Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2012.748296

51 (2013) 2909–2914
March

Taylor & Francis
Taylor & Francis Group

Removal of Cr(VI) from aqueous solution onto chestnut shell: application of full factorial design and equilibrium studies

Raziye Ertaş[a], Neşe Öztürk[b,]*

[a]1st Air Supply & Maintenance Support Center Command, Eskisehir 26320, Turkey
[b]Department of Chemical Engineering, Faculty of Engineering and Architecture, Eskisehir Osmangazi University, Meselik Campus, Eskisehir 26480, Turkey
Tel. +90 222 2393750 3678; Fax: +90 222 2393613; email: nozturk@ogu.edu.tr

Received 9 December 2011; Accepted 27 September 2012

ABSTRACT

Adsorption of chromium VI [Cr(VI)] from aqueous solutions on chestnut shell was studied. In order to optimize the adsorption process, 2^3 full factorial design was applied to investigate the influence of the Cr(VI) concentration (100 and 150 mg/L), contact time (2 and 6 h), and pH (2 and 5) on the amount of Cr(VI) adsorbed. Statistical analysis of the results showed the significance of the individual factors and their interactions on the adsorption process. The best conditions for Cr(VI) adsorption were pH 2 and a contact time of 6 h for both the initial concentrations tried. Adsorption equilibrium was modeled by the Freundlich and Langmuir isotherm for Cr(VI). Equilibrium adsorption data followed Langmuir isotherm. The experimental results showed that chestnut shell could be used for adsorption of Cr(VI) ions from aqueous solutions.

Keywords: Adsorption; Cr(VI); Removal; Chestnut shell; Experimental statistical design

1. Introduction

The use of chromium chemicals in several industrial processes such as metal cleaning, plating, and electroplating leads to contamination of water. In aqueous systems, chromium can exist in both trivalent and hexavalent oxidation states. Because of its great toxicity Cr(VI) must be removed from wastewater before being discharged [1,2]. According to Turkish Water Pollution Control Regulation, the maximum levels permitted for trivalent chromium in wastewater are 5 mg/L and for hexavalent chromium are 0.05 mg/L [3]. The methods used for the removal of chromium ions from wastewater can be divided into five main categories: (i) chemical reduction by using ferro-sulfates, sodium meta bisulfite, sodium sulfite, sulfur dioxide, and similar chemicals, followed by precipitation (ii) ion exchange by using anion exchange resins (Cr(VI)) and cation exchange (Cr (III)), (iii) electrochemical reduction followed by precipitation, and finally (iv) adsorption [4]. Although different technologies are available the adsorption process is one of the efficient methods for chromium removal due to its clean operation and complete removal of heavy metal ions even from dilute solutions [5]. The most widely used adsorbent is activated carbon, which

---

*Corresponding author.

Third International Conference on Environmental Management, Engineering, Planning and Economics (CEMEPE 2011) & SECOTOX Conference, 19–24 June 2011, Skiathos Island, Greece

1944-3994/1944-3986 © 2013 Balaban Desalination Publications. All rights reserved.

is not cost-effective. Various agricultural by-products and wastes were also used for the removal of Cr(VI) from aqueous solutions. However, some of the adsorbents do not have good adsorption capacities or need long adsorption equilibrium times. Hence there is a need to search for more effective adsorbents [6].

Many by-products of agriculture have proved to be suitable low-cost adsorbents for Cr(VI) and Cr(III) removal from water. Lignocellulosic residues, which include both wood residues and agricultural residues, have adsorption capacity comparable to other natural sorbents, but they have the advantage of very low or no cost, great availability, and simple operational process [2]. Park et al. (2008) studied the Cr(VI) removal efficiency by different lignocellulosic wastes such as banana skin, oak leaf, walnut shell, peanut shell, and rice husk. Banana skin was screened as the most efficient biomaterial to remove toxic Cr(VI) from aqueous solution. Banana skin completely removed 50 mg/L of Cr(VI) in 0.5 h. The removal rate of Cr(VI) was remarkably pH dependent, decreasing with increasing pH value [7].

In this work, the use of chestnut shell as a low-cost adsorbent for the removal of Cr(VI) from aqueous solutions is presented. Two level factorial design was applied to investigate the effects of the parameters and their interactions on Cr(VI) removal by adsorption. The effects of the initial concentration, contact time, and pH for Cr(VI) adsorption onto the chestnut shell were investigated. In addition, the equilibrium isotherms (Freundlich and Langmuir models) were determined using the conditions selected from the statistical design of experiments.

2. Materials and methods

2.1. Adsorbent preparation

Chestnut shell supplied by a food factory (Bursa in Turkey) was milled by an automatic grinder (Retsch SK100) and was dried at 105˚C throughout 24 h.

2.2. Adsorption experiments

The aqueous solution of $K_2Cr_2O_7$ was prepared by using analytical grade Merck product. Two different initial concentrations were used in statistical design of adsorption experiments. The solutions were prepared in such a manner that the two initial Cr(VI) concentrations were held at 100 mg/L and 150 mg/L, respectively. Experiments were conducted for two different initial pH values of 2 and 5 and for two different contact times of 2 and 6 h at these initial concentrations. The effect of initial concentration on removal efficiency was also investigated at pH 5 by using solution samples having concentrations of 25, 50, 75, 100, 150, and 200 mg Cr(VI)/L for 4 h. Batch adsorption experiments were conducted in a series of beakers covered with stretch film to prevent contamination. 50 mL of solution of known concentration and pH was put in contact with 1 g of natural chestnut shell, and placed on a magnetic stirrer (WiseStir MH-20D) maintained for known contact time at 250 rpm and at the ambient temperature (25˚C). Final solutions were filtered (Whatman 4, pore size: 20–25 μm) and the filtrate was analyzed for remaining Cr(VI) concentrations by spectrophotometer (CECIL CE 4003). The pH adjustments of the solutions were made with H_2SO_4 or NaOH solutions by using pH meter (WTW N 280 A). All the experiments were duplicated. Langmuir and Freundlich isotherms were employed to study the adsorption modeling.

2.3. Statistical design of experiments

The principal steps of statistically designed experiments are: determination of response variables, factors, and factor levels; choice of the experimental design; and statistical analysis of the data. Today, the most widely used experimental design to estimate main effects, as well as interaction effects, is the 2^n factorial design, where each variable is investigated at two levels. Research can be designed for multiple factors and treatments [8].

3. Results and discussion

3.1. Statistical analysis

A 2^3 full factorial design was employed to study the influence of initial Cr(VI) concentration (x_1, 100 and 150 mg/L), contact time (x_2, 2 and 6 h), and pH (x_3, 2 and 5) on the amount of adsorbed Cr(VI). Eight experiments were required and all of them were done in duplicate. The following variables were kept constant: solid/ liquid ratio, 1/50 (g/mL), and temperature (25˚C). X_1, X_2, and X_3 are the corresponding values in coded forms. The experimental matrix along with natural and coded scales are present and shown in Table 1. The regression equation for the matrix is represented by the following expression [9]:

$$Y_i = b_o + b_1X_{1i} + b_2X_{2i} + b_3X_{3i} + b_{12}X_{1i}X_{2i} + b_{13}X_{1i}X_{3i} + b_{23}X_{2i}X_{3i} + b_{123}X_{1i}X_{2i}X_{3i} \quad (1)$$

The main and interaction coefficients have been calculated by following relations [10]:

Table 1
Experimental matrix

Serial number (i)	Initial concentration (mg/L)		Contact time (h)		pH value		Response (Y_i)	
	Actual (x_1)	Coded (X_1)	Actual (x_2)	Coded (X_2)	Actual (x_3)	Coded (X_3)		
1	100	−	2	−	2	−	Y_1	Y_9
2	150	+	2	−	2	−	Y_2	Y_{10}
3	100	−	6	+	2	−	Y_3	Y_{11}
4	150	+	6	+	2	−	Y_4	Y_{12}
5	100	−	2	−	5	+	Y_5	Y_{13}
6	150	+	2	−	5	+	Y_6	Y_{14}
7	100	−	6	+	5	+	Y_7	Y_{15}
8	150	+	6	+	5	+	Y_8	Y_{16}

$$b_0 = \sum \frac{Y_i}{N} \quad b_j = \sum \frac{X_{ji} Y_i}{N} \quad b_{nj} = \sum \frac{(X_{nj} X_{ji}) Y_i}{N} \tag{2}$$

where Y_i is the response (adsorbed Cr(VI) amount); and X_{ji} values ($j = 1, 2, 3$; $i = 1, 2, 3, \ldots, 16$) represent the corresponding parameters in their coded forms (Table 1); b_0 gives the average value of the results obtained for the adsorbed Cr(VI) amount; b_1, b_2, and b_3 are the linear coefficients (independent parameters); b_{12}, b_{13}, b_{23}, and b_{123} are the interaction coefficients and N is the number of total experiments. Coefficients b_1, b_2, and b_3 show, respectively, the effect of initial concentration, contact time, and pH. Coefficients b_{12}, b_{13}, and b_{23} show the interacting effects of two variables at a time and b_{123} shows the interacting effect of all three variables taken at a time.

Table 2
The values of model coefficients

Main and interaction coefficients	Values
b_0	6.1675
b_1	1.2319
b_2	0.0163
b_3	−0.0316
b_{12}	0.0037
b_{13}	−0.0191
b_{23}	0.0091
b_{123}	0.0072

The values of main and interaction model coefficients determined are given in Table 2. The design matrix and the results showing adsorbent Cr(VI) amount are shown in Table 3. The results obtained from the trial runs are incorporated in the regression Eq. (1) and thus, the equation becomes:

$$\begin{aligned} Y = {} & 6.1675 + 1.2319 X_{1i} + 0.0163 X_{2i} - 0.0316 X_{3i} \\ & + 0.0037 X_{1i} X_{2i} - 0.0191 X_{1i} X_{3i} + 0.0091 X_{2i} X_{3i} \\ & + 0.0072 X_{1i} X_{2i} X_{3i} \end{aligned} \tag{3}$$

The effect of individual variables and interactional effects can be estimated from the above equation. According to this equation, pH of solution have a negative effect while initial concentration and contact time have positive effect on the adsorbed Cr(VI) in

Table 3
Design of trial runs for Cr(VI) removal by adsorption in two replicate experiments

Trial No.	X_1	X_2	X_3	X_1X_2	X_1X_3	X_2X_3	$X_1X_2X_3$	Y adsorbed Cr(VI) (mg/g)	Y adsorbed Cr(VI) (mg/g)	Y average adsorbed Cr (VI) (mg/g)
1	−	−	−	+	+	+	−	4.95	4.93	4.94
2	+	−	−	−	−	+	+	7.45	7.44	7.45
3	−	+	−	−	+	−	+	4.96	4.96	4.96
4	+	+	−	+	−	−	−	7.45	7.46	7.45
5	−	−	+	+	−	−	+	4.91	4.91	4.91
6	+	−	+	−	+	−	−	7.32	7.30	7.31
7	−	+	+	−	−	+	−	4.94	4.93	4.94
8	+	+	+	+	+	+	+	7.38	7.39	7.39

Table 4
Experimental and calculated value of adsorbed Cr(VI)

Serial Number	Adsorbed Cr(VI) (mg/g)	
	Experimental Y (average)	Calculated Y (average)
1	4.94	4.93
2	7.45	7.44
3	4.96	4.95
4	7.45	7.45
5	4.91	4.90
6	7.31	7.31
7	4.94	4.93
8	7.39	7.39

Table 5
According to analysis of variance F ratios and decisions

Source of variation	F ratio	Decision ($\alpha = 0.1$)	Decision ($\alpha = 0.05$)	Decision ($\alpha = 0.01$)
X_1	323408	Effective	Effective	Effective
X_2	56	Effective	Effective	Effective
X_3	5.33	Effective	Effective	Non-effective
X_1X_2	225	Effective	Effective	Effective
X_1X_3	75	Effective	Effective	Effective
X_2X_3	16	Effective	Effective	Effective
$X_1X_2X_3$	12	Effective	Effective	Effective

the range of variation of each variable selected for the present study.

Experimental and calculated values of adsorbed Cr(VI) amount are given in Table 4. Since the differences between the experimental and calculated values of adsorbed amount are negligible, it can be said that the model equation is adequate.

The regression equation was tested to see how it fitted with the observations, using Fisher's adequacy test at the 90, 95, and 99% confidence levels (probability levels: $\alpha = 0.1$; $\alpha = 0.05$; $\alpha = 0.01$, respectively). According to analysis of variance, calculated F ratios and decisions are given in Table 5. Comparing the calculated F values with Fisher's F values, it seems that in all cases calculated F is greater than Fisher's F values [$F_{0.1}(1,8)$]: 3.46; [$F_{0.05}(1,8)$]: 5.32; [$F_{0.01}(1,8)$]: 11.26 ($\alpha = 0.1$, $\alpha = 0.05$). So, initial concentration, contact time, pH, and all of the interactions of parameters were found to be effective on adsorbed Cr(VI) by adsorption.

According to the F values, the initial concentration was the most important parameter affecting the uptake of Cr(VI) by adsorption. The pH of solution was less effective parameter.

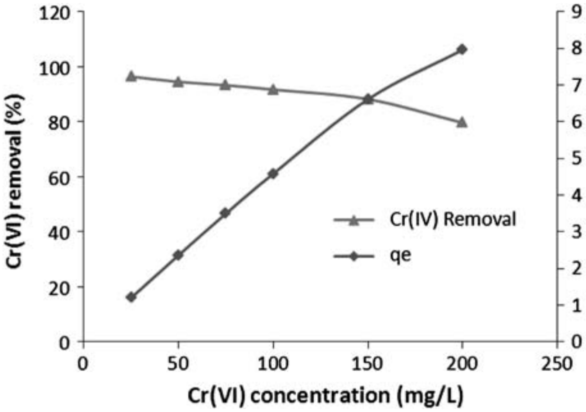

Fig. 1. Effect of initial concentration on the removal of Cr (VI) (pH: 5, temp: 25°C, mix rate: 250 rpm, contact time: 4 h, and adsorbent dose: 1 g/50 mL).

3.2. Effect of initial Cr(VI) concentration

A higher initial concentration provides an important driving force to overcome all mass transfer resistances of the Cr(VI) between the aqueous and solid phases, thus increases the uptake.

The effect of initial concentration on the uptake of Cr(VI) was studied by treating 1 g chestnut shell with 50 mL Cr(VI) solution for 4 h at pH 5. Experimental studies were carried out at Cr(VI) concentrations ranging from 25 to 200 mg/L. The results of experiments were given in Fig. 1. The equilibrium adsorption capacity of chestnut for the Cr(VI) enhanced with raising initial Cr(VI) concentration up to 200 mg/L while the removal of Cr(VI) showed an opposite trend. The amount of Cr(VI) adsorbed increased from 1.21 to 7.96 mg/g with the change of initial Cr(VI) concentration from 25 to 200 mg/L due to the increase of the number of ions competing for the available binding sites on the adsorbent. Cr(VI) removal (%) decreased from 96.4 to 79.6 with increasing Cr(VI) concentration because of nearly complete coverage of the binding sites of adsorbent at higher Cr(VI) concentrations.

3.3. Adsorption isotherms

Adsorption isotherm describe the relationship between the amount of adsorbed and adsorbate concentration remaining in solution. There are several isotherms for analyzing experimental adsorption equilibrium data. The equation parameters of these isotherms often provide some insight into the adsorption mechanism.

Langmuir isotherm is represented by the following equation [10]:

$$\frac{C_e}{q_e} = \frac{1}{q_0 b} + \frac{C_e}{q_0} \tag{4}$$

where C_e is the concentration of the Cr(VI) solution (mg/L) at equilibrium and q_e is the amount adsorbed at equilibrium (mg/g). The constant q_0 signifies the adsorption capacity (mg/g) and b is related to the energy of adsorption (L/mg). For obedience to the Langmuir isotherm, values derived from the slopes and intercepts of plots of C_e/q_e against C_e should remained constant [10].

The Freundlich isotherm model is given by the following equation [10]:

$$\log q_e = \log K_f + (1/n) \log C_e \tag{5}$$

where K_f and n are the Freundlich adsorption isotherm constants, being indicative of the adsorption capacity and intensity of adsorption. Values of K_f and n were calculated from the intercept and slope of the plots of $\log q_e$ vs. $\log C_e$. In general, as the K_f value increases, the adsorption capacity of the adsorbent increases.

In this study, Langmuir and Freundlich adsorption isotherms were used to describe the relationship between the adsorbed amount of Cr(VI) and its equilibrium concentration in solution (Fig. 2 and Table 6).

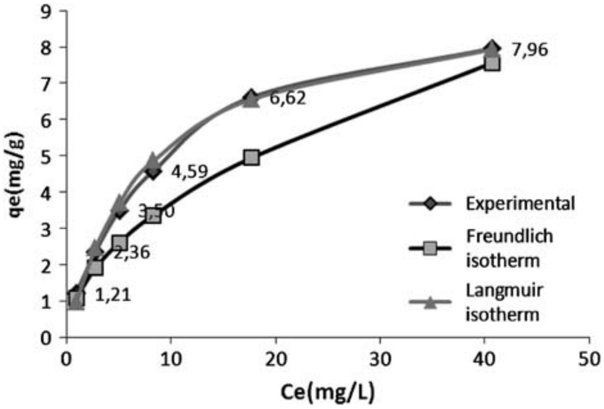

Fig. 2. Isotherms of adsorption of Cr(VI) on chestnut shell (pH: 5, temp: 25℃, mix rate: 250 rpm, contact time: 4 h, and adsorbent dose: 1 g/50 mL).

Table 6
Langmuir and Freundlich constants

Adsorbent	Langmuir constants			Freundlich constants		
	q_0 (mg/g)	b (L/mg)	R^2	K_f	n	R^2
Chestnut shell	9.47	0.127	0.995	1.141	1.96	0.975

According to Fig. 2 the equilibrium data for the adsorption of Cr(VI) using chestnut fits into Langmuir isotherm model. The regression coefficient shows that adsorption follows a Langmuir isotherm (Table 6). The applicability of the Langmuir isotherm suggests the monolayer coverage of the Cr(VI) adsorption onto chestnut shell. Langmuir isotherm assumes that all the adsorption sites are equivalent and there is no interaction between adsorbed species. According to K_f value and q_0 value, chestnut shell is effective (Table 6). It has been shown using mathematical calculations that n was between 1 and 10 representing beneficial adsorption.

To determine if the Cr(VI) adsorption process is favorable or unfavorable for the Langmuir type adsorption process, the isotherm shape can be classified by a term "R_L", a dimensionless constant separation factor, which is defined below [9]:

$$R_L = 1/(1 + bC_0) \tag{6}$$

where R_L is a dimensionless separation factor and C_0 is the initial Cr(VI) concentration (mg/L). The parameter R_L indicates the shape

Of the isotherm accordingly:

$R_L > 1$ unfavorable
R_L=1 linear
$0 < R_L < 1$ favorable
$R_L = 0$ irreversible

Table 7
Adsorption capacity of various adsorbents as reported in literature

Adsorbent	Maximum adsorption capacity (mg/g)	References
Hydrolyzing product of ferric chloride impregnated-saponified sugar beet pulp	5.123	[11]
Coal	6.78	[12]
Cactus	7.82	[12]
Almond	10.616	[12]
Wool	41.15	[12]
Rice Straw	3.15	[2]
Paddy straw	21.50	[2]
Pine needles	21.50	[2]
Present study	9.47	

The fact that all the R_L values are in the range 0.04–0.23 indicates that the adsorption of Cr(VI) is favorable.

Batch adsorption capacity was obtained as 9.47 mg/g. A comparison of the adsorbent capacity with various adsorbents studied in literature is given in Table 7.

4. Conclusions

From the statistical analysis it was found out that the pH has a negative effect, while contact time and initial concentration have positive effects on the Cr(VI) removal by adsorption.

Maximum Cr(VI) removal was obtained at 6 h and pH 2 for both initial Cr(VI) concentrations.

At low pH, the functional groups in the surface of chestnut may be protonated and restrict the approach of cationic species as a result of repulsive forces. In solution, pH values between 2–6 Cr(VI) ions are probably $HCrO^{4-}$ and $Cr_2O_7^{2-}$ species, at lower pH ($pH < 2$) the principal species are $Cr_4O_{13}^{2-}$ and $Cr_3O_{10}^{2-}$. These anionic species can be adsorbed to the protonated active sites of the chestnut [2].

The Langmuir isotherm is obeyed better than the Freundlich isotherm, as is evident from the values of regression coefficients. The batch adsorption capacity was found in 9.47 mg/g.

Symbols

b — parameter of the Langmuir equation, L/mg
b_0 — average adsorbed Cr(VI) amount, g/L
b_1, b_2, b_3 — linear coefficients
b_{12}, b_{13}, b_{23}, b_{123} — interaction coefficients
C_e — concentration of Cr(VI) at equilibrium, mg/L
C_0 — initial Cr(VI) concentration, mg/L
F — the value of Fisher table
K_f — parameter of the Freundlich equation, (mg/g) $(L/mg)^{1/n}$
n — Freundlich adsorption constant
N — the number of total experiments
q_e — amount of Cr(VI) adsorbed at equilibrium, mg/g
q_0 — monolayer capacity of the adsorbent, mg/g
R_L — a dimensionless constant, separation factor
Y_i — performance value of *i*th experiment
x — parameters
X_{ji} — corresponding parameter in coded forms

Greek letters

α — probability level

References

[1] P. Suksabye, P. Thiravetyan, W. Nakbanpote, S. Chayabutra, Chromium removal from electroplating wastewater by coir pith, J. Hazard. Mater. 141(3) (2007) 637–644.
[2] P. Miretzky, A.F. Cirelli, Cr(VI) and Cr(III) removal from aqueous solution by raw and modified lignocellulosic materials: A review, J. Hazard. Mater. 180(3) (2010) 1–19.
[3] The ministry of environment and urban planning, Water Pollution Control Regulations, Turkish Official Newspaper, No. 25687, 31.12.2004.
[4] M. Uysal, I. Ar, Removal of Cr(VI) from industrial wastewaters by adsorption Part I: determination of optimum conditions, J. Hazard. Mater. 149 (2007) 482–791.
[5] R. Chand, T. Watari, K. Inoue, T. Torikai, M. Yada, Evaluation of wheat straw and barley straw carbon for Cr(VI) adsorption, Sep. Purif. Technol. 65 (2009) 331–336.
[6] C. Namasivayam, M.V. Sureshkumar, Removal of chromium (VI) from water and wastewater using surfactant modified coconut coir pith as a biosorbent, Bioresour. Technol. 99 (2008) 2218–2225.
[7] D. Park, S.-L. Lim, Y.-S. Yun, J.M. Park, Development of a new Cr(VI)-biosorbent from agricultural biowaste, Bioresour. Technol. 99 (2008) 8810–8818.
[8] D.C. Montgomery, G.C. Runger, Applied Statistics and Probability for Engineers, third ed., John Wiley & Sons, New York, NY, 2003.
[9] N. Öztürk, D. Kavak, Boron removal from aqueous solutions by adsorption on waste sepiolite and activated waste sepiolite using full factorial design, Adsorption 10 (2004) 245–257.
[10] B. Crittenden, W.J. Thomas, Adsorption Technology and Design, Reed Educational and Professional Publishing Ltd., Oxford, 1998.
[11] H.S. Altundoğan, Cr(VI) removal from aqueous solution by iron (III) hydroxide loaded sugar beet pulp, Process Biochem. 40 (2005) 1443–1452.
[12] M. Dakiky, M. Khamis, A. Manassra, M. Mer'eb, Selective adsorption of chromium(VI) in industrial wastewater using low cost abundantly available adsorbents, Adv. Environ. Res. 6 (2002) 533–540.