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A method for the removal of Cu(II) from aqueous solutions by sulfide precipitation employing heavy oil fly ash

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ABSTRACT

This research concerns the treatment of aqueous solutions by precipitation of Cu(II) with employing heavy oil fly ash (HOFA) which is preferred due to the comparatively low cost of sulfide precipitant for the removal of heavy metals. In this study, HOFA and NaOH were added to enhance sulfide precipitation which results in the reduction of heavy metal concentration to an acceptable level for discharging. The effects of different experimentally controlled factors including HOFA dose, time, pH, initial concentration of Cu(II), and NaOH concentration were investigated through the model equations which were designed by a two-leveled fractional factorial design in a batch system. Using the experimental results, a linear mathematical regression model representing the influence of the significant factors and their interactions were obtained. At last, results indicated that among the main interaction factors which are pH, dose of HOFA, NaOH concentration, and interaction of time and initial concentration had the most significant effects. Besides, it was observed that pH of the solution was the most influencing parameter on the removal of metal ion. Furthermore, based on the results, HOFA as a waste material, had a high efficiency in Cu (II) removal.

Keywords: Sulfide precipitation; Heavy oil fly ash; Cu(II); Fractional factorial design

1. Introduction

Heavy metals such as copper, lead, cadmium, zinc, nickel, and chromium(III) have been used widely by several mining and chemical industries [1,2]. Recently, as industrial activities develop, heavy metal pollution changes to a serious concern [3]. Heavy metals can indeterminately persist in nature and their toxic effects are very dangerous to humans and may cause a serious risk to the environment as well. These metals associate negatively with kidney, lung, liver, circulatory, and nerve tissues [3]. Therefore, it is urgent to remove these toxic heavy metals from wastewater.

Nowadays, many processes have been applied to remove heavy metal ions from polluted water which

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include chemical oxidation and precipitation, ion exchange, adsorption, electrochemical applications, and membrane technologies [4–8]. Among these methods, chemical precipitation is widely used for heavy metal removal from various wastewaters because it is inexpensive to operate and comparatively simple [9,10]. Chemical materials react with metal ions to form insoluble solid precipitates in this process. The formed precipitates can be separated from the water by filtration and the treated water will be remained. Based on the variety of reactant chemicals, the chemical precipitation processes can be classified to hydroxide precipitation, chelating precipitation, and sulfide precipitation [11].

In chemical and metal industries, hydroxide precipitation is usually used for metal removal due to its simplicity, low costs, and ease of automatic pH control [4], but sulfide precipitation was superior over hydroxide precipitation and had more advantages such as lower solubility of metal sulfide precipitates in solutions, less problems caused by interference of chelating agents in the wastewater, lower sludge volumes production, ability to selective metal removal, high reaction rates, better settling properties, very low solubility of the metal sulfides, and capability of sulfide precipitates reusing. Metal sulfide precipitations are important for metal recovery in metal industries [4,12]. Precipitation as a sulfide salt is an effective way to achieve high degrees of separation of various heavy metals from industrial wastewater [13]. Sulfide compounds are the main materials for sulfide precipitation. In sulfide precipitation processes, solid materials (FeS, CaS), aqueous (Na_2S, NaHS, NH_4S), or gaseous sulfide sources (H_2S) can be used [4,14,15]. The thermodynamic equilibrium involved in metal sulfide precipitation can be expressed as:

$$M^{2+} + S^{2-} \leftrightarrow MS \tag{1}$$

Power generation from coal and heavy oil produces solid residues after combustion which is called fly ash (HOFA). Generally, HOFA is one of the most abundant waste materials. The annual production of fly ash from power plants is being increased which tempts to look for possible industrial applications [16]. Heavy oil includes different impurity materials. Therefore, it seems heavy oil fly ash (HOFA) is not applicable as commercial adsorbent for wastewater treatment due to existence of different materials, but it may have potentials as an ideal seeding material for sulfide precipitates as HOFA is a source of sulfur compounds. Use of HOFA reduces costs of precipitation process as a result of being cheaper than use of sulfide components at pure state.

Basically, in order to obtain metal sulfide precipitates with good removal ratio, effective control of the precipitation process is necessary. For proper design of the precipitation process, the influence of operational and material parameters on the precipitation process must be known [13]. Latest researchers were concentrated on individual effects in the precipitation ratio, but it is important to know the significance of each factor and their interactions, so experimental designs are vital [17,18].

In the present work, HOFA was used to remove heavy metals (Cu(II) as a case) from solutions. Factorial design was used to study effects of factors and select important factors in Cu(II) removal from aqueous solutions.

2. Materials and methods

2.1. HOFA characterization

HOFA used in this study was obtained from the gas and thermal power plant of Tabriz, Iran. HOFA was sieved to less than 188 micrometers. The sieved samples were analyzed by X-ray fluorescence (XRF). XRF is the emission of characteristic "secondary" (or fluorescent) X-rays from a material which was excited by bombarding with high-energy X-rays or gamma rays. The phenomenon is widely used for elemental analysis and chemical analysis, particularly in the investigation of metals, glass, ceramics, and building materials. Chemical compositions of fly ash are presented in Table 1.

As can be seen in Table 1, there was a high level of sulfur compounds in HOFA. The main part of materials in HOFA is loss on ignition (LOI) (56.69% of total). The LOI is an index of the amount of unburned carbon remaining in the HOFA [19].

The pore structures of raw HOFA were characterized by SEM. The SEM micrograph (Fig. 1) shows that HOFA consists of spherical particles ranging in size from a few to several micrometers and several impurities. The spherical particles are mostly porous in nature similar to honeycomb voids. The pores were individually situated and randomly located on the particle surface.

The surface of HOFA was fixed by N_2 adsorption isotherms at 77 K. The surface area was determined by applying the isothermal Brunauer–Emmett–Teller (BET). The results for specific surface area for HOFA are shown in Table 2. According to the results, the surface area and total pore volume of HOFA are too low and probably because of high impurities in

Table 1
Chemical composition and physical characteristics of the considered fly ash by XRF analyze

	Samples	(%)		Samples	(ppm)		Samples	(ppm)
1	SiO_2	0.340	15	Cl	85	29	As	19
2	Al_2O_3	0.210	16	Ba	37	30	U	1
3	Fe_2O_3	5.510	17	Sr	8	31	Th	2
4	CaO	0.120	18	Cu	91	32	Mo	4
5	Na_2O	0.090	19	Zn	34	33	Ga	19
6	K_2O	0.020	20	Pb	17	34	Nb	4
7	MgO	0.020	21	Cr	28			
8	V_2O_5	19.860	22	Ce	9			
9	NiO	7.860	23	La	5			
10	TiO_2	0.021	24	W	2			
11	MnO	0.004	25	Zr	34			
12	P_2O_5	0.005	26	Y	3			
13	S	9.210	27	Rb	16			
14	L.O.I	56.690	28	Co	24			

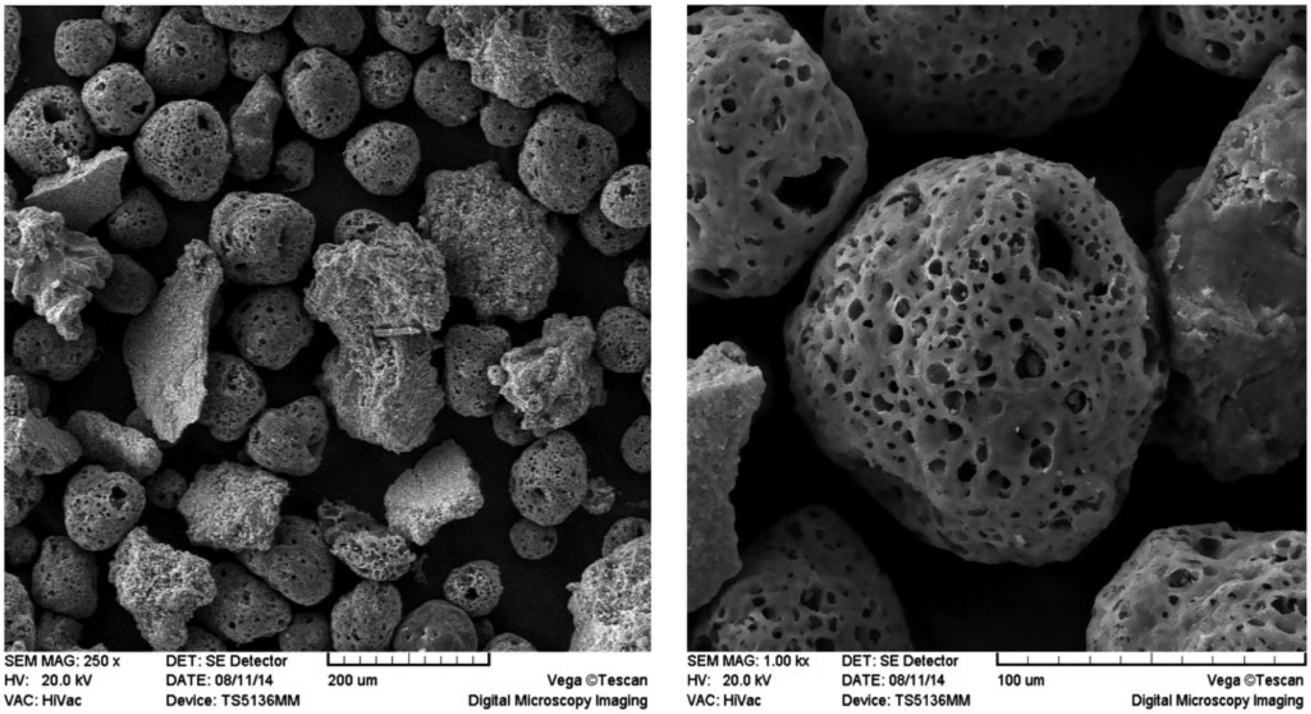

Fig. 1. SEM images of a raw HOFA.

Table 2
Result for specific surface area for HOFA

Sample	Total surface area (m^2 g^{-1})	Total pore volume (cm^3 g^{-1})	Micropore volume (cm^3 g^{-1})	Mesopore volume (cm^3 g^{-1})
HOFA	1.05	0.004	0.001	0.003

HOFA, it has no capacity of adsorption in this condition.

2.2. Reagents and solutions

The Cu(II) solution was prepared by dissolving $CuSO_4$ (Merck, Germany) in distilled water. The solutions of different concentrations required for the precipitation 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 $Ba(OH)_2$ solutions using a pH/mV hand-held meter handy lab HANNA instruments with combined glass electrode with same model. Consequently, solution of NaOH was used for precipitation process.

2.3. Experiment design

The factorial design was selected to study parameters in the removal of Cu(II) in aqueous solutions. In order to determine the significant factors and their interactions that influence the removal of Cu(II) metal ion, a pre-experimental design should be used. Factorial design was employed to decrease the total number of experiments in order to reduce time and costs of experimental studies or their cost effectiveness. In order to determine effects of various parameters, a two-leveled, five-factored, 1/2 fraction factorial design with one replicate was applied. From the literature survey, the experimental factors which might be effective on the precipitation of Cu(II) in aqueous solutions such as HOFA dose, time, initial concentration, pH and NaOH concentration were chosen and are manifested in Table 3. The total number of experiments for a two-leveled design with five factors is $2^5 = 32$ runs that are large. When the number of factors is more than four, fractional factorial design can be used [20]. A $2^{(5-1)}$ fractional factorial design is 1/2 the fraction of a 2^5 full factorial experiment. This way, studying five factors at two levels in just 16 (i.e. $2^{(5-1)}$) experimental runs instead of 32 trials (2^5) is possible.

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

Factor	Symbol	Levels	
		−1	+1
Dose of HOFA (g/L)	A	2.5	5
Time (min)	B	10	30
Initial concentration (ppm)	C	100	300
pH	D	3	10
NaOH concentration (molar)	E	3	5

2.4. Precipitation experiments

The precipitation experiments were performed in batch system at room temperature. For each experimental run, 200 mL of the aqueous solution in specific concentration of Cu(II) was taken in a batch reactor including HOFA in specific weights. The initial pH of solutions was adjusted by using HCl and $Ba(OH)_2$. These samples were stirred on magnetic hot plate stirrer model IKA-RCT in fixed mixing speed (200 rpm). After specified times, NaOH solution was added to the samples to form metal sulphides. For sedimentation of salt sulphides, 1 min was given for each sample. Then, precipitations were separated from solutions using filter papers.

An experiment for analyzing adsorption capacity of HOFA was designed. For this purpose, 200 ml of the aqueous solution of Cu(II) (40 mg L^{-1}) was taken in batch reactor containing pre-weighted amount of HOFA (1 g L^{-1}). These samples stirred on a magnetic hot plate stirrer model IKA-RCT for 10 h in pH of solution.

2.5. Determination of Cu(II)

Remaining Cu(II) concentration in the solution was measured using a graphite furnace atomic absorption spectrometer model Varian Spectra 220.

3. Results and discussion

3.1. Precipitation process

The probability production of chemical species in multicomponent batch system for the minimization of the Gibbs free energy can be calculated by a EQUILIB computer program under web version [21]. Sulfur reacts with NaOH and produces Na_2S. Na_2S which is soluble in water is a source of sulfide precipitation. The input of this program is species of reactant and amounts of those in room temperature and atmospheric pressure. For this study, equilibrium reaction for precipitation of Cu_2S from $CuSO_4$ and Na_2S is given in Eq. (2):

$$Na_2S(aq) + CuSO_4(aq) \rightarrow Cu_2S(S) + Na_2SO_4 \quad (2)$$

As presented in Table 1, HOFA has amounts of different metals such as Pb, Zn, and Cr which might be soluble in water. In the performed experiments for sulfide precipitation of Cu(II), other metals formed sulfide precipitation too. In the final analyzed solutions, values of remained metals were negligible. When the removal efficiency of Cu(II) was high, removal percentage of other metals reached to 100%.

3.2. Sulfide precipitation experiments

The coded values of experimental design for factors and response in terms of percent removal efficiency of Cu(II) are shown in Table 4. The metal removal percentage (R) was calculated by the following equation:

$$R = \left(\frac{C_i - C_f}{C_i}\right) \times 100 \tag{3}$$

where C_i and C_f are the initial and final concentrations of the metal ions (mg L^{-1}). The results were analyzed by employing Minitab release 16 and the main effects and interaction between factors were determined. Additionally, the removal efficiency of Cu(II) for adsorption experiment was 3.9%. So, it was clear that results of sulfide precipitation process are not under influence of adsorption process.

The general coded mathematical model utilized for factorial designs can be given as:

$$R = \beta_0 + \sum_{i=1}^{k} \beta_i y_i + \sum_{i=1}^{k} \sum_{j=1}^{k} \beta_{ij} y_i y_j \tag{4}$$

where β_0 is the global mean, β_i and β_j represent the regression coefficient relating to the main factor effects and interactions (y_i, y_j) [22]. The regression coefficients, estimate effects (EE), and percent contribution (PC) are shown in Table 5. PC for each factor was calculated using the following equation:

$$\text{PC}_i = \left(\frac{\text{SS}_i}{\text{SS}_{\text{total}}}\right) \times 100 \tag{5}$$

where SS_i is the sum of square for each factor and SS_{total} is the sum of SS_i [23]. By substituting the coefficients β_i in Eq. (4) with their values from Table 5, it can be driven a model equation relating the level of parameters and Cu(II) removal efficiency. The regression equation is:

$$\begin{aligned} \text{Removal} = {} & 67.7 - 7.023\,\text{Dose of HOFA} + 1.198\,\text{Time} \\ & - 0.184\,\text{I.C.} + 22.827\,\text{pH} + 5.954\,\text{NaOH} \\ & + 0.708\,\text{Dose of HOFA} \times \text{Time} \\ & + 1.048\,\text{Dose of HOFA} \times \text{I.C.} \\ & - 1.868\,\text{Dose of HOFA} \times \text{pH} \\ & + 0.852\,\text{Dose of HOFA} \times \text{NaOH} \\ & + 4.329\,\text{Time} \times \text{I.C.} - 0.334\,\text{Time} \times \text{pH} \\ & + 0.468\,\text{Time} \times \text{NaOH} + 1.518\,\text{I.C.} \times \text{pH} \\ & + 0.218\,\text{I.C.} \times \text{NaOH} - 0.511\,\text{pH} \times \text{NaOH} \end{aligned} \tag{6}$$

Table 4
Factorial design for experimental data

Run number	Dose of HOFA	Time	I.C.	pH	NaOH concentration	Removal percentage
1	−1	−1	−1	−1	1	61.26
2	−1	1	−1	−1	−1	43.46
3	−1	1	−1	1	1	99.85
4	−1	−1	1	−1	−1	36.81
5	1	−1	−1	−1	−1	35.88
6	1	1	1	−1	−1	37.68
7	1	1	−1	1	−1	67.70
8	1	−1	1	1	−1	72.12
9	1	1	1	1	1	96.95
10	1	−1	−1	1	1	87.67
11	1	−1	1	−1	1	39.61
12	1	1	−1	−1	1	45.90
13	−1	1	1	1	−1	98.96
14	−1	1	1	−1	1	58.78
15	−1	−1	−1	1	−1	99.45
16	−1	−1	1	1	1	99.61

Table 5
Statistical parameters for a 2^{5-1} fractional factorial design

Factor	Coefficient	EE	SS	PC
A	−7.023	−14.046	789.2	7.769934
B	1.198	2.396	23	0.226443
C	−0.184	−0.369	0.5	0.004923
D	22.826	45.654	8,337.1	82.0815
E	5.954	11.909	567.3	5.585256
$A \times B$	0.708	1.416	8.0	0.078763
$A \times C$	1.048	2.096	17.6	0.173278
$A \times D$	−1.868	−3.736	55.8	0.549369
$A \times E$	0.851	1.704	11.6	0.114206
$B \times C$	4.329	8.659	299.9	2.952614
$B \times D$	−0.334	−0.669	1.8	0.017722
$B \times E$	0.468	0.936	3.5	0.034459
$C \times D$	1.518	3.036	36.9	0.363293
$C \times E$	0.218	0.436	0.8	0.007876
$D \times E$	−0.511	−1.021	4.2	0.041350

Pareto plot shows the absolute values of the effects of main factors and interaction of factors. A reference line is drawn to specify that which factors are important? It can be seen from Fig. 2 that pH had the greatest effect on the removal of Cu(II). The effects that are above the reference line are statistically significant at 95% confidence level.

3.3. Analysis of variance

For determining the significant level and interaction effects of factors by influencing the removal efficiency of Cu(II), an analysis of variance (ANOVA) was carried out. Because there was one replicate, ANOVA could not be done. Therefore, based on the contribution percent values (shown in Table 5), main effects and interaction of factors with PC values were more than three and it was chosen for ANOVA [23]. The sum of squares (SS) and mean square of each factor, *p*-value, and the *F*-ratio are shown in Table 6. *p*-value is the probability value that is used to determine the statistically significant effects in the model [24]. The importance of the data can be judged by its *p*-value, with values less than 0.05 and closer to zero meaning greater significance. According to the *F*-ratio and *p*-value (Table 6), it seems the effect of pH (D), dose of HOFA (A), NaOH concentration (E), and the interaction effect of time and initial concentration of Cu(II) ($B \times C$) are statistically significant. The normal probability plot of standardized effects has been provided in Fig. 3 showed the same results of ANOVA.

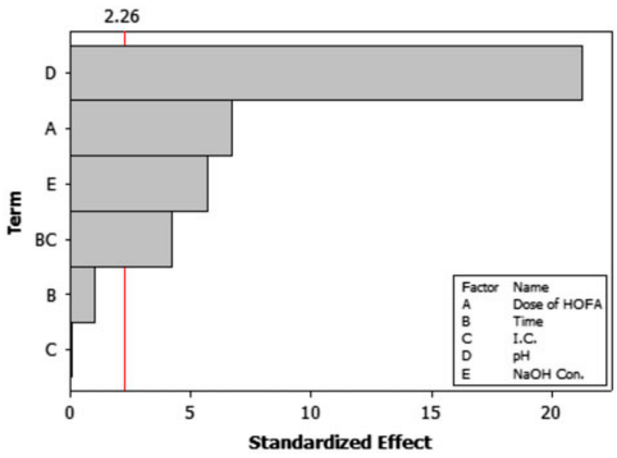

Fig. 2. Pareto chart for standardized effects.

3.4. Effects of main and interaction factors

As can be seen in the *F*-values (Table 6 and Fig. 2), the solution pH had the highest effect on the removal of Cu(II). Also, positive sign of coefficient (Fig. 4) for this factor shows increasing pH was favored in the precipitation of Cu(II) metal ions. Increasing the pH from 3 to 10 increased the removal efficiency by 46.07%. Solubility of metals increase by pH decreasing and sulfide precipitation is always conducted under alkaline conditions to promote sulfide ion formation [25,26], though similar result was reported that effectively removed metal ions by sulfide precipitation in a neutral pH range (at pH 8.5) [27–29].

Second significant factor according to Fig. 2 was dose of HOFA. As it can be seen in Fig. 4, the increase in HOFA dose would lead to reduced removal rate. By increasing dose of HOFA from 2.5 to $5.0\,\mathrm{g\,L^{-1}}$ would lead to the decrease in removal efficiency by 14.11%. Also, increase in HOFA dose would lead to the increases in acidity state of solution which caused to decreases in the removal ratio. Reaction of sulfur compounds in HOFA with water reduces pH of

Table 6
Analysis of variance for a 2^{5-1} fractional factorial design

Factor	DF	*F*-value	*p*-value
A	1	44.96	0.000
B	1	0.97	0.350
C	1	0.00	0.971
D	1	450.33	0.000
E	1	32.55	0.000
$B \times C$	1	17.51	0.002
Residual error	9	–	–
Total	15	–	–

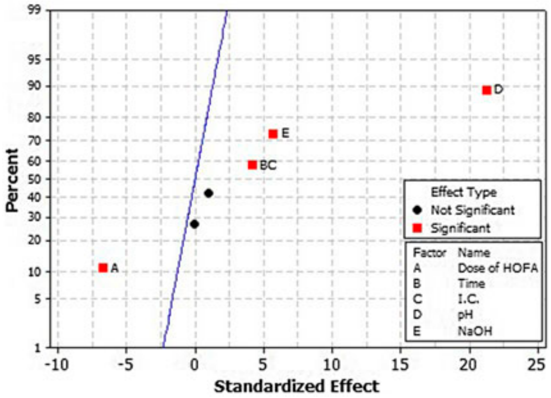

Fig. 3. Normal probability plot of standardized effects at $p = 0.05$.

solution to acidic state. In addition, an increase in HOFA dose enhances the amount of sulfur compounds in wastewater. When more stoichiometric amount of HOFA was added, increasing acidic state results in decrease of the copper precipitation level [30]. Similar results in the previous studies has been reported that by increasing sulfur source, the removal ratio would be decreased [13,31].

The third important factor was concentration of NaOH. Positive value of coefficient shows that increase in sodium hydroxide concentration was favored in the precipitation of Cu(II) metal ions. Enhancing the concentration of NaOH from 3 to 5 mol L^{-1} would lead to an increase in the removal efficiency by 11.96%. By adding NaOH solution in high concentration to samples, pH will be increased to weak acidic or neutral pH as well as production rate of Na_2S. So, it increases the removal of Cu(II) in higher NaOH concentration.

Interaction of time and initial concentration was the last significant factor. The interaction effect plots are shown in Fig. 5. The plots provide the mean response of two factors. If the lines are not parallel, it is an indication of interaction between the two factors. The positive value of the coefficient of this interaction means that an increase in the time and initial concentration leads to an addition of the amount of metallic ion precipitation.

Based on *F*-values and *p*-values, other main and interaction effects were neglected. As shown in Fig. 4, slopes of time and initial concentration as main factors are very low, but with considering high interaction of time and initial concentration (shown in Figs. 5 and 6), time and initial concentration were selected as important main factors.

The effect of other main factors and several interaction effects which were statistically insignificant

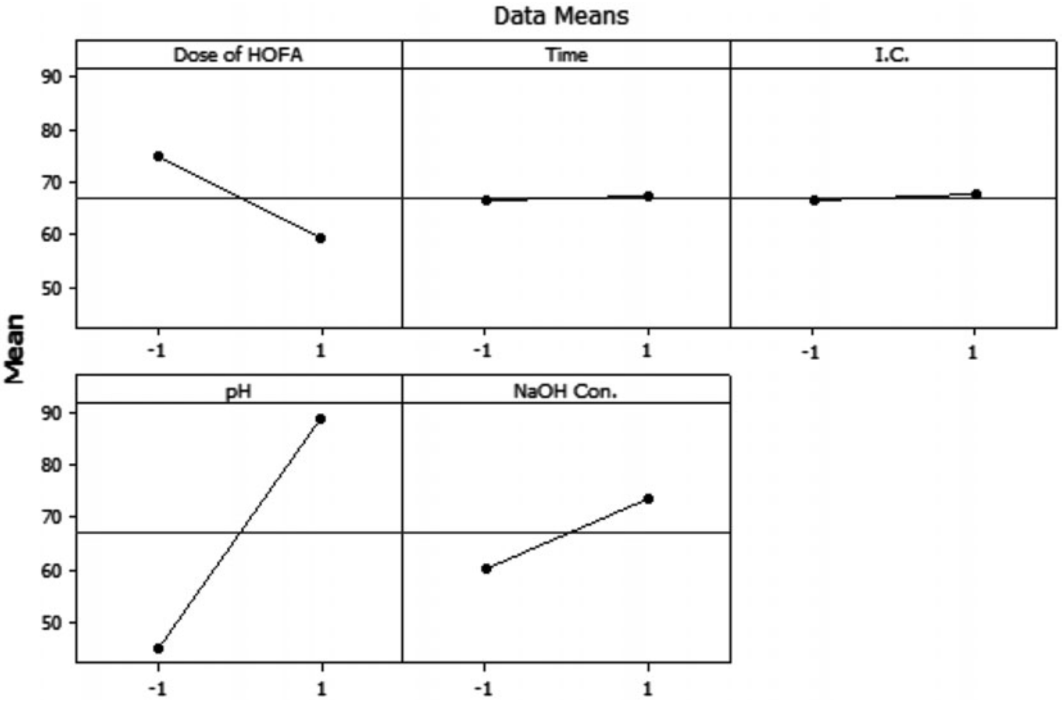

Fig. 4. Main effects plot for Cu(II) removal.

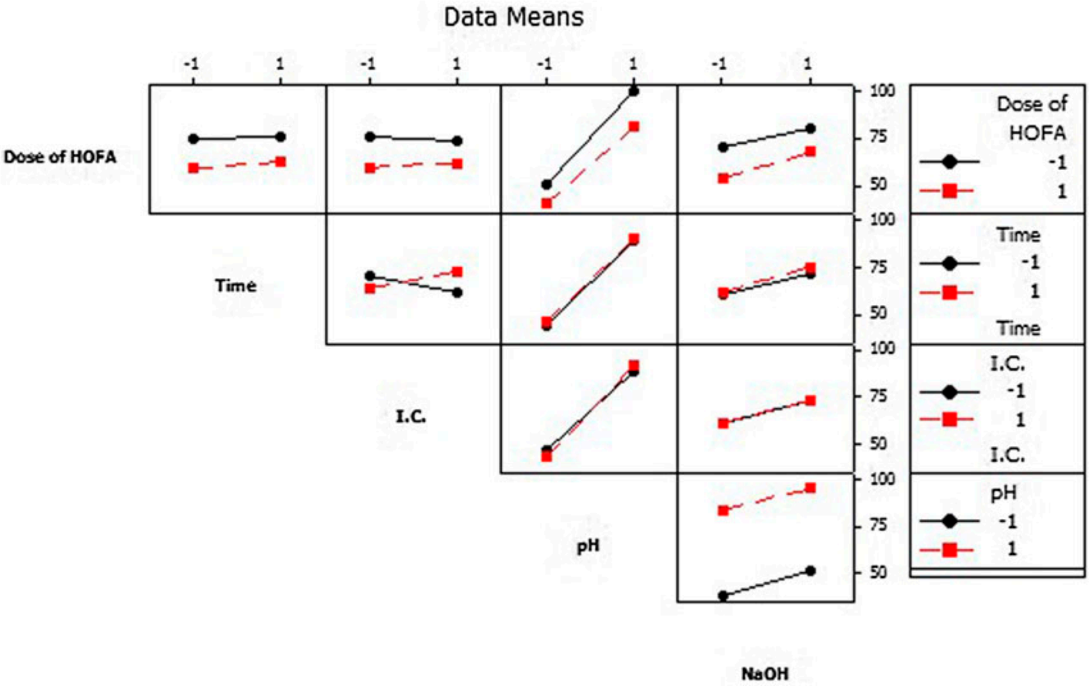

Fig. 5. Interaction effects plot for the removal of Cu(II).

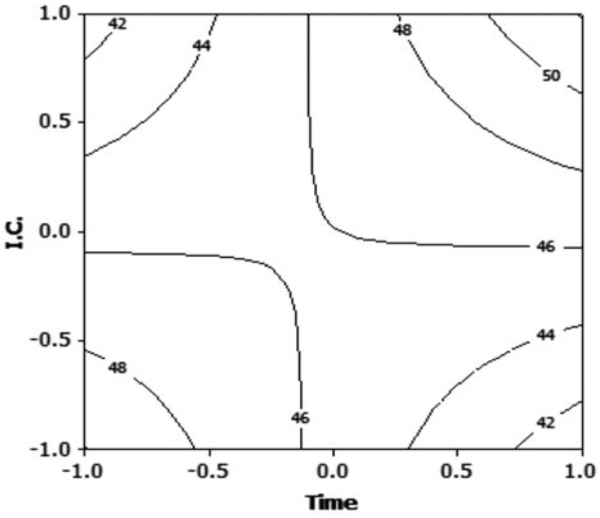

Fig. 6. Contour of removal percentage vs. time, initial concentration.

compared to the other effects were discarded and with remaining variables. The new and simple regression models proposed are as follows:

$$\text{Removal} = 67.7 - 7.02\,\text{Dose of HOFA} + 1.20\,\text{Time} - 0.184\,\text{I.C.} + 22.8\,\text{pH} + 5.95\,\text{NaOH} + 4.33\,\text{Time} \times \text{IC} \tag{7}$$

The new regression equation is so simple. R^2 for Eq. (7) is 98.6% that shows high accuracy of this model. Using simple equation is so applicable instead of other complex equations. The applicable range of all the parameters of the regression model is provided in Table 3.

3.5. Normal probability plot of residuals

It is important for the statistical analysis of the experimental data to assume that the data come from a normal distribution [32]. To determine whether or not the data-set is normally distributed, the normal probability plot of residual values is shown in Fig. 7. It can be understood that the points fall with a good approximate close to the straight line. Therefore, data from the experiments come from a normally distributed population and they can be used for this study.

The summary of results is presented in Table 7, where R^2 estimates the amount of the variation in the response around the mean that can be accounted by the model. According to Table 7, the full regression model gave 98.38% significant models (R^2) that suggest good adjustments to the experimental results. Adjusted R^2 (Adj-R^2) is a modification of R^2 that adjusts for the number of explanatory terms in a model. The Adj-R^2 (97.30%) is more suitable for comparing models with different numbers of independent variables.

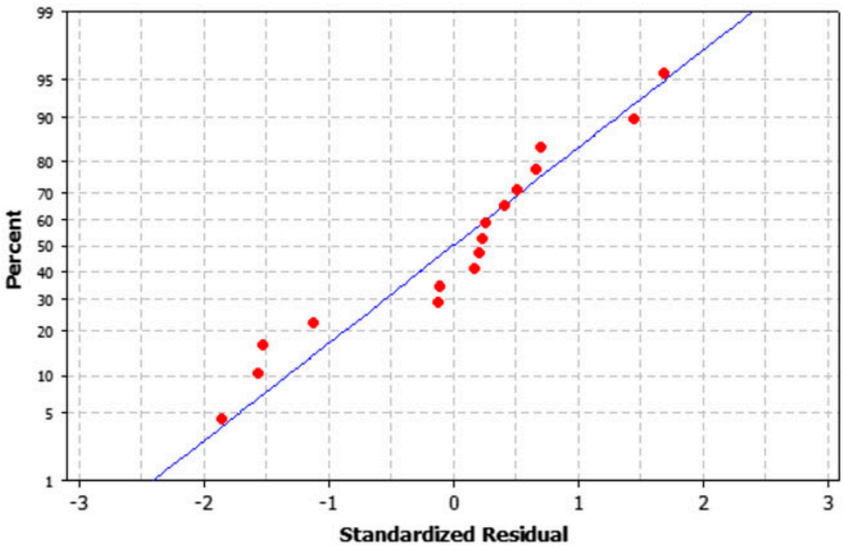

Fig. 7. Normal probability plot of residuals for Cu(II) removal efficiency.

Table 7
Summary of fit

R^2	0.9838
R^2 adj.	0.9730

4. Conclusion

In conclusion, the precipitation of heavy metals with NaOH in the presence of fly ash has been manifested to be successful in reducing the level of soluble heavy metals in solution. Employing HOFA as a sulfide precipitant for the removal of heavy metals from aqueous solutions was suggested due to its comparatively low cost and high performance. Cu(II) removal reached to 99% in this process. In addition, important factors in the precipitation process were identified by applying factorial design method. Six main experimentally factors such as pH, time, HOFA dose, initial concentration, NaOH concentration at two levels have been studied. Studying the results, pH of solution had the highest effect on the removal of Cu(II) with a positive influence. Significance of other parameters in sulfide precipitation for this study falls in the order:

pH > dose of HOFA > NaOH concentration > interaction between time and initial concentration.

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