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Factorial experimental design for optimizing the removal of lead ions from aqueous solutions by cation exchange resin

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ABSTRACT

Full factorial design of experiments were used to screen the factors affecting the lead removal effiency using cation exchange resin. The obtained linear model was statistically tested using analysis of variance (ANOVA), Student's *t*-test, lack of fit test, and test of curvature. The percentage removal of lead was examined by varying experimental conditions with center points. The factors and levels used during the experiments were; initial pH (3.5, 4.5 and 5.5), temperature (25, 35 and 45°C), initial lead concenteration (20, 60, and 100 mg/L) and resin dosage (0.02, 0.26, and 0.5 g). A steepest ascent based optimization procedure was implemented to seek better conditions in terms of maximizing the removal of lead(II) ions. The results showed that approximately 99% removal of Pb(II) was obtained when initial pH, temperature, initial lead concentration, and resin dosage are roughly set to 5, 34, 32, and 0.74, respectively.

Keywords: Lead; Heavy metal removal; Cation exchange resin; Factorial design; Optimization; Steepest ascent

1. Introduction

Toxic heavy metals in air, soil and water are global problems that are a growing threat to the environment. Heavy metals enter the environment by natural and anthropogenic means. They are among the chief pollutants of surface and groundwater [1]. As known, industrial and municipal wastewaters contain metal ions that can be harmful to aquatic life and human health such as kidney, nervous system, reproductive system, liver and brain disease. The permissible level of lead in drinking water is 0.05 mg/L [2]. The permissible limit of lead in wastewater as set by the Environment Protection Agency is 0.1 mg/L [3]. Major sources of water pollution with heavy metals are plating plants, mining, metal finishing, welding, and alloy manufacturing.

Classical techniques of heavy metal removal from solutions include the following processes: precipitation, electrolytic methods, ion exchange, evaporation and adsorption. Among these methods ion exchange receives considerable interest with high efficiency, low operational costs and fast kinetics [4]. Furthermore, ion exchange is particularly effective for treat-

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ing water including low concentration of heavy metals which is very common in practice [5].

Among the materials used in ion exchange processes, synthetic resins are commonly preferred as they are effective to remove the heavy metals from the solution. The most common cation exchangers are strongly acidic resins with sulfonic acid groups ($–SO_3H$) and weakly acidic resins with carboxylic acid groups (–COOH). Hydrogen ions in the sulfonic group or carboxylic group of the resin can serve as exchangeable ions with metal cations. As the solution containing heavy metal passes through the cations column, metal ions are exchanged for the hydrogen ions on the resin with the following ion exchange process:

$$n\text{R–SO}_3\text{H} + \text{M}^{n+} \rightarrow \left(\text{R–SO}_3^-\right)_n\text{M}^{n+} + n\text{H}^+ \quad (1)$$

$$n\text{R–COOH} + \text{M}^{n+} \rightarrow (\text{R–COO}^-)_n\text{M}^{n+} + n\text{H}^+ \quad (2)$$

The uptake of heavy metal ions by ion-exchange resins is rather affected by certain variables such as pH, temperature, initial metal concentration and contact time. Ionic charge also plays an important role in ion exchange process [6,7].

A number of investigators have studied the removal of inorganic metal ions Pb^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+} and Ni^{2+} from aqueous solution using different resins [8]. Gode [6] and Demirbaş [9] reported on the removal of Pb^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Ni^{2+} and Cr^{3+} from aqueous solution using ion exchange resins. Ion exchange resins such as IRN-77 [10], Ionac SR-5 [11], Amberlite [11–13], Purolite S-930 [14–15], SKN-1 [16] and others are also often employed for extraction of heavy metal ions.

The technique of statistical design for the experiments can be used for process characterization, optimization and modelling. It is widely accepted in the manufacturing industry for improving the product performance and reliability, the process capability and yield. In the statistical design of the experiments, the factors involved in an experiment at their respective levels can be simultaneously varied. Thus, a lot of information can be taken with a minimum number of experiment trials. Basically, the classical parameter design is complicated and not easy to use. Especially a large number of experiments must be conducted when the number of the process parameters increased. For this reason, the design of experiments is a useful tool to study the interactions between two or more variables at reduced number of experimental trials [17,18]. Factorial designs are widely used in experiments involving several factors where it is necessary to study the joint effect of the factors on a response [19]. It determines which factors have the important effects on the response as well as how the effect of one factor varies with the level of the other factors.

The main objectives of this work were, on the one hand, to investigate the effects of initial pH, temperature, initial lead concenteration and resin dosage on the ion exchange of Pb(II) onto the Lewatit SP 112 cation exchange resin and to optimize the conditions for Pb(II) removal.

2. Materials and methods

2.1. Ion exchange resin

Commercial synthetic Lewatit MonoPlus SP 112 cation exchange resin in hydrogen form was obtained from Fluka Co. The properties of the resin are given in Table 1. The resin was washed with double distilled water (2 L) to remove impurities and dried in an oven at 105˚C for 24 h. Dried resin was used for further experimental studies.

2.2. Solution preparation and reagents

A 1,000 mg/L Pb(II) stock solution was prepared by dissolving $Pb(NO_3)_2$ in distilled water. The solutions of different concentrations required for the

Table 1
The physical and chemical characteristics of strongly acidic Lewatit MonoPlus SP 112 macroporous cation exchange resin

Characteristics	Value
Physical characteristics	
Appearance	Beige–grey, opaque
Ionic forms as shipped	H^+
Mean particle size (mm) (>90%)	0.65 ± 0.05
Temperature limitations (˚C)	1–120
Chemical characteristics	
Structure	Macroporous
Matrix	Cross-linked-polystyrene
Functional group	Sulfonic acid
pH range	0–14
Total exchange capacity (eq/L)	1.7
Uniformity coefficient (max.)	1.1
Shipping weight (g/L)	740
Density (g/mL)	1.18
Water retention (%)	56–60
Bulk density (g/L)	1.24
Storability (max. year)	2

ion exchange experiments were prepared by the dilution of the stock solution with distilled water. All the chemicals used in this study were analytical or reagent grade products from Fluka Co. Distilled water was used throughout the study to prepare the required solutions.

2.3. Scanning electron microscopy analysis

The surface of Lewatit SP 112 cation exchange resin was also characterized by scanning electron microscopy (SEM) (JEOL-JSM-5600 LV) before and after the ion exchange experiments. Samples were gold-palladium coated prior to SEM observation. Images were collected with a beam potential of 20 kV.

2.4. Ion exchange experiments

The ion exchange of Pb(II) was studied using a batch procedure and results were indicated in the form of the percentage of Pb(II) ion removal. For each run, weighted amounts of resins were added to centrifuge tubes containing 20 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 centrifuge tubes were agitated in a temperature controlled shaker (Memmert) at 150 rpm for 4 h, then the tubes were centrifuged at 6,000 rpm for 10 min and the supernatant was acidified to <pH 2 by adding nitric acid and the lead content was determined through air acetylene flame atomic absorption spectrophotometer (Perkin Elmer, Analyst A400).

The removal efficiency, $R(\%)$ of Lewatit SP 112 was calculated according to Eq. (3):

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

where C_i and C_f represent the initial and final concentrations of the lead ions (mg/L), respectively.

2.5. Experimental planning

In the study, 2^4 full factorial design with center points was selected for conducting percentage of Pb (II) removal experiment. Based on the preliminary research, the factors chosen were initial pH, temperature, initial lead concentration, and resin dosage. The levels of the factors are given in Table 2.

Table 2
Factors and levels used for 2^4 full factorial design

Factors	Symbols	Range and levels		
		Low	Base	High
Initial pH	X_1	3.5	4.5	5.5
Temperature (°C)	X_2	25	35	45
Initial lead concentration (mg/L)	X_3	20	60	100
Resin dosage (g)	X_4	0.02	0.26	0.50

3. Results and dissussion

3.1. Factorial design

Base level experiments were carried out to determine critical factors and respected levels, and to test adequacy of the model. The first order model for k factors and all interactions among them may be represented in closed form as follows:

$$Y = \beta_0 + \sum_{i=1}^{k}\beta_i X_i + \sum_{i=1}^{k}\sum_{j>i}^{k}\beta_{ij}X_iX_j + \sum_{i=1}^{k}\sum_{j>i}^{k}\sum_{m>j}^{k}\beta_{ijm}X_iX_jX_m + \sum_{i=1}^{k}\sum_{j>i}^{k}\sum_{m>j}^{k}\sum_{n>m}^{k}\beta_{ijmn}X_iX_jX_mX_n + \varepsilon \quad (4)$$

where Y = percentage of Pb(II) removal; β_0 = grand average, β = empirical model coefficients for main and interaction effects; X = dimensionless coded factors for initial pH, temperature, initial lead concentration, resin dosage and ε is the residual error, respectively. The relations between coded and actual levels of the factors are designated using Eq. (5):

$$X_{\text{Coded}} = \{x_{\text{Actual}} - [(x_{\text{High}} + x_{\text{Low}})/2]\}/[(x_{\text{High}} - x_{\text{Low}})/2] \quad (5)$$

The coded and actual levels of factors for 2^4 full factorial design and the results showing percentage of Pb(II) removal are given in Table 3.

The coefficients of the empricial model for percentage of Pb(II) removal were calculated through regression analysis and tested for significance by Student's t-test at 95% confidence level. The estimated effects and coefficients are given in Table 4.

Table 4 shows that the interactions of $X_1X_2X_3$ and $X_1X_2X_3X_4$ are statistically insignificant ($p > 0.05$) and remaining main and interactions effects are statistically significant at 95% confidence level. On omitting

Table 3
Results of 2^4 factorial design

Exp. no	Coded levels of factors				Actual levels of factors				Removal%
	X_1	X_2	X_3	X_4	X_1	X_2	X_3	X_4	
1	−1	−1	−1	−1	3.5	25	20	0.02	85.187
2	+1	−1	−1	−1	5.5	25	20	0.02	93.496
3	−1	+1	−1	−1	3.5	45	20	0.02	79.906
4	+1	+1	−1	−1	5.5	45	20	0.02	91.497
5	−1	−1	+1	−1	3.5	25	100	0.02	68.172
6	+1	−1	+1	−1	5.5	25	100	0.02	73.442
7	−1	+1	+1	−1	3.5	45	100	0.02	68.150
8	+1	+1	+1	−1	5.5	45	100	0.02	75.775
9	−1	−1	−1	+1	3.5	25	20	0.50	92.612
10	+1	−1	−1	+1	5.5	25	20	0.50	93.215
11	−1	+1	−1	+1	3.5	45	20	0.50	92.070
12	+1	+1	−1	+1	5.5	45	20	0.50	93.877
13	−1	−1	+1	+1	3.5	25	100	0.50	97.959
14	+1	−1	+1	+1	5.5	25	100	0.50	97.926
15	−1	+1	+1	+1	3.5	45	100	0.50	98.119
16	+1	+1	+1	+1	5.5	45	100	0.50	98.088
17	0	0	0	0	4.5	35	60	0.26	87.521
18	0	0	0	0	4.5	35	60	0.26	87.860
19	0	0	0	0	4.5	35	60	0.26	87.051
20	0	0	0	0	4.5	35	60	0.26	87.695

Note: X_1: initial pH; X_2: temperature (℃); X_3: initial lead concentration (mg/L); X_4: resin dosage (g); −1: low level; 0: base level; +1: high level.

Table 4
Estimated effects and coefficients of the empirical model

Term	Effect	Coef	SE Coef	T	p
β_0		87.468	0.08723	1,002.76	0.000
β_1	4.393	2.196	0.08723	25.18	0.000
β_2	−0.566	−0.283	0.08723	−3.24	0.048
β_3	−5.529	−2.764	0.08723	−31.69	0.000
β_4	16.03	8.015	0.08723	91.89	0.000
β_{12}	0.855	0.428	0.08723	4.9	0.016
β_{13}	−1.185	−0.592	0.08723	−6.79	0.007
β_{14}	−3.806	−1.903	0.08723	−21.82	0.000
β_{23}	1.224	0.612	0.08723	7.02	0.006
β_{24}	0.676	0.338	0.08723	3.88	0.030
β_{34}	10.608	5.304	0.08723	60.81	0.000
β_{123}	−0.266	−0.133	0.08723	−1.53	0.224*
β_{124}	−0.554	−0.277	0.08723	−3.17	0.050
β_{134}	0.566	0.283	0.08723	3.25	0.048
β_{234}	−1.174	−0.587	0.08723	−6.73	0.007
β_{1234}	−0.034	−0.017	0.08723	−0.2	0.856*

*Insignificant coefficients at 95% confidence level ($p > 0.05$).

the coefficients not significant at 95% confidence level, the model given in Eq. (4) becomes:

$$Y = 87.468 + 2.196X_1 - 0.283X_2 - 2.764X_3 + 8.015X_4 + 0.428X_1X_2 - 0.592X_1X_3 - 1.903X_1X_4 + 0.612X_2X_3 + 0.338X_2X_4 + 5.304X_3X_4 - 0.277X_1X_2X_4 + 0.283X_1X_3X_4 - 0.587X_2X_3X_4 \quad (6)$$

In order to test whether the reduced model is adequate regarding with lack of fit and curvature effects, analysis of variance (ANOVA) was carried out. The result of ANOVA for percentage of Pb(II) removal is given in Table 5.

It is observed from Table 5 that neither curvature nor lack of fit effect exists for the reduced model ($p > 0.05$), meaning that the first order model is suitable for the process concerned. All main effects and interactions among them are statistically significant at 95% confidence level. By focusing on the F values in Table 5, X_4 is considered as the most important factor, the interaction between X_3 and X_4 is the second important, X_3 is the third, and so on. The least important factor and interactions are X_2, $X_1X_2X_4$, and $X_1X_3X_4$, respectively. In addition, the model provides higher R^2 (99.96%) and adjusted R^2 (99.88%), and lower standard error of prediction (0.3342), respectively. These conclude that the reduced model may be used for precisely estimating the percentage of Pb(II) removal.

In order to estimate the percentage of Pb(II) removal using the reduced model given in Eq. (6), the appropriate levels for statistically significant main and interaction effects should be determined by means of main and interaction effects plots. The main effects and interaction effects plots are depicted in Figs. 1 and 2, respectively.

It is observed from Fig. 1 that the percentage of Pb (II) removal is affected by each level of the factors in a different way. While high levels of initial pH and resin dosage provide higher percentage of Pb(II) removal, low level of initial lead concentration provides higher percentage of Pb(II) removal. On the other hand, neither low nor high level of temperature provides an important effect in terms of percentage of Pb(II) removal. In addition, resin dosage is considered the most important factor among others due to a steep slope appear in Fig. 1.

As far as interactions concerned, it is stated from Fig. 2 that all of the interactions among respected factors are significant and the most important interaction effect exists between initial lead concentration (X_3) and resin dosage (X_4). The X_3X_4 interaction indicates that resin dosage has little effect at low initial lead concentration but a large positive effect at high initial lead concentration. Therefore, higher percentage of Pb (II) removal would appear to be obtained when X_3 and X_4 are at the high levels ($X_3 = 100$ mg/L and $X_4 = 0.50$ g, respectively). The X_1X_4 and X_2X_3 interaction plots from Fig. 2, and $X_2X_3X_4$ interaction plots from Fig. 3 reveal that high levels of pH and tempera-

Table 5
ANOVA for percentage of Pb(II) removal

Source	df	SS	MS	*F*	*p*
X_1	1	77.19	77.19	694.71	0.000
X_2	1	1.28	1.28	11.52	0.015
X_3	1	122.27	122.27	1100.47	0.000
X_4	1	1,027.87	1,027.87	9,251.41	0.000
X_1X_2	1	2.93	2.93	26.35	0.002
X_1X_3	1	5.61	5.61	50.51	0.000
X_1X_4	1	57.94	57.94	521.48	0.000
X_2X_3	1	5.99	5.99	53.94	0.000
X_2X_4	1	1.83	1.83	16.46	0.007
X_3X_4	1	450.14	450.14	4,051.5	0.000
$X_1X_2X_4$	1	1.23	1.23	11.04	0.016
$X_1X_3X_4$	1	1.28	1.28	11.55	0.015
$X_2X_3X_4$	1	5.51	5.51	49.58	0.000
Residual error	6	0.67	0.11		
Curvature	1	0.01	0.01	0.1	0.766
Lack of fit	2	0.29	0.14	1.18	0.418
Pure error	3	0.37	0.12		
Total	19	1,761.72			

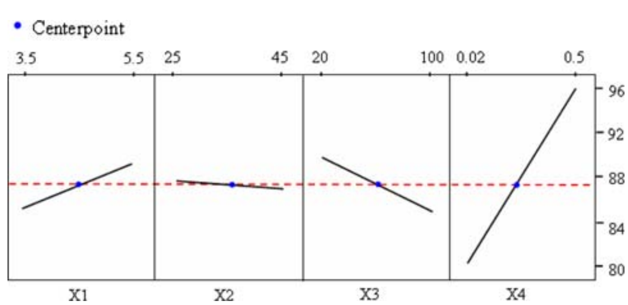

Fig. 1. Effect plots for main factors.

ture provide higher percentage of Pb(II) removal ($X_1 = 5.5$ and $X_2 = 45$, respectively).

By taken into consideration of the appropriate levels of the factors, the percentage of Pb(II) removal can be estimated approximately using Eq. (6) as 98.24 which is slightly better than the ones obtained from the experimental trials. The 95% confidence interval may be calculated as [97.38; 99.10] by using the pure error of 0.34 obtained from the analysis. The estimated percentage of Pb(II) removal is appeared to be within the confidence level, meaning that the reduced model provides reliable results inside the experimental region regarding with the chosen levels of the factors from the analyses.

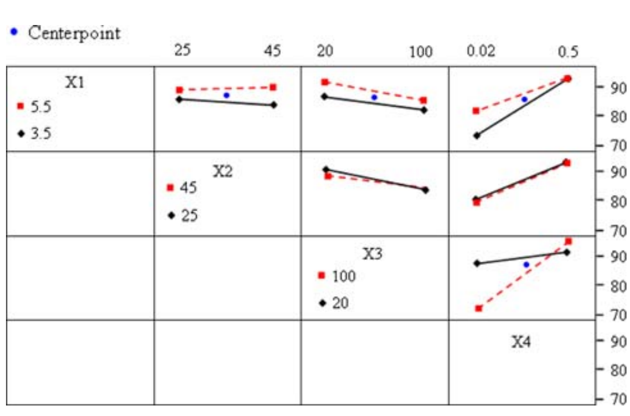

Fig. 2. Effect plots for interactions.

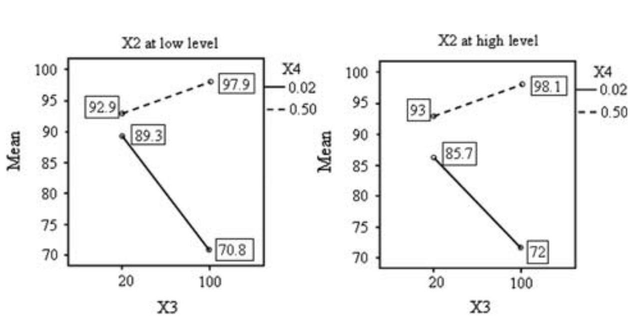

Fig. 3. Effect plot of interaction for X_2, X_3, and X_4.

3.2. Optimization study

The objective of optimization is to investigate whether a set of operating condition better than the currently determined exists to improve the performance for the process concerned. For this reason, additional set of experiments was conducted by steepest ascent method to retrieve optimized process condition for maximum percentage of Pb(II) removal.

The method of steepest ascent involves moving through the experimental region along a path that yields increases in the response. After a first-order model has been fit, the regression coefficients from this model are used to determine the coordinates along the path. The movement in X_j along the path of steepest ascent is proportional to the magnitude of the regression coefficient β_j, with the direction based on the sign of the coefficient [20]. The steepest ascent method aims to find an optimal region of the response and leave the job for finding the optimal points to the further stages. The optimized process conditions were evaluated using the regression equation given in Eq. (6) and unit changes were calculated. The details are given in Table 6.

The actual operating conditions and results obtained from the optimization study are given in Table 7. In this set of experiments, initial pH and resin dosage were increased as they have positive effect, whereas temperature and initial lead concentration were decreased due to negative effect. By focusing on the operating conditions and the corresponding percentage of Pb(II) removal given in Table 7, the experiment no. 22, as depicted in Fig. 4, was considered the optimum because in the next experiments (experiments 23 and 24), a downward trend appears in terms of percentage of Pb(II) removal. Based on the experiment no. 22, it is stated that approximately 99% removal of Pb(II), higher than the previous experimental trials, may be achieved when initial pH, temperature, initial lead concentration, and resin dosage are roughly set to 5, 34, 32, and 0.74, respectively.

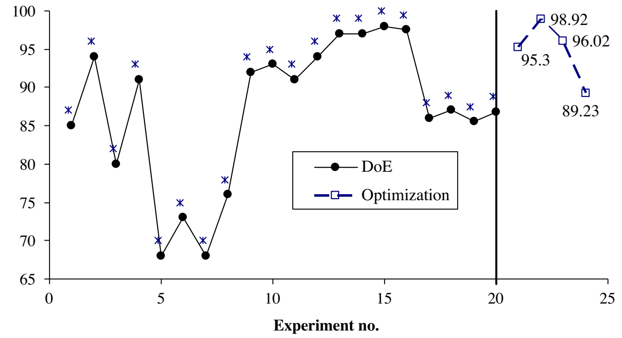

Fig. 4. Scatter plot of percentage of Pb(II) removal for experiments.

3.3. SEM analysis of the resin

The SEM images of the cation exchange resin before and after lead(II) ion exchange are shown in Fig. 5(a) and (b), respectively.

As seen from the Fig. 5(a) and (b), a visible change of the surface morphology in the lead (II) sorbed resin

Table 6
Results of evaluation of optimized factors

	X_1	X_2	X_3	X_4
Base level (Z_j)	4.5	35	60	0.26
Unit change (ΔZ_j)	1.0	10	40	0.24
Coefficient (β_j)	2.196	−0.283	−2.764	8.015
$\beta_j^{*}\Delta Z_j$	2.196	−2.83	−110.56	1.924
Normal steps	0.27	−0.35	−13.79	0.24

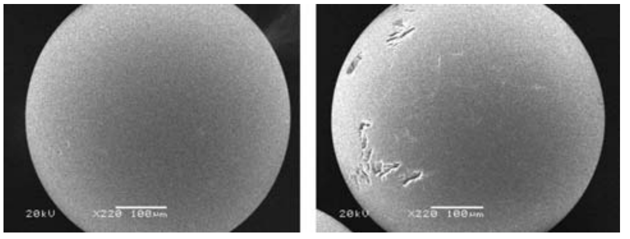

Fig. 5. SEM micrographs of Lewatit MonoPlus SP 112 Resin (a) before and (b) after Pb (II) ion exchange.

Table 7
Results of optimization study

Exp. no	Initial pH	Temperature	Initial lead concentration	Resin dosage	Removal of Pb(II) (%)
–	4.50	35.00	60.00	0.26	87.530
21	4.77	34.65	46.21	0.50	95.300
22	5.05	34.29	32.41	0.74	98.920
23	5.32	33.94	18.62	0.98	96.020
24	5.60	33.59	4.82	1.22	89.230

demonstrated that the ion exchange of lead (II) ions occured onto the resin.

4. Conclusions

The aim of the work was to investigate the removal of lead(II) from aqueous solutions by using Lewatit SP 112 cation exchange resin.

In order to determine the effects of various operating conditions (initial pH, temperature, initial lead concentration and resin dosage) and their interactions on the ion exchange of lead(II) ions by Lewatit SP 112, a full 2^4 factorial design with center points was performed.

Analysis of variance (ANOVA) showed that all main effects and interactions among them were statistically significant at 95% confidence level. Resin dosage (X_4) is considered as the most important factor, the interaction between initial lead concentration (X_3) and resin dosage (X_4) is the second important, initial lead concentration (X_3) is the third, and so on. The least important factor and interactions are temperature (X_2), initial pH-temperature-resin dosage ($X_1X_2X_4$), and initial pH-initial lead concentration-resin dosage ($X_1X_3X_4$), respectively.

Based on the plots of main and interaction effects, high level of each factor was selected ($X_1 = 5.5$, $X_2 = 45$, $X_3 = 100$ and $X_4 = 0.50$) and the percentage of lead(II) removal was calculated as 98.42 by means of reduced model given in Eq. (6).

Additional set of experiments was conducted by steepest ascent method to retrieve optimized process condition for maximum percentage of lead(II) removal. It is found out from the optimization study that approximately 99% lead(II) removal efficiency may be achieved when initial pH, temperature, initial lead concentration and resin dosage are roughly set to 5, 34, 32, and 0.74, respectively.

Experimental and theoretical results of this study demonstrate that Lewatit SP 112 cation exchange resin is suitable for the removal of lead ions from aqueous solutions.

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