

REMOVAL OF CR(VI) FROM ALKALINE AQUEOUS SOLUTIONS USING CHEMICALLY MODIFIED MAGNETIC CHITOSAN RESINS

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ABSTRACT

Chitosan was cross-linked using glutaraldehyde in the presence of magnetite. The resin obtained was chemically modified through the reaction with tetraethylenepentamine followed by glycidyl trimethylammonium chlorid to produce chitosan bearing amine (R1) and chitosan bearing both amine and quaternary ammonium chloride moieties (R2), respectively. The quaternary amine resin (R2) showed a higher affinity towards the uptake of Cr(VI) from alkaline medium, where an uptake value of 2.8 mmol/g was reported at pH 8 and 25°C. The nature of interaction of R2 with chromate in alkaline medium was clarified. The resin Kinetics at different temperatures and thermodynamic parameters of the uptake process in alkaline medium were obtained. The uptake of Cr(VI) from different electrolyte solutions was studied. Regeneration curves for the desorption of Cr(VI) from R2 were studied. The adsorbed chromate anions was regenerated effectively (desorption ratio ~ 98%) using a mixture of 2 M NaCl and 0.5 M NaOH.

Keywords: Chitosan; Magnetic; Chromate oxyanions; Quaternary amine

1. INTRODUCTION

Heavy metals with the potential to have an impact on environmental quality and human health are a great risk. Amongst them Chromium(IV) which exists in oxidation states from +2 to +6, but only Cr(III) and Cr(IV), are of environmental significance and out of these two forms the latter is a well-documented toxic metal [1]. chromium(VI) is a highly toxic metal that has been linked to cancer in humans following prolonged inhalation, and is toxic to aquatic life at relatively low concentrations (US Environmental Protection Agency (EPA), 1998). The maximum permitted level of chromium for drinking water is 0.05 mg/L [2,3].

The chromium enters the aquatic systems through discharge of concentrated effluents mainly from tanning, electroplating, paint, textile, etc. industries [4]. Chemical reduction, precipitation, solvent extraction and ion exchange are some of the conventional techniques for removal of Cr(VI) from aqueous solutions and industrial effluents [5].

Anion exchange resins are versatile adsorbents that are used to remove a wide variety of anions from different aqueous media. However most of chromate anion exchange resins work only in acidic medium [6], therefore the development of anion exchange resins able to adsorb chromate anions from neutral and alkaline medium is of a great interest. Anion exchange resins could be generated from low-cost agricultural by-products as starting materials such as cellulose, chitosan and lignin. Chitosan has been classified as one of the potentially low-cost sorbents with high adsorption capacity [7]. The addition of cationic groups through the quaternization of these materials to produce anion exchange resins represents a potential alternative to currently available commercial anion exchange resins [8]. The ultimate goal of this study is the development of a new magnetic resins based on chitosan for the removal of chromate anions from acidic, neutral and alkaline aqueous solutions. These methods are cheap and often highly scalable. Moreover, techniques employing magnetism are more amenable to automation [9]. The factors affecting the removal behaviour will be studied. Thermodynamic as well as kinetic properties of the removal process will also be clarified.

2. EXPERIMENTAL

2.1. Chemicals

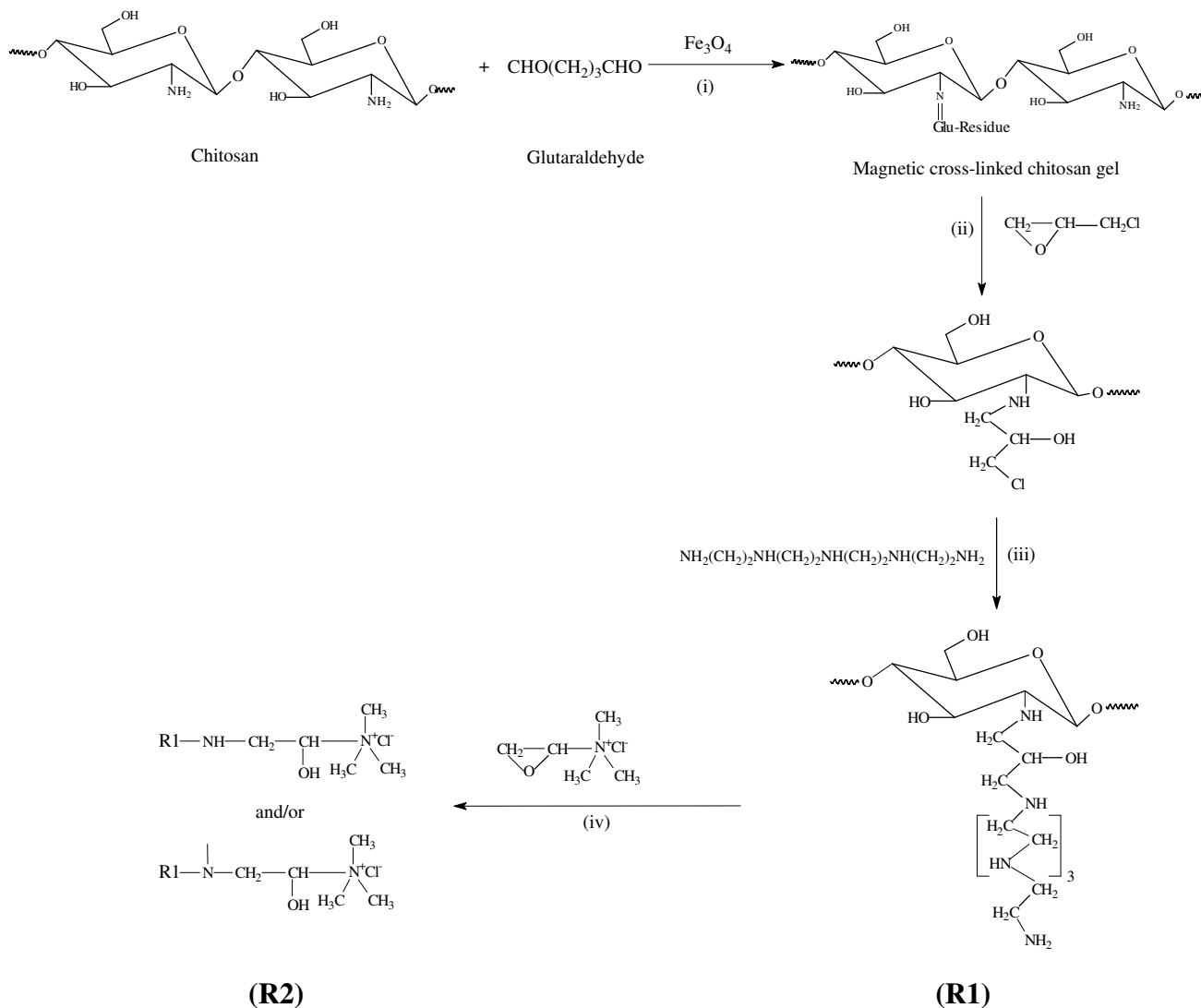
Chitosan with deacetylation degree (DD) of 82.1%, glutaraldehyde, tetraethylenepentamine (TEPA) and glycidyl trimethylammonium chloride (GTMAC) were Aldrich products. Diphenylcarbazine (DPC) was Hach product, USA. All other chemicals were Prolabo products and were used as received. Potassium dichromate ($K_2Cr_2O_7$) was used as a source of Cr(VI). $FeSO_4 \cdot 7H_2O$ and $FeCl_3 \cdot 6H_2O$ were used for preparing magnetite particles as reported earlier using modified Massart method [10,11].

2.2. Preparation of modified magnetic chitosan resins

The process of preparation takes place through subsequent steps (Scheme 1).

(i) Preparation of the magnetic chitosan gel

Three grams of chitosan was dissolved in 20% aqueous solution of acetic acid. One gram of very fine magnetite powder previously prepared was added to chitosan solution and stirred to distribute magnetite equally in all parts of the solution. Then 2 mL of glutaraldehyde solution (25%) was added and the solution was stirred with heating until gelatinous product was obtained. The gel obtained was washed with distilled water several times and kept for use.



(Scheme 1)

(ii) Reaction with epichlorohydrine

The cross-linked chitosan gel obtained in the above step (i) was suspended in 70 mL isopropyl alcohol. Then 7 mL epichlorohydrine (62.5 mmol) dissolved in 100 mL acetone/water mixture (1:1 v/v) was added. The above mixture was stirred for 24 h at 60 °C. The solid product obtained was filtered off and washed several times with water followed by ethanol.

(iii) Reaction with tetraethylenepentamine (TEPA)

The product obtained in the step (ii) was suspended in 100 mL ethanol/water mixture (1:1 v/v) and then treated with 5 mL TEPA. The reaction mixture was stirred at 60 °C for 12 h. The product obtained was washed with water followed by ethanol. The produced chitosan/pentamine resin was dried in air and referred by (R1). The amine content in R1 was estimated using volumetric method of HCl according the early reported method [12] and was found to be 4.9 mmol/g.

(iv) Reaction with glycidyl trimethylammonium chloride (GTMAC)

The chitosan/pentamine product obtained in the step (iii) was suspended in 50 mL of water and treated with GTMAC. The reaction mixture was stirred at 60 °C for 24 h. The product was filtered off and washed with distilled water, methanol, and acetone then dried in air and referred by (R2). The mass of the obtained dried (R2) resin was 4.92 g.

The concentration of quaternary amine groups on the modified chitosan resin (R2) was estimated by conductometric titration [13] using Hanna conductivity meter model EC215. A 0.1 g of resin was suspended in 200 mL of distilled water. Standard silver nitrate solution (0.01 M) was added dropwise to the suspension of the resin with continuous stirring and the conductivity was recorded. The end point was obtained from plotting the conductivity of a suspension of R2 against mL added of 0.01 M AgNO₃ (conductometric titration curve). The end point was detected at 35 mL AgNO₃. The concentration of quaternary ammonium sites (mmol/g) was calculated from equation:

$$\text{concentration of quaternary ammonium sites (mmol/g)} = \frac{M \times V}{W} \quad (1)$$

where M and V are the molarity (mol/L) and the volume (mL) of the titrant, respectively, and W is the weight of the resin. The concentration of quaternary ammonium groups was found 3.5 mmol/g resin.

2.3 Characterization of the resins

2.3.1. FT-IR analysis

Infra red spectra were performed using Nicolet IR200 FT-IR Spectrometer.

2.3.2. Water regain

Water regain factor, W%, represents the percentage of water held intrinsically by the resin for water regain determination; resin samples were centrifuged for 30 min at 1000 rpm to remove excess water and then weighed. These samples were then dried at 50-60 °C until complete dryness then weighed again. To calculate this factor, the following equation was applied:

$$W\% = \frac{100(W_w - W_d)}{W_w} \quad (2)$$

where W_w and W_d are weights (g) of the wet and dried resin respectively. Water regain values are (52 ± 3%) and (58 ± 3%) for R1 and R2 respectively, with insignificant differences when changing conditions. This value reflects the hydrophilic character of the resin type.

2.3.3. Surface area

The surface area of the prepared resins was measured by methylene blue adsorption as this material is known to be adsorbed as a monolayer only on solid sorbents [14]. A standard solution of this material was prepared (0.02 g/L). A calibration curve for methylene blue was drawn ($\lambda = 660$ nm) by measuring diluents from standard stock. To calculate the surface area, 0.1 g of resin was treated with 25 ml of methylene blue of concentration 0.02 g/L. The treatment lasted until there was no further decrease in absorbance. The amount of methylene blue adsorbed was calculated based on concentration difference between the initial and equilibrium values, which were measured by DR 5000 spectrophotometer (HACH) USA. The surface area of the resin was calculated using the following equation [15]:

$$A_s = \frac{G N_{Av} \emptyset 10^{-20}}{M M_w} \quad (3)$$

where A_s is the gel resin surface area in m^2/g , G the amount of methylene blue adsorbed (g), N_{Av} the Avogadro's number (6.02×10^{23}), \emptyset the methylene blue molecular cross-section (197.2 \AA^2), M_w the molecular weight of methylene blue (373.9 g/mol) and M is the mass of adsorbent (g). The surface area of the prepared resins was calculated to be 110 and 126 m^2/g for R1 and R2, respectively.

2.4. Solutions

A stock solution (2×10^{-2} M) of Potassium dichromate ($K_2Cr_2O_7$) as Cr(VI) was prepared in distilled water. HCl (0.5 M) and NaOH (0.5 M) were used to change the acidity of the medium. NH_4OH/NH_4Cl buffer (pH 10), 2 M NaCl and 0.5 M NaOH were prepared and used as an eluent for chromate anions.

2.5. Uptake measurements

2.5.1. Batch method

(i) Effect of pH

Adsorption of chromate anions on the resins obtained under controlled pH was carried out. A 0.1 g of dry resins (R1 or R2) were placed in a series of flasks containing 40 mL of distilled water for 1 h. Thereafter 50 mL of chromate solution (1×10^{-2} M) as Cr(VI) was added to each flask. The desired pH was obtained using HCl or NaOH. The volume of solution in each flask was completed to 100 mL. The initial concentration of Cr(VI) becomes (5×10^{-3}). The contents of the flasks were equilibrated for 3 h on a Vibromatic-384 shaker at 300 rpm and 25 ± 1 °C. The residual concentration of the metal ion was estimated spectrophotometrically at 540 nm using Diphenylcarbazide method [16]. The measurements were taken on DR/2010 spectrophotometer, Hach, USA.

(ii) Effect of time

A 0.1 g of dry resins (R1 or R2) were swelled in a flask containing 50 mL of distilled water for 1 h. Fifty milliliters of Cr(VI) solution (1×10^{-2} M) was added to the flask. The initial concentration of the Cr(VI) becomes (5×10^{-3} M) and pH was adjusted to 8 using NaOH. The contents of the flask were shaken for 3 h on a Vibromatic-384 shaker at 300 rpm and $25 \pm 1^\circ\text{C}$. Five milliliters of the solution was taken at different time intervals, where the residual concentration of metal ion was estimated (samples taken for metal ion concentration analysis were not returned to the flask) according to the above method [16]. The adsorbed amount of Cr(VI) per unit weight of the resin beads q_t (mmol/g), at time t was calculated from the mass balance equation as:

$$q_t = \frac{\sum_{i=1}^n (C_{t(i-1)} - C_{ti}) V_{t(i-1)}}{m} \quad (4)$$

where C_{ti} (mmol/L) is the measured concentration of the drawn sample number i at time t and $C_{t0} = (C_0)$, V_{ti} (mL) is the volume of the solution in the flask at sample number i and time t , and m is the weight of the resin beads added into the flask.

(iii) Adsorption isotherms

Complete adsorption isotherms were obtained by soaking 0.1 g of dry resins (R1 or R2) in a series of flasks containing 48 mL of distilled water for 1h. Fifty milliliters of Cr(VI) with different concentrations were added to each flask. The initial pH of each solution was adjusted to 8 and the volume was completed to 100 mL. The flasks were conditioned at 300 rpm while keeping the temperature at 30, 40, 50 or 60 °C for 3 h. Later on, the residual concentration of metal ion was determined as Cr(VI) according the above method [16].

2.6. Effect of electrolyte

The effect of electrolyte on the uptake of chromate by R2 was carried out at pH 8 and 25 °C. The effect of NaCl, Na_2SO_4 and NaNO_3 were tested as competitor anions at different concentrations. The adsorption experiments were performed by placing 0.1 portions of resin R2 in a series of flasks. In each flask 100 mL (5×10^{-3}) was added while keeping the ionic strength at the desired concentration using NaCl, NaNO_3 or Na_2SO_4 . After equilibration for 2 h, the residual concentration of chromate anions in each flask was determined.

2.7. Regeneration experiments

Regeneration experiments were performed in a plastic column with a length of 10 cm and a diameter of 1.0 cm. A small amount of glass wool was placed at the bottom of the column to keep the contents. One g of the resin under investigation was placed in

the column. Cr(VI) solution having an initial concentration of 5×10^{-3} M and pH 8.0 was flowed downward through the column at flow rate of 1 mL/min. Samples were collected from the outlet of the column at different time intervals and analyzed for metal ion concentration. The operation of the column was stopped when the outlet metal ion concentration matches its initial concentration. The resin loaded by chromate oxyanions was then subjected to elution using 2 M NaCl or a mixture of and 0.5 M NaOH. The concentration of the released chromate as Cr(VI) at 10 mL portions of the down-flow was determined. The elution process continued till the down-flow became free of chromate anions. The resin was then prepared for the next loading cycle by careful washing with distilled water through the column.

3. RESULTS AND DISCUSSIONS

3.1. Characterization of the resins

The infrared bands of the chitosan/pentamine (R1), shown in Fig. 1, appeared in close proximity to those of its salt (R2). The band at 1646 cm^{-1} can be attributed to an imine bond (N=C) of Schiff's base moiety formed as a result of crosslinking with glutaraldehyde. The most striking difference between the two spectra is the band of the salt positioned at 1483 cm^{-1} , which corresponds to an asymmetric angular bending of methyl groups of quaternary hydrogen [17].

The amine active sites of R1 determined using HCl was found to be 4.9 mmol/g, whereas the quaternary amino group concentration of R2 was 3.5 mmol/g. The lower value of concentration of quaternary amine sites of R2 compared to the amine active sites of R1 may be explained on the basis of not all amine sites are not suitable to react GTMAC.

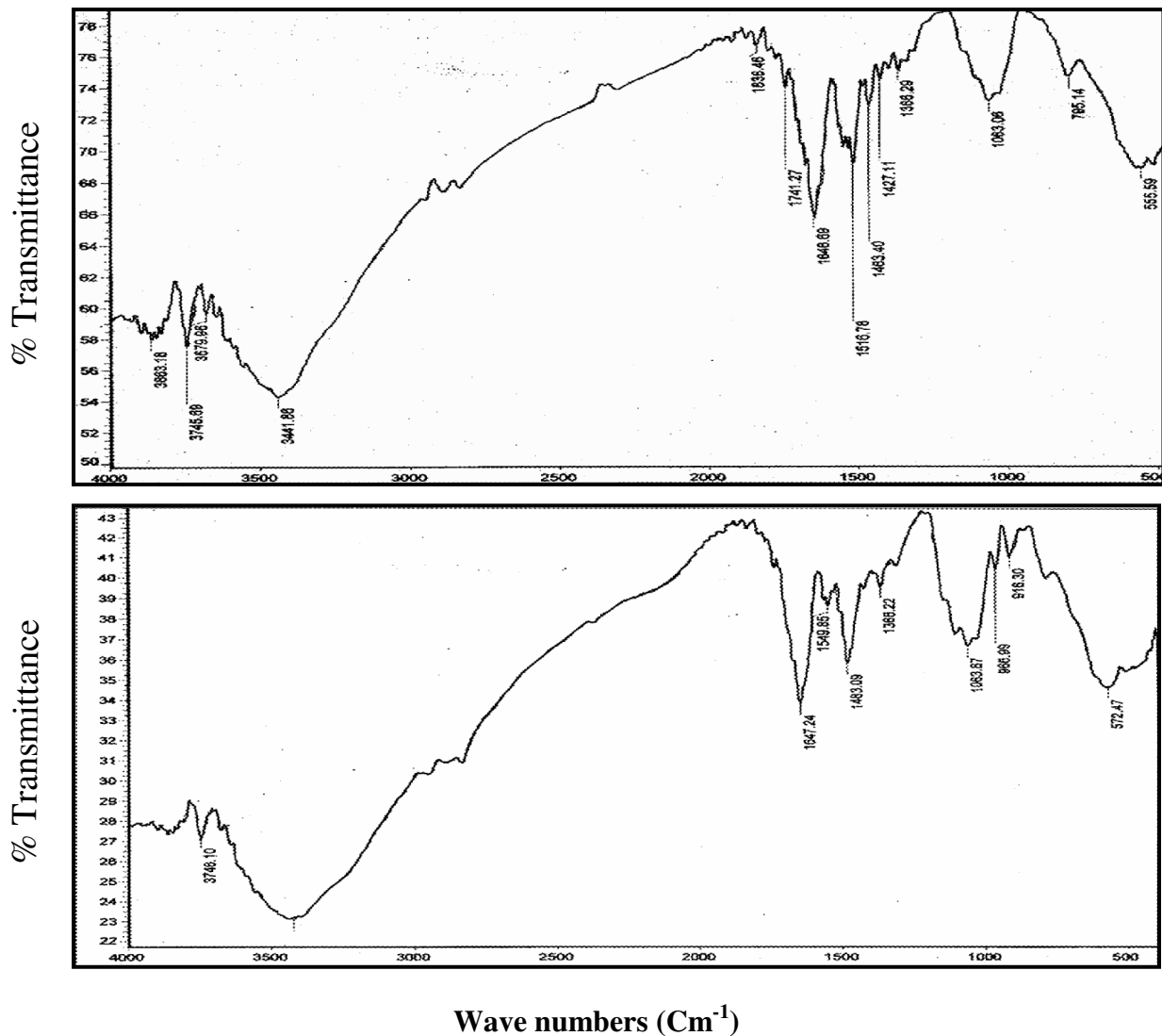


Fig. (1) FT-IR Spectra of R1 and R2 resins

3.2. Uptake studies using batch method

The effect of the acidity of the medium on the uptake of chromate anions by R1 and R2 is given in Fig. 2. Generally, it is seen that, for both resins the maximum uptake value was obtained at $\text{pH} \approx 2.8$. The observed decrease in the uptake value at $\text{pH} < 2.8$ for both resins may be attributed to the higher concentration of Cl^- which compete the chromate anions for interaction with the protonated amine active sites. Above $\text{pH} = 2.8$, R1 displays a sharp decrease in the uptake value as pH increases, whilst R2 shows a slow decrease. This behaviour can be explained on the basis of the lower extent of protonation of amino group with rising pH . The observed higher uptake value of R2 than that of R1 at all pH values may be attributed to the presence of trimethylammonium chloride moiety (which works in acid/neutral/basic media) in addition to amine moiety. It has been reported that HCrO_4^{4-} , CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ are the predominant species at $\text{pH} < 6.5$ while CrO_4^{2-} is the dominant species at $\text{pH} > 7.5$ [18,19].

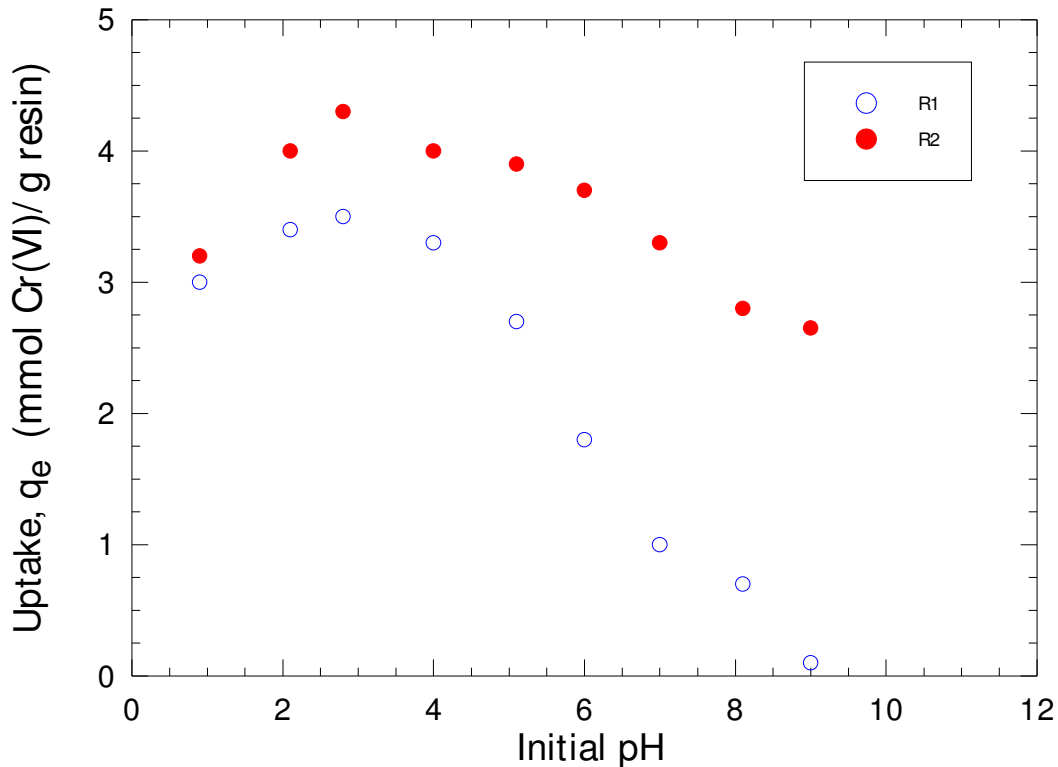


Fig. (2) Effect of pH on the uptake of chromate anions by resins at 30°C and the initial concentration of Cr(IV) is 5×10^{-3} M

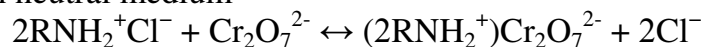
The mechanism of interaction of chromate anions with R1 and R2 can be represented as follows:

For R1 resin:

i) in acidic medium.

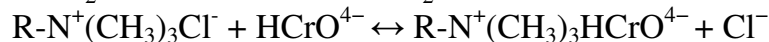
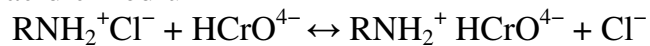


ii) in neutral medium

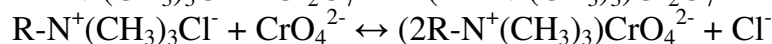
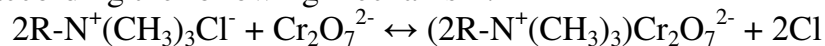


For R2 resin:

i) in acidic medium



ii) in neutral and basic media, the states of Cr(VI) are $\text{Cr}_2\text{O}_7^{2-}$ and CrO_4^{2-} and trimethyl ammonium chloride moiety which work as anion exchanger according the following mechanism:



It is seen that R1 works efficiently towards the removal of chromate in acidic medium, whilst R2 works efficiently in all pH ranges (acidic/neutral/basic).

3.2.1. Kinetic studies

Figure 3 shows the change in the uptake of Cr(VI) by the given resins as a function of time at initial concentration of 5×10^{-3} M, pH 8 and different temperatures. It could be seen that the uptake increases at elevated temperature and about 95% of the total uptake of Cr(VI) could be achieved within 80 min. The data in Fig. 3 were treated according to pseudo-first and pseudo-second order kinetic models. The pseudo first order model is expressed as [20]:

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right) t \quad (5)$$

where k_1 is the pseudo first order rate constant (min^{-1}) of adsorption and q_e and q_t (mmol/g) are the amounts of metal ion adsorbed at equilibrium and time t , respectively. The pseudo second order model is expressed as [21]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right) t \quad (6)$$

where k_2 is the pseudo second order rate constant of adsorption ($\text{g mmol}^{-1} \text{min}^{-1}$). The kinetic parameters in both two models are determined from the linear plots of $\log(q_e - q_t)$ vs. t for pseudo-first order or (t/q_t) vs. t for pseudo-second order (Fig. 4). The validity of each model is checked by the fitness of the straight line (r^2) as well as the consistence between experimental and calculated values of q_e . Accordingly, and as shown in Table (1), pseudo second order model is the more valid for adsorption process than pseudo first order one at all studied temperatures. The value of the calculated q_e increases with temperature increasing and consistent with the experimental values indicating that the adsorption reaction is more favourable at higher temperatures. Most adsorption reactions take place through multistep mechanism comprising (i) external film diffusion, (ii) intraparticle diffusion and (iii) interaction between adsorbate and active site. The first step is excluded by shaking the solution. So the rate determining step is one of the two other steps. To know if the intraparticle diffusion is the rate determining step or not the uptake/time data (Fig. 3) was treated according to Fickian diffusion law [22]:

$$q_t = K_i t^{0.5} + X \quad (7)$$

where q_t is the amounts of metal ion adsorbed at time t and K_i is intraparticle diffusion rate ($\text{mmol/g min}^{-0.5}$). As the value of X decreases the effect of external diffusion on the reaction rate decreases. In our case, the plot of q_t against $t^{0.5}$ gave straight line. The decrease of intercept value (X) at elevated temperature indicates that the boundary layer diffusion effect (external film resistance) decreases as the temperature increase. This may be attributed to the high hydrophilicity of the resin. The slopes of the first portions of the straight lines (K_i values) are 0.309, 0.308 and 0.361 ($\text{mmol/g min}^{-0.5}$) at 25, 35 and 45 °C, respectively. Fig. 5 shows that the straight-line portion does not pass through the origin. This indicates that the overall rate of adsorption reaction for both resins is controlled by the intraparticle diffusion along with the boundary layer diffusion [23].

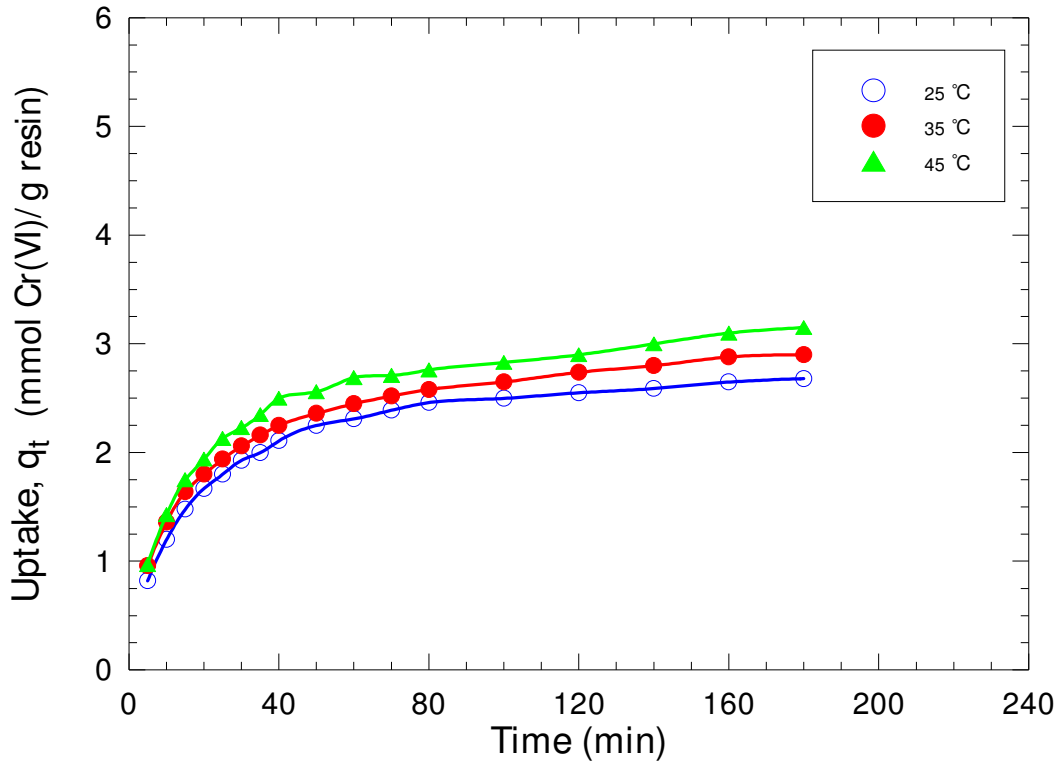
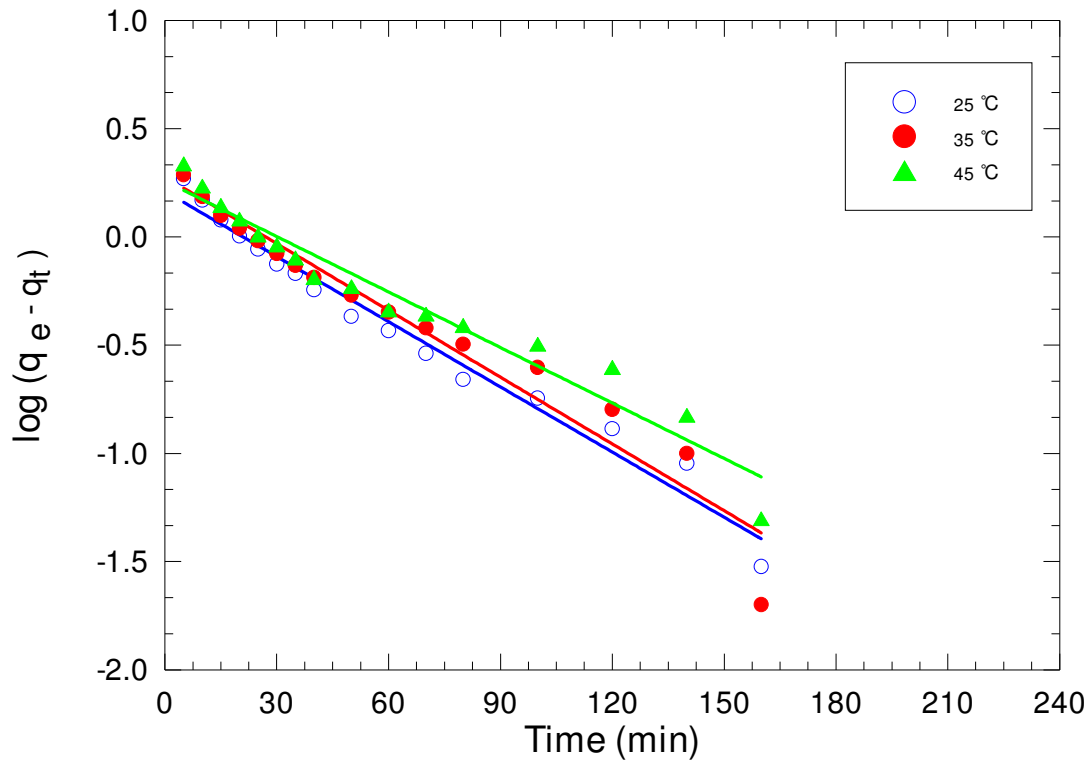


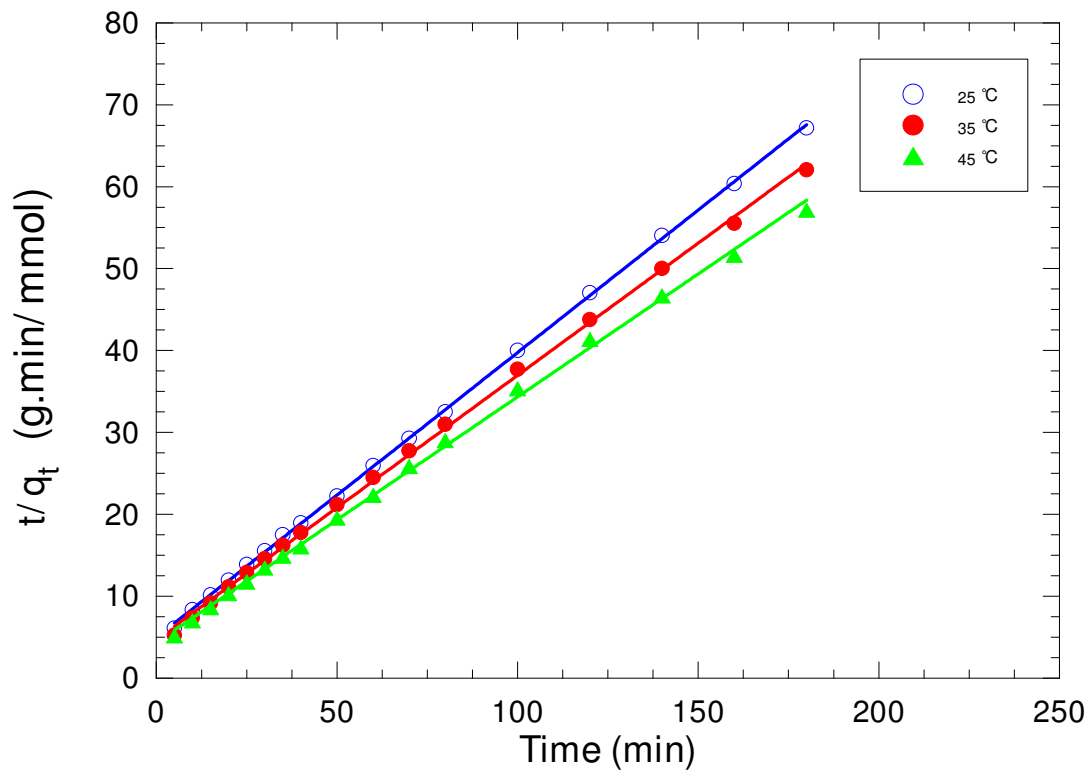
Fig. (3) Effect of time on the uptake of chromate anions from the initial concentration of Cr(IV) is 5×10^{-3} M using R2 at different temperatures and pH 8.0

Table (1) Parameters of the pseudo-first order and pseudo-second order for the adsorption of chromate anions on R2 from initial concentration of 5×10^{-3} , at pH 8 and different temperatures

Temp. (°C)	$q_{e, exp}$	Pseudo-First order			Pseudo-Second order		
		k_1 (min ⁻¹)	$q_{e, calc}$ (mmol/g)	r^2	k_2 (g/mmol min)	$q_{e, calc}$ (mmol/g)	r^2
25	2.68	0.484	0.997	0.975	0.024	2.874	0.999
35	2.90	0.64	0.976	0.947	0.022	3.098	0.999
45	3.15	0.595	0.980	0.949	0.020	3.333	0.998



(a)



(b)

Fig. (4) (a) Pseudo first-order and (b) pseudo second-order kinetics of the uptake of chromate anions by R2

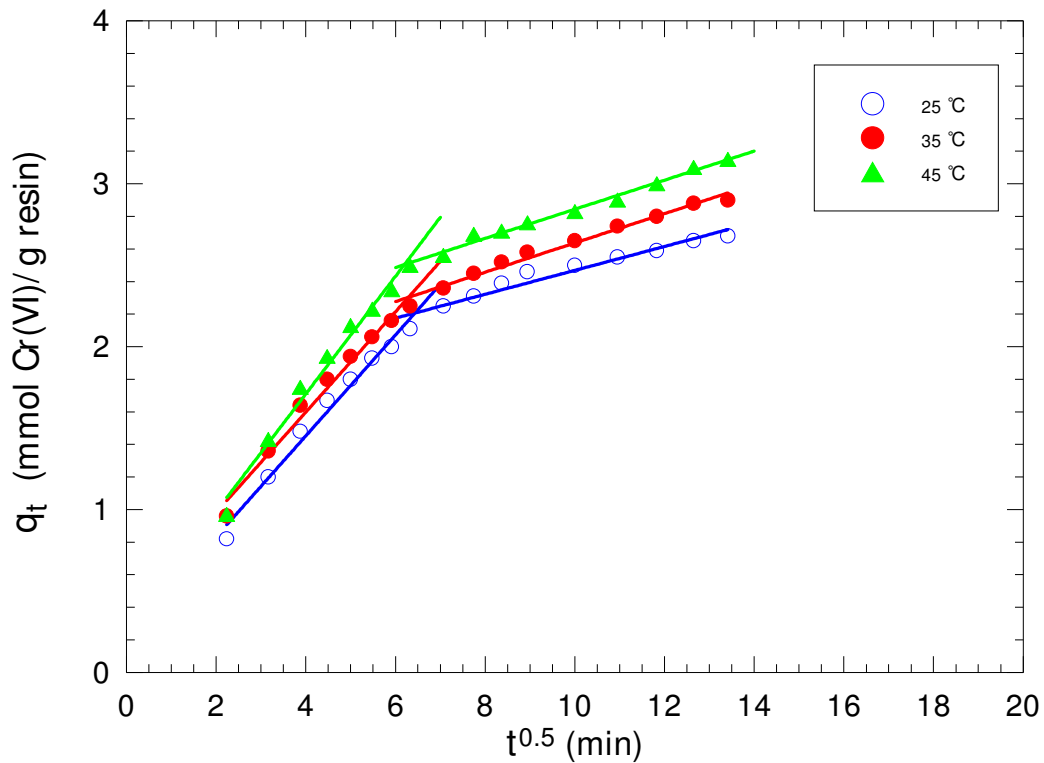


Fig. (5) The intraparticle diffusion kinetics model of the uptake of chromate anions by R2

3.2.2. Adsorption isotherms

Figure 6 shows the adsorption isotherms of Cr(VI) by R2 at different temperatures and pH 8.0. The adsorption data in Fig. 6 were treated according to the following Langmuir equation:

$$\frac{C_e}{q_e} = \frac{C_e}{Q_{\max}} + \frac{1}{K_L Q_{\max}} \quad (8)$$

where C_e is the equilibrium concentration of chromate anions in solution (mmol/L), q_e the adsorbed value of chromate anions at equilibrium concentration (mmol/g), Q_{\max} is the maximum adsorption capacity (mmol/g) and K_L is the Langmuir binding constant which is related to the energy of adsorption (L/mmol). Plotting C_e/q_e against C_e gives a straight line with slope and intercept equal to $1/Q_{\max}$ and $1/K_L Q_{\max}$, respectively. The values of K_L and Q_{\max} at different temperatures for adsorption of chromate anions were obtained from Fig. 7 and reported in Table (2). It is seen that, at all investigated temperatures the values of Q_{\max} obtained from Langmuir plots are mainly consistent with the experimental ones. This indicates that the adsorption process is mainly monolayer at all temperatures.

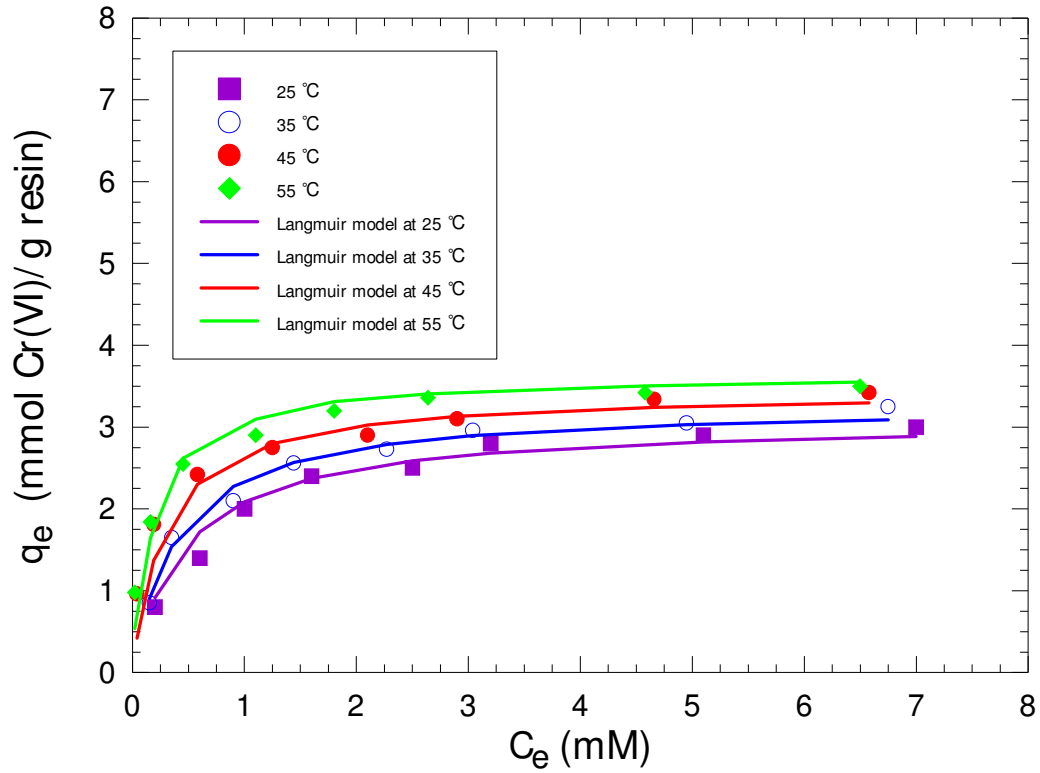


Fig. (6) Adsorption isotherms for the adsorption of chromate anions by R2 at different temperatures and pH 8.0

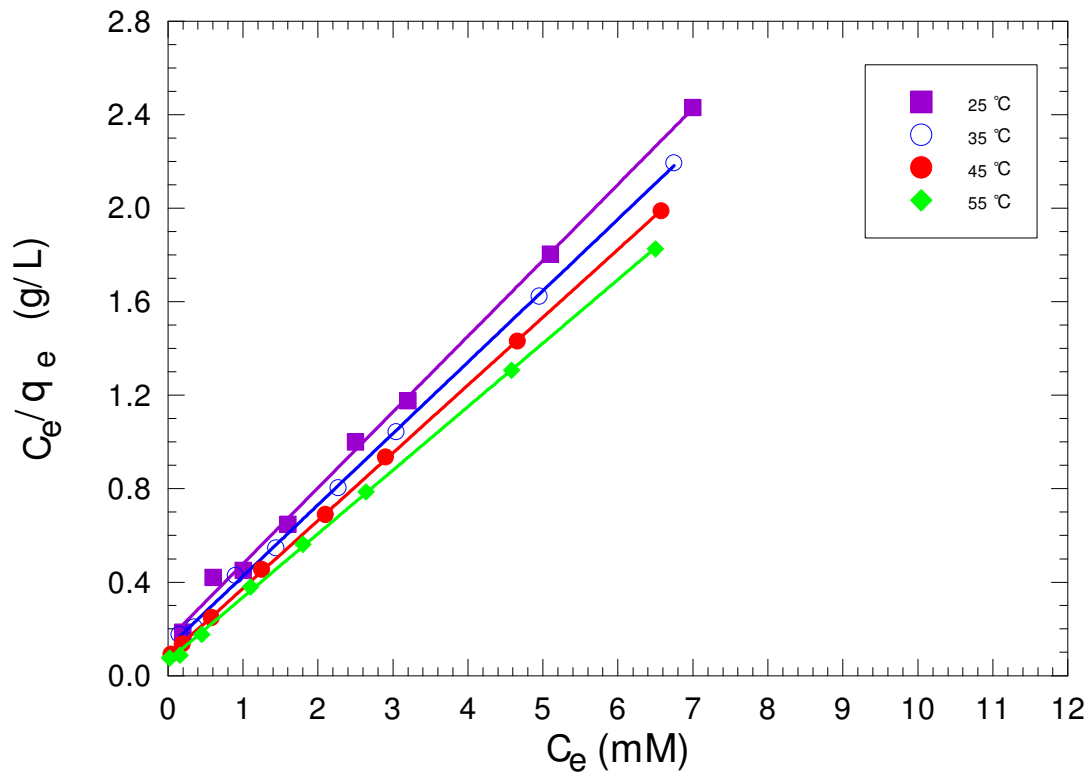


Fig. (7) Langmuir isotherms for the adsorption of chromate anions by R2

Table (2) Langmuir constants for adsorption of chromate anions on the studied resin

Temp. (°C)	Langmuir parameters				Thermodynamic parameters			
	Q _{max} (mmol/g)		K _L (L/mmol)	r ²	ΔH° (kJ/mol)	ΔS° (J/mol.K)	ΔG° (kJ/mol)	TΔS° (kJ/mol)
	exp	calc						
25	3.00	3.08	2.10	0.997	19.70	129.55	-18.90	38.60
35	3.25	3.27	2.54	0.999			-20.20	39.90
45	3.42	3.44	3.48	0.999			-21.49	41.19
55	3.50	3.68	4.25	0.999			-22.79	42.49

The degree of suitability of the investigated resin towards chromate anions was estimated from the values of the separation factor (R_L) using the following relation [24].

$$R_L = \frac{1}{1 + K_L C_o} \quad (9)$$

where K_L is the Langmuir equilibrium constant and C_o is the initial concentration of metal ion. Values of $0 < R_L < 1$ indicates the suitability of the process. The values of R_L for the investigated resins towards the adsorption of chromate lie between 0.02 and 0.32 for all concentration and temperature ranges. This indicates the suitability of resins for chromate adsorption.

The comparable values of K_L for both resins at all studied temperatures indicating the same mechanism of interaction (anion exchange). It is also seen that, for both resins as the temperature increases the value of K_L increases. This may be related to the increased electrostatic attraction between chromate anions and active sites due to the dehydration effect. To obtain the thermodynamic parameters of the adsorption reaction, the values of K_L at different temperatures were processed according to the following van't Hoff equation [25]:

$$\ln K_L = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (10)$$

where ΔH° and ΔS° are enthalpy and entropy changes, respectively, R is the universal gas constant (8.314 J/mol K) and T is the absolute temperature (in Kelvin). Plotting $\ln K_L$ against $1/T$ gives a straight line with slope and intercept equal to $-\Delta H^\circ/R$ and $\Delta S^\circ/R$, respectively. The values of ΔH° and ΔS° were calculated from Fig. 8 and reported in Table (2). The positive values of ΔH° indicate the endothermic nature of adsorption process. The positive values of ΔS° may be related to the increased randomness due to the liberation of water of hydration during the adsorption of

chromate. The Gibbs free energy of adsorption (ΔG°) was calculated from the following relation and given in Table (2):

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

The negative values of ΔG° obtained indicate that the adsorption reaction is spontaneous. The data given in Table (2) also show an increase in the values of $T\Delta S^\circ$ with increasing temperature and $|T\Delta S^\circ| > |\Delta H^\circ|$. This indicates that the adsorption process is dominated by entropic rather than enthalpic changes [23].

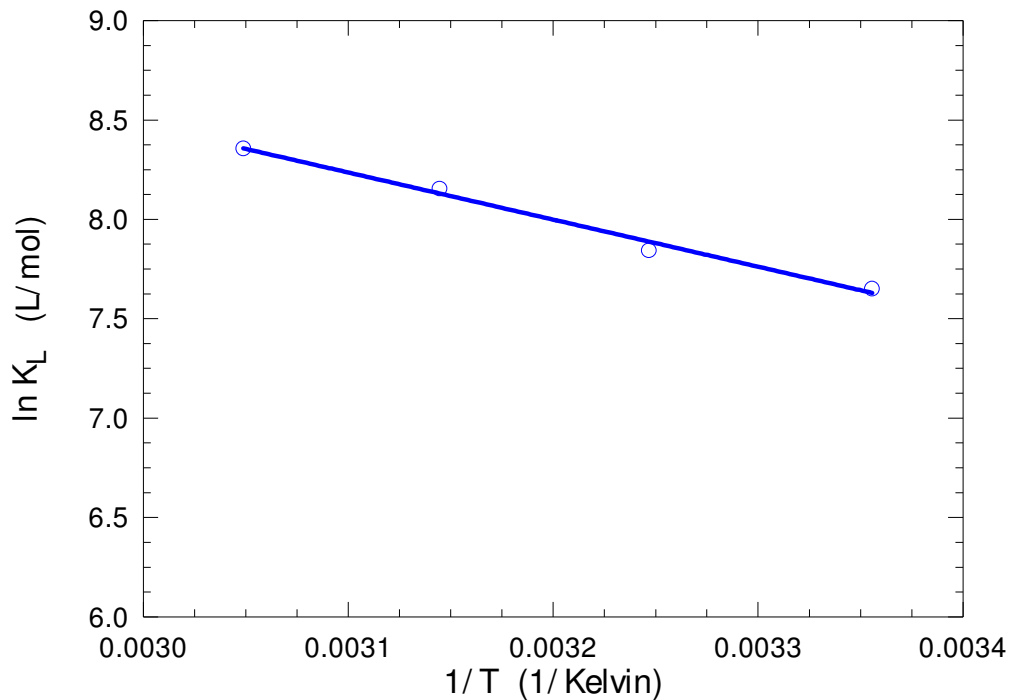


Fig. (8) Van't Hoff plots for the uptake of chromate anions on the studied resin

3.3. Effect of electrolyte

Figure 9 shows the effect of electrolyte on the uptake of chromate ($C_0 = 5 \times 10^{-3}$) on R2 at pH 8 and at 25 °C. Obviously, the uptake of chromate decreased with 13% and 29% of the blank uptake in presence of 0.5 M NaNO_3 and 0.5 M Na_2SO_4 , respectively. Meanwhile, the uptake of chromate was greatly affected in presence of NaCl and almost depressed at 1.0 M NaCl. This indicates strong competition between Cl^- and chromate anions for the interaction with R2 active sites. Consequently, NaCl was used as an eluent for regeneration of R2 for the repeated use.

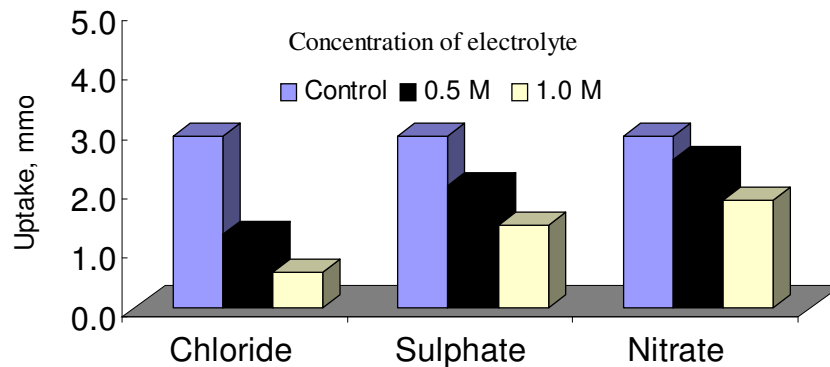


Fig. (9) Effect of chloride, sulphate and nitrate anions with different concentrations on the adsorption of chromate anions by R2 at pH 8.0 and 25 °C

3.4. Resin regeneration

Figure 10 shows that the highest Cr(VI) concentration in the effluent was detected after flowing 20 mL of a mixture of 2 M NaCl and 0.5 M NaOH through the column as an eluent, then the concentration of Cr⁶⁺ gradually decreased until zero concentration, also the fastest elution process was obtained using this eluent. While 2 M NaCl or NH₄OH/NH₄Cl buffer show a slower elution with a little enhanced efficiency. The desorption ratio of chromate anions using the above eluents was calculated using the following equation and reported in Table (3):

$$\text{Desorption ratio (\%)} = \frac{\text{Amount of Cr(VI) anions desorbed to the elution medium}}{\text{Amount of Cr(VI) anions sorbed on the resin}} \times 100 \quad (12)$$

Accordingly, and as shown in Table (3), the process of loading/elution was repeated for three successive cycles and the resin showed slight decrease in the uptake capacity during successive cycles. It is seen in Table (3) that the alkaline eluents (2 M NaCl + 0.5 M NaOH and NH₄OH/NH₄Cl buffer) showed higher elution efficiency than neutral NaCl and the highest desorption ratio for Cr(VI) oxyanions was achieved using a mixture of 2 M NaCl and 0.5 M NaOH \approx 98%. The higher elution efficiency of Cr(VI) anions in alkaline medium can be interpreted according to the following mechanism:

The mechanism of elution of chromate could be:

- Deprotonation of exchange-phase Cr₂O₇²⁻
 $(2\text{RNH}_2^+)\text{Cr}_2\text{O}_7^{2-} + 2\text{NaOH} \leftrightarrow (2\text{RNH}_2^+)\text{CrO}_4^{2-} + \text{Na}_2\text{CrO}_4 + \text{H}_2\text{O}$
 Therefore, alkali addition is required for the deprotonation of the chromate species.
- Removal of exchange-phase CrO₄²⁻ with brine:
 $(2\text{RNH}_2^+)\text{CrO}_4^{2-} + 2\text{NaCl} \leftrightarrow (2\text{RNH}_2^+)\text{Cl} + \text{Na}_2\text{CrO}_4$

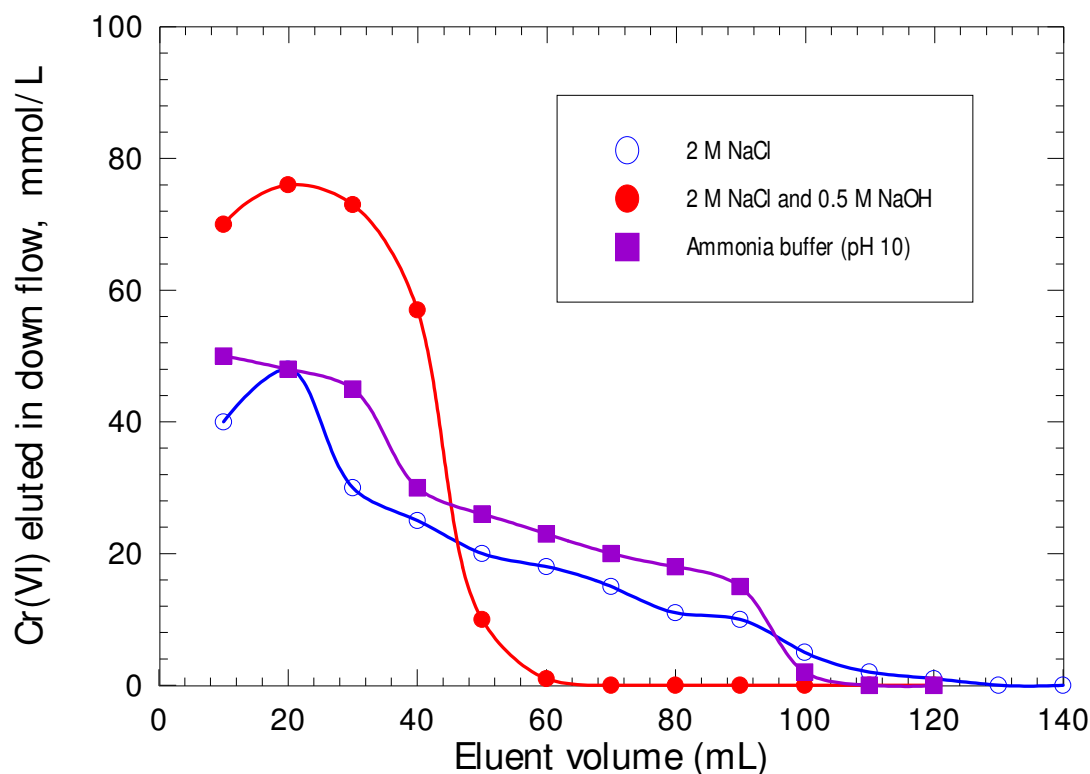


Fig. (10) Elution of chromate anions from R2 using a mixture of 2 M NaCl and 0.5 M NaOH

Table 3 Desorption ratio of chromate anions for repeated cycles

Elution cycle	Desorption ratio (%)		
	NaCl	NH ₄ OH/NH ₄ Cl buffer	NaCl + NaOH
1	77	95	98
2	77	94	96
3	77	93	95

4. CONCLUSIONS

Two chemically modified chitosan magnetic resins (R1 and R2) were prepared. The uptake behaviour of R2 towards Cr(VI) as chromate anions was studied in alkaline medium. The nature of interaction between the anions and the resin was found to be anion exchange. R2 was found to be efficient for removal of Cr(VI) as chromate in basic media. R2 displays a higher uptake capacity than that of R1 at all experimental conditions. Kinetic studies referred that the uptake reaction is pseudo second order. The uptake reaction is a monolayer and found to be endothermic. The resin was regenerated effectively (desorption ratio \approx 98%) using a mixture of 2 M NaCl and 0.5 M NaOH.

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