Application of Raw and Alkaline-modified Coconut Shaft as a Biosorbent for Pb^{2+} Removal

Edwin Andrew Ofudje,[a,*] Olubunmi Kolawole Akiode,[b] Gabriel Opeoluwa Oladipo,[c] Adebusayo Emmanuel Adedapo,[d] Lateefah Olanike Adebayo,[e] and Ayodeji Olushola Awotula[f]

The sorption capacity of untreated and alkaline-treated coconut shaft biosorbents for the removal of Pb^{2+} from aqueous solution was investigated in batch experiments. Effects of contact time, biosorbent dose, initial metal concentration, and pH on the sorption capacity were investigated. Optimum Pb^{2+} removal of 17.6 and 22.1 mg/g by untreated and alkaline-treated biomass was achieved at an initial metal concentration of 150 mg/L, a biomass dose of 0.7 g, a contact time of 80 min, and a pH of 4.0. The sorption data fitted well into the Langmuir isotherm, while kinetic modeling of the data from untreated biomass indicated conformity with the Lagergren pseudo-first-order model, whereas data from the treated biomass fit well with the Elovich model. FT-IR results gave indications of possible functional groups on the cell walls of the coconut shaft, including alcohols, amines, carboxylic acids, ester, and ethers. Thus, alkaline treatment of the coconut shafts enhanced the biosorption ability of Pb^{2+} onto the coconut shaft biomass.

Contact information: a: Department of Chemical Sciences, McPherson University, Seriki-Sotayo, Ogun State, Nigeria; b: Institute for Human Resources Development, Federal University of Agriculture, Abeokuta, Ogun State, Nigeria; c: Department of Science Laboratory Technology, D.S. Adegbenro ICT Polytechnic, Ogun State, Nigeria; d: Department of Chemistry, College of Science And Technology, Covenant University, Ota, Ogun State, Nigeria; e: Department of Chemical Sciences, Crescent University, Abeokuta, Ogun State, Nigeria; f: Department of Biological Sciences, McPherson University, Seriki-Sotayo, Ogun State, Nigeria;*Corresponding author: ofudjeandrew4real@yahoo.com

INTRODUCTION

Lead is one of several major toxic pollutants often released into the environment by industries and human activities. Some of the causes of environmental contamination include industrial uses such as lead-acid batteries, tire wears, lead gasoline, pipes, paints, metal recycling, and foundry lubricating oil and grease (Gilbert and Weiss 2006; Manay *et al*. 2008; Rossi 2008). One of the major sources of lead exposure in adults is occupational exposure (Needleman 2004). People working in factories that produce lead-containing products such as radiation shields, ammunition, certain types of surgical equipment, fetal monitors, circuit boards, jet engines, ceramic glazes, and plumbing products can be exposed to lead contamination (Patrick 2006). Exposure to lead poisoning could result in a variety of symptoms depending on the individual and the duration of lead exposure (Karri *et al*. 2008).Symptoms of lead poisoning in humans include insomnia, delirium, hallucinations, memory loss, kidney failure, weakness, diarrhea, constipation, muscle pains, malaise, fatigue, decreased libido, unusual tastes in the mouth, and personality changes (Patrick 2006; Pearce 2007; Karri *et al*. 2008). Chronic effects of lead poisoning can lead to multiple system defects but are generally associated with neurological, neuromuscular, and gastrointestinal damage (Pearce 2007; Adeogun *et al*. 2013). The

permissible limit of lead (II) ions as stipulated by EPA (2007) and WHO (2007) are 0.015 mg/L and 0.01 mg/L in drinking water, respectively.

Various techniques have been used to eliminate heavy metals in polluted environments. However, most of these methods are expensive and only partially remove pollutants while producing excess sludge (Pehlivan and Altun 2007;Odoemelam*et al.* 2011). Thus, there is a need for a more plausible and unconventional means of removing contaminated heavy metal ions from polluted environments. Biosorption has been anticipated as a possible substitute for conservative methods for the cost-effective removal of toxic wastes through the use of bacteria, fungi, and algae, which have shown potential to bind metal ions (Pehlivan and Altun 2007;Odoemelam *et al.* 2011). Some of the recently used biosorbents for pollutant removal are: corncob (Adeogun *et al.* 2011), palm flower (Elangovan *et al.* 2007), maize husks (Adeogun *et al.* 2013), *Trichoderma* (Padma and Bajpai 2004), *Parmelina tiliacea* (Uluozlu *et al.* 2008*)*,sawdust and peanut(Li *et al.* 2006), rice husk (Wong *et al.* 2003), neem bark and sawdust (Naiya *et al.* 2008), activated alumina (Naiya *et al.* 2009a), clarified sludge (Naiya *et al.*2009b),rice husk ash (Naiya *et al.* 2009c),walnuts, hazelnuts, and almond shells, (Pehlivan and Altun 2007), baobab shells (Chigondo *et al.* 2013), maize cobs (Nale *et al.* 2012), and oyster snail and periwinkle shells (Odoemelam *et al.* 2011). These biosorbents contain functional groups such as hydroxyl, carbonyl, carboxylic acid, and amine groups, which serve as adsorption sites for metal ions in solution (Naiya *et al.*2008; 2009a,b,c).

The search for food production and the need to boost the Nigerian economy is on the rise. This trend has led to the generation of various agricultural wastes, such as coconut shaft. Coconut is widely cultivated in Nigeria, and the shafts are often designated as environmental pollutants once the seed has been removed. This work evaluates the potential of both raw and alkaline-modified coconut shafts as effective biosorbents in the elimination of Pb(II) ions from aqueous solution. The effects of initial metal concentrations, time of contact, biomass dosage, and solution pH were evaluated in batch experiments. Adsorption isotherms and kinetic modeling were performed as well.

EXPERIMENTAL

Preparation of the Biosorbent and Adsorbate

Coconut pods were obtained from the village of Ajebo in Obafemi Owode, Local Government Area of Ogun State, Nigeria. The shaft was removed from the pod and washed with distilled water, sun-dried, pulverized, and sieved to obtain the desired particle size of 150 µm. Alkaline-modification was done by dispersing about 200 g of the biosorbent in 0.2M KOH for 12 h. It was then filtered, washed with distilled water, and oven dried at 80 °C for 2 h. The stock solution of Pb^{2+} was prepared by dissolving 1.6 g of $Pb(NO_3)_2$ (Merck, Germany) in 1000 mL of distilled-deionized water.

Characterization of the Coconut Shaft

The physical and chemical properties of raw and treated coconut shafts both before and after treatment were evaluated following the adsorption of Pb^{2+}. The pH values of the two biomasses were determined by adding each biomass to distilled-deionized water, and the pH of the solution was then recorded. A G. Vario EL analyzer (Germany) was used to determine the percentage abundance of C, H, N, and S. The element O was estimated by mass difference, *i.e.*, 100%- (% abundance of C+H+N+S). A Quantachrome NOVA 2200C

(USA) surface area and pore size analyzer was used in the analysis of surface area, pore volume, and pore size. Fourier Transform Infrared Spectroscopy (Fourier Transform Infrared Spectrophotometer, FT-IR-8300, Shimadzu) was used to identify the various functional groups present in the biomass. Pellets were formed using 0.1 g of coconut shaft which was mixed with 0.3 g of KBr and pressed at 6 to 8 bar pressure.

Determination of Point of Zero Charge (pH$_{ZPC}$)

The point of zero charge (pH$_{ZPC}$) was evaluated by the solid addition method (Mall *et al*. 2006). Briefly, a 0.1M standard solution of the metal ion was prepared, and this was adjusted in series of 250 mL stopped glass flask from 1 to 12 by either the addition of 0.1M HCl or 0.1M NaOH. The initial pH (pH$_o$) of the solutions before the addition of the coconut shaft was noted, and 0.1 g of the coconut shaft was added to the flask and shaken for 24 hours. The final pH (pH$_f$) was then measured. Thus, the difference between the initial and final pH values (*i.e.* ΔpH = pH$_o$ − pH$_f$) was plotted against the initial pH and the intersection of the plots gave the zero point charge (pH$_{ZPC}$).

Batch Experiments

The method used by Adeogun *et al.* (2013) was followed. Several concentrations of lead (ranging from 20 to 150 mg/L) containing different masses (between 0.1to 1.5 g) of the biosorbent were briefly placed in 100 mL Erlenmeyer flasks with a working capacity of 20 mL in each flask. Solutions used for the sorption experiments were placed in a rotator thermostatic shaker at a speed of 150 rpm and at ambient temperature. After 2 h of equilibrium contact time, the mixture was filtered using Whatman No. 1 filter paper, and the resulting filtrate was analyzed for Pb^{2+} contents using an Atomic Absorption Spectrophotometer (Unicam model 929). The pH of the solution was adjusted within the range of 1 to 7 by means of 0.1M HNO$_3$ or 0.1M NaOH. All experiments were carried out in triplicate, and the mean values were used to determine the results. The amount adsorbed, q$_e$, was evaluated using the equation,

$$q_e \;=\; \frac{C_o - C_e}{W} V \tag{1}$$

Where q_e is the amount adsorbed in mg/g, C_o and C_e are the initial and equilibrium concentrations of Pb^{2+} in mg/L, respectively, *V* is the volume in L, and *W* is the weight of the CS used in g. The sorption percentage was evaluated as follows:

$$Sorption\ percentage = \frac{C_o - C_e}{C_o} \times 100 \tag{2}$$

RESULTS AND DISCUSSION

Characterization of Coconut Shaft

The chemical and physical properties of untreated and treated coconut shaft were determined, and the results are presented in Table 1. The results obtained from surface area and pore volume analysis indicated the high surface area and porous nature of CS. Elemental analysis depicted the composition of untreated CS as C (42.3%), H (4.8%), N (1.3%), S (2.4%), and O (49.2%). The composition of treated CS was C (49.6%), H (5.3%), N (0.8%), S (1.9%), and O (42.4%).

Table 1. Chemical and Physical Composition of Coconut Shaft

Elemental analysis of coconut shaft before and after treatment					
Element/Biomass	C	H	N	S	O
UTCS	42.3	4.8	1.3	2.4	49.2
ATCS	49.6	5.3	0.8	1.9	42.4
Surface area and pore size analysis of coconut shaft before and after treatment					
	Surface Area BET (m^2/g)		Pore Volume (cm^3/g)		Pore Diameter (A°)
UTCS	30.8		0.42		20.6
ATCS	39.3		0.75		32.4

The FT-IR spectra of coconut shaft before and after adsorption displayed a number of absorption bands which imply the presence of various functional groups in the biomass as shown in Fig. 1, and the values are interpreted in Table 2. It was observed from the spectra of coconut shaft before and after biosorption of Pb^{2+} that there were slight changes in the absorption bands, which indicated that there was a metal binding process taking place on the surface of the biomass. The FT-IR results gave an indication of the possible functional groups located on the cell walls of the CS. These groups presumably influence the biosorption of Pb^{2+} and are likely the mechanism of adsorption, which largely depends on the functional groups present such as alcohols, amines, carboxylic acids, esters, or ether. Bonds such as –OH, –NH, –C=O, –C=C–, and –SO_3 have been reported as important adsorption sites that enhance the removal of contaminants from aqueous solution (Ertugay and Bayham 2008; Gupta and Rastogi 2008; Qaiser *et al.* 2009).

Table 2. FT-IR Characterization of Coconut Shaft

| Wave number before adsorption (cm^{-1})	Wave number before adsorption (cm^{-1})	Functional groups
3460.41	3483.56	-OH and –NH bands in alcohols and amines.
2974.33	2962.76	-C-H band in aliphatic alkanes
2874.03	2848.96	-CH_2 symmetric stretching
2515.26	2511.40	S-H stretching
1799.65	1797.72	-C=O stretching in carboxylic acid, esters, or aldehydes
-	1620.26	-C=C band in unsaturated compounds
1261.49	1261.49	-SO_3stretching
1099.46	1105.26	-C-O stretching in alcohols, ether, or carboxylic acids.
1030.02	1041.60	-C-N stretching
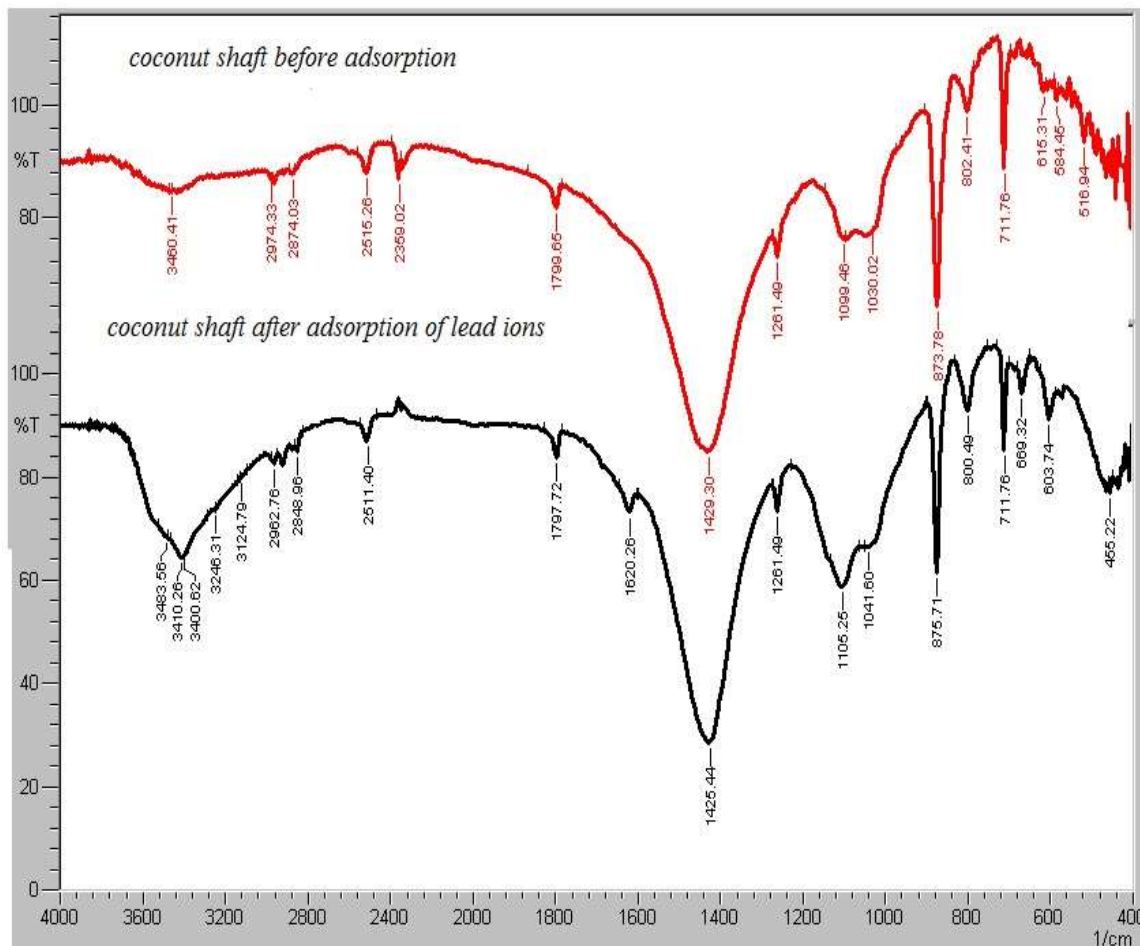
Fig. 1. FT-IR spectra of coconut shaft before and after adsorption of Pb^{2+}

The Point of Zero Charge (pH$_{ZPC}$)

The point of Zero Charge (pH$_{ZPC}$) is the point that determines the pH at which the adsorbent surface has net electrical neutrality in which neither the acicidic nor basic functional groups no longer contribute to the solution pH (Yu *et al.* 2011). Above the pH$_{ZPC}$, the surface charge of adsorbent is negative and below it, the surface charge is positive. The point of interception of ΔpH against pH showed that the pH$_{ZPC}$ of coconut shaft occurred at 1.8, as indicated in Fig. 2. This value is, however, lower than the solution pH of 4.0. Thus the negative charge density on the surface of coconut shaft increased, which enhances the adsorption of cationic metal ions. Similar findings had been reported in literature (Janos *et al.* 2003; Yu *et al.* 2011; Thilagavathy and Santhi 2014).
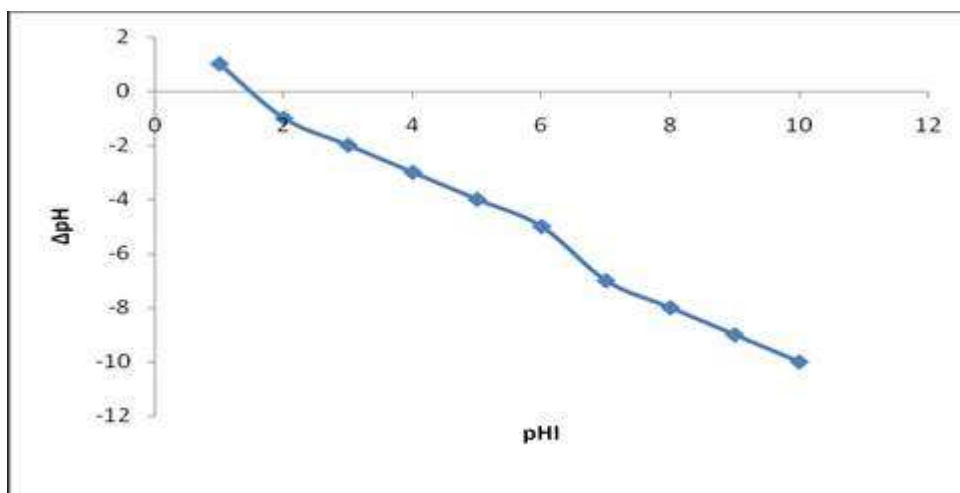
Fig. 2. Zeta Point of Charge of coconut shaft

Effect of Contact Time and Initial Metal Concentrations

Six different contact times were investigated for the removal of Pb^{2+} by UTCS and ATCS at different initial concentrations of Pb^{2+} at an ambient temperature. Figures 3a and 3b show the plots of Pb^{2+} adsorbed for treated and untreated coconut shafts with respect to time. The effects of the initial concentration of Pb^{2+} on the sorption capacity of the biosorbents were investigated by using varying initial Pb^{2+} concentrations from 25 to 150 mg/L, while keeping other parameters constant. It can be inferred from the plots that the amount of Pb^{2+} adsorbed increased from 3.2 to 9.1 mg/g and from 9.9 to 17.6 mg/g when the initial metal concentration was increased from 25 to 150 mg/L and as the contact time was adjusted from 20 to 120 minutes when untreated coconut shaft was used. On the other hand, when alkaline modified biomass was used, the amount of Pb^{2+} adsorbed was found to increase from 5.2 to 10.1 mg/g and from 11.4 to 22.1 mg/g after increasing the initial Pb^{2+} concentration from 25 to 150 mg/L and the contact time from 20 to 120 minutes, respectively.

Alkaline treatment of biological biomasses has been found to enhance their biosorption efficiencies as a result of the hydrolysis of the reactions (Chen and Yang 2005; Bulgariu *et al*. 2011; Bulgariu and Bulgariu 2014). This hydrolysis reaction can result in the formation of more carboxylic and hydroxyl groups, which enhances the metal-binding capacities of the biological molecules (Gupta and Rastogi 2008). According to Bulgariu and Bulgariu (2014), alkaline treatment of biomass results in hydrolysis processes that transform the inactive superficial groups into available functional groups for interaction with heavy metals and thus enhances the biosorption efficiency. Thus, this change of superficial functional groups as a result of the chemical treatment leads to an increase of the adsorption capacity of treated CS.

The results also showed that a contact time of 80 min was sufficient to attain equilibrium, and the sorption capacity did not change significantly with further increase in the contact times above 80 min. The reaction was, however, very fast during the initial stage of the biosorption process and slowed down as the reaction approached equilibrium. This observation is in agreement with earlier works (Ertugay and Bayham 2008; Adeogun *et al*. 2011; Ofudje *et al*. 2013).
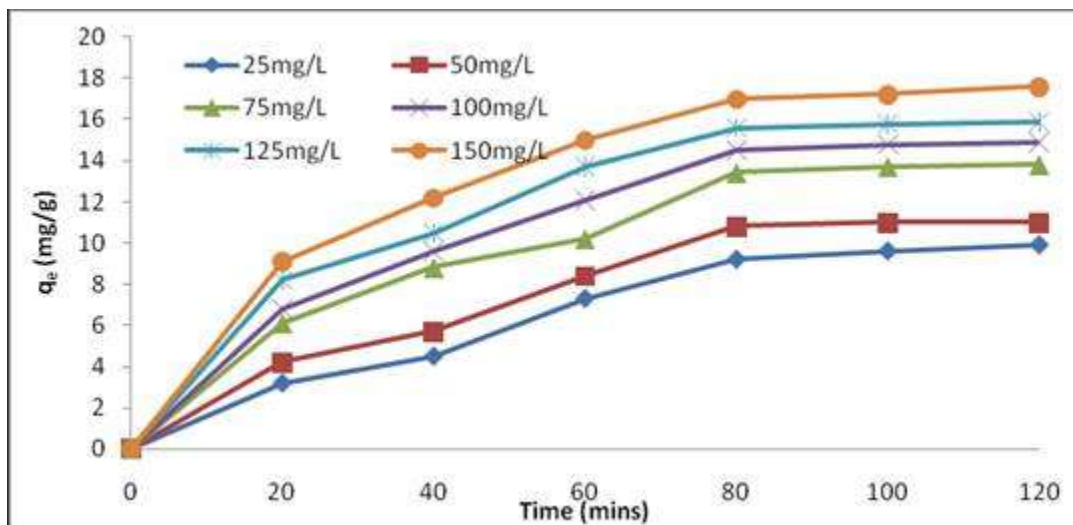
Fig. 3a. Effect of contact time on the biosorption of Pb^{2+} by raw coconut shaft at different initial Pb^{2+}concentrations (25 to 150 mg/L), pH of 4.0,temperature of 25 °C, biosorbent size of 150 μm and biomass dose of 0.7 g
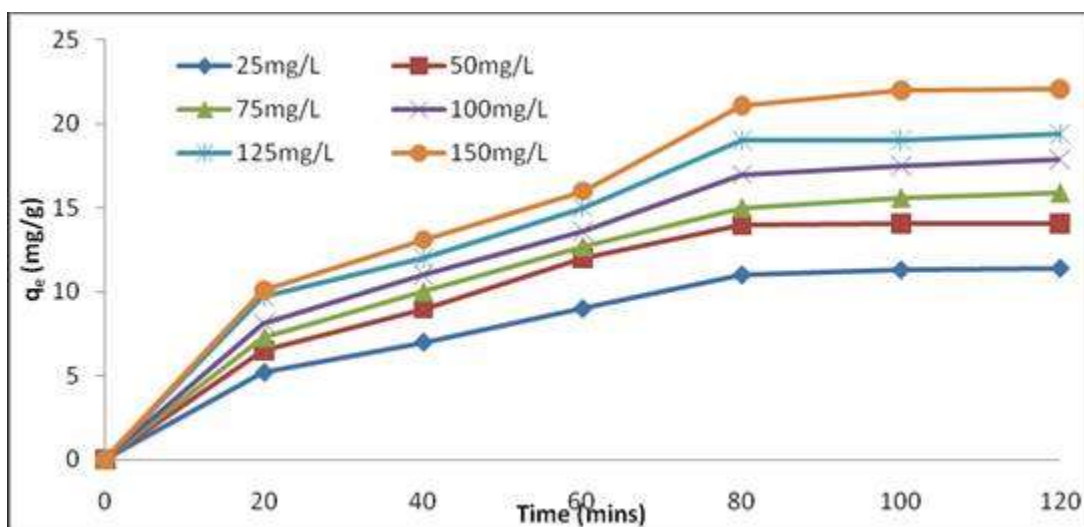

Fig. 3b. Effect of contact time on the biosorption of Pb^{2+} by alkaline-treated coconut shaft at different initial Pb^{2+} concentrations (25 to150 mg/L), pH of 4.0,temperature of 25 °C, biosorbent size of 150 μm,and biomass dose of 0.7 g

Effect of Biomass Dose

To examine the effect of biomass dose on the sorption of Pb^{2+}, varying biomass doses from 0.1 to 1.5 g were used at initial concentrations of 150 mg/L, contact times of 80 min, and pH 4.0. Results are presented in Fig. 4. The amount of Pb^{2+} removed increased with an increase in the biomass dose; however, no appreciable adsorption was observed at a dose higher than 0.7 g. This could be due to the formation of clusters of Pb^{2+} on the surface on the surface of the active sites of the biomass that subsequently decrease the surface area of the biosorbent. Abdel-Ghani *et al*. (2007) observed that with certain doses of adsorbent, maximum adsorption is attained where the amount of adsorbate ions bond to the adsorbent and the amount of free ions remains constant, even after further additions of

adsorbent. Optimum yields of 78.1% and 85.6% were achieved by untreated and alkaline-treated coconut shaft, respectively.
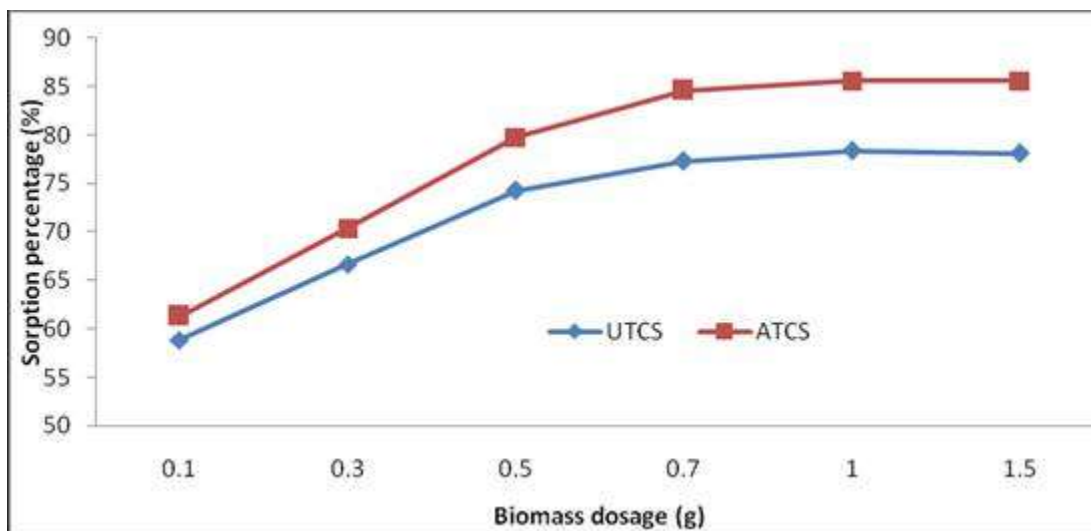

Fig. 4. Sorption percentage against biomass dosage for the biosorption of Pb^{2+} by raw and alkaline-treated coconut shafts at an initial Pb^{2+} concentration of 150 mg/L, contact time of 80 min, pH 4.0, temperature of 25 °C, and biosorbent size of 150 μm

Effect of Solution pH

The uptake of Pb^{2+} by untreated and chemically-treated coconut shafts was studied in various aqueous solutions with pH of 1, 3, 4, 6, and 8, while other parameters were kept constant. Figure 5 shows the plots of the sorption percentage against the pH of the solution. It was observed that maximum uptake of Pb^{2+} by both biomasses was attained in an acidic medium. When untreated coconut shaft was used, the sorption percentage increased from 45.4% to 68.4% when the solution pH was raised from 1.0 to 4.0 and then decreased to 49.3% upon adjusting the pH to 8.0. With treated biosorbent, the sorption percentage increased from 56.3 to 75.6% when the solution pH was increased from 1.0 to 4.0 and then decreased to 50.6% when the pH was adjusted to 8.0. The solubility of adsorbate and the functional groups of the biosorbent cell walls are greatly affected by the solution pH. The FT-IR spectra of coconut shafts indicates the participation of functional groups such as –NH_2, –C=O, and –OH. These functional groups are positively charged when protonated at low pH and negatively charged at higher pH. Thus, deprotonation enhanced the sorption capacity of the biosorbent. This implies that at low pH, the high positive charge density of the biomass due to protons on the surface sites intensively decreased the adsorption of Pb(II) ions as a result of the competition for adsorption sites between protons and Pb(II) ions. However, with an increase in pH, electrostatic repulsion decreases as a result of the reduction in positive charge density on the adsorption sites of the biomass, which enhances the adsorption of lead ions (Farajzadeh and Monji, 2003; Naiya *et al*. 2008). The formation of lead hydroxide at a pH of 7.0 and above resulted in a decrease in the sorption capacity of the biosorbents.
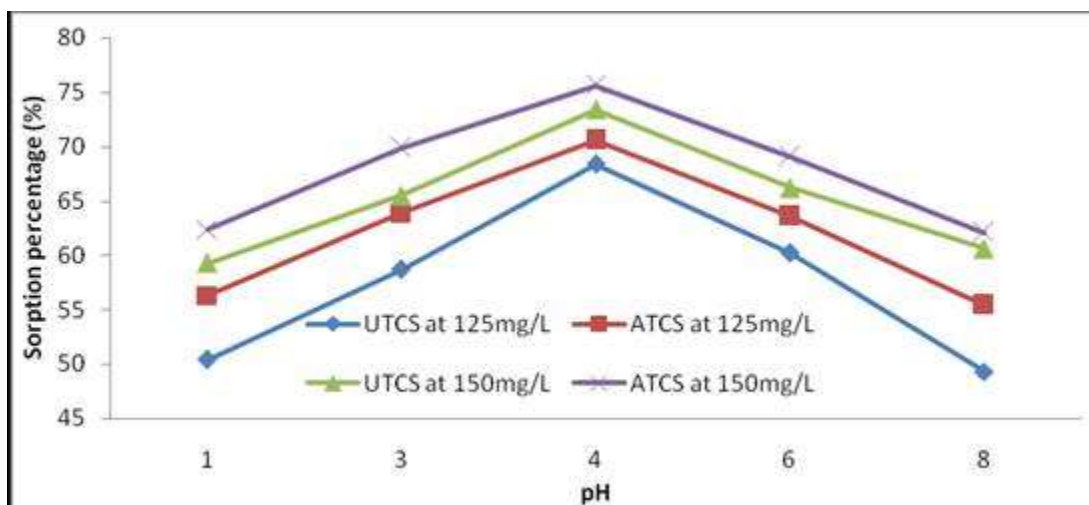
Fig. 5. Sorption percentage versus the pH for the biosorption of Pb^{2+} by raw and alkaline-treated coconut shaft at initial Pb^{2+} concentration of 150 mg/L, contact time of 80 min, biomass dose of 0.7 g, temperature of 25 °C, and biosorbent size of 150 µm

Isothermal Studies

The adsorption data for the sorption of Pb^{2+} by untreated and alkaline-treated coconut shafts at different initial metal concentrations were evaluated using Langmuir and Freundlich Isotherms. The linear form of the Langmuir Isotherm is given as,

$$\frac{C_e}{q_e} = \frac{1}{bQ_o} + \frac{C_e}{Q_o} \tag{3}$$

where Q_o represents the maximum sorption capacity (mg/g) and b is an affinity parameter (dm^3/mg) related to the energy of adsorption (Adeogun *et al.* 2011; Lin *et al.* 2014). Weber and Chakraborti (1974) defined the most important character of the Langmuir isotherms which can be expressed in terms of a dimensionless factor, R_L, as:

$$R_L = \frac{1}{1 + bC_0} \tag{4}$$

The Freundlich model proposes a monolayer sorption with heterogeneous energy distribution of active sites in which there is interaction between adsorbed molecules. The linear form is given as:

$$Inq_e = InK_F + \frac{1}{n}InC_e \tag{5}$$

where 'K_F' and 'n' are the adsorption capacity (mg/g)(1/mg)$^{1/n}$ and adsorption intensity (dm^3/g)^n(Sengil *et al.* 2009; Niu *et a*l. 2014). The greater the value of *n*, the greater the bonding onto the surface of the biosorbent, wherein n=1 indicates linear adsorption. Figure 6 shows the plots of C_e/q_e versus C_e from the Langmuir isotherm. The physical parameters obtained from the slopes and intercepts are presented in Table 3. Figure 7 shows the plots of Inq_e versus InC_e from the Freundlich isotherm, and the physical parameters obtained from the slopes and the intercepts are presented in Table 3 as well. The values of the correlation coefficients (R^2) for both the Langmuir and Freundlich Isotherms were high

enough, suggesting that both isotherms could be applied in the study of the adsorption data. However, a closer look at the values of the correlation coefficients revealed that the adsorption data of Pb^{2+} fitted well with the Langmuir isotherm. The values for adsorption intensity (R_L) were found to be between 0 and 1; this suggests that the adsorption process is favourable.

Comparing the maximum adsorption capacity of CS (Q_{max}) before alkaline treatment and after treatment showed an increased from 8.5 to 17.6 mg/g and 10.2 to 22.1 mg/g for UTCS and ATCS, respectively, as presented in Table 2.

Table 3. Langmuir and Freundlich Model Parameters for the Adsorption of Pb^{2+} at 25 °C

Biomass	C_o	Q_{max}	Langmuir Isotherm			Freundlich Isotherm		
			b	R^2	R_L	N	K_F	R^2
UTCS	70	8.5	0.12	0.990	0.32	5.30	1.40	0.945
ATCS	70	10.2	0.33	0.992	0.46	6.18	3.35	0.968
UTCS	125	13.6	0.53	0.985	0.63	7.12	5.22	0.976
ATCS	125	14.9	0.72	0.987	0.82	9.73	7.20	0.986
UTCS	150	17.6	1.47	0.974	1.25	8.52	6.96	0.979
ATCS	150	22.1	2.42	0.995	1.83	10.24	9.85	0.997

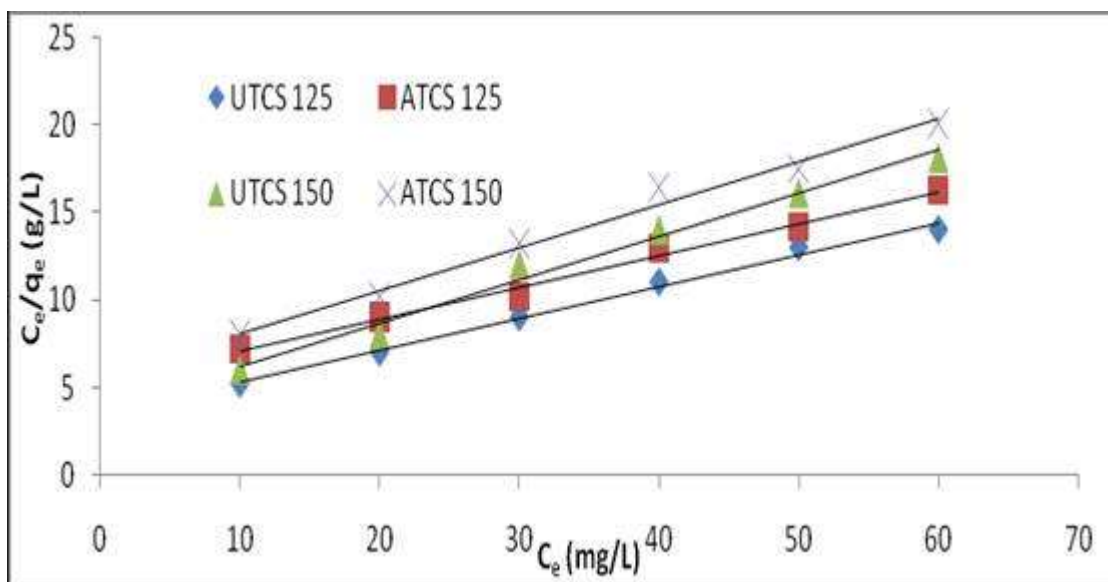Note: C_0 = mg/L, Q_{max} = mg/g, b = L/mg, K_F = (mg/g)(1/mg)$^{1/n}$

Fig. 6. Langmuir adsorption isotherms of Pb^{2+} for untreated and alkaline-treated coconut shaftsat pH = 4, adsorbent dosage = 0.7 g, contact time = 80 min, initial metal concentration = 125 mg/L and 150 mg/L
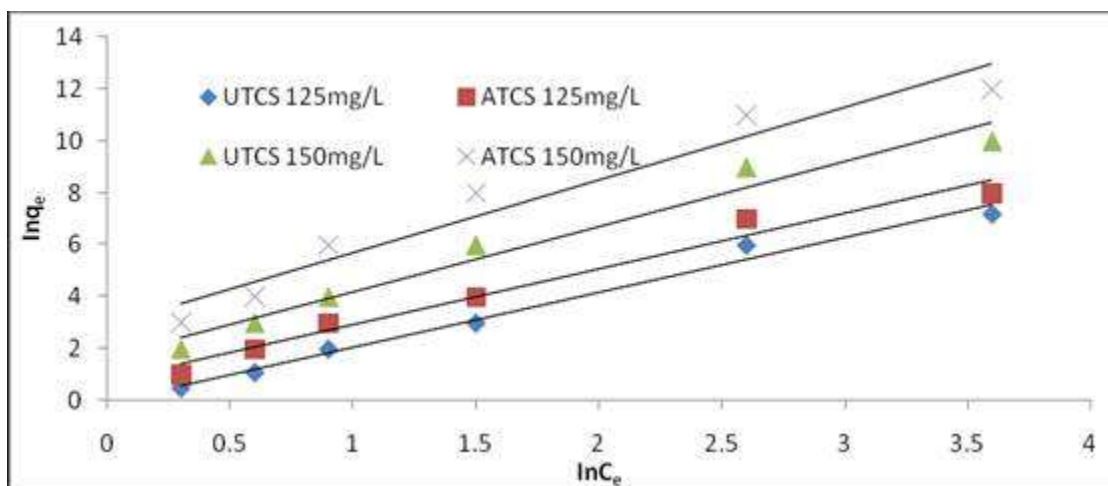
Fig. 7. Freundlich adsorption isotherms of Pb^{2+} for untreated and alkaline-treated coconut shaftsat pH = 4, adsorbent dosage = 0.7 g, contact time = 80 min, initial metal concentration = 125 mg/L and 150 mg/L

Kinetics Studies

Lagergren's pseudo-first-order, Ho's pseudo-second-order, and the Elovich kinetic models were employed to appraise the kinetics of the sorption of Pb^{2+} by UTCS and ATCS. The logarithmic form of Lagergren's pseudo-first-order model can be given as,

$$\log(q_e - q_t) = logq_e - \frac{k_{p1}}{2.303}t \tag{6}$$

where q_e and q_t (mg/g) are the amount of Pb^{2+} adsorbed at equilibrium, time is t (min), and the Lagergren rate constant is k_{p1}(min^{-1}) (Ho 2004; Jaikumar 2009). The plot of $Log(q_e - q_t)$ versus t is shown in Fig. 8.The values of k_{p1} and q_e were determined by the slopes and intercepts of the plot, and their values are presented in Table 4.

The linear form of Ho's pseudo-second-order model is given as:

$$\frac{t}{q_t} = \frac{1}{k_{p2}q_e^2} + \frac{1}{q_e}t \tag{7}$$

wherek_{p2} (g/mg^{-1}min^{-1}) is the rate constant for the pseudo-second-order model (Ho, 2006; Vegheti *et al*. 2009). The plot of t/q_t versus t is shown in Fig. 9, and the values of $k_{p2}$and q_e were evaluated from the slopes and intercepts of the plot; their values are presented in Table 4.

The Elovich model was also used in the evaluation of the biosorption process of Pb^{2+}, using unmodified and alkaline-modified coconut shafts. The simplified form of the Elovich model is given as,

$$q_t = {}^1\!/_\beta (\ln \alpha\beta) + \left({}^1\!/_\beta\right)\ln t \tag{8}$$

where α is the initial adsorption rate in mg/g min, and β is the desorption constant in g/mg (Sag and Aktay 2002; Ho and Mckay 2004; Kazmi *et al*. 2012). The slopes$\left({}^1\!/_\beta\right)$and the

intercepts $^1/_\beta$ $(\ln \alpha\beta)$ from linear plots of q_t against $\ln t$ were used to evaluate the constants as shown in Fig. 10, and its physical parameters are presented in Table 4.

Test of kinetics models

The sorption data were subjected to the sum of error squares (SSE %) in order to examine the applicability of better kinetic models. This was achieved by the application of the formula below:

$$SSE\% = \sqrt{\frac{\varepsilon(q_{e(exp.)} - q_{e(cal.)})^2}{N}} \tag{9}$$

where (q_{eexp}) and ($q_{ecal.}$) are the experimental adsorption capacity and the calculated adsorption capacity in mg/g, and N is the number of data (Vegheti *et al*. 2009). If the values of SSE % are low with higher values of R^2, it implied a better fitness to the respective kinetic model. As shown in Table 3, the values of the correlation coefficients (R^2) of all the models are close to identical. However, after comparing the values of the experimental adsorption capacity ($q_{eexp.}$) with the calculated adsorption capacity ($q_{ecal.}$), the experimental adsorption data of untreated coconut shaft was closer to the pseudo-first-order model. This implied that the sorption of Pb^{2+} by UTCS was governed by the pseudo-first-order model. Also, it was observed that the values of the rate constants for the alkaline treated coconut shaft were found to be higher in comparison with the untreated biomass, which is an indication of more active functional groups to interact with the Pb(II) ions in the solution.
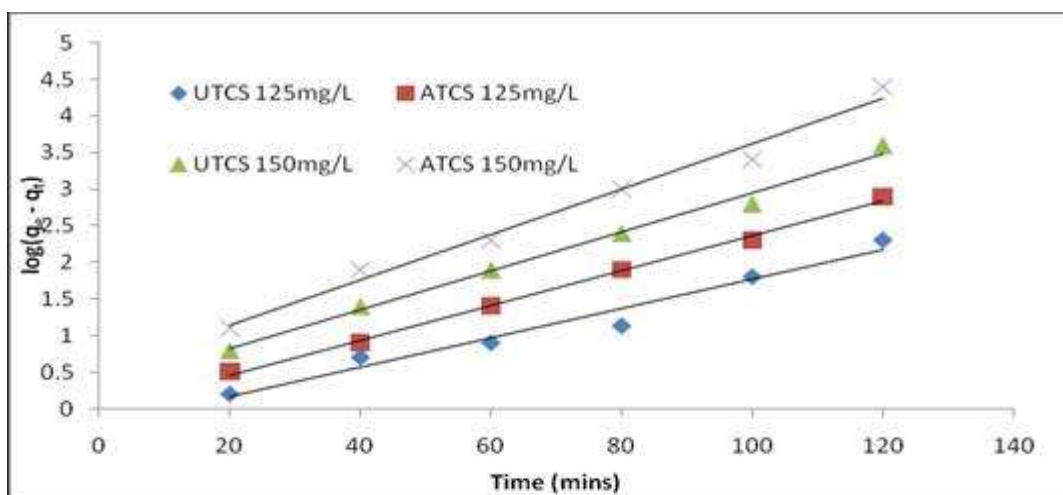

Fig. 8. Graph of the pseudo-first-order kinetic model for the adsorption of Pb^{2+} of raw and alkaline-treated coconut shaftat pH = 4, adsorbent dosage = 0.7 g, initial metal concentration = 125 mg/L and 150mg/L
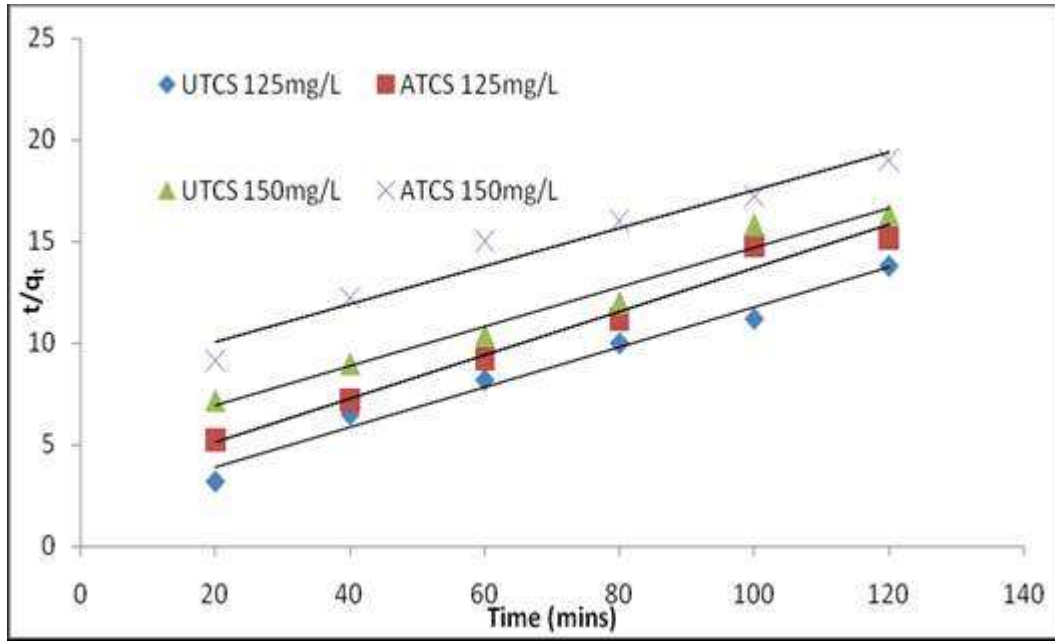
Fig. 9. Graph of the pseudo-second-order kinetic model for the adsorption of Pb^{2+} of raw and alkaline-treated coconut shaftat pH = 4, adsorbent dosage = 0.7 g, initial metal concentration = 125 mg/L and 150mg/L

Fig. 10. Graph of the Elovich kinetic model for the adsorption of Pb^{2+} of raw and alkaline-treated coconut shaft at pH = 4, adsorbent dosage = 0.7 g, initial metal concentration = 125 mg/L and 150 mg/L
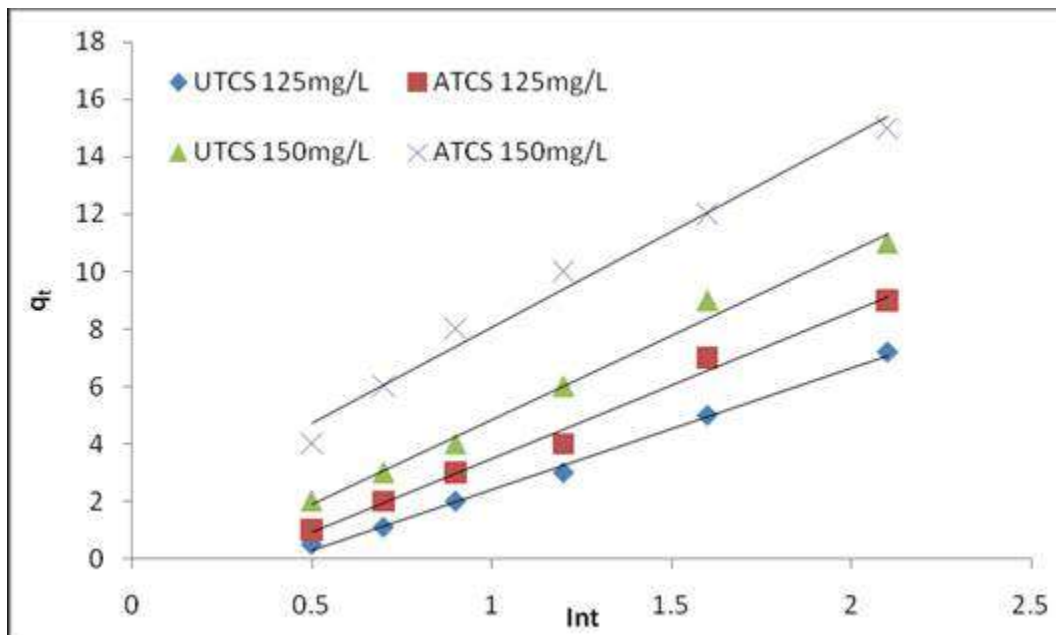
Table 4. Kinetic Model Parameters for the Adsorption of Pb^{2+}

	C_o/biomass	70mg/L UTSC	70mg/L ATSC	125mg/L UTSC	125mg/L ATSC	150mg/L UTSC	150mg/L ATSC
First-Order Model	q_{eexp}	3.20	3.57	17.6	22.1	10.21	16.10
	k_{p1}	0.12	0.22	0.43	0.56	0.72	0.94
	$q_{ecal.}$	2.14	6.11	15.41	14.63	9.12	8.24
	R^2	0.921	0.940	0.940	0.921	0.931	0.961
	SSE %	0.014	0.026	0.014	0.064	0.032	0.074
Second-Order-Model	k_{p2}	0.31	0.42	0.60	0.74	1.42	3.35
	q_{ecal}	9.40	11.92	10.81	14.47	6.52	10.14
	R^2	0.955	0.967	0.977	0.979	0.965	0.971
	SSE %	2.31	4.61	0.95	1.54	6.35	8.81
Elovich Model	A	0.22	0.47	0.82	0.96	1.22	1.74
	B	4.63	6.81	8.26	10.72	15.27	18.83
	q_{ecal}	0.96	2.52	11.12	19.84	7.62	14.71
	R^2	0.97	0.96	0.98	0.94	0.96	0.99
	SSE %	0.08	0.14	0.16	0.26	0.23	0.54

The experimental data were further fitted by pseudo-second-order kinetic model and the results showed that the equilibrium biosorption capacities (q_e, mg/g) calculated from the pseudo-second-order equation was different from the experimental values. This suggest that the pseudo-second-order kinetic model is not adequate to describe the kinetic data of Pb(II) ions adsorption onto untreated and alkaline treated coconut shaft.

When the values of the experimental adsorption capacity ($q_e exp$) were compared to the calculated adsorption capacity ($q_e\ cal.$) for ATCS, more similarity was observed with the Elovich model, which implies that the sorption of Pb^{2+} by ATCS was governed by this model. This was further corroborated by the application of sum of error squares (SSE %) to all the tested models with low values for first-order and Elovich models.

Table 5. Comparison of Sorption Capacity, Q_e, (mg/g) of Pb^{2+} by Different Biosorbents

Biosorbents	Q_e(mg/g)	Reference
Parmelina tiliacea	75.8	Uluozlu *et al.* 2008
Aspergillum niger	32.6	Arzu 2006
Peanut husk	29.14	Li *et al.* 2006
Sawdust	21.05	Li *et al.* 2006
Rice husk	120.48	Wong *et al.* 2003
Bagasse fly ash	2.5	Gupta and Ali 2004
Maize husk	1.18	Adeogun *et al.* 2013
Activated alumina	83.33	Naiya *et al. 2009[a]*
Clarified sludge	92.51	Naiya *et al. 2009[b]*
Rice husk ash	91.74	Naiya *et al. 2009[c]*
Maize cob	3.15	Nale *et al.* 2012
Sawdust	88.49	Naiya *et al.* 2008
Neem bark	88.49	Naiya *et al.* 2008
Untreated coconut shaft	17.6	Present study
Alkaline-treated coconut shaft	22.1	Present study

CONCLUSIONS

1. This work showed that agricultural wastes, such as coconut shafts, can be used for the effective removal of Pb^{2+} from aqueous solutions and can be utilized in solving problems of environmental pollution.

2. The biosorption process is dependent on parameters such as initial concentration of Pb^{2+}, contact time, pH, and biomass dose with the adsorption capacity varying with each of the parameters

3. The Langmuir isotherm model was the closest fitting model for interpreting the adsorption data for the removal of Pb^{2+} from aqueous solutions by both biomasses, indicating the involvement of monolayer surface sites.

4. Kinetic studies revealed that the adsorption data for the untreated coconut shaft was governed by the Lagergren pseudo-first-order model, while that of the alkaline-treated biomass was more closely aligned with the Elovich model.

5. Alkaline treatment of the coconut shafts enhanced the biosorption ability of Pb^{2+} onto the coconut shaft biomass.

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