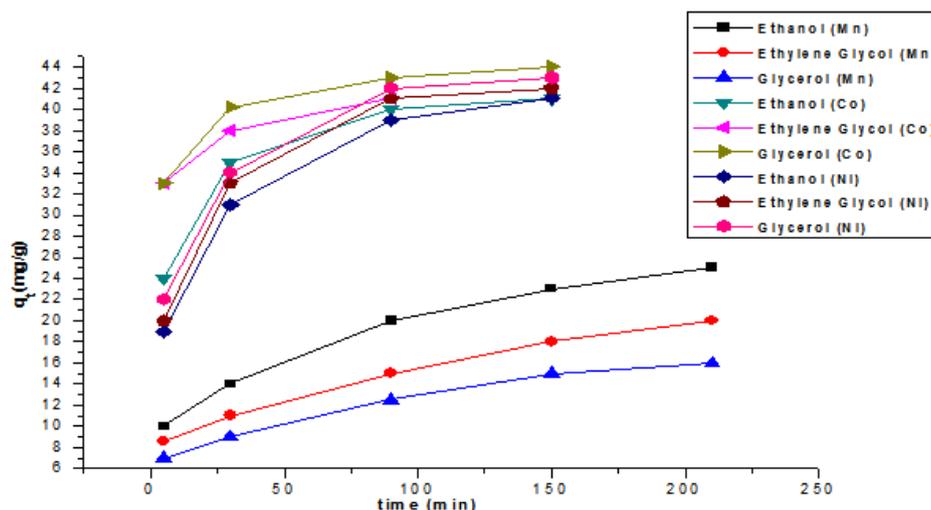
Adsorption studies were carried out in a batch mode by shaking 0.5 g resin in 50 mL solution of Mn (II), Co(II) and Ni(II) onto the water bath shaker at 100 rpm stirring speed. Effect of aqueous-alcoholic solution on the Mn(II), Co(II) and Ni(II) adsorption onto Resinex™K-8 was conducted through varying the concentration in the range 0.01–0.1 M. Furthermore the adsorption studies were also carried out by varying time interval (5–210 min) at 452mg/l of Mn(II), Co(II) and Ni(II) to optimize the time required for the adsorption of these metal ions.

## Results and Discussion

### 1- Study the effect of contact time on adsorption of divalent metal ions:

These studies were carried out at metal ion concentration of 452 mg/L at 25<sup>0</sup>C in aqueous-alcoholic solutions, the time taken at constant manganese concentration and alcohols of 25% for the uptake of Mn(II), Co(II) and Ni(II) in both aqueous-Ethanol, Ethylene Glycol and Glycerol solutions. From the data obtained and illustrated in (Fig. 1), as for kinetic studies the preliminary results show that the time taken for manganese Mn(II) equilibrium uptake is obtained within 5–210 min. Then no appreciable changes in adsorption were noticed after 210 min. Therefore the phase contact time of 210 min was used for the other batch tests.

In general, the ion exchange rate of the order; Mn(II) follows Ethanol>Ethylene Glycol >Glycerol solutions. It is therefore likely that the size of the ligands played great role in the order of the manganese Mn(II)-complex adsorption, where the adsorption capacities was influenced by the steric hindrance and the crowding effect. While for cobalt Co(II) and nickel Ni(II) uptake within 5–150 min. Then no appreciable changes in adsorption were noticed after 150 min. The adsorption rate for both cobalt Co(II) and Ni(II) uptake follows reverse order; Ethanol < Ethylene glycol < Glycerol solutions these mean that the size of ligands has not played a role in the order of these divalent metal -complexes adsorption, but the stability constants of the complexes has important role in adsorption processes.



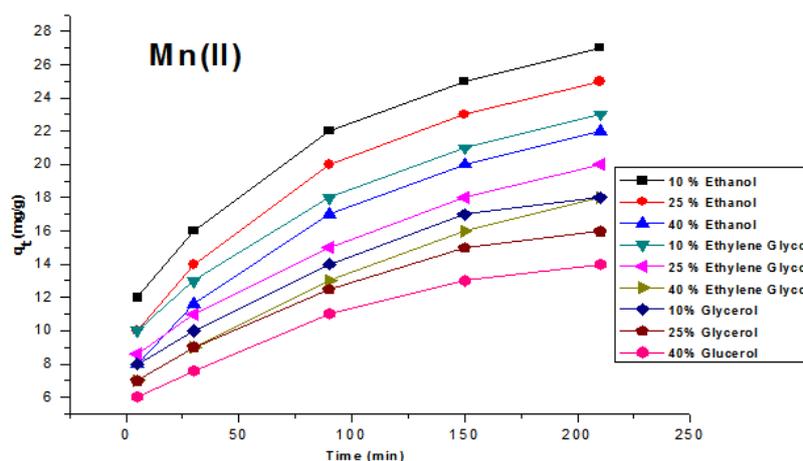
**Fig. 1:** Effect of contact time on the adsorption uptake of Mn (II), Co (II) and Ni (II) in case of alcohols at 25<sup>0</sup>C

Among the three aqueous- alcoholic complexes solutions taken for the study, the order of the manganese Mn(II) percentage uptake (%) is follows; Ethanol (59.1%) > Ethylene Glycol (47.3%) >Glycerol (37.8%), for cobalt Co(II); Glycerol (97.0%) >Ethylene Glycol (92.6%)>Ethanol (90.4%), but in case of nickel Ni(II)Glycerol(95.1%) >Ethylene Glycol (92.9%) > Ethanol (90.7%) % uptake.

The introduction of alcohols to adsorption system may cause the change of the surface characteristics of the resin, competitive distribution of metal ions between resin surface and organic ligands in the solution (Yanzhenget *al.*,2003).

## 2- Study the Effect of different alcohols and its concentrations on adsorption processes:

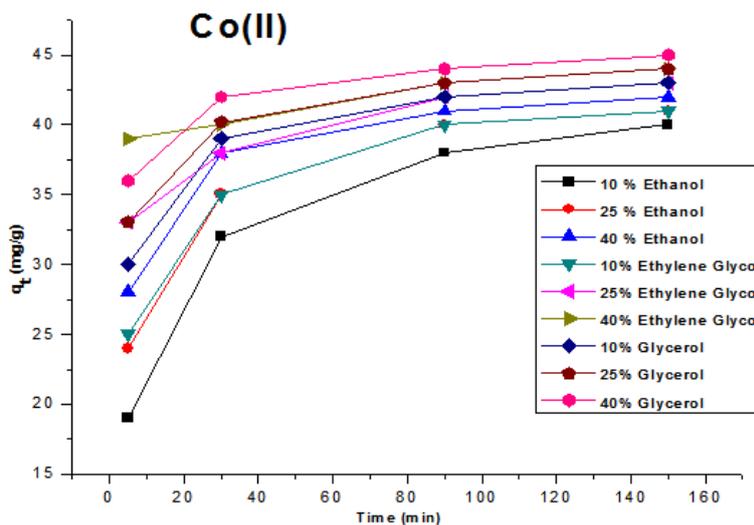
From the data obtained and illustrated in (Figs.2-4), when the concentration of organic ligands in adsorption solution is low(0.01M) manganese Mn(II) in adsorption solution would be bound by organic ligands adsorbed to the adsorbent (El Qada *et al.*, 2006 and Mane *et al.*, 2007), which on the whole, will lead to the reduction of Mn(II) adsorption in the presence of low concentrations of each aqueous-Ethanol, Ethylene Glycol and Glycerol solutions. However, with the continuous enhancement of alcohols percentages in adsorption solution, the ratio of organic ligands concentration in solution to the divalent metal-ligands adsorbed by the resin becomes larger.



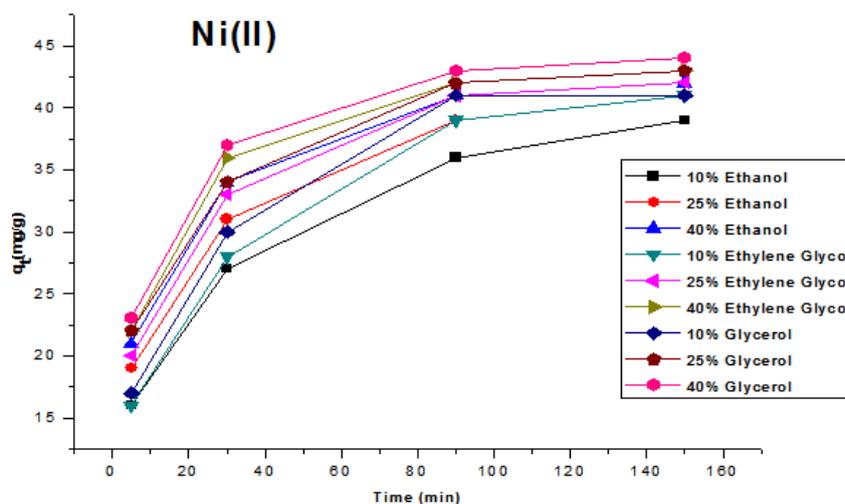
**Fig. 2:** Effect of the Mn (II) adsorption by Resinex K-8 at different concentrations in case of different alcohols at 25<sup>0</sup>Co.

An increased competition ability of organic ligands in the solution for binding Mn(II) led to inhibition of adsorption, as a result lower Mn(II) uptake with increments of alcohols percentages. However, the percentage uptake for Mn(II) at different concentrations of aqueous-Ethanol was 63.8, 59.1 and 52%, for aqueous-Ethylene Glycol was 54.4, 47.3 and 42.6%, but 42.6, 37.8 and 33.1% for aqueous-Glycerol respectively. In opposite trend when the alcohols percentages changed from 10% to 40%, Co(II) and Ni(II) adsorption was enhanced directly,

and no inhibition was shown for the given alcohols percentages, for this reason, the uptake of cobalt Co(II) and nickel Ni(II) increased when initial alcohols percentages increased. However, the percentage uptake for Co(II) at different concentrations of aqueous-Ethanol was 88.1, 90.4 and 92.6%, for aqueous-Ethylene Glycol was 90.4, 92.6 and 94.8%, but 94.8, 97 and 99.2% for aqueous-Glycerol respectively, and for Ni(II) the percentage uptake at different concentrations of aqueous-Ethanol was 63.8, 59.1 and 52%, for aqueous-Ethylene glycol was 54.4, 47.3 and 42.6%, but 42.6, 37.8 and 33.1% for aqueous-Glycerol respectively.



**Fig. 3:** Effect of the Co (II) adsorption by Resinex K-8 at different concentrations in case of different alcohols at 25 °C.



**Fig. 4:** Effect of the Ni (II) adsorption by Resinex K-8 at different concentrations in case of different alcohols at 25 °C.

### 3- Study the adsorption mechanisms and effect of steric hindrance:

To examine the effect of steric hindrance imposed by the bulkiness of the alcohols coordinated with manganese Mn(II), cobalt Co(II) and nickel Ni(II). The metal complexes adsorption data were fitted to the empirical correlations; Freundlich, Langmuir (Nasir *et al.*, 2007), and Temkin (Jha *et al.*, 2008) isotherm models. The linear form of the Freundlich isotherm is given by the following equation:

$$\log q_e = \log K_F + (1/n) \log C_e \quad (3)$$

where ( $q_e$ ) is the amount of the metal adsorbed (mg/g), ( $C_e$ ) is the equilibrium concentration of the divalent metal solution (mg/L). ( $K_F$ ) and ( $n$ ) are the Freundlich constants which indicate the capacity and the intensity of the adsorption, respectively. The values of the Freundlich constant ( $n$ ) (Tables 1a,b,c) showing that the

adsorption process may be favorable. ( $R^2$ ) value ( $<0.99$ ) for Co(II) and Ni(II) in aqueous-Alcohols indicating that Freundlich model is not suitable. While ( $R^2$ ) value obtained ( $>0.99$ ) for Mn(II) in aqueous-alcoholic solutions, indicating that, the adsorption process of manganese ions Mn(II) onto Resinex<sup>TM</sup>K-8 is better described by Freundlich isotherm.

Langmuir isotherm was applied to equilibrium adsorption assuming monolayer adsorption onto the surface with a finite number of identical sites. The following Langmuir adsorption isotherm equation was used:

$$C_e/q_e = 1/K_L Q_m + C_e/Q_m \quad (4)$$

where ( $q_e$ ) is the amount of the metal adsorbed on adsorbent (mg/g) at equilibrium, ( $C_e$ ) is the equilibrium concentration (mg/L) of the divalent metal in solution, ( $Q_m$ ) is the monolayer adsorption capacity (mg/g) and ( $k_L$ ) is the Langmuir constant (L/mg) related to the free energy of adsorption. The values of ( $Q_m$ ) and ( $k_L$ ) were calculated from the slopes ( $1/Q_m$ ) and intercepts ( $1/k_L Q_m$ ) of the linear plots of  $C_e/q_e$  Vs.  $C_e$  are given in (Tables 1a,b,c). The linearity of plots revealed that the adsorption followed Langmuir isotherm model. The essential characteristic of the Langmuir isotherm can also be evaluated by dimensionless adsorption intensity  $R_L$  given from equation.

$$R_L = 1/1 + K_L C_o \quad (5)$$

where ( $C_o$ ) (mg/L) is the initial concentration of the divalent metal adsorbed and  $k_L$  (L/mg) is the Langmuir constant.  $R_L$  values represent the type of isotherm and its value between (0 and 1) indicates favorable adsorption. The ( $R_L$ ) values evaluated from the ( $k_L$ ) values for Mn(II), Co(II) and Ni(II) at various temperatures were found to be between 0 and 1, further suggesting that the adsorption of Mn(II), Co(II) and Ni(II) onto Resinex<sup>TM</sup>K-8 was favorable. The lower ( $R_L$ ) values implied that the interaction of Co(II) and Ni(II) ions with Resinex<sup>TM</sup>K-8H is stronger than Mn(II). The adsorption process of these divalent metal ions onto Resinex<sup>TM</sup>K-8H is better described by Langmuir isotherm.

**Table 1-a:** Adsorption isotherm parameters for (7.7 mmol/L) of Mn(II) on Resinex<sup>TM</sup> K-8 in aqueous-alcoholic solution.

ALCOHOLS	Langmuir parameters				Freundlich parameters			Temkin parameters		
	$Q_o$ (mg/g)	$b$ (L/mg)	$R_L$	$R^2$	$n$	$K_f$ (mg/g)	$R^2$	$K_t$ (L/g)	$B_t$ (J/mol)	$R^2$
ETHANOL	16.0	0.016	0.1290	0.99893	2.00	329.9	0.92857	0.0014	1.03	1.0000
ETHYLENE GLYCOL	11.9	0.011	0.177	0.99238	1.10	2655.2	0.99660	0.0007	1.00	0.7990
GLYCEROL	7.9	0.007	0.2500	0.98976	0.74	28645.0	0.96838	0.0019	0.81	0.99787

**Table 1-b:** Adsorption isotherm parameters for (7.7 mmol/L) of Co(II) on Resinex<sup>TM</sup> K-8 in aqueous-alcoholic solution.

ALCOHOLS	Langmuir parameters				Freundlich parameters			Temkin parameters		
	$Q_o$ (mg/g)	$b$ (L/mg)	$R_L$	$R^2$	$n$	$K_f$ (mg/g)	$R^2$	$K_t$ (L/g)	$B_t$ (J/mol)	$R^2$
ETHANOL	40.0	0.85	0.0026	0.99715	20.7	49.1	0.88087	$2.5 \times 10^{-14}$	8.50	0.6536
ETHYLENE GLYCOL	40.6	0.73	0.0030	0.99976	10.6	58.1	0.98649	$4.0 \times 10^{-8}$	8.66	0.98918
GLYCEROL	43.4	4.20	0.0005	0.99974	57.5	46.1	0.94702	$1.5 \times 10^{-29}$	8.69	0.92045

**Table 1-c:** Adsorption isotherm parameters for (7.7 mmol/L) of Ni(II) on Resinex<sup>TM</sup> K-8 in aqueous-alcoholic solution.

ALCOHOLS	Langmuir parameters				Freundlich parameters			Temkin parameters		
	$Q_o$ (mg/g)	$b$ (L/mg)	$R_L$	$R^2$	$n$	$K_f$ (mg/g)	$R^2$	$K_t$ (L/g)	$B_t$ (J/mol)	$R^2$
ETHANOL	40.7	2.3	0.0010	0.99919	42.4	45.5	0.63008	$5.2 \times 10^{-20}$	16.70	0.63070
ETHYLENE GLYCOL	42.1	3.5	0.0006	0.99894	48.7	45.1	0.45778	$1.3 \times 10^{-20}$	11.05	0.97797
GLYCEROL	42.8	5.5	0.0004	0.99977	47.2	45.9	0.74611	$2.4 \times 10^{-25}$	23.90	0.80877

The Temkin isotherm can be expressed by the following equation:

$$q_e = (RT/b_T) \ln A_T + (RT/b_T) \ln C_e \quad (6)$$

where  $B_T = RT/b_T$ ,  $b_T$  is the Temkin constant (J/mol) related to adsorption heat, (T) is the absolute temperature (K), R is the gas constant (8.314 J/mol K), and ( $A_T$ ) is the Temkin isotherm constant (L/g). ( $B_T$ ) and ( $A_T$ ) can be calculated from the slopes (B) and intercepts ( $B \ln A_T$ ) of the plot of ( $q_e$ ) Vs. ( $\ln C_e$ ). The Temkin constants B,  $b_T$ , and  $A_T$  together with the ( $R^2$ ) values are shown in (Tables 1a,b,c).

#### 4- Study the adsorption kinetics:

Kinetic studies were carried out on divalent metal ion concentration of 452 mg/L at different temperatures, namely, 25, 35 and 45°C in aqueous –Alcoholic solution and 25% of used alcohol. Pseudo-first order, pseudo-second order and Weber-Morris's intraparticle diffusion models were analyzed the experimental data.

The pseudo-first-order rate model is based on solid adsorbent capacity and generally expressed as follows:

$$\text{Log } (q_e - q_t) = \text{log } q_e - \frac{k_1}{2.303}t \quad (7)$$

where ( $q_e$ ) is the amount of solute adsorbed at equilibrium per unit weight of the adsorbent (mg/g), ( $q_t$ ) is the amount of solute adsorbed at any time (mg/g) and ( $k_1$ ) (min/1) is the adsorption rate constant. Values of  $k_1$  calculated from the plots of  $\text{Log } (q_e - q_t)$  Vs. ( $t$ ) at different temperatures are summarized in (Tables 2a,b,c). Based on the pseudo first-order and the pseudo second-order models. The values of correlation coefficients ( $R^2$ ) for the adsorption of  $[\text{Mn}(\text{OA})]^{n+}$  complexes at Mn(II)-Ethylene Glycol solution was fitted for the pseudo first-order kinetic model. Consequently, the pseudo first-order equation was selected as the most adequate to the model adsorption of Mn(II) complexes with aqueous- Ethylene Glycol solution. The pseudo-second order model can be expressed as:

$$(t/q_t) = (1/k_2q_e^2) + (1/q_e)t \quad (8)$$

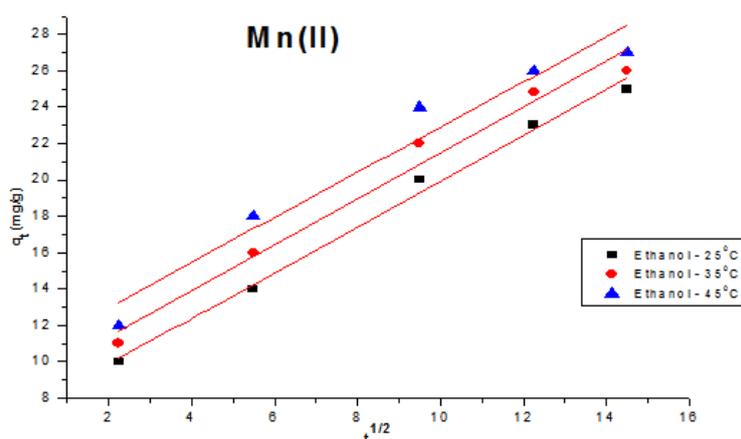
Where ( $k_2$ ) (g/mg min) is the rate constant of the pseudo-second-order equation,  $q_e$  (mg/g) is the maximum adsorption capacity and ( $q_t$ ) (mg/g) is the amount of adsorption at time  $t$  (min). The plot of  $(t/q_t)$  Vs. ( $t$ ) shows a linear relationship.

The value of  $q_e$  (mg/g) and  $k_2$  (g/mg min) are determined from the slope and intercept of the plot. The results are summarized in (Tables 2a,b,c). It can be seen that the calculated values of correlation coefficients ( $R^2$ ) for the adsorption of  $[\text{Co}(\text{OA})]^{n+}$  and  $[\text{Ni}(\text{OA})]^{n+}$  complexes at aqueous-Ethanol, aqueous-Ethylene aqueous-Glycol and Glycerol solutions indicated that the second-order equation are close to the experimental results than those for first-order model. Consequently, the pseudo second-order equation was selected as the most adequate to the model adsorption of these complexes with the three alcohols.

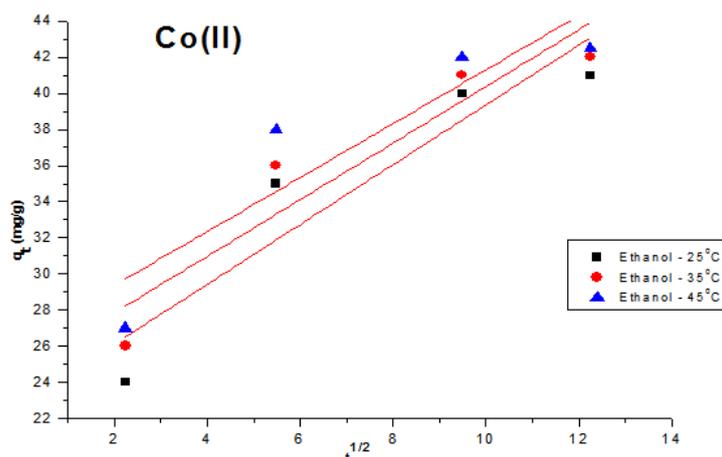
To gain insight into the mechanisms and rate controlling steps affecting the kinetics of adsorption, the intraparticle diffusion plays an important role in the extent of adsorption and can be expressed as:

$$q_t = k_i t^{0.5} + C \quad (9)$$

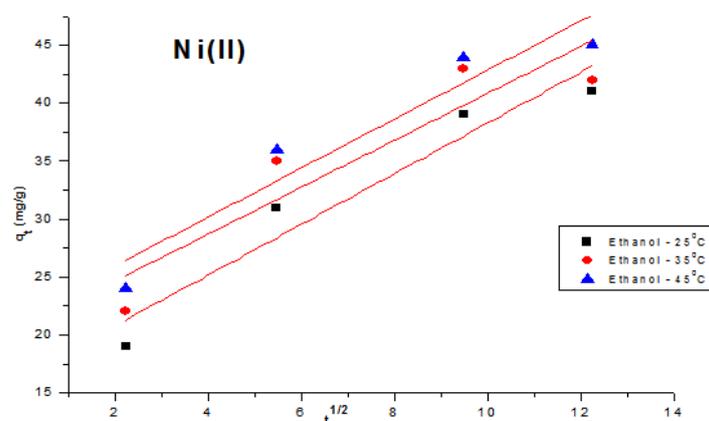
where ( $k_i$ ) is the intraparticle diffusion constant (mg/g min) and the intercept ( $C$ ) reflects the boundary layer effect. The values of  $k_i$  were calculated from slopes ( $k_i$ ) of the plots of  $(q_t)$  Vs. ( $t^{0.5}$ ) (figs. 5-7) and are presented in (Tables 2a,b,c). The plot of  $(q_t)$  Vs. ( $t^{0.5}$ ) should be linear if intraparticle diffusion is involved in the adsorption process and if these lines pass through the origin then intraparticle diffusion is the rate controlling step. When the plots do not pass through the origin, this is indicative of some degree of boundary layer control and further shows that the intraparticle diffusion is not the only rate limiting step, but also other kinetics models may control the rate of adsorption, all of which may be operating simultaneously. In the present work the plots for Mn(II), Co(II) and Ni(II) of  $(q_t)$  Vs. ( $t^{0.5}$ ) do not pass through the origin, showing that intra-particle diffusion is not the only rate controlling step.



**Fig. 5:** Weber plot for the Mn (II) adsorption (7.7mmol/L) by resinx K-8 in case of Ethanol 25% at different temperatures.



**Fig. 6:** Weber plot for the Co (II) adsorption (7.7mmol/L) by resin K-8 in case of Ethanol 25% at different temperatures.



**Fig. 7:** Weber plot for the Ni (II) adsorption (7.7mmol/L) by resin K-8 in case of Ethanol 25% at different temperatures.

##### 5- Study the temperatures and Thermodynamics parameters ( $\Delta H$ , $\Delta S$ , $\Delta G$ and $E_a$ ):

These studies were carried out at divalent Mn(II), Co(II) and Ni(II) metal ion concentration of 452 mg/L at different temperatures, namely, 25, 35 and 45°C in aqueous-Alcoholic solutions and 25% of used alcohol. As seen in each certain temperature and weight percentage of both Ethanol, Ethylene Glycol and Glycerol, the uptake values of Mn(II) in water-Glycerol solutions are less than that in other two water-Alcohols solutions. We can observe that the uptake of manganese Mn(II) increases with the increase of temperature. However, the percentage uptake for Mn(II) at different temperatures of aqueous-Ethanol was 59.1, 61.5 and 63.8%, for aqueous-Ethylene Glycol was 47.3, 52.3 and 59.1%, but 37.8, 44.9 and 45.6% for aqueous-aqueous-Glycerol respectively. As can be seen also from (Figs.8-10), the uptake values of Co(II) and Ni(II) have opposite trend than for obtained in Mn(II) uptake where, uptake of Co(II) and Ni(II) from water-Glycerol solutions are higher than those in other two water-alcoholic solutions.

**Table 2-a:** Kinetic parameters for (7.7 mmol/L) of Mn(II) on Resinex™ K-8 in aqueous-alcoholic solution.

ALCOHOLS	Temp. K	Pseudo first-order model			Pseudo second-order model				Intraparticle diffusion model		
		$q_{e,1,cal}$ (mg/g)	$K_1$ (min <sup>-1</sup> )	$R^2$	$q_{e,2,cal}$ (mg/g)	$K_2$ (g/mg min)	$h$ (mg/g min)	$R^2$	$K_{int}$ mg/g min <sup>-0.5</sup>	$C$ (mg/g)	$R^2$
ETHANOL	298	16.6	0.014	0.9972	26.6	0.00184	1.30	0.9846	1.257	7.40	0.9915
	308	16.9	0.0172	0.9938	27.5	0.00224	1.70	0.9922	1.258	8.90	0.9713
	318	17.6	0.0174	0.8767	28.3	0.00273	2.20	0.9966	1.240	10.50	0.9379
ETHYLENE GLYCOL	298	10.8	0.015	0.9967	22.2	0.0021	0.94	0.9731	0.950	6.16	0.9954
	308	13.4	0.016	0.9559	23.4	0.0020	1.10	0.9781	1.060	6.72	0.9940
	318	14.6	0.017	0.9667	26.7	0.0016	1.14	0.9737	1.270	6.77	0.9359
GLYCEROL	298	12.8	0.0119	0.9787	17.1	0.0029	0.85	0.9809	0.770	5.12	0.9905
	308	14.3	0.0127	0.9871	20.4	0.0024	1.00	0.9825	0.950	5.79	0.9876
	318	17.0	0.0124	0.9904	22.5	0.0023	1.16	0.9862	1.030	6.71	0.9845

**Table 2-b:** Kinetic parameters for (7.7 mmol/L) of Co(II) on Resinex™ K-8 in aqueous-alcoholic solution.

ALCOHOLS	Temp. K	Pseudo first-order model			Pseudo second-order model				Intraparticle diffusion model		
		$q_{e,1,cal}$ (mg/g)	$K_1$ ( $\text{min}^{-1}$ )	$R^2$	$q_{e,2,cal}$ (mg/g)	$K_2$ (g/mg min)	$h$ (mg/g min)	$R^2$	$K_{int}$ $\text{mg/g min}^{-0.5}$	$C$ (mg/g)	$R^2$
ETHANOL	298	18.3	0.0330	0.98732	42.3	0.0047	8.4	0.99962	1.65	22.8	0.81358
	308	17.4	0.0320	0.99235	43.2	0.0051	9.5	0.99957	1.57	24.7	0.83316
	318	17.0	0.0400	0.98852	33.5	0.0065	12.3	0.99987	1.49	26.4	0.74895
ETHYLENE GLYCOL	298	8.2	0.0160	0.84960	43.6	0.0079	15.0	0.99947	0.92	31.96	0.85576
	308	10.8	0.0290	0.99670	43.5	0.0085	16.1	0.99961	0.97	31.91	0.88531
	318	8.8	0.0280	0.98430	43.8	0.0110	21.1	0.99978	0.81	34.20	0.85679
GLYCEROL	298	10.7	0.0027	0.94480	44.8	0.0079	15.1	0.99978	1.06	32.3	0.81310
	308	9.7	0.0028	0.96730	45.0	0.0085	20.3	0.99982	0.92	34.3	0.83274
	318	8.0	0.0240	0.96580	45.5	0.0110	21.7	0.99964	0.78	36.2	0.88651

**Table 2-c:** Kinetic parameters for (7.7 mmol/L) of Ni(II) on Resinex™ K-8 in aqueous-alcoholic solution.

ALCOHOLS	Temp. K	Pseudo first-order model			Pseudo second-order model				Intraparticle diffusion model		
		$q_{e,1,cal}$ (mg/g)	$K_1$ ( $\text{min}^{-1}$ )	$R^2$	$q_{e,2,cal}$ (mg/g)	$K_2$ (g/mg min)	$h$ (mg/g min)	$R^2$	$K_{int}$ $\text{mg/g min}^{-0.5}$	$C$ (mg/g)	$R^2$
ETHANOL	298	24.4	0.028	0.99712	44.7	0.0026	4.9	0.99792	2.20	16.4	0.89802
	308	26.5	0.036	0.99994	46.0	0.0030	6.4	0.9989	2.02	20.6	0.77326
	318	25.4	0.035	0.99978	47.4	0.0032	7.1	0.99895	2.11	21.7	0.87050
ETHYLENE GLYCOL	298	26.3	0.036	0.99880	44.7	0.0024	4.8	0.99980	2.20	17.9	0.85350
	308	40.8	0.058	0.95280	46.0	0.0025	5.3	0.99585	1.60	21.1	0.35935
	318	29.0	0.030	0.98870	47.4	0.0026	5.8	0.99749	2.30	19.9	0.90298
GLYCEROL	298	25.7	0.036	0.99841	45.0	0.0031	6.3	0.99882	2.10	19.8	0.86712
	308	29.6	0.045	0.99730	46.4	0.0033	7.1	0.99585	2.21	20.2	0.81858
	318	26.2	0.044	0.99996	46.8	0.0038	8.3	0.99749	2.06	22.7	0.78714

In general, we can observe that the uptake of cobalt Co(II) increase with the increase of temperature showing endothermic process. This may be due to low stability constant of these divalent metals complexes with the **RESINEX™ K-8**. However, the percentage uptake for Co(II) at different concentrations of aqueous-Ethanol was 90.4, 92.6 and 93.7%, for aqueous-Ethylene glycol was 92.6, 93.7 and 95.4%, and 97, 98.1 and 99.2% for aqueous-Glycerol respectively, and for Ni(II), the percentage uptake for Ni(II) at different temperatures of aqueous-Ethanol was 90.7, 97.3 and 99.8%, for aqueous-Ethylene glycol was 92.9, 95.6 and 99.5%, but 95.1, 98 and 99.5% for aqueous-Glycerol respectively.

The thermodynamic parameters were determined for temperatures ranging from 25 to 45°C using the equilibrium constant  $K_D = (q_e/C_e)$ . The parameters of enthalpy ( $\Delta H$ ) (kJ/mol) and entropy ( $\Delta S$ ) (J/mol) related to the adsorption process were calculated from the following equation:

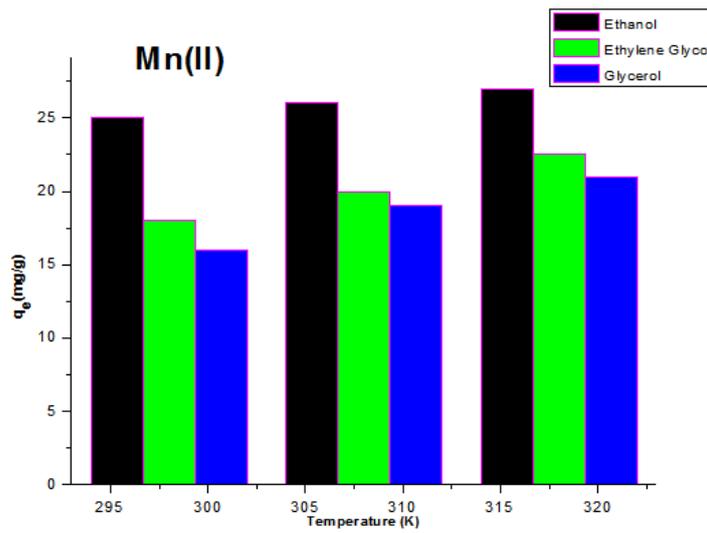
$$\log K_D = \Delta S/2.303R - \Delta H/2.303RT \quad (10)$$

The parameters of enthalpy ( $\Delta H$ ) and entropy ( $\Delta S$ ) can be calculated from the slope and the intercept of the linear plot of  $\ln K_D$  versus  $1/T$ . The data obtained from the thermodynamic parameters are collected in (Tables 3a,b,c). From the data we can observe that the values of ( $\Delta H$ ) were positive for Mn(II), Co(II) and Ni(II) indicating that the adsorption process is endothermic in nature. However, the positive values of ( $\Delta S$ ) showed the increased randomness at the solid/solution interface during the adsorption process. The adsorbed water molecules, which were displaced by the adsorbate species, gained more translational energy than was lost by the adsorbate ions, thus allowing the prevalence of the randomness in the system. In addition, the change in free energy ( $\Delta G$ ) was determined as follows:

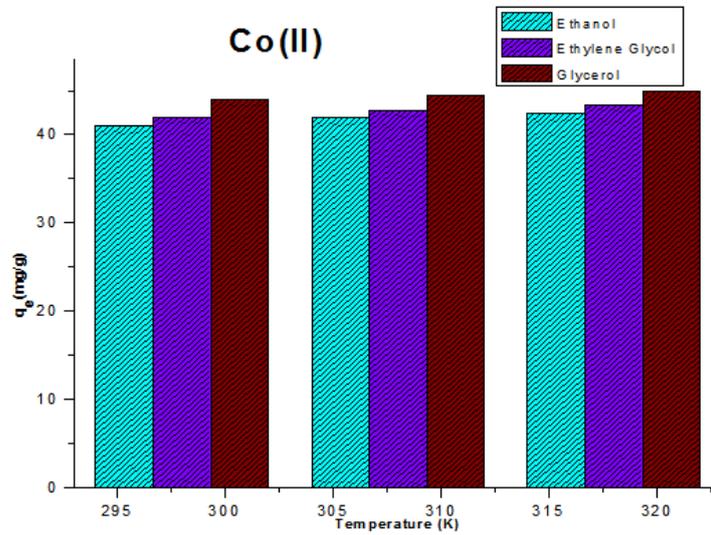
$$\Delta G = -RT \ln K_D \quad (11)$$

where, ( $\Delta G$ ) is the standard free energy (kJ/mol), R is the ideal gas constant (8.314 J/mol K). Depending on the types of the divalent metal ions. The values of standard free energy change ( $\Delta G$ ) were negative for Co(II) and Ni(II) under the conditions applied and was spontaneous. The values of ( $\Delta G$ ) becomes more negative with the increase of temperature indicated more efficient adsorption at high temperature and hence its adsorption become more favorable. While for Mn(II) values of ( $\Delta G$ ) becomes positive with the increase of temperature indicated non-spontaneous processes and lower efficient adsorption at high temperature and hence its adsorption become less favorable at high temperature. The result derived from the references and this work indicates that the thermodynamic parameters are related to the nature of metal ions (Arias and Sen, 2009, Samiey and Toosi, 2010, Sephraet *et al.*, 2013, Francoet *et al.*, 2013 and Sharmaet *et al.*, 2013). The activation energy ( $E_a$ ) (kJ mol<sup>-1</sup>) can also be calculated using the following equation:

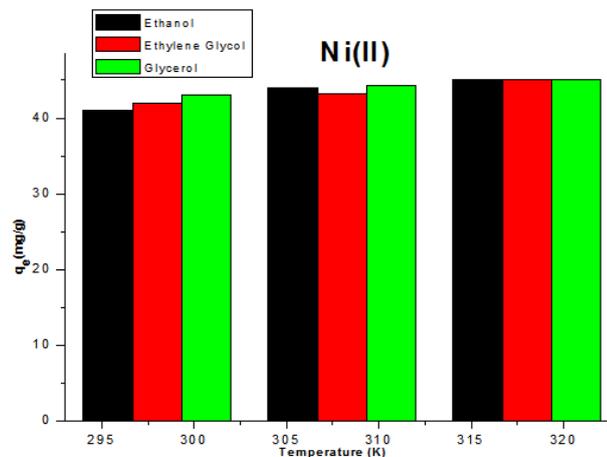
$$\log k_2 = \log A - E_a/2.303RT \tag{12}$$



**Fig. 8:** Effect of temperature on the adsorption uptake of Mn(II) in presence of different alcohols 25% at 25, 35 and 45 °C



**Fig. 9:** Effect of temperature on the adsorption uptake of Co(II) in presence of different alcohols 25% at 25, 35 and 45 °C



**Fig. 10:** Effect of temperature on the adsorption uptake of Ni(II) in presence of different alcohols 25% at 25, 35 and 45 °C

The positive values of activation energy in (Tables 3a,b,c) indicated that the minimum energy is required and endothermic process. The order of activation energy to facilitate the ion exchange processes for the divalent metal ions was observed. The higher activation energy for  $M^{2+}-H^+$  exchange as compared to other  $M^{2+}-H^+$  exchange may be considered due to higher ionic radii even though ionic mobility for the metal ions is same (Alothmanet *al.*, 2012). Our results shows that the removal process is nonactivation chemical adsorption for both cobalt Co(II) and nickel Ni(II), whereas for manganese removal was physical adsorption processes.

**Table 3-a:** Thermodynamic parameters for (7.7 mmol/L) of Mn(II) on Resinex™ K-8 in aqueous-alcoholic solutions.

ALCOHOLS	Temp.K	$\Delta G$ (kJ/mol)	$\Delta S$ (J/mol k)	$\Delta H$ (KJ/mol)	A	Ea (KJ/mol)
ETHANOL	298	4.87	2.4	5.5	0.1700	4.81
	308	4.69	-	-	-	-
	318	4.53	-	-	-	-
ETHYLENE GLYCOL	298	5.97	22.4	12.6	0.0001	-3.30
	308	5.70	-	-	-	-
	318	5.12	-	-	-	-
GLYCEROL	298	6.94	23.0	13.7	0.00018	-2.90
	308	6.42	-	-	-	-
	318	6.13	-	-	-	-

**Table 3-b:** Thermodynamic parameters for (7.7 mmol/L) of Co(II) on Resinex™ K-8 in aqueous-alcoholic solutions.

ALCOHOLS	Temp.K	$\Delta G$ (kJ/mol)	$\Delta S$ (J/mol k)	$\Delta H$ (KJ/mol)	A	Ea (KJ/mol)
ETHANOL	298	-0.16	80.6	24.1	0.13	3.60
	308	-0.56	-	-	-	-
	318	-2.30	-	-	-	-
ETHYLENE GLYCOL	298	-5.41	50.5	14.3	0.26	3.74
	308	-1.30	-	-	-	-
	318	-1.94	-	-	-	-
GLYCEROL	298	-2.88	129.7	35.6	0.45	4.30
	308	-4.15	-	-	-	-
	318	-6.54	-	-	-	-

**Table 3-c:** Thermodynamic parameters for (7.7 mmol/L) of Ni(II) on Resinex™ K-8 in aqueous-alcoholic solutions.

ALCOHOLS	Temp.K	$\Delta G$ (kJ/mol)	$\Delta S$ (J/mol k)	$\Delta H$ (KJ/mol)	A	Ea (KJ/mol)
ETHANOL	298	-0.08	345.2	102.7	0.029	2.6
	308	-3.32	-	-	-	-
	318	-9.90	-	-	-	-
ETHYLENE GLYCOL	298	-0.67	324.4	96.1	0.008	1.4
	308	-1.96	-	-	-	-
	318	-8.14	-	-	-	-
GLYCEROL	298	-1.65	210.9	60.7	0.025	2.3
	308	-4.06	-	-	-	-
	318	-8.14	-	-	-	-

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