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Removal of lead from aqueous solutions by using chestnut shell as an adsorbent

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ABSTRACT

Adsorption of lead 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 adsorbent dosage (0.5–1.0 g/50 mL), stirring speed (50–200 rpm), and pH (2–5) on the amount of lead adsorbed. Statistical analysis of the results showed the significance of the individual factors and their interactions on the adsorption process. The best conditions for lead removal were the adsorbent dosage: 1 g/50 mL, stirring speed: 200 rpm, and pH 5 for the initial concentrations essayed (150 mg/L). In addition, adsorption equilibrium was modeled by the Freundlich and Langmuir isotherm for lead. The results obtained from the study on parameters showed that as the selected variables increased the lead removal by adsorption also increased.

Keywords: Adsorption; Heavy metal; Removal; Chestnut shell; Low-cost adsorbent

1. Introduction

Increase in industrial activities without stringent control on the effluent quality has led to the contamination of environment [1]. Heavy metal ions are reported as priority pollutants, due to their toxicity. The presence of copper, zinc, cadmium, lead, mercury, iron, nickel, and other metals has a potentially damaging effect on human physiology and other biological systems when the tolerance levels are exceeded. Hence, it becomes mandatory to control and reduce the levels of these metal ions in wastewaters and bring them to permissible values [1,4]. Many physicochemical methods have been proposed for their removal from industrial effluents, such as electro-chemical precipitation, ultra filtration, ion exchange, and reverse osmosis [1]. However, these methods have several disadvantages that include high cost and toxic sludge [2]. Adsorption using commercial activated carbon is an effective purification and separation technique used in industry especially in water and wastewater treatments that can remove heavy metals from wastewater [3]. Activated carbon has been the most used adsorbent, nevertheless it is relatively expensive. In order to obtain cheaper adsorbents, lignocellulosics materials have been studied. For the removal of heavy metal ions using low-cost

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abundantly available adsorbents, agricultural wastes, such as tea waste and coffee, hazelnut shells, peanut hull, saw dusts, pinus bark coconut husk, peanut skins, rice hulls, almond shells, banana and orange, and different agricultural by-products, were used and investigated [4].

In this work, the use of chestnut shell as a low-cost adsorbent for the removal of lead from aqueous solutions is presented. Two-level factorial design was applied to investigate the effects of the parameters and their interactions on lead removal by adsorption. The effects of the adsorbent dosage, stirring speed, and pH on the shell capacity were investigated for removing lead contaminant. 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 a automatic grinder (Retsch SK100) and was dried at 105˚C for 24 h.

2.2. Adsorption experiments

Lead solution was prepared with commercial Pb calibration solutions (1,000 mg/L). The initial Pb concentration in adsorption experiments were held at 150 mg/L. For the contaminant, batch adsorption experiments were conducted in a series of beakers covered with stretch film to prevent contamination. The 50 mL of solution was put in contact with natural chestnut shell of known amount, and placed on a magnetic stirrer (WiseStir MH-20D) maintained for known pH value and stirring speed at the ambient temperature (25˚C) for 4 h contact time. Final solutions were filtered (Whatman 4, 125 mm) and analyzed for remaining Pb concentrations by Atomic Absorption Spectrometer (Perkin Elmer AAnalyst 400). The pH adjustments of the solutions were made with NaOH solutions by using pH meter (WTW N 280 A). All of the experiments were duplicated. Langmuir and Freundlich isotherms were employed to study the adsorption capacity of the adsorbent.

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 [5].

3. Results and discussion

3.1. Statistical analysis

In order to characterize the adsorption process of lead onto chestnut shell, the effect of adsorbent dosage, stirring speed, and initial pH of the solutions was investigated. Among the parameters affecting metal removal by adsorption, initial solution pH is the most important. Surface characteristics of adsorbents and ionization degree of metals in aqueous solution depend on pH value. When pH value is adjusted to a value higher than 6 lead precipitations appears due to increase of the OH^- ions in the solution [6]. So, the initial solution pH lower than 6 values was examined. Adsorbent dosage is another parameter affecting removal. The adsorbed amount (per unit mass) decrease with the increase of the adsorbent dosage. It can be depends on to the increase of unsaturated adsorption sites by increasing the adsorption dose. Another reason of the depression may be due to the particle interaction, such as aggregation, resulted from high adsorbent concentration. Such aggregation would lead to decrease in total surface area of the sorbent and an increase in diffusion path [7]. Adsorbent dosage is important factors for designing the treatment plants. Stirring speed affects kinetics and mechanism [8]. So, 2^3 full-factorial design was employed to study the influence of adsorbent dosage (x_1, 0,5–1,0 g), stirring speed (x_2, 50–200 rpm), and pH (x_3, 2–5) on the amount of adsorbed contaminant. Eight experiments were required and all of them were done in duplicate. The following variables were kept constant: initial concentrations (150 mg/L), contact time (4 h), and temperature (25˚C). The X_1, X_2, and X_3 are the corresponding values in coded forms. The experimental matrix along with natural and coded scales is shown in Table 1. The regression equation for the matrix is represented by the following expression [9]:

$$Y_i = b_0 + b_1X_{1i} + b_2X_{2i} + b_3X_{3i} + b_{12}X_{1i}X_{2i} + b_{13}X_{1i}X_{3i} + b_{23}X_{2i}X_{3i} + b_{123}X_{1i}X_{2i}X_{3i} \quad (1)$$

The main and interaction coefficients have been calculated by the following relations [9]:

Table 1
Experimental matrix

Serial number (i)	Adsorbent dosage (g/50 mL)		Stirring speed (rpm)		pH value		Response (Y_i)	
	Actual (x_1)	Coded (X_1)	Actual (x_2)	Coded (X_2)	Actual (x_3)	Coded (X_3)		
1	0.5	–	50	–	2	–	[Y_1]	[Y_9]
2	1.0	+	50	–	2	–	[Y_2]	[Y_{10}]
3	0.5	–	200	+	2	–	[Y_3]	[Y_{11}]
4	1.0	+	200	+	2	–	[Y_4]	[Y_{12}]
5	0.5	–	50	–	5	+	[Y_5]	[Y_{13}]
6	1.0	+	50	–	5	+	[Y_6]	[Y_{14}]
7	0.5	–	200	+	5	+	[Y_7]	[Y_{15}]
8	1.0	+	200	+	5	+	[Y_8]	[Y_{16}]

Table 2
Values of model coefficients

Main and interaction coefficients	Values for Pb
b_0	8.2963
b_1	−2.4994
b_2	0.7856
b_3	1.7081
b_{12}	−0.4494
b_{13}	−0.4769
b_{23}	−0.2619
b_{123}	0.0381

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

where Y_i is the response (adsorbed lead amount); 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 lead 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, stirring speed, 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.

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

$$\begin{aligned} Y = {} & 8.2963 - 2.4994X_{1i} + 0.7856X_{2i} + 1.7081X_{3i} \\ & - 0.4494X_{1i}X_{2i} - 0.4769X_{1i}X_{3i} - 0.2619X_{2i}X_{3i} \\ & + 0.0381X_{1i}X_{2i}X_{3i} \end{aligned} \tag{3}$$

Table 3
Design of trial runs for lead 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 Pb (mg/g)	Y adsorbed Pb (mg/g)	Y average adsorbed Pb (mg/g)
1	–	–	–	+	+	+	–	7.00	7.22	7.11
2	+	–	–	–	–	+	+	4.04	4.04	4.04
3	–	+	–	–	+	–	+	10.02	10.34	10.18
4	+	+	–	+	–	–	–	5.16	5.16	5.16
5	–	–	+	+	–	–	+	12.32	11.84	12.08
6	+	–	+	–	+	–	–	6.91	6.99	6.95
7	–	+	+	–	–	+	–	13.76	14.14	13.95
8	+	+	+	+	+	+	+	7.16	7.19	7.18

Table 4
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	3,000	Effective	Effective	Effective
X_2	296	Effective	Effective	Effective
X_3	97	Effective	Effective	Effective
X_1X_2	1,402	Effective	Effective	Effective
X_1X_3	109	Effective	Effective	Effective
X_2X_3	32	Effective	Effective	Effective
$X_1X_2X_3$	0.70	Non effective	Non effective	Non effective

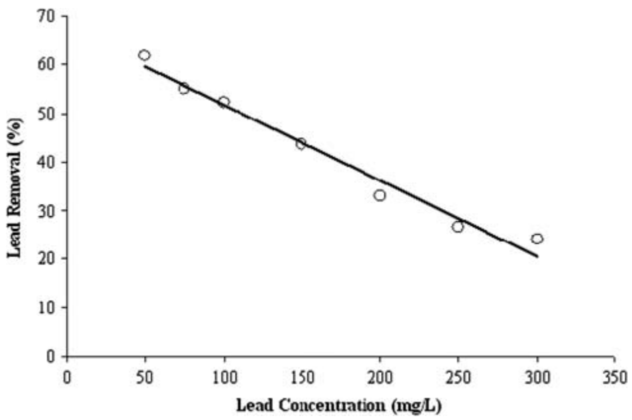

Fig. 1. Effect of initial concentration on the removal of Pb.

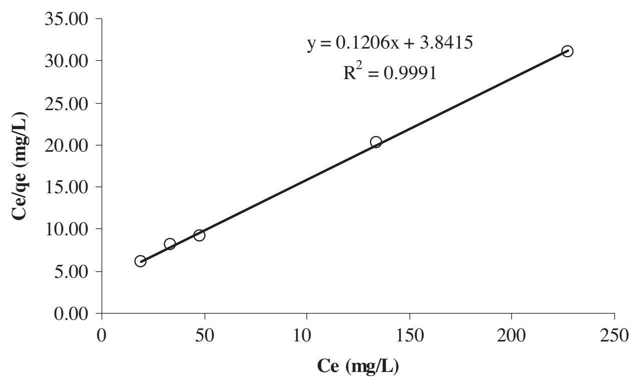

Fig. 2. Langmuir plots for Pb adsorption on the chestnut shell (at pH <2 and 25˚C).

The effect of individual variables and interactional effects can be estimated from the above equation. According to this equation, adsorbent dosage has a negative effect, while stirring speed and pH of solution have positive effect on the lead removal by adsorption in the range of variation of each variable selected for the present study.

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: $\alpha = 0.1$; $\alpha = 0.05$; and $\alpha = 0.01$, respectively). According to analysis of variance, the calculated F ratios and decisions are given in Table 4. Comparing the calculated F values with Fisher's F values, it seems that all of the parameters and interactions of two variables were effective for the lead removal (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).

According to the F values, the adsorbent dosage was the most important parameter effecting the lead removal by adsorption, which was followed the interaction between adsorbent dosage-stirring speeds. The interaction between the three variables was noneffective parameter.

3.2. Effect of initial concentration

Fig. 1 gives the removal percentage of Pb as a function of initial concentration. The experiments were carried out at initial concentrations varied from 50 to 300 mg/L and at original pH (<2). The results indicate

Table 5
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	8.29	0.031	0.999	1.259	2.98	0.941

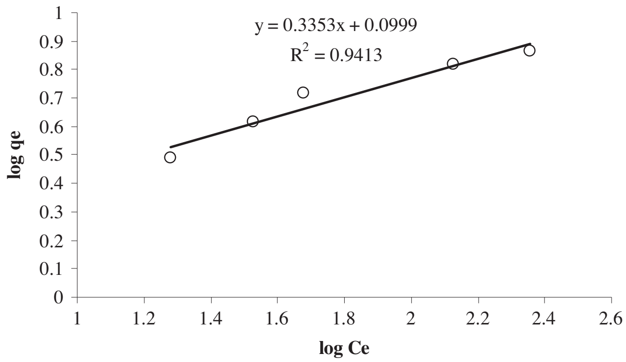

Fig. 3. Freundlich plots for Pb adsorption on the chestnut shell (at pH <2 and 25˚C).

Table 6
Adsorption capacities of different adsorbents in the literature for lead

Adsorbent	Capacity (mg/g)	Reference
Bacterial cellulose	22.56	[11]
Carboxymethylated-bacterial cellulose	60.42	[11]
Unmodified absorbent cotton	10.78	[6]
Thiol-modified absorbent cotton	28.67	[6]
Palm fibers	18.622	[12]
Petiole	20.040	[12]

that the increase in initial concentration decreased the removal efficiency.

3.3. Adsorption isotherms

In this work, the Langmuir and Freundlich adsorption isotherms were used to describe the relationship between the adsorbed amount of Pb and its equilibrium concentration in solution. 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 lead in solution (mg/L) at equilibrium and q_e is the amount adsorbed at equilibrium (mg/g). The constant q_o 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 linear plot of C_e/q_e vs. C_e shows that adsorption follows a Langmuir isotherm (Fig. 2). The applicability of the Langmuir isotherm suggests the monolayer coverage of the lead adsorption onto chestnut shell (Table 5).

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 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 $\log q_e$ versus $\log C_e$ (Fig. 3). In general, as the K_f value increases, the adsorption capacity of the adsorbent increases. According to K_f value and q_o value, chestnut shell is effective (Table 5). It has been shown using mathematical calculations that n was between 1 and 10 representing beneficial adsorption.

The lead adsorption capacities of some adsorbents are given in Table 6. It can be seen from Table 6 that the capacity of chestnut shell is close to unmodified adsorbent cotton. Modification may be increase the capacity.

4. Conclusions

From the statistical analysis it was found out that the adsorbent dosage, stirring speed, and pH have positive effects on the lead removal by adsorption. Maximum lead removal was obtained at adsorbent dosage: 1 g/50 mL, stirring speed: 200 rpm, and pH 5. 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 to be 8.29 mg/g.

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