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Pol. J. Environ. Stud. Vol. 29, No. 1 (2020), 1-13
DOI: *10.15244/pjoes/103027* ONLINE PUBLICATION DATE:

Original Research

A Thermodynamic and Kinetic Evaluation of the Adsorption of Pb(II) Ions Using Peanut *(Arachis Hypogaea)* Shell-Based Biochar from Aqueous Media

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Received: 30 November 2018
Accepted: 19 January 2019

Abstract

In this study, biochar from peanut shells was used to remove Pb(II) ions from aqueous media using a batch method. Adsorption studies were conducted to optimize the adsorption parameters, such as contact time, the initial pH of aqueous media, temperature, initial concentration of lead ions, and the dosage of biochar. The optimum adsorption conditions were found to be contact time: 180 min, initial pH of aqueous media: 5.5 0.02, temperature: 293 K, initial concentration of lead ions: 100 ppm, and the dosage of biochar: 2 g/L. The adsorption yield of Pb(II) ions on the biochar was found to be 89% under these conditions. The experimental results were evaluated by applying the Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich (D-R) isotherm models. We found that the Langmuir isotherm describe the adsorption data very well. The theoretical maximum adsorption capacity (q_o) was determined as 56.5 mg/g using the Langmuir isotherm. In the concept of the research, kinetic investigations also were conducted. Pseudo first-order, pseudo second-order, intraparticle diffusion, and Endovich kinetic models were used to calculate the kinetic parameters and determine the ideal mechanism of the adsorption process. It was found that the pseudo second-order model could be used to explain the experimental data. The adsorption was a controlled chemisorption mechanism. The thermodynamic parameters (ΔH^o, ΔS^o, and ΔG^o) were calculated using basic thermodynamic equations, and they indicated that the adsorption process was spontaneous at all temperatures and that the process was exothermic. Consequently, it was concluded that the peanut shell-based biochar can be used as a suitable and economical adsorbent for the removal of Pb(II) ions from aqueous media.

Keywords: adsorption, Pb(II) ions, biochar, FTIR-SEM, thermodynamic and kinetic evaluation

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Introduction

The treatment of wastewater that contains heavy metal pollutants is very important because it decreases negative effects on public health and on the ecological balance [1,2]. Therefore, wastewater discharge limits, which depend on whether the discharges go into the sea, lakes, or rivers, along with standards for drinking water are determined by laws and regulations [2,3]. The permissible limits of Pb(II) ions for drinking water are 0.005 mg/L, according to the U.S. Environmental Protection Agency (EPA) standard, and 0.01 mg/L, according to the World Health Organization (WHO) standard. Also, the EPA has set a maximum guideline Pb(II) ion concentration of 0.05 mg/L in wastewater [4, 5]. In order to provide these limit values, various conventional processes (such as precipitation, solvent extraction, electroplating, evaporation, ion exchange, reverse osmosis, and adsorption) have been used to remove Pb(II) ions from wastewater [6-13]. Several parameters (the content and quantity of the waste, chemical and energy requirements, process performance, and process economics) are very significant in the selection of suitable treatment processes. Although the adsorption process is more efficient and less expensive than other conventional treatment methods, the cost of adsorption processes depend largely on the properties of the adsorbent, such as the ability to regenerate/reuse the adsorbent and its adsorption capacity. To decrease the amount of by-products and to improve the quality of the treated water, several studies have been carried out on the adsorption of heavy metal ions onto various adsorbent materials [3-5, 14-27]. In these studies, it was presented that the surface properties of adsorbent (the mean diameter of the pores, the distribution of the pores, polarity) directly affect the adsorption yield and adsorbent capacity [10]. Therefore, it is concluded that special works should be done for each heavy metal ion and adsorbent pair to identify superior adsorbents. In recent years, although research on this subject is ongoing, to date, researchers have not yet been able to determine the most suitable adsorbent to remove Pb(II) ions from waste water.

Peanuts are an important food around the world, and about 90% of the peanuts produced annually are grown in Asia and Africa. Annually, almost 18.5 million tons of peanuts are harvested, producing about seven million tons of peanut shells. Peanut shells are nonedible and renewable as a waste biomass resource. Peanut shell, which can be used directly as an economic and inexhaustible adsorbent, has a high metal-binding capacity [9, 20, 26, 27]. In order to further enhance existing sorption capacity, peanut shells can be used as raw material in the production of modified adsorbents such as activated carbon, biochar, ash, etc. Biochar is the solid product of thermal degradation in an inert atmosphere. It cannot be called activated carbon since no activation (chemical or physical activation) is applied during production. Because it does not require additional processes and chemicals, biochar production is more economical and easier than activated carbon production. In previous studies [28], activated carbons derived from peanut shells (by a physical or chemical activation process) were used to remove Pb(II) ions from aqueous solutions. And the optimum adsorption conditions were investigated for removal of Pb(II) ions from aqueous solutions. However, in the previous studies biochar-based peanut shell was not used for this aim. And biochar and activated carbon adsorption capacities/activities were not compared with each other. In this respect, it is predicted that the study may contribute to the literature.

In view of this information, the main objective of this study was to determine the feasibility of using biochar produced from peanut shells as an adsorbent for the removal of Pb(II) ions from aqueous media in a batch system. The biochar produced from peanut shells was characterized. Then its performance as an adsorbent was investigated depending on various adsorption parameters, such as contact time, initial pH of the aqueous media, temperature, initial concentration of Pb(II) ions, and the dosage of the biochar. Kinetic and thermodynamic analyses of the adsorption process were performed. The results were compared with the current literature, especially raw peanut shell and peanut shell-based activated carbon.

Material and Methods

Production of Biochar and Characterization

Peanut shells *(Arachishypogaea)* from a local market in Adana, Turkey, were dried in an oven at 353 K. To produce biochar, the shells were milled in a food mill and then sieved. The fraction between 50 and 100 mesh of the shells was carbonized. The carbonization process was conducted in an ash oven at 823 K for 30 min in a nitrogen atmosphere. The biochar was stored in desiccators during all of the experiments.

Prior to the adsorption experiments, the biochar was characterized with instrumental and analytical analysis methods. The pH drift method was used to determine the pH of the zero point of charge (pH_{zpc}) of the biochar [29]. An ATI Unicam Mattson 1000 FTIR spectrometer was used to determine the functional groups on the surface of the biochar. Pore volume, average pore diameter, single-point BET surface area, and pore size distribution were among the morphological properties of the biochar that were obtained at optimum conditions using pure nitrogen adsorption at 77 K using a Micromeritics ASAP 2020 BET Surface Area Analyzer.

Preparation of Stock Solution

The stock solution that contained Pb(II) ions was prepared with a concentration of 1 g/L. $Pb(NO_3)_2$,

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which is of analytical reagent grade supplied by Merck. The dilute standard solutions that were used during the experiment were prepared by diluting the stock solution. In addition, during the adsorption experiments, especially in studies in which the effects of pH were examined, solutions of 0.1 M and 1 M NaOH and 1 M HNO_3 were used to adjust the pH values of the aqueous media. The pH values were measured by a Thermo Scientific Orion 1112000 3-star pH meter.

Experimental Procedure of the Adsorption Process

The adsorption experiments were conducted using a batch system, and the experiments determined the effects of temperature (293-313 K), pH (1.5-6.5), contact time (5-240 min), and initial concentration of Pb(II) ions (100-350 ppm). All of the parameters were performed using at least two parallel, 100-ml Erlenmeyer flasks, which were prepared in the same conditions using a temperature-adjustable water bath with an agitation speed of 180 rpm. The biochar was separated from the aqueous media at the end of the contact time by centrifuging at 5000 rpm for 5 min. The filtrate was analyzed using a Perkin Elmer Analyst 400 AAS by the direct air-acetylene flame method to determine the concentration of Pb(II) ions in the residue. The average of two experimental results was reported. The adsorption capacity (q_e) (Eq. 1) and adsorption efficiency (Y_a) (Eq. 2) of the biochar based on the experimental conditions were calculated using the following equations:

$$q_e = \frac{Vx(C_0 - C_e)}{m} \quad (1)$$

$$Y_a(\%) = \frac{(C_0 - C_t)}{C_0} \times 100 \quad (2)$$

…where m (grams) is the mass of the biochar; V (liters) is the volume of the aqueous media; C_0 (mg/L),C_e(mg/L), and C_t(mg/L) are the initial, equilibrium, and final concentrations of the Pb(II) ions in the aqueous media, respectively;and q_e is the equilibrium adsorption capacity, which represents the amount of Pb(II) ions adsorbed by the activated peanut shells (in mg/g) at equilibrium conditions.

Kinetic Analysis of the Adsorption Process

To better understand the mechanisms associated with the adsorption of Pb(II) ions on the surfaces of the biochar, we modeled the experimental data that were obtainedusing the following kinetic model equations (Table 1).

The Arrhenius equation (Eq. 3) was used to calculate the activation energy of the adsorption process of Pb(II) ions by the biochar:

$$\ln k = ln\ A - \frac{E_a}{RT} \quad (3)$$

…where A (g/mg min) is the Arrhenius constant; E_a (J/mol) is the activation energy; T (K) is the temperature of the solution; and R (8.314 J/mol K) is the ideal gas constant.

Thermodynamic Analysis of the Adsorption Process

The adsorption isotherm defines the amount of adsorbate on the adsorbent as a function of its concentration at constant temperature. The equilibrium adsorption isotherm data must be calculated to design an adsorption system, and the adsorption capacity, mean free energy, intensity, and the mechanism of adsorption should be determined for this isotherm. Thus, we evaluated our experimental results by applying the Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich (D-R) isotherm models, which have been used extensively to describe the adsorption process (Table 2).

The van't Hoff equation (Eq. 4) indicates the relationship between temperature and the adsorption equilibrium constant.

Table 1. Adsorption kinetic models and their parameters used in this paper.

Kinetic Model	Linearized form of equations	Parameters
Lagergren's pseudo-first order model [30]	$\ln(q_e - q_t) = lnq_e - k_1 t$	t (min): the contact time k_1 (min^{-1}): the pseudo first-order rate constants. q_t (mg/g): the adsorption capacity at t. q_e (mg/g): the adsorption capacity at equilibrium.
Pseudo-second order kinetic model [31]	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$	k_2 (g/mg.min): the pseudo second-order rate constants
Elovich kinetic model [32]	$t = (1/\beta)ln(\alpha\beta) + (1/\beta)lnt$	α(mg/g.min): the initial adsorption rate. β(g/mg): the desorption constants
Intraparticle diffusion [24]	$qt = k_{id} t^{0.5} + C$	k_{id} (mg $g^{-1}min^{0.5}$): the intra particle diffusion rate constant. C (mg/g) : the constant which is proportional to the boundary layer thickness

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Table 2. Adsorption isotherm models and their parameters used in this paper.

Isotherm Model	Linearized form of equations	Parameters
Langmuir Isotherm [33]	$\frac{C_e}{(x/m)} = \frac{1}{q_{max}K} + \frac{C_e}{q_{max}}$	C_e(mg/L): the equilibrium concentration of the Pb(II) ions q_{max}(mg/g): the maximum adsorption capacity of biochar K (L/mg): the Langmuir constant $x/m = q_e$ (mg/g) : the amounts of Pb(II) ions on the surface of the biocharat equilibrium. C_0(mg/L): the highest initial Pb(II) concentration.
Freundlich Isotherm [34]	$ln(x/m) = lnK_f + \frac{1}{n}lnC_e$	K_f(mg/g): the adsorption capacity n :the adsorption intensity, respectively.
Temkin Isotherm [35]	$(x/m) = BlnK_T + BlnC_e$	K_T (mg/g): the temkinisotherm constant B : a constant associated with the heat of adsorption.
D-R Isotherm [36]	$ln(x/m) = lnQ_m - \beta\varepsilon^2$ $\varepsilon = RTln(1 + \frac{1}{C_e})$ $E = (2\beta)^{-2}$	B(mol²/J²): the adsorption energy constant. ε (J/mol): the polanyi potential. E (J/mol): the mean free energy. Q_m(mg/g): the theoreticaladsorption capacity for D-R isotherm.

$$\frac{d(lnK)}{dT} = \frac{\Delta H^{\circ}}{RT^2} \quad (4)$$

Eq. (5) is obtained by integrating Eq. (4):

$$-lnK = \frac{\Delta H^{\circ}}{R}\left(\frac{1}{T}\right) + C \quad (5)$$

Eq. (6) is obtained if the fixed expression is written instead as (*-ΔS°/R*) and the equality is regulated:

$$lnK = \frac{\Delta S^{\circ}}{R} - \frac{\Delta H^{\circ}}{R}\left(\frac{1}{T}\right) \quad (6)$$

…where *K* is the adsorption equilibrium constant, *T* is the absolute temperature, and *R* is the universal gas constant (8.314 J/mol.K).

When Eq. (6) is combined with ΔGº = -RTlnK and rearranged, the following equation is obtained:

$$\Delta G° = \Delta H° - T\Delta S° \quad (7)$$

…where ΔGº, ΔHº, and ΔSº are changes in free energy, enthalpy, and entropy, respectively.

Results and Discussion

Results of the Characterization of Biochar

Results of BET Analysis

Based on the results of the BET analysis performed by the nitrogen adsorption method, it was determined that biochar had pore diameters of 20.55 angstroms (Aº) and a single-point BET surface area of 1.78 m^2/g. The mean pore volume was calculated as 0.002103 cm^3/g, and the untreated peanut shells had pore diameters of 20.72 Aº, an average pore area of 0.84 m^2/g, and a pore volume of 0.00047 cm^3/g. The carbonization process resulted in an increase in the single-point BET surface area and the mean pore volume.

Results of SEM Analysis

Fig. 1a) shows the SEM images of the biocharthat was obtained by carbonization of the peanut shells (at x1000 magnification), and Fig. 1b) shows the peanut shells (at x1000 magnification). A more porous structure resulted from the carbonization process. The development of the pore structure determined by

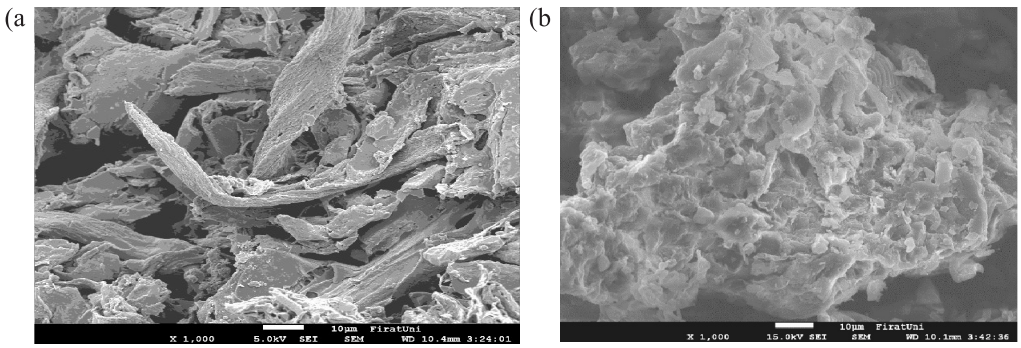

Fig. 1. SEM images of the peanut shells before and after carbonization: a) peanut shell, b) biochar from peanut shell.

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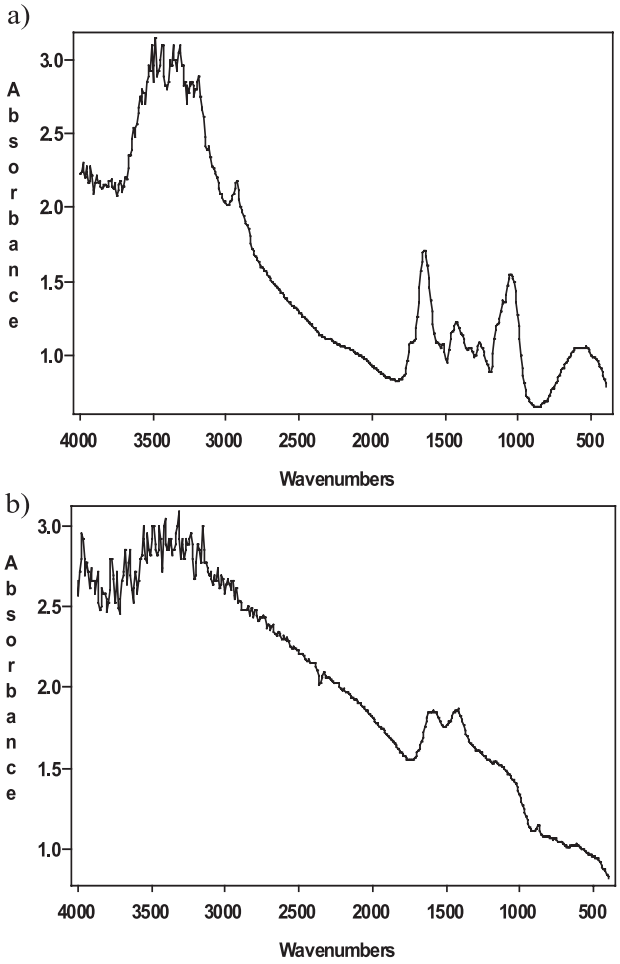

Fig. 2. FTIR spectrum of the peanut shells before and after carbonization.

the SEM analysis was consistent with the results of the BET analysis.

Analysis of FTIR Results

When the adsorption process was used to remove heavy metals from the wastewater, the functional groups found in the active centers of the adsorbent were highly related. These functional groups may be joined with heavy metal ions. Thus, heavy metal ions can be removed from the wastewater. Therefore, in this study, we conducted FTIR analyses of the peanut shells and the biochar, and the functional groups that were obtained from the FTIR spectrum (Fig. 2) are summarized in Table 3.

When the FTIR spectrum of the peanut shell was examined, the following peaks were determined. The peak at 3398 cm^{-1} shows the presence of O–H stretching vibrations due to inter- and intra-molecular hydrogen bonding in the polymeric macromolecules such as cellulose, lignin and pectin. Thus, showing the presence of "free" hydroxyl groups. The peak aliphatic at 2936-2851 cm^{-1} indicates the asymmetric C-H stretching of $-CH_3$ and $=CH_2$ groups of aliphatic acids, and the peak at 1742 cm^{-1} indicates the C=O stretching of aldehyde group peaks of hemicellulose. 1653 cm^{-1} represents asymmetric stretching vibrations of the C=O bond of the carbonyl groups of lignin. 1460 cm^{-1} aromatic ($-CH_3$) group C-H refers to deformation vibration. This is due to the aliphatic portions of the peak lignin. Other peaks seen in the structure are 1377 cm^{-1}; aliphatic C-H bending vibration of methyl and phenyl alcohols, 1261 cm^{-1}; C-O stress vibration in ring structure of lignin and xylan, 1050 cm^{-1}; C-OH stress vibration of cellulose and hemicellulose.

When the FTIR spectrum of biochar was examined, it was determined that the hemicellulose and cellulose in the structures of the peanut shells were degraded significantly by the carbonization process that was conducted at 800 K, but the aliphatic and aromatic structures of lignin were preserved. As stated in Table 3, the peaks of 3398, 1651 and 1457 cm^{-1}, which were determined in the spectrum, are due to the aliphatic and aromatic structures of lignin. Since lignin has higher thermal stability than other components (hemicellulose, cellulose), it was determined that lignin did not undergo thermal degradation and remains in biochar structure.

Table 3. FTIR spectra of the biochar and peanut shells.

Frequency (cm^{-1})		Assignment
Peanut shell	Biochar	
3398	3398	–OH stretching (It was indicated that the presence of p-coumaryl, coniferyl and sinapyl alcohols which were the main building blocks of lignin.)
2936	-	C−H stretching (It was indicated that the presence of methyl and methylene groups.)
1742	-	C=O stretching (It was indicated that the presence of hemicelluloses)
1653	1651	Aromatic C=O stretching (It was indicated that the presence of conjugated carbonyl groups of lignin)
1460	1457	Methyl ($-CH_3$) groups vibrations (It was indicated that the presence of aliphatic part of lignin)
1377	-	Aliphatic CH stretching (It was indicated that the presence of methy and phenol alcohols)
1261	-	Syringyl ring breathing and C−O stretching (It was indicated that the presence of xylan)
1050	-	C−OH stretching vibration (It was indicated that the presence of cellulose and hemicelluloses)

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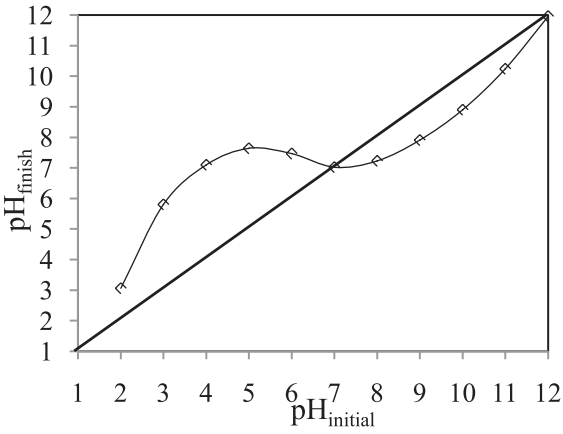

Fig. 3. Zeta potential of biochar made from peanuts shells

Results of the pH_{zpc} Test

It is well known that the point of zero charge (pH_{zpc}), which is indicative of the types of active centers on the surface and the adsorption mobility of the surface, is an important factor in adsorption processes. Fig. 3, which was drawn using the pH drift method, shows that the value of pH_{zpc} was approximately 6.9. The experimental results indicated that the surface of the biochar had a positive charge when the pH of the initial aqueous media that contained Pb(II) ions was less than approximately 6.9 and could attract anions from the aqueous media. The opposite is true, so the cationic ion removal efficiency is significantly increased if the pH value is run at above 6.9. But it is well known that, at pH levels greater than 6.0 in Pb(II) solutions, $Pb(OH)_2$ is formed and precipitates in the aqueous media. For these reasons, the pH range of 5-6 is considered to be more suitable for the removal of Pb(II) ions.

Experimental Adsorption Results

Effect of the pH of the Initial Solution

As detected in the pH_{zpc} test, there is a significant relationship between the acidity of the aqueous media and the surface charge of the active centers of the biochar. So, the acidity of the initial solution is one of the most important factors that affect the adsorption of metal ions. The effect of pH on the adsorption of Pb(II)ions by biochar was investigated in the pH range of 1.5 to 6.5. Fig. 4 shows that the adsorption capacity of the biochar increased rapidly in the pH range of 2 to 5.5., and it reached its maximum value (45 mg/g) at pH 5.5. When the pH exceeded 5.5, a rapid decrease in adsorption capacity occurred. This decrease was the result of the decrease in the degree of ionization of the functional groups of the adsorbent and the change in the solubility of the Pb(II) ions. It is known that, at pH levels greater than 6.0 in Pb(II) solutions, $Pb(OH)_2$ is formed and precipitates in the aqueous media. It also

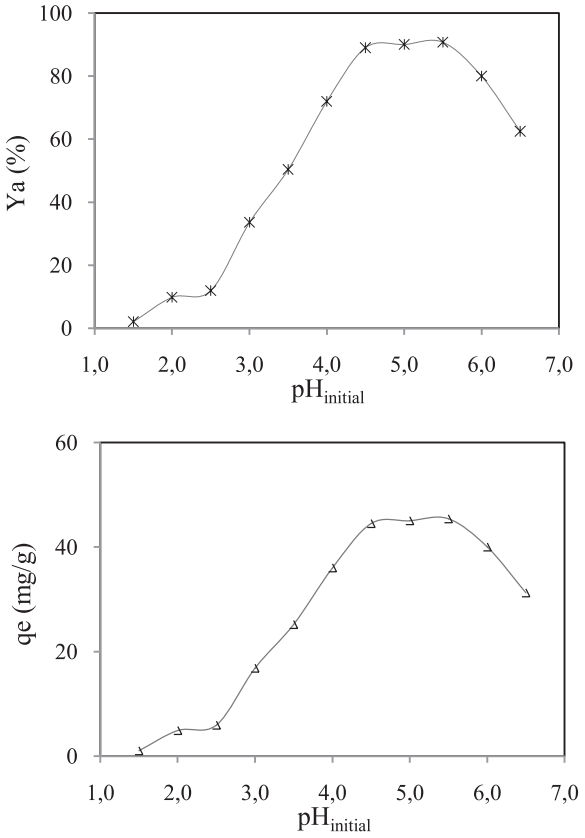

Fig. 4. Effect of the initial pH of the aqueous media (pH: 1.5-6.5; biochar concentration: 2 g/L; temperature: 273 K; initial Pb(II) ion concentration: 100 ppm; contact time: 240 min).

has been stated in studies in the literature that pH values below 6.0 should be studied to prevent the precipitation of $Pb(OH)_2$ on the surface of the adsorbent and to prevent experimental errors [3, 17, 37, 38].

Effect of the Dosage of the Adsorbent

According to the experimental results (Fig. 5), the capacity of the adsorbent increased from 30 to 44.5 mg/g when the concentration of the adsorbent was increased from 1 to 2 g/L. It was determined that the adsorption capacity of the biochar reached its maximum when the dosage of the adsorbent was 2 g/L. When the dosage exceeded 2 g/L, the value decreased sharply. When the adsorbent concentration was 15g/L, the capacity of the absorbent decreased to 6.5 mg/g. Hence, it was determined that the optimum dosage of the adsorbent for the removal of Pb(II) ions was 2 g/L. The Pb(II) removal efficiency increased as the concentration of the absorbent increased to a certain level, and then it remained constant (Fig. 5). This occurred due to the increase in the active areas in the adsorbent, resulting in the Pb(II) ions being absorbed much more easily. A similar trend also has been reported for the removal of metal ions by some other materials [4, 17, 39].

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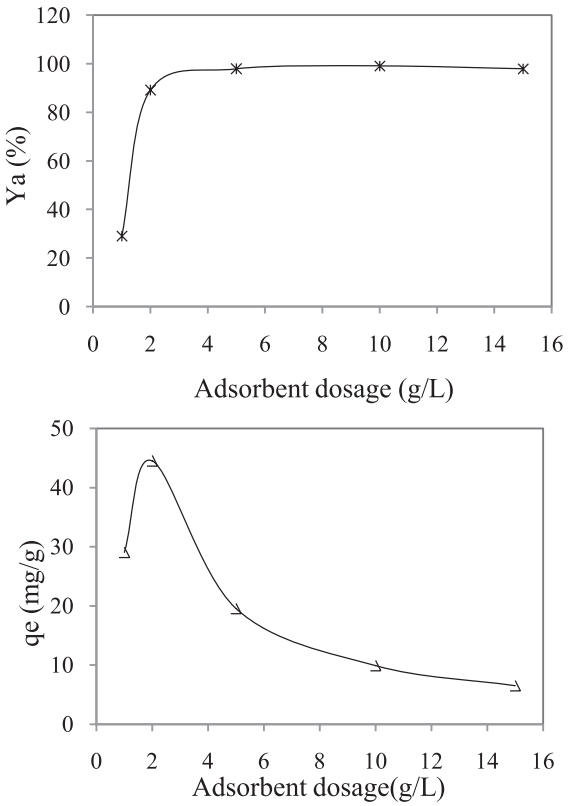

Fig. 5. Effect of the concentration of biochar (pH: 1.5-6.5; biochar concentration: 1-15 g/ L; temperature: 273 K; initial Pb(II) ion concentration: 100 ppm; contact time: 240 min).

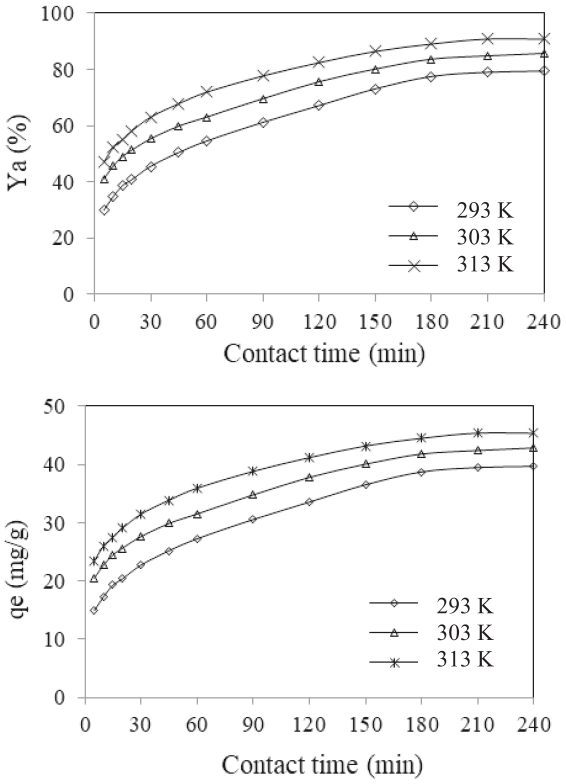

Fig. 6. Effect of temperature and contact time (pH: 1.5-6.5; biochar concentration: 1-15 g/ L; temperature: 273, 283, 293 K; initial Pb(II) ion concentration: 100 ppm; contact time: 240 min).

Effect of Temperature and Contact Time

In order to calculate the kinetic and thermodynamic parameters and to determine whether the process of adsorption is endothermic or exothermic, the effect of temperature on the adsorption process was investigated. The effect of the temperature of the solution on the adsorption of Pb(II) ions was evaluated in the temperature range of 293-313 K with the optimum values of the initial pH. The adsorption yields and adsorption capacities of biochar that were obtained at different temperatures of the solution are shown as functions of time in Fig. 6, which shows that the adsorption efficiency increased relatively faster for the first 30 minutes, after which a certain constant equilibrium value was attained. The adsorption efficiency reached the equilibrium value in 180 minutes, and the adsorption efficiency was determined to be 89% under these conditions. As the active centers of the biochar were occupied by the Pb(II) ions, both the rate of adsorption and the speed at which the Pb(II) ions moved from the outer surface to the inner areas of the biochar were reduced during the adsorption process.

Also, it is well known that adsorption processes are affected significantly by temperature. Our experimental results indicate that the adsorption capacities decreased as the temperature increased. It was determined that, at equilibrium, 45.5 and 39.7 mg of Pb(II) were adsorbed per gram of the biochar at 293 K and 313 K, respectively. The decreasing adsorption capacity of the biochar with increasing temperature showed the exothermic nature of the adsorption process, and these adsorption reactions clearly were favored at the lower temperatures. The interaction (hydrogen bonds and the Van der Waals interaction) between the Pb(II) ions and the biochar was not strong. Similar results were given in Sabri et al. [41], and Ghasemi et al. [4] for the adsorption of Pb(II) ions.

Effect of the Initial Concentration

The effect of the initial concentration of Pb(II) ions on the adsorption capacity of the biochar was investigated at pH 5.5, 293 K, and the concentration range of 100 to 350 mg/L. Fig. 7 shows the results. When the equilibrium data were taken into consideration, the adsorption yields were determined to decrease as lead concentration increased. Unlike the adsorption yields, the adsorption capacities of the biochar increased as the initial concentration of Pb(II) ions increased.

It is well known that an increase in the concentration of an adsorbate causes an increase in the forces that are driving the adsorption process. Thus, the adsorption capacity increases linearly with an increase in the initial concentration of the adsorbate. Thus, the maximum

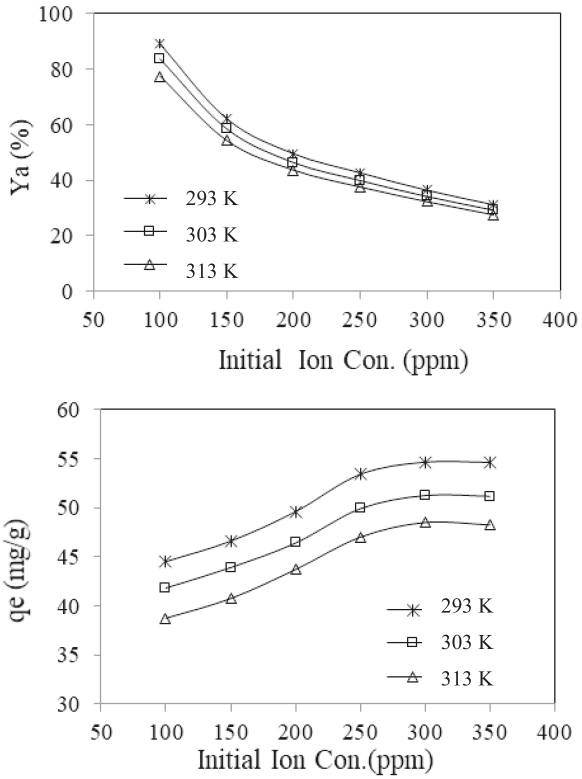

Fig. 7. Effect of initial ion concentration of Pb(II) ions (pH: 1.5-6.5; bio-char concentration: 1-15 g/ L; tempera-ture: 273 K; initial Pb(II) ion concentration: 50-350 ppm; contact time: 240 min).

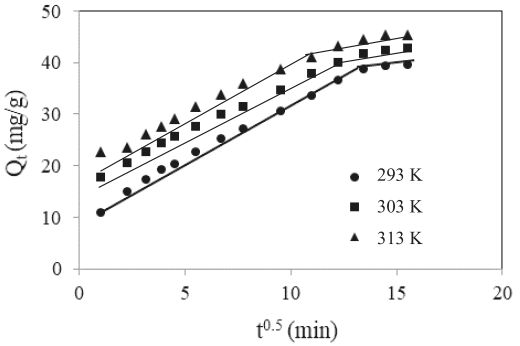

Fig. 8. Intraparticle diffusion models for adsorption of Pb(II) ions onto bio-char.

adsorption capacity was obtained as 54.6 mg/g at 293 K and at the highest initial concentration of the Pb(II) ions (350 mg/L).

The Kinetic Analysis Results

Table 4 gives the correlation coefficients (R^2) and the values of the parameters of the kinetic model, which were calculated in accordance with the equations of the kinetic model presented in the materials and methods section.

When we examined the difference between the experimental adsorption capacity (q_e) and the calculated

Table 4. Parameters of the kinetic model for the adsorption of Pb(II) by biochar.

Temperature (K)	q_e(mg/g)	Pseudo first-order kinetic model constants			
		R^2	k_1(min^{-1})	q_{ec1}(mg/g)	Equations
293	45.38	0.993	0.013	22.64	$\ln(q_e-q_t) = -0.013t + 3.120$
303	42.86	0.987	0.013	23.45	$\ln(q_e-q_t) = -0.013t + 3.154$
313	39.70	0.984	0.014	25.89	$\ln(q_e-q_t) = -0.014t + 3.254$
Temperature (K)	q_e(mg/g)	Pseudo second-order kinetic model constants			
		R^2	k_2 (g/mg.min)	q_{ec2} (mg/g)	Equations
293	45.38	0.990	0.0040	45.45	$t/q_t = 0.025t + 0.422$
303	42.86	0.998	0.0076	43.47	$t/q_t = 0.023t + 0.279$
313	39.70	0.993	0.0112	40.00	$t/q_t = 0.022t + 0.102$
Temperature (K)	q_e(mg/g)	Enovich kinetic model constants			
		R^2	α(mg/g.min)	B(g/mg)	Equations
293	45.38	0.9122	149.63	0.202	$Q_t = 4.9386\ln(t)+16.846$
303	42.86	0.9227	58.47	0.194	$Q_t = 5.1648\ln(t)+12.533$
313	39.70	0.9283	15.27	0.172	$Q_t = 5.8229\ln(t)+5.615$
Temperature (K)	q_e(mg/g)	Intraparticle diffusion kinetic model constants			
		R^2	k_{id}(g/mg.min$^{1/2}$)	C	Equations
293	45.38	0.9806	1.7089	21.4	$q_t = 1.7089t^{0.5}+21.40$
303	42.86	0.9887	1.7843	17.318	$q_t = 1.7843t^{0.5}+17.318$
313	39.70	0.9881	2.0049	11.063	$q_t = 2.005t^{0.5}+11.063$

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maximum adsorption capacity (q_{ec}) and examined the correlation coefficient, it was concluded that the pseudo second-order model equation was the most suitable model for the multi-component adsorption of Pb(II) ions on the surface of the biochar. In other words, the chemisorption process controlled the adsorption of lead (II) ions onto biochar. Also, it was observed that the values of q_{ec2} decreased and the values of k_2 increased as the temperature increased. The values of k_2 indicated that the adsorption of Pb(II) ions by biochar occurred more rapidly at higher temperatures.

Fig. 8 shows that the adsorption process was divided into two parts and that the rate of adsorption was different for the two parts. The first step, which might be attributable to external surface adsorption, had a higher adsorption rate than the other step at all temperatures. The second step could be viewed as a gradual adsorption stage in which intra particle diffusion is initiated, thereby decreasing the adsorption rate in this step. The intra particle diffusion stage controls and limits the rate of adsorption. Similar comments and rate trends were presented by Dil et al. [2]. Table 4 provides the total adsorption rate (k_{id}) as the average of the rates for the two steps for all temperatures. The kinetic calculations indicated that the values of k_{id} increased as the temperature increased.

Similar results for the adsorption of Pb(II) ions onto different adsorbents have been reported in the literature, e.g., active carbon from palm oil mill effluent [24], cucumber peel [25], active carbon from cows' bones [3], active carbon from coconut shells [18], porous starch [13], agricultural waste-based ash and Fe nanoparticle-loaded ash [4], and polymer-modified carboxymethyl cellulose from wheat straw [17].

According to Eq. (7), which was presented in the materials and methods section, ln k values are plotted against 1/T values. Using the values of the slope and the slip, the activation energy and Arrhenius constant "A" for the process were determined to be 42.4 kJ/mol and 1.09 g/mg.min, respectively. The values of the activation energy indicated that chemical adsorption mechanisms had occurred.

Thermodynamic Analysis Results

The adsorption data were analyzed with Langmuir, Freundlich, Temkin, and D-R isotherm models, and the parameters of the isotherm are given in Table 5. Since the correlation coefficients for the Langmuir isotherm were closer to one (0.99), it was concluded that the Langmuir isotherm was the most suitable model for describing the processes involved in the adsorption of Pb(II) ions onto the biochar. These results

Table 5. Parameters of thethermodynamic model for the adsorption of Pb(II) by biochar.

Temperature (K)	Langmuir Isotherm Constants				
	q_{max} (mg/g)	R_L	K (L/mg)	R^2	Equations
293	56.49	0,077	0.1195	0.994	$C_e/(x/m) = 0.0177C_e + 0.1481$
303	53.19	0,089	0.1029	0.997	$C_e/(x/m) = 0.0188C_e + 0.1837$
313	50.76	0,112	0.0795	0.991	$C_e/(x/m) = 0.0197C_e + 0.2476$
Temperature (K)	Freundlich Isotherm Constants				
	K_f(mg/g)		n	R^2	Equations
293	36.49		13.89	0.876	$\ln(x/m) = 0.1018(\ln C_e) + 3.317$
303	32.52		12.35	0.903	$\ln(x/m) = 0.0817(\ln C_e) + 3.482$
313	28.13		9.900	0.921	$\ln(x/m) = 0.0724(\ln C_e) + 3.597$
Temperature (K)	Temkin Isotherm Constants				
	B (J/mol)		K_T (L/mg)	R^2	Equations
293	3.572		16306.23	0.8631	$x/m = 3.572(\ln C_e) + 34.643$
303	3.789		2819.19	0.8915	$x/m = 3.789(\ln C_e) + 30.099$
313	4.419		223.14	0.9104	$x/m = 4.419(\ln C_e) + 23.896$
Temperature (K)	D-R Isotherm Constants				
	β(mol²/kJ²)	Q_m(mg/g)	E (kJ/mol)	R^2	Equations
293	3.454	51.82	0.269	0.5179	$\ln(x/m) = -3.4542\beta + 3.9478$
303	7.112	48.69	0.187	0.5494	$\ln(x/m) = -7.1118\beta + 3.8854$
313	14.26	45.97	0.132	0.5848	$\ln(x/m) = -14.263\beta + 3.828$

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Table 6. Thermodynamic parameters for the adsorption of Pb(II) ions by biochar.

Temperature (K)	ln K	-ΔG° (kJ/mol)	-ΔH°(kJ/mol)	ΔS°(kJ/mol K)	R^2
293	10.12	24.69	15.46	0.315	0.98
303	9.960	25.00			
313	9.710	25.32			

Table 7. Summary of the literature related to the adsorption of Pb(II) ions.

Adsorbent	$q_{max\ (mg/g)}$	References
Peanut Shell	7.10	[26]
Fixed bacteria	10.79	[1]
Phytolaccaamericana L. biomass (the raw P. Americana)	13.19	[40]
Phytolaccaamericana L. biomass (the HNO_3-modified)	15.51	[40]
Active carbon from biomass of Prunusdomestica	12.00	[15]
Synthetic ferrihydritef	13.75	[19]
Coffee grounds	22.90	[23]
Groundnut hull	31.54	[20]
Peanut shell activated carbon	35.50	[28]
Peanut shell	38.91	[27]
Phosphoric acid dehydrated carbon (Moistened carbon)	41.50	[42]
Commercial activated carbon	47.20	[18]
Active carbon from Cow bone	47.62	[3]
Eucalyptus camaldulensis	52.63	[41]
Activated carbons from tropical almond shells	53.10	[21]
Biochar from peanut shell	**56.49**	**This study**
Activated carbon from walnut wood	58.82	[44]
Solanum melongena leaf powder	71.42	[14]
Brassica Compestris Stem (BCS)	78.50	[39]
Sulphuric acid-treated palm tree leaves	88.61	[43]
Activated carbons from dinde stones	92.90	[21]
Activated carbon from palm oil mill effluent	94.34	[24]
Citric acid modified rubber leaf powder	97.19	[22]
Apple juice residue	108.0	[45]
Monosodium glutamate modified rubber leaf powder	109.9	[22]
Activated carbons from guava seeds	114.8	[21]
Cucumber peel	133.6	[25]
Spirodelapolyrhiza (L.) Schleiden biomass	137.0	[5]
Eucalyptus camaldulensis – HNO_3modified	138.8	[41]
Tomato waste	152.0	[45]
Chemically modified agricultural waste	166.7	[16]
The dried aquatic plant, LemnaperpusillaTorr.	196.0	[46]
Ash from rosacanina-l leaves	588.0	[4]
Polymer-modified wheat straw carboxymethyl cellulose	822.1	[17]
Nanoparticles loaded ash (nFe-A) using Rosa Canina-L leaves	833.0	[4]

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were in agreement with other studies, which also have shown that the Langmuir model provides a good fit for the adsorption of Pb(II) [3, 4, 13, 17, 18, 25, 39, 42, 43].

Using the equation for the Langmuir isotherm model, the maximum monolayer adsorption capacities (q_{max}) for 293, 303, and 313 K were calculated as 56.5, 53.2 and 50.8 mg/g, respectively. The decreases in the values of q_{max} and the Langmuir constant (K) with temperature indicated that the Pb(II) ions were adsorbed favorably by the biochar at lower temperatures. It is known that R_L, which is the dimensionless separation factor, is calculated by the following equation.

$$R_L = \frac{1}{1+C_0K} \quad (8)$$

The value of R_L is informed about whether the adsorption is favorable or not. The R_L values (0.077-0.112), which were calculated as less than unity and greater than zero, showed that the adsorption process was favorable. The ratio 1/n is the heterogeneity factor of adsorption, and the calculated values of 1/n were in the range of 0.101-0.072. The calculated values of 1/n were less than 1.0 at all temperatures, which indicated that the Pb(II) ions were adsorbed favorably and that their adsorption was a chemical-driven process.

Table 6 provides the thermodynamic parameters for the process that were calculated by van't Hoff. The negative value of ΔGº indicated that the adsorption was feasible and spontaneous in the specified temperature range. Also, the decrease in the values of ΔGº as the temperature increased indicated that the adsorption of Pb(II) ions on the biochar became more favorable at lower temperatures. The value of ΔHº (-15.46 kJ/mol) indicated that the adsorption process was exothermic. The fact that the absolute value of ΔHº was less than 40 kJ/mol indicated that the process was controlled by a physical mechanism rather than a chemical mechanism. The positive value of ΔSº indicated the affinity of the biochar for the Pb(II) ions.

Comparison

The maximum adsorption capacities (q_{max}) of the adsorbents were the most important parameter for comparing their efficiencies. In order to compare and interpret the sorption capacity of biochar with various adsorbents, Table 7 provides a summary of the experimental data that have been published recently related to the adsorption of Pb(II) ions.

Based on a survey of the literature and the experimental results obtained in this study, it was concluded that biochar can be used as an effective, low-cost, eco-friendly adsorbent for the removal of Pb(II) ions from aqueous media.

Conclusions

The adsorption of Pb(II) ions using peanut shell-based biochar was evaluated in this study.

The biochar was characterized by FTIR, SEM, and BET techniques as well as pH_{zpc}analysis.

The adsorption of Pb(II) ions was found to be dependent on the initial pH of the Pb(II) solution, the dosage of the biochar, the initial concentration of Pb(II) ions, and the contact time. The optimum values of temperature, pH, contact time, adsorbent dosage, and initial concentration of Pb(II) ions were 293 K, 5.5±0.02, 180 min, 2 g/L, and 100 ppm, respectively. The adsorption yield of Pb(II) ions and the adsorption capacity (q_e) of the biocharat the optimum conditions were determined to be 89% and 44.5 mg/g, respectively.

The adsorption followed pseudo second-order kinetics, and the equilibrium data were well fitted with the Langmuir isotherm. It was determined that the maximum Langmuir biosorbent capacity (q_{max}) was approximately 59 mg/g.

The changes in the entropy (ΔSº) and the enthalpy (ΔHº) were calculated to be 31.48 J/mol.K and -15.24 kJ/mol, respectively. The change of free energy (ΔGº) was calculated as-24.59, -24.91, and -25.22 kJ/mol for 293, 303, and 313 K, respectively.

The results indicated that the adsorption process was feasible and spontaneous at all temperature values that were tested and that the process was exothermic.

Consequently, it was concluded that peanut shell-basedbiochar can be used as a high-performance adsorbent for the removal of Pb(II) ions from aqueous media.

Conflict of Interest

The authors declare no conflict of interest.

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