

Adsorption Studies of Cu^{2+} from Aqueous Solutions Using Unmodified and Citric Acid – Modified Plantain (*Musa paradisiaca*) Peels

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Abstract

Natural plantain peel biomass and the citric-acid-modified form were used to study the adsorption of Cu^{2+} from a simulated aqueous solution in a batch adsorption system. The adsorption was strongly pH-dependent as maximum adsorption was recorded at a pH of 5 for the modified biomass and pH of 4 for the unmodified. The kinetics of the adsorption processes was studied with Pseudo-first-order, Pseudo-second-order, Intra-particle diffusion, Elovich and Fractional power kinetic models and the results were best fitted by the pseudo-second-order model. The experimental data were also subjected to Langmuir, Freundlich and Temkin isotherms for adsorption studies and the unmodified biomass was best fitted by the Temkin adsorption isotherm while the modified biomass, on the other hand was best fitted by the Freundlich isotherm. Thermodynamic studies revealed that the heat of adsorption of the unmodified biomass was higher than the modified. The maximum adsorption capacity obtained was 48.31 mg/g.

Keywords: Adsorption; citric acid; copper (II); plantain peels.

1. Introduction

Heavy metals, which are non-biodegradable substances that can constitute adverse health effects to man and livestock remains one of the main causes of pollution of water bodies. One of these is copper which when inadequately controlled as an industrial effluent has been responsible for notable havocs around the world.

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For instance, several incidences of copper poisoning in sheep were reported in the United Kingdom in summer, 2015 [1]; over 3,000 birds and 19,000 tons of fish died from water polluted by sewage leak from copper mines in Montana, United States and Fujian, China respectively [2,3]. Ingesting contaminated foods and water exposes human to the risk of copper pollution as well [4]. The limited access to safe water has therefore encouraged search for efficient ways of purifying available ones for better applications. To this end, a lot of attention has been channeled towards research bothering on efficient and sustainable ways of removing Cu^{2+} from aqueous systems. Notable conventional methods that have been employed include chemical precipitation, biodegradation, membrane filtration, chemical coagulation, electrolysis, ion exchange, chemical degradation, electro-coagulation and adsorption [4-6]. However, adsorption has been the most desired process because of its high efficiency. The vast abundance of different carbonaceous materials that have high adsorption capacity has also contributed in the versatility of this method of remediation. Adsorbents like activated carbon, biopolymers, metal oxides and biochars have been exploited. Recent studies have employed the use of hazelnut shell powder, raw pomegranate peel [7]. In some other studies, the various naturally occurring adsorbents used were first modified in order to increase their sorption performance [8,9] This could be achieved by physical (heating), chemical (acid / alkali treatment or impregnation of catalytic materials) or biological approach (incorporating species like bacteria for additional bioadsorption) [9]. Acid treatment has been established to contribute to acidic functional groups on adsorption sites and improves chelation with metal species [9]. Thus, Polyacrylonitrile, carboxylic acids and tetraethylene pentamine have been used in this regard [10-12]. Reactions like a 'click reaction' between 1,3-dipolar cycloaddition of azide and propargyl have also been used for modification [13].

In contribution to the discovery of cheap materials whose adsorption properties can be exploited to remediate Cu^{2+} in aqueous systems, the ability of plantain peels to adsorb these ions was investigated in this study. Plantain has a wide array of applications and it is abundantly cultivated in Africa [14] where only the fruit is sufficiently consumed and the peels are discarded as wastes while being allowed to degrade naturally. These peels constitute more than 40% of the total weight of the plantain [15] and thereby represent a cheap and easily-accessible raw material. This comparative advantage (in comparison with other adsorbents) coupled with the potentials of achieving chemical modification of the plantain peel biomass with an environment-friendly modifier like citric acid serves as the key motivation of this research work.

2. Materials and Methods

2.1 Materials and Instrumentation

CuSO_4 , citric acid, HNO_3 , NaOH used were of analytical grade. Laboratory test sieve (Endecotts Ltd London, England, Serial No: 6085504) was used to sieve biomass used. Atomic Absorption Spectrophotometer (Buck Scientific). Fourier transform-Infra spectrophotometer (Shimadzu Corporation) was used for functional group identification. Whatman filter paper (No. 1) filter paper was used to separate metal laden biomass from aqueous solution.

2.2 Methods

2.2.1 Preparation of plantain peels adsorbent – unmodified and modified

Peels plantain peels were collected from small scale local plantain roasters in Akure, Ondo state, Nigeria. Two roasters were from around the Federal University of Technology Akure (FUTA) area, one from Akure main market and the last from Akure-Ilesa road, Akure, Ondo state. The peels were thoroughly washed with deionized water and dried. After complete drying, they were ground and sieved to particle sizes between 300 – 1100 μm . Peels were treated with HNO_3 and NaOH . Following the method of [12] with slight modification, 500 g of ground plantain peels (GPP) were treated with 5 litres 0.1 M HNO_3 for 2 h in order to demineralise peels. Peels were then washed with 5 litres of deionized water and dried. Next, 350 g of acid treated-ground plantain peels (AT-GPP) were treated with 7 litres, 0.1 M NaOH by soaking for 2 h, filtered and rinsed thrice with a total of 10 litres of deionized water and dried. Base treated ground plantain peel (BT-GPP) was modified with citric acid. Ground Plantain peel obtained after both acid and base treatment (AT-GPP and BT-GPP) will be referred to as Unmodified Ground Plantain Peels (Un-GPP). Ninety grams of Un-GPP was treated with 900 ml, 0.6 M citric acid at 80 C for 1.5 h in order to introduce carboxylate groups on its surface referred to as citric-acid modified ground plantain peels (CA-GPP). CA-GPP was washed thrice with a total of 2 L of deionized water. Finally, it was dried at 60° C. Fourier transform – Infrared Spectroscopy (FT-IR) was employed for the characterization of Un-GPP and CA-GPP.

2.2.2 Preparation of synthetic Cu^{2+} aqueous solution

All synthetic Cu^{2+} aqueous solution used for this study were prepared from a 1000 mg/L stock solution. Typically, the 1000 mg/L stock solution was prepared by dissolving 2.5118 g of CuSO_4 in 1 L deionized water.

2.2.3 Batch adsorption studies

All batch adsorption studies were undertaken at room temperature except otherwise stated. 0.5 g of adsorbent was contacted with 50 ml, 50 mg/L synthetic Cu^{2+} aqueous solution without shaking. pH studies were undertaken by varying pH of Cu^{2+} solution from 3 – 8. Contact time studies were undertaken by varying time from 30 - 180 min at pH 7 for Un-GPP and pH 5 for CA-GPP. For Un-GPP, time studies was extended to 10 and 20 mins after obtaining maximum adsorption at 30 mins. Adsorbent dose was varied from 30 - 70 mg at same pH used in contact time study but for 30 min (using Un-GPP) and 120 min (with CA-GPP). Temperature and adsorbate concentration studies were co-undertaken by variation of temperature from 308 – 328 K and adsorbate concentration from 25 - 100 mg/L. In this study, adsorbent dose was 0.4 g for Un-GPP and 0.5 g for CA-GPP. Percentage Cu^{2+} adsorbed was calculated using the equation below:

$$\frac{C_i - C_f}{C_o} \times 100 \quad (1)$$

where C_i = initial Cu^{2+} concentration

C_f = final Cu^{2+} concentration after adsorption

2.2.4 Kinetic, isotherm and thermodynamic studies

2.2.4.1 Adsorption Kinetics

The adsorption kinetics of Cu²⁺ on the natural plantain peel biomass and the citric-acid modified form was studied using the following models:

The pseudo-first-order model: This model assumes that the amount of adsorbate that is adsorbed by an adsorbent is directly proportional to the difference in concentration saturation level [16]. Mathematically, the non-linear and linear forms of the model are represented by equations (2) and (3) respectively:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (2)$$

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right)t \quad (3)$$

where: k_1 (min⁻¹) is the rate constant of the pseudo-first-order reaction; q_e denotes the adsorption amount (mg g⁻¹) and q_t represents adsorption amount at a specific time, t .

The pseudo-second-order-model: This kinetic model states that there is a chemical interaction between the adsorbate and the surface of the adsorbent leading to the formation of a chemical bond [17]. Equations (4) and (5) show the non-linear and linear forms of the model respectively:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (4)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (5)$$

where: k_2 (g mg⁻¹ min⁻¹) is the rate constant of the pseudo-second-order reaction; q_e denotes the adsorption amount (mg g⁻¹) and q_t represents adsorption amount at a specific time, t .

The Weber-Morris equation or intra-particle diffusion model: This model states that adsorption occur in stages and these include transportation of adsorbate from the loaded solution, film diffusion, intra-particle diffusion into pores consequently followed by adsorption on the active centres. The model is represented by Equation (6):

$$q_t = K_p t^{1/2} + C \quad (6)$$

where: K_p is the intra-particle rate constant (g/mg.min^{-0.5})

Elovich Kinetic model: This model has been applied for kinetic studies of Cu²⁺ in heterogeneous systems. The non-linear and linear forms represented mathematically by Equation (7) and (8) respectively:

$$q_t = \beta \ln(\alpha\beta t) \quad (7)$$

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t) \quad (8)$$

where: q_t is the quantity of adsorbate adsorbed at time, t (mg/g); α is a constant related to chemisorptions rate and β is a constant that shows extent of surface coverage.

Fractional power kinetic model: This model shows the amount of metal ions sorbed at a specific time [13]. Mathematically, the non-linear and linear forms are shown by Equations (9) and (10):

$$q_t = Kt^v \quad (9)$$

$$\log q_t = \log K + v \log t \quad (10)$$

where: q_t is the amount of Cu^{2+} sorbed at a given time; k and v are constants with $v < 1$.

2.2.4.1 Adsorption Isotherms

Langmuir isotherm: Langmuir isotherm defines a mono-molecular layer arrangement of adsorbate on the surface of the adsorbent and it states that there is no interaction between the adsorbed molecules [22]. The non-linear and linear forms are shown in Equations (11) and (12) respectively:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (11)$$

$$\frac{1}{q_e} = \frac{1}{K_L q_m} \left(\frac{1}{C_e} \right) + \frac{1}{q_m} \quad (12)$$

where q_e is the amount of Cu^{2+} adsorbed per unit mass at equilibrium (mg/g); q_m is the maximum adsorbate that can be adsorbed per unit mass of adsorbent (mg/g); K_L is the adsorption equilibrium constant and C_e is the concentration of adsorbent (mg/L). To obtain a suitable graph, a plot of $1/q_e$ against $1/C_e$ was made to yield values for the constants.

Freundlich isotherm: This model suggests that adsorption occurs in form of a mono molecular layer or multilayer on heterogeneous adsorbent surfaces and that there is an interaction between the adsorbed molecules [18]. The non-linear and linear forms of the isotherm are mathematically represented by Equations (13) and (14) respectively:

$$q_e = K_F C_e^{1/n} \quad (13)$$

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (14)$$

where C_e (mg/L) and q_e (mg/g) are the equilibrium concentration of adsorbent in the solution and the amount of adsorbent adsorbed at equilibrium respectively; n represents adsorption intensity and K_F ($\text{mg}^{1-1/n} \text{L}^{1/n} \text{g}^{-1}$) denotes the adsorption capacity for the adsorbent. The values of the constants were obtained by plotting $\log q_e$

against $\log C_e$.

Temkin Isotherm: This model suggests that there is an indirect interaction between an adsorbate and the adsorbent and this occurs by a decrease in the heats of adsorption of molecules for the first layers and consequently followed by an increase in coverage [19]. The non-linear forms of the isotherm are mathematically represented by Equations (15) and (16) respectively:

$$q_e = BLn(A_T C_e) \quad (15)$$

$$q_e = BLnA_T + BLnC_e \quad (16)$$

where C_e is the equilibrium concentration of Cu^{2+} in the solution (mg/L); q_e is the equilibrium concentration of copper on the adsorbent (mg/g); A_T is known as Temkin binding constant (L/g); B is a constant that is related to heat of adsorption and it is represented mathematically by Equation (17):

$$B = \frac{RT}{b} \quad (17)$$

where b is the Temkin constant; T is the temperature (Kelvin) and R is the molar gas constant ($8.314J.mol^{-1}.K^{-1}$)

3. Results and Discussion

3.1 Modification and Characterization of plantain peels

The citric acid modification was undertaken to provide potentially additional binding sites in the form of carboxylic groups on the surface of Un-GPP. Fig. 1a and Fig. 1b show FT-IR spectra of unmodified and modified plantain peels. Prominent among the peaks in Fig. 1a are those at 3417, 3350, 3308, 2924, 2359, 1641, 1076 and 1024 cm^{-1} . The peaks from 3417 to 3308 cm^{-1} represent OH stretch (alcohol and carboxylic acid). This assignment is confirmed by the presence of a peak at 2924 cm^{-1} which also represents OH from carboxylic acid. Tannins (e.g. gallic acid), present in plantain peels may be responsible for the observed carboxylic functional group [19]. Also, cellulose and hemicelluloses which have appreciable amount of OH groups may be responsible for some of the OH signals observed [20]. The peak at 1641 cm^{-1} represents a C=C stretch. Unsaturated carbon-carbon bonds are found in some polyphenols. Last, the peak at 1024 cm^{-1} refers to =C-O-C symmetric and asymmetric stretch. Ether linkages of this type are again found in some polyphenols like tannin [19]. Fig. 1b presents IR spectrum of modified plantain peels. It is observed that two new sharp peaks at 1716 and 1541 cm^{-1} appear. Peak at 1716 cm^{-1} hints at a C=O stretch in carboxylic acids. It can also depict C=O stretch in esters. This assignment can be confirmed by the equally present peak at 1238 cm^{-1} (C=O for esters), 1157 cm^{-1} (for aliphatic carboxylates) and 1317 cm^{-1} (for aromatic carboxylates). It is very likely that free carboxylic groups remain on the surface of modified biomass since not all are esterified by OH groups in the biomass (Figure 5). Consequently, the peak at 1716 cm^{-1} hints at the fact that the plantain was modified with citric acid.

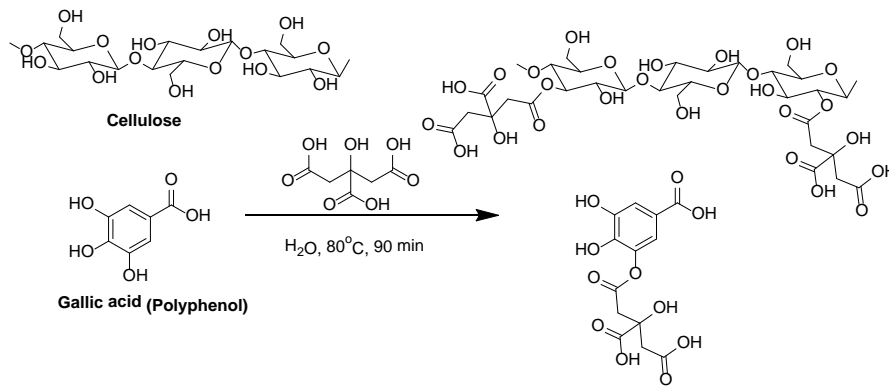


Figure 5: Proposed/suggested scheme for citric acid modification of plantain peels.

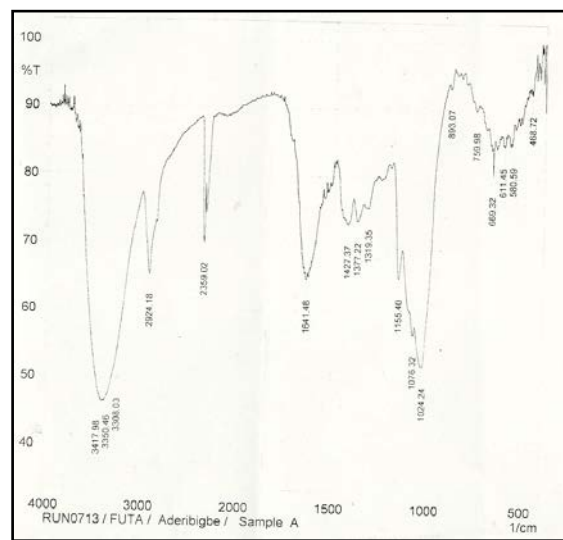


Figure 1a: FT-IR spectra of unmodified plantain peels

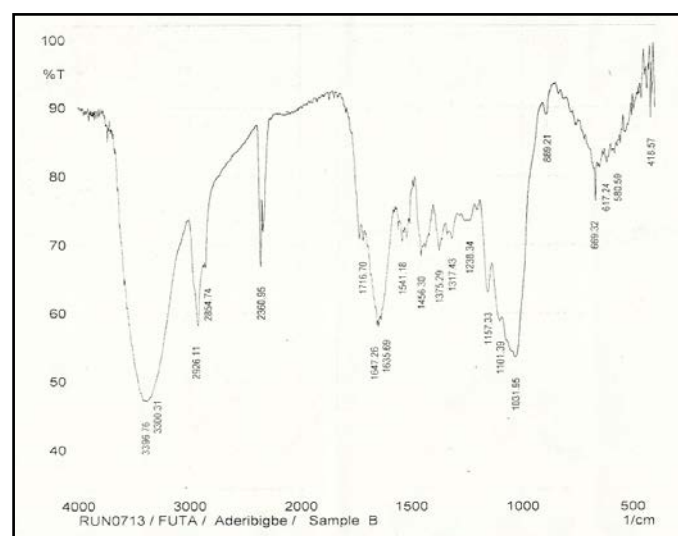


Figure 1b: FT-IR spectrum of citric acid-modified plantain peel

3.2 Effect of pH

Adsorption is a pH-dependent process and the effect of pH on the removal of Cu^{2+} was investigated at a range of 3.0 – 8.0 for both the unmodified and modified biomass. Maximum adsorption was recorded at pH values of 4 and 8 for the unmodified and modified biomass respectively. At low pH values, there is a large availability of H^+ ions and these compete with the Cu^{2+} for active sites on the adsorbent consequently causing lower adsorption; this was observed in adsorption capacity of the biomass at low pH. It has been observed that at pH values greater than 6, adsorption is not the only process responsible for the removal of Cu^{2+} [7] as precipitation occurs and hydroxides like $\text{Cu}(\text{OH})^+$, $\text{Cu}(\text{OH})_2$, $\text{Cu}_2(\text{OH})_2^{2+}$ and $\text{Cu}(\text{OH})_3^-$ are produced. This perhaps may be the reason why the highest adsorption for the modified biomass was noticed at pH 8; the remaining concentration of Cu^{2+} in the reaction vessel at this pH is not due to the action of adsorption only but in addition, precipitation. Therefore, maximum adsorption before pH 6 will be considered; meaning that pH 5 produced maximum adsorption of Cu^{2+} and started experiencing a drop in value as the pH approached 6. This was consistent with results obtained in [7,25].

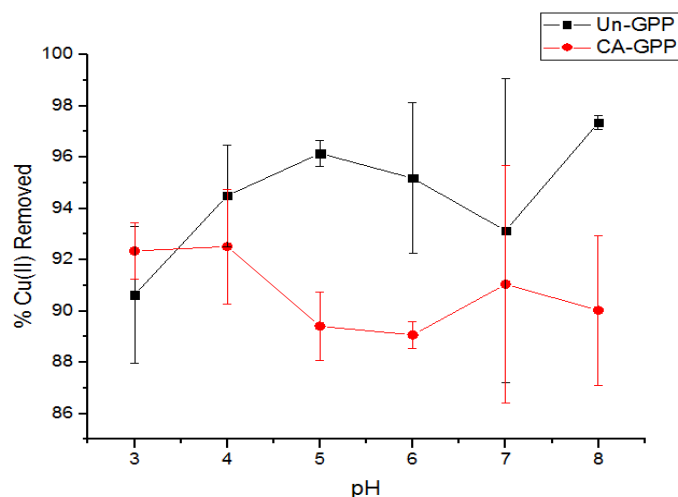


Figure 2: Effect of pH on the adsorption of copper from aqueous solution using Un-modified (Un-GPP) and Citric acid modified ground plantain peels (CA-GPP)

3.3 Effect of contact time

This study was carried out at different contact times between 30-240mins at an interval of 30mins. There was a steady decrease in amount of Cu^{2+} adsorbed from 30-120mins as equilibrium was experienced between 60 and 90mins followed by a steady increase in amount of Cu^{2+} adsorbed from 150-240min. However, a different twist was observed for the modified biomass: there was a steady increase in the amount of Cu^{2+} adsorbed from 30-180mins followed by a decrease between 210 and 240mins. This two-stage adsorption mechanism was reported in [28,34] and it suggests that the availability of active sites at initial contact times led to a sorption of more amount of Cu^{2+} than at final contact times when a repulsive force occurs between the Cu^{2+} in the solution and the ones already adsorbed [7].

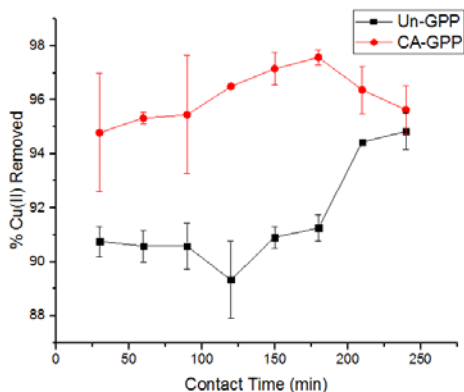


Figure 3: Effect of contact time on the adsorption of copper from 50mg/l aqueous solution using Un-modified (Un-GPP) and Citric acid modified ground plantain peels (CA-GPP)

3.4 Effect of adsorbent dosage

The dependence of varying adsorbent dose on the adsorption of Cu^{2+} was studied at a dose range of 0.1-0.7g of plantain peel biomass. For the unmodified biomass, the percentage removal of Cu^{2+} increased from 92.20% to 96.20% when adsorbent dosage was increased from 0.1-0.2g. This is as a result of the additional active sites that were introduced due to increase in area of adsorbent. However, there was a steady decrease afterwards in the percentage amount of Cu^{2+} that was adsorbed when adsorbent dose was increased sequentially. This suggests that an adsorbent dose of 0.2g can produce enough active sites sufficient for Cu^{2+} removal and further increase in dose will perhaps result into increase in adsorption density which causes an aggregation of adsorption sites hence limiting the capacity for effective adsorption. Therefore, a high removal efficiency is observed for the adsorbent. At dose value of 0.1g, the modified biomass adsorbed 97.40% as against the 92.20% observed for the unmodified and it continued this trend until a maximum adsorption of 99.43% was obtained at dose value of 0.3g. This indicates the effect of the citric acid modification on the biomass as it increased sorption capacity rapidly. Further increase beyond dose value of 0.3g for the modified biomass led to a consistent decrease in the amount of adsorbed ions.

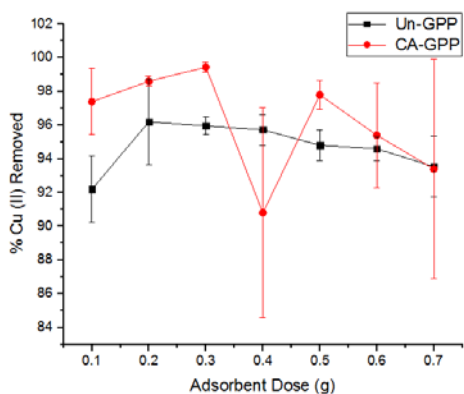


Figure 4: Effect of adsorbent dosage on the % copper removed from 50mg/l aqueous solution using Un-modified (Un-GPP) and Citric acid modified ground plantain peels (CA-GPP)

3.5 Kinetic Studies

Different adsorption kinetic models were applied to the experimental data to study the mechanism of adsorption. The values of the constants were obtained by making necessary plots as guided by the kinetic models and the results are shown in TABLE 1:

Table 1: Values of constants obtained when experimental data was fitted to kinetic models.

Pseudo-first-order kinetic model

	q_e	K_1	R^2
Unmodified	5.9786	0.0028	0.5966
Modified	2.4221	0.0018	0.2569

Pseudo-second-order kinetic model

	q_e	K_2	R^2
Unmodified	47.62	0.0048	0.9984
Modified	48.31	0.0809	0.9997

Intra-particle diffusion model

	K_i	C	R^2
Unmodified	0.1955	43.6130	0.4687
Modified	0.0868	47.0840	0.3884

Elovich kinetic model

	β	α	R^2
Unmodified	1.2140	1.0199×10^{22}	0.3477
Modified	2.1706	0.8128×10^{43}	0.4566

Fractional power kinetic model

	K	v	R^2
Unmodified	42.0920	0.0178	0.3450
Modified	45.9198	0.0096	0.4598

The correlation values obtained show that the pseudo-second-order kinetic model fitted the data for both the unmodified and modified biomass suggesting a chemisorption process [17] with the modified biomass showing

an higher adsorption capacity. The intra-particle diffusion model gave a multi-linear plot which shows that more than one step is involved in the adsorption process [21]. These steps can include external surface adsorption, gradual adsorption, external diffusion and intra-particle diffusion. If a linear graph is obtained and the plot passes through the origin, then intra-particle diffusion is said to be the only rate-limiting step. In the case of this study, the plot did not pass through the origin.

The Elovich kinetic model showed that the extent of surface coverage of the Cu²⁺ was higher for the modified biomass, perhaps as a result of the multiple available bonding sites leading to the attraction of the Cu²⁺ in different directions. The chemisorption rate of the modified biomass was also discovered to be about twice the value of that of the unmodified biomass. The fractional power model shows that the amount of Cu²⁺ sorbed at unit time i.e. $t=1$ will be higher for the modified biomass than the unmodified because the former has a higher value of K.

Table 2: Maximum copper adsorption capacities of previous studies in comparison with data obtained from this research work.

Adsorbent	q _e (mg/g)	References
Sawdust	1.79	Yu and his colleagues [27]
Pomegranate peel	1.32	El-Ashtoukhy and his colleagues [28]
Rice shells	2.95	Ayidin and his colleagues [29]
Lentil shells	9.52	Ayidin and his colleagues [29]
Kolubara lignite	4.05	Milicevic and his colleagues [32]
Litchi pericarp	8.83	Kong and his colleagues [33]
Phosphoric-acid-modified-activated carbon from olive stones	17.66	Bohli and his colleagues [31]
Sodium-hydroxide-modified loquat leaves	28.33	Awwad and his colleagues [30]
Plantain peel biomass	47.62	This research work
Citric-acid-modified plantain peel biomass	48.31	This research work

3.6 Adsorption Isotherms

To understand the mechanism that governed the adsorption process of Cu²⁺ unto Un-GPP and CA-GPP, the experimental data obtained from this study were fitted into Langmuir, Freundlich and Temkin isotherms and results obtained are displayed in TABLE 3.

The correlation values show that the experimental data for the unmodified biomass were better described by the Temkin isotherm which suggests that there must have been an indirect interaction between the adsorbate and adsorbent unlike a Langmuir situation where there is a dominant monolayer adsorption and no interaction

between the molecules of the adsorbate. On the other hand, the modified biomass were better fitted by the Freundlich isotherm; signifying a heterogeneous adsorption. This was consistent with results obtained in [25] and [26]. This can be traced to the effect of the modifying agent (citric acid) which brings in additional surface sites-causing an interaction between the adsorbate molecules and the adsorbent surface. The value of K_L for modified biomass was close to 5 times larger than that of the unmodified; thereby signifying that the adsorption of the Cu^{2+} was stronger for the modified biomass. The Temkin model also shows that the value of B which indicated heat of adsorption was higher for the unmodified than the modified biomass.

Table 3: Values of constants obtained when experimental data for the unmodified and modified biomass were fitted to Langmuir, Freundlich and Temkin isotherm models.

Langmuir isotherm model

	q_m	K_L	R^2
Unmodified	0.0040	1.2114	0.0498
Modified	0.0049	5.8936	0.1866

Freundlich isotherm model

	n	K_F	R^2
Unmodified	3.2906	0.0053	0.0135
Modified	2.9878	0.0079	0.2088

Temkin isotherm model

	B	A_T	R^2
Unmodified	0.01	0.9324	0.1415
Modified	0.0023	0.0147	0.0877

4. Conclusion

Citric acid was sufficiently capable of modifying natural plantain peel biomass; thereby increasing the adsorption capacity of the biomass to remove Cu^{2+} from an aqueous solution. Various parameters such as pH, dosage and contact times were used to study the behavior of the biomass and the effects of modification. The sorption process was largely a pseudo-second-order process and fitting of the experimental data into some kinetic models showed that the Temkin model fitted the unmodified form and best fitting for the citric-acid-form was achieved by the Freundlich isotherm model which suggests that the latter involved an heterogeneous adsorption.

This study has also shown and increased the suitability of plantain peel as an excellent biosorbent for the

remediation of Cu^{2+} in a simulated aqueous system as the maximum adsorption obtained was higher than what was derived in various adsorption studies of Cu^{2+} .

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