EXPERIMENTAL INVESTIGATION OF COPPER REMOVAL FROM AQUEOUS SOLUTION USING *MUSA PARADISIACA* AS A NOVEL ADSORBENT

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ABSTRACT
The adoption of agricultural waste materials in the removal of heavy metals from contaminated waters has gained more recognition in recent times. This study capitalizes on the production of adsorbents from one of the predominant agricultural waste materials (Plantain Peel) in Ado-Odo Ota, to access its metal-removal efficiency. This work investigated Cu^{2+} adsorption using activated carbon processed from chemically modified unripe plantain (*Musa paradisiaca*) peel. Adsorption studies were performed using batch experiments wherewith the influence of pH of the solution, initial concentration, temperature and contact time have been cross-examined. The results displayed a 99.8% removal efficiency of Cu^{2+} at pH 7.5, 30°C and 150 mg/L concentration. The equilibrium adsorption capacity of unripe *Musa paradisiaca* peel has been obtained using linear models of Langmuir and Freundlich isotherms. The result is poised to elucidate the metal retention mechanism as a process involving ion exchange as the divalent metal ion binds to the activated unripe plantain peel.
Keywords: plantain peel, copper, heavy metal, adsorption, activated carbon.

1 INTRODUCTION

One of the environmental problems experienced around the world originates from heavy metal pollution in wastewater [1], [2]. When these effluents (heavy metals) are discharged without proper treatment, the quality of receiving waters get degraded over time [3], causing severe harm to the environment and humans. Although copper is a required micronutrient for humans, severe complications such as stomach ulcers, liver damage and mental disability in humans and animals arise when copper intake is in excess [4], [5]. Therefore, urgent attention should be directed to the treatment of wastewater polluted with copper ions Cu(II) even if the concentration is low.

Several methods have been used to remove Cu(II) from polluted waters. They include ion exchange [6], ultrafiltration, solvent extraction, membrane filtration [7], biological process, chemical precipitation [8] and adsorption [9], [10]. Among these treatment methods, adsorption has proven to be cheap and efficient in the removal of pollutants from water [11].

In the adsorption process, several adsorbents have been used; they include activated carbon [12], bentonite, algae and agricultural waste products [13]–[15]. It is imperative to note that activated carbon has been widely used due to its high adsorption capacity and large surface area, but the broad application is limited due to its expensive nature and challenging regenerating attributes [16], [17]. Hence, the need to develop novel adsorbent has led to the use of biomass resources from agricultural wastes as a potential adsorbent for heavy metal removal. This area is being explored due to the cheap and abundant nature of agricultural waste and availability in local regions. In line with this, we investigated the performance of plantain peel (*Musa paradisiaca*) in the removal of copper ions from aqueous solution.

WIT Transactions on Ecology and The Environment, Vol 216, © 2017 WIT Press
www.witpress.com, ISSN 1746-448X (on-line)
doi:10.2495/WS170161

2 METHODS AND MATERIALS

2.1 Adsorbent

Unripe plantain peels (UPPs) were obtained from a Plantain Chips factory located in Ota, Ogun State, Nigeria. The UPPs was washed with tap water thrice to remove all adhering dirt, soil particles, and debris during acquisition and later rinsed with distilled water twice. They were dried in an oven at 105ºC to a stable dry weight and stored in a desiccator before use. The dried UPPs were then ground to fine powder using a roller mill and sieved to obtain individual particle sizes. The sieved particles were washed again with distilled water, allowed to dry in an oven at 105ºC for 60 hours, and stored in a desiccator for further use. The sieved samples were carbonated using a muffle furnace operated at 250ºC for 80 min and washed with 0.1 M HCL to remove adhering ash. The samples were then stabilized to 7.0 pH using 0.1 M NaOH, rinsed with distilled water and then dried in an oven for 48 hours. The dried sample was then activated with 0.15 mol/dm^3 KOH at ambient temperature for 12 hours. The activated UPPs were then taken to pH 7.0 using 0.1 M HCL and, after that, rinsed with distilled water. Then the sample was placed in an oven for 18 hours, to be dried at 105ºC.

2.2 Adsorbate

The stock solution was prepared by dissolution of copper sulphate in distilled water to make up for 1000 mg/L of the solution. The working solutions were obtained by diluting required volumes prepared daily from stock solutions. The concentration of copper ions in the solution were gotten using the atomic AA spectrophotometer (RAYLEIGH). pH measurements were recorded with a HANNA H198130 Waterproof Instrument. The distilled water used throughout was obtained from the Department of Microbiology, Covenant University, Ota, Ogun State, while all chemicals used throughout the experiment are of analytical grade and were supplied by ARIKEN Chemicals, Nigeria.

2.3 Adsorption studies

Adsorption studies were carried using batch experiments to evaluate the adsorption of copper ions on the alkali activated UPPs. Tests were conducted by agitating appropriate mass of the adsorbent with 20 ml of the copper stock solution with an initial concentration of 150 mg/L. To obtain continuous mixing throughout the experimental process, an agitation speed of 800 rpm was adopted for a different time interval ranging from 5 to 65 mins at 30°C. The solution was then passed through Whatman 1003-055 Quantitative Filter Paper after equilibration, and then the concentration of copper ion left in the filtrate solution was analysed with an absorption AA spectrophotometer (RAYLEIGH), making use of air-acetylene flame in which calibration was done using 1 mg/l, 2 mg/L and 4 mg/L standard solutions.

The impact of certain parameters such as solution pH, contact time and initial solution concentration were investigated. Adjustment of the pH of the solution throughout the experimental process was made using 0.1 M NaOH and 0.1 M HCL. To ensure reliability and credibility of the results, all quantified experiments were performed in triplicates, and the average values were considered.

3 RESULTS AND DISCUSSION

3.1 Effect of initial concentration and contact time

The results of the copper adsorption onto UPPs at different concentrations (100 mg/L and 150 mg/L) is displayed in Fig. 1. An adsorption equilibrium was attained after 55 mins. Therefore, all other experiments were conducted using 55 min equilibrium time. From Fig. 1, it could be seen that 82% removal efficiency for Cu(II) was attained after 25 min. It is also worthy to note that 99.8% removal efficiency of Cu(II) removal was reached at 65 min for an initial concentration of 150 mg/L while 84.34% removal efficiency was noticeable for an initial concentration of 100 mg/L. In addition, from Fig. 1, the rapid rate of uptake of copper was observed between 5 min and 15 min owing to deep available sites for adsorption.

3.2 pH Influence on adsorption

It was reported that an increase in metal adsorption is characterized by an increase in the pH of the aqueous phase [18]. Hence, the adsorption capacity of a certain metal ion, using a specific adsorbent, is favoured by increased pH value [19]. This experiment investigated the influence of pH on Cu(II) ions adsorption using a batch experiment. The experiments were conducted using 20 ml of Cu solution containing an initial concentration of 150 mg/L, 1 g of adsorbent at temperature 30°C. Meanwhile, a varying pH of 5.5 and 7.5 was monitored for 5–65 min. The results obtained, as displayed in Fig. 2, show that 99.8% and 89.91% Cu(II) removal efficiency for pH 7.5 and pH 5.5 respectively occurred at 55 min. This conforms with the results of previous studies that used other kinds of adsorbents. In agreement with this, Ofomaja and Naidoo [20] reported an increase in Cu(II) removal from pH 2 to pH 5 using activated pine cone as adsorbents.

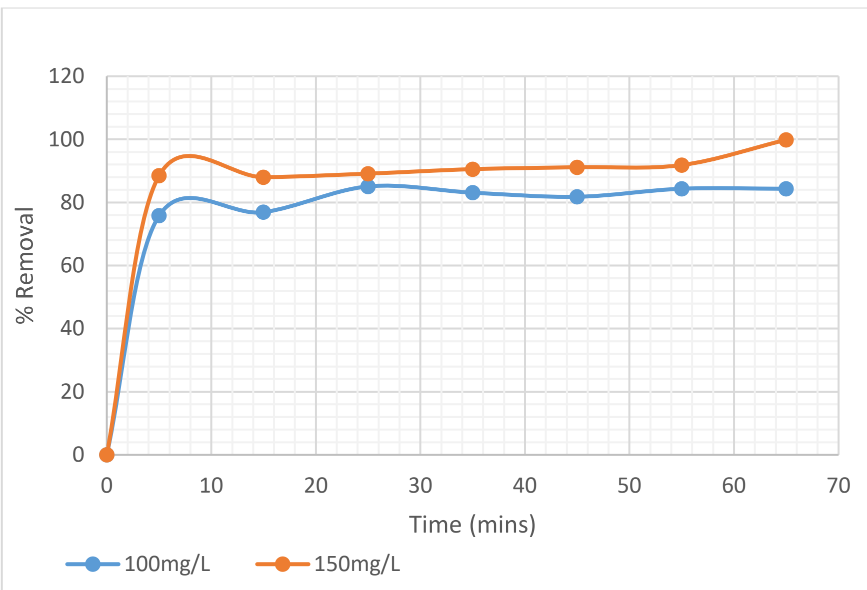

Figure 1: Influence of contact time and initial concentration on Cu(II) adsorption: UPP dose 1 g, pH 7.5.

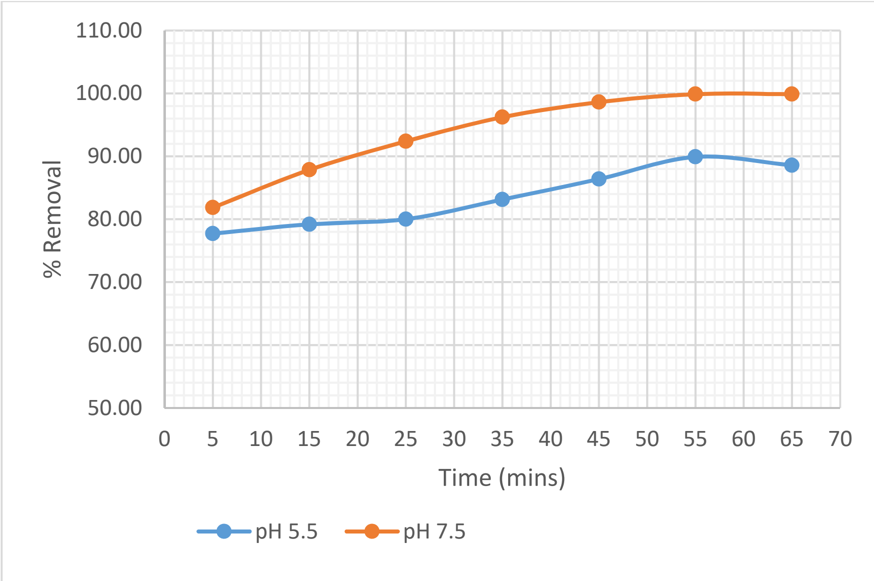

Figure 2: pH influence on Cu (100 mg/L) adsorption at 30°C.

3.3 Adsorption isotherm studies

The study adopted the use of linearized form of Langmuir model (eqn (1)) and Freundlich model (eqn (2)) to fit the adsorption results [21], [22]. The representative models are shown below:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{1}{q_m} C_e \; derived\ from\ q_e = \frac{K_L q_m C_e}{(1+K_L C_e)}, \tag{1}$$

$$Logq_e = Logk_f + \left({}^{1}/_{n}\right) LogC_e \; derived\ from\ q_e = k_f C_e^{\,1/n} \, . \tag{2}$$

C_e denotes equilibrium concentration in (mg/L), K_L represents the constant for equilibrium adsorption, q_e (mg/g) represents adsorbed copper at equilibrium, q_m (mg/g) stands for the saturated/maximum monolayer adsorption capacity, k_f accounts for the adsorption constant for the Freundlich model and ${}^{1}/_{n}$ is the adsorption intensity for the Freundlich model.

Isotherm experimental study was conducted using copper concentrations between 100 mg/L and 200 mg/L, an adsorbent dose of 2 g, temperature of 30°C at 5.5 pH. The results of the Langmuir plot and the Freundlich plot of ${}^{C_e}/_{q_e}$ vs. C_e and $Logq_e$ vs. $LogC_e$ respectively are displayed in Table 1.

Table 1: Adsorption isotherm (Langmuir and Freundlich).

Temperature	Langmuir isotherm			Freundlich isotherm		
30°C	q_m	K_L	R^2	k_f	${}^{1}/_{n}$	R^2
	10.14	0.08	0.999	1.88	0.3859	0.9787

Without doubts, the adsorption of Cu(II) onto UPP is best fitted using the Langmuir model (R^2 = 0.9986). The Freundlich model is characterized with R^2 values of 0.9787 for the temperature considered indicating better conformity with Langmuir model. The interpretation is that an endothermic reaction is associated with the adsorption of Cu(II) onto UPP.

3.4 Kinetics study

One parameter needed to evaluate an adsorption experiment is a kinetic study. The Type 1 pseudo-second-order kinetic model was studied in order to estimate the rate-controlling process of the adsorption experiment [23]. The linearized pseudo-second-order kinetic model [24] is given as:

$$\frac{t}{q_t} = \left[\frac{1}{k_2 q_e{}^2}\right] + \frac{t}{q_e}, \tag{3}$$

where k_2 represents the adsorption rate constant (second order) obtained from the plot of t/q_t vs. t.

The linearized equation of the pseudo-first-order kinetic model [25] is given as:

$$Log(q_e - q_t) = Log q_e - \frac{k_{ad}}{2.303} t, \tag{4}$$

where k_{ad} represents the adsorption rate constant (second order) obtained from the plot of $Log(q_e - q_t)$ vs. t.

To observe this important parameter, a kinetic study was carried out at 30°C, the initial concentration of 150 mg/L for 65 min. The results (Table 2) showed that the time course adsorption for the reaction best fits the pseudo-second-order kinetic model (R^2 = 0.999) when compared to the pseudo-first-order kinetic model (R^2 = 0.8515).

To investigate whether the adsorption procedure was favourable or not, the equilibrium parameter R_L was calculated using eqn (5).

$$R_L = \frac{1}{1 + bC^o}. \tag{5}$$

C^o (mg/L) represents initial metal concentration and b represents the Langmuir constant (L/mg). The adsorption process is favourable when $0 < R_L < 1$, unfavourable when $R_L > 1$, linear when $R_L = 1$ and irreversible when $R_L = 0$ [26]. The R_L values calculated for the adsorption process ranges from 0.0589 to 0.11, suggesting that the process is favourable for Cu(II) adsorption onto UPP.

Table 2: Adsorption kinetics (pseudo-second-order and pseudo-first-order rate constants) for Cu(II) on UPP.

Pseudo-second-order rate constants			Pseudo-first-order rate constants		
q_e (mg/g)	k_2 (g/mg min^{-1})	R^2	k_{ad} (min^{-1})	q_e (mg/g)	R^2
7.9	0.232	0.999	0.128	1.69	0.8515

4 CONCLUSION

The investigation presented in this paper highlights the practical applicability of unripe plantain peel being used as a promising adsorbent for copper removal. In line with the experimental data, the adsorption process fitted well with the Langmuir isotherm while the calculated R_L indicates a favourable adsorption of copper. The maximum adsorption capacity q_m for copper uptake on UPP was found to be 7.84 mg/g at pH 7.5. The adsorption of copper increases as initial concentration increases and equilibrium adsorption was reached at 55 min despite the initial concentration. Hence, UPP adsorbent can be seen as a promising agricultural material for the treatment of Cu metal ion from industrial effluents and water sources laden with copper.

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