# Response surface modeling of Pb(II) removal from aqueous solution by *Pistacia vera* L.: Box–Behnken experimental design

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## ABSTRACT

A three factor, three-level Box–Behnken experimental design combining with response surface modeling (RSM) and quadratic programming (QP) was employed for maximizing Pb(II) removal from aqueous solution by Antep pistachio (*Pistacia vera* L.) shells based on 17 different experimental data obtained in a lab-scale batch study. Three independent variables (initial pH of solution ($pH_0$) ranging from 2.0 to 5.5, initial concentration of Pb(II) ions ($C_0$) ranging from 5 to 50 ppm, and contact time ($t_C$) ranging from 5 to 120 min) were consecutively coded as $x_1$, $x_2$ and $x_3$ at three levels ($-1$, 0 and 1), and a second-order polynomial regression equation was then derived to predict responses. The significance of independent variables and their interactions were tested by means of the analysis of variance (ANOVA) with 95% confidence limits ($\alpha = 0.05$). The standardized effects of the independent variables and their interactions on the dependent variable were also investigated by preparing a Pareto chart. The optimum values of the selected variables were obtained by solving the quadratic regression model, as well as by analysing the response surface contour plots. The optimum coded values of three test variables were computed as $x_1 = 0.125$, $x_2 = 0.707$, and $x_3 = 0.107$ by using a LOQO/AMPL optimization algorithm. The experimental conditions at this global point were determined to be $pH_0 = 3.97$, $C_0 = 43.4$ ppm, and $t_C = 68.7$ min, and the corresponding Pb(II) removal efficiency was found to be about 100%.

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## 1. Introduction

With growing urbanization and rapid industrialization, the problem of the release of toxic heavy metals into the ecosystem has been of increasing concern in many parts of the world. Since heavy metals can significantly contaminate the receiving water bodies even in trace amounts, potential risks of heavy metal pollution cannot be ignored any longer. Therefore, the removal of heavy metals from water and wastewater has recently become the subject of considerable interest due to more strict legislations introduced in many countries to control water pollution [1].

Lead has been recognized one of the most hazardous heavy metals since mining, acid battery manufacturing, metal plating, printing, textile, photographic materials, ceramic and glass industries, explosive manufacturing, and also lead-containing piping material are the main sources of lead contamination [1,2]. The resultant higher concentrations of lead in the ecosystem have substantial impacts on the environment and human health. Lead poisoning causes various severe health problems in vital organs of humans,

such as damage to the kidney, liver, blood composition, nervous system, reproductive system and retardation in mental function [3].

Because lead is non-biodegradable and tends to bioaccumulate in cells of the living organisms, stricter environmental requirements and urgent treatment solutions are needed for lead removal from water and wastewater [3,4]. Current methods for lead removal include precipitation as hydroxide, carbonate and sulfide precipitates [5], coagulation/flocculation [6], membrane process [7], electrochemical process [8], ion exchange [9], biosorption [10], and adsorption techniques [11]. Among these methods, precipitation of heavy metals as metal hydroxides or sulfides has been practiced as the prime method of treatment for heavy metals in industrial wastewater for many years. However, this process may lead to a special problem of sludge handling and costly disposal [3]. Although membrane filtration and electrochemical process are proven techniques, their high costs limit their use in practice. In addition, activated carbon is regarded as an effective adsorbent for removal of metal ions from water, however, due to its high cost and loss during regeneration, unconventional low-cost adsorbents such as fly ash, peat, lignite, bagasse pith, wood, saw dust etc. have attracted the attention of several investigators in recent years [3]. The shell of *Pistacia vera* L. used as an adsorbent in both our previous and the present studies is an agricultural by-product produced in very large

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quantities particularly in the southeastern part of Turkey. The main advantages of Pb(II) removal by using pistachio shells is that it is in abundance and easy availability. This makes it a strong choice in the investigation of an economic way of Pb(II) removal. From the economical point of view, pistachio shells can be used as an alternative media to activated carbon, as well as to gain an understanding of the adsorption process [3].

Even though the dynamic characteristics of the adsorption process is very complicated, a number of attempts in developing an experimental-based optimization methodology may help to provide a better understanding of the process in terms of the effects of independent variables and their interactions on the dependent variable. However, Liu et al. [12] have stated that carrying out experiments with every possible factorial combination of the test variables is impractical because of a large number of experiments required. Hence, response surface modeling (RSM) can be a useful approach for studying the effects of several factors influencing the responses by varying them simultaneously and performing a limited number of experiments [13]. Unlike conventional optimization, suchlike statistical optimization methods can take into account the interactions of variables in generating process responses [14]. Similarly, Guo et al. [15] have reported that the statistical methods are believed to be effective and powerful approach for screening key factors rapidly from a multivariable system for the optimization of a particular process.

Since, many parameters may be responsible for the adsorption of Pb(II) ions from aqueous solution, it is important to select a suitable experimentation technique which will evaluate the effects of important parameters along with possible interactions, with minimum number of experiments, as suggested by Bhunia and Ghangrekar [16]. For this purpose, statistical design of experiments have been widely reported for the process characterization, optimization and modeling in recent years [15,17–22]. Although the experimental design technique has been widely studied by many researchers as an established and promising method for optimization and formulation of various types of processes, however, there are no systematic papers in the literature specifically devoted to a study of the response surface modeling of Pb(II) removal from aqueous solution by *P. vera* L. using an experimental design technique. Therefore, clarification of the place of Pb(II) adsorption by *P. vera* L. in the scheme of experimental design methodology can be considered as a particular field of investigation to develop a continuous control strategy, as well as to achieve an optimum Pb(II) removal.

Based on the above-mentioned facts, the specific objectives of this study were: (1) to apply a three factor, three-level Box–Behnken experimental design combining with RSM and quadratic programming (QP) for maximizing Pb(II) removal from aqueous solution by *P. vera* L.; (2) to examine the effects of three independent variables (initial pH of solution, initial concentration of Pb(II) ions, and contact time) and their interactions on the Pb(II) removal efficiency; and (3) to verify the validity of the proposed model by several additional batch experiments conducted in the experimental area of the Box–Behnken design.

## 2. Materials and methods

### 2.1. Adsorbent preparation

Antep pistachio (*P. vera* L.) shells used in the batch experiments were obtained from lands near to Zohrecik Village of Gaziantep city in the southeastern part of Turkey. Because Pb(II) concentration in the air may affect the Pb(II) amount in the adsorbent, Pb(II) analysis was first in raw pistachio shells prior to determining of Pb(II) ions concentration of aqueous solutions. Our previous results indicated that there was no detectable lead levels present in raw

pistachio shells to have an effect on the experimental data [3]. This was attributed to the fact that the lands near to Zohrecik Village, where the pistachio shells were collected, are quite away from urban freeways, as well as from industrial areas [3]. Elemental analysis was performed with an elemental analyzer (EA 1108, Fisons Instruments). The elemental composition of used pistachio shells (in wt.%) was moisture – 4.22, ash – 0.2, carbon – 47.83, hydrogen – 5.32, nitrogen – 0.34, total sulfur – 0.19, oxygen – 41.9. True density and surface area of pistachio shells were determined as 770 kg/m$^3$ and 0.41 m$^2$/g, respectively [3]. Prior to batch adsorption tests, the shells were washed with distilled water to remove soluble and coloured components, and then dried in an oven (Nuve FN 500) at 80 °C for 24 h. The dried pistachio shells were sieved through a 1 mm sieve (Endecotts Ltd.) and stored in polythene bags for further shake flask studies.

### 2.2. Shake flask studies

A stock solution of 1000 ppm of Pb(II) was first prepared by dissolving analytical grade Pb(NO$_3$)$_2$·6H$_2$O (Merck Chemical Corp.) in distilled water. Then, synthetic wastewater samples were prepared to give Pb(II) concentrations ranging between 5 and 50 ppm by diluting appropriate amounts of Pb(NO$_3$)$_2$·6H$_2$O stock solution with distilled water for batch adsorption experiments. From the physical point of view, experimental ranges of the initial pH of the solution and contact time were chosen between 2.0–5.5, and 5–120 min, respectively. The selected ranges of the present independent variables were considered based on our previous findings [3]. Series of lab-scale shake flask studies were carried out to determine the effects of initial pH (pH$_0$), initial concentration of Pb(II) ions ($C_0$) and contact time ($t_C$) on the Pb(II) removal efficiency. A known amount of the dried adsorbent (1 g) was added into 250 mL glass flasks with 200 mL solution giving a liquid (solution)–solid (adsorbent) ratio of 200. The flasks were then placed in an orbital shaker (Gallenkamp Orbital Incubator Shaker) and agitated up to a total contact time of 120 min at a fixed agitation speed of 250 rpm at an ambient temperature of 30 °C. Samples were taken at predetermined time intervals, and then separated by centrifugation prior to any analysis done.

### 2.3. Box–Behnken experimental design and optimization by RSM

The optimum conditions for maximizing the adsorption of Pb(II) by *P. vera* L. were determined by means of a three factor, three-level Box–Behnken experimental design combining with response surface modeling and quadratic programming. RSM consists of a group of empirical techniques devoted to the evaluation of relationships existing between a cluster of controlled experimental factors and measured responses according to one or more selected criteria [23,24]. In the first step of RSM, a suitable approximation is introduced to find true relationship between the dependent variable (response) and the set of independent variables (factors). If knowledge concerning the shape of true response surface is insufficient, the preliminary model (generally a first-order model) is upgraded by adding high-order terms to it [23]. In the next step, the behaviour of the system is explained by the following quadratic equation [13,23,24]:

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{i=1}^{k} \sum_{j=1}^{k} \beta_{ij} x_i x_j + \varepsilon \qquad (1)$$

where $Y$ is the process response or output (dependent variable), $k$ is the number of the patterns, $i$ and $j$ are the index numbers for pattern, $\beta_0$ is the free or offset term called intercept term, $x_1, x_2, \ldots, x_k$ are the coded independent variables, $\beta_i$ is the first-order (linear)

**Table 1**
Experimental range and levels of independent variables.

| Variables | Range and levels | | | |
|---|---|---|---|---|
| | Low level (−1) | Center level (0) | High level (+1) | $\Delta X_i$[a] |
| Initial pH of solution (pH$_0$), $X_1$ | 2.0 | 3.75 | 5.5 | 1.75 |
| Initial concentration of Pb(II) ions ($C_0$), $X_2$ (ppm) | 5.0 | 27.5 | 50 | 22.5 |
| Contact time ($t_C$), $X_3$ (min) | 5.0 | 62.5 | 120 | 57.5 |

<sup>a</sup> Step change values.

main effect, $\beta_{ii}$ is the quadratic (squared) effect, $\beta_{ij}$ is the interaction effect, and $\varepsilon$ is the random error or allows for discrepancies or uncertainties between predicted and measured values. In developing Eq. (1), the natural (uncoded) independent variables ($X_1, X_2, \ldots, X_k$) are coded according to the following transformation [13,23–25]:

$$x_i(X_i - X_0)/\Delta X_i \tag{2}$$

where $x_i$ is dimensionless coded value of the $i$th independent variable, $X_i$ is the uncoded value of the $i$th independent variable, $X_0$ is the uncoded $i$th independent variable at the center point, and $\Delta X_i$ is the step change value.

For this study, the effects of initial pH of solution (pH$_0$, $x_1$), initial concentration of Pb(II) ions ($C_0$, $x_2$), and contact time ($t_C$, $x_3$) were investigated. Each of independent variables was consecutively coded as $x_1$, $x_2$ and $x_3$ at three levels: −1, 0 and 1. The experimental range and levels of independent variables considered in this study are presented in Table 1. The central values chosen for the experimental design were pH$_0$ = 3.75, $C_0$ = 27.5 ppm and $t_C$ = 62.5 min in uncoded form.

To best determine the effect of various operating parameters such as initial pH of solution, initial concentration of Pb(II) ions, and contact time, requires an organized testing method. Tests that produce several combinations and magnitudes of variables are necessary, but to produce all possible combinations of variables and ranges would be a tremendous task. Therefore, to minimize the number of tests while producing a response surface with statistical meaning, several types of experimental designs (such as Plackett–Burmann design, $2^3$ factorial design, etc.) including various range and levels of independent variables were first tested to obtain the highest correlation between the measured data and predicted values. For the present data, Box–Behnken experimental

design was found to be more suitable than other tested designs. This may be attributed to the characteristics of the performance index, as well as to the complexity of the input vector used in this study.

The advantages of Box–Behnken designs include the fact that they are all spherical designs and require factors to be run at only three levels. The designs are also rotatable or nearly rotatable. Some of these designs also provide orthogonal blocking. Thus, if there is a need to separate runs into blocks for the Box–Behnken design, then designs are available that allow blocks to be used in such a way that the estimation of the regression parameters for the factor effects are not affected by the blocks. In other words, in these designs the block effects are orthogonal to the other factor effects. Yet another advantage of these designs is that there are no runs where all factors are at either the +1 or −1 levels. In all, 17 batch experiments were conducted in triplicate, and the average values of Pb(II) removals were tabulated, as given in Table 2. As seen in Table 2, the design had only 17 experimental runs, instead of having 27 experimental points if the run was done in $3^3$ complete factorial design, as similarly reported by others [17,26]. Therefore, it can be noted that a number of additional experiments as well as time-consuming and laborious laboratory studies were eliminated in this study by selecting the Box–Behnken experimental design, instead of complete factorial design. Consequently, a three factor, three-level Box–Behnken experimental design combining with RSM was selected for maximizing Pb(II) removal from aqueous solution by *P. vera* L.

### 2.4. Analytical procedure

The surface area of the pistachio shells was determined by single point Brunauer, Emmett and Teller (BET) N$_2$ sorption procedure. Elemental analysis was performed with an elemental analyzer (EA 1108, Fisons Instruments). True density of pistachio shells was determined as outlined in our previous work [3]. Pb(II) analysis was done in raw pistachio shells according to EPA Method 3010 (acid digestion of extracts for total recoverable or dissolved metal analysis by FLAA or ICP spectroscopy). The distilled water used in the experiments was supplied from a TKA-GenPure water purification system (Niederelbert, Germany). The pH of synthetic samples was adjusted by the addition of 1N NaOH and 1N HCl solutions using a pH meter (WTW Multiline P4 model). Pb(II) ions concentrations of aqueous phases were analyzed by atomic absorption spectrometric procedure using a flame atomic absorption spectrometer (SpectrAA 220 Fast Sequential Atomic Absorption Spectrometer,

**Table 2**
Box–Behnken design matrix with three independent variables expressed in coded and natural units.

| Batch no. | Initial pH of solution (pH$_0$) | | Initial concentration of Pb(II) ions ($C_0$) (ppm) | | Contact time ($t_C$) (min) | | Pb(II) removal efficiency (%) |
|---|---|---|---|---|---|---|---|
| | $x_1$ (coded) | $X_1$ (uncoded) | $x_2$ (coded) | $X_2$ (uncoded) | $x_3$ (coded) | $X_3$ (uncoded) | $Y_0$ (observed)[a] |
| 1 | −1 | 2.0 | 0 | 27.5 | −1 | 5.0 | 26.45 |
| 2 | 0 | 3.75 | 0 | 27.5 | 0 | 62.5 | 92.18 |
| 3 | +1 | 5.5 | −1 | 5.0 | 0 | 62.5 | 87.30 |
| 4 | 0 | 3.75 | −1 | 5.0 | −1 | 5.0 | 59.60 |
| 5 | −1 | 2.0 | −1 | 5.0 | 0 | 62.5 | 41.70 |
| 6 | +1 | 5.5 | 0 | 27.5 | −1 | 5.0 | 61.96 |
| 7 | 0 | 3.75 | 0 | 27.5 | −1 | 5.0 | 71.22 |
| 8 | 0 | 3.75 | +1 | 50 | 0 | 62.5 | 95.20 |
| 9 | −1 | 2.0 | +1 | 50 | 0 | 62.5 | 53.50 |
| 10 | 0 | 3.75 | +1 | 50 | +1 | 120 | 97.30 |
| 11 | +1 | 5.5 | +1 | 50 | 0 | 62.5 | 97.11 |
| 12 | −1 | 2.0 | 0 | 27.5 | 1 | 120 | 51.20 |
| 13 | 0 | 3.75 | +1 | 50 | −1 | 5.0 | 90.10 |
| 14 | 0 | 3.75 | 0 | 27.5 | +1 | 120 | 94.62 |
| 15 | 0 | 3.75 | −1 | 5.0 | +1 | 120 | 89.70 |
| 16 | 0 | 3.75 | −1 | 5.0 | 0 | 62.5 | 89.10 |
| 17 | +1 | 5.5 | 0 | 27.5 | +1 | 120 | 93.73 |

<sup>a</sup> $Y_0$ indicates the average Pb(II) removal efficiency of triplicate experiments ($n$ = 3).

**Table 3**
Analysis of variance (ANOVA) of the response surface model for the prediction of Pb(II) removal efficiency.

| Factors (coded) | Statistics[a] | | | | |
|---|---|---|---|---|---|
| | SS[b] | df[c] | MSS[d] MSS = SS/df, MSS$_E$ = SS$_E$/df$_E$ | $F$ value $F_{cal}$ = MSS/MSS$_E$ | Probability $(p) > F$ |
| Model | 7987.214 | 9 | 887.468 | 47.31 | 0.000020[e] |
| $x_1$ | 3496.570 | 1 | 3496.570 | 186.40 | 0.000003[e] |
| $x_1^2$ | 2128.834 | 1 | 2128.834 | 113.49 | 0.000014[e] |
| $x_2$ | 433.096 | 1 | 433.096 | 23.09 | 0.001955[e] |
| $x_2^2$ | 7.736 | 1 | 7.736 | 0.41 | 0.541204 |
| $x_3$ | 1374.053 | 1 | 1374.053 | 73.25 | 0.000059[e] |
| $x_3^2$ | 252.955 | 1 | 252.955 | 13.48 | 0.007941[e] |
| $x_1 x_2$ | 0.990 | 1 | 0.990 | 0.05 | 0.824868 |
| $x_1 x_3$ | 12.320 | 1 | 12.320 | 0.66 | 0.444346 |
| $x_2 x_3$ | 131.103 | 1 | 131.103 | 6.99 | 0.033246[e] |
| Error | SS$_E$ = 131.310 | 7 | MSS$_E$ = 18.759 | | |
| Total | 8118.524 | 16 | | | |

[a] E is the subscript indicating the error.
[b] Sum of squares.
[c] Degrees of freedom.
[d] Mean sum of squares.
[e] $p$ values <0.05 were considered to be significant.

Varian Inc.) with an air–acetylene flame and a hollow cathode lamp [27].

### 2.5. Statistical analysis

Each experiment was performed in triplicate and repeated at least three times to observe the reproducibility. STATISTICA (Trial version 8.0, StatSoft Inc., USA) software package was used for regression and graphical analyses of the data obtained. In all calculations, spreadsheets of Microsoft Excel® 2000 were used as ODBC (Open Database Connectivity) data source running under Windows. The significance of independent variables and their interactions were tested by means of the analysis of variance (ANOVA). An alpha ($\alpha$) level of 0.05 was used to determine the statistical significance in all analyses. The standardized effects of the independent variables and their interactions on the dependent variable were also investigated by preparing a Pareto chart. Results were assessed with various descriptive statistics such as $t$ ratio, $p$ value, $F$ value, degrees of freedom (df), coefficient of variation (CV), determination coefficient ($R^2$), adjusted determination coefficient ($R_a^2$), correlation coefficient ($R$), Durbin–Watson (DW) statistic, sum of squares (SS), mean sum of squares (MSS), Mallow's $C_p$ statistic and chi-square ($\chi^2$) test to reflect the statistical significance of the quadratic model. The second-order polynominal coefficients and some descriptive statistics were also analyzed by using DataFit® scientific software (version 8.1.69, Copyright© 1995–2005 Oakdale Engineering) for the verification of the obtained results. The tabulated value of the $F$-statistic corresponding to $n_N$ (numerator = df) and $n_D$ (denominator = $n$ − df + 1) was obtained at the desired probability level (i.e., $\alpha$ = 0.05 or 95% confidence) by using an online statistical calculator (by Petr Kuzmic from BioKin, Ltd., USA). Similarly, the tabulated value of the $\chi^2$ was determined by using another online statistical calculator (by Webster West from Texas A&M University, USA). The quadratic regression equation was solved by a LOQO/AMPL optimization algorithm (designed by the third author) to obtain the global points for maximizing the Pb(II) removal efficiency. For the validation of the regression model, a non-parametric Mann–Whitney (or Wilcoxon rank-sum) $U$-test and a two-sample (unpaired) $t$-test were performed to evaluate the relationship between the additional experimental data and the predicted responses. An online statistical calculator (by Richard Lowry from Vassar College, USA) was used to calculate two-tailed $p$ values for the $z$ score and the $t$ value obtained from the Mann–Whitney $U$-test and the unpaired $t$-test, respectively. The critical $t$ value for

the given values of df and $\alpha$ was obtained by using another online statistical calculator (by David W. Stockburger from Missouri State University, USA). The validation statistics were also checked by using StatsDirect (Trial version 2.7.2, Copyright© 1990–2008 StatsDirect Ltd.) statistical software package for the verification of the obtained results.

## 3. Results and discussion

### 3.1. Determination of the regression model and statistical evaluation

By applying multiple regression analysis on the design matrix and the responses given in Table 2, the following second-order polynomial equation in coded form was established to explain the Pb(II) removal efficiency:

$$Y = 91.6039 + 20.9063x_1 - 23.7018x_1^2 + 6.581x_2 + 1.6058x_2^2$$

$$+ 11.722x_3 - 9.1825x_3^2 - 0.4975x_1x_2 + 1.755x_1x_3 - 5.725x_2x_3$$

$$(3)$$

where $Y$ is the predicted Pb(II) removal efficiency, $x_1$, $x_2$ and $x_3$ are the coded terms for three independent test variables, pH$_0$, $C_0$ and $t_C$, respectively. The optimum values of the selected test variables were obtained by solving the Eq. (3) and also by analysing the response surface contour plots. Sen and Swaminathan [25] have reported that the analysis of variance is essential to test the significance of the model. Therefore, the ANOVA was conducted to test the significance of the fit of the second-order polynomial equation for the experimental data as given in Table 3.

As seen in Table 3, the ANOVA of the regression model (Eq. (3)) showed that the quadratic model was highly significant, as was evident from the Fisher's $F$-test ($F_{model}$ = 47.31) with a very low probability value ($P_{model} > F$ = 0.000020), as suggested by Liu et al. [12]. Furthermore, the calculated $F$ value ($S_r^2/S_e^2 = F_{cal}$ = 47.31) was found to be greater than the tabulated $F$ value ($F_{\alpha,df,(n-df+1)} = F_{0.05,9,7} = S_r^2/S_e^2 = F_{tab}$ = 3.68) at the 5% level, indicating that the computed Fisher's variance ratio at this level was large enough to justify a very high degree of adequacy of the quadratic model and also to indicate that treatment combinations are highly significant, as similarly reported by others [12,25]. Since $F_{cal} > F_{tab}$ (47.31 > 3.68), the Fisher's $F$-test concluded with 95% certainty that the regression model explained a significant amount of the variation in the dependent variable.

**Table 4**
Detailed descriptive statistics of the regression analysis for the entire quadratic model.

| Descriptive statistics | Calculation | Regression results |
|---|---|---|
| Sum of residuals | $\sum_{i=1}^{n}(Y_o - Y_p)$ | $1.599 \times 10^{-9}$ |
| Average residual | $\frac{1}{n}\sum_{i=1}^{n}(Y_o - Y_p)$ | $9.412 \times 10^{-12}$ |
| Residual or error sum of squares (absolute) | $SS_E = \sum_{i=1}^{n}(Y_o - Y_p)^2$ | 131.310 |
| Residual or error sum of squares (relative) | $(SS_E)_R = \sum_{i=1}^{n}[(Y_o - Y_p)^2/\sigma_i^2]$ | 131.310 |
| Error variance of the estimate ($MSS_E$) | $\partial^2 = S_e^2 = \sum_{i=1}^{n}(Y_o - Y_p)^2/(n-p) = SS_E/(n-p)$ | 18.759 |
| Standard error of the estimate ($S_e$) | $\partial = S_e = \sqrt{\sum_{i=1}^{n}(Y_o - Y_p)^2/(n-p)} = \sqrt{SS_E/(n-p)}$ | 4.3311 |
| Determination coefficient ($R^2$) | $R^2 = \dfrac{\sum_{i=1}^{n}(Y_p - \bar{Y}_p)^2}{\sum_{i=1}^{n}(Y_p - \bar{Y}_p)^2 + \sum_{i=1}^{n}(Y_o - Y_p)^2} = \dfrac{SS_{reg}}{SS_{reg} + SS_E}$ | 0.98383 |
| Correlation coefficient ($R$) | $R = \sqrt{\dfrac{\sum_{i=1}^{n}(Y_p - \bar{Y}_p)^2}{\sum_{i=1}^{n}(Y_p - \bar{Y}_p)^2 + \sum_{i=1}^{n}(Y_o - Y_p)^2}}$ | 0.99190 |
| Adjusted determination coefficient ($R_a^2$) | $R_a^2 = 1 - \left(\frac{SS_E}{SS_T}\frac{df_T}{df_E}\right) = 1 - \left[(1 - R^2)\left(\frac{n-1}{n-k-1}\right)\right]$ | 0.96303 |
| Coefficient of variation (CV) | $CV = (\sqrt{MSS_E}/\bar{Y}_o \times 100)$ | 5.698965 |
| Durbin–Watson statistic | $DW = \sum_{i=2}^{n}(e_i - e_{i-1})^2 / \sum_{i=1}^{n}e_i^2$ | 1.784483 |
| Mallow's $C_p$ statistic | $C_p = (SS_E/MSS_E) + 2p - n$ | 9.9902 |
| Chi-square ($\chi^2$) test | $\chi_{cal}^2 = \sum_{i=1}^{n}(O_i - E_i)^2/E_i$ | 1.7183 |

The goodness of fit of the model was checked by the determination coefficient ($R^2$). In this case, the value of determination coefficient ($R^2 = 0.9838$) indicated that only 1.62% of the total variations were not explained by the regression model. In addition, the value of adjusted determination coefficient ($R_a^2 = 0.9630$) was also very high, showing a high significance of the model, as similarly reported by others [12,13,24]. Liu et al. [12] have reported that the $R_a^2$ corrects the $R^2$ value for the sample size and the number of terms in the model. If there are many terms in the model and the sample size is not very large, the $R_a^2$ may be noticeably smaller than the $R^2$. In our case, the $R_a^2$ was found to be very close to the $R^2$ value. Liu et al. [12] observed similar phenomenon for the second-order RSM experiments based on a five-level central composite design employed to explore the effects of various fermentation medium ingredients on production formation. Moreover, a very high value of the correlation coefficient ($R = 0.9919$) signified an excellent correlation between the predicted values (responses) and the experimental results. Furthermore, a very high degree of precision and a good deal of the reliability of the conducted experiments were indicated by a low value of the coefficient of variation (CV = 5.699%), as suggested by others [13,25].

Dawson and Martinez-Dawson [28] have reported that Mallow's $C_p$ statistic can be used to determine how many terms can be omitted from the response surface model. For a response surface model including all terms, $C_p = p$, where $p$ is the number of parameters or variables in the regression model including the intercept term. For response surface models with omitted terms, $C_p \sim p$ indicates a good model with little bias, and $C_p \leq p$ indicates a very good prediction model. The goal is to remove terms from the response surface model until a minimum $C_p$ value near $p$ is obtained. If $C_p > p$, this indicates that too many terms have been removed or some remaining terms are not necessary [28]. In our case, Mallow's $C_p$ statistic ($C_p = 9.9902$) indicated the third condition ($C_p \leq p$ and $p = 10$ including $\beta_0, \beta_1, \ldots, \beta_{13}, \beta_{23}$), showing a very good prediction model.

The Durbin–Watson statistic is another value that shows whether autocorrelation, or correlation between errors, is present in a model [29]. The range of DW statistic is between 0 and 4, and is used for testing the linear association between adjacent residuals [30]. The DW values below 2 can indicate positive autocorrelation and values above 2 can indicate negative autocorrelation [29]. Hewings et al. [30] have reported that for all estimations, analysis was performed to be sure that the DW value would be as close as

**Table 5**
Observed responses and predicted values with residuals.

| Batch no. | Coded factors | | | Pb(II) removal efficiency (%) | | Rounded residuals $(Y_o - Y_p)$ | Error (%) | Absolute rounded residuals |
|---|---|---|---|---|---|---|---|---|
| | $x_1$ | $x_2$ | $x_3$ | Observed, $Y_o$ (%)[a] | Predicted, $Y_p$ (%) | | | |
| 1 | −1 | 0 | −1 | 26.45 | 27.85 | −1.40 | −5.30 | 1.40 |
| 2 | 0 | 0 | 0 | 92.18 | 91.61 | 0.57 | 0.62 | 0.57 |
| 3 | +1 | −1 | 0 | 87.30 | 84.34 | 2.96 | 3.40 | 2.96 |
| 4 | 0 | −1 | −1 | 59.60 | 60.00 | −0.40 | −0.68 | 0.40 |
| 5 | −1 | −1 | 0 | 41.70 | 41.53 | 0.17 | 0.41 | 0.17 |
| 6 | +1 | 0 | −1 | 61.96 | 66.15 | −4.19 | −6.77 | 4.19 |
| 7 | 0 | 0 | −1 | 71.22 | 70.70 | 0.52 | 0.72 | 0.52 |
| 8 | 0 | +1 | 0 | 95.20 | 99.80 | −4.60 | −4.83 | 4.60 |
| 9 | −1 | +1 | 0 | 53.50 | 55.69 | −2.19 | −4.08 | 2.19 |
| 10 | 0 | +1 | +1 | 97.30 | 96.61 | 0.69 | 0.71 | 0.69 |
| 11 | +1 | +1 | 0 | 97.11 | 96.50 | 0.61 | 0.63 | 0.61 |
| 12 | −1 | 0 | 1 | 51.20 | 47.79 | 3.41 | 6.67 | 3.41 |
| 13 | 0 | +1 | −1 | 90.10 | 84.62 | 5.48 | 6.09 | 5.48 |
| 14 | 0 | 0 | +1 | 94.62 | 94.15 | 0.47 | 0.50 | 0.47 |
| 15 | 0 | −1 | +1 | 89.70 | 94.90 | −5.20 | −5.80 | 5.20 |
| 16 | 0 | −1 | 0 | 89.10 | 86.63 | 2.47 | 2.77 | 2.47 |
| 17 | +1 | 0 | +1 | 93.73 | 93.11 | 0.62 | 0.66 | 0.62 |

[a] $Y_o$ indicates the average Pb(II) removal efficiency of triplicate experiments ($n = 3$).

possible to 2. If the DW value is typically around 2, this implies a good fit of the model. In our case, the DW statistic (DW = 1.784) was determined to be very close to 2, indicating the goodness of fit of the model.

The chi-square ($\chi^2$) test was also carried out to check whether there was a significant difference between the expected responses and the observed data. The calculated chi-square value ($\chi^2_{cal} = 1.7183$) was found to be less than the tabulated chi-square value ($\chi^2_{\alpha,(n-1)} = \chi^2_{0.05,16} = \chi^2_{tab} = 26.296$), indicating that there was no statistically significant difference between the observed data and the expected responses. Since $\chi^2_{cal} < \chi^2_{tab}$ (1.7183 < 26.296), the alternative hypothesis ($H_a$) was rejected in favor of the null hypothesis ($H_0$). The $\chi^2$ test concluded with 95% certainty that the quadratic model provided a satisfactory fit to the experimental data. Detailed definitions regarding the above-mentioned descriptive statistics are presented in Table 4.

Liu et al. [12] have reported that checking the adequacy of the model needs all of the information on lack of fit, which is contained in the residuals. The normal (percentage) probability plot of the residuals is an important diagnostic tool to detect and explain the systematic departures from the assumptions that errors are normally distributed and are independent of each other and that the error variances are homogeneous. Therefore, a plot of normal probability of the residuals is depicted in Fig. 1. As seen in Fig. 1, the normal probability of residuals indicates almost no serious violation of the assumptions underlying the analyses. By display-

ing a satisfactory normal distribution, it confirmed the normality assumptions made earlier and the independence of the residuals, as reported by Liu et al. [12]. In addition, the comparison of the residuals with the error variance ($S_e^2$ or MSS$_E$ = 18.759) showed that none of the individual residual exceeded twice the square root of the residual variance, as suggested by Sen and Swaminathan [25].

Table 5 shows the observed and predicted values with raw and absolute residuals, as well as with percent error of responses for all the batches. As mentioned above, the high values of $R^2$, $R_a^2$ and $R$ indicated that the quadratic equation was capable of representing the system under the given experimental domain. This is also evident from the fact that the parity plot depicted in Fig. 2 shows a satisfactory correlation between the predicted and observed values of Pb(II) removal efficiency. As seen in Fig. 2, the points cluster around the diagonal line indicates a good fit of the model, since the deviation between the experimental and predicted values was less, as similarly reported by Imandi et al. [31].

### 3.2. Effects of model components and their interactions on Pb(II) removal efficiency

The significance each coefficient was determined by Student's $t$-test and $p$ values, which are listed in Table 6. The $t$ value repre-
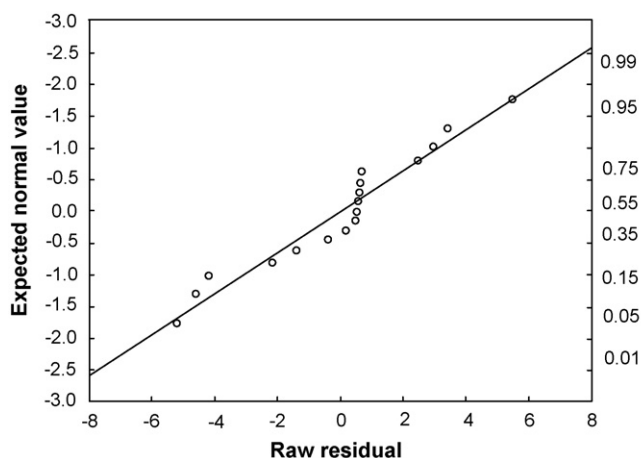


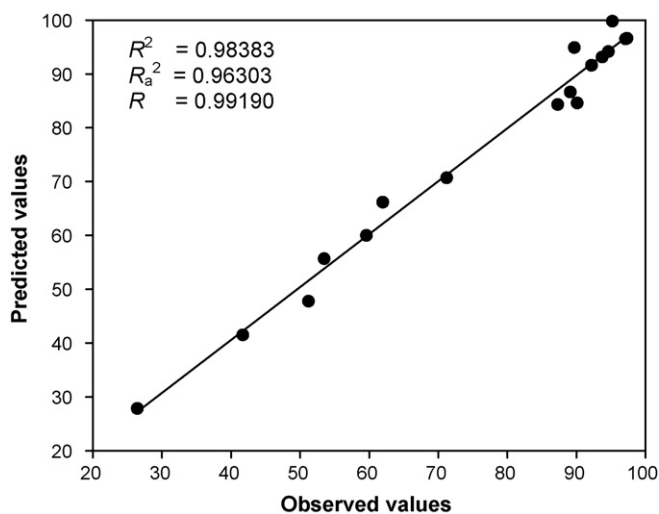**Fig. 1.** The normal probability of the raw residuals.



**Fig. 2.** Parity plot showing the correlation between the experimental and predicted values.

**Table 6**
Multiple regression results and significance of the components for the quadratic model.

| Factor (coded) | Parameter | Coefficient | Effect | SE[a] | $t$ ratio $t = \frac{\text{(Effect)}}{\text{SE}}$ | $p$ value | SS[c] | (PC, %)[d] PC $= \frac{\text{SS}}{\sum \text{SS}} \times 100$ |
|---|---|---|---|---|---|---|---|---|
| Intercept | $\beta_0$ | 91.6089 | | | | | | |
| $x_1$ | $\beta_1$ | 20.9063 | 41.8125 | 3.062559 | 13.6528 | 0.000003[b] | 3496.570 | 44.61 |
| $x_1^2$ | $\beta_{11}$ | −23.7018 | −47.4036 | 4.449795 | −10.6530 | 0.000014[b] | 2128.834 | 27.16 |
| $x_2$ | $\beta_2$ | 6.5810 | 13.1620 | 2.739236 | 4.8050 | 0.001955[b] | 433.096 | 5.53 |
| $x_2^2$ | $\beta_{22}$ | 1.6058 | 3.2117 | 5.001138 | 0.6422 | 0.541204 | 7.736 | 0.10 |
| $x_3$ | $\beta_3$ | 11.7220 | 23.4440 | 2.739236 | 8.5586 | 0.000059[b] | 1374.053 | 17.53 |
| $x_3^2$ | $\beta_{33}$ | −9.1825 | −18.3650 | 5.001138 | −3.6722 | 0.007941[b] | 252.955 | 3.23 |
| $x_1 x_2$ | $\beta_{12}$ | −0.4975 | −0.9950 | 4.331113 | −0.2297 | 0.824868 | 0.990 | 0.01 |
| $x_1 x_3$ | $\beta_{13}$ | 1.7550 | 3.5100 | 4.331113 | 0.8104 | 0.444346 | 12.320 | 0.16 |
| $x_2 x_3$ | $\beta_{23}$ | −5.7250 | −11.4500 | 4.331113 | −2.6437 | 0.033246[b] | 131.130 | 1.67 |

[a] Standard error.
[b] $p$ values <0.05 were considered to be significant.
[c] Sum of squares.
[d] Percentage contribution (%).

sents the ratio of the estimated parameter effect to the estimated parameter standard deviation. Moreover, the $p$ value is used as a tool to check the significance of each of the coefficients. The larger the magnitude of the $t$ value and the smaller the $p$ value, the more significant is the corresponding parameter in the regression model [32]. Results showed that the first-order main effects of initial pH of solution (pH$_0$, $x_1$), initial concentration of Pb(II) ions ($C_0$, $x_2$), and contact time ($t_C$, $x_3$) were found to be more significant than their respective quadratic effects ($x_1^2$, $x_2^2$, and $x_3^2$), as was evident from their respective $t$ ratios and $p$ values (Table 6). These values suggest that the initial pH of the solution, initial concentration of Pb(II) ions and contact time have a direct relationship on the Pb(II) removal efficiency. Can et al. [24] observed similar phenomenon for pH and biomass concentration considered in a response surface optimization based on a $2^3$ full-factorial central composite design conducted to optimize Ni(II) removal from aqueous solution by *P. slyvestris*. As seen in Tables 3 and 6, the most significant component of the regression model was found as the initial pH of solution ($x_1$) for the present application ($t = 13.6528$, $p = 0.000003$, $F = 186.40$). Among all model components, the interaction between $x_1$ and $x_2$ demonstrated the lowest effect on the Pb(II) removal efficiency ($t = 0.2297$, $p = 0.8249$, $F = 0.05$). The quadratic terms of $x_1^2$ and $x_3^2$ were also considerably important ($p = 0.000014$ and $p = 0.007941$, respectively), except the quadratic term of $x_2^2$ ($p = 0.5412$). From the physicochemical point of view, the effect of initial pH, as well as the effects of initial concentration of Pb(II) ions and contact time on the adsorption efficiency were discussed in detail in our previous work [3].

The Pb(II) removals measured for the different batches showed a wide variation ranging from a minimum of 26.45% to a maximum of 97.30% (Table 5). Results clearly indicated that the Pb(II) removal efficiency was strongly affected by the variables selected for the study. This was also reflected by the wide range of values for coefficients of the terms of Eq. (3). The standardized effects of the independent variables and their interactions on the dependent variable were investigated by preparing a Pareto chart (Fig. 3). The length of each bar in the chart indicates the standardized effect of that factor on the response [26]. The fact that the bar for $x_1 x_3$, $x_2^2$, and $x_1 x_2$ remained inside the reference line in Fig. 3, and the smaller coefficients for these terms compared to other terms in Eq. (3), indicated that these terms contributed the least in prediction of the Pb(II) removal efficiency. The negative coefficients for the model components ($x_1^2$, $x_3^2$, $x_2 x_3$ and $x_1 x_2$) indicated an unfavorable or antagonistic effect on the Pb(II) removal efficiency, while the positive coefficients for the model components ($x_1$, $x_2$, $x_3$, $x_1 x_3$, $x_2^2$) showed a favorable or synergistic effect on the Pb(II) removal efficiency.

In the ANOVA, the sum of squares for each individual model component was defined, as given in Table 3. Based on the sum of squares obtained from the ANOVA, the percentage of contributions (PC) for

each individual term were calculated and tabulated in Table 6. As seen in Table 6, the initial pH of solution ($x_1$) showed the highest level of significance with a contribution of 44.61% as compared to other components. As similarly done by Meng et al. [33], the final part of the ANOVA was finished in the same way to obtain the total PC values for the possible first-order, quadratic and interaction terms according to the following equations, respectively:

$$\text{TPC}_i = \frac{\sum\limits_{i=1}^{n} \text{SS}_i}{\sum\limits_{i=1}^{n}\sum\limits_{i=1}^{n} \text{SS}_i + \text{SS}_{ii} + \text{SS}_{ij}} \times 100 \tag{4}$$

$$\text{TPC}_{ii} = \frac{\sum\limits_{i=1}^{n} \text{SS}_{ii}}{\sum\limits_{i=1}^{n}\sum\limits_{j=1}^{n} \text{SS}_i + \text{SS}_{ii} + \text{SS}_{ij}} \times 100 \tag{5}$$

$$\text{TPC}_{ij} = \frac{\sum\limits_{i=1}^{n}\sum\limits_{i=1}^{n} \text{SS}_{ij}}{\sum\limits_{i=1}^{n}\sum\limits_{j=1}^{n} \text{SS}_i + \text{SS}_{ii} + \text{SS}_{ij}} \times 100 \tag{6}$$
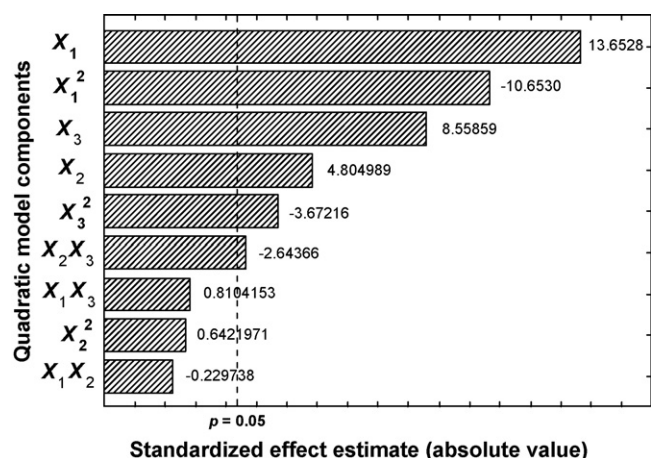


**Fig. 3.** Pareto chart showing the standardized effect of independent variables and their interaction on the Pb(II) removal efficiency.
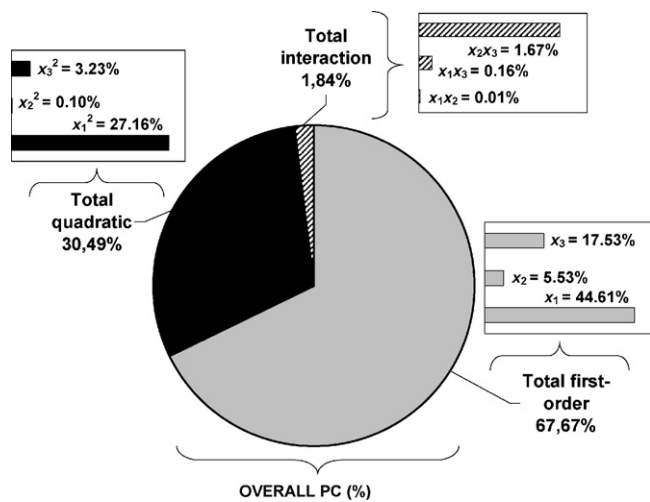
**Fig. 4.** A detailed schematic showing the percentage contributions of components.

where $TPC_i$, $TPC_{ii}$, and $TPC_{ij}$ are the total percentage contributions (TPC) of first-order, quadratic and interaction terms, respectively. Similarly, $SS_i$, $SS_{ii}$, and $SS_{ij}$ are the computed sum of squares for first-order, quadratic and interaction terms, respectively. A detailed schematic showing the percentage contributions of components is depicted in Fig. 4. As seen in Fig. 4, results indicated that the $TPC_i$ of first-order terms demonstrated the highest level of significance with a total contribution of 67.67% as compared to other TPC values. This was followed by the $TPC_{ii}$ of quadratic terms with a total contribution of 30.49%. Among the calculated TPC values, the $TPC_{ij}$ of interaction terms showed the lowest level of significance with a total contribution of 1.84%, indicating that the interaction components did not show a large effect in prediction of the Pb(II) removal efficiency. Hence, TPC values also prove that the first-order independent variables have a direct relationship on the dependent variable as mentioned above.

### 3.3. Three-dimensional (3D) response surfaces and contour plots

Adinarayana and Ellaiah [13] have reported that three-dimensional (3D) response surface plots as a function of two factors, maintaining all other factors at fixed levels are more helpful in understanding both the main and the interaction effects of these two factors. In addition, 3D response surfaces and their corresponding contour plots can facilitate the straightforward examination of the effects of the experimental variables on the responses [34]. Therefore, in order to gain a better understanding of the effects of the independent variables and their interactions on the dependent variable, 3D response surface plots for the measured responses were formed based on the model equation (Eq. (3)) in this study. The relationship between the dependent and independent variables was further elucidated by constructing contour plots. Since the regression model has three independent variables, one variable was held at constant at the center level (for the coded form: $x_i = 0$ or for the uncoded form: $X_i = X_0$) for each plot, therefore, a total of three response 3D plots and three corresponding contour plots were produced for responses. Figs. 5 and 6 show the 3D response surfaces and the corresponding contour plots as the functions of two variables at the center level of other variables, respectively. The nonlinear nature of all 3D response surfaces and the respective contour plots demonstrated that there were considerable interactions between each of the independent variables and the Pb(II) removal efficiency. Furthermore, it can also be concluded that all the contour plots for a high value of Pb(II) removals were found to be nonlinear. This signified that there was no direct linear relationship among the selected independent variables.
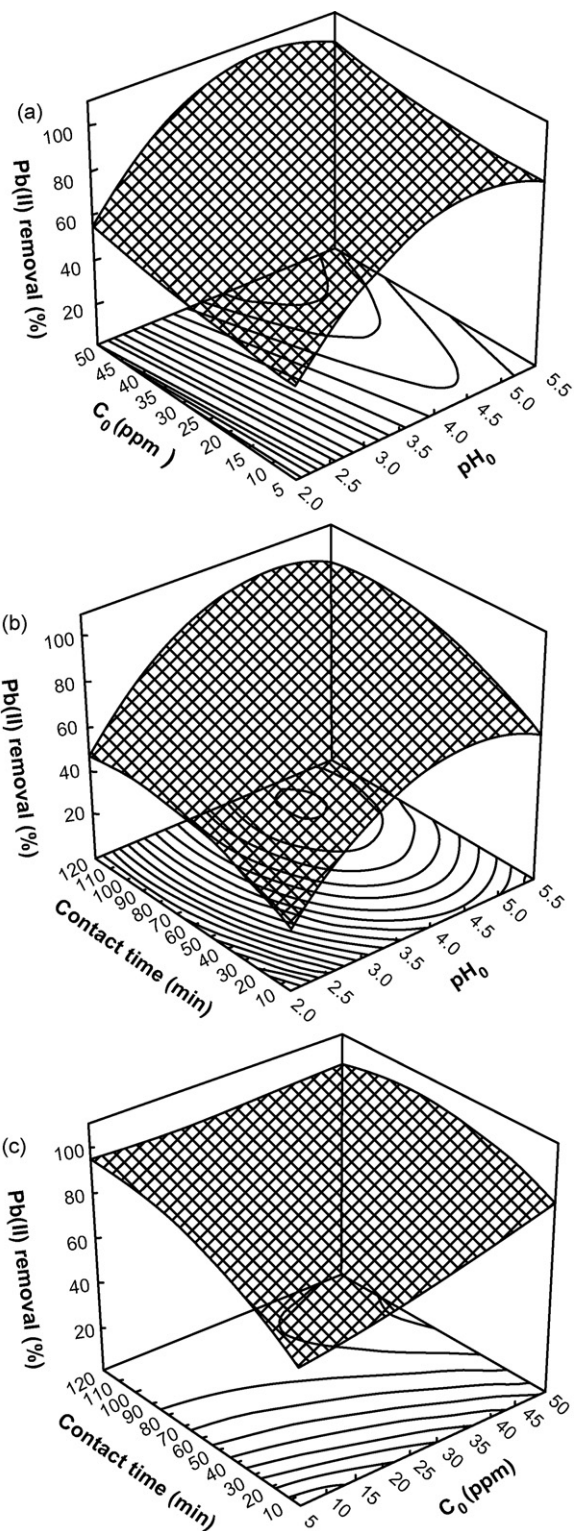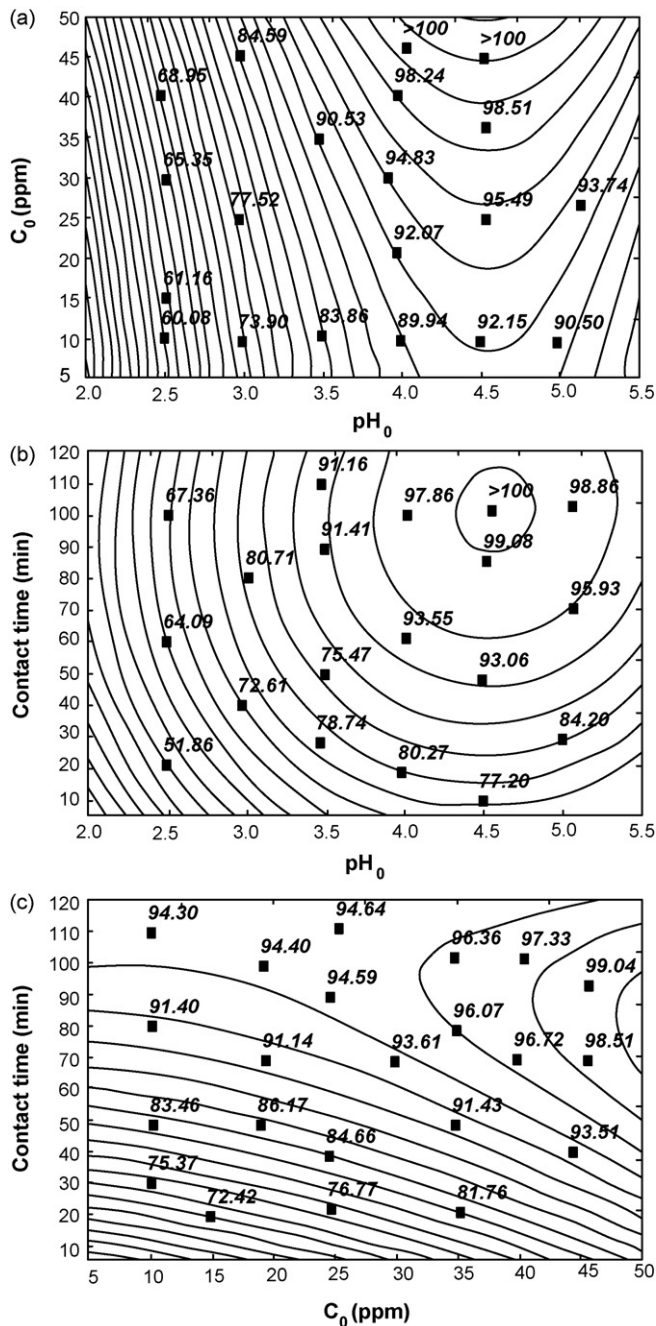


**Fig. 5.** 3D response surface diagrams showing the effects of the mutual interactions between two independent variables (other variables were held at their respective center levels); (a) initial pH of solution ($pH_0$, $X_1$) and initial concentration of Pb(II) ions ($C_0$, $X_2$), (b) initial pH of solution ($pH_0$, $X_1$) and contact time ($t_C$, $X_3$), (c) initial concentration of Pb(II) ions ($C_0$, $X_2$) and contact time ($t_C$, $X_3$).

### 3.4. Optimization studies for maximizing Pb(II) removal efficiency

For the solution of a particular nonlinear model, each iterative step of the nonlinear solver returns the best estimate found so far in the solution process. After each iteration, the merit function is

**Fig. 6.** Contour plots exhibiting the interactive effects between two independent variables (other variables were held at their respective center levels); (a) initial pH of solution ($pH_0$, $X_1$) and initial concentration of Pb(II) ions ($C_0$, $X_2$), (b) initial pH of solution ($pH_0$, $X_1$) and contact time ($t_C$, $X_3$), (c) initial concentration of Pb(II) ions ($C_0$, $X_2$) and contact time ($t_C$, $X_3$).

compared to that from the previous iteration. Since the solver returns the best estimates reached so far, the newly computed merit function will either be better (lower) or unchanged. However, when determining the goodness of fit of the model, a scientific interpretation of the obtained responses is also necessary to see how well the chosen regression model truly describes the actual behaviour of the experimental data. This examination should be carried out as an important task to ensure that the fitted values of any of the variables are scientifically meaningful or should not violate a possible physical reality. In some cases, depending on the characteristics of the data set, some overestimations as well as underestimations may be observed in the prediction modeling based computational

studies. For a particular efficiency model, the unrealistic overestimations (above 100%) and negative predictions (below 0%) can be normally set to the 100% and zero in practice, respectively. However, a number of attempts in developing a proper solution algorithm representing the extension of the experimental data may help to recognize possible technical or scientific faults in the planning stage and also to develop a better understanding of the process. Therefore, considering the above-mentioned facts, some constraints were included into the LOQO/AMPL optimization algorithm used for the solution of the quadratic regression equation, and then the global points were obtained within the realistic limits.

On the basis of the calculation steps defined for the optimization algorithm, the optimal values of the test variables in coded units were found as $x_1 = 0.125$, $x_2 = 0.707$, and $x_3 = 0.107$ with the corresponding $Y = 99.9\%$. The natural values were then determined to be $pH_0 = 3.97$, $C_0 = 43.4$ ppm, and $t_C = 68.7$ min by substituting the respective coded values in Eq. (1). The optimal values of coded factors were also computed for each mutual interaction at the center level of other independent variables. The obtained results are summarized in Table 7.

### 3.5. Validation of the regression model

To verify the validity of the proposed model, several additional batch experiments were carried out in the experimental area of the Box–Behnken design, and each experimental response was compared with the predicted one. As similarly conducted by Caqueret et al. [35] and Wu et al. [34], these extra experiments were chosen randomly in the experimental domain. Table 8 shows the validation results of the model with these experimental points. As seen in Table 8, Pb(II) removals measured for the additional batch experiments showed a wide variation ranging from a minimum of 36.23% to a maximum of 98.43%.

A non-parametric Mann–Whitney (or Wilcoxon rank-sum, WMW) $U$-test was conducted to examine whether there was a noticeable difference between the predicted values and the observed data obtained from the additional experiments. The Mann–Whitney $U$-test is the non-parametric equivalent of a pooled two-sample $t$-test. The basic procedure of the Mann–Whitney $U$-test is to work with the ranked data. Two independent samples are first combined into one column, and then the values are ranked from smallest to largest (where 1 = smallest). Finally, they are broken down into their original samples, and the total rank scores ($U$) of each are summed up. On the basis of the test procedure, an expected score is first determined as follows [36]:

$$E(U) = n_U(N + 1)/2 \tag{7}$$

where $E(U)$ is the expectation of $U$, $n_U$ is the sample size of the sample being tested, and $N$ is the total sample size ($N = n_1 + n_2$). Thereafter, the $z$ score under the normal curve is calculated according to the following equation [36]:

$$z = \frac{U_{max} - E(U)}{\sqrt{n_1 n_2 (N + 1)/12}} \tag{8}$$

where $U_{max}$ is the maximum total rank score, and $n_1$ and $n_2$ are the sample sizes of the independent samples. According to Eqs. (7) and (8), the $z$ score was determined to be 0.3024 for the present validation data. Then, the two-tailed probability associated with the obtained $z$ score under the normal curve was obtained as $p = 0.762$. Since the obtained $p$ value was greater than the chosen $\alpha$ level (0.762 > 0.05), the alternative hypothesis ($H_a$) was rejected in favor of the null hypothesis ($H_0$), indicating that there was no statistically significant difference between the measured data and the predicted responses.

**Table 7**
Optimal values of coded factors and the corresponding natural values for interactions of two independent variables at the center level of other variables.

| Interacted independent variables | Coded factors | | | Uncoded factors $x_i = (X_i - X_0)/\Delta X_i$ | | | Quadratic equations (in coded form) |
|---|---|---|---|---|---|---|---|
| | $x_1$ | $x_2$ | $x_3$ | $X_1$ | $X_2$ | $X_3$ | |
| $pH_0, C_0$ | 0.177 | 0.712 | 0 | 4.06 | 43.5 | 62.5 | $Y = 91.6039 + 20.9063x_1 - 23.7018x_1^2 + 6.581x_2 + 1.6058x_2^2 - 0.4975x_1 x_2$ |
| $pH_0, t_c$ | 0.357 | 0 | 0.523 | 4.38 | 27.5 | 92.6 | $Y = 91.6039 + 20.9063x_1 - 23.7018x_1^2 + 11.722x_3 - 9.1825x_3^2 + 1.755x_1 x_3$ |
| $C_0, t_c$ | 0 | 0.928 | 0.194 | 3.75 | 48.4 | 73.6 | $Y = 91.6039 + 6.581x_2 + 1.6058x_2^2 + 11.722x_3 - 9.1825x_3^2 - 5.725x_2 x_3$ |
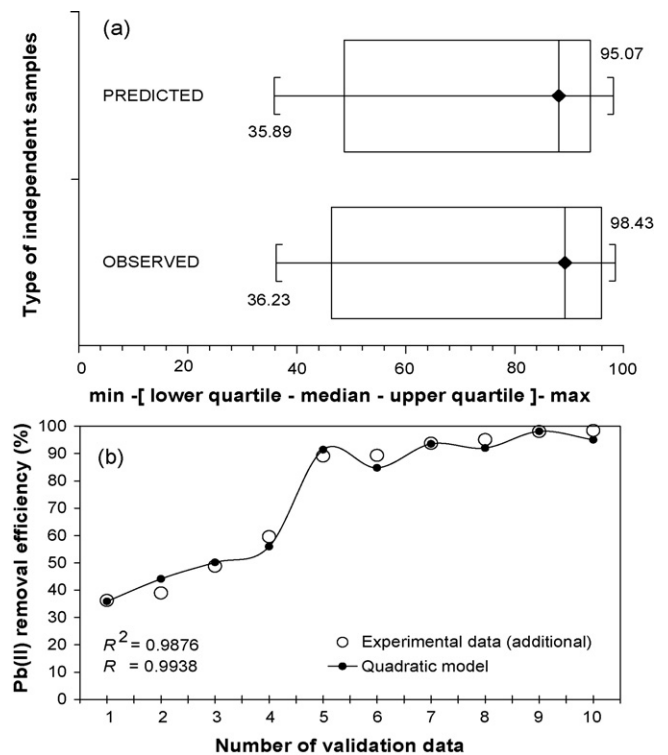


**Fig. 7.** A head-to-head comparison between additional experimental results and predicted responses; (a) Box-and-Whisker plot showing the distribution of two independent samples, (b) agreement between two independent samples.

Besides the Mann–Whitney test, a two-sample (unpaired) $t$-test was also conducted to evaluate the relationship between the model outputs and the observed data, as well as to prove statistical results. The Box-and-Whisker plot depicted in Fig. 7(a) suggests that both distributions are close enough to normal to use a parametric hypothesis such as a two-sample $t$-test, as suggested by Hamilton [37]. In addition, the outputs given in Table 8 indicate that the variances (or standard deviations) are roughly equal. Thus, the standard errors of both samples can be pooled according to the following equation [37]:

$$se_p = \frac{s_1 + s_2}{2} \sqrt{\frac{1}{n_1} + \frac{1}{n_2}} \tag{9}$$

where $se_p$ is the pooled standard error, $s_1$ and $s_2$ are the standard deviations of the samples, and $n_1$ and $n_2$ are the sample sizes of the independent samples as similarly defined in the Mann–Whitney $U$-test. Following calculation of the pooled standard error, the $t$-test statistic is then determined as follows [37]:

$$t_{cal} = \frac{\bar{Y}_1 - \bar{Y}_2}{se_p} \tag{10}$$

where $t_{cal}$ is the calculated $t$-statistic, and $\bar{Y}_1$ and $\bar{Y}_2$ are the mean values of the independent samples. The tabulated $t$ value is obtained for the given values of degrees of freedom (df $= n_1 + n_2 - 2$) and an $\alpha$ level of 0.05. Results indicated that the calculated $t$ value ($t_{cal} = 0.0558$) was found to be less than the tabulated $t$ value ($t_{\alpha,df} = t_{0.05,18} = t_{tab} = 2.101$), indicating that there was no statistically significant difference between the observed data and the expected responses. Since $t_{cal} < t_{tab}$ (0.0558 < 2.101), we failed to reject the null hypothesis ($H_0$) that there was no significant statistical difference between the independent samples. The two-tailed probability associated with the calculated $t$ value was determined as $p = 0.956$ ($t_{cal} = 0.0558$, df $= 18$). Since $p > \alpha$ (0.956 > 0.05), two-sample $t$-test also indicated that there was no sufficient evidence for a signifi-

**Table 8**
Values of coded ($x_i$) and natural ($X_i$) independent variables and corresponding output and ranked data for the statistical model validation.

| Additional batch no. | Coded factors | | | Uncoded factors $x_i = (X_i - X_0)/\Delta X_i$ | | | Pb(II) removal efficiency (%) | | Ranked data for the Mann–Whitney $U$-test | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $x_1$ | $x_2$ | $x_3$ | $X_1$ | $X_2$ | $X_3$ | Observed, $Y_o$ (%)[a] | Predicted, $Y_p$ (%) | Observed | Predicted |
| 1 | +1 | +1 | 0.478 | 5.5 | 50 | 90 | 98.07 | 98.11 | 18 | 19 |
| 2 | +1 | −1 | −1 | 5.5 | 5 | 5 | 59.58 | 55.95 | 8 | 7 |
| 3 | −1 | 0.111 | −0.304 | 2 | 30 | 45 | 38.96 | 44.12 | 3 | 4 |
| 4 | +1 | +1 | +1 | 5.5 | 50 | 120 | 98.43 | 95.07 | 20 | 16 |
| 5 | −1 | 0.111 | −0.739 | 2 | 30 | 20 | 36.23 | 35.89 | 2 | 1 |
| 6 | −1 | 0.111 | 0.478 | 2 | 30 | 90 | 48.76 | 50.17 | 5 | 6 |
| 7 | −0.143 | 0.111 | −0.304 | 3.5 | 30 | 45 | 89.33 | 84.75 | 11 | 9 |
| 8 | −0.143 | 0.111 | 0.478 | 3.5 | 30 | 90 | 95.09 | 91.98 | 17 | 13 |
| 9 | 1 | 0.111 | 0.478 | 5.5 | 30 | 90 | 93.75 | 93.55 | 15 | 14 |
| 10 | 1 | −1 | 0.478 | 5.5 | 5 | 90 | 89.08 | 91.42 | 10 | 12 |

[a] $Y_o$ indicates the average Pb(II) removal efficiency of triplicate experiments ($n = 3$).

cant difference between the measured and the predicted values, as previously found in the Mann–Whitney test. Therefore, both the non-parametric Mann–Whitney test and the two-sample $t$-test concluded with 95% certainty that the proposed quadratic model provided a satisfactory fit to the additional experimental data, as also seen in Fig. 7(b).

In this study, the goodness of fit of the regression model was also checked by the determination coefficient ($R^2$). In this case, the value of determination coefficient ($R^2 = 0.9876$) indicated that only 1.24% of the total variations were not explained by the quadratic model. Furthermore, a very high value of the correlation coefficient ($R = 0.9938$) signified an excellent correlation between the predicted values and the experimental findings. Therefore, the second-order prediction model was finally validated by the statistical analysis of the output data.

Finally, the response of the proposed mathematical model in terms of adsorption capacity (mg Pb(II)/g) was also compared with $q_{max}$ obtained from the equilibrium isotherm. Both experimental results and the model outputs were described by the well-known Langmuir isotherm model as a function of equilibrium Pb(II) concentration ($C_e$) and the corresponding equilibrium adsorption capacity ($q_e$). Results indicated that the adsorption capacity obtained from the model response (26.95 mg/g) was clearly in agreement with that of the equilibrium isotherm (26.53 mg/g). Linear plots of $1/C_e$ versus $1/q_e$ showed that determination coefficients ($R^2$) were found to be about 0.997 and 0.98 for the experimental data and the model outputs, respectively. From the engineering point of view, the proposed model to describe the Pb(II) adsorption process was also validated by means of the adsorption capacity in addition to various descriptive statistics considered in this work.

## 4. Conclusions

The application of a three factor, three-level Box–Behnken experimental design combining with RSM and QP based on a LOQO/AMPL optimization algorithm helped in reaching the global optimal solution for maximizing Pb(II) removal from aqueous solution by *P. vera* L. The proposed mathematical methodology also provided a critical analysis of the simultaneous interactive effects of independent variables, such as initial pH of the solution, initial concentration of Pb(II) ions, and contact time, for better understanding of the Pb(II) removal process. The optimum variables were found to be 3.97 ($x_1 = 0.125$) for initial pH of the solution, 43.4 ppm ($x_2 = 0.707$) for initial concentration of Pb(II) ions, and 68.7 min ($x_3 = 0.107$) for contact time with a predicted Pb(II) removal efficiency of about 100%, which was also higher than any other removals obtained in the initial 17 experimental tests.

The adequacy of the developed mathematical model was checked with the various descriptive statistics. Predicted values

obtained using the quadratic model equation were in very good agreement with the observed values ($R^2 = 0.9838$, $R_a^2 = 0.9630$, $R = 0.9919$, CV = 5.699%, $C_p = 9.9902$, DW = 1.784). The statistical results showed that the first-order main effects of the independent variables (pH$_0$, $C_0$, and $t_C$) were found to be more significant than their respective quadratic effects, indicating that the selected variables had a direct relationship on the Pb(II) removal efficiency. The most significant component of the quadratic model was found as pH$_0$ = for the present application ($t = 13.6528$, $p = 0.000003$, $F = 186.40$, TPC$_i = 44.61\%$). Findings of this study also indicated that the total percentage contributions of first-order terms demonstrated the highest level of significance with a total contribution of 67.67% as compared to the respective TPC values of quadratic and interaction terms.

Finally, the prediction capability of the proposed model was verified by additional batch experiments conducted in the experimental scale of the Box–Behnken design. The validation results clearly confirmed with 95% certainty that a three factor, three-level Box–Behnken experimental design combining with RSM and QP is an effective tool for mathematical modeling and factor analysis of the Pb(II) adsorption process.

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