9.1 Introduction

Application of iron oxide nanoparticles-based nanomaterials for the remediation of toxic elements like heavy metals from water is a well-recognized technique. Nowadays, the materials such as magnetic NMs, carbon nanotubes, activated carbon, and zero-valent iron have wide application in the field of water and wastewater treatment. Among these, iron oxide magnetic NMs, owing to its significant physiochemical property, convenient for magnetic separation, the capability to treat large volume of wastewater, inexpensive method and easy regeneration in the presence of external magnetic field make them as most promising materials for purification of heavy metals (Hu et al., 2010; Xu et al., 2012; Dave & Chopda, 2014). The iron oxide nanomaterials possess unique properties like high surface-area-to-volume ratio, extremely small size, excellent magnetic properties, surface modifiability and great
biocompatibility. Iron oxide nanomaterials have been applied in wastewater treatment, as nanosorbents and photocatalysts in many environmental clean-up technologies (Xu et al., 2012). In remediation of heavy metals from water, surface modification strategy is utilised to improve the heavy metal removal efficiency of iron oxide nanoparticles. Magnetic property of iron oxide nanoparticles enables its easy separation and reusability for further application. The reusability of iron oxide-based nanosorbent decreases its economic burden (Dave & Chopda, 2014).

Surface modification can be done by the attachment of organic molecules and/or inorganic shells, which not only stabilizes the nanoparticles and ultimately prevents their oxidation, but also offers specific functionalities having selectivity for metal ion and thus improve the capacity for heavy metal uptake in water treatment process. Various types of functionalized materials have been employed for grafting the surface of NMs for the removal of heavy metal (Ambashta & Sillanpää, 2010; Girginova et al., 2010). For example, carbon-encapsulated magnetic nanoparticles were applied for the removal of Cu\(^{2+}\) and Cd\(^{2+}\) (Bystrzejewski et al., 2009). Surface sites binding (Hu et al., 2010), magnetic selective adsorption (Ozmen et al., 2010), electrostatic interaction (Zhong et al., 2006), and modified ligands combination (Hao et al., 2010) are the main mechanisms involved in the sorption of contaminants from wastewater by surface modified iron oxide. By surface modification strategy iron oxide nanoparticles can achieve high metal removal efficiency.
Adsorption based treatment technology is considered as the most promising technique in the removal of heavy metal from contaminated water due to its high efficiency, low cost-effective, and simple operation. Adsorption mechanism involves surface complexation i.e., the reaction between adsorbate (an ion or molecule) and the functional group present on the adsorbent surface. The adsorption mechanism is based on the surface complex formed during adsorption. Surface complexes are mainly outer- and inner-sphere surface complexes, which formerly were known as physical and chemical adsorption, respectively. In the outer-sphere surface complex formation, surface charge is a crucial factor, since electrostatic interactions and van der Waals forces (both are weak forces) are involved in the process. But in inner-sphere surface complexation, a covalent or ionic bond (strong forces) is involved, and it is irrespective to the surface charge. Removal of lead and cadmium using functionalised iron oxide nanoparticles such as iron oxide nanoparticles coated with polyvinyl alcohol and gallic acid was studied in this chapter. The results of the removal study were also compared with the results of uncoated iron oxide nanoparticles.

9.2 Materials and Methods

9.2.1 Reagents

All the chemicals and reagents used were AR grade procured from Merck Ltd. India. Iron (III) nitrate nine hydrate \( \{Fe \ (NO_3)_3 \cdot 9H_2O\} \) and ammonium hydroxide \((NH_4OH)\) were used for the synthesis of iron oxide nanoparticles. For functionalization of iron oxide nanoparticles, polyvinyl alcohol (98 % degree of hydrolysis) and gallic acid were utilized.
Polyvinyl alcohol (PVA) is a hydrophilic polymer with a simple chemical structure having high hydroxyl group and form cross linked network within the water solution, which is applied in biomedical and pharmaceutical fields due to its properties such as biocompatibility, nontoxicity, noncarcinogenicity, nonimmunogenicity, and inertness in body fluids. Gallic acid (3,4,5-trihydroxybenzoic acid), an anticancer drug, can be found from a variety of natural products such as gallnut, black tea, and sumac, and it also possesses the properties like antimutagenic, antiviral, anti-inflammatory, and antimicrobial (Dorniani et al., 2014).

Lead and cadmium, synthetic solutions were used in the adsorption studies were prepared using lead nitrate \{Pb(NO$_3$)$_2$\} and cadmium sulphate\{(3CdSO$_4$).8H$_2$O\} respectively. Deionized water was used in all experiments. Stock solution (1000 mg/L) of Pb$^{2+}$ was prepared by dissolving 1.5985g of Pb(NO$_3$)$_2$ in 1000 mL of deionized water and 1000 mg/L Cd$^{2+}$ stock solution was prepared by dissolving 2.2819 g of \((3CdSO$_4$).8H$_2$O\) in 1000 mL of deionized water. Experimental solutions of the desired concentrations were obtained by successive dilutions.

9.2.2 Preparation of nanosorbent

9.2.2.1 Preparation of iron oxide nanoparticles

Iron oxide nanoparticles was prepared by using iron (III) nitrate nine hydrate \{Fe(NO$_3$)$_3$.9H$_2$O\} as inorganic salt and ammonium hydroxide (NH$_4$OH) as precipitating agent. 0.5 M ammonium hydroxide solution was prepared and added drop-wise to 0.1 M iron (III) nitrate
solution under vigorous stirring. The volume ratio of two solutions was 1:1. In this step, instant formation of red precipitate was observed. The supernatant was removed from the red precipitate by decantation. Deionized water was added to the precipitate and the solution was decanted after centrifugation at 3000 rpm. The last procedure was repeated three times to remove the impurities. Dry powder was obtained by filtering and drying under vacuum. Then it was heated at 250°C for 2 h in air to get Fe$_2$O$_3$ particles from Fe$_2$(OH)$_6$ (Park et al., 2001). In this experiment, when NH$_4$OH was added as precipitating agent, the iron oxide particles were formed by following chemical reactions.

$$2\text{Fe(NO}_2\text{)}_3 + 6\text{NH}_4\text{OH} \rightarrow \text{Fe}_2\text{(OH)}_6 \downarrow + 6\text{NH}_4\text{NO}_3$$

Fe$_2$(OH)$_6$ particles were flocculated and precipitated in the aqueous solution immediately after its formation. The Fe$_2$(OH)$_6$ precipitates were transformed into iron oxide by calcination for 2 h at 250 °C by the following reaction (Mahan et al., 1987).

$$\text{Fe}_2\text{(OH)}_6 \rightarrow \text{Fe}_2\text{O}_3 + 3\text{H}_2\text{O} \downarrow$$

9.2.2.2 Preparation of surface modified iron oxide nanoparticles

The prepared iron oxide nanoparticle was dispersed in 100 mL deionized water and mixed with 1 % polyvinyl alcohol. After stirring the mixture for 24 h, the precipitates were collected by a permanent magnet and washed three times to remove the excess polyvinyl alcohol, which does not participate in the coating process and then dried in an oven. The 2 % of gallic acid (dissolved in deionized water) was added into the iron
oxide nanoparticle - polyvinyl alcohol and the mixture was stirred for 24 h. Finally, the coated iron oxide was washed and dried in an oven to obtain iron oxide nanoparticles coated with polyvinyl alcohol and gallic acid (Dorniani et al., 2014).

Plate 9.1: Iron oxide nanoparticles coated with polyvinyl alcohol and gallic acid

![Image of iron oxide nanoparticles coated with polyvinyl alcohol and gallic acid]

(a) Polyvinyl alcohol
(b) Gallic acid

Figure 9.1: (a) Polyvinyl alcohol and (b) Gallic acid

Gallate anion were immobilized on the surface of iron oxide nanoparticles prepared using polyvinyl alcohol (PVA) as a polymer stabilizer, to improve the reducing of the size distribution of the nanoparticles (Dorniani et al., 2014). In this study, iron oxide
nanoparticles were chosen as a core and PVA - gallate anion chosen as shells to be adsorbed on the surface of the core. Removal of lead and cadmium using this surface modified iron oxide nanoparticles were studied in this chapter.

### 9.2.3 Sorption experiment

Contaminated aqueous solutions were artificially prepared by adding appropriate quantities of metals into the deionized water. Sorption experiments were conducted under different conditions, to understand the rate and equilibrium data in single species batch sorption system. The known quantity of the nanosorbents, nanoparticles were transferred into 250 mL screw topped flasks and agitated with 100 mL of known concentration of heavy metal solutions for a predetermined period in a temperature-controlled shaker. After sorption study, the residual concentrations of heavy metals (Pb$^{2+}$ and Cd$^{2+}$) in the aqueous solution were determined using AAS. All the analysis was done in triplicate to check precision and average values are only reported. Five different conditions were applied to study the adsorption behavior. The adsorption behavior was studied under five different conditions of: 1) pH, 2) adsorbent dosage, 3) contact time, 4) initial metal concentration, 5) temperature. A comparison of adsorption capacity of iron oxide nanoparticles (IONPs) and iron oxide coated with polyvinyl alcohol and gallic acid (PG-IONPs) were carried out.

To find the optimum pH for adsorption, 0.1 mol/L HCl and 0.1 mol/L NaOH solutions were used to vary pH from 2 to 12 and the sorbent dosage was also varied from 0.5-10 g/L. The initial metal concentrations
were varied from 5-25 mg/L and mixed with optimum dosage of nanosorbent at optimum pH and room temperature for a predetermined period required for better sorption of Pb\(^{2+}\) and Cd\(^{2+}\). The sorption studies were carried out by mixing nanosorbent and metal solutions (20 mg/L) using a mechanical shaker for 180 min. To investigate the effect of temperature on adsorption, sorption experiments were conducted at four different temperature (333K, 353K, 373K and 393K) using a temperature-controlled shaker with water bath. 150 rpm agitation speed was maintained for study.

The sorption efficiency (%) and amount of adsorbate adsorbed at equilibrium, \(q_e\) (mg/g) were calculated as per equation (1 and 2).

\[
\text{Sorption efficiency (\%) = } \frac{(C_0 - C_e) \times 100}{C_0} \quad (1)
\]

\[
q_e = \frac{(C_0 - C_e)V}{m} \quad (2)
\]

where \(C_0\) and \(C_e\) are the metal concentrations in the solution before and after treatment, respectively. \(V\) is the volume of the heavy metal solution (L), \(M\) is the mass of nanosorbent used (g).

The linearized form of Langmuir, Freundlich, Temkin and Dubinin - Radushkevich adsorption isotherms were used to investigate the adsorption capacity of iron oxide coated with polyvinyl alcohol and gallic acid. Kinetics of the adsorption of Pb\(^{2+}\) and Cd\(^{2+}\) on functionalized iron oxide nanoparticles were studied using pseudo-first order (Lagergren’s first-order) model, pseudo-second order model and intraparticle diffusion kinetic model. The results iron oxide nanoparticles
and iron oxide coated with polyvinyl alcohol and gallic acid were compared. Thermodynamic parameters of PG-IONPs were also studied under different temperatures.

9.2.4 Desorption study of functionalized iron oxide nanoparticles

The Pb$^{2+}$ and Cd$^{2+}$ adsorbed nanosorbents were regenerated using 0.1 M HCl and 0.1 M NaOH. 50 mL of desorbing agents was added to known amount of metal adsorbed, functionalized iron oxide nanoparticles in 250 mL stopped bottle and agitated at 150 rpm for 1 h at room temperature using a mechanical shaker. After separation of nanosorbent, the concentration of metals in solution was measured using AAS.

9.3 Results and Discussions

9.3.1 Characterization of the iron oxide nanoparticles coated with poly vinyl alcohol and gallic acid

Fourier Transform - Infrared Spectrometer was used to identify the functional groups and chemical bonding of the coated materials. FTIR spectrums shows the characteristic peaks of iron oxide nanoparticles, PVA coated iron oxide nanoparticles and the iron oxide nanoparticles coated with poly vinyl alcohol and gallic acid in Figure 9.2, Figure 9.3 and Figure 9.4, respectively. Figure 9.2 shows that the iron oxide nanoparticles (IONPs) have absorption peak at 531.19 cm$^{-1}$ and 448.28 cm$^{-1}$, which is due to Fe–O stretching in Fe$_2$O$_3$. The absorption bands in the range 400 - 750 cm$^{-1}$ indicates Fe–O vibration mode of iron oxide nanoparticles. However, the PG-IONPs nanocomposites show
characteristic peaks of Fe–O at 531.65 cm\(^{-1}\) and 449.13 cm\(^{-1}\) respectively, which confirm the presence of iron oxide nanoparticles in the nanocomposites. PVA coated iron oxide nanoparticles also have absorption peaks between the range of 400 - 750 cm\(^{-1}\). Figure 9.3 shows the presence of absorption band at 3323.18 cm\(^{-1}\) which indicates the hydroxyl (–OH) groups. The absorption bands in the range 3400-3200 cm\(^{-1}\) represents the intermolecular hydrogen bonded –OH group having polymeric association.

**Figure 9.2:** FTIR spectrum of iron oxide nanoparticles (IONPs)

**Figure 9.3:** FTIR spectrum of PVA coated iron oxide nanoparticles
In PG-IONPs nanocomposite (Figure 9.4), the carboxylic acid O–H stretching band was observed at 2969.05 cm\(^{-1}\). 1158 cm\(^{-1}\) is attributable to M–O–C (M=Fe) bond. This evidence confirms the attachment of PVA onto iron oxide nanoparticles via hydrogen bond between hydroxyl group of PVA and protonated surface of the oxide (Kayal & Ramanujan, 2010). FTIR spectrum of the PG-IONPs nanocomposite shows the characteristic peaks for GA, confirming that the surface of PVA is loaded with GA, for example, the peaks observed at 1562.17 and 1372.03 cm\(^{-1}\), which are due to asymmetry and symmetry COO– stretching, respectively (Kayal & Ramanujan, 2010).

![FTIR spectrum of iron oxide nanoparticles coated with polyvinyl alcohol and gallic acid (PG-IONPs)](image)

**Figure 9.4:** FTIR spectrum of iron oxide nanoparticles coated with polyvinyl alcohol and gallic acid (PG-IONPs)

Scanning Electron Microscopy (SEM) was used to study the surface morphology of IONPs and PG-IONPs (Figure 9.5(a-b)). The IONPs were rough and aggregated. The morphological characteristics of PG-IONPs (the iron oxide nanoparticles functionalised with PVA and gallic acid) was different from that of IONPs and which was favourable.
for metal adsorption. EDX spectra of IONPs (Figure 9.6) confirmation the presence of iron and oxygen but the EDX spectra of PG-IONPs (Figure 9.7) shows the presence of iron, oxygen and carbon.

**Figure 9.5:** SEM images of (a) IONPs and (b) PG-IONPs

**Figure 9.6:** EDX spectra of IONPs

**Figure 9.7:** EDX spectra of PG-IONPs
The X-ray diffraction patterns of iron oxide nanoparticles and iron oxide nanoparticles coated with polyvinyl alcohol and gallic acid are shown in Figure 9.8(a) and Figure 9.8(b). For IONPs, characteristic peaks observed at 2θ: 24.22°, 33.22°, 35.71°, 40.91°, 49.56°, 54.14°, 62.51° and 64.08° and for PG-IONPs, peaks observed at 2θ: 23.87°, 32.90°, 35.38°, 40.60°, 49.21°, 53.83°, 62.20° and 63.79°. For both iron oxide nanoparticles and iron oxide nanoparticles coated with polyvinyl alcohol and gallic acid, eight characteristic peaks were observed. The diffraction peaks obtained for iron oxide nanoparticles coated with polyvinyl alcohol and gallic acid were matched with the diffraction peaks of iron oxide nanoparticles which indicates that the coating process for Fe₂O₃ did not affect the phase change of iron oxide.

![X-ray diffraction patterns](image)

**Figure 9.8:** X-ray diffraction patterns for (a) IONPs and (b) PG-IONPs

### 9.3.2 Removal of Pb²⁺ and Cd²⁺ using PG-IONPs and IONPs

#### 9.3.2.1 Effect of pH

The pH of the metal solution played a significant role in the removal of Pb²⁺ and Cd²⁺ and the effect of pH is shown in Figure 9.9(a). Adsorption studies were carried out in the pH range of 2 -12 for both
Pb$^{2+}$ and Cd$^{2+}$ at 303K (equilibrium time: 120 min; adsorbent dose: 1 g/L; adsorbate concentration: 10 mg/L; agitation speed: 150 rpm). The best pH range of Pb$^{2+}$ and Cd$^{2+}$ removal was observed between pH 4 and 12 in PG-IONPs. In the case of IONPs, maximum adsorption of Pb$^{2+}$ and Cd$^{2+}$ was observed from pH 6 and pH 8, respectively. Percentage of sorption and metal uptake increases with increase in pH. The electrostatic repulsion between the cations and surface sites resulted as the pH increases, so less insignificant competitive adsorption of H$^+$ ions and the positively charged metal ions gets adsorbed on the free binding sites, which leads to an increase in the total metal uptake. pH 7 was maintained during further sorption study.

**Figure 9.9:** Effect of (a) pH and (b) adsorbent dosage on adsorption of Pb$^{2+}$ and Cd$^{2+}$

### 9.3.2.2 Effect of adsorbent dosage

Effect of adsorbent dosage on removal of Pb$^{2+}$ and Cd$^{2+}$ from aqueous solution is presented in Figure 9.9(b). Adsorbent dosage was varied from 0.5 to 10 g/L for both Pb$^{2+}$ and Cd$^{2+}$ at 303K (equilibrium time: 120 min; pH: 7; adsorbate concentration: 10 mg/L; agitation speed: 150 rpm). Metal sorption capacity was found to increases with increases
the adsorbent dosage. In the case of PG-IONPs, the percentage removal of Pb\textsuperscript{2+} and Cd\textsuperscript{2+} increased from 99.61 % to 100 % and 98.86 % to 100 %, respectively. The percentage removal of Pb\textsuperscript{2+} and Cd\textsuperscript{2+} increased from 45.69 % to 99.98 % and 64.84 % to 99.83 %, respectively in the case of IONPs. Iron oxide nanoparticles coated with polyvinyl alcohol and gallic acid (PG-IONPs) exhibited maximum removal of Pb\textsuperscript{2+} and Cd\textsuperscript{2+} by using minimum amount of adsorbent dosage than iron oxide nanoparticles (IONPs). The functionalization of iron oxide nanoparticles increases the availability of more binding sites for complexation of metal ion which increases the metal sorption capacity of PG-IONPs. 1 g/L was taken as the adsorbent dosage for further studies.

9.3.2.3 Effect of contact time

![Figure 9.10: Effect of contact time on adsorption of (a) Pb\textsuperscript{2+} and (b) Cd\textsuperscript{2+}](image)

To understand the suitable contact time at which the nanosorbents are saturated and the adsorption is at equilibrium, the effect of contact time was examined from 10 to 180 min at optimal conditions (adsorbent
dose: 1g/L; pH: 7; adsorbate concentration: 20 mg/L; agitation speed: 150 rpm). The influence of contact time on the removal of Pb$^{2+}$ and Cd$^{2+}$ from aqueous solution is depicted in Figure 9.10 (a and b). It was observed that the removal of Pb$^{2+}$ and Cd$^{2+}$ increases with rise in contact time. In the case of PG-IONPs, 91.77 % of Pb$^{2+}$ and 84.89 % of Cd$^{2+}$ was removed within 10 min of contact time and at 180 min, the removal of Pb$^{2+}$ and Cd$^{2+}$ was reached up to 99.85 % and 98.16 %, respectively. After 140 min, the rate of sorption was slow. Only, 22.71 % of Pb$^{2+}$ and 66.72 % of Cd$^{2+}$ was adsorbed by IONPs at 10 min.

Fast removal of metal ions was observed in the case of PG-IONPs compared to IONPs, this may be due to that the functional group present on the PG-IONPs provides more adsorption site for metal ions. The metal removal by PG-IONPs could be due to different sorption processes: adsorption (physisorption/chemisorption), co-ordination, complexion as a result of the ion binding groups such as hydroxyl, carboxylic, phenolic functional groups in PG-IONPs. PG-IONPs exhibited maximum sorption capacity of 19.98 mg/g and 19.86 mg/g for Pb$^{2+}$ and Cd$^{2+}$ at 180 min. Initially, the rate of removal was high and then slowed down as move towards the equilibrium condition.

**9.3.2.4 Effect of temperature**

Temperature plays a major role in adsorption of metal ions and the influence of temperature is presented in Figure 9.11. The effect of temperature on sorption were studied under four different temperature (333K, 353K, 373K and 393K) using a temperature-controlled shaker with water bath. The percentage of removal of Pb$^{2+}$ and Cd$^{2+}$ showed a
decreasing trend with increase in temperature for both nanosorbents, PG-IONPs and IONPs. As the temperature increases, the attractive forces between adsorbent surface and metal ions are weakened and the sorption decreases. As the temperature varied from 333 - 393 K, the sorption of Pb$^{2+}$ and Cd$^{2+}$ by PG-IONPs varied from 99.28 - 97.48 % and 99.89 - 91.04 %, respectively. But, in the case of IONPs, the sorption of Pb$^{2+}$ and Cd$^{2+}$ was varied from 98.60 - 44.63 % and 98.87 - 79.31 %, respectively. Compared to PG-IONPs, IONPs showed sharp decrease in the removal of metals with increase in temperature. This may be due to that the bonding between PG-IONPs and Pb$^{2+}$ and Cd$^{2+}$ ions were stronger than the bonding between IONPs and metal ions. In the energy dependent mechanisms in metal removal process, the temperature of the adsorption medium played a significant role.

**Figure 9.11:** Effect of temperature on adsorption of Pb$^{2+}$ and Cd$^{2+}$
9.3.2.5 Effect of initial metal ion concentration

As the initial metal concentration increased from 5 - 25 mg/L, a slight decrease in Pb$^{2+}$ removal (99.98 - 97.93 %) by PG-IONPs was observed but, its sorption capacity was increased from 5.0 - 24.48 mg/g. The influence of initial metal concentration on the removal efficiency and sorption capacity of Pb$^{2+}$ is depicted in Figure 9.12(a). For IONPs, the removal of Pb$^{2+}$ decreased from 97.01 - 67.08 % and sorption capacity varied from 4.85 - 16.77 mg/g. A decreasing trend of Cd$^{2+}$ removal was also observed with increasing initial metal concentration (Figure 9.12(b)). In the sorption of Cd$^{2+}$ by PG-IONPs, the removal efficiency of Cd$^{2+}$ decreased from 99.95 - 93.97 % with increase in initial concentration from 5 - 25 mg/L but for IONPs it decreased from 98.28 - 82.85 %.

![Figure 9.12: Effect of initial concentration of (a) Pb$^{2+}$ and (b) Cd$^{2+}$](image)

Initial metal concentration acted as a driving force to overcomes mass transfer resistance between solution and nanosorbent, so the sorption capacity of the nanosorbent increases with increase in the metal concentration. But, the increase in metal concentration resulted in relative
reduction of available binding sites which leads to the reduction in metal removal efficiency. PG-IONPs showed better results compared to IONPs, this may be due to the availability of more functional groups or active sites on the PG-IONPs.

### 9.3.3 Sorption equilibrium studies

The linearized sorption isotherm models such as Langmuir, Freundlich, Temkin and Dubinin - Radushkevich adsorption isotherms were used to investigate the information about the adsorption mechanisms and adsorbate-adsorbent interactions. The isotherm studies were conducted by varying the initial concentration of Pb$^{2+}$ and Cd$^{2+}$ from 5 - 25 mg/L and maintaining the adsorbent dosage of 1g/L at a constant temperature of 303K and neutral pH. Single species sorption experiments were conducted for each heavy metal. The linearized form of Langmuir, Freundlich, Temkin, and Dubinin - Redushkevich (D-R) isotherm models are detailly described in chapter 7 and 8. Isotherm models were applied to investigate the adsorption capacity of both, PG-IONPs (iron oxide coated with polyvinyl alcohol and gallic acid) and IONPs (iron oxide nanoparticle).

The values of Langmuir constants were calculated from the linear plot of $C_e/q_e$ against $C_e$ (Figure 9.13(a)) for the sorption of Pb$^{2+}$ and Cd$^{2+}$ by PG-IONPs and IONPs. For the metal sorption by PG-IONPs, Langmuir constants, $q_m$ (Pb$^{2+}$: 23.42 mg/g and Cd$^{2+}$: 24.21 mg/g) and $K_L$ (Pb$^{2+}$: 71.17 L/mg and Cd$^{2+}$: 14.75 L/mg) were obtained are presented in Table 9.1. In the case of Pb$^{2+}$ and Cd$^{2+}$ adsorption by IONPs, Langmuir constants obtained were $q_m$ (Pb$^{2+}$: 19.57 mg/g and Cd$^{2+}$: 20.45 mg/g) and
Maximum adsorption capacity was found for sorption of Pb\(^{2+}\) and Cd\(^{2+}\) by PG-IONPs. For the sorption of Pb\(^{2+}\) and Cd\(^{2+}\) by PG-IONPs and IONPs, the separation factor or equilibrium parameter \(R_L\) values found were \(0 < R_L < 1\), which indicates that the sorption of Pb\(^{2+}\) and Cd\(^{2+}\) on both PG-IONPs and IONPs is favourable.

By plotting log \(q_e\) versus log \(C_e\) (Freundlich plots) a straight line was resulted and the values for \(n\) (adsorption intensity) and \(K_f\) (the sorption capacity) can be obtained from the slope and intercept of the plot (Figure 9.13(b)) and are presented in Table 9.1. The values of sorption capacities \(K_f\) and adsorption intensity \(n\) of PG-IONPs were found higher than that of IONPs, for both Pb\(^{2+}\) and Cd\(^{2+}\). For both the metal sorption by PG-IONPs and IONPs, the values of \(n\) were found to be greater than 1, representing the favorable adsorption condition.

Figure 9.13(c) shows the linear form of the Temkin isotherm plot \(q_e\) against ln \(C_e\) and a straight line was observed for the sorption of both the metals by PG-IONPs and IONPs. The values of the Temkin constant \(b\), indicates that the heat of adsorption is presented in Table 9.1. In the case of PG-IONPs, the values of mean free energy \(E\) (Pb\(^{2+}\): 10.10 kJ/mol and Cd\(^{2+}\): 9.21 kJ/mol) was found in the range of 8–16 kJ/mol, indicating that the type of sorption of Pb\(^{2+}\) and Cd\(^{2+}\) on PG-IONPs (iron oxide coated with polyvinyl alcohol and gallic acid) is essentially chemical. But for the sorption of Pb\(^{2+}\) and Cd\(^{2+}\) by IONPs, it was found in the range of 1 to 8 kJ/mol, indicates the physical sorption.
Evaluation of the suitable isotherm model for the sorption of Pb$^{2+}$ and Cd$^{2+}$ by PG-IONPs and IONPs was conducted using the correlation coefficients value ($R^2$). The Langmuir isotherm fits very close to the experimental data of the sorption of both the metals by PG-IONPs and the Langmuir equation assumes a homogeneous distribution of active sites on surface. The values of $q_m$ determined by the Dubinin-Radushkevich isotherm model also fits close to the experimentally determined data for sorption of Pb$^{2+}$ and Cd$^{2+}$ on PG-IONPs. $R^2$ value of Pb$^{2+}$ sorption by PG-IONPs indicates that the Dubinin-Radushkevich isotherm is the best followed by the Langmuir isotherm, Temkin and then
the Freundlich isotherm. The order of adsorption isotherm models fitted the equilibrium data are for Cd\textsuperscript{2+} sorption by PG-IONPs: Langmuir isotherm > Freundlich isotherm > Temkin isotherm > Dubinin-Radushkevich isotherm. For the metal sorption by IONPs, the order of the fitted isotherm model was as follows, Pb\textsuperscript{2+}: Freundlich isotherm > Langmuir isotherm > Temkin isotherm > Dubinin-Radushkevich isotherm and Cd\textsuperscript{2+}: Langmuir isotherm > Dubinin-Radushkevich isotherm > Freundlich isotherm > Temkin isotherm.

**Table 9.1:** Isotherm parameters for adsorption of Pb\textsuperscript{2+} and Cd\textsuperscript{2+} by PG-IONPs and IONPs

<table>
<thead>
<tr>
<th>Isotherm models</th>
<th>Parameters</th>
<th>Pb</th>
<th>IONPs</th>
<th>Cd</th>
<th>IONPs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>$q_m$ (mg/g)</td>
<td>23.42</td>
<td>19.57</td>
<td>24.21</td>
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<td>$K_L$ (L/mg)</td>
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<td></td>
<td>$R_L$</td>
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<td>(0.0027 - 0.0121)</td>
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<tr>
<td></td>
<td>$R^2$</td>
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<td>0.834</td>
<td>0.989</td>
<td>0.9208</td>
</tr>
<tr>
<td>Freundlich</td>
<td>$K_f$ (mg/g) (L/mg)$^{1/n}$</td>
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<td>7.97</td>
<td>22.14</td>
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</tr>
<tr>
<td></td>
<td>$n$</td>
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<td>3.30</td>
<td>4.44</td>
<td>3.51</td>
</tr>
<tr>
<td></td>
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<td>0.8548</td>
<td>0.9813</td>
<td>0.8879</td>
</tr>
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<td>Temkin</td>
<td>$A$ (L/g)</td>
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<td>25.7</td>
<td>2172.9</td>
<td>74.2</td>
</tr>
<tr>
<td></td>
<td>$b$ (kJ/mol)</td>
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<td>911.1</td>
<td>910.7</td>
<td>776.1</td>
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<td></td>
<td>$R^2$</td>
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<td>0.9509</td>
<td>0.87</td>
</tr>
<tr>
<td>Dubinin – Radushkevich</td>
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<td>19.87</td>
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<td></td>
<td>$E$ (kJ/mol)</td>
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<tr>
<td></td>
<td>$R^2$</td>
<td>0.9834</td>
<td>0.6596</td>
<td>0.9355</td>
<td>0.9134</td>
</tr>
</tbody>
</table>
9.3.4 Sorption kinetics

Lagergren’s pseudo-first-order, pseudo-second-order and intraparticle diffusion models were utilized for analysis of sorption kinetics which are discussed in chapter 7 and 8. The pseudo-first-order rate constants $k_1$ and $q_e$ determined from the slope and intercept of the Lagergren’s plot (Figure 9.14 (a and b)) and are listed in Table 9.2 along with the correlation coefficients ($R^2$). It was observed from $R^2$ value that the pseudo first-order model did not fit well. The second-order constants, $k_2$ and $q_e$ were calculated from the intercept and slope of the linear second-order kinetic plot (Figure 9.14 (c and d) and are revealed in Table 9.2. The high correlation coefficient ($R^2$) value indicates that the adsorption data of Pb$^{2+}$ and Cd$^{2+}$ by PG-IONPs and IONPs were well fitted to pseudo-second order equation. $R^2$ value obtained from the adsorption data of Pb$^{2+}$ and Cd$^{2+}$ ranged as, 0.9995 - 1 for PG-IONPs and 0.9542 - 0.9999 for IONPs. For the pseudo second-order kinetic model, a good agreement between experimental and calculated $q_e$ values was also observed which indicates that the pseudo-second-order model better represents the reaction mechanism, directing to a chemisorption character. PVA and gallic acid on the iron oxide nanoparticles provide plenty of surface functional groups as active sorption sites.
Figure 9.14: Pseudo-first-order plot (a) Pb$^{2+}$ and (b) Cd$^{2+}$ and pseudo-second-order (c) Pb$^{2+}$ and (d) Cd$^{2+}$

A rate-limiting step is required for the pseudo-second-order kinetic model which may comprise of chemisorption and the diffusion processes (Ho & McKay, 1999). Weber and Morris proposed model was utilized to understand whether the sorption process is controlled by intraparticle diffusion or bulk diffusion. According to intraparticle diffusion models, if sorption of a solute is controlled by the intraparticle diffusion process, the plot of $q_t$ versus $t^{1/2}$ gives a straight line (Pelit et al., 2011). In the case sorption of Pb$^{2+}$ (Figure 9.15(a)) and Cd$^{2+}$ (Figure 9.15(b)) by both PG-IONPs and IONPs, $R^2$ value of Weber and Morris
plot or intraparticle diffusion model plot was ranged between (0.8376 - 0.9841) and (0.4417 - 0.976), respectively. High R$^2$ value and better correlation between experimental and calculated values indicates that the pseudo second-order model better represents the reaction mechanism involved in the sorption of Pb$^{2+}$ and Cd$^{2+}$ by PG-IONPs and IONPs.

Figure 9.15: Intraparticle diffusion plot (a) Pb$^{2+}$ and (b) Cd$^{2+}$
Table 9.2: Kinetic parameters for the adsorption of Pb^{2+} and Cd^{2+} by PG-IONPs and IONPs

<table>
<thead>
<tr>
<th>Kinetic models</th>
<th>Parameters</th>
<th>Pb</th>
<th></th>
<th></th>
<th>Cd</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>PG-IONPs</td>
<td>IONPs</td>
<td>PG-IONPs</td>
<td>IONPs</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>10 mg/L</td>
<td>20 mg/L</td>
<td>10 mg/L</td>
<td>20 mg/L</td>
<td>10 mg/L</td>
<td>20 mg/L</td>
</tr>
<tr>
<td>q_{e,exp} (mg/g)</td>
<td></td>
<td>10.25</td>
<td>19.98</td>
<td>9.74</td>
<td>17.88</td>
<td>10.78</td>
<td>19.858</td>
</tr>
<tr>
<td>k_{1} (min^{-1})</td>
<td></td>
<td>0.033</td>
<td>0.038</td>
<td>0.025</td>
<td>0.023</td>
<td>0.029</td>
<td>0.038</td>
</tr>
<tr>
<td>q_{e,cal} (mg/g)</td>
<td></td>
<td>0.66</td>
<td>6.80</td>
<td>13.11</td>
<td>21.24</td>
<td>0.50</td>
<td>3.06</td>
</tr>
<tr>
<td>R^2</td>
<td></td>
<td>0.8585</td>
<td>0.5884</td>
<td>0.6558</td>
<td>0.9335</td>
<td>0.7735</td>
<td>0.9776</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.141</td>
<td>0.017</td>
<td>0.002</td>
<td>0.001</td>
<td>0.131</td>
<td>0.029</td>
</tr>
<tr>
<td>k_{2} (g/mg min)</td>
<td></td>
<td>10.29</td>
<td>20.20</td>
<td>11.40</td>
<td>22.78</td>
<td>10.82</td>
<td>20.08</td>
</tr>
<tr>
<td>q_{e,cal} (mg/g)</td>
<td></td>
<td>1</td>
<td>0.9995</td>
<td>0.9542</td>
<td>0.9869</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>R^2</td>
<td></td>
<td>0.9999</td>
<td>0.9915</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.049</td>
<td>0.171</td>
<td>0.625</td>
<td>1.341</td>
<td>0.068</td>
<td>0.240</td>
</tr>
<tr>
<td>\kappa_{id} (mg/g min^{1/2})</td>
<td></td>
<td>1</td>
<td>0.9324</td>
<td>0.9535</td>
<td>0.9841</td>
<td>0.4417</td>
<td>0.7363</td>
</tr>
<tr>
<td>C (mg/g)</td>
<td></td>
<td>9.72</td>
<td>17.71</td>
<td>1.43</td>
<td>0.85</td>
<td>10.02</td>
<td>17.14</td>
</tr>
<tr>
<td>R^2</td>
<td></td>
<td>0.8376</td>
<td>0.9324</td>
<td>0.9535</td>
<td>0.9841</td>
<td>0.4417</td>
<td>0.7363</td>
</tr>
</tbody>
</table>
Adsorption of Pb\(^{2+}\) and Cd\(^{2+}\) on PG-IONPs was confirmed by the EDX spectra of Pb\(^{2+}\) and Cd\(^{2+}\) loaded PG-IONPs. EDX peaks of lead (Figure 9.16) and cadmium (Figure 9.17) observed were clearly confirmed the adsorption of Pb\(^{2+}\) and Cd\(^{2+}\) on PG-IONPs surfaces.

**Figure 9.16:** EDX spectra of Pb\(^{2+}\) loaded PG-IONPs.
9.3.5 Adsorption thermodynamics of metal ions on functionalized iron oxide nanosorbent

The thermodynamic studies were carried out by varying temperature from 303 to 373 K and the values of \( \Delta G^\circ \), \( \Delta H^\circ \) and \( \Delta S^\circ \) are presented in the Table 9.3. The negative value for the Gibbs free energy for \( \text{Cd}^{2+} \) indicates the spontaneous adsorption of \( \text{Cd}^{2+} \) on PG-IONPs with increasing temperature. The calculation of thermodynamic parameters was discussed in chapter 7. Negative value of enthalpy change (\( \Delta H^\circ \)) for \( \text{Pb}^{2+} \) and \( \text{Cd}^{2+} \), implies the exothermic behaviour of the adsorption process. The magnitude and sign of \( \Delta S^\circ \) show a contributing role in reflecting whether the association of the adsorbate at the solid/solution
interface during the adsorption process becomes less random ($\Delta S^o < 0$) or more random ($\Delta S^o > 0$) (Tran et al. 2016). The positive value of entropy change ($\Delta S^o$) reflect an increased degree of disorderliness at the solid/liquid interface during the adsorption of Cd$^{2+}$ on the nanosorbent, PG-IONPs.

**Table 9.3:** Thermodynamic parameters for the adsorption of Pb$^{2+}$ and Cd$^{2+}$ on PG-IONPs

<table>
<thead>
<tr>
<th>Metal ions</th>
<th>T (K)</th>
<th>PG-IONPs</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\Delta G^o$ (kJ/mol)</td>
<td>$\Delta H^o$ (kJ/mol)</td>
</tr>
<tr>
<td>Pb</td>
<td>303</td>
<td>14.39</td>
</tr>
<tr>
<td></td>
<td>333</td>
<td>16.08</td>
</tr>
<tr>
<td></td>
<td>353</td>
<td>17.22</td>
</tr>
<tr>
<td></td>
<td>373</td>
<td>18.36</td>
</tr>
<tr>
<td>Cd</td>
<td>303</td>
<td>-46.19</td>
</tr>
<tr>
<td></td>
<td>333</td>
<td>-46.48</td>
</tr>
<tr>
<td></td>
<td>353</td>
<td>-47.63</td>
</tr>
<tr>
<td></td>
<td>373</td>
<td>-46.46</td>
</tr>
</tbody>
</table>

9.3.6 Regeneration and stability of functionalized iron oxide nanosorbent

The efficiency of functionalized NPs was investigated for multiple adsorptions-desorption cycles. The Pb$^{2+}$ and Cd$^{2+}$ adsorbed nanosorbents were regenerated using 0.1 M HCl and 0.1 M NaOH. 50 mL of desorbing agents was added to 2 g of metal adsorbed, functionalized iron oxide nanoparticles in 250 mL stopped bottle and agitated at 150 rpm for 1h at room temperature using a mechanical shaker. The dried desorbed nanosorbent were reused for another adsorption cycle and the adsorption-desorption process was repeated five
times, separately for Pb\(^{2+}\) and Cd\(^{2+}\). Adsorption was conducted using 10 mg/L metal solution. A decrease in adsorption yield was observed in every cycle. 0.1 M HCl was found as suitable desorbing agent than 0.1 M NaOH. Both, Pb\(^{2+}\) and Cd\(^{2+}\) desorption was favourable using an acidic desorbing agent because at low pH, the competition between H\(^+\) ions and metal ions occurs. In the first cycle Pb\(^{2+}\) adsorption yield was 99.95% but on fifth cycle it reduced to 56%. Cd\(^{2+}\) removal yield was 99.77% in the first cycle and reduced to 52.1% in the fifth cycle. Thus, functionalized iron oxide nanoparticles using PVA and gallic acid can be regenerated and reused for Pb\(^{2+}\) and Cd\(^{2+}\) removal and recovery.

9.4 Summary

The iron oxide nanoparticles (Fe\(_2\)O\(_3\)) were synthesized by co-precipitation and its surface was coated by polyvinyl alcohol and gallic acid. The removal of toxic metals such as lead and cadmium from aqueous solution was studied using functionalized nanoparticles (PG-IONPs) and its metal removal efficiency was compared with the uncoated iron oxide nanoparticles (IONPs). The functionalized iron oxide nanoparticles were characterized using FTIR, SEM EDX and XRD. The presence of functional groups on PG-IONPs were confirmed by FTIR. Batch sorption experiments under different conditions such as pH, adsorbent dosage, contact time, temperature and initial metal concentration were carried out and the results revealed that the maximum sorption of metals by PG-IONPs is possible under a wide range of pH (pH: 4 - 12 for Pb\(^{2+}\) and pH: 6 - 12 for Cd\(^{2+}\)). Better sorption of metals was exhibited by PG-IONPs than IONPs. Compared to IONPs, PG-IONPs
exhibited high removal efficiencies for both Pb$^{2+}$ and Cd$^{2+}$ at minimal adsorbent dosage. The increase in metals concentration from 5 to 25 mg/L leads to an increase in adsorption capacity and observed a maximum adsorption capacity of 24.48 mg/g and 23.52 mg/g for Pb$^{2+}$ and Cd$^{2+}$, respectively by PG-IONPs which was better than that of IONPs. As the temperature increases, both nanosorbents exhibited a decreasing trend in the removal of lead and cadmium. Compared to IONPs, PG-IONPs exhibited only a slight decrease in metal sorption. The results indicate that the bonding between PG-IONPs and metal ions were stronger than the bonding between IONPs and metal ions at higher temperature. In the case of PG-IONPs, 91.77 % of Pb$^{2+}$ and 84.89 % Cd$^{2+}$ removal was attained within 10 min of contact time. Initially, the rate of removal was high and then slowed down as move towards the equilibrium condition. After 140 min, the rate of sorption was slow and reaches equilibrium by PG-IONPs. PG-IONPs showed fast removal of metals than IONPs this may be due to that the functional group present on the PG-IONPs provides more active adsorption site for metal ions.

The sorption equilibrium data was best described by Langmuir equation. The values of $q_m$ determined by the Dubinin-Radushkevich isotherm model also fits close to the experimentally determined data for sorption of Pb$^{2+}$ and Cd$^{2+}$ on PG-IONPs. For the sorption of both Pb$^{2+}$ and Cd$^{2+}$, the values of mean free energy ($E$) was found in the range of 8 - 16 kJ/mol for PG-IONPs, indicating the chemical sorption but the value of $E$ was found in the range of 1 to 8 kJ/mol, indicates involvement of physical sorption in the sorption of Pb$^{2+}$ and Cd$^{2+}$ by IONPs. Sorption dynamics data were best described using pseudo-second-order rate
equation. High $R^2$ value and better correlation between experimental and calculated values indicates that the sorption dynamics data were best described by using pseudo-second-order kinetic model, in the case of both nanosorbents. Thermodynamic studies illustrated that Pb$^{2+}$ and Cd$^{2+}$ adsorption by the functionalised nanosorbent was exothermic in nature. Sorption of Pb$^{2+}$ and Cd$^{2+}$ on the PG-IONPs was confirmed using EDX spectra. The better regeneration of exhausted PG-IONPs was done using desorbing agent, 0.1 M HCl and its reusability were also investigated. Polyvinyl alcohol and gallic acid coated iron oxide nanoparticles (PG-IONPs) can be considered as fast and efficient, nano-adsorbent for Pb$^{2+}$ and Cd$^{2+}$ removal from contaminated waters.