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Determination of significant factors in the removal of Cu(II) from aqueous solutions by applying adsorption method: using factorial design

Saeid Ghanbarian[a], Davood Kahforoushan[b,*], Eghbal Sahraei[a]

[a]*Faculty of Chemical Engineering, Sahand University of Technology, Tabriz, Iran, Tel. +98 41 3447 0559; email: s_ghanbarian@sut.ac.ir (S. Ghanbarian), Tel. +98 41 3345 9140; email: sahraei@sut.ac.ir (E. Sahraei)*
[b]*Faculty of Chemical Engineering, Environmental Engineering Research Center, Sahand University of Technology, Tabriz, Iran, Tel. +98 41 3345 9140; Fax: +98 413 344 4355; email: kahforoushan@sut.ac.ir*

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ABSTRACT

This paper aims to prove that adsorption is one of the most applicable, efficient, and inexpensive processes in the removal of heavy metals from water. In this research, commercially activated carbon and clinoptilolite were used as adsorbents in order to adsorb Cu(II) in the aqueous solutions. The effects of different experiment control factors including pH, time, temperature, adsorbent dose, initial concentration of Cu(II), mixing rate, and type of adsorbent have been investigated through the equations model designed by a two-level fractional factorial design in a batch system. Furthermore, by employing the experimental results, a linear mathematical regression model which represents the influence of each factors and their mutual interactions was established. Finally, the results declared that pH and temperature are significant among the main factors. Besides, the interaction of time and mixing speed was noticeable, so it was observed that the pH level of solution was the most influential parameter in the removal of metal ion.

Keywords: Adsorption; Activated carbon; Clinoptilolite; Cu(II); Fractional factorial design

1. Introduction

Conspicuously, industrial wastewaters are one of the main sources of environmental pollution. Among various pollutants, heavy metals such as Cr, Cu, Ni, As, Pb, and Zn are in majority because of their persistency in the environment. Alive organisms can absorb heavy metals. Obviously, when these metals enter into the food chain, high concentrations of heavy metals might accumulate in the human body. So, some heavy metals like copper in specific concentrations do essential job in animal metabolism, but the excessive absorption of copper causes serious toxicological concerns, such as vomiting, cramps, convulsions, or even death [1]. It is clear that the removal of heavy metal from polluted water is very important for water treatment. Several processes have been suggested to remove heavy metals from waters. These processes include chemical precipitation, coagulation, ion exchange, reverse osmosis, complexion, bio-sorption, membrane technologies, and adsorption processes [2,3]. Most of these methods suffer from some disadvantages such as high operational costs and also they are not suitable for small-scale industries [4]. Among these techniques, the adsorption method is the most applicable, efficient, and inexpensive process and

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*Corresponding author.

creates relatively little sludge [5,6]. Choosing suitable adsorbent is the most prominent part in adsorption processes. Activated carbon (AC) is one of the materials which frequently have been used for removing impurities from liquid solutions [6,7]. So, it has been widely used to treat industrial water due to its large surface area, high adsorption capacity, porous structure, selective adsorption, and high purity standards [8]. However, the high cost of the commercial AC limits its usage in such water and wastewater treatment applications [9]. Therefore, low cost materials have been tested on a large scale for heavy metal removal. Natural materials such as chitosan, zeolites, clay, or certain waste products from industrial operations such as fly ash, coal, and oxides are classified as less charged adsorbents [10,11]. Clearly, in the past decade, natural zeolites were being applied as effective adsorbents for heavy metal removal in water treatment due to its strong ion-exchange ability [12,13]. These low cost adsorbents have lower performance than AC because of their lower surface area and porous structure. Mixing expensive adsorbents such as AC with the low cost adsorbents like natural zeolite is an applicable method to reduce cost of operation.

To decrease the total number of experiments, cost, and time of the research for adsorption of the chosen metallic ion, experimental design is useful [14]. The experimental design determines which factors play a crucial role on the responses as well as how the effect of one factor varies compared to the level of the other factors [15,16]. The determination of factor interactions could only be achieved by using experimental designs, since it cannot be observed when the system study was carried out by varying just one factor at a time and fixing the others [17,18].

Consequently, several studies have been done on the removal of Cu(II) by using a variety of adsorbents such as AC [19], zeolite [19], wheat shell [20], rice husk [21], and carrot residues [22]. In all of these studies, only one kind of adsorbent has been used.

The purpose of this paper is to determine the significant factors' role in the elimination of Cu(II) from aqueous by applying adsorption method, previous studies have employed single variable during the experiments that certified the individual effects of various factors on heavy metals adsorption processes. Although recent studies have focused on the individual effects, it would be useful to comprehend the complexity of the systems and to find interactive effects of the factors and compare effects of each factor together. In this study, in order to investigate the experimental factors in the adsorption process and to determination the importance of factors and their interactions in Cu(II) removal from aqueous solutions experimental design was employed.

2. Materials and methods

2.1. Adsorbent

In this research, Iranian commercial powder AC was selected as the main adsorbent and clinoptilolite (Z) as the second one. These adsorbents were washed with distilled water until cleaned and heated at 60°C.

2.2. Adsorbents characterization

The surface of AC and clinoptilolite were fixed by N_2 adsorption isotherms at 77 K. The surface area was determined by applying the isothermal Brunauer–Emmett–Teller. Results for specific surface area for AC and clinoptilolite are shown in Table 1.

The pore structures of AC and clinoptilolite were characterized by scanning electron microscope (SEM). The SEM micrographs (Figs. 1 and 2) show that AC and clinoptilolite have crystalline particles ranging in size from a few to several micrometers.

In order to obtain the functional groups of AC, FT-IR (Fourier transform infrared) analyze was done. Fig. 3 shows the FT-IR spectra obtained from the AC. In Table 2, the assignment of the bands observed in Fig. 3 is shown, based on the data published by other authors [23,24].

Clinoptilolite characterization was performed by X-ray diffraction (XRD). XRD pattern (Fig. 4) shows that clinoptilolite contains SiO_2 and Al_2O_3.

2.3. Reagents and solutions

A Cu(II) solution was prepared by dissolving $CuSO_4$ (Merck, Germany) in distilled water. The solutions of different concentrations required for the adsorption experiments were prepared by dissolving different values of $CuSO_4$ solid in distilled water. The pH adjustments of the solutions were made with 1.0 mol L^{-1} of HCl and KOH solutions, utilizing a pH mV^{-1} hand-held meter handy lab HANNA

Table 1
Results for specific surface area for AC and clinoptilolite

Adsorbent	Total surface area ($m^2\ g^{-1}$)
Activated carbon	887.10
Clinoptilolite	30.95

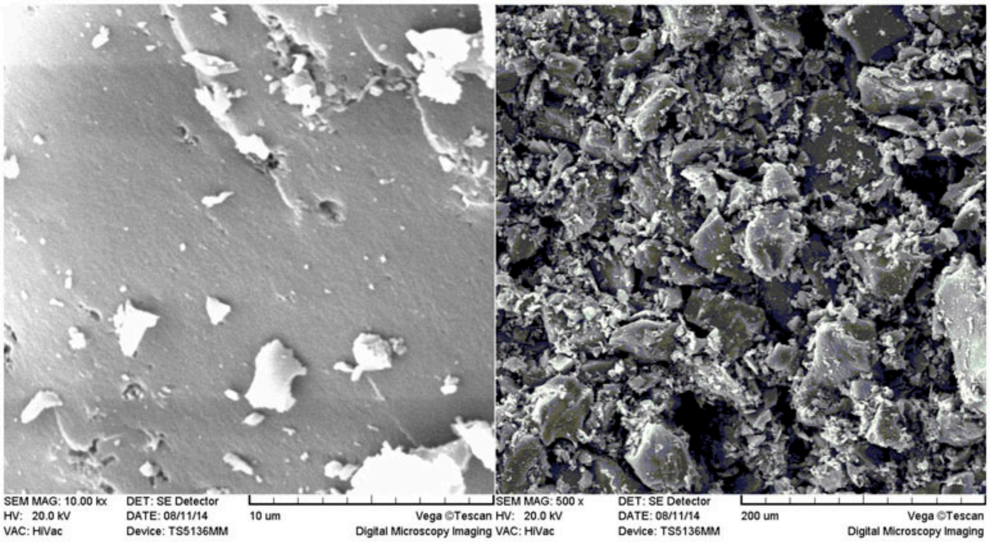

Fig. 1. Scanning electron micrographs of AC.

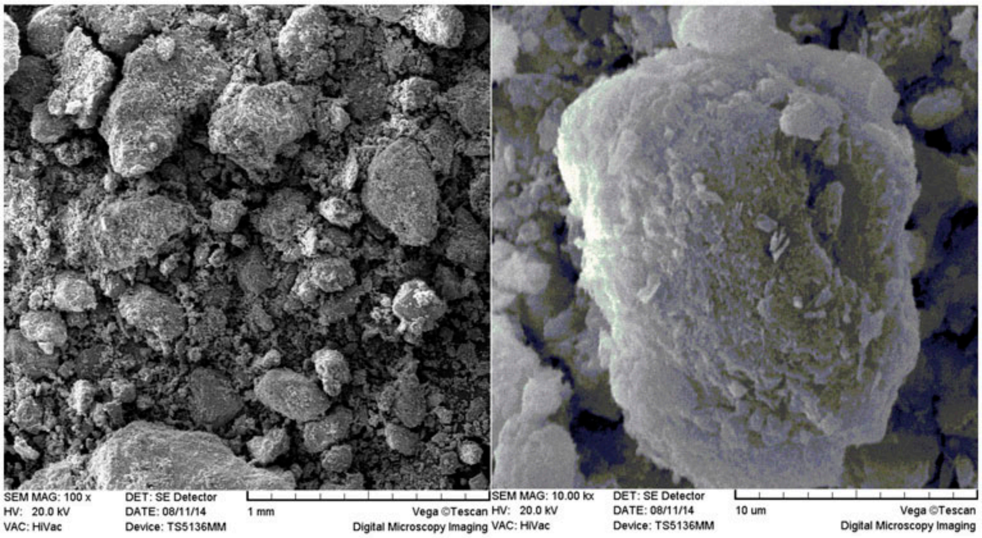

Fig. 2. Scanning electron micrographs of clinoptilolite.

instruments which were provided with combined glass electrode with the same model.

2.4. Experiment design

Factorial method was selected in order to study parameters in the adsorption of Cu(II) metal ion from aqueous solution. Moreover, to determine the factors that are effective in the removal of Cu(II) and to examine the interactional effects of various parameters by AC and AC–Z, seven-factors, a two-levels, 1/4 fraction factorial experimental design with two blocks and one replicate was applied. Consequently, the parametric process could be an effective method on adsorption including pH of the solution, time, temperature, adsorbent dose, initial concentration of Cu(II), rotational speed of the stirrer (mixing rate), and type of adsorbent (AC, AC + Z) which were selected. These factors were chosen based on a literature survey and the minimum number of the experimental runs was carried out for a two levels with seven factorial designs that were

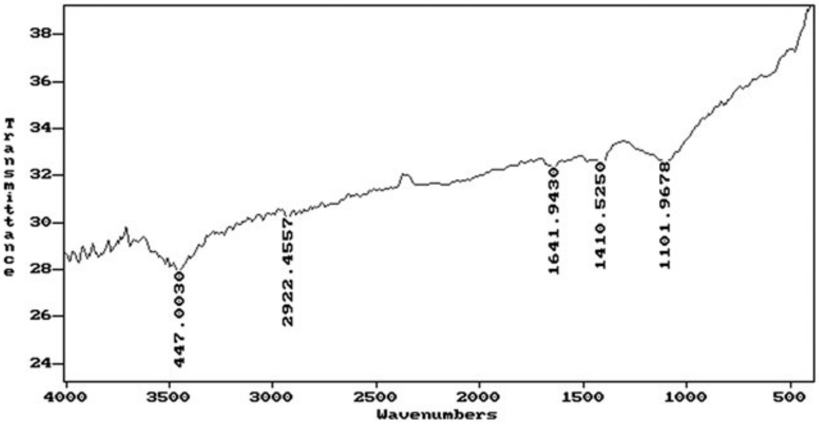

Fig. 3. FT-IR data for AC.

Table 2
The assignment of the FT-IR vibrations shown in Fig. 3

	Peak (cm^{-1})			
No.	This work	In reference	Surface group	Assignment
1	3,447	3,447	–OH	Intra-molecular H-bonded
2	2,922	2,920	CH_2	Asymmetrical and symmetrical stretch of CH_2
3	1,641	1,642	CONH	Stretch of C–O in cyclic amides
4	1,410	1,458	CH_3COO	Stretch of C–O in ethers
5	1,101	1,118	COH	OH stretch

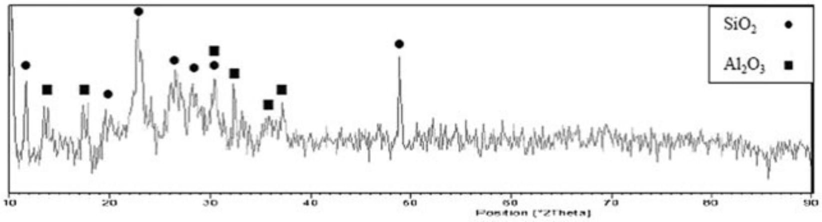

Fig. 4. X-ray powder pattern of clinoptilolite.

$2^7 = 128$ runs, which were more. When the number of factors is more than four, fractional factorial design could be usable [25]. A fractional factorial design was represented by $2^{(k-p)}$, where k was the number of factors and $1/2^p$ represents the fraction of the full factorial 2^k. Type of the adsorbent was blocked, so six factors were remained. A $2^{(6-2)}$ fractional factorial design was 1/4 of the fraction of a 2^6 full factorial experiment. By applying this method, it could be able to study seven factors at two levels in just 16 (i.e. $2^{(6-2)}$).

2.5. *Adsorption experiments*

For each experimental run, 200 mL of the aqueous solution of Cu(II), was taken in batch reactor containing pre-weighted amount of AC for part of the experiments (block 1) and mixture of 50–50% of AC and clinoptilolite for the next part (block 2). These samples stirred on a magnetic hot-plate stirrer model IKA-RCT. Due to the test devotion to pH effect study, the initial solution pH was adjusted by addition of HCl and KOH (1 M) to the solutions including Cu(II) ions.

2.6. Determination of Cu(II)

Cu(II) was measured by applying a flame atomic absorption spectrometer model NOVAA Analytik jena 300 using air–acetylene flame under optimized conditions.

3. Results and discussion

3.1. Factorial design adsorption experiments

For each quantity factor (six factors) two levels were considered that are shown in Table 3 as natural values. This is commonly called as main effect, whereas it refers as the main factors of interest in the experiment [26]. The design of coded values for factors and response in terms of percent removal efficiency of Cu(II) is shown in Table 4. In the efficacy removal percent, R is defined as:

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

C_i and C_f are the initial and final concentrations of the metal ions (mg L^{-1}). The results were analyzed using Minitab version 16, the main and interaction effects were determined. The applied coded mathematical model for factorial designs was:

$$R = A_0 + \sum_{i=1}^{k} A_i X_i + \sum_{i=1}^{k}\sum_{j=1}^{k} A_{ij} X_i X_j \quad (2)$$

whereas X_i and X_j are the independent variables, A_0 shows the constant model and A_i shows the regression coefficient corresponding related to the main factor effects and interactions. A_{ij} are the cross-product coefficients [27]. The estimated effects, regression coefficients and percent contributions (PCs) are shown in Table 5. PC is defined as:

$$\mathrm{PC}_i = \left(\frac{\mathrm{SS}_i}{\mathrm{SS}_{\mathrm{total}}}\right) \times 100 \quad (3)$$

whereas SS_i is the sum of square for each factor [28]. When the effect of a factor is positive, removal efficiency increases. On the other hand, if the effects were negative, removal efficiency decreases. By substituting the coefficients X_i in Eq. (2) with their values illustrated in Table 5, it could drive a model equation connecting to the level of parameters and Cu(II) removal efficiency (R), the regression equation is:

$$\begin{aligned}\%R = {} & 76.9 + 19.1\ \text{pH} + 3.52\ \text{Time} + 8.41\ \text{Temperature} \\ & - 2.56\ \text{Adsorbent dose} \\ & + 5.76\ \text{Initial concentration} + 2.63\ \text{Mixing speed} \\ & - 7.29\ \text{pH} \times \text{Initial concentration} - 4.96\ \text{pH} \\ & \times \text{Mixing speed} + 9.43\ \text{Time} \times \text{Mixing speed} \\ & - 1.30\ \text{pH} \times \text{Time} - 5.45\ \text{pH} \times \text{Temperature} \\ & - 0.275\ \text{pH} \times \text{Adsorbent dose} - 3.05\ \text{Time} \\ & \times \text{Adsorbent dose} + 4.77\ \text{pH} \times \text{Time} \\ & \times \text{Adsorbent dose} - 5.86\ \text{pH} \times \text{Temperature} \\ & \times \text{Adsorbent dose}\end{aligned} \quad (4)$$

Fig. 5 presents the Pareto chart of standardized effects at $p = 0.05$. All the values present an absolute value higher than the standardized effect value (2.776), which was located at the right-hand of the vertical line; and declares significant magnitude effect for the 95% confidence level.

Table 3
Experimental ranges and levels of the factors examined in the factorial design

Factor	Symbol	Levels	
		−1	+1
pH	A	4	8
Time (min)	B	30	90
Temperature (℃)	C	20	40
Adsorbent dose (g)	D	0.3	1.0
Initial concentration (mg L^{-1})	E = ABC	40	100
Mixing speed (Rpm)	F = BCD	200	400

3.2. Analysis of variance

In order to determine the significant and main interaction effects of factors which causes influence on the elimination impact of Cu(II), an analysis of variance (ANOVA) was carried out. Because of being one replicate, ANOVA could not be performed. Therefore, based on PC values which were shown in Table 5, main effects and factors' interaction with PC values more than three, were selected [28]. Although according to the Table 5, some main factors were less than three, such as time, but PC values of time and mixing speed interaction were bigger than 3. Results manifest that other main factors with these conditions should be considered for ANOVA.

By selecting the factors with PC < 3, ANOVA was done. The sum of squares (SS) and mean square (MS) of each factor, p-value and the F-ratio, named ratio of

Table 4
Experimental data of factorial design

Run	Blocks	A	B	C	D	E	F	Cu(II) removal percentage
1	1	1	1	1	−1	1	−1	89.58
2	1	1	−1	−1	1	1	1	78.90
3	1	−1	−1	1	1	1	−1	83.13
4	1	1	−1	1	−1	−1	1	87.02
5	1	−1	1	1	1	−1	1	76.20
6	1	−1	1	−1	−1	1	1	84.80
7	1	1	1	−1	1	−1	−1	84.50
8	1	−1	−1	−1	−1	−1	−1	28.25
9	2	1	−1	−1	−1	1	−1	89.82
10	2	1	1	1	1	1	1	89.84
11	2	−1	−1	−1	1	−1	1	23.90
12	2	−1	−1	1	−1	1	1	66.66
13	2	1	−1	1	1	−1	−1	89.69
14	2	−1	1	1	−1	−1	−1	50.67
15	2	1	1	−1	−1	−1	1	89.22
16	2	−1	1	−1	1	1	−1	28.84

Table 5
Statistical parameters for $2^{(6-2)}$design

Factor	Coefficient	EE	SS	PC
A	19.13	38.26	5,856.8	48.14
B	3.52	7.035	198	1.63
C	8.41	16.82	1,131.6	9.30
D	−2.56	−5.13	105.2	0.86
E = ABC	5.76	11.52	530.4	4.36
F = CDE	2.63	5.26	110.6	0.91
A × B	−1.30	−2.61	27.2	0.22
A × C	−5.45	−10.90	475	3.90
A × D	−0.275	−0.55	1.2	0.01
A × E	−7.29	−14.59	851.2	7.00
A × F	−4.95	−9.91	392.8	3.23
B × D	−3.048	−6.09	148.6	1.22
B × F	9.43	18.86	1,422.8	11.70
A × B × D	4.77	9.54	364.2	2.99
A × C × D (block)	−5.86	−11.72	549.2	4.51

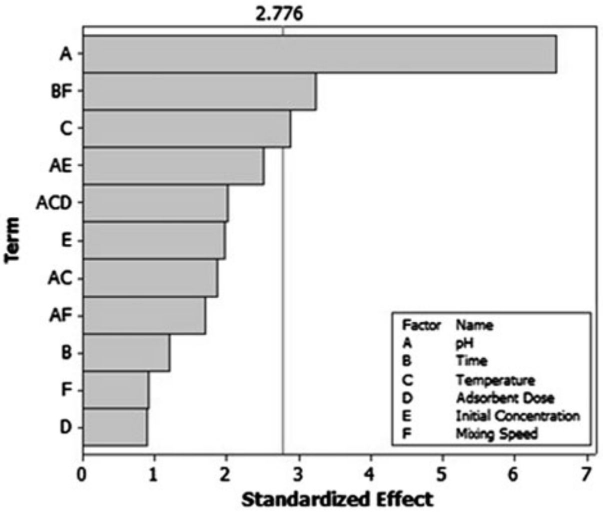

Fig. 5. Pareto chart for standardized effects.

the respective mean square effect and the mean square errors are shown in Table 6. *p*-value is the probability value which was used to determine the statistically significant effects in the model [26]. The importance of data could be judged by its *p*-value, with values closer to zero with greater significance. For a 95% confidence level, the *p*-value should be less than or equal to 0.05, and the effects should be considered statistically significant [25]. According to the obtained *F*-ratio and *p*-value (Table 6), it seems that the effect of pH (A), temperature (C), and the interaction effect of time and mixing speed (B × F) are statistically significant. The normal probability plots of standardized effects are available in Fig. 6. This graph is completely consistent with the analysis performed for significant results.

3.3. Effects of the major and the interaction factors

By analyzing the graphs in Fig. 7, and the *F*-values in Table 6, it could be concluded that pH had a major role in the removal of metal ions. So, the pH (A) was the most noticeable variable among selected parameters, since its coefficient was the highest one (i.e. 19.13). The positive slope in Fig. 7 meant that Cu(II)

Table 6
ANOVA for a $2^{(6-2)}$design

Factor	DF	SS	MS	F	P
A	1	5,856.8	5,856.8	43.28	0.003
B	1	198	198	1.46	0.293
C	1	1,131.6	1,131.6	8.36	0.044
D	1	105.2	105.2	0.78	0.428
E	1	530.4	530.4	3.92	0.119
F	1	110.6	110.6	0.82	0.417
A × C	1	475	475	3.51	0.134
A × E	1	851.2	851.2	6.29	0.066
A × F	1	392.8	392.8	2.9	0.164
B × F	1	1,422.8	1,422.8	10.52	0.032
A × C × D (blocks)	1	549.2	549.2	4.06	0.114
Residual error	4	541.2	135.3	–	–
Total	15	12,164.8	–	–	–

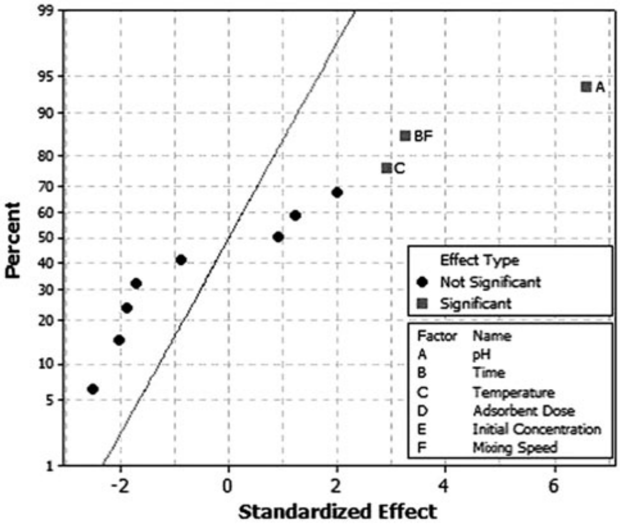

Fig. 6. Normal probability plot of standardized effects at $p = 0.05$.

removal was favored at high pH values. pH enhancement in solution from level 4 to 8, leads to an increase in the adsorption efficiency by 38%. At lower pH values, the active sites of the adsorbent are less available in the metal ions due to protonation of the active sites at higher H^+ concentration. By increasing the pH values, linked H^+ is released out of the active sites and adsorbed amount of the metal ions, again showed a noticeable increase. Due to involving acidic functional groups on AC surface, these groups could have the potentiality to form chelates easily by employing the metal ions and to improve the AC surface. Consequently, such negatively charged groups showed affinity towards the positively charged or neutral metal species because of electrostatic interactions. Similar trends of the adsorption in the copper removal of aqueous solutions were reported [15,29].

The Interaction effect plots are shown in Fig. 8. The plots declare the mean response of two factors; if the lines are not parallel it indicates an interaction between the two factors [25]. Figs. 8 and 9 and Eq. (4) coefficients show positive interaction between time and mixing speed (B × F) as a significant factor. Although, time and mixing speed as main factors showed positive effects on adsorption ratio (Fig. 7), these main factors were not important. The positive value of the coefficient in this interaction declares that an increase in the time of adsorption process and mixing speed of the solution, leads to the accumulation in the amount of metallic ion adsorbed. Other interactions showed no noticeable features for a discussion.

Additionally, the third main factor was temperature (C), so adsorption was favored by an increase in the temperature. Although this was not an expected behavior, it was reported by some researchers when studying the adsorption of different type of metals over several adsorbents. Obviously, an increase in the temperature level may lead to an enhancement in the porosity and total pore volume of the adsorbent or to a sudden rise in the chemical affinity of the adsorbent for metal cautions [30]. Also, it will weak the electrostatic interactions between the heavy metals ions and adsorbent layer [31]. It seems that positive effects are more effective than negative effects. Other researchers reached to the similar results about the effects of temperature [32,33].

According to Fig. 5, other main factors like initial concentration (E), time (B), mixing speed (F) (But the interaction of B × F was significant), adsorbent dose (D), and adsorption type (ACD) were not statistically significant. According to Eq. (4) and Fig. 6, the enhancement of adsorbent dose reduces adsorption rate, so an increase in adsorbent dose causes to encompass the number of adsorbent particles by metal ions increasing in solutions which results to more ions attachment to the adsorbent surfaces, and finally provide more active sites for ions. Furthermore, in a certain dose of adsorbent, the highest rank for that adsorbent will be achieved. Hence, there is no adsorption of metal ion to that adsorbent. The more increase in adsorbent dose, will leads to the more rise in particles density and also results to the solution adsorbent particles contacted with each other, so it will make particles to be larger which reduce the contact surface of the adsorbent with solution and increases the resistance related to the transport phenomena. In conclusion, it will decrease adsorption efficiency. Similar

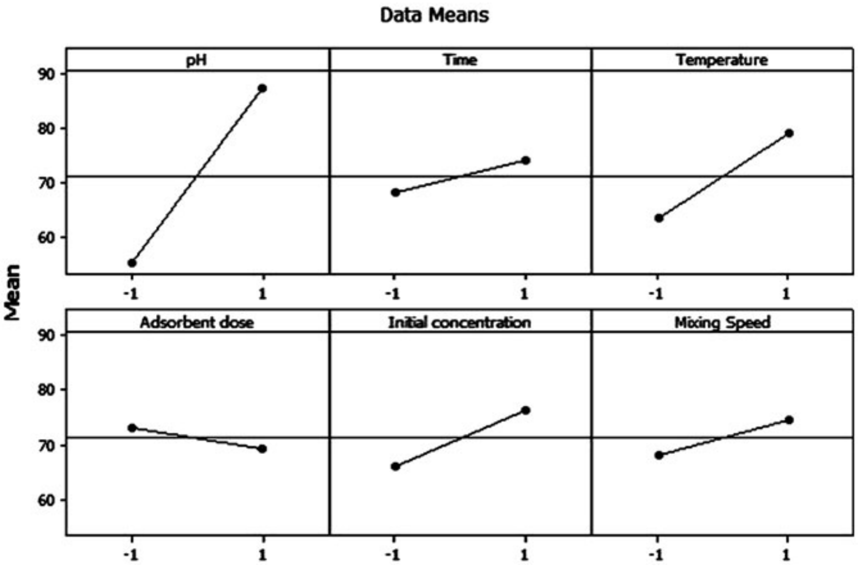

Fig. 7. Main effects plot for Cu(II) removal.

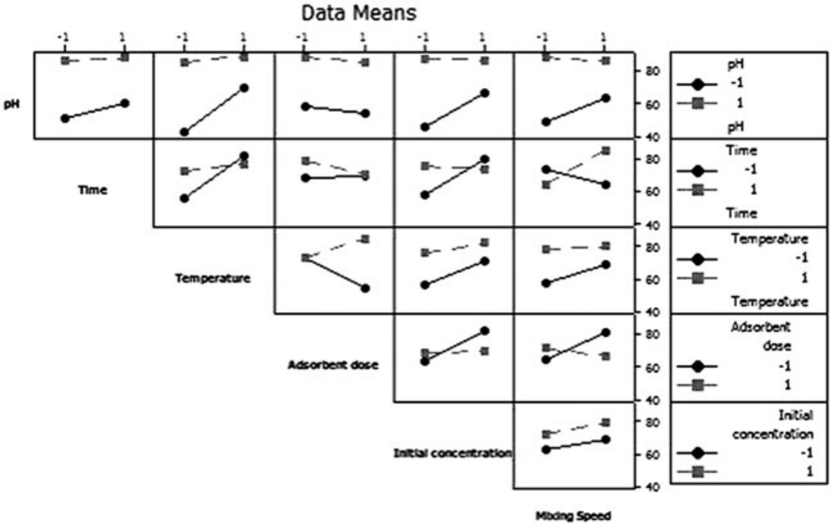

Fig. 8. Interaction effects plot for removal of Cu(II).

results have been reported on adsorption rate for heavy metal ions [34]. At last, the influence of this factor was negligible ($p = 0.428$).

Adsorbent type (AC, AC + Z) showed a negative effect on adsorption process. Because surface area of AC is much larger than clinoptilolite (Table 2), in result mixture of these adsorbents have lesser total surface area than AC. So it would provide less active sites for ion adsorption that decrease adsorption ratio. However, this negative effect was not so considerable.

There is no doubt that coefficient of initial concentration based on Eq. (4) and Fig. 6 is positive. It also shows an increase in the removal percentage of Cu(II) by enhancing Cu concentration. Cu(II) would interact with the binding sites. In the higher concentrations of metal ions, more ions are left unadsorbed because of saturation of binding sites. So, this manifests that energetically less desired sites be involved by increasing metal ions in the solution [35]. Effects of this factor was negligible compared to the other factors ($p = 0.119$).

A detailed study on Cu(II) removal by these adsorbents and involving the significant factors obtained by the fractional factorial analysis will help in understanding the process better.

Based on *F*-values and *p*-values, other interactions effects were neglected. As it is clear in Fig. 7, slopes of time and mixing speed are smaller than other main factors, but by paying attention to the high interaction of time and mixing speed (shown in Figs. 8 and 9), time and mixing speed were selected as the important main factors. The effect of the other main factors and several interaction impacts which were statistically insignificant, compared to the other effects with remaining variables were discarded as well; besides, the new and simple regression model are proposed as follows:

$$R = 76.9 + 19.1\ \text{pH} + 3.52\ \text{Time} + 8.41\ \text{Temperature} + 2.63\ \text{Mixing speed} + 9.43\ \text{Time} \times \text{Mixing speed} \quad (5)$$

Although R^2 was equal to 71.7%, the equation was simplified. Simple equation employed, and it showed that it is applicable compared to the other complex equations.

The applicable range of all parameters related to the regression model is demonstrated in the Table 3.

3.4. Normal probability's residuals plot

Observably, it is important for the statistical analysis of the experimental data to suppose that it comes from a normal distribution [36]. To determine whether the data-set is normally distributed or not, so the normal probability plot of residual values is shown in Fig. 10. It is crystal clear that the points show a noticeable fall approximately close to the straight line. Therefore, experimental data which results from a normally distributed population can be used for this study.

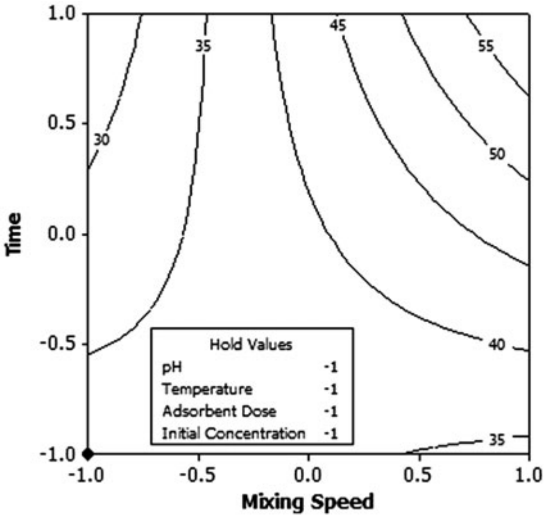

Fig. 9. Contour of removal percentage vs. time, mixing speed.

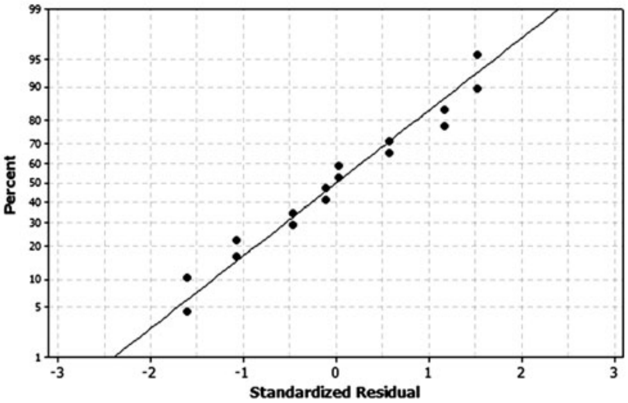

Fig. 10. Normal probability plot of residuals for Cu(II) removal efficiency.

4. Conclusions

Eventually, Factorial design method was employed to analyze the adsorption characteristics of Cu(II), in order to AC and clinoptilolite. So, seven main adsorption factors including pH, time, temperature, adsorbent dose, initial concentration, mixing speed, and type of adsorbent at two levels have been studied. Finally, by considering the results, the adsorption significance of parameters in this study is in this order: pH > interaction between time and mixing speed > Temperature. Also, based on the results, type of adsorbent (AC, AC + Z) had no noticeable effect in the Cu(II) removal, so mixture of adsorbents (AC + Z) can be applicable to reduce the costs of operation.

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