Experimental and Modeling Process Optimization of Lead Adsorption on Magnetite Nanoparticles via Isothermal, Kinetics, and Thermodynamic Studies

Rimmy Singh and Rachna Bhateria*

ABSTRACT: Lead has been a burgeoning environmental pollutant used in industrial sectors. Therefore, to emphasize the reactivity of lead toward magnetite nanoparticles for their removal, the present study was framed to analyze mechanisms involved in adsorption of lead. Batch adsorption studies have shown remarkable adsorption efficiency with only a 10 mg adsorbent dose used to extract 99% Pb\(^{2+}\) (110 mg L\(^{-1}\)) within 40 min at pH 6. Isothermal, kinetic, and thermodynamic studies were conducted, and the equilibrium data was best fit for the Langmuir isotherm model with a maximum of 41.66 mg g\(^{-1}\) adsorption capacity at 328 K. Moreover, a pseudo second order was followed for adsorption kinetics and thermodynamic parameters such as Gibbs energy (\(\Delta G^\circ\)), enthalpy (\(\Delta H^\circ\)), and entropy (\(\Delta S^\circ\)) that were calculated and revealed the spontaneous, feasible, and exothermic nature of the process.

1. INTRODUCTION

Lead (Pb\(^{2+}\)) concentration above prescribed limits in water poses lethal effects to humans as well as the environment. Unmanaged discharge from battery manufacturing industries, steel and paint industries, and aeronautical and automobile sectors has resulted to leapfrogging increase in heavy metal concentration in effluents.\(^1\)\(^,\)\(^2\) The World Health Organization (WHO) and US Environmental Protection Agency (USEPA) have prescribed a permissible limit of 0.1 mg L\(^{-1}\) for lead in drinking water.\(^3\) Lead is absorbed via the digestive tract and lungs and circulates in the blood.\(^4\) Then, it binds to red blood cells and gets distributed in the whole body and accumulates in the bones.\(^5\) In human beings, approximately 20—80% lead get absorbed through inhalation while 5—15% via ingesting inorganic lead.\(^6\) Long-term intake of Pb\(^{2+}\) in high concentration leads to certain health problems such as kidney diseases, premature birth, high blood pressure, hearing loss, and lower IQ in children.\(^7\)\(^,\)\(^8\)\(^,\)\(^9\)

Various methods have been employed for the removal of lead, which includes coprecipitation,\(^10\) membrane filtration,\(^11\) reverse osmosis,\(^12\) ion exchange,\(^13\) adsorption,\(^14\) etc. Among these, adsorption is the most preferred technique as it is simple, facile, economical, and environment-friendly. Till date, several adsorbents have been reported for heavy-metal remediation such as Bajestani et al. fabricated spinel type lithium manganese oxide adsorbents for the removal of lithium ions.\(^15\) Similarly, Gugushe et al. have synthesized a multwalled carbon nanotube/zeolite magnetic nanocomposite for the extraction of arsenic ions from real acid mine drainage.\(^16\) However, magnetite nanoparticles are a viable approach as they are superparamagnetic and hydrophilic and possess high surface area.\(^17\) Magnetic magnetite (Fe\(_3\)O\(_4\)) nanoparticles are paving a path for revolutionizing nanotechnology by their influencing properties such as reduced imperfections, high number of surface atoms, and high surface energy and spatial confinement.\(^18\) Moreover, the literature reveals that magnetite nanoparticles have wide scope and can be further modified to enhance related properties. For the decontamination and elimination of toxicants from wastewater, magnetic nanoadsorbents such as spinel ferrites (M\(^{2+}\)Fe\(^{2+}\)O\(_4\), where M\(^{2+}\) can be Mg\(^{2+}\), Fe\(^{3+}\), Zn\(^{2+}\), Cd\(^{2+}\), Mn\(^{2+}\), Ni\(^{2+}\), or Cd\(^{2+}\)), maghemite, magnetite, and hematite are good adsorbents. Due to their magnetic nature, they can be easily separated from reaction media by applying an external magnetic field. The literature showed various research studies on the use of magnetic nanosorbents for the removal of different metals such as chromium, nickel, arsenic, cobalt, lead, copper, and others in
their ionic forms. Kalantari et al. synthesized Fe₃O₄/ MMT nanocomposites for the removal of Pb²⁺, Cu²⁺, and Ni²⁺ ions from aqueous solution. L-Cysteine functionalized Fe₃O₄ nanoparticles were fabricated by a coprecipitation method to recover lead ions. Furthermore, Wang et al. synthesized and used magnetite nanoparticles for the adsorption of lead ions. Batch experiments were also conducted to study adsorption kinetics and isotherms. With application of magnetic separation technologies, magnetic nanosorbents offer a priceless advantage of fast recovery of toxic metals from wastewater. Various research studies have been conducted on magnetite for the removal of trace metal ions. The successful implementation of magnetic nanosorbents depends on their efficiency of selective uptake of pollutants and surface chemistry involved. In this context, we have successfully fabricated magnetite nanoneedles for the adsorption of lead ions from aqueous solution. The synthesized nanoneedles have shown better adsorption capacity and regenerability. However, adsorption capacity also depends on certain other conditions such as dose and initial Pb²⁺ ion concentration. At optimum conditions, adsorption capacity of magnetite nanoneedles was found to be maximum for Pb²⁺ ion removal. The method used to synthesize nanoneedles is a single-step method with one precursor.

The objective of the present study is to determine and compare the adsorption performance of magnetite nanoparticles for Pb²⁺ elimination from aqueous solution at variable temperatures to analyze equilibrium, kinetics, and thermodynamics of adsorption.

2. EXPERIMENTAL SECTION

2.1. Reagents and Equipment. All chemicals used were of analytical grade. Ferric chloride hexahydrate (98%), sodium borohydride (NaBH₄), and lead nitrate (Pb(NO₃)₂) were purchased from Chemical Drug House (CDH). Stock solutions of lead with variable concentrations were prepared from lead nitrate in double-distilled water. The pH of the solution was determined by a pH meter (Mettler Toledo AG, FEP 20) and adjusted using 0.1 N HCl and 0.1 N NaOH solution. Inductively coupled plasma mass spectrometry (ICP-MS) (Agilent’s 7900, CRF-IIT, Delhi, India). The equilibrium adsorption capacity (qₑ) of magnetite nanoneedles is “the amount of metal adsorbed per unit weight of adsorbent at equilibrium (mg g⁻¹)” and was calculated from the given equation:

\[ q_e = \frac{(C_0 - C_e)V}{m} \]  

where \( C_0 \) is the initial metal ion (Pb²⁺) concentration, \( C_e \) is the metal ion concentration at equilibrium, \( V \) is the volume of the solution (L), and \( m \) is the dry weight of adsorbent.

Moreover, the percentage of lead adsorption (R) was also determined by the following equation:

\[ R = \frac{(C_0 - C_e)}{C_0} \times 100 \]

where \( C_0 \) and \( C_e \) are the initial lead ion concentration (mg L⁻¹) and after equilibrium, respectively.

2.2. Synthesis of Magnetite Nanoparticles. Magnetite (Fe₃O₄) nanoparticles were synthesized by a sodium borohydride chemical reduction method. The detailed procedure involves the reduction of ferric chloride hexahydrate (FeCl₃·6H₂O) by sodium borohydride (NaBH₄), resulting in black precipitates of magnetite nanoparticles. For this, 0.54 g of ferric chloride hexahydrate was dissolved in 30 mL of ethanol water (24/6) solution. Then, 100 mL of 0.1 M sodium borohydride was added to the ferric chloride solution dropwise with hand stirring. At certain time, the reddish brown color of ferric chloride disappears, and then, remaining sodium borohydride solution was added. Black precipitates appear, indicating the formation of nanoparticles. The fabricated nanoparticles were then washed several times with ethanol and heated for 5 h at 80 °C.

2.3. Sample Characterization. The micrographs of synthesized nanoparticles were obtained by a Tecnai G2 20, a high-resolution transmission electron microscope (HRTEM) for the characterization of nanoparticle size. Elemental mapping of Fe₃O₄ nanoparticles was done by energy-dispersive X-ray (EDX) and the selected-area electron diffraction (SAED) pattern was captured in association with HRTEM. The crystallographic phase was computed by X-ray powder diffraction (XRD) (Rigaku Ultima IV, RI), which uses a monochromatic X-ray beam with Cu Kα radiation (\( \lambda = 0.154021 \)). Dynamic light scattering (DLS)/particle size analyzer and zeta potential (Malvern Zetasizer Na) determine the size distribution and zeta potential (“related to the magnitude of the electrical charge at the particle surface”) of Fe₃O₄ nanoparticles, respectively. An Autosorb 1Q-C-MP (Quantachrome) system was used for the determination of surface area and pore size.

2.4. Batch Adsorption Experiment. All studies were carried out in batch experiments to determine the effect of pH, adsorbent dose (magnetite NPs), initial Pb²⁺ concentration, temperature, and contact time. All experiments were conducted in 100 mL of Pb²⁺ ion solution of variable concentrations (10, 30, 50, 70, 90, 110, 130, and 150 mg L⁻¹) (the concentration range was selected from literature studies as high concentrations of lead can be adsorbed by nanoparticles), adsorbent dose of 5, 10, 20, 30, 40, 50, and 60 mg L⁻¹ at 200 rpm with a pH range of 2–9. The contact time studies were conducted at 10, 20, 30, 40, 50, and 60 min. The temperature ranges from 15, 20, 25, 30, 35, 40, 45, and 50 °C. The pH was analyzed and maintained by 0.1 M HCl and 0.1 M NaOH solution. Isothermal studies were conducted with 100 mL of Pb²⁺ solution of variable concentrations (30, 70, 110, and 150 mg L⁻¹) and 10 mg of adsorbent dose for 40 min, and pH 6 was maintained at four temperatures (298, 308, 318, and 328 K). All the experiments were conducted in triplicates, and their mean values were used to evaluate the data. Equilibrium concentrations of Pb²⁺ were determined by inductively coupled plasma mass spectrometry, i.e., ICP-MS (Agilent’s 7900, CRF-IIT, Delhi, India). The equilibrium adsorption capacity (qₑ) of magnetite nanoneedles is “the amount of metal adsorbed per unit weight of adsorbent at equilibrium (mg g⁻¹)” and was calculated from the given equation:

\[ q_e = \frac{(C_0 - C_e)V}{m} \]

where \( C_0 \) is the initial metal ion (Pb²⁺) concentration, \( C_e \) is the metal ion concentration at equilibrium, \( V \) is the volume of the solution (L), and \( m \) is the dry weight of adsorbent.

Moreover, the percentage of lead adsorption (R) was also determined by the following equation:

\[ R = \frac{(C_0 - C_e)}{C_0} \times 100 \]

where \( C_0 \) and \( C_e \) are the initial lead ion concentration (mg L⁻¹) and after equilibrium, respectively.

3. RESULTS AND DISCUSSION

3.1. Characterization of Magnetite Nanoparticles. A high-resolution electron microscope (HRTEM) at CRF IIT Delhi was used to determine the morphology of the nanoparticles. Images at different magnification scales were captured from the same or different locations (Figure 1a,b). HRTEM revealed that bare magnetite nanoparticles have needle-like morphology with tapering ends and have a mean diameter of 9.09 nm (Figure 1c). The average size of synthesized nanoneedles was found to be 100 nm. HRTEM images elucidate lattice fringes, which exhibit a structurally uniform interplanar spacing of about 0.84 nm (Figure 1d). The
SAED pattern confirms the phase identification of magnetite nanoparticles. Figure 1e shows the SAED pattern of the magnetite nanoparticles. The dotted circle represents the estimated size and location of the diffraction aperture used for the SAED pattern at 100 nm scale bar. The synthesized magnetite nanoparticles possess a polycrystalline structure. In addition, EDX spectra (Figure 2) demonstrate the elemental composition of magnetite nanoparticles. Carbon and copper peaks were also detected on the collected spectrum along with iron and oxygen peaks, resulting from the carbon-coated copper grid used to mount the sample. The elemental composition spectra exhibit iron as 9.94% and oxygen as 21.58% while carbon and copper were 65.36 and 2.79% in atomic percent, respectively; additionally, a chlorine peak was also present.

XRD of the powdered nanoparticles elucidate details about the crystallinity of the particles, and for synthesized nanoparticles, XRD peaks are shown in Figure 3.

The lattice constants values were computed and matched with PDF database in crystallography open database (COD) to predict the type of nanoparticles. The value of lattice constant (a) was used to determine the magnetic type of the iron oxide nanoparticles, and for magnetite, it has a value of 8.35. The resulting nanoparticles were of Fe₃O₄ which possess a cubic spinel structure. The multiple peaks produced by magnetite have hkl values of 222, 112, 311, 313, 511, and 404 (COD database, 96-900-2318). The Scherrer equation was used to calculate the mean diameter of nanoparticles \[^{31,32}\] and is given as follows

\[
d = \frac{K\lambda}{B\cos \theta}
\]  

Figure 1. TEM images of Fe₃O₄ nanoneedles at scale bars of (a) 0.5 µm and (b) 100 nm. (c,d) HRTEM of Fe₃O₄ NPs at 10 nm showing lattice fringes. (e) SAED pattern of Fe₃O₄ nanoneedles.

Figure 2. Energy-dispersive spectra of Fe₃O₄ NPs showing different elemental peaks.

Figure 3. XRD spectra of Fe₃O₄ nanoparticles with characteristic peaks from 2θ = 20–80°.
“where factor $K$ is 0.9 (as spherical), $B$ structural $1/4B$ observed—$B$ standard (where $B$ is the full width at half maximum in radians), $\theta$ is half of the Bragg angle (in radians), and $\lambda$ is the wavelength of the X-rays ($1.5418 \text{ Å}$) used”.

Hence, the average crystallite size for the two most intense peaks (112, 313) estimated by the Scherrer equation was found to be 25.30 and 16.60 nm, respectively, for synthesized nanoparticles. The characteristic peaks of Fe$_3$O$_4$ NPs at $2\theta = 27.97$, 29.77, 31.659, 35.672, 45.38, 57.31 and 62.84$^\circ$ are attributed to their 222, 202, 112, 311, 313, 511, and 404 crystal planes, respectively. The Fe$_3$O$_4$ XRD pattern also had the diffraction peaks that can be indexed to cubic phase spinal Fe$_3$O$_4$. The diffraction peak of (112) is the strongest peak, which means that it is the dominant growth planes of Fe$_3$O$_4$.

The DLS measurement results were shown in Figure 4a in the form of a histogram. The DLS measurement for the dispersed Fe$_3$O$_4$ nanoneedles in ethanol has shown an RH of 381, 442, and 450 nm. The DLS histogram RH peaks were larger than the expected and calculated diameter. It showed a high degree of aggregation in particles, and its polydispersity index (PDI) was found to be 1, which should be 0 when there is no aggregation. The stability of the Fe$_3$O$_4$ NPs was analyzed by a zeta potential analyzer. Zeta potential ($\zeta$) is a significant method for understanding the surface of nanoparticles and their stability in solution. Usually, zeta potentials higher than positive 30 mV or lower than negative 30 mV have high stability. Moreover, dispersions with less than +25 mV or greater than −25 mV $\zeta$ value are prone to agglomeration due to interparticle interactions and may result in physical instability. The values less than 5 mV can lead to agglomeration.

The BJH results confirmed that Fe$_3$O$_4$ is a mesoporous material with pore diameter in the range of 2–50 nm and peak point diameter at 10.5 nm.

3.2. Batch Experiments. 3.2.1. Variation of pH. The solution pH has been recognized as one of the important parameters that affects the removal of a solute from the solution and has been termed as a master variable. In this study, the effect of pH on adsorption of Pb$^{2+}$ was investigated, and results are depicted in Figure 6. The Pb$^{2+}$ adsorption efficiency increased linearly from pH 2 to 4 then becomes nearly constant between pH 4 and 5 before increasing toward
pH 6. The pH of the solution affects speciation and surface charge of metal ions. At lower pH values, lesser uptake of Pb\textsuperscript{2+} ions was due to the competition for binding sites between Pb\textsuperscript{2+} and H\textsuperscript{+} ions. At pH 6, adsorption was increased, which may be due to some precipitation of Pb(OH)\textsubscript{2}, as a result of the solution buffering to pH > 6 during agitation. Higher values of pH > 6.0 were avoided due to hydrolysis and precipitation of Pb\textsuperscript{2+} ions. Therefore, all the subsequent experiments in this work were carried out at the optimum pH 6.0 to achieve maximum Pb\textsuperscript{2+} removal.

3.2.2. Variation of Adsorbent Dose. The adsorption of Pb\textsuperscript{2+} ions by magnetite NPs was studied over an adsorbent dose range of 5, 10, 20, 30, 40, 50, and 60 mg by keeping all other factors constant (Figure 7). On increase of adsorbent dose from 5 mg to 20 mg, adsorption efficiency got decreased due to the fact that all active sites were entirely exposed at lower dose whereas only a fraction of active sites was available for higher doses. Therefore, higher adsorbent dose has caused aggregation of nanoparticles, which reduced the total surface area of the adsorbent and thus decreased Pb\textsuperscript{2+} adsorption.

3.2.3. Variation of Temperature. The Pb\textsuperscript{2+} adsorption was studied at a temperature range of 15, 20, 25, 30, 35, 40, 45, and 50 °C as shown in Figure 8. Saturation of the adsorbent surface seems to be reached at 20−40 °C, and Figure 8 revealed that most of the Pb\textsuperscript{2+} ions get removed between this optimal temperature range. With increased temperature from 40 °C to 50 °C, the attractive forces between the adsorbent and adsorbate get weakened, and thus, sorption decreased. However, at high temperature, the thickness of the boundary layer decreased due to the increased tendency of the metal ions to escape from the adsorbent surface to the solution phase, which resulted in decrease in adsorption as temperature increased.

3.2.4. Variation of Contact Time. The Pb\textsuperscript{2+} concentration adsorbed on Fe\textsubscript{3}O\textsubscript{4} NPs versus contact time is represented in Figure 9. The Pb\textsuperscript{2+} adsorption increased with increased contact time and achieved maximum at 40 min. This behavior can be due to availability of a large number of sites for rapid surface metal ion binding during 40 min and their slow intraparticle diffusion of Pb\textsuperscript{2+} ions onto the Fe\textsubscript{3}O\textsubscript{4} surface afterward.

3.3. Adsorption Isotherms. To find out the relation of adsorbed species with their equilibrium concentrations, isotherms mainly Langmuir, Freundlich, and Temkin were applied to the equilibrium data. The isotherm modeling provides significant information on the surface properties, adsorption mechanism, and affinities of the adsorbent. Batch studies were performed at different temperatures (298, 308, 318, and 328 K), 100 mL of Pb\textsuperscript{2+} ion solution with an initial ion concentration of 30−150 mg L\textsuperscript{−1} was taken, and 10 mg of magnetite nanoparticles was added to it and stirred for 40 min to obtain equilibrium. Modeling analysis was carried out to get the best isotherm model.

Langmuir isotherm: This isotherm modeling is applicable to homogenous surface adsorption with uniform energy. From this isotherm, it can be interpreted that there is a fixed number of active sites on the surface of the adsorbent. The linearized-form Langmuir is as follows:

\[ \frac{1}{q_e} = \frac{1}{(K_L Q_m)C_e} + \frac{1}{Q_m} \]

(4)
or

\[
\frac{C_e}{q_e} = \frac{1}{K_q Q_m} + \frac{C_e}{Q_m}
\]

(5)

where \( Q_m \) can be calculated by plotting a curve between 1/\( q_e \) vs 1/\( C_e \) (Figure 10a), which gives maximum adsorption capacity and Langmuir constant as well, which can be related to energy of adsorption. Therefore, the maximum adsorption capacity calculated from the Langmuir model was 41.66 mg g\(^{-1}\) at 328 K (Table 1). A comparative maximum adsorption capacity data of various adsorbents obtained from the literature reviewed is also summarized in Table 2. An important feature of the Langmuir isotherm includes a dimensionless constant, i.e., the separation factor or equilibrium parameter, \( R_L \).

\[
R_L = \frac{1}{1 + K_L C_0}
\]

(6)

Table 1. Parameters for Pb\(^{2+}\) Adsorption

| Isotherm model | Parameters | 25 °C (298 K) | 35 °C (308 K) | 45 °C (318 K) | 55 °C (328 K) |
|---------------|------------|--------------|--------------|--------------|--------------|
| Langmuir      | \( q_m \)  | 13.17        | 3.753        | 3.759        | 41.66        |
|               | \( K_L \)  | 0.011        | 0.20         | 0.063        | 0.011        |
|               | \( R_L \)  | 0.99         | 0.97         | 0.99         | 0.99         |
|               | \( 1/q_m \)| 0.075        | 0.266        | 0.266        | 0.024        |
|               | \( K_L \)  | 0.742        | 0.671        | 0.335        | 0.826        |
|               | \( 1/q_m \)| 0.075        | 0.266        | 0.266        | 0.024        |
|               | \( K_L \)  | 0.742        | 0.671        | 0.335        | 0.826        |
|               | \( 1/q_m \)| 0.075        | 0.266        | 0.266        | 0.024        |

Figure 10. (a) Langmuir adsorption isotherm for Pb\(^{2+}\) adsorption. (b) Freundlich isotherm plots and (c) Temkin plots at different temperatures. (d) Experimental isotherm at (a) 298 K, (b) 308 K, (c) 318 K, and (d) 328 K for different lead ion concentrations of 30, 70, 110, and 150 mg L\(^{-1}\).
In the above equation, \( R_L \) indicates the nature of the adsorption. If the value of \( R_L > 1 \), then adsorption is interpreted as unfavorable; adsorption is linear for \( R_L = 1 \), favorable for \( 0 < R_L < 1 \), and irreversible when \( R_L = 0 \). For magnetite nanoneedles, the value of \( R_L \) ranges from 0.335–0.826, which was found to be less than unity. Hence, there is an effective interaction among Fe₃O₄ nanoneedles and Pb²⁺ ions and hence favors physical sorption.

The adsorption data was further analyzed by using the Freundlich isotherm equation, which frequently gives appropriate explanation of the acquired data over a restricted range of concentration.\(^{57}\) This isotherm is mostly viable to heterogeneous surfaces but also explains both monolayer and multilayer adsorption. The multilayer surface adsorption leads to non-uniform distribution of energy.\(^{58,59}\) It also describes the varied affinities of adsorbent surfaces and heterogeneous surface adsorption.\(^{60}\) The Freundlich equation is

\[
\ln q_e = \ln K_f + \frac{1}{n} \ln C_e
\]

(7)

where \( K_f \) and \( n \) are Freundlich constants, \( K_f \) denotes the adsorption capacity while adsorption intensity of the process was denoted by \( n \). The value of \( 1/n \) less than unity shows a significant adsorption at low concentration. Increase in the adsorbed amount with concentration becomes less significant when the concentration is high or vice versa.\(^{61}\)

The value of \( K_f \) and \( n \) can be derived from a linear equation by plotting a curve \( \ln q_e \) against \( \ln C_e \). The \( K_f \) and \( n \) values lie in between 0.240–6.839 and 0.865–1.710, respectively (Table 1). At four different temperatures (298, 308, 318, and 328 K), a curve was plotted for the Freundlich isotherm (Figure 10b). The minimum value of \( 1/n \), i.e., 0.314 and the maximum value of \( n \), i.e., 1.710 show an active interaction between magnetite nanoparticles and Pb²⁺ ions.\(^{72}\) The increase in \( K_f \) value with decrease in temperature indicates endothermic nature of adsorption.

Unlike Langmuir and Freundlich models, the Temkin isotherm model is based on “the assumption that free energy of sorption is a function of the surface coverage”.\(^{71}\) This model investigates the interactions among the adsorbent and adsorbate at four different temperatures to account for the adsorption process. The linear form of this model can be expressed by the following equation

\[
q_e = \frac{R_T}{B_T} \ln A_T + \frac{R_T}{B_T} \ln C_e
\]

(8)

where \( C_e \) is the equilibrium concentration of the adsorbate (mg L⁻¹), \( q_e \) is the equilibrium adsorbate value (mg g⁻¹), \( A_T \) denotes the equilibrium binding constant (g L⁻¹), and \( B_T \) (J mol⁻¹) is the Temkin constant that is related to heat of adsorption. The curve for the Temkin model is plotted between \( q_e \) vs \( \ln C_e \) over different temperatures (Figure 10c). The value of Temkin constant ranges in between 0.52 and 0.88 kJ mol⁻¹. When heat of sorption is less than 20 kJ mol⁻¹, then it is a characteristic of physisorption.\(^{72}\) In this case, the low value of \( B_T \) indicates feeble interaction between magnetite nanoneedles and Pb²⁺ ions and hence favors physical sorption. The value of \( R^2 \) for the Temkin model ranges from 0.69 to 0.83.

3.4. Kinetics of Adsorption. An adsorption kinetic modeling gives an insight into determining the adsorption rate and adsorption reaction mechanism. Pseudo first order, pseudo second order, and intraparticle diffusion models investigated the kinetics of adsorption (Table 3).

**Table 3. Estimated Kinetic Parameters for Pb²⁺ Adsorption**

| kinetic model          | parameters                                      | \( k_i \) | \( q_i \) | \( R^2 \) |
|------------------------|-------------------------------------------------|-----------|----------|----------|
| pseudo first order     | \( \ln(q_e - q_t) = \ln q_e - k_t t \)          | \( q_i \) | amount of Pb adsorbed on adsorbent (mg g⁻¹) | 1.26     |
|                        |                                                 |           |          | 0.96     |
| pseudo second order    | \( t/q_i = 1/(k_i q_i e^2) + (1/q_i t) \)       |           |          | 0.110    |
|                        |                                                 | \( q_i \) | amount of Pb adsorbed on adsorbent (mg g⁻¹) | 9.52     |
|                        |                                                 |           |          | 0.99     |
| intraparticle diffusion| \( q_i = k_i \sqrt{t} + x_i \)                  |           |          | 0.165    |
|                        |                                                 |           |          | 0.66     |
|                        |                                                 |           |          | 8.12     |

The pseudo-first-order rate equation, "popularly known as the Lagergren equation, generally describes the solute adsorption on adsorbent" and is represented by the following equation\(^{52,57}\)

\[
\ln(q_e - q_t) = \ln q_e - k_i t
\]

(9)

where \( q_e \) is the equilibrium concentration of metal ions per unit weight of adsorbent (mg g⁻¹); \( q_t \) is the rate of metal ions adsorbed at any time (mg g⁻¹); \( k_i \) is the rate constant (min⁻¹). Figure 11a shows the pseudo-first-order kinetic plots between \( \ln(q_e - q_t) \) vs \( t \) at 10 mg L⁻¹ equilibrium concentration and temperature of 298 K.

If the "intercept is not equal to the natural logarithm of equilibrium uptake of metal ions, the reaction is not likely to follow a first-order path even if experimental data have high coefficient of determination".\(^{57}\) The value for the coefficient of determination, i.e., \( R^2 \) for Pb²⁺ adsorption, was observed as 0.96 (Table 3), and from the slope of eq 10, the Lagergren rate constants were calculated.\(^{61}\) The pseudo-second-order kinetics was also applied to the adsorption data.\(^{73,74}\)

However, the pseudo-second-order linear equation is given by

\[
\frac{t}{q_t} = \frac{1}{(k_i q_i e^2)} + \frac{1}{q_i} t
\]

(10)

where \( k_i \) is the rate constant (mg g⁻¹ min⁻¹).

**Table 2. Different Nanoadsorbents with their Adsorption Capacities**

| adsorbent                                  | maximum adsorption capacity (mg g⁻¹) | reference |
|--------------------------------------------|--------------------------------------|-----------|
| graphene oxide                             | 35.6                                  | 62        |
| polysulfone/hydrous ferric oxide NPs       | 13.2                                  | 63        |
| magnetic biochar                           | 0.11 mmol g⁻¹                         | 64        |
| pine wood charcoal                         | 4.13 mg g⁻¹                           | 65        |
| CNTs                                       | 17.44 mg g⁻¹                          | 66        |
| activated carbon                           | 21.2 mg g⁻¹                           | 67        |
| l-cysteine functionalized Fe₃O₄ NPs        | 18.8 mg g⁻¹                           | 68        |
| Fe₃O₄−SO₄,H MNP                             | 108.93 mg g⁻¹                         | 69        |
| mesoporous magnetite (Fe₃O₄) nanospheres   | ~19 mg g⁻¹                            | 70        |
| magnetite nanoneedles                      | 41.66 mg g⁻¹                          | present study |

In the above equation, \( R_L \) indicates the nature of the adsorption. If the value of \( R_L > 1 \), then adsorption is interpreted as unfavorable; adsorption is linear for \( R_L = 1 \), favorable for \( 0 < R_L < 1 \), and irreversible when \( R_L = 0 \). For magnetite nanoneedles, the value of \( R_L \) ranges from 0.69–1.0, and from the slope of eq 10, the Lagergren rate constants were calculated.\(^{61}\) The pseudo-second-order kinetics was also applied to the adsorption data.\(^{73,74}\)
If the pseudo-second-order kinetics gives a linear relation after plotting a curve, then $t/q_t$ against $t$ (Figure 11b) and the value of constant $k_2$ can be obtained. The pseudo-second-order model was the best fit to the obtained equilibrium data. The correlation coefficient ($R^2$) of pseudo-second-order kinetics is 0.99.

The intraparticle diffusion model considers the adsorbate intraparticle uptake and pore diffusion during adsorption. According to this model, transient uptake of the solute varies almost proportionately with the half power of time ($t^{1/2}$) for most of the adsorption processes. It mainly represents the thickness of the boundary layer. The linearized form of this model is represented as follows

$$q_i = k_i \sqrt{t} + x_i$$  \hfill (11)

A kinetic curve for the intraparticle diffusion model was plotted between $q_i$ vs $t^{1/2}$ (Figure 11c) to obtain the value of $x_i$, i.e., 8.12 at 298 K for 110 mg L$^{-1}$ Pb$^{2+}$ concentration. According to the model, the higher the value of $x_i$ the greater will be the boundary layer effect (Table 3). Hence, from the above experimental kinetic results, the order of best fit kinetic model in relation to $R^2$ is pseudo second order > pseudo first order > intraparticle diffusion.

**3.5. Thermodynamics of Adsorption.** To estimate the spontaneity and feasibility of the adsorption processes, thermodynamic parameters have critical importance as they give viable information to design the process of adsorption. Using eqs 12–18, the entropy change [$\Delta S^o$ (kJ mol$^{-1}$ K)], Gibbs free energy of adsorption [$\Delta G^o$ (kJ mol$^{-1}$)], and the enthalpy change [$\Delta H^o$ (kJ mol$^{-1}$)] were determined.$^{76–77}$ For the calculation of the above parameters, $K_d$ (Langmuir constant), $K_d$ (solute coefficient distribution), and $C_e$ (equilibrium Pb$^{2+}$ ion concentration) at different temperatures were calculated (Table 4). Various equations for calculating thermodynamic parameters are given as follows.$^{78–80}$

**Distribution coefficient**

$$\ln K_d = \Delta S^o / R - \Delta H^o / RT$$  \hfill (12)

where $K_d = q_e / C_e$

$$\Delta G = \Delta H - T \Delta S$$  \hfill (13)

**Table 4. Thermodynamic Parameters of Pb(II) Adsorption**

| $C_o$ (mg L$^{-1}$) | 298 | 308 | 318 | 328 | $\Delta H^o$ (kJ mol$^{-1}$) | $\Delta S^o$ (kJ mol$^{-1}$) | 298 | 308 | 318 | 328 |
|---------------------|-----|-----|-----|-----|---------------------------|---------------------------|-----|-----|-----|-----|
| 30                  | 3.09| 0.13| 0.16| 0.05| $-2.60$                   | 0.074                     | $-22.1$| $-22.9$| $-23.6$| $-24.3$|
| 70                  | 3.25| 0.23| 0.21| 0.13| $-2.09$                   | 0.062                     | $-18.5$| $-19.1$| $-19.7$| $-20.4$|
| 110                 | 5.34| 0.34| 0.24| 0.52| $-1.58$                   | 0.053                     | $-15.7$| $-16.3$| $-16.8$| $-17.3$|
| 150                 | 1.59| 0.32| 0.24| 0.25| $-1.415$                  | 0.038                     | $-11.4$| $-11.8$| $-12.2$| $-12.6$|

If the pseudo-second-order kinetics gives a linear relation after plotting a curve, then $t/q_t$ against $t$ (Figure 11b) and the value of constant $k_2$ can be obtained. The pseudo-second-order model was the best fit to the obtained equilibrium data. The correlation coefficient ($R^2$) of pseudo-second-order kinetics is 0.99.

![Figure 11. Kinetic curves: (a) pseudo first order and (b) pseudo second order at 10 mg L$^{-1}$ at 298 K. (c) Intraparticle particle diffusion and (d) kinetic curve at 10 mg L$^{-1}$ at 298 K.](image)

[Table 4. Thermodynamic Parameters of Pb(II) Adsorption](#)

**| $C_o$ (mg L$^{-1}$) | 298 | 308 | 318 | 328 | $\Delta H^o$ (kJ mol$^{-1}$) | $\Delta S^o$ (kJ mol$^{-1}$) | 298 | 308 | 318 | 328 |
|---------------------|-----|-----|-----|-----|---------------------------|---------------------------|-----|-----|-----|-----|
| 30                  | 3.09| 0.13| 0.16| 0.05| $-2.60$                   | 0.074                     | $-22.1$| $-22.9$| $-23.6$| $-24.3$|
| 70                  | 3.25| 0.23| 0.21| 0.13| $-2.09$                   | 0.062                     | $-18.5$| $-19.1$| $-19.7$| $-20.4$|
| 110                 | 5.34| 0.34| 0.24| 0.52| $-1.58$                   | 0.053                     | $-15.7$| $-16.3$| $-16.8$| $-17.3$|
| 150                 | 1.59| 0.32| 0.24| 0.25| $-1.415$                  | 0.038                     | $-11.4$| $-11.8$| $-12.2$| $-12.6$|
Δ = Δ − Δ

KS R H R T

l

ln L

(14)

Δ = − ×

GR T K

ln L

(15)

Equilibrium lead concentration

= − +Δ C K H R

(16)

The Gibbs–Helmholtz equation can be used to calculate Δ

Δ = Δ − Δ

SH G T

() /

(17)

Δ = −

Gn R T

(18)

where \( n \) is the Freundlich constant.

Using the above equations, a thermodynamic curve was plotted between \( \ln K_d \) vs 1/\( T \), \( \ln C_e \) vs 1/\( T \), and \( \ln K_L \) vs 1/\( T \) as shown in Figure 12a–c, respectively. Van’t Hoff plots can be interpreted to determine the thermodynamic parameters from the slope and intercept (Table 4). In this experimental study, low temperature is favorable for adsorption interpreted from \( \Delta G^o \) values at four different temperatures. The negative value of \( \Delta G^o \) indicates the spontaneity and feasibility of the adsorption reaction at a given temperature.\(^{81}\) The increasing value of \( \Delta G^o \) with an increased temperature indicates decrease in the degree of feasibility for Pb\(^{2+}\) adsorption. The \( \Delta H^o \) values lie in the range of \(-20\) to \(40\) kJ mol\(^{-1}\) for physisorption and \(-80\) to \(400\) kJ mol\(^{-1}\) for chemisorption. Moreover, the negative value of \( \Delta H^o \) shows that it is physisorption and exothermic in nature.\(^{81}\) The positive values of \( \Delta S^o \) indicate the increased randomness at the adsorbate–adsorbent interface during Pb\(^{2+}\) adsorption.\(^{32}\) From all the three Van’t Hoff plots, it can be concluded that \( \Delta G^o < 0 \), \( \Delta H^o < 0 \), and \( \Delta S^o > 0 \).

We have demonstrated the ability of Fe\(_3\)O\(_4\) NPs to be used for the elimination of Pb\(^{2+}\) ions from aqueous solution. The process involves physisorption of Pb\(^{2+}\) ions. Therefore, the efficiency of the process and the ability of its facile recovery and regeneration make the entire process viable. Although the method described here is majorly efficient for the removal of Pb\(^{2+}\) with lesser adsorbent dose, the synthesized Fe\(_3\)O\(_4\) NPs can limit their efficiency as they tend to aggregate rapidly. Hence, certain capping agents can work to reduce the aggregation between particles and increase their stability and efficiency. Silica or other polymers can be added as a shell to the nanoparticles to make them stable. Deposition of a thin layer on the nanoparticles is supposed to alter their functions, optical and electronic properties, chemical reactivity, catalytic activity, thermal stability, dispersibility, and magnetic properties as well.

3.6. Regeneration and Desorption Studies. The efficiency of magnetite nanoneedles was investigated in three consecutive adsorption–desorption cycles. The exhausted magnetite nanoneedles were regenerated with HNO\(_3\). Magnetite nanoneedles were agitated with 50 mL of Pb\(^{2+}\) solution of 110 mg L\(^{-1}\) concentration for 40 min, equilibrium concentration was measured, and the NPs were desorbed using 0.01
M HNO₃. The desorbed NPs were dried and again used for adsorption. The adsorption–desorption cycles were repeated thrice (Figure 13). The lead adsorption yield was 98.5% and 88% desorption in the first cycle, and then, reduction to 89% adsorption and 75% desorption was achieved in 20 mL of HNO₃ for Pb²⁺ in the third cycle. Therefore, magnetite nanoneedles can be regenerated with maximum efficiency for Pb²⁺ removal.

4. CONCLUSIONS

In this work, Fe₃O₄ nanoneedles were successfully synthesized and explored for the adsorption of Pb²⁺ ions. Characterization studies (HRTEM, XRD, SAED, DLS, and zeta potential) confirmed the morphological and structural details of nanoneedles. However, it was observed that Pb²⁺ adsorption was highly pH-dependent, and isotherm modeling was obeyed by the Langmuir model, which indicated the monolayer Pb²⁺ adsorption at the homogeneous surface. The overall process involves physisorption of ions. The fabricated Fe₃O₄ NPs could efficiently extract Pb²⁺ ions from the solution, and after repeated adsorption–desorption cycles, the NPs still possess stable adsorption capacity and can be used as an ideal heavy-metal extraction adsorbent. The experiments revealed that Fe₃O₄ nanoneedles can be considered as operative, reckless, and dose-redeemable materials for lead decontamination. Moreover, the synthesized nanoneedles have shown better adsorption capacity (41.1 mg g⁻¹) and regenerability as compared with activated carbon and graphene oxide on the basis of their maximum adsorption capacities, i.e., 21.2 and 35.6 mg g⁻¹, respectively.

Author

Rimmy Singh — Department of Environmental Science, Maharshi Dayanand University, Rohtak 124001, India

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.0c00450

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The Central Research Facility (CRF) and Nanoscale Research Facility (NRF) at IIT Delhi (India) are acknowledged for providing characterization facility of HRTEM along with EDX, SAED, XRD, DLS, zeta potential, and ICP-MS.

REFERENCES

(1) Jalali, R.; Ghaforian, H.; Asef, Y.; Davarpanah, S.; Sephr, S. Removal and recovery of lead using nonliving biomass of marine algae. J. Hazard. Mater. 2002, 92, 253–262.
(2) Iqbal, M.; Edyvean, R. G. J. Biosorption of lead, copper and zinc ions on loofa sponge immobilized biomass of Phanerochaete chryosporium. Miner. Eng. 2004, 17, 217–223.
(3) World Health Organization. Guidelines for drinking-water quality - 4th edition; ISBN 978924 1548151 published by WHO: Switzerland, 2011.
(4) Ihsanullah; Abbas, A.; Al-Amer, A. M.; Laouli, T.; Al-Marr, M. J.; Nasser, M. S.; Khaahe, M.; Atieh, M. A. Heavy metal removal from aqueous solution by advanced carbon nanotubes: critical review of adsorption applications. Sep. Purif. Technol. 2016, 157, 141–161.
(5) Mason, L. H.; Harp, J. P.; Han, D. Y. Pb neurotoxicity: neuropsychological effects of lead toxicity. BioMed Res. Int. 2014, 840547.
(6) Matta, G.; Gyál, L. Mercury, lead and arsenic: impact on environment and human health. J. Chem. Pharm. Sci. 2016, 9, 718–725.
(7) Sekhar, K. C.; Kamala, C. T.; Chary, N. S.; Sastry, A. R.; Rao, T. N.; Vairamani, M. Removal of lead from aqueous solutions using an immobilized biomaterial derived from a plant biomass. J. Hazard. Mater. 2004, 108, 111–117.
(8) Atsdr. U. Toxicological profile for lead (Atlanta, GA: US Department of Health and Human Services, Agency for Toxic Substances and Disease Registry (ATSDR); Public Health Service). Air quality criteria for lead; US EPA (2006). 2007.
(9) Jarup, L. Hazards of heavy metal contamination. Br. Med. Bull. 2003, 68, 167–182.
(10) Kameda, T.; Suzuki, Y.; Yoshioka, T. Removal of arsenic from an aqueous solution by coprecipitation with manganese oxide. J Environ. Chem. Eng. 2014, 2, 2045–2049.
(11) Sunil, K.; Karunakaran, K.; Yadav, S.; Padaki, M.; Zadorozhnyy, V.; Pai, R. K. Al-TiO₂G a mixed metal oxide based composite membrane: a unique membrane for removal of heavy metals. Chem. Eng. J. 2018, 348, 678–684.
(12) Abejón, A.; Garea, A.; Irabien, A. Arsenic removal from drinking water by reverse osmosis: minimization of costs and energy consumption. Sep. Puriﬁ. Technol. 2015, 144, 46–53.
(13) El-Din, A. F. T.; El-Kholy, M. E.; Elshemy, E. A.; Atia, A. A.; El-Said, W. A. Cellulose acetate assisted synthesis of wound-shaped mesopores of MgP ion-exchanger for cesium ions removal from seawater. Microporous Mesoporous Mater. 2018, 265, 211–218.
(14) Dhillon, A.; Kumar, D. Development of a nanoporous adsorbent for the removal of health–hazardous fluoride ions from aqueous systems. J. Mater. Chem. 2015, 3, 4215–4228.
(15) Bajestani, M. B.; Moheb, A.; Masigol, M. Simultaneous Optimization of Adsorption Capacity and Stability of Hydrothermally Synthesized Spinel Ion Sieve Composite Adsorbents for Selective Removal of Lithium from Aqueous Solutions. Ind. Eng. Chem. Res. 2019, 58, 12207–12215.

AUTHOR INFORMATION

Corresponding Author

Rachna Bhateria — Department of Environmental Science, Maharshi Dayanand University, Rohtak 124001, India; orcid.org/0000-0001-5378-6172; Email: bioremediationlab.mdu@gmail.com
(16) Gugushe, A. S.; Nqombolo, A.; Nomungo, P. N. Application of Response Surface Methodology and Desirability Function in the Optimization of Adsorptive Remediation of Arsenic from Acid Mine Drainage Using Magnetic Nanocomposite: Equilibrium Studies and Application to Real Samples. *Molecules* 2019, 24, 1792.

(17) Baghi, Y.; Sarswat, A.; Mohan, D.; Pandey, A.; Solanki, P. R. Lead and chromium adsorption from water using L-cysteine functionalized magnetite (Fe₃O₄) nanoparticles. *Sci. Rep.* 2017, 7, 7672.

(18) Bhatera, R.; Singh, R. A review on nanotechnological application of magnetic iron oxides for heavy metal removal. *J. Water Process Eng.* 2019, 31, 100845.

(19) Badruddoza, A. Z. M.; Shawon, Z. B. Z.; Rahman, M. T.; Hao, K. W.; Hidayat, K.; Uddin, M. S. I onically modified magnetic nanomaterials for arsenic and chromium removal from water. *Chem. Eng. J.* 2015, 235, 607–615.

(20) Lei, Y.; Chen, F.; Luo, Y.; Zhang, L. Three-dimensional magnetic graphene oxide foam/Fe₃O₄ nanocomposite as an efficient absorbent for Cr (VI) removal. *J. Mater. Sci.* 2014, 49, 4236–4245.

(21) Ngomsik, A. F.; Bee, A.; Talbot, D.; Cote, G. Magnetic solid-liquid extraction of Eu(III), La(III), Ni(II) and Co(II) with maghemite nanoparticles. *Sep. Purif. Technol.* 2012, 86, 1–8.

(22) Tan, I.; Xu, J.; Xue, X.; Lou, Z.; Zhu, J.; Baig, S. A.; Xu, X. Multifunctional nanocomposite Fe₃O₄@SiO₂-mPDF/SP for selective removal of Pb(II) and Cr(VI) from aqueous solutions. *RSC Adv.* 2014, 4, 45920–45929.

(23) Tu, Y. J.; You, C. F.; Chang, C. K.; Wang, S. L.; Chan, T. S. Arsenate adsorption from water using a novel fabricated copper ferrite. *Chem. Eng. J.* 2012, 440–448.

(24) Kalantari, K.; Ahmad, M. B.; Masoumi, H. R. F.; Shameli, K.; Basri, M.; Khandanlou, R. Rapid and high capacity adsorption of heavy metals by Fe₃O₄/montmorillonite nanocomposite using response surface methodology: Preparation, characterization, optimization, equilibrium isotherms, and adsorption kinetics study. *J. Taiwan Inst. Chem. Eng.* 2015, 49, 192–198.

(25) Baghi, Y.; Sarswat, A.; Mohan, D.; Pandey, A.; Solanki, P. R. Lead and chromium adsorption from water using L-cysteine functionalized magnetite (Fe 3 O 4) nanoparticles. *Sci. Rep.* 2017, 7, 7672.

(26) Wang, X. S.; Lu, H. J.; Zhu, L.; Liu, F.; Ren, J. J. Adsorption of lead (II) ions on magnetite nanoparticles. *Adsorpt. Sci. Technol.* 2010, 28, 407–417.

(27) Tavares, D. S.; Daniel-da-Silva, A. L.; Lopes, C. B.; Silva, N. J. O.; Amaral, V. S.; Rocha, J.; Pereira, E.; Trindade, T. Efficient sorbents based on magnetite coated with siliceous hybrid shells for removal of mercury ions. *J. Mater. Chem. A* 2013, 1, 8134–8143.

(28) Yuvakkumar, R.; Elango, V.; Rajendran, V.; Kannan, N. Preparation and characterization of zero valent iron nanoparticles. *Dig. J. Nanomater. Biострук.* 2011, 6, 1771–1776.

(29) Ahmadi, S.; Kord Mostafapour, F. K. Adsorptive removal of aniline from aqueous solutions by Pistacia atlantica (Baneh) shells: isotherm and kinetic studies. *J. Sci. Technol. Environ. Inf.* 2017, 5, 327–335.

(30) Balarad, D.; Azarpria, H.; Mostafapour, F. K. Thermodynamics of removal of cadmium by adsorption on Barley husk biomass. *Der Pharma Chem.* 2016, 8, 243–247.

(31) Holzwarth, U.; Gibson, N. The Scherrer equation versus the ‘Debye-Scherrer equation’. *Nat. Nanotechnol.* 2011, 6, 534.

(32) Klug, H. P.; Alexander, L. E. X-ray diffraction procedures for polycrystalline and amorphous materials; New York: Wiley Interscience, 1974, 2.

(33) Haavik, C.; Stříten, S.; Fjellvåg, H.; Hanfland, M.; Häusermann, D. Equation of state of magnetite and its high-pressure modification: Thermodynamics of the Fe-O system at high pressure. *Am. Mineral.* 2000, 85, 514–523.

(34) Challagulla, S.; Nagarjuna, R.; Ganesan, R.; Roy, S. Acrylate-based polymerizable sol–gel synthesis of magnetically recoverable TiO₂ supported Fe₃O₄ for Cr (VI) photoreduction in aerobic atmosphere. *ACS Sustainable Chem. Eng.* 2016, 4, 974–982.
(54) Hao, Y. M.; Man, C.; Hu, Z. B. Effective removal of Cu (II) ions from aqueous solution by amin-functionalized magnetic nanoparticles. *J. Hazard. Mater.* 2010, 184, 392–399.

(55) Langmui, I. The constitution and fundamental properties of solids and liquids. Part I. Solids. *J. Am. Chem. Soc.* 1916, 38, 2221–2295.

(56) Farmer, V.C. (eds.); *The Infrared Spectra of Minerals;* Mineralogical Society: London, 1974.

(57) Lagergren, S. K. About the theory of so-called adsorption of soluble substances. *Sven. Vetensk.-Akad. Handl.* 1898, 24, 1–39.

(58) Gupta, V. K.; Rastogi, A.; Nayak, A. Biosorption of nickel onto treated alga (Undaria pinnatifida): application of isotherm and kinetic models. *J. Colloid Interface Sci.* 2010, 342, 533–539.

(59) Amin, N. K. Removal of reactive dye from aqueous solutions by adsorption onto activated carbons prepared from sugarcane bagasse pith. *Desalination* 2008, 223, 152–161.

(60) Vasiiliu, S.; Bunia, L.; Racovita, S.; Neagu, V. Adsorption of cefotaxime sodium salt on polymer coated ion exchange resin microparticles: Kinetics, equilibrium and thermodynamic studies. *Carbohydr. Polym.* 2012, 89, 1178–1185.

(61) Ho, Y. S.; McKay, G. Sorption of dye from aqueous solution by pet. *Chem. Eng. J.* 1998, 70, 115–124.

(62) Lee, Y. C.; Yang, J. W. Self-assembled flower-like TiO2 on exfoliated graphite oxide for heavy metal removal. *J. Ind. Eng. Chem.* 2012, 18, 1178–1185.

(63) Abdullrah, N.; Gohari, R. J.; Yusof, N.; Ismail, A. F.; Juhaana, J.; Lau, W. J.; Matsuura, T. Polysulphone/hydrous ferric oxide ultrafiltration mixed matrix membrane: preparation, characterization and its adsorptive removal of lead (II) from aqueous solution. *Chem. Eng. J.* 2016, 289, 28–37.

(64) Karunanayake, A. G.; Todd, O. A.; Crowley, M.; Ricchetti, L.; Pittman, C. U., Jr.; Anderson, R.; Mohan, D.; Milsa, T. Lead and cadmium remediation using magnetized and nonmagnetized biochar from Douglas fir. *Chem. Eng. J.* 2018, 331, 480–491.

(65) Mohan, D.; Pittman, C. U., Jr.; Bricka, M.; Smith, F.; Yancey, B.; Mohammad, J.; Steele, P. H.; Alexandre-Franco, M. F.; Gomez-Serrano, V.; Gong, H.; Gong, H. Sorption of arsenic, cadmium, and lead by chars produced from fast pyrolysis of wood and bark during bio-oil production. *J. Colloid Interface Sci.* 2007, 310, 57–73.

(66) Staifje, A.; Pryzynska, K. Solid phase extraction of metal ions using carbon nanotubes. *Microchem. J.* 2008, 89, 29–33.

(67) Shi, Q.; Terracciano, A.; Zhao, Y.; Wei, C.; Christodoulatos, C.; Meng, X. Evaluation of metal oxides and activated carbon for lead removal: Kinetics, isotherms, column tests, and the role of co-existing ions. *Sci. Total Environ.* 2019, 648, 176–183.

(68) Baghi, Y.; Sarswat, A.; Mohan, D.; Pandey, A.; Solanki, P. R. Lead (Pb2+) adsorption by monodispersed magnetite nanoparticles: Surface analysis and effects of solution chemistry. *J. Environ. Chem. Eng.* 2016, 4, 4237–4247.

(69) Chen, K.; He, J.; Li, Y.; Cai, X.; Zhang, K.; Liu, T.; Hu, Y.; Lin, D.; Kong, L.; Liu, J. Removal of cadmium and lead ions from water by sulfonated magnetic nanoparticle adsorbents. *J. Colloid Interface Sci.* 2017, 494, 307–316.

(70) Kumari, M.; Pittman, C. U., Jr.; Mohan, D. Heavy metals (chromium (VI) and lead (II)) removal from water using mesoporous magnetite (Fe3O4) nanospheres. *J. Colloid Interface Sci.* 2015, 442, 120–132.

(71) Chen, Z.; Ma, W.; Han, M. Biosorption of nickel and copper onto treated alga (Undaria pinnatifida): application of isotherm and kinetic models. *J. Hazard. Mater.* 2008, 155, 327–333.

(72) Raghav, S.; Kumar, D. Adsorption equilibrium, kinetics, and thermodynamic studies of fluoride adsorbed by tetrarmetalic oxide adsorbent. *J. Chem. Eng. Data* 2018, 63, 1682–1697.

(73) Hou, Y.; Yu, H.; Gao, S. Solvothermal reduction synthesis and characterization of superparamagnetic magnetite nanoparticles. *J. Mater. Chem.* 2003, 13, 1983–1987.

(74) Marmier, N.; Fromage, F. Sorption of Cs(I) on magnetite in the presence of silicates. *J. Colloid Interface Sci.* 2000, 223, 83–88.

(75) Yao, Z. Y.; Qi, J. H.; Wang, L. H. Equilibrium, kinetic and thermodynamic studies on the biosorption of Cu (II) onto chestnut shell. *J. Hazard. Mater.* 2010, 174, 137–143.

(76) Xu, P.; Zeng, G. M.; Huang, D. L.; Lai, C.; Zhao, M. H.; Wei, Z.; Li, N. J.; Huang, C.; Xie, G. X. Adsorption of Pb (II) by iron oxide nanoparticles immobilized Phanerochaete chrysosporium: equilibrium, kinetic, thermodynamic and mechanisms analysis. *Chem. Eng. J.* 2012, 203, 423–431.

(77) Sheela, T.; Nayaka, Y. A. Kinetics and thermodynamics of cadmium and lead ions adsorption on NiO nanoparticles. *Chem. Eng. J.* 2012, 191, 123–131.

(78) Li, H.; Huang, G.; An, C.; Hu, J.; Yang, S. Removal of tannin from aqueous solution by adsorption onto treated coal fly ash: kinetic, equilibrium, and thermodynamic studies. *Ind. Eng. Chem. Res.* 2013, 52, 15923–15931.

(79) Mohapatra, M.; Haripurasad, D.; Mohapatra, L.; Anand, S.; Mishra, B. K. Mg-doped nano ferricydrite a new adsorbent for fluoride removal from aqueous solution. *Appl. Surf. Sci.* 2012, 258, 4228–4236.

(80) Xue, F.; Xu, Y.; Lu, S.; Ju, S.; Xing, W. Synthesis of hybrid ion exchanger for rhodamine b dye removal: equilibrium, kinetic and thermodynamic studies. *J. Chem. Eng. Data* 2016, 61, 2179–2185.

(81) Erkey, C. Supercritical fluids and organometallic compounds: from recovery of trace metals to synthesis of nanostructured materials; Elsevier, 2011.

(82) Liu, L.; Liu, S.; Zhang, Q.; Li, C.; Bao, C.; Liu, X.; Xiao, P. Adsorption of Au (III), Pd (II), and Pt (IV) from aqueous solution onto graphene oxide. *J. Chem. Eng. Data* 2015, 58, 209–216.