Removal of Pb(II) from aqueous solutions using Acacia Nilotica seed shell ash supported Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ magnetic nanoparticles

Farshad Omidvar-Hosseini and Farid Moeinpour

ABSTRACT

Acacia Nilotica seed shell ash supported Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ magnetic nanoparticles were synthesized by a low-cost, simple, and environmentally benign procedure. The adsorbent was characterized by several methods including X-ray diffraction, scanning electron microscopy and Fourier transform infrared spectroscopy. Then, the potential of Acacia Nilotica seed shell ash supported Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ magnetic nanoparticles was investigated for adsorption of Pb(II). The effect of different parameters including contact time, pH, adsorbent dosage and initial Pb(II) concentration on the Pb(II) removal yield was studied. The experimental data were fitted well with the pseudo-second order kinetic model ($R^2 = 0.999$). The adsorption isotherm was described well by the Langmuir isotherm ($R^2 = 0.900$) with a maximum monolayer adsorption capacity of 37.6 mg g$^{-1}$. The process for purifying water treatment presented here is easy using the magnetic nanoparticles. Therefore, this adsorbent was found to be useful and valuable for controlling water pollution due to Pb(II) ions.

Key words | Acacia Nilotica, adsorption, Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$, Pb(II) ions

INTRODUCTION

The presence of heavy metals in water resources has been an attractive subject for scientists due to their increased leakage, toxic nature, and other harmful effects (Volesky 1990). Lead is used in many important industrial usages, such as storage battery fabricating, printing pigments, fuels, photographic materials, and explosive fabrication (Jalali et al. 2002). The effects of lead toxicity are very extensive and include defective blood synthesis, hypertension, intense stomach-ache, brain, and kidney damage (Toxicological Profile for Lead 1989). The allowed level for Pb(II) in drinking water is 0.05 mg L$^{-1}$ based on the US Environmental Protection Agency requirements. Therefore, a very low concentration of Pb(II) in water is very harmful and toxic (Bhattacharjee et al. 2005). Adsorption was established as an important and economically practical treatment technology for removing the Pb(II) ions from water and wastewater. Activated carbon is usually used as an adsorbent for the removal of Pb(II) ions from aqueous solution. Despite the abundant applications of activated carbon, its uses are sometimes limited due to its high cost and also because of its loss during re-formation (El-Ashtoukhy et al. 2008; Baysal et al. 2009; Senthil Kumar et al. 2013). Therefore, researchers are on the quest for new low-cost substitute adsorbents for water pollution control, especially where cost plays an important role. Much effort has been carried out towards the development of other adsorbents from biological wastes that are effective and low-cost. They can be produced from a wide diversity of raw materials, which are abundant and have high carbon and low inorganic content. Owing to the low cost and high accessibility of these materials, it is not essential to have complex regeneration processes. Such low cost adsorption methods have attracted many researchers. Often, the adsorption capabilities of such adsorbents are not large, therefore the study and investigation of more and more new adsorbents are still under development.
Some of the cheap adsorbents studied for the removal of Pb(II) ions are modified agricultural waste (Senthil Kumar et al. 2015), hazelnut husk (Imamoglu et al. 2016), oak stem (Prasad & Freitas 2000), olive waste (Blázquez et al. 2010), waste coconut buttons (Anirudhan & Sreekumari 2011), magnetically modified tea (Lucia et al. 2014), Botrytis cinerea (Akar et al. 2005), bael leaves (Chakravarty et al. 2010), pomegranate peel (El-Ashtoukhy et al. 2008), multiwalled carbon nanotube magnetic composites (Shao et al. 2012), marine green algae (Jeyakumar & Chandrasekaran 2014), tourmaline (Wang et al. 2011), amino-functionalized Fe3O4 magnetic nano-particles (Tan et al. 2012), Fe3O4@SiO2–NH2 (Zhang et al. 2013), waste maize bran (Singh et al. 2006), coir (Conrad & Hansen 2007), Caulerpa lentillifera (Apiratikul & Pavasant 2008), fraxinus tree leaves (Sangi et al. 2008), lignin (Guo et al. 2008), rice husk ash (Naiya et al. 2009), corn cobs (Tan et al. 2010), and Moringa oleifera bark (Reddy et al. 2010), etc. In recent years, due to economic problems, creating a cheap and efficient alternative method of wastewater treatment as opposed to expensive and inefficient methods is of great importance. One of the most efficient, technical and economic methods in this context is the use of magnetic adsorbent. These adsorbents have magnetic properties, and by using an external magnetic field can be easily separated from the solution. In magnetic separation, high costs of separation, such as centrifugation and filtration, are not included (Shen et al. 2009). Extensive researches in the field of magnetization of materials such as chitosan (Cho et al. 2012), silica (Shi et al. 2012), polymer (Dallas et al. 2006) and activated carbon (Mohan et al. 2011) have been conducted for water contaminant removal. Due to their high specific surface area and adsorption capacity, the use of this property in the nanoparticles is very good (Mak & Chen 2005; Nitayaphat & Jintakosol 2014, 2015). Nickel-zinc ferrites have drawn noticeable consideration from researchers as a result of their remarkable magnetic properties, large permeability, and very high electrical resistivity (Sharma et al. 2010). They have extensive potential applications such as high-density information storage devices, microwave devices, transformer cores, magnetic fluids, etc. (Virden & O’Grady 2005). The use of activated carbon to remove chlorine, separating gases and air pollution treatment recycling of heavy metals from aqueous solutions has many applications. However, because of the high cost, other options have been suggested as an alternative. Ash, due to the low cost of production, is a good alternative to activated carbon (Panday et al. 1985; Mane et al. 2005; Agrafioti et al. 2014; Vázquez-Rivera et al. 2015; Al Haddabi et al. 2016). Ashes can be produced from a wide range of carbon materials such as wood, coal, shell, walnut shell, fruit stones, agricultural waste, etc. (Banat et al. 2005).

In this context, we investigated the capability of the surface modified Ni0.5Zn0.5Fe2O4 magnetic nanoparticles with ash prepared from Acacia nilotica seed shell (Ni0.5Zn0.5Fe2O4/ANSA) as a low-cost adsorbent for removal of Pb(II) ions from aqueous solution, and also studied the adsorption mechanism of Pb(II) ions onto this adsorbent (Figure 1). For this purpose, a set of batch adsorption experiments (pH, contact time, adsorbent dosage and initial Pb(II) ion concentration, on Pb(II) ion removal using this adsorbent) were carried out to test optimum conditions. The characterization of the adsorbent was described by Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD) and scanning electron microscopy (SEM) analyses.

**MATERIALS AND METHODS**

Analytical-grade salt Pb(NO3)2 was obtained from Merck, Germany. A 1,000 mg/L stock solution of the salt was prepared in deionized water. All working solutions were prepared by diluting the stock solution with deionized water. Deionized water was prepared using a Millipore Milli-Q (Bedford, MA) water purification system. All reagents (Fe(NO3)3.9H2O, Zn(NO3)2.6H2O and Ni(NO3)2.6H2O, NaOH and HNO3) used in the study were of analytical grade and purchased from Aldrich, USA. Before each experiment, all glassware was cleaned with dilute nitric acid and repeatedly washed with deionized water. XRD analysis was carried out using a PAN analytical X’Pert Pro X-ray diffractometer. Surface morphology and particle size were studied using a Hitachi S-4800 SEM instrument. FT-IR spectra were determined as KBr pellets on a Bruker model 470 spectrophotometer. All the metal ion concentrations were measured with a Varian AA240FS atomic absorption spectrophotometer.
Experimental

The synthesis of Acacia Nilotica seed shell ash (ANSa)

The Acacia nilotica tree is grown in southern Iran. Acacia nilotica seed shells were collected from Bandar Abbas, Hormozgan, Iran, and were applied as a raw material for the preparation of surface modified adsorbent. The collected Acacia nilotica seed shells were washed and dried in an air oven at 80 °C for 24 h and were then ground and sieved to the desired particle size (2–3 mm). The resultant sieved powder was carbonized in a furnace at 700 °C at a heating rate of 10 °C/min for 2 h. The method for producing carbon materials was similar to other studies (Mane et al. 2013).

Synthesis of Ni0.5Zn0.5Fe2O4/ANSa

As described in Figure 1, Ni-Zn ferrite was initially prepared using stoichiometric ratios of metal nitrates and freshly extracted egg-white (Gabal et al. 2012). The metal nitrates (Fe(NO3)3·9H2O, Zn(NO3)2·6H2O and Ni(NO3)2·6H2O) and 2 g ANSA were dissolved together in a minimum amount of double distilled water to obtain a clear solution. Sixty mL of extracted egg-white was dissolved in 40 mL of double distilled water by vigorous stirring and was added to the nitrate mixture at ambient temperature. After constant stirring for 30 min, the resultant sol-gel was evaporated at 80 °C until dry precursor was obtained. The dried precursors were ground and calcined in a muffle furnace at 550 °C for 2 h.

Adsorption experiments

Batch adsorption of lead ions onto the adsorbent (Ni0.5Zn0.5Fe2O4/ANSa) was investigated in aqueous solutions under various operating conditions viz. pH 2–6, at a temperature of 298 K, for an initial Pb2+ ion concentration of 50 mg L−1. Approximately 0.05 g adsorbent was added to 50 mL of lead nitrate solution (50 mg L−1). Then the mixture was agitated on a shaker at 250 rpm. The initial pH values of the lead solutions were adjusted from 2 to 6 with 0.1 mol L−1 HNO3 or 0.1 mol L−1 NaOH solutions using a pH meter. After equilibrium, the samples were centrifuged and the adsorbent (Ni0.5Zn0.5Fe2O4/ANSa) was removed magnetically from the solution. The Pb(II) concentration in the supernatant was measured by a flame atomic absorption spectrometer. The effects of several parameters, such as contact time, initial concentration, pH and adsorbent dose on extent of adsorption of Pb(II) were investigated.

The Pb(II) removal percentage was calculated as:

\[
\text{%Removal} = \frac{C_0 - C_t}{C_0} \times 100
\]

where \(C_0\) and \(C_t\) (mg L\(^{-1}\)) are the concentration of Pb(II) in the solution at initial and equilibrium time, respectively.
The amount of Pb(II) adsorbed ($Q_e$) was calculated using the following equation:

$$Q_e = \frac{(C_0 - C_e)V}{m}$$  \hspace{1cm} (2)

where $C_0$ and $C_e$ are the initial and equilibrium concentrations of Pb(II) (mg L$^{-1}$), $m$ is the mass of adsorbent (g), and $V$ is the volume of solution (L).

**Adsorption isotherms**

Adsorption isotherms were obtained by using 0.05 g of adsorbent and 50 mL of lead nitrate solution with different concentrations (50–800 mg L$^{-1}$) at 298 K. These solutions were buffered at an optimum pH of 5 for adsorption and agitated on a shaker at 250 rpm until they reached adsorption equilibrium (20 min). The quantity of Pb(II) adsorbed was derived from the concentration change.

**Adsorption kinetics**

Experimental studies were carried out by shaking the adsorption mixture at various predetermined time intervals at the optimum conditions (Pb(II) ions concentration = 50 mg L$^{-1}$, pH 5.0, Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$/ANSA dose = 0.05 g, volume of sample = 50 mL at ambient temperature). The Pb(II) ion concentration in the solution for each contact time was measured using a flame atomic absorption spectrometer. The amount of Pb(II) ions adsorbed onto the Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$/ANSA at time $t$, $q_t$, was calculated by the following expression:

$$Q_t = \frac{(C_0 - C_t)V}{m}$$  \hspace{1cm} (3)

where $C_t$ is the concentration of Pb(II) ions in the solution at time $t$ (mg L$^{-1}$).

**RESULTS AND DISCUSSION**

**Characterization of Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$/ANSA magnetic nanoparticles**

Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ nanocrystallites were prepared according to the reported procedure by Gabal et al. (2012). Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$/ANSA nanocrystallites were characterized by FT-IR (Figure 2), XRD (Figure 3) and SEM (Figure 4). FT-IR spectra of Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$, Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$/ANSA and ANSA are compared in Figure 2. In the FT-IR spectrum of Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$/ANSA (Figure 2(a)), most of the bands of Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ (Figure 2(c)) and ANSA (Figure 2(b)), with a slight shift for some of them, are observable, which shows ANSA has been well supported on the Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$. The bands in the low-frequency region (1,000–500 cm$^{-1}$) due to the iron oxide skeleton, are in agreement with the magnetite spectrum. The peak at 1440.85 cm$^{-1}$ showed the existence of Fe–O (Pol et al. 2009). In Figure 2(a), the presence of –OH stretching mode is evident from the peak close to 3,446 cm$^{-1}$.

To confirm the Ni ferrite formation in the synthesized magnetic nanoparticles, the XRD spectrum of the sample was studied. The XRD patterns (Figure 3) show that Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ nanoparticles have a spinel structure, with all the major peaks matching the standard pattern of bulk Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ (JCPDS 08–0234). The particle size of adsorbent was investigated by the SEM technique. The SEM photograph of the sample (Figure 4) shows that the average size of Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$/ANSA is approximately less than 100 nm.

The magnetic properties of Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$/ANSA was evaluated by a vibrating sample magnetometer (VSM). As shown in Figure 5, the saturation magnetic moments of Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$/ANSA reached approximately 17 emu/g. It showed superparamagnetic behavior that would enable easy recovery of the adsorbent from solution under an applied magnetic field.

**Adsorption and removal of Pb(II) from aqueous solution**

**Effect of contact time**

The effect of contact time on the amount of lead adsorbed was studied at 50 mg L$^{-1}$. It can be observed from Figure 6 that with the increase of contact time, the percentage adsorptions also increased. Minimum adsorption was 94.9% for 5 min to a maximum adsorption value of 98.0% for 20 min. The adsorption characteristic indicated a rapid uptake of the lead. The adsorption rate, however, reduced to a constant value with an enhancement in contact time because all available sites were covered, and no active site was present for adsorbing.
Figure 2 | The FT-IR spectra of: (a) Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$/ANSA; (b) ANSA; (c) Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$. 
Effect of pH

The acidity of the aqueous solution applies a considerable effect on the adsorption process because it can affect the solution chemistry of contaminants and the state of functional groups on the surface of adsorbents (Ren et al. 2008; Zhou et al. 2009; Sheng et al. 2010). The effect of solution pH on Pb(II) adsorption was studied at pH 2–6 at 298 K. As
shown in Figure 7, the adsorption rate of Pb(II) enhances with increasing pH values from 2 to 6. However, at a pH value of 5.9, the Pb(II) ions begin to hydrolyze and then form a small quantity of Pb(OH)₂ or Pb(OH)₃ varieties (Huang et al. 2010). Compared with Pb(II) ions, these species are unfavorable for adsorption, which accounts for the small reduction in the adsorption capacity. Therefore, the maximum adsorption occurs at around pH 5.0 and it is therefore selected for all adsorption experiments in this study.

**Effect of adsorbent dosage**

The effect of change in the adsorbent amount on the process adsorption of Pb(II) was investigated, with different adsorbent doses in the range of 0.02–0.5 g. The results obtained are shown in Figure 7. From Figure 8, it is considered that as the adsorbent dose enhances, the percentage removal also increases, until it approaches a saturation point where the enhancement in adsorbent dose does not alter the percentage removal. An increase in adsorption rate with adsorbent quantity can be ascribed to increased surface area and the availability of more adsorption sites. The best removal of Pb(II) is about 94.8%, using
an adsorbent dosage of 0.05 g in 50 mL of 50 mg L\(^{-1}\) Pb(II) solution (1 g L\(^{-1}\)).

**Effect of initial Pb(II) concentration**

Batch adsorption experiments were performed at different initial Pb(II) concentrations (50, 100, 200, 400, 600 and 800 mg L\(^{-1}\)), at pH 5. An amount of 1 g/L of Ni\(_{0.5}\)Zn\(_{0.5}\)Fe\(_2\)O\(_4\)/ANSA was used for each adsorption experiment, with a contact time of 20 min. Figure 9 shows that the adsorption capacity of Pb(II) increases, but the removal percentage (%R) of Pb(II) decreases with the increase in initial concentration, indicating that the adsorption of Pb(II) on to Ni\(_{0.5}\)Zn\(_{0.5}\)Fe\(_2\)O\(_4\)/ANSA is highly related to the initial Pb(II) concentration. This observation can be described considering the fact that by increasing the initial Pb\(^{2+}\) concentration, more Pb\(^{2+}\) ions are available, while the amount of active sites on the adsorbent is constant which leads to a decrease in %R. The maximum removal of Pb(II) was attained at 50 mg/L of lead solution.

**Adsorption isotherms**

Isotherms study can explain how an adsorbate interacts with an adsorbent. The experimental data were examined by Langmuir, Freundlich and Dubinin–Radushkevich (D–R) models, as shown in Table 1.

![Figure 9](image-url)  
*Figure 9* | Effect of initial Pb(II) concentration on the removal percentage of Pb(II) in blue and adsorption capacity, \(q_e\) (mg/g) in red (adsorbent dose = 1 g L\(^{-1}\), pH = 5, contact time = 20 min. and T = 25 °C). The full colour version of this figure is available in the online version of this paper, at [http://dx.doi.org/10.2166/wrd.2016.073](http://dx.doi.org/10.2166/wrd.2016.073).

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Langmuir, Freundlich, D–R isotherm constants for the adsorption of Pb(II) ions onto Ni(<em>{0.5})Zn(</em>{0.5})Fe(_2)O(_4)/ANSA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>(q_m) (mg g(^{-1}))</td>
</tr>
<tr>
<td>37.6</td>
<td>0.042</td>
</tr>
<tr>
<td>Freundlich</td>
<td>(1/n)</td>
</tr>
<tr>
<td>0.45</td>
<td>2.921</td>
</tr>
<tr>
<td>Dubinin–Radushkevich (D–R)</td>
<td>(q_m) (mg g(^{-1}))</td>
</tr>
<tr>
<td>24.8</td>
<td>(3 \times 10^{-6})</td>
</tr>
</tbody>
</table>

The Langmuir isotherm model, which defines a monolayer adsorption, is given in Equation (4):

\[
\frac{1}{q_e} = \frac{1}{K_Lq_m C_e} + \frac{1}{q_m}
\]

where \(q_e\) = the amount of Pb\(^{2+}\) adsorbed per unit mass at equilibrium (mg g\(^{-1}\)), \(q_m\) = the maximum amount of adsorbent that can be adsorbed per unit mass adsorbent (mg g\(^{-1}\)), \(C_e\) = concentration of adsorbent (in the solution at equilibrium (mg L\(^{-1}\)), \(K_L\) = adsorption equilibrium constant.

A plot of \(1/q_e\) versus \(1/C_e\) gives a straight line, with a slope of \(1/K_Lq_m\) and intercept \(1/q_m\).

The main characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor \(R_L\) that is given by Equation (5) (Hall *et al.* 1966):

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

where \(C_0\) is the highest initial concentration of adsorbate (mg L\(^{-1}\)), and \(K_L\) (L mg\(^{-1}\)) is the Langmuir constant. The value of \(R_L\) shows the shape of the isotherm to be either unfavorable \((R_L > 1)\), linear \((R_L = 1)\), favorable \(0 < R_L < 1\), or irreversible \((R_L = 0)\). The \(R_L\) values between 0 and 1 indicate favorable adsorption. In this study, the value of \(R_L\) is 0.029 and shows the favorable adsorption between Ni\(_{0.5}\)Zn\(_{0.5}\)Fe\(_2\)O\(_4\)/ANSA and Pb(II).

The Freundlich isotherm is expressed by Equation (6). This isotherm model defines a heterogeneous adsorption with different surface energy sites and assumes the change
of uptake with exponential distribution of adsorption sites and energies (Chen et al. 2013; Hou et al. 2011; Kerkez & Bayazit 2014):

\[
\log q_e = \log K_F + \frac{1}{n} \log C_e
\]  

(6)

where \( C_e \) (mg L\(^{-1}\)) and \( q_e \) (mg \( g^{-1}\)) are the equilibrium concentration of adsorbent in the solution and the amount of adsorbent adsorbed at equilibrium, respectively; \( K_F \) (mg\(^{1-(1/n)}\) L\(^{1/n}\) g\(^{-1}\)) and \( n \) are the Freundlich constant, which indicate the adsorption capacity for the adsorbent and adsorption intensity, respectively.

A plot of \( \log q_e \) versus \( \log C_e \) gives a straight line of slope \( 1/n \) and intercept \( \log K_F \). The value of \( 1/n \) indicates the adsorption intensity and the type of isotherm to be favorable (0.1 \( < \) \( 1/n < 0.5 \)) or unfavorable (\( 1/n > 2 \)). The Freundlich parameter, \( 1/n \), is related to the adsorption intensity of the adsorbent. When 0.1 \( < \) \( 1/n \) \( \leq \) 0.5, the adsorption of the adsorbate is easy; when 0.5 \( < \) \( 1/n \) \( \leq \) 1, there is a difficulty with the adsorption; when \( 1/n > 1 \), it is quite difficult to adsorb (Luo & Zhang 2009; Samiee & Goharshadi 2014).

In our study, the value of \( 1/n \) (0.45) shows the favorable adsorption of Pb(II) on Ni\(_{0.5}\)Zn\(_{0.5}\)Fe\(_2\)O\(_4\)/ANSA. In our study, the value of \( 1/n \) (0.45) shows the favorable adsorption of Pb(II) on Ni\(_{0.5}\)Zn\(_{0.5}\)Fe\(_2\)O\(_4\)/ANSA.

In order to discern between physical and chemical adsorption, the sorption data were analyzed using the D–R equation, which is shown in Equation (7):

\[
\ln q_e = \ln q_m - \beta e^2
\]  

(7)

where \( \beta \) is a constant related to the mean energy of adsorption (mol\(^2\) kJ\(^{-1}\)), \( q_m \) is the maximum adsorption capacity of metal ions (mg \( g^{-1}\)), \( e \) is the Polanyi potential given by Equation (8):

\[
e = RT \ln \left( 1 + \frac{1}{C_e} \right)
\]  

(8)

where \( R \) is the gas constant (8.314 J mol\(^{-1}\) K\(^{-1}\)) and \( T \) is the temperature (K). By plotting \( \ln q_e \) versus \( e^2 \) with experimental data, a straight line is obtained. From the intercept and slope, the values of \( q_m \) and \( \beta \) are determined. With the value of \( \beta \), the mean energy \( E \), which is the free energy transfer of one mole of solute from infinity to the surface of adsorbent, can be obtained by Equation (9):

\[
E = \frac{1}{\sqrt{2\beta}}
\]  

(9)

For \( E < 8 \) kJ mol\(^{-1}\), the adsorption process might be performed physically, while chemical adsorption may occur when \( E > 8 \) kJ mol\(^{-1}\) (Tan et al. 2012).

All the parameters are listed in Table 1. From Table 1, in which the Langmuir, Freundlich, D–R isotherm constants for the adsorption of Pb(II) are summarized, it can be derived from \( R^2 \) that the Langmuir model matches the experimental data better than Freundlich and D–R models. Moreover, it is clear that the adsorption of Pb(II) by Ni\(_{0.5}\)Zn\(_{0.5}\)Fe\(_2\)O\(_4\)/ANSA may be explained as a physical adsorption process as the value of \( E \) is 0.408 kJ.

The adsorption capacity is a significant parameter which determines the performance of an adsorbent. Table 2 compares the maximum adsorption capacity of Ni\(_{0.5}\)Zn\(_{0.5}\)Fe\(_2\)O\(_4\)/ANSA for Pb(II) adsorption with that of other adsorbents in the literature.

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>( q_m ) (mg/g)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Modified agricultural waste</td>
<td>166.67</td>
<td>Senthil Kumar et al. (2013)</td>
</tr>
<tr>
<td>Hazelnut husk</td>
<td>109.90</td>
<td>Imamoglu et al. (2016)</td>
</tr>
<tr>
<td>Olive waste</td>
<td>6.57</td>
<td>Blázquez et al. (2010)</td>
</tr>
<tr>
<td>Magnetically modified tea</td>
<td>44.50</td>
<td>Lucia et al. (2014)</td>
</tr>
<tr>
<td>Bael leaves</td>
<td>104.00</td>
<td>Chakravarty et al. (2010)</td>
</tr>
<tr>
<td>Marine green algae</td>
<td>15.62</td>
<td>Jeyakumar &amp; Chandrasekaran (2014)</td>
</tr>
<tr>
<td>Tourmaline</td>
<td>108</td>
<td>Wang et al. (2011)</td>
</tr>
<tr>
<td>Amino-functionalized Fe(_3)O(_4) magnetic nano-particles</td>
<td>40.10</td>
<td>Tan et al. (2012)</td>
</tr>
<tr>
<td>Fe(_3)O(_4)@SiO(_2)–NH(_2)</td>
<td>243.90</td>
<td>Zhang et al. (2013)</td>
</tr>
<tr>
<td>Waste maize bran</td>
<td>142.86</td>
<td>Singh et al. (2006)</td>
</tr>
<tr>
<td>Rice husk ash</td>
<td>91.74</td>
<td>Naiya et al. (2009)</td>
</tr>
<tr>
<td>Corncob</td>
<td>43.40</td>
<td>Tan et al. (2010)</td>
</tr>
<tr>
<td>Ni(<em>{0.5})Zn(</em>{0.5})Fe(_2)O(_4)/ANSA</td>
<td>37.60</td>
<td>This study</td>
</tr>
</tbody>
</table>
Adsorption kinetics

In this study, pseudo-first-order and pseudo-second-order kinetics models were used to test the controlling mechanism of Pb(II) adsorption from aqueous solutions. Adsorption equilibrium was reached in 20 min (Figure 5). The linear form of the pseudo first-order model and pseudo second-order kinetics model can be explained as shown in Equations (10) and (11), respectively:

\[
\ln\left(\frac{q_e}{q_t}\right) = -kt
\]

(10)

\[
\frac{t}{q_t} = \frac{1}{k_2q_e} + \frac{t}{q_e}
\]

(11)

where \( q_e \) and \( q_t \) are the adsorption capacities at equilibrium and at time \( t \) (min) respectively. \( k_1 \) (min\(^{-1}\)) and \( k_2 \) (g/(mg.min)) are the pseudo first-order and pseudo second-order rate constants respectively (Ho 2006). The equilibrium experimental results did not conform well to the pseudo first-order model (Table 3). The values of \( q_e \) and \( k_2 \) can be calculated from the slope and intercept of the plot of \( t/q_t \) versus \( t \). The results listed in Table 3 show that the correlation coefficient is very high (\( R^2 = 0.999 \)). Moreover, the calculated equilibrium adsorption capacity was consistent with the experimental results. These results indicated that the kinetics data were better described with a pseudo second-order kinetics model.

CONCLUSIONS

Ni\(_{0.5}\)Zn\(_{0.5}\)Fe\(_2\)O\(_4\)/ANSA magnetic nanoparticles were used in adsorption of Pb(II) ions from aqueous systems and the maximum Pb(II) adsorption occurred at pH 5 with a maximum adsorption capacity of 37.6 mg g\(^{-1}\) at 25°C. The adsorbent was characterized by FT-IR, SEM, XRD and VSM. These results show ANSA has been supported well on the Ni\(_{0.5}\)Zn\(_{0.5}\)Fe\(_2\)O\(_4\). The XRD patterns show that Ni\(_{0.5}\)Zn\(_{0.5}\)Fe\(_2\)O\(_4\) nanoparticles have a spinel structure, with all the major peaks matching the standard pattern of bulk Ni\(_{0.5}\)Zn\(_{0.5}\)Fe\(_2\)O\(_4\). The SEM photograph of samples shows that the average size of Ni\(_{0.5}\)Zn\(_{0.5}\)Fe\(_2\)O\(_4\)/ANSA is approximately less than 100 nm. The VSM curve shows superparamagnetic behavior of Ni\(_{0.5}\)Zn\(_{0.5}\)Fe\(_2\)O\(_4\)/ANSA. The adsorption isotherm fitted the Langmuir model well, and the kinetic adsorption showed that the pseudo-second-order rate equation characterized the kinetic curves better than the pseudo-first-order rate equation. The prepared magnetic adsorbent can be well dispersed in the aqueous solution and easily separated from the solution with the aid of an external magnet after adsorption. The process of water treatment described here is clean and safe using the magnetic nanoparticles. Thus, this adsorbent was found to be useful and valuable for controlling water pollution due to Pb(II) ions.

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REFERENCES


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