Asian Journal of Chemistry Vol. 18, No. 1 (2006), 145–154

Removal of Chromium(III) by the Adsorbents Produced from Coal Mining Wastes

MEHMET MAHRAMANLIOGLU*, KUBILAY GÜCLÜ and TOLGA MISIRLI
Chemistry Department, Faculty of Engineering, Istanbul University
Avcilar 34320 Istanbul, Turkey
Fax: (90)(212)5911997; E-mail: mehmah@istanbul.edu.tr

The adsorption study of Cr(III) on the adsorbent produced from coal mining waste was carried out as a function of time, initial concentration and pH. The Lagergren equation was used to calculate the adsorption rate constant. The equlibrium data showed that the adsorption of Cr(III) obeyed the Langmuir and Freundlich isotherm equations. Based on the Langmuir isotherm constant it was shown that the adsorbent produced from coal mining waste was more effective compared to most of the other adsorbents. The maximum adsorption for Cr(III) was observed at pH 5.2. Column studies were also performed to simulate the industrial conditions and column capacities for each flow rate were determined.

Key Words: Adsorption, Chromium(III), Chromium(VI), Activated carbon, Coal mining waste.

INTRODUCTION

The mining industry has employed processes and produced products at lower costs and reduced energy consumption due to the development of new technologies and improvements to existing technologies. At the same time, this industry must minimize the adverse environmental, health and safety effects associated with mining products since a great quantity of solid waste remains and contaminates the environment after the mining process.

Environmental policies put pressures on production, processing and product costs in mining industry. Therefore, environmental costs are significant and the future success of the mining industry depends on its relationship with the environment.

Coal mining waste is a mixed alumina-silicate/carbon material. A great quantity of mining waste remains after coal mining processes and contaminates the environment. It contains a considerable amount of carbon material that can be activated. Therefore, coal mining waste can be considered as a starting material to produce a new adsorbent.

Our laboratory has used a program to develop cheap and new adsorbents from cheap raw materials such as used tyres, spent bleaching earth, contaminated soil[1–5] and the adsorbents produced from coal mining wastes were studied extensively.

These studies showed that the adsorbents produced from coal mining wastes had a high capacity for chromium(VI), MCPA and some organic and inorganic pollutants[6, 7].

Activation of coal mining wastes was also the subject of investigation by some researchers in the past. Hu and Vansant[8] used $ZnCl_2$ to produce activated carbon from coal mining waste and reported that the adsorbent produced from coal mining waste exhibited high affinities towards organic compounds. Deng *et al.*[9] used K_2CO_3 to produce activated carbon from coal mining waste and reported that the adsorbents were produced from coal mining wastes.

The nature and behaviour of various Cr forms found in wastewater can be quite altered physicochemical conditions of the effluents originating from various industrial sources. Cr(VI) dominates in wastewater from the metallurgical industry, metal finishing industry, refractory industry and production or application of pigments. Cr(III) is found mainly in tannery, textile and decorative plating industry wastewater[10,11].

The oldest and most frequently used method for removal of Cr(III) from wastewater is the precipitation[12]. This process has some disadvantages as it produces a large amount of sludge[13].

Therefore, in recent years, various studies have been published for the removal process of Cr(III) and a number of materials have been investigated for the adsorption capacity for chromium(III). These materials include bentonite[12], perlite[12], activated carbon[13, 14], inorganic-organic silicon hybrid surface[15], biogas slurry[16], chelating ion-exchanger resin[17] and anion exchanger[18].

In this context, the aim of this study was (1) to develop a new adsorbent from coal mining waste, (2) to study the capacity of the new adsorbent for the removal of Cr(III) and (3) to reduce the amount of coal mining waste.

EXPERIMENTAL

All chemicals used in the study were of analytical grade. A stock solution of 250 mg/L Cr(III) was prepared from $Cr(NO)_3 \cdot 9H_2O$. All solutions were prepared with double distilled water.

Coal mining waste was obtained from a coal mine in Marmara Region. Coal mining waste was crushed and sieved to a particle size < 1 mm. The material used in this study contains; C: 30.2%, SiO_2: 37.1%, Al_2O_3: 17.2% and other oxides (Ca, Mg, Fe, Mn, Cr): 15.5%.

Absorbents were prepared according to a procedure described in the study of Mahamanlioglu[5, 7] and Hu and Vansant[8]. 20 g of sample was blended with 1% $ZnCl_2$ solution and this mixture was preheated at 300°C in flowing N_2 for 4 h. After pretreatment process samples were cooled to room temperature and washed with hot and cold water to remove chloride ions. The material obtained was dried at 110°C for 6 h and stored for activation process.

Activation process

10 g of the pretreated sample was mixed with 5 g of $ZnCl_2$ and pyrolyzed at 700, 800 and 900°C for 1 h. The adsorbents produced at different temperatures will be referred to hereafter as A(700), A(800) and A(900) in the text. After the

activation process, the samples were cooled to room temperature and washed with hot and cold water. The adsorbent obtained was dried at 110°C for 6 h and sieved again to a particle size < 1 mm and then stored for adsorption experiments. It is seen from Table-1 that the surface area decreases with increasing the temperature and increases again with the increasing temperature. This result agrees with the results obtained by Hu and Vansant[8] for the preparation of adsorbent from elutrilithe. Carbon contents of the adsorbent produced from coal mining waste also decrease with higher temperature. The effect of temperature on the carbon content is similiar to that reported for the similar material. Hu and Vansant[8] also reported that the adsorbents produced from coal mining waste at higher temperatures were found to possess a greater micropore volume and smaller total pore volume when higher activation temperatures were employed. These results also agree with the results obtained in this study (Table-1). This result can be explained by the fact that a higher degree of carbon burning occurs at higher temperatures than the boiling point of $ZnCl_2$ (732°C). At higher temperatures, carbon burn off leading to the formation of some new pores, and to the partial removal of meso and macropores and, therefore, the surface area increases. But the activation process at temperatures lower than 732°C results in a low degree of carbon lost, and a porous adsorbent with micropores as well as mesopores was produced. The activation process at temperatures greater than 732°C results in higher degree of carbon lost and a highly microporous with a few mesopores adsorbent is produced. It is seen from Table-1 that A(900) has the greatest surface area. These findings show that carbon burn-off results in the creation of new pores[8].

TABLE-1

THE SURFACE AREA, CARBON CONTENT AND PORE VOLUME OF COAL MINING WASTE AND THE ADSORBENTS PRODUCED FROM COAL MINING WASTE

Sample	Surface area (m^2/g)	Carbon content (%)	Pore volume (cm^3/g)	
			V_t	V_m
Fresh coal mining waste	10.4	30.2	0.0311	—
A(700)	122.4	19.1	0.1115	0.0480
A(800)	119.4	17.8	0.0960	0.0512
A(900)	161.9	16.2	0.0878	0.0752

Outgassing of the adsorbent

Surface area of the adsorbent was measured by nitrogen adsorption experiments. Prior to surface area and batch experiments all the products were outgassed at 300°C for 3 h. Surface areas, pore volumes and carbon contents of coal mining waste and the adsorbents produced from coal mining waste are given in Table-1.

Adsorption process

Batch studies: Experiments were carried out by taking the known amount of adsorbent with 100 mL of aqueous solutions of chromium(III) of a desired concentration in glass bottles and shaking for pre-determined time intervals using a thermostated shaker. The adsorbent and adsorbate were separated by centrifugation at 6000 rpm for 10 min. The concentration of supernatant was measured by atomic absorption spectrophotometry. All the equilibrium and kinetic studies and column studies were carried out only at pH = 5.2 except pH studies since this value was obtained as the optimum pH for the adsorption of chromium(III).

Column studies: The adsorption column was made of glass tube. 2 g of adsorbent was fixed in the column and the column was fully filled with distilled water for 12 h to wet the column to expel all the air existing among adsorbent particles. After flushing with distilled water, the solution was pumped vertically downward inside the column at constant flow rate.

Chromium(III) solutions of concentrations 20 mg/L (pH = 5.2) were passed through the column at different flow rates (0.1, 0.12, 0.14, 0.16 L/h). When C/C_0 ratio reached a constant value, the experiments were considered to be finished. Concentrations in the column outlet were measured with the method mentioned above.

RESULTS AND DISCUSSION

Effects of Contact Time on the Variation of Concentration of Cr(III)

The concentration data obtained from the contact time experiments using different initial concentrations were plotted against time in order to determine the equlibrium time (Fig. 1).

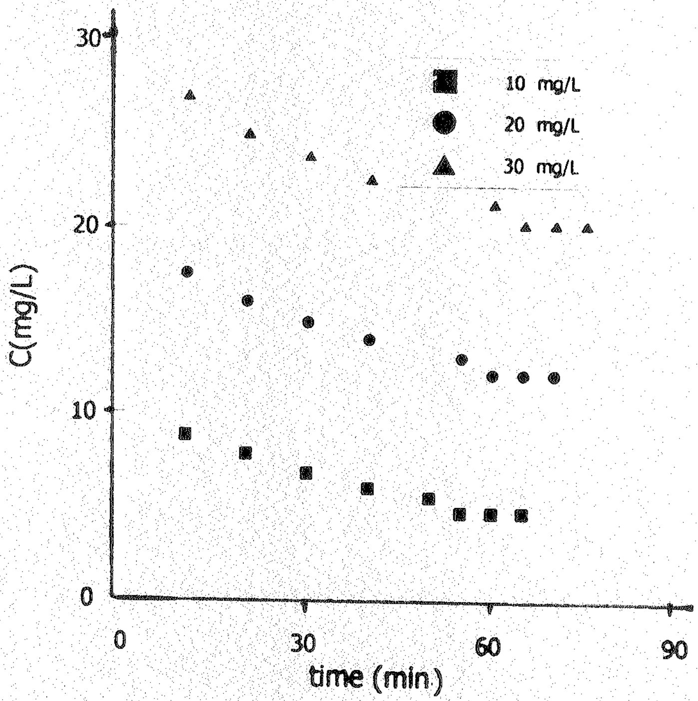

Fig. 1. The variation of concentration of Cr(III) with time

The results show that the equilibrium times for the initial concentrations 10, 20, 30 mg/L was found to be 55, 60 and 65 min, respectively. It is seen from Fig. 1 that the equilibrium time depends on the initial concentration.

The adsorption rate equation

The adsorption of chromium(III) on the adsorption produced from mining waste was found to follow the first order adsorption rate expression of Lagergren given by

$$\ln (q_e - q) = \ln q_e - K \cdot t$$

where q_e and q are the amounts of chromium(III) adsorbed at equilibrium at any time, t, respectively and K is the rate constant of adsorption. The values of K were determined by least square method and found to be 0.038, 0.036 and 0.033 L/min for the concentrations of 10, 20 and 30 mg/L, respectively.

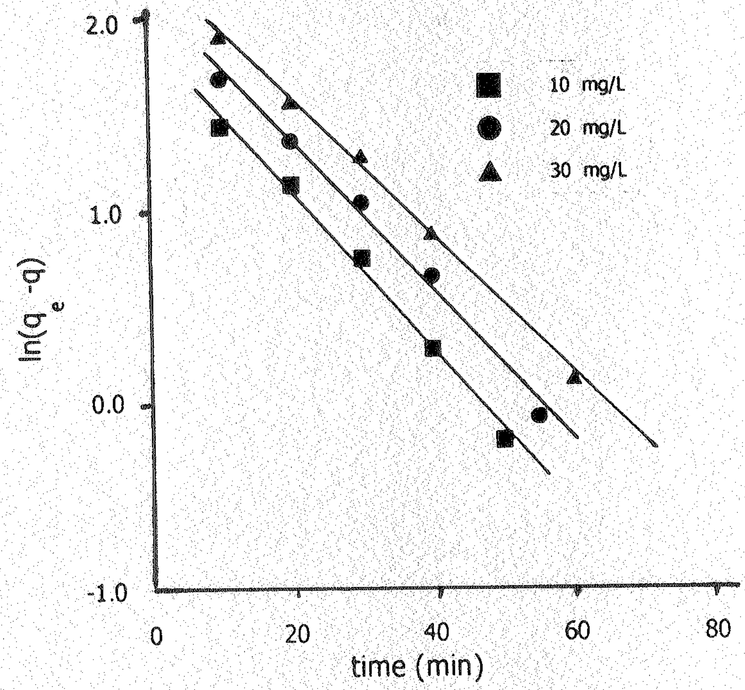

Fig. 2. Lagergren plots for the adsorption of Cr(III)

Effect of pH on the adsorption of Cr(III)

The pH of the aqueous solution is an important variable that controls the adsorption of the solute at the adsorbent-water interface. Therefore, the effect of pH on the adsorption of Cr(III) was examined for the initial concentration of 20 mg/L in the pH range 2.3 and 5.2. A maximum adsorption was attained at pH 5.2. It is seen from Fig. 3 that the adsorption increases with increasing pH. This result can be attributed to the sorbent charge and speciations of Cr(III). Similar results for the sorption of Cr(III) on montmorillonite, activated carbon, Al_2O_3, bentonite and expanded perlite have been reported[12].

Chromium(III) in aqueous solution forms the following complexes[13]:

$Cr(OH)_3 + 3H^+ = Cr^{3+} + 3H_2O$ $pK_1 = 11.83$

$Cr^{3+} + H_2O = Cr(OH)^{2+} + H^+$ $pK_2 = 3.85$

$Cr^{3+} + 2H_2O = Cr(OH)^{2+} + 2H^+$ $pK_3 = 10.06$

$Cr^{3+} + 3H_2O = Cr(OH)^{3+} + 3H^+$ $pK_4 = 18.70$

$Cr^{3+} + 4H_2O = Cr(OH)^{4-} + 4H^+$ $pK_5 = 27.87$

$3Cr^{3+} + 4H_2O = Cr_3(OH)_4^{5+} + 4H^+$ $pK_6 = 8.40$

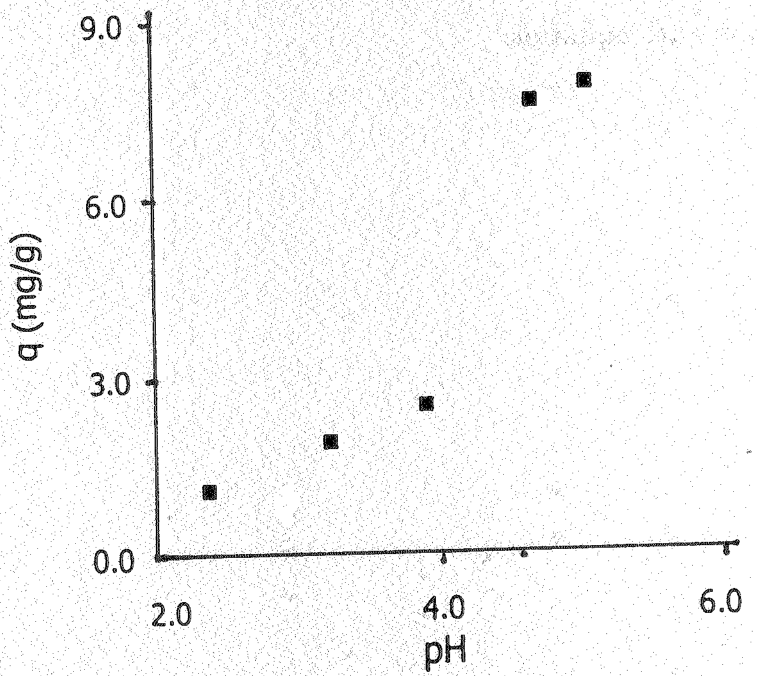

Fig. 3. Effect of pH on adsorption of Cr(III)

According to the values of pK, the predominant species below pH 2 is Cr^{3+}. At pH 4, the Cr^{3+} and $Cr(OH)^{2+}$ species are present in an approximate distribution of 40 and 60% respectively. At pH 5, the $Cr(OH)^{2+}$ species dominates accounting for around 70%[12]. The distribution of species clearly indicates that between pH values of 2 and 4, the complex $Cr(OH)^{2+}$ is selectively adsorbed on the adsorbent, but between pH values of 4 and 6, Cr(III) is adsorbed principally as $Cr(OH)^{2+}$, although $Cr(OH)_4^{5+}$ complex is also adsorbed.[13]

Adsorption isotherms

The capacity of any adsorbent for the removal of substances is generally represented by the Langmuir and Freundlich isotherms. Therefore, the data obtained from equilibrium studies were used to calculate the value of the Langmuir and Freundlich isotherm constant.

Langmuir isotherm: The linearized Langmuir isotherm is

$$C/q = 1/Q_0 \cdot b + C/Q_0$$

where C is the equilibrium concentration, q is the amount of solute adsorbent at equilibrium and Q_0 and b are the Langmuir constants. Q_0 and b were calculated from the least square method applied to the linear relation between C/q and C shown in Fig. 4 and found to be 15.11 and 1.15 L/mg, respectively.

Although the capacity of the adsorbent produced in this study is less than some adsorbents, the capacity for Cr(III) is not low (14.95 mg/g) and the adsorbent produced from coal mining waste has a high capacity for the removal of Cr(VI) and some organic substances mentioned above and reprocessing the coal mining waste reduces the environmental pollution around the coal mines[6–9].

Freundlich isotherm: It is an empirical isotherm and has the following form:

$$q = k \cdot C^n$$

where q is the amount of solute adsorbed, C is the equilibrium concentration, k and n are the Freundlich constants.

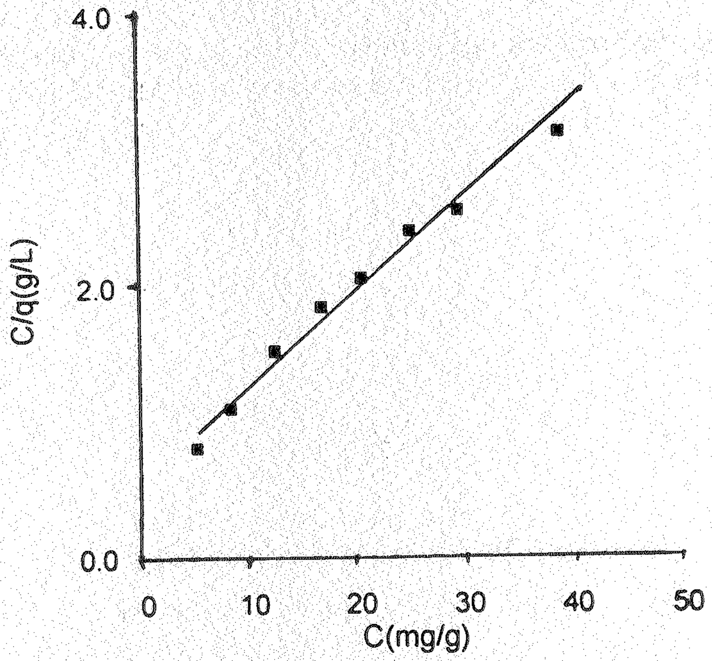

Fig. 4. Langmuir plot for the adsorption of Cr(III)

A linear form of the Freundlich expression can be written as

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

Fig. 5 depicts the results obtained by plotting ln q *vs.* ln C for the adsorption of chromium(III). k and n parameters were calculated from the least square method applied to the straight line in Fig. 5 and found to be 3.19 and 0.36, respectively.

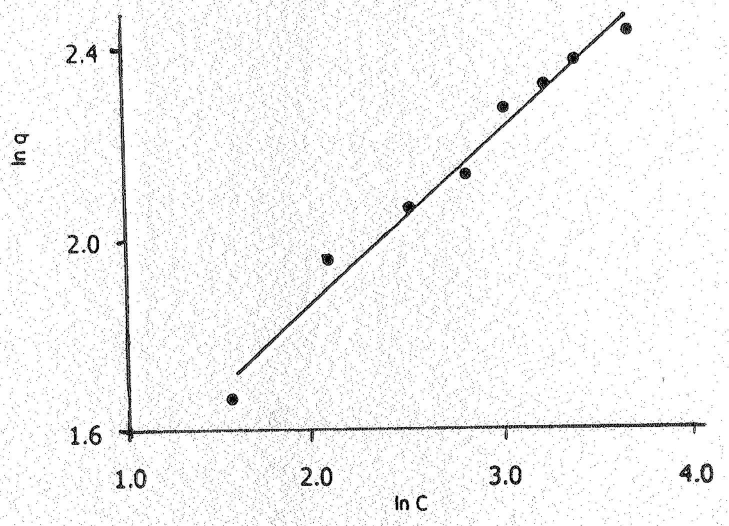

Fig. 5. Freundlich plot for the adsorption of Cr(III)

Column studies

Adsorption isotherms are used for preliminary investigations and obtaining operational parameters before running more costly column tests, but in practice treatment plants use column-type[19]. Therefore, it is necessary to carry out flow tests using columns.

Fig. 6 shows the breakthrough curves obtained from the fixed bed experiments for Cr(III) solutions at four different feed concentrations (0.10, 0.12, 0.14, 0.16 L/h) and at the constant concentration (20m/L). The results obtained from breakthrough curves in Fig. 6 are given in Table-2.

TABLE-2
PARAMETERS CALCULATED FOR DIFFERENT FLOW RATES IN COLUMN STUDIES

	Flow rates (L/h)			
	0.16	0.14	0.12	0.10
V_i (L)	0.60	0.80	1.00	1.40
X_i (mg/g)	6	8	10	14
V_f (L)	3	3.40	3.60	4.00
X_f (mg/g)	15.20	18.60	20.10	24.40
t (h)	18.75	24.29	30.00	40.00
C/C_0	1	1	1	1
Q (mg/g)	30	34	36	40
R	50.50	54.80	55.80	61.00

V_i = volume of effluent at the breakthrough point of the column (L), X_i = amount of Cr(III) adsorbed per g of adsorbent at the breakthrough point (mg/g), V_f = volume of effluent at the close point of the column (when C/C_0 reaches a plateau), t = experiment period (h), Q is the amount of Cr(III) passed through the column until the close point (mg/g) adsorbed per g of adsorbent at the close point, R = removal efficiency of the column (120).

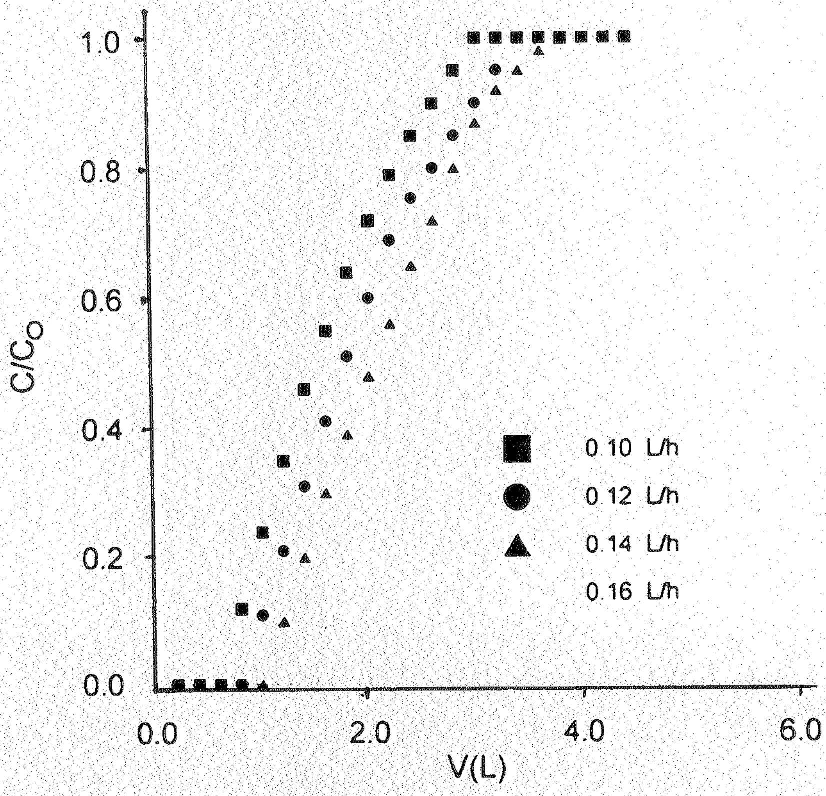

Fig. 6. Breakthrough curves for Cr(III) on the adsorbent produced from coal mining waste

If one compares the results obtained from the fixed bed experiments with those obtained from the batch experiments, it is seen that the amount of Cr(III) adsorbed per g of adsorbent for each flow rate is greater for the fixed bed than for the batch experiments. Several researchers[19–23] have reported the same dissimilarities between the adsorption capacity found by batch and column studies. This result was also expected in the present work due to different conditions such as the different durations of experiments and different adsorbent/solution ratios used in the batch and column studies. Other factors can be explained by the fact that the solution phase concentration is continuously decreasing in the batch system while that concentration is continuously increasing in the column system.

Comparison of the breakthrough curves obtained at four flow rates showed a consistent trend wherein the breakthrough curves for the faster flow rates were shifted leftward of the slow flow rate. The parameters obtained in this part are given in Table-2. When the flow rate increases, the residence time in the column decreases which results in lower bed utilization. Therefore, as can be seen in Table-2, the breakthrough time and the bed capacity decrease with increasing flow rate of Cr(III). Similar findings have been obtained by Ko *et al.*[24]

Conclusion

Adsorbents were produced from coal mining waste and adsorption capacity for Cr(III) was calculated. The contact time results were described with Lagergren equation. The values of Langmuir and Freundlich isotherm constants were calculated. The capacity value obtained from the Langmuir isotherm was found to be higher than some adsorbents. The maximum removal was obtained at pH = 5.2. The column studies showed that the column capacity was higher than batch capacity and this capacity decreased with increasing flow rate. The use of activated coal mining waste as an adsorbent after suitable treatment process can be an option for minimizing solid waste in mining industry. Therefore, it should be borne in mind that a low-cost feedstock can be used in the case of coal mining waste and that reprocessing of coal mining waste into valuable products is associated with appreciable environmental benefits.

ACKNOWLEDGEMENT

This study was supported by Research Fund of Istanbul University, Istanbul, Turkey, Project No. BYP-156/15012003.

REFERENCES

1. M. Mahramanlioglu, *J. Radioanal. Nucl. Chem.*, **256**, 99 (2003).
2. M. Mahramanlioglu, I. Kizilcikli, I.O. Biçer, and M. Tuncay, *J. Environ. Sci. Hlth.*, **B38**, 813 (2003).
3. ———, *J. Environ. Sci. Hlth.*, **B35**, 187 (2000).
4. I. Kizilcikli and M. Mahramanlioglu, *Fresenius Environ. Bull.*, **11**, 1098 (2002).
5. M. Mahramanlioglu, I. Kizilcikli and I.O. Biçer, *J. Flourine Chem.*, **115**, 41 (2002).
6. M. Mahramanlioglu and K. Güçlü, *Energy Sources*, **25**, 1 (2003).
7. ———, *Fresenius Environ. Bull.*, **12**, 1492 (2003).
8. Z. Hu and E.F. Vansant, *J. Colloid Interface Sci.*, **176**, 422 (1995).

9. X. Deng, Y. Yinghong and Z. Gao, *J. Colloid Interface Sci.*, **192**, 475 (1997).
10. J.O. Nriaguds, Chromium in Natural and Human Environments, Wiley-Interscience, New York, pp. 21–81 (1988).
11. J. Kotas and Z. Stasicka, *Environ. Pollut.*, **107**, 263 (2000).
12. A. Charkir, J. Bessiere, K.E. Kacemi and B. Marouf, *J. Hazard. Mater.*, **B95**, 29 (2002).
13. R. Leyva-Ramos, L. Fuentes-Rubio, R.M. Guerrero-Coronado and J. Mendoza-Barron, *J. Chem. Tech. Biotechnol.*, **62**, 64 (1995).
14. P. Millich, F. Möller, J. Piriz, G. Vivo and N. Tancredi, *Sep. Sci. Tech.*, **37**, 1453 (2002).
15. F.R. Farias, A.G. Souza, L.M. Numes and V.A. Cardoso, *Colloids and Surfaces*, **211**, 295 (2002).
16. C. Namasivayam and R.T. Yamuna, *Water Air Soil Pollut.*, **113**, 371 (1999).
17. F. Gode and E. Pehlivan, *J. Hazard. Mater.*, **B100**, 231 (2003).
18. E. Korngold, N. Belayev and L. Aronov, *Sep. Purif. Tech.*, **33**, 179 (2003).
19. S.M. Lee and A.P. Davis, *Water Res.*, **35**, 534 (2001).
20. E. Gonzales-Pradas, M. Villafranca-Sanchez, A. Gallego-Campo, D. Uren-Amate and M. Socias-Viciana, *J. Chem. Technol. Biotechnol.*, **69**, 173 (1997).
21. J.W. Weber (Jr.), P.M. McGinley and L.E. Katz, *Water Res.*, **25**, 499 (1991).
22. W.T. Tan, S.T. Oui and C.K. Lee, *Environ. Technol.*, **14**, 277 (1993).
23. M.T. Yoshikawa and T. Kataoka, *AIChE J.*, **40**, 2034 (1994).
24. D.C.K. Ko, J.F. Porter and G. McKay, *Water Res.*, **35**, 3876 (2001).

(*Received*: 30 November 2004; *Accepted*: 5 September 2005) AJC-4376