

Original Research Article

Biosorption of copper from aqueous solutions by raw and activated spines of *Bombax buonopozense*: Equilibrium, kinetics and thermodynamic studies

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ABSTRACT: Biosorption of copper on raw and activated (AC) spines of *Bombax buonopozense* in a batch system was studied. The percentage removal of copper was found to be a function of pH, contact time, dosage, initial metal concentration and temperature. The experimental results were analyzed with Langmuir, Freundlich, and Dubinin-Radushkevich isotherm models and in each case the Langmuir model appears to have better regression coefficients, R^2 , 0.998 and 0.987 for raw and activated adsorbents respectively. From the kinetic studies the rate constant values for the adsorption process were calculated. Also, various thermodynamic parameters such as ΔG° , ΔH° , ΔS° and E_a were calculated and the result showed that the sorption process was endothermic in nature and that higher solution temperatures favoured metal ion removal by the adsorbents. These results indicated that spines of *Bombax buonopozense* have potential for the uptake of the toxic element (copper) from industrial effluents.

Keywords: Biosorption, Langmuir isotherm, endothermic, kinetic, thermodynamic

INTRODUCTION

Wastewater treatment processes in terms of removal of toxic metals is of great importance in determining the quantity of heavy metals discharged into municipal waters. Discharge of industrial wastewater containing hazardous metals into the environment causes serious environmental problems to human and ecosystems [1, 2]. This is because untreated wastewater from industries and homes end up in rivers and aquatic systems that are sources of livelihood for humans [3]. Most of these rivers are used as sources of drinking water by rural dwellers without any form of treatment and thus increase the chances of several health problems such as cancer, kidney failure, oral ulcer, renal failure and metabolic acidosis [4].

Several techniques are available for the removal of inorganic pollutants (potential toxic metals) from industrial wastewater. The removal of these inorganic pollutants from domestic or drinking water can be achieved through precipitation, flocculation, solvent extraction, ion exchange, reverse osmosis [5], but the process of adsorption has become a preferred method for the

removal of toxic contaminants from water because of its effectiveness, economical value, versatility and simplicity [6].

Adsorption is a mass transfer process by which a substance is transferred from the liquid phase to the surface of a solid and becomes bound by physical or chemical interactions [7]. Adsorption processes mostly involve the use of various low cost agricultural by-products for the elimination of heavy metals from wastewater and these include *Moringa oleifera* pod [8], papaya wood [9], neem bark [10]. Most of these are used in form of granular or powdered activated carbon which have been employed as adsorbents for the removal of both heavy metals and organic pollutants from contaminated water.

The goal of this work was to investigate the sorption capacity, thermodynamics and kinetics of raw and activated adsorbents prepared from spines of *Bombax buonopozense* for copper removal. The potential of this biomaterial as a low cost biosorbent was studied by means of batch sorption tests.

MATERIALS AND METHODS

Biosorbents

The spines of *Bombax buonopozense* were obtained from the bark of this tree collected from farm lands from suburbs of Minna, Nigeria. They were washed with distilled water and thoroughly dried in an oven at 105°C. The sample was ground using pestle and mortar and then sieved to obtain the 250µm fraction used in this experiment. The sample after sieving is divided into two parts: The first part was labeled by “Raw” and second part “AC” was placed in a crucible and positioned at the center of a muffle furnace for 15mins at 500°C. The activated carbon (AC) produced is washed with distilled water and later oven dried.

Metal ion solutions

All reagents used in this study were analytical grade. A stock solution of 1000 mgdm⁻³ copper was prepared by dissolving the appropriate amount of CuSO₄.5H₂O in distilled water. Solutions of lower concentrations were prepared by diluting the stock solution with distilled water. Sodium hydroxide (NaOH) and hydrochloric acid (HCl) were used for pH adjustments.

Analytical techniques

The concentration of copper in the filtrate was measured on an atomic absorption spectrophotometer (AAS), Perkin Elmer; Analyst 200 and the pH were measured with Kent EIL7045/46 pH-Meter.

The specific metal uptake q_e and the percentage removal (Removal %) calculated according to the following equations:

$$q_e = \frac{C_o - C_e}{m} V$$

$$\text{Removal (\%)} = \frac{C_o - C_e}{C_o} \times 100$$

where C_o (mgdm⁻³) is the initial concentration of copper in solution, C_e (mgdm⁻³) the equilibrium copper concentration, q_e (mgg⁻¹) the equilibrium uptake capacity and m (g) the dry weight of the adsorbent.

Adsorption isotherms

The adsorption isotherms were obtained by employing 0.5g of raw and carbonized samples. These were then interacted with 40cm³ of waste solution with different initial concentrations (10, 20, 30, 40 and 50mgdm⁻³) of copper. These solutions were stirred on a mechanical shaker until they reached adsorption equilibrium. The mixtures were shaken for the contact time and then both phases were separated by filtration. The metal contents of the filtrates were determined by atomic absorption spectrometry.

Equilibrium modeling in a batch system

Analysis of equilibrium data is important for developing equation under different operational conditions in order to design and optimize an operating procedure. Equilibrium studies give the capacity of the adsorbent and this can be established on several models.

Freundlich isotherm model

The Freundlich isotherm is an empirical expression which shows the heterogeneity of the surface and multilayer adsorption to the binding sites located on the surface of the sorbent and is expressed as follows:

$$q_e = K_f(C_e)^{1/n}$$

where K_f is the biosorption equilibrium constant and n is a constant indicative of biosorption intensity. C_e is the final concentration of copper in solution (mgdm⁻³). The Freundlich isotherm constants K_f and $1/n$ are evaluated from the intercept and the slope respectively, of the linear plot of $\ln q_e$ versus $\ln C_e$.

Dubinin-Radushkevich isotherm (D-R) model

This isotherm model was chosen to evaluate the mean energy of sorption. It is represented in the linear form by the equation:

$$\ln q_e = \ln Q_m - K\mathcal{E}^2$$

where Q_m is the theoretical maximum capacity (mgg⁻¹) and $\mathcal{E}$ is the Polanyi potential which is expressed as:

$$\mathcal{E} = RT \ln \left(1 + \frac{1}{C_e} \right)$$

The biosorption mean free energy E was calculated from the relation:

$$E = \frac{1}{(-2K)^{\frac{1}{2}}}$$

Langmuir model

The Langmuir treatment is based on the assumption that a maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface and the equation of Langmuir's isotherm model is expressed as:

$$\frac{C_e}{q_e} = \frac{1}{K_L Q_{max}} + \frac{1}{Q_{max}} C_e$$

where q_e is the amount of metal adsorbed (mg g^{-1}), C_e is the equilibrium concentration of solution (mg dm^{-3}). Q_{max} and K_L are Langmuir constants indicating adsorption capacity and energy respectively.

Sorption kinetics

Pseudo first-order kinetic model

The pseudo first-order kinetic model was applied to the experimental data to describe the kinetics of copper metal sorption. This equation is given below:

$$\ln(q_e - q_t) = \ln q_e - k_1 t$$

where q_t and q_e are the amount of solute sorbed per mass of sorbent (mg g^{-1}) at any time and equilibrium respectively and k_1 is the rate constant of first-order sorption (min^{-1}).

Pseudo second-order kinetic model

The pseudo second-order kinetic model equation is represented as:

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

The initial sorption rate is defined by the following equation:

$$h = k_2 q_e^2$$

where k_2 is the rate constant (g/mg.min) and q_t is the metal uptake capacity at any time t .

These equations in this model were used to characterize the adsorption processes of these sorbents.

Thermodynamic studies

Thermodynamic parameters were evaluated by considering the thermodynamic equilibrium constants. The free energy of the biosorption reaction, considering the biosorption equilibrium constant, K_a , is given by the following equation:

$$\Delta G = -RT \ln K_a$$

where ΔG is the change in free energy (kJ/mol), R the universal gas constant 8.314 J/K mol and T is the absolute temperature (K). The equilibrium constant of the biosorption is defined as:

$$K_a = \frac{q_e}{C_e}$$

where q_e is the metal uptake capacity (mgg^{-1}), C_e is the equilibrium concentration of the metal ion in solution (mgdm^{-3}) and K_a is the biosorption equilibrium constant (dm^3/g). The surface coverage (θ) for studying the sticking probability and activation energy was calculated from the equations below.

$$\theta = (1 - \frac{C_e}{C_0})$$

$$S^* = (1 - \theta)e^{-E_a/RT}$$

C_e and C_0 are the equilibrium and initial metal concentrations of the metal respectively while the values of activation energy (E_a) and sticking probability (S^*) were estimated from the experimental data using a modified Arrhenius type equation related to surface coverage as expressed above.

DISCUSSION OF RESULTS

Contact time

Fig. 1 shows the effect of residence time on the removal of copper metal on raw and carbonized adsorbent. Equilibrium was attained within 90 min of shaking time for Cu(II) ions. This shows that there were large number of vacant active binding sites available at the first phase of experiment and large amounts of copper metal were bound rapidly on the adsorbents of spines of *Bombax buonopozense* at a faster adsorption rate. The binding site later became limited and the remaining vacant adsorbents surface sites were difficult to contain more copper ions due to the formation of repulsive forces between the metal ions on the solid surface of the adsorbent and the liquid phase [11]. This was in agreement with the effect of contact time presented by Dhabab [12], on the removal of Fe(II), Cu(II), Zn(II), and Pb(II) ions from aqueous solutions by duckweed.

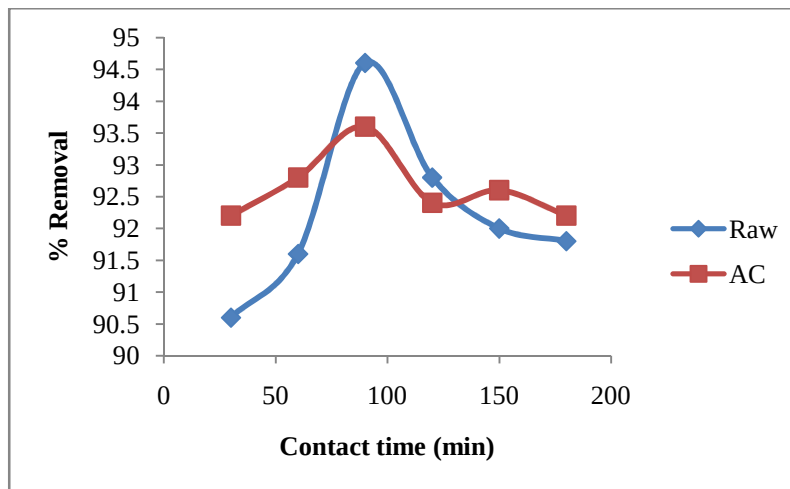


Figure 1. Effect of contact time on the removal of copper ion by adsorption at 5mgdm^{-3} , 0.5g adsorbents weight, pH 6.9 and temperature $28^\circ\text{C} \pm 1$

pH

Cu(II) adsorption increased with increase in solution pH in the range 2-10 as indicated in Fig. 2. These suggest that some functional groups might be involved in the adsorption of copper [13]. At a low pH, adsorption of metal is relatively low due to increase in competition for adsorption sites by hydroxonium ion (H_3O^+). As the pH increased ($\text{pH} > 7$) adsorption increased. The enhanced rate of adsorption with increasing pH implies that the surfaces of adsorbents became more negatively charged. This is in accordance with the findings of Abdel-Halim and Al-Deyab [14].

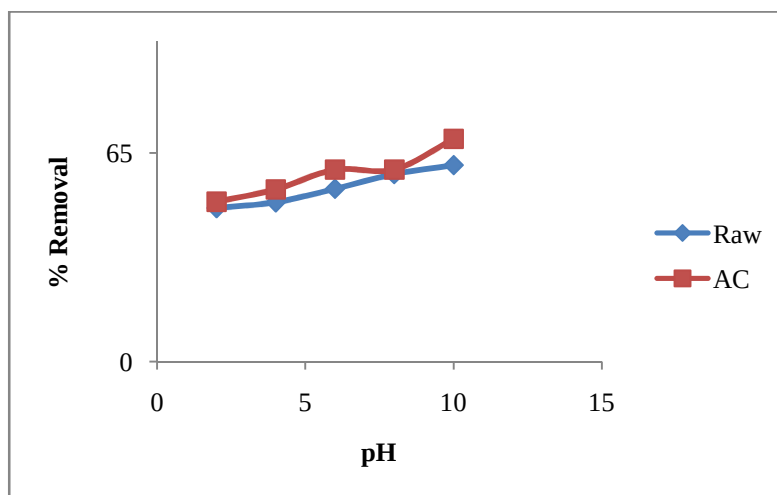


Figure 2. Effect of pH on the removal of copper ion by adsorption at 5mgdm^{-3} concentration and 0.5g adsorbents weight

Initial Concentration

Figure 3 shows the effect of initial metal concentration on the ability of adsorption by raw and activated samples from spines of *Bombax buonopozense* at a range of $10 - 50\text{mgdm}^{-3}$ of copper solution. The initial faster rate of removal of copper could be due to the availability of the vacant surface areas of the adsorbents and increase in the electrostatic interaction between the metal ions and the adsorbent active sites [15, 16]. In contrast, decrease in the percentage removal was due to the availability of limited sites on the adsorbents at higher concentrations [17, 18]. Similar results were observed by El-Ashtoukly et al. [19] that used pomegranate peel for the adsorption of lead and copper.

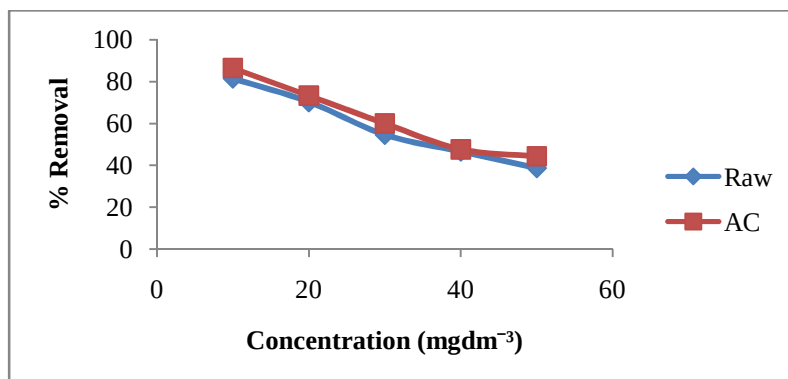


Figure 3. Effect of variation of initial concentration on the removal of copper ion by adsorption at 0.5g adsorbents weight, contact time 90min and pH 6.9

Dosage

The percentage of copper removal in Fig. 4 increased with increasing the weight of the adsorbents. The increase in the weight of adsorbents increased the rate of adsorption due to availability of more adsorption surface sites (overcrowding of particles). This may also be attributed to aggregation of adsorbent surface area available to ion and increase in diffusion path lengths [20]. This conforms to the findings of Asubiojo and Ajelabi, [21]; Khosravan and Lashkari [22].

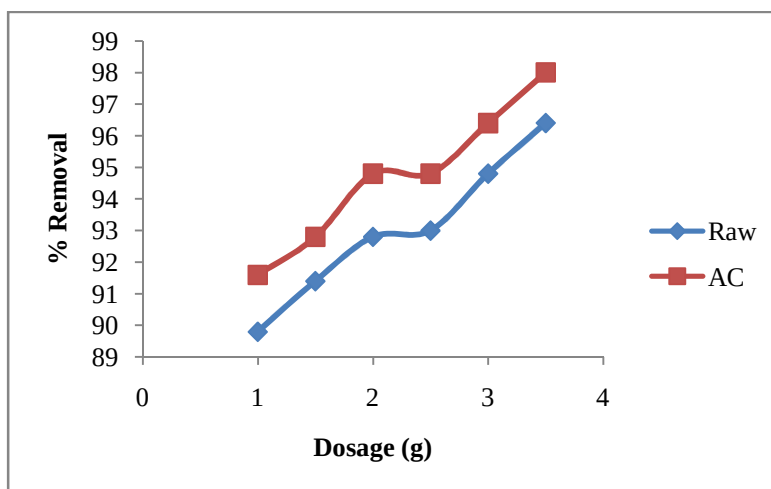


Figure 4. Effect of adsorbent dose on the removal of copper ion by adsorption at contact time 90min, 5mgdm^{-3} concentration and pH 6.9

Temperature

The effect of temperature on the adsorption of copper is illustrated by the results depicted in Figure 5. It is shown that the percentage removal of copper increased with an increase in temperature indicating better adsorption at higher temperatures. The increase in the amount of copper ions adsorbed with increase in temperature may be due to the rise in the kinetic energy of sorbent particles or creation of some new adsorption active sites on the surface of adsorbents [23]. Also the retarding specific or electrostatic interactions probably became weaker and the ions became smaller, because solvation is reduced [24, 25]. This indicates that the adsorption reaction was endothermic in nature. This was similar to the findings of Shen and Duvnjak [26], that found that the uptake of Cd(II) and Cu(II) using corncob particles as adsorbent increased at higher temperatures.

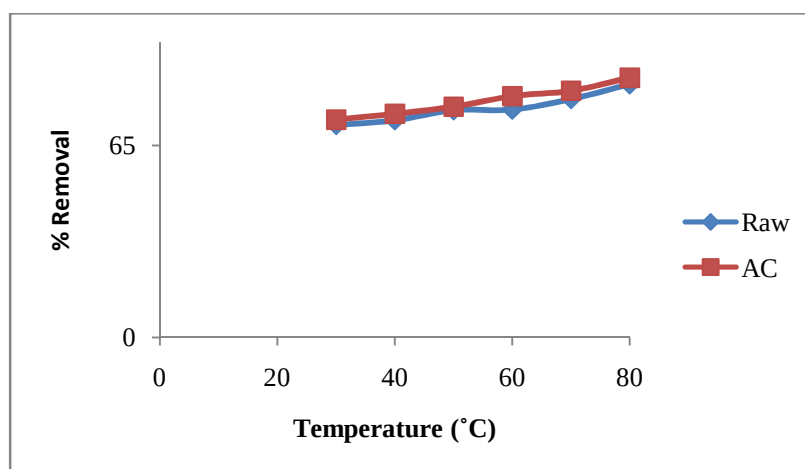


Figure 5. Effect of temperature on the removal of copper ion by adsorption at 5mgdm^{-3} concentration, contact time 90min and pH 6.9

Isothermal studies

The Freundlich isotherm values of K_F and n were calculated and given in Table 1. This shows the increase of negative charge on the surface that enhanced the electrostatic force like Van der Waal's between the surface of the adsorbents and the metal ions which increased the adsorption of copper ions which clearly showed dominance in adsorption capacity. The biosorption intensity n is indicative of the bond energies between the copper ions and the adsorbents which showed a possibility of physisorption and slight chemisorptions and the values of n indicated that the adsorption was favourable [27, 28]. The Freundlich isotherm provides no information on the monolayer adsorption capacity when compared to the Langmuir model.

Table 1. Isotherm model for the sorption of copper ions by spines of *Bombax buonopozense*

Isotherm	Parameter	Raw	AC
Freundlich	$K_F(\text{mgg}^{-1})$	0.557	0.659
	n	3.257	3.367
	R^2	0.957	0.973
Dubinin Radushkevich	$Q_m(\text{mgg}^{-1})$	0.265	2.77
	$K(\text{mol}^2\text{kJ}^{-2})$	7×10^{-8}	5×10^{-9}
	$E(\text{kJ/mol})$	2.672	3.163
	R^2	0.934	0.925
Langmuir	$Q_{\max}(\text{mgg}^{-1})$	1.709	1.876
	$K_L(\text{L/mg})$	0.303	0.318
	R^2	0.998	0.987

The E values of the raw and activated adsorbents were between 2.672 and 3.163 kJ/mol which indicated that the adsorption process might be due to the predominant nature of physisorption process [29]. The correlation coefficients R^2 results of Langmuir isotherm model fitted the results quite well suggesting that the surface of the sorbent is homogenous and at maximum adsorption $Q_{\max}$ only monolayer was formed on the free surface of the adsorbents [30, 31]. The maximum

sorption capacity determined from the experimental equilibrium isotherm showed that activated adsorbent (AC) had a better copper binding ability (1.876mgg^{-1}) than the raw adsorbent (1.709mgg^{-1}). Nevertheless, the maximum biosorption capacities obtained in this for both raw and activated (AC) are found to be lower compared to pristine peat (17.8mgg^{-1}) [32].

Figure 6. Freundlich isotherm plot for adsorption of copper ion onto raw and activated adsorbents

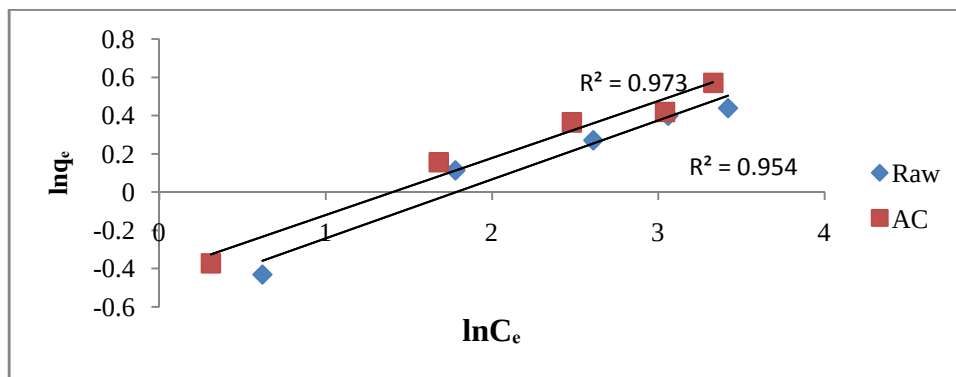


Figure 7. Dubinin-Radushkevich isotherms plot for adsorption of copper ion onto raw and activated adsorbents

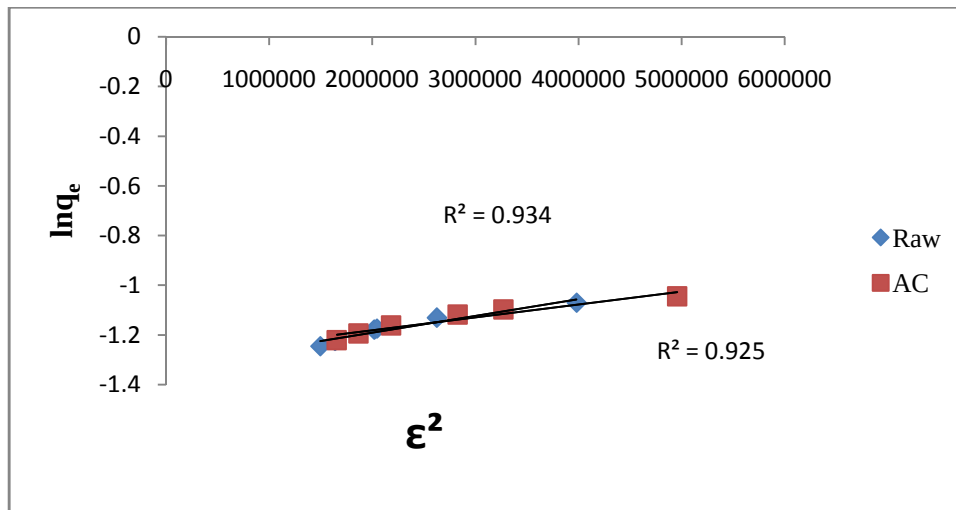
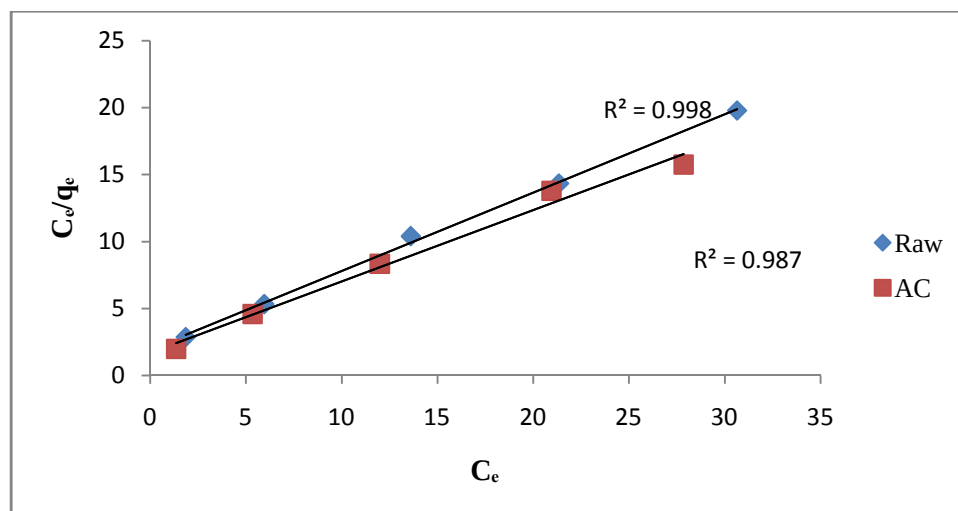


Figure 8. Langmuir isotherm plot for adsorption of copper ion onto raw and activated adsorbents



Biosorption Kinetics

The values of rate constants, correlation coefficients, adsorption capacity and initial sorption rate are given in Table 2. The plots of $\ln(q_e - q_t)$ against t for the pseudo-first-order for raw and activated adsorbents were not linear indicating that more than one mechanism are involved in adsorption process. This confirms that it is not appropriate to use the pseudo-first-order kinetic model to predict the adsorption kinetics for copper ion. The correlation coefficients values of the raw and activated adsorbents at various initial concentration of pseudo second order kinetic model were higher than that of pseudo first order kinetic model. This shows that kinetics of copper biosorption by *Bombax buonopozense* was better described by pseudo second order kinetic model which is similar to the findings of Puello *et al.* [33]; Priyantha *et al.* [34]. This was also in line with the findings of Murthy *et al.* [35] for the removal of Pb(II) from aqueous solution by *Cucumissativus* (Cucumber) Peel. Predicted initial copper sorption rate, h , for activated adsorbent (AC) was higher than the raw adsorbent. The higher initial rate by activated adsorbent may be evidence that carbonization increase the number of active surface sites that are more available for sorption of copper ion.

Table 2. Kinetics rate model for the sorption of copper ions by spines of *Bombax buonopozense*

Kinetic	Parameter	Raw	AC
First-order	$q_e(\text{mgg}^{-1})$	0.333	0.342
	$k_1(\text{min}^{-1})$	1×10^{-8}	5×10^{-5}
	R^2	0.048	0.052
Second-order	$q_e(\text{mgg}^{-1})$	0.033	0.031
	$k_2(\text{g/mg.min})$	3.432	5.14
	$h(\text{mg/gmin})$	3.737×10^{-3}	4.4×10^{-3}
	R^2	0.902	0.987

Figure 9. Pseudo-first-order plot for adsorption of copper ion onto raw and activated adsorbents

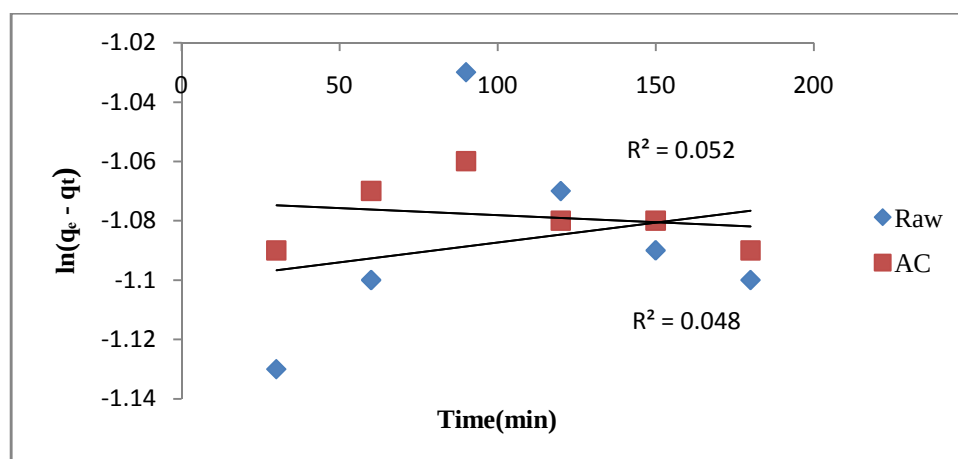
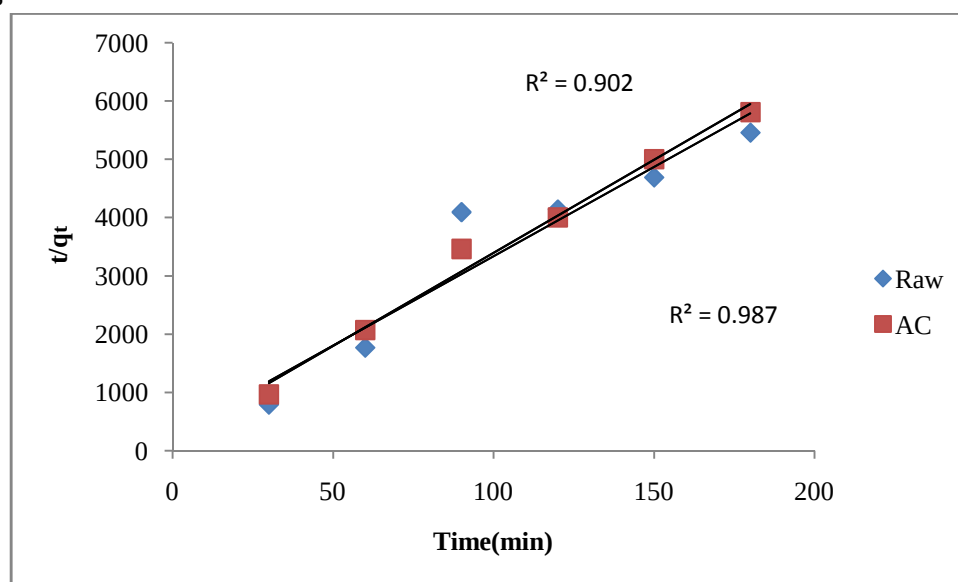


Figure 10. Pseudo-second-order plot for adsorption of copper ion onto raw and activated adsorbents



Thermodynamics Parameter

The thermodynamic parameters in Table 3, the values of enthalpy, ΔH° , and entropy, ΔS° , and Gibbs free energy, ΔG° , of the sorption are useful in defining whether the sorption reaction is endothermic or exothermic and spontaneity or non-spontaneity of the adsorption process. The positive value of enthalpy change, ΔH° , shows that the adsorption of copper ions was endothermic and the positive values of ΔG° at various temperatures indicated the non spontaneous nature of the adsorption process. The numerical values of ΔG° decreased with increased temperature indicating that the reaction became spontaneous and more favourable at higher temperature. The positive values of ΔS° indicated the strong affinity of raw and activated adsorbent materials toward the copper ions.

The sticking probability, S^* , is a function of the adsorbate and adsorbent system under consideration and is dependent of the temperature of the batch system. The activation energy E_a values were found to be 10.875kJ/mol and 13.177kJ/mol for the raw and activated adsorbents

respectively. The positive values of E_a indicated that higher solution temperatures favoured copper metal removal by adsorption and the adsorption process was endothermic in nature.

Table 3. Thermodynamic parameters for the sorption of copper ions by spines of *Bombax buonopozense*

	Raw					AC				
Temp (K)	ΔH° (kJ/mol)	ΔS° (Jmol ⁻¹ K ⁻¹)	E_a (kJ/mol)	ΔG° (kJ/mol)	R^2	ΔH° (kJ/mol)	ΔS° (Jmol ⁻¹ K ⁻¹)	E_a (kJ/mol)	ΔG° (kJ/mol)	R^2
303				4.144					4.428	
313				3.857					3.652	
323	13.036	29.346	10.875	3.557	0.932	27.952	77.636	13.177	2.876	0.717
333				3.242					2.099	
343				2.93					1.323	
353				2.619					0.547	

CONCLUSION

Batch sorption studies for the removal of copper from wastewater have been carried out using spines of *Bombax buonopozense* as low cost and locally available biosorbents. The adsorption process followed pseudo-second-order kinetics and obeyed Langmuir adsorption isotherm for the metal ion studied. The excellent applicability of Langmuir isotherm to the metal ion biosorption showed the occurrence of monolayer adsorption of active sites on the surface of biosorbents. The Laboratory test on copper removal from wastewater showed the potential applicability of this material in the industrial waste treatment. It is therefore necessary to synthesize *Bombax buonopozense* as low cost and effective adsorbent for the removal of potentially toxic metals from aqueous solutions.

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