

Adsorption of Copper by Raw Pinecone

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Authors' contributions

This work was carried out in collaboration between all authors. Author AOA performed the experiment and wrote the first draft of the manuscript. Authors KOA and BIOO designed the study, supervised the work and gave useful advice. All authors read and approved the final manuscript.

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ABSTRACT

This work was carried out in order to study the possibility of using pinecones as inexpensive sorbent material for the removal of copper ions in solution. The experiment was carried out in the Department of Chemistry, University of Ibadan, Ibadan, Oyo State, Nigeria. Batch adsorption studies were conducted to determine the optimum conditions for adsorption of copper ions on pinecone. 20mL of the aqueous metal ion solution was agitated with 1g of the adsorbent and different parameters varied. Langmuir and Freundlich isotherm models were used to analyse the experimental data. Equilibrium data fitted well the Langmuir model ($R^2=0.988$). The monolayer adsorption capacity of Cu^{2+} was found to be 38.46mg/g. The Lagergren's pseudo first order and pseudo second order kinetic models were selected to study the adsorption process. Kinetic data was found to show very good fit with the pseudo second order kinetic model ($R^2 = 1$). This shows that

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the adsorption of copper can be described by the pseudo second order equation, showing that the adsorption process is chemisorption between the metal ions and pinecone. The thermodynamic parameters ΔG , ΔH and ΔS were calculated for predicting the nature of adsorption. The negative value of the calculated Gibbs free energy value obtained for the sorption of Cu^{2+} on raw pinecone shows the adsorption to be spontaneous and feasible. The results show that pinecone can be used as a low-cost and effective adsorbent for removal of heavy metal ions from aqueous solutions.

Keywords: Adsorption; heavy metals; pinecone; kinetics; thermodynamics.

1. INTRODUCTION

Industries such as the textile, mining, plating, automobile, manufacturing and metal processing industries release many toxic heavy metals into the environment [1]. The presence of these toxic metals has become a source of concern. Such heavy metals include Cr, Pb, Ni, Zn, Cd, Cu and Fe. Once released into the environment, these metals are recalcitrant. They bioaccumulate and cannot be degraded or destroyed posing several health problems for animals, plants and human beings.

Although copper is an essential trace elements for animals, plants and microorganisms, it is toxic to organisms even at low concentrations [2]. While its toxicity is not as potent as that of other heavy metals (Cd, Pb and Hg), excessive consumption can still be fatal to many organisms including humans [3].

Methods such as chemical precipitation, reverse osmosis, membrane filtration, solvent extraction, ion exchange and adsorption [4]; have been used for the recovery of heavy metals from industrial wastewater. However, they have drawbacks such as secondary pollution, handling and disposal problems, inefficiency, high operating and/or investment costs, technical constraints etc [5]. This has led to the investigation for cost effective and environmentally sound alternative techniques for treatment of wastewaters containing heavy metals [6,7,8,9,10,11].

Adsorption is one of the most preferred methods for the removal of heavy metals from industrial effluents due to its ease of operation and insensitivity to toxic substances [12,13]. However, the applications of activated carbon are restricted due to its high operational costs [14]. Therefore, there is need for an alternative technique, which is economical and efficient. Studies have concentrated on discovering natural, inexpensive and readily available adsorbents with good sorption properties as an alternative for the treatment of industrial wastewater [15-20].

Adsorption using low cost, readily available agricultural waste materials is a novel technology and has distinct advantages over conventional methods [21]. Its promising results have endeared it to the scientific community as an alternative to traditional methods of wastewater treatment [22]. This work aims at evaluating the possibility of using pinecones as an inexpensive sorbent material for the removal of Cu^{2+} from aqueous solution.

2. MATERIALS AND METHODS

2.1 Pinecone Preparation and Chemicals

The pinecones used as adsorbent were picked and ground to dust, washed with distilled water to remove surface impurities and dried at 105°C for 24 h. The adsorbent was used without further modification.

All chemicals were of analytical grade. 2000mg/L stock solutions of copper was prepared from $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. Atomic absorption spectrometer (AAS) was used to analyse the concentrations of lead and cadmium ions remaining in solution.

2.2 Adsorption Experiments

Batch experiments were conducted in 50mL polyethylene bottles using 20mL of Cu(II) solutions which has been diluted to 200mg/L using deionised water. The pH value of the solutions measured by pH meter was adjusted using 0.1M HCl or 0.1M NaOH and 1g of the adsorbent was added to the solution. The resulting mixture was stirred for a specified amount of time while keeping the pH constant. At the end of each experiment, a sample of the suspension was separated by filtration to remove pinecone particles. The filtrate was then analyzed for residual copper ions.

The effects of varying the pH (3–8), adsorbent mass (1g – 5g), contact time (24 hours) and temperature (299K and 323 K) were studied. All tests were conducted in duplicate and their mean values were used in analyzing the data.

The amount of Cu^{2+} adsorbed, q_e was evaluated using the equation: $q_e = [(C_0 - C_e)/W]V$. In this equation, q_e (mg/g) represents the rate of the adsorbed metal ion per unit mass of the adsorbent and V (L) and W (g) are the volume of the metal ion solution and the weight of the adsorbent respectively.

3. RESULTS AND DISCUSSION

3.1 Effect of pH

pH is the most important variable in the adsorption process. The pH of the solution was varied between 3 and 8 using 0.1M NaOH and 0.1M HCl at room temperature. There was an increase in amount adsorbed up to pH of 6 after which adsorption remained constant. This is shown in Fig. 1. An explanation for this can be because at a lower pH, the amount of H^+ ions present is high. These compete with the metal ions for active sites but as the pH increases, the amount of H^+ decreases and this leads to an increase in the number of sites available for the metal ions to adsorb on which increases the adsorption. Beyond the pH of 6, the surface of the adsorbent is saturated hence the constant adsorption capacity observed.

3.2 Effect of Sorbent Mass

The effect of varying adsorbent mass was studied for 1g, 2g, 3g, 4g and 5g of the pinecone. These were agitated with 20mL of 200mg/L of the metal solution. It was found that an increase in the mass of the adsorbent resulted in a decrease in the amount of Cu(II) ions

adsorbed (Fig. 2). A similar result was observed for the removal of Cd(II) by modified *Tamrix articulata* wastes [23].

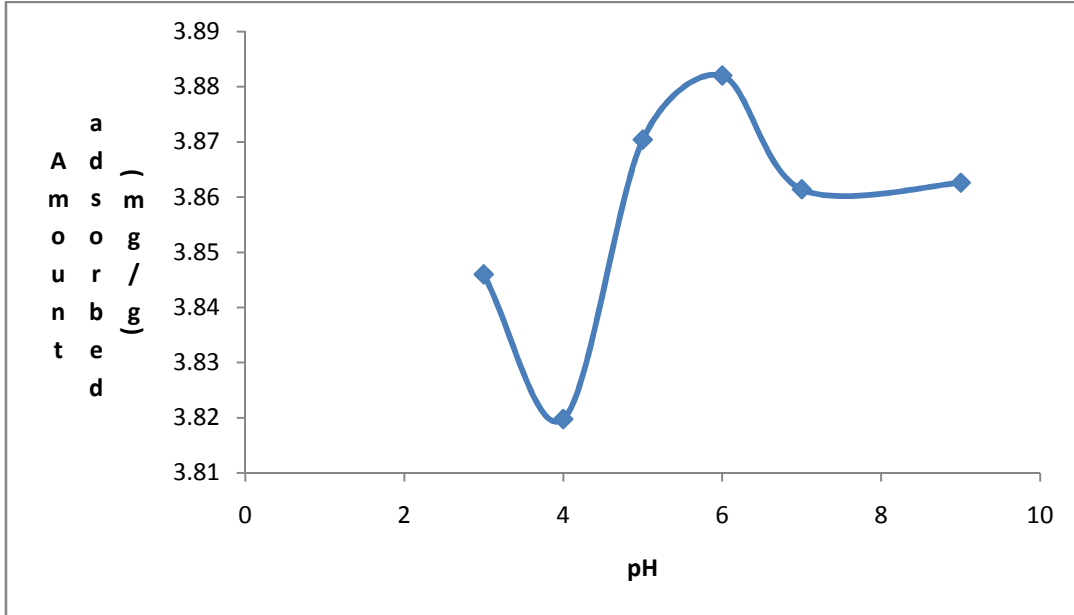


Fig. 1. Effect of pH on adsorption of Cu²⁺ ions by raw pinecone
 (Contact time = 24 hours, mass = 1-5g, initial metal concentration = 100mg/L-500mg/L, Temperature = 299K and 323K)

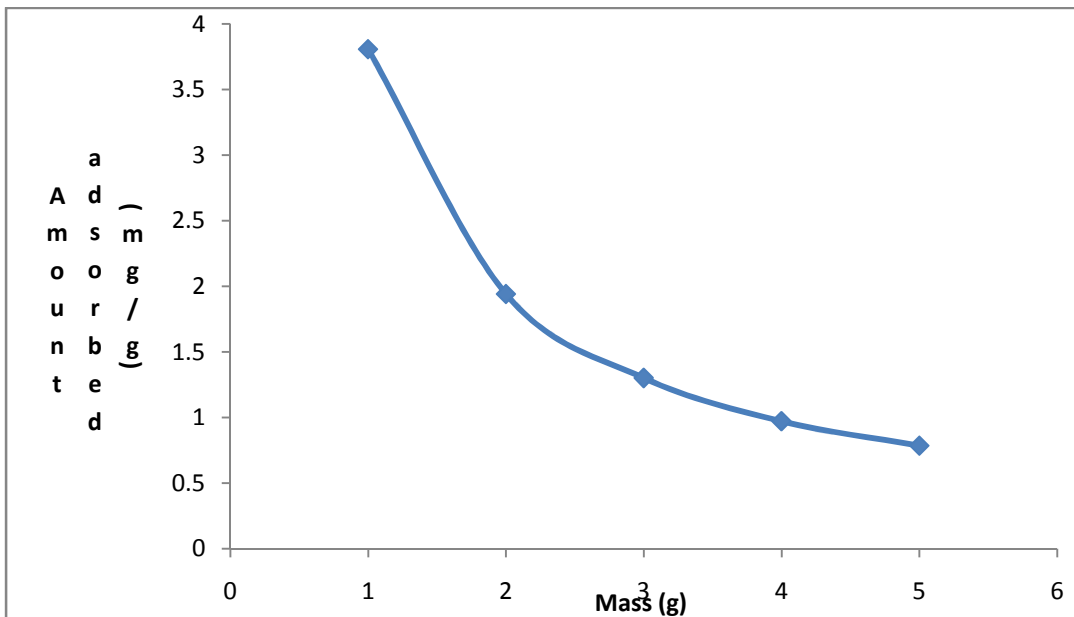


Fig. 2. Effect of adsorbent mass on adsorption of Cu²⁺ ions by raw pinecone
 (Contact time = 24 hours, pH = 3-8, initial metal concentration = 100mg/L-500mg/L, Temperature = 299K and 323K)

3.3 Effect of Contact Time

In order to study the effect of contact time, other parameters were held constant and the suspension agitated at different times of 60, 240, 720, 1080 and 1440 minutes. The adsorption of Cu^{2+} on the pinecone increased as the contact time was increased as shown in Fig. 3. The adsorption did not achieve sorption equilibrium after the period of 24 hours. However, within the time studied, the point of maximum adsorption was obtained at 24 hours. Increase in adsorption as contact time is increased means that the rate of adsorption on the surface of the adsorbent was high up to the maximum point obtained. Therefore, the rate of adsorption depends on the rate at which metal ions are adsorbed from the aqueous solution to the surface of the adsorbent. Subsequent studies will take into account the effect of further increase in contact time on the adsorption of copper ions on pinecones

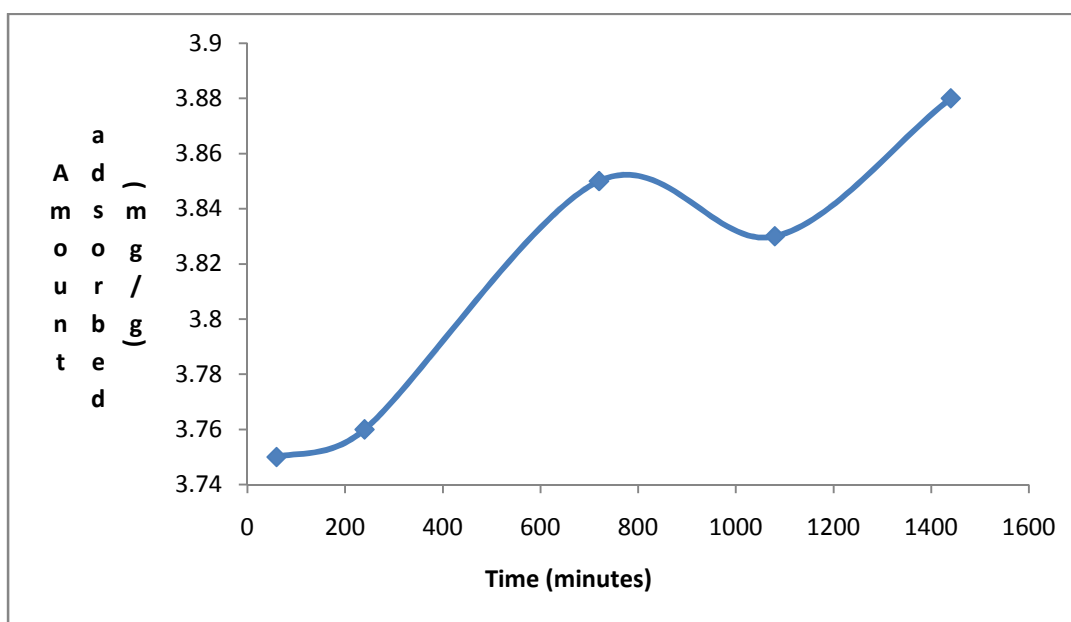


Fig. 3. Effect of contact time on adsorption of Cu^{2+} ions by raw pinecone
($\text{pH} = 3-8$, mass = 1-5g, initial metal concentration = 100mg/L-500mg/L, Temperature = 299K and 323K)

3.4 Effect of Initial Metal Ion Concentration

The effect of sorbate concentration was studied at room temperature by increasing the initial concentration of the metal ion (100mg/L–500mg/L). Adsorption increased as the initial concentration of the metal ion increased (Fig. 4). This may be due to an increase in the number of metal ions available to be adsorbed as well as the availability of active sites for the adsorption. The effect of further increase in initial concentration could be studied to determine the equilibrium concentration at which the adsorbent will adsorb copper ions.

3.5 Adsorption Isotherm

Two sorption isotherms, the Langmuir and Freundlich models were used to fit the experimental sorption data.

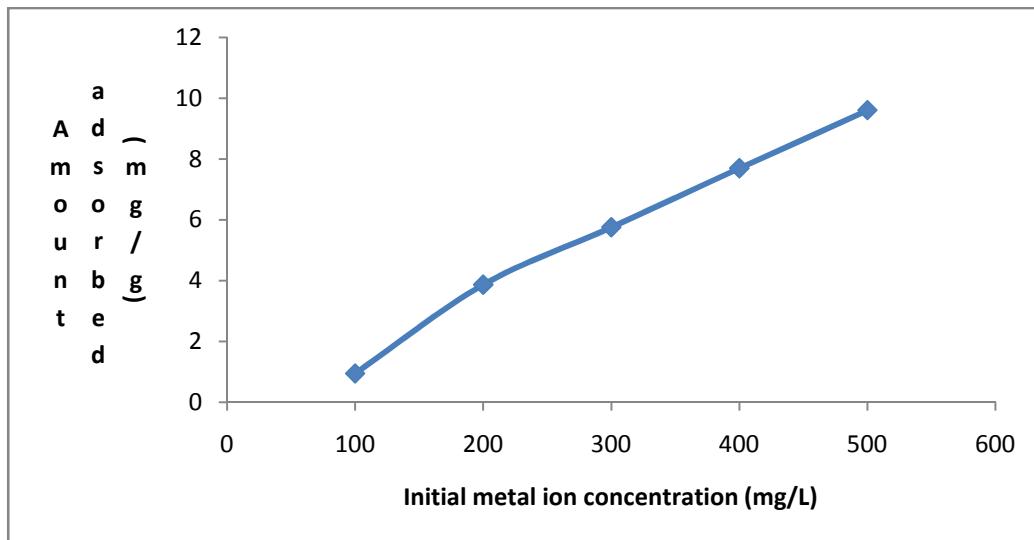


Fig. 4. Effect of initial metal ion concentration on adsorption of Cu^{2+} ions by raw pinecone

(Contact time = 24 hours, mass = 1-5g, initial metal concentration = 100mg/L-500mg/L, pH = 3-8)

Langmuir model is based on monolayer sorption and can be described by the following equation: $C_e/q_e = 1/Q_o b + (1/Q_o)C_e$. It assumes that the uptake of metal ions occur on a homogeneous surface by monolayer sorption without interaction between adsorbed ions. This means that there are uniform energies of adsorption on the surface. The Langmuir constant Q_o , obtained by plotting C_e/q_e against C_e is used to compare the performance of adsorbents. For a good adsorbent, a high Q_o is desirable. The Q_o for the pinecone is 38.46mg/g. Thus, the pinecone is a good adsorbent. Similar results were obtained for the adsorption of Cu(II) ions using low cost adsorbents [24,25]. Adsorption coefficient, b (L/mg) relates to the apparent energy of adsorption. The lower the value of b , the more favourable the adsorption will be. The b and R_L values (as shown in Table 1) of Cu^{2+} show that the adsorption is favourable.

The Freundlich model is based on multilayer sorption and is given by the following equation: $\log q_e = \log K_f + 1/n \log C_e$, where q_e is the equilibrium sorption (mg/g) amount of Cu^{2+} adsorbed on pinecones, C_e is the equilibrium concentration of the adsorbate in aqueous solution (mg/L), K_f is a constant determined by plotting C_e/q_e versus C_e . K_f and $1/n$ are constants related to the sorption of adsorbent and intensity of the sorption respectively. Freundlich isotherm is used to estimate the adsorption intensity of the adsorbent towards the adsorbate by assuming that the adsorption occurs on a heterogeneous surface by multilayer sorption and that the amount of adsorbate adsorbed increases infinitely with increasing concentration. According to Lee [26], n values between 1 and 10 represent favourable adsorption. From the study, the n value of Cu^{2+} on pinecone suggests that the adsorption is favourable at studied conditions.

The experimental sorption data was more suited to the Freundlich isotherm with R^2 value of 0.993. This shows that the Freundlich model was able to adequately describe the relationship between C_e and q_e for the copper. The calculated isotherm constants and correlation coefficients of Langmuir and Freundlich models are listed in the Table 1 below.

Table 1. Isotherm parameters for the adsorption of Cu²⁺ onto pinecone

Freundlich			Langmuir				
1/n	n	K _f	R ²	Q _o (mg/g)	b(g/L)	R ²	R _L
0.84	1.19	1.36	0.993	38.46	0.016	0.615	0.238

3.6 Adsorption Kinetics

The kinetic data was fitted with both the pseudo first order and pseudo-second-order kinetic model. The pseudo-first-order kinetic model is expressed by the following equation:

$$\log (q_e - q_t) = \log q_e - \frac{k_1 t}{2.303}$$

Where q_t (mg/g) is the amount adsorbed at time, t in minutes and k_1 (min^{-1}) is the rate constant of pseudo-first-order adsorption. The values of k_1 and q_e are determined by the plot of $\ln(q_e - q_t)$ versus t . The R^2 value (0.011) of the pseudo first order plot shows that the sorption data was a poor fit for this model. It can be observed that there is a large difference between the calculated equilibrium adsorption capacity and that obtained from the pseudo first order kinetic model.

The pseudo second order kinetic relationship between sorption quantity and time can be described with the following equation:

$$t/q_t = 1/K_2 q_e^2 + t/q_e$$

where q_t and q_e are sorption quantity at time t and equilibrium respectively, K is the rate constant, which can be calculated from the plot of t/q_t vs t . Table 2 lists the kinetic parameters for the removal of Cu²⁺ using pseudo-second-order model. A linear relationship with high correlation coefficient ($R^2 = 0.999$) was obtained, illustrating that the kinetic data were well fitted with the pseudo-second-order model. This indicates that the rate-limiting step is a chemisorption process between the metal ions and the pinecone.

Table 2. Kinetic and Thermodynamic parameters for the adsorption of Cu²⁺ onto pinecone

Pseudo first order model	Q _e	K ₁	R ²	
	0.014		0.011	
Pseudo second order	Q _e	K ₂	R ²	h _o
	3.88	0.07	0.999	1.052
Thermodynamic parameters	S	H	G(299K) (KJ/mol)	G(323K) (KJ/mol)
	214	-42.4	-106.4	-111.6

3.7 Thermodynamic Studies

To determine the thermodynamic parameters for the adsorption, experiments were conducted at two temperatures (299K and 323K). A plot of $\ln q_e/C_e$ versus $1/T$ gave intercept and slope from which the ΔG , ΔH and ΔS were calculated. The values of the thermodynamic parameters for the adsorption of Cu²⁺ on pinecone are given in Table 2. The negative value of the calculated Gibbs free energy value obtained for the sorption of Cu²⁺ on shows that the adsorption was spontaneous and feasible. A decrease in Gibbs value with

increase in temperature was observed for the adsorption and this showed that the adsorption was favourable at higher temperature. The positive value of entropy change for adsorption of Cu^{2+} shows an increase in the randomness at the adsorbent – adsorbate interface during adsorption. The adsorption of Cu^{2+} gave negative values for enthalpy change, which indicate that the adsorption was exothermic.

4. CONCLUSION

This work studied the possibility of using pinecone as an inexpensive sorbent material for the removal of Cu^{2+} as well as the effect of different experimental parameters through tests of sorption equilibrium in batch conditions. Information about its maximum adsorption capacities were analysed using the Langmuir and Freundlich isotherms. The results demonstrate that pinecone can be used as a novel and an effective adsorbent for the removal of Cu^{2+} from aqueous solutions.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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