

## **Removal of Ca(II) and Mg(II) from Aqueous-Organic Solutions on Strong Cation Exchange of Resinex<sup>TM</sup>K-8H**

**A. A. SWELAM, M.B. AWAD and A.M.A. SALEM**

*Department of Chemistry, Faculty of Science, Al-Azhar University, Cairo, Egypt*

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### **ABSTRACT**

The present study was undertaken to evaluate the feasibility of strong cation exchange of Resinex<sup>TM</sup>K-8H ( $H^+$ -form) for the removal of calcium and magnesium ions from aqueous-organic (acetate, citrate, formalin and thiourea) solutions in different concentrations and temperatures. Batch experiments were performed to study the sorption of the two alkaline earth metal ions on the resin in single and binary systems. The experimental isotherm data were analyzed using the Langmuir, Freundlich, Temkin and D-R equations. The equilibrium data fit well in the Langmuir isotherm except for aqueous-citrate system where Freundlich isotherm was more fitness. The experimental data were analyzed using four sorption kinetic models, pseudo-first and second-order equations, the Elovich and the intraparticle diffusion model equation, to determine the best fit equation for the sorption processes. According to type of the employed system, it was found that the sorption on the resin could be described more favorably by the pseudo-second-order or favorably by the pseudo-first-order kinetic model, also the adsorption process has been found to be endothermic or exothermic. The results of the present study suggest that the resin can be used beneficially in treating industrial effluents containing alkaline earth metal ions.

**Key words:** Adsorption; Removal; Kinetics; Thermodynamic; Steric hindrance

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### **Introduction**

Most of the water resources should be treated for purification before consumption. In some countries, groundwater is the main safe drinking water resource (Bruggen and Vandecasteele, 2003). In some cases, the resource does not satisfy to the desirable levels regarding their chemical properties, such as hardness, nitrate contamination, heavy metals, soluble iron, etc. (Teixeira and Rosa, 2006). Among them, water hardness can appear problematic in some cases; it can also be considered as an important aesthetic parameter. However, because public acceptance of hardness differs remarkably according to local conditions, a maximum acceptable level has not been defined. In general, water supplies with total hardness higher than 200 mg/L can be tolerated by consumers but are considered as poor resources; while values higher than 500 mg/L are not acceptable for most of the domestic consumptions. Hardness in water refers to existing divalent ions, such as iron, manganese, calcium and magnesium. Among them, calcium and magnesium are known as the dominant species for water hardening (Yan *et al.*, 2008, Ritchie *et al.*, 2013). Although it has been shown that water hardness does not have serious health impact, it has been demonstrated that hard water is responsible for the formation of deposits in boiler and household facilities, as well as diverse influence on cleaning performances of detergents (Suzuki *et al.*, 2002). Formation of precipitates may cause a decrease of heat transfer in boiler, a decrease of fluid rate, bursting of water pipeline, the formation of stain in dishes and clothes. Furthermore, high concentrations of magnesium in drinking water may induce a bitter taste (Dimirkou and Doula, 2008). In water purification and treatment plant, lime and soda ash are used for the removal of hardness. One of the main drawbacks of this process is the resulting waste, namely the large amount of liquid sludge produced, as well as the need for re-carbonation of the softened water (Sheikholeslami, 2011, Fu *et al.*, 2009). In addition, the use of additional chemicals to prevent sludge production is restricted and hence in most cases water hardness species cannot be fully removed (Park *et al.*, 2007). Ion exchange processes have been considered as an alternative approach which is commercially in use worldwide. However, high power consumption and periodical regeneration of saturated ion-exchanger resins are needed. Potential hazards of the effluent solutions resulting from the regeneration process should also be taken into account (Seo *et al.*, 2010). Recently, various methods including electrodeionization process (Fu *et al.*, 2009), electro membrane processes (Park *et al.*, 2007), capacitive deionization (Seo *et al.*, 2010), membrane and fluidized pellet reactor (Li *et al.*, 2005), ion exchange process (Apell and Boyer, 2010, Faghidian *et al.*, 1999, Kazemian *et al.*, 2003) and adsorption (Torabian *et al.*, 2010, Seifi *et al.*, 2011) have been studied for the removal of a wide variety of ionic and molecular species from various water streams, including those responsible for hardness (e.g. Ca(II) and Mg (II)cations). Amongst the developed processes, adsorption has been widely studied for the uptake of various ionic and molecular species from water.

### Experimental:

#### (A)- Materials:

All the materials and chemicals (Aldrich, USA) were used as received with analytical grade. Stock solution of calcium and magnesium was prepared by dissolving its chloride (AR Grade) in double distilled water. The stock solution was diluted with distilled water to obtain the desired concentrations. Strong cation exchange of Resinex<sup>TM</sup>K-8H used in this work from Jacobi Swedish Company. Prior to use, the resin was converted to the hydrogen ( $H^+$ ) form by washing it in 1 M HCl followed by further washing in deionized water. The resin regeneration procedures follow the recommendations provided by the manufacturers. The resin was dried at room temperature and kept in a desiccator until it was used.

#### (B)- Batch experiments:

The ion exchange properties of the Resinex<sup>TM</sup>K-8H were determined by the batch equilibrium method in 250 mL conical flasks. The resin sample (0.5g) was suspended in mixture of an aqueous-organic solution (50 mL) of different concentration (0.025, 0.05 and 0.1 M) containing calcium or magnesium ions of known concentration (8.4mmol/L). The different organic materials used here are sodium acetate, sodium citrate, formalin and thiourea. The suspension was shaken at 200 rpm (Hanna-Hi 190M, Singapore) for about 12h at room temperature. The metal ion content was determined by titration against standard EDTA. The amount of the metal ion uptake was calculated from the difference between a blank experiment without the resin and the reading in the actual experiments.

The adsorption capacity in mmol/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 metal ion concentrations (mmol/l), respectively, V is aqueous phase volume (ml) and W is the weight of adsorbent used (g). The data of isotherms were obtained after an equilibrium time of 24 h.

#### Theory of adsorption:

The adsorption equilibrium is usually described by an isotherm equation whose parameters express the surface properties and affinity of the adsorbent. To determine the performance of the adsorbent it is important to get an accurate equilibrium relationship between the solid- and liquid-phase concentrations. In the present study, it is essentially required to test the equilibrium data obtained for Ca(II) or Mg(II) removal using Resinex<sup>TM</sup>K-8H resin with different isotherm models.

Langmuir model has been widely applied to many metal ions sorption process. The basic assumption of the Langmuir theory is that uptake of metal ions occurs on a homogenous surface by monolayer adsorption without any interaction between adsorbed ions that is all the adsorption sites have equal adsorbate affinity and that the adsorption at one site does not affect the adsorption at an adjacent site (Altin *et al.*, 1998). The model takes the following linear form:

$$\frac{C_e}{q_e} = \frac{1}{bQ_m} + \frac{C_e}{Q_m} \quad (3)$$

Where  $Q_m$  is the quantity of adsorbate required to form a single monolayer on unit mass of adsorbent (mmol/g) and  $q_e$  is the amount adsorbed on unit mass of the adsorbent (mmol/g) when the equilibrium concentration is  $C_e$  (mmol/l) and b an empirical parameters Langmuir constant that is related to the apparent energy of adsorption (L/mmol). Eq.(3) shows that a plot of ( $C_e/q_e$ ) versus  $C_e$  should yield a straight line if the Langmuir equation is obeyed by the adsorption equilibrium. The slope and the intercept of this line then yield the values of constants  $Q_m$  and b respectively. A further analysis of the Langmuir equation can be made on the basis of a dimensionless equilibrium parameter,  $R_L$ (Koopal *et al.*, 1994), also known as the separation factor, given by Eq. (4):

$$R_L = \frac{1}{1+bC_0} \quad (4)$$

The value of  $R_L$  lies between 0 and 1 for a favorable adsorption, while  $R_L > 1$  represents an unfavorable adsorption, and  $R_L = 1$  represents the linear adsorption, while the adsorption operation is irreversible if  $R_L = 0$ .

The Freundlich isotherm theory says that the ratio of the amount of solute adsorbed onto a given mass of sorbent to the concentration of the solute in the solution is not constant at different concentrations. The heat of adsorption decreases in magnitude with increasing the extent of adsorption (Agrawal *et al.*, 2004). The linear Freundlich isotherm is commonly expressed as follows:

$$\ln q_e = \ln k_f + (1/n) \ln C_e \quad (5)$$

where  $k_f$  (mmol/L) and  $n$  are the Freundlich constants characteristics of the system, indicating the relative adsorption capacity of the adsorbent related to the bonding energy and the adsorption intensity, respectively. A plot of  $\ln q_e$  versus  $\ln C_e$  yielding a straight line indicates the confirmation of the Freundlich isotherm for adsorption. The constants which are  $k_f$ , and  $n$  can be determined from the slope and the intercept respectively (Memon *et al.*, 2009).

Temkin isotherm model (Baker, 2009) assumes that the heat of adsorption of all the molecules in the layer decreases linearly with the coverage of molecules due to the adsorbate–adsorbate repulsions and the adsorption of adsorbate is uniformly distributed (Kumara *et al.*, 2009) and that the fall in the heat of adsorption is linear rather than logarithmic. The linearized Temkin equation is given by Eq. (6) (Ho and Mckay, 1999):

$$q_e = B_T \ln A_T + B_T \ln C_e \quad (6)$$

where  $B_T = RT/b_T$ ,  $T$  is the absolute temperature in K and  $R$  is the universal gas constant ( $8.314 \text{ Jmol}^{-1} \text{ K}^{-1}$ ). The constant  $B_T$  is related to the heat of adsorption,  $A_T$  is the equilibrium binding constant ( $\text{L min}^{-1}$ ) corresponding to the maximum binding energy (Wang and Qin, 2005). The slope and the intercept from a plot of  $q_e$  versus  $\ln C_e$  determine the isotherm constants  $A_T$  and  $B_T$ .

Another equation used in the analysis of isotherms was proposed by Dubinin and Radushkevich, 1947, (D-R). It does not assume a homogeneous surface or constant sorption potential, but it applied to estimate the porosity apparent free energy and the characteristic of adsorption and it has commonly been applied in the following form

$$\ln q_e = \ln X_m - \beta \epsilon^2 \quad (7)$$

Where  $\beta$  is a constant related to the adsorption energy,  $X_m$  the maximum adsorption capacity,  $\epsilon$  can be calculated from Eq. (7) where;

$$\epsilon = RT \ln (1 + 1/C_e)$$

From the plot of  $\ln q_e$  versus  $\epsilon^2$  of the experimental data for the adsorption of the metal ions by the resin the constants  $\beta$  ( $\text{mol}^2 \text{ kJ}^{-2}$ ) and  $X_m$  ( $\text{mmol g}^{-1}$ ) can be calculated from the slope and the intercept, respectively. The mean free energy of sorption,  $E_s$  (kJ/mol) is the free energy change when one mole of ion transferred from infinity in solution to the surface of the sorbent.  $E_s$  is calculated from the  $\beta$  value using Eq. (8):

$$E_s = 1/\sqrt{-2\beta} \quad (8)$$

#### Adsorption kinetics:

Lagergren showed that the rate of adsorption of solute on the adsorbent is based on the adsorption capacity and followed a pseudo-first-order equation (Yang and Al-Duri, 2005, Ho and Mckay, 1998) which is often used for estimating  $k_1$  considered as mass transfer coefficient in the design calculations. The linear form of the pseudo-first-order equation is described by Eq. (9):

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (9)$$

where  $q_e$  and  $q_t$  are the amounts of Ca(II) or Mg(II) adsorbed (mmol/g) at equilibrium time and at any instant of time  $t$ , respectively, and  $k_1$  (L/min) is the rate constant of the pseudo-first-order sorption. The plot of  $\log(q_e - q_t)$  versus  $t$  gives a straight line for the pseudo first-order adsorption kinetics, from the adsorption rate constant,  $k_1$ , is estimated.

Ho developed a pseudo second-order kinetic expression for the sorption system of divalent metal ions using sphagnum moss peat (Ho, 2006). This model has since been widely applied to a number of metal/sorbent sorption systems. The adsorption of Ca(II) or Mg(II) onto the Resinex™K-8H resin at a short time scale may involve a chemical sorption which implies the strong electrostatic interaction between the Resinex™K-8H functional groups surface and Ca(II) or Mg(II).

The second-order kinetics equation is described in the following form:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (10)$$

Where  $k_2$  (g/mmol min) is the second-order rate constant. The product  $k_2 q_e^2$  is the initial adsorption rate "h"(mmol/g min):

$$h = k_2 q_e^2 \quad (11)$$

$h$  can be regarded as the initial sorption rate as  $t$  approaches 0. Under such circumstances, the plot of  $t/q_t$  versus  $t$  should give a linear relationship, which allows the computation of  $q_e$  and  $k_2$ .

Elovich equation is a rate equation based on the adsorption capacity commonly expressed as following Eq. (12) (Zeldowitsch, 1934):

$$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t) \quad (12)$$

Where  $\alpha$  is the initial adsorption rate (mg/g min) and  $\beta$  the desorption constant (g/ mg) related to the extent of surface coverage and activation energy for chemisorption. Eq. (12) is simplified by assuming  $\alpha\beta \gg t$  and by applying the boundary conditions  $q_t = 0$  at  $t = 0$  and  $q_t = q_e$  at  $t = t$  becomes:

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t) \quad (13)$$

Plot of  $q_t$  versus  $\ln(t)$  and the Elovich constants  $\alpha$  and  $\beta$  were obtained from the intercept and the slope.

## Results and Discussions

### Effect of contact time:

The required contact time for sorption to be completed is important to give insight about the kinetics of the sorption process. Also it gives information on the minimum time required for considerable adsorption to occur, and also the possible diffusion control mechanism between metal ions (adsorbate). The required time for equilibrium could give information about the movement of Ca(II) and Mg(II) ions from the bulk solution toward the adsorbent surface. The adsorption of Ca(II) and Mg(II) ions from different aqueous-organic systems onto Resinex™K-8H was studied at different time periods, with keeping other parameters constant (ion concentration, adsorbent concentration and temperature). The effect of contact time on sorption of Ca(II) and Mg(II) ions onto Resinex™K-8H is shown in Figs.1,2. As can be seen from Figs.1,2, initially, after 1h a rapid raise of removal was obtained, which could be due to the availability of adsorbent active groups. Generally the adsorption kinetics depends on: (i) the adsorbent surface area and (ii) the nature and concentration of the surface active groups present on the adsorbent, which could react with Ca(II) and Mg(II) ions. The equilibrium time was reached in the range 125-335 and 215-675 min for calcium and magnesium adsorption depending on the type of metal-aqueous-organic systems, while after 24 h there is no significant increase in removal of Ca(II) and Mg(II) from the different media. This is due to the decreased or lesser number of active sites. Accordingly, for an initial metal concentration of 8.4 mmol/L, uptake percentage was 94, 20.23, 89.29 and 92.86% of calcium and 67.86, 16.67, 69 and 76.19% of magnesium, respectively, showing a higher affinity for calcium over magnesium.

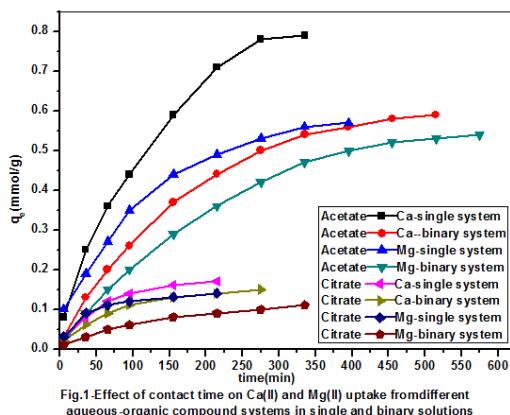


Fig.1-Effect of contact time on Ca(II) and Mg(II) uptake from different aqueous-organic compound systems in single and binary solutions

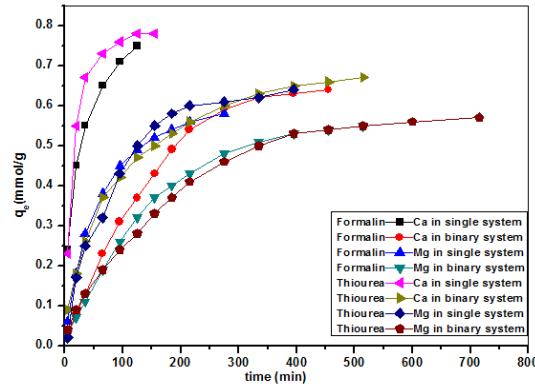


Fig.2-Effect of contact time for Ca(II) and Mg(II) adsorption from different aqueous-organic media in single and binary solutions

### 2- Binary system:

In order to study the interfering effect of Ca(II) and Mg(II) one another, adsorption tests were conducted in the optimal conditions using a mixture of Ca(II) and Mg(II) cations at 8.4 mmol/L for each (Figs.1,2). Cation

uptake was 79.76, 76.19, 70.24 and 17.86% for calcium and 67.86, 65.48, 64.29 and 13.10% for magnesium in aqueous-thiourea, formalin, acetate and citrate systems, respectively. It can be noticed that equilibrium time and adsorption efficiency were lower compared to the values observed in single ion adsorption tests, which can be attributed to a competition between the two cations for occupying the active sites leading to a faster saturation of the adsorbent in the simultaneous presence of calcium and magnesium. Nevertheless and similarly to the single ion adsorption tests, calcium showed higher adsorption compared to magnesium indicating a higher selectivity of the adsorbents for calcium.

### 3- Effect of acetate and citrate solutions on the metal uptake:

The examination of the influence of acetate and citrate at various concentrations (0.025, 0.05 and 0.1M for each) on the position of the equilibrium of Ca(II) and Mg(II)-resin interactions are shown in Fig. 2. As can be seen from the Fig.2 that the amount of both metal ions,  $q_e$ , taken up by the resin sample decreases with increasing concentration of both acetate and citrate solutions. This may be explained in terms of the higher stability constants of the complexes formed by the metal ions with the two electrolytes used in the present study. Comparing with acetate and citrate more significantly inhibited Ca(II) and Mg(II) adsorption, suggest the order of adsorption capacity of the metal complexes, is citrate >acetate complexes. The sizes of the ligands are in the following order; the acetate ( $C_2H_3O_2^-$ ) is the smallest than that of citrate ( $C_6H_7O_7^{2-}$ ). It is therefore likely that the size of the ligands played important role in the order of the metal complex adsorption, where the adsorption capacity of the calcium and magnesium complexes was influenced by the steric hindrance or the crowding effect associated with the comparative bulkiness of the organic ligands in the metal complexes. In general, calcium uptake was higher than that of magnesium, using Resinex<sup>TM</sup>K-8H cation-exchange resin (based on sulfonic acid functional group). Generally, the metal ion forms a complex with the acetate ion and the sorption depends upon the nature of complex formed (Ho and Mckay, 1998). As the concentration of acetate is increased, acetate ion replaces the coordinating water molecule resulting in the formation of complex species of a small positive charge, and consequently  $q_e$  is lowered. A further increase in the concentration of acetate lead to the formation of a neutral species and this also results in decrease of  $q_e$ . When the concentration of acetate is higher and a neutral metal acetate is likely to be present in solution, the predominant species in the resin phase would be  $M^{2+}(OAc)^+$  or  $M^{3+}(OAc)^{2+}$  as inferred by workers (Ho, 2006, Zeldowitsch ,1934).

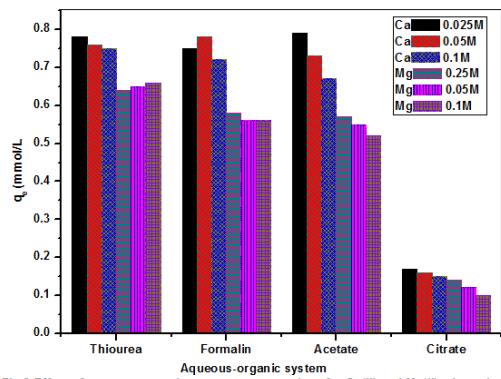


Fig.3-Effect of aqueous-organic system concentrations for Ca(II) and Mg(II) adsorption

### 4- Effect of thiourea and formalin solution.

The effects of thiourea and formaldehyde at various concentrations were also investigated for calcium and magnesium (Fig.3). For aqueous-thiourea system, calcium uptake show slightly decreases with increasing of thiourea concentration, while various concentrations of thiourea does not seem to significantly affect on the magnesium uptake. On the other hand, with increasing of formalin concentration, calcium uptake increases then decrease with higher concentration, while magnesium uptake will decrease then no change with higher formalin concentration. This may be explained in terms of the stability constants of the complexes formed by the metal ions with the organic materials used in the present study (Ying and Yeung2011, Syna *et al.*, 2003, Fernando *et al.*, 2009, Ritchie *et al.*, 2001).

### 5- Adsorption isotherm models:

Further, the obtained sorption data were used to study the sorption isotherms to provide information about the capacity of the resin and to make a comparison between the sorptive capacities for different metal ions under given conditions. The empirical Langmuir and Freundlich isotherms, which in turn correspond to homogeneous

and heterogeneous sorbent surface, respectively, were used to correlate the experimental data. The sorption data obtained for calcium and magnesium-acetate, formalin and thiourea systems onto Resinex<sup>TM</sup>K-8H at three different temperatures (293, 308, and 323 K) were first fitted to the Langmuir sorption isotherm model. The values of the Langmuir constant ( $R_L$ ), the monolayer capacity of sorbent ( $Q_m$ ) and the correlation coefficient ( $R^2$ ) was estimated by linear fit analysis at different temperatures. These values are tabulated in Table 1 and the linear Langmuir sorption isotherm plots for both the metal ions are figured (Figs are hidden). The obtained high values of regression correlation coefficients ( $R^2 = 0.997\text{--}0.999$ ) are in good agreement with the isotherm plots at three different temperature. The plots with high  $R^2$  values confirm that the sorption equilibrium data fitted well to the Langmuir model in these studied conditions for both the metal ions. The fitting of sorption data to Langmuir sorption isotherm reveals that the uniform sorption and strong metal ion-sorbent interactions over the surfaces of the resin. The Langmuir constant,  $Q_m$ , represents the monolayer saturation at equilibrium and  $R_L$  value indicates affinity of sorbent (Sharma *et al.*, 2013). The Langmuir monolayer sorption capacity,  $Q_m$  is found to be higher for Ca(II) sorption on the resin at all temperatures in comparison to that for Mg(II) sorption. The value of  $Q_m$  increases according to the following order; acetate > thiourea > formalin in both the sorption systems *i.e.* Ca(II)-Resinex<sup>TM</sup>K-8H and Mg(II)-Resinex<sup>TM</sup>K-8H. These results reveal that for metal-organic systems was more favorable for the sorption. The increase in sorption intensity and sorption capacity may be due to the change in stability constant of metal complexes. The  $R_L$  values tabulated in Table 1 are found to be positive and less than unity, indicating thereby a highly favorable sorption in both the cases at all the three aqueous-organic systems. The low separation factor  $R_L$  values in case of Ca(II) and Mg(II) sorption on the resin indicate that the metal ions preferred to remain bound to the sorbent surface. The  $R_L$  values obtained from Ca(II)-Resinex<sup>TM</sup>K-8H sorption systems are even lower than those obtained from Mg(II)-resin sorption systems. However, calcium and magnesium-citrate system show opposite trend.

The Freundlich sorption isotherm is the second most widely used mathematical descriptions to characterizing the sorption process. The Freundlich constants  $K_F$  and  $n$  were calculated from the equilibrium data for sorption of Ca(II) and Mg(II) on Resinex<sup>TM</sup>K-8H at three different temperatures (293, 308 and 323 K) and these are reported in Table 1 along with the correlation coefficient ( $R^2$ ) values. The linear Freundlich sorption isotherms plots along with  $R^2$  values corresponding to each plot are given (Fig. is hidden). No satisfactory results were found on fitting the sorption data obtained for both the metal ions onto the resin at aqueous-acetate, formalin and thiourea systems to Freundlich sorption isotherm model. The values of correlation coefficients (0.70–0.99) for each plot reported in Table 1 demonstrate the non-linearity of Freundlich plots. So the calculated values of Freundlich constants could not considered authentic (Sharma *et al.*, 2013). Langmuir sorption isotherm model showed better fit than Freundlich isotherm for both the metal ions. While for calcium and magnesium-citrate system were fitted to the Freundlich sorption isotherm model.

Table 1 summarizes the parameters and correlation coefficients for Temkin and Dubinin–Radushkevich (D-R) isotherms (Figs. are hidden) for Ca(II) and Mg(II) sorption by Resinex<sup>TM</sup>K-8H. The correlation coefficients obtained are  $R^2 \geq 0.98$  for calcium-citrate, formalin systems and magnesium-formalin, thiourea systems, which indicates that the Temkin isotherm fit well the equilibrium data obtained for the adsorption of Ca(II) and Mg(II) onto Resinex<sup>TM</sup>K-8H in these media. However, based on the  $R^2$  value, the Temkin isotherm appears to be less applicable for calcium-acetate, thiourea and magnesium-acetate, citrate systems.

The energy of sorption ( $E_s$ ) calculated from the D-R model indicates uptake of Ca(II) and Mg(II) on the resin sample can be described by the physisorption/ion exchange or chelation mechanism, as  $E_s$  lies between 8 and 16 kJ mol<sup>-1</sup>. Uptake of ions followed a physical adsorption mechanism, as  $E_s$  is less than 8 kJ mol<sup>-1</sup> obeyed a chelating mode of the metal ions trapping, as the  $E_s$  is greater than 16 kJ mol<sup>-1</sup> (Burke, 2013). Projected chemical equations for physisorption/ion exchange of Ca(II) and Mg(II) onto the resin surfaces is given in Eq. while the uptake via chelation is shown in Eq.



The values of correlation coefficients are ranged from 0.92 to 0.63) for calcium in all aqueous-organic media studied here and 0.25 to 0.93 for magnesium-acetate, citrate and thiourea systems, indicating that the D-R model is less fitting to the experimental data in comparable with magnesium-formalin system ( $R^2 \geq 0.99$ ).

According to the above discussion, we can conclude that the Langmuir model appears to be much applicable for most adsorption processes than Freundlich, Temkin and D-R isotherm models.

#### 6- Sorption kinetics:

The kinetics of sorption reaction were studied through performing a series of Ca(II) and Mg(II) sorption experiments onto Resinex<sup>TM</sup>K-8H sorbent at constant initial metal concentration (8.4 mmol/L) and at different temperatures and monitoring the amount sorbed with time. In this study, pseudo-first-order kinetic model, pseudo-second-order kinetic model and Elovich model were investigated to find the best fitted model for the

experimental data. Calculated values of various parameters of all the three models and their correlation coefficients ( $R^2$  values) are summarized in Table 2. As can be seen from the data in Table 2, vary good fitness of the models are observed.

**Table 1:** Adsorption isotherm parameters of calcium and magnesium uptake at different aqueous-organic media.

Metal ion	Langmuir				Freundlich			Temkin			D-R		
	$Q_m$ (mmol/g)	b (L/mmol)	$R_L$	$R^2$	$k_F$ (mmol/L)	n	$R^2$	$A_T$	$B_T$ (L/min)	$R^2$	$q_e$	$E_s$	$R^2$
	Acetate												
Ca(II)	0.78	139	$8.55 \times 10^{-4}$	0.999	0.78	0.07	0.912	0.02	$6.51 \times 10^{-15}$	0.914	0.79	63.23	0.628
Mg(II)	0.55	6.74	0.017	0.985	0.68	8.05	0.742	0.09	$4.92 \times 10^{-4}$	0.779	0.63	65.3	0.252
Citrate													
Ca(II)	0.06	0.22	0.35	0.972	34.41	2.78	0.992	0.61	0.11	0.998	0.09	28.24	0.928
Mg(II)	0.02	0.16	0.42	0.982	33.6	0.13	0.997	0.79	0.12	0.974	3.05	4.87	0.645
Formalin													
Ca(II)	0.56	4.07	0.18	0.996	0.71	7.34	0.393	0.19	0.02	0.993	0.59	260	0.872
Mg(II)	0.45	0.29	0.29	0.999	0.87	1.42	0.929	0.23	0.03	0.997	0.52	170	0.999
Thiourea													
Ca(II)	0.61	6.90	0.02	0.996	0.73	7.08	0.900	0.11	$1.08 \times 10^{-3}$	0.958	0.64	374	0.786
Mg(II)	0.55	3.30	0.04	0.997	0.75	4.39	0.992	0.16	$8.16 \times 10^{-3}$	0.989	0.60	268	0.935

Considering pseudo first order kinetics. The plot give straight lines with good linearity (Fig. is hidden), and the values of first order rate constant ( $k_1$ ) and correlation coefficient ( $R^2$ ) obtained from these plots are listed in Table 2. The first order mechanism could be applied for all Ca(II) and Mg(II)-aqueous-organic systems sorption on Resinex™K-8H sorbent. One of the major discrepancies was observed when  $q_e$  values obtained from Lagergren plot were compared with the experimental  $q_e$  value. The experimental  $q_e$  values differed from the corresponding theoretical values. Thus, good linearity of Lagergren plot is not guarantee that the interactions of the metal ions with the resin will follow first order kinetics. However, Ca(II)-citrate system and Mg(II)-thiourea system could be guarantee that the interactions of the metal ions with the resin will follow first order kinetics. This finding suggests that a pseudo second order sorption could be considered as the predominant mechanism and the overall rate constant of Ca(II) and Mg(II) appears to be controlled by the physisorption process (Zou *et al.*, 2006).

The second order kinetic equation was applied to find more reliable description for reaction kinetics. The plot good linearity (Fig. is hidden) and the correlation coefficient ( $R^2$ ) for Ca(II)-acetate, formalin, thiourea systems and Mg(II)-acetate, citrate, formalin systems, suggesting a strong relationship between the model parameters and explains that the sorption process could follows pseudo second order kinetics. From these data, it was observed that, the calculated correlation coefficient is relatively high and closer to unity for pseudo second order kinetic model than for pseudo first order kinetic model. The calculated equilibrium sorption capacity ( $q_e$ ) is consistent with the experimental data, Table 2.

Based on these results, the sorption reaction could be explained more favorably by the pseudo second order kinetic model. This finding suggests that a pseudo second order sorption could be considered as the predominant mechanism and the overall rate constant of Ca(II) and Mg(II) ions appears to be controlled by the chemisorption process (Yang, 2003). In addition, for both metal ions, the rate constants ( $k_2$ ) for calcium sorption were higher than those observed for magnesium, confirming the higher affinity of the studied adsorbents for calcium over magnesium.

Elovich kinetic model (Fig. is hidden) is often used to interpret the sorption kinetics successfully with describing the chemical sorption on highly heterogeneous sorbents. The Elovich constants  $\alpha$  and  $\beta$  and the correlation coefficients  $R^2$  were reported in Table 2. As can be seen from the data in Table 2, vary good fitness of all calcium and magnesium adsorption systems are observed.

#### 7- Adsorption mechanism:

In this model, it is assumed that the mechanism for calcium and magnesium removal by adsorption on a sorbent material is taking place through four steps: (a) migration of the metal ion from bulk solution to the surface of the adsorbent through bulk diffusion, (b) diffusion of metal ion through the boundary layer to the surface of the adsorbent via film diffusion; (c) the transport of the metal ion from the surface to the interior pores of the particle occur through intra-particle-diffusion or pore diffusion mechanism and (d) the adsorption of the metal ion at an active site on the surface of material by chemical reaction via ion-exchange, complexation and/or chelation. In general, the metal ion sorption is governed by either the liquid phase mass transport rate or through the intra-particle mass transport rate. Pore-diffusion models should be formulated so as to consider not only the particle size but also particle shape. The adsorption process is a diffusive mass transfer process where

the rate can be expressed in terms of the square root of time (t). The intra-particle-diffusion model is expressed as follows (Tofiqhy and Mohammadi, 2011).

$$q_t = k_i t^{0.5} + C \quad (16)$$

**Table 2:** Kinetics parameters of calcium and magnesium uptake by Resinex™K-8H at different aqueous-organic media.

Kinetics parameters	Acetate		Citrate		Formalin		Thiourea	
	Ca(II)	Mg(II)	Ca(II)	Mg(II)	Ca(II)	Mg(II)	Ca(II)	Mg(II)
Pseudo first-order								
$q_1$ (mmol/g)	1.07	0.60	0.16	0.10	0.55	0.54	0.46	0.61
$k_1$ (L/min)	0.143	0.011	0.018	0.016	0.027	0.015	0.032	$6.75 \times 10^{-3}$
$R^2$	0.886	0.956	0.999	0.953	0.994	0.994	0.970	0.998
Pseudo second-order								
$q_2$ (mmol/g)	1.02	0.67	0.20	0.15	0.83	0.70	0.84	0.80
$k_2(g/\text{mmol min})$	$9.73 \times 10^{-3}$	0.002	0.122	0.272	0.161	0.028	0.11	$8.78 \times 10^{-3}$
$h(\text{mmol/g min})$	0.01	$9.02 \times 10^{-3}$	4.94	$6.38 \times 10^{-3}$	0.11	0.01	0.08	$5.61 \times 10^{-3}$
$R^2$	0.966	0.977	0.987	0.998	0.996	0.993	0.999	0.990
Elovic model								
$\beta(g/\text{mg})$	5.53	8.44	25.87	34.09	6.24	7.14	6.27	6.99
$\alpha(\text{mg/g min})$	1.01	2.18	9.24	0.99	5.47	1.73	5.09	1.02
$R^2$	0.904	0.916	0.964	0.995	0.999	0.985	0.925	0.957
Intraparticle diffusion								
$k_i(\text{mmol/g min}^{0.5})$	0.047	0.028	0.012	0.008	0.056	0.037	0.047	0.027
C	0.018	0.049	0.014	0.029	0.175	0.041	0.277	0.039
$R^2$	0.987	0.973	0.944	0.864	0.936	0.933	0.731	0.922

Where  $q_t$  is the fraction the metal ions uptake (mmol/g) at time  $t$ ,  $k_i$  is the intra-particle-diffusion rate constant (mmol/g min $^{0.5}$ ) and C is the intercept (mmol/g). The plot of  $q_t$  versus  $t^{0.5}$  (Fig. is hidden) will give  $k_i$  as slope and C as intercept. The intercept C represents the effect of boundary layer thickness. Minimum is the intercept length, adsorption is less boundary layer controlled.

From the figure, (Fig. is hidden) it seems that for all the cases plots are non linear in nature but careful observation infer that data points can be better represented by double linear with different in slope and intercept. In first straight line, the sudden increase (within a short time period) in slope signifies that the Ca(II) and Mg(II) ions are transported to the external surface of the resin particle through film diffusion and its rate is very fast. After that, the metal ion is entered into the resin particle by intra-particle-diffusion through pore, which is represented in second straight line. From the plots and the data obtained and tabulated in Table 2, we can found that the intercept of the line fails to pass through the origin which may be due to the difference in the rate of mass transfer in the initial and final stages of adsorption. Further, such deviation of the straight lines from the origin reveals that the pore diffusion is not the solerate-controlling step.

#### 8- Effect of the temperature:

This one important parameter can affect the sorption process considerably. So, experiments were made to optimize the favorable temperature to have maximum recovery of alkali metal ions. Experimental results concerning the effect of temperature on Ca(II) and Mg(II) ions sorption at three different temperature (20, 35 and 50°C) were presented in Fig. 4. Results of present temperature study confirm that this resin gave a positive response to an increase in temperature with respect to Ca(II) ion uptake for calcium-acetate, citrate and Mg(II) ion for magnesium-acetate, formalin and thiourea systems. While opposite trends was observed for calcium-formalin, thiourea and magnesium-citrate systems. The increase in temperature is known to increase the rate of diffusion of metal ions across the external boundary layer and in the internal pores of the resin. According to Wang (Wang *et al.*, 2005) changes in temperature also change the equilibrium capacity stability of complex formation of the sorbent-sorbate-aqueous-organic media. The increase in sorption percentage may also be due to the acceleration of some originally slow sorption steps or due to the retardation of the processes such as association of ions, aggregation of molecules, ion pairing and complex formation in the system because of thermal agitation. Furthermore, sometime an increase in temperature will reduce the electrostatic repulsion between the surface and the sorbing species, allowing sorption to occur more readily.

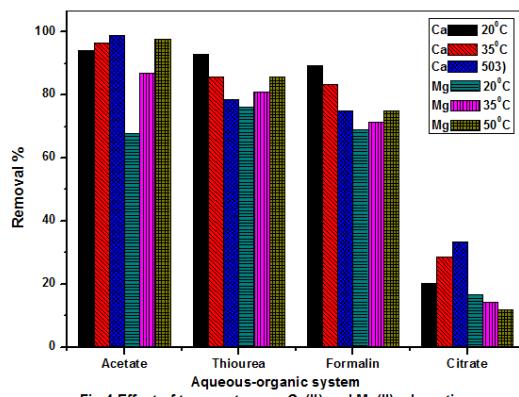


Fig.4-Effect of temperature on Ca(II) and Mg(II) adsorption

Thermodynamic parameters were determined for temperatures ranging from 20 to 50 °C using the equilibrium constant  $k_d$  ( $q_e/C_e$ ). The change in free energy ( $\Delta G^\circ$ ) was determined as follows (Eq. 17):

$$\Delta G^\circ = -RT \ln K_d \quad (17)$$

where,  $\Delta G^\circ$  is the standard free energy (kJ/mol). The parameters of enthalpy  $\Delta H^\circ$  (kJ/mol) and entropy  $\Delta S^\circ$  (J/molK) related to the adsorption process were calculated from the following equation (Eq. 18):

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (18)$$

The parameters of enthalpy ( $\Delta H^\circ$ ) and entropy ( $\Delta S^\circ$ ) can be calculated from the slope and the intercept of the linear plot of  $\ln k_d$  versus  $1/T$ . Fig. 5 shows the thermodynamic plots and the related parameters are collected in Table 3. The values of  $\Delta H^\circ$  were positive for calcium-acetate and citrate systems and magnesium-acetate, formalin and thiourea systems; showing that the sorption reaction was endothermic in nature. While for calcium-formalin and thiourea systems and magnesium-citrate system, the  $\Delta H^\circ$  were negative values; showing that the sorption reaction was exothermic processes.

**Table 3:** Thermodynamic parameters of calcium and magnesium uptake by Resinex at different aqueous- organic media.

Metal ion	$\Delta H$ (kJ/mol)	$\Delta S$ (J/molK)	$\Delta G$ (kJ/mol)	$S^*$	$E_a$ (kJ/mol)	$R^2$
Acetate						
Ca(II)	44.33	154	-1.12	$6.73 \times 10^{-10}$	44.78	0.999
Mg(II)	79.43	265	3.80	$5.49 \times 10^{-4}$	4.89	0.999
Citrate						
Ca(II)	18.02	31.25	8.94	0.07	4.69	0.805
Mg(II)	-10.44	-68.08	9.52	1.43	-1.31	0.820
Formalin						
Ca(II)	-27.34	-94.70	0.438	1.064	22.33	0.907
Mg(II)	8.01	14.76	3.65	0.026	6.06	0.998
Thiourea						
Ca(II)	-33.85	-113.58	-6.33	9701	28.56	0.783
Mg(II)	16.87	47.93	2.77	$8.09 \times 10^{-4}$	13.84	0.975

The positive  $\Delta S^\circ$  value characterized an increase in randomness at the solid/liquid interface during the sorption process, as in calcium-acetate, citrate and magnesium-acetate, formalin and thiourea systems. The negative  $\Delta S^\circ$  value characterized calcium-formalin, thiourea and magnesium-citrate systems showing a decrease in randomness at the solid/liquid interface. In addition, the values of standard free energy ( $\Delta G^\circ$ ) were positive for calcium-citrate, formalin and magnesium-acetate, citrate, formalin and thiourea systems, indicating that the sorption of metals was not thermodynamically spontaneous while for calcium-acetate, thiourea and magnesium-citrate systems,  $\Delta G^\circ$  were negative values, indicating that the sorption processes were spontaneous in nature.

#### 9- Measurement of sticking probability:

The sticking probability in the surface coverage ( $\theta$ ) was evaluated (Singha and Das, 2013) by the following equation.

$$\theta = 1 - \frac{C_e}{C_o} \quad (19)$$

The apparent activation energy ( $E_a$ ) and sticking probability ( $S^*$ ) was estimated by a modified Arrhenius type equation (Fig. is hidden) related to surface coverage as

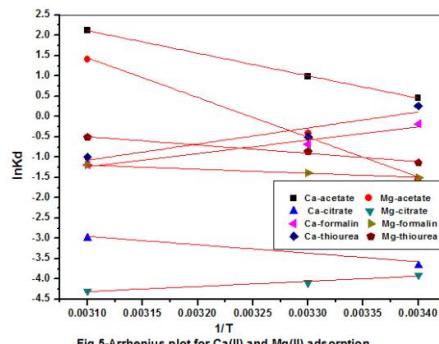


Fig.5-Arrhenius plot for Ca(II) and Mg(II) adsorption

$$S^* = (1 - \theta) \exp\left(-\frac{E_a}{RT}\right) \quad (20)$$

The sticking probability,  $S^*$ , is a measure of metal ion capacity to remain adsorbed indefinitely. The positive values of  $E_a$  for both calcium uptake in aqueous-acetate, citrate and thiourea systems and magnesium in aqueous-acetate, formalin and thiourea systems indicated that the higher solution temperature favors the adsorption process and also the adsorption process is endothermic in nature. Table 3 also indicated that the values of  $S^* \ll 1$ , hence the sticking probability of the Ca(II) and Mg(II) ions onto the resin are very high. While in aqueous-formalin and citrate systems, respectively, calcium and magnesium shows opposite trend.

#### Conclusions:

The process of calcium and magnesium uptake by a selective, cation exchange resin, Resinex™K-8H, was studied through batch kinetic experiments in different aqueous-organic media from single and binary systems. Crowding effect and steric hindrance in the adsorption of these metal ions in single and binary systems on the resin had very important roles. Although pseudo first and second order models described the experimental kinetic data satisfactorily, the model constants (first and second order rate constants) varied significantly with changes in the experimental conditions. Moreover, the applicability of the Elovich model to describe the kinetic data of ion exchange adsorbent was found to be poor compared to the pseudo first and second order models.

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