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Investigation of the efficiency of oyster sell nano particles in removal of lead from aqueous solutions in batch system

Samira Sheikhi[1], Hasan Rezaei[2*], Ali Akbar Hedayati[3]

[1] M.Sc Student in Environmental Science and Engineering, Environmental Pollution, Gorgan University of Agricultural Sciences and Natural Resources. Gorgan, Iran

[2] Assistant Professor of Environmental Pollution, Faculty of Fisheries and Environment, Gorgan University of Agricultural Sciences and Natural Resources. Gorgan, Iran

[3] Associate Professor, Department of Fisheries, Faculty of Fisheries and Environment, Gorgan University of Agricultural Sciences and Natural Resources, Gorgan, Iran

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Corresponding author:
hassanrezaei1979@gmail.com

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Abstract

Wastewater containing heavy metals reduces water quality, has toxic effects, is carcinogenic, and causes irreparable environmental damage. As a result, various methods are used today to remove heavy metals from water sources, with adsorption being one of the most effective. In this study, the removal of lead using binocular oyster shell nanoparticles was investigated due to their high adsorption capacity and low cost. The efficiency of lead ion adsorption by binocular oyster shell nanoparticles was examined under varying conditions, including pH, contact time, temperature, adsorbent concentration, and lead concentration. Experiments were conducted using a batch system. The adsorption process was also modeled using Freundlich and Langmuir isotherms, as well as first-order and pseudo-second-order kinetic models. The optimal conditions for lead removal were found to be pH 6, an initial lead concentration of 50 mg/L, a contact time of 60 minutes, a temperature of 25°C, and an adsorbent concentration of 0.01 g. The results indicated that the adsorption process followed the Freundlich isotherm and the pseudo-second-order kinetic model. Oyster shell nanoparticles demonstrate effective lead ion removal, with several advantages such as low cost, abundance, low energy consumption, minimal sludge production, ease of recycling heavy metals adsorbed onto nanoparticles, and a high adsorption potential for lead from aquatic environments.

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Introduction

One of the most important human needs for a healthy life is the existence of clean fresh water. What makes provision of clean fresh water difficult is the increasing population growth, along with expanding industries and the problems associated with water shortage (Javanshir & Jandaghi, 2008). The entry of industrial wastewater containing heavy metals into water sources leads to reduced water quality, toxic effects and irreversible damage to the environment (Bahmani*et al*, 2013). Heavy metals such as lead and cadmium are a serious threat to living organisms because of their mobility, accumulative, carcinogenic and mutagenic properties even at low levels. (Holan & Volesky, 1994). Lead is a soft gray metal with shades tending to blue-silver-bruised color with 207.119 atomic mass and a specific weight of 11.34 (Inglezakis et al., 2002). Lead pollution is caused by melting and fusion processes, mining and other activities. This element naturally exists in the environment, but in most cases it is generated during human activities, including use of batteries, rubber, insecticides and other industries. Lead is an extremely toxic element. Drinking water containing high concentrations of lead for a long time leads to brain injuries, damage to the kidneys and digestive tract, especially in children (Amarasinghe & Williams, 2007). Studies show that bones, kidneys and liver have the highest amount of lead (Sanai, 1996). One of the most important effects of lead in aquatic ecosystems is the disruption of phytoplankton functions that results to disturbing the balance of aquatic organisms (Nick Azar et al., 2006). Therefore, removal of these metals is an urgent need due to their toxic, bioaccumulation, bio magnification, and numerous adverse effects on the environment and living organisms. Various methods such as chemical precipitation with lime, reverse osmosis, ion exchange, and activated carbon, electrolytic techniques are used to remove heavy metals from aqueous solutions, but each technique may have high technical and investment cost limitations (Wang et al., 2006).The adsorption method is used due to easy operation, low energy consumption, simple maintenance and high adsorption capacity from high volumes of industrial wastewater and sewage (Kumar, 2013). In recent years, the use of nanotechnology as one of the new methods has shown a great deal of efficiency in adsorbing these types of pollutants from the environment. Oyster shells contain a high amount of organic compounds and macromolecules, such as chitin, which have the ability to adsorb various anions and metal ions. (Champagne, 2009 and Liu et al., 2009 Quoted in Yousefi et al., 2013). Jeeon et al., (2006) used oyster shells and sludge to remove cadmium, lead and copper from aqueous solution. They found the oyster shells were able to remove 80% of these metals after 40 minutes. Yan-jiao, (2011) Used oyster shells to remove cadmium and cobalt and found the cadmium to be adsorbed more than cobalt. The best efficiency to remove cadmium was reported as 49.2%. Yousefi et al., in a study involving oyster shells to remove lead from aqueous solutions. The result of this study present high adsorption capacity of mollusk shells to remove bivalent lead ions because of adsorption mechanism and ionic changes (Yousefi et al., 2013). Oyster shells in the east of the Golestan province are found in the form of a mountain due to the retreat of the Caspian Sea. According to provincial press, quoting head of Planning and Budget Organization of Golestan Province, the largest oyster shell mine is in Gonbad Kavoos requiring foreign and state investors to promote and benefit from this resource. In addition, according to statistics provided by FAO in 2002, more than 11 million tons of binocular oysters are produced through aquaculture. Hence, if the high efficiency of this adsorbent is confirmed, its use on the actual scale and its mass production can be proposed. In this study, the efficiency of binocular oyster shell nanoparticles was investigated to remove heavy lead metal from water. In the batch experiment, the effects of pH, adsorption dose, and initial concentration of lead metal, temperature and time on adsorption were investigated. Also, for fitting data from Langmuir and Freundlich adsorption isotherms, the pseudo-first order and pseudo-second order absorption kinetic models were used.

Materials and Methods

Preparation of adsorbent and adsorption tests

Stock solution (1000 mg/L) was prepared by dilution of lead nitrate $(PbNO3)2$ manufactured by Merck (Germany) in deionized water. For making other lead solutions at various concentrations (range from 5 to 200 mg /l), the solution was prepared by dilution of the stock solution with two-time distilled water. pH was adjusted using HCl and NaOH of 0.1 molar.

Experiments were carried out in a discontinuous system with sample volume of 100 mL in 250 mL glass flask at identical conditions. In each step of batch experiment one of the parameters (temperature, pH, contact time, adsorbent dose and metal concentration) was considered constant to obtain optimal condition of sorption, variables and other parameters. The variations of the parameters studied are shown in Table 1.

Table 1. Range of variations of the studied parameters

Variable	Unit	Scope of Change
Contact time	min	15-30-45-60-90-120
Pb concentration	Mg/l	5-10-20-50-100-200
Sorbent dose	gr	0.01-0.02-0.03-0.04-0.05 and 0.06
Temperature	C	15-20-25-30-35-45
pH		3-4-5-6-7-8

All samples were placed in a shaker at ambient temperature (25 ° C) at a speed of 190 rpm. After stirring the adsorbent with different concentrations of lead metal at different times and pH values, the residue concentrations of lead were read by the atomic absorption spectrophotometer.
Capacity of adsorption and removal efficiency of lead was calculated using the following equation:

$$\%A = \frac{C_i - C_e}{C_i} \times 100$$

where Ci and Ce are the initial and equilibrium concentrations of Pb (2) respectively. The amount of lead absorbed by the absorbent was determined using Equation (2).

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

In the above equation, qe (mg/g) is the adsorption capacity of the adsorbent, V is the volume of solution in liters, m is the amount of adsorbent (g), and Ci and Ce are the initial and after adsorption process concentration of lead (mg/L) respectively (Jahangiri and Ameri, 1394)

Sorption isotherms

Sorption equilibrium isotherms are very important for design and analysis of adsorption systems. Adsorption equations for an adsorbent represent the adsorption properties of a sorbent. In this study, Langmuir and Freundlich which are the most common equilibrium models for adsorption system analyses, were used. In the Langmuir isotherm, it is assumed that all active adsorption sites are uniform on the adsorbent surface, and all have the same adsorption capacity, and that adsorption is monolayer. Freundlich's isotherm, unlike the Langmuir model, refers to the heterogeneity of adsorbent surfaces; in the form of a multilayer adsorption (Naqizade and Momeni, 1394).

The linear form of the Langmuir model used to investigate the adsorption phenomena is as follows (Equation 3).

$$\frac{C_e}{q_e} = \frac{1}{b\, q_{max}} + \frac{C_e}{q_{max}}$$

In this equation, q_e is the amount of Pb (2) ions adsorbed per unit weight of adsorbent (mg/g), q_{max} is the maximum adsorption capacity (mg / g), C_e is the equilibrium concentration of lead ions in solution (mg / L), and b is constant in terms of liter per millimeter, which shows the adsorption energy and the binding power of the binding sites. The cardinal parameter obtained from the Langmuir model is the equilibrium constant R_L, which is determined by Equ (4), where b and c are adsorption energy in the Langmuir equation and the initial concentration of metal ions, respectively. If the R_L value is zero, it indicates irreversible isotherm, if $0<R_L<1$, it indicates that isotherm is optimum, if $R_L=1$ it represents Linear isotherm and if $R_L>1$, it is considered undesirable (Ziapoor et al., 1391).

(4) $$R_L = \frac{1}{1+bC}$$

The isotherm linear equation for Freundlich absorption is as follows.

(5) $$Lnq_e = LnK_f + \frac{1}{n}LnC_e \ldots\ldots$$

In this equation, C_e and q_e are the same as those presented in the Langmuir model and k_f is Freundlich constant, which shows sorbent capacity and n is Freundlich power, which indicates the intensity of adsorption. Also, the value of n between 1 and 10 represents the optimal adsorption process (Nemati Thani et al., 2014). The n and k_f parameters are determined by the slope and width of the origin of the linear diagram of Lnq_e versus LnC_e (Freundlich, 1906).

Adsorption kinetics

One of the effective factors in adsorption is contact time, which determines the rate of adsorption reaction. In adsorption kinetics studies, the effect of contact time with adsorption in two pseudo-first-order kinetics and second-order kinetics was investigated. Equation (6) shows the pseudo-first-order model.

(6) $$\text{Ln}\,(q_e - qt) = \text{Ln}\,q_e - K1t$$

In equation (6) q_t and q_e are the amount of lead adsorbed at time t and the equilibrium time (mg / g), respectively and $k_1$is the adsorption rate constant (min^{-1}); Therefore, the constants $k_1$and q_e are obtained from the origin and gradient of the linear graph Ln ($q_e - q_t$) on time t (Ghanizadeh et al., 2012).

One of the most widely used kinetic models is the pseudo-second-order model. This model shows many adsorption mechanisms of heavy metals on different adsorbents (Salariyan et al., 2012).

The quasi-quadratic kinetic equation is also in the form of equation (7).

(7) $$\frac{t}{q_t} = \frac{1}{k_2 qe^2} + \frac{1}{q_t} \quad \ldots\ldots$$

In this equation, q_e and q_t are the same parameters presented in the pseudo-first-order model and K2is the constant velocity of pseudo-second order equation ($g.mg^{-1}.\ min^{-1}$) (Ghanizadeh et al., 2012). Excel 2007 and SPSS version 19 were used to plot Figures and match the data in equations.

Effects of pH

One of the important adsorption factors is pH. The experiments were carried out within the pH range of 3 to 8. Figure 1 shows the effect of pH on lead adsorption. As we can see with increasing pH, the removal percentage and the adsorption capacity of lead ions increased at pH=6, removal percentage and absorption capacity was 90.625 and 181.25 mg /g, respectively, has reached its maximum and was selected as optimal pH. The pH was then reduced from 6 to 8, and the removal percentage and capacity decreased. The reason for this is that in the lower pHs, competition between the positive ions of H and metal ions is created to bind to the adsorbent surface. As a result, the number of available sites for adsorption of metal cations on activated sites decreases and reduces the absorption rate. By increasing the pH of the solution and approaching the neutral state, the availability of cations increases to these sites (Gao et al., 2012 and Estevez et al., 2000). The concentration of ion (OH^-) at pH higher than 6 will increase the competition between the adsorbent ligands and (OH^-) for binding to lead cation. As a result, metallic ions are observed as hydroxide that reduces adsorption percentage (Ramezanpour et al., 2014). Yousefi et al. Examined the effect of pH in the range of 3-9 and announced the highest lead removal efficiency at pH = 6 (Yousefi et al., 2014). Rahman et al. (2008) Reported an optimal pH = 6.5 for the removal of arsenic by nano sized shell. Wu et al. Also obtained a high adsorption efficiency at pH = 5.5 in a study on copper adsorption using shellfish with optimum yields close to the result of the present study (Rehman et al., 2008).

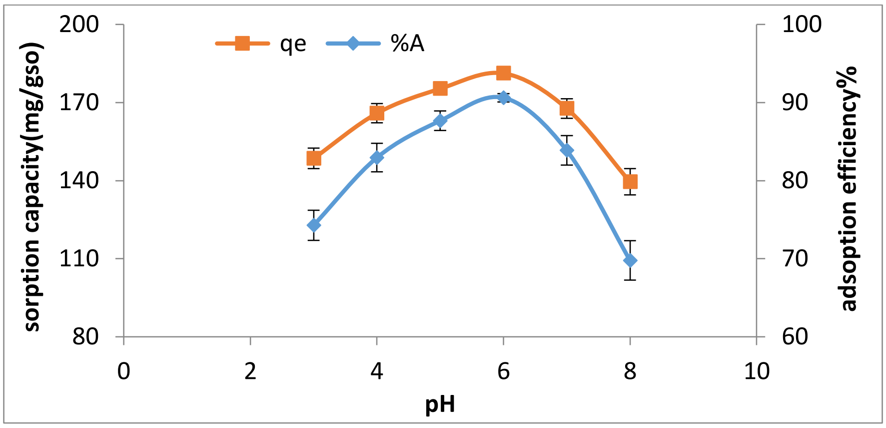

Figure 1. Effect of pH changes on the adsorption process (initial concentration:20 mg / L, adsorbent dose: 0.01 g, contact time: 60 minutes and temperature of 25 °C)

Effect of adsorbent amount

Determining the effective amount of adsorbent to reduce sludge production and reduce the cost of treatment is essential (Yousefi et al., 2013). To investigate the effect of sorbent to adsorb lead ions, the experiments were carried out at pH = 5, initial concentration of 20 mg / L, adsorption range in different amounts ranging (0.01-0.06 g) and 25 °C. Graph 2 shows the effect of the adsorption value on the percentage of the removal of lead ions by the oyster shell nanoparticles.

As we can see, by increasing the adsorbent amount from 0.01 to 0.06 g the elimination percentage of lead ions increases from 87.67 to 95.37 and the adsorption capacity is reduced from 35.17 to 31.79 mg/g, respectively. The main reason for this issue is that with increasing the absorption concentration, the active locations of adsorbent, exchangeable surfaces and the free spaces of the nanoparticles surface have increased. Thus, efficiency of adsorption increases (Ekhlasi et al., 2012). The decrease in adsorption capacity is attributed to the limited number of lead ions and the large number of unsaturated adsorption sites remaining unoccupied (Jahangiri & Ameri, 2015). The results of this study are consistent with those of Nagizadeh and Momeni, who determined the optimal amount of sorbent to be 0.01 g/L (Nagizadeh & Momeni, 2015). Similarly, Edokpayi et al. (2015) conducted a study on the removal of lead from aqueous solutions using chitosan derived from clam shells and found that increasing the amount of adsorbent also increased removal efficiency. This finding aligns with the results of the current research (Edokpayi et al., 2015).

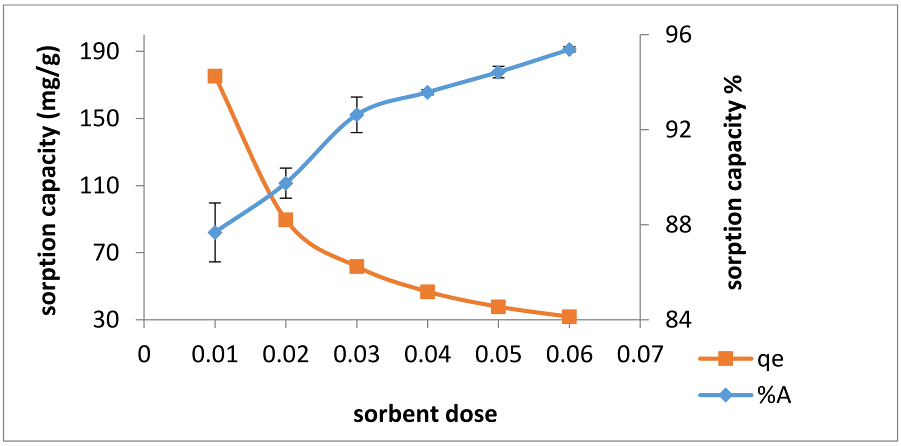

Figure 2. Effect of Adsorption dose (pH: 5, Initial Concentration: 20 mg / L, Contact Time: 60 Minutes and Temperature = 25)

The effect of the primary lead concentration

Another effective parameter on the adsorption rate is the initial concentration of lead. Experiments were carried out with initial concentration of lead on the target adsorbent in constant pH (5), temperature (20°C), and adsorption dose was 0.01 g, and lead concentration range were considered from 5 to 200 mg/liter as shown in Figure 3. The change in the initial concentration of lead metal from 5 to 20 mg/liter reduces the adsorption efficiency and lead concentration higher than 20 mg/l increases the efficiency with a mild slope. This reduction can be attributed to the fact that resistance to lead adsorption decreases because of increased driving force of mass transport. At high concentration due to the high accumulation of metal captions around the adsorbent, the chance of metal contact increases with adsorption sites on the absorbent. On the other hand, in higher concentrations of adsorption capacity, the trend will continue to increase, because most of the adsorption stations are occupied by metal ions (Ekhlasi et al., 2012). Alizadeh et al (2012) concluded that as lead concentration increases, the adsorption rate increases as well (Alizadeh et al., 2012).

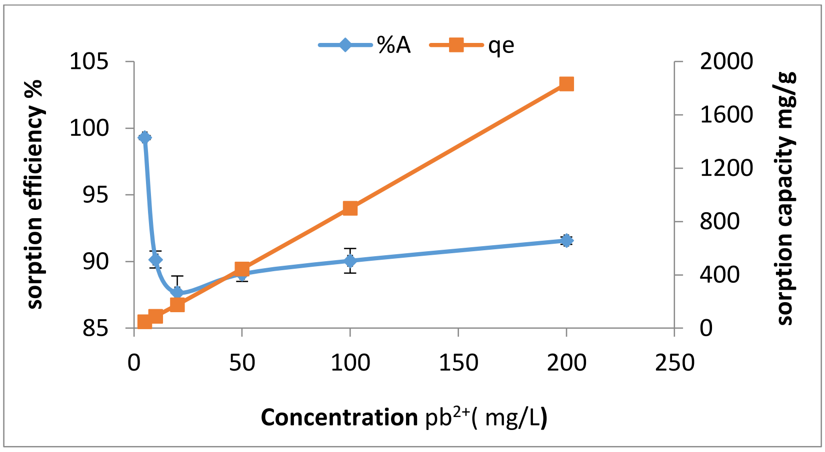

Figure 3. Effect of changes in the initial concentration of lead on the adsorption process (pH: 5, contact time of 60 minutes, adsorbent content: 0.01 grams and temperature of 25 °C)

Effect of Contact Time

In this batch experiment, pH, initial concentration, sorbent dose, and temperature were set at 6, 20 mg/L, 0.01 g, and 25°C, respectively. The variable, contact time, ranged from 15 to 120 minutes, as shown in Fig. 4. The results indicate that lead absorption occurred very rapidly within the first 60 minutes, with a removal efficiency of 67.87% and an adsorption capacity of 175.35 mg/g. However, beyond 60 minutes, the adsorption rate slowed. The initial rapid increase is due to the active sites on the adsorbent quickly colliding with lead cations, facilitating adsorption. As these sites become saturated, the adsorption rate declines (Khosravi et al., 2012).

In this study, extending the contact time to 120 minutes did not result in a significant increase in adsorption, indicating that the system had reached near equilibrium and no further adsorption reactions occurred between the lead ions and the adsorbent. Given the importance of contact time in industrial applications and the minimal change in adsorption rate after 60 minutes, this time was selected as optimal for practical use. These findings are consistent with those of Castaneda et al. (2012), who studied lead ion removal using oyster shell.

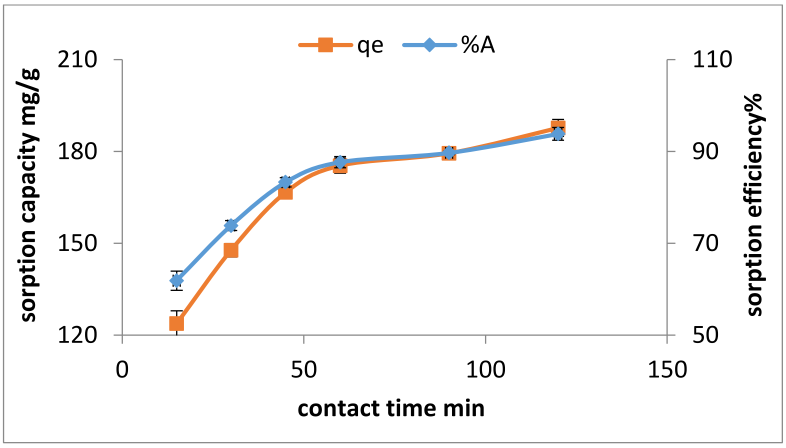

Figure 4. The effect of contact time changes on the adsorption process (pH: 5, initial concentration: 20 mg / L, absorbance: 0.01 g and temperature of 25 ° C)

Temperature effect

Solution temperature is one of the important factors in removing pollutants with different adsorbents. In this stage, experiments were conducted at 15, 20, 25, 30, 35, and 40 °C. Other parameters were considered constant (pH=6, initial concentration=20 mg /liter, initial concentration=20 mg /iter). Figure 5 shows the effect of temperature on the percentage elimination and adsorption capacity by the adsorbent. As the results show, with increasing temperature up to 25°C, the adsorption rate increases markedly, and then with higher temperature increase no major change is not observed. The minimum adsorption level was found at 25 °C, and the maximum percentage of lead removal was obtained at 45 °C. This phenomenon can be explained as: by increasing the temperature up to a certain degree, it causes greater movement of lead ions and increasing their contact rate with absorptive surfaces. At temperatures higher than 25 °C most of adsorbent sites are occupied. Alizadah et al. conducted lead removal by magnetic Fe nanoparticles and found the sorption increased due to temperature increase.

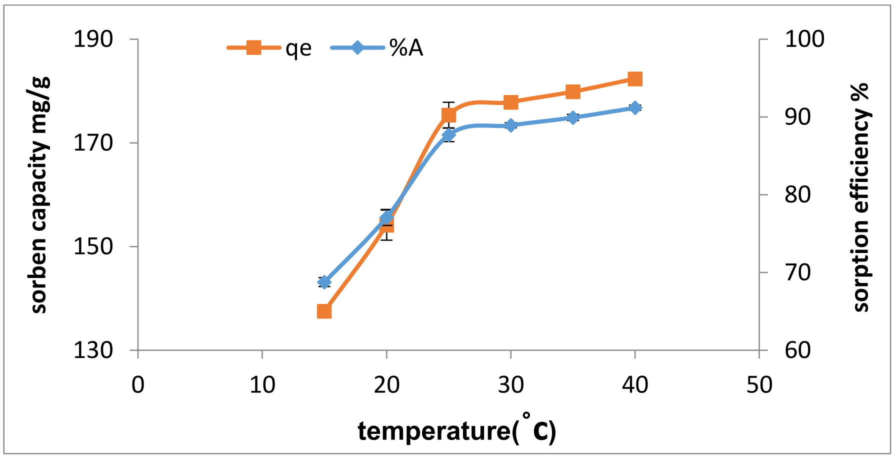

Figure 5. The effect of temperature changes on the adsorption process (pH: 5, contact time 60 minutes, adsorbent amount: 0.01 g and initial concentration 20 mg / L)

Results of isotherm adsorption experiments

The fitting of data from absorption equilibrium experiments was studied using Langmuir and Freundlich models. The constants of each model with their correlation coefficients are given in Table 2. Figures 6 and 7 illustrate the linear form of Langmuir and Freundlich isotherm models for oyster shell adsorbent, respectively. Regarding Figures 6, 7 and Table 1, the Freundlich model, R^2= 0.820 is better than Langmuir, R^2=0.041, which can better describe absorption of lead ions by adsorbent. Also, with respect to the N obtained as 1.78, the fitness of the Freundlich model is confirmed. Since the Freundlich model refers to the heterogeneity of adsorbent surfaces, it can be concluded that the lead absorption by nano sized oyster shell particles is carried out in a multi-layered manner. The isotherm results from Wu et al. research for copper removal with binocular oyster shell in the range of 200 to 30 mg / l (Wu et al., 2014) are consistent with the results of this study. Shokouhi et al., in a study on the removal of lead and cadmium by calcareous coral granules, cited Freundlich model as the best for lead adsorption, (Shokouhi et al., 2014).

Results of kinetic adsorption studies

Figures 8, 9 and Table 3 show the fitting of experimental data with first and second order pseudo-kinetics models. Regarding the correlation coefficient of the pseudo-first order and pseudo-second-order models, which were obtained to be equal to 0.271 and 0.999 respectively, the pseudo-second-order kinetic model shows the mechanism of action of lead adsorption on the desired adsorbent. In a study by Edokpayi et al. in 2015 on removal of lead from aqueous solution using chitosan nanoparticles, it was concluded that a pseudo second order kinetic model has the best matching power in lead absorption (Edokpayi et al., 2015).

Table 2. Parameters of isotherm models used

Model	Kf	B(l/mg)	Qmax	R2	RL	N
Rruendlich	5.257	….	……	0.82	……..	1.78
Longmuir	……	0.011	1000	0.0412	0.819	……….

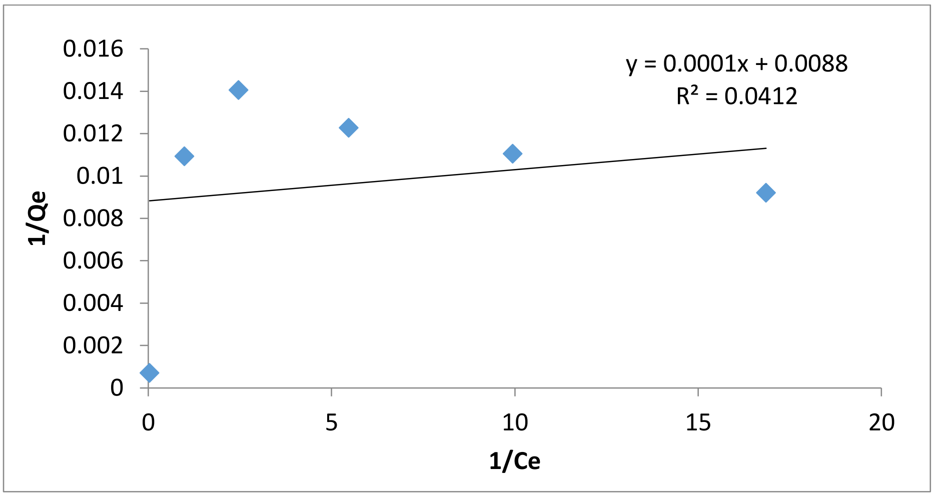

Figure 6. Longmuir lead co-temperature curve

Table 3. Parameters of the used kinetic models

MODEL	QE (MG/G)	K	R2
PSEUDO FIRST ORDER	150	0.013	0.271
PSEUDO SECOND ORDER	250	0.008	0.999

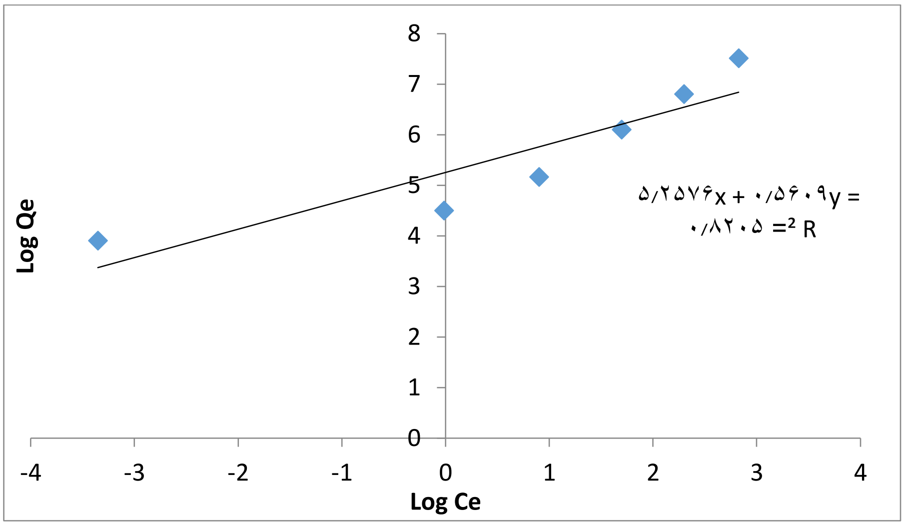

Figure 7. Freundlich Lead co-temperature curve

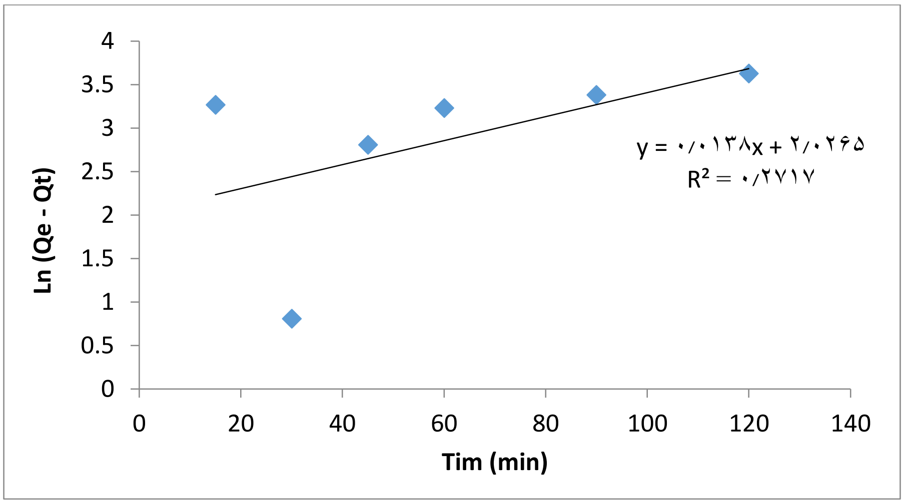

Figure 8. Pseudo-first-order kinetic model of lead

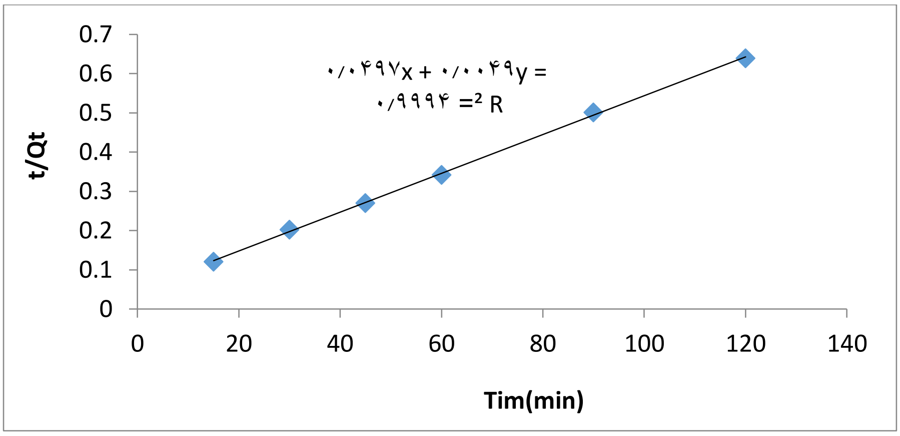

Figure 9. Pseudo second- order kinetic model of lead

Conclusion

In this research, the ability to remove lead using binocular oyster shells under pH parameters, contact time, initial concentration, temperature and adsorbent content were investigated. According to the results, the optimal values of each agent were obtained at pH 6, initial concentration of 50 mg / g, contact time of 60 minutes, temperature of 25 ° C, and adsorbent concentration of 0.01 g, respectively. Based on the results, with increasing pH, the adsorption process increased and eventually reached the highest value at pH 6 and then declined. Also, with increasing contact time, temperature and adsorbent amount, the adsorption efficiency increased as well. While the initial concentration of lead was increased from 5 to 20 mg / l, the adsorption of metal ions decreased and then the incremental trend continued with a gentle slope. Finally, the results showed that the adsorption process of Freundlich isotherm obeyed a pseudo-second-order kinetic model. This method, in addition to a novel method for removing lead metal from industrial solutions and waste, has many advantages, such as low cost, availability, low energy consumption, less sludge production, easier recycling, adsorbed heavy metals on nanoparticles, as well as high adsorption potential, than conventional chemical, physical and biological methods. Therefore, oyster shell nanoparticles can be used on a real scale for lead removal.

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