Chemical Engineering Journal 173 (2011) 743–749

Contents lists available at SciVerse ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Optimization of Pb(II) adsorption onto modified walnut shells using factorial design and simplex methodologies

S. Saadat, A. Karimi-Jashni *

Department of Civil and Environmental Engineering, School of Engineering, Shiraz University, Shiraz, Fars 7134851156, Iran

ARTICLE INFO

Article history:
Received 13 April 2011
Received in revised form 12 August 2011
Accepted 16 August 2011

Keywords:
Adsorption
Walnut shell
Pb(II)
Factorial design
Simplex method

ABSTRACT

The removal of Pb(II) ions from aqueous solutions by chemically modified walnut shells was studied. A 2^4 full factorial design analysis was performed to screen the variables affecting Pb(II) removal efficiency. The effects of solution pH, adsorbent dose, initial concentration of Pb(II) ions, and temperature on metal removal efficiency were examined in a batch system. Using the experimental results, a linear mathematical model representing the influence of the different variables and their interactions was obtained. Analysis of variance (ANOVA), *F*-test and Student's *t*-test showed that Pb(II) ions adsorption is only slightly temperature dependent, but markedly increases with adsorbent dose and solution pH. The initial concentration of Pb(II) ions had a relatively small negative effect on removal efficiency. The optimization of the statistically significant factors was carried out using a modified simplex method. The recommended optimum conditions were: adsorbent dosage of 13.5 g/L, solution pH of 6.3, initial metal concentration of 45.3 mg/L, with the Pb(II) removal efficiency of 98.2%.

1. Introduction

Heavy metal pollution is a significant environmental problem due to its toxic effects, non-biodegradability, accumulation in living tissues and food chain and, hence, in the human body. Heavy metals are released from various industrial processes and increase the concentration of heavy metals in aquatic systems, causing serious environmental problems. Therefore, it is necessary to remove metal ions from industrial wastewater before discharging it into the environment. Lead is an extremely toxic metal listed as a priority pollutant [1]. The major sources of lead pollution are the discharging of waste streams from battery manufacturing, metal plating, mining and finishing, printing, ammunition, metallurgical alloying, and ceramics and glass industries [2,3]. Even at relatively low concentrations, lead can cause serious health issues in the human body, including irreversible brain damage and injury to the blood forming systems [4,5].

General treatment techniques for metal bearing effluents are chemical precipitation, membrane filtration (reverse osmosis, nanofiltration, etc.), electrolyte reduction, solvent extraction, ion exchange, and adsorption [6–8]. Of these metal removal methods, adsorption is the most common practice due to technological and cost advantages. The application of conventional adsorbents such as granular or powdered activated carbon is usually limited due to their high cost [9]. Non-conventional low cost materials have been tested on a large scale for Pb(II) removal, such as sawdust [3,4,10,11], rice bran [12], grape stalk waste [13], hazelnut and almond shells [14], wheat bran [2], peanut husk [10,15], fly ash [16], tea waste [1,17], the carbon of nut shells [18], and rice husk [11].

Instead of the traditional one-variable-at-a-time experiments which were used by the majority of previous researchers to determine the individual effect of various factors on lead adsorption processes [2–4,8,10,11,13,18–22], factorial design technique can be employed to reduce the number of experiments, time and overall research cost. The factorial design method determines which factors have significant effects on a response as well as how the effect of one factor varies according to the level of the other factors [23]. Recently, a number of investigations have been conducted using this technique to model heavy metal adsorption processes [23–31]. However, there are limited studies concerning the application of this method to the adsorption of Pb(II) cations [23,32–36].

The optimization of conditions in pollutant removal is important in waste water treatment. Simplex is a simple and efficient optimization algorithm which has been used previously to optimize phosphorus and phenol removal [37,38]. Ricou-Hoeffer et al. [35] have also optimized two parameters of sorbent concentration and solution temperature for Cu^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} uptake through the application of this technique.

Iran ranks fourth in walnut production worldwide, producing about 290,000 metric tons of walnut per year. Consequently, walnut shell as an agricultural by-product is available in large quantities in Iran [39]. In the present work, a chemically modified walnut

* Corresponding author. Tel.: +98 917 300 7901; fax: +98 711 6473161.
E-mail addresses: ssaadat@shirazu.ac.ir (S. Saadat), ajashni@yahoo.ca, akarimi@shirazu.ac.ir (A. Karimi-Jashni).

1385-8947/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2011.08.042

Table 1
Experimental ranges and levels of the factors studied in the factorial design.

Factor	Coded symbol	Range and level	
		−1	+1
pH	*A*	2	10
Adsorbent dose (g/L)	*B*	1	20
Initial metal concentration (mg/L)	*C*	10	90
Temperature (°C)	*D*	15	45

shell was selected as an effective, economical and readily available adsorbent material for the treatment of lead contaminated aqueous solutions. The main objectives of this work were, on the one hand, to investigate the effect of pH, adsorbent dose, initial metal concentration, and temperature on the adsorption of Pb(II) onto the modified walnut shell, and, on the other hand, to optimize the conditions for Pb(II) removal. Following the determination of the statistically significant parameters through factorial design, the modified simplex method was also applied to find out the optimum conditions for the removal of Pb(II) ions.

2. Materials and methods

2.1. Adsorbent

Walnut shell which is available in large quantities in Iran was selected as adsorbent. Crushed walnut shell was sieved in the size range of 0.6–2.0 mm and then washed with distilled water until the supernatant solution became clear. Next, the shell was dried at room temperature in order to evaporate the moisture. To extract soluble organic compounds from walnut shell, 20 g of dried walnut shell was treated with 200 ml of 1.0 M NaOH in a shaker at 25 °C for 24 h. The mixture was filtered and washed several times with distilled water to remove the excess NaOH from the treated walnut shell. Finally, the material was dried and stored in an airtight container for further use.

2.2. Adsorbate solution

A 1000 mg/l Pb(II) stock solution was prepared by dissolving $Pb(NO_3)_2$ in acidified distilled water (a mixture of 10 ml of HNO_3 and 100 ml of distilled water). The solutions of different concentrations required for the adsorption experiments were prepared by the dilution of the stock solution with distilled water. All the chemicals used in this research were analytical reagent grade products from Merck, Germany. Distilled water was used throughout this research to prepare the required solutions.

2.3. Adsorption experiments

In order to determine the factors that influence the removal of Pb(II) by modified walnut shell, and to investigate the interaction effects of various parameters, a two-level, four-factor, full factorial design of experiments was applied. For this purpose, four factors, namely pH, adsorbent dose, initial concentration of Pb(II) and temperature were varied at two levels as shown in Table 1. The adsorption of Pb(II) was studied using a batch procedure and results were indicated in the form of the percentage of Pb(II) ion removal by use of modified walnut shell. For each run, weighted amounts of adsorbent were added to flasks containing 200 ml of metal aqueous solution and pH was adjusted to the desired value by using 0.1 M NaOH or HCl solutions as needed. The flasks were agitated in an incubated rotary shaker at 65 rpm for 5 h. The suspensions were then filtered and the lead content in the filtrates was determined through air acetylene flame atomic adsorption spectrometry. A Shimadzu A-A 680 (Japan), atomic absorption spectrophotometer was used as detector with hollow cathode lamp source set at 117.0 nm wavelength using 10 mA lamp current and 0.5 nm slit width. Sixteen experiments with all possible combinations of variables were duplicated in random order, and a matrix was created according to their low and high levels, represented by −1 and +1, respectively.

2.4. Simplex method

Simplex is a simple and efficient optimization algorithm that can find the global extreme of functions with fewer trials than the non-systematic approaches or the one-variable-at-a-time method. This method is based on an initial design of $k+1$ trials, where k is the number of variables. After the initial trials, the simplex process is sequential, with the addition and evaluation of one new trial at a time.

In order to improve the performance of the simplex method, many modifications have been proposed. In the modified simplex method, convergence can be achieved more quickly by expansion or contraction along the line of reflection [37,40]. In this study modified simplex optimization was performed using the MultiSimplex® 2.1 software. The implementation of the algorithms is described in detail in the software manual. The three statistically significant main factors of the process (pH, adsorbent dose and Pb(II) initial concentration) were selected as the control variables, with the response variable being the percentage of Pb(II) ion removal. The objective of this project was to maximize the Pb(II) ion removal as much as possible.

The initial design space was constrained with lower and upper bounds on each control variable, which was 2 and 10 for the pH, 1 and 20 g/L for the adsorbent dose and 10 and 90 mg/L for the initial concentration of Pb(II) ions, respectively. When an experiment design is outside of the defined domain, the simplex will determine another experiment within the allowable range of conditions. The starting points of the simplex were determined using the MultiSimplex® software by the assignment of a reference value and a step size for each variable. The assigned values were suggested in such a way so as to cover a wide range of values in the factor space in order to avoid the results being confined to a local minimum all the time.

The basis for the simplex algorithm comes from geometry. For the optimization of three variables, the simplex takes the form of a tetrahedron. Each vertex corresponds to a set of experimental conditions. In the initial simplex, after ranking the vertices from worst to best, the worst one is rejected and a new simplex is established by calculating the conditions of the new vertex corresponding to a contraction on the reflection side using the modified simplex procedure as suggested by Nelder and Mead [41]. This procedure was then repeated until the maximum response value was reached (when the responses could not be improved further).

3. Results and discussion

3.1. Characterization of modified walnut shell

Modified walnut shell was characterized by using a scanning electron microscope. The scanning electron microscopy (SEM) investigations of the modified walnut shell were conducted to examine the morphological and surface characteristics of the adsorbent. Fig. 1 displays the SEM image of NaOH modified walnut shell. It is obvious from this figure that modified walnut shell has an irregular and porous surface which makes it appropriate for adsorption purposes. The specific surface area of walnut shell was $118 \pm 5\ m^2/g$ which was determined according to the technique described by Araujo and Jaroniec [42], using a lab-made thermogravimetric (TG) analyzer.

Table 2
Factorial design experimental data.

Run no.	Coded values of independent variables				Pb(II) removal (%)		Pb(II) removal (%)
	A	B	C	D	Trial 1	Trial 2	Average
1	−1	−1	−1	−1	3.94	6.68	5.31
2	+1	−1	−1	−1	52.48	54.02	53.25
3	−1	+1	−1	−1	87.07	80.29	83.68
4	+1	+1	−1	−1	88.25	89.69	88.97
5	−1	−1	+1	−1	1.31	1.19	1.25
6	+1	−1	+1	−1	75.36	77.88	76.62
7	−1	+1	+1	−1	68.02	60.42	64.22
8	+1	+1	+1	−1	80.54	80.00	80.27
9	−1	−1	−1	+1	5.81	8.65	7.23
10	+1	−1	−1	+1	58.63	49.37	54.00
11	−1	+1	−1	+1	87.09	83.99	85.54
12	+1	+1	−1	+1	91.47	90.55	91.01
13	−1	−1	+1	+1	1.98	1.64	1.81
14	+1	−1	+1	+1	77.00	79.46	78.23
15	−1	+1	+1	+1	69.35	62.47	65.91
16	+1	+1	+1	+1	82.56	79.76	81.16

3.2. Factorial design adsorption experiments

The design matrix of coded values for factors and response in terms of percent removal of Pb(II) is shown in Table 2. The removal efficiency, R, is defined as:

$$R = \left(\frac{C_i - C_f}{C_i}\right) \times 100 \quad (1)$$

where C_i and C_f represent the initial and final concentrations of the metal ions, respectively. The results were analyzed using Minitab release 15.1 and the main effects and interaction between factors were determined. The effect of a factor is defined as the change in response, in this study the percentage of Pb(II) removal, occurring as a result of a change in the level of a factor from a lower to higher level. This is commonly called a main effect as it refers to the major factors of interest in the experiment [40]. The coded mathematical model utilized for 2^4 factorial designs can be given as:

$$\begin{aligned}\%R = {} & X_0 + X_1A + X_2B + X_3C + X_4D + X_5AB + X_6AC + X_7AD \\ & + X_8BC + X_9BD + X_{10}CD + X_{11}ABC + X_{12}ABD \\ & + X_{13}ACD + X_{14}BCD + X_{15}ABCD \quad (2)\end{aligned}$$

where R (%) is the percentage removal of Pb(II), X_0 is the global mean, X_i represents the regression coefficient relating to the main factor effects and interactions, and A, B, C, and D stand for pH, amount of adsorbent, initial concentration of Pb(II), and temperature, respectively. The effects, regression coefficients, standard errors and T values (standardized effects) appear in Table 3. The regression model coefficients are calculated by dividing the net effects by two. The standardized effects were obtained by dividing the regression coefficients by standard error. By substituting the coefficients X_i in Eq. (2) with their values from Table 3 we can derive a model equation relating the level of parameters and Pb(II) removal efficiency:

$$\begin{aligned}\%R = {} & 57.4. + 18.04A + 22.69B - 1.22C + 0.71D - 12.7AB \\ & + 4.85AC - 0.05AD - 5.98BC + 0.1BD - 0.11CD \\ & - 2.28ABC - 0.03ABD + 0.08ACD - 0.05BCD - 0.20ABCD \quad (3)\end{aligned}$$

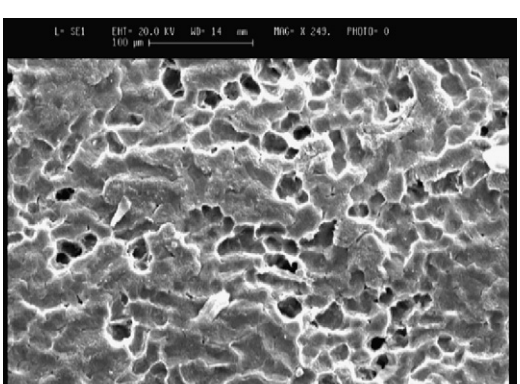

Fig. 1. SEM image of NaOH modified walnut shell.

3.3. Student's t-test

Student's t-test was carried out to determine whether the calculated main and interaction effects were significantly different from zero. Absolute values of the effects of main factors and the interaction of factors are illustrated in the Pareto chart (Fig. 2) in the horizontal columns. With a 95% confidence level and sixteen degrees of freedom, the value of t was equal to 2.12. To indicate the minimum statistically significant effect magnitude for the 95% confidence level, a vertical line is drawn in the Pareto chart. The bars for D, $ABCD$, CD, BD, ACD, BCD, AD, and ABD remained inside the reference line in the Pareto chart, showing that these terms contributed the least to the prediction of Pb(II) removal efficiency.

Table 3
Statistical parameters for a 2^4 design.

Term	Effect	Coefficient	Standard error	T
Constant		57.40	0.5303	108.25
A	36.07	18.04	0.5303	34.01
B	45.38	22.69	0.5303	42.79
C	−2.44	−1.22	0.5303	−2.30
D	1.41	0.71	0.5303	1.33
$A \times B$	−25.55	−12.78	0.5303	−24.10
$A \times C$	9.70	4.85	0.5303	9.15
$A \times D$	−0.09	−0.05	0.5303	−0.09
$B \times C$	−11.97	−5.98	0.5303	−11.29
$B \times D$	0.21	0.10	0.5303	0.19
$C \times D$	−0.23	−0.11	0.5303	−0.21
$A \times B \times C$	−4.57	−2.28	0.5303	−4.31
$A \times B \times D$	−0.06	−0.03	0.5303	−0.06
$A \times C \times D$	−0.15	0.08	0.5303	0.15
$B \times C \times D$	−0.10	−0.05	0.5303	−0.10
$A \times B \times C \times D$	−0.40	−0.20	0.5303	−0.38

Table 4
Analysis of variance.

Factor	Degrees of freedom	Sum of squares (SS)	Mean square (MS)	*F*-Value	*P*-Value
A	1	10408.4	10408.4	1156.69	0.000
B	1	16476.6	16476.6	1831.6	0.000
C	1	47.6	47.6	5.29	0.035
D	1	16.0	16.0	1.78	0.201
$A \times B$	1	5224.5	5224.5	580.60	0.000
$A \times C$	1	753.1	753.1	83.69	0.000
$A \times D$	1	0.1	0.1	0.01	0.932
$B \times C$	1	1146.2	1146.2	127.38	0.000
$B \times D$	1	0.3	0.3	0.04	0.849
$C \times D$	1	0.4	0.4	0.05	0.833
$A \times B \times C$	1	166.9	166.9	18.55	0.001
$A \times B \times D$	1	0.0	0.0	0.00	0.954
$A \times C \times D$	1	0.2	0.2	0.02	0.886
$B \times C \times D$	1	0.1	0.1	0.01	0.924
$A \times B \times C \times D$	1	1.1	1.3	0.14	0.711
Error	16	144.0	9.0		
Total	31	34385.7			

3.4. Analysis of variance (ANOVA)

In order to determine the significant main and interaction effects of factors influencing the removal efficiency of Pb(II), an analysis of variance (ANOVA) was performed. The sum of squares (SS) and mean square (MS) of each factor, *P*-value, and the *F*-ratio, defined as the ratio of the respective mean square effect and the mean square error, are shown in Table 4. Since for a 95% confidence level, 1 degree of freedom and 16 factorial tests $F_{0.05,1,16}$ is equal to 4.49, all the effects with *F*-values higher than 4.49 are significant. *P*-value is the probability value that is used to determine the statistically significant effects in the model. The importance of the data can be judged by its *P*-value, with values closer to zero denoting greater significance. For a 95% confidence level the *P*-value should be less than or equal to 0.05 for the effect to be considered statistically significant [43]. According to the obtained *F*-ratio and *P*-value, it seems that the effect of pH (*A*), adsorbent dose (*B*), initial concentration of metal ion (*C*), and the interaction effect of pH and adsorbent dosage ($A \times B$), pH and initial concentration of metal ion ($A \times C$), adsorbent dosage and initial metal ion concentration ($B \times C$), and pH and adsorbent dosage and initial concentration of Pb(II) ($A \times B \times C$) are statistically significant. The normal probability plot of standardized effects has been provided in Fig. 3. This graph is completely consistent with the analysis performed for significant results. The statistically significant effects are characterized by square signs which are situated away from the center line; however, the circle signs representing the insignificant effects tend to follow a normal distribution.

Table 5
Analysis of variance-reduced model.

Factor	Degrees of freedom	Sum of squares (SS)	Mean square (MS)	*F*-Value
A	1	10408.4	10408.4	1537.43
B	1	16476.6	16476.6	2433.77
C	1	47.6	47.6	7.03
AB	1	5224.5	5224.5	771.71
AC	1	753.1	753.1	111.24
BC	1	1146.2	1146.2	169.30
ABC	1	166.9	166.9	24.65
Residual error	24	162.4	6.77	
Lack of fit	8	18.4	2.3	0.34
Pure error	16	144.0	9.0	
Total	31	34385.7		

According to the student's *t*-test and *F*-test, the effect of temperature and several interaction effects which were statistically insignificant compared to the other effects were discarded, leading to the following equation:

$$\%R = 57.40 + 18.04A + 22.69B - 1.22C - 12.78AB + 4.85AC - 5.98BC - 2.28ABC \quad (4)$$

Based on Eq. (4), the model was recalculated, eliminating the effect of insignificant factors. Table 5 shows the analysis of variance for the reduced model. The lack of fit associated with the elimina-

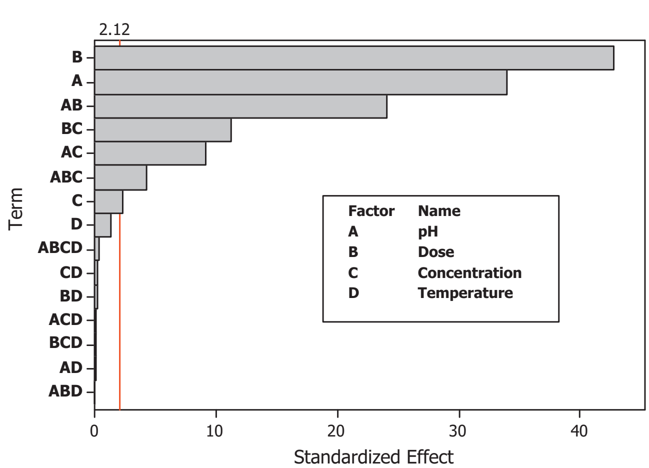

Fig. 2. Pareto chart for standardized effects.

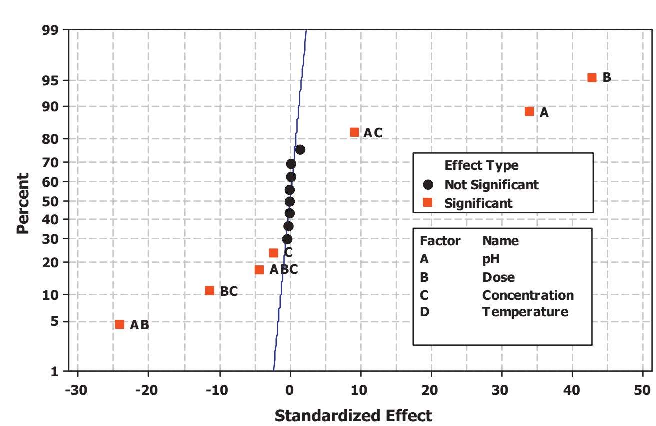

Fig. 3. Normal probability plot of standardized effects at $P = 0.05$.

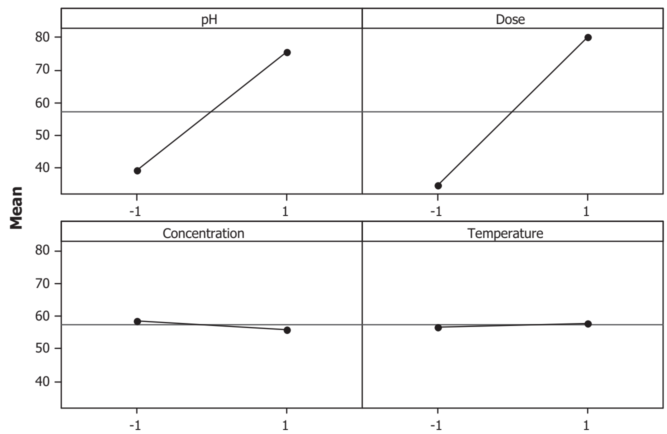

Fig. 4. Main effects plot for Pb(II) removal.

tion of some factors resulted in an *F*-value of 0.34. Since this value is very much lower than the tabulated $F_{0.05,8,16} = 2.59$, these factors did not have statistical significance.

3.5. Main and interaction effects

Analyzing the graphs of Fig. 4 and the coefficients of Eq. (4), it can be inferred that the adsorbent dosage (B) was the most important variable of the overall adsorption procedure since its coefficient was the largest (i.e. 22.69). The positive sign of this coefficient meant that Pb(II) removal was favored at high adsorbent values. Increasing the dose of walnut shell from 1 to 20 g/L increased the adsorption efficiency by 45.38%. This was due to the greater availability of the exchangeable sites or surface area at higher amounts of the sorbent. The same trend was previously reported for the adsorption of lead from aqueous solutions using sawdust [4].

The solution pH (A) also had a considerable effect on Pb(II) removal efficiency. An increase in the pH from 2 to 10 resulted in a 36.07% increase in Pb(II) adsorption. It has been reported in previous studies that the sorption of heavy metal ions is highly sensitive to changes in pH levels and that lead adsorption increases with a rise in pH values [36,44]. A reduction in metal ion removal efficiency at lower pH values is probably due to the existence of a relatively large number of hydrogen ions in the solution, which compete, with the metal ions for the adsorption sites of walnut shell.

The third important main effect regarding the adsorption process was the effect of the initial concentration of Pb(II) ions (C). An increase in the ion concentration from 10 to 90 mg/L decreased adsorption efficiency by 2.44%. This behavior can be attributed to the saturation of sorbent sites above a certain concentration of metal ions. At low concentrations, the ratio of active adsorption sites to the initial Pb(II) ions is larger, resulting in higher removal efficiency. However, at higher concentrations, the numbers of metal ions are relatively higher as compared to the available sorption sites, hence the lower metal removal percentage. The results of the present study for the effect of initial concentration on the removal efficiency of Pb(II) ions using modified walnut shell was in agreement with the previous results for adsorption of heavy metals onto rice bran [12], and removal of Ni(II) by sawdust [45].

According to *F*-ratio and *P*-value, the effect of temperature (*D*) on the removal of Pb(II) ions was not statistically significant and thus was not included in Eq. (4). Increasing the temperature from 15 to 45 °C increased the removal efficiency by 1.41%. Increasing the temperature may lead to an increase in the porosity and total pore volume of the adsorbent or to an enhancement in the chemical affinity of the adsorbent for metal cations [46]. On the other hand, it can weaken the adsorptive forces between the active sites of the adsorbents and the adsorbate material which increases the tendency to desorb metal ions from the interface to the solution. It is likely that these positive and negative effects neutralized each other in the present investigation, resulting in the negligible effect of temperature on Pb(II) cations adsorption. Cordero et al. [47] and Freitas et al. [27] reported an insignificant effect of temperature on Ca(II) and Cu(II) by *Fucus spiralis* and *Ascophyllum nodosum*, respectively.

The interaction effects plots are shown in Fig. 5. The non-parallel lines in this figure are indications of interaction between the two factors. Graphs of Fig. 5 and coefficients of Eq. (4) show negative interaction between pH and adsorbent dosage ($A \times B$), adsorbent dose and initial metal concentration ($B \times C$), and also between pH, adsorbent dosage and initial concentration of metal ion ($A \times B \times C$). A positive interactive effect was also observed between the solution pH and the metal ion concentration ($A \times C$). All of these interactions were more significant than the main factors *C* and *D* (initial concentration of metal ion and temperature).

The interaction plot for $A \times B$ (Fig. 5) indicates that decreasing the solution pH from 10 to 2 reduced Pb(II) removal efficiency by 61.62% (from 65.52 to 3.9%) at 1 g/L dose and 10.51% (from 85.35 to 74.84%) at 20 g/L. This indicates that at lower adsorbent

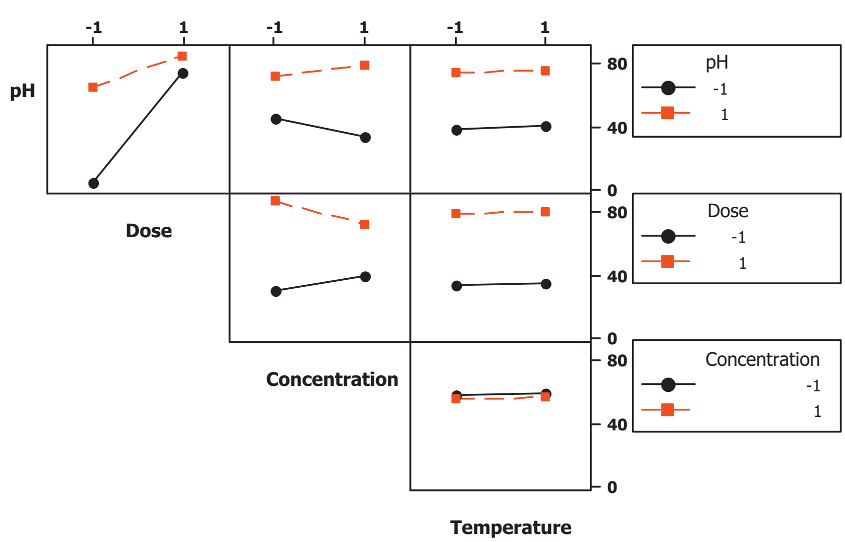

Fig. 5. Interaction effects plot for removal of Pb(II).

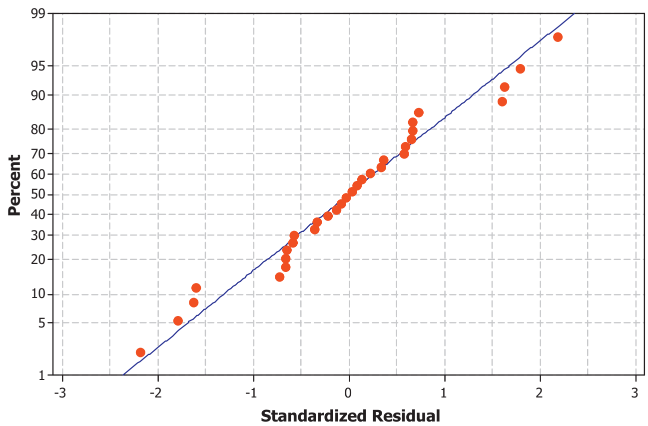

Fig. 6. Normal probability plot of residuals for Pb(II) removal efficiency.

dosages, changes in pH have a greater effect, but at higher adsorbent dosages, these changes were not as significant. Similarly, analyzing the interaction plot of $B \times C$ reveals that at lower metal concentrations (10 mg/L), metal removal efficiency was 29.95 and 87.3% at 1 and 20 g/L adsorbent dosage levels, respectively. However, at higher initial metal concentrations (90 mg/L), increasing the adsorbent dosage from 1 to 20 g/L increased metal removal efficiency from 39.48 to 72.89%. The $A \times C$ interaction plot illustrates that the increase in the pH from 2 to 10, led to a rise in lead removal efficiency from 45.44 to 71.81% at an initial metal concentration of 10 mg/L and 33.30 to 79.07% at 90 mg/L metal ion concentration. What this means is that the effect of pH was higher when the initial metal concentration was high. Other interactions showed no important features for discussion.

3.6. Normal probability plot of residuals

For the statistical analysis of the experimental data, it is necessary to assume that the data come from a normal distribution [48]. To determine whether or not the data set is normally distributed, the normal probability plot of residual values is shown in Fig. 6. The data set has normal distribution if the points fall close enough to the straight line. It is evident from the figure that the experimental points follow a straight line suggesting normal distribution of the data.

3.7. Optimization of Pb(II) adsorption by simplex method

As shown in Table 6, a total of 20 different conditions were tested in the simplex optimization phase: the four starting conditions and 16 additional experiments. Experiment number 16 was considered to be the best alternative due to the fact that it had the maximum response value, while response values decreased in the subsequent experiments. Fig. 7 shows the evolution of the response during these experiments. Improvements of about 15% were observed in Pb(II) removal efficiency in the 16th experiment; however, it was decided for the evolution to be continued to ascertain the achievement of the optimum conditions. The maximum Pb(II) removal efficiency observed in the experimental domain was 98.24%, which was achieved by 13.5 g/L of modified walnut shell at a pH level of 6.3 and initial metal concentration of 45.3 mg/L. The optimum pH condition of 6.3 obtained from the simplex method is in agreement with the findings of previous studies on adsorption of Pb(II) onto rice bran [12], modified wheat bran [2], and treated sawdust [11].

Table 6
Relation between Pb(II) removal efficiency and experimental conditions during simplex optimization.

Experiment number	pH	Adsorbent dose (g/L)	Initial metal concentration (mg/L)	Pb (II) removal (%)
1	2	20	10	85.20
2	2	1	90	2.12
3	10	1	10	54.76
4	10	20	90	82.50
5	4.7	7.3	63.3	78.33
6	7.8	8.4	32.2	63.91
7	5.7	11.7	53.7	89.35
8	6.8	12.8	41.7	86.23
9	7.4	17.4	62.6	83.71
10	4.3	17	31.3	85.77
11	3.8	10.3	21.9	61.12
12	6.5	15.6	52.4	95.27
13	8.4	9.7	67.2	76.51
14	5.3	15.2	40.3	87.26
15	4.9	15.5	55.9	86.00
16	6.3	13.5	45.3	98.24
17	7.0	12	60.6	79.03
18	5.7	14.4	45.4	94.90
19	6.6	17.3	41.7	96.12
20	7.2	16.5	47.5	83.25

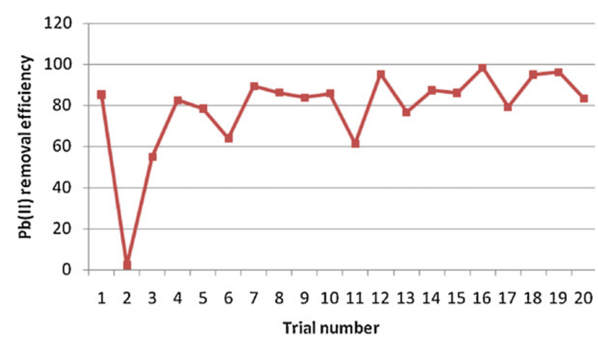

Fig. 7. Evolution of the response of Pb(II) removal efficiency.

4. Conclusions

In order to determine the effects of various operating conditions (pH, adsorbent dose, initial metal concentration and temperature) and their interactions on the overall adsorption of Pb(II) ions by modified walnut shell, a full 2^4 factorial design was performed. Analysis of variance (ANOVA), *t*-test and *F*-test showed that solution pH (A), adsorbent dose (B) and initial metal concentration (C) and also the interactions of $A \times B$, $A \times C$, $B \times C$, and $A \times B \times C$ were statistically significant. The adsorbent dosage was found to have the most significant impact on the Pb(II) removal efficiency, while the effect of temperature on the adsorption process was not significant. Following the determination of significant variables through factorial design, a modified simplex method was employed to achieve the best conditions for Pb(II) uptake. The modified simplex method was able to improve Pb(II) removal efficiency by about 15%. The maximum Pb(II) removal efficiency obtained from the optimization procedure was 98.24%, which was reached in 16 experiments. This optimum removal efficiency was achieved by 13.5 g/L of modified walnut shell at a pH level of 6.3 and initial Pb(II) concentration of 45.3 mg/L.

Acknowledgements

The authors would like to acknowledge Fars Province Water and Wastewater Co. for their partial financial support of this project.

References

[1] M.K. Mondal, Removal of Pb(II) ions from aqueous solution using activated tea waste: adsorption on a fixed-bed column, J. Environ. Manage. 90 (2009) 3266–3271.

[2] A. Ozer, Removal of Pb(II) ions from aqueous solutions by sulphuric acid-treated wheat bran, J. Hazard. Mater. 141 (2007) 753–761.

[3] A. Ahmad, M. Rafatullah, O. Sulaiman, M.H. Ibrahim, Y.Y. Chii, B.M. Siddique, Removal of Cu(II) and Pb(II) ions from aqueous solutions by adsorption on sawdust of Meranti wood, Desalination 247 (2009) 636–646.

[4] B. Yu, Y. Zhang, A. Shukla, S.S. Shukla, K.L. Dorris, The removal of heavy metals from aqueous solutions by sawdust adsorption-removal of lead and comparison of its adsorption with copper, J. Hazard. Mater. B 84 (2001) 83–94.

[5] M. Ahmedna, W.E. Marshall, A.A. Husseing, R.M. Rao, I. Goktepe, The use of nutshell carbons in drinking water filters for removal of trace metals, Water Res. 38 (2004) 1062–1068.

[6] M.M. Rao, G.P. Chandra Rao, K. Seshaiah, N.V. Choudary, M.C. Wang, Activated carbon from *Ceiba pentandra* hulls, an agricultural waste, as an adsorbent in the removal of lead and zinc from aqueous solutions, Waste Manage. 28 (2008) 849–858.

[7] D. Sad, G. Mahajan, M.P. Kaur, Agricultural waste material as potential adsorbent for sequestering heavy metal ions from aqueous solutions—a review, Bioresour. Technol. 99 (2008) 6017–6027.

[8] M. Uçurum, A study of removal of Pb heavy metal ions from aqueous solution using lignite and a new cheap adsorbent (lignite washing plant tailings), Fuel 88 (2009) 1460–1465.

[9] M. Nadeem, M. Shabbir, M.A. Abdullah, S.S. Shah, G. Mckay, Sorption of cadmium from aqueous solution by surfactant-modified carbon adsorbents, Chem. Eng. J. 148 (2009) 365–370.

[10] Q. Li, J. Zhai, W. Zhang, M. Wang, J. Zhou, Kinetic studies of adsorption of Pb(II), Cr(III) and Cu(II) from aqueous solution by sawdust and modified peanut husk, J. Hazard. Mater. 141 (2007) 163–167.

[11] A.K. Meena, K. Kadirvelu, G.K. Mishra, C. Rajagopal, P.N. Nagar, Adsorptive removal of heavy metals from aqueous solution by treated sawdust (*Acacia Arabica*), J. Hazard. Mater. 150 (2008) 604–611.

[12] S.F. Montanher, E.A. Oliveira, M.C. Rollemberg, Removal of metal ions from aqueous solutions by sorption onto rice bran, J. Hazard. Mater. B 117 (2005) 207–211.

[13] M. Martínez, N. Miralles, S. Hidalgo, N. Fiol, I. Villaescusa, J. Poch, Removal of lead(II) and cadmium(II) from aqueous solutions using grape stalk waste, J. Hazard. Mater. B 133 (2006) 203–211.

[14] Y. Bulut, Z. Tez, Adsorption studies on ground shells of hazelnut and almond, J. Hazard. Mater. 149 (2007) 35–41.

[15] P. Brown, I.A. Jefcoat, D. Parrish, S. Gill, E. Graham, Evaluation of the adsorptive capacity of peanut hull pellets for heavy metals in solution, Adv. Environ. Res. 4 (2000) 19–29.

[16] S. Wang, T. Terdkiatburana, M.O. Tadé, Single and co-adsorption of heavy metals and humic acid on fly ash, Sep. Purif. Technol. 58 (2008) 353–358.

[17] B.M.W.P.K. Amarasinghe, R.A. Williams, Tea waste as a low cost adsorbent for the removal of Cu and Pb from wastewater, Chem. Eng. J. 132 (2007) 299–309.

[18] M. Kazemipour, M. Ansari, S. Tajrobehkar, M. Majdzadeh, H.R. Kermani, Removal of lead, cadmium, zinc, and copper from industrial wastewater by carbon developed from walnut, hazelnut, almond, pistachio shell, and apricot stone, J. Hazard. Mater. 150 (2008) 322–327.

[19] J. Anwar, U. Shafique, W. uz-Zaman, M. Salman, A. Dar, S. Anwar, Removal of Pb(II) and Cd(II) from water by adsorption on peels of banana, Bioresour. Technol. 101 (2010) 1752–1755.

[20] N. Feng, X. Guo, S. Liang, Y. Zhu, J. Liu, Biosorption of heavy metals from aqueous solutions by chemically modified orange peel, J. Hazard. Mater. 185 (2011) 49–54.

[21] B.C. Qi, C. Aldrich, Biosorption of heavy metals from aqueous solutions with tobacco dust, Bioresour. Technol. 99 (2008) 5595–5601.

[22] S.K. Chatterjee, I. Bhattacharjee, G. Chandra, Biosorption of heavy metals from industrial waste water by Geobacillus thermodenitrificans, J. Hazard. Mater. 175 (2010) 117–125.

[23] C.G. Passos, F.S. Ribaski, N.M. Simon, A.A. dos Santos Jr., J.C.P. Vaghetti, E.V. Benvenutti, E.C. Lima, Use of statistical design of experiments to evaluate the sorption capacity of 7-amine-4-azaheptylsilica and 10-amine-4-azadecylsilica for Cu(II), Pb(II), and Fe(III) adsorption, J, Colloid Interf. Sci. 302 (2006) 396–407.

[24] M.E.R. Carmona, M.A.P. da Silva, S.G.F. Leite, Biosorption of chromium using factorial experimental design, Process Biochem. 40 (2005) 779–788.

[25] E.C. Lima, B. Royer, J.C.P. Vaghetti, J.L. Brasil, N.M. Simon, A.A. dos Santos Jr., F.A. Pavan, S.L.P. Dias, E.V. Benvenutti, E.A. da Silva, Adsorption of Cu(II) on *Araucaria angustifolia* wastes: determination of the optimal conditions by statistic design of experiments, J. Hazard. Mater. 140 (2007) 211–220.

[26] N.T. Abdel-Ghani, A.K. Hegazy, G.A. El-Chaghaby, E.C. Lima, Factorial experimental design for biosorption of iron and zinc using Typha domingensis phytomass, Desalination 249 (2009) 343–347.

[27] O. Freitas, C. Delerue-Matos, R. Boaventura, Optimization of Cu(II) biosorption onto *Ascophyllum nodosum* by factorial design methodology, J. Hazard. Mater. 167 (2009) 449–454.

[28] E. Da'na, A. Sayari, Optimization of copper removal efficiency by adsorption on amine-modified SBA-15: experimental design methodology, Chem. Eng. J. 167 (2011) 91–98.

[29] S. Chegrouche, A. Bensmaili, Removal of Ga(III) from aqueous solution by adsorption on activated bentonite using a factorial design, Water Res. 36 (2002) 2898–2904.

[30] J.L. Brasil, R.R. Ev, C.D. Milcharek, L.C. Martins, F.A. Pavan, A.A. Santos Jr., S.L.P. Dias, J. Dupont, C.P.Z. Noreña, E.C. Lima, Statistical design of experiments as a tool for optimizing the batch conditions to Cr(VI) biosorption on Araucaria angustifolia wastes, J. Hazard. Mater. B 133 (2006) 143–153.

[31] R. Gottipati, S. Mishra, Process optimization of adsorption of Cr(VI) on activated carbons prepared from plant precursors by a two-level full factorial design, Chem. Eng. J. 160 (2010) 99–107.

[32] W.S. Peternele, A.A. Winkler-Hechenleitner, E.A.G. Pineda, Adsorption of Cd(II) and Pb(II) onto functionalized formic lignin from sugarcane.bagasse, Bioresour. Technol. 68 (1999) 95–100.

[33] N.R. Axtell, S.P.K. Sternberg, K. Claussen, Lead and nickel removal using *Microspora* and *Lemna minor*, Bioresour. Technol. 89 (2003) 41–48.

[34] S.H. Hasan, P. Srivastava, M. Talat, Biosorption of lead using immobilized *Aeromonas hydrophila* biomass in up flow column system: factorial design for process optimization, J. Hazard. Mater. 177 (2010) 312–322.

[35] P. Ricou-Hoeffer, I. Lecuyer, P.L. Cloirec, Experimental design methodology applied to adsorption of metallic ions onto fly ash, Water Res. 35 (4) (2001) 965–976.

[36] G. Vázquez, M. Calvo, M.S. Freire, J. González-Alvarez, G. Antorrena, Chestnut shell as heavy metal adsorbent: optimization study of lead, copper and zinc cations removal, J. Hazard. Mater. 172 (2009) 1402–1414.

[37] Y. Wang, T. Han, Z. Xu, G. Bao, T. Zhu, Optimization of phosphorus removal from secondary effluent using simplex method in Tianjin, China, J. Hazard. Mater. B121 (2005) 183–186.

[38] N. El Hannafi, M.A. Boumakhla, T. Berrama, Z. Bendjama, Elimination of phenol by adsorption on activated carbon prepared from the peach cores: modeling and optimization, Desalination 223 (2008) 264–268.

[39] N. Banaeian, M. Zangeneh, Modeling energy flow and economic analysis for walnut production in Iran, Res. J. Appl. Sci. Eng. Technol. 3 (3) (2011) 194–201.

[40] J.N. Miller, J.C. Miller, Statistics and Chemometrics for Analytical Chemistry, fifth ed., Pearson, London, 2005.

[41] A. Kamoun, M. Jaziri, M. Chaabouni, The use of the simplex method and its derivatives to the on-line optimization of the parameters of an injection moulding process, Chemom. Intell. Lab. Syst. 96 (2009) 117–122.

[42] A.S. Araujo, M. Jaroniec, Determination of the surface area and mesopore volume for lanthanide-incorporated MCM-41 materials by using high resolution thermogravimetry, Thermochim. Acta 345 (2000) 173–177.

[43] A. Srinivasan, T. Viraraghavan, Oil removal from water by fungal biomass: a factorial design analysis, J. Hazard. Mater. 175 (2010) 695–702.

[44] Y. Kikuchi, Q. Qian, M. Machida, H. Tatsumoto, Effect of ZnO loading to activated carbon on Pb(II) adsorption from aqueous solution, Carbon 44 (2006) 195–202.

[45] S.S. Shukla, L.J. Yu, K.L. Dorris, A. Shukla, Removal of nickel from aqueous solutions by sawdust, J. Hazard. Mater. B121 (2005) 243–246.

[46] V. Ponnusami, V. Krithika, R. Madhuram, S.N. Srivastava, Biosorption of reactive dye using acid-treated rice husk: factorial design analysis, J. Hazard. Mater. 142 (2007) 397–403.

[47] B. Cordero, P. Lodeiro, R. Herrero, M.E.S. de Vicente, Biosorption of Cadmium by *Fucus spiralis*, Environ. Chem. 1 (2004) 180–187.

[48] J. Antony, Design of Experiments for Engineers and Scientists, Butterworth-Heinemann, New York, 2003.