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Walnut skin nanoparticles as a novel and fast nano-biosorbent for the fast removal of lead ions from polluted water

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ABSTRACT

Walnut skin nanoparticles are prepared by an innovative vibratory ball mill (Spex). A suitable amount of walnut skin powder (≈ 100 g) together with 200 hard chromium electroplated balls are filled into the tank of Spex, and vibrated by 1,200 rpm for 10 h. SEM and TEM images of the output powder of Spex show that the milled powder includes uniform nanoparticles with 65 nm average diameters. The prepared walnut nanopowder is used as a new nano-biosorbent for the fast removal of lead ions from polluted waters. The obtained experimental data show that the adsorption of lead ions on the surface of walnut skin nano-biosorbent (WSNBS) is acceptably fitted to the Langmuir isotherm model with a maximum adsorption capacity of 17.39 mg g^{-1}. The optimum conditions for the removal of lead ions from water include solution pH 4, sample volume 500 ml or less, WSNBS weight 50 mg or more, contact time less than 2 s at room temperature. The desorption step can be done by 1.5 ml 0.5 M HNO_3. In operation conditions, preconcentration factor, RSD and the detection limit are obtained 200, 4.3% and 0.11 ppb, respectively. The interfering effects of some cations such as Cu^{2+}, Ni^{2+}, Fe^{2+}, Zn^{2+}, Mg^{2+} and Na^+ on the removal efficiency of lead ions are investigated. The presented method is successfully applied for the removal and the determination of lead ions from real samples.

Keywords: Walnut skin; Nanoparticles; Biosorbent; Nanosorbent; Heavy metal; Ion removal

1. Introduction

The existence of heavy metal ions in water and wastewater is of great concern due to their potential effects on human and animal health. The concentration of these metal ions in the environment may rise to a level that can be hazardous to livestock. Heavy metals do not undergo biological degradation and tend to accumulate in the organisms, therefore they can enter the food chains [1–3]. Lead is a well-known inorganic contaminant in tap water [4] and belongs to the group of serious hazardous heavy metals. It is believed that exposure to the toxic metals such as lead even at the trace amount is still a risk to human beings [5]. The primary sources of lead are the lead-acid batteries, corrosion of pipes, faucets, household plumbing systems, mining, solders, pigments, radiation shields, and smelting [6,7]. Inorganic lead compounds may be adsorbed through the gastrointestinal tract, the respiratory system, and the skin. Initially, lead is distributed in the blood, liver, and kidney; after prolonged exposure, about 95% of the body lead is found in bone tissue. The main targets of lead toxicity are the hematopoietic and nervous systems [8]. Children are especially at high risk because lead can reduce intelligence and can cause hearing problems [9]. Several methods extensively have been used for the lead ion removal from the water such as ultrafiltration, reverse osmosis, chemical precipitation [22–24], liquid-liquid extraction [10–12], co-precipitation [13–15], ion exchange, solid- phase Extraction [15–21] and chelating matrices. In recent years, among the separation techniques, contaminant removal by solid sorbents has been extensively used due to

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its advantages such as simplicity of operation, reduced solvent usage, suitability to combine with different detection techniques, reduced disposal costs, shorter extraction times for sample preparation, and the availability of a wide variety of sorbent materials that mainly affects the extraction efficiency [25,26]. A number of sorbents have been widely used for the preconcentration and separation of trace metal ions from various matrices. The most common sorbents include zeolites, activated carbon, natural sorbents, XAD resins, clays, biomass, polymeric materials, complexes [27] and nanometer-sized material [28]. Among these sorbents, nanometer-sized material have gained more attention due to their special abilities [29].

There are many reports for the removal of lead ion and other heavy metal ions from water by nanosorbents. Maghemite (γ-Fe_2O_3) nanoparticles have been used for the selective removal of toxic heavy metals from electroplating wastewater [30]. The ability of nano-hydroxyapatite (nano-HAP) as an inexpensive and efficient sorbent has been investigated to remove Cd, Pb and Cu ions from single-metal and multi-metal ions reaction systems in the aqueous phase [31]. Iron oxide nanoparticle-based sorbents with one-step ligand exchange reaction to introduce an affinity ligand to the nanoparticle surface that is specific to a heavy metal or class of heavy metal contaminants [32]. Removal of lead ion by using physically immobilized [$Bmim^+Tf_2N^-$] as an ion liquid on the surface of nano-silica-amine sorbent were studied [33]. ZrO_2 coated multiwall carbon nanotube (MWCNT) has been used as a new solid phase extractor for metal ion preconcentration [34]. Cellulose/manganese oxide nanocomposite, Oxolane-2,5-dione modified electrospun cellulose nanofibers and carboxylate-functionalized cellulose have been introduced for Pb(II) removal from aqueous solutions [35–37].

On the other hand, biosorption, as an alternative process, is the uptake of heavy metals from aqueous solutions by biological materials. In biosorption, cheaper materials such as naturally abundant plant residues or products of fermentation industries were used as a sorbent. The biosorption process is generally rapid and is suitable for the extraction of metal ions from large volumes of water [38,39].

In the last decade, fungus [39], algae [40], microorganism [41], sunflower stalks [42], lichen [43], palm and coconut fibers [44,45], leaves [46], fibrous network of papaya wood [47], olive stones [48], rice bran [49], carrot residues [50], olive pomace [51], wheat bran [52] and cone biomass [53], activated slag-A blast-furnace waste [54], rice husk ash [55], sawdust and neem bark [56], Poly (itaconic acid)-grafted chitosan [57], and activated carbons [58] have been successfully used as biosorbent for the removal of toxic heavy metal ions. In adsorption studies, the unsaturated surface atoms can bind other atoms possessing strong chemical activities which produce a high adsorption capacity [59].

To the best of our knowledge, there is no report about the production and application of walnut skin nanoparticles as biosorbent for the removal of heavy metal ions from water. For the first time, we introduce the walnut skin nano-biosorbents which produced by vibratory ball mill without any surface modification for the removal of lead ions from polluted water. Because nanometer-sized walnut skin has high surface area, high sorption capacity and high chemical activity, it could be successfully applied for the separation and preconcentration of trace metal ions in environmental samples.

2. Experimental

2.1. Materials

In this work, all materials, including HNO_3, $CuSO_4.5H_2O$, $Zn(NO_3)_2.6H_2O$, $Fe_2(SO_4)_3.H_2O$, $MnSO_4.H_2O$, $NiCl_2$, $Pb(NO_3)_2$, $NaNO_3$, $Al(NO_3)_3.9H_2O$, KNO_3 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 ref. [60] and used for the production of WSNBS. The morphology and the particle sizes of walnut skin nano-biosorbent samples were examined by an England scanning electron microscope (SEM, Vp 455 model) and transmission electron microscope (TEM, Zeiss EM900). Malvern Zetasizer (Ver. 6.32) was used to study the size distribution of the sample. Determination of residual concentrations of metal ions was performed by the Flame Atomic Absorption (FAA; Sens AA model, GBC Company). 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 (8.b, Pars Teb Co., Iran) was used to separate heavy metal ion-loaded nanoparticles from the solution phase in all adsorption experiments. Cellulose acetate membranes (0.45 μ, 47 mm, Empore Co.) were used to separate nanoparticles from solution in all desorption experiments. In desorption studies, determination of the residual concentration of lead ions in the membrane-based filtrated solutions and in the centrifuse-based separated solutions showed that the cellulose acetate membrane can adsorb a less amount of lead ions (lower than 2%). Therefore, cellulose acetate membrane can be used in the desorption studies without any concern. The vacuum pump (DV-42N-2501, Platinum Co., USA) was used to flow the solution through the membrane in the separation of WSNBS from lead ion solutions. Fourier transform infrared spectroscopy (FT-IR, Vector 22, Bruker) is used to study the sorption mechanism of lead ions on walnut skin nanoparticles. A home-made innovative vibratory ball mill apparatus was used for the production of walnut skin nanoparticles.

2.3. Procedures

2.3.1. Preparation of sorbent

Walnut skins were dried in the oven at 80°C for 24 h. A suitable amount of walnut skin (about 100 g) together with 200 hard chromium electroplated iron balls (in three sizes: 5, 10 and 20 mm) were filled in the tank of the innovated vibratory ball mill and vibrated by 1,200 rpm for 10 h. The prepared WSNBS was characterized by SEM, TEM and DLS.

2.3.2. Sorption experiments

To identify the best metal ion which can be removed by WSNBS, some heavy metal ions such as pb^{2+}, Cu^{2+}, Zn^{2+}, Ni^{2+}, Fe^{2+}, Mn^{2+} and Al^{3+} were examined. For this propose, 50 ml of each metal ion with concentration of 5 ppm is separately mixed with 50 mg WSNBS for 30 min at 500 rpm mixing rate. Then, the nanoparticles were separated from solution by using a centrifuge. The residual concentrations of the metal ions were determined by the flame atomic absorption spectrophotometer (FAAS) with respect to the related standard solutions and, the removal efficiency was calculated for each ion.

The effects of sorption parameters such as pH, sample volume, solution temperature, mixing time (contact time of WSNBS with the metal ion solution), sample concentration and WSNBS dosage were investigated and optimized by the "one at a time" method. The adsorption efficiency of metal ions onto the WSNBS 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 initial concentration and the equilibrium concentration of metal ions, respectively; V (ml) is the sample volume and m (mg) is the WSNBS amount.

2.3.3. The effect of mixing time

The effect of contact time was studied on lead ion removal at different times in the range of 1 s to 60 min with the initial metal ion concentration of 5 ppm. After completing of the adsorption, WSNBS was separated from solution 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 WSNBS with lead ion solutions in the range of 5 to 35 μg ml^{-1}. After separation, the residual concentrations of metal ions in the solutions were calculated.

2.3.5. The pH effect

Sorption efficiency of WSNBS as a function of solution pH was studied. The initial pH values were adjusted at 2 to 6, using 0.1 M HNO_3 or KOH solutions. In each pH, the adsorption experiment was done.

2.3.6. Desorption experiments

For desorption of the lead ions from WSNBS, after separating the WSNBS from a lead ion solution via membrane, the WSNBS was first washed with water and then washed with nitric acid solution. 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

The prepared walnut skin was washed and dried. The dried particles of walnut skin were mechanically brushed and processed to walnut skin nanoparticles. The prepared walnut skin nanoparticles were used as WSNBS.

3.1. Characterization of the prepared WSNBS

The morphology, particle size and size distribution of the walnut skin nanoparticles were characterized by SEM, TEM and DLS, respectively. The results of these studies were shown in Fig. 1.

According to the SEM image, the synthesized samples consisted of highly agglomerated particles so it is difficult to determine the particle sizes. According to TEM micrograph, the samples consisted of spherical particles with an average diameter of 65 nm which agglomerated of sticking together. Based on DLS diagram, 90% of sample particles are in the size range of 55 to 85 nm with the mean size of 70 nm. The DLS results confirm those of TEM.

3.2. Sorption studies

In the first step, the removal efficiencies of some heavy metal ions by WSNBS were examined. Fig. 2 shows the obtained results about the ability of WSNBS for the removal of some heavy metal ions from water. Based on Fig. 2, WSNBS is suitable biosorbent to remove lead ions from water. The higher removal of lead ions than the others can be related to strong interaction between a soft acid (lead ion) and soft base (hydroxyl group in WSNBS) [61].

The FT-IR spectra of walnut shell powder (before and after sorption of lead ion) were used to determine the vibrational frequency changes of the functional groups in the adsorbent (Fig. 3). The FT-IR spectra of the adsorbent display a number of absorbance bands indicating the complex nature of the adsorbent. In native walnut shell powder, the broad absorption band at 3,650 cm^{-1} is indicative of the existence of the bonded hydroxyl group. The absorbance peak around 2,850 and 1,400 cm^{-1} is assigned to –CH and CH_2 stretching, respectively. The –OH absorption band was observed to shift to 3,580 cm^{-1} when walnut shell powder is loaded with pb^{2+}. The –CH stretching band also shifted to 2,800 cm^{-1}. It seems that these functional groups participate in metal binding. The changes in FT-IR spectra confirm the complex formation between pb^{2+} ion and functional groups of the adsorbent [62]. The observed chemical interaction between lead ions and WSNBS surface functional groups shows that the chemisorptions process.

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 to 6 was studied. The relationship between the initial pH values and the lead ions removal efficiency was presented in Fig. 4.

Fig. 4 shows that the lead ion removal depends strongly on solution pH. As it can be seen in Fig. 4, when the pH increases from 2 up to 3, the removal efficiency increases from 22% to 90%. Maximum sorption of lead ions on WSNBS takes place at pH 4. Because of high abundance of H^+ at

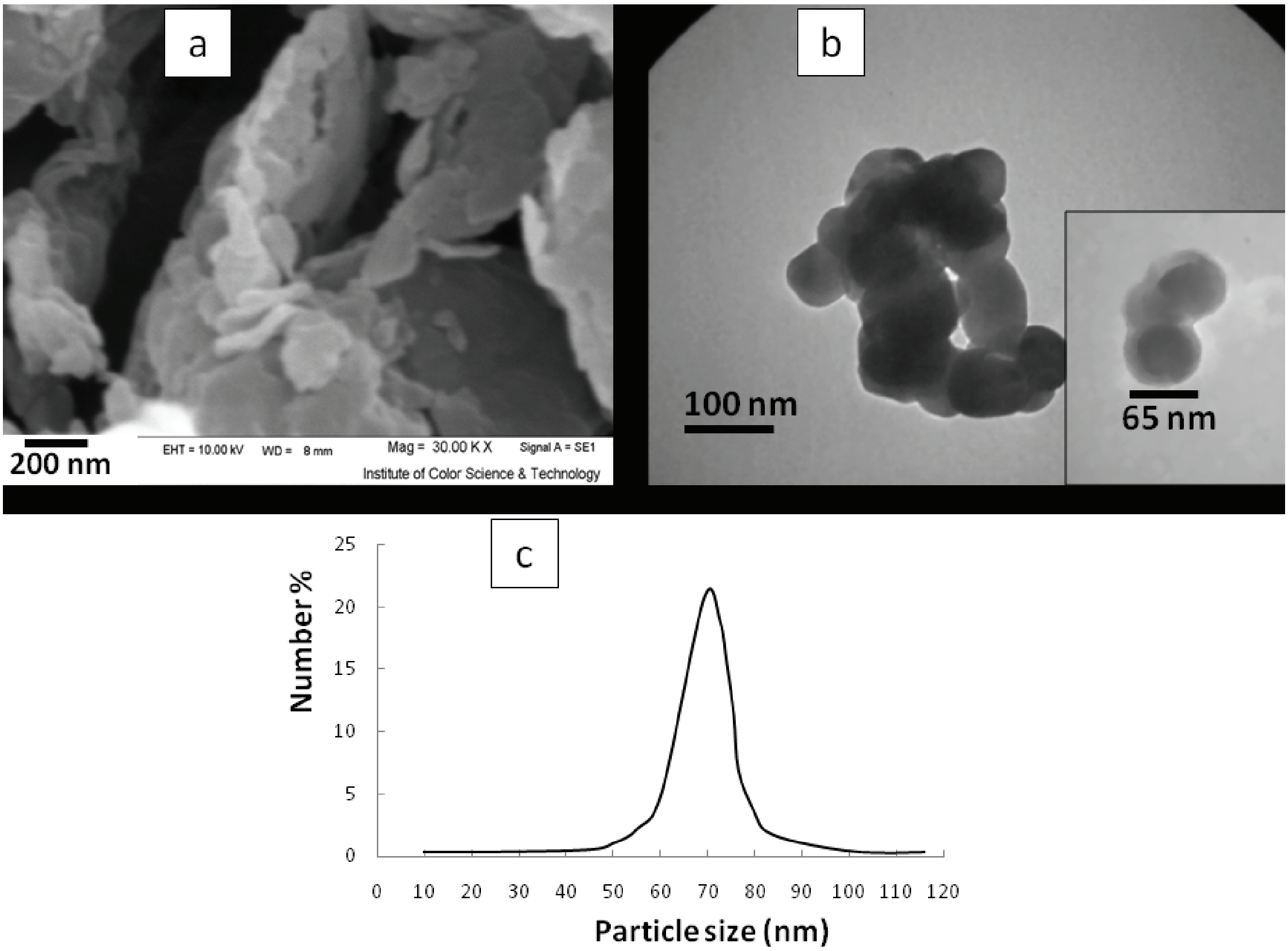

Fig. 1. (a) SEM image, (b) TEM micrograph and (c) size distribution diagram of the walnut skin nanoparticles.

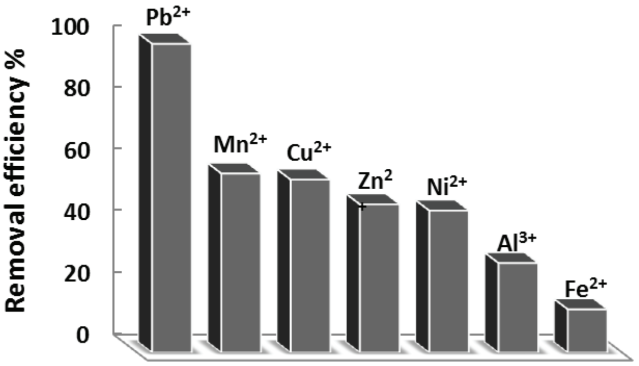

Fig. 2. Application of WSNBS for the removal of some heavy metal ions from water.

pH less than 3, it can interfere on the sorption of Pb^{2+} ions. Therefore, the sorption of lead ions on WSNBS is decreased. In other words, some sorption sites on WSNBS are occupied by hydrogen ions. At the pH above than 4, the percentage of lead ion removal decreases that it is probably due to the formation of sediment of cation like $Pb(oH)^+$ which is less likely to be attracted to the surface of nanoparticles [63,64].

3.2.2. The effect of WSNBS dosage

To study the effects of WSNBS dosage on sorption, the removal experiments were carried out with different biosorbent dosages at the range of 0.2 to 8 mg ml^{-1}. Fig. 5 shows the effect of sorbent dosage on the removal efficiency.

As it can be seen in Fig. 5, by increasing the biosorbent dosage from 0.2 to 1.2 mg ml^{-1} and then from 2 to 6 mg ml^{-1}, the removal value increases from 60% to 90% and 90% to 100%, respectively. In the small amount of biosorbent, because of saturation of the sorption sites by Pb^{2+} ions, the ion removal is not completed [63]. The slowly increasing of lead ion removal in the sorbent dosage of 2 to 6 mg ml^{-1} shows the equilibrium nature of sorption/desorption processes.

3.2.3. Effect of contact time

Sorption kinetics is the important factor in flow systems and industrial applications of sorbents. For example, a sorbent with high kinetics rate can be packed in a column for the continuous water purification in a piping system. The results of sorption studies as a function of contact time (mixing time of lead ion solution with WSNBS) are shown in Fig. 6.

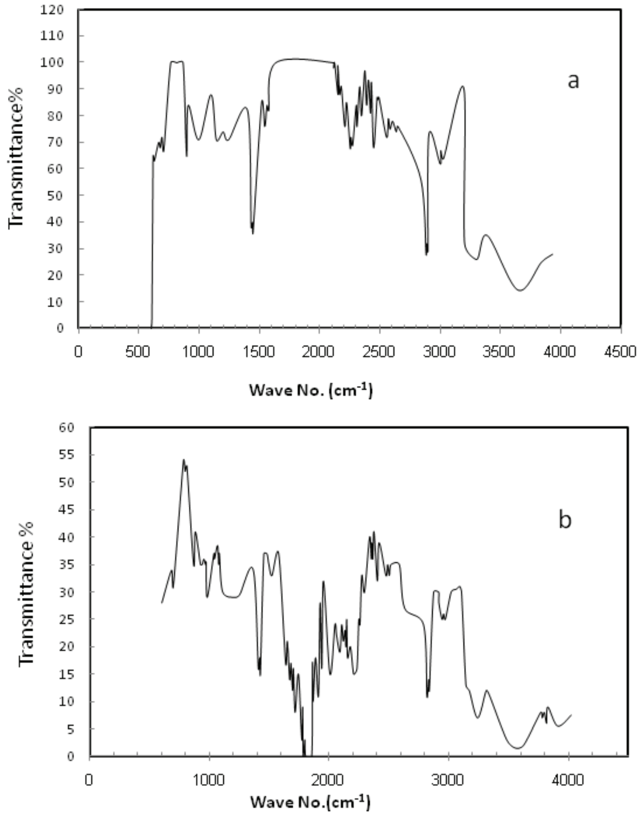

Fig. 3. IR spectrums of the prepared WSNBS before (a) and after treatment with lead ions (b).

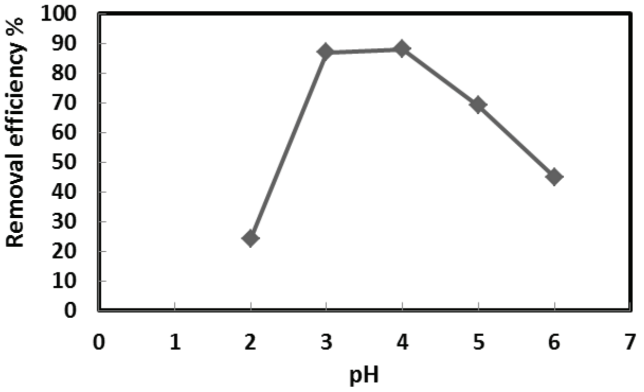

Fig. 4. Effect of pH on the lead ion removal efficiency on WSNBS.

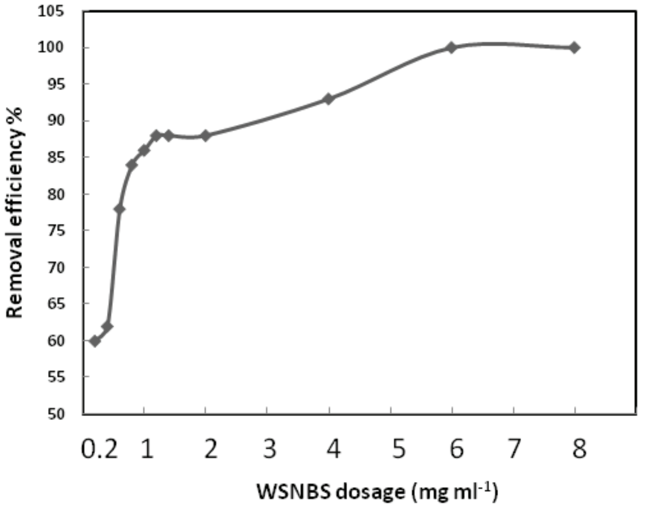

Fig. 5. Effect of WSNBS dosage on the lead ion removal efficiency.

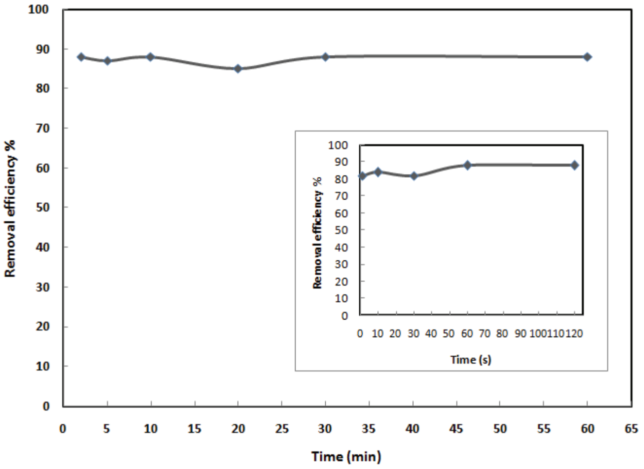

Fig. 6. Effect of contact time on the removal efficiency of lead ions.

According to the Fig. 6, in the time range of 2 to 60 min, the removal efficiency does not depend on contact time. The results of fast sorption studies were shown as inserted in Fig. 6. The results show that the removal value is reached to 80% during the first second. Therefore, it is impossible to determine the time-dependency data for the kinetic studies such as examination of kinetics models. Based on the obtained results, sorption of lead ions on WSNBS has a very fast kinetics. Based on these results, the appropriate contact time for Pb^{2+} ions is 5 s, which is very shorter than those of all previous reports, for example ref. [65].

3.2.4. Isotherm studies

The lead ions removal performance by the WSNBS was investigated as a function of the initial lead ion concentration (at the range of 5–35 ppm) in room temperature and pH 4. In this study, the sorption time was fixed at 5 s. Fig. 7 shows the effect of initial ion concentration on the removal efficiency.

As it can be observed in Fig. 7, by increasing the initial concentration of the sample, the sorption efficiency of lead ions is decreased; this decreasing of sorption indicates that sorption sites on the sorbent surface become saturated [66]. To determine the sorption capacity of WSNBS towards the examined lead ions, the sorption studies in initial concentration range of 50 to 350 µg ml^{-1} were carried out. The sorption mechanism of lead ions adsorption on WSNBS was evaluated using the sorption isotherms such as Langmuir, Freundlich and Temkin models. In the Langmuir model, it is assumed that is a homogeneous surface, the sorption energy

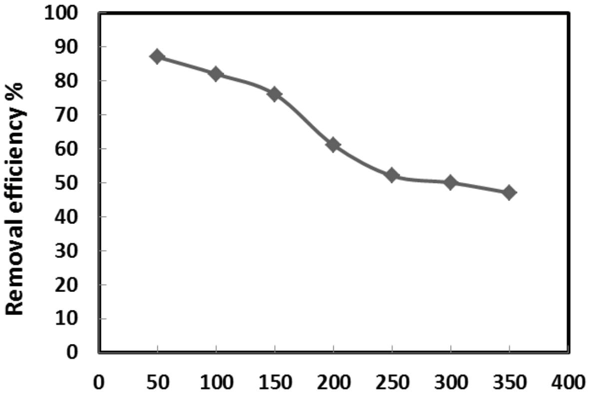

Fig. 7. Effect of initial lead ion concentration on the removal efficiency.

is constant and equal in all places. Sorption on the surface to be performed at the 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 [67]. The Langmuir isotherm equation and its linear form are presented as Eqs. (3) and (4), respectively:

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

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

where, q_e is the equilibrium sorption capacity of the biosorbent for lead ions in mg g^{-1}, C_e is the equilibrium concentration of metal ions in ppm, q_m is the highest amount of metal ions adsorbed in mg g^{-1}, and b is the constant that refers to the bonding energy of 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, and different pieces of the same level do not impact together [67]. 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 log q_e versus log C_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:

$$q_e = \frac{RT}{b} \text{In}(A C_e) \tag{7}$$

In this equation, $\frac{RT}{B} = B$

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

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

where q_e is the equilibrium adsorption capacity of the sorbent 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 and also, b is the constant in j mol^{-1}. The quantitative relationship between initial concentration of pb^{2+} ions and the sorption capacity was analyzed with three different isotherm models which are shown in Fig. 8.

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 model was better fitted to the experimental data ($R^2 = 0.981$). Based on the Langmuir model, the highest sorption capacity of pb^{2+} by WSNBS was calculated 17.39 mg g^{-1}.

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 solutions with 50 mg WSNBS. The experimental data showed that the sample dilution from 25 to 300 ml does not have any significant effect on the lead ion removal. The results show that WSNBS 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 the 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 WSNBS, sorption experiments were done at temperature range 10°C–40°C. The obtained results are presented in Fig. 9. According to the presented data in Fig. 9, increasing of solution temperature causes to decrease slowly the lead ion removal. This result is probably related to the exothermic nature of Pb^{2+} sorption on WSNBS [30].

3.2.7. Application of WSNBS 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 WSNBS, the removal efficiencies of some heavy metal ions such as Mn^{2+}, Cu^{2+}, Zn^{2+}, Ni^{2+}, Al^{3+} and Fe^{2+} were also examined in the optimized conditions of lead ions. The summary of all results was presented in Table 2.

The obtained results show that WSNBS can be used as a selective sorbent for pb^{2+} ions in water samples.

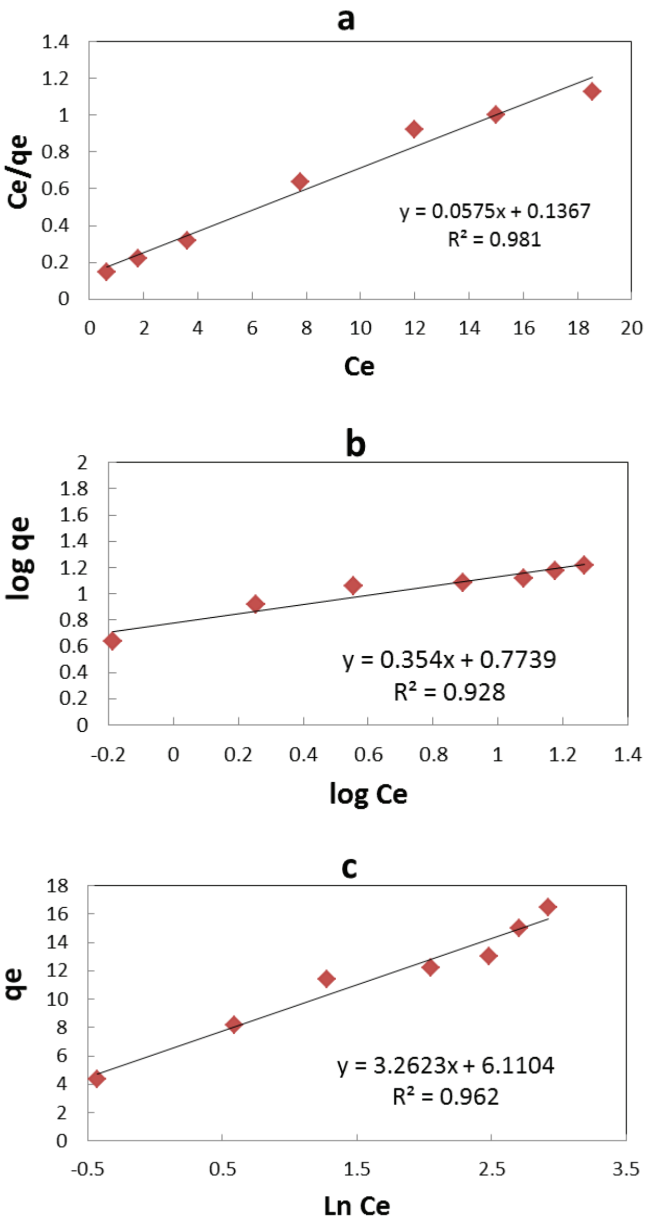

Fig. 8. Comparison of (a) Langmuir, (b) Temkin and (c) Freundlich isotherm models for the sorption of Pb(II) on WSNBS (WSNBS = 0.05 g, pH = 4, sample volume= 50 ml, T = 25°C).

Table 1
The calculated parameters of Langmuir, Freundlich and Temkin isotherm models

Isotherm	Constants	R^2
Langmuir	$q_m = 17.391$ mg g^{-1} $b = 0.419$	0.981
Freundlich	$K_f = 5.929$ $n = 2.825$	0.962
Temkin	$A = 6.507$ $B = 3.262$ $b = 759.525$	0.928

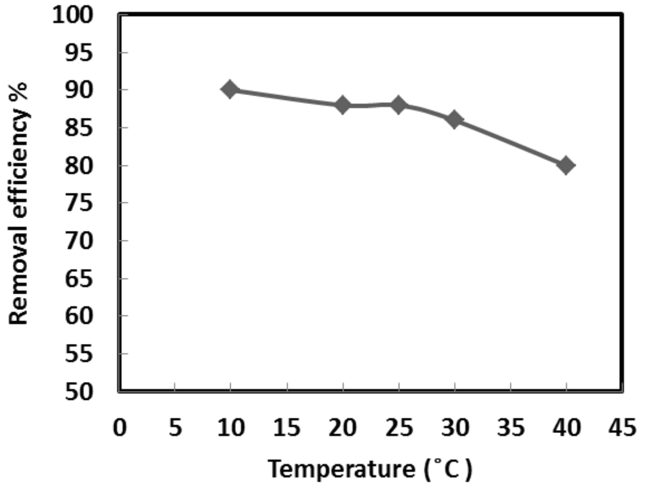

Fig. 9. Temperature-dependency of lead ion sorption on WSNBS.

Table 2
The removal values of some metal ions in separate solutions

Examined ions	Removal (%)
Pb^{2+}	100
Cu^{2}	56
Al^{3+}	29
Zn^{2+}	48
Fe^{2+}	14
Mn^{2+}	58
Ni^{2+}	46
Na^{+}	0.0
K^{+}	0.0

3.2.8. Desorption studies

In desorption step, adsorbed ions on WSNBS 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 HNO_3 concentration on the recovery of pb^{2+} ions was studied at the range 0.1 to 2 M (Fig. 10).

As it can be seen in Fig. 10, by increasing nitric acid concentration from 0.1 to 0.5 M, the recovery of pb^{2+} ions has reached from 83% to 100%, thus, the concentration of 0.5 M nitric acid is enough to be selected as suitable solvent. It is obvious that in the elution process, the adsorbed lead ions on WSNBS are completely replaced with hydrogen ions when the nitric acid is 0.5 M or more.

If WSNBS is used as solid sorbent in the analytical solid phase extraction, the volume of eluent is a main factor that affects on the preconcentration factor. Therefore, the dependency of lead ion recovery on eluent volume was evaluated at the range 0.2–2 ml (Fig. 11). Based on the presented data in Fig. 11, by increasing HNO_3 volume from 0.2 to 0.8 ml, the recovery percentage is increased from 65% to 100%. Therefore, 0.8 ml HNO_3 (0.5 M) can be used as an effective solvent to release the loaded lead ions on WSNBS.

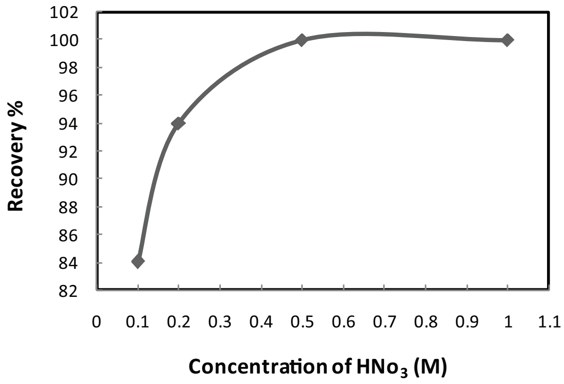

Fig. 10. Effect of HNO_3 concentration on the lead ion recovery.

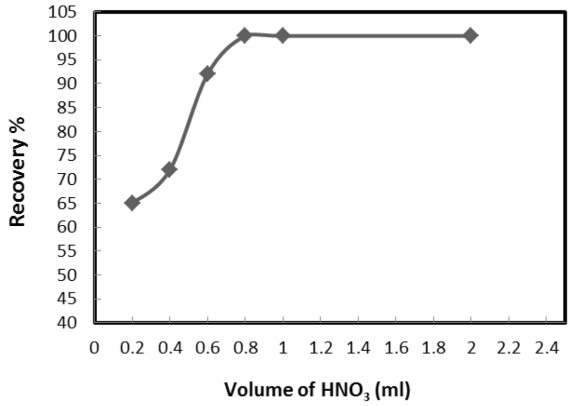

Fig. 11. Effect of HNO_3 volume on the lead ion recovery. HNO_3 concentration is 0.5 M in all experiments.

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 samples, two water samples (well water in the yard of Abhar Payame Noor University and outlet water of Kine Vars dam) were collected. For analytical purpose, the pH of the well water was set in 4 and used in sorption and desorption processes. 200 mg WSNBS was added to 500 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 0.5–3 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. Fig. 12 shows the obtained calibration curve for the determination of lead ion in real samples.

Based on the data presented in Fig. 12, the presented method can be considered as an analytical method for the determination of lead ion in trace level. The analytical RSD and detection limit of the proposed method were calculated 4.32% and 0.11 ppb, respectively. Based on the initial sample volume and the final volume of the sample after desorption step, the preconcentration factor for the presented method was calculated 200.

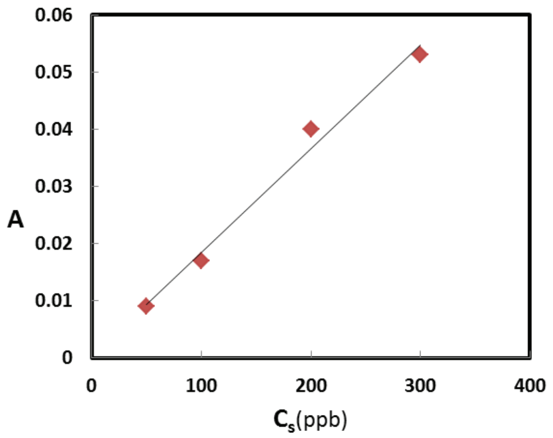

Fig. 12. The obtained calibration curve for the determination of lead ion in real samples.

Table 3
Results of the proposed method in the real samples

Sample	Pb^{2+} (ppb)		Critical t-value	Experimental t-value
	Presented method	ICP-MS		
1	1.275 ± 0.062	1.40 ± 0.03	4.604	3.11
2	0.634 ± 0.019	0.65 ± 0.04	4.604	0.631

The obtained results of lead ion concentration in real samples were compared with those of ICP-atomic emission spectroscopy (ICP- AES) by using the t-test method. All results are summarized in Table 3. To do t-test, the following equation was used:

$$t=\sqrt{\frac{n_1\times n_2}{n_1+n_2}}\times\frac{a_1-a_2}{\sqrt{\frac{(n_1-1)S_1^2+(n_1-1)S_2^2}{n_1+n_2-2}}} \tag{9}$$

where a_1 and a_2 are he mean values for the measured concentrations of lead ion in ppb by the proposed method and ICP-MS method, respectively, and n is the frequency of each measurement.

According to the results, we can conclude the two methods are not significantly different, this means that both methods are suitable, and the average difference between the two methods is related to the random errors.

4. Conclusions

Walnut skin particles can be processed by an innovative ball milling method to spherical nanoparticles with an average diameter of 65 nm. The walnut skin nanoparticles can be 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 level. The highest capacity of lead ions on the nanosorbent based on the Langmuir isotherm method was calculated 17.39 mg g^{-1}. Walnut skins nanoparticles can act as a cheap and very fast nanosorbent to remove completely Pb^{2+} ions in less than 5 s, which is a tremendous advantage. Based on the obtained results, walnut skin nanoparticles can be used as an efficient biosorbent in construction of water purification devices.

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