

Application of waste *Delonix regia* pods and leaves for the sorption of Pb(II) ions from aqueous solution: kinetic and equilibrium studies

Bolanle M. Babalola, Adegoke O. Babalola, Habibat O. Adubiaro, Olushola S. Ayanda, Simphiwe M. Nelana and Eliazer B. Naidoo

ABSTRACT

The removal of Pb(II) ions from synthetic wastewater using *Delonix regia* pods and leaves as low-cost biosorbents was investigated. The elemental, morphological and phase characterization of *Delonix regia* pods and leaves were examined before and after biosorption. The adsorption process at various pH values, contact times, initial concentration of Pb(II) ions and adsorbent doses was studied with the aim of investigating the consequences of these parameters on the process of biosorption. The Langmuir adsorption isotherm provided the best fit for the experimental data of the pods while the Freundlich isotherm gave a better fit for the leaves of *Delonix regia*. The optimum adsorption capacity of 30.27 mg/g for the pods and 27.60 mg/g for the leaves was achieved when 0.5 g of the adsorbent was mixed with 20 mL of 1,000 mg/L Pb(II) ions solution for 30 min at 21 ± 2 °C and a stirring speed of 18 rpm. The data obtained from the time-dependent experiment of the biosorbents followed the pseudo-second-order kinetic model. This study showed that *Delonix regia* pods and leaves could be developed further as a low-cost sorbent that could be harnessed for removing Pb from industrial wastewater and thus limit water pollution from point sources.

Key words | adsorption capacity, *Delonix regia*, Freundlich isotherm, kinetic models, Langmuir isotherm, Pb(II) ions

Bolanle M. Babalola
Habibat O. Adubiaro
Olushola S. Ayanda (corresponding author)
Department of Industrial Chemistry,
Federal University Oye-Ekiti,
Ekiti State,
Nigeria
E-mail: osayanda@gmail.com

Adegoke O. Babalola
Ekiti State Ministry of Works and Infrastructure
Ado-Ekiti,
Ekiti State,
Nigeria

Olushola S. Ayanda
Simphiwe M. Nelana
Eliazer B. Naidoo
Department of Chemistry,
Vaal University of Technology,
Vanderbijlpark 1900,
South Africa

INTRODUCTION

Pollution of heavy metals is an issue requiring great attention all over the world due to their persistent nature and toxicity for living organisms and the environment. Lead (Pb) has been found to be present in many industrial wastewaters (Davydova 2005), thereby causing immense health and environmental issues. It is one of the most toxic pollutants introduced into the environment because of its various uses, such as in pipes, type metal, plumber's solder, lead acid batteries, projectiles, roofing sheets, cables, projectors, lead crystal glassware, ammunition, electrodes in the process of electrolysis, etc. (Gilbert & Weiss 2006). In the human body, Pb has no useful purpose and

its presence has negative effects on every organ or system, and is especially damaging to children (Woolf *et al.* 2007) and the developing foetus. Pb can result in unwanted situations such as kidney damage, disruption of the biosynthesis of haemoglobin, disruption of nervous systems, brain damage, anaemia, subtle abortion, rise in blood pressure, etc. (Niu *et al.* 1993; Gaballah & Kilbertus 1998; Karthika *et al.* 2010; Papandreou *et al.* 2011). Conventionally, heavy metals are removed through various remediation treatment methods which include phytoremediation, pump and treat, chemical precipitation, reverse osmosis and ion exchange, but the major disadvantages of these methods

are their high cost and the generation of large amounts of waste sludge whose disposal will constitute another environmental issue. Therefore, it is very important to find eco-friendly means of removing Pb(II) ions from industrial wastewater as this is a major means through which it enters the environment. Previous studies have investigated the use of various low-cost adsorbents for removing Pb(II) ions. Ayanda et al. (2016) examined the kinetics, equilibrium and thermodynamics of the adsorption of Pb(II) ions onto coal fly ash (a waste generated during the coal combustion process). The authors reported that the maximum percentage removal of Pb(II) ions achieved with fly ash was 98.94% at pH 7. Filote et al. (2019) studied the removal of Pb(II) from aqueous solution by the biorefinery macroalgae waste of *Fucus spiralis*. The maximum adsorption capacity predicted by the Langmuir model was 132 ± 14 mg/g at pH 4.5 and temperature of 20 °C. The application of coffee husk biomass waste for the adsorption of Pb(II) ions from aqueous solutions was investigated by Alhogbi (2017). Alhogbi stated that the adsorption equilibrium of Pb(II) ions was achieved after 60 min with 98% (19.02 mg/g) removal efficiency and that the sorption kinetics data fitted well with the pseudo-second-order model.

Delonix regia is a species of flowering plant in the family *Fabaceae*. It is a moderately sized fast growing deciduous tree. The leaves are bipinnated, and flowers appear in coryms along and at the ends of branches. The pods are green and flaccid when young and turn dark brown and woody. *Delonix regia* is generally regarded as agricultural waste, but the pods and leaves could serve as a good adsorbent by way of having limited valuable use other than seed dispersal. Ponnusami et al. (2009) examined methylene blue removal from aqueous solution using gulmohar (*Delonix regia*) plant leaf powder. Moreover, the application of *Delonix regia* pods as a sorbent for crude oil spill in water was reported by Onwuka et al. (2016). Authors have also reported the development of activated carbon from *Delonix regia* for the treatment of contaminants in aqueous solution, for example, the preparation of activated carbon from *Delonix regia* for the removal of reactive red (RR-120) and reactive blue (RB-4) dyes (Louis et al. 2018). Louis et al. (2018) reported that the decolourization efficiency achieved was approximately 98% for the dyes and that the kinetics of the adsorption process was best represented by the

pseudo-second-order kinetic model. Activated carbon prepared from *Delonix regia* pods was likewise used by Subramani et al. (2014) for the removal of acid blue 15, acid red 114 and acid violet 17. It was stated that the adsorption data fitted the Langmuir isotherm and pseudo-second-order kinetic equation with the highest dye removal (>95%) obtained at pH 2.

There are limited reports on the application of *Delonix regia* pods and leaves for the removal of toxic metal ions in aqueous solution. Therefore, in the present study, the investigation of unmodified low-cost *Delonix regia* pods and leaves for the removal of Pb(II) ions from synthetic wastewater was considered. The investigation involves studying the biosorption capacities, equilibrium and the kinetics of Pb(II) ions biosorption.

MATERIALS AND METHODS

Chemicals and reagents

All the chemicals used throughout the experiments were of analytical reagent grade and were used without further purification. Lead trioxonitrate (V) salt ($\text{Pb}(\text{NO}_3)_2$), nitric acid (HNO_3) and sodium hydroxide (NaOH) were obtained from Sigma Aldrich, USA. A stock solution of 1,000 mg/L of Pb(II) ions was prepared by dissolving $\text{Pb}(\text{NO}_3)_2$ with deionized water in 1 L volumetric flasks. The working standard solutions were prepared from the stock solutions by serial dilution to the required concentration. HNO_3 and NaOH (0.1 M) were used for the adjustment of pH where necessary. *Delonix regia* pods and leaves were collected from Ekiti State University, Ado-Ekiti. The pods and leaves were washed thoroughly with deionized water and air dried, broken down into small pieces, and then the seeds were separated from the pods and were ground in a blender to fine dry powder.

Characterization of *Delonix regia* pods and leaves

The elemental composition of the pods and leaves of *Delonix regia* was determined by energy dispersive spectroscopy (EDS) attached to a scanning electron microscope (Nova Nano SEM 230). The scanning electron microscope and transmission electron microscope (FEI

Tecnai G² 20) were used for the morphological studies, whereas X-ray diffraction (Siemens D8 Advance Bruker XRD) was used for phase characterization.

Biosorption experiments

A quantity of 0.5 g of the ground pods or leaves was weighed into 150 mL tubes, and 20 mL of 100 mg/L Pb(II) solution of pH 1.0–8.0 was added. Stirring was conducted for 5 h, after which the suspensions were centrifuged and analysed for their metal content using inductively coupled plasma-optical emission spectroscopy (ICP-OES; Variance Liberty II). pH values of 4 and 5 were observed to be the optimum Pb(II) ion removal by the pods and the leaves of *Delonix regia*, respectively; these pH values were kept constant and used for further studies. To optimize the sorption process, other parameters such as the effect of contact time, initial Pb(II) ion concentration, biosorbent dose and ionic strength on the sorption capacities of *Delonix regia* pods and leaves were investigated.

Sorption kinetic was conducted by adding 0.5 g of *Delonix regia* (pods or leaves) to 20 mL of Pb(II) ions solution and shaken on a mechanical shaker at 18 rpm; at intervals of 0.5, 1, 3, 5, 15, 30, 60, 120, 180, 240, 300 min, the suspensions were centrifuged and analysed to determine the residual Pb(II) ions concentration in the aqueous solutions. An initial Pb(II) ion concentration of 100 mg/L

was used for all experiments except the experiment for modelling the isothermal parameters in which case 1, 5, 20, 50, 100, 200, 400, 500 and 1,000 mg/L Pb(II) ions were used.

The percentage Pb(II) ions' removal was calculated with Equation (1) and the amount of Pb(II) ions adsorbed (q_e (mg/g)) was calculated using Equation (2) (Omidvar-Hosseini & Moeinpour 2016):

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

$$q_e = \frac{C_o - C_e}{W} \times V \quad (2)$$

where C_o and C_e (mg/L) are the initial and equilibrium concentration of the Pb(II) ions' solution, respectively, V (mL) is the volume of the solution and W (g) is the mass of *Delonix regia* used.

The desorption of bound Pb(II) ions from the spent biomass was achieved with different concentrations of HNO₃.

RESULTS AND DISCUSSION

Characterization

The spongy nature with porous structure of the pods' and leaves' surfaces was indicated by SEM (Figures 1(a) and

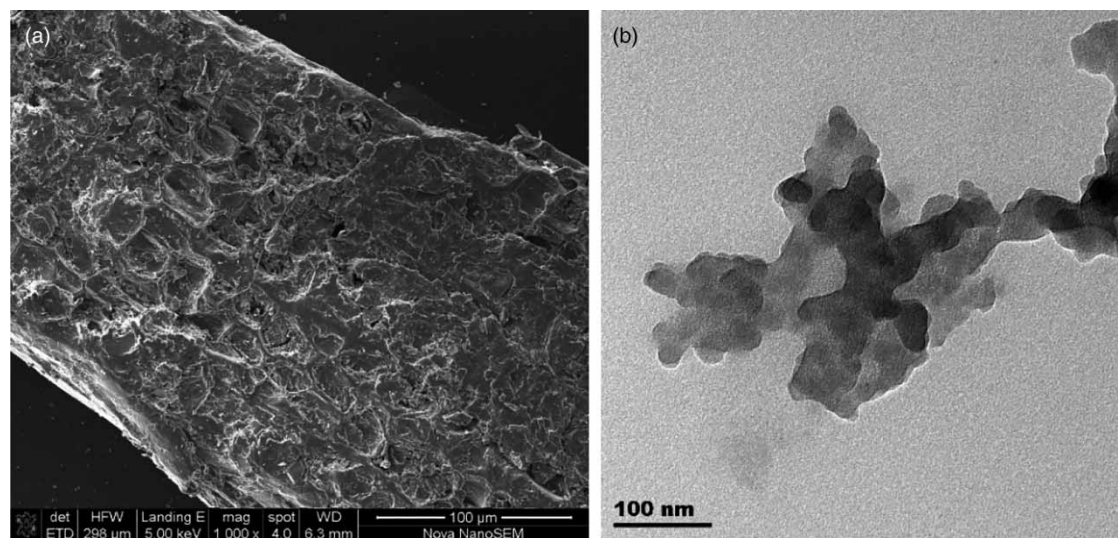


Figure 1 | SEM (a) and TEM (b) micrographs of *Delonix regia* pods.

2(a)) and TEM (Figures 1(b) and 2(b)) micrographs. Such structural characteristics may enhance the uptake of the Pb(II) ions from aqueous solution.

The EDS of *Delonix regia* leaves showed the surface of the adsorbent to be composed of 66.79% C, 32.97% O and traces of Ca and K, whereas the pods are composed of 57.61% C, 41.15% O and traces of K.

The X-ray diffractogram of the pods and leaves of *Delonix regia* (Figure 3) revealed its carbonaceous composition. Native cellulose ((C₆H₁₀O₅)_n) was identified in *Delonix regia*, the peak at 22.15° for pods and 21.36° for the leaves may be due to the amine, hydroxyl, aldehydic

and ketonic groups of the hemicellulosic moieties (Oyediji et al. 2017). Thus, the pods and leaves are rich in cellulosic material (Onwuka et al. 2016), which may provide sites for the binding of organic and inorganic pollutants.

Sorption studies

pH

pH is a crucial factor in the uptake of heavy metals from aqueous solution. The solubility of metals and level of ionization during adsorption is pH dependent as hydrogen ions

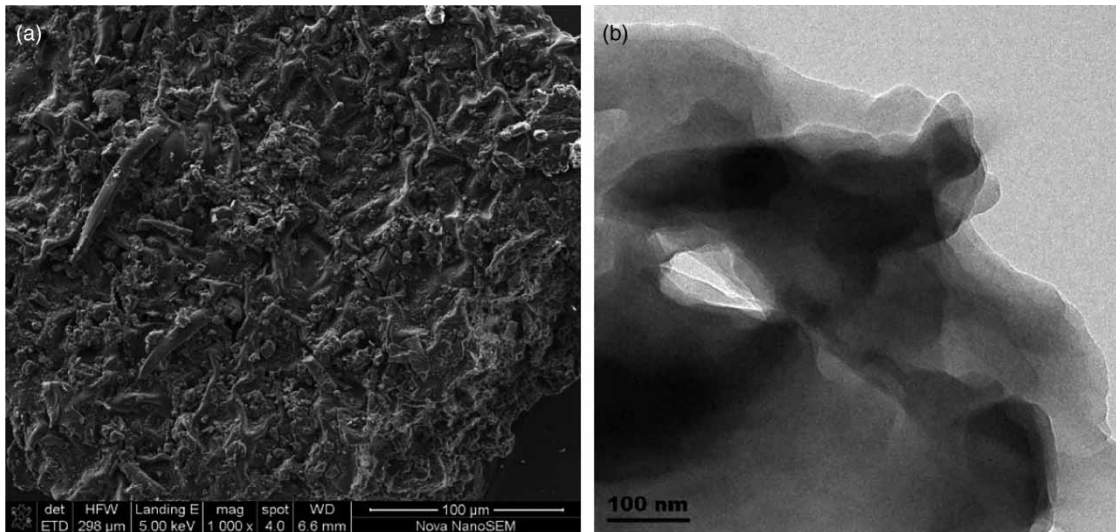


Figure 2 | SEM (a) and TEM (b) micrographs of *Delonix regia* leaves.

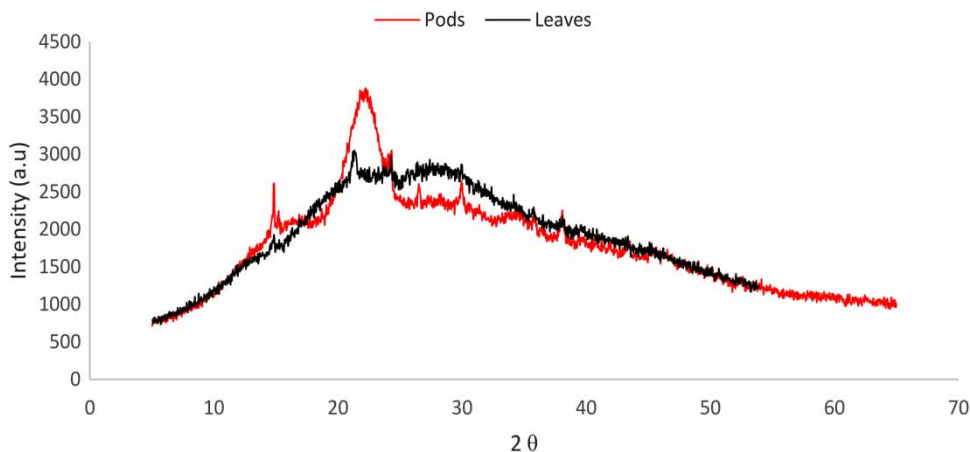


Figure 3 | X-ray diffractogram of *Delonix regia* pods and leaves.

occupy some of the binding sites (Vimala & Das 2009). Figure 4 shows the results for the pH study of the sorption of *Delonix regia* pods and leaves for Pb(II) ions.

From Figure 4, the points of major change in the percentage of Pb(II) ions adsorbed are between pH 1 and 3; after these values the percentage adsorbed was constant throughout the pH range tested in this study. At pH 2, a percentage adsorption of 86.13 was recorded for pods while for the leaves it was 73.98%. These values increased to 97.96 and 86.83% for pods and leaves, respectively, as pH increased to 3. A slight increase to 98.22% (3.6 mg/g) adsorption in pods was recorded at pH 4, while for the leaves, adsorption was 90.22% at the same pH value. An increase in pH to 5 had no effect on the percentage adsorption when the pods of *Delonix regia* were tested while the leaves registered a maximum sorption of 94.66% (2.9 mg/g) at pH 5. Further increase in pH to 6 and 7 resulted in a slight decreased sorption of Pb(II) ions for the leaves while sorption was unchanged in the case of the pods. A decrease to 93.25 and 93.85% was recorded at pH 6 and 7 for the leaves' sorption. The decrease in the percentage sorption at these higher pH values may be the result of hydrolysis of Pb(II) ions to $Pb(OH)_2$ and $Pb(OH)_3^-$ accompanied by precipitation of these metal hydroxides (Pehlivan et al. 2008; Omidvar-Hosseini & Moeinpour 2016). Metal ion uptake by biosorbents may involve complexation, coordination, chelation, ion exchange and adsorption (Volesky 1990). The fact that

the adsorption process is dependent on the pH of the adsorbate shows that electrostatic attraction and ion-exchange are involved in the binding mechanism of Pb(II) ions by *Delonix regia* pods (Pehlivan et al. 2008). During the ion-exchange binding mechanism, the proton on the acidic amine group of the biomass may likely be displaced by Pb(II) ions and thus binding occurs in the anionic sites of the biomass.

All experiments involving pods and leaves of *Delonix regia* were thus conducted at pH 4 and 5, respectively. Researchers who investigated sugar beet pulp and other biosorbents reported similar values in their work (Saeed et al. 2005; Bulut & Baysal 2006; Pehlivan et al. 2008).

Time dependence study and kinetic modelling

For process efficiency, a good biosorbent should be able to sorb a reasonable amount of the adsorbate within a few minutes of contact with the aqueous solutions. The rapid uptake of metals by the biosorbent is desirable, providing for short contact time of solution-biosorbent in the actual process.

The plots in Figure 5 show the time dependence study of the biosorption of Pb(II) ions on *Delonix regia* pods and leaves; approximately 98.4% (4.13 mg/g) uptake was achieved from the first 5 min of contact with the pods and this percentage was maintained throughout the 300 min of this study. For the biosorption involving the leaves, 91.3% adsorption was recorded within 5 min, this was increased

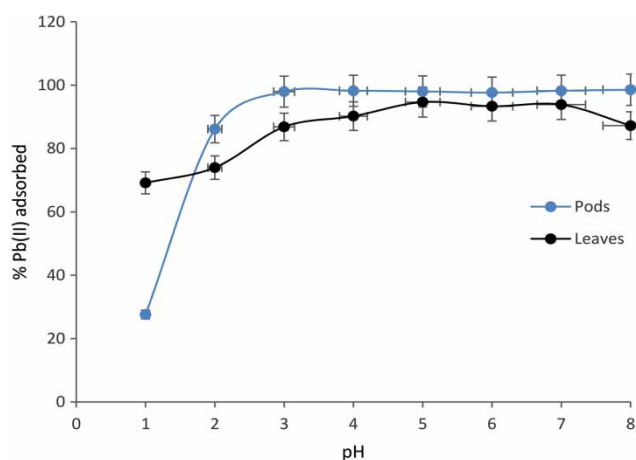


Figure 4 | pH study of the sorption of Pb(II) ions on *Delonix regia* pods and leaves. Experimental conditions: pH: 2–8; contact time: 300 min; Pb(II) ions' concentration: 100 mg/L; volume of Pb(II) ions: 20 mL; biosorbent dose: 0.5 g; stirring speed: 18 rpm; temperature: $21 \pm 2^\circ\text{C}$.

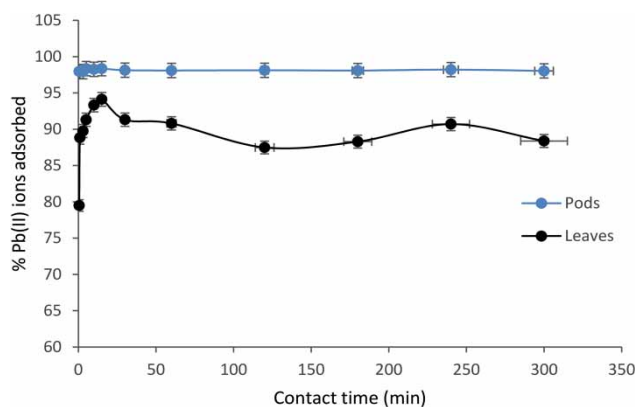


Figure 5 | Time dependence of Pb(II) ions' sorption on *Delonix regia* pods and leaves. Experimental conditions: pH: 4 and 5 for the pods and leaves, respectively; contact time: 0.5–300 min; Pb(II) ions' concentration: 100 mg/L; volume of Pb(II) ions: 20 mL; biosorbent dose: 0.5 g; stirring speed: 18 rpm; temperature: $21 \pm 2^\circ\text{C}$.

to 93.3% in 10 min and 94.1% (2.9 mg/g) in 15 min, after which it reduced to 91.3% and 90.7% at 30 min and 60 min, respectively. At 120 min, a percentage adsorption of 87.5% was observed, and afterwards, an increase to 88.3% and 90.6% was observed at 180 and 240 min. From the result obtained during the adsorption experiment, adsorption and desorption were observed after 15 min of contact with both pods and leaves. In all subsequent experiments in this study, an adsorption time of 30 min was used for easy handling and laboratory setup.

Experimental adsorption data of time dependence was used for the kinetic modelling and it fitted the pseudo-second-order equation shown in Equation (3):

$$\frac{t}{Q_t} = \frac{1}{k_{2,ad}Q_{eq}^2} + \frac{1}{Q_{eq}t} \quad (3)$$

where $k_{2,ad}$ is the pseudo-second-order rate constant for adsorption (g/mg/min); contact time, t , (min); Q_t sorption uptake at any time t and Q_{eq} (mg/g) is equilibrium sorption uptake.

The applicability of the pseudo-second-order kinetics is established by the linearity of the plot of t/Q_t versus t (Figure 6), where Q_{eq} and $k_{2,ad}$ (Table 1) are obtained from the slope and intercept, respectively (Ho & McKay 1998, 1999a, 1999b). The pseudo-second-order kinetic depends on the assumption that chemisorption is the rate-limiting step (Ayanda et al. 2013). Therefore, the Pb(II) ions stick to the biosorbent surface by forming a bond and tend to find

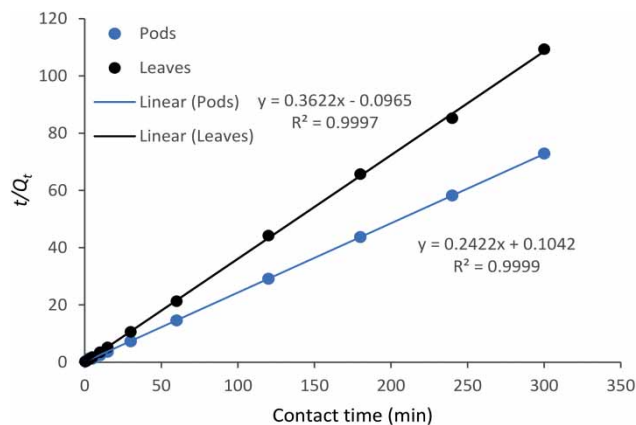


Figure 6 | Pseudo-second-order kinetics plot of the adsorption of Pb(II) ions on *Delonix regia* pods and leaves.

Table 1 | Kinetic parameters

<i>Delonix regia</i>	Q_{eq} (mg/g)	$k_{2,ad}$ (g/mg/min)	R^2
Pods	4.12	0.98	0.9999
Leaves	2.76	0.69	0.9997

sites that maximize their coordination number with the surface.

Equilibrium modelling

To overcome all the mass transfer resistances of the metal between the two phases (aqueous and solid), energy provided by an initial concentration of adsorbate is a major force (Kulkarni et al. 2014).

Figure 7 shows that the percentage adsorption was 99.3% when 20 mg/L of Pb(II) ions' solution was in contact with *Delonix regia* pods. This sorption remained fairly constant until 100 mg/L was used, after which it decreased slightly to 98.2% (7.4 mg/g) at 200 mg/L of Pb(II) ions' solution and a further decrease to 93.4% (21.2 mg/g) was observed at 500 mg/L to 65.8% (30.3 mg/g) at 1,000 mg/L. The percentage of Pb(II) ions adsorbed with the leaves increased from 58.2% at 1 mg/L to 83.3% when 5 mg/L of Pb(II) ions solution was used. The percentage adsorption was 82.7% when 100 mg/L of Pb(II) ions' solution was in contact with *Delonix regia* leaves. It decreased slightly to 81.4% (7.5 mg/g) and 80.2% (16.4 mg/g) at 200 mg/L and 500 mg/L of Pb(II) ions solution, respectively. A decrease

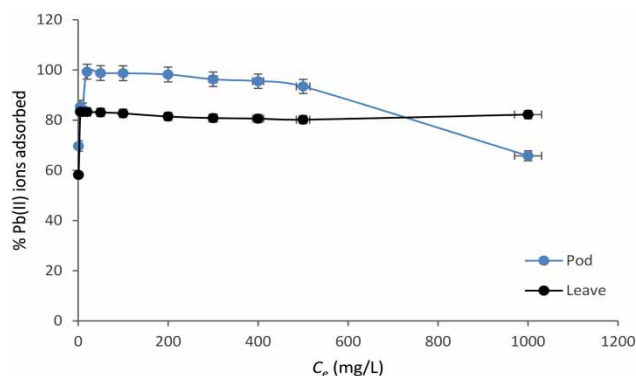


Figure 7 | Effect of initial Pb(II) ions' concentration. Experimental conditions: pH: 4 and 5 for the pods and leaves, respectively; contact time: 30 min; volume of Pb(II) ions: 20 mL; biosorbent dose: 0.5 g; stirring speed: 18 rpm; temperature: 21 ± 2 °C.

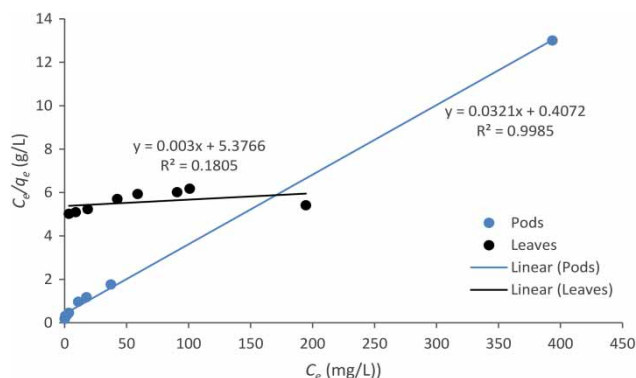


Figure 8 | Plots of the Langmuir isotherm for the adsorption of Pb(II) ions by *Delonix regia* pods and leaves.

to 63.0% (27.6 mg/g) was observed at 1,000 mg/L. This trend observed in the percentage of Pb(II) ions adsorbed was because there is a fixed number of binding sites on the biomass and once these are occupied a further increase in concentration will lead to a decrease in the percentage adsorption; that is, increasing the initial metal concentration will lead to adsorption increase provided the binding sites are not saturated (Igwe & Abia 2007).

An equilibrium isotherm is crucial in the development of the sorption system, as it provides details on the capacity of the sorbent (Aksu & Tezer 2000). It is described by constants that estimate the properties of the surface and its affinity for the pollutant. To determine the isotherm parameters for the adsorption of Pb(II) ions onto *Delonix regia* pods and leaves, the modelling of the equilibrium data for the biosorption of Pb(II) ions were obtained by using the Langmuir and Freundlich isotherms.

The monolayer adsorption capacity (Q_o , mg/g), and b , the Langmuir constant related to the energy of adsorption, were calculated from the Langmuir isotherm represented by Equation (4):

$$\frac{C_e}{Q_e} = \frac{1}{bQ_o} + \frac{C_e}{Q_o} \quad (4)$$

Table 2 | Langmuir and Freundlich isotherm constants

Delonix regia	Langmuir isotherm			Freundlich isotherm			
	Q_o cal (mg/g)	b (L/mg)	R^2	Q_o (exp) mg/g	k_f (mg/g(L/mg) ^{1/n})	n	R^2
Pods	31.15	7.9×10^{-2}	0.9985	30.27	0.95	1.32	0.6242
Leaves	333.3	5.58×10^{-4}	0.1805	27.60	0.14	1.03	0.9772

The plots of C_e/Q_e against C_e shown in Figure 8 were employed to calculate the Langmuir constants, whose values are presented in Table 2. The R^2 values obtained for the Langmuir plots (Figure 8) confirm that the adsorption process of Pb(II) ions onto *Delonix regia* pods suits the Langmuir adsorption model. The calculated adsorption capacity (Q_o cal = 31.15 mg/g) and the experimental adsorption capacity (Q_o (exp) = 30.27 mg/g) for the pods are very close. This is not the same for the leaves (Table 2).

A dimensionless equilibrium separation factor, R_L , expresses important characteristics of the isotherms, represented by Equation (5) (Arami et al. 2005):

$$R_L = \frac{1}{1 + bC_o} \quad (5)$$

R_L shows whether the adsorption is favourable or not. When $R_L = 0$ the isotherm is irreversible; $0 < R_L < 1$ indicates favourable; $R_L = 1$ is a linear isotherm and $R_L > 1$ is termed unfavourable. The R_L values obtained from this study are shown in Figure 9. The R_L for the initial Pb(II) ions' concentrations for the *Delonix regia* pods are found in the range 0.012–0.387, and 0.642–0.988 for the *Delonix regia* leaves. These values suggested favourable biosorption of Pb(II) ions onto *Delonix regia* under the conditions of the experiment.

Equation (6) is the linear equation of the Freundlich isotherm used to explain sorption in heterogenous surfaces (Freundlich 1907). From this equation, $\log Q_e$ was plotted against $\log C_e$ (Figure 10), such that the Freundlich constants k_f and n could be determined from the intercept and slope, respectively.

$$\log Q_e = \log k_f + \frac{1}{n} \log C_e \quad (6)$$

k_f is the Freundlich constant which is related to the adsorption capacity and n is the Freundlich model constant

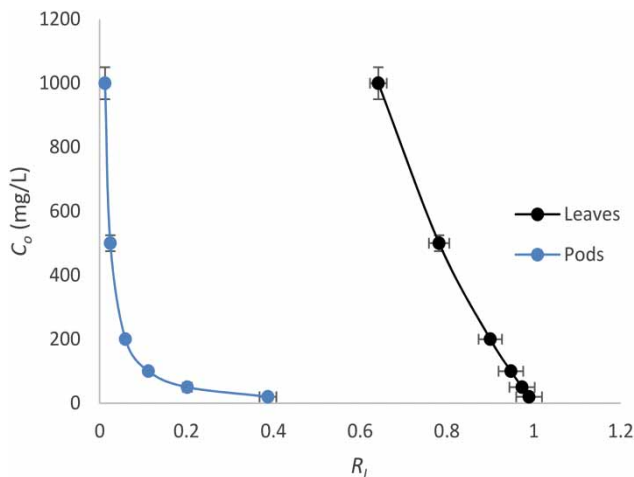


Figure 9 | Plot of the initial Pb(II) ions' concentration versus R_L .

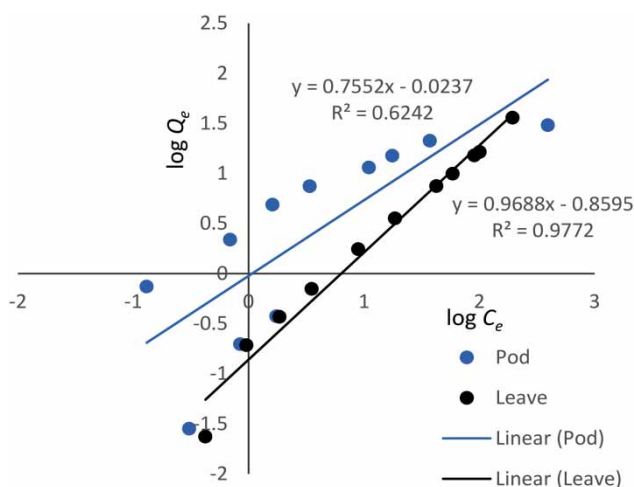


Figure 10 | Plots of the Freundlich isotherm for the sorption of Pb(II) ions on *Delonix regia* pods and leaves.

indicating the intensity of adsorption. The Freundlich isotherm gave a better fit with the sorption of Pb(II) ions on the leaves of *Delonix regia*. The value of n between 1 and 10 is an indication of a favourable adsorption process (Ayanda et al. 2013).

Effect of sorbent dose on adsorption

Figure 11 presents the result obtained when different quantities of *Delonix regia* pods and leaves were used, while keeping all other experimental parameters constant. From the result, changing the doses of the biomass has little effect on the percentage adsorption of Pb(II) ions recorded.

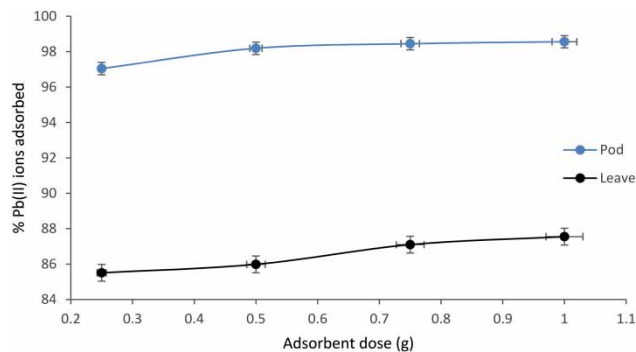


Figure 11 | Effect of sorbent dose on the adsorption of Pb(II) ions on *Delonix regia* pods and leaves. Experimental condition: pH: 4 and 5 for the pods and leaves, respectively; contact time: 30 min; Pb(II) ion concentration: 100 mg/L; volume of Pb(II) ions: 20 mL; biosorbent dose: 0.5 g; stirring speed: 18 rpm; temperature: 21 ± 2 °C.

Approximately 86% adsorption was recorded when 0.25 g and 0.5 g of *Delonix regia* leaves were used but when the doses were increased to 0.75 g and 1.0 g, the percentage adsorption was increased to 87% and 88%, respectively. Percentage adsorptions of 97, 98, 98 and 99% were recorded when 0.25, 0.5, 0.75 and 1.0 g of *Delonix regia* pods were used, respectively. These percentage increases do not correlate with the increase in the doses of the biomass.

Effect of ionic strength

The effect of inorganic salts (NaCl) on Pb(II) ions' biosorption at different ionic strengths was also considered. The results showed that the presence of NaCl has little or no effect on the removal efficiency of Pb(II) ions (Figure 12). With the increase of ionic strength from 0.001 to 0.05 M NaCl, the removal of Pb(II) ions slightly increased from 99.3% to 99.9% for the pods and from 94.7% to 97.7% for the leaves.

There is no appreciable difference in the removal efficiency of Pb(II) ions due to increased competition for the adsorption sites between Pb(II) ions and Na^+ ions present in the solution. Moreover, the increase in the solution ionic strength could have also led to the formation of ion pairs between Pb(II) ions and Cl^- present in solution that reduced the activity of free Pb(II) ions. Other inorganic salts such as KCl, MgCl_2 , ZnCl_2 , Na_2SO_4 or Na_3PO_4 need to be further studied.

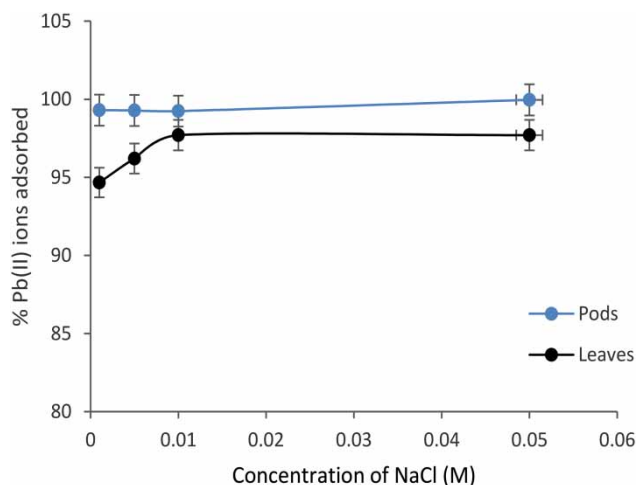


Figure 12 | Effect of ionic strength on the adsorption of Pb(II) ions on *Delonix regia* pods and leaves. Experimental condition: pH: 4 and 5 for the pods and leaves, respectively; contact time: 30 min; Pb(II) ion concentration: 100 mg/L; volume of Pb(II) ions: 20 mL; biosorbent dose: 0.5 g; stirring speed: 18 rpm; temperature: 21 ± 2 °C.

The morphology and EDS analysis of *Delonix regia* pods and leaves after the sorption process was investigated. Figures 13 and 14 show that the surface morphology of the pods and leaves was not changed after adsorption. This indicated that the pods and leaves of *Delonix regia* are not destroyed and their structure is unaffected during Pb(II) ions' adsorption and could be further reused after desorption or activation. The EDS spectrum (Figure 15(a) and 15(b)) also confirm the presence of Pb(II) ions on the

surface of the adsorbent, about 16.33% and 15.4% Pb was present on the pods and leaves, respectively. The presence of Si in traces may result from the chemical composition of $\text{Pb}(\text{NO}_3)_2$ used for the preparation of Pb(II) ions' solution.

Desorption experiment

The recovery experiment was conducted to investigate the possibility of recovering the adsorbed Pb(II) ions from the biomass. The results obtained from the desorption study are shown in Figure 16.

From Figure 16, the trends obtained for the percentage recovery of Pb(II) ions from the pods and leaves of *Delonix regia* are similar at different concentrations of HNO_3 . The figure also reveals that the percentage of Pb(II) ions recovered from the leaves was higher than what was recovered from the pods. The recovery experiment indicated that Pb(II) ions' recovery decreases with increasing concentration of HNO_3 . Thus, HNO_3 at low concentration is required for efficient desorption, and this will, in turn, make the recovery process less expensive. Approximately 57.3% and 47.8% Pb(II) ions were recovered from *Delonix regia* leaves and pods, respectively, when the concentration of HNO_3 used was 0.05 M. The recovery study has proved that the sorption of Pb(II) ions onto the pods and leaves of *Delonix regia* is environmentally friendly and sustainable.

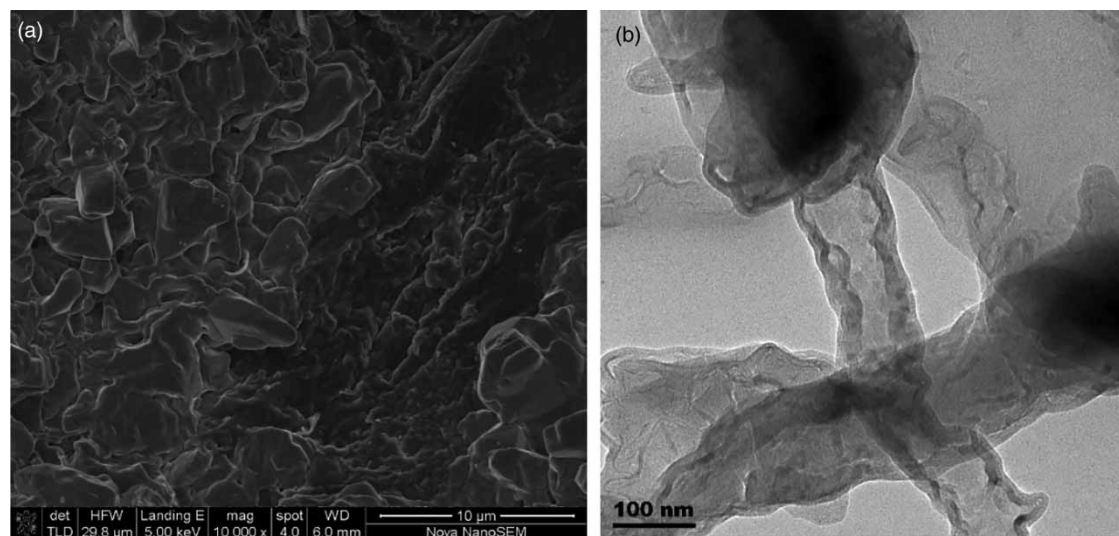


Figure 13 | SEM (a) and TEM (b) micrographs of *Delonix regia* pods after sorption.

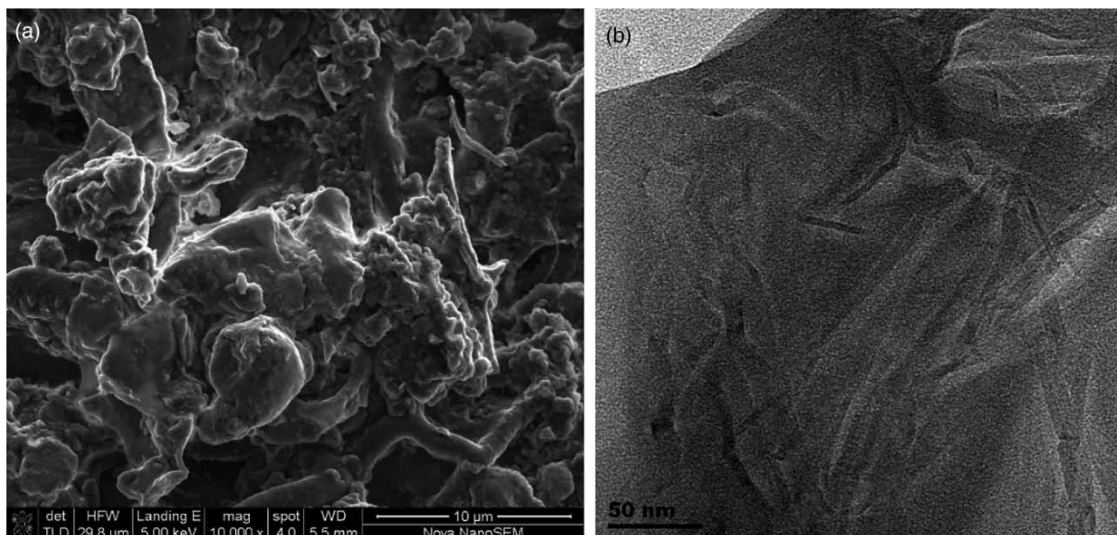


Figure 14 | SEM (a) and TEM (b) micrographs of *Delonix regia* leaves after sorption.

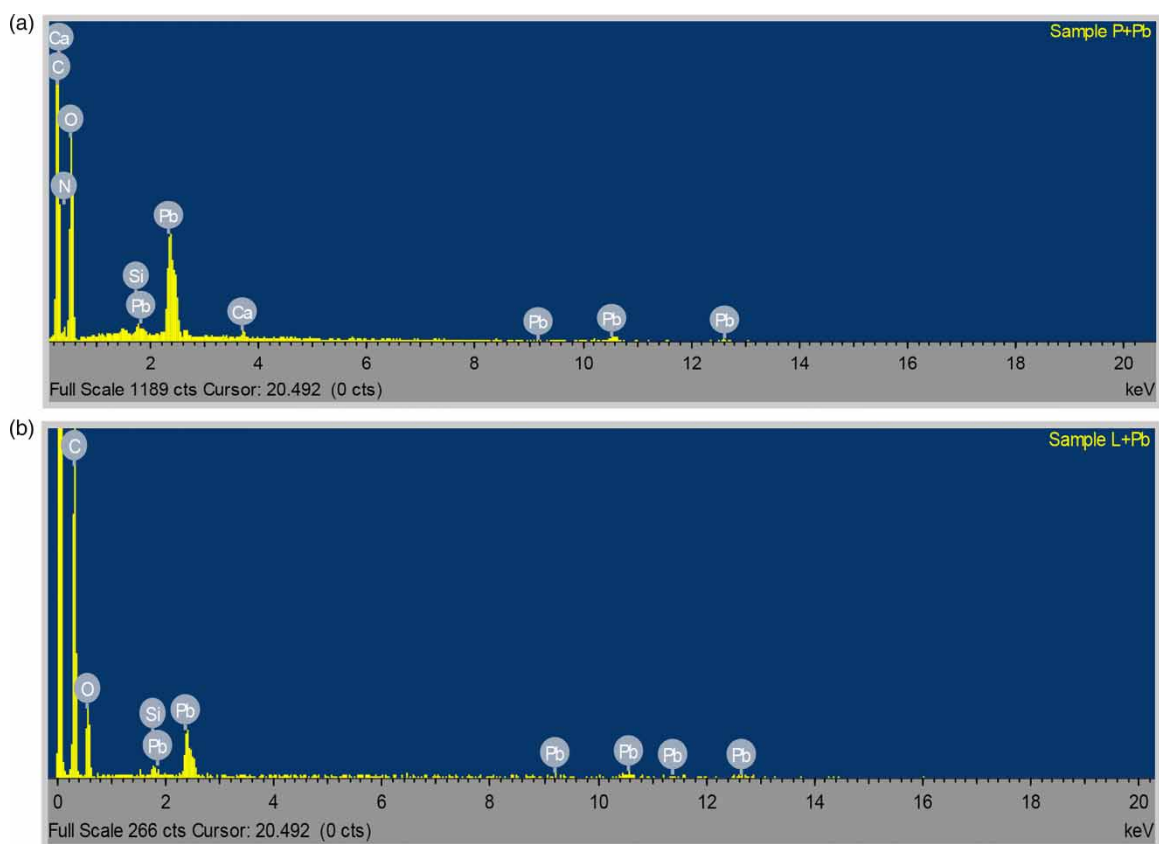


Figure 15 | EDS spectrum of *Delonix regia* pods (a) and leaves (b) after sorption.

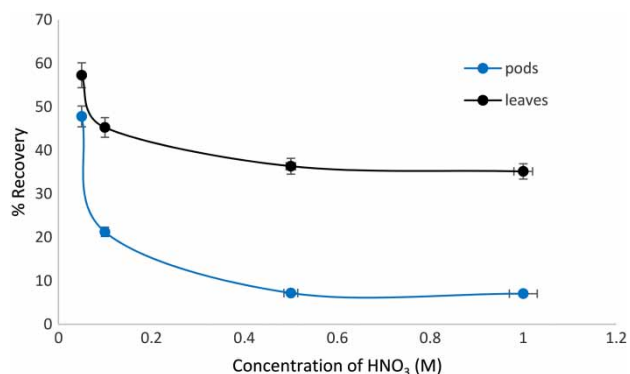


Figure 16 | Recovery study of the adsorbed Pb(II) ions from the pods and leaves of *Delonix regia*.

CONCLUSION

The pods and leaves of *Delonix regia* were used as a low-cost adsorbent for the removal of Pb(II) ions from aqueous solution. The results obtained in this study have shown that *Delonix regia* pods and leaves have varying adsorption capacities for removing Pb(II) ions from aqueous solutions. The pods showed better adsorption capacity than the leaves and this might be due to the more fibrous content of the pods. The XRD peak of the cellulosic material, which may provide sites for the binding of Pb(II) ions, is also prominent for the pods. Thus, *Delonix regia* pods seem a better and viable adsorbent for treating wastewater containing Pb(II) ions than the leaves. The biosorption of Pb(II) ions depends on the initial Pb(II) ions' concentration, contact time, ionic strength and pH of the aqueous solution. Maximum removal of Pb(II) ions by *Delonix regia* pods and leaves is at pH 4 and 5, respectively. The removal of Pb(II) ions by *Delonix regia* was adequately modelled by the Freundlich and Langmuir isotherms and the data of the time dependence experiment of the biosorbents followed the pseudo-second-order kinetic model. *Delonix regia* pods have a capacity of 30.27 mg/g for Pb(II) ions while the leaves have a capacity of 27.60 mg/g. The desorption study also showed that the recovery of the Pb(II) ions from the spent pods and leaves decreased with increasing concentration of HNO₃. Therefore, *Delonix regia* pods and leaves could be effectively used as low-cost biosorbent for removing Pb from

contaminated wastewaters before discharge into the environment.

ACKNOWLEDGEMENT

The authors are grateful to Petroleum Technology Development Fund (PTDF), Nigeria for financing this research work. Bolanle M Babalola appreciates the support received from DGT Research Group, Lancaster University, UK.

REFERENCES

- Aksu, Z. & Tezer, S. 2000 Equilibrium and kinetic modelling of biosorption of Remazol Black B by *Rhizopus arrhizus* in a batch system: effect of temperature. *Process Biochemistry* **36** (5), 431–439.
- Alhogbi, B. G. 2017 Potential of coffee husk biomass waste for the adsorption of Pb(II) ion from aqueous solutions. *Sustainable Chemistry and Pharmacy* **6**, 21–25.
- Arami, M., Limaee, N. Y., Mahmoodi, N. M. & Tabrizi, N. S. 2005 Removal of dyes from colored textile wastewater by orange peel adsorbent: equilibrium and kinetic studies. *Journal of Colloid and Interface Science* **288** (2), 371–376.
- Ayanda, O. S., Fatoki, O. S., Adekola, F. A. & Kimba, B. J. 2013 Removal of tributyltin from shipyard process wastewater by fly ash, activated carbon and fly ash/activated carbon composite: adsorption models and kinetics. *Journal of Chemical Technology and Biotechnology* **88**, 2201–2208.
- Ayanda, O. S., Akintayo, C. O., Mthembu, N. L., Emmanuel, F. C. A. & Kimba, B. J. 2016 A comparative study of the kinetics, equilibrium and thermodynamics of the adsorption of Pb(II) ions onto activated carbon and fly ash from aqueous solution. *Research Journal of Chemistry and Environment* **20** (8), 44–54.
- Bulut, Y. & Baysal, Z. 2006 Removal of Pb (II) from wastewater using wheat bran. *Journal of Environmental Management* **78** (2), 107–113.
- Davydova, S. 2005 Heavy metals as toxicants in big cities. *Microchemical Journal* **79** (1), 133–136.
- Filote, C., Volf, I., Santos, S. C. R. & Botelho, C. M. S. 2019 Bioadsorptive removal of Pb(II) from aqueous solution by the biorefinery waste of *Fucus spiralis*. *Science of the Total Environment* **648**, 1201–1209.
- Freundlich, H. 1907 Über die adsorption in lösungen (Adsorption in solution). *Zeitschrift für Physikalische Chemie* **57** (1), 385–470.
- Gaballah, I. & Kilbertus, G. 1998 Recovery of heavy metal ions through decontamination of synthetic solutions and

- industrial effluents using modified barks. *Journal of Geochemical Exploration* **62** (1), 241–286.
- Gilbert, S. G. & Weiss, B. 2006 A rationale for lowering the blood lead action level from 10 to 2 µg/dL. *Neurotoxicology* **27** (5), 693–701.
- Ho, Y. & McKay, G. 1998 Sorption of dye from aqueous solution by peat. *Chemical Engineering Journal* **70** (2), 115–124.
- Ho, Y. & McKay, G. 1999a Pseudo-second order model for sorption processes. *Process Biochemistry* **34** (5), 451–465.
- Ho, Y. & McKay, G. 1999b The sorption of lead (II) ions on peat. *Water Research* **33** (2), 578–584.
- Igwe, J. & Abia, A. 2007 Adsorption isotherm studies of Cd (II), Pb (II) and Zn (II) ions bioremediation from aqueous solution using unmodified and EDTA-modified maize cob. *Eclética Química* **32** (1), 33–42.
- Karthika, C., Vennilamani, N., Pattabhi, S. & Sekar, M. 2010 Utilization of sago waste as an adsorbent for the removal of Pb (II) from aqueous solution: kinetic and isotherm studies. *International Journal of Engineering Science and Technology* **2** (6), 1867–1879.
- Kulkarni, R. M. R., Srinikethan, G. & Vidyashetty, K. 2014 Equilibrium and kinetic studies for the adsorption of cadmium ion on Zeolite 4A. *Journal of Biochemical Technology* **3** (5), 158–160.
- Louis, M. R., Sorokhaibam, L. G., Bhandari, V. M. & Bundale, S. 2018 Multifunctional activated carbon with antimicrobial property derived from *Delonix regia* biomaterial for treatment of wastewater. *Journal of Environmental Chemical Engineering* **6** (1), 169–181.
- Niu, H., Xu, X. S., Wang, J. H. & Volesky, B. 1993 Removal of lead from aqueous solutions by penicillium biomass. *Biotechnology and Bioengineering* **42** (6), 785–787.
- Omidvar-Hosseini, F. & Moeinpour, F. 2016 Removal of Pb (II) from aqueous solutions using *Acacia nilotica* seed shell ash supported NiO.5ZnO.5Fe₂O₄ magnetic nanoparticles. *Journal of Water Reuse and Desalination* **6** (4), 562–573.
- Onwuka, J. C., Agbaji, E. B., Ajibola, V. O. & Okibe, F. G. 2016 Kinetic studies of surface modification of lignocellulosic *Delonix regia* pods as sorbent for crude oil spill in water. *Journal of Applied Research and Technology* **14**, 415–424.
- Oyediji, O. A., Azeez, L. A. & Osifade, B. G. 2017 Chemical and nutritional compositions of flame of forest (*Delonix regia*) seeds and seed oils. *South Africa Journal of Chemistry* **70**, 16–20.
- Papandreou, A., Stournaras, C., Papias, D. & Paspaliaris, I. 2011 Adsorption of Pb (II), Zn (II) and Cr (III) on coal fly ash porous pellets. *Minerals Engineering* **24** (13), 1495–1501.
- Pehlivan, E., Yanik, B., Ahmetli, G. & Pehlivan, M. 2008 Equilibrium isotherm studies for the uptake of cadmium and lead ions onto sugar beet pulp. *Bioresource Technology* **99** (9), 3520–3527.
- Ponnusami, V., Gunasekar, V. & Srivastava, S. N. 2009 Kinetics of methylene blue removal from aqueous solution using gulmohar (*Delonix regia*) plant leaf powder: multivariate regression analysis. *Journal of Hazardous Materials* **169**, 119–127.
- Saeed, A., Iqbal, M. & Akhtar, M. W. 2005 Removal and recovery of lead (II) from single and multimetal (Cd, Cu, Ni, Zn) solutions by crop milling waste (black gram husk). *Journal of Hazardous Materials* **117** (1), 65–73.
- Subramani, S. E., Kumaresan, D. & Thinakaran, N. 2014 Application of activated carbon derived from waste *Delonix regia* seed pods for the sorption of acid dyes: kinetic and equilibrium studies. *Desalination and Water Treatment* **57** (16), 7322–7333.
- Vimala, R. & Das, N. 2009 Biosorption of cadmium (II) and lead (II) from aqueous solutions using mushrooms: a comparative study. *Journal of Hazardous Materials* **168** (1), 376–382.
- Volesky, B. 1990 *Biosorption of Heavy Metals*. CRC Press, Boca Raton, FL, USA.
- Woolf, A. D., Goldman, R. & Bellinger, D. C. 2007 Update on the clinical management of childhood lead poisoning. *Pediatric Clinics of North America* **54** (2), 271–294.

First received 12 October 2018; accepted in revised form 6 April 2019. Available online 10 May 2019