

Separation and enrichment of Cr(VI) ion in waters using solid phase extraction and evaluation of adsorption, kinetic and thermodynamic parameters

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Abstract: Cr(III) and Cr(VI) ions in waters were separated by using column method containing Amberlite IRA 900 copolymer resin. Cr(VI) ion was separated, pre-concentrated and determined by using flame atomic absorption spectrometry. After oxidizing all Cr(III) into Cr(VI) with H₂O₂, total chromium (Cr(III) + Cr(VI) ions) was determined. Concentration of Cr(III) was obtained by subtracting Cr(VI) level from whole chromium. Recovery of Cr(VI) ion at optimum conditions such as pH (5.5 – 6), type and concentration of eluent solution (5 mL of 1 mol/L HCl + 2% (m/v) ascorbic acid) and flow rate (3 mL/min) obtained was 99 ± 1% for five replicate measurements. Analytical detection and quantification limits were found as 0.11 and 0.38 µg/L, respectively. The enrichment factor of Cr(VI) ion found was about 100 after using optimization conditions. Accuracy of proposed method was checked by analyzing Cr(VI) in CWW-TM-D Wastewater (SRM) containing Cr(III) and Cr(VI) ions and applied to real waters. Langmuir adsorption model was suitable for Cr(VI) ion and maximum adsorption capacity found was 303 mg/g at 298 K. Thermodynamic parameters (ΔG° , ΔH° and ΔS°) and activation energy (E_a) were determined. Adsorption of Cr(VI) ion on resin was chemical ion-exchange, spontaneous and exothermic process.

Keywords: Chromium, Separation, Solid phase extraction, Amberlite IRA 900 resin, Activation energy.

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1. INTRODUCTION

Chromium is widely distributed in the earth crust and exists mainly in the forms of Cr(III) and Cr(VI) ions. Cr(III) is a biologically active ion found in food and it is important in mammalian metabolism. It is responsible for lowering blood sugar levels with insulin which is a critical

hormone for carbohydrates, fat and protein metabolism in the body [1]. However, Cr(VI) is toxic form of chromium originating from industrial pollution. It has toxic effects on biological systems as a result of possible free diffusion in cell membranes and also by a strong oxidative potential. Compounds containing Cr(VI) ion are highly soluble and more bioavailable than

poorly soluble Cr(III) ion. Cr(VI) ion causes extreme diarrhea, eye and skin irritation, kidney dysfunction, ulcers, and probably lung carcinoma in human body (Mohan, and Pittman (2006). The World Health Organization (WHO) states that maximum permissible level of Cr(VI) in drinking water guideline is 50 µg/L (WHO, 1984). Main sources of chromium pollution are mining, leather tanning industry, pigments and paints, ceramics, glass industry, production of steel and the other metal alloys such as photographic and corrosion control materials. Because of these reasons, separation of Cr(III) and Cr(VI) ions in biological and environmental samples has become important in recent years. It is known that distribution and the biological effects of chromium ions depend not only on its concentration but also on chemical forms of its compounds. It is important to determine levels of Cr(III) and Cr(VI) ions in the environment.

Several analytical methods such as flame atomic absorption spectrometry (FAAS) (Tunçeli and Türker, 2022; Hassanien et al., 2008; Narin et al., 2008; El-Shahawi et al., 2008; Tüzen and Soylak, 2007; Chamjangali et al., 2011; Kendüzler et al., 2007; Hashemi et al., 2004; Cavoca et al., 2009; Yalçın and Apak, 2004; Kiran et al., 2008; Uluozlu et al., 2009; Aydın and Soylak, 2009), graphite furnace atomic absorption spectrometry (GFAAS) (Ball and McCleskey, 2003; Gu and Zhu, 2011; Chwastowska et al., 2005; Sadeghi and Moghaddam, 2016, Bahadır et al., 2016; Beni et al., 2007), inductively coupled plasma-atomic emission spectrometry (ICP-AES) (Liang et al., 2003; Sumida et al., 2005, Motomizu et al., 2003), spectrophotometry (Hosseini and Belador, 2009; Yang et al., 2007; Kalidhasan and Rajesh, 2009) and voltammetry (Bobrowski et al., 2004) are sufficiently used in the determination of chromium. However, chromium analysis is difficult to determine in samples because of various factors, especially at low Cr concentrations and high matrix effects. To solve these problems, the separation and enrichment methods such as solid-phase extraction (SPE) (Tunçeli and Türker, 2022; Hassanien et al., 2008; Narin et al., 2008; El-Shahawi et al., 2008; Tüzen and Soylak, 2007; Chamjangali et al., 2011; Kendüzler et al., 2007; Gu and Zhu, 2011; Chwastowska et al., 2005; Liang et al., 2003; Hosseini and Belador, 2009; Yang et al., 2007;

Tunçeli et al., 2022; Li et al., 2023) ion-exchange (Hashemi et al., 2004; Cavoca et al., 2009; Yalçın and Apak, 2004; Ball and McCleskey, 2003; Béni et al., 2007; Yang et al., 2007), cloud point extraction (Kiran et al., 2008; Sadeghi and Moghaddam, 2016; Bahadır et al., 2016; Wang et al., 2010), co-precipitation (uluozlu et al., 2009; Aydın and soylak, 2009; Li et al., 20223) and liquid-liquid extraction (Béni et al., 2007; Kalidhasan and Rajesh, 2009) can be used prior to analyze. The SPE has been widely applied for trace elements due to its advantages such as selectivity, simplicity, fast and low chemical consumption. In many studies, some synthetic polymers from styrene-divinylbenzene such as Amberlite XAD-16 (Tunçeli and Türker, 2002; Hassanien et al., 2008), Amberlite XAD-1180 (Narin et al., 2008; El-Shahawi et al., 2008), polyurethane foams (El-Shahawi et al., 2008), multi walled-carbon nanotubes (Tüzen and Soylak, 2007), nanometer titanium dioxide (Liang et al., 2003), modified silica (Yang et al., 2007) and organic and inorganic sorbents (Türker, 2007) were used as solid phase extraction for speciation and pre-concentration of chromium from waters and wastewaters.

In this study, Amberlite IRA 900 copolymer resin was used as SPE for separation and enrichment of Cr(VI) ion. It is a strong base anion-exchange resin including quaternary ammonium groups such as styrene-divinylbenzene copolymer. The ideal conditions for SPE of chromium were found by examining critical parameters such as the pH of the solution, the type and volume of the eluent, the sample volume, the sample flow rate, and the resin's adsorption capacity. It was used for separation and enrichment of Cr(VI) from Cr(III) ion. Cr(VI) was determined in water samples by using the resin. Effects of foreign ions and adsorption capacity of resin for Cr(VI) were studied. Chromium in standard reference material (SRM, CWW-TM-D Certified Waste Water) was determined for accuracy of method. Analytical parameters (limits of detection (LOD) and quantification (LOQ)), precision and linear working range were studied. The suggested technique was successfully used to analyze samples of tap and dam water. Adsorption isotherm models and adsorption kinetics of Cr(VI), reaction order, adsorption capacities of resin at different temperatures (298, 308, 318 and

328 K), thermodynamic parameters (ΔG° , ΔH° and ΔS°) and the E_a were investigated.

2. EXPERIMENTAL

2.1. Instruments and reagents

Varian AA240-FS model flame atomic absorption spectrometry (Palo Alto, CA, USA) equipped with deuterium lamp for background correction and Varian Cr lamp were used for absorbance measurements. The operating conditions of Cr lamp (12.0 mA lamp current, 357.9 nm wavelength and 0.5 nm slit width) suggested by the manufacturer were used. Acetylene/air flow rate (1.4/13.2 L/min) was used. All pH measurements were performed by WTW 720 model pH meter (Wilhelm, Germany). A shaking thermostatic bath (Nüve ST 402, Turkey) maintained at the desired temperatures (298 K, 308 K, 318 K and 328 K) with a fixed speed of 150 rpm was used.

All chemicals were of analytical reagent grade. All solutions were prepared in ultrapure water (18.3 M Ω cm). Stock solutions of Cr(III) and Cr(VI) ions (1000 mg/L for each) were prepared by dissolving 0.7692 g Cr(NO₃)₃·9H₂O and 0.8269 g K₂Cr₂O₇ (Merck, Darmstadt, Germany) in 0.1 mol/L HNO₃ solution and diluting to 100 mL, separately. 50 mg/L of Cr(III) and 40 mg/L of Cr(VI) standard and model solutions were prepared from these stock solutions by diluting daily. Nitric acid (65%, m/m), hydrochloric acid (37%, m/m), Hydrogen peroxide (30%, m/m), ascorbic acid, sodium fluoride and sodium hydroxide purchased from Merck (Darmstadt, Germany) were used. Amberlite IRA 900 chloride resin purchased from Rohm and Hass (Philadelphia, USA) was used. Basic characteristics of resin are polystyrene cross-linked with divinylbenzene copolymer (macro-reticular) (strongly basic anion exchange), (CH₃)₃RN⁺-Cl⁻ (quaternary ammonium) chemical structure, spherical beads physical form, 20–50 mesh (650–820 μ m) particle size, 80°C maximum temperature range, 0 – 14 operating pH, 55% – 65% moisture, 1 meq/L or 4.2 meq/g exchange capacity (Berbar et al., 2008; Esfandian et al., 2020, Jachuła and Hubicki, 2013; Tan et al., 2018). Due to its macro-reticular structure, it is suitable for water treatment applications such as potable water and for industrial uses (Esfandian et al.,

2020). Amberlite IRA 900 resin was washed with methanol, 1 mol/L HCl solution, and rinsed with ultrapure water, dried at 70 °C for 4 h, respectively and used. The glassware materials were kept an overnight in a 5% nitric acid solution, rinsed with water and dried before using.

2.2. Column preparation and pre-concentration procedure

Glass columns with 1.0 cm inner diameter, 30 cm height and approximately 100 mL volume of solution reservoir at the upper end were used in the studies for separation and enrichment of Cr(III) and Cr(VI) by fixing on Amberlite IRA 900 resin. After the columns were cleaned and dried, a piece of glass cotton was placed at the bottom, and 0.3 g of the resin was placed on glass cotton. Another piece of glass wool was placed on the resin to prevent it from falling apart and to prevent channel formation. 0.1 mol/L HCl solution and ultrapure water were passed through columns for cleaning and regenerating of the resin after each usage.

The 50 mL of model solution including 0.2 μ g/mL of Cr(III) and 0.2 μ g/mL of Cr(VI) was placed in a beaker and pH of solution was adjusted to 6 by adding 0.1 mol/L HCl and 0.1 mol/L of NaOH solutions, separately. After preconditioning column with the solution adjusted to pH 6, model solution was passed through the column at a flow rate about 3 mL/min. A 10 mL volumetric flask was used to elute the adsorbed Cr(VI) on the resin using 5 mL of an eluent solution that contained 0.1 mol/L ascorbic acid and 1 mol/L HCl. Concentration of Cr(VI) in eluent solution was analyzed by using FAAS. The percentage of recovered Cr(VI) was determined by dividing the Cr(VI) concentration determined by FAAS by the starting Cr(VI) concentration, which was theoretically predicted using the previously described approach.

2.3. Oxidation of Cr(III) ion into Cr(VI) ion

Oxidation of Cr(III) into Cr(VI) was carried out using the procedure given in the literature (Tüzen and Soylak, 2007). The pH of Cr(III) solution was adjusted to 10 by adding 0.1 mol/L NaOH solution. After adjusting pH of solution, 10 mL of 3% (v/v) H₂O₂ was added and heated at 80 °C for 40 min. Solution was then boiled for 10 min to

evaporate the excess amount of H_2O_2 . After applying the general procedure for the solution, Cr(VI) was determined by using FAAS.

2.4. Collecting and getting preparing samples

Tap water from laboratory and dam waters from Çubuk Dam Ankara in 2.5 L plastic bottles were collected. The samples were acidified by adding 1 mL concentrated nitric acid into each bottle to prevent adhering of ions onto surface of the vessels. Samples were filtrated from membrane filters (Millipore, 0.45 μ m pore size) and the procedure given above was applied.

2.5. Batch adsorption procedure

Batch adsorption method was used to determine adsorption kinetics of Cr(VI) on Amberlite IRA 900 resin. Batch equilibrium tests were carried out adding 50 mL of Cr(VI) solutions in 100 mL flasks containing 0.05 g of adsorbent. Range of concentrations of Cr(VI) solutions prepared was varied from 25 to 800 mg/L to investigate the effect of mass transfer. pH values of solutions were set to 6 by using 0.1 mol/L HCl and 0.1 mol/L of NaOH solutions. Flasks were placed onto a mechanical shaker and stirred for 2 h at suitable temperatures (298 K, 308 K, 318 K and 328 K) at 150 rpm fixed speed, separately. The suspensions were filtered and Cr(VI) in filtrates were determined by using FAAS after a suitable dilution.

The amount of Cr(VI) ion adsorbed at equilibrium q_e (mg/g) was obtained from Equation (1).

$$q_e = \frac{(C_o - C_e) \cdot V}{m} \quad (1)$$

where, C_o and C_e are initial and equilibrium concentrations (mg/L) of the solutions. V is volume of a solution (L) and m is mass of Amberlite IRA 900 (g).

3. RESULTS AND DISCUSSION

3.1. pH effect of solution

pH of solution containing Cr(III) or Cr(VI) ions for adsorption onto Amberlite IRA 900 resin was investigated. The pH of 50 mL model solution containing 0.2 mg/L Cr(III) or 50 mL model solution containing 0.2 mg/L Cr(VI) was adjusted to 2.0 - 10.0 pH range with 0.1 mol/L HCl and 0.1 mol/L NaOH solutions, separately. At a flow rate of roughly 1 mL/min, they were passed through the column. The adsorbed Cr(III) and Cr(VI) ions on the resin were eluted by adding 5 mL of eluent solution containing 1 mol/L HCl + 0.1 mol/L ascorbic acid. The concentrations of Cr(III) or Cr(VI) in eluent solutions were analyzed by using FAAS. The percent recoveries of Cr(III) and Cr(VI) ions obtained versus pH of the solutions were presented in Figure 1. As shown in Figure 1, the quantitative percent recovery of Cr(VI) (>95%) was obtained at pH 5.5 - 6.0, while the percent recovery of Cr(III) found was lower than 5%. According to these results, it was possible to separate Cr(VI) ion from Cr(III) ion at this pH range.

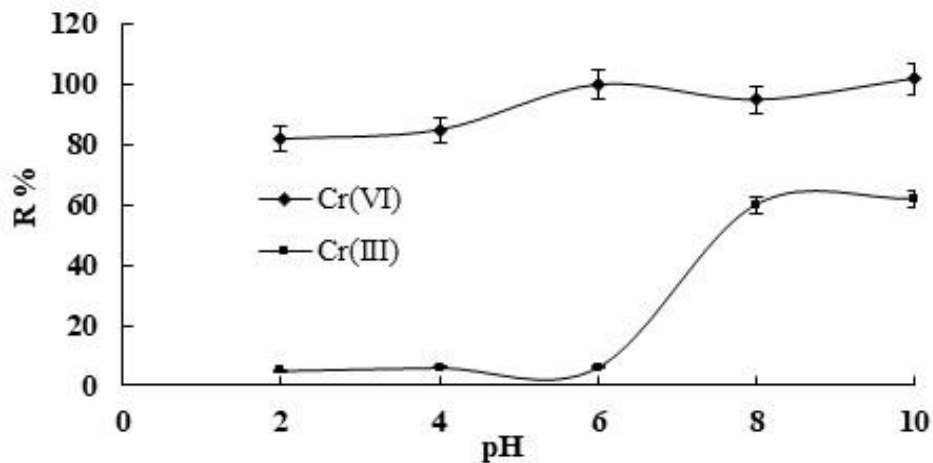


Figure 1. pH effect on adsorption of Cr(VI) and Cr(III) (Sample volume; 50 mL containing 10 μ g Cr(VI) and 10 μ g Cr(III))

3.2. Impact of eluent solution type and concentration and volume

To find a proper concentration and volume of eluent solution type for retaining Cr (VI) onto Amberlite IRA 900 resin, different concentrations (1 or 2 mol/L) and different volumes (5 or 10 mL) of HCl solutions were examined and adequate percent recovery for Cr (VI) was not obtained. When ascorbic acid solution was only used as eluent solution, the percent recovery for Cr(VI) was found as $51 \pm 3\%$ because Cr(VI) ion can be reduced to Cr(III) ion and ascorbic acid in solution can easily oxidize into dehydroascorbic acid and $2H^+$ ions by air oxygen. To prevent this oxidation,

ascorbic acid and HCl mixture solutions were prepared and used as eluent solution. The average values of Cr(VI) recoveries obtained with ascorbic acid solution only or mixtures of HCl + ascorbic acid solutions prepared were given in Table 1. As seen in Table 1, when 5 mL eluent solution containing 1 mol/L HCl + 2% (m/v) ascorbic acid solution was used, the percent recovery of Cr(VI) obtained at pH 6 was about 100%. Therefore, the pH effect of solution containing Cr(III) and Cr(VI) ions for adsorption on the resin was repeated five times by using 5 mL of eluent solution containing 1 mol/L HCl and 2% (m/v) ascorbic acid.

Table 1. Effect of eluent solution type and concentration on the recovery of Cr(VI)

Eluent solution type	R% \pm s ^a
10 mL of 2 % (m/v) ascorbic acid	51 \pm 3
10 mL of 2 mol/L HCl + 2 % (m/v) ascorbic acid	61 \pm 2
10 mL of 2 mol/L HCl + 1 % (m/v) ascorbic acid	64 \pm 1
10 mL of 1 mol/L HCl + 2 % (m/v) ascorbic acid	87 \pm 3
10 mL of 1 mol/L HCl + 1 % (m/v) ascorbic acid	49 \pm 3
5 mL of 2 mol/L HCl + 2 % (m/v) ascorbic acid	98 \pm 3
5 mL of 2 mol/L HCl + 1 % (m/v) ascorbic acid	81 \pm 4
5 mL of 1 mol/L HCl + 2 % (m/v) ascorbic acid	100 \pm 2
5 mL of 1 mol/L HCl + 1 % (m/v) ascorbic acid	90 \pm 4

Note: ^a Mean of the three determinations

3.3. Flow rate effect of sample solution

Flow rate effect of sample solution containing Cr(III) and Cr(VI) ions passing through column was studied. Because a large volume of sample solution was needed to get a high enrichment factor, passing this solution through column was time-consuming. The highest flow rate for passing the sample solution was preferred. On the other hand, adequate contact time may not be obtained to retain the Cr(VI) ions on the resin at high flow rates. Because of this, it was agreed upon that the sample solutions might be run through the column

at an appropriate flow rate in order to maximize recovery. In order to determine the appropriate flow rate, the model solutions were passed through column under optimum conditions (pH of solution and type of eluent solution) with flow rate adjusted in the range of 1 - 6 mL/min. Figure 2 showed the means of the recovery values obtained vs the sample solution's flow rate. The best flow rate was discovered to be roughly 3 mL/min, as seen in Figure 2, as the percent recovery declined above this point. The flow rate of eluent solution was applied as 1 mL min⁻¹ because the volume of elution solution was small.

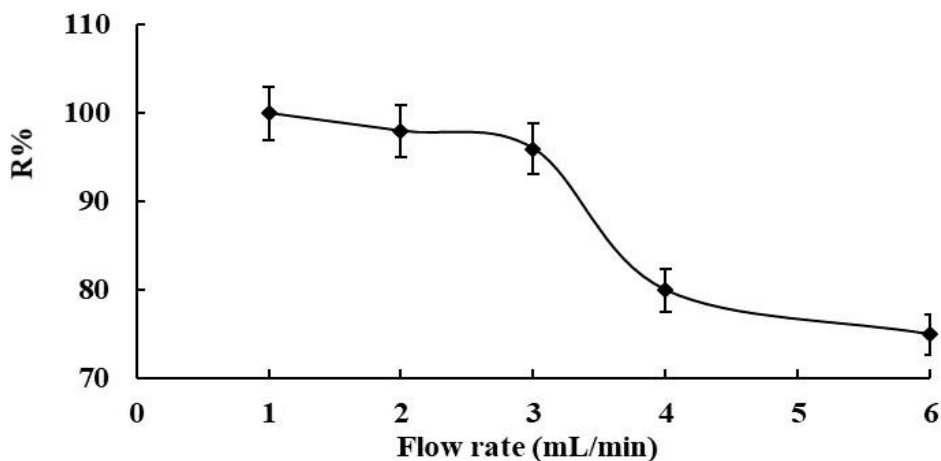


Figure 2. Effect of flow rate of sample solution

3.4. Sample volume effect

Sample volume effect was investigated to determine a suitable and applicable sample volume. For this purpose, 50, 100, 250, 500, 750 and 1000 mL of the model solutions containing 10 μg of Cr(VI) were prepared by applying general procedure given above. The percent recovery of Cr(VI) quantitatively increased up to 100% when the sample volume was about 500 mL. The percent recovery of Cr(VI) ion decreased to 85% when 750 mL or higher sample volume was used. The enrichment factor (EF) of Cr(VI) ion was found as 100 (500 mL of sample/5 mL of eluent). This result showed that Cr(VI) could be pre-concentrated from sample solutions at low concentration (0.020 mg/L) and determined by using FAAS.

3.5. Analytical features

Analytical features such as limits of detection (LOD) and quantification (LOQ), precision and linear working range were calculated for Cr(VI) at optimum conditions obtained. For the precision of method, a general procedure was carried out using 50 mL solution containing 10 μg Cr(VI) and 10 μg Cr(III) and concentration of Cr(VI) ion was determined by using FAAS after pre-concentration. The average values of recoveries obtained from eight determinations for Cr(VI) was about $99 \pm 1\%$ at 95% confidence level, and the percent standard deviation of recovery was about 2.0%. The 50 mL solution containing only 10 μg Cr(III) was first oxidized to Cr(VI) using procedure and pre-concentration /elution cycle was applied. The eluent solution was analyzed as Cr(VI) and $100 \pm 1\%$ recovery for Cr(VI) was

obtained from eight determinations of Cr(III) with standard deviation of recovery about 1.4%. The Linear working range for Cr determination was 0.04 - 5 mg/L using direct calibration graphic method. Calibration equation obtained was $A = 0.07177xC + 0.00069$, where C is Cr concentration (in mg/L) and A is absorbance. The 50 mL blank solution was passed through the column at pH 6.0 to determine the instrumental detection limit and the retained Cr(VI) was eluted using 50 mL of eluent solution containing 1 mol/L HCl + 0.1 mol/L ascorbic acid solution. The ratio of three times the standard deviation of the blank absorbance readings ($N = 17$) to the slope of the calibration curve ($\text{LOD}_i = 3s/m$) yielded the instrumental detection limit, which was determined to be $11.3 \mu\text{g L}^{-1}$ for Cr(VI). Analytical detection limit was obtained as 0.113 $\mu\text{g/L}$ by dividing the instrumental detection limit to enrichment factor (100) (Sahayam, 2002). The instrumental limit of quantification ($\text{LOQ} = 10s/m$) was calculated as 37.5 $\mu\text{g/L}$ and the analytical limit of quantification was calculated as 0.38 $\mu\text{g/L}$.

3.6. Matrix effect

Matrix effect of foreign metal ions in real samples such as waters for the retention of Cr(VI) on Amberlite IRA 900 resin was also studied. For this purpose, solutions containing Fe(III), Cu(II), Zn(II), Cd(II), Mn(II), Ni(II), Na(I), K(I), Ca(II) and Mg(II) ions at different concentrations were prepared from nitrate salts. Appropriate concentrations of foreign ions were separately added to 50 mL - volumetric flask containing 10 μg of Cr(VI) and total volume was diluted to 50 mL. Means of recovery values of Cr(VI) in

different concentrations of foreign ions were given in Table 2. As seen in Table 2, after applying proposed method, Cr(VI) was determined quantitatively (about 100 %) in presence of 250 mg/L of K, 50 mg/L of Na, 25 mg/L of Ca and Mg and 5 mg/L of Cd. In presence of other ions, percent recovery of Cr(VI) decreased seriously. The reason of this decrease could be the formation of metal-chromate aqueous complexes such as

NaCrO_4^- , FeCrO_4^+ , CaCrO_4 , NiCrO_4 , ZnCrO_4 and MnCrO_4 (Tunçeli et al., 2013). The interferences of these ions were prevented by masking them with the addition of sodium fluoride (NaF) and ethylenediamine tetra acetic acid (EDTA) mixture solutions (Table 2). The results showed that Cr(VI) could be determined from water samples by using this proposed method.

Table 2. The concentration effects of some foreign ions on the recovery of Cr(VI)

Foreign ions	Concentration (mg/L)	Recovery ^a (%)	Recovery ^{a,b} (%)
K ⁺	250	104 ± 3	-
	500	83 ± 3	-
Na ⁺	5	100 ± 2	-
	50	95 ± 4	-
	100	85 ± 3	-
Mg ²⁺	25	101 ± 5	-
	100	87 ± 2	-
Ca ²⁺	25	101 ± 5	-
	50	92 ± 4	-
Cd ²⁺	5	96 ± 4	-
	50	82 ± 3	-
Zn ²⁺	5	91 ± 4	101 ± 2
	25	80 ± 1	103 ± 1
	50	-	102 ± 2
Mn ²⁺	25	87 ± 3	96 ± 2
	100	53 ± 2	82 ± 3
Cu ²⁺	1	86 ± 3	99 ± 2
	5	-	102 ± 3
	50	-	97 ± 4
Fe ³⁺	1	82 ± 1	101 ± 3
	2	-	100 ± 5
	5	-	65 ± 1
Ni ²⁺	1	83 ± 3	104 ± 5

^a Mean ± standard deviation for five determination

^b By masking agent (2.0 mL of 0.01 mol/L EDTA and 0.1 mol/L NaF)

3.7. Column reusability, accuracy and application of the method proposed

The reusability of the column containing Amberlite IRA 900 resin was investigated. After regeneration with 10 mL of 1 mol/L HCl solution and water, respectively, a column can be used again. For approximately 25 cycles of adsorption, elution, and regeneration, the resin remained stable with no discernible decrease in Cr(VI) ion recovery.

The chromium-containing standard reference material (CWW-TM-D Waste Water) was examined to assess the precision of the suggested technique and is provided in Table 3. Table 3 illustrates that the results showed a good agreement with the certified value, with a percent relative error of less than 4%. The suggested technique was used to measure the chromium content of the dam and tap waters.

Table 3. Determination of chromium in real samples (Volume of water sample: 50 mL)

Sample	Added (mg/L)		Found (mg/L) ^a			Certified (mg/L)	Relative error for total chromium (%)
	Cr(VI)	Cr(III)	Cr(VI)	Cr(III)	Total Chromium		
CWW-TM-D Waste Water	-	-	98.5±1.2	-	98.5±1.2	100 ± 1	-1.5
Tap Water (Ankara)	-	-	< LOQ	< LOQ	< LOQ		-
	0.200	-	0.193±0.020	-	0.193±0.020		- 3.5
	0.400	-	0.394±0.035	-	0.394±0.035		- 1.5
	-	0.200	-	0.201±0.022	0.201±0.022		+ 0.5
	-	0.400	-	0.398±0.038	0.398±0.038		- 0.5
	0.100	0.200	0.101±0.020	0.203±0.025	0.311±0.032		+ 3.7
Dam Water (Çubuk Ankara)	-	-	< LOQ	< LOQ	< LOQ		-
	0.200	-	0.196±0.016	-	0.196±0.016		-2.0
	0.400	-	0.386±0.028	-	0.386±0.028		-3.5
	-	0.200	-	0.199±0.015	0.199±0.015		- 0.5
	-	0.400	-	0.402±0.030	0.402±0.030		+ 0.5
	0.100	0.200	0.098±0.009	0.202±0.014	0.309±0.017		+ 3.0
	0.200	0.200	0.198±0.014	0.200±0.016	0.401±0.021		+ 0.25

^a Mean of three replicate measurements at 95% confidence level, $\bar{X} \pm t_{\alpha/2} s / \sqrt{N}$.

3.8. Effect of initial Cr(VI) concentration on amberlite IRA 900 resin

A batch approach was employed at pH 6 with four distinct initial Cr(VI) concentrations at temperatures (298 K, 308 K, 318 K, and 328 K) in order to ascertain the impact of the initial Cr(VI) concentration on the adsorption capacity of Amberlite IRA 900. Figure 3 showed the outcomes derived from the mean of three duplicate measurements. Up to the necessary equilibrium, the adsorption capacity of the resin increases as the

starting concentration of Cr(VI) increases. Because the initial concentration of a metal acts as a catalyst to reduce the resistance to mass transfer between the solid phase and aqueous solution. As demonstrated in Figure 3, the adsorption equilibrium capacity grew until it reached 300 mg/L at which point it stabilized as the temperature rose. For the purpose of determining the adsorption kinetics, the equilibrium concentration of Cr(VI) was therefore determined to be 300 mg/L.

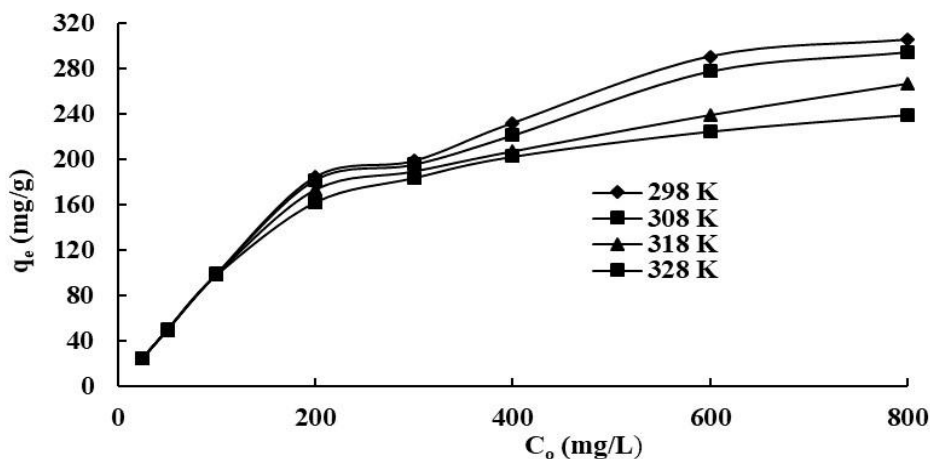


Figure 3. The effect of initial concentration of Cr(VI) on adsorption at different temperatures (Sample volume: 50 mL, pH: 6)

3.9. Adsorption isotherm models

Adsorption isotherm models were used to explain the relationship of metal ions between in aqueous solution and in solid-phase at equilibrium. The Langmuir, Freundlich, and Dubinin-Radushkevich isotherm models were each used independently for this purpose.

For the adsorption of metal ions from aqueous solutions, the Langmuir adsorption isotherm model was frequently employed. A basic assumption of the Langmuir theory is that the adsorption of a metal can be increased until the saturated monolayer adsorption is reached (Tunçeli and Türker, 2002).

The linearized Langmuir isotherm model for the saturated monolayer side was given in Eqn. (2).

$$\frac{C_{eq}}{q_{eq}} = \frac{1}{K_L q_m} + \frac{C_{eq}}{q_m} \quad (2)$$

where, C_{eq} is equilibrium concentration of metal ion (mg/L), q_{eq} is amount of metal ion adsorbed (mg/g) at equilibrium experimentally, q_m is monolayer adsorption capacity of adsorbent (mg/g) and K_L is the Langmuir adsorption constant (L/mg) related to free energy of adsorption. A plot of C_{eq}/q_{eq} versus C_{eq} was depicted in Figure 4. As seen in Figure 4, the slope and the intercept of the calibration graphic were $1/q_m$ and $1/(K_L q_m)$, respectively.

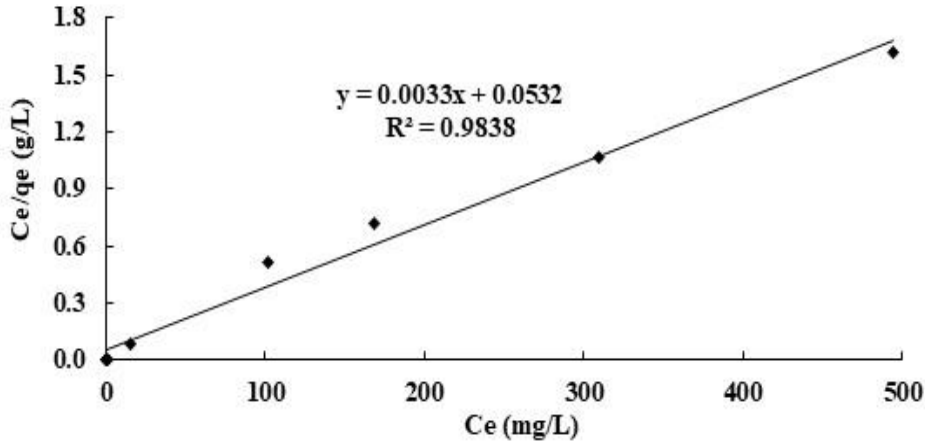


Figure 4. The linearized Langmuir isotherm model at 298 K (pH: 6)

For active sites with varying energies and heterogeneous adsorption, the Freundlich isotherm model may be applied (Zarghami et al., 2016). The Linearized Freundlich model was given in Eqn. (3).

$$\log q_{eq} = \log K_F + \frac{1}{n} \log C_{eq} \quad (3)$$

where, K_F is a constant related to the adsorption capacity and $1/n$ is an empirical parameter related to the adsorption intensity which varies with the heterogeneity of adsorbent. A plot of $\log q_{eq}$ versus C_{eq} was indicated as a straight line with slope $1/n$ and intercept K_F of the calibration graphic, respectively. The parameters obtained from the Langmuir and Freundlich isotherm models were given in Table 4. As seen in Table 4, experimental adsorption capacities ($q_{eq,exp}$) at each temperature were nearly the same with the theoretical

adsorption capacities ($q_{m,cal}$) obtained from the Langmuir adsorption model. The correlation coefficients (R^2) obtained from the Langmuir adsorption model were more acceptable than the Freundlich adsorption model at different temperatures. Because of these, the Langmuir adsorption model was preferred. In addition, the isotherm model's form was utilized to forecast the favorable or unfavorable adsorption system. Equation (4) defined the equilibrium parameter R_L , which was used to describe the Langmuir isotherm model.

$$R_L = \frac{1}{1 + K_L C_0} \quad (4)$$

where K_L is the previously mentioned Langmuir constant and C_0 is the initial Cr(VI) ion concentration (mg/L). Four probabilities are utilized to determine the R_L value: (i)

advantageous adsorption, defined as $0 < RL < 1$, (ii) unfavorable adsorption, defined as $RL > 1$, (iii) linear adsorption, defined as $RL = 1$, and (iv) irreversible adsorption, defined as $RL = 0$. For every starting concentration (10–800 mg/L) at every temperature, the computed RL values ranged from 0 to 1. It was demonstrated that Cr(VI) ion adsorption on Amberlite IRA 900 was advantageous at all temperatures.

The Dubinin-Radushkevich (D - R) isotherm model was fitted to the experimental equilibrium data (q_{eq}) in order to identify whether the adsorption process was physical or chemical [24]. Equation (5) provided an explanation of the linearized D-R isotherm model.

$$\ln q_{eq} = \ln q_m - \beta \epsilon^2 \tag{5}$$

where, q_{eq} is amount of metal ion adsorbed per weight of adsorbent (mol/g), q_m is maximum adsorption capacity (mol/g), β is activity coefficient (mol^2/J^2) related to the adsorption mean

free energy and ϵ is the Polanyi potential [$\epsilon = RT \ln(1 + \frac{1}{C_{eq}})$]. Difference in free energy between the adsorbed phase and the saturated liquid phase was referred to as adsorption potential which was first put forward by the Polanyi and developed by the Dubinin [40]. Free energy E (J/mol) was given by Equation (6).

$$E = \frac{1}{\sqrt{-2\beta}} \tag{6}$$

A plot of $\ln q_{eq}$ versus ϵ^2 was depicted in Figure 5. As seen in Figure 5, the slope of D-R plot was given as β constant and q_m values were calculated from the intercept. The E value explains that adsorption mechanism is the physical or chemical ion-exchange. If E is between 8 and 16 kJ/mol, the adsorption process is chemical ion exchange. When E is less than 8 kJ/mol, adsorption process is explained as physical ion exchange [28]. Mean adsorption energy (E) at each temperature was calculated and given in Table 4. As seen in Table 4, adsorption process was chemical ion exchange.

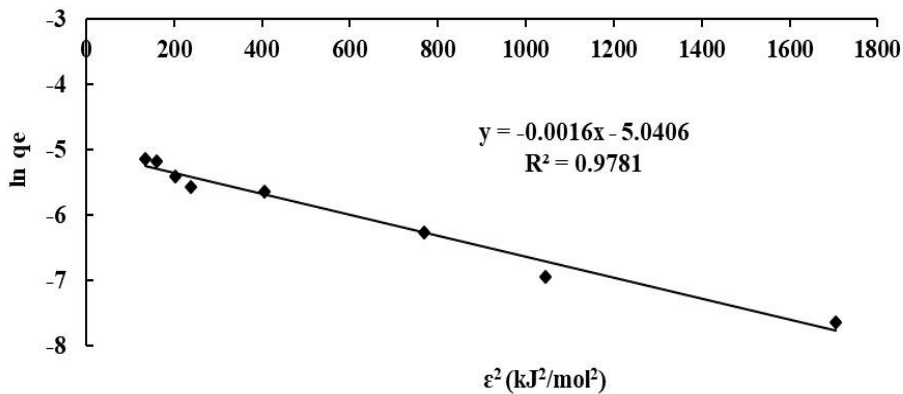


Figure 5. Linearized D-R isotherm at 298 K

Table 4. Parameters obtained from Langmuir, Freundlich and D-R isotherms

Temperature (K)	$q_{e,exp}$ (mg/g)	Langmuir			Freundlich			D-R		
		$q_{m,cal}$ (mg/g)	K_L (L/mg)	R^2	K_F	n	R^2	E (kJ/mol)	q_m (mg/g)	R^2
298	305	303	0.062	0.9838	87.5	4.86	0.9804	17.68	336	0.9781
308	295	294	0.059	0.9835	73.2	4.27	0.9566	16.22	371	0.9767
318	267	263	0.062	0.9874	65.8	4.27	0.9358	16.22	345	0.9722
328	239	238	0.075	0.9946	60.3	4.23	0.9392	16.66	324	0.9748

3.10. Chi-square (X^2) analysis

The Chi-square (X^2) analysis was used to explain a suitable isotherm model for the adsorption of Cr(VI) ions on Amberlite IRA 900 resin from aqueous solutions (Tunçeli et al., 2022; Mustapha et al., 2019; Karthik and Meenakshi, 2015). Mathematical explanation of the X^2 analysis was given by equation (7):

$$X^2 = \sum_{i=1}^n \frac{(q_{e,exp} - q_{m,cal})^2}{q_m} \quad (7)$$

where, q_e and q_m are the experimental equilibrium ($q_{e,exp}$) and theoretical equilibrium adsorption capacities ($q_{m,cal}$) calculated from models (mg/g), respectively. As seen in Table 4, the $q_{e,exp}$ and $q_{m,cal}$ values were close to each other for Langmuir isotherm model at 298, 308, 318 and 328 K and X^2 values were near to zero. When the correlation coefficients (R^2) obtained from isotherm models for Cr(VI) were compared, R^2 values found from the Langmuir model were about 1.0 and higher than the R^2 values from other isotherm models. Therefore, the Langmuir isotherm model was suitable for adsorption process proposed.

3.11. Contact time and temperature

Contact time and temperature for adsorption of Cr(VI) ions are suitable for adsorbents in applications. Adsorption rate may be related to form and structure of adsorbent [29, 43 - 47]. Effects of contact time and temperature on adsorption of Cr(VI) on resin were studied to obtain the optimum contact time and temperature for adsorption process. The means of three replicate measurements with standard deviation (less than 3%) were obtained. The contact times for the adsorption of Cr(VI) on resin at 298, 308, 318 and 328 K were shown in Figure 6. As seen in Figure 6, adsorption of Cr(VI) increased faster by increasing the contact time up to 15 min and slowly increased up to 90 min and after then, it was almost constant. Optimum contact time of Cr(VI) was about 90 min. When temperature of adsorption process was increased from 298 K to 328 K, the adsorption of Cr(VI) decreased slowly. These results were explained that the adsorption of Cr(VI) on the resin was exothermic. Therefore, 298 K was found to be the ideal temperature (Tunçeli et al., 2022; Karthik and Meenakshi, 2015; Wang et al., 2016; Xiong et al., 2015).

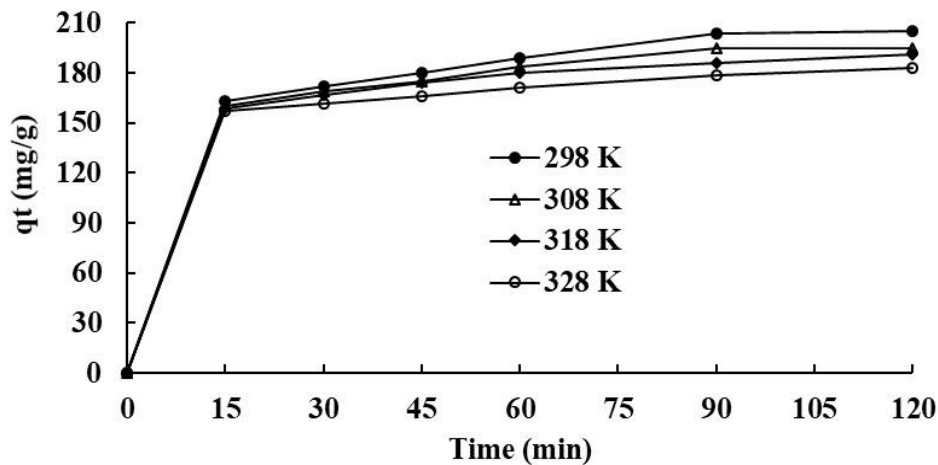


Figure 6. Effect of contact time and temperature for adsorption of Cr(VI) on Amberlite IRA 900 resin at pH 6.0.

3.12. Adsorption kinetics

50 mL of 300 mg/L Cr(VI) ion solutions, including 0.05 g of resin, were agitated at predetermined intervals (15, 30, 45, 60, 90, and 120 min) at a fixed speed of 150 rpm in order to ascertain the adsorption kinetics of Cr(VI) on Amberlite IRA 900. The experimental data was subjected to linearized variants of the pseudo-first order,

pseudo-second order, and second order kinetic models developed by Lagergren (Tunçeli et al., 2013; Aksu, 2002). The following equations (8, 9, 10) provided models:

Pseudo first order:

$$\log(q_{eq} - q_t) = \log q_{eq} - \frac{k_1}{2.303} t \quad (8)$$

Pseudo second order:

$$\frac{t}{q_t} = \frac{1}{k_2 q_{eq}^2} + \left(\frac{1}{q_{eq}}\right) t \tag{9}$$

Second order:

$$\frac{1}{(q_{eq} - q_t)} = \frac{1}{q_{eq}} + k t \tag{10}$$

where, q_{eq} and q_t (mg/g) are metal ions adsorbed by adsorbent at equilibrium and at time t (min), respectively. The k_1 is rate constant of pseudo-first order kinetic model (1/min). The k_2 is rate constant of pseudo second order kinetic model (g/(mg min)) and k is rate constant of second order kinetic model (g/(mg min)).

The adsorption rate constants were determined experimentally by plotting of $\log (q_{eq}-q_t)$, t/q_t and $1/(q_{eq}-q_t)$ versus t , respectively and kinetic parameters obtained were given in Table 5. The plot of t/q_t versus t was depicted in Figure 7 as an example. It was clear from the results given in Table 5 that the adsorption of Cr(VI) on Amberlite IRA 900 resin was suitable for the pseudo-second order kinetic, because its R^2 values (0.9961-0.9981) found at different temperatures were higher than R^2 values of pseudo-first order kinetic (0.8512 - 0.9095) and R^2 values of the second order kinetic (0.6016 - 0.9118) found.

Table 5. Lagergren parameters for kinetics

Temperature (K)	Puseudo first order			Puseudo second order			Second order		
	q_e (mg/g)	k_1 (1/min)	R^2	q_e (mg/g)	k_2 g/(min mg)	R^2	q_e (mg/g)	k g/(min mg)	R^2
298	172.8	0.053	0.9095	208.3	1.14×10^{-3}	0.9987	5.16	0.0123	0.8366
308	170.4	0.059	0.9091	200.0	1.40×10^{-3}	0.9973	2.24	0.0213	0.6016
318	93.2	0.035	0.8673	192.3	1.70×10^{-3}	0.9981	107.5	0.0200	0.9118
328	87.3	0.035	0.8512	185.2	1.83×10^{-3}	0.9979	6.21	0.0024	0.8359

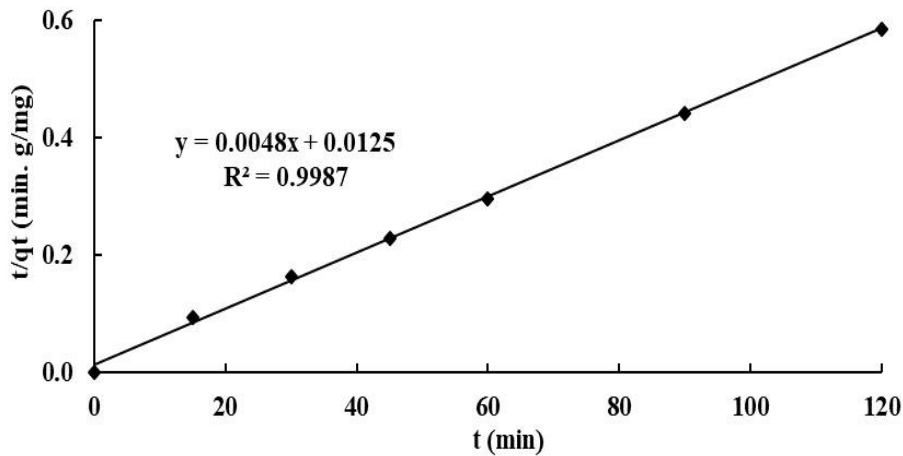


Figure 7. Lagergren Puseudo second order rate kinetic for Cr(VI) absorption.

3.13. Adsorption thermodynamics

Metal ions in solution → Metal ions on adsorbent is one way to explain the adsorption-desorption process of metal ions on adsorbent at equilibrium.

Equation (11) explains the apparent equilibrium constant (K'_c) of the adsorption reaction dependent on concentration.

$$K'_c = \frac{C_{ad.eq}}{C_{eq}} \tag{11}$$

where, $C_{ad.eq}$ and C_{eq} are equilibrium concentrations of metal ions on adsorbent and in solution, respectively. Apparent equilibrium constant values (K'_c) were calculated according to Equation (11) at different initial concentrations of Cr(VI) to obtain thermodynamic equilibrium constant (K_c^0). K'_c versus concentration of Cr(VI) in the solution (C_{eq}) at each temperature was plotted. Obtained-line was extrapolated to zero for infinite dilution and thermodynamic equilibrium constants (K_c^0) were obtained at 298, 308, 318 and 328 K [48].

The thermodynamic parameters (ΔG° , ΔH° and ΔS°) were calculated with the Equations (12) and (13).

$$\Delta G^\circ = -RT \ln K_c^\circ = \Delta H^\circ - T\Delta S^\circ \quad (12)$$

$$\ln K_c^\circ = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (13)$$

where, R is gas constant (8.314 J/mol) and T is temperature (K). ΔG° indicates the spontaneity of chemical reaction. The ΔG° values for adsorption of Cr(VI) on Amberlite IRA900 resin were calculated according to Equation 12 and the results were given in Table 6. As seen in Table 6, all ΔG° values found were negative. Negative values of ΔG° indicated that the adsorption of Cr(VI) on resin was feasible and spontaneous at four different temperatures.

The plot of $\ln K_c^\circ$ values versus $1/T$ according to Equation 13 was depicted in Figure 8. Enthalpy and entropy changes were determined from slope and intercept, respectively. The ΔH° and ΔS°

values obtained were given in Table 6. As seen in Table 6, negative value of enthalpy change (ΔH°) showed that adsorption of Cr(VI) on resin was exothermic. The negative value of entropy change (ΔS°) indicated that regularity at solid/liquid interface was increased during adsorption of Cr(VI) on Amberlite IRA 900 resin.

After determining kinetics of ion exchange reaction related to the adsorption of Cr(VI) ion on the resin as pseudo-second-order, the activation energy (E_a in J/mol) was calculated using Equation (14).

$$\ln k = -\left(\frac{E_a}{R}\right)\frac{1}{T} + \ln A \quad (14)$$

Plotting the rate constant values versus $1/T$ for Cr(VI) at four distinct temperatures (298 K, 308 K, 318 K, and 328 K) was done using pseudo second order kinetics. The results are shown in Figure 9. Activation energy of Cr(VI) ion was obtained from the slope of straight line according to Equation (14) and was given as 13.12 kJ/mol in Table 6.

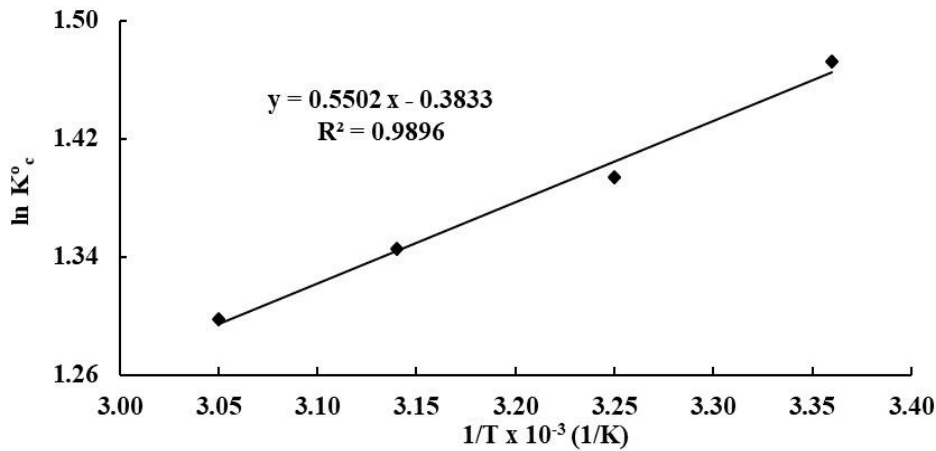


Figure 8. Determination of enthalpy any entropy

Table 6. Thermodynamic parameters for adsorption of Cr(VI) on Amberlite IRA 900 resin

36	K_C°	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° J/(mol/K)	E_a (kJ/mol)
298	4.3570	- 3.65	- 4.57	- 3.19	13.12
308	4.0295	- 3.57			
318	3.8373	- 3.56			
328	3.6632	- 3.54			

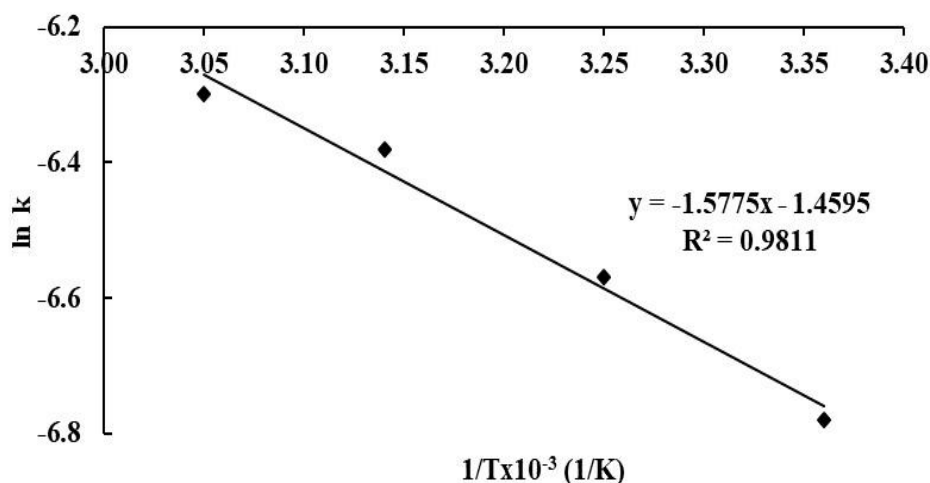


Figure 9. Determination of activation energy for adsorption of Cr(VI) on the adsorbent.

4. CONCLUSION

Amberlite IRA 900 resin as a solid-phase extractor provides a simple, selective, accurate, economic, rapid and precise for separation of Cr(III) and Cr(VI) ions and for the determination of Cr(VI). The Langmuir model is better in application than the Freundlich adsorption isotherm model. Mono layer adsorption capacity of Amberlite IRA 900 for Cr(VI) was found as 305 mg/g at 298 K. From D - R model, Cr(VI) adsorption on the resin was found to be a chemical ion exchange process. The kinetic data revealed that adsorption of Cr(VI) ion on resin followed by pseudo second order kinetic. Negative values of ΔG° support spontaneous and favorable adsorption of Cr(VI) ion and negative value of ΔH° shows exothermic nature of adsorption. Negative value of ΔS° indicated that randomness had decreased at solid liquid interface.

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CONFLICTS OF INTEREST

The authors disclosed no conflicts of interest.

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