Adsorption of Chromium Ions from Aqueous Solution by Carbon Adsorbent

S. Heydari, H. Sharififard, M. Nabavinia, H. Kiani, M. Parvizi

Abstract—Rapid industrialization has led to increased disposal of heavy metals into the environment. Activated carbon adsorption has proven to be an effective process for the removal of trace metal contaminants from aqueous media. This paper was investigated chromium adsorption efficiency by commercial activated carbon. The sorption studied as a function of activated carbon particle size, dose of activated carbon and initial pH of solution. Adsorption tests for the effects of these factors were designed with Taguchi approach. According to the Taguchi parameter design methodology, L9 orthogonal array was used. Analysis of experimental results showed that, the most influential factor was initial pH of solution. The optimum conditions for chromium adsorption by activated carbons were found to be as follows: initial feed pH 6, adsorbent particle size 0.412 mm and activated carbon dose 6 g/l. Under these conditions, nearly %100 of chromium ions was adsorbed by activated carbon after 2 hours.

Keywords—Chromium, Adsorption, Taguchi method, Activated carbon.

I. INTRODUCTION

CHROMIUM compounds are among the most dangerous inorganic water pollutants. Chromium is considered to be one of the priority pollutants, chromium is soluble in water and hence mobile and it possesses a great threat to surface and groundwater quality, which is a threat to human health. The rapid development and proliferation of process industries have made wastewater treatment a major concern in industrial areas. The presence of metal ions in natural (mainly by volcanic activity and weathering of rocks) or industrial wastewater and their potential impact has been a subject of research in environmental science for a long time. Chromium compounds mainly occur in the environment as trivalent, Cr(III), and hexavalent, chromium (VI), chromium. Trivalent chromium is an essential element in humans and is less toxic than the hexavalent one, which is recognized as a carcinogenic and mutagenic agent. The wastewater from the dyes, pigments, metal cleaning, plating, leather and mining industries contain undesirable amount of chromium ions and therefore priority is given to regulate these pollutants at the discharge level. The maximum contaminant level goal of chromium for the drinking water is 0.05 mg/l as per the World Health Organization (WHO) set standard [1]. Adsorption is a versatile treatment technique practiced widely in fine chemical and process industries for wastewater and waste gas treatment.

The usefulness of the adsorption process lies in the operational simplicity and reuse potential of adsorbents during long-term applications. Activated carbon adsorption has proved to be the least expensive treatment option, particularly in treating low concentrations of wastewater streams and in meeting stringent treatment levels. Activated carbon is a black solid substance resembling granular or powder charcoal and are carbonaceous material that have highly developed porosity, internal surface area and relatively high mechanical strength [2], [3]. There are many studies in the literatures relating to the application of activated carbon for the adsorption of gasses [4], heavy metals [5]-[7].

The aim of this study was to investigate the efficiency of commercial activated carbon as adsorbent for the removal of chromium from aqueous solutions.

II. MATERIAL AND PROCEDURE

A. Materials

In this study, commercial activated carbon that used in oil refinery was applied as adsorbent. The specific surface area of this carbon was about $922 m^2/g$. Adsorption of chromium ions with activated carbon (AC) was carried out by batch method and the influence of operating parameters such as initial pH of solution, particle size, and dose of adsorbent were studied. Stock solutions of the tests were prepared by dissolving Chromium nitrate in distilled water. Working solutions were prepared by diluting a different volume of stock solution to achieve the desired concentration. Initial pH of solution was adjusted by HCl and NaOH solution with pH meter (Metrohm780). All of the materials have been used in laboratory grade from Merck Company.

B. Design of Experiments

Chromium adsorption tests were designed by Taguchi method and effectiveness of operating parameters as well as optimum operating condition was determined. These removal parameters and their levels are showed in Table I.

TABLE I
CHROMIUM REMOVAL PARAMETERS AND THEIR LEVELS

Removal parameter	Unit	Level 1	Level 2	Level 3
pH solution		1	3	6
Adsorbent particle size	mm	0.21	0.425	1
Adsorbent dose	g/l	2	4	6

In this study, there are 6 degrees of freedom related to the three sets of three-level separation parameters. In accordance with Taguchi method, the standard orthogonal array L9, with

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World Academy of Science, Engineering and Technology
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Vol:7, No:12, 2013

three columns and nine rows could be used for these experiments [8]. The experimental layout for these parameters using the L9 orthogonal array is listed in Table II.

Batch mode adsorption studies were carried out with known amount of adsorbent with known particle size and 50ml of metal solution (initial concentration 50mg/l) at desired pH in 100ml conical flasks and these flasks were agitated at 250rpm for 2h at room temperature in mechanical shaker. After this time adsorbents was separated with whatman filter paper and residual chromium concentration was determined by inductively coupled plasma (ICP) analyzer (Varian 735ES). The amount of chromium adsorbend by activated carbon was calculated from the difference of chromium concentration in the initial and final solutions.

TABLE II
ARRANGEMENT OF PARAMETERS IN L9 ORTHOGONAL ARRAY

Experiment number	Separation parameter Level		
	pH	Adsorbent particle size	Adsorbent dose
1	1	1	1
2	1	2	2
3	1	3	3
4	2	1	2
5	2	2	3
6	2	3	1
7	3	1	3
8	3	2	1
9	3	3	2

C. Equilibrium Studies

Adsorption equilibrium study was conducted using 0.20g of AC in 50ml chromium solution with a contact time of 24 h at ambient temperature. The initial pH and the concentration of chromium solution were 6 and 10 to 50 mg/l. Subsequently, adsorbents were separated with Whatman filter paper and the solution concentration was analyzed by ICP .The amount of chromium removed by AC, q was determined by (1):

$$q = \frac{V}{m}\left(C_0 - C_e\right) \qquad (1)$$

where C_0 and C_e are initial and final concentration (mg/l) of metal ions in solution, respectively, V is the solution volume (l) and m is the weight of adsorbent (g).

D. Adsorption Equilibrium Isotherms

The adsorption isotherm of chromium onto the AC analyzed in terms of Langmuir and Freundlich isotherm models. The linear Langmuir equation may be written as:

$$\frac{1}{q_e} = \left(\frac{1}{q_{max}L}\right) \cdot \frac{1}{C_e} + \frac{1}{q_{max}} \qquad (2)$$

where q_{max} (mg/g) is maximum adsorption capacity of adsorbent and L (dm3/mg) is the Langmuir constant related to energy of adsorption. L and q_{max} can be calculated from the

intercept and slope of the linear plot of 1/qe versus 1/ Ce.

Linear form of Freundlich model is:

$$\log q_e = \frac{1}{n}\log C_e + \log K_f \qquad (3)$$

where Kf (mg1-(1/n)L1/n/g) is the Freundlich constant related to adsorption capacity of adsorbent and n is the Freundlich exponent related to adsorption intensity. These parameters determine by plotting lnqe versus lnCe.

III. RESULTS AND DISCUSSION

A. Influence of Operating Parameters

In this work, the effect of activated carbon particle size, dose of activated carbon and initial pH of solution on efficiency of adsorption process was investigated. The percent of adsorbed chromium was selected, as responses of the system for analyze by Taguchi method and optimal operating conditions was determined based on this parameter. The results of these experiments are shown in Figs. 1-3. According to Fig. 1, maximum adsorption of chromium takes place in initial pH 6. At pH < 6.9 surface charge of activated carbon is net positive and these can uptake anions of chromium by electrostatic attraction mechanism. In low pH, strong competition adsorption between chloride anions and chromium species restricted metal adsorption. But at higher pH, chloride concentration decreased and this competition effect decreased and metal ions adsorption increased. The optimum operating condition for adsorption of chromium was pH=6, particle size of activated carbon =0.425mm and activated carbon dose = 6gr/l .Under these condition nearly 100% of chromium was adsorbed by activated carbon after only 2hr.

Taguchi-oriented practitioners often use the analysis of variance (ANOVA) to verify the factors that influence the performance characteristic mean response. In ANOVA table, the percentage contribution of each parameter in the total sum of the squared deviations can be used to evaluate the importance of the parameter change on the performance characteristic. In addition, the F- ratio can also be used to determine which parameters have a significant effect on the performance characteristic. The calculated values are then compared with F values predicted by statistical F distribution (in Fischer tables) [9]. ANOVA results for chromium adsorption are shown in Table III. From the Fisher tables with 95% confidence, and F0.05,2,2 = 19. According to these values, the F-value for initial pH is greater than the corresponding values of Fisher tables for 95% confidence and, so the tests are reliable with 95% confidences, and this parameter has great effects on the characteristic of the adsorption process. The contribution of the error is 2.775%, which is in reasonable range of errors. This table indicated that the adsorbent particle size and adsorbent dose did not have an effect on metal adsorption process.

World Academy of Science, Engineering and Technology
International Journal of Environmental and Ecological Engineering
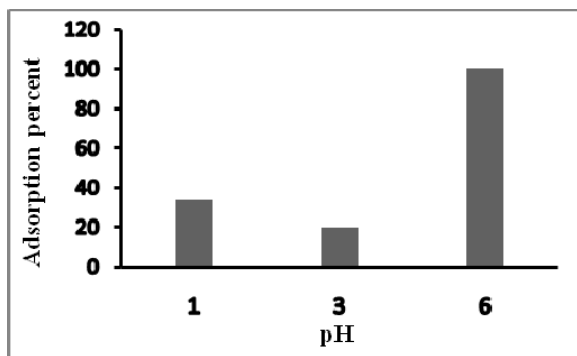Vol:7, No:12, 2013

Fig. 1 Influence of initial pH on chromium adsorption by activated carbon
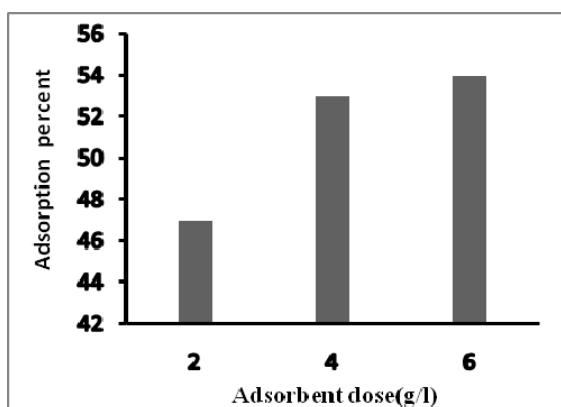

Fig. 2 Influence of adsorbent dose on chromium adsorption by activated carbon
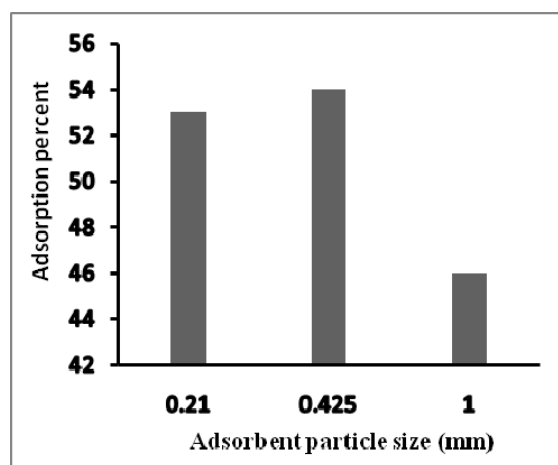

Fig. 3 Influence of adsorbent particle size on chromium adsorption by activated carbon

TABLE III
RESULTS OF THE ANALYSIS OF THE VARIANCE (ANOVA TABLE) FOR CHROMIUM ADSORPTION

Removal parameter	DOF	Sum of Sqrs (S)	Var (V)	F-ratio (F)	Contribution percentage
Initial pH	2	10931	5465.8	136.4	97.1
Activated carbon particle size	2	91.1	45.551	0.868	0.098
Activated carbon dose	2	69.6	34.8	0	0
Other/error	2	80.11	46.06		2.775

B. Influence of Operating Parameters

Various isotherm equations like those of Freundlich and Langmuir have been used to describe the mono-component equilibrium characteristics of adsorption of chromium ions onto activated carbon. Figs. 4, 5 indicated these isotherms. The parameters of each isotherm were listed in Table IV along with the linear regression coefficients, R^2. Results showed that Langmiur isotherm best fitted with the equilibrium data of chromium adsorption on activated carbon. Maximum capacity of activated carbon for adsorbing chromium ions has been reported in Table IV by using (2). Table V shows the comparison of the maximum adsorption capacity of activated carbon for chromium adsorption with other adsorbents [10]-[12]. It is clear that maximum adsorption capacity of activated carbon is higher than several others adsorbents and is good adsorbent for chromium removal from aqueous solutions.
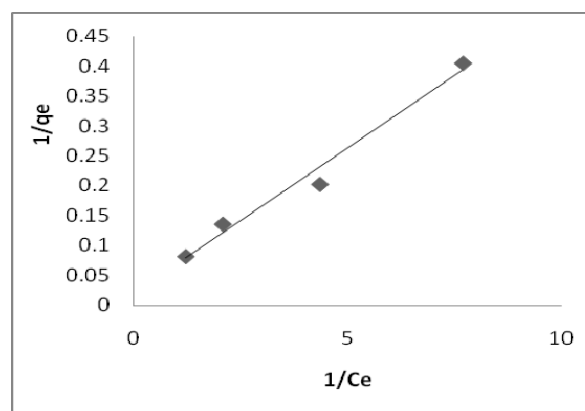

Fig. 4 Linear form of Langmuir isotherm for chromium removal by activated carbon
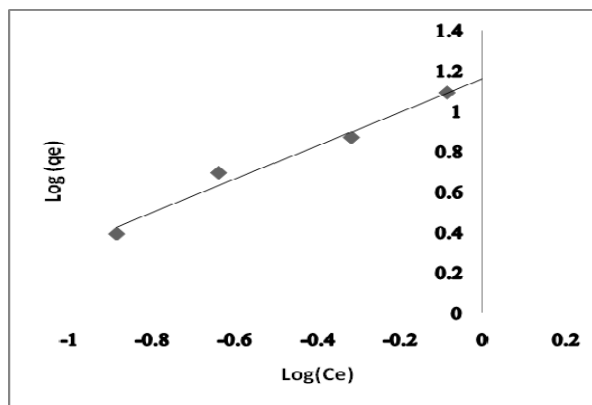
World Academy of Science, Engineering and Technology
International Journal of Environmental and Ecological Engineering
Vol:7, No:12, 2013

Fig. 5 Linear form of Fruendlich isotherm for chromium removal by activated carbon

TABLE IV
CONSTANTS PARAMETERS AND REGRESSION COEFFICIENT FOR LANGMUIR, FREUNDLICH ISOTHERM

Isotherm	Parameters	Activated carbon-Cr
Langmuir	q_{max}	52.6
	L	0.395
	R^2	0.99
Freundlich	K_f	14.45
	n	1.2
	R^2	0.971

TABLE V
ADSORPTION CAPACITY OF DIFFERENT ADSORBENT FOR CHROMIUM ADSORPTION

Adsorbent	Adsorption capacity (mg/g)	Ref
Sugar beet pulp	17.2	[10]
Bentonite clay	49.75	[11]
Coconut shell based activated carbon	20	[12]
Activated charcoal	12.87	[13]
Activated carbon	52.6	this work

IV. CONCLUSION

In this work, adsorption of chromium ions from dilute solution with commercial activated carbon was investigated. The effect of several parameters such as pH of solution, dose and particle size of activated carbon, on the chromium adsorption was studied. According to experimental data, optimum operating condition for chromium adsorption with activated carbon were pH=6, particle size of adsorbent =0.425mm and adsorbent dose = 6gr/l and under these condition nearly 100% of chromium ions was adsorbed by activated carbon after 2 hours. Langmiur model is the best model for describing equilibrium adsorption of chromium on activated carbon. Maximum adsorption capacity of activated carbon was 52.6 mg/g and this result shows that this activated carbon exhibits a reasonable capacity for chromium removal from aqueous solutions.

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