ABSTRACT: Magnetic Fe₃O₄ nanoparticles have been used as adsorbents for the removal of heavy-metal ions. In this study, optimization of the Pb²⁺ adsorption process using Fe₃O₄ has been investigated. The adsorbent was characterized by various techniques such as transmission electron microscopy (TEM), energy-dispersive X-ray spectroscopy (EDX), and Brunauer–Emmett–Teller (BET) analysis. The influence of process variables on adsorption of Pb²⁺ ions in accordance with p < 0.05 was investigated and analyzed by the Box–Behnken design (BBD) matrix with five variables (pH, adsorbent dose, initial Pb²⁺ ion concentration, contact time, and temperature). The pH and temperature were observed to be the most significant parameters that affected the Pb²⁺ ion adsorption capacity from the analysis of variance (ANOVA). Conduction of 46 experiments according to BBD and a subsequent analysis of variance (ANOVA) provide information in an empirical equation for the expected response. However, a quadratic correlation was established to calculate the optimum conditions, and it was found that the R² value (0.99) is in good agreement with adjusted R² (0.98). The optimum process value of variables obtained by numerical optimization corresponds to pH 6, an adsorbent dose of 10 mg, and an initial Pb²⁺ ion concentration of 110 mg L⁻¹ in 40 min at 40 °C adsorption temperature. A maximum of 98.4% adsorption efficiency was achieved under optimum conditions. Furthermore, the presented model with an F value of 176.7 could adequately predict the response and give appropriate information to scale up the process.

1. INTRODUCTION

For industrial development, lead (Pb²⁺) is a versatile and strategically significant metal as it is intrinsically associated with the automotive sector, power backup, and energy storage.¹ Pb²⁺ and its compounds have been used in battery manufacturing, mining, refining, acid industries, smelting, etc.²,³ The extensive use of Pb²⁺ ions results in high levels of contamination in water and thus accumulation via the food chain. Lead is a mutagenic and teratogenic metal, and it exerts toxicological effects on the bone marrow, nervous system, kidney, and immune system, especially in children.⁴⁻¹⁰ Lead, being lethal, is the most extensive environmental pollutant due to its long-term persistence and easy transportability.¹¹ Pb²⁺ occurs in organic and inorganic forms and its rate of absorption in humans mainly depends on the physicochemical nature of the exposed individual. Inorganic lead is incapable of being metabolized; hence, it gets distributed and accumulates in soft tissues and bones and is not excreted directly, whereas organic lead used in gasoline as an additive can be absorbed via the skin and respiratory tract.¹² Therefore, lead is recommended as a priority pollutant on the list of the US Environmental Protection Agency (EPA),¹³ and the concentration of lead should be less than 10 μg L⁻¹ in drinking water according to World Health Organisation (WHO) standards.¹⁰

Heavy-metal remediation of water involves various techniques such as membrane filtration,¹⁴ coprecipitation,¹⁵ electrocoagulation,¹⁶ reverse osmosis,¹⁷ and ion exchange.¹⁸ The above-mentioned conventional techniques possess certain limitations of sensitive operation, high energy requirements, and generation of toxic sludge.¹⁹,²⁰ Hence, sorption methods can be alternatives for heavy-metal adsorption from wastewaters.²¹ In the surface adsorption process, heavy-metal ions diffuse from an aqueous solution toward the opposite charge of the adsorbent by passing the boundary layer and thus the ions are subsequently removed from the solution.²² To date, a number of adsorbents have dominated the market, with excellent mechanical properties, large surface area, facile
Iron oxide nanoparticles, especially magnetite (Fe₃O₄), have been found to be promising candidates due to their structural stability, along with high surface area and excellent removal efficiency. Magnetite NPs have unique properties as they have both trivalent (Fe³⁺) and divalent (Fe²⁺) arrangements of iron. Therefore, they have a cubic inverse spinel structure, where Fe²⁺ ions occupy half of the octahedral positions, whereas Fe³⁺ joined the lateral tetrahedral and octahedral positions. Magnetite NPs exist as both p- and n-type, with a very minor band gap of 0.1 eV. These nanoparticles have a suitable framework for interaction with heavy metals such as lead (Pb²⁺), leading to enhanced functional properties. Recently, Rasoulzadeh et al. carried out a study on Fe₃O₄ NPs and chitosan-coated Fe₃O₄ NPs to optimize Pb²⁺ using the response surface methodology (RSM) and achieved a maximum of 93% removal efficiency. For field-based applicability, efficient adsorbents can be obtained by modeling and optimization studies. In another study, Fe₃O₄/talc NPs were fabricated to adsorb Pb²⁺, Ni²⁺, and Cu²⁺ ions. The process was optimized by RSM and analysis of variance (ANOVA) to achieve maximum adsorption. Similar adsorption studies are summarized in Table 1.

The reasons behind agglomeration may be the low dimensions, the needlelike morphology of the agglomerated nanoparticles. The energy-dispersive spectroscopy (EDS) peaks shown in Figure 2a correspond to iron, oxygen, and chlorine taken from the Fe₃O₄ NP sample, confirming the successful synthesis of the desired product. The EDS spectrum collected after adsorption of Pb²⁺ is represented in Figure 2b.

### Table 1. Comparison Table of Different Adsorbents with Their Experimental Details

| Adsorbent                        | Metal ions | adsorbent properties | initial concentration | contact time | pH | temperature °C | adsorbent dose | adsorption percent (%) |
|----------------------------------|------------|----------------------|-----------------------|--------------|----|----------------|-----------------|------------------------|
| chitosan-conjugated magnetite    | Pb²⁺       | mean size = 10 nm,   | 32.5 mg L⁻¹           | 40 min       | 6.1 | 40             | 0.625 mg L⁻¹    | 93.6                   |
| nanobiocomposite                 |            | monodisperse         |                       |              |    |                |                 |                        |
| thio-urea-functionalized magnetite| Ni²⁺       | mean size < 50 nm,   | 100 mg L⁻¹            | 30 min       | 6.5 | 35             | 0.625 mg L⁻¹    | 93.6                   |
| ZnO/nano cellulose composite     | Cu²⁺       | mean size < 100 nm,  | 11 mg L⁻¹             | 30 min       | 4  | 40             | 0.625 mg L⁻¹    | 93.6                   |
| Fe₃O₄ NPs                        |            | uniform spherical    |                       |              |    |                |                 |                        |
| Fe₃O₄ nanoparticles              |            | uniform spherical    |                       |              |    |                |                 |                        |
| T-Fe₃O₄ NPs with diameter less than 100 nm | Pb²⁺ | mean size < 50 nm,   | 11 mg L⁻¹             | 30 min       | 4  | 40             | 0.625 mg L⁻¹    | 93.6                   |
| Fe₃O₄ nanoparticles              |            | uniform spherical    |                       |              |    |                |                 |                        |
| Fe₃O₄ nanoparticles              |            | uniform spherical    |                       |              |    |                |                 |                        |
| Fe₃O₄ nanoparticles              |            | uniform spherical    |                       |              |    |                |                 |                        |
| Fe₃O₄ nanoparticles              |            | uniform spherical    |                       |              |    |                |                 |                        |
| Fe₃O₄ nanoparticles              |            | uniform spherical    |                       |              |    |                |                 |                        |
| Fe₃O₄ nanoparticles              |            | uniform spherical    |                       |              |    |                |                 |                        |
| Fe₃O₄ nanoparticles              |            | uniform spherical    |                       |              |    |                |                 |                        |
| Fe₃O₄ nanoparticles              |            | uniform spherical    |                       |              |    |                |                 |                        |
| Fe₃O₄ nanoparticles              |            | uniform spherical    |                       |              |    |                |                 |                        |
| Fe₃O₄ nanoparticles              |            | uniform spherical    |                       |              |    |                |                 |                        |
| Fe₃O₄ nanoparticles              |            | uniform spherical    |                       |              |    |                |                 |                        |
| Fe₃O₄ nanoparticles              |            | uniform spherical    |                       |              |    |                |                 |                        |
| Fe₃O₄ nanoparticles              |            | uniform spherical    |                       |              |    |                |                 |                        |
| Fe₃O₄ nanoparticles              |            | uniform spherical    |                       |              |    |                |                 |                        |
| Fe₃O₄ nanoparticles              |            | uniform spherical    |                       |              |    |                |                 |                        |
| Fe₃O₄ nanoparticles              |            | uniform spherical    |                       |              |    |                |                 |                        |

### 2. RESULTS AND DISCUSSION

#### 2.1. Characterization of Fe₃O₄ Nanoparticles

The microscopic morphology of the adsorbent was characterized by a JEOL TEM-1400 transmission electron microscope (TEM). Figure 1a–c shows images acquired by TEM from pure Fe₃O₄ NPs that revealed the porous structure of the adsorbent. The TEM image shown in Figure 1a–c represents the needlelike morphology of the agglomerated nanoparticles. The reasons behind agglomeration may be the low dimensions, magnetic properties, and high surface energies. The Fe₃O₄ NPs comprise nanoneedles with different size distributions. The average size of the nanoparticles was 83.2 nm and the average diameter was 7.03 nm. The selected area electron diffraction (SAED) pattern revealed the polycrystalline structure of the Fe₃O₄ NPs (Figure 1d).

The energy-dispersive spectroscopy (EDS) peaks shown in Figure 2a correspond to iron, oxygen, and chlorine taken from the Fe₃O₄ NP sample, confirming the successful synthesis of the desired product. The EDS spectrum collected after adsorption of Pb²⁺ is represented in Figure 2b.

The process was optimized by RSM and analysis of variance (ANOVA) to achieve maximum adsorption. Similar adsorption studies are summarized in Table 1.
along with iron and oxygen confirms the adsorption of Pb\(^{2+}\) ions on Fe\(_3\)O\(_4\) NPs.

From the Brunauer–Emmett–Teller (BET) analysis, the surface area of Fe\(_3\)O\(_4\) NPs was determined to be 25.37 m\(^2\) g\(^{-1}\) and the pore volume was 0.16 cm\(^3\) g\(^{-1}\). The Barrett–Joyner–Halenda (BJH) method was used to calculate the pore diameter as shown in Figure 3. Moreover, it was found that most of the pore diameters are in the range of 2–50 nm, with a peak diameter at 11.1 nm, revealing the mesoporous nature of the adsorbent.

2.2. Statistical Analysis. According to ANOVA (Table 2), a higher value of \(F\) indicates that most of the variables in the response can be explained by the regression equation, and probability values (\(p\) values) less than 0.005 are considered to be statistically significant. The results compiled by ANOVA predict the adequate representation of the actual relation between the response function, i.e., removal %, and independent variables (pH, adsorbent dose, initial ion concentration, contact time, and temperature) by a second-order polynomial equation.

The empirical relation between the response, which is the amount of Pb\(^{2+}\) ions adsorbed per unit mass of Fe\(_3\)O\(_4\) nanoparticles (mg g\(^{-1}\)), and the independent variable is represented as \(Y\). The positive values show the synergistic effect

Figure 1. TEM images of synthesized nanoparticles at (a, b) 50 nm and (c) 200 nm and (d) SAED patterns of nanoparticles.

Figure 2. Collected EDX spectrum for Fe\(_3\)O\(_4\) NPs (a) before and (b) after Pb\(^{2+}\) adsorption.
of variables and the negative values denote the antagonistic effect.

\[
Y = 98.45 - 10.08A - 0.6756B + 0.3238C + 0.4931D - 1.41E + 0.2250AB + 0.0400AC + 0.2450AD - 0.1150AE + 0.5050BC + 0.5675BD - 0.2500BE - 0.4200CD + 0.8800CE + 0.2050DE - 12.04A^2 - 1.15B^2 - 0.6490C^2 - 9.87D^2 - 6.68E^2 \tag{1}
\]

The quadratic model was found to be significant for the Pb^{2+} ion adsorption mechanism. The significance of the coefficient term is dependent on the p value and the F value. The p values (prob > F) < 0.05 are significant model terms, while p values (prob > F) > 0.05 indicate insignificant terms. For response Y (% lead removal), the model terms A, B, E, A^2, B^2, D^2, and E^2 were significant. The model F value of 179.76 indicated that model terms are significant. The value for the coefficient of determination, i.e., adjusted R^2 (0.98), is in good agreement with the predicted value (0.97). The results also confirmed the adequacy of the selected quadratic model.

Lack-of-fit tests and model summary statistics are summarized in Table 3. The lack of fit of the model was found to be insignificant; hence, the responses are adequately described by the regression equation. The goodness of fit by the regression model was evaluated by the coefficient of regression (Table 4), i.e., R^2, adjusted R^2, standard error of estimate, and mean absolute error. The R^2 statistic indicates 93.8% of the variable Pb^{2+} ion removal efficiency. The adjusted R^2 statistic is suitable for comparing models with different independent variables. For a significant model, the correlation coefficient should have a minimum value of 0.8. The standard deviation of the residuals was found to be 1.18. The "adeq precision" ratio of the model is 47.76 (adeq > 4), which indicates that the noise values to the ratio of the model are in the desirable range. The accuracy estimation of the regression model was evaluated by the parity plots and residual plots as shown in Figure 4a,b.

Predicted versus actual Pb^{2+} ion removal percent is illustrated in Figure 4a. It shows that the maximum data points near the straight line predicting the actual and predicted values are nearly identical and the regression model has predicted these values efficiently. These plots provide insight into the fit criteria for residuals. Similarly, in Figure 4b, the maximum deviation between the predicted and measured Pb^{2+} ion removal is below 4% and reveals a good correlation between them.

**Table 2. Analysis of Variance (ANOVA) Results for Pb^{2+} Removal**

| source     | sum of squares | df  | mean square | F value | p value | significant |
|------------|----------------|-----|-------------|---------|---------|-------------|
| model      | 3696.65        | 20  | 184.83      | 179.76  | <0.0001 | significant |
| A—pH       | 1625.30        | 1   | 1625.30     | 1580.66 | <0.0001 |             |
| B—adsorbent dose | 7.30      | 1   | 7.30        | 7.10    | 0.0133  |             |
| C—initial ion conc. | 1.68      | 1   | 1.68        | 1.63    | 0.2133  |             |
| D—contact time | 3.89      | 1   | 3.89        | 3.78    | 0.0631  |             |
| E—temperature | 31.98     | 1   | 31.98       | 31.10   | <0.0001 |             |
| AB         | 0.2025         | 1   | 0.2025      | 0.1969  | 0.6610  |             |
| AC         | 0.0064         | 1   | 0.0064      | 0.0062  | 0.9377  |             |
| AD         | 0.2401         | 1   | 0.2401      | 0.2335  | 0.6331  |             |
| AE         | 0.0529         | 1   | 0.0529      | 0.0514  | 0.8224  |             |
| BC         | 1.02           | 1   | 1.02        | 0.9921  | 0.3288  |             |
| BD         | 1.29           | 1   | 1.29        | 1.25    | 0.2736  |             |
| BE         | 0.2500         | 1   | 0.2500      | 0.2431  | 0.6263  |             |
| CD         | 0.7056         | 1   | 0.7056      | 0.6862  | 0.4153  |             |
| CE         | 3.10           | 1   | 3.10        | 3.01    | 0.0949  |             |
| DE         | 0.1681         | 1   | 0.1681      | 0.1635  | 0.6894  |             |
| A^2        | 1264.55        | 1   | 1264.55     | 1229.82 | <0.0001 |             |
| B^2        | 11.54          | 1   | 11.54       | 11.22   | 0.0026  |             |
| C^2        | 3.68           | 1   | 3.68        | 3.57    | 0.0703  |             |
| D^2        | 851.01         | 1   | 851.01      | 827.64  | <0.0001 |             |
| E^2        | 389.12         | 1   | 389.12      | 378.43  | <0.0001 |             |
| residual   | 25.71          | 25  | 1.03        |         |         |             |
| lack of fit| 24.29          | 20  | 1.21        | 4.30    | 0.0563  | not significant |
| pure error | 1.41           | 5   | 0.2825      |         |         |             |
| cor total  | 3722.35        | 45  |             |         |         |             |
2.3. Interactive Effect of Variables and Three-Dimensional (3D) Response Surface Plots.

Three-dimensional response surface plots were constructed to determine the individual and interactive effects of variables on the response. Different process variables, i.e., pH, adsorbent dose, initial ion concentration, contact time, and temperature, influenced Pb²⁺ ion adsorption capacity. The adsorbent dose determines the capacity of the adsorbent to remove Pb²⁺ ions from the solution, while the initial Pb²⁺ ion concentration shows a significant impact on the mass transfer resistance between the aqueous and solid phases. Meanwhile, an appropriate contact time quantifies better agitation between the adsorbent and the adsorbate. The Pb²⁺ ion uptake increases with an increase in the initial Pb²⁺ ion concentration, and the low adsorbent dose favors high adsorption. The 3D surface plots of the combined effects of pH, initial Pb²⁺ ion concentration, adsorbent dose, contact time, and temperature are presented in Figure 5a–j.

Metal sorption on the surface of an adsorbent mainly depends on pH, which is related to the ionization state of the adsorbent’s functional groups and metal chemistry in the solution, which affects the availability of active sites.43 Figure 5a clearly shows that the Pb²⁺ ion adsorption efficiency increased rapidly when pH increased from 5 to 6 and no significant increase was observed after that. The reason behind this was the competition of metal ions with hydroxyl ions to acquire adsorption sites and, therefore, the surface charge alteration led to electrostatic repulsion between the metal ions and the adsorbent, resulting in the escape of existing adsorbed ions.44 Similarly, the interactive effect of pH and the initial Pb²⁺ ion concentration was also evaluated (Figure 5b) and it was revealed that merely 75% Pb²⁺ ion adsorption occurs at 130 mg L⁻¹ initial Pb²⁺ ion concentration at pH 7 when agitated for 40 min. Figure 5c depicts a 3D plot for pH and contact time. At pH 7, only 66% adsorption was achieved within 30 min and it increased as the contact time increased.

### Table 3. Lack-of-Fit Statistics and Model Summary Statistics

| source     | sum of squares | df  | Mean square | F value | p value |
|------------|----------------|-----|-------------|---------|---------|
| linear     | 2050.79        | 35  | 58.59       | 207.38  | <0.0001 |
| 2FI        | 2043.76        | 25  | 81.75       | 289.33  | <0.0001 |
| quadratic  | 24.29          | 20  | 1.21        | 4.30    | 0.0563  |
| cubic      | 4.28           | 5   | 0.8562      | 3.03    | 0.1245  |
| pure error | 1.41           | 5   | 0.2825      |         |         |

### Table 4. Standard Fit Statistics

| std. dev. | R²       | R² precision |
|-----------|----------|--------------|
| 1.01      | 0.9931   | 47.7699      |
| mean      | adjusted R² | 0.9876      |
| CV (%)    | predicted R² | 0.9733      |

Figure 4. (a) Parity plots showing the correlation between predicted and actual lead removal efficiency. (b) Plot between residuals and predicted values.
Figure 5. continued
time progressed to 40 min. Subsequently, maximum adsorption (98.5%) was achieved by the Fe₃O₄ NPs at 40 °C at pH 6 (Figure 5d). Furthermore, according to ANOVA, pH is a significant factor in this study as it affects the overall adsorption process.

The combined effect of adsorbent dose and initial ion concentration is represented in Figure 5e. On increasing the adsorbent dose from 5 to 15 mg L⁻¹, the adsorption efficiency decreased by up to 96%. However, the maximum adsorption was achieved at 10 mg of Fe₃O₄ NP dosage. The initial increase in Pb²⁺ ion adsorption may be due to the large number of active sites available for adsorption. In the starting phase, where the adsorbent surface is empty, the adhering probability is high and thus sorption takes place at a higher rate. However, the subsequent adsorption rate was slow due to the saturation of active sites, and equilibrium was achieved with time.⁴⁵

Furthermore, with an increase in the initial ion concentration from 90 to 130 mg L⁻¹, the adsorption efficiency increased, with the maximum (99%) at 110 mg L⁻¹, and declined at 130 mg L⁻¹. The decrease in the sorption rate with increasing initial Pb²⁺ ion concentration may be due to the absence of active sites on Fe₃O₄ NPs. In fact, at lower initial concentrations, adequate numbers of sites are available to bind on, whereas relatively high metal ions are available with respect to sorption sites at higher concentrations.⁴⁶

Figure 5f shows the effect of adsorbent dose and contact time on Pb²⁺ ion adsorption. The adsorption rate increased with an increase in agitation time from 30 to 40 min and achieved the maximum sorption. The Pb²⁺ ion adsorption rate increased up to 40 min and thereafter no further increase was observed with contact time (Figure 5h). The adsorption rate was higher at the initial agitation time as a greater number of binding sites were
equation \(^50\) in 1959, unanimously called the Redlich–Peterson (R–P) isotherm equation (or model). The equation compensates for imperfections of Langmuir and Freundlich isotherm equations in some adsorption systems. The linear form of the R–P equation is given as follows

\[
\ln \frac{C_e}{q_e} = \beta \ln C_e - \ln A
\]

A plot of \(\ln (C_e / q_e)\) versus \(\ln C_e\) (Figure 7a) enables the determination of Redlich–Peterson constants, where \(\beta\) is the slope and \(A\) is the intercept. \(^51\)–\(^55\) where \(\beta\) is also a constant and \(\beta = 0\) favors the Freundlich isotherm. The Redlich–Peterson (R–P) isotherm model was applied to understand the interaction mechanism of Pb\(^{2+}\) ion adsorption on magnetite nanoparticles. However, the accuracy of RP interpretations rigidly depends on the method of fitting. \(^56\) From Table 5, it is clear that the interpreted RP model is in agreement with experimental data on the basis of \(\beta\) value for magnetite nanoparticles, which is lower than 1 (308, 318, 328 K), i.e., 0.13–0.51. \(^57\)

2.5.2. Dubinin–Radushkevich Isotherm. The D–R isotherm is an empirical model generally used to express the adsorption process with a Gaussian energy distribution onto a heterogeneous surface. \(^38\) This isotherm was basically used to distinguish between physical and chemical adsorption of metal ions \(^59\) with its free energy, \(E\), per molecule of adsorbate. The equation to compute \(E\) is given as follows

\[
E = \frac{1}{\sqrt{2K_{DR}}} \quad (3)
\]

where \(K_{DR}\) is the isotherm constant in eq 3 and the \(E\) parameter (eq 4) can be correlated by the given equation

\[
e = RT \ln \left[ 1 + \frac{1}{C_e} \right] \quad (4)
\]

where \(R\) is the gas constant (8.314 J mol\(^{-1}\) K\(^{-1}\)), \(T\) is the absolute temperature, and \(C_e\) is the equilibrium concentration of the adsorbate (mg L\(^{-1}\)). A ln \(q_e\) versus \(E^2\) curve was plotted and the values of parameters \(q_m\) and \(K_{DR}\) were computed from the following equation

\[
\ln q_e = \ln q_m - kE^2 \quad (5)
\]

The type of adsorption, i.e., physical or chemical, is determined by the DR isotherm model. By plotting ln \(q_e\) against \(E^2\) (Figure 7b), the values of \(q_m\) and \(K_{DR}\) can be obtained using the intercept and slope \(^60\) (Table 5).

2.5.3. Elovich’s Isotherm. The equation that defines this model is based on a kinetic principle that assumes that adsorption sites increase exponentially with adsorption; this implies multilayer adsorption. \(^61\) The equation was first developed to describe the kinetics of chemisorption of gas onto solids. \(^62\) The linear forms of the Elovich model are expressed as follows

\[
\ln \frac{q_e}{C_e} = \ln k_e q_m - \frac{q_e}{q_m} \quad (6)
\]

The slope and intercept of the plot of \(\ln (q_e / C_e)\) versus \(q_e\) (Figure 7c) give Elovich’s maximum adsorption capacity and
Elovich’s constant. The coefficient of regression ($R^2$) for Elovich’s isotherm ranges from 0.12 to 0.84 (Table 5).

2.6. Principal Component Analysis (PCA). PCA was the most widely used multivariate statistical analysis technique. PCA
is a data dimension reduction technique that intends to explain most of the variance in the data with a small number of independent variables (termed “principal components”). With PCA, an orthogonal transformation method is used to identify the first principal component accounting for the largest possible variance in the original data. Then, each succeeding component is identified with the constraint that it is orthogonal to all preceding components. It is often conducted by eigenvalue decomposition in a matrix operation. The eigenvectors with the highest eigenvalue are the principal components (PCs) of the data set.

The individual and combined effects of parameters of Pb²⁺ ion adsorption are explained using principal component analysis (see Table 6). The bold numbers in Table 6 represent high correlation values. By conducting 46 adsorption experiments, the effect of pH, adsorbent dose, initial concentration, contact time, and temperature on Pb²⁺ ion adsorption by Fe₃O₄ nanoparticles was studied (see Table 8). The calibration data basically consists of matrix X of dimension 46 × 5 and a response vector of dimension 46 × 1 (adsorption % in this case). The adsorption data presented by only two principal components captures most of the variance. The biplot for the first and second principal components (PC1 and PC2) is shown in Figure 8. PCA was carried out as outlined in the literature using the Origin 2020b version.

A dendrogram is a hierarchical clustering of large amounts of information in a visual form that is easy to understand. On the basis of Euclidean distance, major clustering groups can be evaluated. The horizontal axis of a dendrogram represents dissimilarity or distance between clusters, whereas the vertical axis represents clusters. A dendrogram begins with each run in a separate cluster and at every step, the two most similar clusters join into a single new cluster. In the above dendrogram (Figure 9), two cluster groups A and B were found to be prominent.

Cluster A includes eight experimental runs (1, 28, 20, 43, 37, 26, 21, and 24), while cluster B comprises 38 experimental runs (2, 35, 10, 18, 23, 41, 14, 9, 27, 42, 44, 16, 19, 36, 4, 17, 38, 15, 6, 3, 40, 34, 45, 46, 8, 31, 33, 13, 11, 30, 5, 7, 12, 22, 32, 29, 39, and 25). Both these clusters A and B are grouped on the basis of their initial concentrations. Cluster A has experimental runs with 90 mg L⁻¹ initial Pb²⁺ ion concentration, whereas group B consists of experimental runs with 110 mg L⁻¹ initial Pb²⁺ ion concentration.

3. CONCLUSIONS

This experimental work has detailed the probability of RSM for evaluating the interactive effect of five process variables on Pb²⁺ ion adsorption using Fe₃O₄ NPs as adsorbents. The mean size of the synthesized nanoparticles was 83.2 nm, and they had a needlelike morphology. This study was carried out to correlate the combined influence of different variables including adsorbent dose, pH, initial Pb²⁺ ion concentration, temperature, and contact time using the Box–Behnken design. On summarizing the results, RSM was found to be a highly applicable method for optimization of Pb²⁺ adsorption parameters. In fact, ANOVA showed a high coefficient of regression, i.e., $R^2 = 0.99$, and confirmed that experimental data fit well to the model. Furthermore, pH and temperature are significant terms with $p$ value < 0.0001 in the model that have crucial control over the Pb²⁺ ion adsorption process. The results also revealed that the adsorption rate decreased gradually with an increase in the adsorbent dose and temperature. Fe₃O₄ NPs could be promising adsorbents and the given RSM model could effectively predict the response with a maximum of 98.4% adsorption efficiency and provide information for process scale-up.
4. EXPERIMENTAL SECTION

4.1. Chemicals. Ferric chloride hexahydrate (FeCl₃·6H₂O) and sodium hydroxide (NaOH) were purchased from the Central Drug House, New Delhi, India. Sodium borohydride (NaBH₄), ethanol, and lead nitrate (Pb(NO₃)₂) were purchased from Merck, India. All reagents were used intact as received, without further purification. Double-distilled water was used throughout the experiments for preparing synthetic stock solutions. The pH of the solution was adjusted using 0.1 M HCl and 0.1 M NaOH with a pH meter (Mettler Toledo AG, FEP 20). The initial and equilibrium Pb²⁺ concentrations were analyzed by an inductively coupled plasma mass spectrometer (ICPMS) (Agilent’s 7900 ICPMS).

4.2. Adsorbent Preparation. The magnetic Fe₃O₄ nanoparticles used in this study were synthesized by the sodium borohydride (NaBH₄) chemical reduction method. The synthesis process was carried out in four steps: (i) 0.54 g of ferric chloride hexahydrate (FeCl₃·6H₂O) was dissolved in 30 mL of ethanol–water solution (4/1 (v/v)), (ii) 100 mL of 0.1 M NaBH₄ was added to the solution dropwise with stirring, (iii) black precipitates were formed and were separated, and (iv) the synthesized NPs were dried for 5 h at 90 °C.

4.3. Characterization. Transmission electron microscopy (JEOL JEM-1400) was used to study the morphology of the magnetic nanoparticles, and attached selected area electron diffraction (SAED) was used to study the crystallinity of the sample. A small amount of sample was mounted on a copper grid and analyzed by TEM to capture bright-field images at different magnification scales. Energy-dispersive spectroscopy (EDS) was also performed to analyze the elemental composition of the sample before and after Pb²⁺ adsorption. The Brunauer–Emmett–Teller (BET) model was used to calculate the surface area of the synthesized Pb₃O₄ nanoparticles, and pore size distribution was determined using the Teller (BET) model was used to calculate the surface area of the sample.

4.4. Adsorption Experiment. For the batch experimental study, optimization of the dependent parameters such as adsorbent dose (10–60 mg), Pb²⁺ ion concentration (10–150 mg L⁻¹), agitation time (20–60 min), pH (2–9), and temperature (15–55 °C) was conducted. Optimum conditions obtained from batch experiments were used for the experimental design of process variables in BBD RSM. Furthermore, to optimize the experimental conditions and collect data for isothermal studies, batch experiments were carried out in a 250 mL Erlenmeyer flask with 10 mg of Fe₃O₄ nanoparticles in 100 mL of Pb²⁺ aqueous solution at different concentrations (30, 70, 110, 130 mg L⁻¹) for an equilibrium time of 40 min. The pH of the solution was adjusted to 6. The residual Pb²⁺ ion concentration in the samples was analyzed by inductively coupled plasma mass spectroscopy (ICP-MS) to obtain the final concentration. The percentage of Pb²⁺ ion adsorption and capacity were computed using eqs 7 and 8, respectively.

\[
\text{lead removal \%} = \left(\frac{C_0 - C_e}{C_0}\right) \times 100
\]

(7)

\[
\text{adsorption capacity (q)} = \left(\frac{(C_0 - C_e)V}{m}\right)
\]

(8)

where \(C_0\) is the initial Pb²⁺ ion concentration, \(C_e\) is the Pb²⁺ ion concentration at equilibrium, \(V\) is the volume of the solution, \(m\) is the mass of the adsorbent, and \(q\) is the adsorption capacity.

4.5. Experimental Design: Methodology. For the process optimization of Pb²⁺ ion adsorption, the experimental design was created by the response surface methodology on the basis of optimum conditions obtained from batch experiments. It is based on mathematical and statistical techniques to fit a polynomial equation to the experimental data. This method is well applied to a response influenced by various parameters. In the present experimental investigation, the process variables that estimated Pb²⁺ removal efficiency were pH, adsorbent dose (mg), initial Pb²⁺ ion concentration (mg L⁻¹), contact time (min), and temperature (°C). As RSM is an efficient statistical mathematical approach, it uses quantitative data of apt experiments for the design of a set of experiments and optimization of process variables to achieve the maximum response. A three-level five-factor Box–Behnken design (BBD) was used to optimize five variables. The response surface model generates an empirical equation for describing the corresponding quantity of the process. The BBD is an independent, rotatable quadratic design with no embedded factorial or fractional factorial points where the variable combinations are at the midpoints of the edges of the variable space and at the center. It is ensured by the BBD that not all of the factors are at high levels at the same time. Hence, significant interaction can be identified for batch studies.

Preliminary experiments revealed the significant variables that affect the Pb²⁺ adsorption including pH, adsorbent dose, Pb²⁺ ion concentration, contact time, and temperature. Different ranges adjusted for process variables (A, B, C, D, E) at three different levels (coded as −1, 0, +1) for low, intermediate, and high values, respectively, are summarized in Table 7.

| Table 7. Factors and Low–High Levels in the BBD–RSM Design |
| --- |
| factors | levels |
| A—pH | low (−1) | central (0) | high (+1) |
| B—adsorbent dose (mg L⁻¹) | 5 | 10 | 15 |
| C—initial ion concentration (mg L⁻¹) | 90 | 110 | 130 |
| D—contact time (min) | 30 | 40 | 50 |
| E—temperature (°C) | 35 | 40 | 45 |

According to the RSM statistical matrix, 46 runs were generated to set up the experimental design (Table 8). Using a nonlinear regression method and second-order polynomial, experimental data was fit to identify significant coefficient terms. The response surface methodology gives the empirical relationship between the response function and the independent variables. The quadratic response model is based on all linear terms, square terms, and linear interaction terms according to the following equation:

\[
Y = b_0 + \sum b_i x_i + \sum b_{ii} x_i^2 + \sum b_{ii} x_{ij} x_j
\]

(9)

where \(Y\) denotes the predicted response (Pb²⁺ removal efficiency), \(b_0\) is the model constant, \(b_i\) is the linear coefficient, \(b_{ii}\) is the quadratic effect of the input factor \(x_i\), and \(b_{ij}\) is the linear interaction effect between the input factors \(x_i\) and \(x_j\).

The response function coefficients of experimental data were determined by regression. The standard polynomial quadratic equation was used to approximate the response function for lead removal (%). To analyze the adequacy of the proposed model, analysis of variance (ANOVA) was performed. ANOVA
evaluates the suitability of the response functions and the significance of the effects of independent variables.

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**Notes**

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