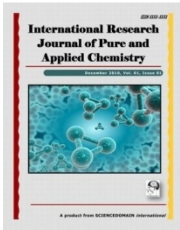

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Adsorption of Copper by Biochar

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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.

Original Research Article

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ABSTRACT

Aims: To study the possibility of using biochar as an inexpensive sorbent material for the removal of copper ions in aqueous solution.
Place of Study: Department of Chemistry, University of Ibadan, Ibadan, Oyo State, Nigeria.
Methodology and Results: Batch adsorption studies were conducted to determine the optimum conditions for adsorption. The biochar was prepared by pyrolysis of pinecones in a furnace at 573K. To create an inert environment, nitrogen gas was introduced into the furnace. The biochar produced was treated with 1M HCl to demineralise it and the slurry separated by vacuum filtration. The residue was washed several times with distilled water and oven dried at 378K. Langmuir and Freundlich isotherm models were used to analyse the experimental data. Equilibrium data fitted well the Langmuir model (R^2=0.961). The monolayer adsorption capacity of Cu^{2+} on the biochar was found to be 8.85mg/g. Kinetic data was found to show very good fit with the pseudo second order kinetic model. The thermodynamic parameters such as ΔG, ΔH and ΔS were calculated for predicting the nature of adsorption and this showed the adsorption to be exothermic.
Conclusion: The results show that pinecone biochar can be used as a low-cost and effective adsorbent for removal of heavy metal ions from aqueous solutions.

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Keywords: Adsorption; biochar; pinecone; heavy metals; copper ions; wastewater.

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].

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 [7]. However, the applications of activated carbon are restricted due to its high operational costs [8]. 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 [9-14].

Of these studies, sorption mechanism of Cu^{2+} and methods to improve its sorption capacity through pyrolysis in a low oxygen environment for the removal of heavy metals is unknown. This work aims at evaluating the possibility of the biochar as an inexpensive sorbent material for the removal of Cu^{2+} from aqueous solution.

2. MATERIALS AND METHODS

2.1 Biochar Preparation and Chemicals

Dried pinecones were obtained from the University of Ibadan, Nigeria and pyrolysed in a furnace at 573K. To create an inert environment, nitrogen gas was introduced into the furnace. The biochar produced was treated with 1M HCl to demineralise it and the slurry separated by vacuum filtration. The residue was washed several times with distilled water and oven dried at 378K.

All chemicals were of analytical grade. 2000mg/L stock solutions of copper was prepared from $CuSO_4.5H_20$. 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 pH (3–9), 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, qe (mg/g) represents the amount of metal ion adsorbed 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 one of the most important variables affecting adsorption. The pH of the solution was conditioned using 0.1M NaOH and 0.1M HCl to pH of 3, 4, 5, 6, 7, 8, 9 while keeping metal ion concentration constant at 200mg/L. There was a decrease in the adsorption capacity as pH was increased up to 6 as shown in Fig. 1. Thereafter, a sharp increase was observed between pH 6 and 7. The amount adsorbed decreased beyond this point (pH 7) as pH was further increased.

3.2 Effect of Adsorbent Mass

The effect of varying adsorbent mass was studied for 1g, 2g, 3g, 4g and 5g of the biochar. These were agitated with 20mL of 200mg/L of the metal solution. It was found that uptake in mg of copper ions for the different masses is almost the same. This is shown in Fig. 2. A similarity in the amount adsorbed shows that the effect of 1g of the adsorbent is almost the same for 4g of the adsorbent and that the variation in adsorbent dosage did not affect the adsorption.

3.3 Effect of Contact Time

The effect of contact time was studied at 60, 240, 720, 1080 and 1440 minutes for 200mg/L of the adsorbate. The sorption of copper ions by the biochar was very fast in the initial stage, reaching an equilibrium in 30 minutes and beginning to decrease gradually thereafter (Fig. 3). This indicates that the adsorption sites available on the biochar are either saturated beyond the equilibrium point or the remaining vacant binding sites present on the biochar are difficult to occupy due to repulsive force between the solute molecules of the solid and bulk phase [15]. The sorption of metal ions on the adsorbent surface depends on the availability of binding sites and the electrostatic interaction between them [16].

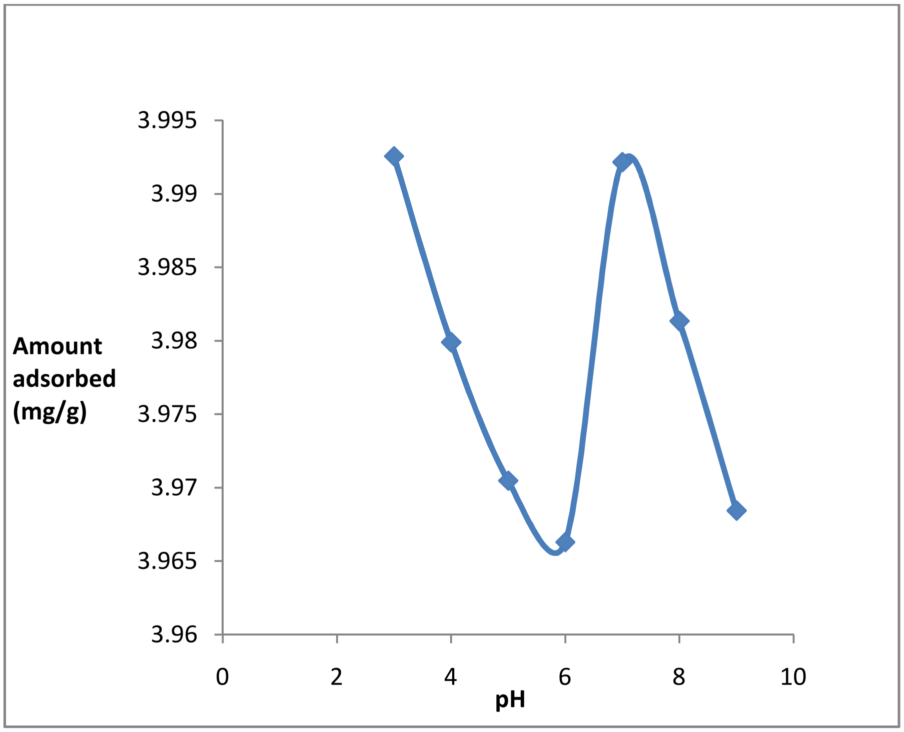

Fig. 1. Effect of pH on the adsorption capacity of Cu^{2+} by pinecone biochar
(Contact time = 24 hours, mass = 1-5g, initial metal concentration = 100mg/L-500mg/L, temperature = 299K)

3.4 Effect of Sorbate Concentration

The effect of sorbate concentration was studied at room temperature by increasing the initial concentration of the metal ion from 100mg/L to 500mg/L. Adsorption increased as the initial concentration of the metal ion increased. This is seen in Fig. 4. The increase 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 Temperature

The varying effect of temperature was observed at 299K and 323K over the initial concentration of 100mg/L – 500mg/L. A rise in adsorption with temperature means that there is an increase in kinetic energy of adsorbent, which suggests an endothermic reaction while a decrease in adsorption as temperature is increased suggests an exothermic reaction. However, an increase in the temperature did not affect the adsorption capacity of the pinecone biochar towards the copper ions (Fig. 5). This suggests that the collision frequency between the biochar and metal ions did not increase which resulted in the constant adsorption observed at the two temperatures. Also, an increase in temperature did not cause the bond rupture of functional groups on adsorbent surface which would have led to an increase in adsorption [17].

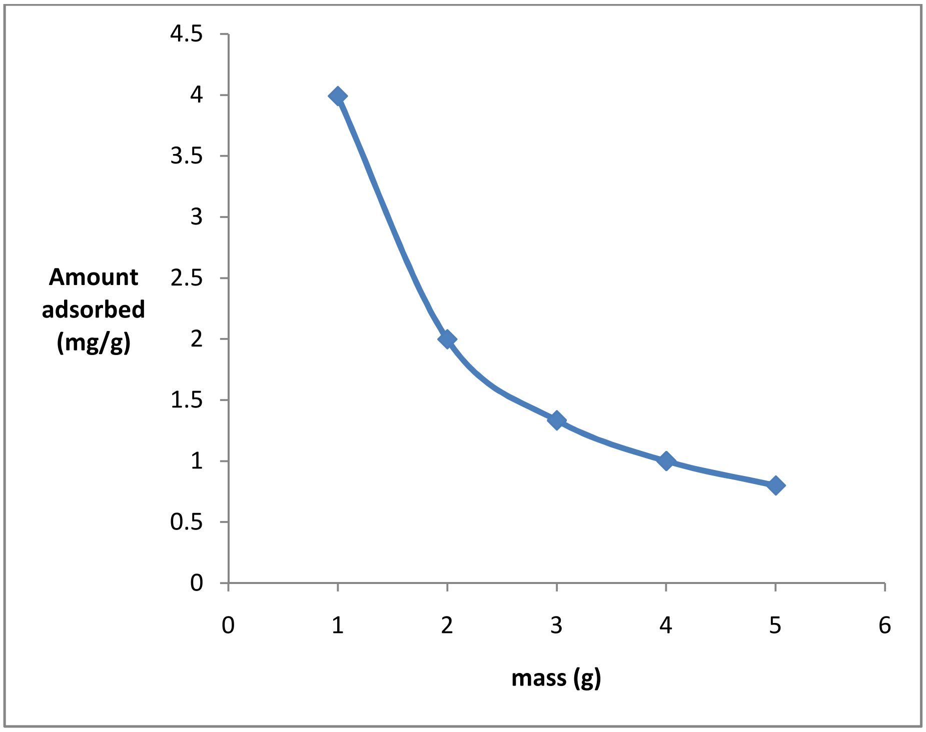

Fig. 2. Effect of adsorbent mass on the adsorption capacity of Cu^{2+} by pinecone biochar

(Contact time = 24 hours, pH = 3-9, initial metal concentration = 100mg/L-500mg/L, temperature = 299K)

3.6 Adsorption Isotherm

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

Langmuir model is based on monolayer sorption and can be described by the following equation: $Ce/q_e = 1/Q_o b + (1/Q_o)Ce$. 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 Ce/q_e against Ce is used to compare the performance of adsorbents. From the Langmuir plot, the equilibrium adsorption capacity was found to be 8.85 mg/g. This result is similar to the results obtained for other low cost adsorbents [18,19]. 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.

$R_{L,}$ equilibrium parameter expresses the essential characteristics of the Langmuir isotherm. It indicates the shape of the isotherm.

$$R_L = \frac{1}{1 + bC_o}$$

According to McKay et al (1982) [20], R_L = 0 shows irreversible adsorption, R_L = 1 shows linear adsorption, R_L>1 shows unfavourable adsorption, R_L<1 shows favourable adsorption. The R_L of Cu^{2+} as shown in Table 1 shows that the adsorption is favourable.

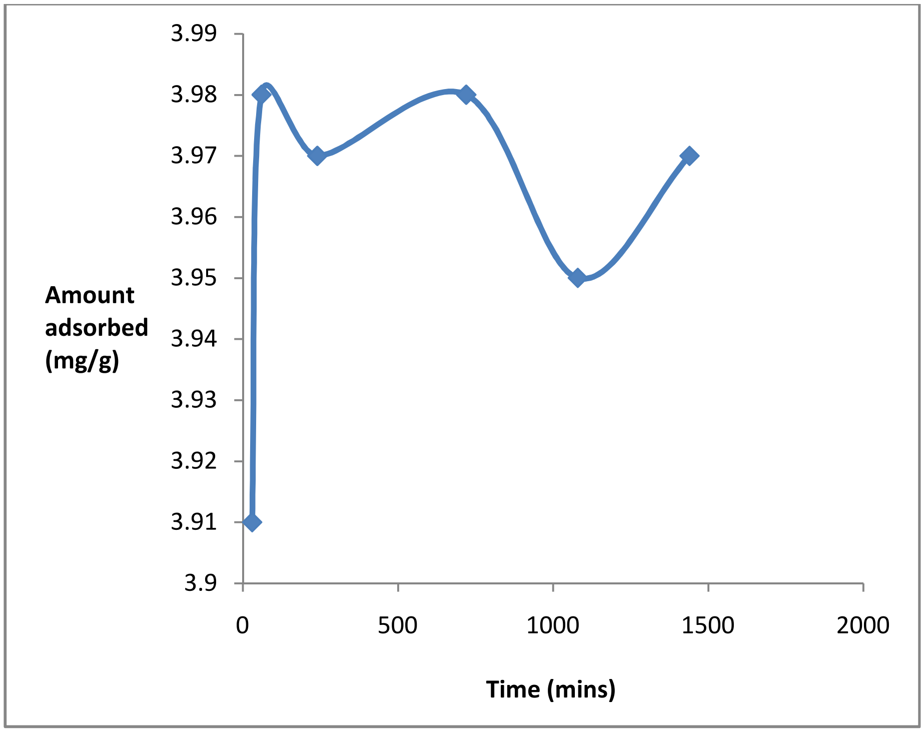

Fig. 3. Effect of contact time on the adsorption capacity of Cu^{2+} by pinecone biochar
(pH = 3-9, mass = 1-5g, initial metal concentration = 100mg/L-500mg/L, temperature = 299K)

Table 1. Isotherm parameters for the adsorption of Cu^{2+} onto pinecone biochar

Freundlich				Langmuir			
1/n	**N**	**K_f**	**R^2**	**Q_o(mg/g)**	**b(g/L)**	**R^2**	**R_L**
0.35	2.88	3.41	0.819	8.85	1.64	0.961	0.003

The Freundlich model is based on multilayer sorption and is given by the following equation: $\log q_e = \log K_f + 1/n \log Ce$, where q_e is the equilibrium sorption (mg/g) amount of Cu^{2+} adsorbed on the biochar, Ce is the equilibrium concentration of the adsorbate in aqueous solution (mg/L), K_f is a constant determined by plotting Ce/qe versus Ce. K_f and 1/n are constants related to the sorption of adsorbent and intensity of the sorption respectively. This 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 [21]. According to Lee [22], n values between 1 and 10 represent favourable adsorption.

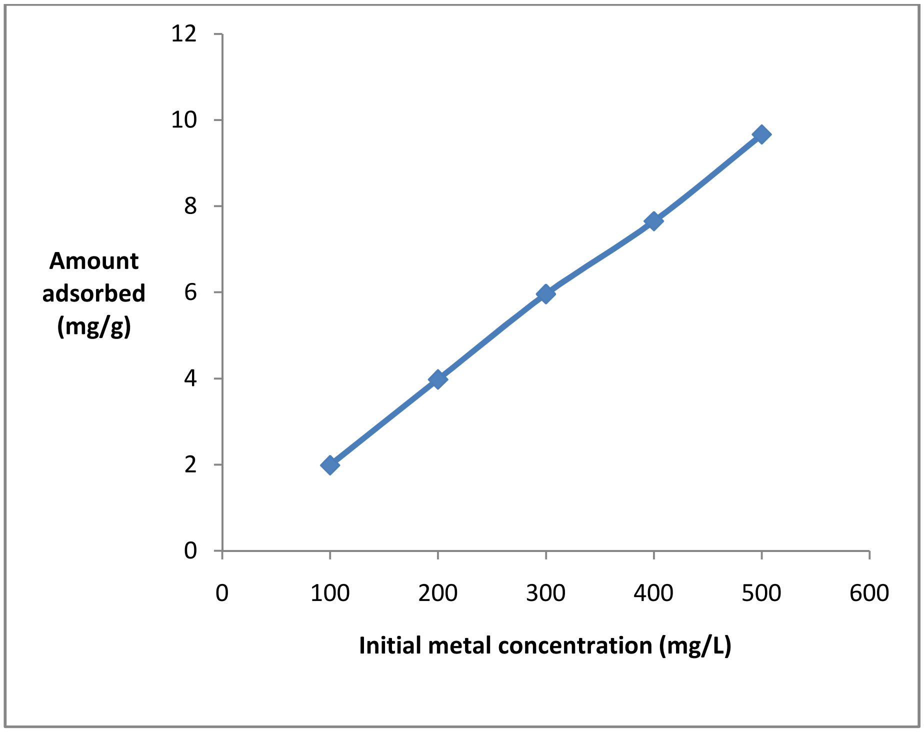

Fig. 4. Effect of initial metal concentration on the adsorption capacity of Cu^{2+} by pinecone biochar

(Contact time = 24 hours, mass = 1-5g, pH = 3-9, temperature = 299K)

From the study, the n value (2.88) of Cu^{2+} adsorption on the biochar suggests that the adsorption is favourable at studied conditions.

The experimental sorption data was more suited to the Langmuir isotherm (R^2 = 0.961), which shows the homogeneous nature of the adsorbent. The calculated isotherm constants and correlation coefficients of Langmuir and Freundlich models are listed in the Table below.

3.7 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 equation:

$$\log (qe - qt) = \log qe - \frac{k_1 t}{2.303}$$

where qt (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 qe are determined by the plot of ln(qe− qt) versus t. The R^2 value (0.143) 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.

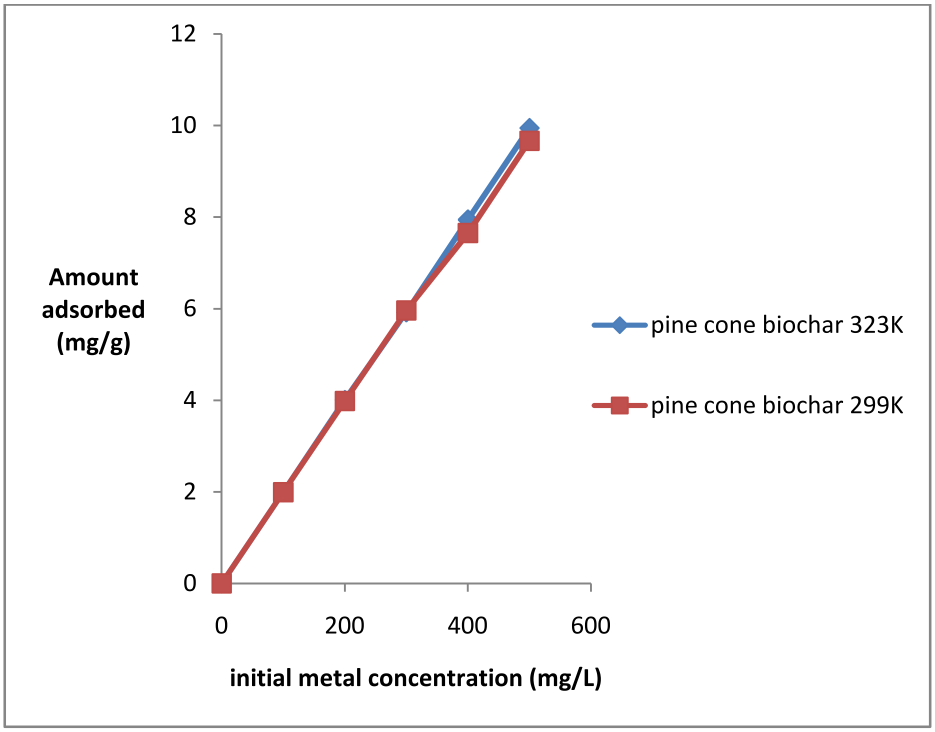

Fig. 5. Effect of temperature on the adsorption capacity of Cu^{2+} by pinecone biochar
(Contact time = 24 hours, mass = 1-5g, initial metal concentration = 100mg/L-500mg/L, pH = 3-9).

The pseudo second order kinetic relationship between sorption quantity and time can be described with the following equation: $t/qt = 1/k_2qe^2 + t/qt$; where qt and qe are sorption quantity at time t and equilibrium respectively, k_2 is the rate constant, which can be calculated from the plot of t/qt vs. t.

Table 2 lists the kinetic parameters for the removal of Cu^{2+} by pinecones using pseudo-second-order model. A linear relationship with high correlation coefficient (R^2 =1) was obtained with the pseudo second order kinetic model illustrating that the kinetic data fitted well with the pseudo-second-order model. This indicates that the rate-limiting step is a chemisorption process between the metal ions and the biochar.

3.8 Thermodynamics Studies

To determine the thermodynamic parameters, experiments were carried out at two temperatures, 299K and 323K. A plot of ln qe/Ce versus 1/T gave intercept and slope from which the ΔG, ΔH and ΔS were calculated. As shown in Table 2, the positive value of the calculated Gibbs free energy value obtained for the sorption of Cu^{2+} on pinecone biochar shows that the adsorption was not spontaneous. The increase in ΔG values with increase in temperature for the adsorption of Cu^{2+} on pinecone biochar shows that the adsorption is not favourable at high temperatures.

Table 2. Kinetic and Thermodynamic parameters for the adsorption of Cu^{2+} onto pinecone biochar

Pseudo first order	**qe (mg/g)**	**K_1**	**R^2**	
	0.019		**0.143**	
Pseudo second order	qe (mg/g)	K_2	R^2	h_o
	3.97	3.34	1	52.64
Thermodynamic parameters	ΔS	ΔH	ΔG(299K) (KJ/mol)	ΔG (323K)(KJ/mol)
	-134.7	61.52	101.8	105.1

The negative value of entropy change for adsorption of Cu^{2+} shows the affinity of the adsorbents for the metals and shows a decrease in the randomness at the adsorbent – adsorbate interface during adsorption. The adsorption of Cu^{2+} gave positive values for enthalpy change, which indicate that the adsorption was endothermic.

4. CONCLUSION

This work studied the sorption potential of pinecone, the possibility of using the biochar 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.

REFERENCES

1. Al-Saadi AA, Saleh AT, Gupta KV. Spectroscopic and computational evaluation of cadmium adsorption using activated carbon produced from rubber tires. Journal of Molecular Liquids. 2013;(188):136–142.
2. Sharma P, Kumari P, Srivastava M, Srivastava S. Removal of cadmium from aqueous system by shelled *Moringa oleifera* Lam. seed powder. Bioresource Technology. 2006;(97):299–305.
3. Spitalny KC, Brondum J, Vogt RL, Sargent HE, Kappel S. Drinking water induced copper intoxication in a Vermont family. Pediatrics. 1984(74):1103–1106.
4. Basso MC, Cerrella EG, Cukierman AL. Activated carbons developed from a rapidly renewable biosource for removal of cadmium (II) and nickel (II) Ions from dilute aqueous solutions. Industrial Engineering Chemical Resources. 2002;(41):180–189.
5. Kurniawan TA, Chan GYS, Lo WH, Babel S. Physicochemical treatment techniques for wastewater laden with heavy metals. Chemical Engineering Journal. 2006;118:83–98.
6. Kumar KY, Muralidhara HB, Nayaka YA, Balasubramanyam J, Hanumanthappa H. Low-cost synthesis of metal oxide nanoparticles and their application in adsorption of commercial dye and heavy metal ion in aqueous solution. Powder Technology. 2013;(246):125–136.
7. Dupont L, Guillon E. Removal of hexavalent chromium with a lignocellulosic substrate extracted from wheat. Environmental Science Technology. 2003;(37):4235–4241.

8. Bhatnagar A, Sillanpaa M. Utilization of agro-industrial and municipal waste materials as potential adsorbents for water treatment e a review. Chemical Engineering Journal. 2010;(157):277- 296.
9. Deng J, Zhang X, Zeng G, Gong J, Niu Q, Liang J. Simultaneous removal of Cd(II) and ionic dyes from aqueous solution using magnetic graphene oxide nanocomposite as an adsorbent. Chemical Engineering Journal. 2013;226:189–200.
10. Seyedi SM, Anvaripour B, Motavassel, Jadidi N. Comparative cadmium adsorption from water by Nanochitosan and Chitosan. International Journal of Engineering and Innovative Technology. 2013;2(9):145 -148.
11. Silva SM, Sampaio KA, Ceriani R, Verhé R, Stevens C, Wim De Greyt, Meirelles AJA. Adsorption of carotenes and phosphorus from palm oil onto acid activated bleaching earth: Equilibrium, kinetics and thermodynamics. Journal of Food Engineering. 2013;118:341–349. Available: http://dx.doi.org/10.1016/j.jfoodeng.2013.04.026.
12. Yang G, Jiang H. Amino modification of biochar for enhanced adsorption of copper ions from synthetic wastewater. Water Research. 2014;48:396-405.
13. Das B, Mondal KN, Roy P, Chattaraj S. Equilibrium, kinetic and thermodynamic study on chromium(VI) removal from aqueous solution using Pistia Stratiotes biomass. Chemical Science Transactions. 2013;2(1):85-104. DOI: 10.7598/cst2013.318.
14. Abbasi Z, Alikarami M, Nezhad ER, Moradi F, Moradi V. Adsorptive Removal of Co^{2+} and Ni^{2+} by peels of banana from aqueous solution. Universal Journal of Chemistry. 2013;1:90-95. DOI: 10.13189/ujc.2013.010303.
15. Saumya PS, Deepa B, Abraham E, Girija N, Geetha P, Jacob L, Koshy M. Biosorption of Cd(II) from aqueous solution using xanthated nano banana cellulose: Equilibrium and kinetic studies. Ecotoxicology and Environmental Safety. 2013;(98):352–360.
16. Anirudhan TS, Fernandez NB, Mullassery MD. Removal of Cd(II) ions from aqueous solution using a cation exchanger derived from banana stem. Journal of Chemical Technology and Biotechnology. 2012;(87):714–722.
17. Tewari N, Vasudevan P, Guha BK. Study on biosorption of Cr(VI) by Mucor hiemalis. Journal of Biochemical Engineering. 2005;68:185–192.
18. Issabayeva G, Aroua MK. Removal of copper and zinc ions onto biomodified palm shell activated carbon. World Academy of Science, Engineering and Technology. 2011;76.
19. Erdem E, Karapinar N, Donat R. The removal of heavy metal cations by natural zeolites. J Colloid and Interface Science. 2004;280:309–314.
20. McKay G, Blair HS, Gardener JR. Kinetics and diffusion processes in colour removal from effluent using wood as an adsorbent. Journal of Applied Polymer Sciences. 1982;27(8):3043–3057.
21. Jain M, Garg VK, Kadirvelu K. Chromium (VI) removal from aqueous system using Helianthus annuus (sunflower) stem waste. Journal of Hazardous Materials. 2009;(162):365–372.
22. Lee SM, Davis AP. Removal of Cu(II) and Cd(II) from aqueous solution by seafood processing waste *Aspergillus niger* biomass, mineral metallurgical process. Journal of Chemical Society. 2000;13(2):52-57.

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