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**Araştırma Makalesi / Research Article**

# Cr(VI) Adsorption Performance of Commercial Anion Exchange Resin

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***Keywords***
Anion exchange resin;
Batch sorption;
Hexavalent chromium;
Langmuir isotherm

## Abstract

Chromium (VI) batch system sorption from aqueous solutions by use of commercial Eichrom 1x4 anion exchange resin was studied at varying pH, temperature, and contact time, adsorbent dosage, desorption study, and starting Cr (VI) concentration. The ideal pH range for Cr (VI) sorption via anion exchange resin (AER) was found as 2.0-6.0. The kinetic of Cr (VI) sorption by resin came after the second-order kinetic model. The greatest chromium sorption emerged at 10 min for AER. The sorption isotherms were investigated with Langmuir, Freundlich and Redlich-Peterson models. The optimum isothermal model for chromium sorption via AER was the Langmuir isotherm. Moreover, the sorption thermodynamic parameters like entropy change (ΔSº), free energy change (ΔGº), and enthalpy change (ΔHº) were also investigated. A rise in the temperature has resulted in a rise of the equilibrium constant (Kc) value for the Cr (VI) sorption by AER.

# Ticari Anyon Değiştirme Reçinesinin Cr(VI) Adsorpsiyon Performansı

***Anahtar kelimeler***
Anyon değişim reçinesi;
Toplu sorpsiyon;
Altı değerlikli krom;
Langmuir izotermi

## Öz

Ticari Eichrom 1x4 anyon değişim reçinesi kullanılarak sulu çözeltilerden krom (VI) kesikli sistem sorpsiyonu, değişen pH, sıcaklık ve temas süresi, adsorban dozajı, desorpsiyon çalışması ve başlangıç Cr (VI) konsantrasyonunda incelenmiştir. Anyon değiştirici reçine (AER) yoluyla Cr (VI) sorpsiyonu için ideal pH aralığı 2,0-6,0 olarak bulundu. Reçine tarafından Cr (VI) emiliminin kinetiği, ikinci dereceden kinetik modelden sonra geldi. AER için en büyük krom sorpsiyonu 10 dakikada ortaya çıkmıştır. Langmuir, Freundlich ve Redlich-Peterson modelleri ile sorpsiyon izotermleri incelenmiştir. AER yoluyla krom sorpsiyonu için optimum izotermal model Langmuir izotermidir. Ayrıca entropi değişimi (ΔSº), serbest enerji değişimi (ΔGº) ve entalpi değişimi (ΔHº) gibi sorpsiyon termodinamik parametreleri de incelenmiştir. Sıcaklıktaki bir artış, AER tarafından Cr(VI) sorpsiyonu için denge sabiti (Kc) değerinin yükselmesine neden olmuştur.

## 1. Introduction

The widespread usage of chromium (Cr) in many practical applications such as dyeing, metallurgical processes, the production of stainless steel, etc., has resulted in the discharge of Cr into the environment and pollution of the natural world. The presence of chromium compounds in the wastewater caused by these industries has transformed into a considerable concern because of its harmful effects on human health and as well as other living beings. Chromium, like $HCrO_4^-$, $Cr_2O_7^{2-}$, and $CrO_4^{2-}$, is extremely poisonous to plants and animals due to oxidation (ASDTR 2000, Zhao *et al* 1998., Edebalı *et al*. 2010). The maximum chromium (VI) polluter level for drinking water is 0.05 mgL$^{-1}$ (US EPA 1990). The limit value for chromium release into the inner surface of water bodies is 0.1 mgL$^{-1}$. Hence, the elimination of chromium from water bodies is of vital importance to the environment. The different methodologies (i.e., ion exchange (Gode *et al.* 2005), solvent extraction (Venkateswaran et al. 2004) nondispersive solvent extraction (Alonso *et al.* 1999) membrane-based methods (Hafiane *et al.* 2000, Cengeloğlu et al. 2003, Tor et al 2004, Yılmaz et al 2008, Palanıvelu *et al.* 2004, Aslan et al. 2010) and adsorption (Hayashi *et al.* 2021, Kobya *et al.*

2004, Khezami *et al* 2005) have been reported for recovery or chromium (VI) elimination from the aqueous solutions. Nevertheless, these methods except ion exchange have significant back draws, including needs for costly materials, deficient metal removal, high energy needs, and production of toxic slush (Dragan *et al.* 2008). Ion exchange resins were employed to dispose of Cr(VI) from water. The essential benefit of employing these resins is owing to their superior ion exchange rate, high ion exchange capacity, and high mechanical and chemical stability (Pehlivan and Çetin 2009). Edebalı *et al*. reported chromium (VI) disposal from an aqueous solution via two resins, Amberlite IRA96 and Dowex 1×8 (3). Korngold et al. used Amberlite 416, and Purolite A420 that the strongly basic anion exchange resins for selective elimination of chromium from tap water (Korngold *et al.* 2003). Rengaraj *et al.* evaluated some ion exchange resins such as 1200H, 1500H, and IRN97H, to remove chromium compounds from an aqueous solution (Rengaraj *et al*. 2003). Zhao *et al.* also indicated a novel anion exchanger, named polymeric ligand exchanger, was of superior chromate selectivity at neutral to alkaline pH (Zaho *et al.* 1998). The main purpose of this research was to examine the equilibrium and kinetic parameters of Eichrom 1x4 anion exchange resin containing quaternary amine group for the Cr(VI) disposal from the aqueous solution. Contact time, temperature, pH, amount of resin and starting Cr(VI) concentration parameters that affect the adsorption were examined and the results were discussed.

## 2. Experimental Section

### *2.1 Materials*

The Eichrom 1x4 anion exchange resin employed in this study was purchased from Eichrom Technologies Inc. (Illinois, USA). The main physicochemical properties of the resin is given in Table 1. Chromium stock solutions were prepared by dissolving $K_2CrO_4$ in ultrapure water (UPW). All the chemicals used were of analytical grade and were purchased from Merck Co. UPW was used to prepare all solutions for the experiments.

**Table 1.** Properties and speciations of Eichrom anion exchange resin

| | **Eichrom anion exchange resin** |
|---|---|
| Type | Strong base anion exchanger |
| Matrix | Styrene–divinyl benzene polymeric beads |
| Chemical functional group | Quaternary amine |
| Ionic form as shipped | $Cl^-$ |
| Moisture holding capacity | 55–63% |
| Total exchange capacity | 1.0 meq/g |
| Stability (at pH range) | 0-14 |

### *2.2. Batch sorption studies.*

The chromium (VI) solution was prepared from $K_2CrO_4$ by dilution of the stock solution at the requested concentrations. The solution pH was set at the required value using 0.1 M NaOH or HCl solutions and determined with an ion meter. Experiments was performed by the batch sorption technique by shaking the resin in 20 mL chromium (VI) solutions at 225 rpm and 20±1 °C. Finally, the solution was filtered.

The effects of contact time (0-250 min), starting Cr(VI) concentration (5-1000 $mgL^{-1}$), the level of adsorbent (1.5-10 $gL^{-1}$) and temperature (20-70 °C) was also investigated for Eichrom AER. The amount of chromium (VI) sorbed was obtained by Eq. 1.

$$q = \frac{(C_o - C_e) \times V}{m} \quad (1)$$

Where q, chromium (VI) sorbed ($mgg^{-1}$); Co, starting concentration of chromium (VI) ($mgL^{-1}$); Ce, chromium (VI) concentration in solution at equilibrium ($mgL^{-1}$); V, volume of solution (L); m, resin dose (g). Concentrations of chromium (VI) were determined using ContrAA 300®Analytik Jena atomic absorption spectrometer in an acetylene torch.

## 3. Results and Discussions

### *3.1 Effect of AER pH*

Chromium ions are present in diverse anionic forms such as $Cr_2O_7^{2-}$, $HCrO^{4-}$, $CrO_4^{2-}$ and, $HCr_2O^{7-}$ in aquatic solution, depending on the concentration and pH. $CrO_4^{2-}$ anion prevails in basic or lightly acidic solution. Additionally, $Cr_2O_7^{2-}$ transforms to $HCrO^{4-}$ anion in acidic a solution when the chromium concentration exceeds about 1000 mgL$^{-1}$ (Pehlivan *et al.* 2008). Thus, in this research, chromium (VI) ions will be present as $HCrO^{4-}$ in the aquatic solution due to the studied Cr(VI) starting concentrations being ≤ 1000 mgL$^{-1}$. Anion exchangers and ions can interact in solutions in two basic ways. The most comprehensive approach requires ion exchange or metal ions chelation. Above mentioned mutual effects are studied based on the resin structure concerning existing functional groups (Lıu *et al.* 1999). In addition, the exchanger surface would be encircled with the hydrogen ions, which would improve the chromium (VI) interaction with the binding sites of the sorbent through superior attractive forces at low pH.

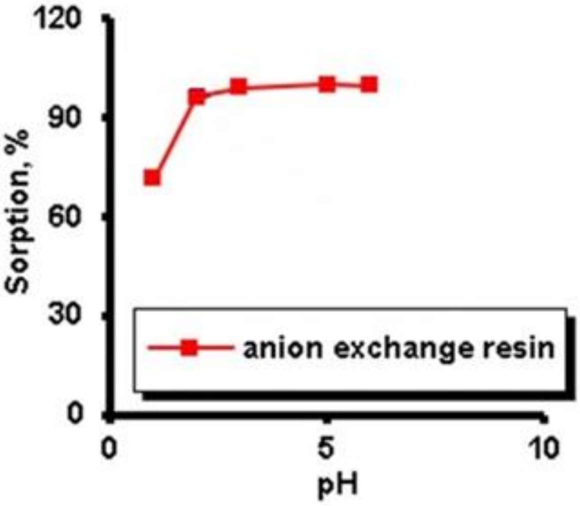

***Fig. 1.*** The effect of pH on chromium (VI) sorption via Eichrom anion exchange resin (chromium (VI) starting concentration: 25 mgL-1; the amount of resin: 5 gL-1; contact time: 1 h; shaking speed: 225 rpm temperature: 20±1 ◦C).

$$R - Cl + HCrO^{4-} \leftrightarrow R - HCrO_4 + Cl^- \qquad (2)$$

When the solution pH decreases, particularly at pH ≤2.0, the reaction in Equation 2 shifts to the left since the pKa of the carboxyl group is 1.8 (Park and Na 2006, Huang *et al.* 2009, Zhang *et al.* 2008, Cangeloğlu *et al.* 2006). Hence, at a pH range of 2.0-8.0, a possible repulsive force between the deprotonated carboxyl group and $HCrO^{4-}$ decreased the sorption. Thus, optimal pH ranges for effective Cr(VI) sorption with Eichrom anion exchange resin 2.0-6.0.

### ***3.2. Effect of Contact Time***

The disposal of Cr(VI) via anion exchange resin depending on contact time is presented in Fig. 2. Sorption equilibrium was reached in 10 min for anion exchange resin.

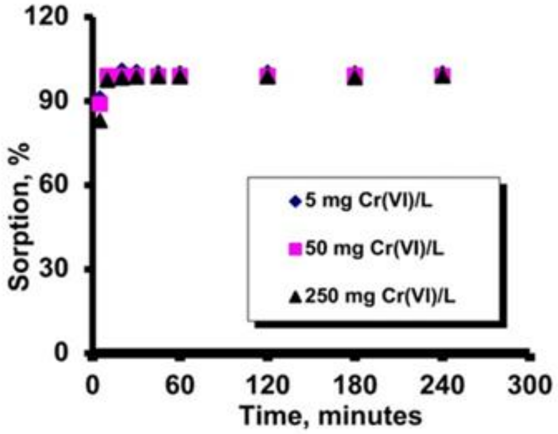

**Fig. 2.** Effect of contact time on the chromium (VI) sorption by Eichrom anion exchange resin and (starting concentration of Cr(VI): 5, 50, and 250 mgL$^{-1}$; the amount of resin: 5 gL$^{-1}$,; solution pH: 1.0 for fiber, shaking speed: 225 rpm, temperature: 20±1 °C)

According to the literature (Brassi *et al.* 1999), the concentration of chemical functional groups on the adsorbent surface allows the rate estimation of the chemisorption through the pseudo-second-order kinetic model. The experimental data were used for the pseudo-second-order kinetic model obtained by Eq. 3 (Ho *et al.* 1999).

$$\frac{t}{q_t} = \frac{1}{(k_2 \times q_e^2)} + \frac{t}{q_e} \qquad (3)$$

Where $q_e$ and $q_t$ are the amounts of chromium (VI) sorbed (mgg$^{-1}$) at equilibrium and at time t (min), respectively, $k_2$ is the rate constant of chemisorption pseudo-second-order (g.mg$^{-1}$.min$^{-1}$). The rate constant ($k_2$) and the theoretical equilibrium sorption capacities, *qe*, were determined from the slope and intercept of the linear plots of the pseudo-second-order kinetic model and are given in Table 2 for the present study. Coefficients of determination (R$^2$) and the theoretical and experimental *qe* values indicate that the chromium (VI) sorption via anion exchange resin and fibers follows second-order reaction kinetic

**Table 2.** The rate constant values of the pseudo-second-order kinetic model for AER.

| **Eichrom anion exchange resin** | | | |
|---|---|---|---|
| | 5 $mgL^{-1}$ | 50 $mgL^{-1}$ | 250 $mgL^{-1}$ |
| $q_e$ (calculated) ($mgg^{-1}$) | 1.040 | 10.309 | 51.546 |
| $q_e$ (experimental) ($mgg^{-1}$) | 1.105 | 10.551 | 52.280 |
| $k_2$ [g/(mg. min)] | 17.829 | 0.753 | 0.058 |
| $R^2$ | 1.000 | 1.000 | 0.999 |

### *3.3 Models of Sorption Isotherm*

The sorption isotherm studies are crucial in terms of design objectives. Hence, experimental data were investigated with widely known adsorption isotherms. Langmuir isotherms (given as Eq. 4 (Langmuir 1916)), the single-layer adsorption surfaces and presumes adsorption occurs on a uniform surface structure of the adsorbent.

$$q_e = \frac{Q_o \times b \times C_e}{(1 + b \times C_e)} \tag{4}$$

The linear form of the Langmuir isotherm may be given as Eq. 5;

$$\frac{C_e}{q_e} = \frac{1}{Q_o \times b} + \frac{C_e}{q_e} \tag{5}$$

Where $C_e$ is the concentration of chromium (VI) ion ($mgL^{-1}$) at equilibrium, $Q_o$ is the single-layer capacity of the adsorbent ($mgg^{-1}$) and $b$ is the Langmuir sorption constant ($Lmg^{-1}$). The plot of $C_e/q_e$ versus $C_e$ shows a straight-line Fig. 3 a, b and $Q_o$ and $b$ can be obtained by the slope and intercept of the plot, respectively.

The Freundlich equation (given as Eq. 6 (Freundlich 1907)) is reproduced for modeling multilayer sorption and sorption on non-uniform surfaces.

$$q_e = k \times C_e^{1/n} \tag{6}$$

The linear form of the Freundlich equation may be presented as Eq. 7;

$$logq_e = logk + (\frac{1}{n}) \times logC_e \tag{7}$$

The plotting of the log $q_e$ versus log $C_e$ shows a straight-line according to Eq.6 (Fig. 3c, d). $n$ and $k$ were obtained by the slope and the intercept of this straight-line, respectively. Where $k$ is an approximate sign of adsorption capacity [($mgg^{-1}$).($mgL^{-1}$)$^{-1/n}$], $C_e$ is the equilibrium concentration ($mgL^{-1}$), and $n$ is an empirical parameter. The Redlich–Peterson equation is given by the following Eq. 8 (Tor *et al.* 2006):

$$q_e = \frac{K_R \times C_e}{(1 + a_R \times C_e^{\beta})} \tag{8}$$

Where, $K_R$ is Redlich–Peterson isothermal constant ($Lmg^{-1}$), $a_R$ is also a constant ($Lmg^{-1}$)$^{\beta}$ and β is the exponent between 0 and 1.

The Redlich–Peterson isotherm is close to the Freundlich isotherm for high concentrations and the Langmuir equation for low concentrations. This isotherm model shows not only a linear concentration dependence in the numerator but also an exponential function in the denominator. Additionally, this model can provide an experimental isotherm combining three parameters. Thus, it may be implemented in uniform or non-uniform systems owing to its sophistication (Marcu *et al.* 2021).

While Eq. 8 reduces to the Langmuir equation for the β value of 1, it reduces to Henry's equation for the β value of 0. The Redlich–Peterson equation (Eq. 9) can be transformed into a linear form by the following:

$$\ln[\left(\frac{K_R \times C_e}{q_e}\right) - 1] = lna_R + \beta \times lnC_e \tag{9}$$

For the Redlich-Peterson isotherm, the values of the constants were calculated from the intercept and slope (Fig. 3 (d) and (e)) of the linear form of the isotherm (Eq. 9). The isotherm constants and coefficients of determination ($R^2$) values for were presented in Table 3. For the comparison of $R^2$ values, it may be determined that Cr(VI) sorption by anion exchange resin may be preferably defined by Langmuir isotherm. Our findings may be deduced from the value of *β* (0.820) given in Table 3, which is close to unity.

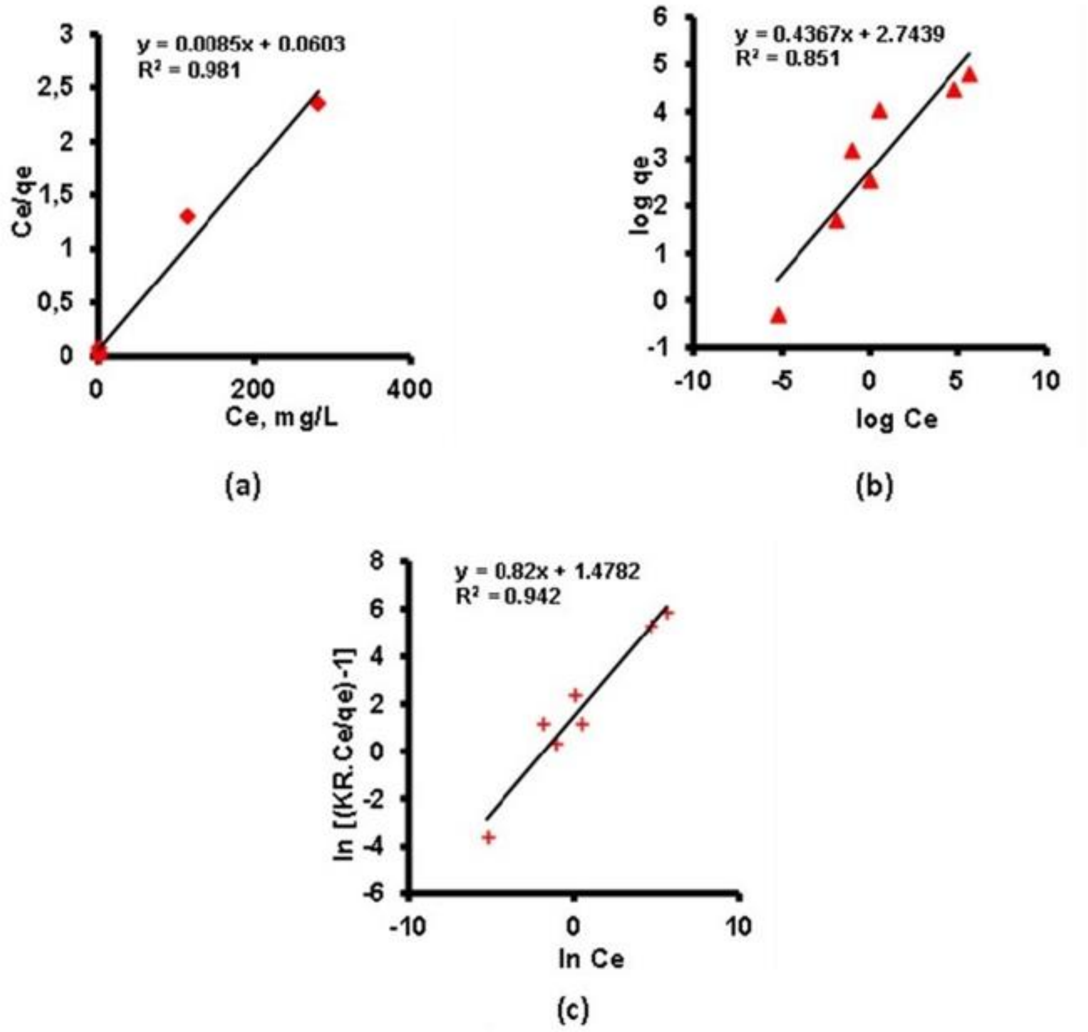

**Fig.3.** The Langmuir isotherm for anion exchange resin (a), The Freundlich isotherm for resin (b), The Redlich-Peterson isotherm for resin (c) (amount of resin and fiber: 5 $gL^{-1}$, respectively, solution pH: 1.0 resin, contact time: 1 h, shaking speed: 225 rpm, temperature: 20±1 °C).

**Table 3.** The parameters of isotherm models for the Cr(VI) sorption from aquatic solution by Eichrom anion exchange resin and FIBAN AK-22-1 anion exchange fiber.

| **Isotherm model** | **Eichrom anion exchange resin** |
|---|---|
| Langmuir model | |
| $Q_o$, ($mgg^{-1}$)<br>*b*, ($Lmg^{-1}$) | 117.647<br>0.141 |
| $R^2$ | 0.981 |
| Freundlich model | |
| *k*, [($mgg^{-1}$). ($mgL^{-1}$)$^{-1/n}$] | 554.498 |
| *n* | 2.290 |
| $R^2$ | 0.851 |
| Redlich-Peterson model | |
| $K_R$, ($Lmg^{-1}$) | 148.993 |
| $a_R$, ($Lmg^{-1}$)$^{\beta}$ | 4.406 |
| $\beta$ | 0.820 |
| $R^2$ | 0.942 |

### *3.4. Effect of Adsorbent Doses*

The percentages of Cr(VI) sorption with various amounts of anion exchange resin is given in Fig. 4. An increase in the adsorbent dose, increases the percentage disposal of the adsorbate. This is consistent with the hypothesis that lower q values are produced by higher adsorbent dosages. Functional group concentrations on the resins related to the amount of these adsorbent through surface site density (Redlich *et al.* 1959, Sujana *et al.* 1998). However, *q* decreased as the unit of *q* is mg Cr(VI) per gram of resin.

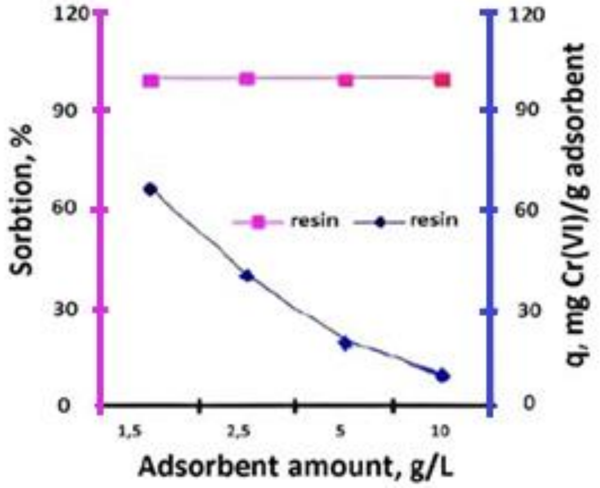

**Fig.4.** Variation of chromium (VI) sorption with the amount of anion exchange resin (concentration of chromium (VI): 100 mgL$^{-1}$, contact time: 1 h, solution pH: 1.0 for resin, shaking speed: 225 rpm, temperature: 20±1 °C).

### *3.5. Effect of Temperature*

Calculation of free energy change (Δ*G*°), enthalpy change (Δ*H*°), and entropy change (Δ*S*°) parameters can be carried out by the following equations.

$$K_c = \frac{C_{Ae}}{C_e} \quad (10)$$

$$\Delta G^0 = -R \times T \times lnK_c \quad (10)$$

$$logK_c = \left[\frac{\Delta S^0}{2{,}303 \times R}\right] - \left[\frac{\Delta H^0}{2{,}303 \times R \times T}\right] \quad (11)$$

Where $K_c$ is the equilibrium constant obtained from the equilibrium concentrations ratio of the metal ions on the ion exchanger and in the solution (Gode *et al.* 2005). $C_{Ae}$ is the solid phase concentration at equilibrium (mgL$^{-1}$) and $C_e$ is the equilibrium concentration in solution (mgL$^{-1}$). Δ*G*°, Δ*S*°, and Δ*H*° are defined as changes in free energy, entropy, and enthalpy, respectively. Mixture temperatures ranged from 20 to 70 °C. Free energy (Δ*G*°) can be calculated by Eq.10. Entropy (Δ*S*°) and enthalpy (Δ*H*°) can be obtained by the plot of log *K*c versus 1/*T by* Eq.11 (Fig. 5). Thermodynamic parameters were presented in Table 4.

The positive Δ*H*° values for anion exchange resin indicate that the endothermic reaction occurred as seen in Table 4. The positive Δ*S*° values were randomly proposed at the ion exchanger solution interface over the chromium (VI) sorption on the resin. The negative Δ*G*° values indicated that the sorption processes via anion exchange resin occurred spontaneously. Besides, a decrease in Δ*G*° values with an increase in temperature demonstrated the sorption through resin was more natural at higher temperatures.

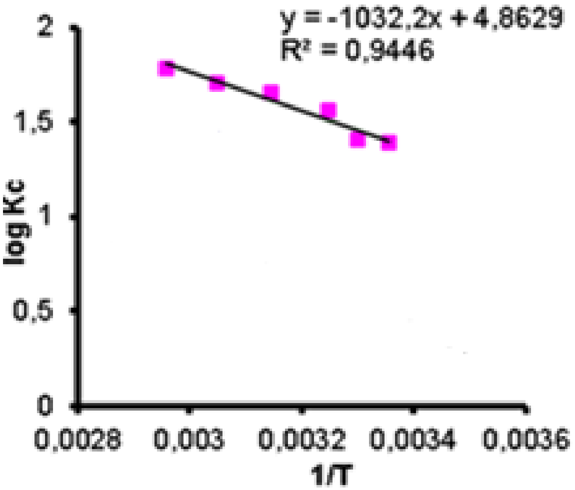

**Fig.5.** Equilibrium constants of chromium (VI) on anion exchange resin as a function of temperature.

**Table 4.** Thermodynamic parameters for the adsorption of Cr(VI) on Eichrom anion exchange resin.

| | **Eichrom anion exchange resin** | | |
|---|---|---|---|
| | **ΔG° (J mol$^{-1}$)** | **ΔH° (J mol$^{-1}$)** | **ΔS° (J kmol$^{-1}$)** |
| T=298 K | -7920.60 | 19764.87 | 93.12 |
| T=303 K | -8020.69 | | |
| T=308 K | -8922.68 | | |
| T=318 K | -9436.12 | | |
| T=328 K | -9756.42 | | |
| T=338 K | -10191.73 | | |

### *3.6. Chromate Desorption Experiment*

NaOH solution was used to carry out the chromate's desorption. Desorption study was carried out by taking hourly measurements of chromate desorption with 2 M NaOH solution under optimum conditions. In addition, the regenerated adsorbents kept their original capacity of around 80%.

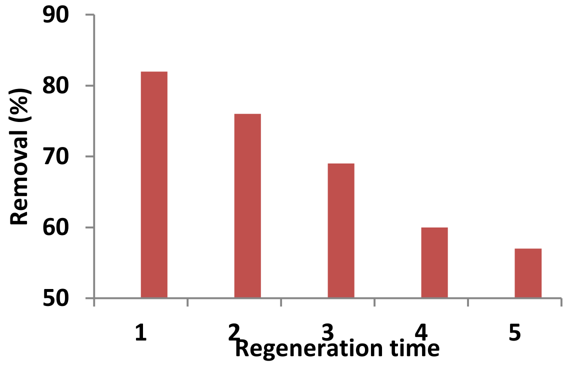

**Fig. 6**. Regeneration of adsorbent by 2M NaOH (concentration of chromium (VI): 100 mgL$^{-1}$, contact time: 5 h, solution pH: 1.0 resin, shaking speed: 225 rpm, temperature: 20±1 ˚C)

## 4. Conclusion

The present study demonstrated that Eichrom anion exchange resin have a remarkable sorption ability for Cr(VI) ions. Optimum pH ranges for ion exchange were 2.0-6.0 for anion exchange resin. The Cr(VI) adsorption reached equilibrium at 10 min for anion exchange resin. The kinetic of Cr(VI) sorption by resin came after the second-order kinetic model. The data for the sorption on the resin was better described by Langmuir isotherm. As a result, Eichrom anion exchange resin may be employed for successful uptake of Cr(VI) from water samples. The equilibrium sorption level for both anion exchange resin increased with increasing temperature.

## 5. Conflict of Interest

The author declares that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## 6. Acknowledgments

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