Application of black walnut (*Juglans nigra*) husk for the removal of lead (II) ion from aqueous solution

O. S. Lawal, O. S. Ayanda, O. O. Rabiu and K. O. Adebowale

ABSTRACT

The biosorption characteristics of Pb (II) ions from aqueous solution using black walnut (*Juglans nigra*) seed husk (WSH) biomass were investigated using batch adsorption techniques. The effects of pH, contact time, initial Pb (II) ion concentration, and temperature were studied. The Langmuir, Freundlich and Temkin isotherms were used to analyze the equilibrium data. It was found that the adsorption of Pb (II) ions onto WSH was best described by the Freundlich adsorption model. Biosorption kinetics data were tested using the pseudo-first order and pseudo-second order models, and it was observed that the kinetics data fitted the pseudo-second order model. Thermodynamic parameters such as standard Gibbs free energy change (ΔG^0), standard enthalpy change (ΔH^0) and standard entropy change (ΔS^0) were evaluated. The result showed that biosorption of Pb (II) ions onto WSH was spontaneous and endothermic in nature. The FTIR study showed that the following functional groups: O-H, C = O, C-O, C-H and N-H were involved in binding Pb (II) ions to the biomass.

Key words | agricultural by-product, biosorption, isotherm, kinetics, lead (II) ion, walnut husk

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INTRODUCTION

Environmental pollution by metal ions in industrial wastewaters is one of the most important causes of contamination to humans (Siddiquee *et al.* 2015). They can accumulate throughout the food chain and environment, due to their great persistence and high toxicity. The removal of heavy metals from contaminated wastewaters is generally accomplished by conventional methods such as chemical precipitation, membrane separations, evaporation, resin ion-exchange, electrowinning, reverse osmosis, etc. However, these conventional methods of removing heavy metals from effluents have major disadvantages such as high energy requirements, incomplete metal removal and large quantities of toxic waste sludge. Moreover, these technologies are most suitable in situations where the concentrations of heavy metal ions are relatively high (Gunatilake 2015). To compare with conventional processes, new methods must be economically viable as well as successful in the removal of environmental contaminants (Amin *et al.* 2014). Biosorbents are alternatives to conventional methods. The term 'biosorbent' includes the usage of dead biomass (agricultural by-products such as fibre, peat and wool) as well as living plants and bacteria as sorbents (Kumar *et al.* 2013). Processing of agricultural products often yields very large proportions of by-products (Zhao *et al.* 2012) that are considered to be of low value. Agricultural by-products are usually composed of lignin and cellulose as major constituents and may also include other polar functional groups of lignin, which include alcohols, aldehydes, ketones, carboxylic, phenolic and ether groups. These groups have the ability to bind heavy metals by the replacement of hydrogen ions for metal ions in aqueous solution (Abdel-Ghani & El-Chaghaby 2014).

Agricultural by-products such as tea waste, coffee waste, watermelon seed hulls, fibre, sawdust, etc. have been applied to the sorption of metal ions (Putra *et al.* 2014). In addition, the biosorption of Pb (II) ions onto cereals (Low *et al.* 2000), *Moringa oleifera* bark (Reddy *et al.* 2010), modified lignin hydrogel (Yao *et al.* 2014), rice husks (Abdel-Aty *et al.* 2013), etc. has been studied. Özcan *et al.* (2007) affirmed the effectiveness of an agricultural by-product (*Capsicum annuum* seeds) for the removal of Pb (II) ions. Özcan *et al.* (2007) stated that the maximum adsorption capacity of Pb (II) onto *Capsicum annuum* seeds was 1.87×10^{-4} mol/g, the adsorption data fitted well to the Langmuir isotherm model, and the pseudo-second order kinetic model described the adsorption data, whereas the thermodynamic

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parameters indicated that the adsorption process is spontaneous. The study of the biosorption of Pb (II) onto an agricultural by-product (date stems) was reported by Yazid & Maachi (2008). It was reported that the equilibrium study obeys the Langmuir and Freundlich isotherm models, while the kinetic study obey the pseudo-second order model. The thermodynamic parameters were also evaluated. Gerola *et al.* (2013) examined the use of the passion fruit skin by-product for the sorption of Pb (II) ions. They reported that the kinetics and equilibrium of biosorption follow the pseudo-second order and the Langmuir models, respectively. Putra *et al.* (2014) investigated the effectiveness of coconut tree sawdust, eggshells and sugarcane bagasse as low-cost biosorbents for the removal of Cu (II), Pb (II) and Zn (II) ions from aqueous solutions. They proposed that the application of agricultural by-products for the sorption of environmental pollutants will provide a solution to the disposal of agricultural wastes. Lastly, the biosorption of Pb (II) ions by untreated and alkali treated dried leaf of *Adhatoda vasica* was considered by Christi & Sandhya Kiran (2014). They likewise established the possibility of cleaning up the environment through the use of agricultural by-products.

Walnut seed husk (WSH) is a by-product of black walnut production. Walnuts (*Juglans nigra*) are plants in the family *Juglandaceae*. They are deciduous trees with wide distribution across the globe. Walnut is grown mainly for its edible nuts, oil and timber production. Medicinal uses have also been reported for the nuts of the walnut (Ekwe & Ihemeje 2013). These uses of walnut have widely enhanced its cultivation, particularly in the tropic zone area. However, the hard husk of the walnut is often seen as waste material after the nut is extracted. In areas where walnut oil is used, the husks often constitute an environmental nuisance due to the large quantity of walnut fruits needed for walnut oil production.

Therefore, the objective of this study was to investigate the possible use of a waste material, WSH, as an alternative biosorbent material for the removal of Pb (II) ions from aqueous solutions. The dynamic behavior of the adsorption was investigated via the effect of the pH of the solution, initial Pb (II) ion concentration, contact time, and temperature.

MATERIALS AND METHODS

Chemicals and reagents

The lead (II) nitrate ($Pb(NO_3)_2$), sodium hydroxide (NaOH) and nitric acid (HNO_3) used are analytical grades purchased from Merck Schuchardt, Germany. Stock Pb (II) solution (1,000 mg/L) was prepared by dissolving $Pb(NO_3)_2$ (1.6 g) in deionized water (100 mL) and diluting quantitatively to 1,000 mL using deionized water. Pb (II) solutions of different concentrations were prepared by adequate dilution of the stock solution with deionized water. The pH of the solution was adjusted with HNO_3 and NaOH solutions for pH studies. All the glassware used were immersed overnight in 10% (v/v) nitric acid and rinsed several times with deionized water before drying.

Preparation of biomass

Walnut fruits were obtained in large quantity from a market in Ibadan, Nigeria. The fruits were soaked and rinsed with deionized water to remove any physical and weakly bound materials on the outer shell. The fruits were cooked to enhance easy breaking and removal of the fruits to collect enough WSH. The WSH were then oven-dried at 60 °C for 24 h. The dried WSH were ground and then sieved using a 150 size mesh screen. The sieved WSH were then packed in polythene bags (2.0 g each) until required for the experiments.

Fourier transform infrared spectroscopy (FTIR) of WSH

The IR spectra of the free and metal-adsorbed biosorbents were run as KBr pellets on an impact 410 Nicolet FTIR spectrometer. Finely ground biomass (10.0 mg) was mixed with KBr (500 mg) and the two were ground together in an agate mortar. To prepare a translucent sample disk, the mixture was transferred into the die and the die placed into the hydraulic press. Pressure was applied, exhausted and the translucent sample disk formed was carefully removed from the die, placed in the FTIR sample holder and the spectra were recorded over the range 4,000–500 cm^{-1}.

Effect of pH on adsorption of Pb (II) ions

The influence of pH on the biosorption process was investigated by adjusting the Pb (II) solution to a desired value within the range 1.0–8.0 with HNO_3 or NaOH. The metal ion solution (25 mL; 100 mg/L) was then contacted with a fixed quantity of WSH (0.5 g, dry weight) in a boiling tube. The mixture was left in a water bath to maintain a constant temperature of 28 °C for 24 h with constant shaking at 75 rpm. The biosorbent was then removed from the mixture by filtration through a Whatmann No. 32 filter paper. All experiments were performed in triplicates.

Effect of initial metal ion concentration on the adsorption of Pb (II) ions

Batch adsorption studies were carried out using initial metal ion concentrations of 25, 50, 100, 150, 200 and 400 mg/L. A fixed quantity of WSH (0.5 g) was packed into boiling tubes, and the desired metal ion solution (25 mL) was added. The mixture was left in a water bath while maintaining a constant temperature of 28 °C for 1 h with constant shaking at 75 rpm. The biosorbent was then removed from the mixture by filtering through a Whatmann No. 32 filter paper. All experiments were performed in triplicates. The data obtained were then used to test the fitness of the sorption process to Langmuir, Freundlich and Temkin isotherms.

Effect of contact time on adsorption of Pb (II) ions

The adsorption of Pb (II) ions onto WSH was studied at various time intervals. A constant concentration of 100 mg/L was used at a constant temperature of 28 °C. A fixed quantity of the biosorbent (0.5 g) was weighed into various boiling tubes, and the metal ion solution (25 mL) was added into each boiling tube and its contents. The biosorbent was filtered at different time intervals of 10, 20, 30, 45, 60, 74, 90, 120, 150 and 180 min. All experiments were performed in triplicates. The data obtained were then used to determine the values of k_1 and k_2 in the Lagergren and Ho's pseudo-first order and pseudo-second order equations.

Thermodynamic studies

For the thermodynamics study, experiments were carried out at 35, 40, 50, 60 and 70 °C using initial metal ion concentration of 100 mg/L. Each experiment was carried out for 1 h with triplicate determinations.

Theories and calculations

The concentration of Pb (II) ions remaining in solution after all the adsorption experiments was determined using the atomic absorption spectrophotometer (Buck 200A Analytical Model) at 283.2 nm. The percentage removal of Pb (II) ions by the WSH was calculated using Equation (1), and the amount of metal ions (mg/g) adsorbed by the biosorbent was calculated by Equation (2)

$$\text{Biosorption } (\%) = \frac{C_o - C_e}{C_o} \times 100 \tag{1}$$

$$q_e \left(\frac{mg}{g}\right) = \frac{(C_o - C_e)V}{1,000W} \tag{2}$$

where C_o and C_e are the initial and equilibrium metal ion concentrations (mg/L) in aqueous solution, q_e is the amount of metal ion adsorbed on the biosorbent in (mg/g), V is the volume of metal ion solution used (mL) and W is the weight of the biosorbent used (g).

Adsorption isotherms

Langmuir, Freundlich and Temkin adsorption isotherms were applied to describe the relationship between the adsorbed amount of Pb (II) ions and its equilibrium concentration in solution.

Langmuir model. The Langmuir model suggests monolayer sorption on a homogeneous surface without interaction between the sorbed molecules. It relates the coverage of molecules on a solid surface to the concentration of a medium above the solid surface at a fixed temperature. It is represented in the linearized form as shown in Equation (3) (Langmuir 1918)

$$\frac{1}{q_e} = \frac{1}{q_m K_L}\left[\frac{1}{C_e}\right] + \frac{1}{q_m} \tag{3}$$

where q_e is the heavy metal adsorbed on the biosorbent (mg/g dry weight), C_e is the final concentration of metal (mg/L) in the solution, q_m is the maximum possible amount of metallic ion adsorbed per unit weight of adsorbent; K_L is the equilibrium constant related to the affinity of the binding sites for the metals. The adsorption constants (q_m and K_L) were obtained by plotting $1/q_e$ against $1/C_e$ (Figure 1), giving a straight line with a slope of ($1/K_L q_m$) and an intercept of ($1/q_m$).

Freundlich model. The Freundlich isotherm model (Freundlich 1907) assumes that the uptake of metal ions occurs on a heterogeneous surface by multilayer adsorption and that the amount of adsorbate adsorbed increases infinitely with an increase in concentration. This model is empirical in nature, and it further assumes that the stronger binding sites are occupied first and that the binding strength decreases with increasing degree of site occupation (Khambhaty *et al.* 2009; Akduman *et al.* 2013). It is represented in the linearized form as shown in Equation (4)

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \tag{4}$$

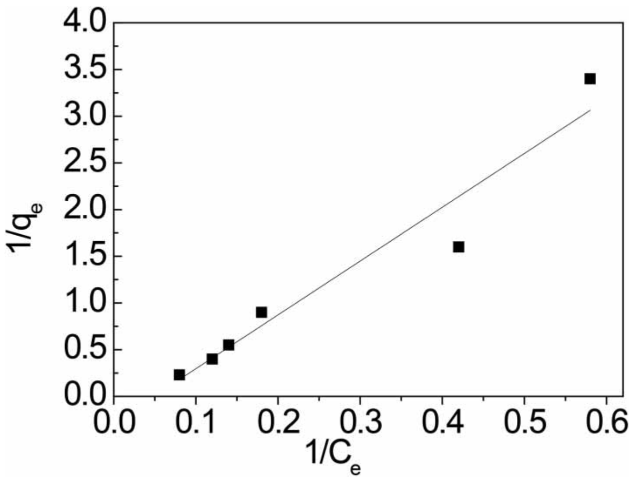

Figure 1 | Langmuir isotherm for sorption of Pb (II) ions onto WSH.

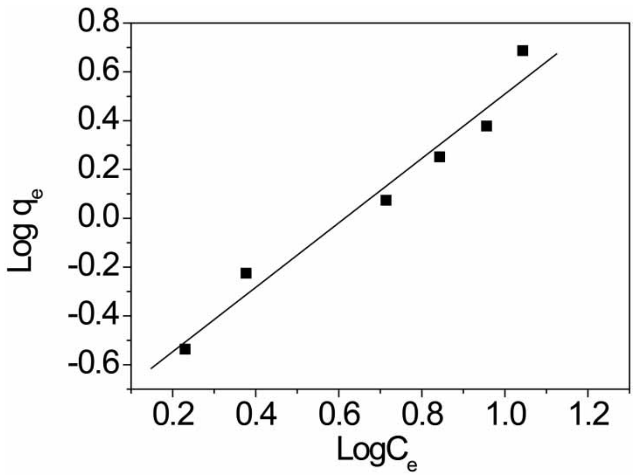

Figure 2 | Freundlich isotherm for sorption of Pb (II) ions onto WSH.

The adsorption constants 1/n and K_F were obtained by plotting log q_e against log C_e (Figure 2), from the slope and the intercept, respectively.

Temkin model. The Temkin isotherm can be expressed in the linearized form as:

$$q_e = B \ln K_T + B \ln C_e. \quad (5)$$

A plot of q_e versus *ln* C_e (Figure 3) enables the determination of the isotherm constants B and K_T from the slope and the intercept, respectively. K_T is the equilibrium binding constant corresponding to the maximum binding energy and the constant, B, is related to the heat of adsorption (Moafi *et al.* 2016).

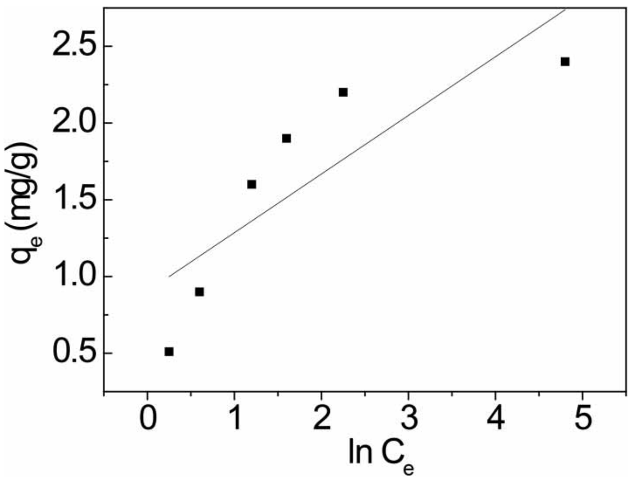

Figure 3 | Temkin isotherm for sorption of Pb (II) ions onto WSH.

Kinetics of adsorption

One of the major characteristics to define the efficiency of sorption is its kinetics. Different biosorbents conform to different models. Here in our investigations, the Lagergren first-order and pseudo-second order models were used to test the adsorption kinetics data with a view to investigating the mechanism of biosorption. The Lagergren rate equation is the most widely used model for the sorption of a solute from a liquid solution, and the first-order rate expression of Lagergren is given as Equation (6) (Ho & McKay 1999; Ayanda *et al.* 2013).

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (6)$$

where q_e and q_t (mg/g) are the amounts of Pb (II) ions adsorbed on the WSH at equilibrium and time *t*, and k_1 is the rate constant of the first-order kinetic. The slope and intercept of the plot of log $(q_e - q_t)$ versus *t* for WSH was used to determine the values of q_e and k_1 (Figure 4).

The pseudo-second order kinetic model in its integrated and linearized form has been used and is given as Equation (7)

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{t}{q_e} \quad (7)$$

where k_2 is the rate constant of second-order adsorption. The plot t/q_t versus *t* gave q_e and k_2 (Figure 5), which were determined from the slope and intercept of the plot, respectively.

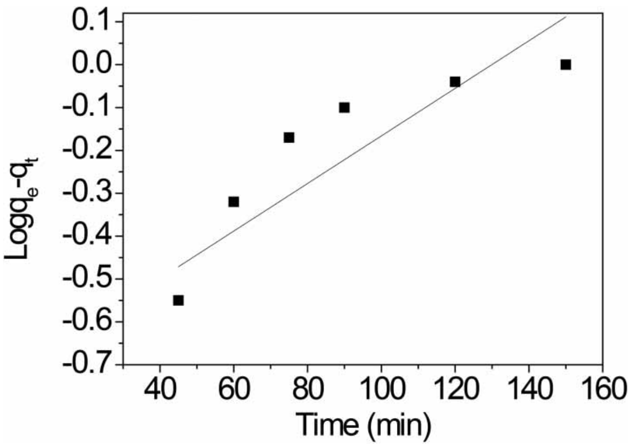

Figure 4 | Pseudo-first order graph for sorption of Pb (II) ions on WSH.

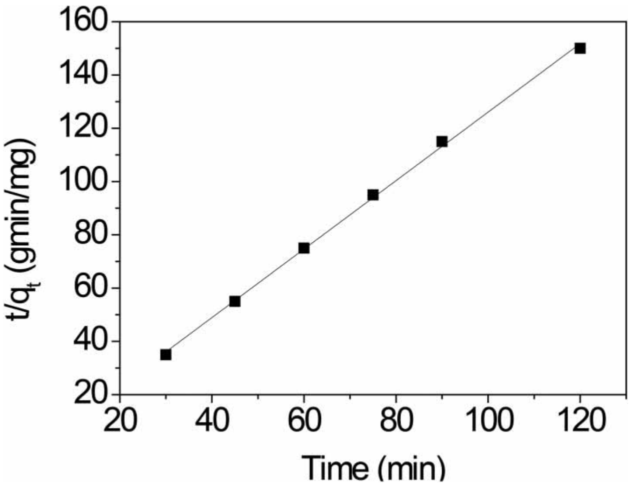

Figure 5 | Pseudo-second order graph for sorption of Pb (II) ions on WSH.

Thermodynamics study

In order to describe the thermodynamic behaviour of the biosorption of Pb (II) ions onto WSH, thermodynamics parameters including the change in free energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) were calculated from Equations (8)–(10).

$$K = C_a/C_e \tag{8}$$

$$\Delta G^0 = -RT \ln K \tag{9}$$

$$\ln K = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \tag{10}$$

where C_a is the amount (mg) of the adsorbate adsorbed per litre, C_e is the equilibrium concentration of solution in mg/L, T is the temperature in Kelvin (K), R is the ideal gas constant having a value of 8.314 J mol^{-1} K^{-1} and K is the thermodynamic equilibrium constant. According to these equations, the ΔH^0 and ΔS^0 can be calculated from the slope and intercept of the plot of ln K versus I/T (Figure 6), respectively (Fatoki *et al.* 2014).

RESULTS AND DISCUSSION

The FTIR study

FTIR was used to investigate the surface functional groups of WSH before and after biosorption. The details of the assignment of bands due to the functional groups present on the surface of the biomass before and after biosorption are given in Table 1. Different adsorption mechanisms including complexation, ion exchange, and electrostatic attraction may be involved in the biosorption process, and these processes depend on the functional groups on the surface of the biomass. In the present study, the broad peak around 3,388 cm^{-1} was assigned to the presence of -OH or -NH groups on the WSH surface, 1,038 cm^{-1} shows C-O groups, 1,639 cm^{-1} shows C = O, the peak at 2,911 cm^{-1} is due to C-H vibration of CH_3 groups, 3,159 cm^{-1} and 3,029 cm^{-1} show the vibration of the aromatics. O-H, C = O, C-O, C-H and N-H were identified as being involved in Pb (II) ions binding to the WSH surface due to the shift in the spectra band after adsorption.

The effect of pH on the adsorption of Pb (II) ions

One of the most important factors affecting biosorption of metal ions is the acidity of the solution. The acidity of the

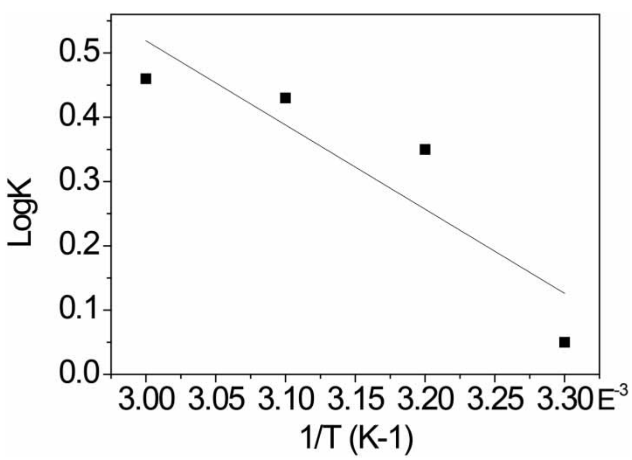

Figure 6 | Thermodynamic profile of sorption of Pb (II) ions onto WSH.

Table 1 | FTIR spectra characteristics of walnut shell before and after biosorption and the corresponding possible groups

WSH (cm^{-1})	WSH with Pb (II) (cm^{-1})	Vibration type
3,388	3,394	Carboxylic/OH
3,123	3,123	C-H stretch
3,070	3,068	Aromatics/C-H stretch
2,929	2,929	C-H saturated
1,639	1,615	Carboxylic/C=O
1,509	1,503	N-H stretch
1,450	1,421	C-H stretch
1,262	1,382	-C-O stretch
1,038	1,056	-C-O stretch
873	872	Phosphoryl groups
785	779	C-H out of plane

medium affects the competition between hydrogen ions and metal ions for the active sites on the biosorbent surface (Zhang *et al.* 2014). The solution pH affects the cell wall metal binding sites and the metal ion chemistry in water. The effect of pH on biosorption is shown in Figure 7. In the current study, the pH was varied from 1.0–8.0. The minimal adsorption capacity (54%) was at pH 1 and the trend increased progressively until it reached 98% at pH 4. It was observed that the adsorption capacity decreased progressively above pH 4. As revealed by the FTIR study, the WSH surface contains acidic functional groups. It is reasonable that at lower pH ($pH \leq 2.0$), the dissociation of the acidic functional groups like carboxylic acids on the surface of the adsorbent did not take place. However, when the pH increased, the acidic functional groups were deprotonated. The deprotonation of the acidic functional groups increased the negative charges on the adsorbent. This means that below pH 3 the overall surface charge on the WSH was less negative when compared with the surface charge on the WSH at higher pH. The increase in the number of negative charges on the WSH surface facilitated the adsorption of the metals ions but reduced on further increase of pH above 4 due to the hydrolysis of lead ions. These observations are consistent with previous studies on the biosorption of Pb (II) ions onto ground and NaOH-treated cereals (Low *et al.* 2000), *Moringa oleifera* bark (Reddy *et al.* 2010) and modified lignin hydrogel (Yao *et al.* 2014).

Effect of initial metal ion concentration on the adsorption of Pb (II) ions

The initial metal ion concentration plays an important role in the biosorption process. The biosorption characteristics of WSH, in the removal of Pb (II) ions, increased with increasing metal ion concentration (Figure 8). This implies that the removal of Pb (II) ions from solution by WSH at higher concentrations will most likely be favourable. Similar observations were reported by Kilic *et al.* (2008) and Lim *et al.* (2016). It is reasonable that the increase in the initial metal ion concentrations enables the mass transfer of Pb (II) ions between the aqueous and solid phases, and this facilitated a higher probability of collision between the

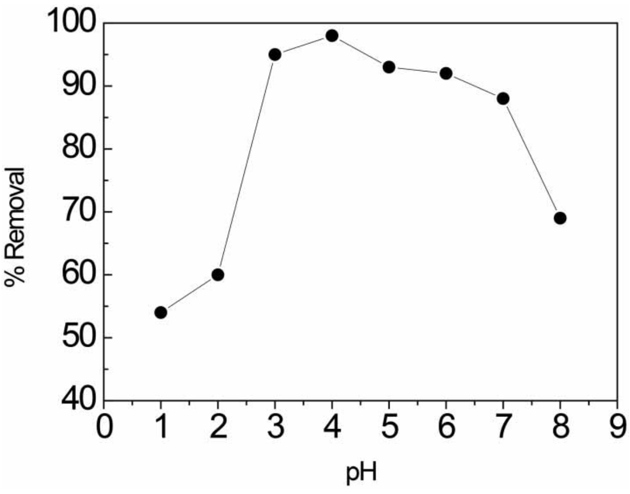

Figure 7 | Graph showing the effect of pH on the sorption of Pb (II) ions from aqueous solution using WSH. Initial Pb (II) ion concentration is 100 mg/L, 0.5 g dry weight biomass with 25 mL of Pb (II) ion solution.

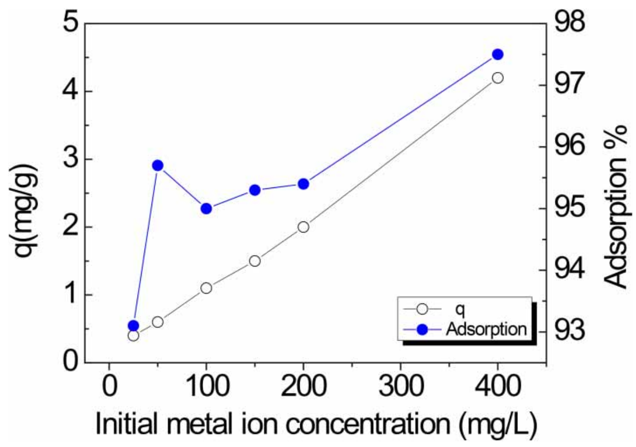

Figure 8 | Effect of initial metal ion concentration on the biosorption of Pb (II) ions from aqueous solution using WSH. 0.5 g dry weight biomass with 25 mL of Pb (II) solution at pH 4.0.

metal ions and adsorbent. An improved probability of collision between the metal ions and adsorbent led to higher metal adsorption.

Effect of contact time on the adsorption of Pb (II) ions

The time variation (Figure 9) for the adsorption of Pb (II) ions onto WSH showed that more than 80% of Pb (II) ions were adsorbed within the first 10 min, but the sorption continued up to 3 h. It was observed that the sorption process reached equilibrium after 60 min when 96% of Pb (II) ions have been adsorbed by the WSH biomass. The observed fast biosorption kinetics are consistent with the biosorption of metal involving non-energy mediated reactions, where metal removal from solution is due purely to physico-chemical interactions between the biomass and the metal solution. Similar observations have been reported for the biosorption of Pb from solution using rice husks (Abdel-Aty *et al.* 2013).

Effect of biosorbent dosage on the adsorption of Pb (II) ions

The effect of biosorbent dosage on the adsorption of Pb (II) ions is depicted in Figure 10. The trend revealed a progressive increase in the amount of Pb (II) ions adsorbed as the adsorbent dosage increased from 0.1 to 0.5 g. The percentage of Pb (II) ions removed increased from 81 to 96%. It is reasonable that increasing the biosorbent dose increased the surface area, thus providing an increase in the available active sites for adsorption. A similar trend was observed for Pb removal using *Moringa oleifera* (Reddy *et al.* 2010; Meneghel *et al.* 2014; Adhiambo *et al.* 2015).

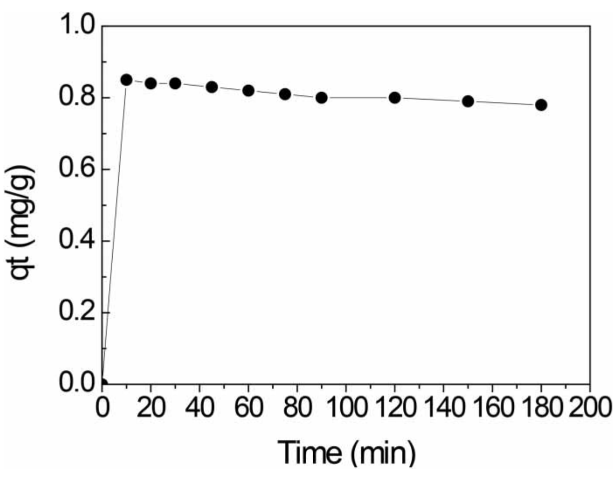

Figure 9 | Time dependent study of the biosorption of Pb (II) ions on WSH. Initial Pb (II) ions concentration is 100 mg/L, 0.5 g dry weight biomass with 25 mL of Pb (II) solution at pH 4.0.

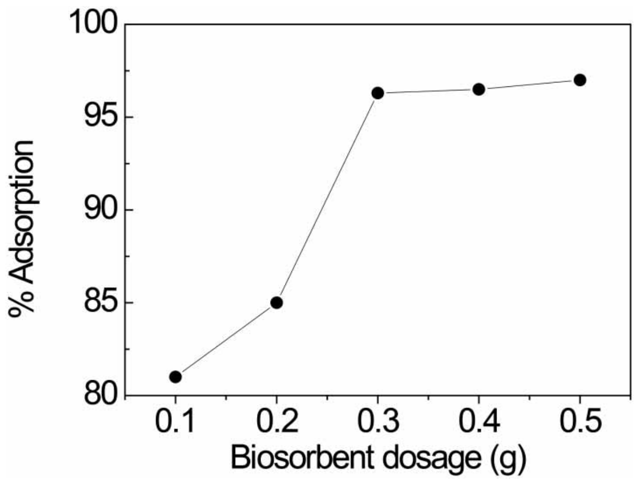

Figure 10 | Effect of adsorbent dose for the adsorption of Pb (II) ions onto WSH.

Effect of temperature on the adsorption of Pb (II) ions

The result obtained from varying temperature within the range 308–343 K showed progressive increase in metal uptake as the temperature increased (Figure 6). A similar increase in metal uptake with increasing temperature had been reported earlier (Liu *et al.* 2014). The increase in adsorption with increasing temperature indicated the endothermic nature of the adsorption process, which may be attributed to either the increase in the number of active surface sites available for sorption on the WSH or the decrease in the boundary layer thickness surrounding the WSH, thereby resulting in strong adsorptive forces between the active sites of the WSH and the Pb (II) ions.

Isotherm, kinetics and thermodynamics

The equilibrium data in Table 2 show the values of regression coefficients R^2 between the adsorbate and adsorbent systems for the Langmuir, Freundlich and Temkin models. The best description of the adsorption process of Pb (II) ions was observed in the Freundlich model, based on the regression coefficient $R^2 = 0.964$ compared with 0.957 and 0.719 for the Langmuir and Temkin isotherms, respectively. Possibly the adsorption process began with the initial monolayer coverage on the outer surface of the

Table 2 | Model parameters for the biosorption of Pb (II) ions on WSH

Freundlich model				Langmuir model				Temkin model			
K_F	R^2	n	SD	K_L	R^2	q_m	S.D	K_T	R^2	B	S.D
0.155	0.964	0.758	0.093	0.059	0.957	3.033	0.281	10.343	0.719	0.381	0.443

Table 3 | Comparison of pseudo-first and second-order biosorption of Pb (II) ions on WSH

Pseudo-first order				Pseudo-second order			
k_1	R^2	q_e	S.D	K_2	R^2	q_e	S.D
−0.013	0.782	0.230	0.1133	−0.680	0.999	0.795	0.4431

adsorbent, after which the sorption progressed to the multilayer dimensions.

The pseudo-first order kinetic model provided a poor description of the data for the biosorption of Pb (II) ions, as is evident from their correlation coefficient (R^2) values in Table 3. In previous reports where the pseudo-first order kinetic model disagrees with experimental values, this discrepancy was attributed to a time lag, which probably caused the presence of the boundary layer or external resistance controlling the beginning of the sorption process. The pseudo-second order kinetic model is more likely to predict the kinetic behaviour of the biosorption with chemical sorption being the rate-controlling step (Unlu & Ersoz 2006; Abbas *et al.* 2012). The linear plot of t/q_t versus t for the pseudo-second order model for the biosorption of Pb (II) ions onto WSH is presented in Figure 5. It is clear from Table 3 that the R^2 value for the pseudo-second order model is high. This result suggests that the biosorption of Pb (II) ions onto WSH follows the pseudo-second order kinetic model well. Several authors that studied the adsorption of divalent metals on heterogeneous sorbents had reported that most metal sorption kinetics follow the pseudo-second order mechanism (Suguna & Kumar 2013; Amer *et al.* 2015).

The negative ΔG^0 values indicate thermodynamic feasibility and spontaneity of the biosorption process. The increase in the magnitude of ΔG^0 values for Pb (II) biosorption with an increase in temperature shows an increase in its feasibility. The slight decrease in the value of ΔG^0 in the biosorption of Pb (II) ions by WSH at 343 K may be due to gradual damage of active binding sites in the biomass (Hannachi 2012) or the tendency to desorb metal ions from the interface to the solution (Saltali *et al.* 2007). The ΔH^0 value for Pb (II) ions was calculated to be 25.35 kJ mol^{-1},

Table 4 | Comparison of the maximum lead adsorption capacities of some adsorbents with WSH

Adsorbents	Adsorption capacity (mg/g)	pH	Reference
Caulerpa lentlifera	28.72	5–6	Pavasant *et al.* (2006)
Modified peanut sawdust	29.1	4	Li *et al.* (2007)
Grape stalks	49.7	5.5	Martinez *et al.* (2006)
Barley straw	15.2	5.5	Conrad *et al.* (2007)
Coir	48.8	4.5	Quek *et al.* (1998)
Syzygium cumini L.	32.47	6.0	King *et al.* (2007)
C. inophyllum	34.51	4.0	Lawal *et al.* (2010)
Tea leaves	2.1	–	Ahluwalia *et al.* (2005)
Rice husk	4.0	5.5	Conrad *et al.* (2007)
Olive pomace	7.0	5.0	Pagnanelli *et al.* (2003)
Walnut seed husk	3.0	4.0	This study

indicating that the binding of Pb (II) ions onto WSH was endothermic. The enthalpy change agrees with previous works in the literature (Tewari *et al.* 2005; Senthilkumar *et al.* 2007). The magnitude of ΔH^0 value gives an indication of the type of adsorption, which can either be physical or chemical. The heat of adsorption, ranging from 2.1–20.9 kJ mol^{-1} is said to be physical adsorption, and the activation energy for chemical adsorption is of the same magnitude as the heat of chemical reactions, 20.9–418.4 kJ mol^{-1} (Yalçin 2014). The ΔH^0 value obtained in the biosorption experiment indicates that the binding of Pb (II) ions to the WSH is by chemical adsorption. Moreover, the ΔS^0 was observed to be positive (86.1 kJ mol^{-1} K^{-1}), indicating the increasing randomness at the solid/liquid interface during biosorption (Fat'hi *et al.* 2014). A comparison of the maximum adsorption capacities for Pb (II) ions adsorption to different adsorbents is presented in Table 4.

CONCLUSION

The study concerns the use of WSH for the removal of a heavy metal, Pb, from the environment. The results obtained indicate that the pH, contact time, temperature and initial concentrations affect the uptake of the metal ions by the biosorbent. It was observed that the adsorption equilibrium data fitted best into the Freundlich model compared with the Langmuir and Temkin isotherms. The pseudo-second order kinetic model agrees with the biosorption of Pb (II) onto WSH. The negative value of ΔG^0 indicates the spontaneity of the biosorption process and the positive values of ΔH^0 and ΔS^0 also showed the endothermic nature and irreversibility of Pb (II) ion biosorption. Results obtained from this study showed that WSH could be useful in removing Pb (II) ions from aqueous solution. The justifications for our report are as follows. (1) WSH is a waste material that constitutes an environmental nuisance in areas where the seed is processed for its oil, hence finding a technical application for WSH becomes reasonable. (2) Since it is a waste material, it is very cheap. (3) Like most other biomaterials, it is an eco-friendly and non-toxic material for the removal of Pb from aqueous solution. (4) Unlike other biomaterials such as rice husk, which can be processed into animal feed, or sawdust, which can be used as a building material after processing, WSH has no other competing utilization to the best of our knowledge. Therefore the strength of this study is that a waste material, WSH, can be used to address an important environmental problem.

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