Adsorption study of Heavy Metals from Aqueous Solutions using Magnetite Nanoparticles

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Abstract. Contamination of heavy metals in wastewater is a significant worldwide problem, which is causing to detrimental effect on human health and environment. In present work, magnetite nanoparticles were used for the expulsion of Pb(II) and Cd(II) ions from aqueous solutions at varying pH conditions, contact time and adsorbent amounts. Magnetite nanoparticles were synthesized by co-precipitation method. Synthesized nanoparticles were characterized by XRD, FTIR, UV-Vis, VSM and SEM techniques for structural, optical, magnetic and morphological properties. The crystalline nature of magnetite nanoparticles with crystallite size 10.16 nm was confirmed by XRD. Optical properties and functional group identification of magnetite nanoparticles were revealed by UV-Vis and FTIR spectroscopy respectively. VSM measurements showed that the saturation magnetization of magnetite nanoparticles was 56.42 emu/g. This indicates that after adsorption, an easy separation of metal loaded magnetite nanoparticles from aqueous solutions can be achieved by applying the external magnetic field. Adsorption experiments results showed that the adsorption capacity of magnetite nanoparticles is higher for Pb(II) ions. At optimum conditions, the maximum removal efficiencies for Pb(II) and Cd(II) ions were 98.6% and 93% respectively. Langmuir and Freundlich adsorption isotherms were found suitable for adsorption processes. The adsorption kinetic data for both the metal ions were best fitted by pseudo second order reaction. Surface images of bare and metal loaded magnetite nanoparticles supported the confirmation of adsorption of metal ions on nanoparticles surface. Thus, it is concluded that magnetite nanoparticles can be effectively used as an adsorbent for expulsion of heavy metals from aqueous solutions.

1. Introduction

Industrialization and urbanization has grown drastically since last few decades, posing as a dangerous threat to aquatic systems. United Nations evaluates that 300-500 million tons quantity of heavy metals, solvents, toxic sludge and other harmful wastes are released to the water supply each year (UNWDPAC, 2011). Heavy metal pollution in aqueous system has become harmful threat because they do not have the capability to reduce and convert themselves to less toxic compounds or to be decomposed by microorganism [1]. These metals can harmfully affect the organisms even at ppm (mg/L) level of concentration. Generally an ionic form of any metal has more toxic nature, since it may form toxic compounds after combining with other ions. An accordance with environmental regulations worldwide, the concentration of these toxic metals must be managed to a permissible level before discharging them into environment [2].

In order to detoxify toxic heavy metals from aqueous system, various conventional methods like coagulation, membrane filtration, ion exchange, chemical precipitation, adsorption, electrochemical
treatment etc. have been used [3] [4]. But most of these methods are appropriate for large scale treatment and incur high equipment cost. Among these techniques, adsorption is found relatively practicable, convenient and effective technique due to its low cost and simple operation [5]. Several types of adsorbents have been found applicable for the expulsion of heavy metals including activated carbon, carbon nanotubes, metal oxides, polymeric adsorbents, bio-adsorbents etc. Among these, iron oxide magnetite NPs have marked themselves by their exclusive and specific properties like high surface to volume ratio, associated sorption sites, tunable pore size, easy regeneration in the presence of external magnetic field etc, which results in a high metal adsorption capacity [6]. Nanomaterials generally show more reactivity and higher ability to adsorb than normal materials. The use of magnetite (Fe₃O₄) nanoparticles as an adsorbent in wastewater treatment confers an appropriate and convenient approach for separating and extracting the pollutants by just applying external magnetic field [1].

In present work, the applicability of magnetite nanoparticles were investigated as an adsorbent for the expulsion of lead and cadmium from their synthetic solutions. Adsorption experiments have been carried out by varying solution pH, contact time and adsorbent doses. A complete and systematic analysis of the experimental outcomes provides the potential application of magnetite nano-adsorbents for metal adsorption from industrial wastewater.

2. Material and methods

2.1. Materials
All the reagents and chemicals were of analytical grade and were used without any purification. Ferric chloride (FeCl₃), ferrous chloride (FeCl₂.4H₂O) and 25% ammonia solution were purchased from Molychem and Fisher chemicals. Cadmium Nitrate Tetrahydrate (Cd(NO₃)₂.4H₂O) and Lead nitrate (Pb(NO₃)₂) were purchased from Molychem and AnalyR respectively.

2.2. Synthesis of Fe₃O₄ nanoparticles
Fe₃O₄ nanoparticles were synthesized by co-precipitation method. FeCl₃ and FeCl₂.4H₂O at 2:1 molar ratio was added in 200 mL distilled water and kept at desired temperature (~80°C). While vigorously stirring the reaction mixture, 25% NH₃ solution was added drop wise until pH of solution becomes 11. The solution was kept additionally under vigorous stirring. Afterward, the black precipitate was achieved to settling down in the flask. In order to separate the magnetite nanoparticles, solution was centrifuged at 6000 rpm for 10 minutes. The black colored nanoparticles were collected and washed various times with distilled water and acetone (until the pH becomes neutral) and dried at 60°C for 6-7 hours. The relevant chemical reaction can be explained as:

Fe₂⁺ + 2Fe³⁺ + 8OH⁻ ➔ Fe₃O₄ + 4H₂O

2.3. Characterization.
The structural parameters of nanoparticles were measured using X-ray diffraction technique. The Crystalline pattern was recorded by Rikagu smart lab X-ray Diffractometer with CuKα radiation (λ= 1.54 Å). FTIR measurements were performed for the identification of functional groups in prepared sample. Thermo scientific 6700™ FTIR spectrometer (ATR technique) was used for recording spectra in the range of 4000-600 cm⁻¹ with resolution 8 cm⁻¹. The reflectance measurements of nanoparticles were analysed using Perkin Elmer Lambda 365 UV-Vis spectrophotometer in the wavelength range of 200-800 nm. Magnetic properties of nanoparticles were determined with PAR 155 Vibrating sample magnetometer manufactured by quantum design. The magnetic measurements were done in room temperature. Surface morphology of magnetite nanoparticles before as well as after adsorption were analysed by JEOL JSM-6610 LV Scanning electron microscope at an electron acceleration voltage of 8kV.
2.4. Adsorption procedure  
The adsorption experiments were conducted in batch mode. The experiments were performed at initial metal ion concentration of 1 ppm (mg/L), 0.5 g and 1 g amount of Fe₃O₄ nanoparticles, different solution pH of acidic, basic, neutral (4.2, 7, 8.9) and at contact time of 15, 30, 45 and 60 minutes. Adsorption process were carried out with an incubator shaker (Bench top model S145) at 250 rpm. After treatment, nanoadsorbents were separated and residual solution was filtered and digested to allow metal concentration measurements.

For all the tests, the residual concentration of metal ions in the filtered solution was measured by atomic absorption spectrometer (GBC Avanta sigma AAS). The air-acetylene flame atomizer with temperature of about 2200°C was used for the excitation of electrons. The removal % is determined by following equation:

\[ \text{Removal} \% = \frac{C_i - C_e}{C_i} \times 100 \quad (1) \]

Where Cᵢ and Cₑ are the initial and residual metal ion concentration respectively.

The absorbed amount of metal ions (mg/g) was obtained by using the following equation:

\[ Q_e = \frac{(C_i - C_e)V}{m} \quad (2) \]

Where Cᵢ and Cₑ are the initial and residual metal ion concentration(mg/L) respectively, V is the volume of metal solution (L) and m is the weight of Fe₃O₄ nanoadsorbents (g).

3. Results and discussion

3.1 Structural properties

The XRD pattern of Fe₃O₄ nanoparticles is shown in figure 1. The strong and sharp peaks are demonstrating the existence of crystalline phase. The XRD peaks of magnetite NPs at 2Θ = 30.24, 35.62, 43.24, 53.92, 57.20 and 62.74 corresponds to crystal planes (220), (311), (400), (422), (511) and (440) respectively, were obtained in accordance with literature [7] [8]. This reveals that magnetite NPs exhibit an inverse spinel structure [9] and no specific peak of impurities are detected in the XRD pattern. The average crystallite size of Fe₃O₄ NPs is calculated using most intense peak by Debye-Scherrer equation as:

\[ D = \frac{k\lambda}{B \cos \theta} \quad (3) \]

Where \( \lambda \) is wavelength of X-ray, B is full width at half-maximum intensity in radian, K is dimensionless constant (~0.93) and \( \Theta \) is the diffraction angle.

The lattice parameter (a), interplanar distance (dhkl) and X-ray density (\( \rho_x \)) were calculated by using following equations:

\[ a = d_{hkl} (h^2 + k^2 + l^2)^{1/2} \quad (4) \]

Where, h,k,l denotes as miller indices and \( d_{hkl} \) is interplanar spacing.

\[ d_{hkl} = \frac{\lambda}{2 \sin \theta} \quad (5) \]

Where \( \lambda \) is X-ray wavelength and \( \Theta \) is diffraction angle.

\[ \rho_x = \frac{2M}{N_Aa^2} \quad (6) \]

Where Z is number of molecules per unit cell, M refers to molecular weight, \( N_A \) is Avogadro number and a is lattice parameter.

The calculated values are presented in table 1.

| Parameters             | Observed Value |
|------------------------|----------------|
| Crystallite size       | 10.16 nm       |
| Interplanar spacing    | 2.51 Å         |
Lattice parameter 8.35 Å  
X-ray density 5.27 g/cm$^3$

![Diffraction pattern of magnetite NPs](image)

**Figure 1.** Diffraction pattern of magnetite NPs.

### 3.2. Functional group identification

In order to identify the functional groups and their respective bands in synthesized MNPs, the nanoparticles were characterized by FTIR spectroscopy. The obtained FTIR spectrum is presented in figure 2. The spectrum consists of a sharp band at 613.25 cm$^{-1}$ of metal-oxide. A broad band about 3151.11 cm$^{-1}$ corresponds to H-O-H stretching and bands about 1619.91 cm$^{-1}$ and 1423.20 cm$^{-1}$ are assigned to H-O-H bending. This confirms the presence of adsorbed water on the surface of magnetite NPs since magnetite NPs were synthesized in aqueous medium. Small band at 2368.15 cm$^{-1}$ corresponds to absorbed atmospheric CO$_2$. 
3.3. Optical properties
Optical properties of magnetite NPs were studied by UV-Vis diffuse reflectance spectroscopy at the wavelength range of 200nm-800nm. The diffuse reflectance spectra of magnetite NPs is shown in figure 3. A strong broad reflection band is observed between 248 and 665 nm, which is in good agreement with previous literature [10].

3.4. Magnetic properties
Magnetization curve of magnetite NPs was measured by VSM at room temperature and shown in figure 4. The M-H curve is the function of magnetic field and magnetization. Magnetization of nanoparticles increases with the increment in magnetic field and saturates at a constant value. The saturation magnetization of Fe$_3$O$_4$ nanoparticles was found to be 56.42 emu/g. This is an advantage of magnetite nanoparticles in adsorption processes. An easy regeneration of nanoadsorbents from aqueous solutions can be attained in the presence of external magnetic field (figure 5).

3.5 Surface morphological properties

3.5.1 SEM analysis

Surface morphology of magnetite nanoparticles before as well as after adsorption is investigated by Scanning electron microscope. Surface images of different samples and different magnifications are shown in figure 6. SEM images shows the spherical shape of magnetite nanoparticles. Due to magnetic nature the nanoparticles tends to aggregate. After metal adsorption, the nanosphere pores are less visible. The Slight difference in surface images of bare and metal loaded nanoparticles supported the confirmation of metal adsorption on the surface of magnetite nanoparticles.
3.6 Adsorption Experiments.

3.6.1 Effect of pH.

The pH of the solution is an essential parameter in heavy metal ion adsorption processes, as reported by previous literature also. Maximum removal of Cd(II) and Pb(II) was observed at basic (8.9) and neutral (7) pH respectively. According to zeta potential data for Fe₃O₄ nanoparticles, surface of magnetite nanoparticles contains positive charge at low pH whereas negative charge at high pH [11]. At low pH, high concentration of protons (H⁺) surrounds the surface of nanoparticles so the positive metal ions experience high electrostatic repulsion with the nanoparticles surface at acidic pH. Increasing pH decays the competition between positive metal ions and the protons for adsorption sites, consequently adsorption of positive metals ions on magnetite nanoparticles increases. While in case of Pb(II) at higher pH precipitation of lead hydroxide [Pb (OH)₂] may occur, resulting in the slower rate for adsorption process.

3.6.2 Effect of contact time.

The effect of interaction time on the effective removal of Pb(II) and Cd(II) metal ions was examined at different time intervals of 15, 30, 45, 60 minutes. Figure 7 describes the effect of interaction time on the expulsion of metal ions from aqueous solutions by magnetite nanoparticles. In case of both metal
ions, it is clearly indicated that the adsorption efficiency were strongly time dependent. The adsorption efficiency increases as the contact time increases. At the initial phase all the adsorption sites are unoccupied on the surface of nanoparticles hence initially the adsorption rate was higher. After 45 minutes, slight difference in metal uptake is observed indicating the saturation state of adsorption.

![Figure 7](image1.png)

**Figure 7.** (Colour) Effect of contact time (a) For Cd(II) ion adsorption (at basic pH) (b) For Pb(II) ion adsorption (at neutral pH).

3.6.3 Effect of adsorbent dosage

To analyse the effect of adsorbent amount on adsorption of Cd(II) and Pb(II) ions, experiments were performed with two amounts of magnetite nanoparticles (0.5g and 1g). The maximum removal % of Cd(II) and Pb(II) was shown by 1g amount of nanoparticles (figure 7 and 8). This is due to increment in surface area where the adsorption phenomenon occurs. Thus it is concluded that the adsorption efficiency increases with increasing the amount of nanoadsorbents.

![Figure 8](image2.png)

**Figure 8.** Effect of adsorbent amount on adsorption of (a) Cd(II) ion (b) Pb(II) ion at different pH conditions.

3.6.4 Adsorption isotherm

Adsorption isotherm indicates the correlation between the amount of substance adsorbed by an adsorbent and equilibrium concentration at any constant temperature. In this work, Freundlich and Langmuir adsorption isotherm models were used to evaluate the experimental outcomes.

Freundlich adsorption isotherm model is based on empirical formula and can be expressed as:

$$\log Q_e = \frac{1}{n} \log C_e + \log k$$  \hspace{1cm} (7)
Where k and n are Freundlich constants. \(Q_e\) is the amount of adsorbate per gram of the adsorbent at equilibrium (mg/g) and \(C_e\) is the equilibrium concentration.

Langmuir adsorption isotherm model is rooted on the assumption that the surface of adsorbent exhibits finite number of equivalent sites which are homogeneously distributed over the surface of adsorbent, having an equal affinity for adsorption. Langmuir isotherm is expressed by the following equation:

\[
\frac{C_e}{Q_e} = \frac{1}{bQ_{max}} + \frac{C_e}{Q_{max}}
\]

(8)

Where \(Q_{max}\) (mg/g) is maximum metal ion adsorbed per unit mass.

Freundlich and Langmuir both the models were analysed with the help of experimental data for the adsorption of Cd(II) and Pb(II) ions from synthetic solutions by magnetite nanoparticles. According to \(R^2\) value, both the models were found to be suitable for adsorption process (figure 9 and 10).

**Figure 9.** Langmuir isotherm curves for (a) Cd(II) adsorption at basic pH condition (b) Pb(II) adsorption at neutral pH condition.

**Figure 10.** Freundlich isotherm curves for (a) Cd(II) adsorption at basic pH condition (b) Pb(II) adsorption at neutral pH condition.

3.6.5 Adsorption kinetics

Adsorption kinetics is an important tool to analyze the adsorption uptake with respect to time at a particular concentration. The systematic study of adsorption kinetics provides important information
about the designing of batch adsorption system. In order to better investigate the rates of Cd (II) and Pb(II) adsorption on Fe$_3$O$_4$ nanoparticles, pseudo first order as well as pseudo second order kinetic model is studied.

Pseudo first order kinetics is based on the assumption that the rate of occupation of adsorption sites is directly proportional to the number of remaining unoccupied sites. The equation is expressed as:

$$\ln(Q_e - Q_t) = \ln Q_e - k_{ad}t$$

(9)

Where $k_{ad}$ (min$^{-1}$) is the pseudo first order rate constant (Laguerre rate constant). $Q_t$ and $Q_e$ are amount of metal ions adsorbed per unit mass (mg/g) at time t and at equilibrium respectively.

Pseudo second order kinetics assumes that the rate limiting step can be chemisorption which involves the exchange and sharing of electrons between adsorbate and adsorbent [12]. Pseudo second order equation is expressed as:

$$\frac{t}{Q_t} = \frac{1}{k_2Q_e^2} + \frac{t}{Q_e}$$

(10)

Where $k_2$ is the rate constant for pseudo second order adsorption $Q_t$ and $Q_e$ are amount of adsorbate adsorbed per unit mass (mg/g) at time t and at equilibrium respectively.

Pseudo first and second order model were analysed for the adsorption of Cd(II) and Pb(II) metal ions. According to the correlation coefficient ($R^2$) values, pseudo second order model was found to followed in well manner (figure 11 and 12).

![Figure 11](image1.png)

**Figure 11.** Pseudo first order kinetic model curves for (a) Cd(II) adsorption at basic pH condition (b) Pb(II) adsorption at neutral pH condition.
Figure 12. Pseudo second order kinetic model curves for (a) Cd(II) adsorption at basic pH condition (b) Pb(II) adsorption at neutral pH condition.

4. Conclusion
The applicability of magnetite nanoparticles were examined for the removal of Cd(II) and Pb(II) metal ions from aqueous solutions. In summary, an economical, simple and environment friendly method was applied to obtain the optimum conditions for adsorption. The experiments were performed under varying conditions like pH, contact time and adsorbent dosage. Magnetite NPs were prepared by co-precipitation method. XRD results confirmed the formation of magnetite NPs with crystallite size 10.16 nm. The reflectance spectrum and identification of functional groups were revealed by UV-Visible and FTIR spectroscopy respectively. Magnetic properties of magnetite nanoparticles were analyzed by VSM technique and the saturation magnetization of Fe$_3$O$_4$ NPs was observed to be 56.42 emu/g, suggesting an easy regeneration of nanoadsorbsents in the presence of external magnetic field. Magnetite NPs were applied as an adsorbent for expulsion of Pb(II) and Cd(II) metal ions from their synthetic solutions. The maximum removal (93%) was observed at basic pH for Cd(II), while in case of Pb(II), neutral pH (maximum removal 98.6%) was found to be most favorable. It is observed that the adsorption capability of magnetite nanoparticles is higher for lead. Langmuir and Freundlich isotherm models were investigated for the adsorption process and both the isotherm models were found to fitted well for adsorption. Pseudo first and second order adsorption kinetic models were analyzed. For the adsorption process, pseudo second order kinetic model was found to be preferably suitable. SEM Images supported the confirmation of adsorption of cadmium and lead ions on the surface of magnetite NPs. Therefore, magnetite nanoparticles can be used as effective adsorbents in order to minimize the heavy metal pollution in wastewater.

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