Preparation and characterization of a new sawdust/MNP/PEI nanocomposite and its applications for removing Pb (II) ions from aqueous solution

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ABSTRACT

A new sawdust/magnetite nanoparticles/polyethyleneimine (SD/MNP/PEI) nanocomposite was synthesized by grafting polyethyleneimine (PEI) to magnetic sawdust. Features of SD/MNP/PEI were characterized using Fourier transform infrared spectroscopy (FT-IR) and X-ray diffraction (XRD), vibrating sample magnetometer (VSM) and scanning electron microscopy (SEM). SD/MNP/PEI was used as an adsorbent for the removal of lead (Pb (II)) from aqueous solution. The effects of independent variables including pH of solution, adsorbent dose and contact time were performed and adsorption isotherms were obtained. Experimental results show that priority effective variables were pH and the amount of nanocomposite, and it was found that the sorption capacity increases with the increasing phase contact time. The adsorption process followed the Langmuir adsorption isotherm. Although SD and SD/MNP do not show a high affinity for the adsorption of Pb (II) in aqueous media, polyethyleneimine cross-linked on SD/MNP showed 40 and 66% increases, respectively, in the adsorption of Pb (II) compared to the SD and SD/MNP. It was found that SD/MNP/PEI removes more efficiently lead ions from aqueous solutions than the SD, SD/MNP. Desorption of the lead from the SD/MNP/PEI was conducted. It was proved that SD/MNP/PEI has excellent properties and can be used as a sorbent of multi-use.

Key words | magnetic nanoparticle, Pb (II), polyethyleneimine, sawdust

INTRODUCTION

Energy cycle and yield in food production and heavy metal pollution has always been a major cause of contamination of the environment and is considered as a major concern for food health. There are several methods for optimization (Sefeedpari et al. 2016; Hosseinzadeh-Bandbafha et al. 2018; Nabavi-Pelesaraci et al. 2018) and modeling of food and related cycles. Recently, various models of mathematical, statistical, computer and artificial intelligence have been used by researchers to protect the environment (Olyaie et al. 2015; Alizadeh et al. 2017; Najafi et al. 2018).

Today, people introduce various notorious toxic heavy metals, dyes, organics and pharmaceuticals into the ecosystem in many ways such as via household products, municipal sewage, industrial wastewaters, mineral weathering, underground toxic waste disposal into streams, lakes, rivers, and seas, thus making water bodies the sinks (Gupta et al. 2015; Hu et al. 2018).

The lead ion, Pb (II), is one of the highly toxic heavy metal ions in the environment. Lead exists intensively in the waste waters of many industries, such as storage batteries, mining, metal plating, painting, smelting, ammunition, oil refining and ceramic glass. Lead has both acute and chronic effects in humans. Toxicity of lead may cause anemia, headache, chills and reduction in hemoglobin formation. The most important health problem of lead poisoning is that it may cause severe damage to the kidneys, nervous system, reproductive system, liver and brain (Googerdchian et al. 2018). The permissible limit for Pb (II) in drinking water is 0.015 mg L$^{-1}$ according to the current US Environmental Protection Agency (EPA) standard (Samuel et al. 2018). Its treatment and removal have received considerable attention because of its significant threat to both human health and the environment (Bertagnolli et al. 2016). Many methods have been used for heavy metal analysis,
such as flame atomic absorption spectrometry (FAAS), and inductively coupled plasma atomic emission spectrometry (ICP-AES). To improve the detection limits and selectivity of FAAS, several preconcentration–separation procedures including ionic liquid dispersive liquid–liquid micro extraction (Soylak & Yilmaz 2011), ionic liquid-linked dual magnetic micro extraction (Yilmaz & Soylak 2013) and solid-phase extraction (Ghaedi et al. 2015) were studied.

Numerous methods have been reported for the removal of Pb (II), mainly including chemical treatment, reverse osmosis, coagulation and flocculation, ion exchange, oxidation, membrane separation, chemical precipitation and adsorption (Yang et al. 2018). Among these, adsorption is the most frequently studied method, proving its advantage over other methods due to its high efficiency, low operating cost, easy handling and lower production of chemical or biological sludge. Adsorption technology can efficiently remove toxic materials from the liquid phase, and chemical surface treatments of adsorbents can significantly enhance the selectivity and capacity of substrates. Use of reliable and low-cost absorbent is an effective method to remove all types of contaminants including heavy metals and organic pollutants (Ali et al. 2016; Yang et al. 2018). Natural materials have many advantages and they have high potential to be used as absorbents for heavy metals removal. Many agricultural and forest waste products have been studied for effluent treatment as an absorbent. Novel approaches include the use of sawdust modified by magnetite nanoparticles for removal of cadmium (Shah et al. 2016). Modification of sawdust by chemical material can improve this action.

Polyethyleneimine (PEI) is a synthetic polymer that finds many applications in products like cosmetics, detergents, gene delivery, adhesives, and water treatment agents. Polyethyleneimine (PEI) is a water-soluble chelating polymer, which contains amine groups. Several papers have reported methods including covalent bonding (Chen et al. 2015), electrostatic interactions (Hu et al. 2014), layer-by-layer self-assembly (Wang et al. 2011) and emulsion polymerization (Pimpha et al. 2012) for the preparation of polymer-modified magnetite nanoparticles. Modification of magnetite nanoparticles with polymeric reagents not only enables surface functional groups but also provides a porous network. In this context, polyethyleneimine has been used as a good absorbent for heavy metals and organic pigments (Ma et al. 2016b). Polyethyleneimine is used for the selective adsorption of heavy metals (Saad et al. 2013). To increase efficiency, selectivity and the ability for removal, polyethyleneimine is stabilized on different bases, such as magnetite nanoparticles (Sui et al. 2015), ethy cellulles (Qiu et al. 2014), halloysite nanotubes (Tian et al. 2015) and so on.

Recently, iron oxide nanoparticles (NPs) have attracted much consideration due to their unique properties, such as surface-to-volume ratio, greater surface area, super paramagnetism and easy separation methodology. Due to these applications, we decided to study MNPs here. Magnetizing the sawdust and the resulting synthesized nanocomposite by MNPs would make easy separation of the adsorbent from the solution, increasing process speed and consequently better absorbent performance. The polymeric nanoparticles can be prepared via two different strategies including (a) magnetite nanoparticles (Fe3O4) coating with a layer of polymer and (b) Fe3O4 nanoparticles precipitated in the presence of a porous polymer. The aim of this study for the first time was synthesis of a new PEI functional magnetic sawdust nanocomposite; its characterization and application for Pb (II) removal is reported. Investigation and comparison of SD, SD/MNP and SD/MNP/PEI efficiency for the removal of Pb (II) ions from aqueous solution in a batch system were performed. At the next stage, investigation of the effectiveness of various operating factors such as adsorbent dose, contact time and solution pH on the sorption of Pb (II) were carried out. Also a desorption study of Pb (II) ions from SD/MNP/PEI was conducted. The desorption operation was carried out by HCl. Analysis of the effects of the process parameters on Pb (II) ions removal was studied and isotherm models were used for investigation of the adsorption mechanism.

**MATERIALS AND METHODS**

**Chemicals**

Sawdust (with a mesh of 470 μm) was prepared from Poplar tree. Polyethyleneimine (PEI, Mw = 2,000 gmol−1) was purchased from Sigma Aldrich. Other chemical reagents used in this work including ferric chloride hexahydrate (FeCl3.6H2O, 98%), ferrous sulfate heptahydrate (FeSO4.7H2O), ammonia solution (25%), epichlorohydrin (EPC), sodium bicarbonate (NaHCO3), sodium hydroxide (NaOH) and lead (II) nitrate (Pb(NO3)2, 99.5%) were purchased from Merck. A stock solution of 1,000 mg L−1 was prepared by dissolving appropriate amounts of Pb (NO3)2 in deionized water. Working solutions ranging from 5 to 50 mg L−1 of Pb (II) was prepared by diluting the stock
solution. The pH values of the prepared solutions were adjusted using 0.1 mol L$^{-1}$ of HNO$_3$ and NaOH.

**Preparation of magnetic sawdust**

Poplar sawdust was first washed with distilled water in order to remove any dust or impurities and then dried at a temperature of about 60 °C for 5 h in an air circulating oven. In order to have uniform modification and reproducible results, sawdust particles were sieved to pass through a 470 μm standard sieve, and stored in an airtight bottle before treatment.

Nanoparticle-loaded sawdust (SD-MNP) was prepared by modified co-precipitation method (Gupta & Nayak 2012; Shah et al. 2014). Briefly, 6.3 g of FeCl$_3$·6H$_2$O and 4.2 g of FeSO$_4$·7H$_2$O was dissolved in 200 mL of distilled water and mechanically stirred at 80 °C under a nitrogen atmosphere. Black precipitates of MNP were formed when 20 mL of 25% ammonia solution was added. For loading of MNP on sawdust, 10 g of SD was added to the solution at 80 °C for 60 min under vigorous stirring. The resultant SD-MNP was separated by a magnet, washed with distilled water until the pH of the filtrate became neutral, and dried in the oven at 70 °C.

**SD/MNP/PEI nanocomposite**

The dried SD-MNP was steeped in epichlorohydrin (5 mL) and NaOH (1.4 M, 10 mL) and stirred for 2 h at 60 °C. The obtained raw product was subsequently rinsed with NaOH (1.4 M, 50 mL) and distilled water (50 mL). The epoxidized SD/MNP was added to a solution of NaHCO$_3$ (50 mM, pH 9, 50 mL) and PEI (2 mM). The reaction system was incubated for 5 h with gentle stirring at 65 °C. The grafted nanocomposite was sequentially rinsed with NaHCO$_3$ and distilled water and dried in vacuum at 40 °C (Ma et al. 2016a) (Figure 1).

**Characterization**

The X-ray diffraction pattern of the nanocomposite was examined by a Philips PW-1730 diffractometer using a Cu Kα radiation ($\lambda = 0.1540$ Å) in the range of 10–90° (20) (X-ray powder diffraction (XRD)). The size and morphology of the described synthesized particles were determined by a scanning electron microscope (SEM, MIRA3, TESCAN). Energy dispersive X-ray spectroscopy (EDX) was used to determine the elemental composition of the nanocomposite utilizing a TESCAN detector. The functional groups and surface elemental of SD, SD/MNP, SD/MNP/PEI were characterized by Fourier transform infrared spectrometer (Perkin Elmer Spectrum RX I). The magnetization and hysteresis loop were measured at room temperature with a vibrating sample magnetometer (VSM, Meghnatis Kavir Kashan Co, Kashan). Pb$^{2+}$ analysis was carried out by using a Varian AA-220 atomic absorption spectrophotometer.

**Batch adsorption experiment**

For the removal of Pb (II) ions, 0.2 g of SD/MNP/PEI nanocomposite was added into 50 mL conical flasks of Pb (II) solutions with initial ion concentrations (C$_0$) of 5 (mg L$^{-1}$). In order to investigate the optimum pH, the values were varied between 2 and 11. The solutions were agitated (60 rpm) at a temperature of 25 °C in contact

![Figure 1](https://iwaponline.com/wst/article-pdf/78/12/2469/525241/wst078122469.pdf)
times of 0–180 min. Finally, the adsorbent was separated from the solution using a permanent magnet.

The amount of Pb (II) adsorbed onto SD/MNP/PEI and the removal efficiency were calculated by the following equations:

\[ q_e = \frac{V}{M} (C_0 - C_e) \]

Removal efficiency(%) = \( \frac{C_o - C_e}{C_o} \times 100 \)

where \( C_0 \) and \( C_e \) (mg L\(^{-1}\)) are the initial and equilibrium concentrations of contaminants respectively. \( q_e \) (mg g\(^{-1}\)) is the adsorbed amount of adsorbate per unit mass of the adsorbent at equilibrium. \( V \) (L) is the volume of adsorption solution, \( M \) (g) is the mass of adsorbent (Googerchian et al. 2018).

**Adsorption isotherms**

The equilibrium sorption isotherm is important in the sorption systems for the evaluation of the metal uptake mechanism and capacity. An adsorption isotherm represents the relationship of the amount of species adsorbed by a unit mass of adsorbent with the concentration of adsorbent remaining in the medium at equilibrium. The adsorption mechanism was described using Freundlich, Langmuir, Tempkin and adsorption isotherm models. The Freundlich isotherm is generally used to describe a heterogeneous adsorption surface with active sites of different energies. The linearized form of the Freundlich isotherm is given as:

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

In which \( q_e \) is the amount of metal ions adsorbed at equilibrium (mg g\(^{-1}\)), \( C_e \) is the equilibrium concentration of metal ions (mg g\(^{-1}\)). The \( n \) and \( K_f \) are the Freundlich constants related to the intensity parameter and the relative adsorption capacity of the adsorbent. The values of \( n \) and \( K_f \) were calculated from the slope \((1/n)\) and intercept \((\log K_f)\) of the plot \( \log q_e \) versus \( \log C_e \). Values of \( n \) greater than 1 show a good adsorption process.

The Langmuir isotherm assumes monolayer coverage of adsorbate on the outer surface of the adsorbent without interactions. The Langmuir isotherm can be expressed as:

\[ \frac{C_e}{q_e} = \frac{1}{(bq_m)} + \frac{C_e}{q_m} \]

where \( q_m \) is the maximum monolayer adsorption capacity (mg g\(^{-1}\)) and \( b \) is the constant of Langmuir related to the affinity of binding sites; it is a measure of the energy of adsorption. The values of \( q_m \) and \( b \) have been evaluated from the intercept and slope of linear plot of \( C_e/q_e \) versus \( C_e \). The essential characteristics of Langmuir isotherm can be explained using a dimensionless constant, \( R_L \), known as the separation factor, which is calculated using the following equation:

\[ R_L = \frac{1}{1 + bC_0} \]

where, \( C_0 \) (mg L\(^{-1}\)) is the initial liquid phase concentration of analyte and \( b \) is the Langmuir adsorption constant (L mg\(^{-1}\)). The \( R_L \) value describes the adsorption process to be unfavorable \((R_L > 1)\), linear \((R_L = 1)\), favorable \((0 < R_L < 1)\) or irreversible \((R_L = 0)\) (Ali et al. 2011).

The Tempkin isotherm is employed to describe the effects of indirect adsorbent/adsorbate interactions. The Tempkin isotherm can be expressed as:

\[ q_e = BlnA + BlnC_e \]

\[ B = \frac{RT}{b_t} \]

In which \( R \) is the ideal gas constant \((8.3134 \text{ J mol}^{-1}\text{ K}^{-1})\), \( T \) is the temperature (K), \( b_t \) is the heat of adsorption (kJ mol\(^{-1}\)), and \( A \) is the equilibrium binding constant (L g\(^{-1}\)). The values of \( b_t \) and \( A \) were obtained from the slope and intercept of the plot of \( q_e \) versus \( \ln C_e \).

**RESULTS AND DISCUSSION**

**Characterization of SD/MNP/PEI**

**FT-IR characterization**

Modification of sawdust by magnetic nanoparticles and the PEI functionalization was proved by the FT-IR spectra (Figure 2). For SD/MNP, the peak at 1,057 cm\(^{-1}\) belongs to the ether C–O–C asymmetric stretching vibration. The aromatic C–H stretch adsorption peak from lignin 2,964 cm\(^{-1}\) appears in both SD/MNP and SD/MNP/PEI samples. The bands at 1,635 and 1,515 cm\(^{-1}\) respectively related to bending and stretching C = C groups in alkene and aromatic (Setyono & Valiyaveettil 2014). The band
around 1,740 cm\(^{-1}\) might be assigned to the carbonyl (C=O) stretching vibration. For SD/MNP, the peak around 550–620 cm\(^{-1}\) belongs to the Fe–O vibration band from the magnetite phase and the same peak also appear in the spectrum of SD/MNP and SD/MNP/PEI, indicating that the main component of the samples was the same. The peaks at 2,861 and 2,890 cm\(^{-1}\) associated with C–H stretching vibration of methyl and methylene group were present in magnetic sawdust carbon. The absorption peaks in the range 1,500–1,300 cm\(^{-1}\) were attributed to C–H stretching vibration of methyl and methoxy groups.

SD/MNP and SD/MNP/PEI exhibited a broad peak between 3,200 and 3,500 cm\(^{-1}\) corresponding to different hydroxyl groups. In contrast, alone Fe\(_3\)O\(_4\) NPs display a weak absorption band at 3,449 cm\(^{-1}\), which may be assigned to the O–H stretching and bending vibrations of physically adsorbed H\(_2\)O and the surface –OH groups of the NPs (Wu \textit{et al.} 2017). After PEI grafting, new bands appeared at 1,470 cm\(^{-1}\) and 1,590 cm\(^{-1}\), which are ascribed to the N–H in-plane bending vibrations. The adsorption bands at 2,923, 2,851 cm\(^{-1}\) for SD/MNP/PEI could be attributed to the CH\(_2\) groups of PEI and the band at 1,129 cm\(^{-1}\) is due to the stretching vibration of the C–N bond, demonstrating that PEI was coated on the surface of SD/MNP successfully (Cai \textit{et al.} 2015; Zhu \textit{et al.} 2017).

**XRD patterns**

An XRD pattern is a plot of the intensity of X-rays scattered at different angles by a sample. The XRD pattern is a fingerprint that lets you figure out what is in your sample. And experimental XRD data are compared to reference patterns to determine what phases are present. The XRD patterns of MNP, SD/MNP and SD/MNP/PEI are shown in Figure 3. The diffraction peak of cellulose (related to sawdust) is located at 2\(\theta\) = 23° (Musapatika \textit{et al.} 2012). For the MNP pattern, the position and relative intensity of all the diffraction peaks (2\(\theta\) = 55.71°, 43.2°, 55.9°, 57°, 63°) suitably matched those of standard MNP (Fe\(_3\)O\(_4\)) (Zeng \textit{et al.} 2007). Therefore, XRD confirmed MNP was coated...
on sawdust. Intensity of 455, 264 and 237 diffraction peaks of magnetite at 35.71° respectively related to MNP, SD/MNP and SD/MNP/PEI, which implies attachment of nanoparticles on the SD and SD/PEI matrix. After PEI modification of SD/MNP, no more new diffraction peaks were observed.

The diffraction peak at 23° in SD/MNP and SD/MNP/PEI is corresponding to the cellulose structure of sawdust. The obtained XRD spectra of SD/MNP and SD/MNP/PEI illustrated low intensity and some noise that may be due to the presence of the sawdust carbon. The XRD patterns indicate that the structures of the MNP are preserved after coating with PEI.

SEM

SEM is an important technique for visual confirmation of the physical nature of the surface and morphology. The SEM images of SD particles, MNPs, SD/MNP and SD/MNP/PEI are given in Figure 4.

Figure 4(a) shows the heterogeneous, porous surface morphology of SD particles. Sawdust is mainly exhibited as small shreds of fibre sheet with a ragged surface. Figure 4(b) shows the spherical morphology of MNP; these Fe₃O₄ nanoparticles are spherical in shape and Figure 4(c) shows a morphology of SD/MNP similar to MNP with more uniformity. Figure 4(d) shows the morphology of SD/MNP/PEI similar to those of SD/MNP but with a much smoother surface. The heterogeneous, porous surfaces in sawdust were covered by MNP. It is clear from the SEM images that the surface morphology of SD/MNP changed after modification with PEI. Particle size in SD/MNP is more homogenous compared with SD/MNP/PEI. SD/MNP diameters are in the range of 25 to 50 nm and for SD/MNP/PEI are in the range of 30 to 60 nm. Due to the physical changes in the reaction process and attaching polyethyleneimine on the surface of SD/MNP, variation of particle size was observed. The SEM images of SD/MNP/PEI beads showed an almost spherical surface and enough monodispersity. The surface of the SD/MNP beads has a tighter structure compared with SD/MNP/PEI beads.

EDX

To further ascertain the main chemical compositions of SD/MNP and SD/MNP/PEI they were examined by EDX and the results are shown in Table 1.

It could be seen that the main compositions of SD/MNP/PEI were Fe, O, C and N elements. Composition of SD/MNP included C, O, and Fe. The content of N element is higher for SD/MNP/PEI than SD/MNP, which clearly demonstrated the presence of nitrogen in SD/MNP/PEI in comparison to SD/MNP.
A VSM is a scientific instrument that measures magnetic properties. VSM measures the magnetization of a small sample of magnetic material placed in an external magnetizing field by converting the dipole field of the sample into an AC electrical signal. Magnetic measurements for MNP, SD/MNP and SD/MNP/PEI were performed using VSM. The typical room temperature magnetization curves of bare MNP, SD/MNP and SD/MNP/PEI samples are shown in Figure 5. The saturation magnetizations (Ms) of MNP, SD/MNP and SD/MNP/PEI are 46.5, 37 and 3.1 emu g⁻¹, respectively. Results of VSM analysis prove that SD/MNP/PEI had typical magnetite behavior.

The reported data for the neat MNP would be decreased when the MNP is presented in sawdust. Also, decreasing could be observed when it was coated with the PEI layer. The decrease in saturation magnetization of the nanocomposite is due to the lower content of magnetic compound, the contribution of the non-magnetic PEI layer on the surface of MNP and the smaller size of Fe₃O₄ nanoparticles (Arabi et al. 2016; Fan et al. 2016; Guo et al. 2017). Although the specific saturation magnetization values of the SD/MNP/PEI have decreased, they could still be efficiently separated from solution with a permanent magnet (Liu et al. 2012).

**Effect of pH**

pH is a critical parameter because it affects the degree of ionization and speciation of adsorbate during a reaction, the surface charge of the adsorbent and the formation of metal complexes. The influence of the pH on the adsorption capacity of Pb (II) was studied in the pH range from 2 to 12 and the results are shown in Figure 6. It can be seen that the adsorption capacity of Pb (II) improved remarkably when increasing the pH from 2 to 11 and then remained unchanged. At low pH values, highly protonated amino groups can strongly act with cations via electrostatic forces and high H⁺ might compete with Pb (II) for active binding sites. When the pH increased, the protonated degree of the adsorbent and competition of H⁺ decreased and amino groups could chelate with Pb (II) easily and strongly, which created increasing adsorption capacity and was in agreement with the zeta potential results (Gao et al. 2006). The result depicts that removal% increased steadily up to pH 6.5; after pH 7, it was more or less the same. The cumulative effect of adsorption and precipitation has enhanced the removal efficiency at higher pH values. Therefore, to ensure true adsorption, all kinetics experiments were carried out at pH 7.
Effect of contact time

The effect of time on the removal of metal ions by SD/MNP/PEI was studied. Figure 7 shows the removal of Pb (II) with contact time. The result shows that the removal of Pb (II) increased as the contact time increased. It is clear that the removal efficiency of lead ions reached a maximum value after 80 min and then no further significant increase was observed for contact times of up to 3 h. This may be due to the fact that initially all adsorbent sites were vacant and the solute concentration gradient was high. Therefore, based on these results, a contact time of 80 min was selected in subsequent isotherm studies.

Effect of adsorbent dose

The effect of adsorbent dose on the adsorption of Pb²⁺ was studied at contact time of 80 min for an initial heavy metals concentration of 5 mg L⁻¹. The maximum adsorption of heavy metals was obtained for the adsorbent dose of 0.2 g (Figure 8). However, it is observed that after a dosage of 0.2 g, there was no significant change in percentage adsorption of Pb²⁺. It may be due to the overlapping of active sites at a higher dosage. There is a decrease in the effective surface area resulting in the conglomeration of adsorbent sites (Rahmani et al. 2010). Therefore 0.2 g was considered as an optimum dose.

Adsorption studies

Linear regression of Freundlich, Langmuir and Temkin isotherm models were performed for Pb (II) adsorption on SD/MNPs/PEI nanocomposite. The obtained Freundlich, Langmuir and Temkin fitted curves, parameters of adsorption and the correlation coefficients R² are shown in Table 2, respectively. Comparing R² values evidently indicated that
the Langmuir model possessed the best fit with the experimental equilibrium data. Therefore it is assumed that a monolayer of the Pb\(^{2+}\) is adsorbed on the heterogeneous surface of the SD/MNPs/PEI nanocomposite. \(R_L = 0.0485\) indicated the adsorption process to be favorable (0 < \(R_L\) < 1). The Freundlich model was investigated for adsorption capacity (\(K_f\)) and adsorption strength (\(n\)). If \(n = 1\) then the partition between the two phases is independent of the concentration. If the value of 1/\(n\) is below one it indicates a normal adsorption. On the other hand, 1/\(n\) being above one indicates cooperative adsorption. However, \(K_f\) and \(n\) are parameters characteristic of the sorbent-sorbate system, which must be determined by data fitting and whereas linear regression is generally used to determine the parameters of kinetic and isotherm models. Specifically, the linear least-squares method and the linearly transformed equations have been widely applied to correlate sorption data where 1/\(n\) is a heterogeneity parameter, the smaller 1/\(n\), the greater the expected heterogeneity. This expression reduces to a linear adsorption isotherm when 1/\(n\) = 1. If \(n\) lies between one and 10, this indicates a favorable sorption process. From the data in Table 2, that value of 1/\(n\) = 0.45 while \(n\) = 2.2 indicates that the sorption of Pb\(^{2+}\) to SD/MNPs/PEI is favorable and the \(R^2\) value is 0.95.

### Adsorbate efficiency

To evaluate the effectiveness of the absorbers, the activity of SD, SD/MNP and SD/MNP/PEI was investigated for the removal of lead (Table 3). The results showed SD/MNP/PEI had maximum efficiency and SD/MNP have minimum efficiency. Maybe due to coating the sawdust surface with MNPs, SD/MNPs have less efficiency for adsorption of lead, because the functional groups on the sawdust surface that can interact with lead ions are covered, whereas -NH\(_2\) groups of PEI in the synthesized nanocomposite can easily adsorb lead ions. The adsorption mechanism of Pb (II) by SD/MNP/PEI was complicated, and may consist of complexation reaction, ion exchange and electrostatic adsorption (Yang et al. 2018). This indicated chemical surface treatments of sawdust by polyethyleneimine can significantly enhance the capacity of substrates for removal of Pb (II).

### Table 2 | Freundlich, Langmuir and Temkin parameters for the adsorption of Pb (II) ions on SD/MNP/PEI

<table>
<thead>
<tr>
<th>Order model</th>
<th>Parameters</th>
<th>STDEVA</th>
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<tbody>
<tr>
<td>Freundlich isotherm model</td>
<td>(n)</td>
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</tr>
<tr>
<td></td>
<td>(K_f) (mg g(^{-1}))</td>
<td>2.17</td>
</tr>
<tr>
<td></td>
<td>(R^2)</td>
<td>0.9503</td>
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<tr>
<td>Langmuir isotherm model</td>
<td>(q_{max}) (mg g(^{-1}))</td>
<td>2.55</td>
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<tr>
<td></td>
<td>(b)</td>
<td>3.92</td>
</tr>
<tr>
<td></td>
<td>(R^2)</td>
<td>0.9875</td>
</tr>
<tr>
<td>Temkin isotherm model</td>
<td>(A) (L g(^{-1}))</td>
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</tr>
<tr>
<td></td>
<td>(b_T) (Kmol(^{-1}))</td>
<td>3.92</td>
</tr>
<tr>
<td></td>
<td>(R^2)</td>
<td>0.9778</td>
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### Table 3 | Adsorbate efficiency

<table>
<thead>
<tr>
<th>Type</th>
<th>SD</th>
<th>SD/MNP</th>
<th>SD/MNP/PEI</th>
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<tr>
<td>%Removal</td>
<td>59.38</td>
<td>33.6</td>
<td>98</td>
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</table>
the Pb (II) cations were adsorbed by NH2 groups of the PEI was fast and pH-sensitive. The sorption capacity indicated that the sorption of Pb (II) ions by SD/MNP/PEI aqueous solution after adsorption. The batch experiments Pb (II) ions and they could be magnetically separated from the sorbent. However, complete regeneration is not always possible.

Desorption study

When a solid sorbent is applied for sorption of pollutants (organics or inorganics), the possibility of regeneration of the sorbent is of great importance from the point of view of application in industries. It is important that the sorbent is easily regenerated and the desorbing agent is effective, cheap, non-polluting and non-damaging to the structure of the sorbent. However, complete regeneration is not always possible.

Desorption study was carried out in a similar way to that of the sorption studies. After sorption, Pb-loaded SD/MNP/PEI was dried. Smeary nanocomposite was first treated with 50 mL of HCl 0.5 mol L\(^{-1}\) for 80 min at 60 rpm, and then rinsed with distilled water. The resulting supernatant was separated by a permanent magnet before AA analysis.

Results are shown in Table 3. Only 0.2 g of nanocomposite could be used in the four experiments without obvious loss in its sorption behavior (Table 4).

<table>
<thead>
<tr>
<th>SD/MNP/PEI(g)</th>
<th>C(ppm)</th>
<th>V(ml)</th>
<th>rpm</th>
<th>Time (min)</th>
<th>%Removal</th>
</tr>
</thead>
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<tr>
<td>0.2</td>
<td>5</td>
<td>50</td>
<td>60</td>
<td>80</td>
<td>97.1</td>
</tr>
<tr>
<td>0.2</td>
<td>5</td>
<td>50</td>
<td>60</td>
<td>80</td>
<td>96.2</td>
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<tr>
<td>0.2</td>
<td>5</td>
<td>50</td>
<td>60</td>
<td>80</td>
<td>96.4</td>
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<tr>
<td>0.2</td>
<td>5</td>
<td>50</td>
<td>60</td>
<td>80</td>
<td>96.8</td>
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</table>

CONCLUSIONS

Herein, magnetically recoverable cross-linked polyethyleneimine nanocomposites with porous structures, in which the sawdust magnetic carriers were embedded, were successfully synthesized via a cost-effective and simple chemical route. It was found that the obtained nanocomposite exhibited significantly enhanced adsorption capability towards Pb (II) ions and they could be magnetically separated from aqueous solution after adsorption. The batch experiments indicated that the sorption of Pb (II) ions by SD/MNP/PEI was fast and pH-sensitive. The sorption capacity increases with increasing phase contact.

Considering the properties of both adsorbents and Pb (II), and the sorption conditions, it was declared that the Pb (II) cations were adsorbed by NH2 groups of the negatively charged SD/MNP/PEI adsorbents via electrostatic interaction over a wide pH. The removal efficiency was highly pH dependent and the optimal adsorption occurred at pH of 7–9. Adsorption of Pb (II) at 80 min reached equilibrium. SD, SD/MNP and SD/MNP/PEI were compared for sorption of Pb (II) ions from aqueous solutions. Under the optimized condition, the maximum removal of Pb (II) on SD, SD/MNP and SD/MNP/PEI was about 59.38, 33.6 and 98% (adsorption capacity 0.74, 0.42 and 2.58 mg g\(^{-1}\)), respectively, which disclosed the effectiveness of modification of SD/MNP. It was found that SD/MNP/PEI removes more efficiently lead ions from aqueous solutions than the SD and SD/MNP. The Langmuir isotherm model fitted to the adsorption data, demonstrating that the adsorption of Pb (II) on SD/MNP/PEI was monolayer adsorption. Additionally, it was shown that Pb (II) could be desorbed from SD/MNP/PEI by 0.5 mol L\(^{-1}\) HCl and used for at least four cycles without any adsorption performance loss, which revealed that the adsorbent is a potential candidate for highly efficient and renewable adsorbent of Pb (II) ions in environmental remediation. No specific equipment, time-consuming and complex processes for other than conventional methods are required. The main advantage of the method is that it can be applied to real water.

REFERENCES


oxide nanoparticles for biomedical applications. ACS Applied Materials & Interfaces 5 (5), 1722–1731.


First received 22 August 2018; accepted in revised form 12 December 2018. Available online 24 December 2018