

## Removal of Cr(VI) from aqueous solution by two Lewatit-anion exchange resins

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### Abstract

The sorption of hexavalent chromium, Cr(VI), from aqueous solutions on macroporous resins containing tertiary amine groups (Lewatit MP 62 and Lewatit M 610) was studied at varying Cr(VI) concentrations, adsorbent dose, pH, contact time and temperatures. The concentration of chromium in aqueous solution was determined by inductively coupled plasma spectrometry (ICP–AES). Batch shaking sorption experiments were carried out to evaluate the performance of Lewatit MP 62 and Lewatit M 610 anion exchange resins in the removal of Cr(VI) from aqueous solutions. The ion-exchange process, which is pH dependent, shows maximum removal of Cr(VI) in the pH range 2–6 for an initial Cr(VI) concentration of 100 ppm. The sorption increases with the decrease in pH and slightly decreases with the increase in temperature. Both ion exchangers had high bonding constants with Lewatit M 610 showing stronger binding. It was observed that the maximum adsorption capacity of 0.40 mmol of Cr(VI)/g for Lewatit MP 62 and 0.41 mmol of Cr(VI)/g for Lewatit M 610 was achieved at pH of 5.0. The thermodynamic parameters (free energy change,  $\Delta G^\circ$ ; enthalpy change,  $\Delta S^\circ$ ; and entropy change,  $\Delta H^\circ$ ) for the sorption have been evaluated. The rise in temperature caused a slight decrease in the value of the equilibrium constant ( $K_c$ ) for the sorption of Cr(VI) ion. The sorption of Cr(VI) on the resin was rapid during the first 15 min and equilibrium was found to be attained within 30 min. The sorption of Cr(VI) onto the resins followed reversible first-order rate kinetics. Such ion exchange resins can be used for the efficient removal of chromium from water and wastewater.

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**Keywords:** Anion-exchange resin; Batch adsorption; Cr(VI); Adsorption isotherms

### 1. Introduction

The problem of removing pollutants from water and wastewater has grown with rapid industrialization. Several industries like paint and pigment manufacturing, stainless steel production, corrosion control, leather tanning, chrome plating, wood preservation, fertilizers, textile, photography, etc. discharge effluent containing hexavalent chromium, Cr(VI), to surface water. Hexavalent chromium is toxic and a suspected carcinogen material and it is quite soluble in the aqueous phase almost over the entire pH range and mobile in the natural environment. Cr(VI) in acidic solution demonstrates a very high positive redox potential which denotes that it is

strongly oxidizing and unstable in the presence of electron donors. Cr(VI) forms several species, the relative proportions of which depend on both pH and total Cr(VI) concentration. Above pH 7, only  $\text{CrO}_4^{2-}$  ions exist in the solution throughout the concentration range; in the pH between 1 and 6,  $\text{HCrO}_4^{2-}$  is predominant. Within the normal pH range in natural waters, the  $\text{CrO}_4^{2-}$ ,  $\text{HCrO}_4^{2-}$  and  $\text{Cr}_2\text{O}_7^{2-}$  ions are forms expected and they constituted a lot Cr(VI) compounds which are quite soluble and mobile in water streams. Chromate compounds, widely used in industry, have been shown to have serious toxic effects on humans. Scientific evidence showed the oxidation of Cr(III) to more mobile Cr(VI) even under ambient conditions. For that reason, this toxic metal must be removed from water reservoirs [1,2].

There are many different ways of treating process and wastewater. Alongside mechanical and physical processes,

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these include thermal, biological and chemical methods. Among the various treatment techniques available, the most commonly used ones are: ion exchange, adsorption, reduction and precipitation. In many cases, the environmentally most compatible and cost effective solution comprises a combination or two or more of these processes. The main advantages of ion exchange are recovery of metal value, selectivity, less sludge volume produced and the meeting of strict discharge specifications. Ion exchange using synthetic resins is the method of choice for removing toxic metal contaminants in water and wastewater [3–8].

Removal of Cr(VI) from cooling water and ground water by an ion-exchanger has been investigated by a number of researchers [9–14]. For removing chromates from water at acidic pH values, weak-base anion exchange resins are generally used [15,16]. The separation of metals with similar properties is a most useful analytical application of ion exchange [15–17]. Obviously, the ion exchange process has been a strong alternative to precipitation because of its ability to reduce dissolved chromate concentration to no detectable levels in the water treatment plants. The concentrations of the substances that have to be removed are normally in the lower ppm range. Lewatit ion exchange resins are particularly suited for this type of applications. There are basically two types of strong base anions, one uses trimethylamine (TMA) and the other uses dimethylethanolamine (DMEA) to functionalize the resin. Lewatit M 610 resin which has DMEA functional group has a greater capacity than Lewatit MP 62 resin which is functionalized with a tertiary amine.

Environmental pollution and its abatement have drawn keen attention for a long time. Direct elimination of Cr(VI) was performed by its fixation on the appropriate resin at industrial scale and the selective recovery and recycling of Cr(VI). Kubrakova et al. [18] have studied the microwave sorption preconcentration of chromium under dynamic conditions followed by determination of the metal in the eluate or in the solid phase of the sorbent by electrothermal atomic absorption spectrometer (ETAAS). Another report by Sule and Ingle [19] describes the adsorption of Cr(III) species by Chelex-100 chelating resin and Cr(VI) species by the anion-exchange resin. According to Donais et al. [20], an automated method was developed for the separation and determination of Cr(VI) and Cr(III) using low-pressure chromatographic separation of the species coupled with on-line ICP–MS detection. The inductively coupled plasma spectrometry (ICP–AES) determination of chromium in water streams requires a preconcentration step, since they have low concentration amount [21–25].

In the present paper, anion exchange resins, weakly and strongly basic were examined for their sorption properties towards Cr(VI) ion not only for different conditions, but also for different temperatures. The parameters that influence adsorption, initial Cr(VI) concentration, agitation time, pH, resin amount, isotherm and kinetic studies were investigated at 25 °C. In addition, the equilibrium and kinetic parameters of Cr(VI) at pH 5 were investigated at 20, 35, 50 and 65 °C.

## 2. Experimental

### 2.1. Reagents and ion exchange media

Double distilled water free from interference at the minimum detection limit of each constituent filtered through a membrane filter was used in all experiment. Solutions of 0.01 M NaOH and HCl (from Aldrich) were used for pH adjustment. Cr(VI) stock solution (from Merck) was prepared from potassium salts of dichromate ( $K_2Cr_2O_7$ ) of analytical grade. This study was conceived for the equilibrium, thermodynamics and kinetics characterization of the following systems: strong-base anion exchanger with a macro-porous structure (Lewatit M 610 from Bayer AG)—synthetic solution of  $K_2Cr_2O_7$ , and the second one, the weak-base anion exchanger with a macroporous structure (Lewatit MP 62 from Bayer AG)—synthetic solution of  $K_2Cr_2O_7$ . The physical properties of the resins are shown in Table 1.

### 2.2. Instrumentation

Inductively coupled plasma spectrometry (Varian Vista ICP–AES) was used for metal analysis. pH was measured by using a glass electrode (Jenway 3010 model pH meter). A shaker with thermostat (Gallenkamp Incubator) of Orbital model was used for adsorption experiments and temperature studies.

### 2.3. Experimental methods

The resins, Lewatit MP 62 and Lewatit M 610, were washed several times with doubly distilled water. Then the resins were conditioned by treating with several 100 mL portion of 1 M HCl. The resins were then left standing for 24 h and washed with distilled water until the washing was free from  $Cl^-$ . After air drying, the resin was stored for sorption studies. Prior to any experiments, the resins were carefully treated for changing the ion-exchanger to RC1 form.

The sorption curves were determined by a batch procedure. The influence of the amounts of the chromium for the sorption procedure was investigated by using 20–100 ppm Cr(VI) solutions. For measurements of the exchange equilibrium, a series of samples of swollen resin (~0.05 g in the dry state) originally completely loaded with  $Cl^-$  was equilibrated with a 0.03 L  $K_2Cr_2O_7$  solution of different concentrations (20–100 mg Cr/L) at room temperature ( $25 \pm 1$  °C) in a thermostatic shaker bath for 2 h. The resins were separated by filtration and washed in distilled water. The filtrate was analyzed by ICP–AES for Cr(VI) content. The concentration of chromium metal ions was calculated from the change in metal concentration in the aqueous solution before and after equilibrium sorption from the weight of the dry resin used. In all cases, mass balance was confirmed.

The effect of initial pH studies on the removal of chromium about 100 mL of chromium solution of desired concentration was taken in bottles and known amount of Lewatit MP 62

Table 1  
Properties and specifications of Lewatit MP 62 and Lewatit M 610 anion exchange resins

Resin	Lewatit MP 62	Lewatit M 610
Type	Anion exchange resin, weakly basic	Anion exchange resin, strongly basic
Functional group	Tertiary amine	Tertiary amine (dimethyl amino ethanol)
Matrix	Macroporous crosslinked polystyrene	Macroporous crosslinked polystyrene
Bead size (mm)	0.31–1.25	0.30–1.20
Operating pH range	0–8	1–14
Total exchange capacity (meq/L)	1.7 eq/L	3.7 meq/g
Thermal stability (°C)	–20 to 100	–20 to 70

and Lewatit M 610 resins was added separately and pH was adjusted using 0.01 M HCl or dilute NaOH solutions. The solutions were agitated in the shaking incubator. The resins were separated and filtrate was analyzed by ICP–AES for Cr(VI) content.

The effect of the resin dosage for adsorption studies was studied in the batch vessel by varying the resin from 0.2 to 1.0 g. Contact time adsorption experiments were conducted at 25 °C in a well-mixed pyrex glass vessel with a cover. The sorption of Cr(VI) on the resins at different temperatures ranging from 20 to 65 °C was investigated in the thermostatic shaker. After the solution's pH was stabilized and equilibrated, the resin was filtered and Cr(VI) content in equilibrium solution was measured.

Kinetics measurements were performed in a glass vessel equipped with a mechanical stirrer in static conditions. Samples of the resins in the swelling form (0.05 g in the dry state) were contacted with a 0.03 L  $K_2Cr_2O_7$  solution of a known concentration (100 ppm) Cr(VI). The concentration of Cr(VI) ions from the aqueous solution was determined at known time intervals. The analysis of Cr(VI) ions was performed by ICP–AES.

### 3. Results and discussion

#### 3.1. Adsorption isotherms

Factors influencing the adsorption rate are mainly, among others, the nature and concentration of competing ions, pH, resin amount, shaking speed and temperature. Three individual composition variables, the nature of polymer matrix and basicity and steric property of the functional group of the anion exchanger, were found to have significant impact on chromate sorption. The two resins are identical in the matrix; the primary difference between them is the functionalities (di-methyl tertiary amine and di-methyl amino ethanol) and in the basicity of these groups. The strong-base anion exchanger offers higher chromate selectivity than the weak-base one. Apparently, therefore, it appears that the sorption is related to the basicity. The capacities of the two resins are not so different. The apparent effects of the basicity on Cr(VI) sorption are also believed to be due to the difference in their steric properties of the functional groups and not only due to the differences in their  $pK_a$  values.

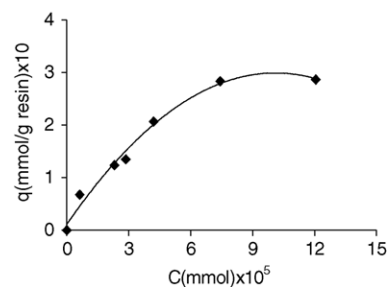


Fig. 1. Sorption isotherm of Cr(VI) ion on Lewatit MP 62 (adsorption conditions: initial concentration of Cr(VI), 20–100 ppm; amount of resin, 0.05 g, volume of adsorption medium, 30 mL; temperature, 25 ± 1 °C; stirring time, 180 rpm; adsorption time, 60 min; initial pH, 5).

A study of the maximum adsorption of Cr(VI) from its solution by 0.05 g of resin was done at pH 5 by varying the concentration of Cr(VI) (20–100 ppm). A remarkable feature of the result is that though the amount of adsorption of Cr(VI) increases with the increase of initial amount of Cr(VI) in solution, the percentage of sorption decreases. The results are given in Figs. 1 and 2. The Langmuir model (Eq. (1)) was applied for ion-exchange equilibrium. The experimental results obtained for the adsorption isotherms were found to obey the Langmuir adsorption isotherm. Analysis of adsorption results obtained at various concentrations showed that the adsorption pattern on the resin followed Langmuir isotherms as seen in Table 2. The maximum Cr(VI) adsorption at an optimum pH of 5.0 is 0.40 and 0.41 mmol/g of weight Lewatit MP 62 and Lewatit M 610 anion-exchangers, respectively (Table 2). The Langmuir constant  $b$  can serve as

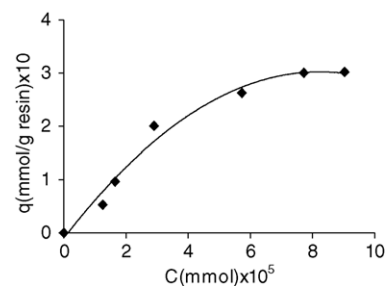


Fig. 2. Sorption isotherm of Cr(VI) ion on Lewatit M 610 (adsorption conditions: initial concentration of Cr(VI), 20–100 ppm; amount of resin, 0.05 g; volume of adsorption medium, 30 mL; temperature, 25 ± 1 °C; stirring time, 180 rpm; adsorption time, 60 min; initial pH, 5).

Table 2  
Parameters of Langmuir isotherm for sorption of chromium on Lewatit MP 62 and Lewatit M 610 anion exchange resin

Resin	Langmuir isotherm		
	$Q_0$	$b$	Correlation coefficient
Lewatit MP 62	0.40	25234	0.94
Lewatit M 610	0.41	35090	0.99

an indicator of isotherm rise in the region of lower residual metal concentrations, which reflects the strength of the resin for the solute.

The adsorption of Cr(VI) by resins is very high, in the range of 95–99% at low initial concentrations, and reaches equilibrium very quickly. This indicates the possibility of the formation of monolayer coverage of the metal ions at the outer interface of resins and suggests that these ion-exchangers can remove most of the chromium ion from aqueous solution if their concentrations are low, below 100 ppm. At a fixed resin quantity, the amount sorbed increased with increasing concentration of solution, but the percentage of sorption decreased. In other words, the residual concentration of Cr(VI) ions will be higher at a higher initial concentration of the Cr(VI) under study. In the case of lower concentrations, the ratio of initial number of Cr(VI) moles to the available sorption sites is low and subsequently the adsorption becomes independent of initial concentration [16]. At higher concentrations, however, the available sites of sorption become fewer and subsequently the removal of metals depends on the initial concentrations of Cr(VI). At higher initial concentration, it is not likely that metal ions are only adsorbed in a monolayer at the outer interface of anion-exchangers.

The Langmuir isotherm is valid for monolayer adsorption onto a surface containing a finite number of identical sites. The Langmuir isotherm is represented by the following equation:

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

where  $C_e$  is the equilibrium concentration (mg/L),  $q_e$  the amount of adsorbed material at equilibrium (mg/g),  $b$  the “affinity” parameter or Langmuir constant (L/mg), and  $Q_0$  is the “capacity” parameter (mg/g) [17,26–30]. The Langmuir isotherm parameter was determined by least-squares fit of the sorption data in Figs. 1 and 2.  $Q_0$  and  $b$  were determined from the slope and intercept of the Langmuir plot and are presented in Table 2. The Langmuir isotherm equation provided an excellent fit to the equilibrium sorption data, giving correlation coefficients of 0.94 and 0.99 on the two resins, respectively. The adsorption capacity,  $Q_0$ , for Cr(VI) calculated from the Langmuir adsorption isotherm was found to be 0.40 and 0.41 and adsorption intensities,  $b$ , 25234 and 35090 for the resins Lewatit MP 62 and Lewatit M 610, respectively. It was found that more than 95% removal was achieved using these anion exchangers.

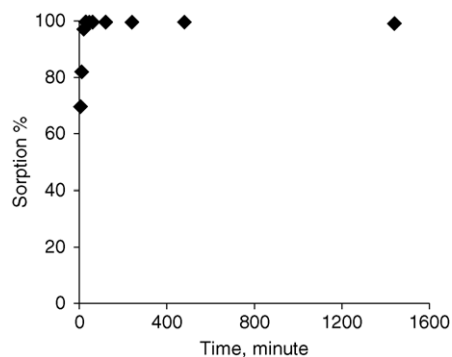


Fig. 3. Effect of contact time on the sorption of Cr(VI) by Lewatit MP 62 (adsorption conditions: initial concentration of Cr(VI), 100 ppm; amount of resin, 1.0 g; volume of adsorption medium, 30 mL; temperature,  $25 \pm 1^\circ\text{C}$ ; stirring time, 180 rpm; initial pH, 5).

### 3.2. Effect of shaking time on the removal of Cr(VI)

Figs. 3 and 4 show the effect of shaking time on the removal by resins. High adsorption rates of chromium for Lewatit MP 62 and Lewatit M 610 resin are observed at the onset, and then plateau values are gradually reached within 15 min. The increasing contact time increased the Cr(VI) adsorption and it remains constant after equilibrium reached in 30 min for initial concentration of 100 ppm. In each case, the decreasing concentration of Cr(VI) remaining in the solution indicates that chromium was adsorbed strongly by both resins. The Cr(VI) adsorption with respect to time curves is smooth and continuous leading to saturation showing monolayer coverage of metal ion on the surface of resin.

### 3.3. Sorption at various pH levels

In aqueous solutions, Cr(VI) exists in the form of chromic acid ( $\text{H}_2\text{CrO}_4$ ) and in the form of dichromate ( $\text{Cr}_2\text{O}_7^{2-}$ ). In this process, the anion is not a simple monovalent anion but rather a series of chromate anions depending upon the pH and concentration of the solution. The total chromate species will be represented as Cr(VI) or chromate. The chromate may

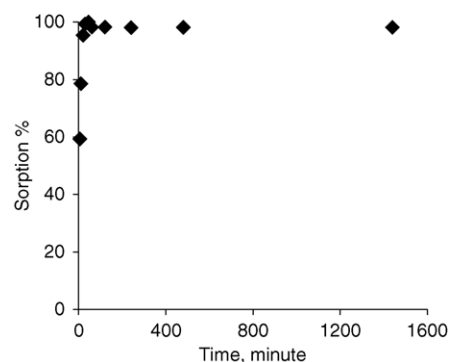


Fig. 4. Effect of contact time on the sorption of Cr(VI) by Lewatit M 610 (adsorption conditions: initial concentration of Cr(VI), 100 ppm; amount of resin, 1.0 g; volume of adsorption medium, 30 mL; temperature,  $25 \pm 1^\circ\text{C}$ ; stirring time, 180 rpm; initial pH, 5).

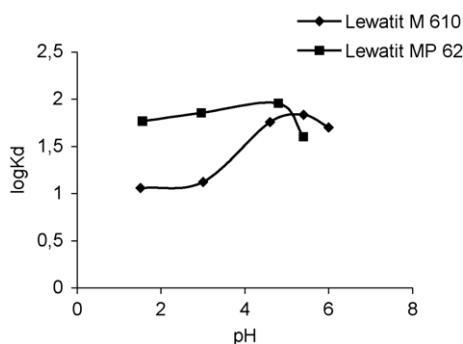
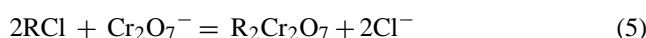
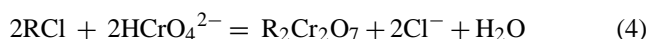
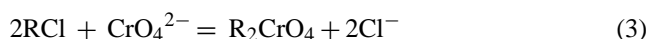
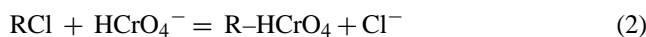


Fig. 5. The distribution coefficients of Cr(VI) metal on the Lewatit MP 62 and Lewatit M 610 as a function of pH (adsorption conditions: initial concentration of Cr(VI), 100 ppm; amount of resin, 1.0 g; volume of adsorption medium, 100 mL; temperature,  $25 \pm 1$  °C; stirring time, 180 rpm).

be represented in various forms such as  $\text{H}_2\text{CrO}_4$ ,  $\text{HCrO}_4^-$ ,  $\text{CrO}_4^{2-}$ ,  $\text{HCr}_2\text{O}_7^-$ , and  $\text{Cr}_2\text{O}_7^{2-}$  in the solution phase as a function of pH and concentration. In the neutral solution at low concentrations, Cr(VI) will be present in the form of  $\text{HCrO}_4^-$  and  $\text{CrO}_4^{2-}$ . At acidic pH,  $\text{HCrO}_4^-$  is the predominant Cr(VI) species in the aqueous phase. The  $\text{pK}_a$  value for the weak-base anion exchanger is about 7.0. By reducing pH of the equilibrium solution, Cr(VI) uptake increases, only up to a certain pH, by forming more  $\text{HCrO}_4^-$  at the expense of  $\text{Cr}_2\text{O}_7^{2-}$ . Once the pH value of about 3 is reached, the further reduction in pH will not increase the Cr(VI) uptake. An anion-exchange resin will absorb chromates from aqueous solution according to the reactions shown in Eqs. (2)–(5) [31].



The explanation for this finding lies in the influence of the functional group of the tertiary ammonium moiety of the resin, which has a significant influence on the uptake of Cr(VI). The interaction of Cr(VI) with both type of resins was investigated at the different pH values. The pH value of the solution is an important factor that controls the sorption of Cr(VI). There are two principal means by which anion-exchanger and ions can interact with each other in aqueous solutions. The most common way involves ion exchange or chelation of metal ions. These interactions are characterized by the resin structure in terms of the functional groups present. Amine groups bound to carbon are considered to be the reaction partner of Cr(VI).

Ion exchange of Cr(VI) was studied at varying pH values to determine the optimum pH range for its removal and the results are shown in Fig. 5. The pH was adjusted with small additions of diluted HCl or NaOH in the experiments. After equilibration, the pH was measured and recorded. In order to find out the optimum pH for maximum removal efficiency,

experiments were conducted with changing the pH of Cr(VI) solution from 2 to 6. About 1.0 g of resins Lewatit MP 62 and Lewatit M 610 was added in the pH range 2–6 to the solution phase. Decreasing the pH of the aqueous solution from 6 to 4, there is a distinct increase in the sorption. The maximum recovery (>95%) was obtained in the range of 4–5.5. The higher chromate removal capacity at the acidic pH is due to the removal of a greater number of Cr(VI) ions as per exchange site of the resin. As also seen in Fig. 5, for Lewatit MP 62 and Lewatit M 610 anion exchange resins, the removal efficiency of Cr(VI) decreased from 95.0 to 70.0, 95.0 to 80.0 as pH of the solution changes from 5.5 to 2. The slight pH increase was observed due to the release of  $\text{H}^+$  ions during the ion exchange process of Cr(VI) ions.

At higher pH values greater than 6, the presence of  $\text{OH}^-$  ions forms the hydroxyl complexes of chromium. For that reason, the uptake decreases at high pH values. Chromate ions exist in the aqueous phase in different ionic forms and pH dictating which particular chromate species will predominate. At pH greater than 7.5,  $\text{CrO}_4^{2-}$  is the only chromate species both in the aqueous and exchanger phases. Although chromate sorption is significantly lower at alkaline pH compared to acidic pH,  $\text{CrO}_4^{2-}$  is still preferred as chloride ions. We are interested in removing chromium atoms, regardless of the ionic species they form at a given condition in the chromate-ion exchange process. It may be noted that, excepting  $\text{CrO}_4^{2-}$ , all Cr(VI) species exist only at acidic pH. For this reason, ion exchange for a chromate removal process is more suitable at acidic pH than at alkaline pH. At slightly acidic pH (below 6.0),  $\text{HCrO}_4^-$  is the most predominant Cr(VI) species; however, during Cr(VI) ion exchange at acidic pH,  $\text{Cr}_2\text{O}_7^{2-}$  is also present inside the ion exchanger. This event may be the reason of a resin-phase dimerization of  $\text{HCrO}_4^-$  into  $\text{Cr}_2\text{O}_7^{2-}$  [30]. The sorption of Cr(VI) ion on the resins is clearly very favorable at pH values between 3.0 and 5.5. Cr(VI) is very soluble in aqueous solutions, and their solubility increases with pH; therefore, it was practical to employ resins at solution pH values of 6 and below.

#### 3.4. Effect of temperature on Cr(VI) adsorption

Sorption of Cr(VI) decreases with temperature and  $K_c$  equilibrium constant for various temperatures are presented in Fig. 6. The adsorption rate and equilibrium adsorption level decrease with increasing temperature. Thermodynamic parameters such as free energy change ( $\Delta G^\circ$ ), enthalpy change ( $\Delta H^\circ$ ) and entropy change ( $\Delta S^\circ$ ) can be calculated using Eqs. (6)–(8) where  $K_c$  is equilibrium constant that is resulted from the ratio the equilibrium concentrations of the metal ion on the resin and in the solution, respectively [3]. The temperature of mixture was ranged from 20 to 65 °C.

$$K_c = \frac{C_{\text{Ae}}}{C_e} \quad (6)$$

$$\Delta G^\circ = -RT \ln K_c \quad (7)$$

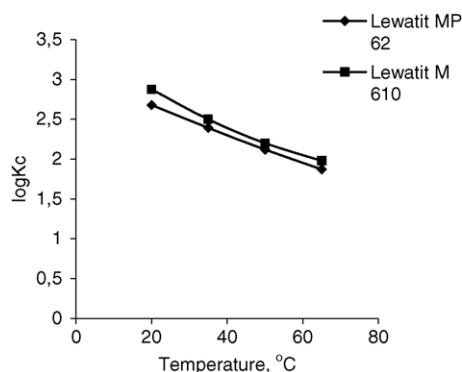


Fig. 6. The equilibrium constants of Cr(VI) on the Lewatit MP 62 and Lewatit M 610 as a function of temperature (adsorption conditions: initial concentration of Cr(VI), 100 ppm; amount of resin, 1.0 g; volume of adsorption medium, 30 mL; initial pH, 5; stirring time, 180 rpm).

$$\log K_c = \frac{\Delta S^\circ}{2.303R} - \frac{\Delta H^\circ}{2.303RT} \quad (8)$$

where  $K_c$  is the equilibrium constant,  $C_e$  the equilibrium concentration in solution (mg/L) and  $C_{Ae}$  is the solid phase concentration at equilibrium (mg/L).  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$  are changes in free energy, enthalpy and entropy, respectively.  $\Delta G^\circ$ ,  $\Delta S^\circ$  and  $\Delta H^\circ$  can be calculated from a plot of  $\log K_c$  versus  $1/T$ . A negative  $\Delta G^\circ$  value indicates the process to be feasible and spontaneous nature of adsorption; negative  $\Delta H^\circ$  value suggests the exothermic nature of adsorption and the  $\Delta S^\circ$  can be used to describe the randomness at the resin-solution interface during the sorption. Increase in the solution temperature has a small effect on the sorption. The sorption of Cr(VI) slightly decreased as the temperature of the solution increased. Therefore, a general temperature range is suggested to be 25–35 °C.

The removal of Cr(VI) from the solution of initial concentration decreases as increasing the temperature and agitation rate of 180 rpm with resin indicates the exothermic nature of the process. This may be attributed to a relative increase in the escaping tendency of the solute from the resin phase to the bulk phase with the rise in the temperature of the solution. As seen from Table 3, the negative values of  $\Delta G^\circ$  and  $\Delta H^\circ$  are indications of exothermic and spontaneous nature of the process and favorable adsorption.

### 3.5. Effect of resin amount

It is apparent from Fig. 7 that by increasing the resin amount, the adsorption efficiency increases but adsorption density, the amount adsorbed per unit mass, decreases. It is

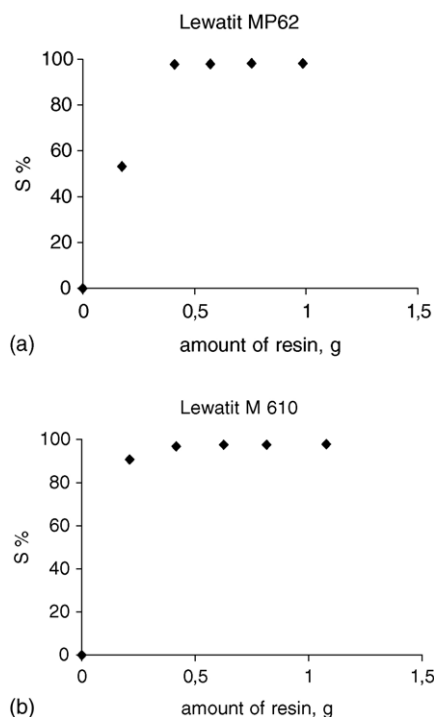


Fig. 7. The effects of the amount of resins for Cr(VI) ion from aqueous solutions (a) Lewatit MP 62 and (b) Lewatit M 610 (adsorption conditions: initial concentration of Cr(VI), 100 ppm; amount of resin, 0.1–1.0 g; volume of adsorption medium, 30 mL; temperature,  $25 \pm 1$  °C; stirring time, 180 rpm; adsorption time, 60 min; initial pH, 5).

readily understood that the number of available adsorption sites increases by increasing the resin amount and it, therefore, results in the increase of removal efficiency.

### 3.6. Adsorption kinetics

Experiments were also performed in order to understand the kinetics of chromium removal by these resins. It is a well-established fact that the adsorption of ions in aqueous system follows reversible first-order kinetics, when a single species is considered on a heterogeneous surface. It must be remembered that the two important physicochemical aspects for parameter evaluation of the sorption process as a unit operation are the kinetics and the equilibrium. Kinetics of sorption describing the solute uptake rate which in turn governs the residence time of sorption reaction is one of the important characteristics defining the efficiency of sorption. Hence, in the present study, the kinetics of chromium removal has been carried out to understand the behavior of this adsorbent.

Table 3  
Thermodynamic parameters for the adsorption of Cr(VI) on Lewatit MP 62 and Lewatit M 610 resin

Resin	$\Delta H^\circ$ (J mol <sup>-1</sup> )	$\Delta S^\circ$ (JK <sup>-1</sup> mol <sup>-1</sup> )	$\Delta G^\circ$ (J mol <sup>-1</sup> )			
			$T=298$ K	$T=308$ K	$T=323$ K	$T=338$ K
Lewatit MP 62	-2.16	24.49	-7177.26	-7544.62	-7911.98	-8279.34
Lewatit M 610	-2.51	35.49	-10402.48	-10934.89	-11467.29	-11999.70

Table 4  
Rate constants for the removal of Cr(VI) with Lewatit MP 62 and Lewatit M 610 system

Resin type	Cr(VI) amount (mmol)	Overall rate constant ( $K = k_1 + k_2$ ( $\text{h}^{-1}$ ))	Forward rate constant ( $k_1$ ( $\text{h}^{-1}$ ))	Backward rate constant ( $k_2$ ( $\text{h}^{-1}$ ))
Lewatit MP 62	0.1150	0.1100	0.1100	0.0005
Lewatit M 610	0.1150	0.0500	0.0490	0.0009

The sorption of chromium from liquid to solid phase may be expressed as:



where  $k_1$  is the forward reaction rate constant and  $k_2$  is the backward reaction rate constant. Using the kinetic equations numbered (2)–(17) in reference [3], the overall rate constant, the forward and backward rate constants were calculated.  $U_t$  is called fractional attainment of equilibrium of chromium and this was calculated by considering chromium adsorption over the resins in 60 min. By plotting  $\ln(1 - U_t)$  versus  $t$  (Fig. 8a and b), the overall rate constant  $k$  for given concentration of chromium was calculated by considering the slope of straight line in Fig. 8a and b and by using Eqs. (5) and (9) [3]. The equilibrium constant,  $K_c$ , forward and backward rate constants,  $k_1$  and  $k_2$ , were calculated and are shown in Table 4. From Table 4, it is seen that the forward rate constants for the removal of chromium were much higher than the backward rate constants, namely the desorption process. The rate for the sorption of Cr(VI) on the resin was rapid during the first 15 min and equilibrium was found to be attained within 30 min. The sorption of Cr(VI) onto the resins followed re-

versible first-order rate kinetics. This suggests that the rate of adsorption is clearly dominant. Both resins have about the same order of magnitude for the ion exchange rates even if they are characterized by different values of the exchange capacities and base strength.

#### 4. Conclusion

The present work demonstrates that both resins have a large collective adsorption with Cr(VI) ion, Lewatit M 610 showing stronger binding. A strong-base and weak-base anion-exchange resin were used to reduce trace concentrations of Cr(VI) in aqueous solution to low levels. The resins are suitable sorbent for the anions, since the amine functionalities using the ion-exchange mechanism are able to bind Cr(VI) ion. The isotherm plots showed a high sorption for pH 3–5.5 for both of the resins. These ion-exchangers can be used as an efficient sorbent for the removal of Cr(VI) from aqueous solution. The sorption is relatively quick and the process is very efficient especially for water containing low concentrations of pollutants. These anion-exchangers are thus attractive sorbents for the treatment of wastewater containing Cr(VI) ion at trace levels. Lewatit anion exchange resins have provided new solutions for removing chromate ions from aqueous solution. The chromate ion exchange process is likely to become a very viable and alternative to other traditional treatment processes. For a given Cr(VI)-bearing wastewater, it is possible to design a batch treatment system to remove Cr(VI) ion at any pH within the range 2–6. A batch contractor requires about 1 h contact time to achieve 90–95% removal percentages from aqueous solution.

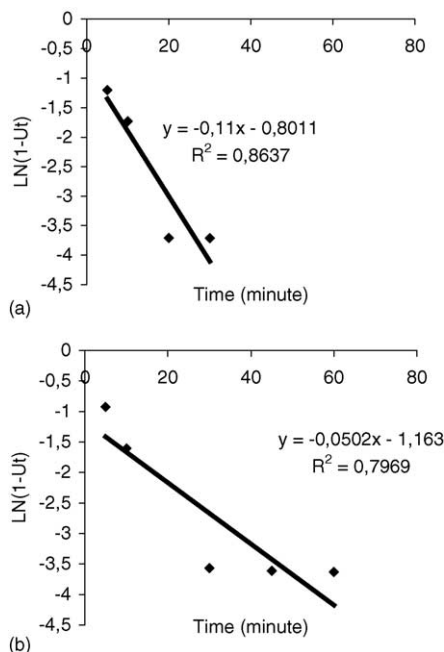


Fig. 8. Kinetic fits for the adsorption of Cr(VI) on (a) Lewatit MP 62 and (b) Lewatit M 610 (adsorption conditions: initial concentration of Cr(VI), 100 ppm; amount of resin, 1.0 g; volume of adsorption medium, 30 mL; temperature,  $25 \pm 1$  °C; stirring time, 180 rpm; initial pH, 5).

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