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Adsorption of Cu(II) and Pb(II) from aqueous solution using Jordanian natural zeolite based on factorial design methodology

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ABSTRACT

Parametric study was conducted to study the adsorption of Cu(II) and Pb(II) from aqueous solution using Jordanian Natural Zeolite (JNZ) as an adsorbent. Two levels factorial design was implemented to determine the main and interaction effects of initial metal ion concentration (20–100 mg/L), pH (2–4), and temperature (20–50ºC) on the ion uptake as a response variable. The effect of initial ion concentration was found the most prominent impact in increasing the ion uptakes ($t = 352.86$, $p = 0.00$ for Cu(II) and $t = 1538.2$, $p = 0.00$ for Pb(II)). Initial pH value was found to have a slight positive effect on the ion uptake ($t = 13.35$, $p = 0.006$ for Cu(II) and $t = 9.49$, $p = 0.011$ for Pb(II)). Overall, the effects of some interactions among the studied parameters were significant on ion uptakes. The highest uptakes obtained were 65 and 122.13 mg/g JNZ for Cu(II) and Pb(II), respectively. Both Langmuir and Freundlich isotherms were found to be appropriately fitting the adsorption data. Factorial design was a powerful method, which revealed the main and interaction effects and their relative magnitudes. The revealed insights will help in searching for a global optimum adsorption conditions.

Keywords: Factorial design; Zeolite; Metal ion; Sorption isotherms

1. Introduction

Jordan has limited water resources. This necessitates the adoption of stringent policies to conserve water consumption, prevent resources pollution, and recycle wastewater for better use. Wastewater from many industries such as smelting, metal plating, mining, pigments, stabilizer and alloy manufacturing contains heavy metals such as Pb, Hg, Cr, Ni, Cd, Cu, and Zn [1, 2]. The increase in the level of heavy metals represents a serious pollutant to human beings and other living organisms [1, 3]. Eexcessive level of Pb(II) in drinking water (>15 μg/L) can damage the kidney, liver, basic cellular processes and brain functions [4]. Also, high concentration of Cu(II) (>2 mg/L) may cause serious toxicological effects on humans and animals [5].

Numerous processes exist for removing soluble heavy metal ions from water including chemical precipitation, ultra filtration, evaporation, and electrodialysis. Among the different treatment methods, adsorption process has been shown to be an economically feasible method for removing heavy metal from industrial wastewater [3, 6]. Activated carbon is a widely used adsorbent, but high production and regeneration costs make it uneconomical [7, 8]. The literature shows a growing interest in finding alternative low cost adsorbents for heavy metal removal from aqueous solution [8–11].

Natural zeolite is an abundant resource of aluminosilicate available in many countries such as Greece, UK, Italy, Mexico, Iran and Jordan. Most common natural zeolites are formed by alteration of glass-rich volcanic rock (tuff) with fresh water in playa lakes or seawater [12]. Natural zeolite has a three dimensional framework structure with a negatively charged lattice which is balanced by cations (e.g. Na, K, Ca, and Mg). Theses cations are exchangeable with certain cations in the solutions such as heavy metal ions [2, 13]. Therefore, natural zeolite has been explored as effective adsorbent for the removal of various heavy metals [14–16]. Jordanian natural zeolite (JNZ) has been investigated as adsorbent for Ni(II) [2], Pb(II) [2, 17, 18], Fe(III) [19], and for treating effluents from electroplating factories [20].

Most adsorption studies adopt univariate optimization strategy to determine the optimum conditions for the adsorption process. Since many interactions of the experimental adsorption parameters are frequently evidenced, experimental factorial design can be more effectively applied to extract more information while requiring a minimum number of experiments [21, 22]. This study is the first attempt to implement factorial design approach in studying adsorption of heavy metal ions using JNZ.

The aim of the present work was to use experimental factorial design in the study of adsorption of Pb(II) and Cu(II) using JNZ. In this research work, a study of the effect of three input parameters (initial ion concentration, initial pH, and temperature) on the uptake of the heavy metal ion has been undertaken.

2. Experimental and methods

2.1. Materials and chemicals

A sample of JNZ was obtained from Tell Rmah area through the Natural Resources Authority (NRA), Amman, Jordan. The chemical compositions of the main compounds are presented in Table 1 [23]. Zeolites rock samples were broken into small pieces, crushed using a jaw crusher, dried at 100°C in an oven, sieved and stored. The particle size of zeolite used was in the range of 500–710 μm. The BET surface area and pore volume were measured by N_2 adsorption-desorption at 77 K using ASAP 2400 (Micromeritics) instrument.

Stock solutions (100 mg/L) of Pb(II) and Cu(II) were prepared by dissolving carefully measured amounts of $Pb(NO_3)_2$ and $CuSO_4.6H_2O$ salts in deionized water. Standard solutions of the required concentrations were prepared by dilution with deionized water.

2.2. Batch adsorption studies

Batch adsorption experiments were conducted in 50 ml polyethylene bottles using 0.02 g of JNZ mixed with 25 ml of solutions. The initial pH of the Cu(II) and Pb(II) solutions was adjusted using H_2SO_4 and HNO_3, respectively. The samples were shaken for 5 days at 300 rpm. Afterwards, the solutions were separated from the adsorbent by filtration through Whatman filter paper (No. 42). The final concentration of ions was analyzed using atomic absorption spectrophotometer (solaar AA series).

The amount of ion uptake was determined using the following equation:

$$q = \frac{C_0 - Ce}{m} V, \tag{1}$$

where q is the amount of ion uptake (mg/g), C_0 and C_e are the initial and equilibrium concentrations of the ions in the solution, respectively (mg/l), m is the mass of adsorbent (g), and V is the volume of the solution (l).

2.3. Experimental factorial design

Initial ion concentration (X_1), initial pH (X_2), and temperature (X_3) of the solution, were chosen as independent input variables and the amount of ion uptake (q) as dependent output response variable. Since the factorial design involves three independent variables at two levels (low designated as – and high designated as +), 2^3 full-factorial design with a center point (designated as 0) has been applied. To quantify the variability in the collected data, the center point run was repeated three times. Table 2 shows the complete design matrix of experiments and the results obtained for the uptakes.

The results of the factorial design were analyzed using MINITAB 14 statistical software to estimate the response of the dependent variable. The behavior of the system was modeled according to the following equation:

$$\begin{aligned} q_i = {} & b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_{12}X_1X_2 + \\ & b_{13}X_1X_3 + b_{23}X_2X_3 + b_{123}X_1X_2X_3, \end{aligned} \tag{2}$$

where q_i is the theoretical response function.

Table 1
Chemical compositions of the main compounds of Jordanian natural zeolites [23].

Chemical compound	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	K_2O	Na_2O
Composition (%)	42.0	12.8	12.1	10.1	8.5	0.8	4.0

Table 2
Experimental design matrix and results for uptake of Cu(II) and Pb(II) from aqueous solution using Jordanian natural zeolite.

Run	Independent variables (levels)			Ion uptake, q (mg/g)	
	X_1 (mg/L)	X_2	X_3(°C)	Cu(II)	Pb(II)
1	20 (–1)	2 (–1)	20 (–1)	16.50	23.70
2	100 (+1)	2 (–1)	20 (–1)	62.50	114.37
3	20 (–1)	4 (+1)	20 (–1)	16.35	23.78
4	100 (+1)	4 (+1)	20 (–1)	65.00	115.63
5	20 (–1)	2 (–1)	50 (+1)	15.75	24.50
6	100 (+1)	2 (–1)	50 (+1)	61.25	121.25
7	20 (–1)	4 (+1)	50 (+1)	16.78	24.63
8	100 (+1)	4 (+1)	50 (+1)	65.00	122.13
9	60 (0)	3 (0)	35 (0)	45.38	71.63
10	60 (0)	3 (0)	35 (0)	45.75	71.78
11	60 (0)	3 (0)	35 (0)	45.52	71.63

2.4. Adsorption isotherms

The adsorption equilibrium is commonly described by Langmuir [24] and Freundlich isotherms [25]. The linearized form of Langmuir isotherms can be represented by the following equation:

$$\frac{C_e}{q} = \frac{1}{bQ_{\max}} + \frac{C_e}{Q_{\max}}. \qquad (3)$$

And the linearized form of Freundlich isotherm can be represented by the following equation:

$$\log q = \log K_F + \frac{1}{n} \log C_e, \qquad (4)$$

where b is the Langmuir affinity constant (L/mg), $Q_{\max}$ is the maximum adsorption capacity of the adsorbate (mg/g), K_F (mg/g) is the Freundlich constant, and n is the Freundlich exponent.

3. Results and discussion

3.1. Properties of Jordanian natural zeolite

The main chemical compositions of JNZ were determined and listed in Table 1. The Al/Si ratio of JNZ was determined based on the chemical composition presented in Table 1. Also, the N_2 adsorption isotherm, presented in Fig. 1, was used to determine the BET surface area as well as the pore volume of JNZ. These results for JNZ are compiled in Table 3 together with those of other natural zeolites from other resources. The data presented in Table 3 show that JNZ is characterized by a high Al/Si ratio, a high BET surface area, and a high pore volume when compared with zeolites from other resources. The high ratio of Al/Si enables JNZ to have a highly negative framework favorable for higher exchange capability [8].

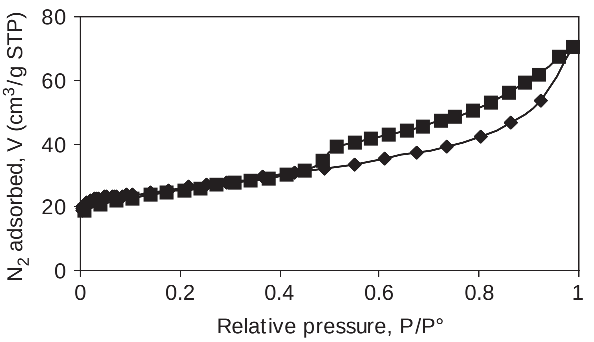

Fig. 1. N_2 adsorption isotherm of Jordanian natural zeolite.

3.2. Factorial design analysis

The characteristic parameters that affect the metallic ion uptake by any adsorbent are the initial ion concentration, solution pH, and temperature. The study of these variables based on the univariate approach is tedious and time-consuming. The main disadvantage of this approach is the difficulty of determining the global optimum conditions. Part of this difficulty is due to neglecting the effect of interactions among all parameters. More importantly, varying the level of input parameters in univariate approach would result in different local optimum conditions [31–33]. To overcome these difficulties and disadvantages, an effective experimental design methodology was used to investigate not only the effects of those input parameters, but also the effect of interactions among them.

Table 3
Al/Si ratio, BET surface area, and pore-volume of Jordanian natural zeolite compared with that of other natural zeolites.

Zeolite's origin	Al/Si (mol/mol)	BET (m^2/g)	Pore volume (cm^3/g)	Reference
JNZ	0.357	84.7	0.11	This work
Polish	–	13.2	0.043	[3]
Australian	0.224	16.0	0.039	[26]
Turkish	0.20	54–95	–	[27]
Greek	0.232	–	–	[13]
	–	20.3	–	[28]
Italian	0.279	–	–	[29]
	–	27.0	–	[30]

As a part of applying this experimental design methodology, the metallic ion uptake was chosen as the response output variable, and initial ion concentration (X_1), initial pH (X_2), and temperature (X_3) of the solution were chosen as the input parameters. These choices enabled us to determine the main effects, and the cross parameters as the interaction effect. These effects are regressed by a linear model with coefficients of statistical significance indicated by the probability (*p*-value) and the student's *t*-test. Based on this methodology, a full 2^3 experimental factorial design was constructed and presented in Table 4. The number of these experiments represents the minimum number necessary to determine the main and interaction effects.

The significance of the model coefficients is determined based on Student's *t*-test and the value of probability p. The higher the '*t*' value and the smaller the *p*-value, the more significant the corresponding coefficient term is [18]. Results presented in Table 4 show that the initial Cu(II) concentration (X_1), solution pH (X_2) and their interaction (X_1X_2) were significant within the 95% confidence interval ($p \leq 0.05$). However, solution temperature (X_3) and its interaction with the initial ion concentration (X_1X_3) were not significant.

For the case of Pb(II) adsorption, the effect of all parameters and most interactions were significant within 95% confidence interval except the interactions between pH and temperature and the interaction among all the parameters ($X_1X_2X_3$) were not significant. The interaction between pH and initial ion concentration with the uptake of both ions suggests that they are related. Such relation would not be clear if experiments were carried out using univariate approach.

Analysis of variance (ANOVA) was further carried out in order to confirm the above conclusions obtained using *t*-test. ANOVA is a statistical technique that subdivides the total variation in a set of data into component parts associated with specific sources of variation for the purpose of testing hypotheses on the parameters of the model [29]. F random variable is used as a test statistic. The higher the value of F and the smaller the value of *p* indicate statistical significance.

Table 5 shows the ANOVA for 2^3 factorial design for the adsorption of each heavy metal studied. For both ions, it was found that the main effects, two way interactions, and curvature were significant at 95% confidence interval ($p < 0.05$). On the other hand, three way interaction effects were insignificant at 95% confidence interval ($p > 0.05$).

The model, which is presented by Eq. (2), was fitted to experimental data shown in Table 4. Based on the above discussion, the insignificant coefficients and their terms were deleted from the general fitting model (Eq. 2). The refined fitting models for the two studied systems in term of coded parameters are as follows:

$$q\,(\mathrm{Cu(II)}) = 23.55X_1 + 0.89X_2 + 0.672X_1X_2 + 0.303X_2X_3 + 39.89, \tag{5}$$

$$q\,(\mathrm{Pb(II)}) = 47.09X_1 + 0.291X_2 + 1.878X_3 + 0.241X_1X_2 + 1.466X_1X_3 + 71.24. \tag{6}$$

3.2.1 Main effects

The main effects of input parameters on metal ion uptake are presented in Fig. 2. It is clear (Fig. 2 and Table 4) that initial ion concentration has a sharp effect in increasing the uptake. This agrees with the intuition that supplying more ions to empty active sites will increase the uptake, while the JNZ still away from saturation. This trend agrees with the results reported in literature regarding the same zeolite [2,19].

The effect of initial pH shows a slight increase in the uptake of Cu(II) and almost no effect for the adsorption of Pb(II) (Fig. 2). However, Table 4 shows that pH is significant for both ions. It is clear that the effect of initial pH is diminished due to the relatively large concentration's effect. In order to clarify the effect of pH, clearer picture of pH effect mechanism should to be discussed. First, at high pH, the hydronium ion will compete with the heavy metal ion for zeolite's active sites [3,13,34].

Table 4
Full 2^3 factorial design for metal ion uptake (q) versus initial ion concentration (X_1), pH (X_2), and temperature (X_3). Coefficients are given in coded units.

Term	Effect	Coefficient	SE	t	p–value
(a) For Cu(II)					
Constant		39.89	0.0667	597.78	0.000
X_1	47.09	23.55	0.0667	352.86	0.000
X_2	1.781	0.89	0.0667	13.35	0.006
X_3	−0.394	−0.197	0.0667	−2.95	0.098
X_1X_2	1.344	0.672	0.0667	10.07	0.010
X_1X_3	−0.231	−0.116	0.0667	−1.73	0.225
X_2X_3	0.606	0.303	0.0667	4.54	0.045
$X_1X_2X_3$	0.0188	0.0094	0.0667	0.14	0.901
$R^2 = 0.9999$					
(b) For Pb(II)					
Constant		71.24	0.0306	2326.9	0.000
X_1	94.19	47.09	0.0306	1538.2	0.000
X_2	0.581	0.291	0.0306	9.49	0.011
X_3	3.756	1.878	0.0306	61.34	0.000
X_1X_2	0.481	0.241	0.0306	7.86	0.016
X_1X_3	2.932	1.466	0.0306	47.87	0.000
X_2X_3	−0.081	−0.041	0.0306	−1.33	0.316
$X_1X_2X_3$	−0.106	−0.053	0.0306	−1.74	0.225
$R^2 = 1.0$					

Table 5
Analysis of variance (ANOVA) for Pb(II) and Cu(II) uptakes using Jordanian natural zeolites for full 2^3 factorial design (coded units).

p-value	F	Adj SS	Seq SS	DF	Source
					a. Cu(II)
0.000	41565.36	4442.3	4442.3	3	Main effects
0.024	41.67	4.45	4.45	3	Two-way interactions
0.901	0.02	0.0	0.0	1	Three-way interactions
0.001	1961.56	69.88	69.88	1	Curvature
		0.07	0.07	2	Residual error
		0.07	0.07	2	Pure error
			4516.7	10	Total
					b. Pb(II)
0.000	789947.54	17773.8	17773.8	3	Main effects
0.001	784.93	17.7	17.7	3	Two-way interactions
0.225	3.01	0.0	0.0	1	Three-way interactions
0.018	53.2	0.4	0.4	1	Curvature
		0.0	0.0	2	Residual error
		0.0	0.0	2	Pure error
			17791.9	10	Total

DF, degree of freedom; Seq SS, sequential sum of squares; Adj SS, adjusted sum of square; F, Fisher's variance ratio; p, probability.

This competition will result in lowering the uptake of heavy metals by JNZ. It is apparent that using solutions with pH of 4 gives the highest uptake. Similar results have been reported for Pb(II) [2] and Cu(II) ions [35, 36]. Second, as a part of the adsorption mechanism, hydronium ion will be consumed, which will result in increasing the value of pH. If the pH value exceeded a certain limit (5.8 for Cu(II) and 5.3 for Pb(II)) the heavy metal

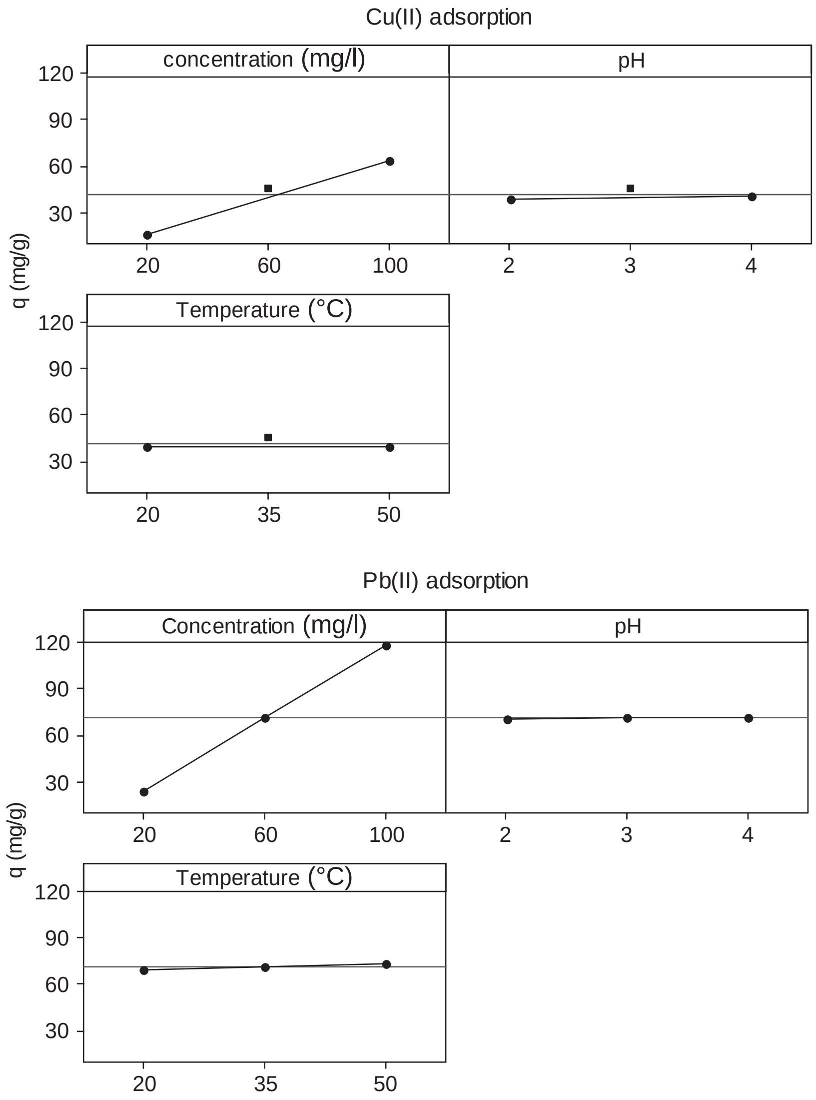

Fig. 2. Main effects of the data means for Cu(II) and Pb(II) adsorption uptakes using Jordanian natural zeolite.

ions would precipitate [35]. Consequently, heavy metal uptake would be due to adsorption and precipitation as hydroxides. While undergoing a heavy metal adsorption experiments, the experimental design matrix was constructed to be away from these limits, and the final pH for all samples was measured (results are not shown).

The slight increase in Pb(II) uptake with temperature (Table 4, Fig. 2) was consistent with the literature [37–39]. This can be attributed to two main reasons. First, increasing the temperature weakened the electrostatic interactions and decreased the ion salvation [37]. This decrease resulted in smaller ion sizes and enhanced the uptake. Second, high temperature might activate the Pb(II) for enhancing adsorption at the coordinating sites of the zeolite [8]. On the contrary, Al Haj Ali et al. [2] found the uptake of Pb(II) independent upon temperature in the range from 20 to 35°C.

For the case of Cu(II) adsorption, the increase of temperature was found insignificant (Fig. 2 and Table 4). Contradictory trends were reported in literature which either stated a slight decrease [40] or increase [36] in ion uptake.

Factorial design analysis helps us to get more insight on the relative magnitude of major effects. It is clearly shown in Table 4 that the value of the effect of ion concentration is at least 25 times higher than the effect of the other two main effects in both cases. This shows clearly that the effect of initial ion concentration is dominant.

The uptake of Pb(II) was higher than that of Cu(II) (Fig. 2). This behavior is in agreement with other studies [35, 37]. The higher Pb(II) uptake can be explained by the following three reasons. First, the hydrated ionic radius of Pb(II) (4.01 Å) is smaller than that of Cu(II) (4.19 Å) [41, 42]. Second, the hydration energy of Cu(II) (Å502 kcal/mol) is higher than that of Pb(II) (Å 354 kcal/mol), and rejection of water molecules increases when hydration energy increases [35, 37]. Third, adsorption of Cu(II) as hydroxy complexes on the surface of zeolite results in a decrease in the surface negative charge and thus a decrease in the uptake.

3.2.2 Interaction effects

One of the major benefits of factorial design approach is that it gives more insight about the interaction between the input parameters. Fig. 3 shows a slight interaction between input parameters (i.e. slight change in slope of the lines in Fig. 3). However, Table 4 shows that some of these interactions have significant effects at 95% confidence interval ($p < 0.05$). The interaction effects might be diminished due to the relatively large effect of concentration or to the narrow ranges of these parameters studied. The interactive effects would have been observed if experiments were carried out in a wider range of parameters studied.

3.3 Adsorption isotherms of Cu(II) and Pb(II) on Jordanian natural zeolite

Chemical equilibrium is described by two fundamental adsorption isotherms (Freundlich and Langmuir). Because of the insignificance of the temperature effect on Cu(II) uptake, all experimental data collected in the range of 20–50°C were used to fit the model isotherms. Values of the fitted parameters of Langmuir and Freundlich isotherms for Cu(II) and Pb(II) are listed in Table 6. The higher correlation coefficients (R^2) for Freundlich model indicated a heterogeneous adsorption of Pb(II) and Cu(II) on JNZ. However, both models show correlation coefficients higher than 0.95 except for the case of Pb(II) adsorption at 50°C when fitted using Langmuir.

To reveal the essential characteristics of Langmuir isotherm, the dimensionless equilibrium parameter (R_L) was calculated based on Eq. (7) [31, 43]. R_L values will determine the type of isotherm to be either favorable ($0 < R_L < 1$), unfavorable ($R_L > 1$), linear ($R_L = 1$) or irreversible

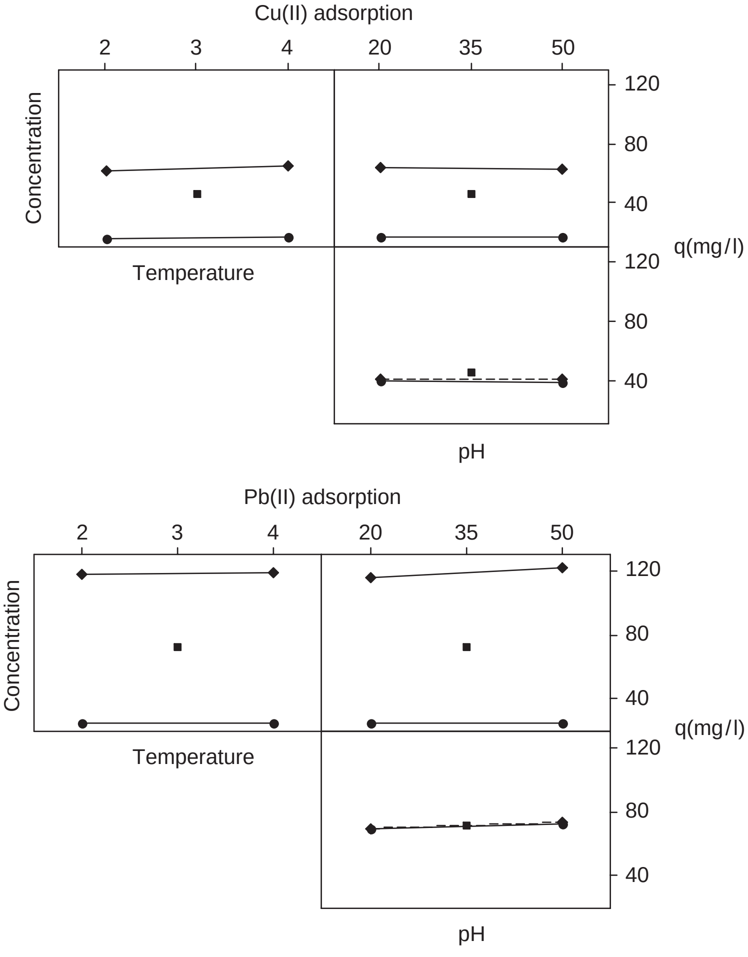

Fig. 3. Interaction effects of the data mean for Cu(II) and Pb(II) adsorption uptakes using Jordanian natural zeolite.

Table 6
Parameters of fitted Lagmuir and Freundlich isotherms for Cu(II) and Pb(II) uptake using Jordanian natural zeolite.

Ion	Temperature	Langmuir				Freundlich		
		Q_{max}	b	R^2	R_L	K_F	$1/n$	R^2
Cu(II)	20–50°C	119.05	0.0234	0.9706	0.3	4.369	0.7014	0.9778
Pb(II)	20°C	256.41	0.1015	0.9764	0.09	56.707	0.775	0.9806
	50°C	285.71	0.2756	0.8377	0.035	23.613	0.7611	0.9973

($R_L = 0$) [31, 43, 44]. The values of R_L listed in Table 5 show a favorable isotherm:

$$R_L = \frac{1}{1 + bC_o}. \tag{7}$$

The maximum adsorption capacities for Pb(II) and Cu(II) were 285.71 and 119.05 mg/g, respectively, using Langmuir isotherm (Table 6). Several investigations have been conducted to obtain adsorption capacity of Pb(II) and Cu(II) on natural zeolite. Berber-Mendoza *et al*. [45] investigated different zeolite samples from Mexico and found the adsorption capacity of Pb(II) in the range of 40–120 mg/g. Sprynskyy et al. [3] found the adsorption capacity of Pb(II) and Cu(II) on natural zeolite to be 26.8 and 25.7 mg/g, respectively. Erdem et al. [16] investigated adsorption of different heavy metal ions on Turkish zeolite and found the adsorption capacity of Cu(II) to be 141 mg/g. Cincotti [46] summarized the results from the previous investigations and their work on various natural zeolite samples and found the adsorption capacity of Pb(II) and Cu(II) in the range of 33.3–393.7 and 5.9–93.3 mg/g, respectively. Clearly, the values of maximum capacity, from this work, are in the range, but higher than most of the published results. This high capacity might be attributed to the high Al/Si ratio as well as to the high BET surface area of JNZ compared to other natural zeolites.

4. Conclusion

The effect of parameters such as initial ion concentration, solution pH, and temperature on the uptake of Cu(II) and Pb(II) from aqueous solution was studied on samples of Jordanian natural zeolites (JNZ). Experimental factorial design was implemented to evaluate the main and interaction effects on the metal ion uptake as a response variable.

It was found that initial ion concentration has the most pronounced effect on the adsorption process and pH has a slight positive effect. It was found that most prominent interaction effect was between initial ion concentration and solution pH.

Langmuir and Freundlich isotherms were employed to model the ion uptake. Both models satisfactorily fitted the data. The adsorption capacities of JNZ were 119.05 mg/g for Cu(II) and 285.71 mg/g for Pb(II), based on Langmuir isotherm. In conclusion, JNZ had excellent capability of removing Cu(II) and Pb(II) from aqueous solutions.

Factorial design methodology was able to predict not only the main effect of each parameter, but also the interaction effects among them. Satisfactory empirical models, which relate the uptakes to the parameter studied, were developed. This study will pave the road in searching for global optimum operating conditions to the adsorption process on JNZ.

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References

[1] I. Kula, M. Ugurlu, H. Karaoglu, and A. Celik, Bioresour. Technol., 99 (2008) 492–501.
[2] A.A.H.j Ali and R.E.Bishtawi, J. Chem. Technol. Biotechnol., 69 (1997) 27–34.
[3] M. Sprynskyy, B. Buszewski, A. P. Terzyk, and J. Namiesnik, J. Colloid Interface Sci., 304 (2006) 21–28.
[4] R. Naseem, S.S. Tahir, Water Res., 35(16) (2001) 3982–3986.[5] E. Eren, J. Hazard. Mater., 159 (2008) 235–244.
[6] J. Peric´, M. Trgo, N.V. Medvidovic´, Water Res., 38 (2004) 1893–1899.
[7] S. Doyurum and A. Celik, J. Hazard. Mater., B138 (2006) 22–28.
[8] S. Babel and T. Kurniawan, J. Hazard. Mater., B97 (2003) 219–243.
[9] N. Balkaya and N. Bektas, DWT, 3 (2009) 43-49.
[10] S. Dib and M. Boufatit, DWT, 5 (2009) 106–110.
[11] B.E. Eswed, R.I. Yousef, M. Alshaaer, F. Khalili and H. Khoury, DWT, 8 (2009) 124–130.
[12] V.B. Almaraz, P. Trocellier, I.D. Rangel, Nucl. Instrum. Methods Phys. Res., B210 (2003) 424–428.
[13] V. Inglezakis, M. Loizidou, and H. Grigoropoulou, Water Res., 36 (2002) 2784–2792.
[14] M.V. Mier, R.L. Callejas, R. Gehr, B.E.J. Cisneros and P.J. J. Alvarez, Water Res., 35 (2001) 373–378.
[15] S.M.D. Bosco, R.S. Jimenez and W.A. Carvalho, J. Colloid. Interface Sci., 281 (2005) 424–431.
[16] E. Erdem, N. Karapinar and R. Donat, J. Colloid Interface Sci., 280 (2004) 309–314.

[17] R.F.E. Bishtawi and A.A.H. Ali, J. Environ. Sci. Health, A36(6) (2001) 1055–1072.
[18] K.M. Ibrahim and T. Akashah, Environ. Geol., 46(6-7) (2004) 865–870.
[19] M.A. Anber and Z.A.Anber, Desalination, 225 (2008) 70–81.
[20] K.M. Ibrahim, T.N.E. Deen, and H. Khoury, Environ. Geol., 41 (2002) 547–551.
[21] D.C. Montgomery, Design and analysis of experiments, 5th edn, NewYork, John Wiley & Sons, 2001.
[22] G.E.P. Box, W.G. Hunter, and J.S. Hunter, Statistics of experiments–-An introduction to design, data analysis and model building, New York, John Wiley & Sons, 1978.
[23] M.K. Nawasreh, S.M. Yasin, and N.A. Zurquiah, Mineral status and future opportunity of zeolitic tuff, Natural Resource Authority (2006), Jordan, accessed on September 17th (2009). http://www.nra.gov.jo/index.php?option=com_content&task=view&id=5&Itemid=39
[24] I. Langmuir, J. A. Chem. Soc., 40 (1918) 1361–1403.
[25] H.M.F. Freundlich, J. Phys. Chem., 57 (1906) 385–470.
[26] S. Wang and Z.H. Zhu, J. Hazard. Mater., B136 (2006) 946–952.
[27] A.H. Őren and A. Kaya, J. Hazard. Mater., B131 (2006) 59–65.
[28] E.Á. Ayuso, A.G. Sánchez, and X. Querol, Water Res., 37 (2003) 4855–4862.
[29] D. Caputo, F. Iucolano, F. Pepe, and C. Colella, Microporous. Mesoporous. Mater., 105 (2007) 260–267.
[30] P. Castaldi, L. Santona, S. Enzo, and P. Melis, J. Hazard. Mater., 156 (2008) 428–434.
[31] B.H. Hameed, I.A.W. Tan, and A.L. Ahmad, J. Hazard. Mater., 158 (2008) 324–332.
[32] K. Ravikumar, B. Deebika, and K. Balu, J. Hazard. Mater., 122 (2005) 75–83.
[33] A.R. Cestari, E.F.S. Vieira, I.A. Oliveira, and R.E. Bruns, J. Hazard. Mater., 143 (2007) 8–16.
[34] S. Wang, T. Terdkiatburana, and M.O. Tadé, Sep. Purif. Technol., 62 (2008) 64–70.
[35] V.J. Inglezakis, M.D. Loizidou, and H.P. Grigoropoulou, J. Collid. Interface Sci., 261 (2003) 49–54.
[36] M.A. Stylianou, V.J. Inglezakis, K. G. Moustakas, S.P. Malamis, M.D. Loizidou, Desalination, 215 (2007) 133–142.
[37] V.J. Inglezakis, M.D. Loizidou, and HP. Grigoropoulou, J. Collid. Interface Sci., 275 (2004) 570–576.
[38] V.J. Inglezakis, M.A. Stylianou, D. Gkantzou, M.D. Loizidou, Desalination, 210 (2007) 248–256.
[39] L. Ćurković, Š.C. Stefanović, T. Filipan, Water Res., 31 (1997) 1379–1382.
[40] A. Woinarski, I. Snape, G. Stevens, S. Stark, Cold Regions Sci. Technol., 37 (2003) 159–168.
[41] R.S. Vieira, E. Guibal, E.A. Silva and M.M. Beppu, Adsorption, 13 (2007) 603–611.
[42] D.H. Lee and H. Moon, Korean J. Chem. Eng., 18 (2001) 247–256.
[43] T.W. Weber and R.K. Chakkravorti, AIChE J., 20 (1974) 228.
[44] I.A.W. Tan, B.H. Hameed, and A.L. Ahmad, Chem. Eng. J., 127 (2007) 111–119.
[45] MS.B.. Mendoza, R.L. Ramos, P.A. Davila, J. M. Barron, P.E.D. Flores, J. Chem. Technol. Biotechnol., 81 (2006) 966–973
[46] A. Cincotti, A. Mameli, A.M. Locci, R. Orrù, and G. Cao, Ind. Eng. Chem. Res., 45 (2006) 1074–1084.