Comparative study of the adsorption capacity of lead (II) ions onto bean husk and fish scale from aqueous solution

Chionyedua T. Onwordi, Cosmas C. Uche, Alechine E. Ameh and Leslie F. Petrik

ABSTRACT

The present study compared the adsorption capacity of Pb (II) ions from aqueous solution onto biopolymer materials (BPMs): (bean husk (BH) and fish scale (FS)). Fourier transform infrared (FTIR), thermogravimetric analysis (TGA), scanning electron microscopy (SEM) and X-ray diffraction (XRD) techniques were used to characterize the BPMs. The optimal conditions of the variables: pH, adsorbent dosage, initial metal concentration, contact time and temperature were ascertained. Experimental data were applied to the Langmuir, Freundlich and Temkin sorption isotherms using the linear equations form. The optimal removal of Pb (II) ions with BH and FS was obtained at pH 7.0 and 6.0, and 0.2 g adsorbent dosage each, respectively. The removal of Pb (II) ions fitted the pseudo-second order kinetic model well for the materials. Equilibrium Langmuir isotherm, which indicated a heterogeneous process, gave a better conformity than the other models used for BH while the Temkin isotherm gave better conformity for FS. The FS reached equilibrium faster (at about 30 min) compared to BH (at about 60 min); however, the processes are both spontaneous and endothermic. The BPMs gave about 90% removal of Pb (II) ions at the optimum dosage when used for textile wastewater. The BPMs, therefore, can be used as effective, low-cost and environmentally friendly adsorbents.

Key words | adsorption capacity, bean husk, biopolymer materials, fish scale, isotherms, lead

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INTRODUCTION

Due to rapid industrialization and technological advancements, the natural environment suffers from the detrimental effects of pollution (Wahid *et al.* 2017). In particular, pollution of the environment through indiscriminate discharge of partially/untreated industrial effluents has been a serious concern in developing countries. Therefore, to protect our environment from these pollutants, this can be achieved either by minimizing the introduction of pollutants into the environment or by their removal from contaminated media (Baker & Khalili 2004). The industrial effluents contain

pollutants in the form of organic and inorganic components. An example of the inorganic component is potential toxic metals (PTMs) which found their way into the environment via the discharge of untreated wastewater/effluents. The PTMs (e.g., cadmium (Cd), lead (Pb), copper (Cu), zinc (Zn)) originate from metal plating/metallurgical processes, mining activities, smelting, battery manufacture, tanneries, petroleum refining, paint manufacture, pesticides, pigment manufacture, printing and photographic industries. These PTMs are not biodegradable and their toxicity poses a significant threat to plant, animal and human health, accumulation in the food chain and persistence in the environment.

Lead is one of the priority toxic pollutants as stated in the *Guidelines for Drinking Water Quality* (WHO 2006).

The health implications of acute lead poisoning in humans include effect on the nervous system, enzyme inhibitor, causing mental retardation and damage to the brain cells in young children (King *et al.* 2007; Nadeem *et al.* 2008). Calcium in the bone is replaced by lead and subsequently released into the blood stream (King *et al.* 2007).

The conventional methods involved in the removal of these pollutants from wastewater include ion exchange, chemical precipitation, reverse osmosis and liquid–liquid extraction, resins, cementation and electrodialysis. However, these methods are often inefficient and very expensive. A promising method, termed adsorption, an economically feasible and environmentally friendly process which uses biological materials as a sorbent, is being looked into as an alternative treatment for removal of pollutants (Tan *et al.* 2010). These agriculture wastes and by-products are considered low value and are quite abundant. Different types of biomass/agriculture wastes have been investigated for biosorption of Pb (II) ions and these include papaya wood (Saeed *et al.* 2005a), bacteria (Jong & Parry 2004), algae (Luo *et al.* 2006), juniper (Min *et al.* 2004), black gram husk (Saeed *et al.* 2005b), rice milling (Tarley & Arruda 2004), cocoa shell (Meunier *et al.* 2003), saw dust (Li *et al.* 2006), banana peel (Anwar *et al.* 2010), banana stalks, corn cob and sunflower achene (Mahmood-ul-Hassan *et al.* 2015).

Lately, studies have reported the use of fish scales as a sorbent for removal of PTMs from wastewater. Nadeem *et al.* (2008) reported the biosorption by *Labeo rohita* fish scale (FS) for the removal of Pb (II) ions from aqueous solutions under different experimental conditions using a batch process. The results showed the maximum lead (II) ions adsorption (196.8 mgg^{-1}) occurred at pH 3.5. Pb (II) ions sorption was found to be pH, dosage, initial metal concentration, contact time and shaking speed dependent, whereas particle size and temperature are independent.

Srividya & Mohanty (2009) investigated the adsorption of hexavalent chromium by *Catla catla* scales from aqueous solution as a function of time, pH, initial Cr (VI) concentration, sorbent dose and agitation speed. Their study revealed that the optimum pH, sorbent dosage, contact time and agitation speed were 1.0, 50 mg/L, 180 min and 200 rpm, respectively. It was reported that the isothermal data could be well described by the Freundlich model and the dynamical data fitted well with the pseudo-second order kinetic model. The Fourier transform infrared (FTIR) spectrum analysis revealed the presence of O–H, N–H and C–O groups as the bond for the Cr (VI) binding.

Othman *et al.* (2016) reported the biosorption of heavy metals by *Mozambique tilapia* (*M. tilapia*) fish scales. The study characterized the fish scales, determined the adsorption isotherm and biosorption kinetics in the removal of zinc (Zn) ion and ferum (Fe) ions from domestic wastewater. FTIR spectrum confirmed the involvement of nitro compounds, as well as carbonyl and amine groups in the biosorption process. It was reported that the isothermal data could be well described by the Langmuir equation, and the dynamical data fitted well with the pseudo-second order kinetic model. The removal of metallic pollutants from wastewater with fish scales was reported by Villanueva-Espinosa *et al.* (2001) and Mustafiz *et al.* (2003) who respectively used *Oreochromis niloticus* (Mojarra tilapia) and Atlantic cod scales in their studies.

Adediran *et al.* (2007) investigated the adsorption of Pb and other divalent ions (Cd, Zn, Cu and Hg) on formaldehyde and pyridine modified bean husks. The study reported that formaldehyde modified bean husks could be employed in the removal of Pb (II) ions from industrial effluent, especially in the battery manufacturing, paints and dyes industries.

Guyo & Moyo (2017) studied the use of acid pre-treated cowpea pod (*Vigna unguiculata*) biomass for removal of Pb (II) ions from aqueous solution. The optimum conditions recorded for the biosorption of lead (II) ions were pH 6.0, contact time 30 min and dosage concentration of 3 g L^{-1}. The biosorption data were best described by the Langmuir isotherm model. The biosorption kinetics followed the pseudo-second order model. The thermodynamics data showed that the adsorption of lead (II) ions onto cowpea pod was endothermic.

Limited studies have used white croaker FS and bean husk (BH) for the adsorption of metals from wastewater. These adsorbent materials are available in abundance as agricultural waste/agri-food by-products, hence the need for the beneficiation/valorization of such waste materials; also, the utilization of the different functional groups present on the surface of the biosorbent, such as amino, carboxylic, ester, hydroxyl, phenolic, phosphate and sulfhydryl to interact with the Pb (II) ions in aqueous solution. In this study, therefore, we set out to quantify and compare the adsorption

capacity of FS and BH for the removal of lead ions from aqueous solution in a batch process. The effect of solution pH, biosorbent dose, initial metal ion concentrations, contact time and temperature were investigated. Kinetic data were analysed with pseudo-first order and pseudo-second order models. The equilibrium parameters were analysed with three of the parameters: Freundlich, Langmuir, and Temkin isotherm models. The thermodynamic equilibrium model was used to estimate changes in standard free energy (ΔG^o), enthalpy (ΔH^o) and entropy (ΔS^o) for the biosorption processes.

MATERIALS AND METHODS

Preparation of biosorbent and the chemicals

The white croaker FS were obtained from a fish merchant while BH was obtained from a popular Alaba Rago market, both locations in Lagos, Nigeria. The fish scales were washed with distilled water and air dried for about 10 days, and stones, dirt and stalks were removed by hand from the BH. Both adsorbents were pulverized with a stainless steel grinder and sieved through a 2 mm mesh. They were separately stored in airtight containers.

The Pb (II) ions aqueous solution was prepared from $Pb(NO_3)_2$ salt. About 1.615 g of $Pb(NO_3)_2$ was used to prepare 1,000 mg/L lead stock solution while about two drops of concentrated nitric acid were added to the solution before making it up with distilled water in 1,000 mL volumetric flasks. The pH of solutions was 3.00. The reagents (lead nitrate, sodium hydroxide, hydrochloric acid and nitric acid) were purchased from Sigma Aldrich, South Africa.

Characterization of the adsorbents and analytical procedure

The dried FS and BH were characterized with various physicochemical techniques such as FTIR, thermogravimetric analysis (TGA), and surface morphology of the material was analysed using scanning electron microscopy (SEM) and X-ray diffraction (XRD). FTIR spectra were recorded from 400 to 4,000 cm^{-1} (Perkin Elmer 400 FT-IR spectrophotometer). The concentrations of Pb (II) ions in the solutions before and after adsorption were determined using an inductive coupled optical emission spectrophotometer ICP/OES (Varian 710 ES model). The samples were filtered with 0.45 µm filter paper prior to analysis in order to obtain a clear solution and also to minimize interference of the biosorbent with the analysis.

Experiment for the batch adsorption procedure

Fifty mL aqueous solutions with known concentration of Pb (II) ions were measured into a predetermined amount of biosorbent in Erlenmeyer flasks which were then placed in an orbital shaker for about 120 min. The effects of pH, biosorbent dosage, initial metal concentration, contact time and temperature on the removal of Pb (II) ions was studied. Sample solutions were withdrawn at intervals to determine the residual Pb (II) ions concentration by using ICP/OES Varian 710 ES model. The percentage of Pb (II) ions removal was obtained with Equation (1) and the amount of Pb (II) ions adsorbed (mg/g biosorbent) was calculated using Equation (2):

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

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

where C_o and C_e (mgL^{-1}) are the initial and equilibrium concentration in the liquid-phase of the Pb (II) ions solution. V (mL) is the volume of the solution, W (g) is the mass of absorbent used and q_e ($mg\,g^{-1}$) is the amount adsorbed.

Effect of pH

The study of the effect of pH on the biosorption was carried out at initial pH range between 1 and 8 using 50 mg/L of the Pb (II) ions initial concentration solution and a 0.5 g biosorbent dosage. The pH was adjusted with 0.1 M HCl or 0.1 M NaOH and measured using a pH meter. Shaking was performed at 25 °C on an orbital shaker at 200 rpm for 120 min. The samples were filtered using 0.45 µm filter paper and the filtrate was analysed for residual Pb (II) ions.

Effect of biosorbent dosage

The effect of biosorbent dosages was investigated for the removal of Pb (II) ions from 50 mg/L solution at different

biosorbent doses ranging from 0.1 to 2.0 g. The Erlenmeyer flasks containing the Pb (II) ions solutions at the optimum pH of the same initial concentration (50 mg/L) and temperature (25 °C) but different biosorbent mass were placed on an orbital shaker at 200 rpm for 120 min. The samples were filtered using 0.45 μm filter paper and the filtrate was analysed for residual Pb (II) ions.

Effects of initial lead concentration and contact time

The effects of initial Pb (II) ions concentration and contact time on the biosorption process were studied with 50 mL Pb (II) ions solutions with initial concentrations ranging from 5 to 100 mg/L in a series of Erlenmeyer flasks with the optimal amount of both biosorbents (0.2 g) and pH (6.0 for FS and 7.0 for BH) on an orbital shaker at 200 rpm for 120 min. The contact time was investigated at varied times between 10 and 180 min at optimal pH, dosage and concentration. The samples were filtered using 0.45 μm filter paper and the filtrate was analysed for residual Pb (II) ions.

Effect of temperature

The effect of temperature was investigated at a range between 293 and 333 K at optimal pH, biosorbent dosage, concentration and contact time.

Adsorption isotherm models

The initial Pb (II) ions concentration provides information on either the adsorption of metal ions on the biosorbent surface that occurs through formation of a monolayer or multilayers, or gas adsorption. Langmuir isotherm type II (Langmuir 1916) was adopted, which describes the monolayer while multilayer adsorption is described by the Freundlich isotherm (Freundlich 1906). The Langmuir isotherm is based on the theoretical principle that only a single adsorption layer exists on an adsorbent. The linear form of the Langmuir model type II is presented in Equation (3):

$$\frac{1}{q_e} = \frac{1}{q_m K_L C_e} + \frac{1}{q_m} \tag{3}$$

where C_e is the equilibrium concentration of the Pb (II) solution (mg/L), q_e is the amount of Pb (II) ions adsorbed per unit mass of the biosorbent (mg/g), q_m is the Langmuir constant representing adsorption capacity (mg/g), and K_L is the Langmuir constant representing energy of adsorption (L/mg). A plot of $\frac{1}{q_e}$ versus $\frac{1}{C_e}$ is linear for a sorption process obeying the basis of this equation with K_L and q_m obtained from the slope and intercept, respectively.

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor R_L that is given by Equation (4):

$$R_L = \frac{1}{1 + K_L C_o} \tag{4}$$

where K_L is the Langmuir constant and C_o is the initial concentration of Pb (II) ions. The value of R_L indicates the shape of the isotherm to be either unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$).

The Freundlich isotherm assumes that the Pb (II) uptake occurs on a heterogeneous surface by multilayer adsorption and that the amount of the adsorbed metal increases infinitely with an increase in Pb (II) concentration. The linear form of the Freundlich equation is written as Equation (5):

$$\log_{10} q_e = \log K_F + \frac{1}{n} \log C_e \tag{5}$$

where C_e is the equilibrium concentration of Pb (II) ions solution (mg/L), q_e is the amount of Pb (II) adsorbed per unit mass of biosorbent (mg/g), n is the number of layers, and K_F is the Freundlich constant. For a sorption process obeying the Freundlich isotherm, the plot of $\log_{10} q_e$ versus $\log_{10} C_e$ is linear with K_F and n obtained from the intercept and slope, respectively.

The Temkin isotherm (Temkin & Pyzhev 1940) contains a factor that clearly taking into the account of adsorbent–adsorbate interactions:

$$q_e = B \log_{10} A + B \log_{10} C_e \tag{6}$$

where $B = RT/b$ (mg/g) represents heat of adsorption, T is the absolute temperature in Kelvin and R is the universal

gas constant, 1/b indicates the adsorption potential of the adsorbent, while A (L/mg) is the equilibrium binding constant corresponding to the maximum binding energy. The plot of q_e versus log C_e enables the determination of isotherm constants A and B.

Adsorption kinetics studies/models

The mechanism of adsorption process was studied. The Lagergren pseudo-first order (Ho & McKay 1998) and pseudo-second order (Ho & McKay 1999) models were applied to describe the kinetics of biosorption of Pb (II) during the process.

The Lagergren pseudo-first order kinetic model is presented by Equation (7):

$$\log_{10}(q_e - q_t) = \log q_e + \frac{k_1}{2.303}t \tag{7}$$

where q_e and q_t are the amounts of the Pb (II) ions adsorbed (mg/g) at equilibrium and at time t (min), respectively, k_1 is the adsorption rate constant (1/min), and t is the time (min). A linear plot of $\log_{10}(q_e - q_t)$ versus t gives the equilibrium adsorption capacity q_e (mg/g) as intercept while the slope gives the pseudo-first order rate constant k_1.

The linear form of the Lagergren pseudo-second order kinetic model as described by Ho & McKay (1999) is given in Equation (8):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \tag{8}$$

where q_e and q_t are the sorption capacity (mg/g) at equilibrium and at time t, respectively and k_2 is the pseudo-second order rate constant (g/mg.min). A linear plot of $\frac{t}{q_t}$ versus t gives the slope as equilibrium adsorption capacity, q_e (mg/g), and the intercept pseudo-second order rate constant k_2.

Thermodynamics of the adsorption process

The thermodynamics provide general information about the influence of temperature on adsorption and is, importantly,

useful to predict the feasibility of the adsorption process. The thermodynamics parameters: standard free energy (ΔG^o), enthalpy (ΔH^o) and entropy (ΔS^o) were calculated from the Gibb's free energy (Sujana *et al.* 2009) and Van't Hoff (Krishna *et al.* 2000; Albadarina *et al.* 2012) using the following Equations (9)–(12):

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

$$K = \frac{C_o - C_e}{C_e} \tag{10}$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{11}$$

$$\log_{10} K = \frac{-\Delta H}{2.303RT} + \frac{\Delta S^0}{2.303R} \tag{12}$$

where $C_o - C_e$ (mg/L) is the concentration after Pb (II) ions adsorption and C_e (mg/g) is the equilibrium concentration ΔH^o and ΔS^o are deduced from the slope and intercept of a plot of log K versus $\frac{1}{T}$; R is the gas constant (8.3142 J/mol/K) and T is the temperature in Kelvin.

Application of the adsorbents for the treatment of real textile wastewater

The efficiency of the biosorbents (BH and FS) for the treatment of real textile effluent was verified. 0.200 g each of the adsorbents was added to 50 mL of the textile effluent in an Erlenmeyer flask and placed on an orbital shaker for the optimum time obtained in the course of the batch process at 200 rpm. The resulting solutions were filtered using 0.45 µm filter paper and the filtrate digested in accordance with the standard method (American Public Health Association (APHA 2017)) for determining metals in industrial effluents. The real textile effluent was digested without using the adsorbent to ascertain the actual level of the Pb (II) ions.

RESULTS AND DISCUSSION

Characterization of the adsorbent

The presence of functional groups on the surface of the biosorbents was confirmed using FTIR, as shown in
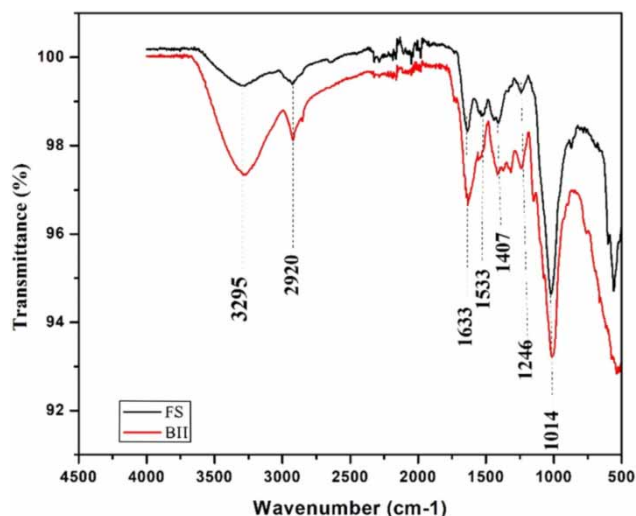
Figure 1 │ The FTIR of the fish scale and bean husk.

Figure 1. FTIR spectra for the FS and the BH showed a similar broad band between 3,200 and 3,400 cm^{-1} which is attributed to the stretching of hydroxyl groups, 2,914 cm^{-1} attributed to CH stretching, 1,315–1,411 cm^{-1} attributed to the aromatic vibration, and 1,009 is due to CH$_3$ stretching. Similar spectra were observed in the FTIR characterization and optimization of Pb (II) biosorption by fish (*Labeo rohita*) scales studied by Nadeem *et al.* (2008) and cowpea pod (*Vigna unguiculata*) biomass for removal of Pb (II) ions from aqueous solution (Guyo &

Moyo 2017). The amide I and amide II stretches at 1,631 and 1,536 cm^{-1} are present in the FS spectra but not in the BH spectra.

The TGA and DTG graphs for the FS and BH are shown in Figure 2. The FS is thermally stable at 330 °C, compared to BH at 270 °C. The DTG graph of FS shows two endothermic peaks at 95 °C and 340 °C, however, BH shows three endothermic peaks at 95 °C, 230 °C and 320 °C.

The SEM images of the FS and BH are shown in Figure 3. The micrographs show that both samples are irregularly spherical in shape with the FS exhibiting agglomeration while the BH is loosely packed. Results similar to this were reported in previous studies (Mondal *et al.* 2012; Hidayati *et al.* 2013).

The XRD patterns for the BH and FS are shown in Figure 4. The FS exhibits more characteristic peaks than the BH. The major characteristic peak value for FS appears at $2\theta = 32$ while for BH the major peaks appear at $2\theta = 22$ and 38. Similar results were recorded by Mondal *et al.* (2012) in the characterization of hydroxyapatite biomaterials from different biowastes. The peak at 32 for the FS shows that it contains hydroxyapatite, a calcium apatite mineral (Ca$_{10}$(PO$_4$)$_6$(OH)$_2$), while BH does not contain noticeable hydroxyapatite. The major peaks at $2\theta = 22$ and 38 in the BH signify the present of cellulosic compound.
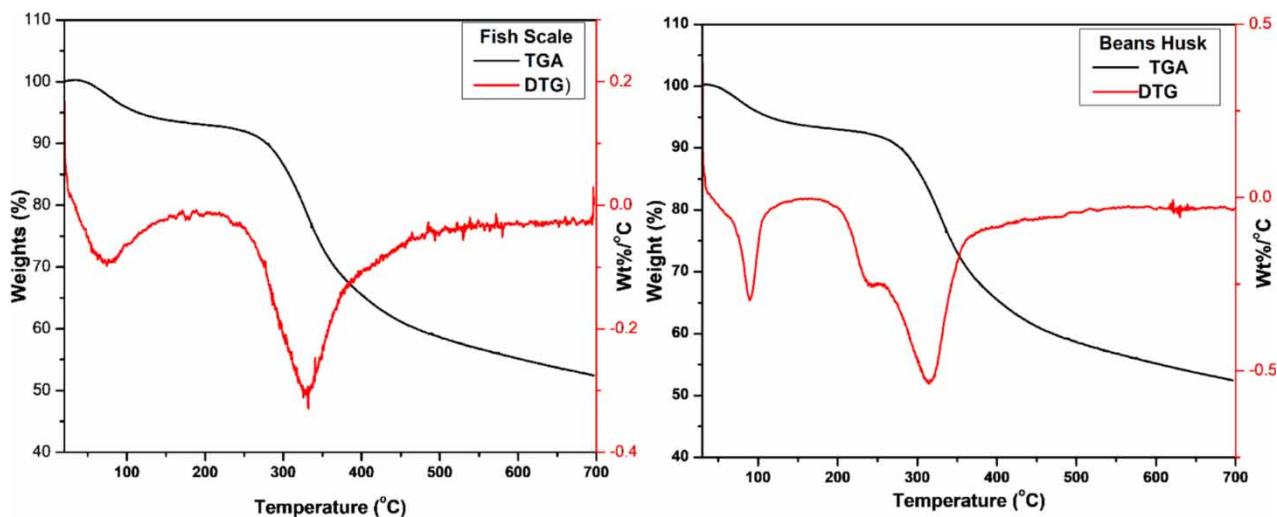

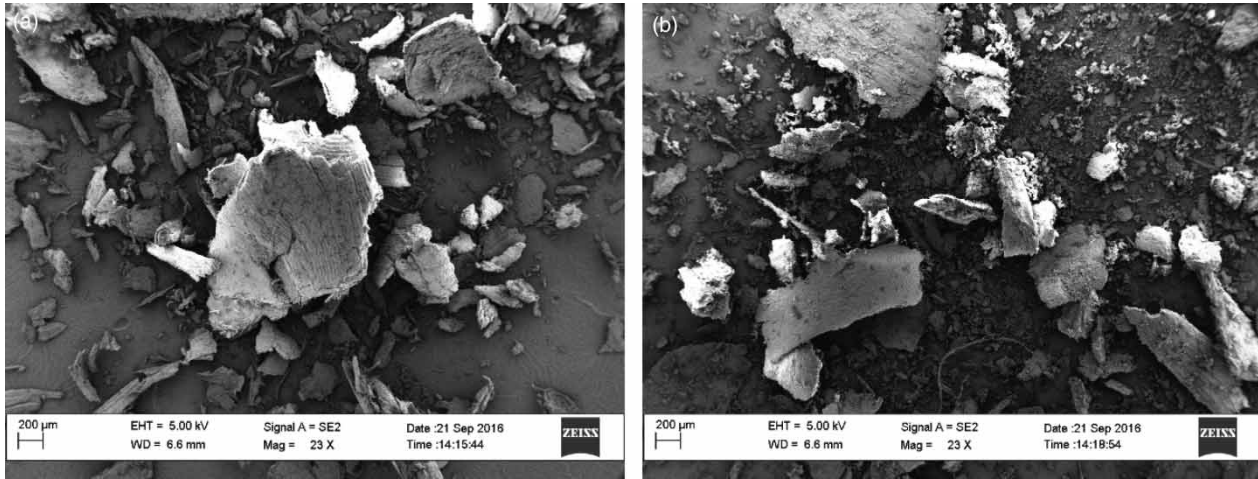**Figure 2** │ The TGA and DTG of the fish scale and bean husk.

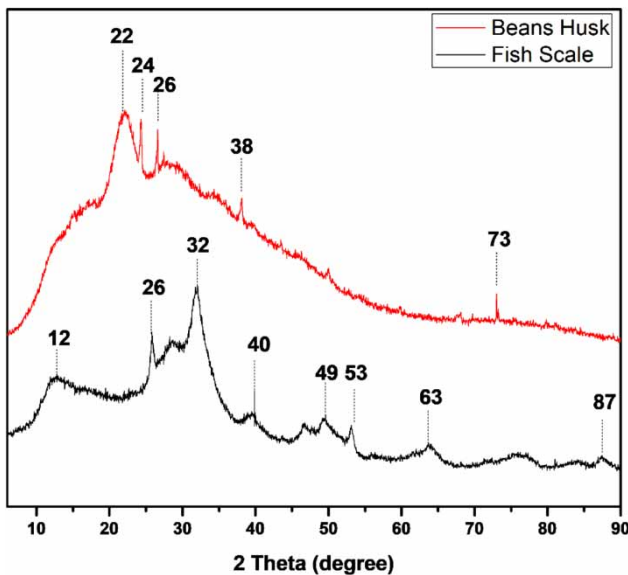**Figure 3** │ The SEM micrographs of (a) fish scale and (b) bean husk.

Figure 4 │ XRD of the fish scale and bean husk.

Batch equilibrium studies

Effect of pH

The adsorption of Pb (II) ions in FS and BH experiments were carried out at the pH range of 1.0–8.0. The changes in the adsorbate pH had significant effects on the surface functional groups of the adsorbent as well as the Pb (II) ions present in the solution, indicating pH is an important parameter in controlling the adsorption (Flaviane *et al.*

2010). The effect of pH on the percentage of Pb (II) ions adsorbed by FS and BH is shown in Figure 5. It is observed that a gradual rise in the adsorption of the Pb (II) ions took place with the increase in pH from 1.0 to 8.0. The lower removal efficiency at low pH may be a result of the positive charge dominating the biosorbent surface as protonation causes repulsion of the Pb (II) ions. The removal of Pb (II) ions increases gradually as pH increases from 1 to 6 and 1 to 7 for FS and BH, respectively. This may be attributed to a reduction in the competition between the H^+ ions and the Pb (II) ions in the solution for the adsorbent sites (Vukovic *et al.* 2011). The highest percentage removal was observed at pH 6 and 7 for FS and BH, respectively.

Similar optimum pH was observed in the study carried out by Zayadi & Othman (2013) in lead ions biosorption using tilapia fish scales; however, Guyo & Moyo (2017)
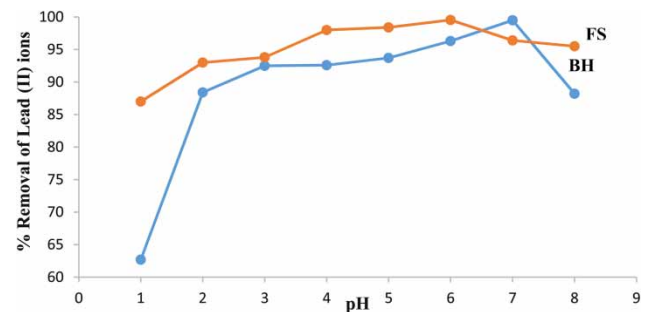

Figure 5 │ Effect of pH on the removal of Pb (II) ions onto fish scale and bean husk.

reported pH 6 as the optimum pH for acid pre-treated cowpea pod.

Effect of adsorbent dosage

The effects of FS and BH biosorbent dosage against the percentage of Pb (II) ions removed from solution is shown in Figure 6. The results show that as the adsorbent dosage was increased from 0.05 to 2.0 g, the Pb (II) ions removal increased from 97.1 to 99.9% for FS and 72.1 to 92% for BH. The range of the mass of the adsorbent was used to establish the optimum biosorbent dosage. The increase in adsorption with adsorbent dose could be attributed to increased adsorbent surface area and availability of more adsorption sites (Alshameri *et al.* 2014; Shaban *et al.* 2018). However, there was no significant increase in the percentage removal for both adsorbents after the 0.2 g dosage. This may be attributed to particle interactions, such as the aggregation or overlapping of active surface area of the adsorbent available to the Pb (II) ions and/or an increase in diffusion paths (Kakavandi *et al.* 2015). 0.2 g of each of the adsorbents were used for further experiments.

Effects of initial lead concentration and contact time

The adsorbate concentration and the contact time between adsorbent and adsorbate species play an important role in the removal of pollutants from water and wastewater. The effect of initial Pb (II) ions concentration on the adsorption process is shown in Figure 7. It was observed that as the concentration increases the percentage adsorption increased.
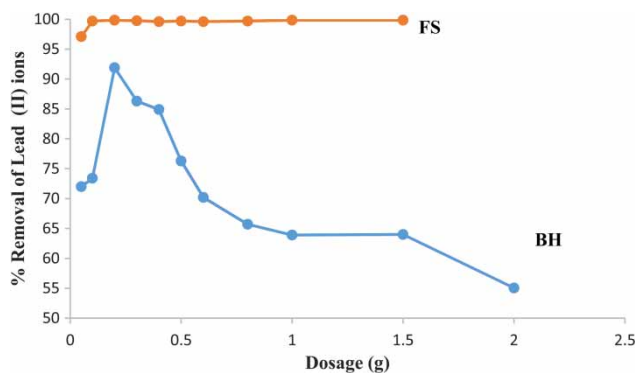

Figure 6 | Effect of dosage on the removal of Pb (II) ions onto fish scale and bean husk.
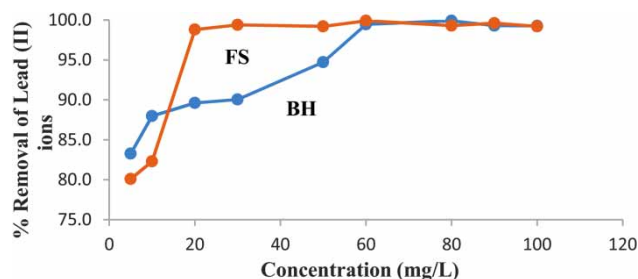

Figure 7 | Effect of initial concentration on the removal of Pb (II) ions onto fish scale and bean husk.

However, it becomes almost constant/steady after 60 mg/L and 80 mg/L for FS and BH, respectively.

The effect of contact time on the efficiency of Pb (II) ions adsorption was used to establish the equilibrium time and the adsorption kinetics. The adsorption of Pb (II) ions against time onto the adsorbents is shown in Figure 8. The rate of uptake of the Pb (II) ions on the adsorbents was rapid, from 10 to 30 min, with maximum uptake for FS observed within the first 30 min while BH maximum uptake occurred at 60 min. There was no significant difference in uptake of the Pb (II) ions as shown after 60 min, indicating equilibrium was achieved at that time.

Optimum time was achieved faster in this study when compared with the study carried out by Zayadi & Othman (2013) while the optimum time was reached faster in the work done by Guyo & Moyo (2017), which used acid pre-treated cowpea pod (*Vigna unguiculata*) biomass.

Effect of temperature

The effect of temperature on the adsorption of Pb (II) ions onto FS and BH adsorbents was studied within the range
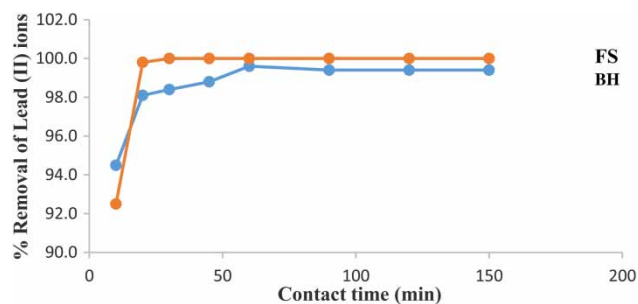

Figure 8 | Effect of contact time on the removal of Pb (II) ions onto fish scale and bean husk.

of 293–338 K, shown in Figure 9(a) and 9(b). It was observed that the adsorption capacity of Pb (II) ions increased with temperature. The maximum adsorption capacity was attained at 321 K (97.5%) and 318 K (93.3%) for FS and BH, respectively, after which, equilibrium was achieved. The results were applied in the thermodynamic study.

Adsorption isotherm models and kinetic studies

The equilibrium data were analysed using Langmuir, Freundlich and Temkin equilibrium models (Equations (3)–(6)) in order to obtain the best fitting isotherm. The isotherms are modelled graphically in Figures 10 and 11 and parameters are listed in Table 1. Comparison of coefficients indicates that the Langmuir isotherm fitted more precisely

($R^2 = 0.898$) than the Freundlich ($R^2 = 0.148$) and the Temkin isotherms ($R^2 = 0.0309$) for BH. The Temkin isotherm fitted best for FS with value (0.520) compared to the Freundlich ($R^2 = 0.228$) and the Langmuir isotherms ($R^2 = 0.07$). The low R^2 value for the FS Temkin isotherm shows the low efficiency in the adsorption capacity of the FS; however, there is a view that if the FS is chemically treated before it is used for adsorption of Pb (II) ions, this might improve the adsorption capacity. The basic assumption of the Langmuir adsorption isotherm is based on monolayer coverage of the adsorbate on the surface of adsorbent (Nadeem *et al.* 2006; Singh *et al.* 2006) which is an indication of the fact that the adsorption of Pb (II) ions onto BH generates monolayer formation. In this study, the Langmuir isotherm dimensionless constant separation factor R_L that was obtained lies between
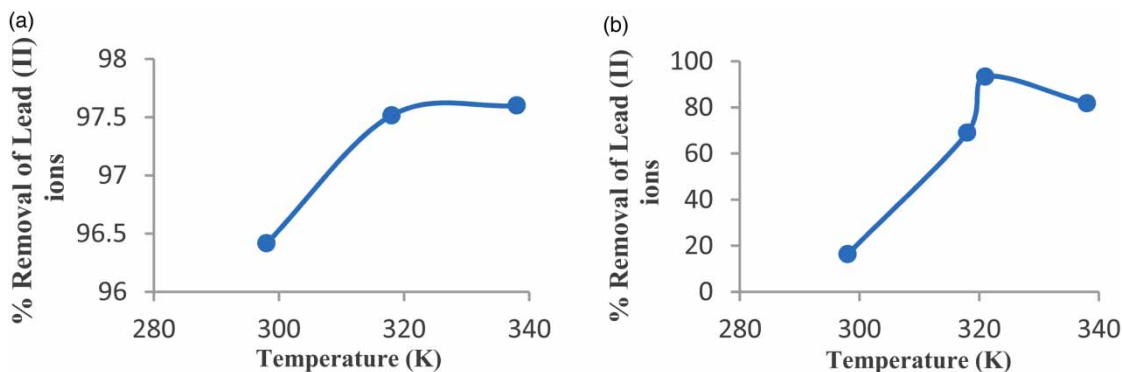
Figure 9 │ Effect of temperature on the removal of Pb (II) ions onto (a) fish scale and (b) bean husk.
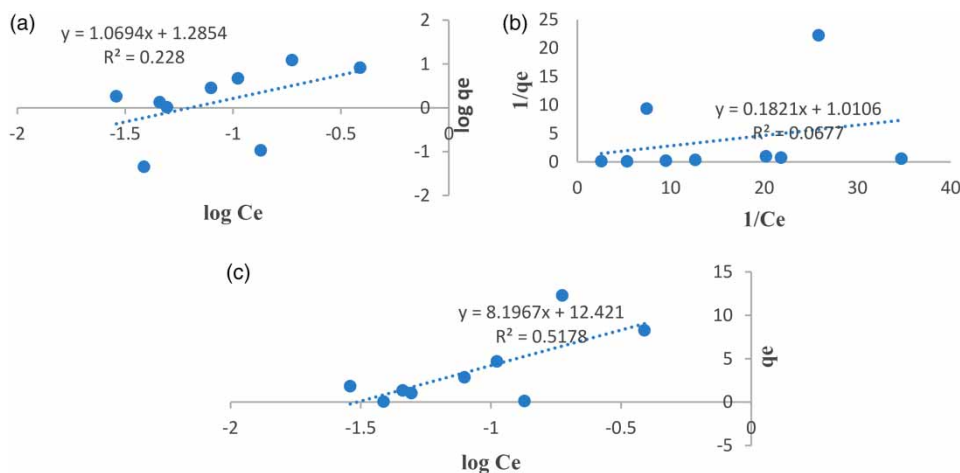
Figure 10 │ Freundlich (a), Langmuir (b) and Temkin (c) adsorption isotherms of Pb (II) ions onto fish scale.
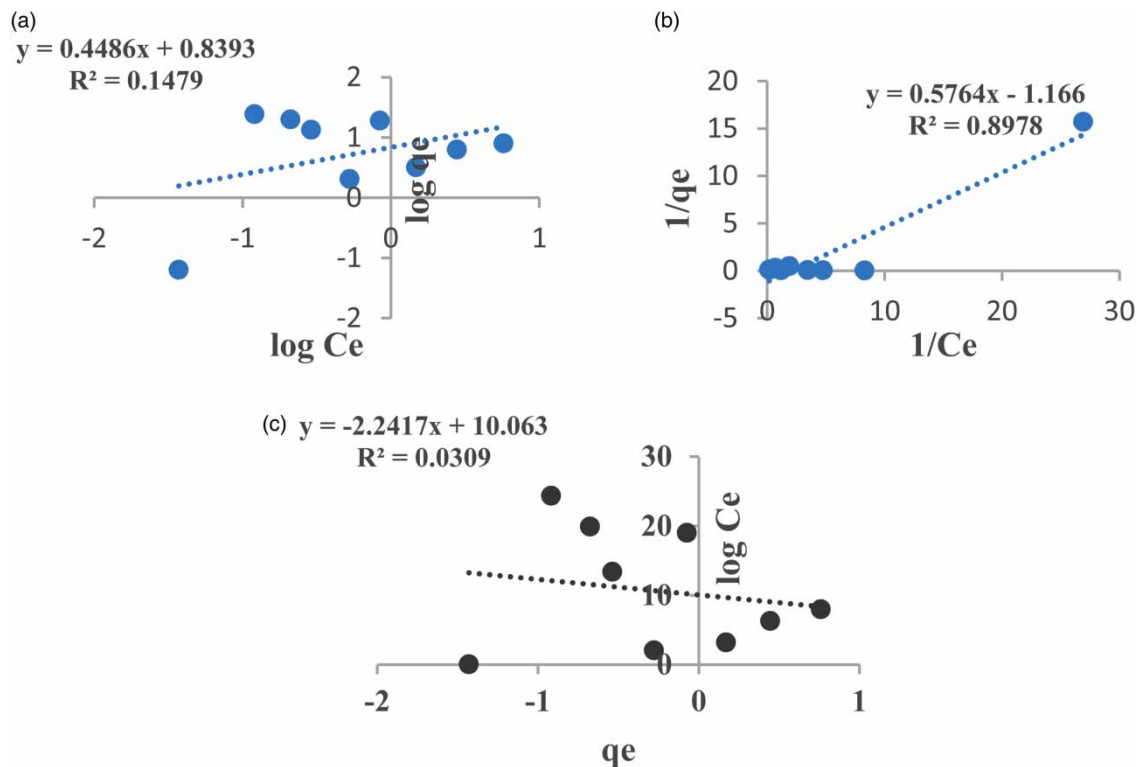
Figure 11 │ Freundlich (a), Langmuir (b) and Temkin (c) adsorption isotherms of Pb (II) ions onto bean husk.

Table 1 │ Isotherm parameters of Pb (II) ions adsorption onto fish scale and bean husk

Freundlich isotherm

Adsorbent	Slope	Intercept	R^2	n	K_F (mgg^{-1}(mg/L)$^{-1/n}$)
Fish scale	1.069	1.285	0.2280	0.935	19.29
Bean husk	0.449	0.89	0.1479	2.23	6.907
Langmuir isotherm					
Adsorbent	Slope	Intercept	R^2	q_m (mgg^{-1})	b (Lmg^{-1})
Fish scale	0.182	1.011	0.0677	0.9895	0.180
Bean husk	0.576	1.166	0.8978	0.858	2.02
Temkin isotherm					
Adsorbent	Slope	Intercept	R^2	B_T (KJ.mol$^-$)	K_T
Fish scale	8.20	12.42	0.5178	0.70	32.7
Bean husk	2.24	10.06	0.0309	3.55	3,100

$(0 < R_L < 1)$, indicating the adsorption process is favourable for the adsorption of Pb ions onto BH.

Various studies have investigated Pb (II) adsorption by different low-cost adsorbents as shown in Table 2. By comparison, it is found that FS and BH are also efficient adsorbents for the removal of Pb (II) ions from water.

The adsorption kinetics were investigated for the contact time of 180 min. The kinetic parameter details of the first order and second order rates are shown in Table 3 and the

Table 2 | Comparison of maximum sorption capacity (q_{max}) for the adsorption of Pb (II) ions with some low-cost adsorbents

| | Experimental conditions | | | |
Adsorbent	pH	°C	q_m (mg/g)	Reference
Bean husk	7	25	0.9895 (99%)	Present study
Fish scale	6	25	0.858 (98%)	Present study
Banana peel	5.5	25	2.18	Anwar et al. (2010)
Bagasse fly ash	6.0	30	2.50	Gupta & Ali (2004)
Rice bran	5	25 ± 1	n.d.	Montanher et al. (2005)
Fluted pumpkin	5	Nd	9.54	Horsfall & Spiff (2005)
Sugar beet pulp	4	20 ± 0.5	50	Gérente et al. (2000)
Sugar beet pulp	5.5	20.0 ± 0.5	73.76	Reddad et al. (2002)
Black gram husk	5	25 ± 2	49.97	Saeed et al. (2005b)
Grape stalks	5.5	25	49.93	Martínez et al. (2006)
Pinus sylvestris sawdust	4	20.5 ± 0.5	15.77	Taty-Costodes et al. (2003)

Table 3 | Kinetic parameters of Pb (II) ions adsorption onto fish scale and bean husk

| | Pseudo-first order | | | Pseudo-second order | | | |
Adsorbent	K_1 (min^{-1})	q_e (mgg^{-1})	R^2	K_2 (gmg^{-1} min^{-1})	q_e (mgg^{-1})	q_{cal} (mgg^{-1})	R^2
Fish scale	0.0343	0.015	0.3539	0.4577	11.507	11.510	1
Bean husk	0.4284	0.428	0.3383	0.1974	12.658	12.660	0.9999

pseudo-second order graph is shown in Figure 12. The pseudo-second order kinetic model best fitted the kinetic data for both FS and BH with R^2 of 1.00 and 0.9999, respectively. The experimental adsorption capacity q_e, for FS and BH (11.493 and 12.64 mg/g, respectively) was close to the calculated q_e, 11.51 and 12.66 mg/g. This suggests high

correlation of adsorption of Pb (II) ions by the adsorbents to the pseudo-second order model. This further indicates/confirms that in the adsorption process, concentrations of both adsorbate (Pb (II) ions) and adsorbents (FS and BH) are involved in the rate determining step, which may be chemisorption (Ho & McKay 1998; Rao et al. 2008).
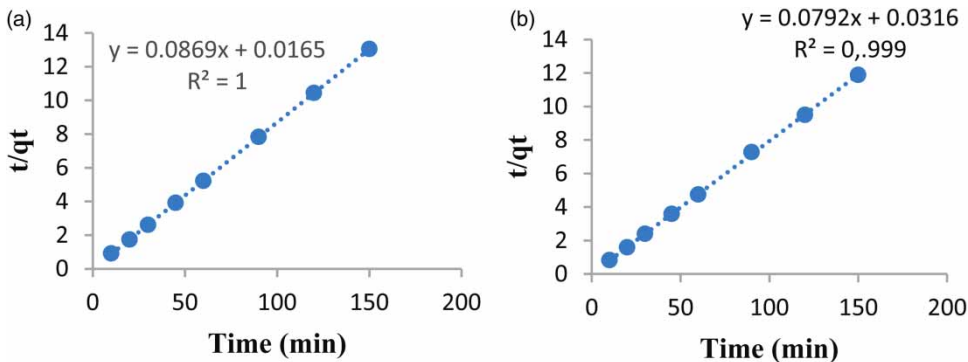
Figure 12 | Pseudo-second order kinetic model for adsorption of Pb (II) ions onto (a) fish scale and (b) bean husk.
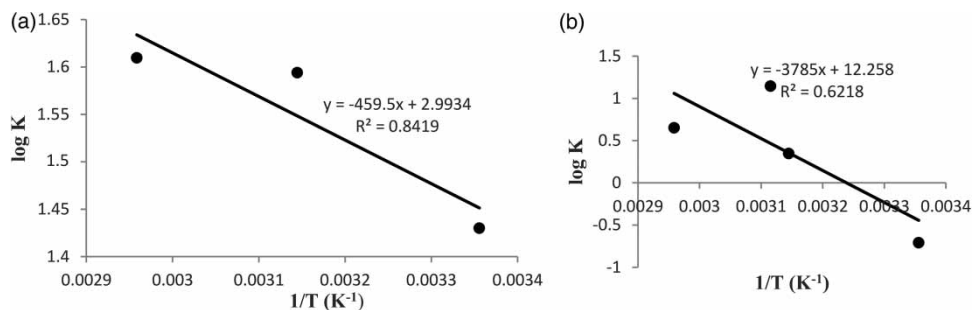
Figure 13 | Van't Hoff plot on the adsorption of Pb (II) ions onto (a) fish scale and (b) bean husk.

Adsorption thermodynamic

The effect of heat of adsorption of the adsorbate onto the adsorbent material was determined using the thermodynamic parameters: free energy change (ΔG^o), enthalpy change (ΔH^o) and entropy change (ΔS^o), and was calculated using the Van Hoff's Equations (9)–(12).

The Van't Hoff plot for the adsorption of Pb (II) ions onto FS and BH is shown in Figure 13. The standard free energy (ΔG^o), enthalpy (ΔH^o) and entropy (ΔS^o) changes for BH and FS were obtained using equilibrium constant K and the data are given in Table 4.

The positive values of ΔH show that the adsorption process is endothermic, while a positive ΔS indicates increased randomness in the interface between adsorbent and adsorbate (solid-solution). Moreover, the negative value of free energy change (ΔG^o) shows that the adsorption process is spontaneous at high temperature, and has good feasibility for Pb (II) ions adsorption onto FS and BH.

Table 4 | Thermodynamic parameters of Pb (II) ions adsorption onto fish scale and bean husk

T(K)	ΔH^o (KJ/mol)	ΔS^o (J/mol K)	ΔG^o (J/mol)	K
Fish scale				
298			−8,159.7	26.9
318	8.8	57.3	−9,706.1	39.3
338			−10,417.4	40.7
Bean husk				
298			1,119.5	0.2
318	72.5 kJ	234.7	−587.6	2.2
321			−1,950.2	14.0
338			−1,168.8	4.5

Treatment of real textile effluent with the adsorbents

The adsorbents were used to treat textile wastewater with initial Pb ions concentration of 2.77 mg/L. The treatment reduced the Pb (II) ions by 95.0% and 98.2% for FS and BH, respectively.

CONCLUSION

In the present study, the capacity of FS and BH to remove Pb (II) ions was investigated. Experimental results showed that the removal of Pb (II) ions increases with increase in pH, initial concentration, contact time and temperature for both biosorbents, but decreases with increase in the dosage for BH. The dosage effect for FS assumed a plateau after a certain amount of the dose was used. The adsorption obeyed the Langmuir model for the BH adsorbent and Temkin model for the FS, while the adsorption kinetics followed the pseudo-second order equation for both. Furthermore, the thermodynamics parameters obtained indicated the adsorption process is endothermic and spontaneous. Both adsorbents effectively removed about 90% of the lead ions in textile wastewater. The study has shown that the adsorbents can serve as a cost-effective alternative adsorbent for the removal of toxic metals, especially Pb (II) effluents, before being discharged into the environment.

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