Development of low-cost bio-adsorbent from agricultural waste composite for Pb(II) and As(III) sorption from aqueous solution

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Abstract: Agricultural waste composite-activated carbon was developed and characterized by means of chemical activation (KCl) to be utilized for the uptake of Pb(II) and As(III) in a batch adsorption process. This study was carried out to minimize the widespread of heavy metals within water source. Batch adsorption studies were carried out with the consideration of factors such as pH, temperature, initial concentration, adsorbent dosage and contact time. The phase identification (XRD), surface chemistry (FTIR), surface area (BET), surface morphology and elemental identification (SEM/EDX) were all investigated in this study, and the BET surface area were 230.242 and 849.630 m²/g resulting in relatively high adsorption capacities of 200 and 250 mg/g for both As(III) and Pb(II), respectively. The adsorption rate of Pb(II) and As(III) onto AWCAC was faster in the first 30 min but it attained equilibrium at 90 min for both metal ions. The Isotherm models studied show that the adsorption process was fitted best to Langmuir model. The result of the kinetic and thermodynamic studies revealed that the adsorption process followed a pseudo-second-order, physical, exothermic, and spontaneous in nature.

ABOUT THE AUTHOR

The Author Obayomi Kehinde Shola did both his Master's and Bachelor's degree at the Federal University of Technology Minna, Niger State Nigeria and his currently on his PhD. The rate of technological advancement, growing industrialization and extensive use of chemicals has resulted in the release of unwanted contaminants (Lead and Arsenic) into various water compartments. The continuous release of these contaminants has led to a decrease in drinking water quality causing various water borne diseases to human and aquatic life. This worrying environmental problem has been recognized as an issue of growing concern in recent years. To address this challenge, it will be important to develop low-cost adsorbent (agricultural waste) that will possess high adsorption capacity towards the removal of this contaminants from waste or polluted water system and that is water this research work is major on, using an economical, efficient and effective adsorbents to tackle pollutant being posed by heavy metals in wastewater body.

PUBLIC INTEREST STATEMENT

Pollutants from the environment and their toxicity are causing a major problem worldwide. Rapid massive industrialization in the last decades has been accompanied with the emergence of new pollutants posing severe health and environmental challenges globally. Water pollution is one of the biggest environmental challenges resulting in serious problems to living beings. The removal of these various toxic substances from water and wastewater has been of core interest to many scientists and researchers around the globe over the past decades. Heavy metals in wastewater have been of major environmental concern for environmentalists for many years due to their toxicity towards human beings, and aquatic biota. As they do not degrade biologically like organic pollutants, their presence in industrial effluents and drinking water is a public health problem. Lead and Arsenic are recognized as a multifunctional metal and their purpose in industrial sector leads to wastewater production.
The adsorption of As(III) and Pb(II) unto agricultural waste composite when compared with other adsorbents in literature gave the highest adsorption capacity.

Subjects: Toxicology; Environment & Society; Environment & Health; Environmental Change & Pollution

Keywords: Agricultural waste; adsorption; heavy metals; kinetic; thermodynamic

1. Introduction

Based on the inaccessibility of water treatment equipment, water pollution amongst other types of pollution became a major issue for undeveloped and fast-rising countries who are more vulnerable. Not only does the upsurge of contamination of aquatic sources with different numbers of pollutants endanger the aquatic biota, it also leads to a wide-reaching recreational water scarcity (Rai, Tripathi, Vajpayee, & Jha, 2002). The rise in population and industrial development has negative impact on the environment due to heavy metal discharged (Majumdar et al., 2010). Heavy metals, that is, metals with high density above 5 g/cm³, amid other pollutants have the most harmful effect because of their tenacity and non-biodegradability in the environment. Environmental pollution and grave poisoning symptoms are caused by the release of metals (toxic) including arsenic, lead, nickel, copper, mercury, and chromium in wastewater. This is as a result of great industrialised operations, which is the reason for the complications experienced in wastewater treatment (World Health Organization, 2004).

Industrial discharge from battery, tannery, paint, fertilizer, mining, petrochemical, and fabric industries comprises heavy metals (non-biodegradable and toxic) that are emitted into the earth and permeate into waterbodies, thus affecting both human and aquatic life (Bilal et al., 2013).

A substantial amount of traditional practices like oxidation, osmosis, reduction, precipitation, ultrafiltration, electro-dialysis, ion exchange and electrochemical are being engaged to help in the adsorption of these toxic metals from wastewater. However, their shortcomings include higher quantity of sludge produced, poor efficiency and incapability to remove metals at higher concentrations (Hydari, Sharififard, Nabavinia, & Parvizi, 2012; Xiao et al., 2019). Researchers have viewed adsorption method as low-cost, effective and proficient for metal ions’ uptake in wastewater and it is the overall preference preferred when accessing a good number of waste products and natural materials (Atar, Olgun, & Wang, 2012).

Researchers have also established the efficacy of activated carbon amongst other adsorbents as one of the best adsorbents for heavy metal uptake from wastewater. Since activated carbon can be prepared from agrarian waste, it is not only considered to be extremely effective but also easily accessible and cost-effective (Herrera-González, Caldera-Villalobos, & Peláez-Cid, 2019). Activated carbon gotten from commercial-based products has been typically employed for adsorption processes but its restriction with reference to cost (high) has motivated researchers to look for substitutes (Won et al., 2006). Activated carbon from agrarian waste materials has revealed a good prospect in connection with their usual abundance, reusability, and cost-effective nature (Auta & Hammed, 2011; Batzias, Sidiras, Schroederb, & Weber, 2009).

This work is aimed at preparing activated carbon as an adsorbent from agricultural waste composite (rice husk, groundnut shell, and soya bean shell) through activation (chemical), using potassium chloride (KCl) for lead and arsenic sorption from an aqueous solution via batch adsorption process. Although researchers have carried out numerous studies on agricultural waste-activated carbon for the purpose of adsorption, but for now no work has been circulated on agricultural waste composite-activated carbon using KCl as the activating agent for the uptake As(III) and Pb(II). Consequently, this work introduces a new adsorbent from agricultural waste composite materials (rice husk, soyabean pod and groundnut shell) using KCl as an activating agent that was used in the uptake of Pb(II) and As (III). The purpose of this study is to limit the spread of heavy metals within water source using an effective and efficient low-cost adsorbent from agricultural waste.
2. Materials and method

2.1. Materials
Analytical grade lead nitrate (Pb(NO$_3$)$_2$), arsenic trioxide (A$_2$O$_3$) and potassium chloride (KCl) were utilized for this experimental study without additional purifications and were acquired from Chloral Chemicals India, Abbott India Limited India, and Muby Chemicals, respectively. The raw material applied for this study was agricultural waste composite (AWC) including rice husk, ground nutshell, and Soya beans, respectively. AWC was gotten from Landmark University Farms Omu-Aran, Kwara State, Nigeria which was pretreated by washing and drying until a constant weight was achieved. The AWC percentage elemental analysis were C = 73.421, O = 25.245, H = 0.766 and N = 0.420 while the proximate analysis gave fixed carbon (45.07%), volatile content (43.56%), ash content (7.65%), and moisture content (3.72%) respectively.

2.2. Method
The research methodology summary for the production and characterization of activated carbon from agricultural waste composite for adsorption of Pb(II) and As(III) is depicted in Figure 1.

2.2.1. Activated carbon preparation
The AWC obtained from Landmark University Farm after washing and drying was charged in a crucible and loaded into a furnace set at 400°C for 30 min at 10°C/min heating rate. The operating condition implemented was as a result of thorough preliminary studies. The oven was turned off and the sample was allowed to cool at room temperature after carbonization. The prepared char with KCl was impregnated and the impregnation ratio between the char and KCl (gchar/gKCl) was 2:1 g/g and was left overnight at room temperature. The activated adsorbent after impregnation was washed with distilled water until a neutral pH of 6.9–7 was attained; it was then left in the oven to dry at 120°C, reduced to a particle size of 125 µm and eventually kept in a container (airtight) for usage.

2.2.2. Characterization
The prepared char was examined prior to activation and afterwards with KCl through X-Ray diffraction (XRD-Rigaku D/Max-III C X-ray diffractometer) method established by the Rigaku International Corporation Tokyo, Japan. It was fixed to produce diffractions at scanning rate of 2°/min at 2–50°C at room temperature through a CuKa radiation fixed at 40 kV and 20 mA for phase identification. Brunauer-Emmett-Teller (BET) (SHIMADZU SS-100) to determine the porosity and surface area, and Scanning Electron Microscopy (SEM) with Energy Dispersive X-ray spectroscopy (EDX) was carried out to determined samples’ element identification and surface morphology. Fourier transform infrared spectroscopy (FT-IR- 84,005, SHIMADZU Kyoto Japan) was used to determine the surface chemistry.
2.2.3. Sorption studies

Scorpion batch studies were undergone through a set of Erlenmeyer flasks (500 mL). Two hundred and fifty milliliters of Pb(II) and As(III) with dissimilar concentrations (50, 100 and 150 mg/L) were charged individually into different containers and 0.25 g of agricultural waste composite-activated carbon (AWCAC) was carefully measured and put into each of the containers containing the adsorbates at a constant pH. The flasks were then put into a water-bath isothermal shaker set at 140 rpm shaker speed, 35°C for 2 h so that equilibrium could be attained. Prior to the achievement of equilibrium state, samples at different time intervals were taken and filtered by means of a microspore filter membrane (45 µm) to establish the adsorbates' concentration remaining in each of the solution with the aid of atomic absorption spectroscopy (PerkinElmer AAS-AAnalyst 200). The water-bath isothermal shaker’s temperature was set to 45°C and 55°C and the entire process was executed once more with a fresh set of flasks for both metals. The uptake at equilibrium of metal ions, \( q_e \), was evaluated as

\[
q_e = \frac{(C_0 - C_e)V}{W}
\]

where \( C_0 \) and \( C_e \) (mg/L) are the adsorbates' initial and equilibrium concentration in solution; \( W \) is the adsorbent mass (g); \( V \) is the adsorbate volume (L).

The pH effects of the study on both Pb(II) and As(III) uptake were conducted in the range of pH 2–11 by modifying it with either 0.1 M HCl or 0.1 M NaOH. The study was investigated using a set of Erlenmeyer flasks (250 mL) charged with 150 mg/L Pb(II) and As(III) and 0.25 g AWCAC in a different flask. The flasks were kept in a water-bath isothermal shaker and were run at 140 rpm, 35°C for 90 min.

The sorption kinetic studies were examined by determining the Pb(II) and As(III) concentration at a pre-set time intervals, \( t \). The adsorbates' uptake \( q_t \) (mg/g) at separate time interval \( t \), was gotten using:

\[
q_t = \frac{(C_0 - C_t)V}{W}
\]

where \( C_t \) is the adsorbates' concentration solution any time \( t \) (mg/L).

3. Results and discussion

3.1. Characterization

The prepared char prior to activation and afterwards with KCl gave BET surface area of 230.242 and 849.630 m\(^2\)/g, Langmuir surface area of 1025.978 and 5072 m\(^2\)/g, average pore diameter of 2.643 and 6.083 nm and collective adsorption pore volume of 0.1351 and 0.4967 cm\(^3\)/g. The high surface area and pore volume development on the AWCAC could be ascribed to the KCl chemical activation (Viswanathan, Indra Neel, & Varadarajan, 2009). The prepared char prior to activation and afterwards was viewed as naturally mesoporous with the pore diameter between 2 and 50 nm.

The infra-red spectra as shown in Figure 2 observed a sharp band at 3954.20 cm\(^{-1}\) indicating the collective presence of hydroxyl, the steep band at 1591.33 cm\(^{-1}\) is linked with the carbon-carbon double bond. The wavelength at 1350.22 cm\(^{-1}\) points to the carbon-oxygen single bond group while 491.86 cm\(^{-1}\) indicated the Fe-O band in the spectra for both the activated carbon (AC) and carbon before activation (CBA) samples, respectively. This range of spectra was corroborated by Aguayo-Villarreal, Bonilla-Petriciolet, & Muñiz-Valencia, 2017; Nejadshafiee & Islami, 2019.

The XRD spectra for AWCAC are illustrated in Figure 3. The result indicated that there was formation of different phases in the adsorbent under study. Quartz was PARTICULARLY detected.
to have dominated the peaks in the spectra. Other phases such as Fe₂O₃ and Na₂SiO₃ characterized the phases formed at 2theta values of 36° and 57°, respectively. However, it is observed that some intermetallic compounds were also formed including C₂S.CaSO₄ and Ca₃Fe₂(SiO₄)₃ at 2theta values of 21° and 47° in that order.

The (SEM/EDX) investigation of carbonized AWC prior to activation and afterwards, is exemplified in Figure 4. The morphological illustration presented in Figure 4(a) indicates a relative sphere-like phase of the AWC char is well distributed in the structure. The EDX spectrum also shows the variation in the elemental composition of the char. However, in Figure 4(b), a honeycomb structure was evident in the activated carbon structure which leads to the development of good pores as a result of activation with KCl. Thus, leading to surface area rise of the adsorbent and porous structure (Tounsadi, Khalidi, Farnane, Abdennouri, & Barka, 2016; Youssef, Ahmed, Amin, & EL-Banna, 2014).

3.2. Initial Pb(II) and As(III) concentration effect

The study of initial concentration is a significant aspect of adsorption study process because it helps to calculate the adsorbate-adsorbent equilibrium position establishment. This is a point where the metal ion uptake on the adsorbent is in a dynamic equilibrium state. The effect of initial Pb(II) and As(III) concentration (50, 100, and 150 mg/L) on the uptake of both metals onto AWCAC was analyzed as shown in Figure 5. The result showed that at the lower concentration of Pb(II) and As(III) adsorption equilibrium was attained faster rather than at greater concentration.
At a concentration lower, several vacant sites were present on the adsorbent sites with less metal ion in solution (low concentration) to occupy thereby promoting rapid adsorption of both metals but at higher concentration, more metal ions present the solution were contending for the limited available adsorbent binding sites (Auta & Hammed, 2011). It was noticed from the graph that at 50 mg/L of Pb(II) (35°C), equilibrium position was attained after 45 min while it took 75 min and 90 min for equilibrium establishment for 100 and 150 mg/L at 35°C. The attainment of equilibrium position for initial As(III) concentration (50 mg/L) at 35°C was 45 min while it took 90 min for both 100 and 150 mg/L. The metal ion concentration increases from 50 to 150 mg/L caused an increment in the uptake at equilibrium for both metals as shown in Figure 6. This fact could be attributed to gradient concentration increase of the driving force to prevail overall resistance of the metal ion mass transfer between the adsorbate and adsorbent phases. Thereby accelerating the probable impact between the adsorbent and the adsorbates, resulting in higher adsorption capacity of both metals (Ahmad & Alrozi, 2010; Chen et al., 2005). In this study, concentration equilibrium was measured for 120 min so as to give room for all other concentrations and the equilibrium time of both metals on AWCAC was 90 min and this was used for further experiment.

3.3. pH effect

The solution pH is one of the substantial variables under study that controls the adsorption process. It measures the solution acidity and alkalinity and also influences surface adsorbent charges. In the experimental study, uptake of Pb(II) and As(III) against pH was studied over
Figure 5. Initial metal ion concentration effect on the adsorption (a) Pb(II) (b) As(III) onto AWCAC at 35°C.

Figure 6. Contact time effect on the uptake (a) Pb(II) (b) As(III) onto AWCAC at 35°C.
the range of 2–11 for a constant AWCAC dosage of 0.25 g, the initial metal concentration of 150 mg/L at 35°C for 90 min. The result portrayed in Figure 7 shows that the uptake of both metals by AWCAC increased dramatically due to increased pH value up to a point (pH 10) whereas further increment beyond this point resulted in no significant change. At pH 10, the maximum amount of Pb(II) and As(III) uptake on AWCAC attained was 139.456 and 121.345 mg/g while at lowest pH 2, 15.446 and 12.456 mg/g was the minimum amount adsorbed by both metals. At a lower pH values, more protons were available in the solution causing the adsorbent sites to be more positive thus encouraging electrostatic repulsion between the positively charged metal ions and the adsorbent (AWCAC) thereby making the adsorbates compete for the fewer space on the adsorbent sites; hence little amount of both metals were adsorbed (Badii, Ardjani, Saberi, Limaee, & Shifaei, 2010; Hameed, 2009). At pH values higher, there was deprotonation and more negatively charged adsorbent surface was formed as a result thereby promoting greater uptake of both Pb(II) and As(III) by electrostatic attraction (Nejadshafiee & Islami, 2019; Salameh, Al-Lagtah, Ahmad, Allen, & Walker, 2010). A similar finding was reported by (Olgun & Atar, 2012).

3.4. Dosage effect
The adsorbent dosage effect onto Pb(II) and As(III) adsorption was carried out with varied AWCAC dosage of 0.1 to 1 g, constant initial Pb(II) and As(III) concentration of 150 mg/L at 35°C for 90 min equilibrium time. The result as depicted in Figure 8 shows that adsorption capacity is increased with increasing adsorbent dosage. A significant increment in adsorbent dosage from 0.1 to 0.6 g resulted in a fast rise in the adsorption capacity of Pb(II) and As(III). At lower adsorbent dosage, the adsorbent sites are less thereby making metal ions contest for adsorption on the limited spaces thus resulting in a lower adsorption capacity but as the amount of AWCAC is increased, more and more binding sites were made present on the adsorbent for metal ions complexation thereby promoting higher uptake of both metals (Olgun & Atar, 2012). However, further increment in AWCAC dosage beyond this point (>0.6 g) resulted in no significant increase in both metals’ adsorption capacity (equilibrium attainment). This could be attributed to the adsorbent site saturation which does not permit more metal ions to be adsorbed. The result obtained revealed higher adsorption of Pb(II) when compared with As(III) on the AWCAC, signifying higher affinity of Pb(II) to the AWCAC (Atar et al., 2012).

Figure 7. pH effect on Pb(II) and As(III) adsorption by AWCAC (C₀ = 150 mg/L, V = 250 mL, W = 0.25 g, shaking speed = 160 rpm, temperature = 35°C, equilibrium time 90 min).

Figure 8. Effect of dosage on Pb(II) and As(III) adsorption by AWCAC (C₀ = 150 mg/L, V = 250 mL, W = 0.25 g, shaker speed = 160 rpm, pH = 7, equilibrium time = 90 min, temperature = 35°C).
3.5. Temperature effect

Adsorption equilibrium of Pb(II) and As(III) onto AWCAC was investigated at diverse temperatures of 35°C, 45°C, and 55°C as depicted in Figure 9. The result revealed that the uptake temperature is inversely proportional to the uptake of both metal ions; thus, decreasing the adsorption process temperature resulted into adsorption capacities increase and this could be attributed to the exothermic nature of the process (Auta & Hammed, 2011).

3.6. Isotherm adsorption studies

The experimental equilibrium data obtained for Pb(II) and As(III) adsorption onto AWCAC at 35°C, 45°C, and 55°C were tested with three widely used isotherm models to determine the level of fitness. Langmuir model assumption is based on the occurrence of homogeneous monolayer surface adsorption within specific site on the adsorbent and that there is no lateral interaction between the molecules adsorbed (Badii et al., 2010). The linearized form is evaluated as (Langmuir, 1918):

\[
\frac{C_e}{q_e} = \frac{1}{q_{max}K_L} + \frac{C_e}{q_{max}} \tag{3}
\]

where \( q_e \) is the amount metal ion uptake at equilibrium (mg/g); \( C_e \) is the metal ion concentration uptake at equilibrium (mg/L); \( q_{max} \) is the maximum adsorption capacity (mg/g); and \( K_L \) is the Langmuir constant (L/mg). Freundlich model predicts that heterogeneous multilayer occurs on adsorbent surface with a non-uniform heat sorption distribution and affinities (Hameed, 2009). The linearized form is calculated as (Freundlich, 1906):

\[
\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{4}
\]

where \( K_F \) is the adsorption capacity (mg/g); and \( n \) is the heterogeneity factor indicating the adsorption process favorability. Temkin model accounts for the effect of both metals' interactions with AWCAC during the adsorption process and also suggests that all molecules adsorbed during heat adsorption decrease linearly with coverage (Salameh et al., 2010). The linearized form of equation is calculated as (Temkin and Pyzher, 1940):

\[
q_e = B \ln A_T + B \ln C_e \tag{5}
\]
where $A_T$ is the binding constant (L/g); $B$ is the heat of adsorption (J/mol).

\[ B = \frac{RT}{b_T} \]  

(6)

where $\frac{1}{b_T}$ indicated the adsorbent potential adsorption, $R$ is gas constant (universal) (8.314 J/Kmol) and $T$ is the absolute temperature in Kelvin (K).

The adsorption isotherm studies on the sorption of Pb(II) and As(III) onto AWCAC was found to be fitted to the three models studied. The values of their regression coefficient ($R^2$) and adsorption constant are tabulated in Table 1. The result shows that Langmuir model best describes the adsorption process (best fit) with a regression correlation of over 0.990 and was followed by Temkin and Freundlich model, respectively (<0.90). Going by Langmuir model assumption, the adsorption process followed a monolayer and homogeneous mechanism, where the adsorbates and adsorbent at the sorption sites are energetically identical. The monolayer adsorption capacity values were 250 and 200 mg/g for Pb(II) and As(III). Higher $K_L$ values result in higher adsorbent affinity to the metal ions and temperature decreased result in a consistent decrease in the $K_L$ value (Zheng, Liu, Zheng, Liang, & Liu, 2009). The isotherm result further confirms that the high adsorption capacity of Pb(II) can be as a result of its higher affinity with AWCAC when compared with As(III) (Atar et al., 2012). The adsorption capacities on Pb(II) and As(III) on various adsorbents from literatures are presented in Table 2.

### 3.7. Adsorption kinetic studies

Kinetic is the study rates of chemical reactions that are essential in predicting how the speed of reaction will change under reaction conditions. This study is important in the adsorption of Pb(II) and As(III) onto AWCAC because revealed reaction mechanism information. The pseudo-first-order linearized form is given as (Lagergren & Svenska, 1898):

\[ \log \left( \frac{q_e}{q_t} \right) = \log \left( \frac{q_e}{k_1 t} \right) + \frac{k_1}{2.303} \]  

(7)

where $q_t$ and $q_e$ are the metal ions adsorbed capacity (mg/g) at time $t$ and at equilibrium; $k_1$ is the constant rate adsorption (min$^{-1}$). The pseudo-second-order linearized equation is calculated as (Ho & McKay, 1990)

\[ \frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2} \]  

(8)

$K_2$ (g/mg min) is the second-order rate constant.

### Table 1. Isotherm model parameters for Pb(II) and As(III) adsorption onto AWCAC

| Isotherms  | Parameters | Pb(II)   | As(III)   |
|------------|------------|----------|-----------|
|            |            | 35°C     | 45°C     | 55°C     | 35°C     | 45°C     | 55°C     |
| Langmuir   | $q_m$ (mg/g) | 250.000  | 166.667  | 142.857  | 200.000  | 145.439  | 128.730  |
|            | $K_L$ (L/mg) | 1.667    | 0.950    | 0.630    | 1.115    | 0.750    | 0.430    |
|            | $R^2$       | 1.000    | 0.997    | 0.994    | 0.993    | 0.994    | 0.995    |
| Freundlich | $K_F$       | 124.462  | 110.609  | 103.544  | 99.286   | 77.324   | 58.616   |
|            | 1/n         | 0.159    | 0.199    | 0.223    | 0.427    | 0.546    | 0.536    |
|            | $R^2$       | 0.663    | 0.513    | 0.518    | 0.697    | 0.795    | 0.846    |
| Temkin     | $A_T$ (L/mg) | 69.884   | 53.687   | 21.250   | 23.351   | 7.202    | 4.338    |
|            | $B$ (kJ/mol) | 0.176    | 0.140    | 0.130    | 0.075    | 0.060    | 0.062    |
|            | $R^2$       | 0.793    | 0.657    | 0.662    | 0.857    | 0.890    | 0.893    |
Two kinetic models were studied to evaluate the adsorption rate of Pb(II) and As(III) onto AWCAC; the result obtained revealed the process is described best by pseudo-second-order as depicted in Table 3 and Figures 10–11 respectively. Comparing the two kinetic models, the values of $R^2$ obtained from the linear plots (linear) of $t/q_t$ against $t$ (Figure 11) for the second-order equations were seen to be closer to unity confirming the model applicability compared to the ones gotten for first-order. Adsorption capacities calculated ($q_{e,\text{cal}}$) to the experimented ($q_{e,\text{exp}}$) values were observed to be very close for second-order when compared to the first-order. The best fit of the second-order on the adsorption of Pb(II) and As(III) by AWCAC can be further confirmed on their adsorption rate constant ($K_2$) smaller values as compared to the rate constant ($K_1$) of the first-order. The adsorption constant rate decreases as the metal ion concentration increases confirmed that the Pb(II) and As(III) uptake onto AWCAC attain equilibrium position faster at a lower initial concentration (Azizian & Yahyaei, 2006; Nanganoa, Ketcha, & Ndi, 2014).

### 3.8. Adsorption thermodynamic studies

The feasibility and spontaneity nature of Pb(II) and As(III) adsorption onto AWCAC were revealed by the adsorption thermodynamic parameters at various temperatures. The entropy change ($\Delta S^o$) and enthalpy change ($\Delta H^o$) were calculated from log $\frac{q_{e,\text{cal}}}{C_0}$ against $\frac{1}{T}$ plots intercept and slope.

$$\log \frac{q_{e,\text{cal}}}{C_0} = -\frac{\Delta H^o}{2.303R} \cdot \frac{1}{T} + \frac{\Delta S^o}{2.303R} \quad (9)$$

where $\Delta H$ is the enthalpy change and $\Delta S$ is the entropy change. Free Gibbs energy is equation is given by:

$$\Delta G^o = \Delta H^o - T\Delta S^o \quad (10)$$

| Adsorbents                | Maximum adsorption Pb(II) capacities (mg/g) | As(III) capacities (mg/g) | References |
|--------------------------|---------------------------------------------|---------------------------|------------|
| AWCAC                    | 250                                         | 200                       | Present study |
| Coconut husk             | –                                           | 146.30                    | Kairvelu, Thamaraiselvi, & Namazivayam, (2001) |
| Rice husk barchar        |                                             | 19.3                      | Samsuri, Sadegh-Zadeh, & Seh-Bardan, (2013) |
| Char carbon              |                                             | 89                        | Pattanayak, Mandal, Mathew, & Lalvani, (2009) |
| Soyabean hull            | 37.37                                       | –                         | Johns, Marshall, & Toles, (1998) |
| Iron-chitosan granules   | –                                           | 2.32                      | Gupta, Chauhan, & Sankararamakrishnan, (2009) |
| Peanut shell              | 35.5                                        | –                         | Xu & Liu, (2008) |
| Pecan shell               | 64.2                                        | –                         | Bansode, Losso, Marshall, Rao, & Portier, (2013) |
| Iron-chitosan flakes     | 16.2                                        | –                         | Gupta et al., (2009) |
| Ce-Ti oxide adsorbent    | 6.8                                         | –                         | Li, Deng, Yu, Huang, & Lim, (2010) |
| Palm nut shell           | 95.2                                        | –                         | Issabayeva, Arousa, & Sulaiman, (2006) |
| Rice husk ash            | 26.11                                       | –                         | Nnaji, Ebeagwu, & Ugwu, (2017) |
| Cotton stalk             | –                                           | –                         | Li, Zheng, Zhang, & Mei, (2010) |
| Groundnut shell          | 86.25                                       | –                         | Isah & Yusuf, (2012) |
| Hazelnut husk            | 13.03                                       | –                         | Imamoglu & Tekir, (2008) |
| Coconut shell            | 76.6                                        | –                         | Kikuchi, Qian, Machida, & Tatsumoto, (2006) |
| Metals | Metal Conc. (mg/L) | \( q_e, \text{cal (mg/g)} \) | Pseudo-first-order | | | | Pseudo-second-order | | |
|---|---|---|---|---|---|---|---|---|
| | | \( q_e, \text{exp (mg/g)} \) | \( K_1, \text{(min}^{-1}) \) | \( R^2 \) | | \( q_e, \text{exp (mg/g)} \) | \( K_2, \text{(g/mg min) (×10}^{-3}) \) | \( R^2 \) |
| Pb(II) | 50 | 42.342 | 38.860 | 0.051 | 0.932 | 50.761 | 2.280 | 0.995 |
| | 100 | 91.343 | 91.876 | 0.055 | 0.965 | 108.696 | 0.753 | 0.996 |
| | 150 | 138.310 | 141.612 | 0.047 | 0.919 | 158.730 | 0.044 | 0.996 |
| As(III) | 50 | 37.634 | 34.650 | 0.076 | 0.952 | 47.175 | 2.998 | 0.988 |
| | 100 | 92.463 | 82.699 | 0.033 | 0.988 | 97.909 | 0.472 | 0.990 |
| | 150 | 133.464 | 121.479 | 0.043 | 0.970 | 151.330 | 0.449 | 0.986 |
The thermodynamic result parameters calculated for Pb(II) and As(III) adsorption are revealed in Table 4. The negative free Gibb’s energy ($\Delta G^\circ$) values obtained at various temperatures for both metals revealed that the adsorbates-adsorbent interactions during the adsorption process are Spontaneous and feasible. This result was further established by the negative enthalpy ($\Delta H^\circ$) and entropy ($\Delta S^\circ$) values gotten signifying that the adsorption processes on both Pb(II) and As(III) onto AWCAC was exothermic, physical, involves weak attraction forces and decrease in
randomness during process adsorption at the liquid-solid interface of both metals on AWCAC surface. The negative enthalpy ($\Delta H^\circ$) values could be attributed to movement restriction when metals are adsorbed on a solid surface thereby causing a decrease in entropy and residual forces on the adsorbent surface thereby resulting in energy surface decrease of the adsorbent (Aravindhan, Fathima, Rao, & Nair, 2007; Li, Yue, Su, Gao, & Sun, 2010).

4. Conclusion
A novel low-cost bio-adsorbent from agricultural waste composite using KCl as an activating agent for the uptake of Pb(II) and As(III) from an aqueous solution in a batch adsorption process has been established. The chemical activation of the char gave rise to the surface area from 230.242 to 849.630 m$^2$/g and also an upsurge in the pore volume from 0.1351 to 0.4967. Owing to the increasing pH, there was an increase in the uptake of Pb(II) and As(III) respectively. The metals' uptake depends significantly on the amount of AWCAC. The equilibrium time for both metal ions to reach equilibrium was 90 min. The adsorption monolayer capacities for Pb(II) and As(III) as informed by the Langmuir model were 250 and 200 mg/g. The obtained parameters from the three isotherm studies proved that Langmuir described best the adsorption process on both Pb(II) and As(III) then followed by Temkin and Freundlich models, respectively. The adsorption of Pb(II) and As(III) onto AWCAC obeyed pseudo-second-order kinetics. The adsorption process is thermodynamically spontaneous, exothermic and physical in nature. The high adsorption capacities of AWCAC alongside their advantages such as reusability, environmental-friendly nature, abundance nature and its effectiveness in terms of cost make it a better alternative to be used than other commercial adsorbents for the uptake of the heavy metal ions.

Acknowledgement

Authors wish to acknowledge Landmark University Centre for Research, Innovation and Development (LUCRID) for their support.

Funding
The authors received no direct funding for this research.

Competing Interests
The authors declared no competing interest.

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Citation information
Cite this article as: Development of low-cost bio-adsorbent from agricultural waste composite for Pb(II) and As(III) sorption from aqueous solution, K. S. Obayomi, J. O. Bello, J. S. Nnoruka, A. A. Adediran & P.O Olajide, Cogent Engineering (2019), 6: 1687274.

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