

Removal of Hardness Agents, Calcium and Magnesium from Different Electrolytes Solutions by ResinexTMK-8H Resin

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ABSTRACT

Experimental measurements have been made on the batch ion exchange of Ca(II) and Mg(II) from aqueous-electrolyte (Cl^- , I^- , Br^- , BrO_3^- , NO_3^- and $\text{S}_2\text{O}_3^{2-}$) solutions in single and binary systems using strong cation exchange of ResinexTMK-8H (Na^+ -form). The ion exchange behavior of two alkaline-earth metals on the resin, depending on contact time, ionic strength and temperature was studied. The adsorption isotherms were described by means of three adsorption isotherms. The fitness order of Langmuir > Temkin >Freundlich for the isotherm models showed the favorability toward monolayer adsorption. The kinetic data were tested using pseudo-second order, pseudo-first-order and Weber-Morris kinetic models. The experimental data for the adsorption processes fitted pseudo second-order kinetic model thereby indicating the chemical nature of the adsorption process. The sorption processes was endothermic in nature. Depending on types of the electrolytes solutions, the ion exchange of these metal ions was spontaneous and non-spontaneous with negative and positive values for ΔG° , respectively.

Key words: Hardness; Electrolytes; Removal; Kinetics; Thermodynamic

Introduction

Hard water is water that has high mineral content mainly calcium and magnesium ions. There are two types of water hardness: temporary and permanent. Temporary hardness is caused by a combination of calcium and bicarbonate ions in water. It can be removed by addition of lime (calcium hydroxide) or by boiling in an open container. Boiling promotes formation of carbonate from bicarbonate and then calcium carbonate is precipitated, and consequently the cooled leaving water is softer. Permanent hardness is usually caused by the presence of calcium and magnesium sulfates in water which become more soluble as temperature rises. Therefore, permanent hardness cannot be removed by boiling. It can be removed by using a water softener which works on the principle of ion exchange in which calcium and magnesium ions are exchanged with sodium ions, reducing the concentration of hardness minerals to tolerable levels and thus making the water softer and giving it a smoother feeling. Water softener gradually loses its effectiveness and must be regenerated. This is accomplished by passing a concentrated brine solution through it, causing the above reaction to be reversed. Most of the salt employed in the regeneration process gets flushed out of the system and is usually released into the soil or drainage systems that can have damaging consequences to the environment, especially in arid regions (Ozer et al., 2013; Cheng et al., 2014).

To avoid the addition of sodium or potassium ions from the softener to the treated water and also the environmental problems of water softeners, developing alternative methods and new materials for hard water softening are important and essential. Among many treatment processes that are currently used for removal of ions from water such as chemical precipitation, evaporation, ion exchange, adsorption, electrodialysis and reverse osmosis, adsorption is a promising and widely applied method due to its cost effectiveness (Rao et al., 2007).

Thus, the present study is focused on the potential of strong-acid cation exchange resin (ResinexTMK-8H, Na^+ -form) in the adsorptive removal of various hazardous metal ions such as calcium and magnesium from aqueous-inorganic salts media and the thermodynamic data discussed in terms of interactions or mechanisms.

Experimental

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.

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Batch experiments

Ion-exchange property of the ResinexTMK-8H (Na^+ -form) was studied with various electrolytes in different concentrations (0.025-0.1M) and temperatures (25-50°C) in a batch system. The exchanger dose was 0.5g/50ml CaCl_2 or MgCl_2 (each 8.4 mmol/l) solution in order to seek the optimum condition for the posterior experiments. The ResinexTMK-8H was mingled with CaCl_2 or MgCl_2 solution at a different initial concentration of Cl^- , I^- , Br^- , BrO_3^- , NO_3^- , SO_3^{2-} and, $\text{S}_2\text{O}_3^{2-}$ in 100 ml conical flask with stopper and then shake for a predetermined period (found out from the kinetic studies) at different temperatures in water bath-cum-mechanical shaker. Afterwards, the concentrations of metal ions were determined.

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

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

$$\text{Ads}\% = \frac{(C_0 - C_e)x100}{C_0} \quad (2)$$

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. After the equilibrium time, the concentrations were determined by AAS varion 6 (Analytik Jena AG Konrad-Zuse-StraBe 1 07745 Jena)

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 ResinexTMK-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 (Hong et al., 2015). The model takes the following linear form:

$$\frac{C_e}{q_e} = \frac{1}{bQ_0} + \frac{C_e}{Q_0} \quad (3)$$

where Q_0 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 (L/mg) is Langmuir constant that is related to the apparent energy of adsorption. 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_0 and b , respectively. A further analysis of the Langmuir equation can be made on the basis of a dimensionless equilibrium parameter, R_L ((Dolinina and Parfenyuk, 2014), 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 (Muhammad et al., 2014). 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 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 $1/n$ can be determined from the slope and the intercept respectively (Memona et al., 2009; Hong et al., 2015).

Tempkin 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 Tempkin equation is given by Eq. (6) (Fathi et al., 2015):

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

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 (L min^{-1}) corresponding to the maximum binding energy (Awual et al., 2014).

The slope and the intercept from a plot of q_e versus $\ln C_e$ determine the isotherm constants A_T and B_T .

D-R isotherm (Dubinin and Radushkevich, 1947; Abdel wahab et al., 2013) was employed to find out the adsorption mechanism based on the potential theory assuming a heterogeneous surface. D-R isotherm is expressed as follows

$$q_e = X_m e^{-\beta \epsilon^2} \quad (7)$$

the linear form was;

$$\log q_e = \log X_m - \beta \epsilon^2 \quad (8)$$

Where X_m is the D-R monolayer capacity (mmol/g), β is a constant related to sorption energy, and ϵ is the Polanyi potential which is related to the equilibrium concentration as follows

$$\epsilon = RT \ln(1 + 1/C_e) \quad (9)$$

Where R is the gas constant (8.314 J/mol K) and T is the absolute temperature. The constant β gives the mean free energy, E, of sorption per molecule of the adsorbate when it is transferred to the surface of the solid from infinity in the solution and can be computed using the relationship.

$$E = \frac{1}{\sqrt{2\beta}} \quad (10)$$

A plot of q_e vs. ϵ^2 (Fig. is hidden) gave a straight line of slope, β and intercept, X_m of different systems were evaluated.

The difference in the free energy between the adsorbed phase and the saturated liquid adsorbate is referred to as the Polanyi potential. Thus the sorption space in the vicinity of the solid surface may be characterized by a series of equipotential surfaces with a given sorption potential. The sorption potential is independent of temperature but varies according to the nature of the adsorbent and adsorbate.

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 (Lidiany et al., 2015) 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:

$$\ln(q_e - q_t) = \ln q_{e,1} - k_1 t \quad (11)$$

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 (Ru et al., 2014).

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:

$$\frac{t}{q_t} = \frac{1}{k_2 q_{e,2}^2} + \frac{t}{q_t} \quad (12)$$

where k_2 (g/mg min) is the second-order rate constant.

Under such circumstances, the plot of t/q_t versus t should give a linear relationship, which allows the computation of $q_{e,2}$ and k_2 (Simon et al., 2015).

Results and Discussion

Evaluation of calcium and magnesium uptake with respect to contact time

Time taken for the adsorption process to attain thermodynamic equilibrium is very important in characterization and prediction of both the efficiency and the feasibility of an adsorbent for its use in water pollution control. Perusal of Figs.1 and 2 reveals that the time taken for the uptake of the calcium and magnesium ions depends on the nature of the electrolyte solutions. As shaking time increases the polymer gets more time for adsorption, hence uptake increases Among the six electrolyte solutions taken for the study, the calcium uptake ($q_e, \text{mmol/g}$) follows the order $I^- > BrO_3^- > Cl^- > NO_3^- > Br^- > S_2O_3^{2-}$ and $BrO_3^- > Cl^- > S_2O_3^{2-} > NO_3^- > I^- > Br^-$ for magnesium.

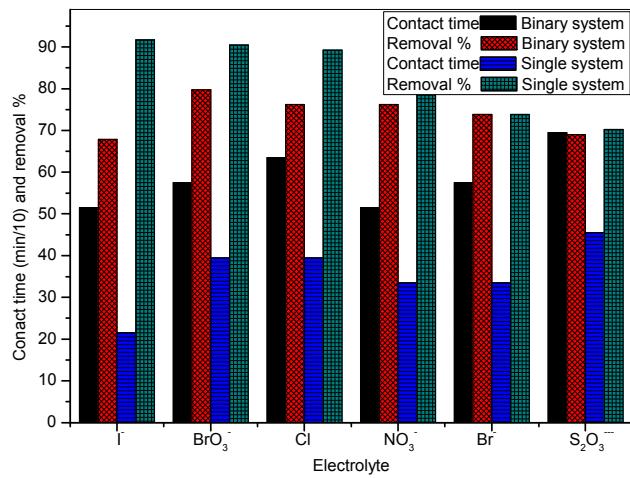


Fig.1-Effect of contact time on Ca(II) adsorption in single and binary systems

The observation indicates that the time required for the metal ion uptake depends on the nature of the metal ions and the ionic size of the metal ions. In general, the ion exchange rate of Ca(II) was faster than that of Mg(II) and the equilibrium exchange capacity of Ca(II) was higher than that of Mg(II) in this study. The Lewis acidity of the cations should follow the charge density of the ions. For this reason considering the charge/ionic radius ratio (Mg^{2+} 0.72°A, Ca^{2+} 0.99°A) the less acidic (Ca^{2+}) cation would be also the higher active (Navalon et al., 2009). Agrawal et al., 2004 have used the Amberlite IRC 718 resin as Na^+ form to treat the waste water containing Ca(II) and Mg(II). They found the equilibrium exchange capacity for Ca(II), was higher than Mg(II).

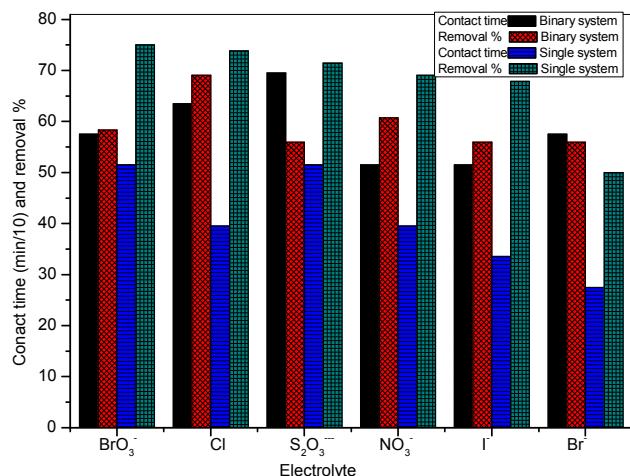


Fig.2-Effect of contact time on Mg(II) adsorption in single and binary systems

Binary system

To examine the competitive effects the metal exert on each other in binary-metal solutions, the removal efficiencies of Resinex™K-8H for each metal (50 ml/0.5g) and binary solutions (100 ml/1.0g) in electrolytes 0.025M Cl^- , I^- , Br^- , BrO_3^- , NO_3^- and $S_2O_3^{2-}$ solutions and at 25°C were compared are shown in Figs.1,2. It can be seen that the percentage removal of Ca^{2+} and Mg^{2+} ions in single-metal system (non-competitive) slightly increased than the binary-metal system, Ca^{2+} - Mg^{2+} ions. It can be also noticed that equilibrium time were higher compared to the equilibrium time 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 slower 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 (q_e) compared to magnesium indicating a higher selectivity of the adsorbent for calcium for all electrolytes systems studied. These results also showed the efficiency of the resin for the removal of calcium and magnesium from water streams.

Evaluation of calcium and magnesium uptake in different electrolytes solutions

The influences of Cl^- , I^- , Br^- , BrO_3^- , NO_3^- and $\text{S}_2\text{O}_3^{2-}$ at various concentrations (0.025, 0.05 and 0.1 M) on the equilibrium state of the metal-resin interaction have been studied at 25°C. The results are shown in the column graphs in Fig. 3. It reveals that the amount of metal ion taken up by the given amount of Resinex™K-8H (Na^+ -form) depends on the nature and concentration of the electrolytes (Singru and Gurmule, 2010).

Generally as the electrolyte concentration increases, the ionization decreases, in the solution which form the complex with fewer amounts of metal ions and still more ions are available for adsorption. The variable metal ions uptake capacity of Resinex™K-8H (Na^+ -form) may be due to the strong and weak complex formation between electrolyte solution and the metal ions.

Electrolyte solution + metal ion solution + Resin \rightarrow electrolyte–metal ion complex + Resin–metal ion complex. If electrolyte–metal ion complex is weaker than the resin–metal ion complex, the resin can break easily the electrolyte–metal complex which generates more number of free metal ions which can easily complexes with the resin and hence uptake of metal ion increases. Further, if electrolyte–metal ion complex is stronger than the Resin–metal ion chelates, more number of metal ions will try to form strong complex with the electrolyte which in turn decreases the metal uptake capacity of the resin. In our studies we observed that in the electrolytes Cl^- , I^- , Br^- , BrO_3^- , NO_3^- and $\text{S}_2\text{O}_3^{2-}$ –calcium system, the amount of Ca^{2+} ions uptake increase with increasing the electrolyte concentration. This may be explained in terms of the stability constants of the complexes formed by the metal ions with the anions used in the present study, where calcium form weak chelates with the electrolyte ions solution.

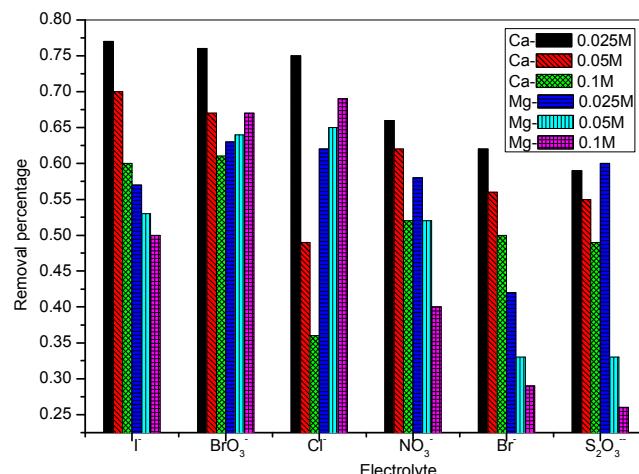


Fig.3-Effect of different electrolyte concentrations on removal percentage of $\text{Ca}(\text{II})$ and $\text{Mg}(\text{II})$.

On the other hand the uptake of magnesium ion by the above polymer increases with decreasing concentration of Cl^- and, BrO_3^- . This may be due to these anions form strong chelates with Mg^{2+} ion, while I^- , Br^- , NO_3^- and $\text{S}_2\text{O}_3^{2-}$ ions form weak complex with the same metal ion leading to increases of Mg^{2+} ion uptake with increase of these electrolytes concentration.

The influences of most anions-calcium systems in general, are higher on the position of metal chelates at equilibrium compared to that of these electrolytes-magnesium systems. This may be explained on the basis of the stability constants of the complexes with these metal ions. The stability of the complexes depends on the charge of the metal ions and nature of the electrolyte. Hence the overall calcium uptake capacity by the resin is higher compared to magnesium. These types of trends has already been observed by other investigators (Azarudeen et al., 2011; Dutta and Das, 2007; Jadhao et al., 2008).

Adsorption isotherms

Equilibrium data, commonly known as adsorption isotherms, are basic requirements for the design of adsorption systems. Ion-exchange equilibrium of calcium and magnesium onto Resinex™K-8H resin was measured at 8.4 mmol/l under different temperatures and the experimental data were analyzed by the Langmuir,

Freundlich and Temkin isotherm models. The calculated adsorption parameters and correlation coefficient (R^2) for the three isotherm models by linear regression are listed in Table 1. Based on

Table.1a: Adsorption isotherm parameters of Ca(II) and Mg(II) in aqueous solution.

| Salts | | Langmuir parameters | | | | Freundlich parameters | | |
|---|----|----------------------------|-------------|-----------------------|----------------|-----------------------|----------------------------|----------------|
| | | Q ₀ (mmol/g) | b (L/mg) | R _L | R ² | n | K _F (mmol/g) | R ² |
| NaCl | Ca | 0.74 | 162 | 7.71x10 ⁻⁴ | 0.99909 | 34.48 | 0.74 | 0.79794 |
| | Mg | 0.54 | 3.95 | 0.03 | 0.99874 | 4.52 | 0.71 | 0.98024 |
| NaNO ₃ | Ca | 0.63 | 12.19 | 0.009 | 0.99681 | 8.5 | 0.69 | 0.93658 |
| | Mg | 0.44 | 1.88 | 0.07 | 0.99976 | 3.04 | 0.75 | 0.98872 |
| KBr | Ca | 0.53 | 3.67 | 0.03 | 0.99923 | 4.6 | 0.7 | 0.99598 |
| | Mg | 0.3 | 0.89 | 0.12 | 0.98872 | 1.67 | 0.95 | 0.98249 |
| KI | Ca | 0.48 | 2.75 | 0.05 | 0.99451 | 56 | 0.76 | 0.95772 |
| | Mg | 0.77 | 1300 | 9.61x10 ⁻⁵ | 1.0 | 3.89 | 0.71 | 0.97325 |
| KBrO ₃ | Ca | 0.75 | 309 | 0.004 | 0.99931 | 48.24 | 0.75 | 0.96086 |
| | Mg | 0.55 | 4.6 | 0.03 | 0.99807 | 5.45 | 0.7 | 0.99407 |
| Na ₂ S ₂ O ₃ | Ca | 0.54 | 5.13 | 0.02 | 0.99344 | 5.19 | 0.69 | 0.96655 |
| | Mg | 0.5 | 2.99 | 0.04 | 0.99911 | 3.85 | 0.72 | 0.98598 |
| Na ₂ SO ₃ | Ca | Ppt. | | | | | | |
| | Mg | 0.42 | 1.7 | 0.07 | 0.9991 | 2.67 | 0.78 | 0.99797 |
| Thiourea | Ca | 0.65 | 26.24 | 4.74x10 ⁻³ | 0.99968 | 11.85 | 0.69 | 0.95507 |
| | Mg | 0.6 | 8.56 | 0.01 | 0.99761 | 7.11 | 0.69 | 0.94143 |

the correlation coefficient (R^2) value for these isotherm models, it was found that the experimental data of calcium and magnesium adsorption on this adsorbent could be described best by the Langmuir model. The correlation coefficient of the isotherm models for Resinex™K-8H adsorbent followed the order: Langmuir >Freundlich>Temkin. It was known that Langmuir isotherm model applied to homogeneous adsorbent surface. (Low et al., 2011; Zhang et al., 2010).

The values of the separation factor (R_L) were calculated for different temperatures and constant initial metal concentration (8.4 mmol/l) and were found between 0 and 1 (0.001–0.009 and 0.001–0.12 for calcium and magnesium adsorption on Resinex™K-8H, respectively), indicating a favorable adsorption process, as confirmed from the values of the Langmuir model. Maximum sorption capacities according to the Langmuir constant (Q_0) for calcium and magnesium adsorption using various electrolyte solutions are listed in Table 1 to allow comparison with the results from the present work. In addition and for various electrolyte solutions, the experimental q_e values for calcium sorption were higher than those observed for magnesium, confirming the higher affinity of the studied adsorbent for calcium over magnesium.

Table.1b: Adsorption isotherm parameters of Ca(II) and Mg(II) in aqueous solution.

| Salts | | D-R parameters | | | | Temkin parameters | | |
|---|----|---|----------------------------|---------------|----------------|-------------------------|---------------------------|----------------|
| | | B (mg ² /J ²) | X _m (mmol/g) | E (kJ/mol) | R ² | K _T (L/g) | B _T (J/mol) | R ² |
| NaCl | Ca | 0.75 | 0.001 | 20 | 0.62735 | 3.5x10 ⁻¹⁴ | 0.02 | 0.91431 |
| | Mg | 0.58 | 0.06 | 2.94 | 0.93766 | 6.81x10 ⁻³ | 0.14 | 0.9903 |
| NaNO ₃ | Ca | 0.66 | 0.01 | 8.33 | 0.732 | 1.47x10 ⁻⁴ | 0.08 | 0.93658 |
| | Mg | 0.61 | 0.06 | 2.94 | 0.73749 | 0.02 | 0.22 | 1.0000 |
| KBr | Ca | 0.58 | 0.07 | 2.94 | 0.98775 | 0.08 | 0.14 | 0.99598 |
| | Mg | 0.38 | 0.47 | 1.03 | 0.91784 | 0.06 | 0.3 | 0.99514 |
| KI | Ca | 0.77 | 6.58x10 ⁻⁴ | 0.887 | 0.9800 | 11x10 ⁻¹⁹ | 0.21 | 0.95772 |
| | Mg | 0.54 | 0.09 | 2.44 | 0.90109 | 0.01 | 0.17 | 0.98108 |
| KBrO ₃ | Ca | 0.76 | 8.64x10 ⁻⁴ | 2.50 | 0.92471 | 2.74x10 ⁻¹⁶ | 0.02 | 0.96086 |
| | Mg | 2.01 | 0.13 | 1.96 | 0.98485 | 0.004 | | 0.98485 |
| Na ₂ S ₂ O ₃ | Ca | 0.58 | 0.04 | 3.45 | 0.88656 | 0.004 | 0.12 | 0.97019 |
| | Mg | 0.58 | 0.06 | 2.86 | 0.9569 | 0.01 | 0.16 | 0.99028 |
| Na ₂ SO ₃ | Ca | ppt | | | | | | |
| | Mg | 0.5 | 0.16 | 1.79 | 0.98222 | 0.028 | 0.21 | 0.99928 |
| Thiourea | Ca | 0.66 | 0.01 | 7.14 | 0.89316 | 1.36x10 ⁻⁵ | 0.06 | 0.9675 |
| | Mg | 0.63 | 0.02 | 5.00 | . 0.70020 | 7.785x10 ⁻⁴ | 0.1 | 0.95675 |

The Freundlich isotherm model that is appropriate for heterogeneous systems is expressed by Eq. (5). Large values of K_F reveal high affinity of the adsorbate. For a favorable adsorption, the value of the adsorption affinity constant (n value) obtained from the Freundlich equation ranged from 1 to 10, which implied favorable adsorption of calcium and magnesium for this adsorbent, Temkin constants B_T and A_T were calculated at all temperatures. These isotherm parameters are given in Table 1. The obtained A_T values indicated a good

potential for Ca(II) and Mg(II), the heat of adsorption B_T increased by increasing the temperature (Shaikh et al., 2013).

A comparison of calculated and measured results for different adsorption models at various temperatures is tabulated in Table 1. It is obviously that, the Langmuir equation provides the best correlation for Ca(II) and Mg(II) ions. From the above discussion we can concluded that, the fitness order of Langmuir > Temkin > Freundlich for the isotherm models for magnesium and calcium uptake, showed the favorability toward monolayer adsorption.

Adsorption kinetics

For a successful scale-up of hard water softening using the kinetic studies are essential since they describe the adsorbate uptake rate, which in turn controls the residence time in the adsorbent–solution interface. In order to analyze the adsorption kinetics of hard mineral ions, three kinetic models including the pseudo-first-order (Lagergren, 1898), the pseudo-second-order (Ho and McKay, 1998) and intra-particle diffusion kinetic models. (Tofiqhy and Mohammadi, 2011) were applied to fit the experimental data (Figs. is hidden). The effect of the temperatures was investigated to find the best kinetic model.

The slope and the intercept of each linear plot are used to calculate the adsorption rate constants (k_1 , k_2 and k_p) and the amount of adsorption in equilibrium (q_e). The calculated kinetic parameters for adsorption of hard mineral ions onto the Resinex™K-8H under different initial hard mineral ion concentrations are listed in Tables 2a and 2b. As can be observed, the correlation coefficients (R^2) of the pseudo-second-order kinetic model are higher than those of the pseudo-first-order and intraparticle diffusion kinetic model. Also, the experimental q_e values are closer to q_e values calculated from the pseudo-second-order kinetic model especially at lower temperature. With increasing temperature, the deviation of the q_e values calculated from the pseudo-second-order kinetic model from the experimental q_e values increases. In addition 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.

Table.2a: Kinetic parameters of Ca(II) and Mg(II) in aqueous-inorganic salt solutions.

| Salts | Temp.K | Intraparticle diffusion model | | | Pseudo first-order model | | | Pseudo second-order model | | | | |
|-------------------|--------|--|-------------|----------------|----------------------------------|--|----------------|----------------------------------|---------------------------------|-----------|----------------|---------|
| | | K _P (mg/g min ^{-0.5}) | C (mg/g) | R ² | q _{e,1,cal} (mmol/g) | K ₁ (min ⁻¹) | R ² | q _{e,2,cal} (mmol/g) | K ₂ (g/mg min) | h | R ² | |
| NaCl | Ca | 301 | 0.03729 | 0.06094 | 0.96697 | 0.76 | 0.01004 | 0.97686 | 0.88 | 0.0152447 | .012 | 0.97867 |
| | | 313 | 0.03883 | 0.06027 | 0.96667 | 0.77 | 0.01024 | 0.98856 | 0.91 | 0.0146625 | 0.012 | 0.98071 |
| | | 323 | 0.04018 | 0.06633 | 0.95135 | 0.77 | 0.01075 | 0.99842 | 0.93 | 0.0152737 | 0.013 | 0.98307 |
| | Mg | 301 | 0.02876 | 0.09876 | 0.94963 | 0.57 | 0.01070 | 0.95409 | 0.69 | 0.027224 | 0.013 | 0.99294 |
| | | 313 | 0.02890 | 0.12824 | 0.95717 | 0.59 | 0.01121 | 0.97562 | 0.72 | 0.0286940 | 0.015 | 0.99015 |
| | | 323 | 0.03003 | 0.14804 | 0.94963 | 0.63 | 0.01248 | 0.97815 | 0.76 | 0.0285028 | 0.017 | 0.98966 |
| NaNO ₃ | Ca | 301 | 0.03779 | 0.03452 | 0.94331 | 0.67 | 0.01276 | 0.99757 | 0.80 | 0.017994 | 0.012 | 0.98473 |
| | | 313 | 0.04113 | 0.04279 | 0.94075 | 0.73 | 0.01310 | 0.99787 | 0.87 | 0.017073 | 0.013 | 0.99167 |
| | | 323 | 0.04118 | 0.10476 | 0.87583 | 0.71 | 0.01538 | 0.99737 | 0.88 | 0.024143 | 0.019 | 0.99706 |
| | Mg | 301 | 0.03063 | 0.02745 | 0.96094 | 0.64 | 0.01157 | 0.98324 | 0.71 | 0.011962 | 0.009 | 0.98289 |
| | | 313 | 0.03023 | 0.06560 | 0.93554 | 0.60 | 0.01224 | 0.99484 | 0.70 | 0.022863 | 0.011 | 0.98826 |
| | | 323 | 0.03256 | 0.07579 | 0.94309 | 0.65 | 0.01397 | 0.96491 | 0.71 | 0.027404 | 0.014 | 0.98716 |
| KBr | Ca | 301 | 0.0354 | 0.03332 | 0.95822 | 0.73 | 0.01486 | 0.98118 | 0.76 | 0.018693 | 0.011 | 0.97641 |
| | | 313 | 0.03501 | 0.06504 | 0.94343 | 0.69 | 0.01480 | 0.99056 | 0.75 | 0.023749 | 0.013 | 0.98368 |
| | | 323 | 0.03529 | 0.11072 | 0.90305 | 0.63 | 0.01469 | 0.99664 | 0.77 | 0.030655 | 0.018 | 0.99376 |
| | Mg | 301 | 0.02365 | 0.04250 | 0.92113 | 0.42 | 0.0127 | 0.96547 | 0.50 | 0.035558 | 0.009 | 0.99652 |
| | | 313 | 0.02599 | 0.06422 | 0.92888 | 0.46 | 0.01344 | 0.99455 | 0.56 | 0.036769 | 0.011 | 0.99229 |
| | | 323 | 0.02813 | 0.09693 | 0.94039 | 0.52 | 0.01364 | 0.98583 | 0.63 | 0.036824 | 0.015 | 0.99298 |
| KI | Ca | 301 | 0.04215 | 0.10260 | 0.95738 | 0.71 | 0.01352 | 0.98109 | 0.91 | 0.021712 | 0.018 | 0.94616 |
| | | 313 | 0.04298 | 0.10991 | 0.95259 | 0.94 | 0.01911 | 0.93706 | 0.91 | 0.0236285 | 0.020 | 0.98024 |
| | | 323 | 0.04239 | 0.13389 | 0.93705 | 0.88 | 0.01903 | 0.95329 | 0.91 | 0.0263752 | 0.022 | 0.98486 |
| | Mg | 301 | 0.03171 | 0.05133 | 0.93254 | 0.59 | 0.01420 | 0.98989 | 0.68 | 0.024664 | 0.011 | 0.99788 |
| | | 313 | 0.03486 | 0.05791 | 0.91246 | 0.64 | 0.01527 | 0.99316 | 0.74 | 0.022807 | 0.013 | 0.99770 |
| | | 323 | 0.03736 | 0.07677 | 0.90747 | 0.68 | 0.01486 | 0.99416 | 0.80 | 0.022994 | 0.015 | 0.99900 |

Accordance of the experimental data with the pseudo-second-order kinetic model indicates that the adsorption of hard mineral ions onto the Resinex™K-8H is controlled by chemical adsorption (Lichun et al., 2014). Chemical adsorption as one basic type of the adsorbate–adsorbent interactions involves valence forces through sharing or exchanging electrons between adsorbent and adsorbate. In chemical adsorption, it is assumed that the adsorption capacity is proportional to the number of active sites occupied on the adsorbent. Generally, the adsorption process can be either electrostatic or chemical in nature, and frequently involves both (Ghaedi et al., 2014). The results demonstrated that the adsorption process of hard mineral ions onto the Resinex™K-8H

involves both electrostatic and chemical interactions. At higher temperature, adsorption is controlled by electrostatic interactions, while at low temperature, adsorption is controlled by chemical interactions.

To identify the diffusion mechanisms, the intraparticle diffusion model was also tested (Tofighy and Mohammadi, 2011):

$$q_t = k_p t^{1/2} + C \quad (13)$$

where k_p (mg/g min^{1/2}) is rate parameters for intraparticle diffusion q_t is the amount of Ca(II) or Mg(II) adsorbed on ResinexTMK-8H resin at different instances of time t (min). According to this model, it can be assumed that the mechanism involves the diffusion of the species if a straight line is obtained passing through the origin from the plot of Eq. (10), and the slope of the linear curve is the rate constant of intraparticle transport (k_p). Such plots indicated that two or more steps take place. The first, sharper portion is the external surface adsorption or instantaneous adsorption stage. The second portion is the gradual adsorption stage, where intraparticle diffusion is rate-controlled. The third portion is the final equilibrium stage where intraparticle diffusion starts to slow down due to extremely low adsorbate concentrations in the solution. In general, the slope of the line in stage 2 is called as intraparticle diffusion rate constant. The rate parameters, k_p , together with the correlation coefficients are also listed in Table 2b. From the data obtained we can conclude that the intraparticel diffusion is not the only rate limiting step, but also other kinetic models may control the rate of adsorption, all of which may be operating simultaneously. A comparison of calculated and measured results for different kinetic models at 8.4 mmol/l of calcium or magnesium concentrations for various temperatures were tabulated in Table 2b. It is obviously that, the pseudo-second-order kinetic model provides the best correlation for both calcium and magnesium adsorption.

Table.2b: Kinetic parameters of Ca(II) and Mg(II) in aqueous-inorganic salt solutions.

| Salts | Te mp. K | Intraparticle diffusion model | | | Pseudo first-order model | | | Pseudo second-order model | | | | |
|---|----------|--|----------|----------------|--------------------------------|-------------------------------------|----------------|--------------------------------|---------------------------|----------|----------------|---------|
| | | K _p (mg/g min ^{-0.5}) | C (mg/g) | R ² | q _{e,1,cal} (mmol /g) | K ₁ (min ⁻¹) | R ² | q _{e,2,cal} (mmol /g) | K ₂ (g/mg min) | h | R ² | |
| KBrO ₃ | Ca | 301 | 0.03741 | 0.09848 | 0.92793 | 0.75 | 0.01208 | 0.98691 | 0.87 | 0.019984 | 0.015 | 0.99577 |
| | | 313 | 0.03725 | 0.11704 | 0.91690 | 0.74 | 0.01264 | 0.99314 | 0.88 | 0.021963 | 0.017 | 0.99604 |
| | | 323 | 0.03632 | 0.16039 | 0.88906 | 0.67 | 0.01262 | 0.99829 | 0.88 | 0.027398 | 0.021 | 0.99633 |
| | Mg | 301 | 0.02768 | 0.06696 | 0.93926 | 0.61 | 0.00855 | 0.99068 | 0.73 | 0.016865 | 0.009 | 0.99381 |
| | | 313 | 0.02796 | 0.10135 | 0.89454 | 0.56 | 0.00852 | 0.99008 | 0.75 | 0.020107 | 0.011 | 0.99753 |
| | | 323 | 0.02881 | 0.13500 | 0.85696 | 0.52 | 0.00880 | 0.98051 | 0.79 | 0.022454 | 0.014 | 0.99671 |
| Na ₂ S ₂ O ₃ | Ca | 301 | 0.02733 | 0.06104 | 0.95752 | 0.53 | 0.00846 | 0.99831 | 0.68 | 0.019795 | 0.009 | 0.98640 |
| | | 313 | 0.02906 | 0.08567 | 0.94411 | 0.61 | 0.01013 | 0.99606 | 0.74 | 0.020611 | 0.011 | 0.98820 |
| | | 323 | 0.03597 | 0.09013 | 0.94331 | 0.74 | 0.01209 | 0.98789 | 0.84 | 0.019997 | 0.014 | .99169 |
| | Mg | 301 | 0.02620 | 0.05735 | 0.96938 | 0.62 | 0.00853 | 0.98595 | 0.70 | 0.015860 | 0.008 | 0.98086 |
| | | 313 | 0.03040 | 0.07333 | 0.93389 | 0.64 | 0.01052 | 0.99592 | 0.76 | 0.018001 | 0.011 | 0.98395 |
| | | 323 | 0.03277 | 0.09735 | 0.90735 | 0.66 | 0.01247 | 0.98791 | 0.77 | 0.024202 | 0.014 | 0.98788 |
| Na ₂ SO ₃ | Ca | 301 | Ppt. | | | | | | | | | |
| | | 313 | Ppt. | | | | | | | | | |
| | | 323 | Ppt. | | | | | | | | | |
| | Mg | 301 | 0.02791 | 0.05899 | 0.95674 | 0.58 | 0.01187 | 0.99105 | 0.66 | 0.022345 | 0.010 | 0.98180 |
| | | 313 | 0.02841 | 0.85160 | 0.94088 | 0.57 | 0.01189 | 0.99629 | 0.67 | 0.027841 | 0.012 | 0.98860 |
| | | 323 | 0.03109 | 0.10061 | 0.93915 | 0.58 | 0.01423 | 0.99285 | 0.69 | 0.032695 | 0.016 | 0.99142 |
| Thiourea | Ca | 301 | 0.05926 | 0.12465 | 0.89734 | 0.79 | 0.03283 | 0.97496 | 0.89 | 0.053282 | 0.043 | 0.99313 |
| | | 313 | 0.05736 | 0.11525 | 0.94092 | 0.67 | 0.02460 | 0.99027 | 0.88 | 0.050084 | 0.040 | 0.99223 |
| | | 323 | 0.04221 | 0.13493 | 0.84908 | 0.65 | 0.02676 | 0.99707 | 0.75 | 0.057400 | 0.032 | 0.99657 |
| | Mg | 301 | 0.02546 | 0.08099 | 0.91413 | 0.61 | 0.00762 | 0.99278 | 0.81 | 0.010557 | 0.007 | 0.98246 |
| | | 313 | 0.02856 | 0.10013 | 0.89793 | 0.67 | 0.00791 | 0.99752 | 0.91 | 0.098440 | 0.008 | 0.98566 |
| | | 323 | 0.02869 | 0.13313 | 0.87133 | 0.64 | 0.00793 | 0.99587 | 0.93 | 0.011009 | 0.010 | 0.98616 |

Whereas, the pseudo-first-order equation also fits the experimental data well. The pseudo-first-order equation and the intraparticle equation do not give good fits to the experimental data (Hong et al., 2015) for the sorption of calcium and magnesium onto ResinexTMK-8H resin.

Effect of the temperature

The effect of ionic strength (0.025M Cl⁻, I⁻, Br⁻, BrO₃⁻, NO₃⁻and, S₂O₃²⁻ solutions) at different temperatures (25, 35 and 50 °C on calcium and magnesium adsorption on strong cation exchange of ResinexTMK-8H (Na⁺-form) is illustrated in Fig.4. As can be seen, the calcium removal tended to increase with

the increase of temperatures in all electrolyte systems. A similar trend was also observed for magnesium adsorption.

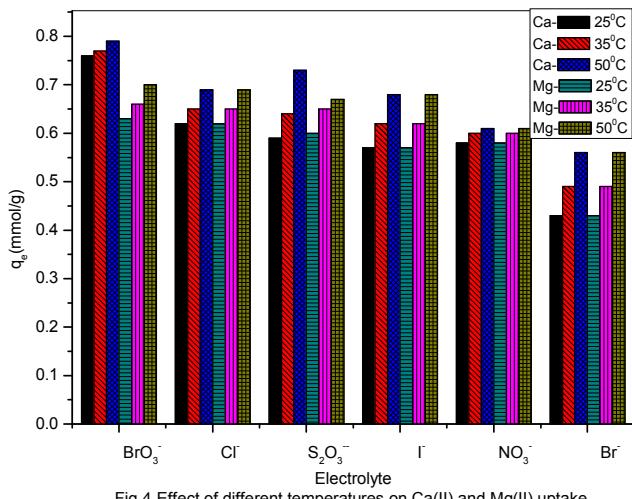


Fig.4-Effect of different temperatures on Ca(II) and Mg(II) uptake

In magnesium-0.025M Cl^- , I^- , Br^- , BrO_3^- , NO_3^- and $\text{S}_2\text{O}_3^{2-}$ solutions, the q_e values show increase with increase of temperatures, as well as for calcium-0.025M Cl^- , I^- , Br^- , BrO_3^- , NO_3^- and $\text{S}_2\text{O}_3^{2-}$ solutions. Enhancement of the adsorption capacity at higher temperatures may be attributed to the enlargement of pore size and/or activation of the adsorbent surface (Jhaa et al., 2008).

From Figs.5 and 6, thermodynamic parameters were determined for temperatures ranging from 25 to 50°C using the equilibrium constant K_D (q_e/C_e). The change in free energy (ΔG°) was determined as follows:

$$\Delta G^\circ = -RT \ln K_D \quad (14)$$

where, ΔG° is the standard free energy (kJ/mol), R is the ideal gas constant (8.314j/mol K). The parameters of enthalpy ΔH° (kJ/molK) and entropy ΔS° (J/mol) related to the adsorption process were calculated from the following equation:

$$\ln K_D = \Delta S^\circ / R - \Delta H^\circ / RT \quad (15)$$

The values of ΔH° were positive for all systems used herein indicating that the adsorption process is endothermic in nature.

The positive values of ΔS° 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, Depending on types of the electrolytes solutions,

The parameters of enthalpy (ΔH°) and entropy (ΔS°) 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 plots and the related parameters are collected in Table 3.

The values of standard free energy change (ΔG°) were negative under the conditions applied, the ion exchange of the metal ions was spontaneous. The values of ΔG° becomes more negative with the increase of temperature, indicated more efficient adsorption at high temperature and hence its adsorption become more favorable or non-spontaneous with the positive values for ΔG° ((Yoon et al., 2014); Samiey and Toosi, 2010; Sepehra et al., 2013; Franco et al., 2013; Sharma, 2013).The result derived from the references and this work indicates that the thermodynamic parameters are related not only to the nature of metal ions, but also to the nature of aqueous-electrolyte solutions.

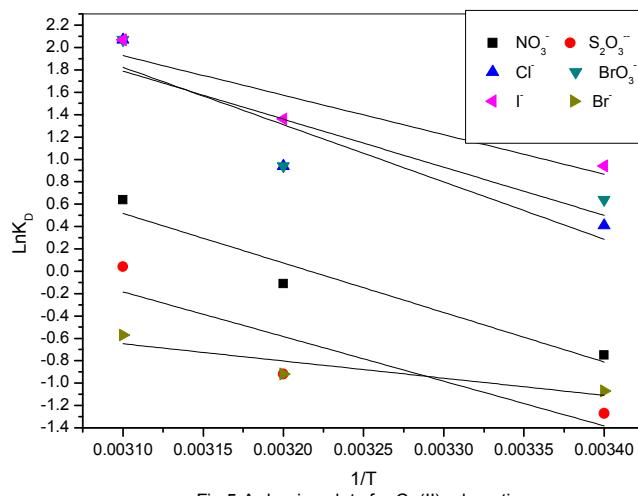


Fig.5-Arrhenius plots for Ca(II) adsorption

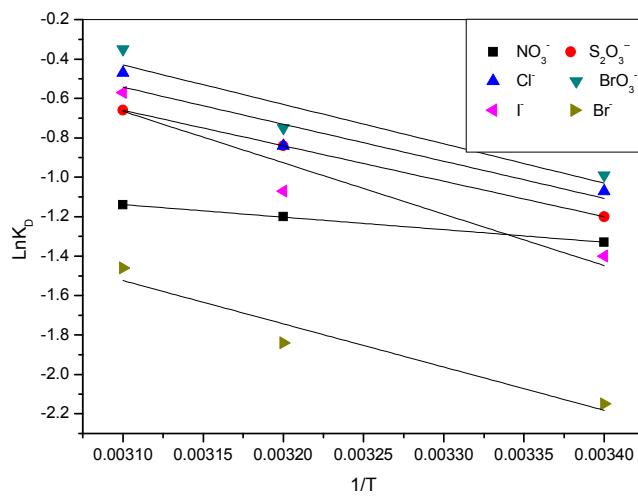


Fig.6-Arrhenius plots for Mg(II) adsorption

Table 3: Thermodynamic parameters of Ca(II) and Mg(II) in aqueous solutions.

| | NaCl | | KI | | KBr | | KBrO ₃ | | NaNO ₃ | | Na ₂ S ₂ O ₃ | | Na ₂ SO ₃ | | Thiourea | |
|--------------------------|--------|--------|--------|--------|--------|--------|-------------------|--------|-------------------|--------|---|--------|---------------------------------|--------|----------|--------|
| | Ca(II) | Mg(II) | Ca(II) | Mg(II) | Ca(II) | Mg(II) | Ca(II) | Mg(II) | Ca(II) | Mg(II) | Ca(II) | Mg(II) | Ca(II) | Mg(II) | Ca(II) | Mg(II) |
| ΔS^0 (J/molK) | 147.16 | 43.90 | 106.9 | 61.66 | 34.1 | 43.8 | 125.7 | 47.9 | 118.4 | 6.92 | 101.3 | 40.9 | ppt. | 17.5 | -4.00 | 50.73 |
| ΔH^0 (kJ/mol) | 42.58 | 15.62 | 29.34 | 21.68 | 12.77 | 18.23 | 35.75 | 16.63 | 36.82 | 5.29 | 33.20 | 14.97 | | 8.73 | -1.48 | 16.92 |
| ΔG^0 (kJ/mol) | | | | | | | | | | | | | | | | |
| 301K | -1.00 | 2.61 | -2.29 | 3.41 | 2.61 | 5.24 | -1.56 | 2.41 | 1.83 | 3.24 | 3.09 | 2.92 | | 3.56 | 0.34 | 2.24 |
| 313K | -7.76 | 2.15 | -0.48 | 2.74 | 2.36 | 4.71 | -7.76 | 1.92 | 0.28 | 3.07 | 2.36 | 2.15 | | 3.25 | 0.13 | 2.82 |
| 323K | -5.56 | 1.26 | -5.56 | 1.53 | 1.53 | 3.92 | -5.56 | 9.40 | 1.72 | 3.06 | 0.11 | 1.77 | | 3.06 | 3.65 | 1.10 |

Author contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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