

Exploration of Industrial potential of *Camellia sinensis* Biochar Biomass for Heavy Metal Remediation: Isotherm and Kinetic Modelling

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ABSTRACT

This study evaluates *Camellia sinensis* leaves waste biochar as a low-cost, sustainable adsorbent for removing Hg(II) from industrial wastewater, combining physicochemical characterization, batch adsorption experiments, isotherm fitting and kinetic analysis. SEM imaging revealed a visibly porous morphology that contracted after sorption, indicating pore plugging by Hg(II) and supporting uptake inferred from spectral shifts. FTIR analysis identified hydroxyl, carbonyl and carboxylic acid functionalities that provide active sites for cation exchange, complexation and hydrogen bonding with mercury species. Batch experiments optimized pH, contact time, adsorbent dose and initial metal concentration, reporting an optimum pH of 6.0 and rapid equilibrium within 40 minutes. Percent removal increased with dose and reached a maximum removal of 92.35% under selected conditions while adsorption capacity rose with initial concentration to a highest observed value near 0.628 mg g⁻¹. Equilibrium data fitted both Langmuir and Freundlich models, with Langmuir providing a superior fit indicative of monolayer adsorption on a relatively homogeneous surface ($R_2 \approx 0.93$). Kinetic modelling favored a pseudo-second-order mechanism, suggesting chemisorption with rate dependence on available surface sites. Overall, the results demonstrate that *Camellia sinensis* leaves waste biochar is an effective, inexpensive and environmentally friendly material for mercury remediation and warrants further investigation for scale-up and real effluent applications. Complementary studies on regeneration, lifetime performance, interference from coexisting ions and pilot-scale column tests are recommended to validate operational feasibility and inform design of low-cost treatment systems tailored to industrial wastewater streams. This work supports circular valorization by converting tea leaves into functional adsorbents for contaminant control.

Keywords: *Camellia sinensis* biochar; mercury remediation; adsorption isotherm; kinetic modelling; low-cost adsorbent

INTRODUCTION

Heavy metals are terms which have been generally used to describe metals with atomic weight greater than iron (56) (Abdel-Rahman, 2012). Also, the term "heavy metals", have been used to describe metals having density greater than 5 gcm^{-3} (Sani, 2011). The actual definition of heavy metals is any metallic element that has a proportionally high density and is poisonous at low concentrations such as As, Pb, Cd, Hg and Cr (Appenroth, 2010). Generally, heavy metals are non-biodegradable in natural environment and are categorized in two groups. The first group is toxic metals (i.e. Pb, Cd and As etc.) which are undesirable: do not have biological benefits for human health and toxic at any concentrations. The second group is essential metals (i.e. Cu, Zn, Mn, Fe, Ni and Cr etc.) which are desirable and have biological benefits for human health at low concentrations, but it become toxic at high concentrations (Chen, 2012).

Cadmium, lead, arsenic and mercury are generally toxic to soil microbial populations, plants as well as humans (Liu *et al.*, 2007; Lenart and Wolny-kotadka, 2013; Mohammadi *et al.*, 2018), while copper, nickel and zinc act as micronutrients in low concentrations but can still be toxic when contents are high (Akbari *et al.*, 2012; Sobhan. 2016). They enter the food chain when accumulated in plant tissues resulting in further accumulation in human organs over time (Seenivasan *et al.*, 2008), that eventually can cause adverse health effects (Lai *et al.*, 2010).

Toxic levels of lead affect neurobehavioral development, brain function and have been associated with encephalopathy, seizures and mental retardation (Mason *et al.*, 2014). Cadmium has been implicated in kidney dysfunction, hepatic damage and hypertension (Madrigal *et al.*, 2019). Mercury's harmful effects, such as kidney damage, neurotoxicity, and bioaccumulation through the food chain, make it an important pollutant to control. Excess copper accumulates in the liver, brain, skin, pancreas and myocardium and the most toxic form of copper is thought to be Cu(I) (Tarnacka *et al.*, 2021). The effects of iron exposure on human health include respiratory problems, heart attack, seizures, tissue damage and depression (Jaishankar *et al.*, 2014).

Because of the above reasons, different methods can be used to treat the industrial wastewater such as advanced oxidation processes (AOPs), reverse osmosis, adsorption, ion exchange, ozonation, precipitation, filtration with coagulation and coagulation process (Park *et al.*, 2011).

Tea (*Camellia sinensis*), also known as shayi in Hausa, tii in Igbo and ti in Yoruba language belonging to the *Theaceae* family, was extensively cultivated in Asian, African, Latin American, and Oceanian countries (Cherotich *et al.*, 2013; Katoh *et al.*, 2015), which was believed to originate from northeast India, north Myanmar, and southwest China (Bora, 2016; Mukherjee *et al.*, 2018). Tea trees are generally divided into three types: shrubs, arbors, and minor arbors. In the harvest season, the shoot removed usually includes the bud and the two youngest leaves (Figure 1) (Wang *et al.*, 2022).

The word Biochar means a solid formed from the pyrolysis of biomass at a temperature below $700 \text{ }^\circ\text{C}$ under low or in the absence of oxygen (Park *et al.*, 2011). The resulting solid is rich in carbon and presents a promising adsorption potential allowing it to remove organic and inorganic contaminants from wastewater (Ambaye *et al.*, 2020).

Different waste materials such as straw, faeces, sludge have been tested as raw materials for biochar production (Ambaye *et al.*, 2020).

Different methods such as pyrolysis, hydrothermal carbonization, gasification can be used to produce biochar as proved by Park *et al.* (2016). Important attention has been devoted for effective techniques for eliminating harmful organic and inorganic compounds from water. A variety of techniques have been used for the removal of organic compounds from contaminated water and waste water, such as coagulation, filtration, electrocoagulation, precipitation, floatation, electrodialysis, membrane, adsorption, ion exchange, reverse osmosis, and advanced oxidation processes (Singh *et al.*, 2013; Nageeb, 2013). Although the traditional methods such as chemical precipitation, ion exchange, membrane separation process and electrocoagulation have been used to remove inorganic pollutants such as heavy metals, these methods have shown some limitations for high capital and operating cost (Tan *et al.*, 2012; Manyangadze *et al.*, 2020; Babel *et al.*, 2003). For example, the process of precipitation generates harmful sludge that it furthermore, needs another treatment. The downside of ion exchange technique is the lack of recyclability. The key drawbacks of the membrane filtration system are the problems of regeneration, high cost and getting rid of the produced sludge (Fiyadh *et al.*, 2019). The technique of flocculation and coagulation suffers from the volume of sludge produced, while the long duration needed is the downfall of the photocatalytic process. The method of electrodialysis is extremely successful, but requires high energy consumption and operating costs (Ihsanullah *et al.*, 2016). Owing to their relatively high expenditure and maintenance costs and the disposal of residual metal sludge, reverse osmosis and ion exchange don't seem to be low cost potential (Ivanov *et al.*, 2004). The previous methods from literature costs from US\$ 10 to US\$ 450 for the treatment of one cubic meter, excluding adsorption. Water treatment with adsorption costs between US\$ 5.0 and US\$ 200 per m³ (Ali *et al.*, 2012). Due to its universal existence, inexpensiveness in both initial costs and land requirements, easy design and ease of operation, adsorption is considered the best wastewater treatment process (Badruddoza *et al.*, 2013; Nageeb *et al.*, 2013). Adsorption can also reduce organic compounds that are soluble and insoluble (Ali *et al.*, 2012). Therefore, adsorption has been used for the treatment of a number of organic and inorganic contaminants from different polluted waterbodies (Amro *et al.*, 2020).

Adsorption ability of biochar has been used to manage waste resources (Park *et al.*, 2011), improve soil performance (Lu *et al.*, 2014), mitigate the climate change and as renewable biofuels (Kotodynska *et al.*, 2012). The practicability of biochar prepared from animal manure, plant residues and biosolids for the adsorption of pesticides, pharmaceuticals, hormones and potentially toxic metals has been studied by many scientists (Downie *et al.*, 2009; Joseph *et al.*, 2010; Sun *et al.*, 2014). They showed that biochar exhibited high efficiency for adsorbing pollutants when compared to activated carbons. Organic and inorganic pollutants can be removed by the adsorption mechanism of biochar which can be based on electrostatic interaction, ion exchange, pore filling and precipitation. This depends upon the physiochemical characteristics of biochar such as dosage, pyrolysis temperature, pH of the medium/ effluent (Pellera *et al.*, 2012; Ahmad *et al.*, 2014; Lam *et al.*, 2016; Mubarak *et al.*, 2016; Vithanage *et al.*, 2016; Younis *et al.*, 2016; Rehman *et al.*, 2017; Qayyum *et al.*, 2017).

Adsorption is basically the accumulation on the surface or interface (solid or liquid) by a substance (gas or liquid) (Singh *et al.*, 2015). The process of adsorption takes place in the case of water treatment at the interface between solid adsorbent and polluted water. When the solution and adsorbent contact together, the solute molecules attract to the surface of adsorbent via the functional groups over the surface (Ali *et al.*, 2012). Adsorbate is the solute that accumulates (on the solid interface) in adsorption processes, while the solid on which it is stored is named an adsorbent (Gehrke *et al.*, 2015).

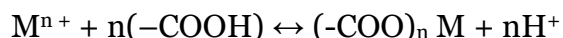


Figure 1. Cation Exchange Mechanism with the Carbon Surface Carboxylic Group (Yin *et al.*, 2007)

However, due to rapidly growing urbanization and industrialization in developing countries, a large volume of wastewater is generated, which contains chemicals generating high environmental risks which could affect health and socioeconomic activities. Consequently, understanding the application of biochar in wastewater treatment and water purification has gained increasing attention despite the scarcity of data (Ambaye *et al.*, 2020).

MATERIALS AND METHODS

Adsorbent Preparation

Camellia sinensis leaves waste material was bought from Kakara tea in Sardauna Local Government Area, Taraba State, Nigeria. It was washed with running water to remove any soluble impurity within it. This washed *Camellia sinensis* leaves waste were then dried in an oven, ground into powder in accordance with the method described by Tatak *et al.*(2022). The ground sample was preserved in polythene bags.

Synthesis of *Camellia sinensis* Leaves Waste Biochar

About 10 g of *Camellia sinensis* leaves waste was measured using analytical weighing balance into five crucibles with each containing 10 g. The crucible was put into a furnace and the temperature of the furnace was adjusted to 350 °C. The process was allowed to run for twenty minutes before the furnace was off and allowed to cool, the furnace was opened and the crucible was transferred to a desiccator using a pair of tongs in order to prevent moisture uptake from atmosphere. After some time, the crucible was removed

and biochar synthesized was transferred into an air tight container kept for further experiment.

Characterisation of Adsorbent

Fourier Transformed Infrared (FTIR) Spectrophotometer was carried out for functional group elucidation of the *Camellia sinensis* leaves waste biochar. Preparation of the samples were done by diluting the *Camellia sinensis* leaves waste biochar to 5% KBr and cast into disks for analysis. Moreover, Scanning Electron Microscopy (SEM; Hitachi S4800) was carried out to assess the morphology of the *Camellia sinensis* leaves waste biochar. Characterisation of the *Camellia sinensis* leaves waste biochar biomass was done before and after adsorption according to the method adopted by Tatah *et al.* (2017).

Preparation of Stock Solution

All solutions for this study were prepared from spectroscopic-grade reagents. A 1000 mg L⁻¹ synthetic Hg(II) stock solution was produced by dissolving 1.48 g of mercury sulphate (Hg₂(SO₄)) in 1 L of distilled water, and working concentrations were obtained by serial dilution. The pH of the subsequent test solutions was carefully adjusted and maintained at pH 5.0 ± 0.05 using 0.1 M HCl or 0.1 M NaOH, with values verified on a calibrated pH meter.

Batch Equilibrium Adsorption Study

The Adsorption of mercury on *Camellia sinensis* leaves waste biochar was studied by batch technique. The method used for this study was as follows;

I. A known weight of *Camellia sinensis* leaves waste biochar (1.5 g, 2.0 g, 3.0 g, 4.0 g and 5.0 g) was equilibrated with 100 mL Hg²⁺ solution of known concentration (5 ppm, 10 ppm, 15 ppm, 20 ppm, and 25 ppm) in different conical flask at a fixed temperature (30 °C) in an orbital shaker for a known period (5 min, 20 min, 40 min, 60 min, 90 min and 120 min) of time.

II. Then 10 mL of sample was collected from each flask at each stipulated time intervals (5 min, 20 min, 40 min, 60 min, 90 min and 120 min) and the suspension of the adsorbent were separated from solution by filtration using Whatman no1 filter paper.

III. The Concentration of heavy metal ion (Hg²⁺) remaining in solution were measured by Atomic Adsorption Spectrometer (AAS).

IV. The effect of some parameters, such as: pH, contact time, adsorbate concentration and adsorbent dose were studied. The pH of the adsorptive solution was adjusted using H₂SO₄ and NaOH to pH 2.4, 6.00, 7.00, 8.52 and 9.13. The adsorbent dose was varied (1.5 g, 2.0 g, 3.0 g, 4.0 g and 5.0 g). The amount of metal ions adsorbed was calculated from the following equations adopted from (Dawodu and Akpomie, 2014).

$$q_e = V (C_o - C_e)/m \quad (1)$$

$$\% \text{Removal} = 100 \times [(C_o - C_e)/C_o] \quad (2)$$

where q_e (mg/g) is the adsorption capacity of the adsorbent for the adsorbate at equilibrium, C_o (mg/L) and C_e (mg/L) are the initial and equilibrium concentrations of

metal ions in solution, m (g) is the mass of adsorbent and $V(L)$ is the volume of solution used.

RESULTS AND DISCUSSION

FTIR and SEM Analysis

FTIR spectra for *Camellia sinensis* leaves waste biochar before adsorption was determined to identify the surface functional groups which were present on the surface as shown in Figure 3.1. and Figure 3.2. The result revealed that the biochar before adsorption had frequencies at 3408.00 and at 1427.00 which depict that hydroxyl groups from alcohols are present, 2927.00 and 2353.08, 1642.00 depict the presence of alkenes, 1737.39 portray the presence of carbonyl C=O groups (Esters), 1515.91 depict the presence of aromatic compounds, 1378.42, 1327.57, 1261.00 and 1043.28 depict that alcohols (C-O stretching) are present, 670.07, 610.14 and 528.43 cm^{-1} are known as finger print region which is unique to each molecule and can be used to confirm the identity of compounds. This is indicative of different functional groups with different affinities for different heavy metals.

The result for FTIR spectra of *Camellia sinensis* leaves waste biochar material after adsorption is shown in Figure 3.2. The findings equally showed peaks of different frequencies, indicative of different functional groups present in the *C. sinensis* leaves waste biochar after adsorption of mercury. The peak frequencies decreased from 3830.00 to 3773.00, 3408.00 to 3395.00, 2927.00 to 2921.57, peak frequencies rose from 2353.08 to 2353.17, 1737.39 to 2153.00, 1642 to 1728.23, 1515.91 to 1635.17, 1427.00 to 1504.26, 1378.42 to 1428.47, 1327.57 to 1373.62, 1261.00 to 1327.95, 1043.28 to 1251.50, 670.07 to 1051.00, 610.14 to 833.94, 528.43 to 659.55. Additional frequencies were seen in 605.54 and 528.44.

The result for characterisation of the *C. sinensis* leaves waste biochar using SEM in Figures 3.3 A and 3.3 B shows the pore size before and after adsorption respectively. The findings showed that the pore size of the biochar before adsorption was 100 μm . However, the pore size for the biochar after adsorption was seen to be 20 μm , signifying a reduction in the pore size as it underwent adsorption.

Before

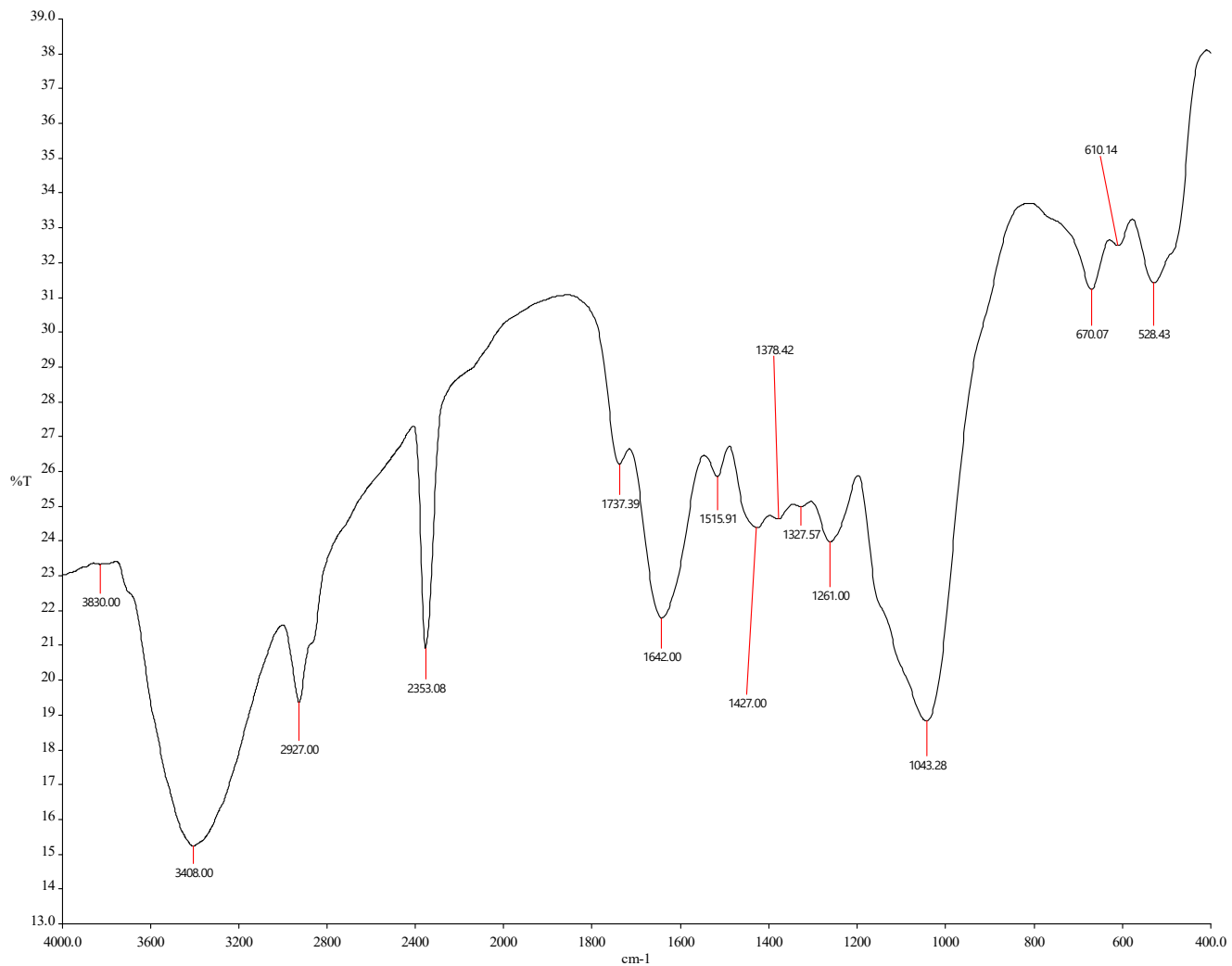


Figure 3.1: FTIR Spectra for *Camellia sinensis* Leaves Waste Before Sorption.

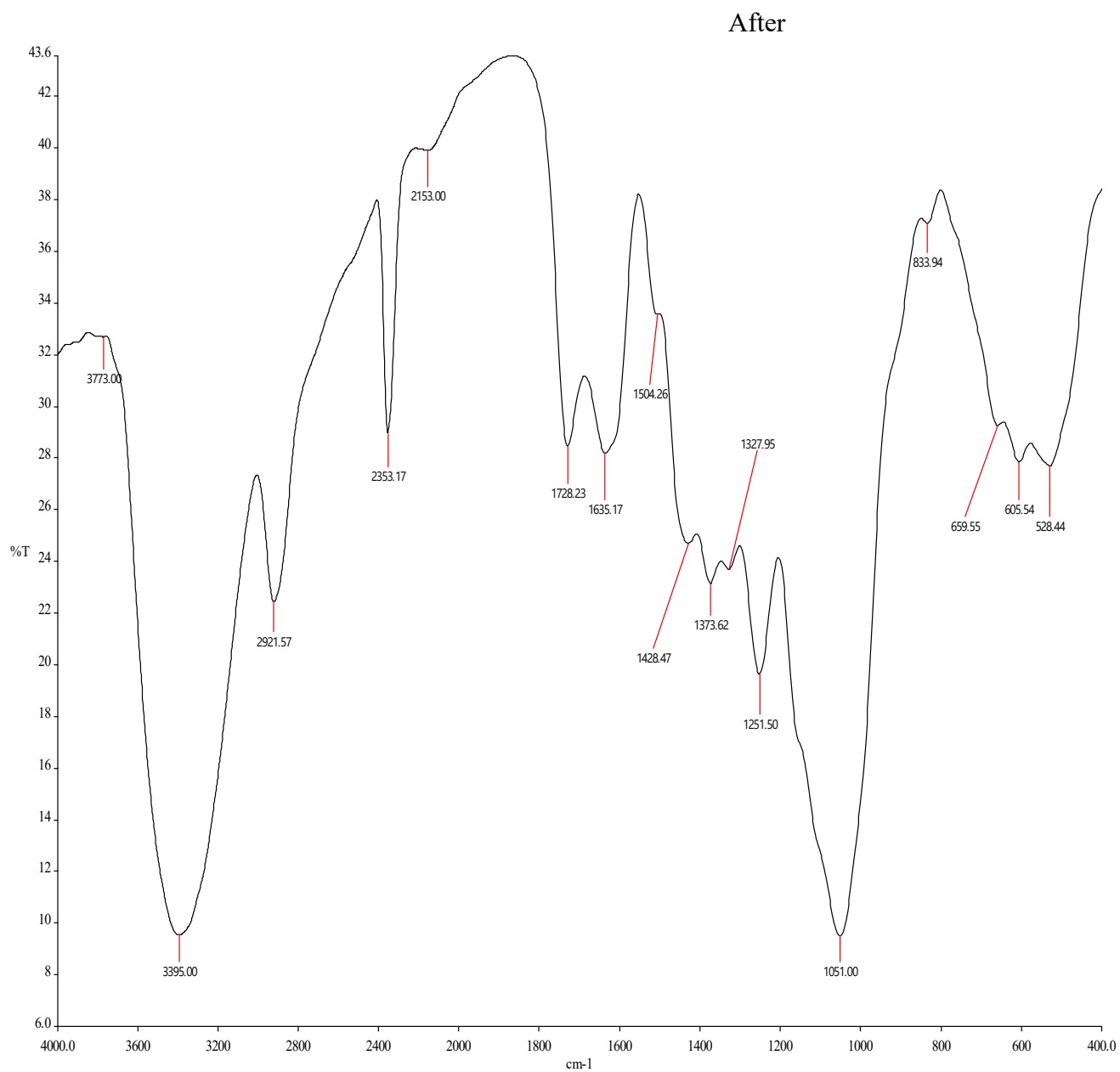


Figure 3.2: FTIR Spectra for *Camellia sinensis* Leaves Waste After Sorption.

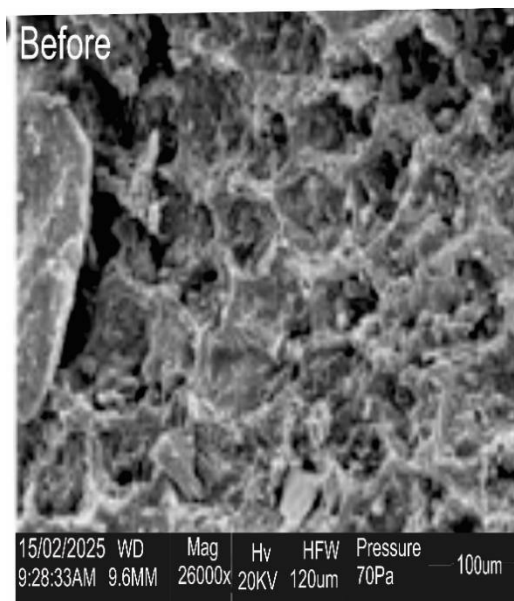


Figure 2A

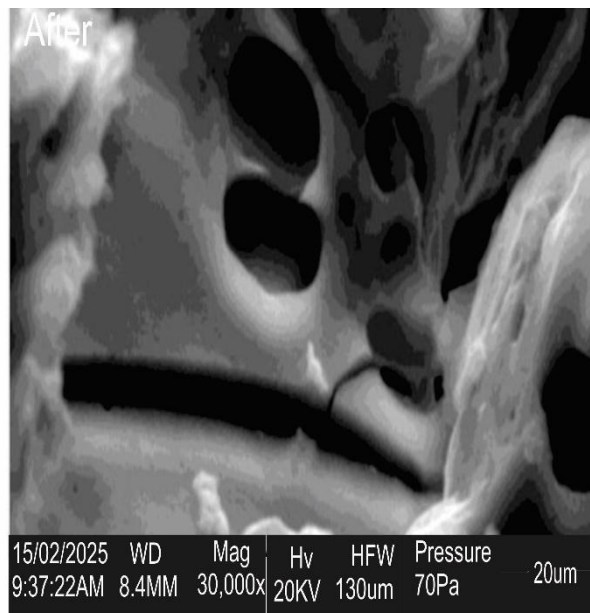


Figure 2B

Figure 2 A and B: SEM images of porous structure of *Camellia sinensis* leaves waste biochar.

Effect of pH

This study indicated that pH has a significant effect on the adsorption process. The result seen in table 3.1 showed a swift increase in percentage removal of mercury with increase in the pH, then a sudden decline as the pH increased beyond optimum. The result showed that at pH 2.4, the percentage removal of mercury was 56.79%, as the pH was increased to 6.00, the percentage removal of mercury increased to 66.78%. Conversely, as the pH was increased to 7.00, the percentage removal dropped to 41.81%. The percentage removal further increased to 56.04% as the pH was increased to 8.52. The percentage removal equally dropped to 52.37% as the pH was increased to 9.13.

Table 1: Effect of pH on Absorption of mercury (Hg) by *Camellia senesis* biochar

No	PH	Initial Absorbance (Abs1)	Final Absorbance (Abs2)	Adsorption capacity (q)	% Removal
1	2.4	1.523	0.658	0.268	56.79
2	6.00	1.999	0.664	0.240	66.78
3	7.00	1.148	0.668	0.434	41.81
4	8.52	1.547	0.680	0.369	56.04
5	9.13	1.411	0.672	0.433	52.37

The result showed that at a low pH of 2.4, the removal efficacy of biochar was 56.79% due to the protonation of functional groups on its surface. At a neutral pH of 6.0, the highest removal efficacy was observed to be 66.78%. After pH 6.0, efficiency decreased

to 41.81% at pH 7.0 and 52.37% at pH 9.13, suggesting that higher pH led to lesser protonation of functional groups on the surface of the adsorbent. Gao *et al.* (2016) and Wang *et al.* (2020) highlighted the importance of pH in optimizing the adsorption of heavy metals onto biochar.

Effect of Initial Metal Ion Concentration

Results from Table 3.2 showed that at low concentrations of 5 to 15 ppm, caused mercury removal efficiency to rise from 85.71 to 92.35% as seen in Table 3.2, suggesting that at neutral concentration of 15 ppm, recorded the highest mercury removal efficiency of 92.35%. After 15 ppm, it decreased to 90.4% and 87.57 respectively, most likely as a result of active adsorption sites becoming saturated. Higher mercury uptake is indicated by the adsorption capacity (q), which rose with increasing starting concentration. The slight decrease in $\log q_e$ values, however, indicated a diminishing rate of adsorption, which implies decreased efficiency at higher concentrations. This is in line with research by Kurniawan *et al.*, (2018), who found that mercury adsorption onto biochar made from agricultural wastes followed a similar pattern. The interfacial reactions between hydroxyl groups and Hg^{2+} in the *Camellia sinensis* leaves waste biochar structure might include hydrogen bonding and van der Waals forces Medykowska *et al.*, (2022).

Table 2: Effect of Concentration on absorption of mercury (Hg) by *Camellia sinensis* leaves waste biochar

N o	Concentrati on (ppm)	Initial Absorbanc e (Abs1)	Final Absorbanc e (Abs2)	Adsorpt ion capacit y (q)	% Remov al	Ce/qe	Log qe	Log Ce
1	5ppm	0.875	0.125	0.375	85.71	0.33	0.425	0.903
2	10ppm	1.078	0.158	0.46	85.34	0.34	0.34	0.801
3	15ppm	0.933	0.118	0.488	92.35	0.29	0.311	0.958
4	20ppm	0.945	0.119	0.513	90.4	0.23	0.29	0.92
5	25ppm	0.945	0.297	0.524	87.57	0.56	0.28	0.53

The adsorption equilibrium was assessed using the Freundlich and Langmuir isotherm models. A fair fit is suggested by the Langmuir model's $R^2 = 0.932$, which implies monolayer adsorption on a homogeneous surface. With a reduced $R^2 = 0.5321$, the Freundlich model suggests that surface heterogeneity or multilayer adsorption are less important. These findings are consistent with research by Mohan *et al.* (2014) and Foo and Hameed. (2010), who found that the Langmuir model was preferred for explaining heavy metal adsorption onto biochar.

Table 3: Equilibrium Isotherm Results for Hg (II) Adsorption by *Camellia sinensis* leaves waste biochar.

Isotherm model	Hg (II)
Langmuir model	
q _L (Mg/g)	8.023
K _L (L/mg)	0.012
R ²	0.931
Freundlich model	
K _F (L/g)	1.011
1/n	0.210
R ²	0.148

Effect of dosage

This study found a relationship between the amount of biochar and the effectiveness of mercury adsorption. Because of the small surface area, the efficiency was 50.14% at 1.5 g. It improves to 74.42% as the dosage rose to 4.0 g, suggesting more binding sites. It reached 84.96% at 5.0 g, suggesting ideal adsorption conditions. The general idea that adsorbent dose increases removal efficiency by providing more active sites is supported by the observed trend. At higher dosages, however, a plateau effect suggests that additional dosage do not correspondingly increase efficiency. The results of other investigations, like those by Onyango *et al.* (2017) and Adejumo *et al.* (2020) which documented comparable patterns for heavy metal adsorption using biochar and other inexpensive adsorbents are in line with this behaviour.

Table 5: Effect of dosage on the absorption of mercury (Hg) by *Camellia senensis* biochar

Abs runs	Dosage (gram)	Initial Absorbance (Abs1)	Final Absorbance (Abs2)	Adsorption capacity (q)	% Removal
1	1.5g	1.008	0.432	0.288	50.14
2	2.0g	0.928	0.432	0.248	53.44
3	3.0g	0.931	0.432	0.249	65.59
4	4.0g	1.689	0.432	0.628	74.42
5	5.0g	1.659	0.432	0.614	84.96

Effect of Contact time on Adsorption

The impact of contact time on the adsorption process is shown in Table 4.5. The effectiveness of mercury removal rose intensely from 85.71% at 5 minutes to 92.35% at 40 minutes, indicating the quick initial adsorption brought on by the large number of vacant active sites. As active sites became saturated, the rate of clearance decreases between 40 and 120 minutes, After 120 minutes, equilibrium is reached, and the highest removal effectiveness is 92.35%.

Table 6: Effect of Contact Time on the Adsorption of Mercury (Hg) by *Camellia senesis* Biochar

No	Contact time (mins)	Initial Absorbance (Abs1)	Final Absorbance (Abs2)	Adsorption capacity (q)	% Removal	Log(qe-qt)	t/qt
1	5mins	1.323	0.941	0.191	85.71	0.282	26
2	20mins	1.340	0.941	0.199	85.34	0.492	50
3	40mins	1.628	0.941	0.344	92.35	0.728	116
4	60mins	1.750	0.941	0.405	90.4	0.935	148
5	90mins	1.912	0.941	0.486	68.57	1.559	185
6	120mins	1.983	0.941	0.521	85.71		230

The strong R^2 value of 0.978 seen in Table 3.6 below indicated that the pseudo-first order kinetic model fits the adsorption process well. This suggests that the predominant mechanism might be chemisorption, which involves valence forces or electron sharing. Studies by Zhang *et al.*, (2019) and Chen *et al.*, (2018) have reported similar outcomes, seeing equilibrium for heavy metal adsorption using adsorbents based on agricultural waste in less than 120 minutes.

Table 7: Kinetic Parameters for the Adsorption of Hg (II) Ions onto *Camellia sinensis* Leaves waste biochar.

Kinetic models	Hg(II)
q_{eexp} (Mg/g)	15.91
Pseudo-first order	
q_{ecal} , (Mg/g)	17.43
K_1 , (min ⁻¹)	0.023
R^2	0.978
Pseudo-second order	
q_{ecal} , (Mg/g)	5.84
K_2 (gmg ⁻¹ min ⁻¹)	0.032
h (Mg/gmin)	1.321
R^2	0.685

Kinetic Studies on the Biosorption of Hg(II) Ions by *Camellia sinensis* Leaves Waste Biochar

Kinetics of sorption describes the rate of solute adsorption which in turn control the residence time of sorption reaction that defines efficiency of sorption (Onyancha *et al.*, 2008). The most used kinetic models are Pseudo-first-order, Pseudo-second-order and Intraparticle diffusion models. These models provide information on the types or order of reactions that is taking place between the adsorbent and the adsorbate.

Pseudo-first-order or Lagergren Equation

The pseudo-first order or Lagergren equation, is based on the assumption that the rate of adsorption site occupation is proportional to the number of unoccupied sites (Lagergren, 1898). Lagergren, 1898 derived the Pseudo-first-order equation to calculate the rate of adsorption. The rate of adsorption is given by equation (1)

$$dq_t/dt = k(q_e - q_t) \quad (1)$$

The linear form of the equation after integration with boundary condition from $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$ becomes:

$$\log (q_e - q_t) = \log q_e - (k/2.303)t \quad (2)$$

Where k (min^{-1}) is the rate constant and q_t and q_e are the amounts of metal ion adsorbed at time t (min) and equilibrium respectively.

The values of q_e and k at different initial concentrations are calculated from the slope and intercept of the plots of $\log (q_e - q_t)$ versus t which gives a straight line if the kinetic data correlate with Pseudo–first-order (Mondal *et al.*, 2018).

Pseudo-second-order

The Pseudo-second-order Kinetic Model is based on the assumption that chemisorption is the rate determining step, provided a good fit to the experimental data as adopted by Tатаh *et al.* (2022).

The rate of adsorption for Pseudo-second-order is given by equation (1)

$$dq_t/dt = k_2(q_e - q_t)^2 \quad (1)$$

Where k_2 (min^{-1}) is the rate constant and q_t and q_e are the amounts of metal ion adsorbed at time t (min) and equilibrium respectively.

By applying the boundary conditions after integration of both sides from $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, the integrated form of the equation becomes:

$$t/q_t = 1/k_2q_e^2 + (1/q_e) t \quad (2)$$

The rate constant k_2 (g/mg.min) and equilibrium adsorption capacity q_e are calculated from the slope and intercept of the linear plot of t (time) Vs t/q_t (Ali *et al.*, 2016; Ingole *et al.*, 2017).

Table 8: Kinetic Parameters for the Adsorption of Hg (II) Ions onto *Camellia sinensis* Leaves waste biochar.

Kinetic models	Hg(II)
q_{eexp} (Mg/g)	15.91
Pseudo-first order	
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Pseudo-second order	
q_{ecal} , (Mg/g)	5.84
K_2 (gmg ⁻¹ min ⁻¹)	0.032
h (Mg/gmin)	1.321
R^2	0.685

Isotherm Studies on the Biosorption of Cadmium by *Camellia sinensis* Leaves Waste Biochar

Equilibrium adsorption isotherms are used to show the relationship between adsorbate concentration in solution and the amount on the adsorbent at equilibrium (Ayranci and Duman, 2005). These parameters often provide fundamental information on the sorption mechanism, surface properties and the affinity of adsorbents, which helps to determine the applicability of sorption as a unit operation (Dawodu and Akpomie, 2014).

Langmuir Isotherm Model

This model called isotherm models which are: The Langmuir model, Freundlich model, Temkin model and The Dubinin–Radushkevich Isotherm model.

One of the best known, scientifically understood, and commonly used models is the Langmuir model, introduced in 1916 by Langmuir. The Langmuir equation is based on the assumption that maximal adsorption occurs on the adsorbent surface of a saturated mono-layer of adsorbate molecules (there is no interaction between adsorbed molecules at the neighboring adsorption

sites) and that the adsorption energy is constant (Hameed and Rahman, 2008; Mondal *et al.*, 2018). The linearized form is given in the bellow equation:

$$C_e/q_e = 1/b Q_m + (1/Q_m) c_e$$

Where, q_e is the capacity of adsorbent in (mg/g) when the concentration of solution reach C_b , Q is the flow rate (mL/min), and M is adsorption mass packed in the column (g).

The plot of C_e versus C_e / q_e gives a linear form if the adsorption equilibrium obeys Langmuir equation.

Freundlich Isotherm Model

Freundlich equation is a practical equation that commonly describes the procedure of adsorption from wastewater for heavy metals and organics. It is based on heterogeneous

or multilayer adsorption sites (Liang *et al.*, 2013; Dada *et al.*, 2012). It also implies that before the lesser one, the stronger binding sites are occupied and that the adsorption strength decreases with the degree of occupation (Bhandari and Ranade, 2014). The linear form for Freundlich equation is given by the bellow equation:

$$\log q_e = \log k_f + 1/n(\log c_e)$$

Where k_f (mg/g), and $1/n$ (mg/L) are the constants for adsorption capacity and intensity, respectively.

The value of $1/n$ is between 0 and 1 if the value of $1/n$ is below the unit it means that the process of adsorption is chemical; if the value is above the unit, the more the physical process is adsorbed; the more heterogeneous the surface, the more the value of $1/n$ approaches zero (Dada *et al.*, 2012).

Table 9: Equilibrium Isotherm Results for Hg (II) Adsorption by *Camellia sinensis* leaves waste biochar.

Isotherm model	Hg (II)
Langmuir model	
q_L (Mg/g)	8.023
K_L (L/mg)	0.012
R^2	0.931
Freundlich model	
K_F (L/g)	1.011
$1/n$	0.210
R^2	0.148

CONCLUSION

Properties of *Camellia sinensis* leaves waste biochar for Hg(II) ions bioremediation from industrial waste water through batch adsorption studies was promising, in this study, Hg(II) ions adsorption was highly dependent on the experimental parameters such as contact time, initial metal concentration, pH, and adsorbent dosage. Based on the isotherm modeling of the experimental data, Langmuir isotherm model provided the best fit to the experimental data for Hg(II) ions compared to the other isotherm models tested. Moreover, pseudo-second order model provided the best fit to the experimental data after kinetic modeling, suggesting that the adsorption process followed a second order rate mechanism. Therefore, from this study it could be inferred that *Camellia sinensis* leaves waste biochar possessed the potential that can be used for the bioremediation of wastewater and industrial effluent contaminated with Hg(II) ions.

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CONFLICT OF INTEREST

The authors declare no conflicts of interest in relation to the work presented in this manuscript.

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