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ADSORPTION CHARACTERISTICS OF ZIZYPHUS JUJUBA SEED SHELL ACTIVATED NANO POROUS CARBON FOR REMOVING COPPER (II) IONS FROM WASTE WATER

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Abstract

In the present study, adsorption of copper (II) ions from aqueous solution by Activated Zizyphus Jujuba shell Nano Carbon 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 6.5. 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 (ΔG^0), the enthalpy (ΔH^0) and the entropy change of sorption (ΔS^0) have also been evaluated and it has been found that the adsorption process was spontaneous, feasible and endothermic in nature. The results indicated that Activated Zizyphus Jujuba shell Nano Carbon can be used as an effective and low-cost adsorbent to remove copper (II) from aqueous solution.

Keywords: Copper; Activated Zizyphus Jujuba Shell Nano Carbon; Isotherms and Kinetics Models.

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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

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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 beings[1]. 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 disposal[2]. In particular, Cu^{2+} 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 Cu^{2+} is detrimental for human health [3]. 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 methods[6]. 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 concentration[7].

In the present investigation the adsorption of Copper ion on activated nano carbon prepared from Zizyphus Jujuba shell by carbonization with sulphuric acid has been achieved. The kinetic and equilibrium adsorption data obtained were utilized to characterize the sample prepared[8]. 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 & Methods

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 ($CuSO_4$, $5H_2O$) was prepared by dissolving accurately weighed 3.9296 grams of copper sulphate in 1000 ml 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 Elemer 2380).

2.1.Preparation of Adsorbent

The natural plant material Zizyphus Jujuba shellused in the present investigations was collected from Antipalayam nearby Thiruvarur district the seed shell were washed with distilled water several times to remove the dirt and dust and was subsequently dried in a hot air oven at 110^0C. Afterward, carbonization of the Zizyphus Jujuba shellwas carried out by w/v ratio of concentrated sulphuric acid for 24 hour; the primary carbon was activated at 1100^oC for 6 hrs under optimized conditions to obtain activated nano carbon. The activated nano carbon was thereafter looked to room temperature in an insert atmosphere of nitrogen and washed with hot distilled water and 0.5 N Hydrochloric and until the pH of the material reached 7.0 the activated

nano carbon was also dried in a hot air oven at 110^0C, to obtain the desired particular size (40nm) and stored in desiccators for further use.

Figure1: Zizyphus Jujuba seed shell

2.2.Batch Adsorption Studies

Preliminary batch adsorption studies were conducted to determine the equilibrium time. Batch studies were performed by mixing 0.025g of Copper ion with some of solution of different initial concentrations of Copper ion in 250 ml stoppered conical flask. The dose of adsorbent was decided experimentally. All the adsorption experiments were conducted at 30 ^{o} C to 60 ^{o}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 from the age use phase by centrifugation at 1000 rpm for to 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, qe (mg/g) was calculated using the following relationships.

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

Amount of adsorbed copper ions molecules per g of solid

$$Q_e = \left(C_o\text{-}C_e\right) \text{v/w} \ldots\ldots\ldots\ldots(2)$$

Where, C_o (mg/L) is the initial concentration of malachite green, 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. Result and Discussion

3.1.Characterization of Adsorbent

Effect of operating variables on the adsorption of heavy copper ions onto Activated Zizyphus Jujuba shell the nano adsorbent of materials, AZJ-NC were used to absorb some mg of Copper ion respectively.

The adsorption capacity of AZJ-NC is better than other, with the increase amount of AZJ-NC the removal of Copper ion increased obviously.

Table 1: Characteristics of the Adsorbent

Analysis	Value
pH_{slurry}	5.5
pH_{zpc}	6.00
Moisture content, %	0.105
Particle density, g cm^{-3}	0.285
Conductivity, μS/cm	41.63
Surface area, m^2/g	25.25

3.2.Effect It Contact Time

Figure 2 illustrates the effects of contact time on the removal of Copper ion ions respectively for different initial copper ions concentrations; 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. There after it continued at a slower rate and finally reached equilibrium as a result of saturation it as surface sites, for all copper ions, at the storied initial copper ions concentrations a sufficient contact time was determined as 45 min.
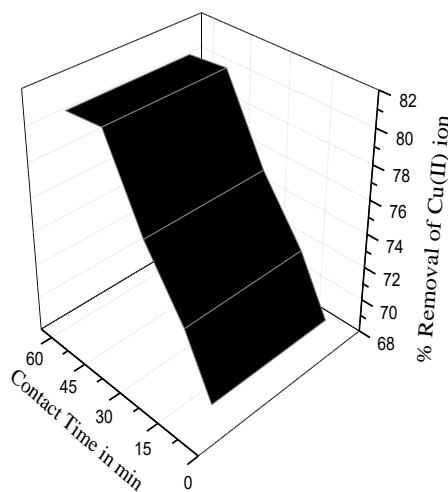

Fig:2- Effect of Contact Time on the Removal of Cu(II) ion
[Cu(II)]=20 mg/L; Temprature=30°C; Adsorbent dose=0.025g/50ml

3.3.Effect of Adsorbent Concentration

AZJ-NC with different concentrations were combined with a fixed 50ml, 20 mg/L of Copper ion respectively the adsorption of heavy copper ions increased with the increase of absorbent dose, and reached to a plateau at the appropriate dose of 125 mg of AZJ-NC. The results were shown in the figure 3.
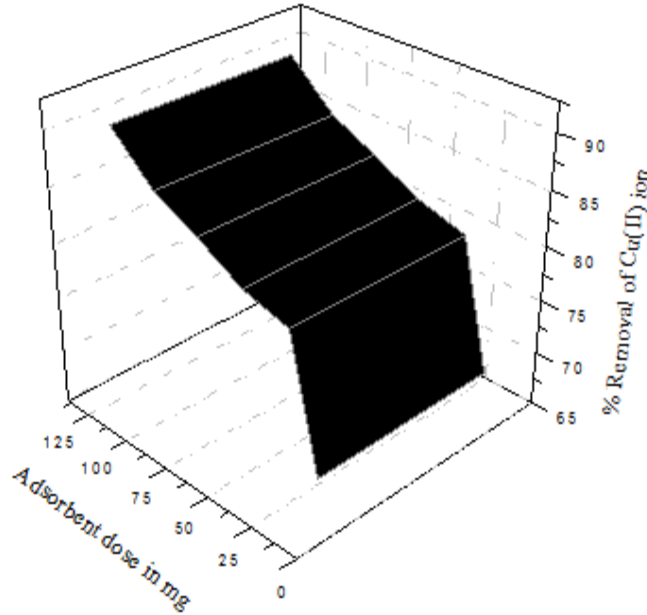
Fig;3- Effect of Adsorbent dose on the removal of Cu(II) ion
[Cu(II)]=20mg/L;Contact Time 45 min;Temprature 30^{0}C

3.4.Effect of Intoned pH on Adsorption

The pH value of the solution was important controlling parameters in the adsorption process, the removal of copper ions increase significantly with increasing pH from 1 to 7. The removal efficiencies of copper ions were low at pH<4. The obvious decreasing of removal might be attributed to the repulsive forces between the positive surface charge of adsorbate and the positive copper ions. The result shows that the figure 4.
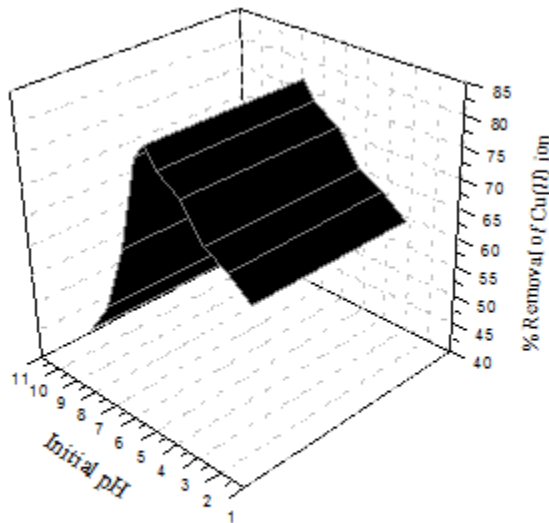
Fig;4- Effect of Initial pH on the removal of Cu(II) ion
[Cu(II)]=20 mg/L;Temprature 30°C;Adsorbent dose=0.025g/50m1

3.5.Adsorption Isotherms

Adsorption isotherm [4-8] 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 20 mg/L with 0.025 g of activated nano carbon at 30 ^{0}C with a constant agitation. Agitation was provided for 1.0 h, which is more than 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

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

Which, can be linearized as

$$\ln q_e = \ln K_F + \frac{1}{n_F} \ln C_e \quad \ldots\ldots\ldots\ldots\ldots(4)$$

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 $1/n_F$ are the Freundlich constants related to adsorption capacity and sorption intensity, respectively.

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 AZJ-NC 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 adsorption[9]. A $1/n_F$ value of less than 1 indicated that Cu(II) is favorably adsorbed by AZJ-NC. 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 isotherm[10] in a linear form can be represented as:

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

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, and the data so obtained were also 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) defined in the following equation:

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

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 AZJ-NC 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 AZJ-NC surface, since the Langmuir equation assumes that the adsorbent surface is energetically homogeneous.

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 interactions[11] The Temkin isotherm equation is given as:

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

Which, can be represented in the following linear form

$$q_e = \frac{RT}{b} \ln K_T + \frac{RT}{b} \ln C_e \quad \ldots\ldots\ldots\ldots (8)$$

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 AZJ-NC can be described reasonably well by the Temkin isotherm.

3.5.4. Hurkins-Jura Adsorption Isotherm

The Hurkins-Jura[12] adsorption isotherm can be expressed as:

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

This can rearranged as follows:

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

Where, A_H (g^2/L) and B_H (mg^2/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 of $1/q_e^2$ versus $\log C_e$ enables the determination of model parameters A_H and B_H from the slope and intercept.

3.5.5. Halsay Adsorption Isotherm

The Halsay[13] adsorption isotherm can be given as

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

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

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

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_{Ha} and K_{Ha} 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. The experimental data and the model predictions based on the non-linear form of the Halsay models. The model parameters are listed in Table 3. This result also shows that the adsorption of Cu(II) on AZJ-NC was not based on significant multilayer adsorption. The Halsay model is also not suitable to describe the adsorption of Cu(II) on AZJ-NC, because this model also assumes a multilayer behavior for the adsorption of adsorbate onto adsorbent.

3.5.6. Redlich-Peterson Adsorption Isotherm

The Radlich-Peterson[14] 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:

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

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

$$\ln \frac{C_e}{q_e} = g \ln C_e - \ln K_R \quad \text{..............(14)}$$

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 the AZJ-NC decreased with an increase temperature. Furthermore, the value of g lies between 0 and 1, indicating favorable adsorption.

3.5.7. *Dubinin-Radushkevich Adsorption Isotherm*

The Dubinin-Radushkevich [15] adsorption isotherm is another isotherm equation [32]. 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:

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

Where, Q_D is the maximum sorption capacity (mol/g), and B_D is the Dubinin-Radushkevich constant (mol^2/kJ^2). A plot of $\ln q_e$ Vs $R_T\ln(1+1/C_e)$ enables the determination of isotherm constants B_D and Q_D from the slope and intercept.

3.5.8. *Jovanovic Adsorption Isotherm*

The model of an adsorption surface considered by Jovanovic [16] is essentially the same as that considered by Langmuir. The Jovanovic model leads to the following relationship [29]:

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

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

$$\ln q_e = \ln q_{max} - K_J C_e \ldots\ldots\ldots\ldots(17)$$

Where, K_J (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. Their related parameters are listed in Table 3.

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 AZJ-NC. Both models show a high degree of correlation. This 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 Concentration ranges from 10 to 50 mg/L corresponding to a monolayer coverage lying between 20 and 30 mg/L. Its extinction model related to liquid–solid interface is exhibited as:

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

Where, CBET, Cs, qs and qe 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,
In the linear form as used is represented as

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

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).

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 applied[18]. 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	Number of Equation
Pseudo-first-order	$dq_t/d_t = k_1(q_e - q_t)$	$\ln(q_e - q_t) = \ln q_e - k_1 t$	(20)
Pseudo-second-order	$dq_t/d_t = k_2(q_e - q_t)^2$	$t/q_t = 1/k_2 q_e^2 + (1/q_e)t$	(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 estimation of the surface adsorption reaction rate. The values of $\ln(q_e - q_t)$ were linearly correlated with t. The plot of $\ln(q_e - q_t)$ Vs t should give a linear relationship from which the values of k_1 were 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/qt 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 6, 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.

3.6.1. Simple Elovich Model

The simple Elovich model[21] is expressed in the form,
$$q_t = \alpha + \beta \ln t \ldots\ldots\ldots\ldots(22)$$

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 lnt should give a linear relationship for the applicability of the simple Elovich kinetic. The Elovich kinetics of Cu(II) on to AZJ-NC for various initial concentrations (10, 20, 30, 40 and 50 mg/L) of volume 50 mL (each), adsorbent dose 0.025g, temperature 30 ^{o}C and pH 6.5.

3.6.2. The Elovich Equation

The Elovich model equation is generally expressed as

$$dq_t / d_t = \alpha \exp(-\beta q_t) \ldots\ldots\ldots(23)$$

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

$$q_t = 1/\beta \ln(\alpha\beta) + 1/\beta \ln t \qquad (24)$$

If Cu(II) ions adsorption fits with the Elovich model, a plot of q_t vs. $\ln(t)$ should yield 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) are summarized in table 6. The experimental data such as the initial adsorption rate (α) adsorption constant (β) and the correlation co-efficient (γ) calculated from this model indicates that the initial adsorption (α) increases with temperature similar to that of initial adsorption rate (h) in pseudo-second–order kinetics models. This may be due to increase the pore or active site on the AZJ-NC adsorbent.

3.6.3. The Intraparticle Diffusion Model

The kinetic results were analyzed by the Intraparticle diffusion model[22] to elucidate the diffusion mechanism. The model is expressed as:

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

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 6. The K_{id} value was higher at the 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 6 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 agree with the experimental data in the case of pseudo-second-order kinetic model. It is also evident from Table 6 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 parameters[23] were evaluated to confirm the adsorption nature of the present study. 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:

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

By plotting ln K as ordinate and 1/T as abscissa, we will get ΔS, ΔH and by using the following equation. We can get the value of have ΔS, ΔH and by this equation, get the value of ΔG.

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

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

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

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

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

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

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 7 to 72 kJ/ mol in literature[24]. The value of –ΔH range from -8 to -11 kJ/mol from Table-5 which indicate that the nature of adsorption of Cu(II) on AZJ-NC is physical adsorption. The negative value of ΔH & ΔG indicate exothermic and spontaneous process of adsorption of Cu(II) on AZJ-NC respectively.

In order to support that physical adsorption is the predominant mechanism, the values of activation energy (Ea) 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:

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

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

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 Ea and S* can be calculated from slope and intercept of the plot of ln(1-θ) versus 1/T respectively. The calculated values were listed in Table 5.

From Table 5 it is clear that the reaction is spontaneous in nature as ΔG^0 and ΔH^0 values are negative at all the temperature studied. Again positive value confirms that the sorption is endothermic in nature. The positive value of ΔS^0 reflects the affinities of the adsorbents for the Cu(II). The result as shown in Table 5 indicate that the probability of the Cu(II) to stick on surface of biomass is very high as S*<< 1, these values confirm that, the sorption process is physisorption.

3.8. 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 used for desorption studies. 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 AZJ-NC through physisorption as well as by chemisorptions mechanisms.

4. Conclusion

In this study, natural Activated Zizyphus Jujuba shell Nano Carbon 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 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 2.0-6.5. 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 AZJ-NC 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 AZJ-NC was a spontaneous and exothermic process. The present findings suggest that AZJ-NC 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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Appendix

Table: 2. Equilibrium Parameters for the Adsorption of Copper Ion onto AZJ-NC

M_0	Ce (Mg / L)				Qe (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	1.813	1.313	1.064	1.038	16.37	17.37	17.87	17.92	81.87	86.87	89.36	89.62
20	3.313	3.064	2.824	2.314	33.37	33.87	34.35	35.37	83.44	84.68	85.88	88.43
30	6.584	6.014	5.313	4.964	46.83	47.97	49.37	50.07	78.05	79.95	82.29	83.45
40	9.334	8.584	8.172	7.700	61.33	62.83	63.66	64.60	76.67	78.54	79.57	80.75
50	13.56	13.11	12.84	12.11	72.87	73.78	74.33	75.79	72.87	73.78	74.33	75.79

Table 3: Langmuir and Freundlich Isotherm Parameter for the Adsorption of Copper Ion onto AZJ-NC

Model	Constant	Temperature (°C)			
		30	40	50	60
Freundlich	K_f (mg/g) $(L/mg)^{1/n}$	12.025	15.471	18.018	19.290
	n	1.3919	1.5836	1.7164	1.7258
Langmuir	Q_m (mg/g)	141.07	116.57	106.94	107.12
	b (L/mg)	0.0799	0.1298	0.1745	0.1954
Temkin	b_T (J/mol)	27.452	24.581	23.022	23.433
	K_T (L/mg)	0.9934	1.0813	1.1250	1.1439
Hurkins-Jura	A_H (g^2/L)	-270.69	-329.46	-371.94	-387.81
	B_H (mg^2/L)	-1.0397	-1.0202	-1.0030	-0.9756
Halsay	K_{Ha} (mg/L)	31.865	76.502	142.964	165.286
	n_{Ha}	1.3919	1.5836	1.7164	1.7258
Radlich-Peterson	g	0.2815	0.3685	0.4174	0.4206
	K_R (L/g)	0.0832	0.0646	0.0555	0.0518
Dubinin-Radushkevich	q_s (mg/g)	63.108	60.232	59.834	62.970
	$K_D \times 10^{-4}$ mol^2 kJ^{-2}	1.4865	1.4693	1.4632	1.4725
Jovanovic	K_J (L/g)	0.1142	0.1129	0.1105	0.1153
	q_{max} (mg/g)	18.558	20.359	21.943	22.738
BET	C_{BET} (L/mg)	4.7517	6.9696	9.8542	11.3460
	qs (mg/g)	0.2105	0.1435	0.1015	0.0881

Table 4: Dimensionless Seperation Factor (R_L) for the Adsorption of Copper Ion onto AZJ-NC

(C_i)	Temperature °C			
	30°C	40°C	50°C	60°C
25	0.3336	0.2356	0.1865	0.1699
50	0.2002	0.1335	0.1028	0.0928
75	0.1430	0.0932	0.0710	0.0639
100	0.1112	0.0715	0.0542	0.0487
125	0.0910	0.0581	0.0438	0.0393

Table 5: Thermodynamic Parameter for the Adsorption of Copper Ion onto AZJ-NC

C_0	$\Delta G°$				$\Delta H°$	$\Delta S°$	E_a	S^*
	30° C	40° C	50° C	60° C				
10	-3797.8	-4917.0	-5715.8	-5968.0	18.490	74.183	15948.4	0.0003
20	-4072.9	-4449.0	-4848.7	-5631.2	11.226	50.242	9652.92	0.0037
30	-3196.4	-3599.9	-4125.1	-4479.8	10.080	43.809	8152.13	0.0086
40	-2996.5	-3376.2	-3651.4	-3969.7	6.0622	32.029	5266.54	0.0287
50	-2489.5	-2691.7	-2855.1	-3159.1	4.0686	21.596	3023.76	0.0820

Table 6: The Kinetic Parameters for the Adsorption of Copper Ion onto AZJ-NC

C_0	Temp °C	Pseudo second order				Elovich model			Intraparticle diffusion		
		q_e	k_2	γ	h	α	β	γ	K_{id}	γ	C
25	30	16.58	0.0163	0.9901	4.469	90.30	0.4615	0.9939	0.0167	0.9889	1.903
	40	18.66	0.0099	0.9902	3.434	125.1	0.4787	0.9866	0.1327	0.9881	1.697
	50	18.65	0.0166	0.9959	5.784	75.26	0.7172	0.9868	0.0830	0.9909	1.799
	60	18.65	0.0177	0.9929	6.165	147.9	0.7557	0.9879	0.0783	0.9920	1.809
50	30	36.71	0.0035	0.9963	4.676	53.94	0.2003	0.9922	0.1706	0.9942	1.605
	40	36.97	0.0039	0.9909	5.277	80.66	0.2097	0.9877	0.1589	0.9909	1.635
	50	37.33	0.0044	0.9943	6.129	130.4	0.2200	0.9872	0.1472	0.9935	1.667
	60	37.83	0.0049	0.9904	7.081	311.4	0.2427	0.9889	0.1285	0.9952	1.710
75	30	49.84	0.0037	0.9912	9.272	735.1	0.1997	0.9926	0.1174	0.9892	1.671
	40	51.57	0.0041	0.9970	10.83	595.3	0.1837	0.9867	0.1231	0.9883	1.683
	50	53.59	0.0034	0.9955	9.895	249.8	0.1576	0.9890	0.1413	0.9875	1.664
	60	53.21	0.0050	0.9971	14.14	104.6	0.1856	0.9868	0.1164	0.9877	1.719
100	30	65.78	0.0037	0.9945	15.98	580.3	0.1362	0.9906	0.1302	0.9896	1.660
	40	67.27	0.0035	0.9904	15.68	585.5	0.1336	0.9883	0.1302	0.9905	1.668
	50	67.92	0.0037	0.9934	17.09	805.5	0.1369	0.9930	0.1248	0.9926	1.684
	60	68.88	0.0037	0.9965	17.58	921.8	0.1370	0.9886	0.1227	0.9937	1.694
125	30	77.80	0.0022	0.9912	13.13	519.9	0.1162	0.9888	0.1314	0.9924	1.615
	40	78.84	0.0021	0.9972	13.25	516.8	0.1145	0.9881	0.1317	0.9945	1.620
	50	79.02	0.0023	0.9906	14.30	851.5	0.1212	0.9888	0.1226	0.9892	1.640
	60	80.76	0.0021	0.9930	13.70	588.8	0.1133	0.9917	0.1295	0.9892	1.634

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