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Original Research Article

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

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 fitted well to the Langmiur isotherm. 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 *Moriga 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.

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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 105^0C. The sample was ground using pestle and mortar and then sieved to obtain the 250μm fraction used in this experiment.

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 $CuS0_4.5H_2O$ 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) and the pH was measured with pH-Meter.

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

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

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

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 $40cm^3$ of waste solution with different 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:

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$$q = K_f(C)^{1/n}$$

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 $\ln q C_e$.

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:

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

Where Q_m is the theoretical maximum capacity (mgg^{-1}) and $\mathcal{E}$ is the Polanyi potential. The biosorption mean free energy E was calculated from the relation:

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

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:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{1}{q_m} C_e$$

Where q_e is the amount of metal adsorbed (mgg^{-1}), C_e is the equilibrium concentration of solution (mgdm^{-3}). q_m 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 (mgg^{-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:

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

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:

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

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_o 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.

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DISCUSSION OF RESULTS

Contact time

Fig. 1 shows the effect of residence time on the removal of copper metal. 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.

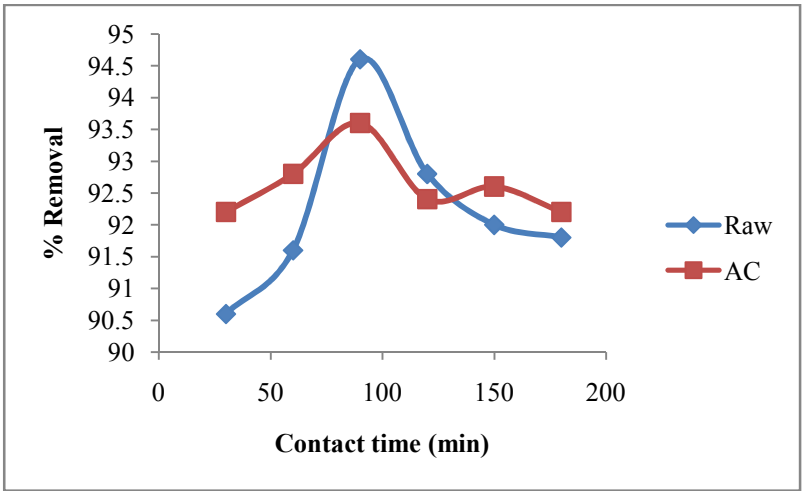

Figure 1. Effect of contact time on the removal of copper metal by adsorption at 5mgdm^{-3}, 0.5g adsorbents weight and temperature 28^{0}C $\pm$ 1

pH

Cu 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 completion for adsorption sites by hydroxonium ion (H_30^+). As the pH increased, 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].

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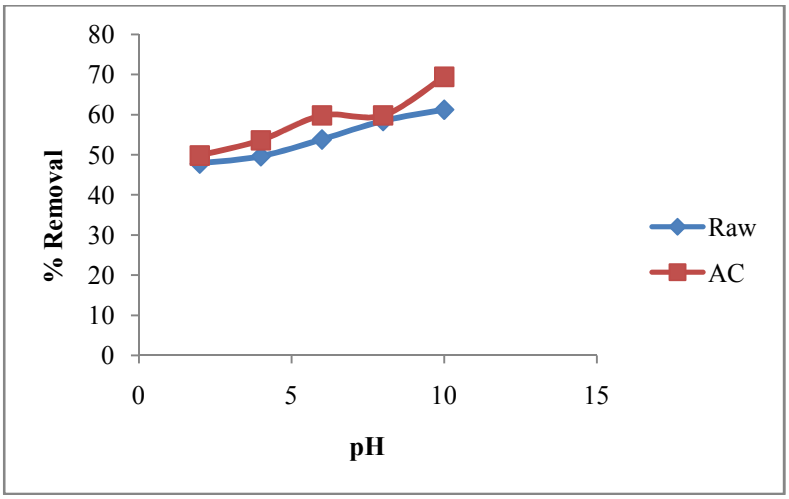

Figure 2. Effect of pH on the removal of copper metal by adsorption at 5mgdm^{-3} and 0.5g adsorbents weight

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 – 50mgdm^{-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 absorbent active sites, since adsorption kinetics depend on the surface area of the adsorbent [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.

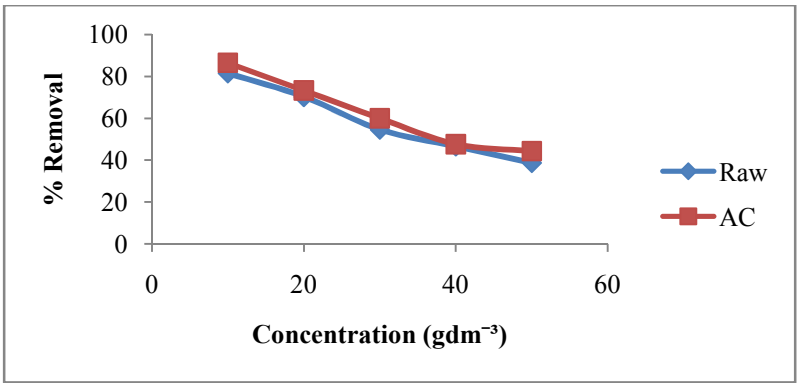

Figure 3. Effect of variation of initial concentration on the removal of copper metal by adsorption at 0.5g adsorbents weight

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

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lengths [20]. This conforms to the findings of Asubiojo and Ajelabi, [21]; Khosravan and Lashkari, [22].

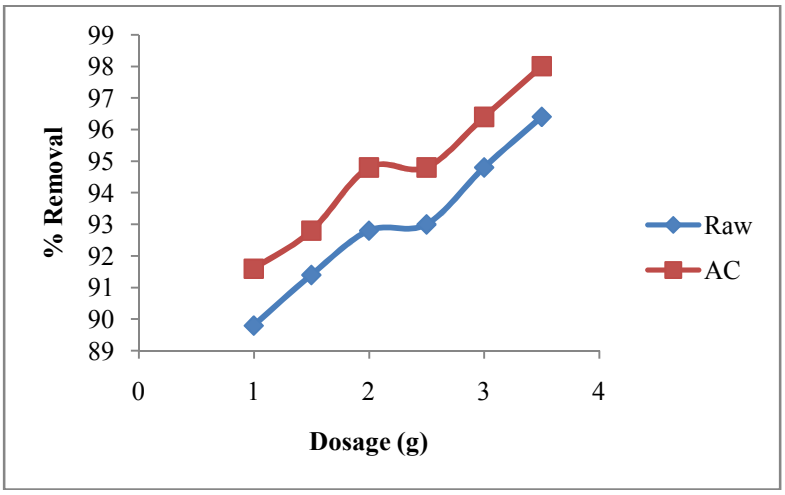

Figure 4. Effect of adsorbent dose on the removal of copper metal by adsorption at 5mgdm^{-3}

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 and Cu using corncob particles as adsorbent increased at higher temperatures.

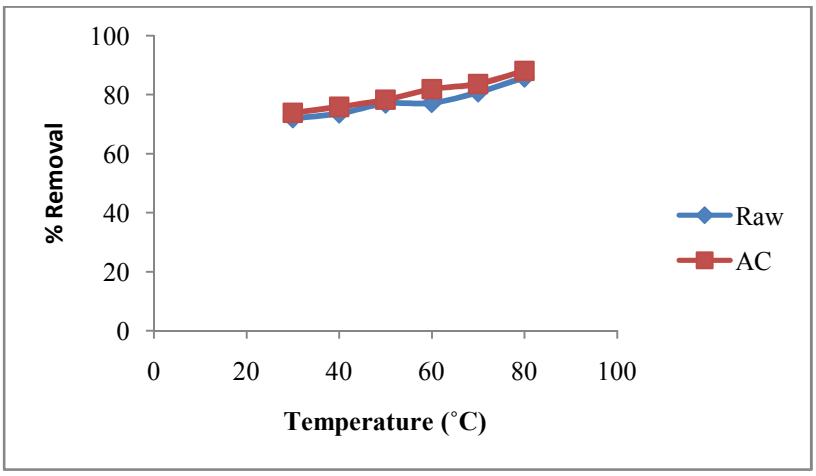

Figure 5. Effect of temperature on the removal of copper metal by adsorption at 5mgdm^{-3}

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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 physiosorption and slight chemisorptions and the values of n indicated that the adsorption was favourable [27] [28].

	K_F	n	R^2
Raw	0.557	3.257	0.954
AC	0.659	3.367	0.973

Table 1. Freundlich adsorption isotherm parameters

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.

	Q_m	K	E	R^2
Raw	0.265	7×10^{-8}	2.672	0.934
AC	2.77	5×10^{-8}	3.163	0.925

Table 2. Dubinin-Radushkevich isotherm parameters

The correlation coefficients R^2 results in Table 3 showed that 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 [29][30].

	Q_{max}	K_L	R^2
Raw	1.709	0.303	0.998
AC	1.876	0.318	0.987

Table 3. Langmuir adsorption isotherm parameters

Biosorption Kinetics

The values of rate constants, correlation coefficients, adsorption capacity and initial sorption rate are given in Table 4 and 5. 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 similar to the finding of [31] [32]. This was also in line with the findings of Oo *et al*. [33] for *Rhizophora apiculata* mangrove polyflavonoid tannins in the adsorption of copper(II) and lead(II).

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	R^2	K_1	q_e
Raw	0.048	1×10^{-8}	0.333
AC	0.052	5×10^{-8}	0.342

Table 4. Pseudo first-order kinetics rate constant for copper sorption

	R^2	K_2	q_e	h
Raw	0.902	3.432	0.033	3.737×10^{-3}
AC	0.987	5.14	0.031	4.4×10^{-3}

Table 5. Pseudo second-order kinetics rate constant for copper sorption

Thermodynamics parameter

The thermodynamic parameters in Table 6, 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 13.177kJ/mol and 10.875kJ/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.

	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	

Table 6. Thermodynamic parameters for the adsorption of copper

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

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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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