Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2017.1754

58 (2017) 120–128
January

Application of sawdust nanoparticles as a cheap and nontoxic biosorbent for the removal of lead ions from polluted waters

Hassan Karami[a,b,*], Farzaneh Yaghoobi[b], Fariba Goli[b]

[a]*Department of Chemistry, Payame Noor University, 19395-4697, Tehran, Iran, Fax: +98 24 352 26932; email: karami_h@yahoo.com (H. Karami)*
[b]*Nano Research Laboratory, Department of Chemistry, Payame Noor University, Abhar, Iran, Fax: +98 24 352 26932; email: karami_h@yahoo.com (H. Karami); Fax: +98 24 352 33556; email: yaghobifarzaneh@yahoo.com (F. Yaghoobi);*

Received 14 December 2015; Accepted 14 May 2016

ABSTRACT

In this study, sawdust nanoparticles are prepared by an innovative vibratory ball mill (Spex). DLS, SEM, and TEM images show that the milled powder includes spherical nanoparticles with 20 nm average diameters. The prepared sawdust nano- biosorbent (SNBS) is used as a new and green nano- biosorbent for the removal of lead ions from polluted waters. Experimental data shows that the sorption of lead ions on SNBS is acceptably fitted to the Langmuir isotherm model. Based on the Langmuir isotherm, a maximum adsorption capacity of 10 mg g^{-1} is achieved for adsorption of lead ions on SNBS. FT-IR is used to describe the sorption mechanism of lead ions on SNBS. The experimental optimum conditions for the lead ion removal include pH of 5, 50 ml sample volume, 50 mg SNBS and 20 min contact time in the room temperature. In these conditions, the removal efficiencies of Pb^{2+}, Cu^{2+}, Ag^{+}, Zn^{2+}, Fe^{2+}, Mn^{2+}, and Ni^{2+} are obtained 97, 64, 55, 44, 37, 36, and 34%, respectively. Desorption studies showed the adsorbed lead ions on sawdust surface can be done by using 1 ml 1.5 M HNO_3.

Keywords: Sawdust, Nanoparticles, Biosorbent, Nanosorbent, Heavy metal, Ion removal

---

1. Introduction

Today, water pollution, including heavy metals, radioactive, organic, and inorganic compounds is a serious problem. The main sources of heavy metal pollutions in groundwater and surface water resources, soil and ultimately human are the natural phenomena such as proximity to a mine or contaminated litter, and as a result of industrial or agricultural activities with high concentrations of a substance. Heavy metals in fertilizers, pesticides, herbicides and insecticides, household and industrial wastewater, and sewage sludge are added to soil to increase crop production, causing contamination of water sources with heavy metal compounds.

There is a variety of methods for the removal and separation of heavy metal ions from aqueous solutions. The most important methods that can be used for this purpose are chemical precipitation and co- precipitation [1], ion exchange [2], reverse osmosis [3], membrane separation [4], solvent extraction [5], and adsorption methods [6]. Most of these methods have disadvantages such as high cost of equipment and operation, production of toxic sludge, or other waste requires lots of energy and space requirements. Among these methods, the attention of many scientists in recent years has attracted to adsorption and specially biosorption processes, because of a simple, low- cost and high efficiency of the removal of heavy metal ions in low and medium concentrations. Biosorption, as an alternative process, is the uptake of heavy metals from aqueous solutions by biological materials. Biosorption uses cheaper materials such as naturally abundant plant residues or products of fermentation industries. The biosorption process is generally rapid and is suitable for the extraction of metal ions from large volumes of water [7,8].

---

* Corresponding author.

There are many reports about the removal of heavy metal ions by bio- sorbents such as adsorption of copper (II), chromium (III), nickel (II), and lead (II) ions from aqueous solutions by meranti sawdust [9], removal of lead ions from aqueous solutions by agricultural waste adsorbent [10], adsorption of Pb (II) ions from aqueous solutions by date bead carbon activated with $ZnCl_2$ [11], wastewater treatment by date palm adsorbent [12], removal of water pollutants by palm biomass- based adsorbents [13], and etc.

In this study, the sawdust powder without any additive was processed to sawdust nanoparticles by using an innovative ball mill [14]. The prepared sawdust nanoparticles were used as sawdust nano biosorbent (SNBS) for the quantitative removal of lead ions from water.

2. Experimental

2.1. Materials

In this work, all materials, including HNO_3, $CuSO_4.5\,H_2O$, $Zn(NO_3)_2.6\,H_2O$, $Fe_2(SO4)_3.H_2O$, $MnSO_4.H_2O$, $NiCl_2$, $Pb(NO_3)_2$, $NaNO_3$, $Mg(NO_3)_2.6\,H_2O$, $AgNO_3$, and NaOH were in analytical grade and were purchased from Merck and used without any purification. Double- distilled water was used in all experiments.

2.2. Instrumental

A vibratory ball mill was made according to reference [14] and used for the production of SNBS. The morphology and the particle sizes of sawdust samples were studied by scanning electron microscopy (SEM, Σigma/VP model) and transmission electron microscope (TEM, Zeiss EM900). Size distribution diagram of the samples was obtained by DLS (Malvern, Zetasizer Nano ZS3600). Flame Atomic Absorption spectrometer (FAAS; Sens AA model, GBC company) was applied for the determination of residual concentrations of metal ions. The pH values were controlled with a pH meter (Metrohm-827). Circulating device (PE 26 1NF model, Grant Co., England) was used to adjust the solution temperature. The centrifuge (K240 model, Wagtech Co.) and cellulose acetate membranes (0.45 μ, 47 mm, Empore Co.) were used to separate nanoparticle from solution in adsorption and desorption experiments, respectively. Fourier transform infrared spectroscopy (FT-IR, Vector 22, Bruker) is used to study the sorption mechanism of lead ions on sawdust nanoparticles. The vacuum pump (DV-42N-2501, Platinum Co., USA) was used to flow the solution through the membrane in the separation of SNBS from lead ion solutions.

2.3. Procedures

2.3.1. Preparation of biosorbent

Sawdust powder was dried in oven at 80°C for 12 h. Some sawdust (about 400 ml) together 200 hard chromium electroplated iron balls (in three sizes: 5, 10, and 20 mm) are filled in the tank of the innovated vibratory ball mill and vibrated with a frequency of 40 Hz for 10 h. The prepared SNBS is characterized by SEM, TEM, and DLS.

2.3.2. Sorption experiments

To identify the best metal ion which can be removed by SNBS, 50 ml solution with pH of 5 including 5 ppm from any of metal ions including pb^{2+}, Cu^{2+}, Zn^{2+}, Fe^{2+}, Mn^{2+}, Ni^{2+}, and Ag^{+} is separately mixed with 50 mg SNBS for 30 min at mixing rate of 650 rpm. The residual concentration of metal ions was determined by the flame atomic absorption spectrophotometer.

The effects of sorption parameters including initial solution pH, sample volume, solution temperature, mixing time (contact time of SNBS with the metal ion solution), sample concentration, and biosorbent dosage were investigated and optimized by the "one at a time" method. The adsorption efficiency of metal ions onto the SNBS was calculated according to the following equation Eq. (1):

$$\text{Removal efficiency }(\%) = \frac{C_i - C_f}{C_i} \times 100 \tag{1}$$

where, C_i and C_f are the initial and final concentrations of the proposed ion in ppm, respectively. The equilibrium adsorption capacity, q_e(mg g^{-1}) of heavy metal ions was calculated using the mass balance equation Eq. (2):

$$q_e = \frac{(C_i - C_e)V}{m} \tag{2}$$

where, C_i (ppm) and C_e (ppm) are the initial and the equilibrium concentrations of metal ions, respectively; V (ml) is the sample volume and m (g) is the sawdust amount.

2.3.3. Effect of mixing time

The effect of contact time on the lead ion removal was studied at different times in the range of 5–40 min with the initial metal ion concentration of 5 ppm. After completing of the contact time, SNBS was separated from solution phase and the residual concentration of lead ions was measured.

2.3.4. The effect of initial lead ion concentration

Sorption isotherms were obtained by equilibrating SNBS with lead ion solutions of different initial concentrations in the range of 5–30 ppm. After separation, the final concentrations of metal ions in the solutions were calculated.

2.3.5. The pH effect

The sorption efficiency of as a function of solution pH was studied. The initial pH values were adjusted from 2 to 6, using 0.1 M HNO_3 or NaOH solutions. After mixing for constant time and in constant stirring rate, the nanoparticles were separated and the residual concentrations of lead ions were measured.

2.3.6. Desorption experiments

For desorption of the lead ions from SNBS, after separating the SNBS nanoparticles from a lead ion solution via membrane, the SNBS was first washed with water and then washed with nitric acid solutions. The concentration of lead ions in the eluted sample was determined by FAAS. The concentration and volume of nitric acid as an eluent was optimized.

3. Results and discussion

Sawdust from woodworking, located in the city of Abhar was prepared. The obtained sawdust was washed and dried. The dried sawdust particles were mechanically brushed and processed to sawdust nanoparticles. The prepared sawdust nanoparticles were used as SNBS.

3.1. Characterization of the prepared SNBS

The morphology and the particle sizes of the sawdust nanopowder were characterized by SEM, TEM and DLS (Fig. 1).

According to the SEM image, observed samples containing small particles that are highly agglomerated and then, large aggregate particles make difficult to calculate the smarter size of the nanoparticles. Nevertheless, SEM images show the sample includes uniform nanoparticles with diameter lower than 20 nm. According to TEM image Fig. 1(b), the sample consists the spherical particles with the wide range of particle sizes (5–50 nm). Based on TEM image, the bulk sample is made up of particles with a diameter smaller than 20 nm. For more clarification, the sample was exactly analyzed by DLS Fig. 1(c). As it can be seen in Fig. 1(c), the major particles of the sample are in the range of 3–65 mm. The average diameter of the particles is 20 nm which it confirms the result of TEM.

The characterized sawdust nanoparticles were mixed with 100 ppm lead (II) ion solution for 1 h and then, the lead ions loaded nanoparticles were filtered, washed, and dried. The finalized nanoparticles were analyzed by SEM (Fig. 2). Comparison between Figs. 1(a) and 2 shows that there is not any significant difference in the morphology and the particle size of SNBS before and after contact with the lead ion solution.

3.2. Sorption studies

In the first step, the removal efficiencies of some heavy metal ions by SNBS were examined. Fig. 3 shows the obtained results about the ability of SNBS for the removal of some heavy metal ions from water.

Based on Fig. 3, SNBS is suitable biosorbent to remove lead ions from water. The higher removal of lead ions than the others can be related to soft acid (lead ion)- soft base (hydroxyl group in SNBS) [15].

The infrared spectroscopy was used to determine the vibrational frequency changes of SNBS functional groups. Fig. 4 shows the IR spectrums of the SNBS sample before and after contact with the lead ion solution.

In comparing the two spectrums, the greatest difference is the peak corresponding to the stretching vibration of functional group *O-H* that Dative bond between non-bonding electron pairs of oxygen and the cation Pb^{2+} alters the *O-H* bond energy and consequent displacement of the vibration of functional group *O-H*. Therefore, the band at 3441.31 cm^{-1} is

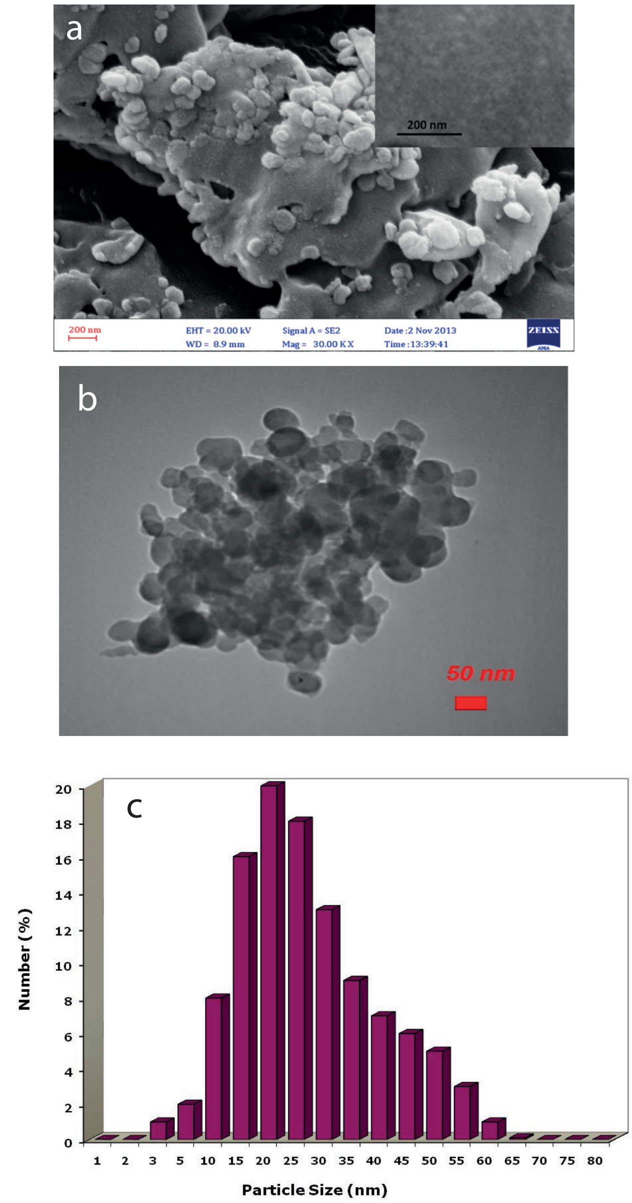

Fig. 1. SEM image (a) TEM image (b) and DLS diagram (c) of the prepared SNBS.

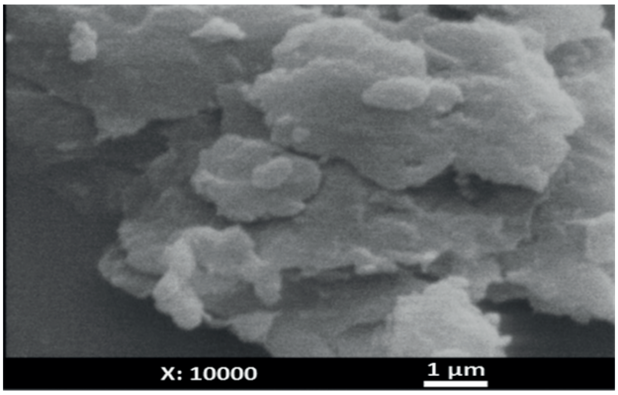

Fig. 2. SEM image of lead ion loaded SNBS.

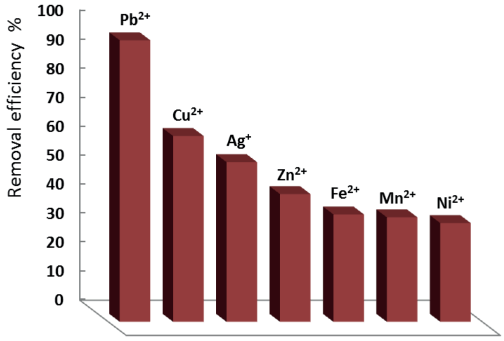

Fig. 3. The removal efficiencies of SNBS for some heavy metal ions from water.

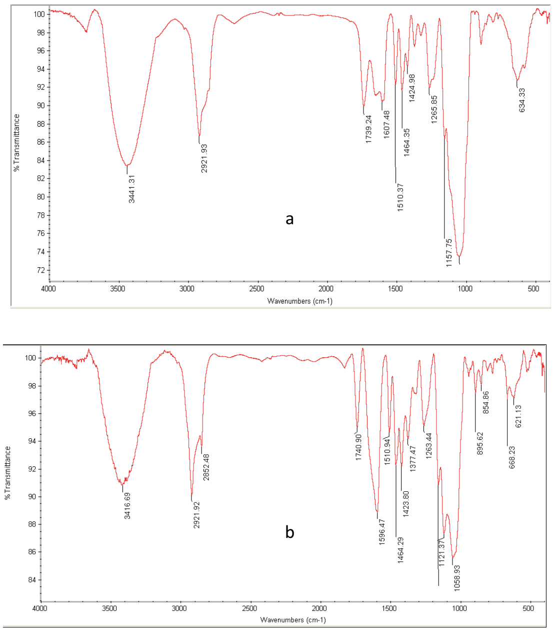

Fig. 4. IR spectrums of the prepared SNBS before (a) and after (b) contact with lead ion solution.

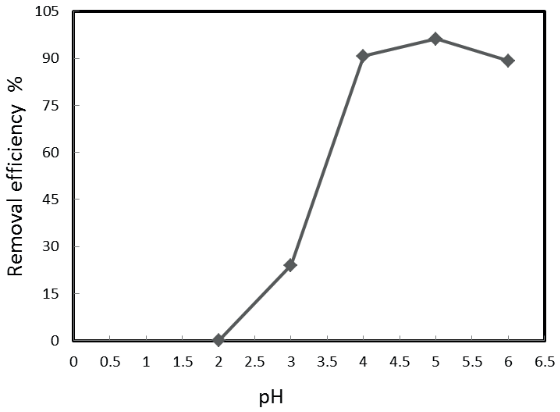

Fig. 5. Effect of solution pH on the lead ion removal efficiency on SNBS.

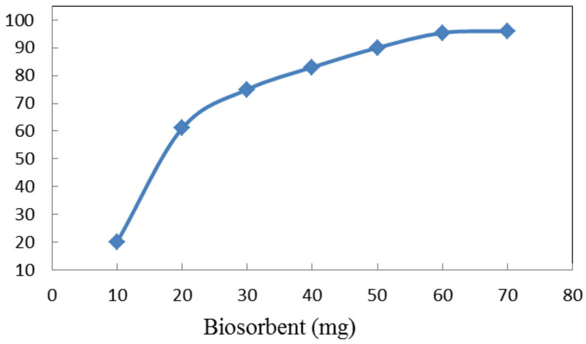

Fig. 6. Effect of SNBS amount on the lead ion removal efficiency.

shifted to 3416.69 cm^{-1}. After the contact of SNBS with a lead ion solution, the additional peaks at the wave number range of 500–900 cm^{-1} (such as the band in 854.86 and 668.23 cm^{-1}) show the formation of metal- oxygen bondings [16]. Based on the IR spectrum data, the SNBS can adsorb lead ions with a chemical mechanism. Lead ions can be removed from water by SNBS through complex formation between lead ions and hydroxyl groups on SNBS.

3.2.1. The effect of pH

To investigate the effect of initial pH on the sorption of lead ions, the pH range of 2–6 was studied. The relationship between the initial pH value and the lead ions removal efficiency was presented in Fig. 5.

The maximum adsorption of lead ions takes place at pH of 5. Because, based on the experimental data (not presented), the zero charge pH of SNBS takes place in pH of 4. At higher pH than 4, there is a negative charge on SNBS particles as well as positive charge at smaller than 4. On the other hand, at low pH, because of the high abundance of protons (H^+) than Pb^{2+}, the sorption of lead ions on SNBS is decreased. In other words, some sorption sites on SNBS are occupied by hydrogen ions. By increasing the pH to more than 5, the percentage of lead ion removal decreases that it is probably due to the formation of sediment of cations like $Pb(oH)^+$ which is less likely to be attracted to the surface of nanoparticles [17,18].

3.2.2. The effect of SNBS amount

To study the effects of absorbent values on the lead ion sorption with keeping constant other factors, the removal experiments were carried out with different biosorbent weights in a range of 10–70 mg. Fig. 6 shows the effects of biosorbent values on the lead ion removal efficiency.

As it can be seen in Fig. 6. With the increasing amount of biosorbent, the removal percentage gradually increases and reaches to the maximum amount (at 50 mg SNBS) and then remains constant. In the small amount of biosorbent, due to the saturation of the sorption sites by Pb^{2+} ions, the ion removal is not completed [18].

3.2.3. The effect of contact time

The results of sorption studies as a function of contact time (mixing of lead ion solution with SNBS) are shown in Fig. 7.

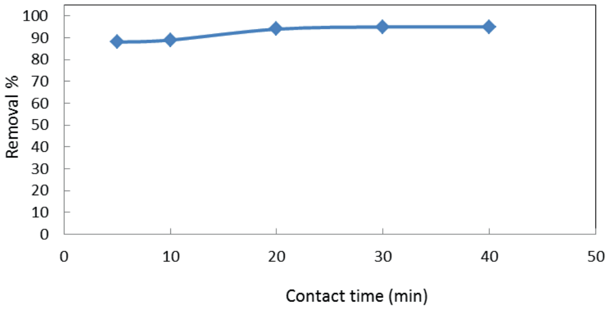

Fig. 7. Effect of contact time between lead ion solution and SNBS on the lead ion removal efficiency.

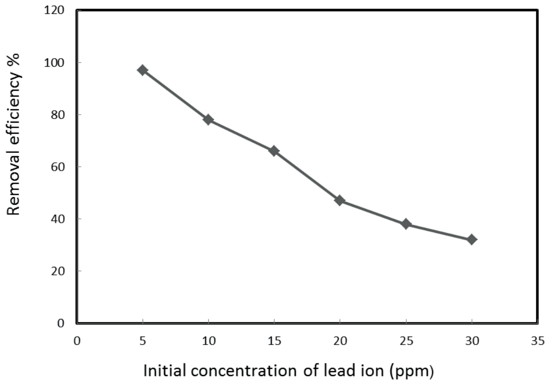

Fig. 8. Effect of initial lead ion concentration on the lead ion removal efficiency.

According to the Fig. 7, the lead ion removal is reached to 88% before 5 min. The results show the fast kinetics of lead ion adsorption by SNBS. Based on the presented data, the lead ion removal is completed at a contact time less than 20 min.

3.2.4. Isotherm studies

The lead ions removal performance by the SNBS was investigated as a function of the initial lead ion concentration (from 5 to 30 ppm) in room temperature. In this study, the sorption time was fixed at 20 min. Fig. 8 shows the effect of initial ion concentration on the removal efficiency.

As it can be observed in Fig. 8, by increasing the initial concentration of the sample, the sorption of lead ions is decreased. The drop in the removal efficiency indicates that sorption sites on the sorbent surface become saturated [19]. To determine the sorption capacity of SNBS toward examining lead ions, sorption studies on an initial concentration range from 5 to 30 ppm were carried out. The sorption mechanism of lead ions adsorption on SNBS was evaluated using the sorption isotherms such as Langmuir, Freundlich, and Temkin. The Langmuir isotherm equation and its linear form are presented as Eq. (3) and, respectively.

$$q_e = \frac{q_m b C_e}{1 + bC_e} \tag{3}$$

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \tag{4}$$

where, q_e is the equilibrium sorption capacity of the biosorbent for metal ions in mgg^{-1}, C_e is the equilibrium concentration of metal ions in ppm, q_m is the maximum amount of metal ions adsorbed in mg.g^{-1}, and b is the constant that refers to the bonding energy of the sorption process in L mg^{-1}. The constants b and q_m can be determined from the intercept and slope of the linear plot C_e/q_e vs. C_e On the contrary, the Freundlich model is based on a reversible heterogeneous sorption. In the Freundlich model, it is assumed that the level of energy distribution is non-uniform, different pieces of the same level are not impact together [20]. Freundlich isotherm equation is presented as follows:

$$q_e = k_f C_e^{1/n} \tag{5}$$

The linear form of Freundlich equation is as follows:

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \tag{6}$$

where q_e is the equilibrium sorption capacity of the biosorbent in mg g^{-1}, C_e is the equilibrium concentration of heavy metal ions in ppm, K_f is the constant related to the sorption capacity of the biosorbent in ppm, and n is the constant related to the sorption intensity. The constants n and K_f can be determined from the slope and intercept of the linear plot logq_e vs. logC_e. The Temkin model contains a factor that clearly shows the interactions between the Sorbent particles and adsorbed ions. Temkin isotherm can be presented as following equation:

$$q_e = \frac{RT}{b} \ln(AC_e)$$

In this equation, $\frac{RT}{b} = B$ (7)

The linear form of the Temkin isotherm equation is as follows:

$$q_e = B \ln A + B \ln C \tag{8}$$

where, q_e is the equilibrium sorption capacity of the biosorbent in mg g^{-1}. C_e is the equilibrium concentration of heavy metal ions in ppm. A is the binding constant related to the maximum binding energy in L mg^{-1}. B is the constant proportional to the heat of sorption. b is the constant in j mol^{-1}. The quantitative relationship between initial pb^{2+} ion concentration and the sorption capacity was analyzed with three different isotherm models which were shown in Fig. 9. The calculated parameters (b, q_m, n, K_f, B, b, and A) and linear regression coefficient (R^2) values for all models are summarized in Table 1. The Langmuir isotherm was better fitted to the experimental data. In the Langmuir model, it is assumed

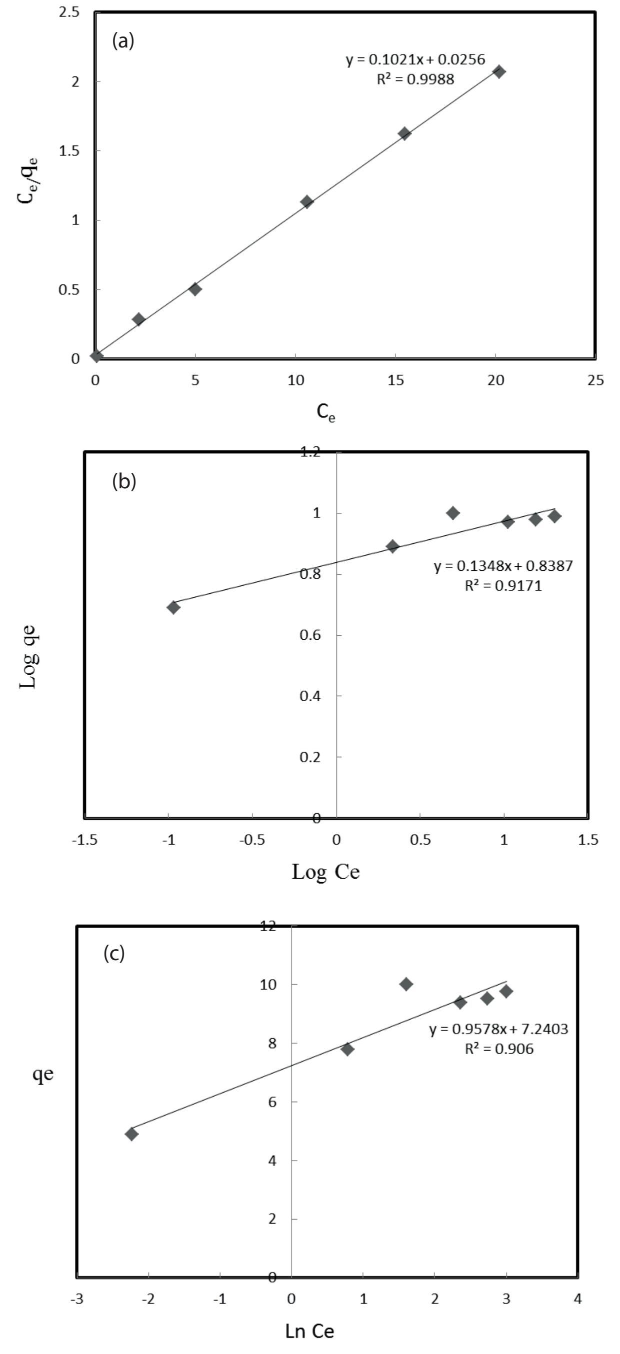

Fig. 9. Adsorption isotherms of pb^{2+} ions by SNBS; (a) Langmuir isotherm, (b) Freundlich isotherm, and (c) Temkin isotherm.

Table 1
The calculated parameters of Langmuir, Freundlich, and Temkin isotherms

Isotherm	Constants	R^2
Langmuir	q_m = 9.803 mg g^{-1}	0.998
	b = 4.080	
Freundlich	K_f = 6.886	0.917
	n = 7.462	
Temkin	A = 1,930	0.906
	B = 0.95	
	B =2589.05	

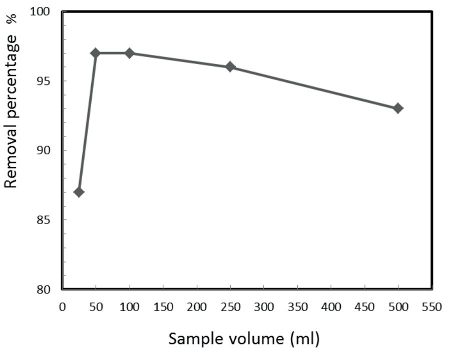

Fig. 10. Effect of initial sample volume on the lead ion removal efficiency.

the sorbent surface is a homogeneous, the sorption energy is constant and equal in all sites. Sorption on the surface to be performed at certain sites, each site can only accommodate a single ion, and also monolayer sorption takes place and none of adsorbed molecules are interactive with each other [20]. The result showed that the value of correlation coefficient (R) for the sorption of pb^{2+} on SNBS was 0.998 which demonstrated the best fitting of experimental data by the Langmuir model. Based on the Langmuir model, maximum sorption capacity of pb^{2+} by SNBS was calculated 10 mg g^{-1}. Mono layer sorption can confirm the chemosorpion of lead ions on SNBS and confirm the data of FT-IR.

3.2.5. The effect of sample volume

The effect of sample solution volume on the pb^{2+} ions removal efficiency was studied by using different volumes (25–500 ml) of aqueous solution with 50 mg SNBS. Fig. 10 shows the results of these studies. In all of the samples, the absolute amount of lead ions was same (0.25 mg). As illustrated in Fig. 10, in sample volume of 25 ml (lead ion concentration is 10 ppm), the removal efficiency is 87%, but in that of 50 ml, lead ion removal is reached to 97%. The lead ion removal slightly decreases when the initial volume increases from 50 to 500 ml. The observed results of lead ion removal in the last range imply that the sorption of lead ions on SNBS is equilibrium process. For more clarification, the lead ion sorption can be shown in the following equations:

$$\mathrm{Pb}^{2+}_{\mathrm{aq}} + \mathrm{Site}_{\mathrm{SNBS}} \Leftrightarrow \mathrm{Pb}^{2+}.\mathrm{Site}_{\mathrm{SNBS}} \tag{9}$$

$$\mathrm{K} = \frac{\left[\mathrm{Pb}^{2+}.\mathrm{Site}_{\mathrm{SNBS}}\right]}{\left[\mathrm{Pb}^{2+}_{\mathrm{aq}}\right]\left[\mathrm{Site}_{\mathrm{SNBS}}\right]} \tag{10}$$

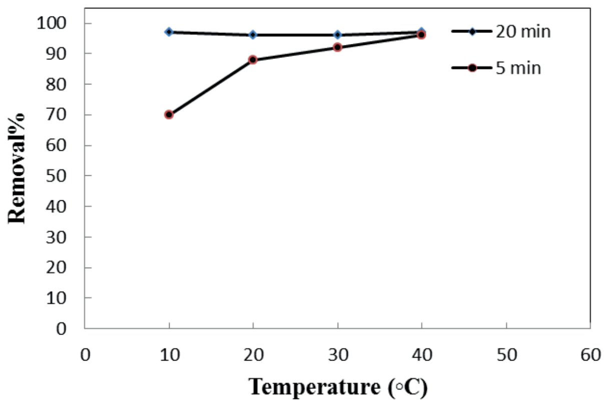

Fig. 11. Effect of solution temperature on the lead ion removal efficiency.

where, Pb^{2+}_{aq} is lead ion in solution, $Site_{SNBS}$ is the active site on SNBS, $Pb^{2+}\bullet Site_{SNBS}$ is the occupied site via lead ions on SNBS and K is the equilibrium constant. In more diluted solutions (initial volume bigger than 200 ml), the residual concentration (mole L^{-1}) is decreased. Therefore, to keep constant the equilibrium, much more lead ions should be free in solution.

The results show that SNBS can be not only used for the removal of lead ions from water at low levels, but also can be used in solid phase extraction for the preconcentration and determination of lead ion concentration.

3.2.6. The effect of solution temperature on removal efficiency

To investigate the temperature dependency of pb^{2+} ion removal by SNBS, the sorption studies were carried out at a temperature range of 10°C–40°C in two contact times. The obtained results are summarized in Fig. 11.

According to the presented data in Fig. 11, in contact time of 20 min, the temperature in the range of 10°C to 40°C has no significant effect on the sorption of lead on SNBS because, the removal efficiency is almost complete in 20 min. Based on the effect of contact time (Fig. 7), it is expected that the effect of temperature on the removal efficiency is visible in contact time of 5 min. Therefore, the effect of solution temperature was studied on the lead ion removal in contact time of 5 min (Fig. 11). In contact time of 5 min, the removal efficiency increases with increasing the solution temperature. The observed data in contact time of 5 min show that the sorption is an endothermic reaction.

3.2.7. Application of SNBS for the removal of some other metal ions

To ensure the right choice of lead ion as the main cation that can be adsorbed on SNBS, two series experiments were done. In the first series, the removal efficiencies of some heavy metal ions such as Pb^{2+}, Cu^{2+}, Ag^{+}, Zn^{2+}, Fe^{2+}, Mn^{2+}, and Ni^{2+} in the optimized conditions of lead ions were evaluated.

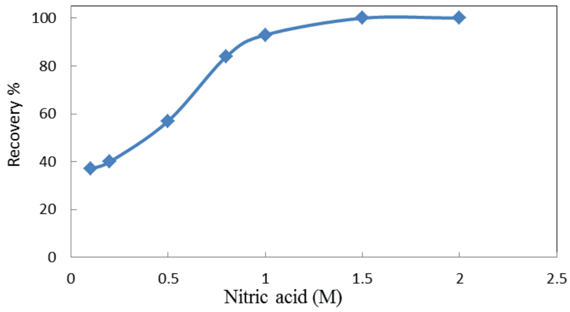

Fig. 12. Effect of HNO_3 concentration as an eluent on the lead ion recovery.

In the second series, to evaluate the ability of SNBS to adsorb heavy metals in a mixed solution, the removal of each cation by SNBS was measured. The summary of all results was presented in Table 2.

The obtained results show that SNBS is selective sorbent for the removal of lead ions not only from sparse matrixes but also from complex matrixes. In a previous report, Zhou et al. reported that the citric acid-modified pine sawdust (CA-PS) for the removal of Pb^{2+}, Cu^{2+}, and Cd^{2+} ions from aqueous solutions [21]. They reported the competitive adsorption behavior of Cu^{2+}, Cd^{2+}, and Pb^{2+} in the binary systems (Cu^{2+}+Pb^{2+}, Cu^{2+}+Cd^{2+}, and Pb^{2+}+Cd^{2+}) and the preference of adsorption onto CA-PS can be ordered as $Pb^{2+} > Cu^{2+} > Cd^{2+}$. The difference between removal efficiencies of Pb^{2+} and Cu^{2+} in reference [21] is smaller than that's of the observed in Table 2. Comparing the results shows that the surface modification of sawdust particles with citric acid can decrease the selectivity of SNBS to Pb^{2+} against Cu^{2+}.

3.2.8. Desorption studies

In desorption step, adsorbed ions on SNBS are eluted with a little volume of a suitable solvent. In this study, the experimental data showed that the nitric acid can be used for the reliable desorption of lead ions. The influence of eluant concentration on the recovery of pb^{2+} ions was studied at nitric acid concentration range of 0.1–2 M (Fig. 12).

As it can be seen in Fig. 12, by increasing nitric acid concentration from 0.1 to 1.5 M, the recovery of pb^{2+} ions from 37% has reached to 100%. Therefore, the concentration of 1.5 M nitric acid was selected as suitable solvent. It is obvious that in the elution process, the adsorbed lead ions on SNBS are completely replaced with hydrogen ions when the nitric acid is 1.5 M or more.

If SNBS is used as solid sorbent in the analytical solid phase extraction, the volume of eluent is a main factor that

Table 2
The removal efficiencies of some heavy metal ions in the optimized removal conditions of pb^{2+} ions in separate and mixed solutions

Examined ions		Pb^{2+}	Cu^{2+}	Ag^{+}	Zn^{2+}	Fe^{2+}	Mn^{2+}	Ni^{2+}
Removal %	Separate solutions	97	64	55	44	37	36	34
	Mixed solutions	95	67	40	27	24	22	20

affects on the preconcentration factor. Therefore, the dependency of lead ion recovery on eluent (nitric acid) volume was evaluated in a range of 0.5–3 ml (Fig. 13).

Based on the presented data in Fig. 13, by increasing the eluant volume from 0.5 to 1.0 ml, the recovery percentage is reaches to 100. In the nitric acid volume more than 1 ml, the lead ion recovery is constant.

3.2.9. Application of the presented method in real sample

To evaluate the applicability of the presented analytical method for the preconcentration and the determination of lead ion in real sample, a well water sample was collected from the yard of Abhar Payame Noor University. For this purpose, the pH of well water was set in 5 and used in sorption and desorption processes. 200 mg SNBS was added to 250 ml sample and the other sorption and desorption steps were exactly done according to experimental section. To determine the concentration of Pb^{2+} ions in the sample, four standard solutions of lead ion in the concentration range of 1–7 ppb were used. The standard solutions as well as the sample passed the sorption and desorption processes. All measurements were repeated three times. The lead ion concentration was determined by FAAS. The presented method can be considered as an analytical method for the determination of lead ion concentration in trace level. Based on the initial sample volume and the final volume of the obtained sample after desorption step, the preconcentration factor for the presented method was calculated 250. The obtained results of lead ion concentration in real sample were compared with those of ICP- atomic emission spectroscopy (ICP-AES) and summarized in Table 3.

The initial lead ion concentrations in this section are very lower than those of section 3.2.4 (and other previous sections). It should be noted that in the previous sections (3.2.1–3.2.7), 50 ml lead ion solution was mixed with suitable amount of SNBS, centrifuged and then, the residual lead ion concentration in the centrifuged solution was determined by FAAS. The detection limit of FAAS for lead ions is about 0.2 ppm therefore, the initial concentrations of lead ions were chosen in the range of 5–30 ppm. In this initial concentration range, the residual concentration of lead ion can be measured by FAAS. In the current section, 250 ml real samples of lead ions (with an approximate initial concentration of 2 ppb) was mixed with SNBS, filtered by the membrane, and the adsorbed ions was desorbed by 1 ml HNO_3 solution. The approximate lead ion concentration in the desorbed solution will be 500 ppb (0.5 ppm) therefore, the lead ion concentration in the desorbed solution will be higher than the FAAS detection limit and it can be measured.

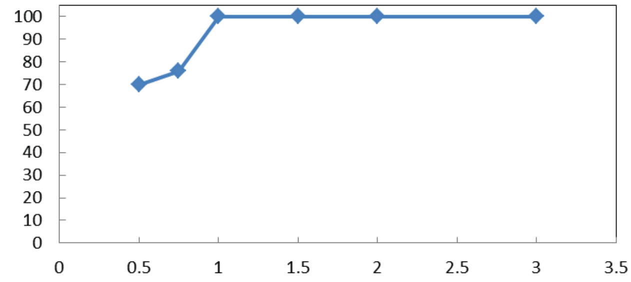

Fig. 13. Effect of HNO_3 solution volume as an eluent on the lead ion recovery.

Table 3
The results of the proposed method for the determination of lead ion concentration in well water (Obtained in Abhar city)

The proposed method	ICP-MS	Critical *t*-value (In level of 95%)	Experimental *t*-value	Significant differences
1.378 ± 0.09	1.4 ± 0.03	2.78	2	No

The average concentration of lead ions in the sample in two methods (Proposed method and ICP- MS) were calculated and compared together using *t*-Test to determine the accuracy of the analytical method. Based the presented data, the result of the current method is confirmed by ICP-AES.

4. Conclusions

Sawdust particles can be processed by an innovative ball milling method to uniform nanoparticles with an average diameter of 20 nm. The sawdust nanoparticles can used as a powerful biosorbent to remove lead ions from polluted waters. The presence of other metal ions in the samples cannot considerably decrease the removal efficiency of lead ions. The proposed biosorbent can be recovered by nitric acid solution and can be reused. In addition, the presented biosorbent, can be used as a solid sorbent in the analytical solid phase extraction for the reliable preconcentration and the determination of lead ions in trace concentrations.

Acknowledgement

We gratefully acknowledge the support of this work by Abhar Payame Noor University Research Council.

References

[1] C. Lertchai, Heavy metals removal by chemical coagulation and precipitation, Water Sci. Technol., 39 (1999) 135–138.

[2] A.Z.P.E. Dąbrowski, Z. Hubicki, P. Podkościelny, E. Robens, Selective removal of the heavy metal ions from waters and industrial wastewaters by ion- exchange method, Chemosphere, 56 (2004) 91–106.

[3] Y. Benito, M.L. Ruiz, Reverse osmosis applied to metal finishing wastewater, Desalination, 142 (2002) 229–234.

[4] H.A. Qdais, H. Moussa, Removal of heavy metals from wastewater by membrane processes: a comparative study, Desalination, 164 (2004) 105–110.

[5] C.H. Yun, R. Prasad, A.K. Guha, K.K. Sirkar, Hollow fiber solvent extraction removal of toxic heavy metals from aqueous waste streams, Ind. Eng. Chem. Res., 32 (1993) 1186–1195.

[6] Y.H. Chen, F.A. Li, Kinetic study on removal of copper (II) using goethite and hematite nano- photocatalysts, J. Colloid Interface Sci., 347 (2010) 277–281.

[7] S. Karthikeyan, R. Balasubramanian, C.S.P. Iyer, Evaluation of the marine algae Ulva fasciata and Sargassum sp. for the biosorption of Cu (II) from aqueous solutions, Bioresour. Technol., 98 (2007) 452–455.

[8] B. Volesky, Advances in biosorption of metals: selection of biomass types, FEMS Microbiol. Rev., 14 (1994) 291–302.

[9] M. Rafatullah, O. Sulaiman, R. Hashim, A. Ahmad, Adsorption of copper (II), chromium (III), nickel (II) and lead (II) ions from

aqueous solutions by meranti sawdust, J. Hazard. Mater., 170 (2009) 969–977.

[10] M.N. Ibrahim, W.S. Ngah, M.S. Norliyana, W.R. Daud, M. Rafatullah, O. Sulaiman, R. Hashim, A novel agricultural waste adsorbent for the removal of lead (II) ions from aqueous solutions, J. Hazard. Mater., 182 (2010) 377–385.

[11] M. Danish, R. Hashim, M. Rafatullah, O. Sulaiman, A. Ahmad, Govind, Adsorption of Pb (II) ions from aqueous solutions by date bead carbon activated with $ZnCl_2$, Clean Soil, Air, Water, 39 (2011) 392–399.

[12] T. Ahmad, M. Danish, M. Rafatullah, A. Ghazali, O. Sulaiman, R. Hashim, M.N.M. Ibrahim, The use of date palm as a potential adsorbent for wastewater treatment: a review, Environ. Sci. Pollut. Res., 19 (2012) 1464–1484.

[13] T. Ahmad, M. Rafatullah, A. Ghazali, O. Sulaiman, R. Hashim, Oil palm biomass–based adsorbents for the removal of water pollutants—a review, J. Environ. Sci. Health C, 29 (2011) 177–222.

[14] H. Karami, A. Akbari Nia, S.R. Hosseini, The process of organic nano fertilizer by ball milling method, Iranian Patent No. 62129, (2009).

[15] J. P. Glusker, A.K. Katz, C.W. Bock, Metal ions in biological systems, Rigaku J., 16 (1999) 8–17.

[16] B. Volesky, Sorption and Biosorption, Montreal, BV Sorbex: Canada, 2003.

[17] J. Lurie, Handbook of Analytical Chemistry, Mirb Pub: Moscow, 1975.

[18] M. Tuzen, E. Melek, M. Soylak, Solid- phase extraction of copper, iron and zinc ions on *Bacillus thuringiensis* israelensis loaded on Dowex optipore, J. Hazard. Mater., 159 (2008) 335.

[19] N. Ahalya, R.D. Kanamadi, T.V. Ramachandra, Cr(VI) and Fe(III) removal using Cajanus cajan Husk, J. Environ. Biol., 28 (2007) 765–769.

[20] S. Liang, X. Guo, N. Feng, Q. Tian, Adsorption of Cu^{2+} and Cd^{2+} from aqueous solution by mercapto- acetic acid modified orange peel, Coll. Surf. B, 73 (2009) 10–14.

[21] Y. Zhou, R. Zhang, X. Gu, J. Lu, Adsorption of divalent heavy metal ions from aqueous solution by citric acid modified pine sawdust, Sep. Sci. Technol., 50 (2015) 245–252.