



ORIGINAL RESEARCH PAPER

Chemistry

REMOVAL KINETICS AND THERMODYNAMICS OF COPPER ION BY ACTIVATED BORASSUS FLABELLIFER BARK NANO CARBON

KEY WORDS: Copper, Activated Borassus *flabellifer* bark nano carbon, Isotherms and kinetics models, Thermodynamics, etc.

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ABSTRACT	In the present study, adsorption of copper (II) ions from aqueous solution by activated Borassus <i>flabellifer</i> bark nano carbon (ABNC) was investigated under batch mode. The influence of solution pH, sorbent dose, copper concentration, contact time and temperature was studied. The copper adsorption was favored with maximum adsorption at pH 6.6. Sorption equilibrium time was observed in 60 min. The equilibrium adsorption data were correlated with Langmuir, Freundlich, Temkin, Dubinin-Radushkevich, Hurkins-Jura, Halsay, Radlich-Peterson, Jovanovic and BET isotherm models. The kinetics of the adsorption process was tested by pseudo-first-order, pseudo-second order, Elovich and Intra-particle diffusion models. It was shown that adsorption of copper could be described by the pseudo-second order kinetic model. Thermodynamic parameters such as Gibbs free energy change (ΔG°), the enthalpy change (ΔH°) and the entropy change of sorption (ΔS°) have also been evaluated and it has been found that the adsorption process was spontaneous, feasible and endothermic in nature. The results indicated that ABNC can be used as an effective and low-cost adsorbent to remove copper (II) from aqueous solution.
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1. Introduction

In view of rapid industrialization, the people all over the world are migrating to cities in search of jobs. This resulted into rapid increase in industrial activities which are important sources of environmental pollution. Industrial effluents contain high content of several heavy metal ions. Heavy metals are widely distributed in the environment and are ecologically important due to their high toxicity for living organisms including human beings¹. Unlike organic pollutants, the majority of which are susceptible to biological degradation, heavy metals will not degrade into harmless end products. Thus, treatment of aqueous wastes containing soluble heavy metals requires concentration of the metals into a smaller volume followed by a secure disposal². In particular, Cu²⁺ is a common metal ion found in effluents of a large number of industries. This metal is an essential element for life and is a micronutrient in trace amounts. However, a chronic exposure to Cu²⁺ is detrimental for human health³. To curtail heavy metal pollution problems, many processes have been developed that include chemical precipitation, electrode deposition, solvent extraction, ion exchange, activated carbon adsorption^{4, 5} and biological methods⁶. The main limitations of these techniques are their low efficiency in metal ion removal at trace levels or the high cost. Hence adsorption is reported to be the most effective method for this purpose, which works at low concentration⁷.

In the present investigation the adsorption of copper ion on activated nano carbon prepared from Borassus *flabellifer* bark by carbonization with sulphuric acid has been achieved. The kinetic and equilibrium adsorption data obtained were utilized to characterize the sample prepared⁸. The amounts and rates of adsorption of copper using above activated nano carbon from water were then measured. Three simplified kinetic models including pseudo first order, Pseudo second order equations and Elovich equations were used to describe the adsorption process.

2. Materials and Methods

2.1 Chemicals

All reagents used in the experiments were of analytical (AR) grade and were obtained from Scientific Equipment Company, Trichy. Stock solutions of the test reagents were prepared by dissolving the copper ions in distilled water. 1000 mg/L of stock solution of

copper was prepared by dissolving accurately weighed 3.9296 grams of copper sulphate (CuSO₄, 5H₂O) in 1000 ml of distilled water. All experimental solutions were prepared by diluting the stock solution to the required concentration. The pH of each experimental solution was adjusted to the required initial pH value using dilute HCl (or) NaOH before mixing the adsorbent. The concentration of residual copper (II) was determined with atomic absorption spectrophotometer (Perkin Elmer 2380).

2.2 Preparation of adsorbent

The natural plant material Borassus *flabellifer* bark used in the present investigations was collected from Muthupet nearby Thiruvarur district the bark wastes were washed with distilled water several times to remove the dirt and dust and was subsequently dried in a hot air oven at 110°C. Afterthat, carbonization of the Borassus *flabellifer* bark was carried out by w/v ratio of concentrated sulphuric acid for 24 hours; the primary carbon was activated at 1100°C for 6 hours under optimized conditions to obtain activated nano carbon. The activated nano carbon was thereafter transferred to room temperature in an inert atmosphere of nitrogen and washed with hot distilled water and 0.5 N hydrochloric acid until the pH of the material reached 7.0. The activated nano carbon was also dried in a hot air oven at 110°C, ground and sieved to obtain the desired particular size (45nm) and stored in desiccators for further use.

2.3 Batch Adsorption studies

Preliminary batch adsorption studies were conducted to determine the equilibrium time. Batch studies were performed by mixing 0.025g of ANBC ion with the solution of 10 - 50 mg/L of initial concentrations of copper ion each in 250 ml stoppered conical flask. The dose of adsorbent was decided experimentally. All the adsorption experiments were conducted at 30°C to 60°C at an agitation speed of 150 rpm on the thermostat sharing water bath. The progress of adsorption was noted and equilibrium was achieved in 45 min. After equilibrium, the adsorbent was separated by centrifugation at 1000 rpm for 10 min using a centrifuge (Remi 24, India). The residual concentration of copper ions in the supernatant was determined by a UV-Visible spectrophotometer at 618 nm. The percentage removal of copper ions at equilibrium and the amount of copper ions transferred

onto the surface of the adsorbent, q_e (mg/g) was calculated using the following relationships.

$$\text{Percentage removal} = 100 (C_o - C_e) / C_o \dots\dots\dots(1)$$

Amount of adsorbed copper ions per g of solid

$$Q_e = (C_o - C_e) v/w \dots\dots\dots(2)$$

Where, C_o (mg/L) is the initial concentration of copper ions, C_e (mg/L) is the equilibrium concentration of copper ions, V is the volume of the solution (L), and w (g) is the mass of the adsorbent.

3. Results and discussion

3.1 Characterization of Adsorbent

Effect of operating variables on the adsorption of heavy copper ions onto activated Borassus *flabellifer* bark nano carbon adsorbent material (ABNC) were studied. The adsorption capacity of ABNC is increased with the increased amount of ABNC

Analysis	Value
pH _{lurry}	7.0
pH _{ZPC}	6.6
Moisture content, %	0.125
Particle density, g cm ⁻³	0.223
Conductivity, μS/cm	21.66
Surface area, m ² /g	18.22

Table 1-Characteristics of the Adsorbent

3.2 Effect of contact time and initial concentration:

Figure-1 illustrates the effects of contact time on the removal of copper ions. The changes in contact time exhibit approximately the same effects on the metal. Because of the utilization of the readily available active adsorption sites on the as surface, the adsorption of copper ions was rapid for the first 45 min for all the investigated initial copper ions concentrations 10-50 mg/L. There after it continued at a slower rate and finally reached equilibrium as a result of saturation. Sufficient contact time was determined as 45 min. Experiments were conducted by varying the initial concentration of copper ion. The obtained equilibrium results are shown in in table.1. Whenever the initial concentration of copper ion increases the adsorption decreases due to the minimization of adsorption sites for occupation of copper ions.

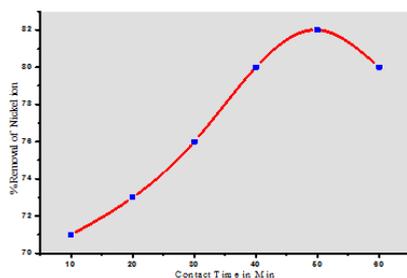


Fig.1-Effect of contact time on the adsorption of Cu(II) onto ABNC

M0	C _e (Mg / L)				Q _e (Mg / L)				Removal %			
	30° C	40° C	50° C	60° C	30° C	40° C	50° C	60° C	30° C	40° C	50° C	60° C
10	3.5	2.1	1.4	1.3	12.	15.	17.	17.	64.	78.	85.	86.
	335	201	151	429	933	760	170	314	665	799	849	571
20	7.7	7.0	6.3	4.9	24.	25.	27.	30.	61.	64.	68.	75.
	737	703	900	486	453	859	220	103	132	649	050	257
30	17.	15.	13.	12.	25.	29.	33.	35.	43.	48.	55.	58.
	019	409	427	441	962	182	145	118	270	637	242	530
40	24.	22.	21.	20.	30.	34.	36.	39.	38.	43.	46.	49.
	794	674	508	175	412	652	984	651	015	315	230	564
50	36.	35.	34.	32.	26.	29.	30.	34.	26.	29.	30.	34.
	748	474	691	631	503	053	618	739	503	053	618	739

Table: 2. Equilibrium parameters for the adsorption of Cu(II) onto ABNC

3.3 Effect of adsorbent concentration:

ABNC with different concentrations were combined with a fixed 50ml, 20 mg/L of copper ion and the effect of adsorbent concentration was investigated. The adsorption of heavy copper ions was increased with the increase of adsorbent dose and reached to a plateau at the appropriate dose of 125 mg of ABNC. The results were shown in the fig. 2. This was due to increased surface area along with pores for occupation of copper ions.

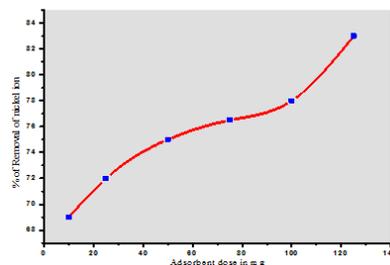


Fig.2-Effect of adsorbent dose on the adsorption of Cu(II) onto ABNC

3.4 Effect of pH on adsorption:

The pH value of the solution was important controlling parameter in the adsorption process. The removal of copper ions increases significantly with increasing pH from 1 to 6.6. The removal efficiencies of copper ions were low at pH above 7. The obvious decrease in removal might be attributed to the attractive forces between the negative surface charge of adsorbent by hydroxyl ions and the positive copper ions. The results are predicted in the fig 3.

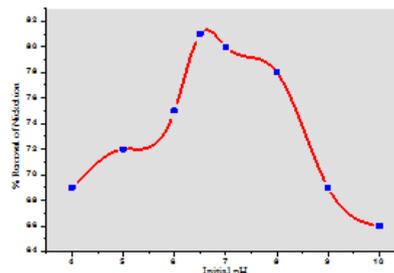


Fig.3-Effect of initial pH on the adsorption of Cu(II) onto ABNC

3.5. Adsorption Isotherms

Adsorption isotherm⁴⁻⁸ describes the relation between the amount or concentration of adsorbate that accumulates on the adsorbent and the equilibrium concentration of the dissolved adsorbate. Equilibrium studies were carried out by agitating a series of beakers containing 50 mL of Cu(II) solutions of initial concentration 10-50 mg/L with 0.025 g of activated nano carbon at 300C with a constant agitation speed. Agitation was provided for 1.0 hour, which is more than a sufficient time to reach equilibrium.

3.5.1 Freundlich adsorption isotherm

The Freundlich adsorption isotherm is based on the equilibrium sorption on heterogeneous surfaces. This isotherm is derived from the assumption that the adsorption sites are distributed exponentially with respect to heat of adsorption. The adsorption isotherm is expressed by the following equation

$$q_e = K_F C_e^{1/nF} \dots\dots\dots(3)$$

$$\ln q_e = \ln K_F + \frac{1}{nF} \ln C_e \dots\dots\dots(4)$$

Where, q_e is the amount of Cu(II) adsorbed at equilibrium (mg/g) and C_e is the concentration of Cu(II) in the aqueous phase at equilibrium (ppm). K_F (L/g) and $1/nF$ are the Freundlich constants related to adsorption capacity and sorption intensity, respectively.

Model	Constant	Temperature (°C)			
		30	40	50	60
Freundlich	K_f (mg/g) (L/mg) ^{1/n_f}	10.471	14.369	17.198	18.057
	n	3.2716	4.0809	4.6472	4.2345
Langmuir	Q_m (mg/g)	29.96	31.62	32.66	37.04
	b (L/mg)	0.3715	0.8131	2.3326	1.1962
Temkin	b_T (J/mol)	6.081	5.641	5.331	6.217
	K_T (L/mg)	1.0202	1.0291	1.0340	1.0408
Hurkins-Jura	A_H (g ² /L)	-239.67	-413.77	-549.37	-549.27
	B_H (mg ² /L)	-1.6838	-1.7749	-1.8100	-1.6848
Halsay	K_{Ha} (mg/L)	2172.7	52878.8	551393.8	209518.8
	n_{Ha}	3.2716	4.0809	4.6472	4.2345
Radlich-Peterson	g	0.6943	0.7550	0.7848	0.7638
	K_r (L/g)	0.0955	0.0696	0.0581	0.0554
Dubinin-Radushkevich	q_s (mg/g)	28.454	30.394	32.382	35.718
Jovanovic	$K_d \times 10^{-4}$ mol ² kJ ⁻²	1.3170	1.3220	1.3300	1.3502
	K_j (L/g)	0.0170	0.0158	0.0148	0.0177
BET	q_{max} (mg/g)	17.027	20.037	22.364	23.469
	C_{BET} (L/mg)	2.5767	-0.7835	1.6261	-0.5820
	q_s (mg/g)	0.3881	-1.2763	0.6150	-1.7182

Table 3. Isotherms parameter for the adsorption of Cu(II) onto ABNC

The Freundlich constants K_f and $1/n_f$ were calculated from the slope and intercept of the $\ln q_e$ Vs $\ln C_e$ plot and the model parameters are shown in **Table 3**. The magnitude of K_f showed that ABNC had a high capacity for Cu(II) adsorption from the aqueous solutions studied. The Freundlich exponent, n_f , should have values in the range of 1 and 10 (i.e., $1/n_f < 1$) to be considered as favourable adsorption⁹. A $1/n_f$ value of less than 1 indicated that Cu(II) is favorably adsorbed by ABNC. The Freundlich isotherm did not show a good fit to the experimental data as indicated by SSE and Chi-square statistics.

3.5.2 Langmuir adsorption isotherm

The Langmuir adsorption isotherm is based on the assumption that all sorption sites possess equal affinity to the adsorbate. The Langmuir isotherm¹⁰ in a linear form can be represented as:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \dots\dots\dots (5)$$

Where, q_e is the amount of Cu(II) adsorbed at equilibrium (mg/g), C_e is the concentration of Cu(II) in the aqueous phase at equilibrium (ppm), q_m is the maximum Cu(II) uptake (mg/g), and K_L is the Langmuir constant related to adsorption capacity and the energy of adsorption (g/mg). A linear plot of C_e/q_e Vs C_e was employed to determine the value of q_m and K_L . The data so obtained are presented in Table 3. The model predicted a maximum value that could not be reached in the experiments. The value of K_L decreased with an increase in the temperature. A high K_L value indicates a high adsorption affinity. Weber and Chakraborti expressed the Langmuir isotherm in term of dimensionless constant separation factor or equilibrium parameter (R_L) as defined in the following equation:

$$R_L = \frac{1}{1 + K_L C_0} \dots\dots\dots (6)$$

Where, C_0 is the initial Cu(II) concentration (ppm). Four scenarios can be distinguished: The sorption isotherm is unfavorable when $R_L > 1$, the isotherm is linear when $R_L = 1$, The isotherm is favorable when $0 < R_L < 1$ and the isotherm is irreversible when $R_L = 0$. The values of dimensionless separation factor (R_L) for Cu(II) removal were calculated at different concentrations and temperatures. As shown in Table 4, at all concentrations and temperatures tested the values of R_L for Cu(II) adsorptions on the ABNC were less than 1 and greater than zero, indicating favorable adsorption. The

Langmuir isotherm showed a better fit to the adsorption data than the Freundlich isotherm. The fact that the Langmuir isotherm fits the experimental data well may be due to homogeneous distribution of active sites on the ABNC surface, since the Langmuir equation assumes that the adsorbent surface is energetically homogeneous.

(C)	Temperature °C			
	30°C	40°C	50°C	60°C
10	0.0972	0.0469	0.0169	0.0324
20	0.0511	0.0240	0.0085	0.0164
30	0.0346	0.0161	0.0057	0.0110
40	0.0262	0.0121	0.0043	0.0083
50	0.0211	0.0097	0.0034	0.0066

Table 4. Dimensionless separation factor (rl) for the adsorption of Cu(II) onto ABNC

3.5.3 Temkin adsorption isotherm:

The Temkin adsorption isotherm assumes that the heat of adsorption decreases linearly with the sorption coverage due to adsorbent-adsorbate interactions¹¹. The Temkin isotherm equation is given as:

$$q_e = \frac{RT}{bT} \ln(K_T C_e) \dots\dots\dots (7)$$

Which, can be represented in the following linear form

$$q_e = \frac{RT}{bT} \ln(K_T C_e) \dots\dots\dots (7)$$

Where, K_T (L/g) is the Temkin isotherm constant, b_T (J/mol) is a constant related to heat of sorption, R is the ideal gas constant (8.314 J/mol K), and T is absolute temperature (K). A plot of q_e versus $\ln C_e$ enables the determination of isotherm constants K_T and b_T from the slope and intercept. The model parameters are listed in Table 3. The Temkin isotherm appears to provide a good fit to the Cu(II) adsorption data.

The adsorption energy in the Temkin model, b_T , is positive for Cu(II) adsorption from the aqueous solution, which indicates that the adsorption is endothermic. The experimental equilibrium curve is close to that predicted by Temkin model. Consequently, the adsorption isotherm of Cu(II) on ABNC can be described reasonably well by the Temkin isotherm.

3.5.4 Hurkins-Jura adsorption isotherm

The Hurkins-Jura¹² adsorption isotherm can be expressed as:

$$q_e = \sqrt{\frac{A_H}{B_H + \log C_e}} \dots\dots\dots (9)$$

This can be rearranged as follows:

$$\frac{1}{q_e^2} = \frac{B_H}{A_H} - \frac{1}{A_H} \log C_e \dots\dots\dots (10)$$

Where, A_H (g²/L) and B_H (mg²/L) are two parameters characterizing the sorption equilibrium. The isotherm equation accounts for multilayer adsorption and can be explained by the existence of a heterogeneous pore distribution. The Harkins-Jura isotherm parameters are obtained from the plots of $1/q_e^2$ versus $\log C_e$. This enables the determination of model parameters A_H and B_H from the slope and intercept.

3.5.5 Halsay adsorption isotherm

The Halsay¹³ adsorption isotherm can be given as

$$q_e = \exp\left(\frac{\ln K_{Ha} - \ln C_e}{n_{Ha}}\right) \dots\dots\dots (11)$$

and, a linear form of the isotherm can be expressed as follows:

$$\ln q_e = \frac{\ln K_{Ha}}{n_{Ha}} - \frac{\ln C_e}{n_{Ha}} \dots\dots\dots (12)$$

Where, K_{Ha} (mg/L) and n_{Ha} are the Halsay isotherm constants.

A plot of $\ln q_e$ Vs $\ln C_e$, enables the determination of n_{FH} and K_{FH} from the slope and intercept. This equation is suitable for multilayer adsorption and the fitting of the experimental data to this equation attest to the heteroporous nature of adsorbent. It also shows that the experimental data and the model predictions based on the non-linear form of the Halsey models. The model parameters are listed in Table 3. This result also shows that the adsorption of Cu(II) on ABNC was not based on significant multilayer adsorption. The Halsey model is not suitable to describe the adsorption of Cu(II) on ABNC, because this model assumes a multilayer behavior for the adsorption of adsorbate onto adsorbent.

3.5.6 Radlich-Peterson adsorption isotherm

The Radlich-Peterson¹⁴ adsorption isotherm contains three parameters and incorporates the features of Langmuir and Freundlich isotherms into a single equation. The general isotherm equation can be described as follows:

$$q_e = \frac{K_R C_e}{1 + a_R C_e^g} \dots\dots\dots(13)$$

The linear form of the isotherm can be expressed as follows:

$$\ln \frac{C_e}{q_e} = g \ln C_e - \ln K_R \dots\dots\dots(14)$$

Where, K_R (L/g) and a_R (L/mg) are the Radlich-Peterson isotherm constants and g is the exponent between 0 and 1. There are two limiting cases: Langmuir form for $g = 1$ and Henry's law for $g = 0$.

A plot of $\ln C_e/q_e$ versus $\ln C_e$ enables the determination of isotherm constants g and K_R from the slope and intercept. The values of K_R , presented in Table 3, indicate that the adsorption capacity of ABNC decreased with the increase in temperature. Furthermore, the value of g lies between 0 and 1 indicates favorable adsorption.

3.5.7 Dubinin-Radushkevich adsorption isotherm

The Dubinin-Radushkevich¹⁵ adsorption isotherm is another isotherm equation. It is assumed that the characteristic of the sorption curve is related to the porosity of the adsorbent. The linear form of the isotherm can be expressed as follows:

$$\ln q_e = \ln Q_D - B_D \left[RT \ln \left(1 + \frac{1}{C_e} \right) \right]^2 \dots\dots\dots(15)$$

Where, Q_D is the maximum sorption capacity (mol/g) and B_D is the Dubinin-Radushkevich constant (mol²/kJ²). A plot of $\ln q_e$ Vs $R \ln(1 + 1/C_e)$ enables the determination of isotherm constants B_D and Q_D from the slope and intercept, and are shown in table 3.

3.5.8 Jovanovic adsorption isotherm

The model of an adsorption surface considered by Jovanovic¹⁶ is essentially the same as that considered by Langmuir. The Jovanovic model leads to the following relationship [29]:

$$q_e = q_{max} \left(1 - e^{-K_1 C_e} \right) \dots\dots\dots(16)$$

$$\ln q_e = \ln q_{max} - K_1 C_e \dots\dots\dots(17)$$

Where, K_1 (L/g) is a parameter. q_{max} (mg/g) is the maximum Copper (II) uptake.

The q_{max} is obtained from a plot of $\ln q_e$ and C_e , as shown in table.3. Comparison of the obtained experimental data with Jovanovic model is also done. By comparing the values of the error functions, it was found the Langmuir and Temkin models are best to fit the Cu(II) adsorption on the ABNC. Both models show a high degree of correlation and is clearly confirming the good fit of Langmuir and Temkin models with the experimental data for removal of Cu(II) from the solution.

3.5.9 The Brunauer-Emmett-Teller (BET) isotherm model

Brunauer Emmett Teller (BET)¹⁷ isotherm is a theoretical equation, most widely applied in the gas-solid equilibrium systems. It was developed to derive multilayer adsorption systems with relative pressure ranges from 0.05 to 0.30 corresponding to a monolayer

coverage lying between 0.50 and 1.50. Its extinction model related to liquid-solid interface is exhibited as:

$$q_e = \frac{q_s C_{BET} C_e}{(C_s - C_e) [1 + (C_{BET} - 1)(C_e / C_s)]} \dots\dots\dots(18)$$

Where, C_{BET} , C_s , q_s and q_e are the BET adsorption isotherm (L/mg), adsorbate monolayer saturation concentration (mg/L), theoretical isotherm saturation capacity (mg/g) and equilibrium adsorption capacity (mg/g), respectively. As C_{BET} and $C_{BET} (C_e / C_s)$ is much greater than 1, the linear form is represented as

$$\frac{C_e}{q(C_s - C_e)} = \frac{1}{q_s C_{BET}} + \left(\frac{C_{BET} - 1}{q_s C_{BET}} \right) \left(\frac{C_e}{C_s} \right) \dots\dots\dots(19)$$

Where, C_e is equilibrium Concentration (mg/l), C_s is adsorbate monolayer saturation concentration (mg/l) and C_{BET} is BET adsorption relating to the energy of surface interaction (L/mg). The results of BET model is shown in table 3. The obtained result clearly shows monolayer coverage of adsorbate Cu(II) and physisorption.

3.6 Kinetic parameters

The rate and mechanism of the adsorption process can be elucidated based on kinetic studies. Cu(II) adsorption on solid surface may be explained by two distinct mechanisms: (1) An initial rapid binding of Cu(II) molecules on the adsorbent surface; (2) relatively slow intra-particle diffusion. To analyze the adsorption kinetics of the Cu(II), the pseudo-first-order, the pseudo-second-order, and intra-particle diffusion models were applied¹⁸. Each of these models and their linear modes of them equations presented in below.

Kinetic Models and Their Linear Forms		
Model	Nonlinear Form	Linear Form
Pseudo-first-order	$dq/dt = k_1(q_e - q_t)$	$\ln(q_e - q_t) = \ln q_e - k_1 t \dots\dots(20)$
Pseudo-second-order	$dq/dt = k_2(q_e - q_t)^2$	$t/q_t = 1/k_2 q_e^2 + (1/q_e)t \dots\dots(21)$

Where, q_e and q_t refer to the amount of Cu(II) adsorbed (mg/g) at equilibrium and at any time t , (min), respectively and k_1 (1/min), k_2 (g/mg.min) are the equilibrium rate constants of pseudo-first order and pseudo-second order models, respectively.

Pseudo-first order model is a simple kinetic model, which was proposed by Lagergren during 1898 and is used for estimating of the surface adsorption reaction rate. The values of $\ln(q_e - q_t)$ Vs t should give a linear relationship from which the values of k_1 will be determined from the slope of the plot. In many cases, the first-order equation of Lagergren does not fit well with the entire range of contact time and is generally applicable over the initial stage of the adsorption processes.

In the pseudo-second order model, the slope and intercept of the t/q_t Vs t plot were used to calculate the second-order rate constant, k_2 . The values of equilibrium rate constant (k_2) are presented in Table 6. According to Table 5, the value of r^2 (0.999) related to the pseudo-second order model revealed that Cu(II) adsorption followed this model, which is in agreement with the results obtained by Karagoz et al.¹⁹ Hameed et al.²⁰. Nevertheless, pseudo-first order and pseudo-second order kinetic models cannot identify the mechanism of diffusion of Cu(II) into the adsorbent pores.

(C _e)	G°				H°	S°	E _a	S°
	30°C	40°C	50°C	60°C				
10	-1522.4	-3416.4	-4841.3	-5159.4	36.11 9	125.3 29	27963 .2	0.000 00489
20	-1140.8	-1570.8	-2030.4	-3079.6	17.75 8	61.99 3	12123 .38	0.003 3
30	-682.3	-142.0	-565.1	-954.0	17.74 29	56.34 2	9046. 67	0.015 7
40	-1231.6	-700.1	-405.7	-848.3	12.89 22	38.66 6	5641. 86	0.065 6
50	-2569.5	-2323.4	-2196.7	-1745.7	10.39 05	25.72 9	3162. 62	0.210 4

Table 6. Thermodynamic parameter for the adsorption of Cu(II) onto ABNC

3.6.1 Simple Elovich Model:

The simple Elovich model²¹ is expressed in the form,

$$q_t = \alpha + \beta \ln t \dots\dots\dots(22)$$

Where, q_t is the amount adsorbed at time t , α and β are the constants obtained from the experiment. A plot of q_t Vs $\ln t$ gives a linear relationship for the applicability of the simple Elovich kinetics. The Elovich kinetics of Cu(II) on to ABNC for various initial concentrations (10, 20, 30, 40 and 50 mg/L) of volume 50 mL (each), adsorbent dose 0.025g, temperature 30°C and pH 6.6 were studied.

3.6.2 The Elovich equation

The Elovich model equation is generally expressed as

$$dq_t/dt = \alpha \exp(-q_t) \dots\dots\dots(23)$$

Where; α is the initial adsorption rate ($\text{mg g}^{-1} \text{min}^{-1}$) and β is the desorption constant (g/mg) during any one experiment. To simplify the Elovich equation. Chien and Clayton (1980) assumed $t \gg \tau$ and by applying boundary conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$ Eq.(23) becomes:

$$q_t = 1/\ln(\beta) + 1/\ln \dots\dots\dots(24)$$

If Cu(II) ions adsorption fits with the Elovich model, a plot of q_t vs. $\ln(t)$ yields a linear relationship with a slope of $(1/\beta)$ and an intercept of $(1/\beta)\ln(\alpha\beta)$. The Elovich model parameters α , β , and correlation coefficient (γ) calculated from this model indicates that the initial adsorption rate (α) increases with temperature similar to that of initial adsorption rate (h) in pseudo-second-order kinetics models. This may be due to increase in the pore or active site on the ABNC adsorbent.

Table: 5. The kinetic parameters for the adsorption of Cu(II) onto ABNC

C ₀	Temp C	Pseudo second order				Elovich model			Intra\particle diffusion		
		q _e	k ₂	γ	h	α	β	γ	K _{id}	C	C
10	30	19.10	0.0009	0.9901	0.3369	1.6E-07	1.26E+00	0.9939	0.0371	0.9889	1.6791
	40	25.83	0.0009	0.9902	0.6124	1.2E+00	1.69E-01	0.9866	0.5485	0.9881	1.9081
	50	20.53	0.0035	0.9959	1.4868	4.5E+00	2.54E-01	0.9868	0.2816	0.9909	1.4220
	60	20.36	0.0039	0.9929	1.6321	5.6E+00	2.67E-01	0.9879	0.2613	0.9920	1.4622
20	30	27.64	0.0003	0.9963	0.2192	1.1E+00	7.09E-02	0.9922	0.3618	0.9942	1.6502
	40	433.2	0.0000	0.9909	0.3945	1.3E+00	7.42E-02	0.9877	0.0222	0.9909	1.0244
	50	85.38	0.0001	0.9943	0.6486	1.6E+00	7.78E-02	0.9872	0.7914	0.9935	1.4211
	60	52.31	0.0004	0.9904	1.0492	2.2E+00	8.59E-02	0.9889	0.5861	0.9952	1.8146
30	30	51.39	0.0001	0.9912	0.2738	1.1E+00	7.06E-02	0.9926	0.1964	0.9892	1.5386
	40	194.1	0.0000	0.9970	0.5940	1.7E+00	6.50E-02	0.9867	0.9073	0.9883	1.0913
	50	426.5	0.0000	0.9955	0.6312	1.9E+00	5.57E-02	0.9890	0.9668	0.9875	1.0499
	60	66.23	0.0003	0.9971	1.3367	2.7E+00	6.57E-02	0.9868	0.6545	0.9877	1.6370
40	30	16.21	0.0008	0.9945	0.2065	1.7E+00	4.82E-02	0.9906	0.7347	0.9896	1.3651
	40	62.06	0.0001	0.9904	0.4199	1.9E+00	4.72E-02	0.9883	0.3150	0.9905	1.6172
	50	37.88	0.0000	0.9934	0.6982	2.2E+00	4.84E-02	0.9930	0.0446	0.9926	1.1249
	60	167.0	0.0000	0.9965	0.9609	2.6E+00	4.85E-02	0.9886	0.8978	0.9937	1.1539
50	30	1.467	0.0080	0.9912	0.0173	9.2E-01	4.11E-02	0.9888	0.7117	0.9924	1.4871
	40	68.74	0.0000	0.9972	0.2292	1.0E+00	4.05E-02	0.9881	0.3210	0.9945	1.8256
	50	12.367	0.0095	0.9906	1.4480	1.1E+00	4.29E-02	0.9888	0.0445	0.9892	1.5366
	60	9.818	0.0044	0.9930	0.4211	1.2E+00	4.01E-02	0.9917	0.8974	0.9892	1.2513

3.6.3 The Intraparticle diffusion model

The kinetic results were analyzed by the Intraparticle diffusion model²² to elucidate the diffusion mechanism. The model is expressed as:

$$q_t = K_{id} t^{1/2} + I \dots\dots\dots(25)$$

Where, I is the intercept and K_{id} is the intra-particle diffusion rate constant. The intercept of the plot reflects the boundary layer effect. Larger the intercept, greater is the contribution of the surface sorption in the rate controlling step. The calculated diffusion coefficient K_{id} values are listed in Table 5. The K_{id} value was higher at higher concentrations. Intraparticle diffusion is the sole rate-limiting step if the regression of q_t versus $t^{1/2}$ is linear and passes through the origin. In fact, the linear plots at each concentration did not pass through the origin. This deviation from the origin is due to the difference in the rate of mass transfer in the initial and final stages of the sorption. This indicated the existence of some boundary layer effect and further showed that Intraparticle diffusion was not the only rate-limiting step.

It is clear from the Table 5 that the pseudo- second-order kinetic model showed excellent linearity with high correlation coefficient ($r^2 > 0.99$) at all the studied concentrations in comparison to the other kinetic models. **In addition the calculated q_e values also in agree** with the experimental data in the case of pseudo-second-order kinetic model. It is also evident from Table 5 that the values of the rate constant k_2 decrease with increasing initial Cu(II) concentrations. This is due to the lower competition for the

surface active sites at lower concentration but at higher concentration the competition for the surface active sites will be high and consequently lower sorption rates are obtained.

3.7 Adsorption Thermodynamics

Thermodynamic parameters²³ were evaluated to confirm the adsorption nature. The thermodynamic constants, free energy change, enthalpy change and entropy change were calculated to evaluate the thermodynamic feasibility and the spontaneous nature of the process. Enthalpy change (ΔH), and entropy change (ΔS) may be determined from Van't Hoff equation:

$$\ln K = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \dots\dots\dots(26)$$

By plotting $\ln K$ as ordinate and $1/T$ as abscissa, ΔS and ΔH values are obtained by using the following equation and from ΔS and ΔH values, ΔG was obtained.

$$\Delta G = \Delta H - T\Delta S \dots\dots\dots(27)$$

Where, ΔG is the free energy change (kJ mol^{-1}), R is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), K the thermodynamic equilibrium constant and T is the absolute temperature (K).

$$\Delta G = \Delta H - T\Delta S = -RT \ln K_c \dots\dots\dots(28)$$

$$\ln K_c = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \dots\dots\dots(29)$$

$$2.30 \log \frac{q_e}{C_e} = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \dots\dots\dots(30)$$

$$\log \frac{q_e}{C_e} = \frac{\Delta S}{R \times 2.303} - \frac{\Delta H}{RT \times 2.303} \dots\dots\dots(31)$$

The values of ΔS, ΔH, ΔG was obtained from a plot of log (q_e/C_e) vs. 1/T.

Heat of reaction (ΔH) for physical adsorption is reported to be 1 to 93 kJ/mol in literature²⁴. The values of ΔH range from 10 to 36 kJ/mol from Table-6 indicate that the nature of adsorption of Cu(II) on ABNC is physical adsorption. The positive value of ΔH and negative ΔG indicate endothermic and spontaneous process of adsorption of Cu(II) on ABNC respectively.

In order to support that physical adsorption is the predominant mechanism, the values of activation energy (E_a) and sticking probability (S*) were calculated from the experimental data. They were calculated using modified Arrhenius type equation related to surface coverage (θ) as follows:

$$\theta = \left(1 - \frac{C_e}{C_i} \right) \dots\dots\dots(32)$$

$$S^* = (1 - \theta)_e \frac{-E_a}{RT} \dots\dots\dots(33)$$

The sticking probability, S*, is a function of the adsorbate/adsorbent system under consideration but must satisfy the condition 0 < S* < 1 and is dependent on the temperature of the system. The values of E_a and S* can be calculated from slope and intercept of the plot of ln(1-θ) versus 1/T respectively. The calculated values are listed in Table 5.

From Table 6 it is clear that the reaction is spontaneous in nature as ΔG⁰ is negative and ΔH⁰ values are positive at all the experimental temperatures. Again the positive value confirms that the sorption is endothermic in nature. The positive value of ΔS⁰ reflects the affinities of the adsorbents for the Cu(II). The result shown in Table 6 indicate that the probability of the Cu(II) to stick on surface of biomass is very high as S* << 1, and these values confirm that, the sorption process is physisorption.

3.8 EFFECT OF OTHER IONS

The effect of other ions like Cl⁻ on the adsorption process studied at different concentrations. The chloride ions added to 20 mg/L of Cu(II) solutions and the contents were agitated for 60 min at 30°C. The results shown in the Figure 4 reveals that low concentration of Cl⁻ ions does not affect the percentage of adsorption of Cu(II) on ABNC, because the interaction of Cl⁻ ions at available sites of adsorbent through competitive adsorption is not so effective. While the concentration of Cl⁻ ions increases, the interference of these ions at available surface sites of the sorbent through competitive adsorption increases and thus, decreases the adsorption percentage. This is so because ions with smaller hydrated radii decrease the swelling pressure within the sorbent and increase the affinity of the sorbent for such ions^{1,2}.

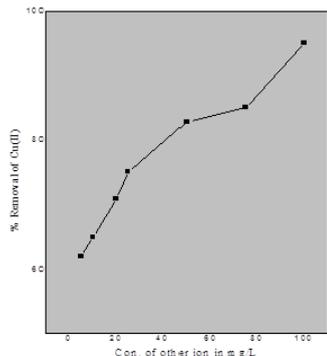


Fig. 4- Effect ionic strength on the adsorption of Cu(II) [Cu]=20mg/L;

Contact time e=60 min; Dose=25mg/50ml

3.9 DESORPTION STUDIES

Desorption studies help to elucidate the nature of adsorption and recycling of the spent adsorbent and the copper ions. If the

adsorbed copper ions can be desorbed using neutral pH water, then the attachment of the copper ion of the adsorbent is by weak bonds. The effect of various reagents were studied for desorption process. The results indicate that hydrochloric acid is a better reagent for desorption, because we could get more than 90% removal of adsorbed copper ion. The reversibility of adsorbed copper ion in mineral acid or base is in agreement with the pH dependent results obtained. The desorption of copper ion by mineral acids and alkaline medium indicates that the copper ion was adsorbed onto the ABNC through physisorption as well as by chemisorption mechanisms.

4. CONCLUSION

In this study, natural activated Borassus flabellifer bark nano carbon (ABNC) of Indian origin was tested and evaluated as a possible adsorbent for removal of copper from its aqueous solution using batch sorption technique. The adsorption process is also dependent on numerous factors such as the solution pH, adsorbent dosage, temperature, initial concentration of adsorbate and contact time. The percentage removal of copper ions decreased with an increase in the copper concentration while it increased with increase in contact time and adsorbent dose. The maximum removal was found between the pH ranges 2.0-6.6. The isotherm study indicates that the sorption data can be modeled by both Langmuir and BET isotherms. According to Dubinin-Radushkevich (D-R) isotherm model, adsorption of copper onto ABNC was physisorption. The adsorption kinetics followed pseudo-second-order kinetic model. Intra-particle diffusion was not the sole rate controlling factor. Thermodynamic analysis suggests that the removal of copper from aqueous solution by ABNC was a spontaneous and endothermic process. The present findings suggest that ABNC may be used as an inexpensive and effective adsorbent without any treatment or any other modification for the removal of copper from aqueous solutions.

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