Research Article

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Green synthesis of manganese-doped superparamagnetic iron oxide nanoparticles for the effective removal of Pb(II) from aqueous solutions

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Abstract: In the current study, pure and manganese-doped superparamagnetic iron oxide nanoparticles (Mn-doped SPIONPs) were successfully prepared by a green approach using a fresh aqueous extract of Asparagus officinalis as a reducing and stabilizing agent. Magnetic behaviors of pure and Mn-doped SPIONPs were measured at room temperature against various field strengths by a vibrating sample magnetometer (VSM). The saturation magnetization was in the range of 5.39–2.07 emu. Absorption at 340 nm in the UV-visible spectrum confirmed the presence of iron oxide nanoparticles (IONPs). The presence of plant extract as a capping agent was confirmed by Fourier transform infrared (FTIR) spectroscopy. The crystalline nature of IONPs was confirmed by X-ray diffraction. A gradual increase in size was observed with increasing concentration of Mn. The synthesized materials were applied successfully as sorbent for the effective removal of lead ions (Pb(II)). Experimental results of adsorption were also analyzed by Langmuir and Freundlich isotherm equations at different temperatures. The results suggested that sorption processes were spontaneous, and the synthesized SPIONPs displayed Pb(II) removal capacity at higher loadings with qm of 21.3 and 29.56 mg g⁻¹ for undoped and 7% Mn-doped IONPs, respectively, as compared to the commercial activated carbon.

Keywords: green synthesis, Asparagus officinalis, magnetization, heavy metal, drinking water

1 Introduction

Nanotechnology is now an established field of science that deals with the conversion and development of materials having unique characteristics, making it an ultimate choice to be used in diverse fields of life. Nanoscale materials have at least one dimension in a nanoscale range and, in contrast to a bulk scale, exhibit excellent physical, chemical, optical, thermal, electrical, and magnetic properties, possessing a wide range of applications [1–3]. At the nanoscale range, iron oxide has been extensively studied due to its low toxicity, high biocompatibility, large surface area, and good magnetic behavior. The applications of iron oxide nanoparticles (IONPs) include biological sensing, antimicrobial activity, preservation of food, magnetic storage media, cancer treatment, and drug delivery [4,5]. In the literature, several methods have been reported for the synthesis of iron oxide including polyol, sol–gel, hydrothermal, micro-emulsion, and co-precipitation methods. Among these, the co-precipitation method is widely used due to its simplicity and cost-effectiveness; however most importantly, the surface of prepared materials can be treated with other substances easily increasing its suitability for medical and technical applications [6].

Due to the regular release of hazardous materials such as heavy metals, dyes, and pigments into the atmosphere, ecological integrity is in threat. The textile, paper,
plastics, leather, food, and cosmetics industries contribute significantly to environmental pollution by releasing colored effluents into the environment, both consciously and unconsciously [7,8]. Rapid urbanization and industrialization have resulted in exponential development in the industry in the recent decades, resulting in massive amounts of harmful effluents being released into natural water bodies. These industrial effluents contain various harmful substances, including dyes, heavy metals, phenolic compounds, pharmaceuticals, among others, which enter the water immediately and have a detrimental impact on the ecosystem [9,10]. Clean water is one of the major requirements of human beings, both for their better health and survival, but most of the countries are facing shortage of clean drinking water [11,12]. Health and environmental concerns are associated with heavy metal contamination, and it is becoming serious day by day due to the rapidly growing industry and population. Water polluted with heavy metals has become a global problem, most importantly in densely populated countries [13,14]. Among the different heavy metals, lead is one of the most toxic contaminants released into water bodies from different industrial activities such as oil refining, metal plating, battery manufacturing, paint, and pigment industries [15]. Pb can enter our body through skin contact, ingestion, and inhalation. Thus, its exposure to the body can act as a cumulative poison. Pb accumulates largely in the kidneys, brain, muscles, and bones and causes severe disorders such as nervous disorders, kidney diseases, and anemia [16,17]. Lead replaces calcium, which is a major essential mineral for strengthening of teeth and bones. Pb also acts as an inhibitor of enzymes and replaces Zn from heme enzymes. The elevated level of Pb damages cognitive development in children [18]. According to the US Environmental Protection Agency, the maximum allowed concentration of lead in drinking water is 15 ppb [19]. Due to the toxic effects of lead ions, their removal from water and wastewater is important in terms of the protection of public health and environment [20]. Conventional methods used to remove Pb(II) from drinking water include ion-exchange, chemical precipitation, electrolysis, adsorption on activated carbon, membrane filtration, coagulation, and reverse osmosis [21–24]. However, these methods have limited application due to their high operational costs. In the recent past, considerable work has been published demonstrating the use of superparamagnetic iron oxide nanoparticles (SPIONPs) as a sorbent for the removal of heavy metals and other pollutants from polluted water and after sorption treatment these SPIONPs can be separated easily [25–27]. It has been shown that when a metal is added to an oxide, it increases its affinity toward the analyte compared to the native oxide; keeping in view the adsorption properties of iron oxide and manganese oxide, it has been suggested to develop IOPNs doped with manganese.

Based on these facts and in continuation of our work dealing with the development of materials for wastewater treatment [28–31], here, in this work, IOPNs were prepared as a host material. This synthesis was achieved by adopting the green chemistry approach. The prepared iron oxide nanomaterials were doped with varying concentration of Mn(II) using a sonicator in order to minimize the use of any extra chemicals.

2 Materials and methods

2.1 Materials

Ferric nitrate (Fe(NO$_3$)$_3$·9H$_2$O), ferrous nitrate (Fe(NO$_3$)$_2$·9H$_2$O), hydrazine hydrate, manganese sulfate (MnSO$_4$), and potassium permanganate (KMnO$_4$) used were obtained from Merck, Germany. Sodium hydroxide (NaOH), nitric acid (HNO$_3$), and lead acetate Pb(CH$_3$COOH)$_2$ were obtained from BDH Chemicals, UK. Analytical-grade ethanol and de-ionized water used were purchased from the local market and used as such without further purification.

2.2 Preparation of plant extract

Plant leaves of Asparagus officinalis were collected from the local hills of Kohat. For the preparation of the aqueous extract, 20 g of fresh leaves was washed with tap water, followed by washing with distilled water three times. The leaves were then crushed with 100 mL of distilled water, and then the mixture was placed in a water bath at 60°C for 1 h; the broth was filtered with Whatman filter paper No. 42 and stored in a refrigerator for further use.

2.3 Synthesis of SPIONPs

For the synthesis of SPIONPs, a 0.05 M solution of ferrous nitrate and ferric nitrate was prepared separately and
then mixed in a 1:2 ratio, i.e., 50 and 100 mL, respectively; then 100 mL of A. officinalis extract was added. The basic pH of the mixture was adjusted by dropwise addition of 100 mL of 0.05 M aqueous hydrazine hydrate solutions while stirring. The appearance of dark brownish color indicated the formation of SPIONPs. The reaction mixture was stirred on a magnetic stirrer at 70°C for 2 h. The synthesized product was collected via centrifugation at 8,000 rpm for 30 min and dried in an oven at 80°C.

### 2.4 Manganese doping

Mn-doped SPIONPs were synthesized via a co-precipitation method in aqueous solutions. The above-synthesized SPIONPs were doped with 1%, 3%, 5%, and 7% concentration of manganese following the method reported in the literature [32]. For the synthesis of 1% Mn-doped SPIONPs, 1 g of SPIONPs was suspended in 50 mL of water and sonicated for 30 min. Then, 0.5 mL of MnSO₄ solution was added and stirred for 50 min, and in the end, 5 mL of KMnO₄ solution, having the same concentration as MnSO₄, was added. The whole mixture was further stirred for 1 h, and the product was collected via centrifugation at 8,000 rpm for 30 min and dried at 120°C in an oven for 1 h. The same procedure was used for 3%, 5%, and 7% samples by adjusting the concentration of MnSO₄ and KMnO₄ accordingly.

### 2.5 Heavy metal removal

All the adsorption experiments were carried out by the batch method [33] at 25°C, 35°C, and 40°C. Briefly, 2 g of SPIONPs was added to 20 mL of Pb(II) solution (500 ppm) and the resulting mixture was shaken to ensure good interaction between SPIONs and the adsorbate. The pH of the medium was adjusted to 5.6 with the controlled addition of 0.01 M HNO₃/NaOH solution, and the samples were placed on an orbital shaker for 2.5 h. After the completion of adsorption, SPIONPs were separated by an external magnet while the concentration of residual Pb(II) was measured by an atomic absorption spectrophotometer. All the experiments were performed in triplicate under identical conditions. The mean values were calculated to ensure the reproducibility of the experiments.

### 2.6 Reusability study

In the adsorption of Pb(II), the reusability of the prepared SPIONPs was investigated. The reusability of 7% Mn-doped SPIONPs was studied in the absorption of Pb(II) at pH 6.5. To investigate reusability, 7% Mn-doped SPIONPs were rinsed with distilled water three times after adsorption and utilized for the next reaction at the very same time.

### 2.7 Characterizations of nanomaterials

X-ray diffraction (XRD) patterns of synthesized nanomaterials were measured on the Bruker XRD machine using kα 1.54, over the 2θ range of 5–70°, at room temperature in the continuous scan mode. The presence of various functional groups on the surface of NPs was analyzed using Fourier transform infrared (FTIR) (Bruker) in the range of 3,500–500 cm⁻¹ at room temperature. The shape and morphology were studied using a scanning electron microscope (JSM-6490). The optical properties or the absorbance of electromagnetic radiation were studied by a UV-vis spectrophotometer (UV-900 BMS) at room temperature in the range of 200–450 nm wavelength. The magnetization of pure and doped SPIONPs was measured with a vibrating sample magnetometer (VSM, Lake Shore) at room temperature. The adsorption of lead ions (Pb(II)) was measured using an atomic absorption spectrometer (Perkin Elmer Analyte 100).

### 3 Results and discussion

#### 3.1 Optical properties of IOPNs

UV-visible spectroscopic analysis was carried out at room temperature using water as the solvent; the samples were scanned in the range of 250–450 nm. SPIONPs showed the maximum absorption at 340 nm (Figure 1), which confirmed the presence of iron oxide in accordance with the literature arising from the absorption and scattering of electromagnetic radiation [34,35]. The electrons’ specific vibration mode also confirmed the particles size and shape [36].
3.2 FTIR analysis

FTIR spectra of pure and Mn-doped SPIONPs were recorded in the range of 500–3,500 cm\(^{-1}\) to identify the biomolecules responsible for stabilization and covering the surface of nanoparticles. Figures A1–A5 (in the Appendix) show the FTIR spectra of pure, 1, 3, 5, and 7% Mn-doped SPIONPs, respectively. In all spectra, an intense and strong absorption band was observed in the region of 500 cm\(^{-1}\), which is due to the stretching vibrations of Fe–O. Thus, the strong band at 500 cm\(^{-1}\) confirmed the synthesis of SPIONPs [37]. The other major peaks observed at 3,887 and 3,738 cm\(^{-1}\) were due to the –OH group, while the band at 2,965 cm\(^{-1}\) was due to the stretching of the aliphatic C–H group [38–40]. Similarly, the band at 1,745 cm\(^{-1}\) was due to the C=O stretching of the carbonyl functional group, while the absorption band at approximately 1,638 cm\(^{-1}\) could be attributed to C=C bending vibrations [41]. The above explanation of FTIR results confirmed the synthesis of SPIONPs, and their surface stabilized with plant extract and was coated by amino and carbonyl groups, which could boost the adsorption of Pb\(\text{II}\) to nanomaterials through electrostatic attraction.

3.3 SEM analysis

The morphology of SPIONPs was investigated by SEM (Figure 2). It has been reported in the literature that the optical and electronic properties of nanoparticles considerably depend on the shape and size of nanoparticles. SEM images of pure and Mn-doped IONPs showed spherical NPs with soft agglomeration; dense and dispersed in a regular manner on the whole surface. The average size calculated from SEM images was in the range of 96–110 nm for SPIONPs and indicated a gradual increase in size upon doping.

3.4 XRD analysis

XRD is a useful technique applied for finding the crystal structure, phase composition, and average crystallite size of nanomaterials. In the XRD pattern of pure and Mn-doped SPIONPs, Bragg’s reflection peaks were observed at 2\(\theta\) values of 24.0, 33.22, 35.44, 41.0, 49.52, 53.94, 57.49, 63.0, and 64.01 representing the (012), (104), (110), (113), (024), (116), (122), (214), and (300) planes, respectively, which are the characteristic patterns of IONPs (hematite JCPDS Card No. 00-024-0072) [42].

XRD patterns of pure and Mn-doped SPIONPs are shown in Figure 3. Scherrer’s equation was used to calculate the average crystallite size of nanomaterials [36,43]. The calculated average sizes were 50.3, 54.57, 62.27, 63.57, and 65.74 nm for pure, 1-, 3-, 5-, and 7%-doped SPIONPs, respectively. From the assessment of XRD patterns of doped SPIONPs, it was clear that the patterns were similar to the XRD pattern of pure SPIONPs. No peaks related to manganese oxides were present, and a gradual increase in size was observed with increasing concentrations of the dopant confirming the successful synthesis of Mn-doped IOPNs [44].

3.5 Magnetism

Magnetic properties in terms of saturation magnetization (\(M_s\)) were measured at room temperature via VSM considering the variable field strength as a basic parameter. The results of the magnetic measurements of prepared nanomaterials showed a gradual decrease in the magnetic moment with increasing concentration of Mn. The magnetization (\(M_s\)) of pure SPIONPs was 5.39 emu and the coercivity (Hci) was 48.64 G. Ms, and the magnetization of 1% Mn-doped SPIONPs was 5.12 emu and the coercivity was 48.927 G, respectively. Similarly, Ms of 3% Mn-doped was 4.30 emu, while coercivity was 46.38 G. For 5%, the Ms and coercivity were 2.89 emu and 38.92 G, respectively. The Ms and Hci for 7% were 2.07 emu and 52.24 G, respectively, as shown in Figure 4. There was a marked decrease in Ms as the concentration of manganese increased, which is due to the fact that Mn(II) occupies the \(T_d\) site of the host SPIONPs during doping [32].
Figure 2: SEM images of (a) undoped IONPs, (b) 1% Mn-doped IONPs, (c) 3% Mn-doped IONPs, (d) 5% Mn-doped IONPs, and (e) 7% Mn-doped IONPs.

Figure 3: XRD pattern of undoped and Mn-doped IONPs.

Figure 4: VSM analysis of undoped and Mn-doped IONPs.
4 Adsorption studies

4.1 Removal efficiency of adsorbent

The adsorption capacity and potential of undoped and Mn-doped IOPNs for Pb(II) ions were checked, considering the role of dopant concentration in the uptake of ions compared to the undoped native iron oxide. In all the samples, the obtained data clearly demonstrate a gradual increase in the adsorption efficiency as the Mn concentration increases. Many reasons are there behind this gradual increase in adsorption as the dopant concentration increases as described above, and the introduction of another metal as a dopant to the native oxide increases its adsorption capacities. The ionic radii of Mn$^{2+}$ are greater than Fe$^{3+}$ ions; so when Mn is introduced as a dopant, it expands the lattice parameters of the native oxide and hence ultimately increases the adsorption of lead ions. The crystalline iron oxide is insoluble in aqueous medium which is also another factor contributing much to the capacity of lead ions [45]. During doping, Mn$^{2+}$ substitute Fe$^{3+}$ ions, but there is a strong chance of Mn$_2$O$_3$ over the surface which increases the porosity and hence the capacity of lead ion removal [46]. The results and parameters for the lab sample are shown in Table 1. Figure 6b illustrates the graphical representation efficiency of the adsorbent.

4.2 Effect of Mn doping on Pb(II) capture

Fresh water and underground water samples were spiked with Pb(II) before contact with the sorbent to determine the effect of Mn doping on the sorption properties of SPIONPs. The uptake was calculated with the solid-phase partition coefficient ($K_d$), as presented in Eq. 1. The removal of the total analyte was calculated as % capture. Here, $C_0$ and $C_f$ are initial and final concentrations of Pb(II), respectively; $V$ is the solution's volume (mL); and $M$ is the mass of SPIONPs (g)

$$K_d = \frac{C_0 - C_f}{C_f} \frac{V}{M}$$  \hspace{1cm} (1)

Higher $K_d$ values indicate a better collection and retention of Pb(II). During the experiments, it was observed that the increase of Mn concentration resulted in the marked affinity of the analyte toward the sorbent. The increase in dopant concentration resulted in a dramatic increase in $K_d$ from pure to 7%-doped SPIONPs in comparison to other materials’ affinity toward the analyte with increasing Mn content. This interesting increase in the affinity of metal ions with the increase in Mn concentration is certainly due to the changes in the surface chemistry. As fresh water and underground water samples were under consideration, such samples pose a complicated situation as these contain numerous pollutants, e.g., carbonates, bicarbonates, humic acid, and several dissolved organic carbons. The increase in the affinity of Pb(II) with the increase in the dopant affected the surface contents. The sorbent response is always very complicated in fresh water samples because of the presence of interferences, such as humic acid, carboxylic moieties, and various dissolved organic species. XRD data also suggested the lattice expansion, which may alter the surface behavior based solely on M–O distances; the affinity of Pb(II) increased with increasing Mn content because of the similarity in ionic radii of Pb(II). From this work, we suggest that ferrite may be doped by varying the concentrations of different metal dopants to tailor the selectivity and affinity of the SPIONPs for the metallic species.

4.3 Effect of pH

The pH of the solution was measured using an AB15 plus pH meter (Fisher Scientific, Toronto). The adsorptions studies were carried out at pH 2.5, 3.5, 4.5, 5.5, and 6.5. During the process, 2 g of the adsorbent was used, while the operating time was 150 min. The concentration of Pb(II) solution was 50 mg L$^{-1}$. The presence of hydrogen ion concentration has considered an important parameter that influences the adsorption phenomena. It can affect the ionization of the adsorbate and replace positive ions found at active sites of the adsorbent and also the solubility of metal ions [47]. Considering the importance of pH in the process of adsorption, experiments were carried out in this regard. The range of pH in the adsorption of lead ions on both undoped and Mn-doped IONPs was

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**Table 1: Parameters and results of samples at pH 5.6 and 25°C**

| Sample no. | Fe$_{1-x}$Mn$_x$O (%) | Time (min) | Efficiency (%) | Nanosorbent (g) |
|------------|-----------------------|------------|----------------|-----------------|
| 1          | 0                     | 150        | 75.65          | 2               |
| 2          | 1                     | 150        | 84.04          | 2               |
| 4          | 5                     | 150        | 84.23          | 2               |
| 5          | 7                     | 150        | 85.58          | 2               |
| 6          | 9                     | 150        | 87.26          | 2               |
set between 3.5 and 6.5 and did not extend to pH 7, as at this pH, the lead ion may get precipitated and hence adsorption is not possible [48]. Figure 5 clearly demonstrates the effect of solution pH on the removal percentage of lead ions, both by undoped and by Mn-doped IONPs; from the obtained results, it was found that the removal efficiency increases from pH 3.5 to 6.5. As the pH increases, the presence of negative charged ions increases, which ultimately enhances the uptake of lead ions by the adsorbent. On the other hand, at lower pH, the positive charged sites increase, which develops a repulsive situation thus decreasing adsorption [49].

4.4 Effect of contact time

To find out the equilibrium time at which the maximum removal of lead ions takes place by the undoped and Mn-doped IONPs, the adsorption of lead ions on the adsorbent was carried out as a function of contact time, as shown in Figure 6c. The amount of adsorbent used was 2 g at pH 5.6 and 25°C. The time of shaking was 150 min. During the experiment, the time was divided into intervals of 15 min each; initially, the adsorption was very quick due to the presence of the active site in excess. Within 60 min, equilibrium was achieved; however, the process was extended to 90 min to confirm the equilibrium. The achievement of equilibrium in a short period of time is due to the small size of the nanosorbent. The shorter period of equilibrium is also important from an economic point of view, thus making IONPs as valuable adsorbents [50]. At the start, the adsorption was quick, due to the availability of large active sites on the surface of nanoparticles. Thus, the maximum adsorption efficiency was achieved in 60 min. Later on, the process was continued but with low speed due to the attachment of adsorbate ions with these active sites [51].

![Figure 5: Effect of solution pH on the removal of Pb(II) by (a) undoped IONPs, (b) 1% Mn-doped IONPs, (c) 3% Mn-doped IONPs, and (d) 5% Mn-doped IONPs.](image-url)
4.5 Catalyst reusability

In today’s catalysis sector, the reusability and regeneration of efficient catalysts are a major challenge. Most catalysts are only utilized for a first or second cycle. Apart from catalytic performance, photocorrosion, recyclability, durability, and stability are also important aspects to consider when evaluating a catalyst’s effectiveness because they can significantly reduce the cost of the process [52]. Catalyst’s activity in the form of colloidal nanoparticles has been effectively documented in the literature; however, recovery from the reaction medium and reusability for further usage remain a problem. As a result, catalysts that are stable and totally separate are essential for the recyclability and reuse process.

Figure 6d shows the recyclability study and the adsorption of Pb(II) by using 7% Mn-doped IONPs for four cycles. For the first use, the adsorption efficiency of 7% Mn-doped IONPs was 87.26%, and for the second use, the adsorption efficiency was 83.1%. For the third and fourth uses, the adsorption efficiency was 81.14 and 76.76%, respectively.

4.6 Adsorption isotherm

To check the validity of the results and find a relation between the initial concentration of Pb(II) and adsorption capacity, an adsorption was carried out by using the initial concentration of Pb(II) from 20 to 50 mg·L⁻¹. Langmuir and Freundlich adsorption isotherms were employed in the adsorption data obtained for undoped and 7% Mn-doped IONPs. Figure 7a and b show the Freundlich isotherm, whereas Figure 7c and d show the Langmuir adsorption isotherm of the undoped and Mn-doped IONPs. The calculated constants \( b, n, k_r, q_m \), maximum adsorption capacity, and the regression coefficient for Langmuir and Freundlich isotherms are presented in Tables 2 and 3.

![Figure 6: (a) Effect of pH on Pb(II) removal by 7% Mn-doped IONPs; (b) efficiency of undoped and doped IONPs; (c) effect of contact time for the removal of Pb(II), by undoped and doped IONPs; and (d) reusability study of 7% Mn-doped IONPs.](image-url)
The amounts of adsorption of SPIONPs were calculated by the following equation:

\[
q_{\text{eq}} = \frac{C_0 - C_{\text{eq}}}{m} V
\]

where \( q_{\text{eq}} \) is the adsorption capacity of Pb(II) ions over SPIONPs (\( \text{mg} \cdot \text{g}^{-1} \)); \( C_0 \) and \( C_{\text{eq}} \) are initial and equilibrium concentrations, respectively, of Pb(II) (in ppm); and \( V \) and \( m \) represent the volume of aqueous solution (mL) and weight of SPIONPs (g), respectively.

The rate of pseudo-first-order kinetic was calculated using Eq. 3, pseudo-second-order data by using Eq. 4, and initial sorption rates were calculated using Eq. 5 as:

\[
\ln(q_{\text{eq}} - q_t) = \ln q_{\text{eq}} - kt
\]

\[
\frac{t}{q_t} = \frac{1}{k_2 q_{\text{eq}}^2} + \frac{t}{q_{\text{eq}}}
\]

\[
k_0 = k_2 q_{\text{eq}}^2
\]

**Table 2:** Comparison of maximum adsorption capacity with recent literature

| Adsorbent                                      | \( q_m \) (mg-g\(^{-1}\)) | Reference |
|------------------------------------------------|-----------------------------|-----------|
| l-Cysteine-functionalized magnetite Fe\(_3\)O\(_4\) nanoparticles | 18.8                        | [61]      |
| *P. chrysosporium*                             | 12.34                       | [62]      |
| Iron oxide nanoparticles                      | 36                          | [63]      |
| \( \alpha \text{Al}_2\text{O}_3\)-supported iron oxide | 28.98                       | [64]      |
| Pure iron oxide nanoparticles                 | 21.3                        | Present study |
| Mn-doped iron oxide                           | 29.56                       | Present study |
| Mn-doped iron oxide nanoparticles             |                             |           |

Weber Morris IPD model:

\[
q_t = k_i t^{1/2} + C
\]

where \( q_t \) is the amount of adsorbate adsorbed on the surface of adsorbent (mg-g\(^{-1}\)); \( K_i \) is the rate constant of IPD;
Table 3: Constant and correlation coefficients of Langmuir and Freundlich adsorption isotherms for the adsorption

| IONPs                   | Langmuir isotherm | Freundlich isotherm |
|-------------------------|-------------------|---------------------|
|                         | \( q_a \) (mg·g\(^{-1}\)) | \( b \) | \( R_L \) | \( R^2 \) | \( n \) | \( R^2 \) | \( K_f \) |
| Undoped IONPs           | 21.3              | 0.74              | 0.23              | 0.9823        | 0.66       | 0.6764       | 11.78       |
| 7% Mn-doped IONPs       | 29.56             | 0.75              | 0.24              | 0.9966        | 0.288      | 0.8539       | 25.77       |

\( q_e \) and \( q_i \) are the concentrations (mg·g\(^{-1}\)) equilibrium and time (min); and \( k_1 \), \( k_2 \), and \( k_i \) are rate constants.

During the adsorption of Pb(II) on SPIONPs, the activation energy of the process was calculated using Eq. 7:

\[
k = A_{exp} \left( \frac{E_a}{RT} \right)^{1/2}
\]

where \( E_a \) is the activation energy (kJ·mol\(^{-1}\)); \( k \) is the rate constant (g·mg\(^{-1}\)·min\(^{-1}\)); \( R \) is the gas constant (8.314 J·mol\(^{-1}\)·K\(^{-1}\)); \( A \) is the Arrhenius constant (g·mg\(^{-1}\)·min\(^{-1}\)); \( T \) is the solution’s temperature (K). Activation energy and Arrhenius constant were calculated by plotting \( k \) versus \( T \) at three different temperatures.

Langmuir and Freundlich adsorption isotherm models were applied to evaluate the adsorption process; equilibrium time of adsorption of the Pb(II) process was 60 min at 298 K and the highest adsorbed quantity was 21.3 and 29.56 mg·g\(^{-1}\) for undoped and 7% Mn-IONPs, respectively, proved Langmuir’s isotherm (iii) as monolayer adsorption of Pb(II) on SPIONPs’ surface. In contrast, Freundlich adsorption isotherm (iv) takes the multilayer adsorption mechanism; it was observed that the increase of temperature favored adsorption of Pb(II) suggested the strong adsorbate–adsorbent interaction.

\[
C_e/q_e = 1/q_m b + 1/q_m C_e
\]

where \( q_m \) is the maximum amount of metal ions adsorbed per unit mass of adsorbent (mg·g\(^{-1}\)); and \( b \) is the Langmuir constant. The plot of \( q_e \) vs \( C_e \) gives a straight line with 1/q_m·b intercept and 1/q_m the slope.

\[
q_e = K_f C_e^{1/n}
\]

The linear form of this equation is represented by Eq. 10:

\[
\log q_e = \log K_f + 1/n \log C_e
\]

In the above equation, \( K_f \) and 1/n are the Freundlich isotherm constant, and these two quantities can be calculated from the slope and intercept by plotting \( \log q_e \) vs \( \log C_e \), respectively, while the favorability of the process can be found from the value of 1/n. This isotherm describes the relationship between \( q_e \) (mg·g\(^{-1}\)) the adsorption capacity and \( C_e \) (mg·L\(^{-1}\)), the metal concentration in solution at equilibrium [53,54]. Each experiment was performed in triplicate.

Langmuir adsorption isotherm includes an interesting dimensionless constant, \( R_L \): the separation factor or equilibrium factor which is presented in Eq. 11 [55,56]. This dimensionless factor is used to check the favorability of the process:

\[
R_L = 1 + b C^o
\]

where \( C^o \) is the initial concentration of Pb(II).

From the comparison between the results of two isotherms, we can say that results well fit the Langmuir adsorption isotherm as compared to the Freundlich adsorption isotherm. Moreover, the increased adsorption capacities are also in agreement with increased efficiency [32,57,58]. In the case of the Langmuir isotherm, the value of \( R_L \) for undoped and Mn-doped IONPs is in between 0 and 1, which confirms that the obtained data best follow the Langmuir adsorption isotherm [59]. The value of \( R^2 > 0.98 \) is higher both for undoped and 7% Mn-doped IONPs in case of Langmuir adsorption isotherm than Freundlich adsorption isotherm. The value of \( R_L < 1 \) confirmed that the adsorptions of lead ions on the adsorbate surface are good. Similarly, the value of 1/n in the case of the Freundlich model indicates more deviation toward the Langmuir model as well as the value of n is less than 1, which confirms that the process of adsorption follow chemisorptions [57,60].

4.7 Kinetic studies

Activation energy and Arrhenius constant were calculated by plotting \( k \) versus \( T \) at three different temperatures. The obtained data for \( E_a \) remained lower, indicating the possibility of chemisorption as well as physisorption.

Kinetic models can be helpful to understand the mechanism of metal adsorption and evaluate the performance
of the adsorbent for metal removal. A number of kinetic models have been developed to describe the kinetics of heavy metal removal: (1) a pseudo-first-order kinetic model of the Lagergren-based equation on solid capacity, (2) a pseudo-second-order kinetic model based on solid-phase sorption, and (3) intra-particle diffusion model of Weber and Morris.

The results of the adsorption of lead ions carried out as a function of contact time are shown in Figure 6c. From the figures, it is clear that the adsorption was quick in early stages till the equilibrium was achieved. To find out the rate constant, pseudo-first-order and pseudo-second-order kinetics were applied. If the pseudo-first-order kinetics describe the process of adsorption, then there should be a well linear relationship between \( t \) and \( \log(q_e - q_t) \). On the other hand, if the adsorption is described by the pseudo-second-order kinetic equation, then the linear relationship should exist between \( t/q_t \) and \( t \). \( k_2 \), the rate constant for pseudo-second-order kinetics, is obtained from the intercept. During the process, the data fitted into pseudo-first-order kinetics equation and were found to be nonlinear for the entire range of time, suggesting that more than one mechanism is involved in the process. While on the other hand the obtained data well fitted in the pseudo-second-order kinetics. Figure 8c and d show the pseudo-second-order plot for undoped and 7% Mn-doped IONPs. \( k_2, k_1, R^2 \) for both pseudo-first-order and pseudo-second-order kinetic are shown in Table 4. Similarly, from the comparison of the \( R^2 \) value, we can deduce that which kinetic model will best describe the process. In our work, the \( R^2 \) value for pseudo-second-order kinetics is much better than the pseudo-first-order kinetic, and its theoretical and experimental data are also in close agreement with each other. In Table 4, the values of kinetic model parameters of Pb(II) adsorption on undoped and 7% Mn-doped IONPs are listed. Higher values of \( R^2 \) for the pseudo-second-order kinetic model than pseudo-first-order indicate that
pseudo-second-order kinetic best fit the experimental data. Its experimental and calculated data are in close agreement with each other. From these facts about the pseudo-second-order kinetic models, we confer that both adsorbate and adsorbent link to the rate controlling step of the process. Hence, we can confer that predominant process is chemisorption. We know that chemisorption is restricted to the monolayer. Moreover, adsorption on the outer surface of the adsorbent, the movement of lead ions from the solution to the pores may also be considered as a rate limiting stage during quick shaking conditions. We analyzed this phase of the process through the intra-particle diffusion model shown in Figure 9a and b. However, the low value of $R^2$ of the IPD model indicates that the pore diffusion is not the rate controlling step. In Tables 4 and 5, we see that the value of $C_i$ is not zero, which marks us that the IPD is not the sole controlling process in this adsorption [66]. Similar results about the adsorption of lead ions on multiwall carbon nanotubes, activated carbon, and ash of rice husk have been previously reported [67,68]. The validity of the applied other kinetic and IPD model can also be checked by the value of the sum squared error value, which could be calculated by Eq. 12. $N$ is the number of data points, if the value of the error sum of squares (SSE) is lower for a particular model, that model will describe the data well and vice versa. The SSE values for the pseudo-first-order and pseudo-second-order kinetic model and the IPD model are listed in Table 6.

\[
\text{SSE} = \left[ \frac{\sum(q_{e,exp} - q_{e,cal})^2}{N} \right]^{1/2}. \tag{12}
\]

5 Conclusion

IOPNs were synthesized by adopting the co-precipitation method using an aqueous extract of *A. officinalis*. The prepared IONPs were doped with various concentrations of Mn through the ultrasonic-assisted method. Physical techniques such as UV-visible spectroscopy, FTIR, XRD, VSM, and SEM confirmed the successful synthesis of NPs and also showed various aspects related to morphology and internal structure of these nanomaterials. The synthesis of SIONPs was confirmed through UV-visible spectroscopy, which gives a characteristic peak at 340 nm, while the intense absorption peak at 500 cm$^{-1}$ at FTIR spectra
confirm the Fe–O bond. The SEM analysis reveals dispersed spherical nanoparticles. XRD confirms the crystalline structure of nanoparticles, while the VSM analysis confirms that the magnetic properties of IONPs decrease with Mn doping. The prepared IONPs act as a nonadsorbent for the removal of Pb(II) ions and show increased efficiency with Mn doping. Our study showed that Pb(II) adsorption is susceptible to the pH of the medium, and this adsorbent works well under mild acidic conditions. The obtained equilibrium data were explained by the Langmuir isotherm. Similarly, dynamic data were best described using the pseudo-second-order kinetic equation. Considering the low cost, easy and fast synthesis, low toxicity, and satisfactory adsorptions results, we can confirm IONPs and manganese-doped IONPs as an excellent adsorbent for reclamation of heavy metal-polluted water.

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**Data availability statement:** The authors confirm that the data supporting the findings of this study are available within the article.

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**Table 5: Adsorption kinetic model constants of Pb(II) adsorption onto 7% Mn-doped IONPs**

| Mode           | ESS | $K_1$ | $R^2$ | $q_{e,cal}$ (mg·g$^{-1}$) | $q_{eq,exp}$ (mg·g$^{-1}$) | $k_0$ |
|---------------|-----|-------|-------|--------------------------|--------------------------|-------|
| Undoped IONPs | 3.02| 0.05  | 0.93  | 17.82                    | 23.56                    | —     |
| 7% Mn-doped IONPs | 2.34| 0.27  | 0.999 | 24.13                    | 23.56                    | 0.86  |

**Table 6: SSE values for pseudo-first-order, pseudo-second-order kinetics, and intra-particle diffusion model**

| Mode           | SSE | $k_d$ | $C_1$ | $R^2$ | $q_{e,cal}$ (mg·g$^{-1}$) | $q_{eq,exp}$ (mg·g$^{-1}$) | $k_0$ |
|---------------|-----|-------|-------|-------|--------------------------|--------------------------|-------|
| Undoped IONPs | 42.17 | 0.674 | 0.929 | 24.14 | 23.56                    | —                        |       |
| 7% Mn-doped IONPs | 24.13 | 0.55  | 0.21  | 24.14 | 23.56                    | —                        |       |

**Table 5: Adsorption kinetic model constants of Pb(II) adsorption onto 7% Mn-doped IONPs**

| Pseudo-first-order kinetics | $K_1$ | $R^2$ | $q_{e,cal}$ (mg·g$^{-1}$) | $q_{eq,exp}$ (mg·g$^{-1}$) | $k_0$ |
|-----------------------------|-------|-------|--------------------------|--------------------------|-------|
| Undoped IONPs               |       |       |                          |                          |       |
| 7% Mn-doped IONPs           |       |       |                          |                          |       |

| Pseudo-second-order kinetics | $K_2$ | $R^2$ | $q_{e,cal}$ (mg·g$^{-1}$) | $q_{eq,exp}$ (mg·g$^{-1}$) | $k_0$ |
|-------------------------------|-------|-------|--------------------------|--------------------------|-------|
| Undoped IONPs                |       |       |                          |                          |       |
| 7% Mn-doped IONPs            |       |       |                          |                          |       |

**Intra-particle diffusion model**

| Mode           | $k_d$ | $C_1$ | $R^2$ | $q_{e,cal}$ (mg·g$^{-1}$) | $q_{eq,exp}$ (mg·g$^{-1}$) | $k_0$ |
|---------------|-------|-------|-------|--------------------------|--------------------------|-------|
| Undoped IONPs |       |       |       |                          |                          |       |
| 7% Mn-doped IONPs |       |       |       |                          |                          |       |
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Appendix

A1 FTIR spectra of prepared materials

FTIR spectra of pure and Mn-doped SPIONPs were recorded in the range of 500–3,500 cm\(^{-1}\) to identify the biomolecules responsible for stabilization and covering the surface of nanoparticles. Figures A1–A5 show FTIR spectra of pure, 1, 3, 5, and 7% Mn-doped SPIONPs, respectively. In all spectra, an intense and strong absorption band was observed in the region of 500 cm\(^{-1}\), which is due to stretching vibrations of Fe–O.

![FTIR spectra of pure SPIONPs](image)

**Figure A1:** FTIR spectra of pure IONPs.
Figure A2: FTIR spectra of 1% Mn-doped IONPs.

Figure A3: FTIR spectra of 3% Mn-doped IONPs.
Figure A4: FTIR spectra of 5% Mn-doped IONPs.

Figure A5: FTIR spectra of 7% Mn-doped IONPs.