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CIVIL & ENVIRONMENTAL ENGINEERING | RESEARCH ARTICLE

Assessment of KOH-activated unripe *Musa paradisiaca* peel for adsorption of copper from aqueous solution

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Abstract: Adsorption of copper ions out of aqueous solution by preparing activated carbon from unripe *Musa paradisiaca* peel (UmpP) with KOH was investigated. Estimation of the adsorption constants was achieved by adopting the Langmuir and Freundlich models. Results revealed that the adsorption process was fast and equilibrium was reached at 55 mins. The adsorption efficiency was highly influenced by the pH of the solution, and the maximum adsorption was attained at pH 7.5. In addition, an increase in adsorption capacity was observed with increase in contact time and initial copper concentration. The adsorption process was explained by both Langmuir and Freundlich models having R^2 value of 0.9977 and 0.9959 at 303 K respectively and R^2 value of 0.9922 and 0.9904 at 308 K respectively. The maximum adsorption capacity of KOH-modified UmpP at the specified conditions was found to be 9.980 and 9.766 mg/g at 303 and 308 K respectively. Sequel to modelling the kinetic data, the Pseudo-second-order model gave the best fit with $R^2 = 0.9990$



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PUBLIC INTEREST STATEMENT

Several industrial activities such as mining, leather tanning, metal plating, battery production, metallurgical processes, and manufacturing of electronics generate effluents containing metal ions, which are deposited directly or indirectly into the environment. This work is aimed at developing an efficient method of removal of copper which is one of the heavy metals that tend to pollute the soil and major sources of water resources thereby causing an environmental hazard, which must be eliminated to comply with the recent legislative standards. The presence of copper in the human body can cause an adverse effect on the liver, skin, kidney, heart, and pancreas, mental retardation, brain damage and stomach ulcer in humans. Therefore, cheap and reliable means of metal removal is needed to reduce their concentration. This study focuses on using available agricultural waste materials for copper removal at over 80% efficiency from aqueous solution.

and 0.9977 at 303 and 308 K respectively, indicating that the adsorption process is restricted to chemisorption. KOH-modified *UmpP* can serve as an economically and environmentally viable sorbent for the removal of copper from contaminated waters.

Subjects: Resource Management - Environmental Studies; Ecology - Environment Studies; Environmental Change & Pollution; Environmental Chemistry; Environmental Health

Keywords: adsorption; *Musa paradisiaca*; equilibrium isotherm; heavy metals; copper(II) removal

1. Introduction

Heavy metals are non-biodegradable. Therefore, its accumulation in living organisms culminates into several health complications as well as environmental deterioration (Gupta & Gogate, 2016). Copper, as seen in most aquatic environment (Barros et al., 2008), is one of the most abundant and harmful metals to living organisms. It occurs naturally (Yargıç, Şahin, Özbay, & Önal, 2015) in soluble form (Cu^{2+}) and can cause environmental pollution and health hazard to humans. Copper is mainly used in its raw state by industrial processes (mining, brass manufacture, plating and petroleum refining) that produces large amount of wastewater laden with copper-containing sludge (Demirbas, Dizge, Sulak, & Kobya, 2009). When copper is ingested in heightened concentration, it causes adverse effect to the liver, skin, kidney, heart and pancreas (Gupta & Gogate, 2016; Turan, Elevli, & Mesci, 2011). Zhu, Wang, and Chen (2009) reported that copper ions might induce severe health complications such as mental retardation, brain damage and stomach ulcer in humans and animals. Solisio, Lodi, Torre, Converti, and Borghi (2006) added that the intake of copper in high concentrations could cause anemia and intestinal disorder. Manzoor, Nadeem, Iqbal, Saeed, and Ansari (2013) also mentioned that the presence of copper in the marine ecosystem had caused severe damage to the gills, kidneys, liver and alteration of the nervous system and reproductive systems of fishes. Hence, attention should be focused on the treatment of wastewater polluted with copper to ensure the protection of aquatic lives and the environment at large.

Several conventional treatment techniques have been used to eliminate copper from polluted waters before discharge into the environment. These include coagulation, membrane separation, chemical precipitation, ion exchange, biological treatment, and solvent extraction (Abdel-Aziz, Nirdosh, & Sedahmed, 2013; Agwaramgbo, Magee, Nunez, & Mitt, 2013; Amuda, Amoo, Ipinmoroti, & Ajayi, 2006; Feng, Sugiura, Shimada, & Maekawa, 2003; Fu & Wang, 2011; Sa'idi, 2010). Good results have been achieved from utilizing these methods. However, their application is limited by incomplete removal, high cost, huge energy requirements and production of secondary waste (sludge) (Li, Zhai, Zhang, Wang, & Zhou, 2007; Soetaredjo, Kurniawan, Ki, & Ismadji, 2013). Among these methods, adsorption has, however, proven to be an efficient and economical means of treating polluted waters having toxic heavy metals. Its flexibility in operation and simple design (Fu & Wang, 2011; Singh & Kaushal, 2013) has made researchers to continually search for novel materials that can serve as adsorbents. Due to the high costs of commercially-sourced activated carbon (Chen et al., 2010), researchers have directed attention towards the use of agricultural wastes for the production of adsorbents due to its abundance, cheap and non-toxic nature, availability in local regions and reusability (Demirbas, 2008). In addition to the listed advantages, the different functional groups such as carboxyl, phenolic, amide, carbonyl, alcoholic, thiol, amine and phosphate present in agricultural waste materials enhances the attraction potentials with heavy metals by forming metal chelates and/or complexes (Witek-Krowiak & Reddy, 2013).

The removal of copper from contaminated waters have been achieved using several agricultural by-products such as papaya wood, sugar beet pulp, black gram husk, cassava peel, onion skins, apple wastes, palm kernel husk, corn cob, pine cone bark and sunflower stalks (Febrianto et al., 2009; Nurchi & Villaescusa, 2008; Pehlivan, Cetin, & Yanik, 2006). Bailey, Olin, Bricka, and Adrian (1999) and Emenike, Omole, Ngene, and Tenebe (2016) reported that natural materials that are by-products of

agricultural and industrial process might possess capabilities as low-cost adsorbents provided they are readily available in substantial quantities. This could ensure its sustained availability in local markets, while also attracting patronage by industries having heavy metals in their effluents (Demirbas, 2008).

Musa paradisiaca or plantain (common name) is regarded as the tenth most important staple food cultivated in tropical parts of the world. In Nigeria, plantain is widely cultivated and consumed by almost every ethnic group. Food and Agriculture Organisation (2005) reported that Nigeria produces over 2,110 million kilograms of plantains annually. The peels (ripe or unripe), which constitutes up to 40% of the original weight are, however, not edible and contribute substantially to the volume of refuse generated. Considering the volume of plantain peels generated in several tropical countries. Limited studies have investigated the use of unripe plantain peel for copper extraction from aqueous solution. However, the purpose of this study is (1) to prepare activated carbon from unripe plantain peel with combined activation (physical and chemical) to enhance the surface characteristics of the resultant product that will be used for copper removal from aqueous solution (ii) to investigate the adsorption characteristics of unripe *Musa paradisiaca* towards copper adsorption from aqueous solution (iii) to calculate the thermodynamic parameter obtained from pseudo-first-order and pseudo-second-order kinetic models. Copper adsorption experiments were conducted in batch mode, and the kinetic and equilibrium data were evaluated and analyzed. Parameters that may affect the adsorption potentials such as pH, temperature, the initial concentration of the metal solution and contact time were investigated.

2. Material and methods

2.1. Preparation of KOH-Activated *Musa paradisiaca* adsorbent

Unripe and fresh *Musa paradisiaca* peels (UmpP) were collected from a local plantain chips manufacturing factory. The UmpP was initially washed with tap water twice to remove debris and further washed with distilled water twice. The UmpP was immediately placed in an oven operated at 105°C for 48 h. The dry samples were placed in a desiccator for cooling and then ground to fine powder with a roller mill and passed through a set of sieves ranging from 75 to 850 µm to obtain particle sizes <450 µm.

The KOH-activated UmpP was prepared via two methods: Carbonization of the dried samples at 250°C for 1 h 20 min in a muffle furnace in the absence of air. The carbonized precursor was cooled in a desiccator and washed with 0.1 M HCl to eliminate ash, rinsed with distilled water and brought back to pH 7.0 using 0.1 M NaOH. Further drying was done at 105°C for 2 days. The dried carbonized sample was soaked with 0.15 mol/dm³ KOH at room temperature for 720 min. The activated precursor was brought back to neutral pH with 0.1 M HCl, washed with distilled water repeatedly, dried at 105°C for 18 h to attain a stable weight and stored in a dry glass bottle for further use.

2.2. Chemicals

A synthetic stock copper solution (1,000 mg/l) was prepared by dissolving anhydrous CuSO₄ in distilled water. To obtain the working solutions, the stock solution was diluted further. The pH of the working solutions was adjusted and measured using HANNA H198130 pH meter. The experiment made use of chemicals of analytical grades while the concentration of copper after each experiment was obtained by atomic absorption spectrophotometer (Thermo Electron Corporation S SERIES AA Spectrometer).

2.3. Morphological study

The surface morphology of KOH-activated UmpP was obtained from Scanning Electron Microscopy (SEM) imagery by using a PHENOM proX SEM (MVE0224651193). Before analysis, the particles were placed on an aluminium sampling stubs with colloidal graphite ribbon and double coated with a sputter coater (QISOR ES).

3. Experimental dynamics

3.1. pH effect

Batch studies were used to investigate the effect of pH on the rate of copper removal. This was achieved by placing 0.4 g of KOH-activated *UmpP* in copper solution of adjusted pH values of 3.5, 5.5 and 7.5 respectively. The mixture of *UmpP* and copper aqueous solution was agitated at 800 rpm (revolutions per minute) for 65 min. The selected dose for the experiment was applied to 20 mL of the copper solution of 100 mg/L.

3.2. Effect of contact time

A study of absorbance based on time variation was carried out by putting 0.4 g of adsorbent in 100 mg/L Cu solution that has been adjusted to pH 3.5 and 5.5 respectively and allowed to stay for 65 min. At stipulated time intervals (5, 15, 25, 35, 45, 55 and 65 min respectively). The samples were filtered, and the filtered solution was analyzed for the leftover Cu ions in the solution.

3.3. Effect of initial Cu concentration

From the setup of 3.1, one of the pH (i.e. pH 3.5) was selected to investigate the effect of different initial Cu concentration on adsorption. Similarly, 0.4 g of the adsorbent was added to 20 mL of different aqueous copper solution (100 and 150 mg/L), and the mixtures were agitated for various contact time (5, 15, 25, 35, 45, 55 and 65 min respectively). At the expiration of the specified time, the sample-solution was filtered, and the separated solution was analyzed for the remaining Cu concentration.

3.4. Adsorption isotherm experiments

The experiment was achieved by soaking 0.4 g of KOH-activated *UmpP* sorbent in 20 mL copper solution. The concentration of copper in the solution was varied (100 to 200 mg/L), for a contact time of 5–65 min, at a constant temperature of 303 and 308 K at pH 7.5. The solution was centrifuged for 10 min at 800 rpm and then filtered using a Whatman filter paper (1003–1055). The filtrate was analyzed for the concentration of copper left in the solution by atomic absorption spectrophotometer.

3.5. Kinetic experiments

The adsorption kinetics of Cu onto KOH-activated *UmpP* was carried out by batch experiments using a THERMO Scientific MaxQ Shaker (Model 4330) at 303 and 308 K. 0.4 g of KOH-activated *UmpP* was added to 100 mL copper solution (150 mg/L) at pH 5.5. Samples were collected at different intervals (5 to 65 min) and filtered instantly with Whatman filter paper. The concentration of Cu left in the filtrate at the selected intervals was analyzed with atomic absorption spectrophotometer. The amount of copper uptake onto *UmpP* at equilibrium q_e (mg/g) can be computed using Equation (1).

$$q_e = \frac{(C_o - C_e)V}{w} \quad (1)$$

where C_o and C_e are the initial and equilibrium copper ion concentration in (mg/L), q_e (mg/g) is the amount of metal adsorbed at equilibrium, V is the volume of the solution in (L) and w is the mass of *UmpP* adsorbent in (g).

4. Theoretical foundation

4.1. Equilibrium isotherm models

The relationship that exists between the quantities of copper adsorbed as well as the remaining concentration can be explained using adsorption isotherms. Several equations have been used in analyzing equilibrium data obtained from experimental adsorption. A proper insight into the surface characteristics and adsorption mechanism of the adsorbent depends on certain thermodynamic postulates and equilibrium parameters of the equilibrium adsorption models. This work tested the equilibrium data of Cu removal by KOH-activated *UmpP* with two common models available in the

literature—Langmuir model and Freundlich model. These models were used to describe the best-fit models as well as their coefficient of determination, R^2 .

4.2. Langmuir isotherm

According to Langmuir (1918), the Langmuir isotherm model regards adsorption as a chemical process involving monolayer adsorption with fixed number of identical sites attracting the adsorbates to the surface. The model also assumes that all sites possess equal energy and an ion can only be attracted to one site. In the same vein, the model stands on another assumption that ions do not interact with each other.

4.3. Freundlich isotherm

The Freundlich isotherm model describes the equilibrium parameter and adsorption properties for a heterogeneous surface (Freundlich, 1906). Being different from the Langmuir model, the Freundlich model cannot be restricted by saturation limitation and Henry's law. This indicates that multilayer sorption occurs on the heterogeneous surface, which can be predicted mathematically (Table 1).

4.4. Adsorption kinetics

One way to describe the potentials of an adsorbent for the removal of pollutant from an aqueous phase is by studying the adsorption kinetics. The conclusion grafted from the kinetic studies tends to provide adequate information on the adsorption mechanism of the system. This paper studied the kinetics of adsorption by using the Pseudo first-order and Pseudo second-order model. Several reports have shown that most adsorption system conforms to the Pseudo-second-order model

Table 1. Some isotherm models commonly used for adsorption of metals

Adsorption isotherm	Non-linear model	Linear model	Plot	References
Freundlich	$q_e = K_f C_e^{1/n}$	$\log q_e = \log K_f + \frac{1}{n} \log C_e$	$\log q_e$ vs $\log C_e$	Freundlich (1906)
Langmuir	$q_e = \frac{Q_{\max} b C_e}{1 + b C_e}$	(I) $\frac{C_e}{q_e} = \frac{1}{b Q_{\max}} + \frac{C_e}{Q_{\max}}$ (II) $\frac{1}{q_e} = \frac{1}{Q_{\max}} + \frac{1}{b Q_{\max} C_e}$ (III) $\frac{q_e}{C_e} = b Q_{\max} - b q_e$ (IV) $q_e = Q_{\max} - \frac{q_e}{b C_e}$	$\frac{C_e}{q_e}$ vs. C_e $\frac{1}{q_e}$ vs. $\frac{1}{C_e}$ $\frac{q_e}{C_e}$ vs. q_e q_e vs. $\frac{q_e}{C_e}$	Langmuir (1918)
Tempkin	$q_e = \frac{RT}{b_T} \ln A_T C_e$	$q_e = \frac{RT}{b_T} \ln A_T + \left(\frac{RT}{b_T}\right) \ln C_e$	q_e vs. $\ln C_e$	Tempkin and Pyzhev (1940)
Dubinin–Radushkevich	$q_e = (q_s) \exp(-k_{ad} \epsilon^2)$	$\ln(q_e) = \ln(q_s) - k_{ad} \epsilon^2$	$\ln(q_e)$ vs. ϵ^2	Dubinin and Radushkevich (1947)
Redlich–Peterson	$q_e = \frac{K_R C_e}{1 + a_R C_e^b}$	$\ln\left(K_R \frac{C_e}{q_e} - 1\right) = g \ln(C_e) + \ln(a_R)$	$\ln\left(K_R \frac{C_e}{q_e} - 1\right)$ vs. $\ln(C_e)$	Redlich and Peterson (1959)
Sips	$q_e = \frac{K_S C_e^{\beta_S}}{1 + a_S C_e^{\beta_S}}$	$\beta_S \ln(C_e) = -\ln\left(\frac{K_S}{q_e}\right) + \ln(a_S)$	$\ln\left(\frac{K_S}{q_e}\right)$ vs. $\ln(C_e)$	Sips (1948)
Flory–Huggins	$\frac{\theta}{C_o} = K_{FH} (1 - \theta)^{n_{FH}}$	$\log\left(\frac{\theta}{C_o}\right) = \log(K_{FH}) + n_{FH} \log(1 - \theta)$	$\log\left(\frac{\theta}{C_o}\right)$ vs. $\log(1 - \theta)$	Horsfall and Spiff (2005)
Toth	$q_e = \frac{K_T C_e}{(a_T + C_e)^{1/T}}$	$\ln\left(\frac{q_e}{K_T}\right) = \ln(C_e) - \frac{1}{T} \ln(a_T + C_e)$	$\ln\left(\frac{q_e}{K_T}\right)$ vs. $\ln(C_e)$	Toth (1971)

Notes: C_e is the equilibrium concentration, q_e is the amount of metal adsorbed at equilibrium, Q_{\max} is the maximum amount of metal adsorbed, n is the adsorption intensity, K_f is the Freundlich isotherm constant, R is the gas constant, T is the absolute temperature, θ represents the degree of surface coverage, K_{FH} is the Flory–Huggins equilibrium constant, n_{FH} is the Flory–Huggins model exponent, A_T is the Tempkin isotherm equilibrium constant, b_T is the Tempkin isotherm constant, q_s is theoretical isotherm saturation capacity, K_{ad} is Dubinin–Radushkevich isotherm constant, K_R is Redlich–Peterson isotherm constant, K_T is the Toth isotherm constant, t is temperature, K_S is Sips isotherm constant.

(Ammari, Al-Labadi, Tahboub, & Ghrair, 2015; Vadivelan & Kumar, 2005). A linearized description of the Pseudo first-order and Pseudo second-order models are represented in Equations (2) and (3) respectively.

$$\text{Log}(q_e - q_t) = \text{Log } q_e - \frac{k_{ad}}{2.303} t \quad (2)$$

$$\frac{t}{q_t} = \left[\frac{1}{k_2 q_e^2} \right] + \frac{t}{q_e} \quad (3)$$

From the plot of $\text{Log}(q_e - q_t)$ vs. t (pseudo first-order model), k_{ad} (adsorption rate constant for first-order) can be derived from the slope. For pseudo second-order model, q_t (mg/g) stands for the adsorption capacity at time, t , whereas the values $1/k_2 q_e^2$ and $1/q_e$ are obtained from the intercept and slope of the straight-line plot of t/q_t against t . It is vital to note that the q_e obtained from the slope is also known as the $q_{e(\text{calculated})}$.

In order to evaluate the adsorption process, i.e. whether the process is favourable or unfavourable, Hall, Eagleton, Acrivos, and Vermeulen (1966) proposed an equilibrium parameter R_L —an important characteristic of the Langmuir isotherm. Four conditions with respect to R_L were itemized; For the adsorption process to be favourable, $0 < R_L < 1$, unfavourable, $R_L > 1$. If $R_L = 1$, then the adsorption process is linear and a R_L value of 0 shows that the adsorption process is irreversible. The expression of R_L is given by Equation (4).

$$R_L = \frac{1}{(1 + bC_i)} \quad (4)$$

where b represents the Langmuir constant and C_i is the initial fluid-phase concentration.

5. Results and discussion

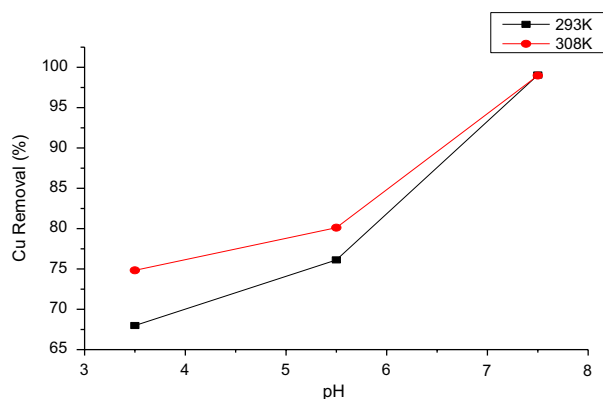
Plate 1 represents the granular KOH-activated UmpP before and after analysis on SEM to show the porous structure characterized by deep pores.

5.1. Effect of pH of the solution

The role of pH of the solution in the entire adsorption process cannot be overemphasized. A change in pH value may alter the adsorbent surface characteristics. According to Nouri, Ghodbane, Hamdaoui, and Chiha (2007), any adsorbent surface is characterized by positive or negative charge, which is proportional to the solution pH surrounding the particles of the adsorbent. In addition, Ammari et al. (2015) outlined that as the pH of the solution increases, metal adsorption increases as well, up to a point where a decline in metal adsorption is experienced or remains unchanged.

As the effect of pH of the solution on the adsorption of copper onto KOH-activated UmpP was being monitored in this study, we discovered that the adsorption of copper onto KOH-activated UmpP increased regardless of the pH value (Figure 1). It was also observed that Cu removal increased from the initial acidic phase (pH 3.5) of the solution to the weak acid zone (pH 5.5). As the solution approach neutral (pH 7.5), there was a sharp increase in adsorption of Cu ions. From Figure 1, about 67.99% Cu removal was attained at pH 3.5 when the investigation was conducted at 293 K. Correspondingly, about 74% Cu removal efficiency was observed at the same pH value but at a temperature of 308 K. As the pH value moved to the weak acid zone (pH 5.5), Cu removal efficiency improved to 76.12% at 293 K and 80.12% at 308 K respectively. The reduced adsorption experienced at the strong acidic medium could be attributed to the presence of H_3O^+ ions surrounding the surface of the KOH-activated UmpP. Within this phase, a repulsive force between the binding sites and the Cu^{2+} ions is created (Ngah & Hanafiah, 2008). In a similar vein, Cu removal increased from 76.12 to 99.04% at temperature 293 K and from 80.12 to 98.98% at 308 K respectively as the pH increased from pH 5.5 to 7.5. This increase can be attributed to the decrease in electrostatic repulsion caused

Figure 1. Copper removal by KOH-activated UmpP (0.4 g in 20 mL) influenced by pH of the solution (100 mg/L Cu concentration) at varied temperature.



by the reduction of positive charge resulting in the attraction of the positively charged Cu^{2+} onto the free binding sites on the surface of the sorbent (Yang et al., 2010). Yargıç et al. (2015) obtained similar results in the removal of Cu^{2+} , Gupta, Kushwaha, and Chattopadhyaya (2011) in the removal of Pb^{2+} , Co^{2+} and Ni^{2+} and Feng and Guo (2012) in the removal of Cu^{2+} , Zn^{2+} , and Pb^{2+} .

In addition, a more detailed pattern of the effect of pH on Cu adsorption is shown in Figure 2. With respect to the pH values presented in Figure 3 (pH 3.5 and pH 5.5), 69.342% Cu absorbance occurred within 25 min contact time at pH 5.5 while 59.149% Cu absorbance occurred within the same time mentioned above at pH 3.5. The respective absorbance within specified time interval is also presented in Figure 2.

5.2. Effect of contact time and initial concentration

In order to develop a water technology that uses adsorption mechanism, the rate of metal removal is a fundamental phenomenon that needs to be studied. The current study investigated the effect of contact time (Figure 3) in order to establish the time required for Cu adsorption to attain equilibrium.

From Figure 3, the equilibrium time needed for the sorption of Cu onto KOH-activated UmpP is about 55 min, and the amount of Cu adsorbed onto KOH-activated UmpP increased as the time increased. Nouri et al. (2007) outlined that the time required to reach equilibrium adsorption also depends on the initial concentration of the metal solution. Therefore, the sorption capacity with respect to the initial concentration using 100 and 150 mg/L of copper solution was investigated. From the results (Figure 3), maximum efficiency for Cu removal onto KOH-activated UmpP occurred at 55 min regardless of the initial concentration. Progressively, the adsorption capacities were improved because of the initial concentration. Cu removal increased from 2.53 mg/g (for 100 mg/L initial concentration) to 2.58 mg/g (for 150 mg/L initial concentration) at 5 min contact time. As the contact time increased, the adsorption capacity was enhanced from 2.53 to 3.76 mg/g at 55 min (for 100 mg/L

Figure 2. Copper absorbance by KOH-activated UmpP (0.4 g in 20 mL) as affected by pH of the solution (100 mg/L Cu concentration) within specified time.

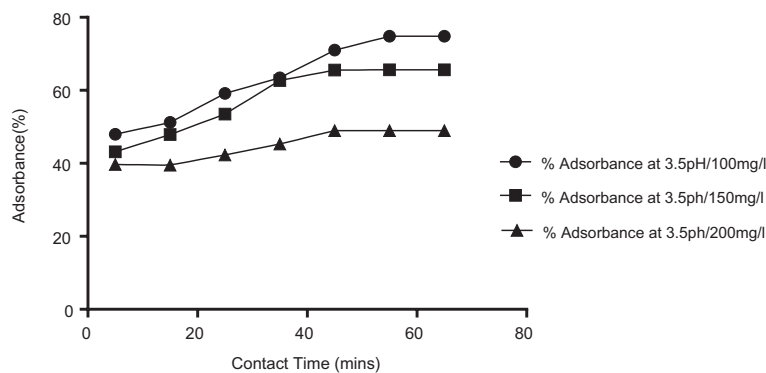
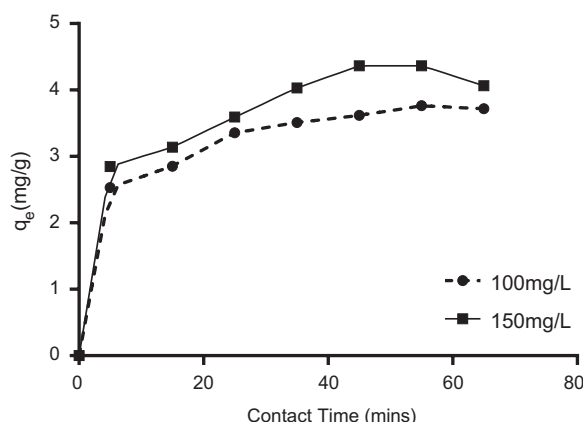


Figure 3. Copper removal by KOH-activated UmpP (0.4 g in 20 mL) as affected by initial concentration (100 and 150 mg/L Cu concentration) and contact time.



initial concentration) and from 2.85 to 4.37 mg/g (for 150 mg/L initial concentration). The results indicate that as the Cu ions increases, the mass transfer process is intensified because of the differential increase in concentration between the surface of the sorbent and the bulk solution. The adsorption rate obtained in this study is of great importance to the practical application of the adsorption mechanism. Kalavathy and Miranda (2010) reported equilibrium time of 4 h using *moringa oleifera* for Cu removal, Ngah and Hanafiah (2008) reported 60 min using treated rubber leaf powder and Hossain, Ngo, Guo, and Setiadi (2012) reported equilibrium time of 6 h using garden grass.

5.3. Adsorption isotherm study

It is important to note that one the basic requirement for the design of any adsorption system is the adsorption equilibrium isotherms. The equilibrium isotherms give a holistic representation of the distribution of the adsorbate between the solid and liquid phase at equilibrium. The experimental data of the Cu adsorption onto KOH-activated UmpP have been analyzed using the Freundlich model and Langmuir model. The correlation coefficients (R^2) are displayed in Table 2. The R^2 values describe the applicability of the models to the experimental data (Figures 4 and 5).

From Table 2, Langmuir model ($R^2 = 0.9977$) best fits the experimental data over the concentration of Cu studied (100–200 mg/L) when compared to the Freundlich model due to its high R^2 values ($R^2 = 0.9959$). The q_{max} value for the range of Cu concentration studied are 9. mg/g and 9.766 mg/g at temperature 303 and 308 K respectively for Langmuir model while Freundlich model reported 1.656 and 1.666 mg/g at 303 and 308 K respectively. The b evaluated from the intercept are 0.651 and 0.642 L/mg at 303 and 308 K. The fitness of the experimental data to Langmuir model indicates that there is uniformity on the surface as well as equivalent active sites. This clearly indicates that there is no competition between any two Cu ions and the formation of a monolayer on the adsorbent culminates into equilibrium. Other observations indicated that the adsorption capacity dropped when the temperature increased from 303 to 308 K indicating that increasing the temperature will result in energy release. Tong, Kassim, and Azraa (2011), obtained a similar report. Several adsorbents have been utilized for the removal of Cu from aqueous solutions. Table 3 displays the different adsorption capacities as compared to the present study.

Table 2. Langmuir and Freundlich constants obtained from the analysis of Cu adsorption onto KOH-activated UmpP biomass; $C_i = 100\text{--}200$ mg/L, 0.4 g biomass, pH 7.5, 800 rpm

Temperature	Langmuir isotherm			Freundlich isotherm		
	q_m (mg/g)	b	R^2	k_f	n	R^2
303 K	9.980	0.651	0.9977	1.656	1.451	0.9959
308 K	9.766	0.642	0.9922	1.666	1.440	0.9904

Figure 4. Equilibrium isotherm at 303 K.

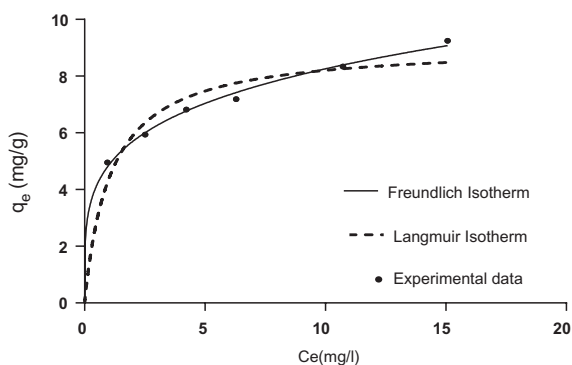


Figure 5. Equilibrium isotherm at 308 K.

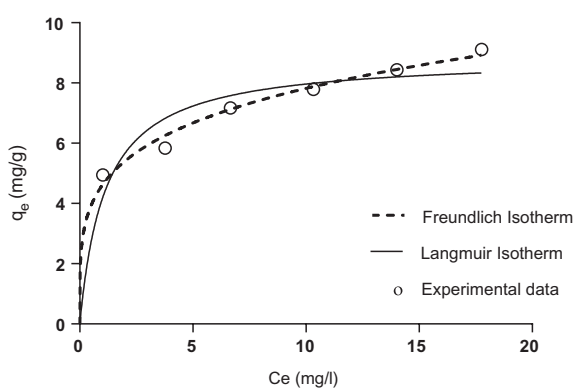


Table 3. Comparison of different sorbent used for Cu removal and their maximum adsorption capacity

Sorbent used	Q_{max}	Reference
Potato peel	0.39	Aman, Kazi, Sabri, and Bano (2008)
Cassava waste	0.95	Abia, Horsfall, and Didi (2003)
Rice shell	1.85	Aydın, Bulut, and Yerlikaya (2008)
Pretreated <i>Aspergillus niger</i>	2.61	Mukhopadhyay, Noronha, and Suraishkumar(2007)
Herbaceous peat	4.84	Gündoğan, Acemioğlu, and Alma (2004)
Pine cone powder	6.80	Ofomaja, Naidoo, and Modise (2009)
Wheat shell	7.39	Aydın et al. (2008)
<i>Atriplex canescens</i> stems of saltbush	7.40	Sawalha, Peralta-Videa, Romero-González, Duarte-Gardea, and Gardea-Torresdey (2007)
Dye loaded groundnut shells	7.60	Shukla and Pai (2005)
Dye loaded sawdust	8.07	Shukla and Pai (2005)
Lentil shell	8.98	Aydın et al. (2008)
Unripe <i>Musa paradisiaca</i> peel	9.98	<i>This study</i>
Spent grain	10.47	Lu and Gibb (2008)
Tree fern	10.60	Ho, Huang, and Huang (2002)
Base treated rubber leaves	14.97	Ngah and Hanafiah (2008)
Cashew nut shell	20.0	SenthilKumar, Ramalingam, Sathyaselvabala, Kirupha, and Sivanesan (2011)

Table 4. Kinetic models and their constants for biosorption of Cu onto KOH-activated UmpP biomass; $C_i = 150$ mg/L, 0.4 g biomass, pH 5.5, 800 rpm

Temp (K)	$q_{e(\text{observed})}$ (mg/g)	Pseudo-second-order rate constants			Pseudo-first-order rate constants		
		$q_{e(\text{calculated})}$ (mg/g)	k_2 (g/mg min ⁻¹)	R^2	k_{ad} (min ⁻¹)	q_e (mg/g)	R^2
303 K	4.939	5.061	0.090	0.9990	0.0820	1.989	0.4965
308 K	5.654	5.845	0.0502	0.9972	0.0815	3.301	0.4533

5.4. Kinetics study

The experimental results obtained from the adsorption of Cu onto KOH-activated UmpP was tested with pseudo first-order and pseudo second-order models to understand the control mechanism of the entire adsorption process e.g. chemical reaction. As presented in Table 4, there is a good relationship between the experimental results obtained from the adsorption of Cu onto KOH-activated UmpP and the pseudo second-order model following the values gotten from the correlation coefficient R^2 (Table 4 complimented with Figure 6(a) and (b)).

At 303 K (Table 4), the $q_{(\text{observed})}$ from the experimental results was 4.939 mg/g while the $q_{e(\text{calculated})}$ was 5.061 mg/g (differential value of 0.122 and R^2 value of 0.9990). Also at 308 K (Table 4), the value of $q_{(\text{observed})}$ is 5.654 mg/g while the $q_{e(\text{calculated})}$ obtained from the pseudo second-order model is 5.845 mg/g (difference of 0.019 and R^2 of 0.9972). This indicates that adsorption capacity of Cu onto KOH-activated UmpP improved when the temperature was raised which is in accordance with the findings of Tong et al. (2011). In addition, the results suggest adsorption via chemisorption.

Figure 6. Plot of pseudo second-order kinetic model for Cu adsorption using KOH-activated UmpP; 150 mg/L initial Copper concentration, 0.4 g biomass, pH 5.5 at 800 rpm (a) 303 K (b) 308 K.

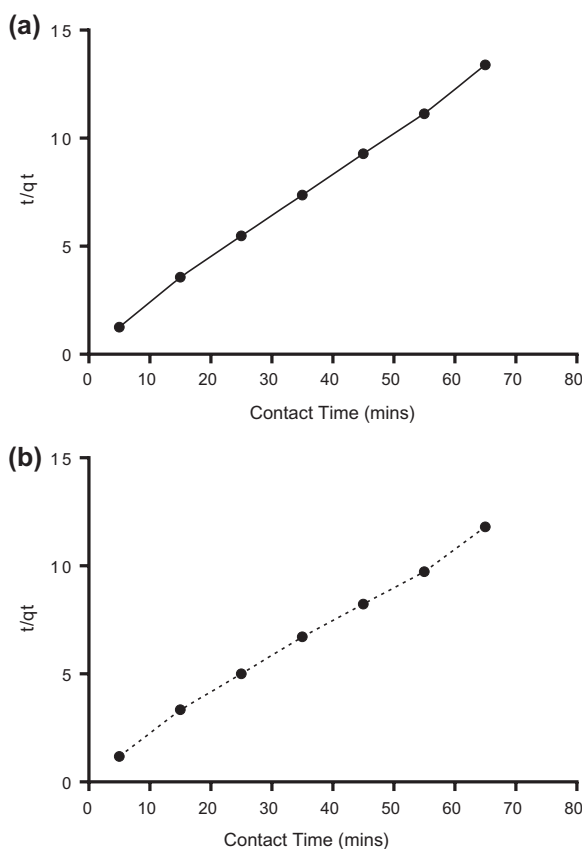
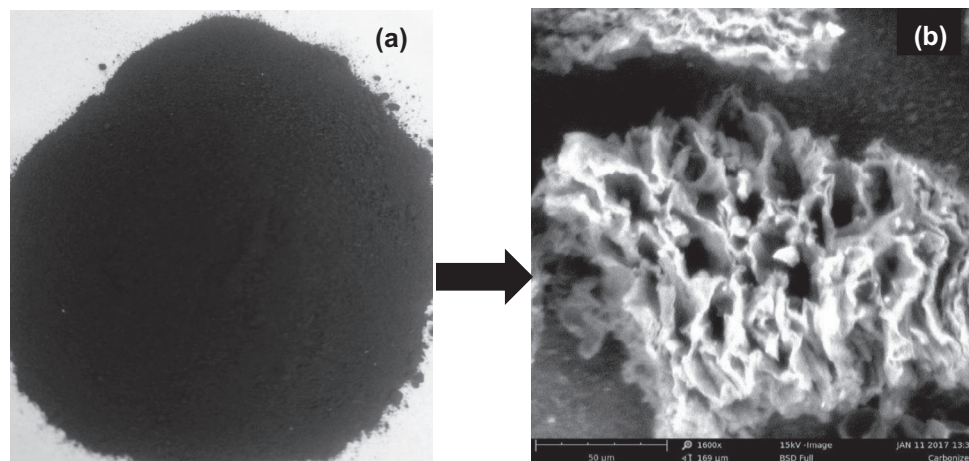


Plate 1. KOH-activated *Musa paradisiaca* peel (a) Granular sample (b) SEM image.



To understand the favourability of the adsorption process, the equilibrium parameter R_L was calculated from Equation (8). From the results, R_L values ranged from 0.008 to 0.015 indicating that sorption of Cu onto KOH-activated UmpP is favourable and reversible.

6. Conclusion

Unripen *Musa paradisiaca* peel (plantain peel), a waste generated from solid food, was utilized as a viable and low-cost adsorbent for removal of Cu from aqueous solution. It is clear that copper adsorption is achievable with KOH-activated unripe plantain peel adsorbent. The operational condition adopted in this study revealed that initial concentration of copper in the solution, pH, temperature and contact time affects the overall adsorption process. The adsorption of copper was found to increase as the initial concentration increased and the equilibrium value was obtained at 55 min contact time regardless of the initial concentration. The adsorption process was affected by the solution pH, initial concentration, temperature and contact time. The model adopted (Langmuir model and Freundlich model) in the adsorption process explained the experimental data, but Langmuir model gave the best fit. The adsorption process followed a reversible and favourable pattern considering the equilibrium parameter R_L . The maximum capacity q_{max} obtained from the Langmuir plot was 9.980 mg/g at 303 K. The kinetic data followed pseudo second-order model indicating adsorption via chemisorption. Results obtained from this study demonstrated that KOH-activated UmpP could be used as biosorbent in place of commercial activated carbon, for the efficient removal of Cu from aqueous solution as well as solving the waste disposal problem of plantain peels.

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