ARAŞTIRMA MAKALESİ/RESEARCH ARTICLE

ROLE OF ALUMINA IN Cr (VI) REMOVAL FROM AQUEOUS SOLUTIONS

Halil HASAR[1,2] and Yakup CUCI[1]

ABSTRACT

This paper presents the adsorption characteristics for the removal of Cr (VI) from aqueous solutions using alumina obtained from Etibank Aluminum Plant. In order to define the optimum conditions, the effects of contact time, activation process, pH of solution, initial concentration, adsorbent dose and salinity on the removal of Cr (VI) have been investigated. It is shown that the Freundlich Isotherm Model adequately described batch adsorption data. Although the removal percentage of Cr(VI) on activated alumina under optimal conditions is high, in practice, it could not be used as a potential sorbent for removal of Cr(VI) because high dose of adsorbent.

Key Words: Adsorption, alumina, chromium (VI), Freundlich Isotherm, removal

SULU ÇÖZELTİLERDEN Cr(VI) GİDERİMİNDE ALÜMİNANIN ROLÜ
ÖZ

Bu makale, Etibank Alüminyum Fabrikasından temin edilen alumina ile sulu çözeltilerden Cr(VI) giderimi için adsorpsiyon karakteristiklerini sunmaktadır. Optimum şartları tayin etmek amacıyla, temas süresinin, aktivasyon prosesinin, çözelti pH'nın başlangıç konsantrasyonunun, adsorbent dozajının ve tuzluluğun Cr(VI) giderimindeki etkisi incelenmiştir. Freundlich İzoterm Modelinin adsorpsiyon verilerini oldukça iyi tanımladığı görülmüştür. Optimum şartlarda Cr(VI)'nın aktif alumina üzerindeki giderim yüzdesi yüksek olmasına rağmen, yüksek adsorbent dozajı gerektirdiğinden uygulamada Cr(VI) giderimi için potansiyel bir sorbent olarak kullanılamaz.

Anahtar Kelimeler: Adsorpsiyon, alumina, krom (VI), Freundlich izothermi, giderim

1. INTRODUCTION

Aquatic media have been contaminated with chromium originating from metal plating, chrome leather tanning, point and pigment, glass and ceramic, photography, and alloy preparation industries. Chromium occurs in aqueous systems as both trivalent and hexavalent forms. The hexavalent chromium must be removed from aquatic media before being discharged into sewage system because of its toxic effect. In general, advanced treatment processes are used such as chemical precipitation, ion exchange, reverse osmosis, electrodialysis, and activated carbon adsorption. Since most of these processes are rather expensive, the use of industrial by-product or agricultural residues having biological activates has been received considerable attention.

Interest has arisen recently in the investigation of some unconventional methods and materials for scavenging heavy metal ions from industrial wastewater. A number of agricultural residues such as moss (Lee and Low, 1989; Sharma and Forster, 1993), coconut husk (Low, et.al., 1995), sawdust (Ajmal, et.al., 1998; Raji and Anirudhan, 1998), chitosan (Saucedo, et.al., 1992), rise husk (Munah and Zein,1997; Suemitsu et.al.,1986; Cici and Keles,1990), sugar beet pulp (Özer, et.al., 1997), tea leaf (Tee and Khan, 1988) have been reported to be able to remove toxic metals from aqueous solutions. However, various other materials such as bituminous coal (Rawat and Singh,1992), bentonite (Kapoor and Viraraghavan, 1998)) and hematite (Chakravarty, et.al 1998) have also been studied for the removal of heavy metals from aqueous solutions.

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The present work examines the removal of Cr (VI) from aqueous solutions by using alumina which is a by-product of an aluminum factory.

2. MATERIAL AND METHOD

2.1 Preparation of Adsorbent

Alumina used in this study was obtained from Etibank Aluminum Factory, Seydisehir. The obtained alumina contains 98% Al_2O_3, and 2% some impurities such as silica and alkalizes. However, it was found that nearly 35% of Al_2O_3 was in a-Al_2O_3 form.

The samples of alumina were sieved to particle size of –200 mesh, and this fraction was used in the experiments. In this study, the alumina was used both in conditions with and without activated form. The activation process was made as follows:

1. 100 g of alumina having size of –200 mesh were boiled through 500 ml of 1 M HCl under condenser for two hours.

2. In the end of two hours, the sample was filtrated, and the cake was obtained.

3. 100 ml of distilled water was passed through the cake.

4. The washed cake was dried for 12 hours in oven adjusted to 90 ºC.

5. Then, the cake was crushed and sieved to have particles of size of –200 mesh.

It is shown that the alumina has increased about 10% in weight by the activation process. To investigate the effect of salinity on adsorption process, solution of 0.1 M NaCl was used in the second series.

2.2 Adsorbate Solution

The stock solutions of Cr (VI) were prepared to be 1000 mg/L by dissolved potassium chromate ($K_2CrO_4.4H_2O$) in distilled water. All working solution were prepared by diluting the stock solution with distilled water. All other reagents used were analytical grade.

2.3 Adsorption Studies

Batch adsorption experiments were carried out by shaking desired amount of alumina with 100 ml of Cr (VI) solutions of specified concentrations at various pH between 1 and 5, and at various contact time between 5 and 60 minutes. The initial pH of the solutions was adjusted with either 1 N NaOH or HCl solutions by using a pH meter. The samples were shaken at 400 rpm. At the end of the contact time, the adsorbent was removed

from solutions by filtration, and the equilibrium concentrations were analyzed by atomic absorption spectrometry (Unicam 929) for total chromium. The removal percentages of Cr (VI) were calculated from the differences between the concentration of chromium in the initial solutions and filtrate.

2.4 Adsorption Isotherms

The distribution of metal ions between the liquid phase and the solid phase can be described by several mathematical model equations such as the standard Langmuir model and Freundlich model equations (Chacravarty and et.al., 1998).

The Freundlich model assumes that the uptake of metal ions occur on a heterogeneous by monolayer adsorption. The model is described by the equation

$$\frac{x}{m} = k_f . C_e^{1/n} \tag{1}$$

or

$$Log\left(\frac{x}{m}\right) = Log(k_f) + \frac{1}{n}Log(C_e) \tag{2}$$

where Ce is the equilibrium concentration (mg/L), x/m is the amount adsorbed per specified amount of adsorbent (mg/g), kf and 1/n are Freundlich constants describing adsorption capacity and intensity, respectively.

3. RESULT AND DISCUSSION

3.1 Salinity Effect

In order to investigate the effect of salinity on the adsorption of Cr (VI), the experiments were carried out by addition of sodium chloride to 10 mg Cr(VI)/L solution. The concentration of NaCl used was 0.58 g/100 ml, that is 0.1 M NaCl. Then, 100 ml of Cr (VI) soluti-
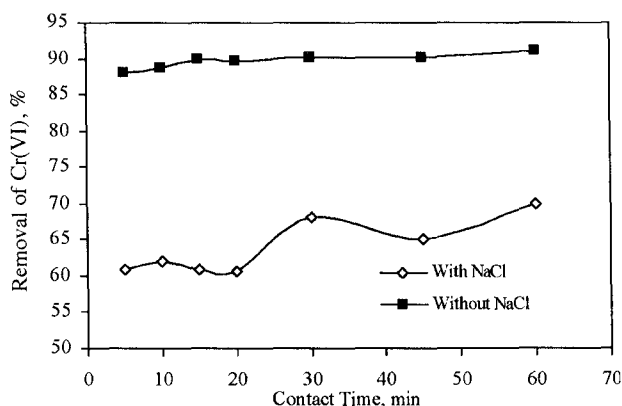

Figure 1. Effect of salinity and contact time on removal of Cr(VI) species using activated alumina as an adsorbent (Conditions: Initial concentration of Cr(VI)=10 mg/l, pH=3.0, adsorbent dose = 5g/100ml).

ons both with and without NaCl solution were shaken by the activated alumina at various contact times.

The results of the removal of Cr (VI) both in the presence and absence of sodium chloride are shown in Figure 1. As can be seen Figure 1, the removal percentage of Cr (VI) reduces in the presence of sodium chloride. At pH 3, Cr(VI) has dominant species, $Cr_2O_7^{-2}$, $HCrO_4^-$. These species are most easily excharged with Cl⁻ (Raji and Anirudhan, 1998). Thus, adsorption capacity of Cr(VI) on alumina are limited. In the presence of sodium chloride, it is shown that Cr(VI) removal has reached nearly 60 % at contact time of 30 minutes. According to the results, the contact time is selected to be 30 minutes for future experiments.

3.2 Effect of pH

Figure 2 shows the removal of Cr(VI) from aqueous solutions without of sodium chloride by both activated and non-activated alumina at pH values between 1 and 5. However, its effect on Cr(VI) removal was also investigated when alumina was activated. At pH 2, Cr(VI) removal by activated and non-activated alumina took place in levels of approximately 68 and 57 %, respectively. The pH value of the solution is an important factor that controls the sorption of (Cr VI). As can be seen in Figure 2, the optimum pH for Cr(VI) removal is about 2. For very acidic pHs, the amount of Cr(VI) removed increases with the increase of pH up to a maximum then decreasing sharply and continuously for pH values higher than 2. Adsorption capacity decreases as pH of solution increases. The maximum removal for Cr(VI) occurs to be 68% at pH 2 by activated alumina. It is shown that an acidic medium is needed for Cr(VI) adsorption.

Cr(VI) removal by activated alumina is governed by adsorption of $HCrO_4^-$ ions which are mainly speci-

es of Cr(VI). Cr (VI) at acidic pHs have different species such as $Cr_2O_7^{-2}$, $HCrO_4^-$, $Cr_3O_{10}^{-2}$, $Cr_4O_{13}^{-2}$ (Weckhuysen et.al.,1996; Raji and Anirudhan,1998). Chromate ion tends to form dichromate ion which is a good oxidizing agent.

$$2CrO_4^{-2} + 2H^+ \Leftrightarrow Cr_2O_7^{-2} + H_2O \qquad (3)$$
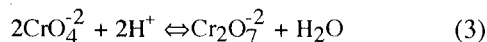
At acidic pH, Cr(VI) ions are either CrO_4^{-2} or $Cr_2O_7^{-2}$ in solutions. At lover pHs, $Cr_3O_{10}^{-2}$, $Cr_4O_{13}^{-2}$ species are formed. That is, decreasing of the pH results in the formation of more polymerized chromium oxide species. Consequently, chromium ions are found in Cr(VI) form due to absence of organic matter in medium.

3.3 Effect of Dosage on the Adsorption Process

The effect of the activated alumina dose on the adsorption of Cr(VI) can be understood from Figure 3 which depicts the variation of the removal of metal ions versus dosage of the activated alumina. The data indicates that the adsorption increases by an increase in the dose. It has been observed in this figure that the removal of chromium (VI) reaches about 97 % at 10 g of adsorbent/100ml. This is because at the higher dose of sorbent due to increased surface area, more adsorption sites are available causing higher removal of Cr(VI).

3.4 Effect of Initial Concentration

The effect of the initial concentrations on Cr (VI) removal is shown in Figure 4. The initial concentrations of metal ions in the samples are within range of 5 to 50 mg/l. pH of samples were kept to be 2.0, adsorbent dosage was taken to be 10 g per 100 ml of sample, and the contact time was selected to be 30 min. All this conditions are optimal at last experiments.
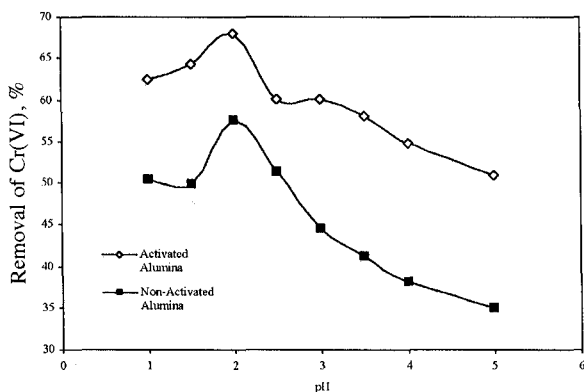

Figure 2. Effect of pH on removal of Cr(VI) species using acti vated and non-activated alumina as an adsorbent (Conditions: Initial concentration of Cr(VI) = 10 mg/l, contact time= 30 min., adsorbent dose = 1g/100ml).
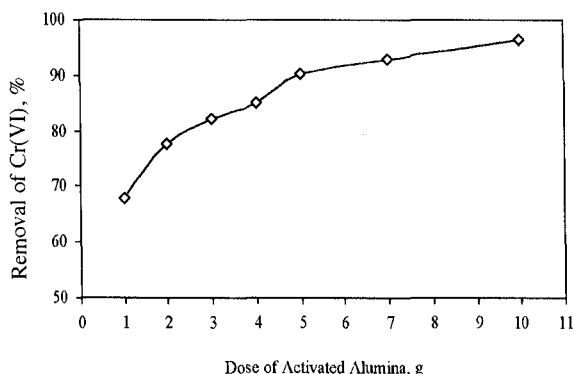

Figure 3. Effect of adsorbent dose on removal of Cr(VI) speci es using activated alumina as an adsorbent (Conditions: Initial concentration of Cr(VI) = 10 mg/l, pH=2, contact time=30 min).
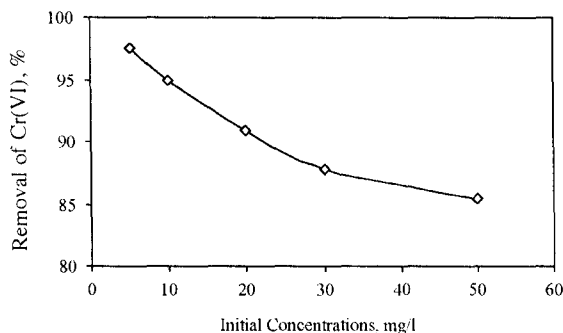
Figure 4. Effect of initial concentrations on removal of Cr(VI) species using activated alumina as an adsorbent (Conditions:pH=2, contact time=30 min, adsorbent dose = 10 g).
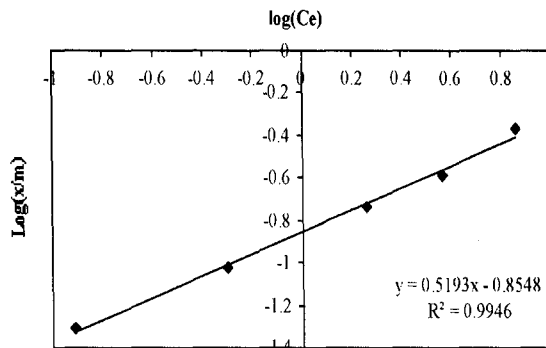

Figure 5. Freundlich plot for the adsorption of Cr(VI) species by activated alumina (conditions: pH=2, contact time=30 min, adsorbent dose=10g/100ml).

It is shown that the adsorption density increased from 0.04878 to 0.427 mg/g for Cr(VI) ions while the removal percentage decreased by increasing the initial concentrations of Cr(VI).

3.5 Adsorption Isotherms of the Activated Alumina

Figure 5 presents the applicability of Freundlich isotherm. The Freundlich type adsorption isotherm is an indication of surface heterogeneity of the adsorbent (Low et.al.,1995). This leads to the conclusion that the surface of alumina is made up of small heterogeneous adsorption. A linear relationship was observed among the plotted parameters which indicates the applicability of the Freundlich aquation. As can be seen the results of Freundlich isotherm, k_f is 0.14, and 1/n is 0.5193. The values of the Freundlich parameters k_f and 1/n for the adsorption of Cr(VI) in different adsorbents in the literature with the adsorbent of the present work are summarized in Table 1. The values of 0.1<1/n<1.0 shows that adsorption of Cr(VI) on the anion exchanger is favorable (Mckay et al., 1982). However, it has been reported that the magnitude of 1/n is 0.5 for intraparticle diffusion to be the rate limiting step (Morris and Weber, 1963). 1/n value for Cr(VI) uptake on activated alu-

mina, 0.5193, indicated that the intraparticle diffusion is the rate limiting step. It may be observed from Table 1 that the uptake of Cr(VI) on activated alumina is lower than other adsorbents. If Table is investigated, it is shown that the value of k_f is lower in activated alumina than in other adsorbents. This means that the amount of activated alumina is greater than other for an effective removal.

4. CONCLUSION

The removal of Cr(VI) by alumina from on aqueous solution has been investigated at various conditions of medium, such as pH of solutions, contact time of aqueous solution including Cr(VI) ions with adsorbent, dosage of alumina in the presence and absence of sodium chloride, and activation process. The study reveals that the pH of solution, the adsorbent dose and the presence of sodium chloride strongly influence the adsorption process.

The investigations are quite useful in developing an appropriate technology for designing a wastewater treatment plant. Although the removal of Cr(VI) was high level, process is not economically feasible and easy to carry out since the adsorbent dose to be used is too high.

Table 1. Freundlich parameters for the adsorption of Cr(VI) in different adsorbent.

Freundlich Parameters			
Adsorbent	k_f **(mg/g)**	**1 / n**	**References**
Activated groundnut carbon	5.61	0.21	Periasamy et.al. (1991)
Activated coconut shell carbon	2.2	0.14	Alaerts et.al.,(1989)
Activated bagasse carbon	0.19	0.981	Chand et.al. (1994)
Activated coconut jute carbon	1.55	0.368	Chand et.al. (1994)
Activated carbon	13.2	- - -	Srinivasan et.al. (1988)
Granular activated carbon	5.09	0.566	Ramos et al. (1994)
Amberlite IRA-900 (Cl⁻ form)	149.9	0.319	Beas et al. (1997)
Amine modified coconut coir (Cl⁻ form)	16.6	0.089	Beas et al. (1997)
Sawdust (PGSD-AE)	12.4	0.503	Raji and Anirudhan (1998)
Activated alumina	0.14	0.519	Present work

In conclusion the activated alumina in practice could not be used as a potential sorbent for removal of Cr (VI) ions from wastewater. But the column experiments must also be made to understand the treatment mechanism.

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