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Evaluating the performance of nanoparticle zero-valent iron and goethite in lead and cadmium removal from aqueous solutions

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Studying the removal of environmental pollutants such as heavy metals is important from various aspects, particularly human health-related issues. Lead (Pb) and cadmium (Cd) are two of the hazardous metals in the environment due to their acute and chronic effects on human health. The present study evaluated the effect of zero-valent iron nanoparticles (nZVI) and goethite on the removal of lead and cadmium from aqueous solutions. Batch experiments were conducted to investigate the effects of various solution properties such as pH, initial concentration, sorbent dosage, and reaction time on Pb and Cd removal by nZVI and goethite. The removal efficiencies of Pb and Cd increased with the increasing initial pH value and reached a maximum at pH 10.0 recorded 98.1 and 94.2% for Pb and Cd by nZVI, respectively, while reached 97.8 and 93.2% for Pb and Cd by goethite. However, enhancing the initial Pb and Cd concentration caused a considerable decrease in Pb and Cd removal efficiency. The results indicate that with increasing initial Pb and Cd concentration the removal efficiency rate has dropped linearly from 78.4 to 51.1% and from 70.8 to 54.9% for Pb by nZVI and goethite, respectively. And from 71.6 to 49.1% and from 68.0 to 31.7% for Cd by nZVI and goethite with increasing the concentration of Pb and Cd from 0.5 to 10.0 mg/L. When the nZVI dosage was increased from 0.2 to 1.0 g/L, the removal percentage of Pb and Cd increased from 93.2 and 73.4 % at 0.2 g L^{-1} to 96.2 and 85.7 % at 1.0 g/ L nZVI, when the goethite dosage was increased from 0.2 to 1.0 g L^{-1}, the percent of Pb and Cd removal increased from 92.3 and 68.6 % at 0.2 g L^{-1} to 95.9 and 79.9 % at 1.0 g L^{-1}. The removal efficiency was increased from 88.8 to 91.2 % for Pb onto nZVI, and from 87.2 to 90.1 % for Pb onto goethite with increasing reaction time from o min to 40 min. Also, the removal efficiency was increased from 73.80 to 88.8 % for Cd onto nZVI, and from 70.6 to 79.8 % for Cd onto goethite with increasing reaction time from o min to 40 min. The distribution coefficient (Kd) was extremely dependent on the initial metal concentration, so that with increase of the initial Pb and Cd concentration from 0.5 to 10.0 mg/L, Kd values decreased for both Pb and Cd. Also, the results indicated that the values of RL (Express of adsorption favorability) decreased with increased the initial concentration of metal ions and take the following order: Cd-goethite > Pb-nZVI > Cd-nZVI > Pb- goethite. The results showed that the adsorption characteristics of Cd and Pb are well described by the Langmuir adsorption isothermal. In conclusion, this study revealed that nZVI and goethite can be used as a promising adsorbent to remove Pb and Cd from aqueous solutions. The proposed method is simple, fast, low cost-effective, and safe for the environment.

Keywords: Lead, Cadmium, Adsorption, Nano zero-valent iron, Goethite, pH

INTRODUCTION

Water has a major role in the environment and subsequently in human life. The population increment followed by industrial and agricultural development has led to generation of large amounts of waste water. Industries are one of the major sources of environmental pollution and heavy metals are one of them. Agricultural pollution occurs due to using fertilizers which consist of heavy metals. Heavy metals are hazardous for human life because of their intake and bioaccumulation in human bodies through food chain (Shibamoto and Bjeldanes, 2009). The common way of exposure to lead (Pb) is water and edible food. Pb-based dyes, aerosols, combustion gases of fossil fuel, and battery manufacturing industries are other potential sources of exposure to Pb (Sarkar, 2002). As for, cadmium (Cd) intake can occur via food and water. Phosphate fertilizers are the major sources of Cd pollution. Aerosols, dyes, Ni-Cd battery manufacturing industries, heating process systems like iron, and cement production are other sources of Cd environmental pollution (Sarkar, 2002).

To date, various methods have been applied for the removal of heavy metals; owing to the capability of this method to adsorb heavy metal ions rapidly, efficiently, inexpensively and adaptive to environment, compared to other methods. Nowadays, nanotechnology has become one of the most efficient solutions for wastewater treatment in the world. This new technology has been an advantageous replacement of the traditional practices for water treatment (Karn et al.2009). Nano zerovalent iron (nZVI), an emerging technology, is being used to successfully treat various metallic ions in aqueous solutions (Jegadeesan et al. 2005).Nano iron particles are particularly attractive for remediation purposes due to their significant surface area to weight ratio leading to a greater density of reactive sites and heavy metal removal capacity (Zhu et al. 2009).Moreover, the magnetic properties of nano iron facilitate the rapid separation of nano iron from soil and water, via magnetic field (Yavuz et al.2009).

A number of researchers have studied the adsorption of heavy metals on goethite and other hydrous oxides. Ion adsorption on oxides is due to the existence of a surface charge. Oxides and hydroxides of Al, Fe, and Mn are amphoteric and do not possess any permanent surface charge (McBride 1989). Adsorbates' affinity for the goethite surface has been examined as a function of pH, temperature, ionic strength and adsorbate and goethite concentration. Coughlin and Stone (1995) studied the adsorption and release of heavy metals on goethite as a function of pH. They observed typical, S-shaped adsorption edges for all metals; with increasing pH, adsorption increased from zero to almost 100% over a narrow pH range of approximately 1.5 units. This change indicates that cation adsorption on goethite is favored as pH increases and surface charge decreases.

Hydrous oxides have long been recognized as reactive soil materials that control the availability of metal nutrients and toxins to plants. Goethite (α-FeOOH) is the most abundant and most stable of all forms of iron-oxides in soil and its surface chemistry affects the distribution of soluble species in soil. Synthetic goethite have been extensively study and applied for the removal of heavy metal contaminants from industrial solutions, radionuclides from nuclear reactor plants and for municipal water treatment (Grossl et al.1997).

MATERIALS AND METHODS

Batch experiments were carried out to evaluate the efficiency of nano zero-valent iron (nZVI) and goethite for adsorb and removal efficiencies of metals (Pb, Cd). Batch adsorption experiments were conducted using four factors reaction time, adsorbent weight, initial metals concentrations and different pH of solution. Different adsorbent weights (0.2, 0.4, 0.8 and 1.0 g/L) of nano particle (nZVI) and goethite were weighed into the centrifuge tubes with 50 ml of water contaminant solutions at different metals concentrations, i.e. 0.5, 1.0, 5.0,10.0 mg/L and different contact time (0,10,20,40 and120 min). In this study pH value of 5, 7, 9 and 10 (the pH was adjusted with 0.1 M HCl and 0.1 M NaOH solutions) were also examined throughout the experiments at room temperature (25ºC).Then samples were shaken vigorously. After batch experiments, each samples were collected and centrifuged at 5000 rpm for 5 min and then filtered via whatman no 42. Samples were collected after shaking and the concentrations of the studied metal ions were determined. The metal ions concentration in the solution determined using atomic absorption spectrometer. The amount of metal ions adsorbed per unit mass of the adsorbent evaluated by using the following mass balance equation,

$qe = (Co-Ce) V / M$

Removal (%) $= Co - Ce / Co \times 100$

Where qe is the equilibrium adsorption capacity (mg/g), Co and Ce are the initial and equilibrium liquid-phase concentrations of solute in aqueous solution (mg/L), respectively. V is the liquid phase volume (L) and M is the mass of sorbent used (g). Other definition of adsorption is a mass transfer process by which a substance is transferred from the liquid phase to the surface of a solid, and becomes bound by physical and/or chemical interactions.

Adsorption Isotherms

An adsorption isotherm is the presentation of the amount of solute adsorbed per unit weight of adsorbent as a function of the equilibrium concentration in the bulk solution at constant temperature. Langmuir and Freundlich adsorption isotherms are commonly used for the description of adsorption data**. (**Langmuir,1918 and Frundlich ,1926). Adsorption isotherm studies carried out with different initial concentrations of metal ions from 0.5 mg/L to 10.0 mg/L at the adsorption optimum pH and dose. All the investigations carried out in duplicate to confirm reproducibility of the experimental results. Metal ions adsorption isotherm experiments using nZVI and goethite were implemented under a range of circumstances. Langmuir and Freundlich's isotherms model calculates the quantity of adsorption at equilibrium. The Langmuir isotherm model is represented by:

$C / q = 1 / kb + C / b$

In addition, the Freundlich isotherm is expressed as:

$\log q = \log k + 1 / n \log C$

Where, q is the weight of metal ions adsorbed per unit weight of nZVI or goethite (mg/g), C is the equilibrium concentration of metal ions (mg/L), b is a constant related to the free energy of adsorption (L/mg), and b is the maximum adsorption capacity (mg/g). The Freundlich constant (k) showed the relative adsorption capacity of the nZVI and goethite (mg/g), and n was the adsorption intensity

RESULTS AND DISCUSSION

Effect of pH value on the removal of Pb and Cd by nZVI and goethite:

Aqueous phase pH strongly influences the adsorption process as it affects the surface charge of the adsorbent and the degree of ionization and speciation of the metal contaminant. In this study four different pH values (5, 7, 9, and 10) were employed to study the effects of pH on Pb and Cd removal efficiency by nZVI and goethite. It is known that the speciation of heavy metals in the water depend on the pH value, and different forms could exist: Cd^{2+}, $Cd(OH)^+$ and $Cd(OH)_2(s)$ Pb^{2+}, $Pb(OH)^+$ and $Pb(OH)_2(s)$. Fig (1) and Table (1) showed the effect of initial pH value on the removal of Pb and Cd. The removal efficiencies of Pb and Cd increased with the increasing initial pH value. When the initial pH was 5, about 82.76 and 72.84 % of Pb and Cd was reduced in 20 min by nZVI, while the removal efficiencies increased to (83.48, 96.44 and 98.12 % for Pb) and (75.32, 91.60 and 94.20% for Cd) when the initial pH values were 7, 9 and 10 with coefficients of determination (r^2) of 0.93 and 0.94 for Pb and Cd by nZVI, respectively. As for, goethite the removal efficiencies were 80.8, 82.08, 95.96 and 97.84 % for Pb while were 58.68, 63.12, 90.12 and 93.20 % for Cd when the initial pH values were 5, 7, 9 and10 with coefficients of determination (r^2) of 0.94 and 0.94 for Pb and Cd, respectively. This suggests that the reduction of Pb and Cd could be well performed in alkaline conditions. In fact, the reduction of Pb and Cd proceeded on the surface of iron particles at high pH, would dissolve away ferrous hydroxide and other protective layers at the surface of goethite yielding more fresh reactive sites for chemical reduction of Pb and Cd. The removal increases as the pH increases. Heavy metal ions tend to a precipitate at pH higher than 6 and therefore adsorption is difficult to quantify at the higher pH value of 6. Thus, pH 6 was used for further experiments. This finding was in agreement with Neha Gupta et al. (2011). General increase in adsorption with increasing pH of solution was observed for all the metal ions up to a pH value of 5.25. A similar behavior has been reported by many authors (Angove et al. 1999; and Mohapatra et al. (2007).

Data also observed that, the performance of nZVI is expected to be superior to that of goethite. The relative increased in removal of Pb and Cd by nZVI reach about 1.15 and 9.45 % compared to goethite, due to nZVI, is essentially elemental iron that has an excess of electrons owing to the nature of iron being characteristically stable as Fe^{+2} and Fe^{+3}. nZVI form acts as an electron donor, facilitating the reduction of a variety of contaminants. At the nano-scale (particle diameter <100 nm) this reductive capacity is greatly increased due to the much larger surface area that accompanies a reduction in particle diameter. In the core-shell model of nZVI particle the core remains nZVI, while the shell which forms as a result of oxidation reaction, is largely composed of iron oxides and hydroxides. It is the mixed oxide shell (Fe^{+2} and Fe^{+3}) that provides sites for chemosorption, which is, a complex chemical formations (Li et al. 2006 and Salim, and Mohsin 2013).

Lead and cadmium ions have a higher adsorption affinity to the nZVI and goethite. This affinity is related to a number of factors, such as molecular mass, ion charges, ionic radius, hydrated ionic radius and hydration energy of the metals. The results observed that the relative increased in removal of Pb compared to Cd by nZVI and goethite reach about 8.04 and 16.89 %, respectively.(Boparai et al.2013 and Arancibia-Miranda et al.2014),).

The effect of pH on Pb and Cd sorption is also related to the changes in the surface charge and can be explained in terms of point of zero charge (pHpzc). Below the pHpzc, the adsorbent surface is protonated, and an electrostatic repulsion exists between the positively charged surface and Pb^{2+} or Cd^{2+} ions, inhibiting the adsorption. At pH above the pHpzc, the nZVI and goethite surface acquires a net negative charge making the surface electrostatically favorable for higher adsorption of Pb^{2+} or Cd^{2+} ions. In the present study, the pHpzc of nZVI and goethite are 7.90 and 7.78 but most of the Pb^{2+} or Cd^{2+} ions were adsorbed below this pH. This suggests that the nonspecific sorption (physisorption) due to electrostatic attractions between both $Cd^{2+}$and Pb^{2+} with nZVI or goethite surface is unlikely to be the major mechanism for Pb^{2+} or Cd^{2+} adsorption. This further supports that Pb^{2+} or Cd^{2+} ions are adsorbed on the nZVI or goethite surface by specific sorption (chemisorption). The other aspect to be considered is the metal speciation which is strongly influenced by pH and can affect the adsorption process (Kadirvelu and Namasivayam, 2003) and (Boparai et al. 2013).

Effect of initial concentration on the removal of Pb and Cd by nZVI and goethite:

Four different initial concentrations of Pb and Cd (0.5, 1.0, 5.0, and 10 mg/L) were employed to study their removal efficiency by nZVI and goethite show in Fig. (2) and Table (2). At lower Pb and Cd concentrations, the ratio of initial moles of Pb and Cd to the available adsorption sites was low, and thus, complete adsorption occurred. However, at higher Pb and Cd concentrations, the available adsorption sites decreased compared to the moles of Pb and Cd present in the solution, and thus, the percentage sorption of metal decreased. This can be attributed to increasing driving force of the Pb^{+2} and Cd^{+2} ions towards the adsorptive sites on nZVI and goethite surface (Kumar et al. 2010). At the lower concentration (0.5 mg/L), 78.4 and 71.6% for Pb and Cd were removed by the nZVI, while at the same concentration 70.8 and 68.0% for the Pb and Cd was removed by the goethite. The decrease in removal efficiency to 51.1 and 49.14 % for Pb and Cd by nZVI, while were 54.9 and 31.7% for Pb and Cd by the goethite, at the higher concentration (10.0 mg/L). The results indicate that with increasing initial Pb and Cd concentration from 0.5 to 10.0 mg/L in the presence of nZVI, the removal efficiency rate has dropped linearly from 78.4 to 51.1% for Pb and from 71.6 to 49.1 for Cd. While, with increasing initial Pb and Cd concentration from 0.5 to 10.0 mg/L in the presence of goethite, removal efficiency rate has dropped linearly from 70.8 to 54.9% for Pb and from 68.0 to 31.7 % for Cd. Therefore, the best removal efficiency of Pb and Cd were at 0.5 mg/L of its initial concentration. Some studies obtained results similar to this reported in the present study. They reported that efficiency of Pb and Cd removal were decreased with increasing initial Pb and Cd concentrations with nZVI dosages (Zhang et al. 2010). Though, the study of Cheng et al. (2015) revealed that 100 mg/L was the optimal concentration for Lead removed by C-nZVI (Coated nZVI).

The relative increased in Pb and Cd removal by nZVI were 5.52 and 14.78 % compared with goethite, respectively. While the relative increased in Pb removal compared to Cd by nZVI and goethite were 6.38 and 15.71%, respectively. In case of Pb and Cd, loading capacity increased as the metal ion concentration increased and reach to 5.11 and 5.49 (mg/g) for Pb onto nZVI and goethite at the higher concentration (10.0 mg/L). While, the loading capacity recorded 4.91 and 3.17 (mg/g) for Cd onto nZVI and goethite at the higher concentration (10.0 mg/L).This finding is in according with Mohapatra et al. (2010). The initial rapid phase may involve physical adsorption or ion exchange at the surface and the subsequent slower phase may involve other mechanisms such as aggregation, precipitation or saturation of binding sites. Metal ions removal decreased with the increase of initial metal concentration.

The distribution coefficient (Kd)

Distribution of metals between soil and solution at equilibrium can be indicated by distribution coefficient (Kd). Kd is a valuable parameter for investigating the adsorption capability of different material**.** The Kd parameter is very important in estimating the potential for the adsorption of dissolved metal. As typically used in fate and metal transport calculations, the Kd is defined as the ratio of the metal concentration associated with the solid to the metal concentration in the surrounding aqueous solution when the system is at equilibrium. The Kd is expressed as:

$$Kd = C0 – Ce/ Ce \times V/M$$

Where Kd is the distribution ratio (ml/g), C0 is the initial concentration of metal ions (mg/L); Ce is the equilibrium concentration of metal ions (mg/L); M is the adsorbent mass (g), and V is the volume of aqueous solution (ml).

The Kd values for Pb and Cd adsorption onto nZVI and goethite obtained from this study ranges from 1044 to 3545 ml/g for Pb onto nZVI and 964 to 2571 ml/g for Cd onto nZVI, respectively. Lower Kd values are recorded from Pb onto Goethite, ranging from 1217 to 2471 and 464 to 2125 ml/g for Cd onto Goethite, respectively. Higher Kd value means that the material has higher sorption capacity. Anderson and Christensen (1988) stated that high values of Kd indicate that metal has been retained by the solid through sorption reactions, while low Kd indicate that most metal remains in solution where it is available for transport. The value of Kd was calculated at varying initial Pb and Cd concentrations (Table, 3). The Kd was extremely dependent on the initial metal concentration, so that with increase of the initial Pb and Cd concentration from 0.5 to 10.0 mg/L, Kd values decreased for both Pb and Cd. This proves that the adsorption capacity of nZVI and goethite decreases with high Pb and Cd concentrations. The Kd values depend on the type of the adsorbent, and they decrease in the following order: Pb-nZVI > Cd-nZVI > Pb-Goethite > Cd-Goethite (Erdem et al. 2004). These results indicate that energetically less favorable sites become involved with increasing metals concentration in the aqueous solution.

Effect of adsorbent dosage on the removal of Pb and Cd by nZVI and goethite:

Adsorbent dosage is an important factor because it presents the adsorption capacity for obtaining the initial amount of the adsorbent. The desired amount of adsorbent required for adsorption of Pb and Cd from solutions was obtained by studying the effects of different amounts of nZVI and goethite ranging from 0.2 to 1.0 g/L. The adsorbent dosage strongly affects the metal removal efficiency of a system. When the nZVI dosage was increased from 0.2 to 1.0 g/L, the percent of Pb and Cd removal increased from 93.2 and 73.4 % at 0.2 g/L to 96.2 and 85.7 % at 1.0 g/L nZVI ,while the goethite dosage was increased from 0.2 to 1.0 g/L, the percent of Pb and Cd removal increased from 92.3 and 68.6 % at 0.2 g/L to 95.9 and 79.9 % at 1.0 g/L goethite (Fig. 3) and Table (4). The relative increased in Pb and Cd removal by nZVI were 0.75 and 6.25 % compared with goethite, respectively. The relative increased in Pb removal compared to Cd were 17.84 and 24.5 % by nZVI and goethite. The removal percentages increased with increases of nZVI and goethite dosage. This is due to the greater surface and availability of more adsorption sites at higher dosages of the adsorbent. Although the metals removal percentage increased with increasing nZVI and goethite dosage, the metal uptake (i.e., the amount of metal adsorbed per unit mass of nZVI and goethite) decreased with increasing loading at higher nZVI and goethite dosages. When the dosages of nZVI was 0.2 g/L, about 23.3 and 18.4 (mg/g) of Pb and Cd was adsorbed by nZVI, while the metal uptake decreased to (11.83, 5.97 and 4.81 (mg/g) with Pb) and (9.96, 5.11 and 4.28 (mg/g) with Cd) when the dosages of nZVI were 0.4, 0.8 and 1.0 (g/L) with coefficients of determination (r^2) of 0.92 and 0.93 for Pb and Cd by nZVI, respectively. As for, goethite when the dosages was 0.2 g/L, about 23.07 and 17.6 (mg/g) of Pb and Cd were adsorbed by goethite, while the metal uptake decreased to (11.70, 5.93 and 4.79 (mg/g) with Pb) and (9.44, 4.90 and 3.99 (mg/g) with Cd) when the dosages of goethite were 0.4, 0.8 and 1.0 (g/L) with coefficients of determination (r^2) of 0.92 and 0.93 for Pb and Cd, respectively. The decrease in metal uptake thereafter may be attributed to the unsaturation/partial filling of sorption sites as the number of sorption sites increased with increase in nZVI and goethite content, but the dosages of sorbate remained constant (i.e., the nZVI and goethite has not reached its adsorption capacity) (Boparai et al.2013).

Therefore, 0.2 g/L from nZVI and goethite was considered sufficient for quantitative removal of Pb and Cd from aqueous solutions, and was selected as the optimum value for the adsorption experiment. Above 0.2 g/L removal of metal ions becomes very slow, as the surface Pb and Cd and the solution Pb and Cd concentration come to equilibrium with each other. Therefore adsorbent dose of 0.2 g/L was sufficient for quantitative removal of Pb and Cd.

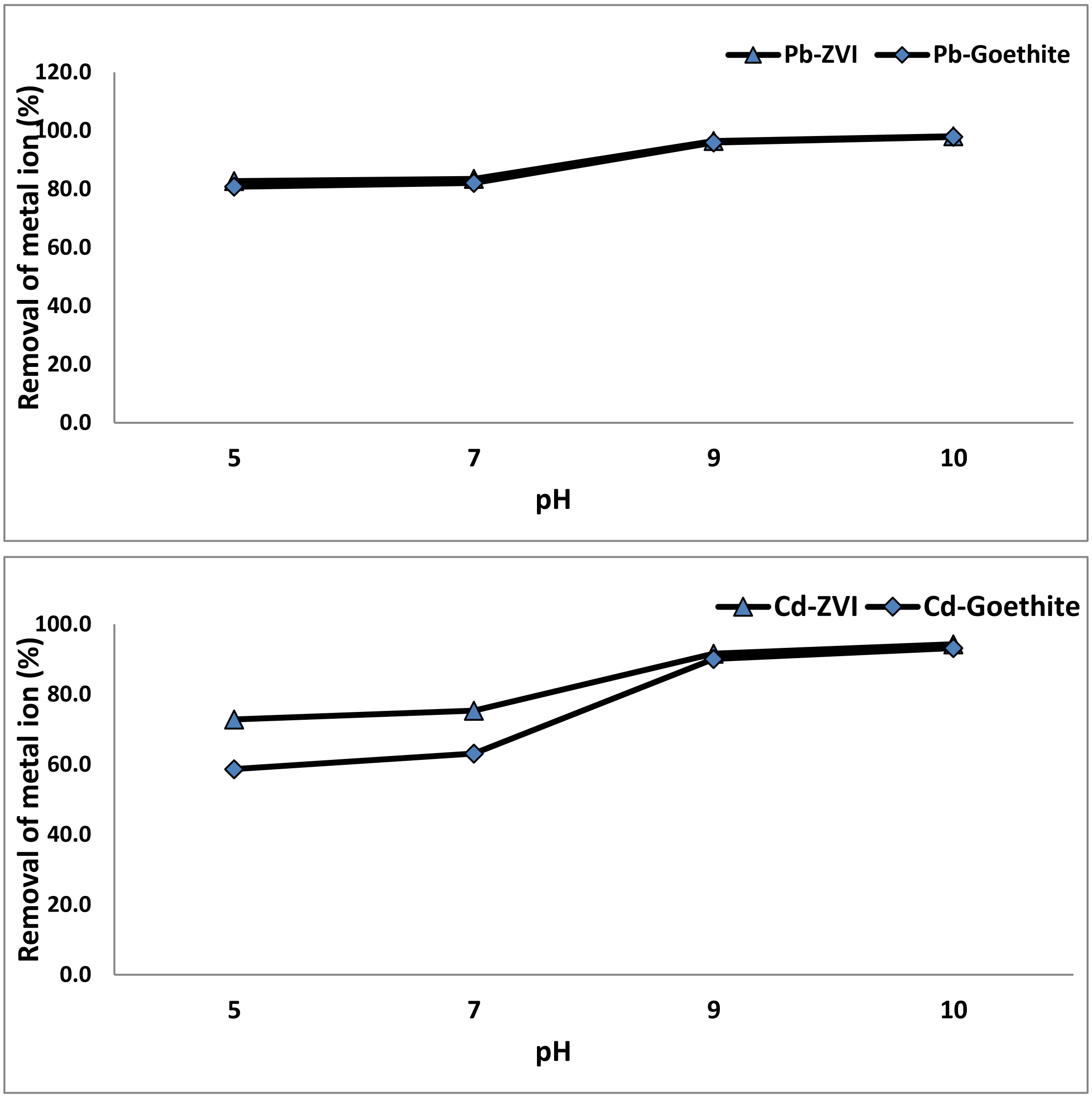


Figure1: Effect of pH values on the amount of metal ion removal of Pb and Cd by ZVI and Goethite.

Table 1: Effect of pH values on the amount of metal ion adsorbed (q_e) and removal of Pb and Cd nZVI and Goethite.

pH values	Pb-nZVI		Pb-Goethite		Cd-nZVI		Cd-Goethite	
	q_e (mg/g)	Removal (%)	q_e (mg/g)	Removal (%)	q_e (mg/g)	Removal (%)	q_e (mg/g)	Removal (%)
5	4.14	82.76	4.04	80.8	3.64	72.84	2.93	58.68
7	4.17	83.48	4.10	82.08	3.77	75.32	3.16	63.12
9	4.82	96.44	4.79	95.96	4.58	91.60	4.51	90.12
10	4.91	98.12	4.89	97.84	4.71	94.20	4.66	93.20
LSD 0.05	0.07	1.59	0.06	1.24	n.s	3.84	0.31	6.10

Table 2: Effect of initial concentration on the amount of metal ion adsorbed (q_e) and removal of Pb and Cd by nZVI and Goethite.

Initial conc. (mg/L)	Pb-nZVI		Pb-Goethite		Cd-nZVI		Cd-Goethite	
	q_e (mg/g)	Removal (%)	q_e (mg/g)	Removal (%)	q_e (mg/g)	Removal (%)	q_e (mg/g)	Removal (%)
0.5	0.39	78.40	0.36	70.80	0.36	71.60	0.34	68.00
1.0	0.74	74.00	0.67	67.00	0.70	70.00	0.63	63.00
5.0	3.51	70.12	3.33	66.60	3.32	66.46	3.07	61.40
10.0	5.11	51.10	5.49	54.90	4.91	49.14	3.17	31.70
LSD 0.05	0.09	2.31	0.14	3.68	0.06	1.79	0.25	2.92

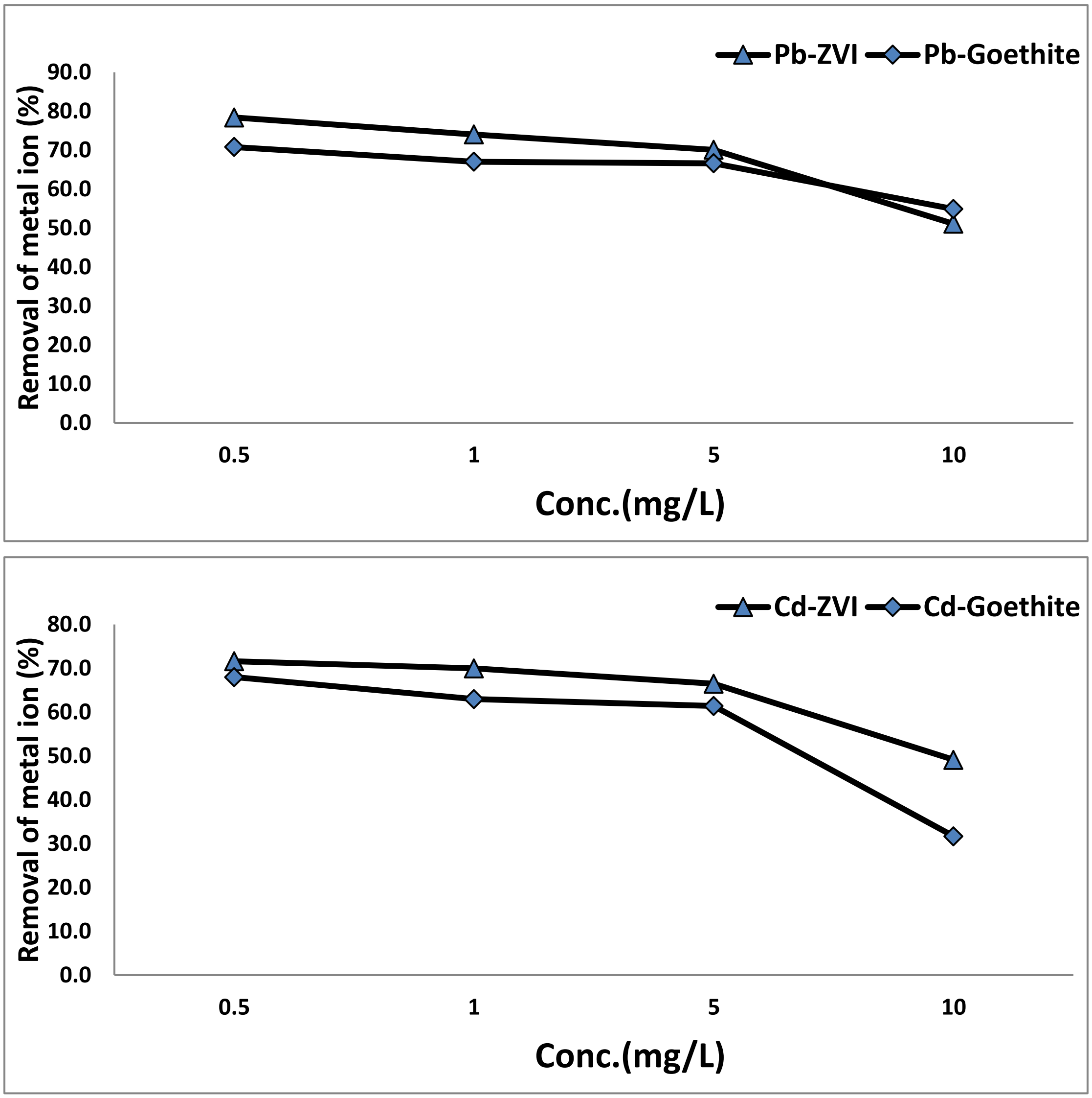


Figure2: Effect of initial concentration on the removal of Pb and Cd by ZVI and Goethite.

Table 3: **The distribution coefficient (Kd) for adsorption of Pb and Cd ions on nZVI and goethite (ml/g).**

Initial conc. (mg/L)	Pb-nZVI	Pb-Goethite	Cd-nZVI	Cd-Goethite
0.5	3545	2471	2571	2125
1.0	2846	2030	2333	1702
5.0	2355	1994	1976	1590
10.0	1044	1217	964	464

Table 4: Effect of weight of adsorbent on the amount of metal ion adsorbed (q_e) and removal of Pb and Cd by nZVI and Goethite.

Weight (g/L)	Pb-nZVI		Pb-Goethite		Cd-nZVI		Cd-Goethite	
	q_e (mg/g)	Removal (%)	q_e (mg/g)	Removal (%)	q_e (mg/g)	Removal (%)	q_e (mg/g)	Removal (%)
0.2	23.30	93.20	23.07	92.30	18.36	73.45	17.16	68.65
0.4	11.83	94.62	11.70	93.60	9.96	79.75	9.44	75.55
0.8	5.97	95.40	5.93	94.85	5.11	83.15	4.90	78.45
1.0	4.81	96.25	4.79	95.90	4.28	85.70	3.99	79.87
LSD 0.05	0.87	n.s	0.47	n.s	0.83	5.47	1.02	6.95

Table 5: Effect of reaction time on the amount of metal ion adsorbed (q_e) and removal of Pb and Cd by nZVI and Goethite.

Time (min)	Pb-nZVI		Pb-Goethite		Cd-nZVI		Cd-Goethite	
	q_e (mg/g)	Removal (%)	q_e (mg/g)	Removal (%)	q_e (mg/g)	Removal (%)	q_e (mg/g)	Removal (%)
0	4.44	88.85	4.36	87.20	3.69	73.80	3.53	70.60
10	4.48	89.70	4.43	88.70	4.02	80.40	3.70	74.00
20	4.53	90.70	4.49	89.85	4.26	85.20	3.89	77.80
40	4.56	91.20	4.50	90.10	4.37	87.40	3.98	79.80
120	4.53	90.55	4.49	89.95	4.44	88.80	3.93	79.20
LSD 0.05	n.s	n.s	0.04	0.97	0.04	0.89	0.08	1.63

Table 6: Langmuir and Freundlich adsorption isotherms of Pb on different type of material under study.

Initial conc. of Pb (mg/L)	C mg/L	q (mg/g)	C/q	Log C	Log q
Pb-nZVI					
0.5	0.11	0.39	0.282	-0.9586	-0.4089
1.0	0.26	0.74	0.351	-0.5850	-0.1308
5.0	1.49	3.51	0.424	0.1732	0.5453
10.0	4.89	5.11	0.957	0.6893	0.7084
Pb-Goethite					
0.5	0.14	0.36	0.389	-0.8539	-0.4437
1.0	0.33	0.67	0.492	-0.4815	-0.1739
5.0	1.67	3.33	0.501	0.2227	0.5224
10.0	4.51	5.49	0.821	0.6542	0.7396

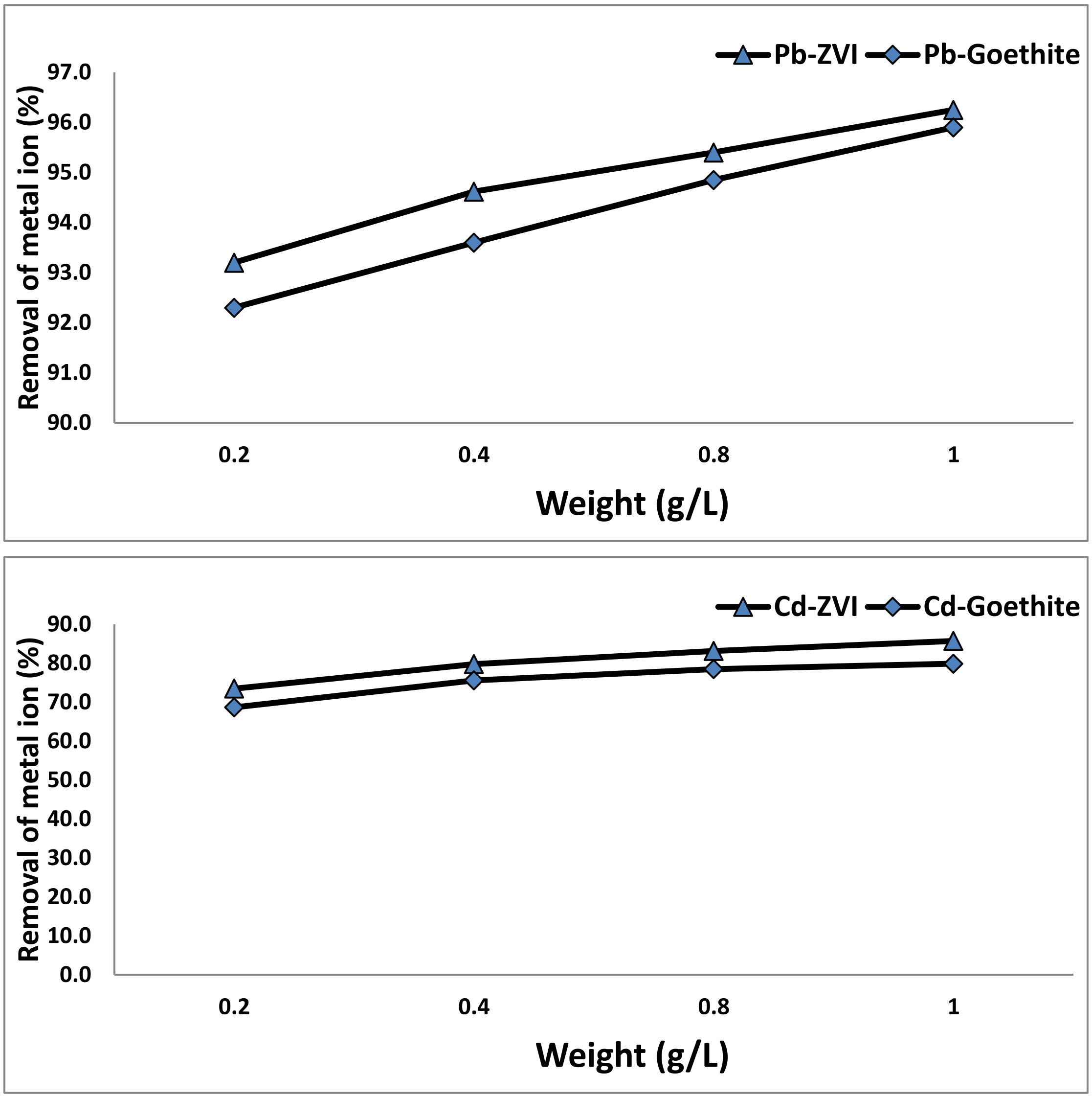


Figure 3: Effect of weight of adsorbent on the removal of Pb and Cd by ZVI and Goethite.

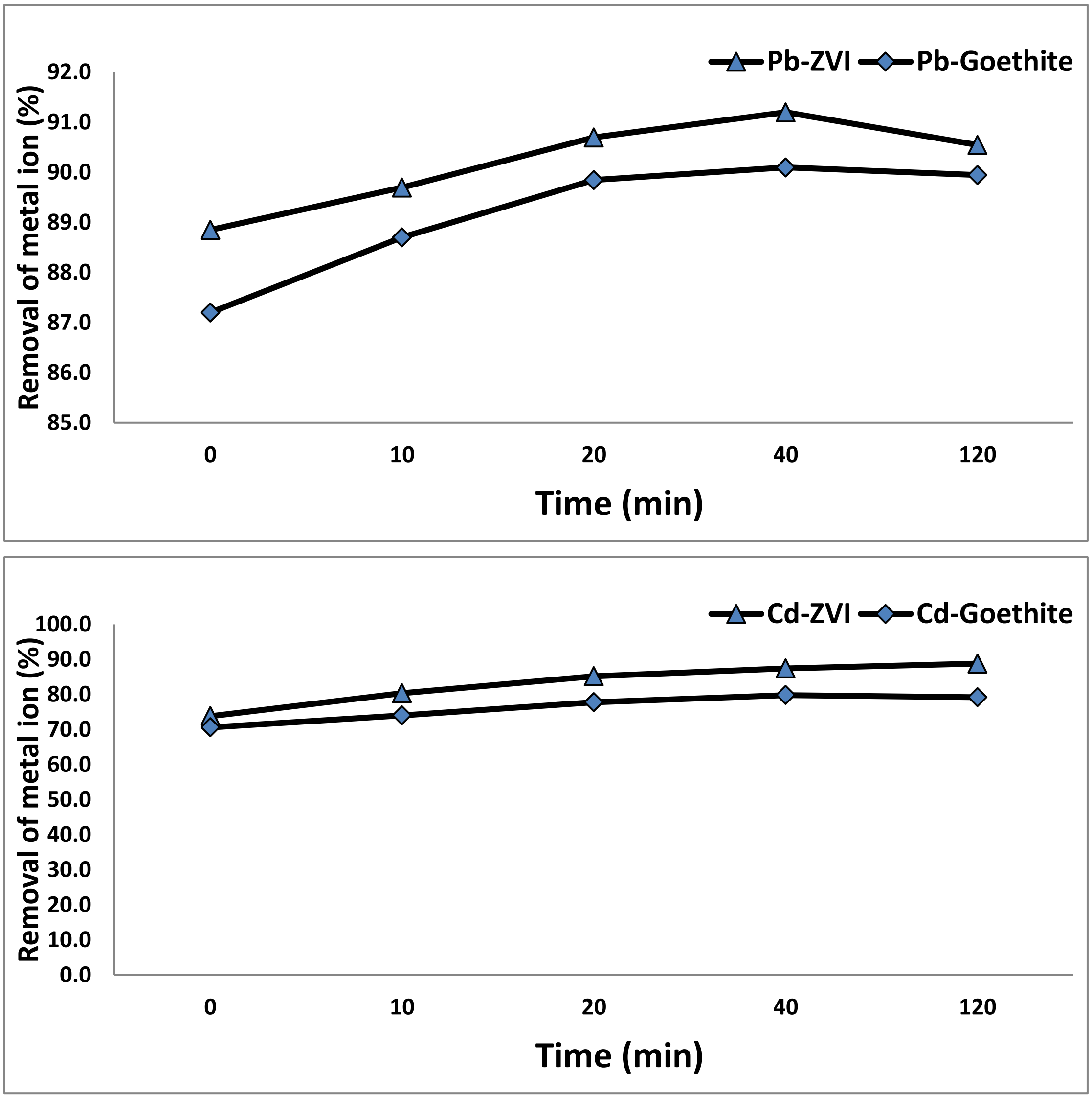


Figure 4:Effect of reaction time on the removal of Pb and Cd by nZVI and Goethite.

This finding is in accordance with that reported by Neha Gupta et al. (2011) and Hamed et al. (2014).

Numerous studies indicated that Pb and Cd removal increased significantly with increasing nZVI dosages, when other parameters were constant (Zhang et al. 2010). It is a belief that at a low adsorbent dosage, the dispersion of adsorbent particles in aqueous solution is good because all active sites on the adsorbent surface are completely uncovered and they cannot accelerate the accessibility of lead molecules to a large number of adsorbent active sites (Arshadi et al.2014 and Wang et al.2015) reported that lead removal efficiency increased with increasing nZVI concentration (0.1 g/L) and then increased or decreased marginally with further increase in nZVI concentration from 0.1 to 0.4 g/L (Wang et al. 2014)

Effect of contact time on the removal of Pb and Cd by nZVI and goethite:

Reaction time is always considered as a one of the most crucial variables in batch systems. The influence of reaction time on Pb and Cd removal was investigated in batch experiments using 1.0 g/L nZVI and goethite, initial concentration of Pb and Cd 5.0 mg/L, at pH 7 at various time intervals from 0 to 120 min, Fig. (4) and Table (5). The adsorption of Pb and Cd onto nZVI and goethite was rapid for the first 1 min of the experiment for metal ions and then increases slowly till saturation levels were completely reached at equilibration points. During the initial stage of adsorption a large number of vacant surface sites are available for adsorption, and after time, the rest of sites are difficult to be occupied due to repulsive forces between the solute molecules on the solid and bulk phases. Equilibrium was achieved almost within 40 min for Pb^{2+} and Cd^{2+} metal ions. Since reaction time increased, the removal efficiency rose significantly until 40 min after reaction for Pb^{2+} and Cd^{2+}. In this order, the removal efficiency was increased from 88.85 to 91.20 % for Pb onto nZVI, from 87.20 to 90.10 % for Pb onto goethite with increasing reaction time from zero min to 40 min. Also, the removal efficiency was increased from 73.80 to 88.8 % for Cd onto nZVI, and from 70.60 to 79.80 % for Cd onto goethite with increasing reaction time from zero min to 40 min. In consequence, 40 min was set as an equilibrium reaction time of Pb and Cd removal. From these findings, it can be postulated that by increasing the reaction time, majority of reactive sites on the surfaces of nZVI and goethite were occupied by Pb^{2+} and Cd^{2+}. Afterwards, the interaction between (nZVI and goethite) and (Pb^{2+} or Cd^{2+}) decreased significantly that attributed to the filling of reactive sites. The relative increased in Pb and Cd removal by nZVI were 1.17 and 8.97 % compared with goethite, respectively. The relative increased in Pb removal compared to Cd by nZVI and goethit were 8.52 and 16.88 %, respectively. A similar study showed that removal percentage of lead using K-nZVI and nZVI at the optimum 30 minutes contact time was 97% and 51.2%, respectively (Zhang et al.2010).

Adsorption Isotherm

The adsorption isotherms are fundamental in describing the interactive behavior between solute and adsorbent Ofomoja and Ho (2006). The analysis of the isotherms data by fitting them into different isotherm models is an important step to find the suitable model that can be used for design process. To determine the absorptivity properties of Pb and Cd on nZVI and goethite, Langmuir and Freundlich adsorption isotherms were investigated. Langmuir isotherm refers to non-interactive monolayer adsorption of ions on a homogenous surface of adsorbent. Freundlich isotherm comes from multilayer adsorption of metal ions on heterogeneous surfaces. The capacity of nZVI and goethite for adsorption of Pb and Cd ions was achieved by measuring the initial and final concentration of the desired ions in the solution in a batch system. Both Langmuir and Freundlich isotherms were computed to realize the adsorption behaviors of Pb and Cd on nZVI and goethite adsorbents. The isotherms data are given in Tables (6 and 7) and Figs.(5,6,7 and 8).

The Langmuir model it is assumed that the adsorption surface sites have identical energy and each adsorbate molecule has been located on a single site and hence this model predicts the formation of monolayer of a adsorbate on the adsorbent surface (Vasconcelos et al. 2008).The Langmuir isotherm is given as:

$$C / q = 1 / kb + C / b$$

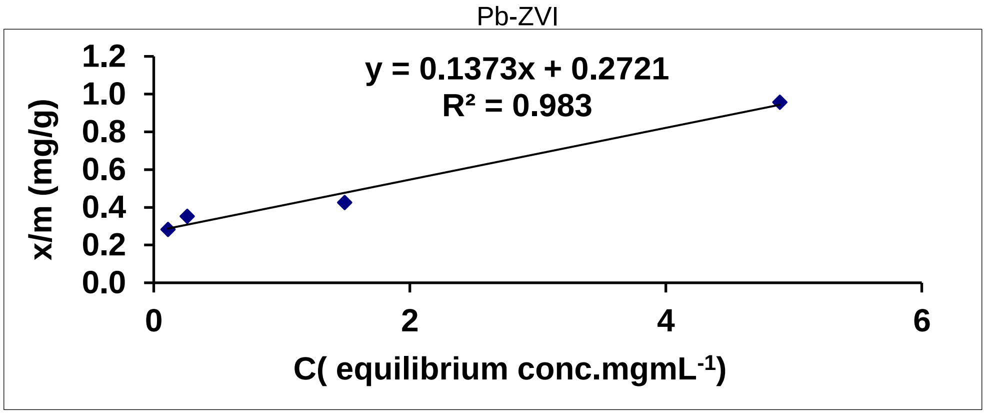
where C (mg/L) is the equilibrium concentration of the metal ions in the solution, q (milligram of metal ions per gram of adsorbent) is the equilibrium adsorption amount of metal ions, b is the maximum adsorption amount of metal ions per milligram of adsorbent (mg/g), and K is the Langmuir affinity binding energy constant in liter per milligram of adsorbent (L/mg).

Sorption parameters for nZVI and goethite showed variability among the two studied metals, as reflected by their sorption maximum (b) and Langmuir affinity constant (k) Table, (8). The results showed that the correlation coefficients (R^2) were 0.983 and 0.932 for Pb onto nZVI and goethite, while were 0.976 and 0.960 for Cd onto nZVI and goethite. The maximum sorption capacity (b) remained highest for Pb sorption onto goethite followed by Cd sorption onto nZVI and Pb sorption onto nZVI then the lowest one was found for Cd sorption onto goethite, respectively. Sing and Yu (1998) concluded that higher is the value of (b), the higher is the affinity of adsorbent for the metal sorbed. The results also indicated that the binding energy constant (k) showed the following order: Cd-goethite > Pb-nZVI > Cd-nZVI > Pb-goethite. This is may be due to the equilibrium process should be affected by the characteristics of sorbent and type of the exchangeable cation.

The maximum sorption capacity (b) is used to calculate RL, a dimensionless separation factor given by equation:

$$RL = 1/1+bC_o$$

Where C_o is the initial concentration (mg/l), RL values will tell if the adsorption is unfavorable (RL > 1), favorable (0 < RL < 1), irreversible (RL=0) (Sari et al. 2007**).** The values of RL for adsorption of Pb and Cd ions onto nZVI and goethite are shown in Table (9). The results indicated that the values of RL decreased with increased the initial concentration of metal ions and take the following order: Cd-goethite > Pb-nZVI > Cd-nZVI > Pb- goethite.



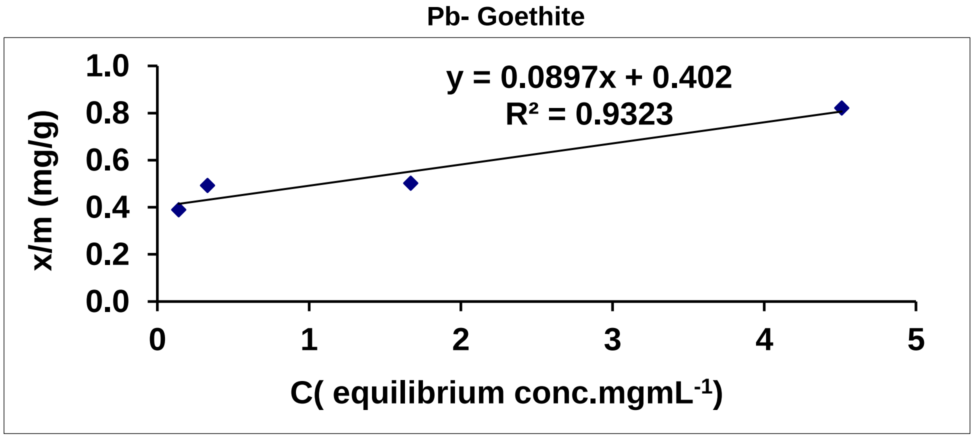


Figure 5: Langmuir plots for Pb^{2+} ions adsorption onto nZVI and goethite.

Table7: Langmuir and Freundlich adsorption isotherms of Cd on different type of material under Study.

Initial conc. of Cd (mg/L)	C mg/L	Q (mg/g)	C/q	Log C	Log q
Cd-nZVI					
0.5	0.14	0.36	0.389	-0.8539	-0.4437
1.0	0.30	0.70	0.428	-0.5229	-0.1549
5.0	1.68	3.32	0.506	0.2253	0.5211
10.0	5.09	4.91	1.037	0.7067	0.6911
Cd-Goethite					
0.5	0.16	0.34	0.471	-0.7959	-0.4685
1.0	0.37	0.63	0.587	-.04318	-0.2007
5.0	1.93	3.07	0.629	0.2856	0.4871
10.0	6.83	3.17	2.155	0.8344	0.5011

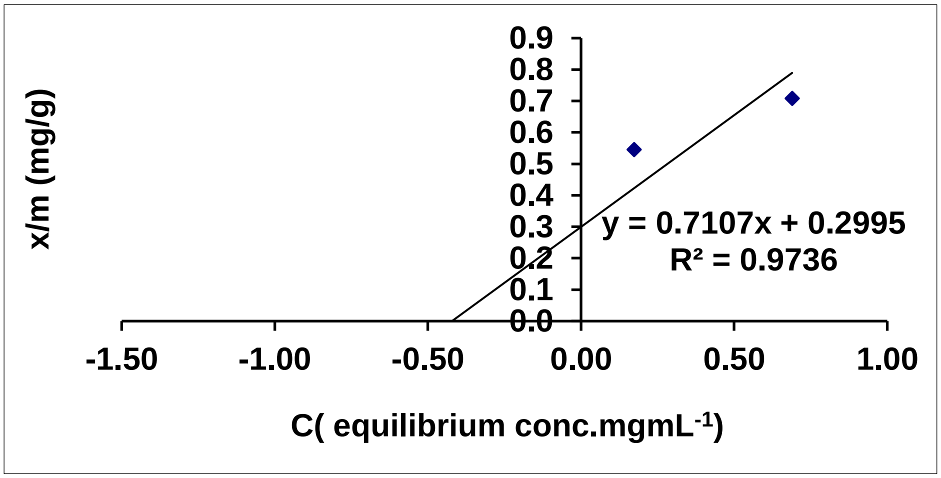
Table 8: Characteristic parameters and determination coefficient of the experimental data according to Langmuir adsorption isotherm equation.

Metal and Adsorbent	b (mg/g)	K (L/g)	R^2
Pb-nZVI	7.28	0.505	0.983
Pb-Goethite	11.15	0.223	0.932
Cd-nZVI	7.71	0.364	0.976
Cd –Goethite	3.97	0.666	0.961

Table 9: The values of RL for adsorption of Pb and Cd ions on nZVI and goethite.

Initial conc. (mg/L)	Pb-nZVI	Pb-Goethite	Cd-nZVI	Cd-Goethite
0.5	0.210	0.150	0.206	0.335
1.0	0.120	0.082	0.115	0.201
5.0	0.027	0.018	0.025	0.048
10.0	0.013	0.009	0.013	0.025

Pb-ZVI



Pb-Goethite

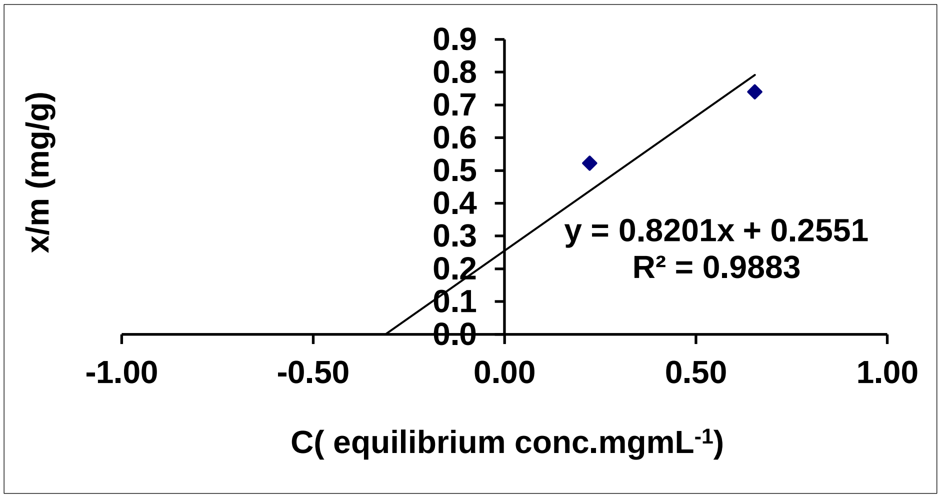
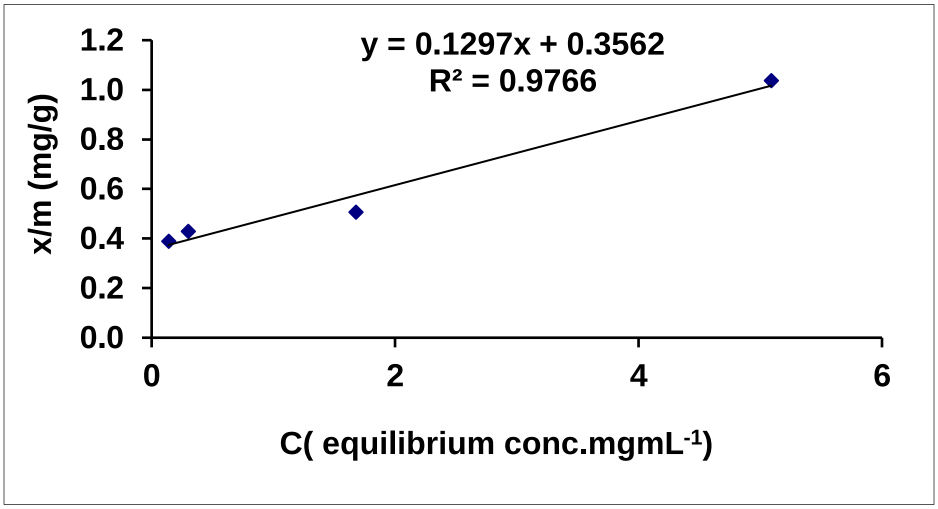


Figure 6: Frundlich plots for Pb^{2+}ions adsorption onto nZVI and goethite.

Cd-ZVI



Cd- Goethite

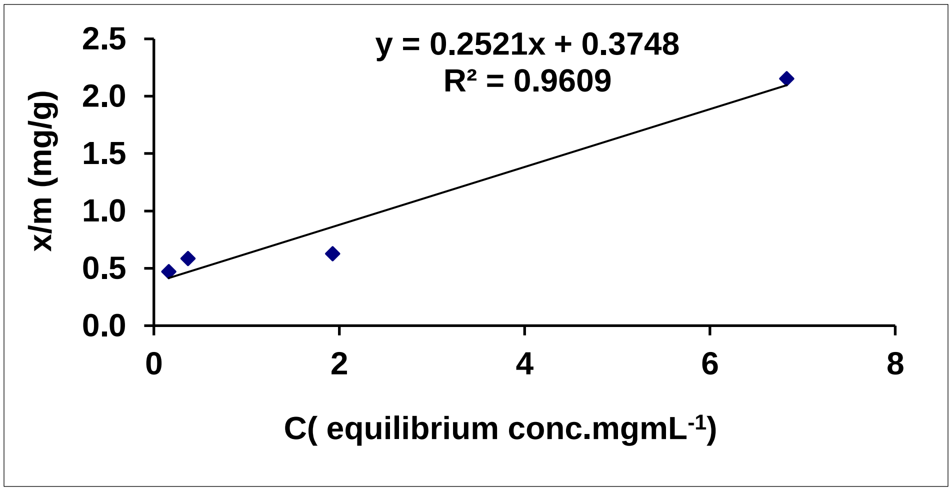
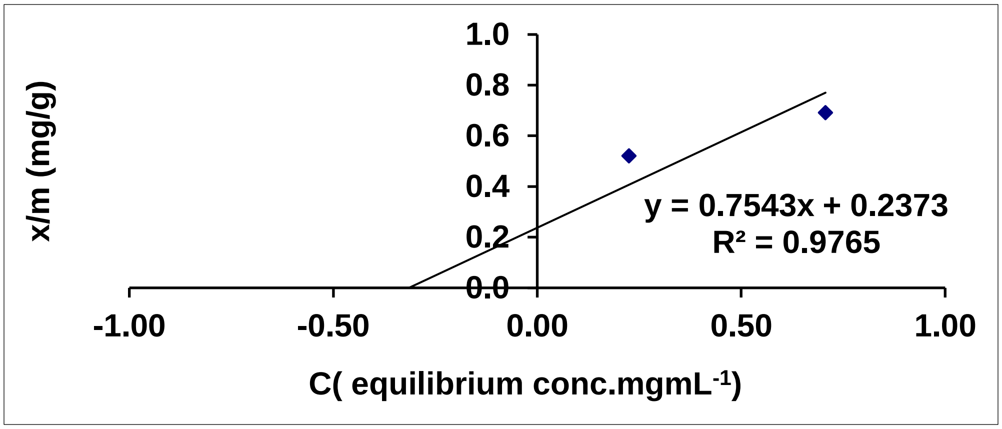


Figure 7 : Langmuir plots for Cd^{2+} ions adsorption onto nZVI and goethite.

Cd-ZVI



Cd- Goethite

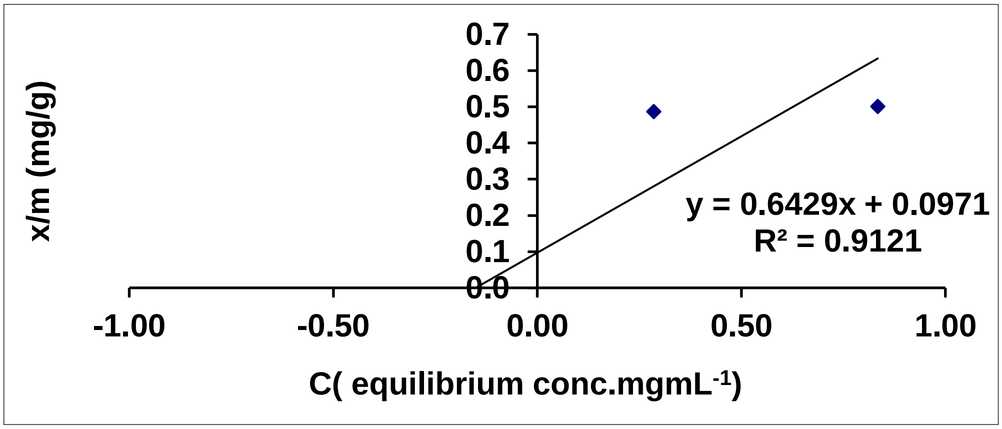


Figure 8: Frundlich plots for Cd^{2+} ions adsorption onto nZVI and goethite.

The values of RL at concentration from 0.5 to 10.0 mg/l for Pb onto nZVI ranged from 0.013 to 0.210, and for Pb onto goethite ranged from 0.009 to 0.150, while for Cd onto nZVI and goethite the LR ranged from 0.013 to 0.206 and from 0.025 to 0.335, respectively. These results indicated that adsorption of Pb and Cd onto nZVI and goethite were favorable.

The Freundlich sorption isotherm, one of the most widely used mathematical adsorption, usually fits the experimental data over a wide range of concentrations. This isotherm gives an expression encompassing the surface heterogeneity and the exponential distribution of active sites and their energies. The Freundlich isotherm is given as:

$$\log q = \log K + 1/n \log C$$

where C (mg/L) is the equilibrium concentration of the metal ions in the solution, q (milligram of metal ions per gram of adsorbent) is the adsorption amount of metal ions, K is the constant related to the adsorption capacity of the adsorbent in (mg/l) and n is the constant related to the adsorption intensity of the adsorbent. The constants K and n were calculated for each metal and adsorbent, (Table, 10).

Table 10: Characteristic parameters and determination coefficient of the experimental data according to Freundlich adsorption isotherm equation.

Metal and Adsorbent	k (mg/g)	n	R^2
Pb-nZVI	1.993	0.71	0.973
Pb-Goethite	1.799	0.82	0.988
Cd-nZVI	1.727	0.75	0.976
Cd –Goethite	1.250	0.64	0.912

The results showed that the correlation coefficients (R^2) were 0.973, 0.988, 0.976 and 0.912 for Pb-nZVI, Pb-goethite, Cd-nZVI and Cd-goethite, respectively. The sorption affinity, as represented by Freundlich sorption coefficient (K) was higher with Pb-nZVI and lowest value was conjugated with Cd-goethite. The data shows highest (K) value for Pb adsorption and lowest (K) value for Cd adsorption indicating the greatest binding of lead ion. Empirically, (K) values may be used to predict differences in the abilities of adsorbents to adsorb a particular adsorbate.

As for (n) constant the results showed that the Pb-goethite presented higher value and lowest value was conjugated with Cd-goethite. Lead ions have a preferential uptake compared to the cadmium metal. This may be attributed to the low tendency of lead ions to form strong complex although it can form hydrated ions (Inglezakis et al. 2002).An isotherm with $1/n < 1$ are classified as L-type isotherms reflecting a high affinity between adsorbate and adsorbent and is indicative of chemisorption (Taha et al. 2009).

CONCLUSION

In conclusion, this study revealed that nZVI and goethite can be used as a promising adsorbent to remove Pb and Cd from aqueous solutions. The proposed method is simple, fast, cost-effective, and safe for the environment. This result should be taken into consideration when the purification of water from Pb and Cd is needed. Nano particle is easy to be obtained and to be used in manufacturing the columns of water purifiers. Beside the advantages of nano particle, there is a disadvantage of it which could not last for long time and could be decomposed.

CONFLICT OF INTEREST

The authors declared that present study was performed in absence of any conflict of interest.

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AUTHOR CONTRIBUTIONS

This search is a search of single author and there are no participants with him.

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