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Mechanically produced Hazelnut Skin Micro and Nano Biosorbents for the Fast Removal of Lead Ions from Polluted Waters

Hassan Karami* , **Seyyed Kazem Kazemi**

Department of Chemistry, Payame Noor University, Tehran, Iran

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Abstract

The work is a feasible study about the performance of woody skin and outer soft shell of Hazelnut for the removal of lead ions from water. The Hazelnut woody skin and soft outer shell are crushed by an innovative ball mill to prepare micro and nano powders. TEM images show that the produced nano powder includes uniform nanoparticles with 8-10 nm average diameters. The produced nanoparticles were used as a suitable and effective biosorbent to remove lead ions from water. Experimental data shows that the adsorption of lead ions on the surface of hazelnut skin nanoparticles is acceptably fitted to Langmuir isotherm model. Based on the Langmuir isotherm, a maximum adsorption capacity of 91 mg g^{-1} is achieved for adsorption of lead ions on the surface of hazelnut skin nanoparticles. The obtained results showed that the best removal of lead ions can be done under conditions includes 50 ml initial solution, pH=4, 120 mg L^{-1} initial concentration of lead ions per 70 mg biosorbent for contact time of 20 minutes at room temperature. The adsorbed ions are easily eluted by 1.5 ml 0.7 M HNO_3 solution. Under the optimal conditions, preconcentration factor of 200, %RSD of less than 5% with detection limit of 100 ppb are obtained. The effects of some interfering ions such as Fe^{2+}, Cu^{2+}, Mg^{2+}, Zn^{2+}, Mn^{2+} and Ni^{2+} on the removal efficiency of lead ions were studied. The presented method is successfully applied for removal and determination of lead ions from real samples.

Keywords
Ball mill; Hazelnut skin; nanosorbent; biosorbent; lead ion removal.

1. INTRODUCTION

Unfortunately, the contamination of surface and underground water with heavy metal ions is a serious, increasing and dangerous problem. One of the serious pollutants is lead ions, which various zoon of the world such as Zanjan and some of villages around this city, are affected by polluted water with lead ions. The mechanism of the toxicity of lead ions is caused by the strong affinity to sulfur to disrupt the activity of vital enzymes in living organisms. The lead ions makes the arteries less flexible and the heartbeat irregular and exposes people to high blood pressure. Decreased IQ, children's hyperactivity, irritability and insomnia are symptoms of increased lead in the body [1,2]. Heavy metal ions are usually removed from aqueous media by chemical precipitation processes [3], ion exchange [4], solvent extraction [5], reverse osmosis [6], electrode coagulation and membrane filtration [7] and surface adsorption [8]. Today, surface adsorption is one of the most widely used methods to remove heavy metals due to its high efficiency and ease of implementation. Biosorption is a surface adsorption method that is the ability of biomass to collect heavy metals from contaminated water through physical or chemical adsorption pathways. The skin and roots of fruits, algae, molds, yeasts, bacteria and fungi are examples of biosorbents. The biosorbents have many advantageous such as high efficiency in low concentrations, performance in a wide range of temperature and pH, easy recycling of biosorbents, and the existence of cheap sources and availability [1, 2].

As mentioned, adsorption technology has been developed using biological adsorbents, In the meantime, nano-biosorbents are more desirable than other biosorbents due to their small particle size and high surface area, which increase chemical reactivity and adsorbend/adsorbant interactions and have a high adsorption capacity. The disadvantage of this method is the saturation of the biomass due to the occupation of all the interaction sites by irreversible adsorption [1, 2].

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* Corresponding author:
H. Karami; E-mail: karami.hassan@pnu.ac.ir

Isotherm is the most important parameter in the design of adsorption systems and describes the relationship between the concentration of the adsorbed material and the adsorption capacity of an adsorbent. In other words, the graph of the concentration of dissolved species on the solid phase q_e against the concentration dissolved in the solution C_{eq} in the equilibrium state expresses a surface adsorption isotherm. Adsorption isotherms are mathematical equations that show the relationship between the amount of adsorption of an ion by the solid phase and its concentration in the equilibrium solution at a constant temperature and are used as tools to describe and predict the amount of adsorption, the type and intensity of the interaction between the adsorbent and the adsorbent. The most famous of them are Langmuir [9], Freundlich [10] and Temkin [11] equations. Kinetic equations are equations that are used before balancing, and the time parameter plays a major role in them. Adsorption kinetics is used to investigate the controlling mechanism in the biological adsorption process such as mass transfer and chemical reaction. Adsorption kinetics is important for adsorption studies because it can predict the removal rate of a pollutant from aqueous solutions in advance and provide valuable information for understanding the mechanism of adsorption reactions. In order to study the mechanisms controlling the adsorption process, pseudo-first-order and pseudo-second-order kinetic models are used [1, 2].

2. EXPERIMENTAL

2.1. Materials

All chemicals such as Nitric acid, Hydrochloric acid and metal were purchased from Merck and used without any purifications. In all experiments, distilled water was used.

Hazelnut seeds along with wooden skin and outer soft shell were collected from the gardens of Tarom region in Zanjan province. Figure 1 shows the photo of the collected Hazelnuts.

Fig. 1. Photo of the collected Hazelnuts.

The soft shell and wooden skin of the Hazelnuts were carefully separated and dried in separate vessels in an electrical oven at 70°C for 48 h. The dried soft skin as well as wooden skin were crushed by an innovated fixed tank ball mill in deferent times to prepare micro and nano powders.

2.2 Instrumentals

A new and innovative ball mill with Iranian patent number of 105404 (2023) was used to prepare micro and nano powders of both Hazelnut soft skin and wooden skin. The scheme of the designed tank of the innovated ball mill was shown in Fig. 2.

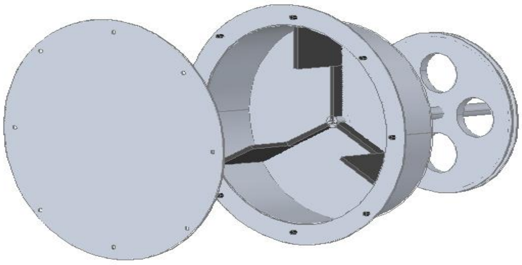

Fig. 2. Scheme of the tank of the desired ball mill.

In Fig. 3, scheme of the desired ball mill was pictured.

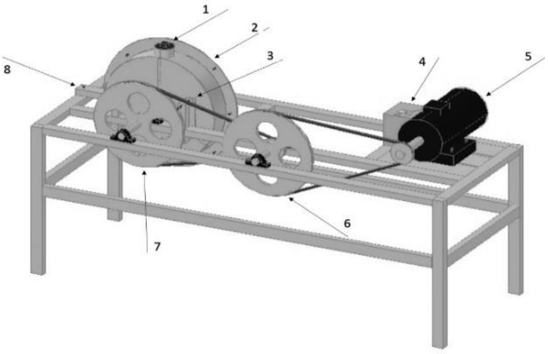

Fig. 3. The scheme of the invented ball mill. 1: Loading and unloading valve, 2: Sealing edge, 3 and 8: Tank stabilizers, 4: Inverter, 5: Electromotor, 6 and 7: pulleys and belts.

The samples were imaged by a transmission electron microscope (TEM, Model LEO912-AB, England) and the size distribution studies were done by Molvern Zeta sizer DLS. FTIR Spectrum GX Perkin Elmer was used to identify the chemical intercation between biosorbent and lead ions. A Sartorius TE123S weighing product with accuracy of ±0.0001 g was used in all weighing experiments. A heater stirrer model 1203 Jenway and a pH meter model 3510 Jenway were used to stir solutions and to adjust pH of solutions, respectively. Laboratory Circulator model D1 (3063-001) manufactured by HAAKE Germany was used to adjust the temperature of the solutions. A flame atomic absorption spectrophotometer (FAA, Sens AA model, GBC, Australia) was used to determine the concentration of metal ions. The cellulose acetate membrane with a 47 mm diameter and 0.2 µm diameter of pores was used to separate the adsorbent nanoparticles from the solution. A vacuum pump model (DN-42N-2501) made by the American Platinum Company was used to create a vacuum in order to pass the solution from membrane.

2.3. Procedures

2.3.2. Sorption experiments

Hazelnuts have two skins, the soft and outer skin and the hard and wooden skin, both skins were tested and according to the results obtained, it can be said that the soft or outer skin of the hazelnut has a higher efficiency in adsorbing all ions than the hard and wooden skin of the hazelnut. According to the obtained results, it can be said that the soft or outer skin of hazelnut showed a higher efficiency for adsorbing all metal ions, especially lead ion, compared to the hard and woody skin of hazelnut. To conduct experiments, The first solutions with a concentration of 100 ppm of heavy metal ions Fe^{2+}, Cu^{2+}, Mg^{2+}, Pb^{2+}, Zn^{2+}, Mn^{2+} and Ni^{2+} And the control solution with a pH equal to 4 was prepared from heavy metal salts, then 0.1 g of wood and outer bark was weighed separately and each of them was poured into 50 cc of a 100 ppm solution of heavy metal ions. It was stirred with a mixer heater at 600 rpm for 30 minutes Then, the mixture of metal ions and hazelnut skins adsorbent was placed separately in the centrifuge and centrifuged at 2500 rpm for about 8 minutes, and the amount of metal ion adsorption of the supernatant solution obtained from the centrifuge was calculated by the flame atomic adsorption device. The obtained results showed that the outer shell of hazelnut with high adsorption and better efficiency was chosen as the main adsorbent and lead ion was chosen as the main cation.

The obtained results shown in Fig.2 can be said that the soft or outer shell of hazelnut has a higher efficiency to adsorb all metal ions than the hard and woody shell of hazelnut. Also, Fig.2 shows that the adsorption rate of lead ion is higher than that of all metals. Finally, according to the above results, the soft or outer skin of hazelnut was chosen as the adsorbent and lead metal ion was chosen as the main cation.

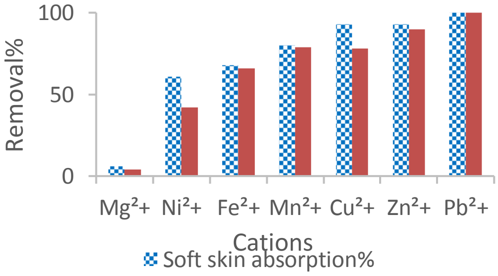

Fig.2. Percentage of adsorption of cations and selection of the main cation and hazelnut skin

The effects of adsorption parameters including pH of the sample, initial concentration of lead ion, gram value of adsorbent, temperature of solution, volume of solution, stirring time and contact of lead ion with adsorbent were calculated according to equation (eq.1).

$$\mathrm{Removal}(\%) = \frac{C_i - C_f}{C_i} \times 100 \qquad \text{(eq.1)}$$

In this regard, C_i is the initial concentration of lead solution in ppm and C_f is the residual concentration of lead ion in ppm after contact with hazelnut skin bio-nanoparticles.

Also, the equilibrium adsorption capacity q_e in terms of $mg.gr^{-1}$ of lead ion was calculated using the mass balance equation (eq.2).

$$q_e = \frac{(c_i - c_e)v}{m} \qquad \text{(eq.2)}$$

In it, C_i is the initial concentration of lead solution in ppm, C_e is the equilibrium concentration of lead ion in ppm, v is the volume of the sample in milliliters and m is the gram value of the adsorbent of the hazelnut skin.

2.3.3. The effect of pH

The effect of solution pH to achieve the removal efficiency of lead ion by hazelnut outer skin nanoparticles was prepared with several 100 ppm solutions at different pHs which were adjusted with 0.1 M nitric acid and sodium hydroxide solutions. 50 ml of each solution, 100 mg of hazelnut outer skin bio-particles were added and the percentage of lead ion removal and the amount of lead ion remaining in the solution at each pH were calculated by flame atomic adsorption device.

2.3.4. The effect of the initial concentration of the main ion

To investigate this important factor, several solutions with different concentrations of lead ions were prepared by adjusting the pH to 4. 50 ml of solution, 100 mg of hazelnut outer skin nano-adsorbent was added. The resulting mixture was stirred with the help of a magnet and a magnetic stirrer at a speed of 600 rpm for 30 minutes to adsorb the lead ion on the surface of the nano-adsorbent. The residual lead ion concentration was calculated with the help of flame atomic adsorption device.

2.3.5. The effect of amount of nano-adsorbent

To investigate the effect of the amount of nano-adsorbent, all variables were kept constant and the pH of the solutions was set to 4. Several solutions with specific concentration of lead ion were prepared. 50 ml of the solution with different amounts of hazelnut skin nanoparticles in terms of mg were added. The residual lead ion

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concentration was calculated with the help of flame atomic adsorption device.

2.3.6. The effect of initial sample volume

To investigate the effect of sample dilution on the efficiency of lead ion removal, a solution with a certain concentration of lead ion was prepared. Several solutions with different volumes of lead ions with equal number of moles were prepared from the above solution. The prepared solutions have equal moles of lead ions, but because they do not have the same volume, they will not have equal concentrations. The amount of 50 ml of each of these solutions was added to them in addition to the specific milligram amount of bio-nano-particles from the outer skin of hazelnuts at a specific temperature. The residual lead ion concentration was calculated with the help of flame atomic adsorption device.

2.3.7. The effect of nano-adsorbent contact time

The contact time of the analyte with the adsorbent surface is one of the factors that can affect the adsorption process. In order to investigate the effect of this factor on the amount of lead ion inhibition on the surface of the outer shell nano-adsorbent of hazelnut, several solutions with specific concentration of lead ion were prepared. To 50 ml of each of the prepared solutions, a specific amount of hazelnut skin bio-adsorbent was added. Then the mixtures were stirred for different times to adsorb the lead ion on the surface of the nano-adsorbent of the outer skin of the hazelnut. The residual lead ion concentration was calculated with the help of flame atomic adsorption device.

3. RESULTS AND DISCUSSION

3.1. Properties of the prepared hazelnut skin

The particle size of the prepared hazelnut skin was determined by transmission electron microscopy (TEM, Fig.3) and dynamic light scattering (DLS, Fig.4) and infrared spectroscopy (IR or FTIR, Fig.5). TEM images show that the shape of the prepared particles is spherical and regular, and DLS diagrams show that the size of the particles is in the range of nano particles.

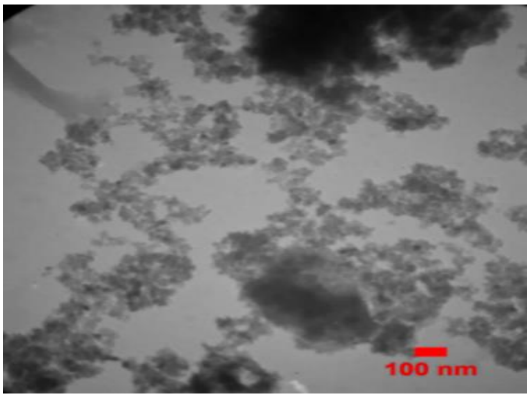
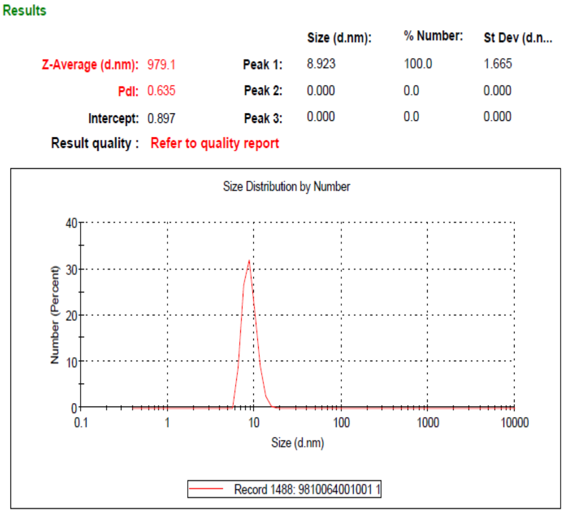


Fig. 3. TEM image with 100000 magnification

According to the Fig.3, From the dark and light points and the spherical shape of the particles, we conclude that the size of the particles is in the nano range [12].


Results

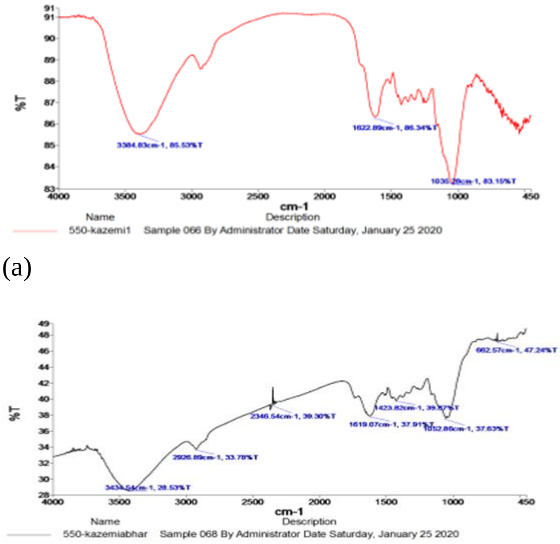
			Size (d.nm):	% Number:	St Dev (d.n...
Z-Average (d.nm):	979.1	Peak 1:	8.923	100.0	1.665
PdI:	0.635	Peak 2:	0.000	0.0	0.000
Intercept:	0.897	Peak 3:	0.000	0.0	0.000

Result quality : Refer to quality report

Fig.4. DLS image of numerical percentage of particles - particle size

According to the diagram of numerical percentage of particles according to particle size Fig.4, it can be concluded that almost 100% of the sample has been converted into particles with a size of 8.923 nm.

Using the IR or FTIR spectrum of the adsorbent, after contact with the analyte solution, it can be determined whether the adsorption of the analyte on the adsorbent is physical or chemical. And if it is chemical adsorption, how is it adsorbed? The IR spectrum was prepared from the outer skin of hazelnut nanoparticles before interacting with lead ion and after interacting with the outer skin of hazelnut, which is shown in Fig.5.



(a)

(b)

Fig.5. FTIR diagram for hazelnut skin nanoparticles before interaction with lead ion (a) and FTIR diagram for hazelnut skin nanoparticles after interaction with lead ion (b).

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In Fig.5 a, it can be seen that there are several indicative peaks for hazelnut skin in wave numbers 1035, 1622 and 3364 cm^{-1}. The vibrational band 1035 cm^{-1} is related to c-o symmetric and asymmetric stretching vibrations, which is weakened but shifted to higher wavenumbers 1052 cm^{-1} after contact with lead ion. The vibrational band 1622 cm^{-1} is assigned to c=o vibrations, whose intensity is also weakened and shifted to smaller wavenumbers 1619 cm^{-1}, and the vibrational band 3364 cm^{-1} is related to It corresponds to the O-H stretching vibrations, which are weakened after the interaction with the lead ion and shifted to higher wavenumbers 3434 cm^{-1}. Considering that both the peaks have shifted and their intensity has decreased, we conclude that the connection of lead ions with the hazelnut shell nano-adsorbent is through chemical adsorption.

3.2. Adsorption studies

3.2.1. The Effect of solution pH

To investigate the effect of pH of the initial solution on the adsorption of lead ions, the case was studied in the range of 1-8. The relationship between initial pH values and Pb^{2+} removal efficiency was presented in Fig.6. The maximum adsorption by the outer skin nanoparticles of hazelnuts takes place at pH = 4. The results presented in the figure show that at low pH due to the high abundance of hydrogen ions H^{+} compared to lead ions Pb^{2+} ,the amount of adsorption of lead ions by the nano-adsorber of hazelnut skin is reduced. In other words, some adsorption sites on the surface of the nano-adsorbent of the outer skin of hazelnuts are occupied by H^{+} ions. With an increase in pH above 4, probably Pb^{2+} ion reacts with these ions due to the increase in the concentration of OH ion and forms the $Pb(OH)_2$ precipitate, which tends to form a complex with zinc functional groups. The outer shell nanoparticles of hazelnuts are less than Pb^{2+} ions, so the adsorption percentage decreases.

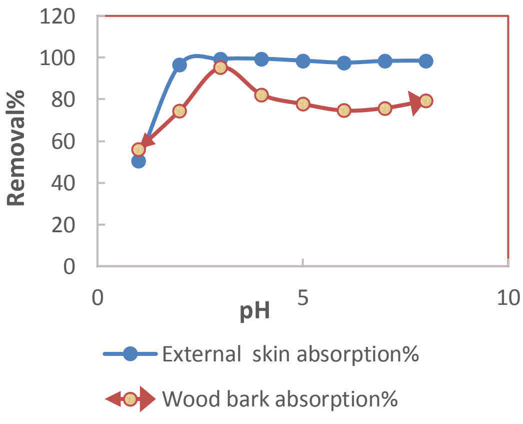

Fig.6. Graph of sample pH effect on lead ion removal

According to Fig.6, At pH lower than 4, most likely due to the increase in the concentration of hydrogen ions, the competition between hydrogen ions and metal ions to occupy the active sites on the adsorbent increases, and the effect of this phenomenon causes a decrease in adsorption. At pH higher than 6, Pb^{2+} ion probably reacts with these ions due to the increase in OH ion concentration and forms $Pb(OH)_2$ precipitate, which tends to form a complex with functional groups on skin particles. Hazelnut is less than Pb^{2+} ion, so the adsorption percentage decreases [13,14].

3.2.2. The effect of the initial concentration of lead ion

In order to investigate the effect of the initial concentration of lead ion on the removal of lead ion by the outer shell nano-adsorbent of hazelnut, solutions with different concentrations were prepared.

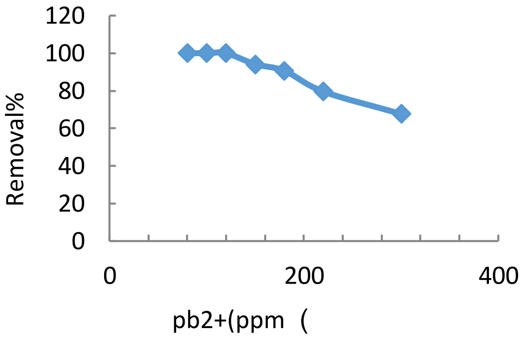

Fig.7. The effect of the initial concentration of the solution on the percentage of lead ion adsorption

As seen in Fig.7, the amount of unadsorbed lead ion species increases with the increase of the initial concentration of the sample. This decrease in lead ion adsorption shows that the capacity of the adsorbent is limited and after the concentration of 120 ppm (per 50 ml of solution and 100 mg of adsorbent) the adsorption sites on the surface of the adsorbent are saturated with lead ions.

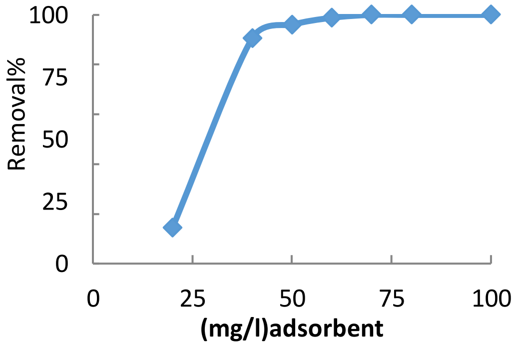

Fig.8. Examining the effect of adsorbent amount on the percentage of lead adsorption

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3.2.3. The effect of adsorbent amount

The study of the effect of the amount of adsorbent on the process of lead ion removal by the nano adsorbent of the outer shell of hazelnut with different masses of adsorbent was carried out.

Fig.8 shows the results of this investigation that with the increase of the amount of adsorbent, with a volume of 50 ml and with a concentration of 120 ppm of lead ion, the percentage of inhibition gradually increases until it reaches 100% at the point of 70 mg and then remains constant. In low amount of adsorbent, due to the saturation of the adsorbent surface with Pb^{2+} ions, the percentage of inhibition decreases, and with the increase of the amount of adsorbent, due to the increase of free and active sites on the surface of the nano-adsorbent, the percentage of inhibition increases [15].

3.2.4. The effect of temperature on lead ion removal

In order to investigate the effect of temperature on the process of lead ion removal by the outer shell nano-adsorbent of hazelnut, the removal of lead ion by the nano-adsorbent was carried out at different temperatures.

The obtained results are shown in Fig.9. The results show that the removal process of lead ion by the outer skin nano-adsorbent of hazelnut was exothermic, and with the increase in temperature, the mobility of lead ion increased and therefore the amount of desorption of lead ion from the surface of the nano-adsorbent increased. According to the mentioned contents, we consider the optimal temperature to be 25 degrees Celsius or the same as the ambient temperature [16-18].

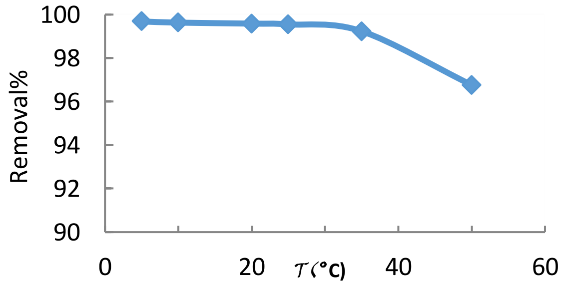


Fig.9. Examining the effect of temperature on the inhibition percentage of lead ion

3.2.5. The effect of solution volume on lead ion removal

To investigate the effect of sample volume (the effect of sample dilution) on the removal efficiency of lead ions, solutions of lead ions with equal number of moles and different volumes were prepared and all steps of inhibition, separation and measurement of the concentration of the remaining lead ions in the solution were performed at 25 degrees Celsius. The decrease in inhibition due to dilution can be justified by the fact that with the increase in the volume of the solution, the concentration of lead ions in the solution decreases, so the balance of adsorption/desorption is less in favor of adsorption [8]. To clarify the matter, the adsorption of lead ion on the outer shell nano-adsorbent of hazelnut can be explained according to the equation (eq.3) and (eq.4).

$$Pb^{2+} + \text{site}_{NONS} \leftrightarrow Pb^{2+}.\text{site}_{NONS} \quad \text{(eq.3)}$$

$$K = \frac{[Pb^{2+}.\text{site}_{NONS}]}{[Pb^{2+}][\text{site}_{NONS}]} \quad \text{(eq.4)}$$

In these two relationships, Pb^{2+} represents lead ions in solution, site_NONS the active sites on the outer shell nanoparticles of hazelnuts, Pb^{2+}.site_NONS the sites occupied by lead ions, and K also represents the equilibrium constant of the reaction. In dilute solutions whose initial volume is greater than 100 ml, the residual lead ion concentration in ppm decreases, so there must be more lead ions freely in the solution to maintain a constant equilibrium.

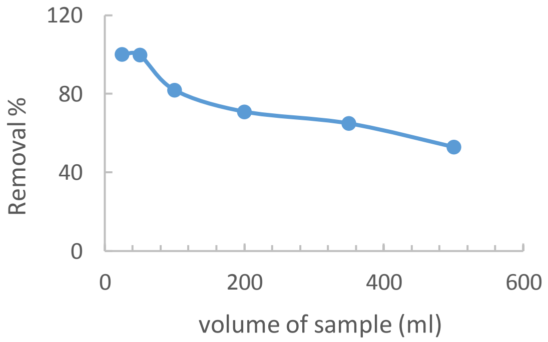


Fig.10. The effect of sample volume on the percentage of lead ion inhibition

Fig.10 shows the effect of changing the volume of the sample solution (dilution) on the inhibition of lead ion. By increasing the solution volume from 25 ml to 500 ml, the inhibition percentage decreases from 100% to 53%.

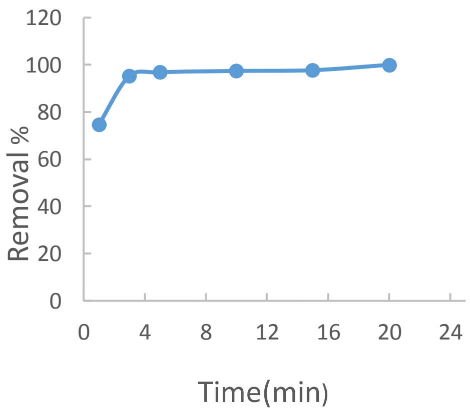


Fig.11. The effect of contact time on the percentage of lead ion adsorption

3.2.6. The effect of nano-adsorbent contact time on removal efficiency

The contact time of the analyte or sample with the adsorbent surface is one of the factors that can affect the adsorption process. To investigate the effect of this factor on the amount of lead ion inhibition on the surface of the nano-adsorbent, solutions were prepared and the amount of lead ion adsorption was obtained by the atomic adsorption device.

the results of which are shown in (Fig.11), The graph of the effect of stirring time shows that the interaction of lead ion with the nano-adsorbent or the amount of penetration of lead ion on the surface of the nano-adsorbent increases with increasing time and the adsorption rate reaches 100% in 20 minutes.

3.2.7. Adsorption isotherms

As mentioned in the study of the effect of the initial concentration of lead solution on removal, the adsorption of lead ions decreases with the increase of the initial concentration of the sample. This decrease in lead ion adsorption shows that the capacity of the adsorbent is limited and after the concentration of 120 ppm, the adsorption sites on the surface of the adsorbent are saturated with lead ions. The maximum adsorption capacities of the hazelnut outer shell nano-adsorbent for lead ions were evaluated using adsorption, Isotherms such as Langmuir, Freundlich and Temkin. The assumptions of the Langmuir model indicate that the adsorption of lead ions is probably in the form of a single layer, and the adsorbed ions do not interact with each other, and the surface of the nano-adsorber of the outer skin of the hazelnut is homogeneous, and surface adsorption is carried out in certain places, that is, the adsorbed lead ions are adsorbed in certain and defined adsorption places, and also every They adsorption site can accommodate only one ion [9-11]. The Langmuir isotherm equation is written as follows [9]:

$$q_e = \frac{K_L\, C_e}{1 + a_L\, C_e} \qquad \text{(eq.5)}$$

where in:

q_e: amount of adsorbed substance in mg per gram of adsorbent.

C_e: the concentration of organic matter in ppm in the liquid phase in the state of equilibrium or adsorption.

K_L: isotherm constant in terms of $L.g^{-1}$.

a_L: constant value in terms of $L.mg^{-1}$.

The linear form of the Langmuir equation is as follows [9].

$$\frac{C_e}{q_e} = \frac{1}{K_L.Q_{max}} + \frac{C_e}{Q_{max}} \qquad \text{(eq.6)}$$

Q_{max}: maximum adsorption value in terms of $mg.g^{-1}$ by one gram of adsorbent.

By drawing $\frac{C_e}{q_e}$ in terms of c_e, a line is drawn whose width from its origin is $\frac{1}{K_L.Q_{max}}$ and the slope of the line is $\frac{1}{Q_{max}}$ [9].

Freundlich isotherm describes heterogeneous systems well [10]. The assumptions that govern the Freundlich isotherm are: the surface has a non-uniform energy distribution and places with the same energy are next to each other and different pieces of the surface do not affect each other.

The Freundlich equation is written as follows [10]:

$$q_e = K_F\, C_e^{bf} \qquad \text{(eq.7)}$$

where K_f and b_f are the constants of the Freundlich equation, and q_e and c_e are the concentration of adsorbed material per gram of adsorbent material and the concentration of organic material in equilibrium in the liquid phase.

The linear form of the Freundlich equation is as follows:

$$\ln q_e = \ln K_F + b_f \ln C_e \qquad \text{(eq.8)}$$

q_e: amount of adsorbed substance in mg per gram of adsorbent.

C_e: concentration of organic matter in ppm in the liquid phase in equilibrium or adsorption.

K_F: Freundlich equation constant in terms of $(mg.g^{-1})(L.mg^{-1})^{\frac{1}{n}}$.

b_f: constant of the Freundlich equation in terms of $L\,g^{-1}$.

where $\ln K_F$ is the width from the origin and b_f is the slope of the line. Usually, b_f is smaller than one, and the smaller it is, the more nonlinear the equation becomes [10].

Temkin isotherm contains a factor that clearly shows the interactions between adsorbent and adsorbed particles [11].

The equation of the Temkin isotherm is written as follows [11]:

$$q_e = \frac{RT}{b} \ln(AC_e) \qquad \text{(eq.9)}$$

Considering: $B = \frac{RT}{b}$

A linear form of the isotherm of Temkin would be:

$$q_e = B \ln A + B \ln C_e \qquad \text{(eq.10)}$$

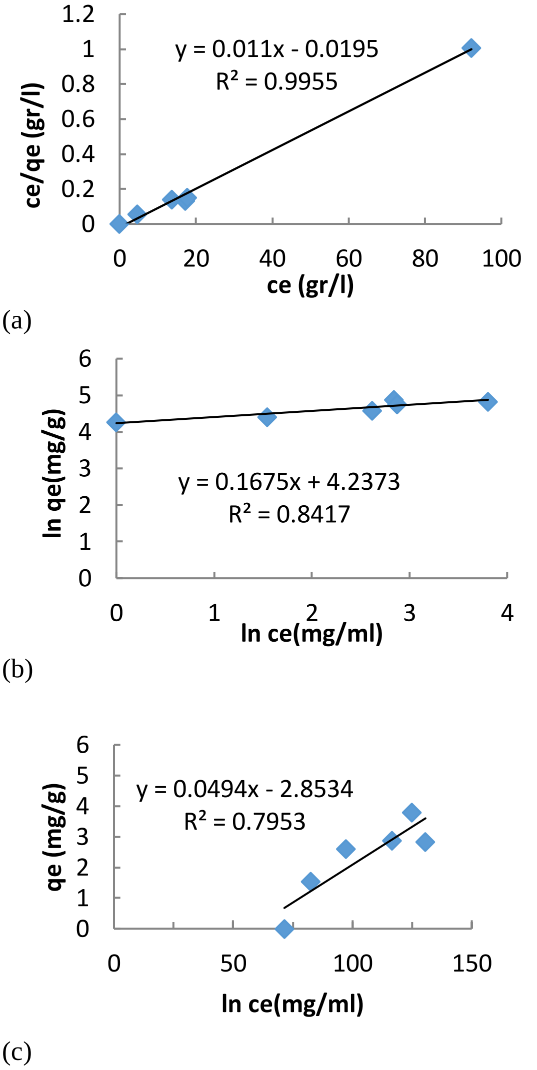
A: In terms of $L.mg^{-1}$, it is equivalent to the bond constant associated with the maximum bond energy.

b: Temkin isotherm constant in terms of $J.mol^{-1}$.

R: universal gas constant 8.314 $J.mol^{-1}K^{-1}$.

T: absolute temperature in Kelvin.

Finally, the quantitative relationship between the initial Pb^{2+} ion concentration and adsorption capacity was analyzed with three different isotherm models, as shown in Fig. This information can be used to describe how the metal ion is adsorbed on the adsorbent material and the reactions of the adsorbed material and the adsorbent.



(a)

(b)

(c)

Fig.12. Langmuir isotherm (a), Freundlich isotherm (b) and Temkin isotherm (c) for the adsorption process of Pb^{2+}ions on the nano-adsorbent outer skin of hazelnut

The calculated parameters Q_{max} , k_l , K_F , b_F , A, B& b and linear regression coefficient values (R^2) for Langmuir [9], Freundlich [10] and Temkin [11] models are summarized in the table. According to the data correlation coefficient values and comparing them together in the Langmuir isotherm, Freundlich isotherm and Temkin isotherm, Fig.12 shows that the adsorption of Pb^{2+}has a better compliance with the Langmuir model and its value is equal to 0.995. Using slope and width from the origin of the regression equation of the graph and Langmuir constants, the maximum adsorption capacity of Pb^{2+} by the nano-adsorber of the outer skin of hazelnut was calculated at the optimum temperature of 91 mg gr^{-1} (Table.1).

3.2.8. Examining the effect of interfering ions

To investigate the effect of the presence of other ions on the inhibition percentage of the main ion on the nano-adsorbent, solutions with all different ions such as $Mn^{2+}, Ni^{2+}, Pb^{2+}, Mg^{2+}, Cu^{2+}$ and Fe^{2+}were prepared with a concentration of 120 ppm. Then, the amount of unadsorbed lead ion was measured by flame atomic adsorption device and the inhibition percentage of lead ion was calculated in the presence of all these ions. The obtained results are shown in (Table.2). These results show that other disturbing ions reduce the efficiency of lead ion adsorption in a small way, and by increasing the amount of adsorbent, the efficiency of the system can be increased.

Table.1. Constants related to Langmuir, Freundlich and Temkin isotherms in surface adsorption

Temperature 25°C	parameters	isotherm	Cation
91	Q_{max} (mg g^{-1})		
0.5640	k_l (L. mg^{-1})	Langmuir	Lead
0.9955	R^2		ion
69	K_F	Freundlich	
0.1675	b_F		Lead
0.8417	R^2		ion
	A	Temkin	
0.7953	B		Lead
	R^2		ion

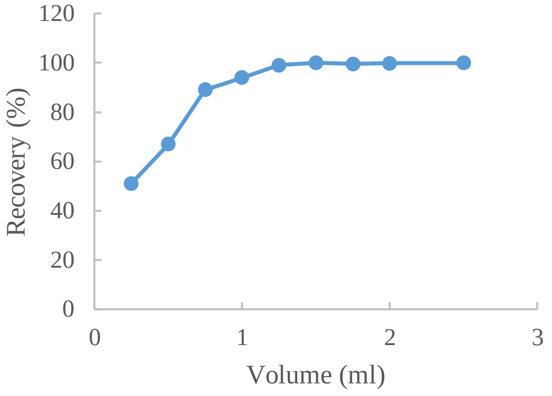


Fig.11. The effect of the volume of HNO3

3.2.9. The desorption studies

In the washing step, the ions adsorbed by the nano-adsorbent are desorbed by a small volume of a suitable detergent, in the meantime, the correct determination of the composition and concentration of the detergent, as well as the use of the minimum amount of detergent, will increase the capability of the analytical method. Nitric acid was used to wash the adsorbed lead ions, which was able to wash up to 100%. Detergent volume is one of the important factors in the extraction of inhibited ions. One molar nitric acid was used for washing.

Table.2. The effect of disturbing ions on the adsorption of lead ions by the nano-adsorbent outer shell of hazelnut

	Residual concentration ppm	Abs	RSD
Standard solution 1	2	0.020	3.92
Standard solution 2	3	0.032	2.72
Standard solution 3	4	0.043	2.82
Standard solution 4	5	0.056	4.48
Blank sample solution	-	0.003	-
Sample solution of all ions with 0.1 g of adsorbent	4.885	0.054	4.98
Sample solution of all ions with 0.7 g of adsorbent	2.182	0.022	4.72

Fig.11 shows the effect of the volume of nitric acid on the removal efficiency, with 1.5 ml of one molar nitric acid, the desorption efficiency reached 100%, which is the optimal condition of the detergent. After determining and measuring the effect of the volume of nitric acid on the release of lead ions from the nano-bio-sorbent surface of the outer shell of hazelnut, the effect of nitric acid concentration on the release of lead ions from the surface of the adsorbent was investigated. 1.5 ml of nitric acid was used for washing.

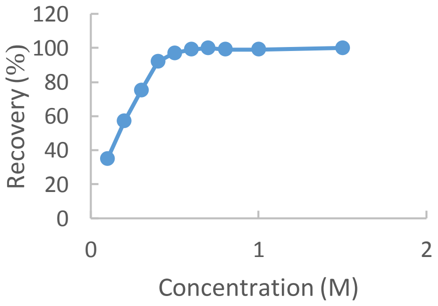


Fig.12. The effect of HNO3concentration

Fig.12 shows the effect of nitric acid concentration on extraction efficiency, with the increase of nitric acid concentration from 0.1 M to 0.7 M, the removal percentage has reached 100% from 35%. The effect of the number of times the nano adsorbent was used on the extraction of lead ions from aqueous solutions was repeated 10 times in all stages of inhibition and washing.

Fig.13 shows the results of this stage that after 10 repetitions, the adsorption percentage of lead ion has decreased from 100% to 72%, which one of the influential factors in this decrease in efficiency can be caused by the physical removal of the adsorbent in each stage. It should be washed. Finally, the results show that it is possible to repeatedly use hazelnut skin nano-adsorbent to remove lead ions from polluted water.

3.2.10. Comparison with similar works

The efficiency of hazelnut skin nano-adsorbent was compared with some previous similar works in terms of maximum adsorption, and the results are shown in Table 3.

Table 3. Comparison of results

References	Max adsorption $mg.gr^{-1}$	adsorbers
]19[	6.35	Sawdust bio-adsorbent
]20[	17	Walnut skin bio-adsorbent
]21[	19.86	Tea leaf bio-adsorbent

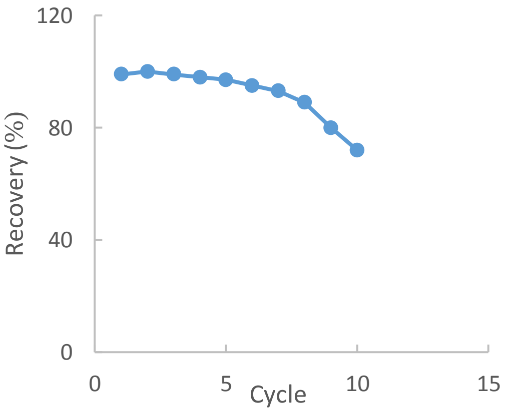


Fig.13. The effect of the number of times

According to (Table.3), it can be seen that the proposed method has a higher adsorption capacity and its efficiency is better than the proposed methods mentioned in the mentioned references. The important feature of the proposed method is having a higher adsorption capacity than similar cases, easy and cheap adsorbent preparation.

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4. CONCLUSION

The main results of the research are as follows:

1) Hazelnut skin nano-adsorbent has the ability to remove most heavy metal ions, especially lead ions.

2) Adsorption of lead ions and other heavy metals on nanoparticles depends on the amount of adsorbent, sample pH, solution temperature, sample volume and contact time.

3) Adsorption of lead ions on the aforementioned nano-adsorbent follows the pseudo-second-order kinetic model and the Langmuir isotherm.

4) The maximum adsorption capacity of lead ions on the hazelnut shell nano-adsorbent is 91 mg per gram of the adsorbent.

5) The washing results show that the nano-bio-sorbent of the outer shell of hazelnut can be used repeatedly to remove lead ions from polluted water.

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میکرو و نانوذرات بیوجاذب پوست فندق تولید شده به روش مکانیکی برای حذف سریع یون‌های سرب از آب‌های آلوده

حسن کرمی[*] ، سیدکاظم کاظمی

بخش شیمی، دانشگاه پیام نور، تهران، ایران
* E-mail: karami.hassan@pnu.ac.ir

تاریخ دریافت: ۱۱ مرداد ۱۴۰۲ **تاریخ پذیرش:** ۲۴ شهریور ماه ۱۴۰۲

چکیده

با استفاده از آسیاب گلوله‌ای، میکرو و نانوذرات بیوجاذب پوست چوبی و پوسته بیرونی نرم فندق تولید شده و از آنها برای حذف یون‌های سرب از آب استفاده شد. پوست خشک چوبی و پوسته بیرونی نرم فندق پس از خشک شدن، توسط یک آسیاب گلوله‌ای نوآورانه به پودرهای میکرو و نانو خردایش شد. تصاویر TEM نانوپودر حاصل شان داد که پودر آسیاب شده شامل نانوذرات یکنواخت با قطر متوسط ۸–۱۰ نانومتر است. نانوپودر حاصل به عنوان یک بیوجاذب مناسب برای حذف یون‌های سرب از آب استفاده شد. داده‌های تجربی نشان داد که جذب یون‌های سرب روی سطح نانوذرات پوست فندق به طور قابل قبولی با مدل ایزوترم لانگموير برازش می‌شود. بر این اساس، بیشینه ظرفیت جذب $\mathrm{mg\ g^{-1}}$ ۹۱ بر گرم برای جذب یون‌های سرب در سطح نانوذرات پوست فندق به دست آمد. نتایج نشان داد که حذف بهینه یون‌های سرب در شرایط تجربی شامل ۵۰ میلی‌لیتر محلول اولیه، pH محلول برابر ۴، غلظت اولیه یون سرب حداکثر $\mathrm{mg\ L^{-1}}$ ۱۲۰ میلی‌گرم به ازای ۷۰ میلی‌گرم نانوبیوجاذب در مدت ۲۰ دقیقه و دمای اتاق قابل انجام است. یون‌های جذب شده می‌توانند با ۱/۵ میلی‌لیتر محلول ۰/۷ مولار اسید نیتریک به آسانی واجذب شوند. در شرایط بهینه،فاکتور پیش‌تغلیظ برابر ۲۰۰ با انحراف استاندارد کمتر از ۵٪ و حد تشخیص ppb ۱۰۰ برای یون سرب قابل دسترس است. اثر برخی از یون‌ها نظیر Fe^{2+}، Cu^{2+}، Mg^{2+}، Zn^{2+}، Mn^{2+} و Ni^{2+} بر کارآیی حذف یون سرب بررسی شد. روش ارائه شده با موفقیت برای حذف یون سرب از نمونه‌های حقیقی استفاده شد.

کلید واژه ها

آسیاب گلوله‌ای؛ پوست فندق؛ نانوجاذب؛ بیوجاذب؛ حذف یون سرب.

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