Attenuation Kinetics and Desorption Performance of *artocarpus altilis* Seed Husk for Co (II), Pb (II) and Zn (II) Ions

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ABSTRACT: *The potential of Bread Fruit (artocarpus altilis) Seed Husk (BFSH) as low-cost biosorbent for the removal of Pb (II), Zn (II) and Co (II) ions from aqueous solution was investigated. The adsorbent was characterized by the Fourier Transform InfraRed (FT-IR) spectroscopy, Scanning Electron Microscopy (SEM) and X-Ray Diffraction (XRD). The batch methodology was utilized to determine the effect of pH, metal ion concentration, adsorbent dose, contact time and temperature on biosorption. Data generated were fitted into appropriate isotherm, kinetic and thermodynamic models. The effect of pH showed an increase in adsorption of metals with an increase in pH and an optimum pH of 5.0 was obtained for Pb (II), while 6.0 were obtained for Co (II) and Zn (II) ions biosorption. An equilibrium sorption contact time of 30, 40 and 60 min was obtained for Co (II), Zn (II) and Pb (II) ions respectively. The biosorption of metal ions was in the order Co (II) > Pb (II) > Zn (II). In general, the Freundlich model provided a better fit than the Langmuir, Tempkin, and Dubinin-Radushkevich isotherm models with R^2 values greater than 0.9. The pseudo-first-order kinetic model was applicable in the adsorption of Pb (II) and Zn (II) ions while the pseudo-second-order model provided the best fit for Co (II) ion adsorption. The adsorption mechanism was found to be controlled by the liquid film diffusion model ($R^2>0.9$) rather than the intraparticle diffusion model ($R^2<0.9$). Thermodynamics revealed a spontaneous, feasible, exothermic physisorption process and over 60% of the metal ions were desorbed using 0.1M HCl and 0.1M NaOH as eluent. The results showed that BFSH could be utilized as low-cost adsorbent for the removal of toxic heavy metals from solution.*

KEYWORDS: *Biomass, Biosorption, Breadfruit, seed husk, heavy metals, isotherm, kinetics*

INTRODUCTION

Metals and their compounds are useful for the industrial, technological and agricultural development of any nation. As a result of increasing development in science and technology, the number of applications

of metals for commercial purposes continues to increase. These industrial processes generate a large number of metallic waste products which are subsequently discharged into wastewaters and land sites. It has been observed that the harmful effect of heavy metals discharged annually into the environment far exceeds the combined total toxicity of all radioactive and organic wastes [1]. This accounts for the reason why the release of heavy metals into the environment has become a problem of great concern over the last few decades. Some of the industrial activities that led to the release of heavy metals into the environment include leather tanning, battery manufacturing, electroplating, metal finishing, steel fabrication, paint production, ceramics, glass, dyes, and paper production. Heavy metals such as lead, cadmium, arsenic, mercury, nickel, chromium, cobalt, zinc and copper are known to be toxic at certain concentrations [2]. The contamination of the environment with lead is mainly due to anthropogenic activities, which makes this metal the most ubiquitous toxic metal in the environment. Lead is non-biodegradable, has the potential to bio-accumulate in the food chain causing human health hazards, when present in high concentrations can damage the brain and nervous system [3]. The assimilation of relatively small amounts of lead in humans can lead to chronic toxicity and malfunctioning of the organs. Lead is also an enzyme inhibitor, general metabolic poison and affects the functioning of the blood, liver, and kidney. Exposure to cobalt may cause weight loss, dermatitis, bleeding, vomiting, sterility, hair loss, coma, respiratory hypersensitivity and even death [4]. Similarly, although small amounts of zinc are necessary for the normal development of the biological cycle, long term ingestion of zinc contaminated drinking water causes skin, lungs and kidney cancer, gastrointestinal disease, bone marrow disorder, cardiovascular diseases and other diseases [1].

Due to the magnitude of the problem resulting from these metals pollution, researches on the removal of these metals from effluents have become a dominant topic for an environmental scientist. The traditional techniques which have been used for the removal of heavy metals from industrial wastewaters include chemical precipitation and filtration, chemical oxidation or reduction, electrochemical treatment, reverse osmosis, solvent extraction, ion-exchange and evaporation [5]. These techniques have the disadvantages of high cost, low selectivity, incomplete metal recovery, high energy requirement, difficult to apply and the generation of toxic slurries which are difficult to dispose of [6].

Adsorption has been discovered to be one of the most effective methods for the removal of these toxic metals from aqueous solution due to its high efficiency, low cost of maintenance and very easy to apply. Activated carbon is the most widely used adsorbent, it has a high adsorption capacity and surface area but has the disadvantage of high cost, and this limits its application to small scale industries and developing nations [2]. As a result, a search for cheaper alternative adsorbents has become a major area of interest for researchers. A good number of researchers have made use of low-cost adsorbent materials for adsorption of pollutants [3, 5, 7- 10].

There is an abundance of Bread Fruit Seed Husk (BFSH) deposit in Nigeria. The waste from this material usually, constitute a nuisance to the environment or serve as a source of energy for burning purposes. Despite a wide variety of agricultural waste biomass utilized for the removal of heavy metals, there is limited information on the use of BFSH for the biosorption of Pb (II), Co (II) and Zn (II) ions. In the search for cheaper biomass materials for the adsorption of heavy metals from effluent, this study, therefore, investigates the potential of BFSH as low-cost materials for the removal of these heavy metals from solution. The effect of various experimental factors such as pH, metal concentration, adsorbent dose and contact time were investigated. Equilibrium and kinetic models were applied in order to help understand the adsorption mechanism.

EXPERIMENTAL SECTION
Adsorbate Preparation

All the chemicals used in the study were of analytical grade and were used without further purification. A laboratory solution of cobalt (II), lead (II) and zinc (II) ions were prepared by dissolving appropriate amounts of $Co(NO_3)_2$, $Pb(NO_3)_2$ and $Zn(NO_3)_2$, respectively in 50 mL of de-ionized water in a beaker and stirred properly with a glass, rod to ensure proper dissolution. Thereafter the 50mL solution was then placed in a 1 Liter volumetric flask and made up to the meniscus mark with de-ionized water to obtain the stock solution of concentration 1000 mg/L of each metal ion. Several lower

concentrations of the metal ions which include 200, 400, 600, and 800 mg/L were then prepared from the stock solution by serial dilution using de-ionized water.

Preparation of the adsorbent

The Breadfruit was obtained from Ogbete market, Enugu, Nigeria, after which it was sliced and the seeds were removed manually. The seeded were washed with distilled water and then sundried for 21 days after which it was oven dried at 80^{0}C for 2 h to get rid of moisture. The seed husk was then removed manually and sundried further for 14 days after which it was pulverized. The powdered seed husk was then passed through 100 μm mesh sieve to obtain the Bread Fruit Seed Husk (BFSH) adsorbent and was stored in a plastic container until use.

Batch adsorption experiments

The batch adsorption technique was applied to determine the effect of pH (2.0 – 8.0), initial metal ion concentration (200 – 1000 mg/L), adsorbent dose (0.1 – 0.5 g), contact time (5 – 120 min) and temperature (300 – 323K) on the biosorption of Co (II), Pb (II) and Zn (II) ions on BFSH. This was carried out by adding 0.1 g of BFSH to 20 mL of 400 mg/L concentration of metal ions solution in a pretreated bottle, which was placed in a thermostated water bath for temperature regulation when the effect of temperature was studied. To investigate the effect of a particular parameter, that parameter was varied while others were kept constant at the optimum conditions of pH 5.0 for Pb and 6.0 for Co and Zn, contact time (120 min) and temperature 300K. At the end of the given contact time for each experiment, the mixture was filtered and the residual metal ions concentration in the filtrate was determined by the Atomic Absorption Spectrophotometer (AAS) (Buck Scientific Model 210VGP). Each experiment was performed twice and the mean value was computed in order to ensure quality assurance. The percentage sorption of Co (II), Pb (II) and Zn (II) ions by BFSH and sorption capacity for metal ions were calculated from the equations are given below respectively:

$$\text{adsorption}(\%) = \frac{100[Co - Ce]}{Co} \qquad (1)$$

$$qe(mg/g) = \frac{v[Co - Ce]}{m} \qquad (2)$$

Where *qe* (mg/g) is the adsorption capacity, *Co* (mg/L) is the initial metal ion concentration in solution, *Ce* (mg/L) is the metal ion concentration remaining in solution at equilibrium, *v* (L) represents the volume of solution used for the adsorption and *m* (g) is the mass of the adsorbent used [11].

Desorption studies

Desorption experiment was conducted by contacting 0.2 g of metal loaded BFSH (obtained under optimum biosorption conditions) with 50 mL of 0.1 M HCl (pH 1.4) in 120 mL bottles. The solution was agitated for 60 min then filtered and the concentration of metal ions desorbed infiltrate was checked by the AAS. The procedure was repeated using 0.1M NaOH (pH 12.8) as a desorbing agent. The percentage desorption was then calculated from the equation:

$$\% \text{Desorption} = 100[C_D V_D]/q_e m \qquad (3)$$

Where C_D (mg/L) is the concentration of metal ions desorbed in solution, V_D (L) is the volume of eluent used for desorption, m (g) is the mass of BFSH used for desorption and q_e (mg/g) is the adsorption capacity of the adsorbent for metal ions obtained under optimum biosorption conditions.

Adsorbent characterization

The specific surface area of the adsorbent was determined by the methylene blue absorption test method [12] while pH point of zero charges (pH$_{pzc}$) was obtained by the solid addition method [13]. The moisture content, ash content and volatile matter of BFSH were determined according to ASTM standard [14]. The fixed carbon, pore volume, and bulk density were determined by the method described by *Horsfall et al.* [15]. The Fourier Transform Infrared (FT-IR) spectra of the soil were obtained by the FT-IR spectrophotometer (Shimadzu FT-IR 8400s), while the surface morphology was assessed with the Scanning Electron Microscope (SEM) (Hitachi S4800 model). X-Ray Diffraction (XRD) of BFSH was determined by the model MD 10 Randicon diffractometer operating at 25kv and 20mA.

RESULTS AND DISCUSSION

Initial pH of the solution

The effect of the initial pH of the solution is a very important parameter to be considered in adsorption because it affects the adsorbent surface charge and the degree of specification and ionization of the adsorbate [16]. Heavy metal ions, for example, may form a complex with groups such as OH thereby affecting metal biosorption. The extent of these compounds formation varies with pH, ionic composition and adsorbate ion [17]. Due to the strong influence of pH, its effect on the biosorption of Co (II), Pb (II) and Zn (II) ions on the adsorbents are shown in Fig. 1. An increase in percentage removal with an increase in pH for the metal ions on BFSH was observed. With the increase in pH of the solution from 2.0 to 8.0 an increase in the percentage biosorption of Co (II), Pb (II) and Zn (II) from 5.5 to 66.75%, 4.75 to 63.75% and 4 to 60% was obtained respectively. Therefore, with an increase in pH, the surface of BFSH tends to acquire a negative charge favoring the biosorption of the positively charged ions [6, 11].

It was observed that Pb (II) was adsorbed higher at pH values of 3.0 to 5.0 than Co (II) and Zn (II), also attaining an optimum pH of sorption at 5.0. At pH 5.0, an optimum percentage biosorption of Pb (II) on BFSH was 62%. Optimum biosorption pH for Co (II) and Zn (II) ions was obtained at 6.0. At optimum pH, the trend of metal ions biosorption on BFSH was Co > Pb > Zn ions. The optimum pH of 5.0 was maintained for the removal of Pb (II) and 6.0 for Co (II) and Zn (II) ions in subsequent biosorption experiments in this work. pH 7.0 and 8.0 were avoided despite the slightly higher biosorption recorded at these values. This is because it has been reported that at pH values greater than 6.0 there is the possibility of precipitation of metal ions from solution in the form of insoluble hydroxide. It is, therefore, possible that precipitation may have accounted for some of the metal ion removed at pH values of 7.0 to 8.0. The general increase in biosorption of metal ions on BFSH with an increase in pH can be explained thus; at low pH values, the solution is acidic and has excess H$^+$ ions in solution competing with the positively charged metal ions for the active sites of the adsorbents leading to a decrease in the removal of metal ions [18]. Also, the repulsive forces between the protons and metal ions were greater at lower pH values due to similar charge hindering the sorption of
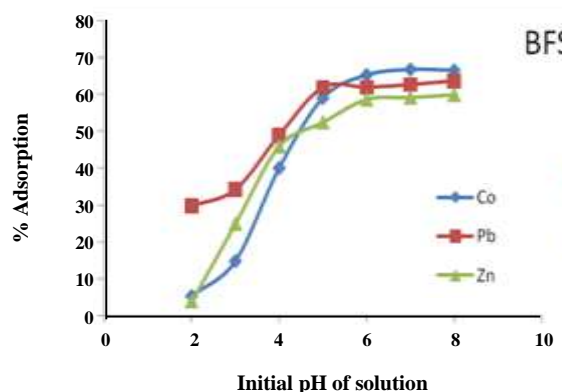

Fig. 1: Effect of initial pH of the solution on the percentage adsorption of metal ions

metal on the surface of BFSH [19]. However, as the pH increases, the solution becomes less acidic and the number of H$^+$ ions in solution decreases, this reduces the repulsive force and competition between the protons and metal ions for the active sites making more sites available for metal biosorption and a higher biosorption obtained [18]. Similar results on the increase in sorption of metal ions with an increase in pH of solution have been reported by many researchers [6, 9, 17, 18].

Initial metal concentration

The amount of metal ion sorbed by an adsorbent depends greatly on the initial concentration of metal ions in solution which makes it an important factor to be considered in sorption study. The effect of the initial concentration of Co (II), Pb (II) and Zn (II) ions on the biosorption capacity of BFSH is shown in Fig. 2. It was observed that an increase in biosorption capacity for the three metal ions with an increase in initial metal ion concentration from 200 – 1000 mg/L was recorded. In fact, the biosorption capacity of BFSH for Co, Pb and Zn ions increased with increase in metal concentration (200 – 1000 mg/L) from 33.8 to 82.8 mg/g, 32.8 to 79.8 mg/g and 31.8 to 74.4 mg/g respectively. The increase in sorption capacity with an increase in initial metal ion concentration recorded is attributed to increasing concentration gradient which acts as a driving force to overcome the resistance to mass transfer of metal ions between the aqueous and solid phase [20]. An increase in initial concentration enhances the interaction between metal ions and the active sites of the adsorbent as a result
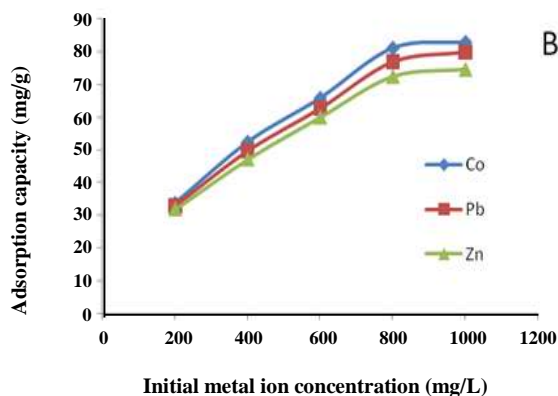
Fig. 2: Effect of initial metal ion concentration on the adsorption capacity of breadfruit seed husk.

Fig. 3: Effect of initial metal ion concentration on the percentage adsorption of metal ions.

of the increase in collision thereby increasing biosorption [21]. In fact, a higher concentration in solution implies higher metal ions fixed at the surface of BFSH and maximum utilization of the active sites [3].

The effect of initial metal ion concentration on the percentage biosorption of Co (II), Pb (II) and Zn (II) ions on BFSH is shown in Fig. 3. It was observed that a decrease in percentage biosorption of all the metal ions on BFSH with an increase in initial metal ion concentration was recorded. With the increase in metal ion concentration from 200 to 1000 mg/L the percentage biosorption of Co (II), Pb (II) and Zn (II) decreased from 84.5 to 41.4%, 82 to 39.9% and 79.5 to 37.2% respectively. The decrease in biosorption with an increase in metal ion concentration is due to the saturation of the active sites on the biomass surface [22]. At lower concentrations, more metal ions would be removed by the abundant active sites on the adsorbent surface but at higher concentrations, more metal ions would be left unadsorbed due to saturation of the active sites [23]. Also, as an increase in metal concentration led to the saturation of the adsorbent surface, most of the metal, adsorption would involve pore diffusion [19]. Furthermore, it was also observed that the trend of metal ion biosorption on BFSH was in the order Co > Pb > Zn ions. Several factors such as the electronegativity of metal ions, ionic radius of the metals, pK$_{OH}$ of the metal hydroxides in solution and the strength of acidity of the metals are known to affect the adsorption of a metal ion relative to another [3]. The trend of adsorption recorded can be explained based on the electronegativity of the metal ions; Co (II) (1.88) > Pb (II) (1.87) > Zn (II) (1.65).
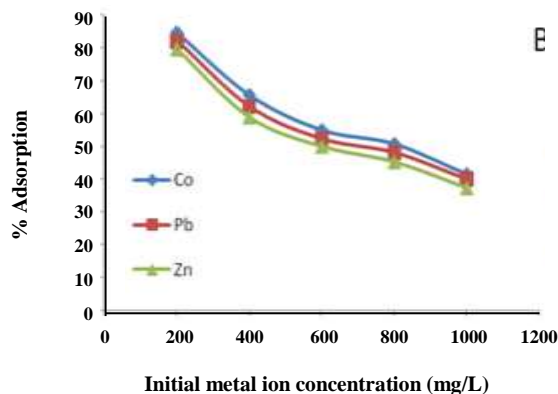
Metals with higher electronegativity tend to be attracted to the surface of the adsorbents i.e to the functional groups containing electrons thus leading to a higher adsorption capacity [19]. Although Co (II) and Pb (II) have close electronegativity, the higher biosorption recorded for Co (II) than Pb (II) ions may be due to the smaller ionic radius of Co (II) (0.74Å) than Pb (II) (1.20Å) which allows for an easy diffusion of Co (II) ions to get to the adsorbent surface than the larger Pb (II) ions [19]. In general, the trend of increase in adsorption capacity and a decrease in percentage removal with an increase in metal ion concentration have been reported by many researchers [10, 11, 22].

Adsorption isotherms

In this work, the Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherm models analysis [10, 24-26] were applied in the biosorption of Co (II), Pb (II) and Zn (II) ions on BFSH. The most suitable isotherm is determined by the linear regression coefficient (R^2). The closer the R^2 value of the model plots to one the best the fit of the model [6].

The Langmuir isotherm refers to homogenous monolayer adsorption represented in its linear form as [27].

$$C_e/q_e = 1/q_L K_L + C_e/q_L \qquad (4)$$

Where q_e (mg/g) is the sorption capacity of the adsorbent, K_L (L/mg) is the Langmuir adsorption constant related to the energy of adsorption, which quantitatively reflects the affinity between the adsorbents and adsorbate,

q_L (mg/g) is the maximum monolayer adsorption capacity of the adsorbents. The Langmuir isotherm parameters obtained for the sorption of metal ions on BFSH are presented in Table 1. It is observed that the values of the linear regression coefficient (R^2) obtained were high and gave good fits to the experimental data (R^2 values < 0.9). The good fit of the Langmuir isotherm suggests that the adsorption process is likely a monolayer one on the homogenous surface of the adsorbents. This, however, can only be verified by comparing the R^2 values of this model with that of the Freundlich model in order to know which best represents the sorption process. However, the essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant or separation factor (R_L) defined by the relationship [28]:

$$R_L = 1/[1 + K_L C_\circ] \qquad (5)$$

Where C_o (mg/L) is the initial metal ion concentration in solution, K_L (L/mg) is the Langmuir equilibrium constant. The value of the separation factor provides important information about the nature of the adsorption process. The adsorption is said to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) and unfavorable ($R_L > 1$) [11]. The values of R_L obtained for the biosorption of Co (II), Pb (II) and Zn (II) on BFSH was in the range 0 to 1. This corresponds to a favorable adsorption process indicating that BFSH is useful and applicable for the removal of toxic heavy metals such as Co (II), Pb (II) and Zn (II) ions from polluted solution.

The Freundlich isotherm describes multilayer heterogeneous adsorption[26, 29]. The linear form of the Freundlich model is given in the equation [30]:

$$\log q_e = \log K_f + [1/n] \log C_e \qquad (6)$$

Where K_f (mg/g) is the Freundlich constant related to the adsorption capacity and n is related to the adsorption intensity of the adsorbents. The isotherm parameters obtained are given in Table 1. It is observed that the Freundlich isotherm also provided a good fit to the adsorption process for the three metal ions on BFSH as R^2 values were all greater than 0.9. Also, comparing the R^2 values obtained from the Langmuir and Freundlich model, it is observed that the Freundlich values were higher and closer to 1 than the Langmuir isotherm model. The better fits presented by the Freundlich model than Langmuir's indicated that the biosorption of metal ions on BFSH is a multilayer one on a heterogeneous surface of the adsorbent and not a monolayer homogenous sorption as suggested earlier when good fits were obtained in the Langmuir isotherm model. Furthermore, if the values of n lie between 1 and 10, it indicates a favorable adsorption process between the adsorbent and adsorbate [22]. The values of n obtained for the adsorption of Co (II), Pb (II) and Zn (II) ions on BFSH as shown in Table 1 showed favorable sorption which corroborated the deduction of Langmuir R_L. This suggested the usefulness of BFSH in the removal of metal ions from solution.

The Temkin isotherm model was applied in its linear form as [31, 32]:

$$q_e = 1 B \ln A + B \ln C_e \qquad (7)$$

Where C_e (mg/L) is the concentration of metal ions at equilibrium, q_e (mg/g) is the number of metal ions adsorbed at equilibrium, $B = RT/b_T$, where T (K) is the absolute temperature, R is the ideal gas constant (8.314 J/molK) and b_T (J/mol) is the Temkin constant. The constant B is related to the heat of adsorption and A (L/mg) is the equilibrium binding constant corresponding to the maximum binding energy. The values of the Tempkin isotherm parameter obtained from the plots are presented in Table 1. The linear regression coefficient (R^2) obtained from the Temkin model for the three metal ions on all the adsorbents were also high and presented good fits ($R^2 > 0.9$). However, all the values were lower than those obtained by the Langmuir and Freundlich isotherm model. The calculated Tempkin heat of adsorption (b_T) was 0.145, 0.144 and 0.152 kJ/mol for Co (II), Pb (II) and Zn (II) ions respectively. These values were less than 20.9 kJ/mol and suggested a physisorption process of metals removal on BFSH [6]. However, these values cannot solely be relied on to arrive at such a conclusion, since the Tempkin model did not provide the best fit for the biosorption process. Therefore a reasonable conclusion was obtained from the values of enthalpy changes (ΔH^0) calculated from thermodynamic parameters.

The Dubinin-Radushkevich (D-R) model does not assume a homogenous surface or a constant sorption potential as the Langmuir model [6, 18, 22,]. The linear form of the D-R isotherm is given in the equation [26, 33]:

$$\ln q_e = \ln q_m + \beta \varepsilon^2 \qquad (8)$$

Table 1: Equilibrium isotherm constants of biosorption of metal ions on BFSH.

Isotherm/Adsorbent	Co (II)	Pb (II)	Zn (II)
Langmuir			
q_L (mg/g)	100	100	90.91
K_L (L/mg)	0.011	0.009	0.009
R^2	0.984	0.981	0.983
Freundlich			
K_F	11.17	9.91	9.27
N	3.13	3.05	3.06
R^2	0.986	0.987	0.985
Tempkin			
B (mg/g)	17.44	17.29	16.34
A (L/g)	0.193	0.157	0.147
R^2	0.958	0.955	0.958
Dubinin-Radushkevich			
qm (mg/g)	70.53	67.29	63.62
B (mol^2/J^2)	0	0	0
R^2	0.786	0.772	0.773

Where q_e (mg/g) is the adsorption capacity, q_m (mg/g) is the theoretical saturation capacity, β (mol^2/J^2) is a constant related to the mean free energy of adsorption per mole of the adsorbate and ε is the Polanyi potential expressed in the equation:

$$\varepsilon = RT \ln \left(1 + 1/C_e \right) \qquad (9)$$

Where C_e (mg/L) is the equilibrium concentration of metal ion in solution, T (K) is the absolute temperature and R is the gas constant (8.314 J/molK). The D-R isotherm parameters obtained from the biosorption are presented in Table 1. The values of the linear regression coefficient (R^2) indicated that this model did not provide a good fit to the adsorption process as all the R^2 values were less than 0.9. This model therefore presented the least fit for the sorption of the three metal ions on BFSH and is therefore not suitable in the description of the mechanism of the process. In general, the best fits presented by the Freundlich isotherm model suggest a multilayer heterogenous adsorption process. This explains why a favorable adsorption process between metal ions and the adsorbents were obtained from the Langmuir R_L and Freundlich n values. This is because

the presence of various kinds of active sites (heterogenous surface) on BFSH with different affinity for metal ions and the possibility of metal ions to be adsorbed on already adsorbed layers favored biosorption.

Adsorbent dose

The influence of adsorbent dosage is a very important parameter to be considered in adsorption study because it affects significantly the adsorption of metal ions on adsorbents [9, 34]. The effect of adsorbent dose on the adsorption capacity of BFSH for Co (II), Pb (II) and Zn (II) ions is shown in Fig. 4. A decrease in the adsorption capacity of all the adsorbents for the three metal ions with an increase in adsorbent dose was obtained. With the increase in adsorbent dose from 0.1 to 0.5 g a decrease in the adsorption capacity of BFSH from 52.4 to 13.48 mg/g, 49.6 to 12.96 mg/g and 47 to 12.72 mg/g for Co (II), Pb (II) and Zn (II) ions were obtained respectively. This decrease in biosorption capacity with an increase in adsorbent dose is attributed to the higher adsorbent dose providing more active sorption sites which resulted in the sorption sites remaining unsaturated during the adsorption process [35]. The decrease in the solid-liquid ratio
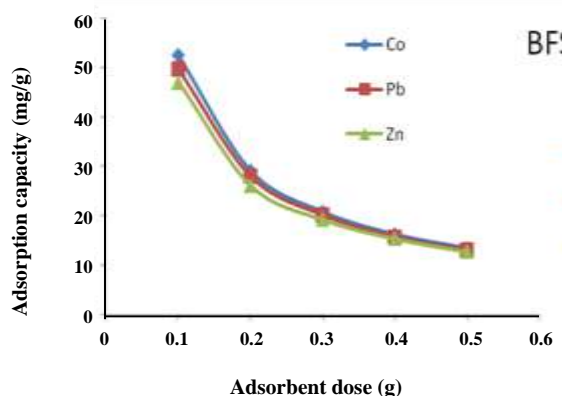
Fig. 4: Effect of adsorbent dose on the biosorption capacity of breadfruit seed husk.

Fig. 5: Effect of adsorbent dose on the percentage biosorption of metal ions.

will allow for dispersion of the particles which will increase the available sorption sites between the particles [35]. This decrease can also be attributed to a decrease in the total adsorption surface area and an increase in diffusion path length resulting from overlapping or aggregation of adsorption sites [18]. The aggregation becomes increasingly significant as the weight of the adsorbent increase. Although, the number of adsorption sites per unit mass of an adsorbent should be constant, independent of the total adsorbent mass, yet increasing the adsorbent dose in a fixed volume of the metal solution decreased the effective surface area as a result of a decrease in the number of available sites. Thus with an increase in the adsorbent mass, the amount of metal adsorbed unto a unit mass of the adsorbent get reduced [36]. Similar results have been reported [10, 37].

However, the opposite trend was obtained when the effect of adsorbent dose on the percentage adsorption of metal ions was studied. Fig. 5 shows the effect of adsorbent dose on the percentage biosorption of Co (II), Pb (II) and Zn (II) ions on BFSH. It was observed that an increase in the percentage sorption of the three metal ions was obtained. With the increase in adsorbent dose from 0.1 to 0.5 g the percentage adsorption of Co (II), Pb (II) and Zn (II) increased from 65.5 to 84.25%, 62 to 81% and 58.75 to 79.5% respectively. The increase in biosorption of metal ions with an increase in adsorbent dose is due to an increase in the number of available active sites and surface area of BFSH [36]. It may also be attributed to increase negative charge and decrease in the electrostatic potential near the solid surface that favors sorbent-solute
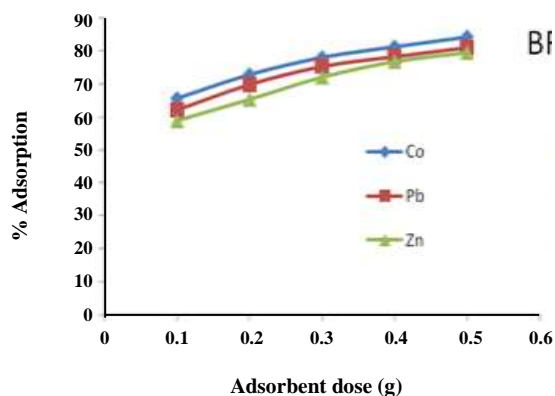
interactions [6]. Similar results have been reported [8, 22]. Consequently, in order to optimize the use of a given amount of adsorbent i.e obtain both high adsorption capacity and high percentage removal, it would be efficient to implement the adsorbent in several adsorption units in parallel rather than in a single large adsorption unit [19]. The maximum adsorption capacity of an adsorbent can, however, be determined from column experiment by the use of large excess of the adsorbate [26]. The trend of sorption of metal ions on BFSH was in the order Co > Pb > Zn. The adsorbent dose of 0.1 g was chosen and utilized in this study in all biosorption experiments due to its higher adsorption capacity which enables maximum utilization of the active sites of BFSH. The observed trend on the effect of adsorbent dose on biosorption in this study is in accordance with the findings by other researchers [38, 39].

Contact time

It is necessary to determine the time dependence of an adsorption system because the time it takes metal ions and adsorbent to reach equilibrium is of considerable importance as it provides information on the processing mechanism [40]. Adsorption kinetics usually involves a rapid initial stage followed by a much slower stage before equilibrium is established [41]. The effect of contact time on the biosorption of Co (II), Pb (II) and Zn (II) ions on BFSH is shown in Fig. 6.

It was observed that the rate of removal of metal ions from solution was initially rapid and then diminished gradually until an equilibrium time beyond which there
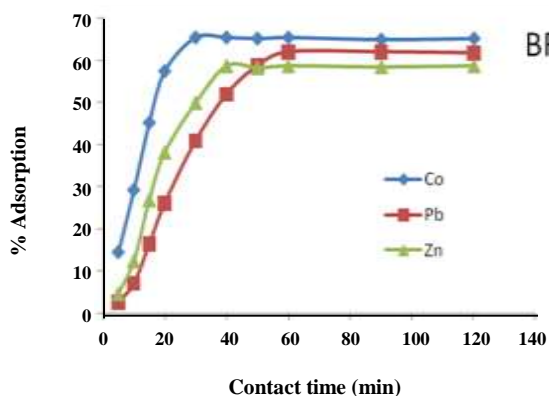
Fig. 6: Effect of contact time on the percentage adsorption of metal ions.

was no significant increase in the rate of removal. An equilibrium contact time of 30, 60 and 40 min was observed for biosorption of Co, Pb, and Zn, respectively. It has been reported that the nature of the adsorbent and its available sorption sites affects the time needed to reach equilibrium [19]. The ionic radius of metal ions has been reported to play the most significant role in determining the equilibrium adsorption time attained by metal ions on adsorbents [42]. Metals with smaller ionic radii tend to diffuse faster and get to the surface of the adsorbent for their adsorption consequently attaining equilibrium faster. On the other hand metals with larger ionic radii tend to encounter resistance in their diffusion due to larger sizes and a longer time to get to the surface and be adsorbed [19]. Comparing the ionic radius of the three metal ions; Co (0.74Å), Zn (0.74Å) and Pb (1.20Å) and the equilibrium times recorded for their adsorption Co (30 min), Zn (40 min) and Pb (60 min), it was observed that Co and Zn ions were biosorbed faster than Pb ions due to their relatively smaller sizes. The faster rate of sorption equilibrium attainment by Co than Zn ion is due to the higher electronegativity of Co (1.88) than Zn (1.65) which makes Co ions to have a stronger attraction for the active sites of BFSH and thus a faster rate of biosorption [3]. The trend of increase in adsorption with contact time until equilibrium attainment can be explained thus; initially, the rapid biosorption rate is due to the external mass transfer of metal ions onto the adsorbent surface and the rapid filling of the unoccupied active sites at the start of the reaction [10]. The trend can be explained that initially all the abundant active sites on

BFSH surface were vacant and the solution concentration was high, this high concentration gradient generated a high driving force for the rapid filling of adsorption sites. Therefore the sorption rate of metal ions decreased with time as less number of vacant sites was made available on the surface and the decrease in the driving force of metal ions to occupy the active sites due to a lower concentration of metal ions in solution. After a certain point of contact, it reached equilibrium, where there was no significant change in the concentration of metal ions in solution as the active sites were completely used up [20]. The fast adsorption kinetics indicates the applicability of the biosorption process. A contact time of 120 min was chosen in this study in order to ensure equilibrium sorption of all metal ions on BFSH was achieved. Similar results have been reported by many researchers [16, 28, 41].

Kinetic modeling

In this study, the kinetics of sorption that defines the efficiency of biosorption of Co (II), Pb (II) and Zn (II) ions on BFSH was analyzed by the pseudo first order, pseudo-second order, intraparticle diffusion, and film diffusion rate equations [43- 45].

The first order kinetics is due to electrostatic attraction between the metal ions and the external surface of the adsorbent which is likely a physical adsorption mechanism [22, 25]. The linear form of the Lagergren model is given in equation [6]:

$$\log(q_e - q_t) = \log q_e - (K_I t / 2.303) \tag{10}$$

Where q_e and q_t in mg/g are the amounts of metal ions adsorbed at equilibrium and time t, respectively. K_I (min^{-1}) is the pseudo-first order rate constant. The pseudo-first-order constants obtained for the biosorption of Co (II), Pb (II) and Zn (II) on BFSH are shown in Table 2. From the R^2 values obtained, it is observed that the pseudo-first order model provided a good fit to the experimental data, as the values were all greater than 0.9. However the experimental q_e values showed some discrepancy to the calculated q_e values.

The pseudo-second-order model is based on the assumption that chemisorption is the rate controlling step [40]. The linear form of the pseudo-second-order model is given in the equation [9]:

$$t/q_t = 1/K_2 q_e^2 + t/q_e \tag{11}$$

Table 2: Kinetic model constants for the biosorption of metal ions on BFSH.

Kinetic/Adsorbent	Co (II)	Pb (II)	Zn (II)
qe_{exp} (mg/g)	52.4	49.6	47
Pseudo-first-order			
qe_{cal} (mg/g)	86.69	86.30	71.94
K_I (min^{-1})	0.122	0.062	0.074
R^2	0.956	0.952	0.981
Pseudo-second-order			
qe_{cal} (mg/g)	58.82	200	71.43
h(mg/g min)	6.061	0.843	1.681
K_2(g/mg min)	1.8×10^{-4}	2.1×10^{-5}	3.3×10^{-4}
R^2	0.979	0.150	0.735
Intraparticle diffusion			
K_d (mg/g min$^{1/2}$)	4.054	6.273	5.116
C	18.42	-6.93	2.93
R^2	0.595	0.842	0.730
Film diffusion			
K_{fd}	0.122	0.063	0.075
D	0.505	0.556	0.427
R^2	0.956	0.952	0.981

Where q_t and q_e in mg/g are the adsorption capacity at the time, *t* and equilibrium respectively. K_2 (g/mg min) is the equilibrium constant of pseudo-second order biosorption? The initial sorption rate (*h*) can be calculated from the equation:

$$h = K_2 q_e^2 \qquad (12)$$

The pseudo-second-order parameters obtained for the biosorption process is given in Table 2. This model has been found to give the best fit in most adsorption studies [3, 29, 42]. It was observed from Table 2 that the pseudo-second-order model presented a very good fit for the biosorption of Co (II) than the pseudo-first-order model ($R^2 > 0.95$). However, this model did not provide good fits for the biosorption of Pb (II) and Zn (II) as R^2 values were low. Also, the experimental q_e values were close to the calculated q_e for Co (II). This showed the pseudo-second-order model to be applicable in the description of the kinetics of biosorption of Co (II). In general, the better fit presented by the pseudo-first-order model suggests

a physisorption process on BFSH [10, 19]. The shape and coefficients of the adsorption kinetics of the system were affected by the interaction between metal ions and the surface of the adsorbent [31]. Another very important deduction obtained from the pseudo-second-order model is that the initial sorption rate (*h*) showed a faster rate of adsorption of Co (II) followed by Zn (II) and a much slower rate for Pb (II) ions. This result corroborated that obtained from the effect of contact time when equilibrium times of 30, 40 and 60 min were obtained for Co (II), Zn (II) and Pb (II) ions respectively. The faster rate of Co (II) adsorption was attributed to its small ionic radii (0.74Å) and higher electronegativity (1.88) while the slower the rate of Pb (II) ion adsorption is due to its higher ionic radii (1.20Å) making for a more difficult diffusion to the surface of the adsorbents.

Metal ions are transported from the aqueous phase to the surface of the adsorbent and consequently they can diffuse into the interior of the particle if they are porous and thus follow the intraparticle diffusion mechanism [17].
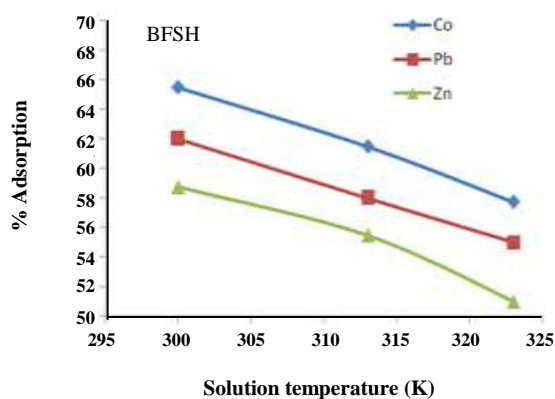
Research Article

Fig. 7: Effect of temperature on the percentage adsorption of metal ions.

To explore the possibility of intraparticle diffusion resistance affecting biosorption, it was necessary to use the intraparticle diffusion model. The intraparticle diffusion model is given in the equation [17]:

$$q_t = K_d t^{1/2} + C \tag{13}$$

Where q_t (mg/g) is the adsorption capacity at time t, K_d (mg/g min$^{1/2}$) is the intraparticle diffusion rate constant. Intraparticle diffusion is the sole rate-limiting step if the regression of q_t versus $t^{1/2}$ is linear and passes through the origin ($C = 0$). The occurrence of the intercept (C) reflects the boundary layer effect. The larger the intercept, the greater the contribution of the surface sorption (film diffusion) in the rate controlling step [10]. The intraparticle diffusion model parameters obtained for biosorption of Co (II), Pb (II) and Zn (II) on BFSH are given in Table 2. The linear regression coefficient (R^2) obtained from the plots were low ($R^2 < 0.9$), which indicated a poor fit of the intraparticle diffusion model to the experimental data and suggest that intraparticle diffusion is not the rate controlling mechanism of the biosorption process. Also, the plots did not pass through the origin due to the occurrence of the intercept C, indicating again that intraparticle diffusion cannot be the sole rate controlling step even if present [22]. The deviation of the straight lines from the origin might be due to the differences in the rate of mass transfer in the initial and final stages of the process [10]. Furthermore, the lower R^2 values and the occurrence of the intercepts suggest that surface phenomenon (film diffusion) might be the major determining mechanism in the biosorption

of metal ions from solution. This was verified by applying the liquid film diffusion model.

When the transport of the adsorbate from the liquid phase up to the solid phase boundary plays the most significant role in adsorption, the process would likely conform to the film diffusion model [17]. The liquid film diffusion mechanism can be expressed in the equation [19]:

$$\ln(1-F) = -K_{fd} t \tag{14}$$

Where F is the fractional attainment of equilibrium, ($F = q_t/q_e$) and K_{fd} (mg/g min) is the adsorption rate constant of film diffusion model. Also, the occurrence of the intercept may indicate that film diffusion is not the only rate controlling mechanism [17]. The liquid film diffusion model parameters for the biosorption of Co (II), Pb (II) and Zn (II) on BFSH are shown in Table 2. As observed all the R^2 values were high (> 0.9) and much better than the intraparticle diffusion model. This confirms that film diffusion played a dominant and relevant role as the rate controlling mechanism in the biosorption of metal ions. However, the occurrence of the intercept suggests that it was not the sole rate determining step but intraparticle diffusion mechanism might have been involved even though it wasn't the major mechanism of biosorption. Similar results have been reported [19, 36].

Biosorption thermodynamics

The influence of solution temperature on the simultaneous biosorption of Co (II), Pb (II) and Zn (II) ions on BFSH is shown in Fig. 7. A decrease in biosorption of the three metal ions with an increase in temperature was observed. This indicated that the biosorption is exothermic in nature. The decrease in biosorption of metal ions with an increase in temperature is attributed to the increase in kinetic energy of the metal ions which enhanced desorption from the surface of BFSH into the bulk solution.

The standard free energy (ΔG^0), enthalpy change (ΔH^0) and entropy change (ΔS^0) were determined to evaluate the feasibility of biosorption. The ΔG^0 is related to a thermodynamic equilibrium constant (Kc) by the following equation [6]:

$$\Delta G^0 = -RT \ln Kc \tag{15}$$

Where T (K) is the absolute temperature, R (8.314J/molK) is the ideal gas constant and Kc is defined by the equation:

$$Kc = Ca/Ce \qquad (16)$$

Where Ca (mg/L) is the metal ion concentration biosorbed at equilibrium, Ce (mg/L) is the residual metal ion concentration at equilibrium. Kc, a dimensionless thermodynamic equilibrium constant provides information on the spontaneity of the biosorption process related to ΔG^0. The biosorption is said to be spontaneous ($Kc > 1$), non-spontaneous ($Kc < 1$) and in equilibrium (equal distribution of the adsorbate on the surface of the adsorbent and in the bulk of the solution) if $Kc = 1$. Also, Gibb's free energy is also related to the enthalpy change and entropy change by the Van"t Hoff [7] equation:

$$\ln Kc = -\left(\Delta H^0/RT\right) + \left(\Delta S^0/R\right) \qquad (17)$$

The values of ΔH^0 and ΔS^0 were calculated from the slope and intercept of the plot $lnKc$ versus $1/T$ (not shown). The calculated thermodynamic parameters of biosorption are given in Table 3.

The negative ΔH^0 values obtained for the three metal ions indicated an exothermic biosorption on BFSH, which explains the decrease in biosorption with temperature obtained. Negative values of ΔS^0 indicate that the process is enthalpy driven. The reaction was found to be spontaneous in nature as Kc values were all greater than 1 and negative values of ΔG^0 were obtained at all temperatures. The type of biosorption can be explained based on the magnitude of ΔH^0. The heat of physisorption generally lies in the range of 2.1-20.9kJ/mol, while the heats of chemisorptions fall in the range of 80-200kJ/mol [6, 10]. From Table 3, the values of ΔH^0 for Co (II), Pb (II) and Zn (II) ions are -11.43, -10.11 and -9.15 kJ/mol respectively. This indicated that biosorption on BFSH is physisorption and corroborated the suggestion obtained from the Tempkin heat of adsorption (b_T) discussed previously. This is the reason why a multilayer biosorption of metal ions was obtained with the Freundlich model as discussed earlier and also suggest easy desorption of metal ions from the surface of metal loaded BFSH.

Desorption analysis

The result of desorption of Co (II), Pb (II) and Zn (II) from metal loaded BFSH showed percentage desorption of 84.6, 80.3 and 75.5% in acid media respectively. That obtained in the basic media was 70.7, 64.9 and 60.2% for the respective metal ions. This indicated the effectiveness of using 0.1M HCl in the removal of biosorbed metal ions from the surface of BFSH than using 0.1M NaOH. Several studies have shown HCl to be more effective than other eluents such as HNO_3, H_2SO_4, and NaOH in desorbing metals from adsorbents [26]. The high percentage desorption obtained using both eluents indicated the suitability of BFSH as a good adsorbent which can easily be reused. Also, the fact that over 60% of all metals were desorbed suggests physisorption which corroborated the deduction obtained from biosorption thermodynamics.

Characterization of breadfruit seed husk

The physicochemical characterization of BFSH is shown in Table 4. The low value of percentage moisture, volatile and ash content indicated that BFSH would be good raw material for use as an adsorbent [46]. A high pore volume is desirable in the removal of large molecules from solution; therefore the pore volume of 3.6×10^{-3} m^3/g indicated that BFSH would be suitable for the removal of large molecules from contaminated solution. The specific surface area (SSA) which is the accessible area of adsorbent surface per unit mass of material was calculated as 42.3 m^2/g for BFSH. The higher the SSA, the more efficient the adsorption potential of the biomass. The SSA of 42.3m^2/g is high which suggest again the suitability of BFSH as an effective adsorbent for heavy metals. The pH_{pzc} of BFSH was 4.8 and implies that at pH values greater than 4.8 the surface of BFSH would be negatively charged favoring the adsorption of cationic species [6]. This accounts for the reason why optimum pH values of biosorption of the three metal ions were achieved at higher values of 5.0 and 6.0 when the surface of BFSH was negatively charged.

The Fourier Transform InfraRed (FT-IR) and Scanning Electron Microscopy (SEM) were used to characterize the adsorbents in order to determine the surface functional groups and the porous nature of the adsorbents respectively. FT-IR allowed the spectrophotometric observation of

Table 3: Thermodynamic parameters for the biosorption of heavy metals on breadfruit seed husk.

Metal ion	Temp (K)	Kc	ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (J/molK)	R^2
	300	1.90	-1.59			
Co (II)	313	1.60	-1.22	-11.43	-32.70	0.995
	323	1.37	-0.84			
	300	1.63	-1.22			
Pb (II)	313	1.38	-0.84	-10.11	-29.63	0.999
	323	1.22	-0.54			
	300	1.42	-0.88			
Zn (II)	313	1.25	-0.57	-9.15	-27.50	0.994
	323	1.09	-0.24			

Table 4: Physicochemical characterization of breadfruit seed husk.

Parameters	Value
Moisture content	16.4%
Volatile matter	12.3%
Ash content	4.8%
Fixed carbon	60.2%
Pore volume	3.6×10^{-3} m^3/g
Specific surface area	42.3 m^2/g
pH$_{pzc}$	4.8

the adsorbent surface in the range $400 - 4000$ cm^{-1} which helped in the identification of the surface functional groups responsible for binding of the positively charged metal ions [6]. The FT-IR spectrum of BFSH is shown in Fig. 8.

Several absorption bands were found which indicated that BFSH consist of functional groups responsible for the binding of cations. Absorption bands at 3406.4 cm^{-1} correspond to the O-H stretching group on the adsorbent surface, while the bands at 2422.7 cm^{-1} represented the C-H stretching of aliphatics [47]. The C=O group of esters was observed by the strong and intense peak at 1647.26 cm^{-1} while absorptions at 1498.7 cm^{-1} were attributed to the C=C of alkenes and could also be attributed to the symmetric -C=O- stretching vibrations of carboxylic groups [10]. The characteristic band at 1120.7 cm^{-1} corresponded to the C-O stretching vibration while the band at 624.96 cm^{-1} represented the C-Cl stretching and could also be attributed to the out of plane C-H bands of alkanes [10, 47]. The SEM image helped to determine the porous nature of the adsorbent surface which is necessary for an efficient and effective biosorption of metal ions by adsorbents [6]. The SEM image of BFSH is shown in Fig. 9. The SEM image showed a porous surface, a considerable number of heterogeneous pores, an irregular surface and particle aggregation of various shapes and sizes where there was a possibility for metal ions to be trapped and adsorbed. The presence of pores enables easy diffusion of metal ions to the surface of the adsorbent and also indicates that physisorption would be the mechanism of biosorption of metal ions [6]. Similar results have been reported [11, 45, 46]. The XRD gives very useful information about the changes in the crystalline and amorphous portions of BFSH. The XRD spectrum of BFSH is shown in Fig. 10, the broad but weak peaks indicate the amorphous nature of the adsorbent suggesting that metal ions could easily penetrate into its surface [48]. Similar results have been reported previously [6, 11].
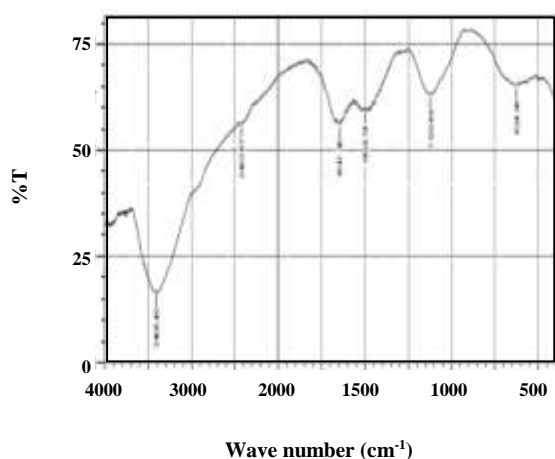
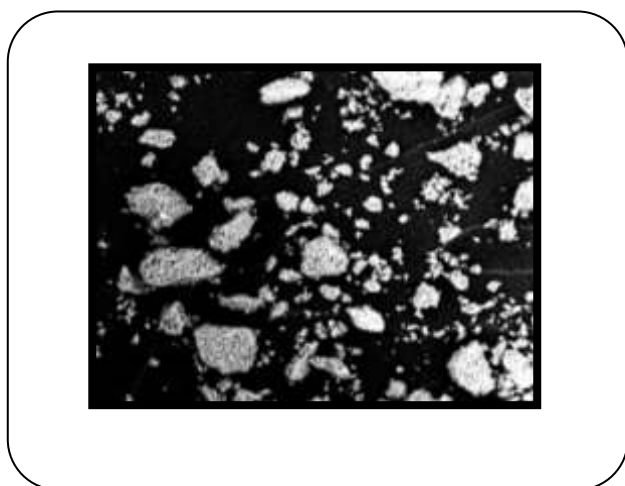***Fig. 8: Fourier transforms infrared spectrum of breadfruit seed husk.***

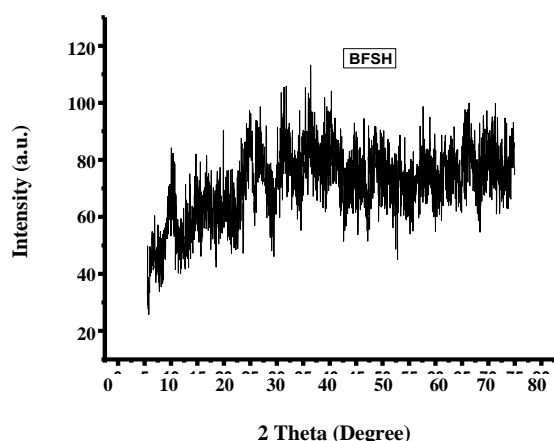***Fig. 9: Scanning electron microscopy of breadfruit seed husk.***

Fig. 10: X-ray diffraction spectra of breadfruit seed husk.

CONCLUSIONS

The results of this study suggest the good potentials of breadfruit seed husk as a suitable low-cost adsorbent for the biosorption of Co (II), Pb (II) and Zn (II) ions from polluted solution. This adsorbent could be applied as an alternative material to solve the problem of the high cost involved in the use of activated carbon.

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