



Removal of Ca(II) and Mg(II) from potassium chromate solution on Amberlite IRC 748 synthetic resin by ion exchange

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ABSTRACT

Experimental measurements have been made on the batch ion exchange of Ca(II) and Mg(II) from potassium chromate solution using cation exchanger of Amberlite IRC 748 as K⁺ form. The ion exchange behavior of two alkaline-earth metals on the resin, depending on contact time, pH, temperature and resin dosage was studied. The adsorption isotherms were described by means of the Langmuir and Freundlich isotherms. For Ca(II) ion, the Langmuir model represented the adsorption process better than the Freundlich model. The maximum ion exchange capacity was found to be 47.21 mg g⁻¹ for Ca(II) and 27.70 mg g⁻¹ for Mg(II). The kinetic data were tested using Lagergren-first-order and pseudo-second-order kinetic models. Kinetic data correlated well with the pseudo-second-order kinetic model, indicating that the chemical adsorption was the rate-limiting step. Various thermodynamic parameters such as Gibbs free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were also calculated. These parameters showed that the ion exchange of Ca(II) and Mg(II) from potassium chromate solution was feasible, spontaneous and endothermic process in nature. The activation energy of ion-exchange (E_a) was determined as 12.34 kJ mol⁻¹ for Ca(II) and 9.865 kJ mol⁻¹ for Mg(II) according to the Arrhenius equation.

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1. Introduction

Chromium trioxide is an important chromium compound and accounts for nearly 60% of all chromium derivatives. In the industrial manufacture of chromium trioxide, the traditional method of decomposing sodium dichromate using sulfuric acid is widely applied [1]. However, the long-flow process discharges large amounts of high chromium-containing waste solutions that can cause serious environmental problems [2]. As hexavalent chromium Cr(VI) is one of the most dangerous heavy metals, the maximum permissible concentration for Cr(VI) in waste water is 0.05 mg l⁻¹ legally [3]. Exposure to hexavalent chromium can cause dermatitis, allergic skin reactions and gastrointestinal ulcers. It has also been reported that micro-solubility chromate salts can be a teratogen and a carcinogen [4,5]. Therefore, manufacturing chromium trioxide by electrolyzing chromate salts as a green process with zero emission of waste is studied widely now [6]. However, the key problem of electro-synthesis method is the requirement for high quality chromate salts in the cells; otherwise the polyvalent metal ions, especially Ca(II) and Mg(II), would penetrate the ion exchange membrane to form particles with OH⁻ which

block the pores of the membrane. It would result in reducing the flow rate of the electrolytic solution, decreasing current efficiency, increasing the electrical resistance of the membrane, and shorting the service life of the membrane. Even the membrane itself might be rapidly destroyed. So, it is essential to refine chromate salts before electro-synthesis of chromium trioxide.

The usual methods for removal of alkaline-earth metals from aqueous solution can be ordered as chemical precipitation, ion exchange, ultrafiltration, reverse osmosis, electrodialysis and adsorption [7–9]. But the selected method is based on the concentration of metal ions and the cost of treatment [8,9]. Ion exchange is a well-established technique, particularly in water purification, the concentration and removal of metal ions at very low concentrations in chemical process industries [10]. The main advantages of ion exchange over other techniques are the recovery of the metals' value, high selectivity, less sludge volume produced and the ability to meet strict discharge specifications. In addition, the simplicity of ion exchange operation makes it attractive to the chemical purification field. In this regard, ion-exchange resins hold great potential for the removal of metals from water and industrial wastewater [11–13].

Ion-exchange resins with chelating functional groups such as iminodiacetic acid (IDA), aminophosphonic acid, and amidoxime have a particularly high selectivity for heavy metals from waste waters. Applications of polymeric resins containing iminodiacetate

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groups as active sites such as Chelex 100, CR-10, Dowex A-1, Amberlite IRC 748 (formerly, IRC 718), Purolite S930, and Lewatit TP 207 have been extensively applied for the recovery of Ca^{2+} , Mg^{2+} from aqueous solution [1,14–19]. This is because IDA group could provide electron pairs so that the binding forces for alkaline-earth metals is 5000 times than those for alkali metals like Na^+ , which react with divalent metals to form a stable coordination covalent bond. Among the commercially available products, Amberlite IRC 748 is one of the most well characterized regarding its applications [15–17]. However no detailed kinetic and equilibrium studies for this resin as K^+ form on the adsorption of alkaline-earth metals from potassium chromate solution.

In order to evaluate the performance of ion exchange process, predictions of the ion exchange partitioning between an aqueous solution and ion exchanger's surface are required. For this purpose, batch adsorption techniques are performed to obtain the distribution function of a solute between the solid and solution phase at equilibrium.

In this study, Amberlite IRC 748 as K^+ form was used for the removal of $\text{Ca}(\text{II})$, $\text{Mg}(\text{II})$ from potassium chromate solution. The main objective of this study was to investigate the parameters that influence ion exchange, such as agitation time, pH of solution, temperature and resin dosage. In addition, the equilibrium, kinetics and thermodynamics parameters were also evaluated from the ion-exchange measurements.

2. Experimental

2.1. Reagents and ion-exchange resin

The resin used in the experiments was Amberlite IRC 748 from Rohm Haas. The physical and chemical properties of the resin are shown in Table 1. Double deionized water (Milli-Q Millipore $18.2 \text{ M}\Omega \text{ cm}^{-1}$ conductivity) was used for all dilutions. Analytical grade reagent of potassium chromate (K_2CrO_4) was purchased from Tianjin Fucheng Chemical Reagent Co. Guaranteed grade reagent of CaCl_2 , MgCl_2 and other inorganic chemicals including HCl, KOH were purchased from Beijing Chemical Reagent Co.

2.2. Apparatus

Inductively coupled plasma spectrometry (PE 5300-DV) was used for metal analysis. pH was measured by using a glass electrode (mettler toledo S20 meter). A thermo stated shaker (Jiangsu Taicang Laboratorial Equipment Factory, DSHZ-300A) was used for ion exchange experiments.

2.3. Batch adsorption procedure

Prior to use, the resins were washed with HCl and KOH, converted to K^+ form and then, the K^+ form resins decanted and washed with deionized water to remove possible organic and inorganic impurities sticking to the surface. They were then dried in vacuum oven at 60°C to constant weight. The working solutions containing 400 g l^{-1} K_2CrO_4 and $50\text{--}250 \text{ mg l}^{-1}$ $\text{Ca}(\text{II})$ (or $\text{Mg}(\text{II})$) were prepared

Table 1
Characteristics of Amberlite IRC 748.

Matrix	Macroporous styrene divinylbenzene
Functional groups	Iminodiacetic acid
Physical form	Opaque, beige beads
Ionic form as shipped	Na^+
Total exchange capacity	$\geq 1.35 \text{ equiv. l}^{-1}$ (Na^+ form)
Particle size	0.50–0.65 mm
Maximum operating temperature	90°C
pH range	1.5–14 (depending on application)

by dissolving a certain amount of K_2CrO_4 and CaCl_2 (or MgCl_2) in double deionized water. The adsorption of $\text{Ca}(\text{II})$, $\text{Mg}(\text{II})$ on resin was studied by the batch technique. The general method was used for this study is described as follows: resins and solution dumped into a vessel and after mixing, the solution and the resins allowed for equilibrium for 24 h in the shaker. The resins were separated by filtration and washed in deionized water. The filtrate was analyzed by ICP-AES. All experiments were performed in triplicate and the results were the average value.

The concentration of metal ion on the resin was calculated as the difference between the original concentration in the solution and the concentration in solution, after contact. The amount of metal ion adsorbed at time t , q_t , was obtained as follows:

$$q_t = \frac{(C_0 - C_t) \times v}{m} \quad (1)$$

where q_t (mg g^{-1}) is the equilibrium adsorption capacity, C_0 and C_t (mg l^{-1}) are the liquid phase concentrations of solutes at the initial and given time t , v (l) is the volume of solution and m (g) is the weight of resin. When equilibrium was reached; $C_t = C_e$ and $q_t = q_e$, then the amount of metal ion adsorbed at equilibrium, q_e was calculated using Eq. (1) [11].

The initial pH of the sample solutions were adjusted in the range of 8.5–13.5 by using HCl or KOH solution. Adsorption isotherms were carried out with different initial concentrations varying from 50 to 250 mg l^{-1} of metal ions while keeping the resin amount at constant value at room temperature (25°C). Resin amount in the batch vessel was varied from 0.02 to 0.12 g for ion exchange studies. Contact time ion exchange experiments were conducted at 25°C in a well-mixed plastic vessel with a cover. The ion exchange of $\text{Ca}(\text{II})$, $\text{Mg}(\text{II})$ on the resin at different temperatures ranging from 25 to 60°C was investigated. The agitating speed was 180 rpm to maintain resin particles in suspension.

3. Results and discussion

Amberlite IRC 748 was studied in removal of $\text{Ca}(\text{II})$, $\text{Mg}(\text{II})$ from potassium chromate solution under different experiment conditions such as contact time, pH, temperature and resin dosage. The experimental results and the relevant observations are discussed in the following sections.

3.1. Effect of contact time on removal of $\text{Ca}(\text{II})$, $\text{Mg}(\text{II})$

Fig. 1 shows the effect of contact time on the removal of $\text{Ca}(\text{II})$, $\text{Mg}(\text{II})$ from potassium chromate solution by Amberlite IRC 748. It is clear that the uptake of $\text{Ca}(\text{II})$, $\text{Mg}(\text{II})$ increased with the lapse of time. The percentage of metal ions adsorbed increased rapidly

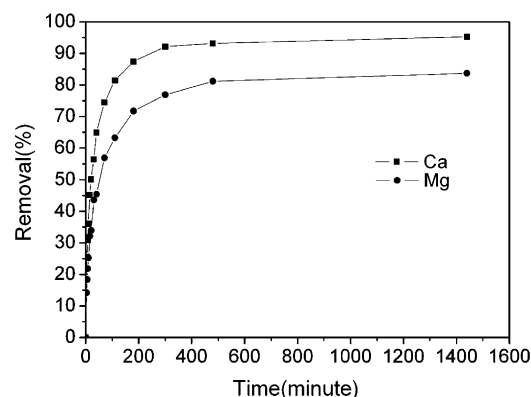


Fig. 1. Effect of contact time on removal of $\text{Ca}(\text{II})$, $\text{Mg}(\text{II})$ (pH, 9.8 for $\text{Ca}(\text{II})$ and 9.5 for $\text{Mg}(\text{II})$; amount of resin, 0.05 g; temperature, 25°C ; agitating rate, 180 rpm).

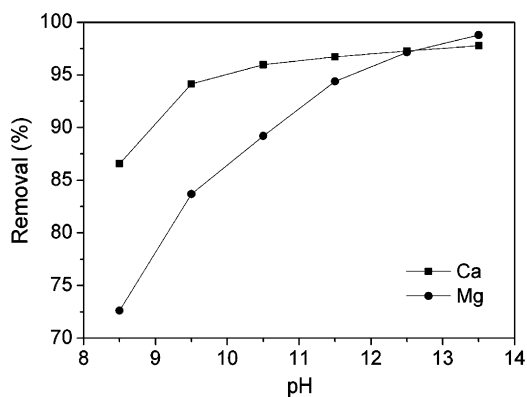


Fig. 2. Effect of pH on removal of Ca(II), Mg(II) (temperature, 25 °C; agitating rate, 180 rpm; amount of resin, 0.05 g; initial metal concentration, 100 mg l⁻¹).

during a few minutes at first, and then increased slowly until the equilibrium state was reached. The figure reveals that over 65% adsorption was occurred within 40 min for Ca(II), over 45% adsorption was occurred within 40 min for Mg(II) and the equilibrium were both attained within 480 min. A further increase in contact time had a negligible effect on the removal. The initial adsorption rate was very fast may be due to the existence of greater number of resin sites available for the adsorption of metal ions. It results in the amount of adsorbate accumulated on the resin surface increased rapidly. As the remaining vacant surface sites decreasing, the adsorption rate slowed due to formation of repulsive forces between the alkaline-earth metals on the solid surface and in the liquid phase. These lead to a decrease of adsorption rate and were well exhibited by plateau lines after 480 min adsorption occurred. The curves of metal uptake versus time are single, smooth and continuously leading to saturation, suggesting the possible monolayer coverage of metal ions on the surface of the resin. 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 exchange capacities for Ca(II) and Mg(II) were 19.06 and 16.73 mg g⁻¹, respectively. The maximum removal were 95.34% and 83.67% for Ca(II) and Mg(II), respectively. Agrawal et al. [18] 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 is 2.30 mequiv. g⁻¹ for Ca(II), 2.13 mequiv. g⁻¹ for Mg(II).

3.2. Effect of pH

The variable that has the most significant effect on the affinity of a resin for a particular ion is pH. In order to study the effect of this parameter on the alkaline-earth metal adsorption from potassium chromate solution by Amberlite IRC 748, solution initial pH was varied within the range of 8.5–13.5. The effect of pH on the removal of Ca(II), Mg(II) by the ion-exchange resins was shown in Fig. 2.

The results (Fig. 2) show that the pH value is very significant for the performance of exchangers, thus pH adjustment may be a feasible alternative to prepare effluent for ion exchange. The ion exchange of Ca(II) increased sharply at pH range of 8.5–9.5. At pH > 9.5, the exchange percentage increased slowly with pH increasing. The percentage of removal for Mg(II) increased rapidly when the pH is increased above 9.5 due to formation of Mg(II) precipitation. It has been reported that alkaline-earth metals are bonding to the IDA functional group by dual mechanisms involving ion exchange and chelation, and ion-exchange is a weaker binding mechanism than chelation. The increase in solution pH may cause the shift from ion exchange to chelation binding mechanism for calcium and magnesium ions [15]. In this study, all

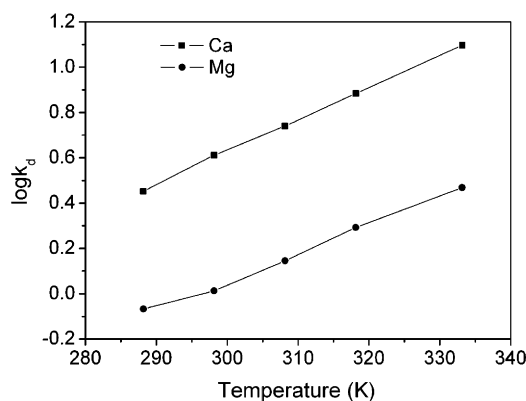


Fig. 3. Effect of temperature on removal of Ca(II), Mg(II) (pH, 9.8 for Ca(II) and 9.5 for Mg(II); agitating rate, 180 rpm; amount of resin, 0.05 g; initial metal concentration, 100 mg l⁻¹).

the experiments were conducted at pH of 9.8 for Ca(II), 9.5 for Mg(II).

3.3. Effect of temperature

To study the effect of temperature on the ion exchange of Ca(II), Mg(II) from potassium chromate solution by Amberlite IRC 748 resin, we selected the following temperatures: 298.15, 308.15, 318.15 and 333.15 K.

In general, the experimental conditions such as metal ion concentration and temperature have strong effects on equilibrium distribution coefficient value (k_d); so it can be used as a comparative measure to the efficiencies of various exchangers. Equilibrium distribution coefficient value (k_d) was calculated using the following equation [20]:

$$K_d = \frac{q_e}{C_e} \quad (2)$$

where q_e is the amount of metal ion adsorbed at equilibrium (mg g⁻¹), and C_e is the equilibrium concentration of metal ion in solution (mg l⁻¹).

Fig. 3 illustrates the relationship between temperature and distribution coefficient (K_d). The K_d values for Ca(II), Mg(II) were very high and they increased with temperature increasing, and the reaction products were favored at high temperatures, as seen in Fig. 3. This is probably due to the endothermic ion exchange reactions of divalent cations.

3.4. Effect of resin dosage

The resin amount is an important parameter to obtain the quantitative uptake of metal ion. The retention of the metals was examined in the relation to the amount of the resin. Fig. 4 shows the removal of Ca(II), Mg(II) as a function of resin dosage using Amberlite IRC 748. The resin amount varied from 0.02 to 0.12 g and equilibrated for 24 h at the initial metal ion concentration of 100 mg l⁻¹ in 400 g l⁻¹ potassium chromate solution. It is apparent that the equilibrium concentration in liquid phase and contact time required to reach equilibrium decreased with increasing resin dose for a given initial metal concentration. These results were anticipated because increasing adsorbent dose could provide a great of surface area or ion-exchange sites for a fixed initial solute concentration [21]. It may be also concluded that the removal efficiency increases and ion-exchange density decreases with the increasing of adsorbent dose. The decrease in ion-exchange density can be attributed to the fact that some of the ion exchanger remains unsaturated during the adsorption process, whereas the number of

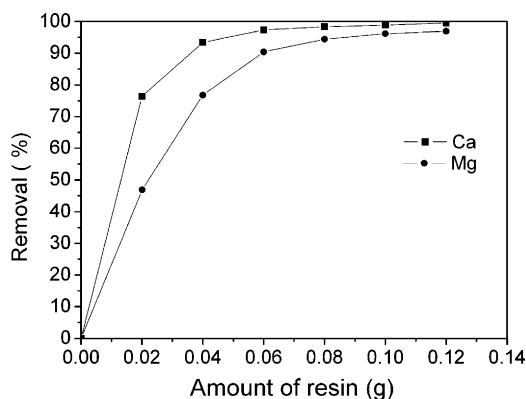


Fig. 4. Effect of resin dosage on removal of Ca(II), Mg(II) (pH, 9.8 for Ca(II) and 9.5 for Mg(II); agitating rate, 180 rpm; temperature, 25 °C; initial metal concentration, 100 mg l⁻¹).

available ion-exchange sites increases with the increasing of resin dosage and results in an increase in removal efficiency. It is clear from Fig. 4 that for the quantitative removal of 100 mg l⁻¹ calcium and magnesium in 10 ml solution, a minimum resin dosage of 0.06 g for Ca(II) and 0.08 g for Mg(II) is required.

3.5. Ion-exchange isotherms

Adsorption isotherms are very powerful tools for the analysis of adsorption process. Adsorption isotherms establish the relationship between the equilibrium pressure or concentration and the amount of adsorbate adsorbed by the unit mass of adsorbent at a constant temperature. The Langmuir and Freundlich isotherm models are widely used to investigate the adsorption process. The model parameters can be construed further, providing understandings on adsorption mechanism, surface properties, and an affinity of the adsorbent.

The Langmuir isotherm is expressed as [22]:

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

where C_e is the equilibrium concentration (mg l⁻¹) in solution, q_e is the solid phase adsorbate concentration at equilibrium (mg g⁻¹). The constant Q_0 gives the theoretical monolayer adsorption capacity (mg g⁻¹) and b is related to the energy of adsorption (l mg⁻¹). The Langmuir isotherm is applied to adsorption on a completely homogenous surface with negligible interaction between adsorbed molecules. The model assumes uniform energies of ion exchange on to the surface and no transmigration of the adsorbate in the plane of the surface.

The Freundlich isotherm model is expressed as [23]:

$$\log q_e = \log k_f + (1/n) \log C_e \quad (4)$$

where k_f is related to adsorption capacity and n is related to intensity of adsorption. The Freundlich isotherm described as a fairly satisfactory empirical isotherm used for non-ideal adsorption is related to heterogeneous process as well as multilayer adsorption.

The linearized Langmuir and Freundlich adsorption of Ca(II), Mg(II) are given in Figs. 5 and 6. The Langmuir and Freundlich adsorption constants evaluated from isotherms and their correlation coefficients are presented in Table 2. It is clear that the Langmuir isotherm model provide an excellent fit to the equilibrium adsorption data, giving correlation coefficients of 0.9972 for Ca(II) and 0.9939 for Mg(II), respectively.

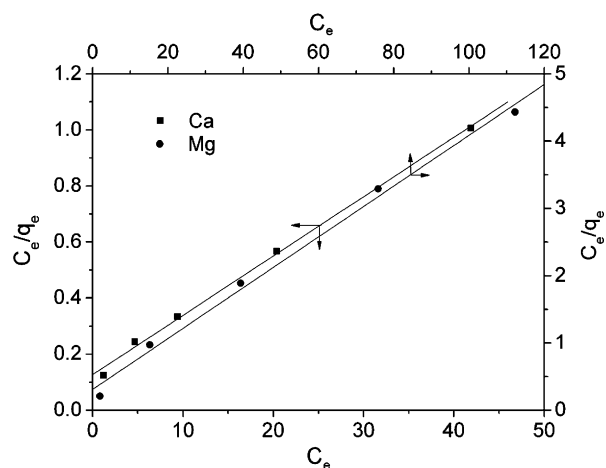


Fig. 5. Langmuir isotherm for ion exchange of Ca(II), Mg(II) on Amberlite IRC 748 (pH, 9.8 for Ca(II) and 9.5 for Mg(II); agitating rate, 180 rpm; temperature, 25 °C).

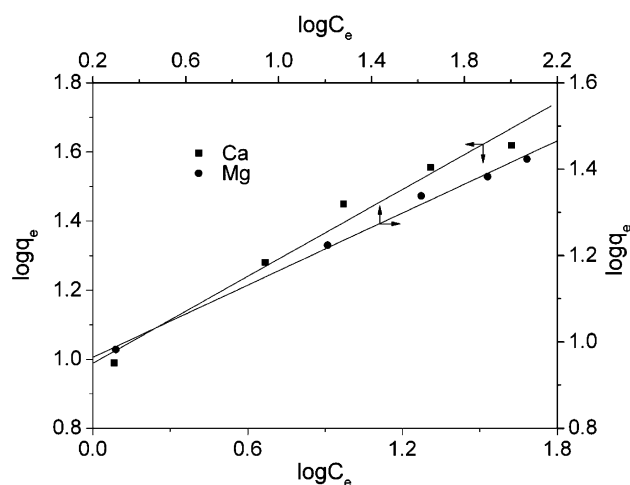


Fig. 6. Freundlich isotherm for ion exchange of Ca(II), Mg(II) on Amberlite IRC 748 (pH, 9.8 for Ca(II) and 9.5 for Mg(II); agitating rate, 180 rpm; temperature, 25 °C).

The essential feature of the Langmuir equation can be expressed in terms of a dimensionless separation factor, R_L , defined as

$$R_L = \frac{1}{1 + bC_0} \quad (5)$$

where b is the Langmuir constant (l mg⁻¹) and C_0 is the initial concentration (mg l⁻¹). The value of R_L indicates the shape of the isotherm to be unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$) [24,25]. The variation of R_L with the initial metal concentration of solution is shown in Fig. 7. R_L values were found to be between 0 and 1 for all the concentrations of Ca(II), Mg(II) and, therefore, ion exchange of Ca(II), Mg(II) are both favorable. From Fig. 7 we can also see that the R_L values decreased with initial alkaline-earth metal concentration increasing. This indicates that ion exchange is more favorable for the higher initial Ca(II), Mg(II) concentrations than for the lower ones.

Table 2

Parameters of Langmuir and Freundlich isotherms for ion exchange of metals on Amberlite IRC 748.

Metal	Langmuir constants			Freundlich constants		
	Q_0 (mg g ⁻¹)	b (l mg ⁻¹)	R^2	k_f	$1/n$	R^2
Ca(II)	47.21	0.1672	0.9972	9.732	0.4195	0.9731
Mg(II)	27.70	0.1181	0.9939	8.681	0.2506	0.9952

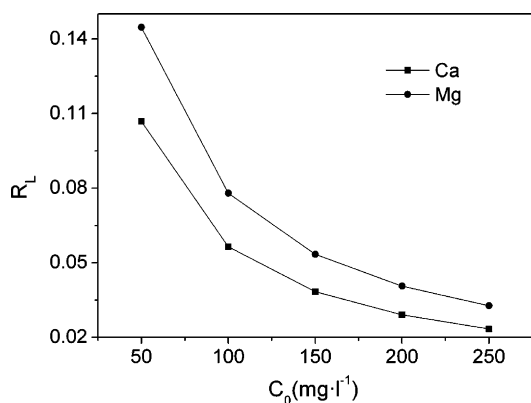


Fig. 7. Variation of adsorption intensity R_L with initial metal concentration C_0 .

The constants k_f and n of the Freundlich model are, respectively, obtained from the intercept and the slope of the linear plot of $\log q_e$ versus $\log C_e$ according to Eq. (4). The constant k_f can be defined as an adsorption coefficient which represents the quantity of adsorbed metal ion for a unit equilibrium concentration (i.e., $C_e = 1$). Higher values of k_f indicate higher affinity for Ca(II), Mg(II). The slope $1/n$ is a measure of the adsorption intensity or surface heterogeneity [26,27]. For $1/n = 1$, the partition between the two phases is independent of the concentration. The situation $1/n < 1$ is the most common and corresponds to a normal L-type Langmuir isotherm, while $1/n > 1$ is indicative of a cooperative adsorption which involves strong interactions between the molecules of adsorbate. Values of $1/n < 1$ show favorable ion exchange of metals on ion-exchange resin from potassium chromate solution.

3.6. Ion-exchange kinetics

The two important physicochemical factors for parameter evaluation of the adsorption process as a unit operation are the kinetics and the equilibrium. Kinetics of adsorption describing the solute uptake rate, which in turn governs the residence time of adsorption reaction, is one of the important characteristics defining the efficiency of adsorption. Hence, in the present study, the kinetics of metal removal has been carried out at 298.15–318.15 K to understand the behavior of this resin.

In this study, Lagergren-first-order equation and pseudo-second-order equation were used to test the experimental data. The Lagergren-first-order equation is expressed as [28,29]:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (6)$$

where k_1 (min^{-1}) is the rate constant of first-order adsorption, q_e is the amount of metal adsorbed at equilibrium and q_t is the amount adsorbed at time “ t ”. Plotting $\ln(q_e - q_t)$ against “ t ” at 298.15–318.15 K provided first-order adsorption rate constant (k_1) and q_e values from the slope and intercept (Table 3).

Table 3

Comparison between adsorption rate constants, estimated q_e and coefficients of correlation associated to the Lagergren-first-order and to the pseudo-second-order kinetic models (pH, 9.8 for Ca(II) and 9.5 for Mg(II); amount of resin, 0.05 g; temperature, 25 °C; agitating rate, 180 rpm).

Metal	T (K)	$q_{e,\text{exp}}$ (mg g^{-1})	First-order kinetic model			Second-order kinetic model				
			$k_1 \times 10^3$ (min^{-1})	q_e (mg g^{-1})	R^2	$k_2 \times 10^{-3}$ ($\text{g mg}^{-1} \text{min}^{-1}$)	q_e (mg g^{-1})	h ($\text{mg g}^{-1} \text{min}^{-1}$)	$t_{1/2}$ (min)	R^2
Ca(II)	298.15	19.07	9.90	10.21	0.9592	2.772	19.39	1.042	18.61	0.9998
	308.15	19.30	9.55	9.703	0.9513	3.040	19.50	1.156	16.87	0.9999
	318.15	19.49	9.86	8.295	0.8972	3.796	19.71	1.475	13.36	1.000
Mg(II)	298.15	16.73	6.00	11.08	0.9476	2.316	16.89	0.6608	25.56	0.9976
	308.15	17.49	6.30	10.75	0.9343	2.622	17.61	0.8127	21.66	0.9983
	318.15	18.15	6.50	10.32	0.9252	2.974	18.02	0.9656	18.66	0.9988

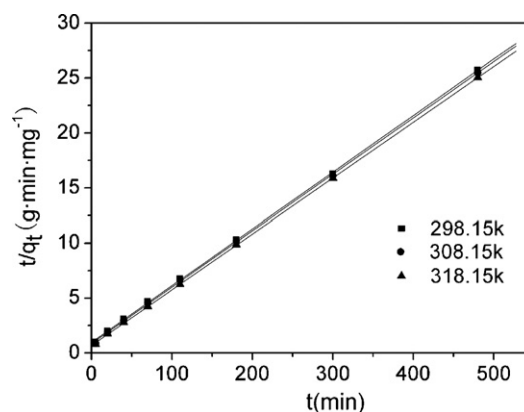


Fig. 8. Test of pseudo-second-order equation for adsorption of Ca(II) from potassium chromate solution on Amberlite IRC 748 at different temperatures (pH, 9.8 for Ca(II) and 9.5 for Mg(II); amount of resin, 0.05 g; agitating rate, 180 rpm).

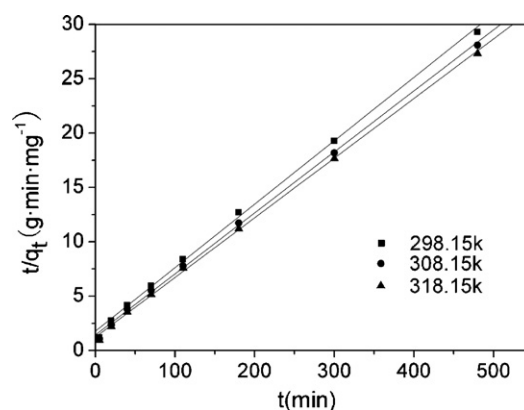


Fig. 9. Test of pseudo-second-order equation for adsorption of Mg(II) from potassium chromate solution on Amberlite IRC 748 at different temperatures (pH, 9.8 for Ca(II) and 9.5 for Mg(II); amount of resin, 0.05 g; agitating rate, 180 rpm).

The pseudo-second-order equation is expressed as [30,31]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (7)$$

The product $k_2 q_e^2$ is the initial adsorption rate “ h ” ($\text{mg g}^{-1} \text{min}^{-1}$):

$$h = k_2 q_e^2 \quad (8)$$

The half-adsorption time is time required to uptake half of the maximal amount of adsorbate at equilibrium. It characterizes the adsorption rate as well. In the case of pseudo-second-order process, its value is given by the following relationship:

$$t_{1/2} = \frac{1}{k_2 \times q_e} \quad (9)$$

Table 4
Thermodynamic parameters of Ca(II) and Mg(II) adsorption onto Amberlite IRC 748.

Metal	ΔH° (kJ mol ⁻¹ K ⁻¹)	ΔS° (kJ mol ⁻¹ K ⁻¹)	ΔG° (kJ mol ⁻¹)				R^2
			298.15 K	308.15 K	318.15 K	333.15 K	
Ca(II)	26.188	0.0994	-3.495	-4.369	-5.391	-7.000	0.9986
Mg(II)	22.735	0.0770	-0.0707	-0.8558	-1.7794	-2.9865	0.9895

where k_2 (g mg⁻¹ min⁻¹) is the pseudo-second-order rate constant, q_e is the amount adsorbed at equilibrium, $t_{1/2}$ is the half adsorption time and q_t is the amount of metal adsorbed at time “ t ”. Plotting t/q_t against “ t ” at 298.15–318.15 K (Figs. 8 and 9) provided second-order adsorption rate constant (k_2) and q_e values from the slope and intercept (Table 3).

The values of correlation coefficient indicate a better fit of pseudo-second-order model with the experimental data compared to the Lagergren-first-order model at all studied temperatures. The Lagergren model fits well for the first 70 min for Ca(II), 40 min for Mg(II) and thereafter the data deviate from the theory. This shows that the model can be applied but is not appropriate to describe the entire adsorption process. In many cases the first-order kinetic process was used for reversible reaction with an equilibrium being established between liquid and solid phases. Whereas, the second-order kinetic model assumes that the rate-limiting step may be chemical adsorption. Values of q_e calculated from the second-order kinetic model agree very well with the experimental values, and regression coefficients are always more than 0.99 for different temperatures. Therefore, the second-order model can be applied for the entire adsorption process. These suggest that the adsorption system studied belong to the second-order kinetic model based on the assumption that the rate determining step may be chemical adsorption or chemisorption involving valence forces through sharing or exchange of electrons between adsorbent and adsorbate. The rate constant k_2 increased with temperature increasing (Table 3) shows that the process is endothermic.

3.7. Thermodynamic evaluation of the process

Temperature dependence of the adsorption process is associated with several thermodynamic parameters. Thermodynamic considerations of an ion-exchange process are necessary to conclude whether the process is spontaneous or not. Thermodynamic parameters such as Gibbs free energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) can be estimated using equilibrium constants changing with temperature. The Gibbs free energy change of the adsorption reaction is given by the following Eq. (10):

$$\Delta G^\circ = -RT \ln k \quad (10)$$

where R is universal gas constant (8.314 J mol⁻¹ K⁻¹), T is absolute temperature (K) and k (q_e/C_e) is the distribution coefficient [32,33].

Relation between ΔG° , ΔH° (enthalpy change) and ΔS° (entropy change) can be expressed by the following equations [34–36]:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (11)$$

Eq. (10) can be written as

$$\ln k = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (12)$$

where values of ΔH° and ΔS° can be determined from the slope and the intercept of the plot between $\ln k$ versus $1/T$. The values of ΔG° , ΔH° and ΔS° along with relation coefficients are given in Table 4.

The magnitude of ΔG° decreased with rising of temperature, indicating that the adsorption is favorable at high temperatures. The negative values confirm the feasibility of the process and the spontaneous nature of adsorption of Ca(II), Mg(II) on Amberlite IRC

748 synthetic resin. The values of ΔH° were positive, indicating that the ion-exchange reaction is endothermic. This is also supported by the increase in value of uptake capacity of the adsorbent with rising of temperature. The positive values of ΔS° reflect the affinity of Ca(II), Mg(II) for adsorbent used. In addition, positive values of ΔS° show the increasing randomness at the solid/liquid interface during the adsorption of Ca(II), Mg(II) on Amberlite IRC 748. Obviously, it is shown from the results reported in Table 4 that the temperature affects the adsorption process of metal ion adsorption onto the resin in which the higher temperature provided more energy to enhance the adsorption rate.

3.8. Activation energy

Activation energy E_a is determined according to the Arrhenius equation [3,21]:

$$\ln k_2 = \frac{\ln A - E_a}{RT} \quad (13)$$

where k_2 is the rate constant value for the metal adsorption, E_a is the activation energy in kJ mol⁻¹, T is the temperature in Kelvin and R is the gas constant (8.314 J mol⁻¹ K⁻¹) and A is constant called the frequency factor. Value of E_a can be determined from the slope of $\ln k_2$ versus $1/T$ plot (Fig. 10). Thus, the rate constants k_2 of the Arrhenius law are given by Eqs. (14) and (15):

$$k_{2,\text{Ca}} = 0.3938 \times \exp\left(\frac{-12.34 \times 10^3}{8.314 \times T}\right) \quad \text{for Ca(II)} \quad (14)$$

$$k_{2,\text{Mg}} = 0.1237 \times \exp\left(\frac{-9.865 \times 10^3}{8.314 \times T}\right) \quad \text{for Mg(II)} \quad (15)$$

The activation energy for the adsorption of Ca(II), Mg(II) on Amberlite IRC 748 synthetic resin was calculated and its value was found to be 12.34 and 9.865 kJ mol⁻¹, respectively. These values are of the same magnitude as the activation energy of activated chemisorption. It is known that when activation energy is low the rate is controlled by intra-particle diffusion mechanism and hence it can be concluded that process is governed by interactions of physical nature. The positive values of E_a also suggest that rise

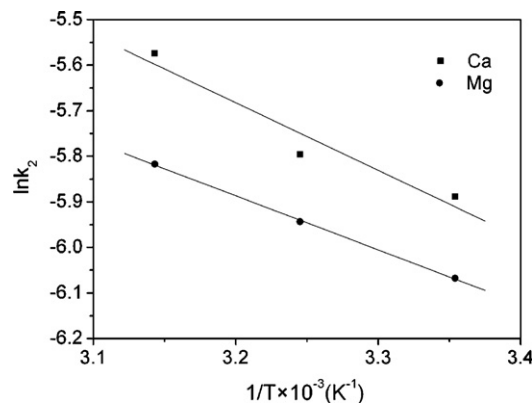


Fig. 10. Plots of $\ln k_2$ against reciprocal temperature for adsorption of Ca(II) and Mg(II) onto Amberlite IRC 748.

in temperature favors the adsorption and adsorption process is an endothermic process in nature.

4. Conclusions

The present investigation shows that Amberlite IRC 748 is an effective adsorbent for the removal of Ca(II), Mg(II) from potassium chromate solution. The effects of process parameters such as contact time, pH, temperature and resin dosage on process equilibrium were studied. The optimum pH obtained for Ca(II), Mg(II) adsorption onto Amberlite IRC 748 from potassium chromate solution is 9.8 and 9.5, respectively. It was also noted that an increase of temperature and resin dosage resulted in a higher Ca(II), Mg(II) adsorption, and the equilibrium conditions were both attained within 480 min.

The linear Langmuir and Freundlich isotherm models were used to represent the experimental data, and the experimental data could be relatively well interpreted by the Langmuir isotherm. R_L values between 0 and 1.0 further indicate a favorable adsorption of Ca(II), Mg(II). The monolayer adsorption capacity of Ca(II), Mg(II) calculated from the Langmuir model was obtained 47.21 and 27.70 mg g^{-1} , respectively. By applying the kinetic models to the experimental data, it was found that the adsorption of Ca(II), Mg(II) onto Amberlite IRC 748 synthetic resin from potassium chromate solution both follow the pseudo-second-order rate kinetics. The negative ΔG° values showed that the ion exchange of Ca(II), Mg(II) onto Amberlite IRC 748 was feasible and spontaneous. The positive ΔH° values depicted endothermic nature of the adsorption. The positive ΔS° values revealed the increased randomness at the solid–solution interface. The activation energy of adsorption evaluated with the second-order rate constants according to the Arrhenius Equation also showed that both the alkaline-earth metals adsorption process was endothermic.

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