



# Cr(III) REMOVAL FROM AQUEOUS SOLUTIONS BY ADSORPTION

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## ABSTRACT

The adsorption of Cr (III) on the adsorbent produced from lignite coal was studied as a function of time, amount of adsorbent, pH and temperature. Cr (III) adsorption data obeyed Freundlich, Langmuir and Lagergren equations. The values of  $\Delta H^0$ ,  $\Delta S^0$  and  $\Delta G^0$  were calculated. The results showed that adsorption is endothermic. The negative free energy values indicate that the process of Cr (III) adsorption is spontaneous and favoured at high temperatures. The adsorption of Cr (III) in the presence of different cations was also studied at 20<sup>0</sup> C. The results were correlated with the ionic potential of cations.

**Key Words :** Adsorption, Cr(VI) , Cr (III), Thermodynamics parameters, Adsorption isotherm

## SULU ÇÖZELTİLERDEN ADSORPSİYON İLE Cr (III) UZAKLAŞTIRILMASI

### ÖZET

Linyit kömüründen elde edilen adsorbent üzerine Cr (III) adsorpsiyonu zamanın, adsorbent miktarının, pH'nın ve sıcaklığın fonksiyonu olarak çalışıldı. Cr (III) adsorpsiyon verileri Freundlich, Langmuir ve Lagergren eşitliklerine uydu.  $\Delta H^0$ ,  $\Delta S^0$  ve  $\Delta G^0$  değerleri hesaplandı. Sonuçlar adsorpsiyonun endotermik olduğunu gösterdi. Negatif serbest enerji değerleri Cr (III) adsorpsiyonunun kendiliğinden olduğunu ve yüksek sıcaklıklarda daha uygun olduğunu gösterdi. Cr (III) adsorpsiyonu, çeşitli katyonların varlığında 20 °C'de çalışıldı. Sonuçlar katyonların iyonik potansiyelleri ilişkilendirildi.

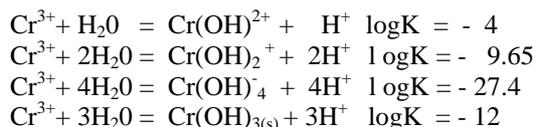
**Anahtar Kelimeler :** Adsorpsiyon, Cr (VI), Cr(III), Termodinamik parametreler, Adsorpsiyon izotermi

## 1. INTRODUCTION

Chromium in waters originates from natural sources such as wet precipitation, dry fall out from the atmosphere and run off from the terrestrial systems. The land increase in chromium concentrations in waters may be originated from by discharge of waste water from industries such as metal, electroplating and chemical (Kotas and Stasicka, 2000). Under environmental conditions chromium exists in two stable oxidative states. Cr (III) and Cr (VI) (Kotas and Stasicka, 2000). These two states are different in charge, physicochemical properties as well as chemical and biochemical reactivity. Cr (VI) is

water soluble, extremely toxic and potentially carcinogenic in humans whereas it is presumed that Cr (III) is an essential trace element for mammals including man and nontoxic to aquatic organisms. It was reported to be responsible for the control of glucose and lipid metabolism in mammals (Anderson, 1989). This hypothesis was also supported by the discovery of the so called glucose tolerance factor which contains Cr (III), nicotinic acid, glycine, glutamic acid and cysteine (Nieber and Jisys, 1988).

The dominant Cr (III) species in water depends on pH, according to the following equilibrium reactions (Selomulya et al., 1999).



$\text{Cr}(\text{OH})_2$  species is dominant at pH values between 6 and 8, while  $\text{Cr}(\text{OH})_2^+$  and  $\text{Cr}^{3+}$  predominate in more acidic conditions.  $\text{Cr}(\text{OH})_4^-$  and  $\text{Cr}(\text{OH})_{3(s)}$  are most likely to be found in alkaline medium.

Although disposal of Cr (III) can be considered to be less problematic than Cr (VI), the hazard of Cr (III) is tantamount to Cr (VI) if oxidation occurs.

Removal of Cr (III) from waste water can be achieved by addition of lime in a basic medium to precipitate a  $\text{Cr}(\text{OH})_3$ . But this process produces a large volume of waste sludge (Macchi et al., 1991). Adsorption seems an alternative process to remove metals from waters. In our laboratory adsorbents produced from coal have been used to remove some inorganic and organic pollutants (Mahramanlioglu et al. 1998a; Mahramanlioglu et al. 1998b). Although various studies have been published on the adsorption of hexavalent chromium on different adsorbents, the adsorption of Cr (III) on the adsorbents has been the subject of relatively few studies (Huang and Wu, 1975; Alaerts et al., 1989; Periasamy et al. 1991; Ramos et al., 1995; Ajmal et al., 1996; Low et al., 1997; Ozer and Özer, 1997; Ozer et al., 1998; Raji and Anirudhan, 1998; Selomulya et al., 1999; Navasivayam and Yamuna, 1999; Krishna et al., 2000).

Activated carbon has been widely used as an adsorbent for the removal of the inorganic and organic pollutants from waste waters since they have both high surface areas and porosities. They can be produced from different raw materials such as coal, coconut-shell, almond shell olive and peach stones, oil palm trunks (Hussein et al., 1996). Coal is the most commonly used precursor due to its low cost and large supply, and also activated carbon produced from coal is superior to those derived from lignocellulosic materials in terms of mechanical properties (Ahmadpour and Do. 1996).

In our laboratory, adsorbents produced from coal have been tested to understand their adsorption capacity using some pollutants such as cobalt, uranium, nylomine blue, p-toluene sulphonic acid in recent years (Mahramanlioglu et al., 2000a; Mahramanlioglu and Biçer, 2000; Mahramanlioglu et al., 2001). Coal can be found abundantly in our country and it is possible to notably increase the surface area and porosity of the coal by means of activation methods.

In the present study, Kemerburgaz coal has been chosen as precursor of activated carbon within the above scope. The present study is devoted to the adsorption of Cr (III) on the adsorbent produced from coal.

## 2. MATERIAL AND METHOD

All the chemicals used in the study were obtained from Merck Company. All the solutions used in the study were prepared with distilled water.

The coal samples obtained from Kemerburgaz were crushed and sieved to the particle size  $< 0.1$  mm. These samples were dried at  $105^\circ\text{C}$  for two hours.

There are two different processes to produce activated carbon: chemical and physical activation.

Physical activation consists of carbonization and activation by suitable gases. The chemical activation consists of carbonization at a relatively low temperature with the addition of a dehydrating agent (eg.  $\text{ZnCl}_2$ ,  $\text{KOH}$ ,). In our study physical activation was chosen to produce activated carbon.

### 2. 1. Carbonization

Carbonization of coal samples were performed in a furnace under a stream of  $\text{N}_2$ . The samples were heated at  $25^\circ\text{C}/\text{min}$  from room temperature to  $550^\circ\text{C}$  and then kept at  $550^\circ\text{C}$  for 1 hour.

### 2. 2. Activation

Following the carbonization of the coal the chars obtained were subject to activation in  $\text{CO}_2$  at  $850^\circ\text{C}$  for one hour in order to increase the surface area and pore volumes of the coal. The samples obtained were cooled to room temperature and washed with  $0.1$  M  $\text{HCl}$  wash to remove ash. Then the samples were washed with pure water. The prepared adsorbents were dried for 6 hours at  $105^\circ\text{C}$ . Prior to use as adsorbent, the product was sieved again according to the particle size  $< 0.1$  mm and stored in air tight containers.

### 2. 3. Outgassing of the Adsorbent

All physisorbed material has to be removed from the surface of the adsorbent before the determination of the surface area of the adsorbent and adsorption studies (Gregg and Singh, 1982).

This can be achieved by exposing of the surface to high vacuum, the exact conditions required being dependent on the particular gas-solid system.

In routine determinations of the surface area it is generally advisable not to remove any chemisorbed species which may be present: thus the hydroxylated oxides are usually outgassed at 150 °C. Activated carbons which has micropores require higher temperatures since the complete removal of physisorbed material from their narrow pores. Therefore adsorbent produced in our study was outgassed by exposure of the surface area at  $10^{-3}$  torr and 350 °C.

Prior to use as adsorbent, the product was sieved again according to the particle size  $< 0.1$  mm and stored in air tight containers. Surface area of the adsorbent produced was determined by an 'one point'  $N_2$  gas adsorption method using Quantochrome Monosorb BET equipment (Quantochrome Corp.) and found to be  $838 \text{ m}^2 \cdot \text{g}^{-1}$ .

## 2. 4. Adsorption Procedure

Adsorption experiments were carried out by a batch method at constant temperature (20, 30, 40, 50 °C). A known amount of adsorbent was shaken with 100 mL of Cr (III) solution. The solutions were centrifuged and then concentrations of Cr (III) were measured. Cr (III) concentration was determined using atomic absorption spectrophotometer.

All the equilibrium and kinetic studies were carried out at pH = 6.00 except pH studies, since this value is the optimum for the adsorption process of Cr (III). pH of the solutions was adjusted by HCl or NaOH.

## 3. RESULT AND DISCUSSION

### 3. 1. Effect of Contact Time

Figure 1 shows the adsorption of Cr (III) on the adsorbent produced from lignite coal with shaking time for different initial concentrations. The concentration of Cr (III) decreases rapidly initially. But the decrease of Cr (III) concentration slows down. It is seen from the Figure 1 that the equilibrium time is 100 minutes for all the concentrations.

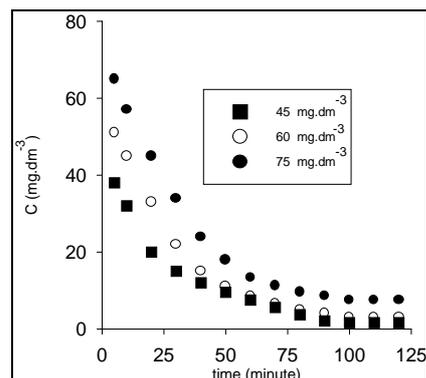


Figure 1. Effect of contact time on the adsorption of Cr(III)

### 3. 2. Adsorption Kinetics

The Lagergren equation was applied to the kinetic data in the form (Kızılcıklı et al., 1999).

$$\ln(q_e - q) = \ln q_e - k_a t$$

Where  $q_e$  and  $q$  are the amounts of Cr (III) adsorbed at equilibrium time and time,  $t$ ,  $k_a$  is the Lagergren equation constant.

Plots of  $\ln(q_e - q)$  versus  $t$  for different initial concentrations are given in Figure 2. The values of  $k_a$  obtained from the slopes were found to be as 0.0421, 0.0435, 0.044  $\text{min}^{-1}$  for the initial concentrations 45, 60 and 75  $\text{mg} \cdot \text{dm}^{-3}$  respectively. It is seen from the values of the rate constants that concentration does not affect the values of  $k_a$  significantly.

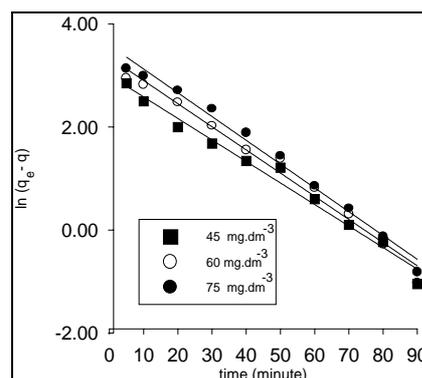


Figure 2. Lagergren plots for the adsorption of Cr(III)

### 3. 3. Effect of Adsorbent Concentration

The effect of the adsorbent concentration on the adsorption of Cr (III) is shown in Figure 3. It is seen from the figure that concentration decreased with the rise in the concentration of adsorbent. The

maximum removal was exhibited at a dosage 0.325g/100 mL. This is due to the increase in the number of active sites with an increase in amount of adsorbent.

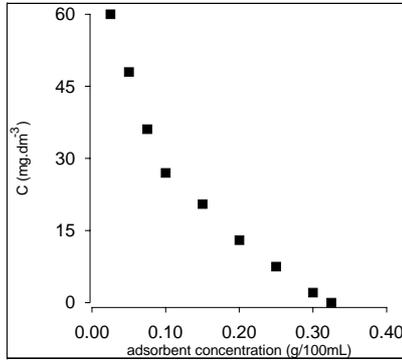


Figure 3. Effect of the adsorbent concentration on the adsorption of Cr (III)

### 3. 4. Adsorption Isotherm

In order to calculate the adsorption capacity of the adsorbent, the equilibrium data were fitted using the Langmuir and Freundlich isotherms.

The Freundlich equation can be written as,

$$q = k.C^n$$

Where  $q$  is the amount of Cr (III) adsorbed per weight of the adsorbent,  $C$  is the equilibrium concentration,  $k$  and  $n$  are the Freundlich isotherm constants.

This equation can be linearized as follows.

$$\ln q = \ln k + n \cdot \ln C$$

The values of  $k$  and  $n$  were calculated from the slope and the intercept of the plot and were found to be as 16.76 and 0.186 (Figure 4).

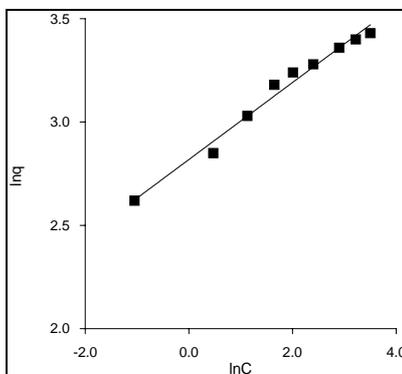


Figure 4 . Freundlich isotherm for the adsorption of Cr (III)

The Langmuir equation can be written as  $C/q = C/Q_0 + 1/Q_0 \cdot b$

Where  $Q_0$  and  $b$  are the Langmuir isotherm constants. A straight line is obtained by plotting  $C/q$  versus  $C$  indicated that the Langmuir equation can be applied in the concentration studied (Figure 5).

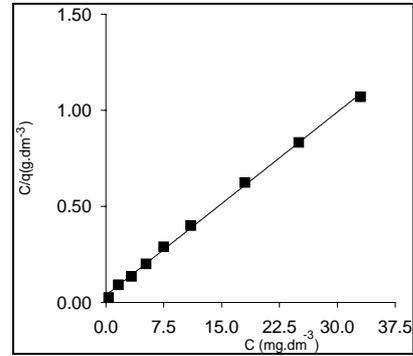


Figure 5. Langmuir isotherm for the adsorption of Cr (III)

The values of  $Q_0$  and  $b$  were calculated from the slope and intercept of the plot in the Figure 5 and were found to be as  $31.55 \text{ mg.g}^{-1}$  and 0.896.

The authors examined some studies on the adsorption of Cr (III) in the literature. The values of  $Q_0$  obtained in these studies are given as 2.7, 25.3, 0.2, 18.9, 7.8, 23.037  $\text{mg.g}^{-1}$  for activated carbon, activated carbon oxidised with  $\text{HNO}_3$ , activated carbon oxidised with  $\text{HNO}_3$  and heated at 873 K in a  $\text{N}_2$  flow in 2 hr, natural moss, biogas residual slurry and activated carbon with mineral origin respectively (Ramos et al., 1995; Namasivayam and Yamuna, 1999).

If the  $Q_0$  value obtained in this study is compared with those adsorbents, it is seen that the adsorption capacity of the adsorbent produced for this study is greater than the adsorbents used in other studies.

In order to predict the adsorption efficiency of the adsorption process, the dimensionless equilibrium parameter was determined by using the following equation (Mahramanlioğlu et al., 2000b).

$$r = \frac{1}{1 + b.C_0}$$

Values of  $r < 1$  represent favourable adsorption and values greater than 1.0 represent unfavourable adsorption. The  $r$  value for the initial concentration of  $60 \text{ mg.dm}^{-3}$  was found to be as 0.019. The value obtained shows that our system is favourable

### 3. 5. Effect of pH

It is known that pH of the solution affects the adsorption. Therefore pH experiments were carried out for the initial concentration of  $60 \text{ mg.dm}^{-3}$ .

The adsorption of Cr (III) on the adsorbents produced from coal as a function of pH is shown in Fig 6. It is seen from the Figure 6 that the adsorption of Cr (III) has a strong pH dependent characteristics and removal of Cr (III) ions decreases with the increase in pH. The influence of pH on Cr(III) adsorption can be explained as follows: At low pH (i.e.3), the surface is protonated resulting in lower removal of Cr (III) by the adsorbent and the surface has the negative charges while pH increases so the negative charges on the surface increase and Cr (III) ions are adsorbed through electrostatic attractions.

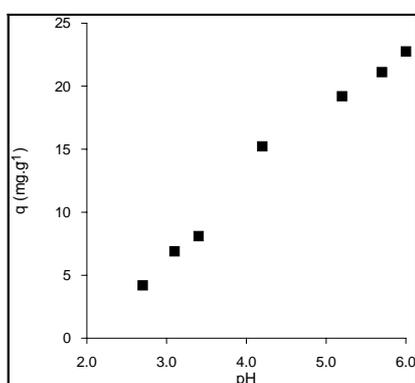


Figure 6 . The effect of pH on the adsorption of Cr (III)

### 3. 6. Thermodynamic Parameters

In order to calculate the values of  $\Delta H^0$  and  $\Delta S^0$  the adsorption experiments were carried out at different temperatures (20, 30, 40, 50 °C ).

The values of enthalpy and entropy changes were calculated using the following equation.

$$\ln K = \Delta S^0 / R - \Delta H^0 / R.T$$

Where K is the equilibrium constant at different temperatures, R is the universal gas constant,  $\Delta H^0$  and  $\Delta S^0$  are the enthalpy and entropy changes. The linear plot of  $\ln K$  vs  $1/T$  indicates the applicability of the above equation (Figure 7). The values of  $\Delta H^0$  and  $\Delta S^0$  were calculated from the slope and intercept of the linear plot and were found to be as  $22914 \text{ J.mol}^{-1}$  and  $96.50 \text{ J.deg.mol}^{-1}$ . The positive values of  $\Delta H^0$  show that the adsorption process is endothermic and the positive values of  $\Delta S^0$  shows

the increase of randomness at adsorbent /solution interface.

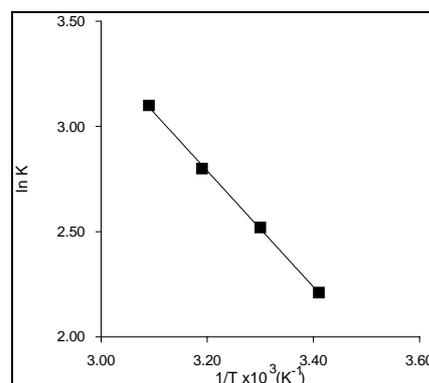


Figure 7.van't Hoff plot for the adsorption of Cr (III).

The standart free energy change was calculated by the equation,

$$\Delta G^0 = \Delta H^0 - T.\Delta S^0$$

The values of  $\Delta G^0$  were calculated as -5361, - 6326, -7290, -8255  $\text{J.mol}^{-1}$ . The results indicate that the adsorption process is more spontaneous at high temperatures.

### 3. 7. The Effect of Different Cations

The other substances in the medium affect the reaction kinetic, adsorption kinetic and adsorption capacity (Tuncay et al.1999; Mahramanlioglu et al., 2000c). Therefore the effect of different cations such as  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{La}^{3+}$  on the adsorption of Cr (III) was also studied. In order to predict the adsorption capacity of the adsorbent in the presence of different cations,  $Q_0$  values of the Langmuir isotherm were calculated. The  $Q_0$  values were calculated since the value of  $Q_0$  indicates the adsorption capacity of the adsorbent. The concentrations of cations were fixed at  $30 \text{ mg.L}^{-1}$ . But the concentrations of Cr (III) was different to calculate the  $Q_0$  constants of the Langmuir equation. The values of  $Q_0$  constants of the Langmuir equation were calculated with the least square method using the Langmuir equation above in the text and was given in Table 1.

Table 1. Langmuir Isotherm Constant,  $Q_0$ , For the Adsorption of Cr(III) in the Presence of Different Cations

Cations	$Q_0(\text{mg.g}^{-1})$	Ionic potential ,Z/r
Only Cr (III)	31.55	-
$\text{La}^{3+}$	23.89	2.830
$\text{Co}^{2+}$	24.71	2.778
$\text{Zn}^{2+}$	25.12	2.707
$\text{Cd}^{2+}$	28.15	2.062

It is seen from the results that the adsorption of Cr (III) is lowered since these cations are coadsorbed alongwith Cr(III) on the adsorbent. The cations reduce the adsorption of Cr (III) in order of  $La^{3+} > Co^{2+} > Zn^{2+} > Cd^{2+}$ . This result indicates that the cation which larger Z/r values has greater effect on the adsorption of Cr (III).

#### 4. CONCLUSION

Removal of Cr (III) by activated carbon increased with an increase in solution pH. Kinetic experimental studies showed that adsorption reached equilibrium in 100 minutes. Adsorption followed Languir and Freundlich isotherms. Adsorption capacity of the adsorbent used in the study for Cr (III) is greater than the adsorbent used in other studies.

The results showed that adsorption is endothermic and the process of Cr (III) adsorption is spontaneous and favoured at high temperatures. The adsorption of Cr(III) in the presence of different cations decreased.

The authors think that the data obtained can be helpful for the engineers who work in waste water treatment plants for the removal of Cr (III).

Based on these findings, the adsorbent used in the study can be proposed to be used to treat Cr (III) containing wastes.

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