INTRODUCTION
Heavy metal pollution in the aquatic environments have become sources of great concern because these heavy metals are usually present in wastewater which is released to the environment from various industrial complexes. This concern is genuine and especially so since the heavy metals are non-biodegradable and accumulate in living systems resulting in various diseases. This fear has been heightened in recent times due to advancements in technology (Ameh et al., 2016). The removal of contaminants in industrial wastewater is an important issue in countries with limited economic resources due to advancements in technology (Ameh et al., 2016). The removal of contaminants in industrial wastewater is an important issue in countries with limited economic resources due to advancements in technology (Ameh et al., 2016). The removal of contaminants in industrial wastewater is an important issue in countries with limited economic resources due to advancements in technology (Ameh et al., 2016).

MATERIALS AND METHODS
The chemicals used are commercially available Analar grade reagents and require no further purification. The distilled and deionized water used were fully characterized. Annona senegalensis is a species of flowering plant in the custard apple family, Annonaceae. It is also known as the African custard apple, wild custard apple, wild soursop, sunkungo (Mandinka language), dorgot (Wolof language), and ukpokpo (Igala language). The specific epithet senegalensis refers to the nation where the original specimen was found, translates to “of Senegal.” The fruits of A. senegalensis, a traditional food plant in Africa, may enhance nutrition, increase food security, promote rural development, and aid in sustainable land management. Annona senegalensis stem bark was collected from the Muslim High School farm in Anyigba, Kogi State and stored in polyethylene bag before taking to the laboratory facility of the Department of Pure and Industrial Chemistry, Kogi State University, Anyigba. Sample pre-treatment was carried out in the laboratory. The plant was identified by a staff of the Plant
Science and Technology Department of Kogi State University, Anyigba. The stem bark was thoroughly washed with water and then pulverized before washing extensively with deionized water to remove any adhering dirt. The sample was sundried for two weeks and oven-dried at 105°C for 6h and thereafter, ground into powder using the grinding mill. The dried stem bark powder was sieved into different particle sizes (0.154, 0.180, 0.280, 0.450 and 0.900 mm) mesh sizes. The individually sieved fractions were stored in plastic containers for use as adsorbents.

Carbonization and activation
Carbonization of the adsorbent was carried out according to the method of Ekere et al., 2018. A 50 g mass each of dried A. senegalensis Stem Powder was carbonized in a muffle furnace at different temperature ranges (300°C, 350°C, 400°C, 450°C and 500°C) for 2 h each. At the end of 2 h, each of the samples was cooled in a desiccator for 3 h and then stored in air-tight bottles. The carbonized A. senegalensis Stem bark was activated via a chemical process. About 40 g were soaked in 250 mL of 25% ZnCl₂ solution in five different 300 mL beakers for 24 h. After 24 hours, the mixture was filtered, and the residue was neutralized with diluted HCl before being cleaned with deionized water to a pH of 7.0. The samples were then dried at 105°C in a thermostatically controlled oven, and the product, which was given the name Modified Activated Annona Senegalensis Carbon, was then allowed to cool to room temperature (MAASC). The MAASC (stem-activated carbon from A. senegalensis) was kept in airtight bottles.

Physicochemical characterizations
Using a pH and conductivity meter that was already calibrated, the pH and conductivity were determined (Hanna instruments, model 0801). Using ASTM-recommended techniques, the percentages of moisture, ash, and volatile matter were measured. Using this technique, bulk density and porosity were determined according to Horsefall et al., 2011. The crystalline size and phases of the produced MAASC powders were determined using XRD spectroscopy. Before and after the batch adsorption investigations, the size, shape, and morphological characteristics of the adsorbents were examined using the SEM technique. The JCM-6000 NeoScopeTM with connected energy dispersive X-ray spectroscopy was used to take all micrographs. Before and after metal adsorption investigations, the MAASC adsorbents' species and functional groups were identified using FT-IR spectroscopy. An Agilent Technologies Microlab FT-IR spectrometer with a Universal Single bounce Diamond ATR adapter was used to analyze the samples. Both FT-IR spectra were recorded in the range from 650 to 4000 cm⁻¹ in steps of 4 cm⁻¹.

Adsorption procedure
Unless otherwise noted, all stock solutions were made using analytical-grade reagents. Each day, new working standards were created by properly diluting the stock solutions. The effects of pH (2, 4, 6, 8 and 10) and adsorbent dosage (0.5, 1.0, 1.5, 2.0, and 2.5g), agitation time (5, 10, 20, 30, 40, 60, 80, and 100 minutes), initial adsorbate solution (5, 10, 15, 20 and 25 mg/L), and solution temperature were examined in the range from 650 to 4000 cm⁻¹ of sorbent towards the adsorbate. It is given by

\[ q_e = \frac{(C_0 - C_e) \cdot V}{W} \quad (1) \]

where \( C_0 \) and \( C_e \) (mg L⁻¹) are the liquid-phase concentrations of metal ions at initial and equilibrium, respectively. V is the volume of the solution (l), and W is the mass of dry adsorbent used (g). The equation below was used to calculate the proportion of metal ions removed from the aqueous solutions

\[ \text{Percentage removal of metal ion, } E_q = \frac{C_0 - C_e}{C_0} \times 100 \]

Adsorption isotherm studies
The experimental data for the metal ion adsorption onto A. senegalensis was fitted to the four-parameter isotherm models. The Langmuir equation is given by

\[ q_e = \frac{q_{\text{max}} \cdot K_L \cdot C_e}{1 + K_L \cdot C_e} \quad (3) \]

where \( C_e \) is equilibrium adsorbate concentration(mg g⁻¹). \( K_L \) is Langmuir constant related to adsorption capacity(mg g⁻¹), which means that a large surface area and pore volume will lead to a higher adsorption capacity and is related to the variation of the adsorbent's porosity and surface area. The following linear form can be used to represent the equation:

\[ \frac{1}{q_e} = \frac{1}{q_{\text{max}}} \cdot \frac{1}{K_L} + \frac{1}{q_{\text{max}}} \cdot \frac{1}{C_e} \quad (4) \]

A plot of 1/qe against 1/Ce gives a straight line with a slope of (1/qmaxKL) and an intercept of 1/qmax. Or

\[ \frac{C_e}{q_e} = \frac{C_e}{q_{\text{max}}} + \frac{1}{q_{\text{max}}} \cdot \frac{1}{K_L} \]

A plot of Ce/qe against Ce also gives a straight line. The Freundlich model is an empirical equation just like the Langmuir model. It is used to estimate the adsorption intensity of sorbent towards the adsorbate. It is given by

\[ q_e = K_F \cdot C_e^{1/n} \quad (5) \]

where \( K_F \) is adsorption capacity (L/mg) and 1/n is adsorption intensity; it also indicates the relative distribution of the energy and the heterogeneity of the adsorbate sites. Linearizing equation (5) we have

\[ \log q_e = \log K_F + \frac{1}{n} \log C_e \quad (6) \]

a plot of \( \log q_e \) against \( \log C_e \) gives a straight line with \( 1/n \) as the slope and \( \log K_F \) as the intercept. The corresponding constants and coefficient of correlation (R²) associated with each linearized model at 25°C for the metal ions would be calculated. The Temkin equation is

\[ Q_e = \frac{R \cdot T \cdot n \cdot A}{b \cdot T} + \frac{R \cdot T \cdot n \cdot A}{b} \quad \text{or} \quad q_e = B \cdot \ln A + B \cdot \ln C_e \quad (7) \]

where B = RT/br relating to the heat of adsorption, R is the universal gas constant, br is the adsorption potential of the adsorbent (J/mol) and A is the equilibrium binding constant (L/mg). The parameters for the Temkin model are obtained from the plot of qe against ln Ce.
The Dubinin-Radushkevich (D-R) equation is represented in a linear form by
\[ \ln q_e = \ln q_0 - K_D \varepsilon^2 \]  
(8)
where \( K_D \) (mol/KJ²) is a constant related to the mean adsorption energy and \( \varepsilon \) is the Polanyi potential which is derived from the equation
\[ \varepsilon = R T (1 + \frac{1}{t^5}) \]  
(9)
In \( q_e \) is plotted against \( \varepsilon^2 \) and the slope gives \( K_D \) and the intercept yields the sorption capacity, \( Q_0 \) (mg/g).

Kinetic modelling studies

The rate of adsorption of trace components onto porous solid surfaces has been described using a variety of adsorption kinetic models. Pseudo-first order and pseudo-second-order kinetic models are the most often employed types. Based on the results of the experiments, the Langergren pseudo-first-order and pseudo-second-order kinetic models are used to examine the metal ion adsorption kinetics. The sorption rates would be calculated as follows,
\[ \ln (q_e - q_t) = \ln q_e - K_1 t \]  
(10)
Where \( q_e \) is the amount of metal ions adsorbed at equilibrium (mg/g); \( q_t \) is amount of metal ions adsorbed at time, \( t \) (mg/g); \( K_1 \) is Pseudo-first-order rate constant (g/mg/min) and \( t \) is the time (min). A graph of \( \ln (q_e - q_t) \) versus \( t \) is plotted where the pseudo-first-order rate constant, \( k_1 \) and \( q_e \) are estimated from the slope and the intercept.

The linear form of second-order kinetic equation is
\[ \frac{1}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \]  
(11)
where \( q_e \) is the amount of metal ions adsorbed at equilibrium (mg/g); \( q_t \) is the amount of metal ions adsorbed at time, \( t \) (mg/g), \( K_2 \) is Pseudo-second-order rate constant (g/mg/min) and \( t \) is time (min).

Just like in the first order, a graph is drawn between \( 1/q_t \) versus \( t \). The pseudo-second-order rate constant, \( K_2 \) and \( q_e \) are obtained from the intercept and slope respectively.

The initial rate of intra-particle diffusion is determined using the following equation in accordance with the intra particle model proposed by Weber and Morris (1963).
\[ q_t = K_{diff} t^{0.5} + C \]  
(12)
where \( q_t \) is the amount of adsorbate deposited on the adsorbent (mg/g), and \( K_{diff} \) (mg/g min ⁰.⁵) gives the intra-particle diffusion rate constant, \( t \) is the time of contact between adsorbate and adsorbent (min) and \( C \) is the intercept.

From concentration versus time data, \( q_t \) is obtained for different agitation times. A graph is drawn between \( q_t \) and \( t^{0.5} \). The standard free energy (\( \Delta G^\circ \)), standard enthalpy change (\( \Delta H^\circ \)) and standard entropy change (\( \Delta S^\circ \)) were evaluated to assess the feasibility of the adsorption process. \( \Delta G^\circ \) is given by the equation:
\[ \Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \]  
(13)
The \( \Delta G^\circ \) is standard Gibbs free energy related to the thermodynamic equilibrium constant (\( K_c \)) thus:
\[ \Delta G^\circ = RT \ln K_c \]  
(14)
Where, 
T = temperature (K); R = ideal gas constant (8.314 J/mol K) and \( K_c \) is defined by the equation:
\[ K_c = \frac{C_a}{C_e} \]  
(15)
where \( C_a \) and \( C_e \) are the metal ion concentration adsorbed from solution at equilibrium (mg/L) and the equilibrium metal ion concentration in the solution (mg/L) respectively. The Gibbs’s free energy (\( \Delta G^\circ \)), the enthalpy change (\( \Delta H^\circ \)) and the entropy change (\( \Delta S^\circ \)) have a relationship at a constant temperature by the Van’t Hoff equation as shown below:
\[ \ln K_c = \left( \frac{\Delta H^\circ}{RT} \right) + \left( \frac{\Delta S^\circ}{R} \right) \]  
(16)
The values of enthalpy change (\( \Delta H^\circ \)) and the entropy change (\( \Delta S^\circ \)) were estimated from the slope and intercept of the plot of \( \ln K_c \) versus 1/T. This equation is used to study the variation of the thermodynamic equilibrium constant with temperature.

RESULTS AND DISCUSSION

Table 1 displays the results of the physicochemical analyses of Annona senegalensis stem bark. Volatile matter, bulk density, porosity, pH, moisture and ash levels, and electrical conductivity are only a few of the characteristics examined.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>6.3 ± 0.61</td>
</tr>
<tr>
<td>Moisture content (%)</td>
<td>11.73 ± 0.2</td>
</tr>
<tr>
<td>Ash content (%)</td>
<td>7.21 ± 0.02</td>
</tr>
<tr>
<td>Volatile matter (%)</td>
<td>18.2 ± 1.00</td>
</tr>
<tr>
<td>Bulk density (g/cm³)</td>
<td>0.18 ± 0.07</td>
</tr>
<tr>
<td>Porosity</td>
<td>0.995 ± 0.08</td>
</tr>
<tr>
<td>Electrical conductivity (µS/cm)</td>
<td>180.00 ± 2.09</td>
</tr>
<tr>
<td>Fixed carbon (%)</td>
<td>62.85 ± 0.94</td>
</tr>
</tbody>
</table>

All parameters were determined in triplicates and values are Mean±SD.

Microscopic and Spectroscopic characterization

Fig. 1a displays the raw adsorbent’s XRD pattern. In Fig. 1a, some distinctive peaks are seen at 2θ values between 150 and 250° and 300° and 400°. The carbonized adsorbent’s peak pattern (Fig. 1b) has a somewhat different shape. The peaks in 1a are broad, but the peaks in 1b are often pointy and sharp. The amorphous nature of the adsorbent in its raw powder form in Fig. 1a explains why the activated product in 1b is crystalline. Sharp peaks with unique shapes were seen at positions 2θ = 27°, 29°, 33°, 36°, 38°, 39°, 43°, 48°, 49°, 58°, 59°, 65°, and 66°. The XRD peaks show nanoscale crystalline. Sharp peaks with unique shapes were seen at positions 2θ = 27°, 29°, 33°, 36°, 38°, 39°, 43°, 48°, 49°, 58°, 59°, 65°, and 66°. The XRD peaks show nanoscale particles and are near the carbon allotrope of graphite. A non-destructive method that exposes a compound’s crystalline structure is XRD (Syed et al., 2016).
The SEM analysis findings for raw and chemically activated MAASC, respectively, are shown in Figures 2a and b. The outcome demonstrated the presence of sheet particles that appear to be scattered hexagons (Fig 2a). The activated adsorbent's morphology (Fig. 2b) was noticeably different since it was found to be rather rough and uneven in shape, but it also had pores with white sheets where heavy metal binding is presumed to have occurred.
The presence of several of the adsorbent's peaks was confirmed by the FTIR spectra (Fig 3a and b). The raw adsorbent's spectrum before activation is shown in Fig. 3a. O-H stretching group is indicated by the large peak found at 3339.7 cm\(^{-1}\) in the raw biosorbent. The other notable peaks at wavenumbers (cm\(^{-1}\)) 2918.5 - 2847.7 are associated with the C-H stretching vibrations of aliphatic groups, 1736.9 with the C=O vibrations of carbonyl groups, 1599.0 with the C-O stretching vibrations of carboxyl groups, and 1032.5 and 875.9 with the S-O stretching and S=O bands, respectively. The main peaks changed to 3488.8, 1446.2, 1066.0, and 700.7 cm\(^{-1}\) after chemical activation, metal ion adsorption, and functionalization (3b). The best intensities for these peaks ranged from 98.47 to 98.67%. The fact that some of the peaks present in the raw biosorbent's spectra disappeared after activation indicated that the raw adsorbent had changed as a result of chemical treatment.
Effect of solution pH

Figure 4 depicts how solution pH affects the metal ion adsorption to MAASC. The findings show that uptake steadily rose to a maximum of 6 with a higher pH. At pH 4, Co\(^{2+}\), Pb\(^{2+}\), and Ni\(^{2+}\) maximal biosorption rates of 99.69, 88.20, and 85.93\% respectively, were noted. Due to the positively charged proton in the solution competing with the metal ions for the active site, adsorption was significantly hindered at pH 2 to 5. Biosorption significantly increased as pH rose between 6 and 7, and some of the best outcomes were noted during this time. However, at higher pH levels (7–9), the biosorption of metal ions was again dramatically reduced, partially as a result of the production of the hydroxide anion, which reduced the concentrations of metal ions in the solution. This is consistent with studies conducted by Rahman and Sathasivan, (2015); and Xu et al., (2017).
Effect of adsorbent dose
Adsorbent dosage is crucial in a variety of ways because it establishes the extent of metal ion removal and, consequently, can be used to calculate the cost of remediation. Studies on the effects of different metal ions on MAASC were conducted at 30°C, pH 6, and variable doses between 0.5 and 2.5 g. The effects of the changes are shown in Fig. 5, where it can be seen that an increase in MAASC mass resulted in a proportionate increase in the quantity of adsorption. At the maximum dosage of 2.5 g, the absorption of all the examined metals was at its highest. This is explained by the abundance of accessible adsorption sites. This presumption is consistent with previous works by Ameh et al., (2016) and Ekere et al., (2018).

![Figure 5: Effect of adsorbent dose on heavy metal biosorption onto MAASC](image)

Effect of agitation time
Results from an investigation into how metal ion intake influences time are displayed in Fig. 6. The findings showed that, except for Pb\(^{2+}\), which reaches its maximum uptake after 40 minutes, the maximum uptake of 97.03, 59.40, and 86.76% for Co\(^{2+}\), Pb\(^{2+}\), and Ni\(^{2+}\) occurred at times over 80 minutes. Additionally, the reduced uptake of the metal ions seen after about 80 minutes is indicative of the MAASC active site becoming saturated. However, several academic works asserted that the equilibrium biosorbent and contact time for biomass are reached around 90 minutes (Rahman and Sathasivan, 2015 and Ekere et al., 2018).

![Figure 6: Effect of agitation time on heavy metal biosorption onto MAASC](image)

Effect of initial metal ions concentration
Using different concentrations ranging from 5 to 25 mg/L, it was examined how the initial concentration of metal ions affected the effectiveness of their removal. According to the findings, the removal percentages of Co\(^{2+}\), Pb\(^{2+}\), and Ni\(^{2+}\) metal ions decreased steadily from 99.27 to 90.00%, 69.60 to 53.20%, and 92.39 to 81.92%, respectively. Since the initial concentration must have occupied all of the accessible active sites, this observation may be explained by the adsorbent’s fixed nature. This outcome, as displayed in Fig. 7, is consistent with the studies of Yusuf et al., 2017.
Effect of solution temperature
Over a temperature range of 30 to 50°C, the impact of temperature on the removal of metal ions by MAASC was investigated. Fig. 8 displays the study’s findings. All of the metal ions under study had already reached equilibrium at 45°C, with the exception of Co^{2+}, which did so at 40°C. The observation revealed that Pb^{2+} and Ni^{2+} reached equilibrium at 45°C with 65.05 and 73.92%, respectively. At 40°C, however, Co^{3+} achieves equilibrium with a removal rate of 97.71% by biosorbent. This is a spontaneous occurrence, and it can be explained by the activation of MAASC biosorbent at higher temperatures, which led to the identification of more active sites for metal ion adsorption. Furthermore, the increased kinetic energy and mass transfer of metal ions may be the cause of reaching equilibrium before 50°C. This is consistent with work done by others (Oluwashola et al., 2019 and Umeh et al., 2021).

Effect of particle size
The MAASC was used to study the adsorption of metal ions with particle sizes of 0.154, 0.180, 0.280, 0.450, and 0.900mm. The results showed that as the particle size rose, the removal of metal ions reduced, as illustrated in Fig. 9. This suggests that the rate of uptake increases as the diameter of the particle decreases. This might be explained by the fact that smaller particles have more surface area and, consequently, more adsorption-active sites. Larger particle size, on the other hand, leads to less adsorption. This might be because there aren’t enough active sites for metal ion biosorption, which causes diffusion to mass transfer to be resistant.
Effect of carbonization temperature

To test the impact of the carbonization temperature on the metal ions by MAASC biomass, the temperature ranging from 300 to 500°C were employed. Fig. 10 presents the evaluation's findings. The observed results showed that there was a commensurate rise in metal ion uptake when the temperature rose from 300°C to 350°C. The rate of metal uptake gradually increased when this occurred and started to decline beyond 400°C. This is due to material rearrangement brought on by the action of increased heat, which results in the opening up of new active sites. However, as the temperature increased, adsorption rapidly attained saturation, which prevented absorption. This view is consistent with earlier research by Ekere et al., (2015) that found that at carbonization temperatures above 400°C, uptake substantially decreases while carbonization temperatures below 400°C increase the level of internal re-arrangement of materials by opening up more pores as heat is increased.

Adsorption isotherm studies

The link between the concentration of the adsorbate and its degree of adsorption onto the adsorbent surface, as well as details on the sorption mechanism, surface characteristics, and affinity of the adsorbent at a constant temperature, are all revealed by the adsorption isotherm. The equilibrium results were analyzed using the Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich isotherm models to maximize the MAASC's ability to adsorb Co(II), Pb(II), and Ni(II) ions from aqueous solution. Table 2 displays the analysis findings.

<table>
<thead>
<tr>
<th>Model</th>
<th>Parameter</th>
<th>Co²⁺</th>
<th>Pb²⁺</th>
<th>Ni²⁺</th>
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</thead>
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<tr>
<td></td>
<td></td>
<td>Co²⁺</td>
<td>Pb²⁺</td>
<td>Ni²⁺</td>
</tr>
<tr>
<td>Langmuir</td>
<td>qₑₒₚ (mg/g)</td>
<td>45.05</td>
<td>22.73</td>
<td>3.2248</td>
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<tr>
<td></td>
<td>Kₑ (L/mg)</td>
<td>0.03154</td>
<td>0.04927</td>
<td>0.0082</td>
</tr>
<tr>
<td></td>
<td>Rₑ</td>
<td>0.0016</td>
<td>0.092</td>
<td>0.0004</td>
</tr>
<tr>
<td></td>
<td>R²</td>
<td>0.9995</td>
<td>0.9171</td>
<td>0.9987</td>
</tr>
<tr>
<td></td>
<td>R_L</td>
<td>0.0016</td>
<td>0.092</td>
<td>0.0004</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Freundlich</td>
<td>Kₓ</td>
<td>46.45</td>
<td>8.71</td>
<td>38.66</td>
</tr>
<tr>
<td></td>
<td>n</td>
<td>25.58</td>
<td>1.6445</td>
<td>7.19</td>
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<td></td>
<td>R²</td>
<td>0.8792</td>
<td>0.9531</td>
<td>0.993</td>
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<tr>
<td>Temkin</td>
<td>A_r (L/mg)</td>
<td>4.394</td>
<td>97.56</td>
<td>0.427</td>
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<td></td>
<td>b_r (KJ/mol)</td>
<td>563.853</td>
<td>25.395</td>
<td>5.802.2</td>
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<tr>
<td></td>
<td>R²</td>
<td>0.5703</td>
<td>0.936</td>
<td>0.9832</td>
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<tr>
<td>Dubini-Radushkevich</td>
<td>qₑₒₚ (mg/g)</td>
<td>3.8584</td>
<td>3.7094</td>
<td>3.8389</td>
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<tr>
<td></td>
<td>Kₑₑₑ (mol²/KJ²)</td>
<td>3 x 10⁶</td>
<td>3 x 10⁶</td>
<td>1 x 10⁷</td>
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<tr>
<td></td>
<td>Rₑₑₑ</td>
<td>0.4171</td>
<td>0.8969</td>
<td>0.9663</td>
</tr>
<tr>
<td></td>
<td>Eₑₑₑ</td>
<td>0.408</td>
<td>0.408</td>
<td>2.236</td>
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</table>

The Langmuir isotherm model predicts that monolayer sorption will result in homogenous sites inside the adsorbent with no interaction between adsorbed species. Kₑ and R_L, respectively, provide the Langmuir equilibrium constant (L/mg) and the characteristics of the adsorption process. Adsorption is therefore regarded as irreversible if R_L equals zero (R_L = 0), favorable if R_L is less than one (R_L < 1), linear if R_L is equal to one (R_L = 1), and unfavorable if R_L is higher than one (R_L > 1). The R_L of all the metal ions examined was 0.0016 for Co²⁺, 0.092 for Pb²⁺, and 0.0004 for Ni²⁺, all of which are below 1, indicating that they will all adsorb favorably.
Due to its superior correlation coefficient ($R^2$), which is close to 1, the Langmuir isotherm provided a good conformation analysis of the equilibrium data when the correlation coefficients of all other isotherms used were compared. The Freundlich isotherm came next. The isotherm order for the metal ions' adsorption onto MAASC is as follows: Langmuir > Freundlich > Temkni > Dubinin-Radushkevich. When specific metal ions are taken into account, the Langmuir and Ni isotherms were shown to be the best fits for Co, with correlation coefficients ($R^2$) of roughly 1.00 and 1.00, respectively. With a correlation coefficient of roughly 0.95, Freundlich's isotherm was, however, the one that fit Pb the best.

**Adsorption kinetic studies**

To analyze the obtained data and determine the rate and potential adsorption process, adsorption kinetic models were fitted. The findings are shown in Table 3 for the applied models, which include pseudo-first order, pseudo-second order, and intra-particle diffusion kinetic model equations. All of the kinetic model's equations were applied to the kinetic data.
UPTAKE OF Co(II), Pb(II) AND Ni(II) IONS… Omale et al., FJS FU DMA Journal of Sciences (FJS) Vol. 8 No. 2, April, 2024, pp 59 - 72

Table 3: Biosorption kinetic models for the adsorption of metal ions onto MAASC biosorbent

<table>
<thead>
<tr>
<th>Kinetic Models</th>
<th>Parameters</th>
<th>Metal ion</th>
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<tbody>
<tr>
<td></td>
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<td>Co^{2+}</td>
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<tr>
<td>PFO</td>
<td>$K_1$ (min^{-1})</td>
<td>0.0106</td>
</tr>
<tr>
<td></td>
<td>$q_o$ (mg/g)</td>
<td>24.31</td>
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<tr>
<td></td>
<td>$R^2$</td>
<td>0.885</td>
</tr>
<tr>
<td></td>
<td>$K_2$ (g/mg min)</td>
<td>0.00389</td>
</tr>
<tr>
<td>PSO</td>
<td>$h$ (mg/g min)</td>
<td>39.22</td>
</tr>
<tr>
<td></td>
<td>$t_{1/2}$ (min)</td>
<td>5.983</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.167</td>
</tr>
<tr>
<td></td>
<td>$k_d$ (mg/g min^{0.5})</td>
<td>0.997</td>
</tr>
<tr>
<td>IPD</td>
<td>$C$ (mg/g)</td>
<td>3.0159</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>13.54</td>
</tr>
<tr>
<td></td>
<td>$k_d$</td>
<td>0.9423</td>
</tr>
</tbody>
</table>

According to the findings, pseudo-first-order kinetic model data is very helpful in characterizing the adsorption kinetics of the metal ions, particularly for Pb and Ni, which have $R^2$ values of 1.00 and 0.98, respectively. This excludes Co with a value of 0.89, hence it is insufficient to describe the kinetics of metal ions adsorbing on MAASC. Similar observations regarding the biosorption kinetics of metal ions have been published in the literature (Rahman and Sathasivan, 2015; Arshadi et al., 2014).

In Table 3 and Fig. 14, the solutions to the pseudo-second order kinetic model equations are also displayed. The pseudo-second-order equation demonstrated to be a superior model in explaining the experimental data, with the $R^2$ exhibiting superiority among the tested kinetic models with 1.00, 1.00, and 1.00 approximately for Co^{2+}, Pb^{2+}, and Ni^{2+} correspondingly. Given the initial uptake rate, $h$ (2.090 to 12.581 mg/g min) in the first few minutes, where more than 75% of adsorption occurred, it was determined that the rate constant, $k_2$, ranged from 0.00064 to 0.00831g/mg min. This indicated that the spontaneity of the adsorption process was quick and favorable. Diffusion was therefore the process rate-limiting stage. The duration of half-adsorption to take place, $t_{1/2}$, ranged from 0.07795 to 0.476 minutes showing high sorbate-sorbent affinity. This finding is consistent with other works published in the literature (Akpmie et al., 2015; Rahman and Sathasivan, 2015).

Figure 14: Pseudo-first-order kinetic model for metal ions biosorption onto MAASC

$y = -0.0046x + 1.3857 \quad R^2 = 0.885$

$y = -0.0164x + 0.9272 \quad R^2 = 0.9971$

$y = -0.0101x + 0.985 \quad R^2 = 0.9841$
UPTAKE OF Co(II), Pb(II) AND Ni(II) IONS… Omale et al., FJS

Figure 15: Pseudo second order kinetic model for metal ions biosorption onto MAASC

The Weber-Morris intra-particle diffusion model was also applied to the kinetic data; the results are shown in Table 3 and Fig. 15. Molecular diffusion is regarded as the most emblematic of all the transport processes out of all the physicochemical phenomena, including dimensional micelle creation, electro-kinetic interactions, and molecular diffusion. This might be because people frequently obstruct the gradient-oriented movement of migratory species. According to the results, \( K_d \) is the rate constant for intra-particle diffusion, and \( C \) is the intercept that veered away from the origin, suggesting that there are other rate-determining processes outside intra-particle diffusion. As a result, a boundary layer effect can be seen in the first curved part of Fig. 16. Furthermore, the regression coefficients of 0.94 (Co\(^{2+}\)), 0.92 (Pb\(^{2+}\)), and 0.99 (Ni\(^{2+}\)) show that intra-particle diffusion plays a substantial role in the adsorption of the metal ions. The latter, linear-appearing segment of the curve illustrates this outcome. Although the \( R^2 \) of the intra-particle diffusion model was lower than that of the pseudo second order model, it was still higher than that of the pseudo first order model. This suggests that because the PSO kinetic model had the best regression coefficient, it provided a better treatment of the data. This result was anticipated, and additional researchers and the literature have confirmed this (Yusuf et al., 2017; Ekere et al., 2018 and Umeh et al., 2021).

Figure 16: Intra-particle diffusion model for the metal ions biosorption onto MAASC

Adsorption thermodynamic studies
The values of the thermodynamic parameters for the metal ion biosorption onto MAASC are presented in Table 4. The linear form of Van’t Hoff plots of \( \ln K_D \) versus \( 1/T \) is depicted in Fig. 16.

Table 4: Thermodynamic parameters for the adsorption of metal ions onto MAASC biosorbent

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>( \Delta H ) (KJ/mol)</th>
<th>( \Delta S ) (KJ/molK)</th>
<th>308K</th>
<th>313K</th>
<th>318K</th>
<th>323K</th>
<th>328K</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co(^{2+})</td>
<td>27.5077</td>
<td>109.73</td>
<td>-6.4799</td>
<td>-6.9507</td>
<td>-6.5851</td>
<td>-7.5476</td>
<td>-7.8684</td>
<td>0.9364</td>
</tr>
<tr>
<td>Pb(^{2+})</td>
<td>19.7009</td>
<td>83.74</td>
<td>-6.1657</td>
<td>-6.6987</td>
<td>-6.2658</td>
<td>-7.0637</td>
<td>-7.3037</td>
<td>0.9385</td>
</tr>
<tr>
<td>Ni(^{2+})</td>
<td>13.3739</td>
<td>65.92</td>
<td>-6.9208</td>
<td>-7.3370</td>
<td>-7.7469</td>
<td>-7.7469</td>
<td>-7.9860</td>
<td>0.9883</td>
</tr>
</tbody>
</table>
The negative values of $\Delta G^\circ$ at the different temperatures show that the thermodynamic process of metal ion adsorption onto MAASC was both possible and spontaneous. Additionally, the increase in metal ion uptake with the rise in solution temperature from 308 to 328 K led to a positive change in enthalpy, which was a sign of an endothermic process. The magnitude of the enthalpy values is also indicative of the several kinds of biosorption mechanisms, including physisorption, chemisorption, and combinations of the two. For physical adsorption, $\Delta H$ lies between 2.1 – 20.9 KJ/mol, for physical and chemical adsorption combined, $\Delta H$ lies between 20.9 – 80.0 KJ/mol while for chemical adsorption, $\Delta H$ lies between 80.0 – 200 KJ/mol. From our studies, Co$^{2+}$ with $\Delta H$ of 27.51 KJ/mol was adsorbed by a combination of both physical and chemical adsorption while Pb$^{2+}$ and Ni$^{2+}$ with $\Delta H$ of 19.70 and 13.37 KJ/mol were clearly adsorbed by physisorption. The D-R isotherm model results, which showed that E values less than 8 KJ/mol are suggestive of physisorption, provide unambiguous proof for this claim. Additionally, a significant degree of disorderliness at the solid-liquid interface during the biosorption of metal ions onto MAASC is suggested by the thermodynamic parameter $\Delta S^\circ$, which is completely positive.

CONCLUSION
The process of heavy metal adsorption onto biomass derived from agriculture involves several different mechanisms. Adsorbent dose, beginning metal ion concentrations, solution pH, solution temperature, agitation or contact time, as well as initial concentrations of metal ions (Co, Pb, and Ni), were all significant factors in our investigation since they affected the rate and efficiency of the process. The outcomes demonstrated that maximum metal ion uptake was accomplished at contact times of 88 minutes, pH values of 6.0 and 30 degrees Celsius, metal ion concentrations of 5 mg/L, and adsorbent doses of 2.5 g. We looked at the adsorption of Co(II), Pb(II), and Ni(II) onto chemically activated MAASC. Since $RL < 1$ and the adsorption capacities of Co$^{2+}$, Pb$^{2+}$, and Ni$^{2+}$ were 45.05 mg/g, 22.73 mg/g, and 3.22 mg/g at 30°C, respectively, the equilibrium values fit the Langmuir isotherm model well. All of the studied metal ions’ kinetic data fit the PSO kinetic model better because it highlighted the rate-limiting step for sorbate-sorbent interactions and provided the best conformation for the sorption mechanism. IPD is another process that play a significant role in the adsorption process. The heavy metal adsorption onto MAASC was endothermic, practicable, and spontaneous, according to the thermodynamic analysis. According to research using the Dubinin-Radushkevich isotherm model with fewer than 8 KJ/mol and thermodynamic results of the enthalpy change with less than 80 KJ/mol, the primary transport mechanism of the examined heavy metals is physisorption. As a result, this study demonstrated that activated carbon made from A. senegalensis can be used as an inexpensive, low-tech, ecologically friendly adsorbent for the removal of heavy metals from contaminated environment.

REFERENCES


