Removal of chromium(III) from aqueous solutions using Lewatit S 100: The effect of pH, time, metal concentration and temperature

Fethiye Gode [a], Erol Pehlivan [b],*

[a] *Faculty of Art and Science, Department of Chemistry, Suleyman Demirel University, 32260 Isparta, Turkey*
[b] *Faculty of Engineering and Architecture, Department of Chemical Engineering, Selcuk University, 42031 Konya, Turkey*

Abstract

The removal of the Cr(III) ion from aqueous solutions with the Lewatit S 100 ion-exchange resin is described; and the performance of this resin was compared with Chelex-100 resin. The effect of adsorbent dose, initial metal concentration, contact time, pH and temperature on the removal of Cr(III) was investigated. Lewatit S 100 shows a remarkable increase in sorption capacity for Cr(III). The Batch ion-exchange process was relatively fast; and it reached equilibrium after about 150 min of contact. The ion-exchange process, which is pH dependent show maximum removal of Cr(III) in the pH range 2.8–4.0 for an initial Cr(III) concentration of 1.0×10^{-3} M. The equilibrium constants were 36.67 at pH value 3.5 for Lewatit S 100 and 6.64 at pH value 4.5 for Chelex-100 resin. Both of the resins had high-bonding constants. The equilibrium related to their ion-exchange capacity and the amount of the ion exchange was obtained by using the plots of the Langmuir adsorption isotherm. It was observed that the maximum ion-exchange capacity of 0.39 mmol of Cr(III)/g for Lewatit S 100 and 0.29 mmol of Cr(III)/g for Chelex-100 was achieved at optimum pH values of 3.5 and 4.5, respectively. The thermodynamic equilibrium constant and the Gibbs free energy flow were calculated for each system. The ion exchange of Cr(III) on these cation-exchange resins followed first-order reversible kinetics. The intra-particle diffusion of Cr(III) on ion-exchange resin represented the rate-limiting step. The rise in temperature caused a slight increase in the value of the equilibrium constant (K_c) for the sorption of Cr(III) ion for both resins.
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1. Introduction

In recent years, there has been a growing concern with environmental protection. The presence of heavy metals in the environment has been shown to be detrimental to a variety of living species including human beings. The treatment and removal of heavy metals received considerable attention because of their association with various health problems. Companies that use chromic acid for electroplating, anodizing and other surface finishing operations have a difficult and costly problem of waste chromic acid solution disposal and the treatment of water to wash parts.

In all metal-finishing operations, chromic acid is reduced to Cr(III) and metal salts are formed by dissolution of the met-

als. Toxicological studies have shown that the degree of toxicity of some elements depends on the chemical form in which the element is present. Cr(III) is considered as an essential micronutrient for human, plant and animal metabolism. However, the increasing accumulation of Cr(III) in the environment from industrial outputs caused great concern [1]. Cr(III) has been reported to be toxic to animals and humans and is known to be carcinogenic. Major anthropogenic sources of Cr(III) in the environment include metal extraction, metal fabrication, and textile, leather tanning facilities, electroplating, surface finishing, paints, pigments and manufacture of batteries [2–4].

There are many different ways of treating wastewater. Alongside numerous processes are available for removing dissolved heavy metals from industrial effluents, including thermal, biological and chemical methods such as; coagulation, chemical precipitation, solvent extraction, electrolysis, ultra filtration, membrane separation, adsorption and electro dialysis [5]. Sorption operations, including adsorption and ion exchange, are potential alternatives for aqueous solutions [6–11].

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* Corresponding author at: Department of Chemical Engineering, Selcuk University, Konya 42079, Turkey. Tel.: +90 332 2232127; fax: +90 332 2410635.
 E-mail address: erolpehlivan@yahoo.com (E. Pehlivan).

Modern ion-exchange materials were prepared from synthetic polymers such as styrene-divinylbenzene copolymers, which were sulfonated to form strongly acidic cation exchangers. Ion-exchange resins are used in their entire range to improve water quality, depending on the types and concentrations of the impurities.

Selective resins were deemed major options for treating wastewater. Traces of environmentally harmful substances accumulate on the Lewatit S 100 ion-exchange resins and are thereby removed from the wastewater.

They can be used for the elimination or separation of heavy metals from aqueous solutions, accumulation and recovery of heavy metals, removal of heavy metals from water and process water. Lewatit S 100 is a strongly acidic, gel-like cation-exchange resin with beads of uniform size based on a styrene-divinylbenzene copolymer. Its high exchange capacity, very good chemical, mechanical and thermal stability, good ion-exchange kinetics make it suitable for the treatment of electroplating rinse waters. Gel resins usually have higher efficiencies and cost less.

A macro-pore gives better physical stability, because of its sponge like structure that gives more stress relief. Lewatit S 100 is suitable for a variety of applications involving the treatment of the solutions containing metal salts. Lewatit S 100 has sulfonic acid groups and a greater affinity for ions with higher valances so a predominance of high valance ion can cause a higher rate of reaction. This resin operates at any pH and requires a substantial amount of regenerant. Chelex-100 is weakly acidic cation-exchange resin and has carboxylic groups as the exchange site. Chelex-100 shows a good capacity, improved kinetics of ion exchange, high resistance to osmotic shock and efficiency for uptake of Cr(III) from aqueous solution. Of an ion-exchange process, ions in a fluid phase diffuse to the surface of adsorbent, where they bond with the solid surface or are held there by weak intermolecular forces [12–16]. Biological materials or certain waste products from industrial or agricultural operations have also been recognized as inexpensive materials for the sorbents in the removal of toxic metals but regeneration of used materials are not possible [17].

Ion exchange is one of the proposed mechanisms for metals used in the cation metal sorption and the improved sorption capacity of ion-exchange resins may have advantages over such non-specific adsorbents.

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 this regard, ion-exchange resins hold great potential for the removal of heavy metals from water and industrial wastewater [18–24].

Some research scientists studied the recovery of chromate from cooling towers with ion-exchange resins and the pretreatment of tannery wastewaters by ion-exchange process for the removal of Cr(III) and the removal of Cr(III) from water and wastewater by ion-exchange resins [25,26].

Lewatit S 100 is a gel which is a strongly acidic resin of the sulfonated polystyrene group. Its principal characteristics are excellent physical, chemical and thermal stability, good ion-

exchange kinetics and high exchange capacity [25]. Utilization of Lewatit S 100 is gaining attention as a simple, effective and economic means of treating wastewater containing heavy metals.

In the present study, Lewatit S 100 and Chelex-100 were used for the removal of Cr(III) from aqueous solution. The main objective of this study was to investigate the equilibrium and kinetic parameters of these ion-exchange resins. In addition, the parameters that influence ion exchange, such as initial Cr(III) concentration, pH, isotherm and kinetic studies were investigated.

2. Experimental studies

2.1. Materials

The resins used in the experiments are Lewatit S 100 from Bayer and Chelex-100 from Merck. The physical and chemical properties of the resin were shown in Table 1. All solutions were prepared from analytical grade chemicals and Milli-Q filtered deionized water. Analytical grade reagent of $CrCl_3 \cdot 6H_2O$ was used from Merck and the pH of which was adjusted and maintained constant by adding a small amount of HCl or NaOH. A stock solution of 1×10^{-3} mol/l of $CrCl_3 \cdot 6H_2O$ was prepared by dissolving 0.2664 g of $CrCl_3 \cdot 6H_2O$ in deionized water. The working solutions 1×10^{-4} to 1×10^{-3} mol/l Cr(III) were prepared by appropriate dilution of the stock solutions immediately prior to their use.

2.2. Batch studies by varying reaction time, pH, initial concentration of Cr(III), resin amount and temperature of solution

Batch ion-exchange studies were conducted by shaking the flasks for a period of time at a controlled temperature to achieve equilibration. Batch experiments were carried out at $25 \pm 1\,^{\circ}C$ in stoppered glass tubes by shaking (200 rpm) a fixed mass of 0.1 g of dry resin, with 30 ml, 1×10^{-3} mol/l Cr(III) solution until equilibrium was reached. After agitation for 150 min, the solid was removed by filtration through cellulose filter paper. The final metal concentration in the filtrates as well as in the initial solution was determined by ICP-AES (Varian Vista AX CCD Simultaneous ICP-AES). All experiments were performed in triplicate and the result was taken as the average value of the experiment.

Table 1
General description and some properties of resin

Resin	Lewatit S 100	Chelex-100
Ionic form	Na^+	Na^+
Functional group	Sulfonic acid	Iminodiacetic acid
Matrix	Crosslinked polystyrene	Polystyrene-divinylbenzene
Structure	Gel type beads	Macroporous
pH range	0–14	0–14
Bead size	0.315–1.25 mm	0.3–1.0 mm
Capacity	2.0 eq/l	0.4 mmol/ml
Appearance	Light brown, translucent	White, translucent

The concentration of metal 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 sorbed at time t, q_t, was calculated from the mass balance equation:

$$q_t = \frac{[(C_0 - C_t)V]}{m} \qquad (1)$$

when equilibrium was reached; $C_t = C_e$ and $q_t = q_e$, then the amount of metal ion sorbed at equilibrium, q_e, was calculated using Eq. (1) [20].

Sorption isotherms were determined with different initial concentrations varying from 0.003 to 0.03 mmol/l of metal, while holding the resin amount at constant value at room temperature. The resin amount in the batch vessel varied from 0.2 to 1.0 g for ion-exchange studies. The shaking speed was 200 rpm to maintain resin particles in suspension. After the solution's pH was stabilized and equilibrated, the resin was filtered and Cr(III) content in equilibrium solution was measured. Sorption isotherms were plots of the Cr(III) uptake and the final equilibrium concentration of the residual sorbate remaining in the solution. The Langmuir model of ion exchanges was used to compare the single metal sorption performance and to determine the capacity of resins for Cr(III) ion.

For the pH effect experiment, 4 h time period was sufficient to reach equilibrium. The ion-exchange experiments were carried out at room temperature ($25 \pm 1\,^\circ$C). The initial pH of the sample solutions were adjusted in the range of 1.5–6 with 0.1N HCl or diluted NaOH. All pH measurements were performed with a Jenway 3010 digital pH meter.

After equilibrium was reached, the pH of the solution was measured and recorded. Temperature effects on the sorption experiments were carried out in incubator (Gallenkamp Incubator) with 30 ml solution of 1×10^{-3} mol/l chromium solution at 20, 35, 50 and 65 $^\circ$C. The effect of the adsorbent amount was studied with a 30 ml solution of 1×10^{-3} mol/l chromium solution and varying amounts of adsorbent from 100 to 1000 mg.

3. Results and discussion

3.1. Effect of pH

In order to optimize the pH for maximum removal efficiency, the experiments were conducted with 0.03 mmol/l of metal solution containing 0.1 g of Lewatit S 100 cation-exchange resin and Chelex-100 in the pH range 2.0–6.0. The effect of the pH on the removal of Cr(III) by the ion-exchange resins was presented in Fig. 1. In general, the experimental conditions such as metal concentration and pH level have strong effects on the equilibrium constant, K_c; so it can be used as a comparative measure of the efficiencies of various exchangers.

The interactions of metals with Lewatit S 100 resin are complex, probably simultaneously dominated by adsorption and ion exchange. The pH dependence of ion exchange may suggest that the metal ions are adsorbed according to the ion-exchange mechanism. The effect of pH on ion exchange of Cr(III) was studied at room temperature by varying the pH of metal solution-ion
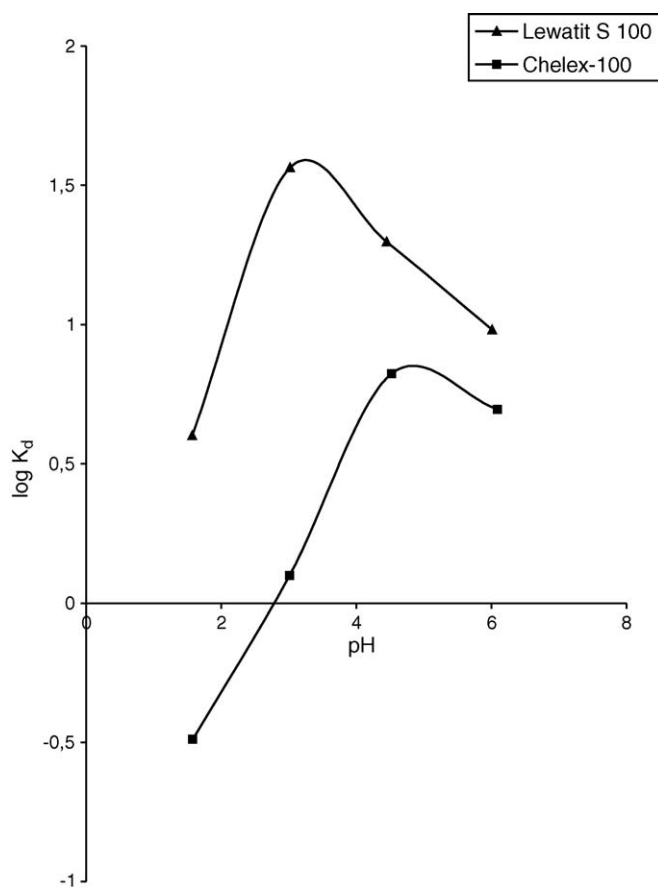

Fig. 1. Effect of pH on the ion exchange of Cr(III) using the Lewatit S 100 and Chelex-100. Ion-exchange conditions; initial concentration of Cr(III): 1×10^{-3} mol/l, amount of resin: 0.5 g, volume of ion-exchange medium: 30 ml, temperature: $25 \pm 1\,^\circ$C and stirring time: 200 rpm.

exchanger from 2.0 to 6.0. In pH range of 2.0–2.8, there is little or no sorption.

The percent ion exchange increases in the pH range of 3.0–4.0. This shows the maximum ion exchange at pH 3.5 for Lewatit S 100 resin. The sorption of Cr(III) ion on Chelex-100 is favorable at a pH value of 4.5. After pH 6, because of precipitation of Cr(III), the optimum pH was chosen as pH 3.5 for Lewatit S 100 resin and pH 4.5 for Chelex-100 resin. It was observed that the maximum ion-exchange capacity of 0.39 mmol of Cr(III)/g for Lewatit S 100 and 0.29 mmol of Cr(III)/g for Chelex-100 was achieved at optimum pH values of 3.5 and 4.5, respectively.

Lewatit S 100 showed a remarkable increase in sorption capacity for Cr(III) in the solution having low pH values. The equilibrium constant increased from a value of 3.98 (at approximately pH 2) to 36.67 at pH 3.5 for Lewatit S 100 and 0.1–6.64 for Chelex-100. The sites responsible for the ion-exchange process are due to the –SO$_3$H groups in the Lewatit S 100 matrix [27].

This sorption trend can likely be ascribed to the effect of competitive binding between Cr(III) and hydrogen ions for the binding sides on the surface of the resins. At low pH, an excess of hydrogen ions can compete effectively with Cr(III) for bonding sites, resulting in a lower level of Cr(III) uptake. This increase is rational for Chelex-100 because the exchanger being weakly
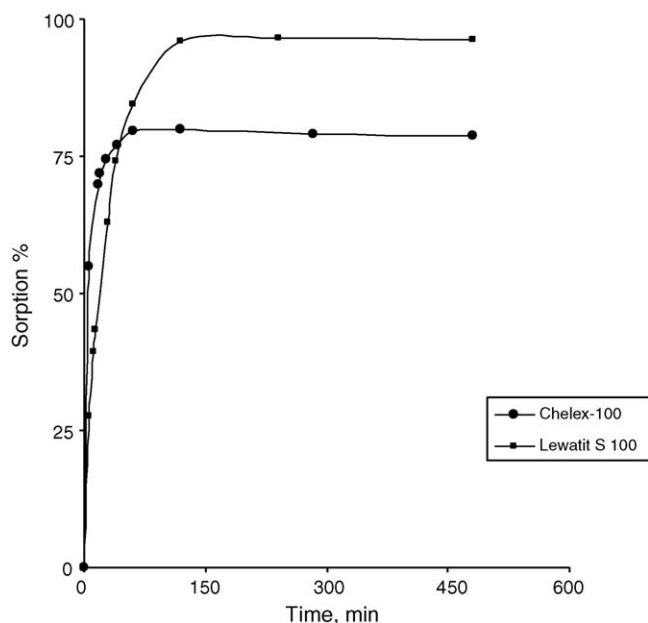
Fig. 2. Effect of contact time on the ion exchange of Cr(III) using Lewatit S 100 and Chelex-100. Ion-exchange conditions; initial concentration of Cr(III): 1×10^{-3} mol/l, amount of resin: 0.5 g, volume of ion-exchange medium: 30 ml, temperature: $25 \pm 1\,^\circ$C, stirring time: 200 rpm and initial pH: 3.8.

acidic, is practically in the hydrogen form at pH 2 and is gradually converted into metal form as the pH was increasing. To avoid precipitation of the metal ions, all the experiments were conducted at a maximum pH of 6.0 [28]. The percentage of ion-exchange decreases rapidly when the pH is increased above 6.0 due to the formation of Cr(III) precipitation and the formation of hydroxyl complexes of chromium, $Cr(OH)_3$ at higher pH values [18].

3.2. Effect of reaction time

Fig. 2 shows the effect of reaction time on the removal of Cr(III) by Lewatit S 100 and Chelex-100. The Cr(III) removal

increased with time and attained equilibrium at about 150 min for Cr(III) for 1×10^{-3} mol/l chromium ion concentration used [29,30]. The percentage of metal removal increased rapidly up to approximately 70 min for Lewatit S 100 and 45 min for Chelex-100 resin and thereafter, rose slowly before attaining a saturation value in 150 min for Lewatit S 100 and 120 min for Chelex-100 resin. A further increase in contact time had a negligible effect on the percent removal.

The percentage metal removal is higher in the beginning due to greater number of resin exchange sites available for the sorption of the metal. The ion-exchange process is the major mechanism for the removal of metal ions from solution within the pH range of 2.0–6.0 for Lewatit S 100 and the basic process is essentially competitive ionic attraction for the ionic site.

When considering Chelex-100 resin involving, it is accepted that a coordinate bond is formed between Cr(III) and the carboxyl group on the surface during the exchange process. Chelation exchange invariably involves an ion-exchange process in conjunction with the formation of a coordinate bond.

In all subsequent experiments, the equilibrium time was maintained at 150 min, which was considered as sufficient for the removals of Cr(III) ion by both resins [6,27,28,31–33]. The metal uptake versus time curves, are single, smooth and continuously leading to saturation suggesting the possible monolayer coverage of metal ions on the surface of the adsorbent. The Batch ion-exchange process was relatively faster for Chelex-100 than Lewatit S 100 but the cation-exchange capacities of Lewatit S 100 is higher than Chelex-100 reached in this study and the exchange capacities are 0.39 and 0.29 mmol for Cr(III) per gram of resins, respectively. The maximum recoveries of Cr(III) (about 99% for Lewatit S 100 at pH 3.5 and about 80% for Chelex-100 at pH 4.5) were found as shown in Fig. 2.

3.3. Sorption isotherms as a function of initial metal concentration

The percentage uptake is highly dependent upon the initial concentration of the Cr(III) ion and the resin. The initial Cr(III)
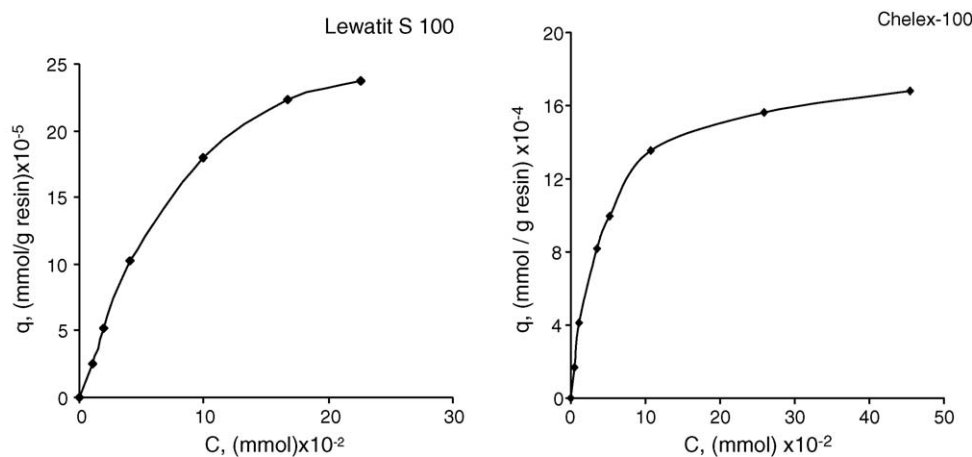

Fig. 3. Sorption isotherm of Cr(III) on Lewatit S 100 and Chelex-100 as a function of initial metal concentration. Ion-exchange conditions; initial concentration of Cr(III): $1 \times 10^{-4} - 1 \times 10^{-3}$ mol/l, amount of resin: 0.5 g, volume of ion-exchange medium: 30 ml, temperature: $25 \pm 1\,^\circ$C, stirring time: 200 rpm, at pH: 3.8 for Lewatit S 100 and pH: 4.5 for Chelex-100.

concentrations tested were 1×10^{-4}, 2×10^{-4}, 4×10^{-4}, 6×10^{-4}, 8×10^{-4}, 1×10^{-3} mol/l at an amount of adsorbent of 0.5 g (Fig. 3). The data indicates that the initial metal concentration determines the equilibrium concentration, and also determines the uptake rate of metal ion and the kinetic character of the process.

In the case of low concentrations, the ratio of the initial number of moles of Cr(III) ion to the available surface area is larger and subsequently, the fractional ion exchange becomes independent of initial concentrations. The rapid metal removal has significant practical importance, as this will facilitate with the small amount of resins to ensure efficiency and economy.

Equilibrium isotherm, the relation between the amount exchange (q_e) and the remaining concentration in the aqueous phase (C_e), is important to describe how solutes interact with the resins and so is critical in optimizing the use of the resins.

Cr(III) sorption isotherms of Chelex-100 and Lewatit S 100 resins are presented in Fig. 3 as a function of the equilibrium concentration of metal ions in the aqueous medium at room temperature (25 °C) for 150 min of contact time.

The amount of Cr(III) ions adsorbed per unit mass of the resin increased with the initial metal concentration as expected. To obtain maximum sorption capacities or reach the plateau values that represent saturation of the active groups which are available for interaction with Cr(III) ions on the resins, the initial concentration were increased from 0.1 to 1.0 mmol/l Cr(III) for both resins. Both resins were saturated at relatively low concentrations indicating strong binding for Cr(III).

3.4. Effect of resin amount on ion exchange

Fig. 4 presents the removal of Cr(III) as a function of resin amount using Lewatit S 100 in a solution at pH 3.5 and Chelex-100 in a solution pH 4.5. The resin amount varied from 0.1 to 1.0 g; and it was equilibrated for 24 h. It is clear that the

maximum removal of 10 mg/1 of Cr(III) ion in 100 ml requires a minimum resin amount of 100 mg for Lewatit S 100 resin. For the quantitative removal of 0.001 M Cr(III) in 30 ml, a minimum resin dosage of 0.8 g of Chelex-100 resin is required.

It is apparent that, the amount of adsorbed metal ion per unit mass increases by increasing the resin amount and the sorption density. It was found that the retention of Cr(III) increased with increasing amount of the Lewatit S 100 up to 0.50 g and the Chelex-100 up to 0.80 g. These values were taken as the optimum amount for other trials. Since the fraction of metal removed from the aqueous phase increases as the sorbent dosage is increased in the batch vessel with a fixed initial metal concentration, the curves in Fig. 4 approach asymptotic values from 0.5 to 1.0 g resin. An increase in the sorbent amount resulted in a decrease in the contact time required to reach the equilibrium.

It may be concluded that by increasing the adsorbent dose the removal efficiency increases but ion-exchange density decreases. The decrease in ion-exchange density can be attributed to the fact that some of the ion exchange remains unsaturated during the sorption process; whereas the number of available ion-exchange sites increases by an increase in sorbent and this results in an increase in removal efficiency [33]. As expected, the equilibrium concentration decreases with increasing adsorbent doses for a given initial Cr(III) concentration, because increasing adsorbent doses provide a greater surface area or ion-exchange sites for a fixed initial solute concentration [6,18,27,30,32,33].

3.5. Thermodynamic evaluation of the process

The ion exchange of Cr(III) ions at different temperatures using Lewatit S 100 at pH 3.5 and Chelex-100 at pH 4.5 are presented in Fig. 5. The effect of temperature on the equilibrium constant, (K_c) for the ion exchange of metal ions onto resins was investigated in this stage. Equilibrium constants for Cr(III) were
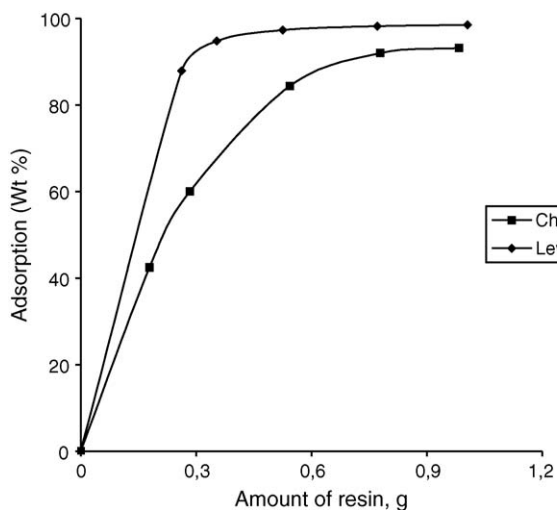

Fig. 4. Effect of amount of resin on the ion exchange of Cr(III) using the Lewatit S 100 and Chelex-100. Ion-exchange conditions; initial concentration of Cr(III): 1×10^{-3} mol/l, amount of resin: 0.1–1.0 g, volume of ion-exchange medium: 30 ml, temperature: 25 ± 1 °C, stirring time: 200 rpm and initial pH: 3.8 and 4.5.
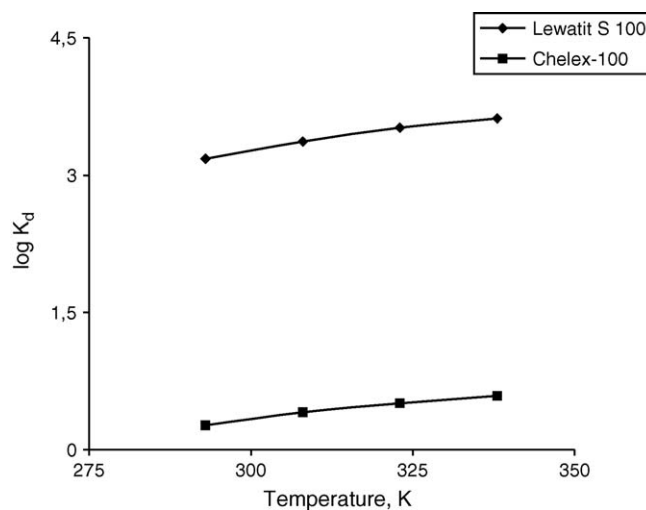

Fig. 5. Effect of temperature on the ion exchange of Cr(III) using the Lewatit S 100 and Chelex-100. Ion-exchange conditions; initial concentration of Cr(III): 1×10^{-3} mol/l, amount of resin: 0.5 g, volume of ion-exchange medium: 30 ml, initial pH: 3.8 and stirring time: 200 rpm.

high and ion exchange increased slightly with temperature for both resins.

This is due to the exothermic ion-exchange reactions of Cr(III) ion with resins. The equilibrium constants for such reactions slightly increase with temperature. The carboxylic groups of iminodiacedic acid resin are partially protonated at all temperatures but their deprotonation degree increases with temperature, resulting in slight increase in metal capacities at high temperature. Where only ion exchange is involved, the temperature effect on retention time is relatively small.

The ion-exchange mechanism (i.e., chemical or physical) is often an important indicator to describe the type and level of interactions between the adsorbate and adsorbent. If ion exchange decreases with increasing temperature, it may be indicative of physical ion exchange and the reverse is generally true for chemisorption. The type of ion exchange may be determined through such thermodynamic quantities as free energy of ion exchange (ΔG^0) and the enthalpy of ion exchange (ΔH^0) both of which can be obtained from the ion-exchange data given in Fig. 5.

The "chelate effect" concerns a large positive change in entropy on formation of a chelate complex, which means that the change of Gibbs free energy with temperature will be negative. Considering other thermodynamic factors, it is possible that the entropy change in chelation reactions may have less important bearing effects on temperature than the enthalpy of sorption. Thus, as the temperature increases, the resulting ΔG^0 will become negative and so the equilibrium constant will decrease slightly as temperature increases for Chelex-100.

Another very important thermodynamic parameter in determining the type of ion-exchange is the heat of ion exchange (ΔH^0). This can be obtained from the Clausius-Clapeyron Eq. (3):

$$\frac{\mathrm{d} \ln K_c}{\mathrm{d}(1/T)} = \frac{-\Delta H^0}{R} \tag{2}$$

The slopes of $\ln K_c$ versus $1/T$ are used via Eq. (3) to calculate the ΔH^0 for each model. The results are presented in Table 2 along with the entropy values calculated using Eq. (3) given below:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 < 0 \tag{3}$$

The ion-exchange reaction that occurs spontaneously is always associated with a decrease in free energy of the system. Gibbs free energy is of the utmost importance since it enables us to predict which reaction will occur and which will not. The ion-exchange process is comprised of two contributions enthalpy and entropy, which characterize whether the reaction is spontaneous.

The negative value of free energy of ion exchange calculated according to all models indicates that the ion exchange of Cr(III) ions onto resin is spontaneous [27,32–36].

3.6. Ion-exchange isotherm

Sorption process modeling is a topic of interest for the prediction of metal partitioning between the aqueous solution and the solid surface. In particular, the non-competitive Langmuir and Freundlich isotherms have been useful tools for the description and comparison of heavy metal sorption by different sorbents [37,38]. These isotherms relate metal uptake per unit weight of adsorbent q to the equilibrium adsorbate concentration in the bulk fluid phase C_e.

The Langmuir isotherm is given as:

$$\frac{C_e}{q} = \frac{1}{(A_s b)} + \frac{C_e}{A_s} \tag{4}$$

where A_s and b are Langmuir constants related to ion-exchange capacity and energy of ion exchanges, respectively. The Langmuir model represents one of the first theoretical treatments of non-linear sorption, and has been successfully applied to a wide range of systems that exhibit limiting or maximum sorption capacities. The model assumes uniform energies of ion exchange onto the surface and no transmigration of the adsorbate in the plane of the surface [11].

The Freundlich isotherm is the most widely used non-linear sorption model and is given by the general form:

$$q = kC_e^{1/n} \tag{5}$$

where k relates to sorption capacity and n to sorption intensity [6,9,18,20]. The ion-exchange capacities (k) and ion-exchange intensities (n) are presented in Table 3. Values of $1 < n < 10$ show favorable ion exchange of metals on ion-exchange resin. Higher value for k indicates higher affinity for Cr(III) [30].

The essential feature of Langmuir equation can be given in terms of a dimensionless separation factor, R_L, for defined as:

$$R_L = \frac{1}{(1 + bC_0)} \tag{6}$$

where C_0 is the highest initial metal concentration. The value of R_L indicates the shape of the isotherm to be favorable ($0 < R_L < 1$). In our work, the value of R_L obtained is 0.99 and listed in Table 3.

The data for the uptake of Cr(III) ion by the resin has been processed in accordance with a linear form of the Langmuir isotherm equation. The linear model, which describes the accu-

Table 2
Thermodynamic parameters for Cr(III) on resin

Resin	ΔH^0 (J mol^{-1})	ΔS^0 (J K^{-1} mol^{-1})	ΔG^0 (J mol^{-1})			
			$T = 298.15$ K	$T = 308.15$ K	$T = 323.15$ K	$T = 338.15$ K
Lewatit S 100	−103.23	383.89	−112373.92	−118132.13	−123890.35	−129649.57
Chelex-100	−37.36	113.30	−33158.24	−34857.67	−36557.11	−38256.54

Table 3
Freundlich and Langmuir isotherm parameters on Lewatit S 100 and Chelex-100 resin with Cr(III)

Resin	Freundlich isotherm			Langmuir isotherm			
	k	n	R^2	A_s	b	R^2	R_L
Lewatit S 100	45081.68	0.71	0.89	0.39	6445.75	0.97	0.999
Chelex-100	0.03	1.48	0.89	0.29	0.09	0.90	0.999

k and A_s: mmol/g resin (capacity of ion exchanger), R^2: correlation coefficient.

mulation of solute by sorbent was directly proportional to the solution concentration. The Langmuir isotherm applies to ion exchange on a completely homogenous surface with negligible interaction between adsorbed molecules.

The Langmuir treatment is based on the assumption that maximum ion exchange depends on the saturation level of a monolayer of adsorbate molecules on the adsorbent surface, that the energy of ion exchange is constant, and that there is no trans-migration of adsorbate molecules in the surface plane.

The Langmuir isotherm parameter was determined by least-squares fit of the sorption data in Fig. 3. A_S and b were determined from the slope and intercept of the Langmuir plot and than were shown in Table 3. The Langmuir isotherm equation provided an excellent fit to the equilibrium sorption data, giving correlation coefficients of 0.90 and 0.97 on the two sorbents, respectively. The results obtained showed that resins have the largest capacity and affinity for the removal of Cr(III) ions from solutions under the conditions studied.

3.7. Ion-exchange kinetic model

The kinetics of Cr(III) ion exchange on Lewatit S 100 followed the first-order rate expression given by Lagergren:

$$\log(q_e - q) = \log q_e - k_{ad} \left(\frac{t}{2.303} \right) \qquad (7)$$

where q and q_e are the amounts of Cr(III) adsorbed (mg/g) at time t (min) and at equilibrium time, respectively, and k_{ad} is the rate constant of ion exchange [30,32].

Various mechanisms and steps in ion-exchange phenomena can control the kinetics. Four major rate-limiting steps are generally cited [39,40]: (1) mass transfer of solute from solution to the boundary film; (2) mass transfer of metal ions from boundary film to surface; (3) sorption and ion exchange of ions onto sites; (4) internal diffusion of solute. The third step is assumed to be very rapid and non-limiting in this kinetic analysis: sorption is a rapid phenomenon. The first and the second steps are external mass transfer resistance steps, depending on various parameters such as agitation and homogeneity of solution. The fourth one is an internal particle diffusion resistance step.

Experiments were also performed to understand the kinetics of Cr(III) removal by The Lewatit S 100 resin. It was well established that the ion exchange of ions in aqueous system followed reversible first-order kinetics, when a single species is considered on a heterogeneous surface. Kinetics of sorption describing the solute uptake rate, which, in turn, governs the residence time of the sorption reaction, is one of the important characteristics defining the efficiency of sorption.
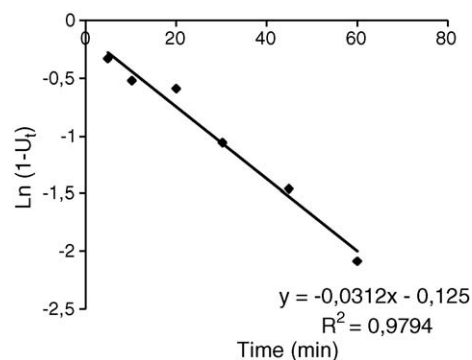

Fig. 6. Kinetic fits for the ion exchange of Cr(III) on Lewatit S 100. Ion-exchange conditions; Cr(III) amount: 0.06 mmol, amount of resin: 0.5 g, volume of ion-exchange medium: 30 ml, initial pH: 3.8 and stirring time: 200 rpm.

Table 4
Rate constants for the removal of Cr(III) with Lewatit S 100

Resin	Cr(III) amount (mmol)	Overall rate constant $K = k_1 + k_2$ (h^{-1})	Forward rate constant k_1 (h^{-1})	Backward rate constant k_2 (h^{-1})
Lewatit S 100	0.060	0.030	0.030	0.001
Chelex-100	0.060	0.034	0.027	0.007

Hence, in the present study, the kinetics of Cr(III) removal has been carried out to understand the behavior of these adsorbents. By using Eq. (7), and the equations given in our earlier previous work [20] and plotting $\ln(1-U_t)$ versus t (Fig. 6), the equilibrium constant K, forward and backward rate constants k_1 and k_2 were calculated and shown in Table 4. The forward rate constants for the removal of Cr(III) were much higher than the backward rate constants namely the desorption process (Table 4). This suggests that the rate of ion exchange is clearly dominant. The kinetics of the resin Chelex-100 were determined to be slower than Lewatit S 100.

4. Conclusion

The results here, show that Lewatit S 100 and Chelex-100 can efficiently remove traces of Cr(III) present in aqueous solutions. The kinetic data would be useful for the fabrication and designing of wastewater treatment plants. Ion-exchange of the Cr(III) is dependent on the initial concentrations of the adsorbent, sorbate, time of contact and pH level. Metal sorption is pH dependent and maximum sorption for Cr(III) ion was found to occur at a pH level of about 3.5 for Lewatit S 100 and 4.5 for Chelex-100; and the equilibrium conditions are attained after nearly 150 min for Lewatit S 100 and 120 min for Chelex-100.

Isothermal data of Cr(III) ion exchange on Lewatit S 100 can be modeled with the Langmuir isotherm. The capacity of the resins for ion exchange of Cr(III) can be calculated with this model. The values for ion-exchange capacity (K_b) and intensity of ion exchange (A_s) indicate the greater affinity for Cr(III) by these resins.

The kinetics of Cr(III) ion exchange by these ion-exchange resin followed first-order reversible kinetics. A batch contactor requires about 120–150 min contact time to achieve 80–96% removal from aqueous solution.

The strong acid cation resin took up Cr(III) ion relatively efficient and can be used for removal of Cr(III) from aqueous solutions and application of this ion-exchange resin to wastewater treatment is expected to be economical and efficient.

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References

[1] K.S. Low, C.K. Lee, A.Y. Ng, Bioresource Technol. 68 (1999) 205.
[2] S. Kocaoba, G. Akcin, Talanta 57 (2002) 23.
[3] T. Stephenson, Sources of heavy metals in wastewater, in: J.N. Lester (Ed.), Heavy Metals in Wastewater, CRC Press, Boca Raton, 1987.
[4] T.N. De Castro Dantas, A.A. Dantas Neto, M.C.P. De, A. Moura, Water Res. 35 (9) (2001) 2219.
[5] I.M.M. Kenawy, M.A.H. Hafez, M.A. Akl, R.R. Lashein, Anal. Sci. 16 (2000) 493.
[6] J.L. Cortina, N. Miralles, M. Aguilar, A.M. Saster, Hydrometallurgy 40 (1996) 195.
[7] M. Soylak, L. Elçi, Int. J. Environ. Anal. Chem. 66 (1) (1997) 51.
[8] B. Yu, Y. Zhang, A. Shukla, S.S. Shukla, K.L. Dorris, J. Hazard. Mater. B80 (2000) 33.
[9] A. Seco, C. Gabaldon, P. Marzal, A. Aucejo, J. Chem. Technol. Biotechnol. 74 (1999) 911.
[10] P.A. Brown, S.A. Gill, S.J. Allen, Water Res. 34 (16) (2000) 3907 (Review Paper).
[11] M. Yu, W. Tian, D. Sun, W. Shen, G. Wang, N. Xu, Anal. Chim. Acta 428 (2001) 209.
[12] R.-S. Juang, F.-C. Wu, R.-L. Tseng, Water Res. 33 (10) (1999) 2403.
[13] S. Chah, J.S. Kim, J.H. Yi, Sep. Sci. Technol. 37 (3) (2002) 701.
[14] J.S. Kim, J.H. Yi, J. Chem. Technol. Biotechnol. 75 (5) (2000) 359.
[15] J.S. Kim, J.C. Park, J. Yi, Sep. Sci. Technol. 35 (12) (2000) 1901.
[16] B. Mattuschka, G. Straube, J. Chem. Technol. Biotechnol. 58 (1993) 57.
[17] S. Rengaraj, C.K. Joo, Y. Kim, J. Yi, J. Hazard. Mater. 102 (2–3) (2003) 257.
[18] S. Lacour, J.-C. Bollinger, B. Serpaud, P. Chantron, R. Arcos, Anal. Chim. Acta 428 (2001) 121.
[19] S.H. Lin, S.L. Lai, H.G. Leu, J. Hazard. Mater. B76 (2000) 139.
[20] F. Gode, E. Pehlivan, J. Hazard. Mater. 100 (1–3) (2003) 231.
[21] S. Rengaraj, S.-H. Moon, Water Res. 36 (7) (2002) 1783.
[22] G. Tiravanti, D. Petruzzelli, R. Passino, Water Sci. Technol. 36 (2–3) (1997) 197.
[23] S. Chiarle, M. Ratto, M. Rovatti, Water Res. 34 (11) (2000) 2971.
[24] G.P. Miller, D.I. Norman, P.L. Frisch, Water Res. 34 (4) (2000) 1397.
[25] Lewatit Catalog, Removing traces, Bayer, 1998.
[26] C.W. Cheung, J.F. Porter, G. Mckay, Water Res. 35 (3) (2001) 605.
[27] L.J. Yu, S.S. Shukla, K.L. Dorris, A. Shukla, J.L. Margrave, J. Hazard. Mater. B100 (1–3) (2003) 53.
[28] C. Namasivayam, S. Senthilkumar, Sep. Sci. Technol. 34 (2) (1999) 201.
[29] D. Mohan, S. Chander, Colloids Surf. A: Phys. Eng. Aspects 177 (2001) 183.
[30] J. Pradhan, S.N. Das, R.S. Thakur, J. Colloid Interf. Sci. 217 (1999) 137.
[31] B. Bayat, J. Hazard. Mater. B95 (2002) 275.
[32] C. Namasivayam, R.T. Yamuna, Water Air Soil Pollut. 113 (1999) 371.
[33] M. Dakiky, M. Khamis, A. Manassra, M. Mer'eb, Adv. Environ. Res. 6 (4) (2002) 533.
[34] S.L.C. Ferreira, C.F. de Brito, A.F. Dantas, N.M.L. de Araujo, A.C.S. Costa, Talanta 48 (1999) 1173.
[35] C. Raji, T.S. Anirudhan, Water Res. 32 (12) (1998) 3772.
[36] M. Kara, H. Yuzer, E. Sabah, M.S. Celik, Water Res. 37 (2003) 224.
[37] K.H. Chong, B. Volesky, Biotechnol. Bioeng. 47 (1995) 451.
[38] Q. Yu, P. Kaewsarn, Sep. Sci. Technol. 34 (8) (1999) 1595.
[39] Y.S. Ho, G. Mckay, Adsorption 5 (1999) 409.
[40] B.S. Krishna, D.S.R. Murty, B.S. Jai Prakash, J. Colloid Interf. Sci. 229 (1) (2000) 230.