# Thermodynamic, Kinetic and Isotherm Studies on the Removal of Copper (II) ION using Activated Nano Carbon

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**Abstract :** In this study activated carbon prepared from Solanum trilobatum was used as adsorbent to remove copper (II) ion from industrial waste water.  A series of experiments were conducted in batch system to evaluate the effect of the variables.  The effect of pH, initial copper concentration dose of adsorbents and contact time were considered.  Adsorption data were fitted to Langmuir, Freundlich, Temkin, Hurkins-Jura, Halsay, Radlich-Peterson, Dubinin-Radushkevich, Jovanovic and BET equations.  The kinetics of adsorption is found to be second order with intra particle diffusion as the rate determining step.  The various thermodynamic parameters like $\Delta H^o$, $\Delta S^o$, and $\Delta G^o$ were analyzed to observe the nature of adsorption.  Generally, these results indicated that ASTNC can be used as an effective and low cost adsorbent for the removal of copper (II) ions from aqueous solutions.

**Keywords :** Adsorption,Copper(II)ion, Activated SolanumTrilobatum Nano Carbon, Isotherm, Kinetic and Thermodynamic studies.

## 1. Introduction

Heavy metal pollution of wastewater is a common environmental hazard, since the toxic metal, metal ion dissolved can ultimately reach the top of the food chain and thus become a risk factor for human health[1].Ions of heavy metalslike copper, nickel, zinc, cadmium, lead, chromium and mercuryhave a significant impact on the environment. They are highlytoxic as ions or in compound forms; they are soluble in waterand may be readily absorbed into living organisms. Out ofthese ions, copper ($Cu^{2+}$) is present in the wastewater of several industries, such as metal cleaning and planning baths, refineries, paper and pulp, fertilizer and wood preservatives [2].  According WHO, the maximum acceptable concentration of Cu(II) in drinking water is 1.5 mg/L.  The adult human body contains 100-150 mg of Cu (II), but excess of copper in the body can be toxic [3].  Copper can be accumulated in human body, causing erythrocycle destruction, nausea, salivation, diarrhea and muscular cramps, renal degradation, chronic pulmonary problems and skeletal deformity [4]. Various techniques like precipitation, ion exchange, chemical oxidation and adsorption have been used for the removal of toxic pollutant from wastewater. Among several chemical and physical methods, the adsorption onto activated carbon has been found to be superior to other techniques in water-re-use methodology because of its high surface area, micro porous character and chemical nature of their surface have made them potential adsorbents for the removal of heavy metal ions from industrial wastewater [5].  In the present investigation, the activated carbon prepared from Solanum trilobatum (ASTNC) used for the removal of copper (II) ions from aqueous solution has been studied and the applicability of the kinetic and equilibrium models for the copper (II) ion- ASTNC system has also been discussed.

## 2. Materials and Methods

### 2.1 Preparation of The Adsorbate

All the reagents used for the current investigation were of GR grade from Scientific Equipment Company, Trichy, India. Stock solution (1000 mg/L) of copper was prepared by dissolving 3.9296g of (CuSO$_4$, 5H$_2$O)in double distilled water. The solution was further diluted to the required concentrations before use. Before mixing the adsorbent, the pH of each Cu (II) solution was adjusted to the required value by 0.1 M NaOH or 0.1 M HCl solutions.

### 2.2 Preparation of The Adsorbent

The Solanum trilobatum obtained from Agricultural fields was carbonized with concentrated sulphuric acid and washed with water and activated around 400$^o$C in a muffle furnace for 5hrs then it was taken out, ground well to fine powder and stored in a vacuum desiccator.



**SolanumTrilobatum**

### 2.3 Batch Experiments

The effect of various parameters on the removal of copper (II) ion onto ASTNCwas studied batch adsorption experiments were conducted at (30-60$^o$C).For each experimental run, 50 ml of copper solution of known initial concentration and pH were taken in a 250 ml plugged conical flask. A 25 mg adsorbent dose is added to the solution and mixture was shaken at constant agitation speed (200 rpm) sample were withdrawn at appropriate time intervals (10-60 min) and the adsorbent was separated by filtration. The residual solutions were analyzed to determine the copper (II) ion concentration. The effect of dosage of adsorbent on the removal of copper (II) ion was measured by contacting 50 ml of 50 mg/L of copper (II) ion solution with 25 mg of ASTNC till equilibrium was attained. Adsorption equilibrium isotherm is studied using 25 mg of ASTNCdosage per 50 ml of copper (II) ion solution. The initial concentration were ranged from (25 to 250 mg/L) in all sets of experiments. The plugged conical flask was shaken at a speed of 200 rpm for 60 minutes. Then the solution was separated from the mixture and analyzed for copper (II) ion concentration. The adsorption capacity was calculated by using a mass equilibrium equation as follows:

$q_e = (C_o – C_e)$ V/M …………………………………….(1)

Where $C_o$ and $C_e$ being the initial copper (II) ion concentration (mg/L) and equilibrium concentration, respectively V is the experimental volume of copper (II) ion solution expressed in liters [L] and M is the adsorbent mass expressed in grams [g]. The copper (II) ions percentage can be calculated as follows:

%Removal = $(C_o – C_t) \times 100/C_o$ ……………………… (2)

The effect of pH on the rate of adsorption was investigated using copper concentration of 75 mg/L constant ASTNC dosage. The pH values were adjusted with dilute HCl and NaOH solution. The adsorbent-adsorbate mixture was shaken at room temperature using agitation speed (200 rpm) for 60 minutes. Then the concentration of copper in solution was determined.

## 3. Result and Discussion

### 3.1 Effect of Contact Time

The effect of contact time on the amount of dye adsorbed was investigated at 1000 mg/L concentration of the dye (Fig. 1). It was observed that the percentage removal of dye increases rapidly with an increase in contact time initially, and thereafter, beyond a contact time of about 50 min, no noticeable change in the percentage removal was observed the percentage removals after 50 min were 93%. Therefore, the study found that the optimum contact time is considered to be 50 min. This is also the equilibrium time of the batch adsorption experiments, since beyond a contact time of 50 min, adsorption is not changed. The rapid removal of dye was observed at the beginning of the contact time due to the percentage of large number of binding sites available for adsorption.



Fig.1 - Contact Time in Min　　　Fig.2 - Adsorbent dose in mg
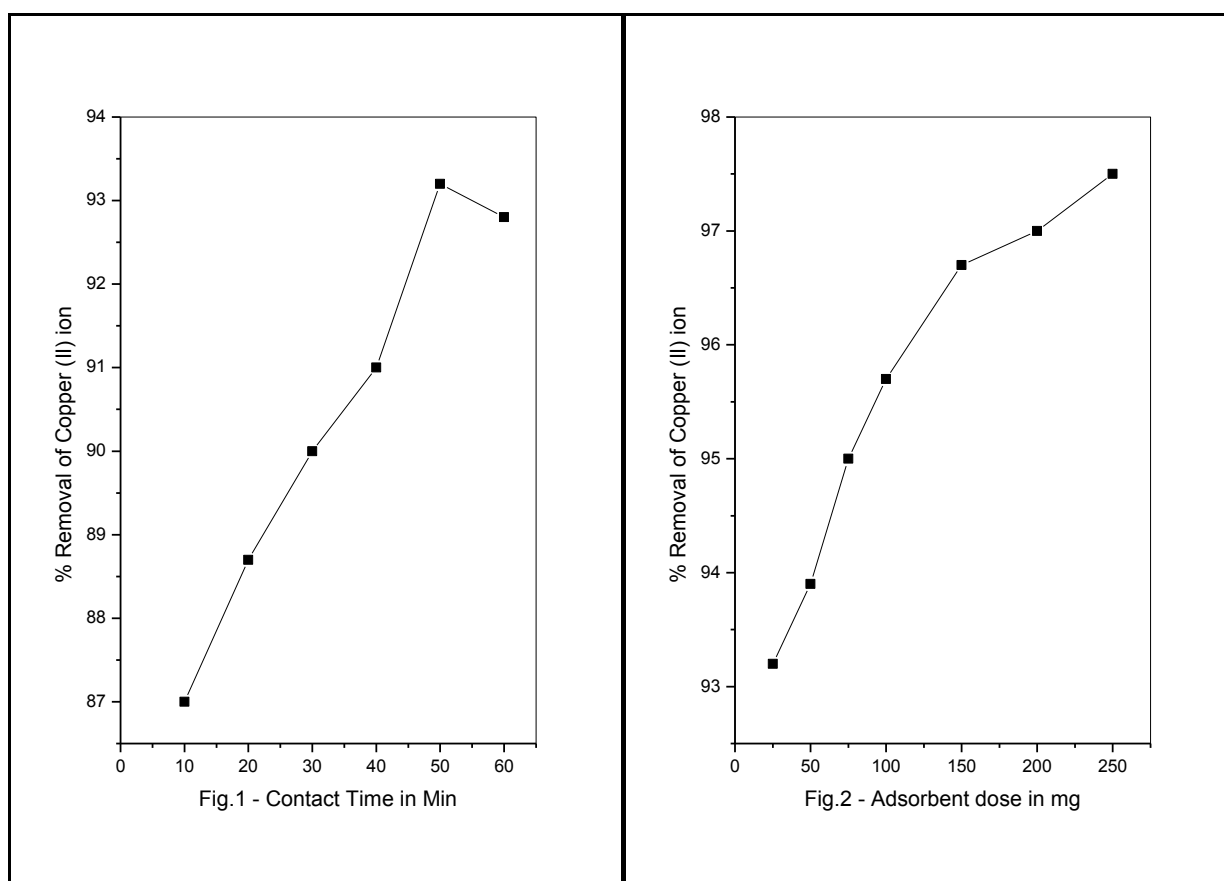
### 3.2 Effect of Adsorbent Dosage

The adsorbent dosage is an important parameter, which influence the extent of metal uptake from the solution. The effect of varying doses of 25 mg to 250 mg of ASTNC was investigated using 50 mg/L of initial copper (II) ion concentration at initial pH 6.5 shows an increase in percentage removal at initial pH 6.5 shows an increase in percentage removal of copper with increase in dose of adsorbent up to certain limit shown in Fig.2, increase in the adsorption with increasing dose of adsorbent is expected due to increase in adsorbent surface area and availability more adsorption site.

### 3.3 Effect of Solution pH

The solution pH is one of the most important factors that control the adsorption of metal ion on the sorbent materials. The adsorption capacity can be attributed to the chemical form of metal ion in the solution at specific pH. In addition, due to different functional groups on the adsorbent surface, which become active sites for the metal ion binding at a specific pH the effect of adsorption can vary substantially. Therefore, an increase in pH may cause an increase or decrease in the adsorption, resulting different optimum pH values dependent on the type of adsorbent. To examine the effect of pH on the % removal of copper (II) ion, the solution pH were

varied from 2.0 to 10.0 by adding acid and base to the stock solution this increases may be due to the presence of negative charge on the surface of the adsorbent ASTNC that may be responds for the metal ion binding. However, as the pH is lowered, the hydrogen ions compete with metal ion for the adsorption sites in the adsorbent ASTNC, the overall surface charge on the particles become positive and hinds the binding of positively charged metal ion.  On other hand, decrease in the adsorption under pH>6.3 may be due to occupation of the adsorption sites by OH⁻ ions which retard the approach of such metal ion further toward the adsorbent ASTNC surface.  From the experimental results, the optimum pH range for the adsorption of the copper (II) ion is 2.0 to 6.5 shown in Fig.3.



Fig.3 - Initial pH
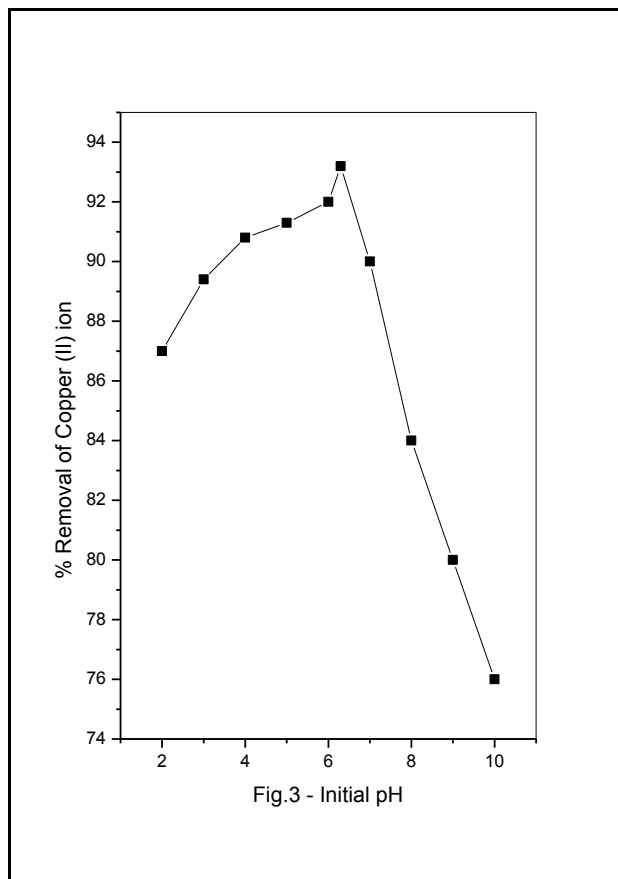
**Table: 1. Equilibrium Parameters for The Adsorption of Copper (II) ION onto ASTNC**

| $M_0$ | $C_e$ (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 | 2.0504 | 1.5504 | 1.3010 | 1.2755 | 15.899 | 16.899 | 17.398 | 17.449 | 79.496 | 84.496 | 86.990 | 87.246 |
| 20 | 3.5504 | 3.3016 | 3.0609 | 2.5510 | 32.899 | 33.397 | 33.878 | 34.898 | 82.248 | 83.492 | 84.696 | 87.245 |
| 30 | 6.8210 | 6.2515 | 5.5505 | 5.2015 | 46.358 | 47.497 | 48.899 | 49.597 | 77.263 | 79.162 | 81.499 | 82.662 |
| 40 | 9.5714 | 8.8216 | 8.4090 | 7.9373 | 60.857 | 62.357 | 63.182 | 64.125 | 76.072 | 77.946 | 78.978 | 80.157 |
| 50 | 13.800 | 13.349 | 13.073 | 12.344 | 72.399 | 73.301 | 73.855 | 75.313 | 72.399 | 73.301 | 73.855 | 75.313 |

### 3.4 Adsorption Isotherms

It is important to determine the most appropriate correlation for equilibrium adsorption isotherm, to optimize the design of a sorption system. The Freundlich, Langmuir, Temkin, Hurkins-Jura, Halsay, Redlich-Peterson, Dubinin-Radushkevich, Jovanovich and BET isotherm models were used to analyses the adsorption equilibrium. Experimental isotherm data were obtained at an adsorption time of 60 min at different temperatures.

### 3.4.1 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

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

Which, can be linearized as

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

Where, $q_e$ is the amount of copper(II) ionadsorbed at equilibrium (mg/g) and $C_e$ is the concentration of copper (II) ionin 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 $\ln q_e$ Vsln$C_e$ plot, as shown in Fig. 4, and the model parameters are shown in Table2. The magnitude of $K_F$ showed that ASTNChad a high capacity for copper (II) ionadsorption 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. A $1/n_F$ value of less than 1 indicated that copper (II) ionis favorably adsorbed by ASTNC. The Freundlich isotherm did not show a good fit to the experimental data as indicated by SSE and Chi-square statistics.

**Table: 2. Isotherm Parameters for the Adsorption of Copper (II) ION onto ASTNC**

| Model | Constant | Temperature (o C) | | | |
|---|---|---|---|---|---|
| | | 30 | 40 | 50 | 60 |
| **Freundlich** | Kf (mg/g) (L/mg)1/n | 10.472 | 13.462 | 15.672 | 16.810 |
| | N | 1.3033 | 1.4641 | 1.5724 | 1.5812 |
| **Langmuir** | Qm (mg/g) | 162.83 | 129.27 | 116.64 | 117.06 |
| | b (L/mg) | 0.0600 | 0.0996 | 0.1341 | 0.1481 |
| **Temkin** | bT (J/mol) | 28.975 | 26.317 | 24.903 | 25.354 |
| | KT (L/mg) | 0.9414 | 1.0344 | 1.0832 | 1.1028 |
| **Hurkins-Jura** | AH (g2/L) | -243.65 | -294.11 | -329.92 | -344.21 |
| | BH (mg2/L) | -1.0463 | -1.0261 | -1.0088 | -0.9834 |
| **Halsay** | KHa (mg/L) | 21.348 | 44.989 | 75.718 | 86.676 |
| | nHa | 1.3033 | 1.4641 | 1.5724 | 1.5812 |
| **Radlich-Peterson** | G | 0.2327 | 0.3170 | 0.3640 | 0.3676 |
| | KR (L/g) | 0.0955 | 0.0743 | 0.0638 | 0.0595 |
| **Dubinin-Radushkevich** | qs (mg/g) | 64.102 | 61.220 | 60.885 | 64.279 |
| | KD ×10-4 mol2 kJ-2 | 1.4937 | 1.4775 | 1.4721 | 1.4816 |
| **Jovanovic** | KJ (L/g) | 0.1158 | 0.1144 | 0.1120 | 0.1168 |
| | qmax (mg/g) | 17.614 | 19.364 | 20.909 | 21.654 |
| **BET** | CBET (L/mg) | 4.2265 | 5.3179 | 7.3467 | 8.5948 |
| | qs (mg/g) | 0.2366 | 0.1880 | 0.1361 | 0.1163 |

### 3.4.2 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 in a linear form can be represented as:

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

Where $q_e$ is the amount of copper (II) ionadsorbed at equilibrium (mg/g), $C_e$ is the concentration of copper (II) ionin the aqueous phase at equilibrium (ppm), $q_m$ is the maximum copper (II) ionuptake (mg/g), and $K_L$ is the Langmuir constant related to adsorption capacity and the energy of adsorption (g/mg).



Fig.4 - Freundlich adsorption isotherm



Fig.5 - Langmuir adsorption isotherm
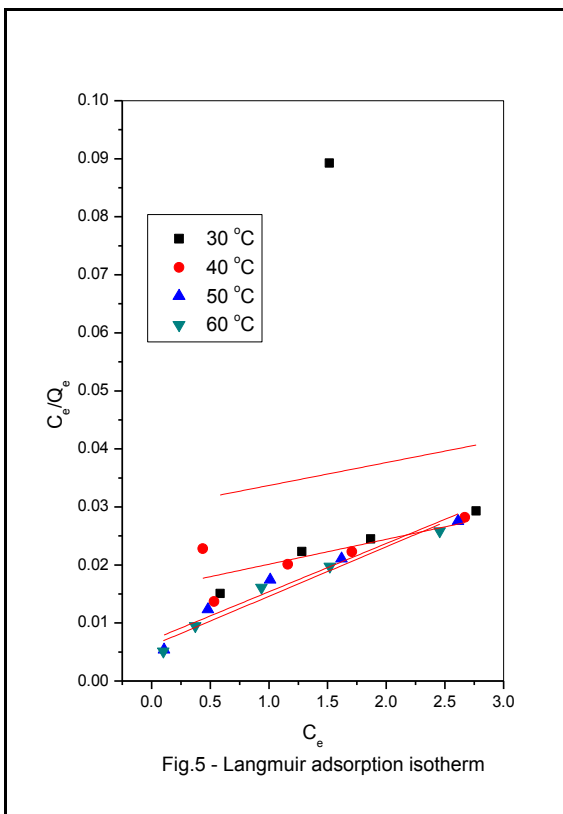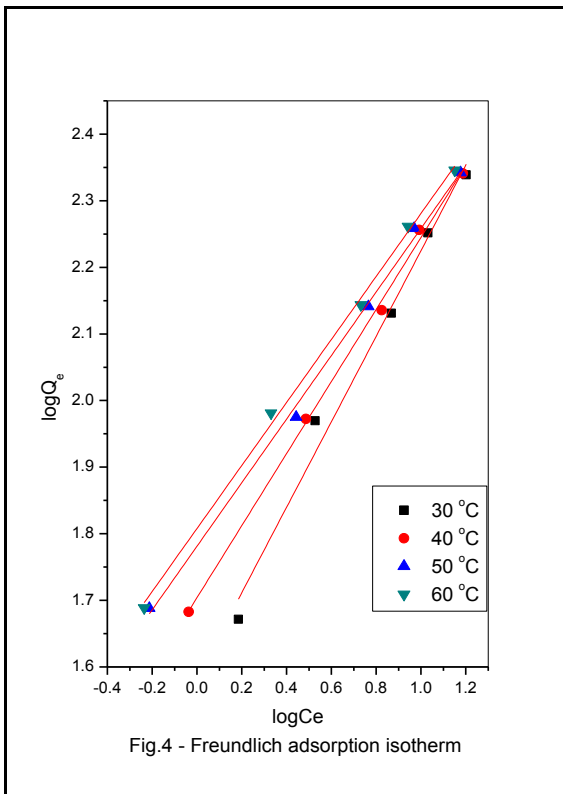
A linear plot of $C_e/q_e$ Vs $C_e$ was employed to determine the value of $q_m$ and $K_L$, as shown in Fig. 5, and the data so obtained were also presented in Table 2. The model predicted a maximum value that could not be reached in the experiments. The value of $K_L$ decreased with an increase in the 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 copper (II) ionconcentration (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 copper (II) ionremoval were calculated at different concentrations and temperatures. As shown in Table 3, at all concentrations and temperatures tested the values of $R_L$ for copper (II) ionadsorptions on the ASTNCwere 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 as shown in Fig. 4 and Fig. 5. The fact that the Langmuir isotherm fits the experimental data well may be due to homogeneous distribution of active sites on the ASTNCsurface, since the Langmuir equation assumes that the adsorbent surface is energetically homogeneous.

### 3.4.3 Temkin Adsorption Isotherm

The Temkin adsorption isotherm assumes that the heat of adsorption decreases linearly with the sorption coverage due to adsorbent-adsorbate interactions. 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 $q_e$ Vs $\ln C_e$ enables the determination of isotherm constants $K_T$ and $b_T$ from the slope and intercept, as shown in Fig. 6 The model parameters are listed in Table 2. The Temkin isotherm appears to provide a good fit to the copper (II) ionadsorption data.

The adsorption energy in the Temkin model, $b_T$, is positive for copper (II) ionadsorption 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 copper (II) ionon ASTNCcan be described reasonably well by the Temkin isotherm.
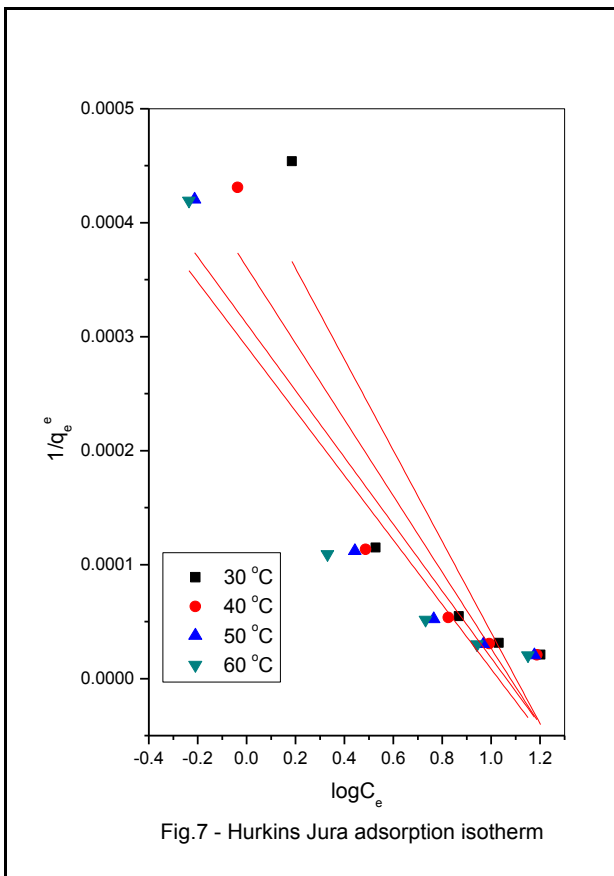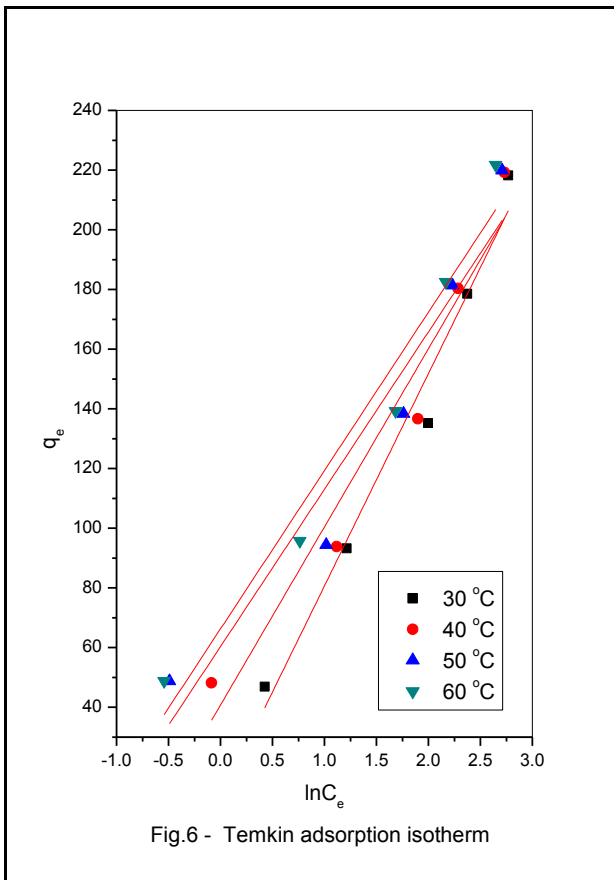
### 3.4.4 Hurkins-Jura Adsorption Isotherm

The Hurkins-Jura adsorption isotherm can be expressed as

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

This can rearranged as follows:

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

Where, $A_H$ ($g^2$/L) and $B_H$ ($mg^2$/L) are two parameters characterizing the sorption equilibrium.



Fig.6 - Temkin adsorption isotherm



Fig.7 - Hurkins Jura adsorption isotherm

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 $1/q_e^2$ Vslog $C_e$ enables the determination of model parameters $A_H$ and $B_H$ from the slope and intercept in Fig. 7. The values presented in table 2 conclude the multilayer adsorption of copper (II) ion by ASTNC.

### 3.4.5 Halsay Adsorption Isotherm

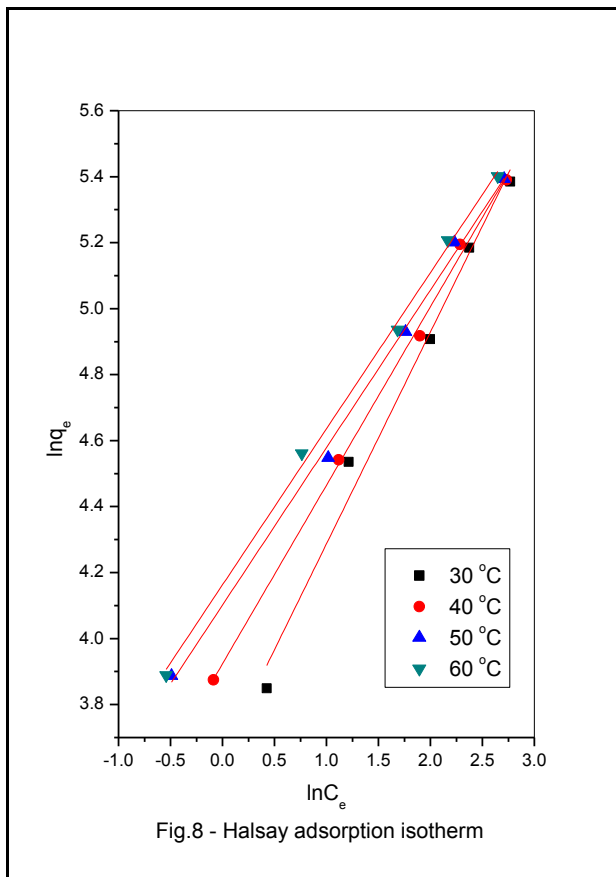The Halsay adsorption isotherm can be given as

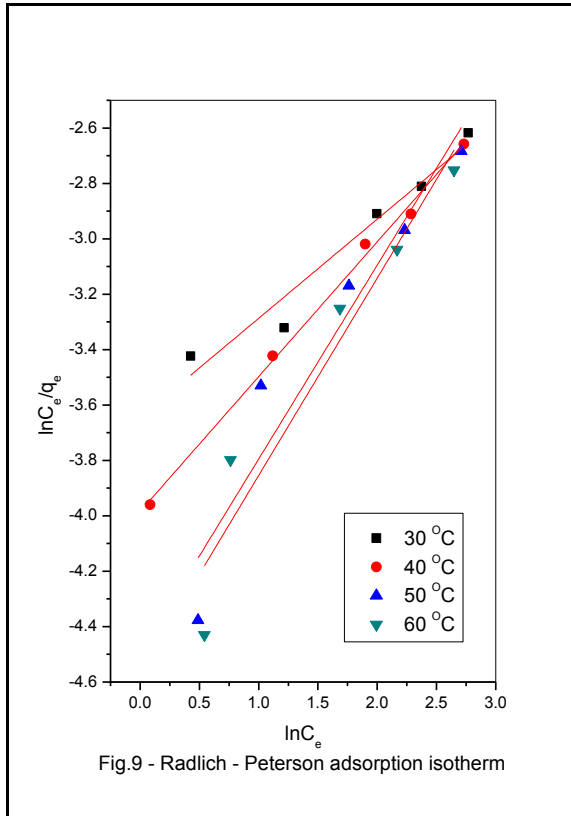$$q_e = \exp\left(\frac{\ln K_{Ha} - \ln C_e}{n_{Ha}}\right) \ldots\ldots\ldots\ldots(11)$$

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

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

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

A plot of $\ln q_e$ Vsln $C_e$, shown in Fig. 8, 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. Fig. 8 also shows that the experimental data and the model predictions based on the non-linear form of the Halsay models. The model parameters are listed in Table 2. This result also shows that the adsorption ofcopper (II) ionon ASTNCwas not based on significant multilayer adsorption. The Halsay model is also not suitable to describe the adsorption of copper (II) iononASTNC, because this model also assumes a multilayer behavior for the adsorption of adsorbate onto adsorbent.



Fig.8 - Halsay adsorption isotherm

Fig.9 - Radlich - Peterson adsorption isotherm

### 3.4.6 Redlich-Peterson Adsorption Isotherm

The Redlich-Peterson 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

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

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

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

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 $\ln C_e/q_e$ Vs $\ln C_e$ shown in Fig.9 enables the determination of isotherm constants g and $K_R$ from the slope and intercept. The values of $K_R$, presented in Table 2, indicate that the adsorption capacity of the ASTNCdecreased with an increase temperature. Furthermore, the value of g lies between 0 and 1, indicating favorable adsorption.

### 3.4.7 Dubinin-Radushkevich Adsorption Isotherm

The Dubinin-Radushkevich 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

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

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, as shown inFig. 10.
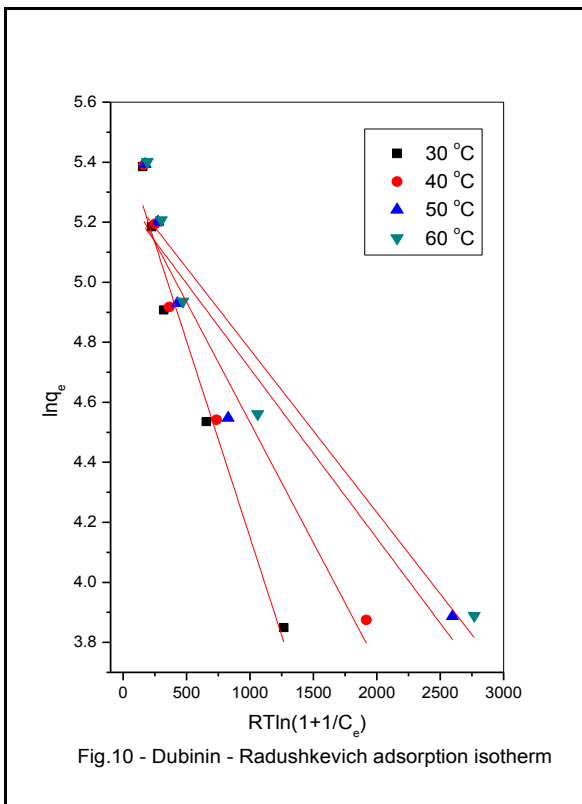


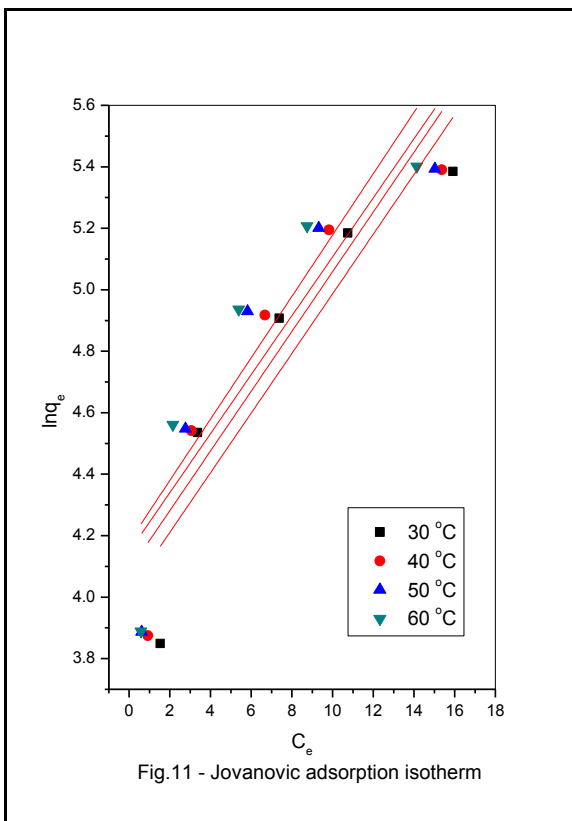Fig.10 - Dubinin - Radushkevich adsorption isotherm



Fig.11 - Jovanovic adsorption isotherm

### 3.4.8 Jovanovic Adsorption Isotherm

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

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

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

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

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

The $q_{max}$ is obtained from a plot of $\ln q_e$ and $C_e$, as shown in Fig. 11. Comparison of the experimental data and Jovanovic model is also shown in Fig. 11. Their related parameters are listed in Table 2.

By comparing the values of the error functions, it was found the Langmuir and Temkin models are best to fit the copper (II) ionadsorption on theASTNC. Both models show a high degree of correlation. This is clearly shown in Fig. 11, confirming the good fit of Langmuir and Temkin models with the experimental data for removal of copper (II) ionfrom the solution.

### 3.4.9 The Brunauer–Emmett–Teller (BET) ISO Therm Model

Brunauer–Emmett–Teller (BET) 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:

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

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

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

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) the BET model is also shown in Fig. 12.

Fig.12 - BET adsorption isotherm
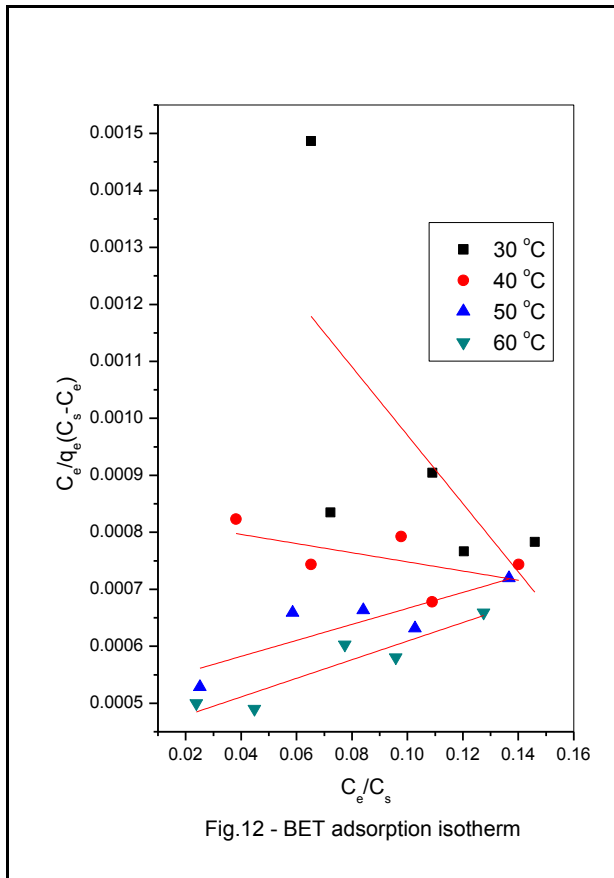
### 3.5 Adsorption Kinetics

The rate and mechanism of the adsorption process can be elucidated based on kinetic studies. Metal ion adsorption on solid surface may be explained by two distinct mechanisms: (1) An initial rapid binding of metal ion molecules on the adsorbent surface; (2) relatively slow intra-particle diffusion. To analyze the adsorption kinetics of the metal ion, the pseudo-first-order, the pseudo-second-order, and intra-particle diffusion models were applied. 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** | $dq_t/dt = k_1(q_e - q_t)$ | $\ln(q_e - q_t) = \ln q_e - k_1 t$ | (20) |
| **Pseudo-second-order** | $dq_t/dt = k_2(q_e - q_t)^2$ | $t/q_t = 1/k^2 q_e^2 + (1/q_e)t$ | (21) |

Where, $q_e$ and $q_t$ refer to the amount of copper (II)ionadsorbed (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/qtVs 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 5. According to Table 5, the value of $R^2$(0.999) related to the pseudo-second order model revealed that copper (II) ionadsorption followed this model, which is in agreement with the results obtained by Karagoz et al., Hameed et al., and

Altenor et al.. Nevertheless, pseudo-first order and pseudo-second order kinetic models cannot identify the mechanism of diffusion of metal ion into the adsorbent pores.

**Table: 3. Dimensionless Separation Factor ($R_L$) For The Adsorption Of Copper (II) ION onto ASTNC**

| ($C_i$) | Temperature °C | | | |
|---|---|---|---|---|
| | **30°C** | **40°C** | **50°C** | **60°C** |
| **10** | 0.4001 | 0.2866 | 0.2297 | 0.2126 |
| **20** | 0.2501 | 0.1672 | 0.1297 | 0.1190 |
| **30** | 0.1819 | 0.1181 | 0.0904 | 0.0826 |
| **40** | 0.1429 | 0.0913 | 0.0694 | 0.0632 |
| **50** | 0.1177 | 0.0744 | 0.0563 | 0.0512 |

**Table: 4. Thermodynamic Parameter for The Adsorption of Copper (II) ION onto ASTNC**

| ($C_0$) | $\Delta G^0$ | | | | $\Delta H^0$ | $\Delta S^0$ | $E_a$ | $S^*$ |
|---|---|---|---|---|---|---|---|---|
| | **30°C** | **40°C** | **50°C** | **60°C** | | | | |
| **10** | -3413.7 | -4412.4 | -5102.5 | -5323.5 | -16.161 | 65.172 | 13547.3 | 0.0009 |
| **20** | -3862.5 | -4218.1 | -4594.5 | -5323.4 | -10.4873 | 47.128 | 8891.57 | 0.0053 |
| **30** | -3081.5 | -3473.3 | -3981.8 | -4324.1 | -9.77390 | 42.418 | 7826.11 | 0.0102 |
| **40** | -2913.6 | -3285.5 | -3554.4 | -3865.2 | -6.55385 | 31.316 | 5122.87 | 0.0311 |
| **50** | -2429.3 | -2628.2 | -2788.7 | -3087.9 | -4.02044 | 21.239 | 2968.80 | 0.0853 |

**Table: 5. The Kinetic Parameters for the Adsorption of Copper (II) ION onto ASTNC**

| $C_0$ | Temp °C | Pseudo second order | | | | Elovich model | | | Intraparticle diffusion | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $q_e$ | $k_2$ | $\gamma$ | $h$ | $\alpha$ | $\beta$ | $\gamma$ | $K_{id}$ | $\gamma$ | $C$ |
| **10** | **30** | 16.1048 | 0.0161 | 0.9899 | 4.1806 | 1.7E-25 | 3.56E+00 | 0.9962 | 0.0171 | 0.9900 | 1.8894 |
| | **40** | 18.1990 | 0.0098 | 0.9900 | 3.2322 | 1.0E+02 | 4.79E-01 | 0.9889 | 0.1369 | 0.9892 | 1.6769 |
| | **50** | 18.1772 | 0.0165 | 0.9957 | 5.4641 | 5.4E+03 | 7.17E-01 | 0.9891 | 0.0854 | 0.9920 | 1.7832 |
| | **60** | 18.1811 | 0.0176 | 0.9927 | 5.8266 | 1.0E+04 | 7.56E-01 | 0.9902 | 0.0806 | 0.9931 | 1.7934 |
| **20** | **30** | 36.2614 | 0.0034 | 0.9961 | 4.5281 | 4.9E+01 | 2.00E-01 | 0.9945 | 0.1734 | 0.9953 | 1.5931 |
| | **40** | 36.5103 | 0.0038 | 0.9907 | 5.1142 | 7.3E+01 | 2.10E-01 | 0.9900 | 0.1615 | 0.9920 | 1.6237 |
| | **50** | 36.8663 | 0.0044 | 0.9941 | 5.9442 | 1.2E+02 | 2.20E-01 | 0.9895 | 0.1495 | 0.9946 | 1.6565 |
| | **60** | 37.3643 | 0.0049 | 0.9902 | 6.8752 | 2.8E+02 | 2.43E-01 | 0.9912 | 0.1305 | 0.9963 | 1.7005 |
| **30** | **30** | 49.3782 | 0.0037 | 0.9910 | 9.0685 | 6.7E+02 | 2.00E-01 | 0.9949 | 0.1187 | 0.9903 | 1.6642 |
| | **40** | 51.1039 | 0.0041 | 0.9968 | 10.6000 | 5.5E+02 | 1.84E-01 | 0.9890 | 0.1245 | 0.9894 | 1.6765 |
| | **50** | 53.1279 | 0.0034 | 0.9953 | 9.6894 | 2.3E+02 | 1.58E-01 | 0.9913 | 0.1428 | 0.9886 | 1.6572 |
| | **60** | 52.7379 | 0.0050 | 0.9969 | 13.8616 | 9.6E+02 | 1.86E-01 | 0.9891 | 0.1176 | 0.9888 | 1.7123 |
| **40** | **30** | 65.3124 | 0.0037 | 0.9943 | 15.7185 | 5.4E+02 | 1.36E-01 | 0.9929 | 0.1313 | 0.9907 | 1.6546 |
| | **40** | 66.8058 | 0.0035 | 0.9902 | 15.4333 | 5.5E+02 | 1.34E-01 | 0.9906 | 0.1313 | 0.9916 | 1.6626 |
| | **50** | 67.4525 | 0.0037 | 0.9932 | 16.8214 | 7.5E+02 | 1.37E-01 | 0.9953 | 0.1258 | 0.9937 | 1.6789 |
| | **60** | 68.4127 | 0.0037 | 0.9963 | 17.3124 | 8.6E+02 | 1.37E-01 | 0.9909 | 0.1236 | 0.9948 | 1.6891 |
| **50** | **30** | 77.3320 | 0.0022 | 0.9910 | 12.9515 | 4.9E+02 | 1.16E-01 | 0.9911 | 0.1323 | 0.9935 | 1.6101 |
| | **40** | 78.3805 | 0.0021 | 0.9970 | 13.0655 | 4.9E+02 | 1.14E-01 | 0.9904 | 0.1327 | 0.9956 | 1.6150 |
| | **50** | 78.5508 | 0.0023 | 0.9904 | 14.1083 | 8.0E+02 | 1.21E-01 | 0.9911 | 0.1235 | 0.9903 | 1.6351 |
| | **60** | 80.2982 | 0.0021 | 0.9928 | 13.5178 | 5.6E+02 | 1.13E-01 | 0.9940 | 0.1304 | 0.9903 | 1.6298 |

### 3.5.1 Simple Elovich Model

The simple Elovich model is expressed in the form,

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

Where, $q_t$ is the amount adsorbed at time t, α and β are the constants obtained from the experiment. A plot of $q_t$ against ln t should give a linear relationship for the applicability of the simple Elovich kinetic. The following figure shows the simple Elovich kinetics of copper (II) ionon to ASTNCfor various initial concentrations (25, 50, 75, 100, 125 and 250 mg/L) of volume 50 mL (each), adsorbent dose 0.025g, temperature 28°C and pH 6.5

### 3.5.2 Intra-Particle Diffusion Model

The adsorption process on a porous adsorbent is generally a multi-step process. In order to analyze the mechanism of the adsorption of copper (II) ionbyASTNC, the experimental data were tested against the intra-particle diffusion model. The adsorption mechanism of the adsorbate on to the adsorbent follows three consecutive steps: mass transfer across the external film of liquid surrounding the particle, adsorption at the surface of pores and the intra-particle diffusion. The slowest of these steps determines the overall rate of the process. The possibility of intra-particle diffusion resistance which could affect the adsorption is explored by using the intra-particle diffusion model given in the equation,

$$q_t = K\, t^{1/2} + I \qquad ..................(23)$$

Where, K is the intra-particle diffusion rate constant and I is the intercept. A plot of $q_t$ against $t^{1/2}$ is drawn to analyze the possibility of intra-particle diffusion as the ratedetermining step. A two stage adsorption mechanism with first was rapid and second was slow has been observed from the experimental data. The plot of $q_t$ against $t^{1/2}$ is multi-linear and deviating from the origin, indicating more than one process has affected the adsorption. Hence, the first portion of the plot indicates the external mass transfer and the second portion is due to intra-particle or pore diffusion.

### 3.6 Thermodynamic Treatment of The Sorption Process

In order to study the feasibility of the adsorption process, the thermodynamic parameters such as free energy, enthalpy and entropy changes can be estimated from the following equations.

$$K_c = C_{Ae}/C_e \qquad ............... (24)$$

$$\Delta G^o = -RT\, \ln K_c \qquad ........... (25)$$

$$\text{Log } K_c = \Delta S^o/2.303R - \Delta H^o/2.303RT \qquad ............. (26)$$

Where $C_e$ is the equilibrium concentration in solution in mg/L and $C_{Ae}$ is the equilibrium concentration on the sorbent in mg/L and $K_c$ is the equilibrium constant. The Gibbs free energy ($\Delta G^o$) for the adsorption of copper (II) iononto biomass at all temperatures was obtained from Eq.24 and is presented in Table 4. The values of $\Delta H^o$ and $\Delta S^o$ were calculated from the slope and intercept of the plot log $K_c$ against 1/T (Figure not shown) and are also listed in Table 4.

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:

$$\theta = \left( 1 - \frac{C_e}{C_i} \right) ............... (27)$$

$$S^* = (1 - \theta)_e\, \frac{-E_a}{RT} ........... (28)$$

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 (Figure not shown) and are listed in Table 4.

From Table 4 it is clear that the reaction is spontaneous in nature as $\Delta G^o$ values are negative at all the temperature studied. Again positive $\Delta H^o$ value confirms that the sorption is endothermic in nature. The positive value of $\Delta S^0$ reflects the affinities of the adsorbents for thecopper (II) ion. The value of Ea was found to be 217.59 kJ mol$^{-1}$ for the adsorption of copper (II) iononto biomass. The positive value of $E_a$ indicates the endothermic nature of the adsorption process which is in accordance with the positive values of $\Delta H^o$. The result as shown in Table 4 indicate that the probability of the copper (II) ionto stick on surface of biomass is very high as S*$<<$ 1, these values confirm that, the sorption process is physisorption.

## Conclusion

The efficiency of ASTNCas a cheap adsorbent and the results revealed that ASTNCwas an appropriate adsorbent for removing copper (II) ion from the aquatic environments. pH also plays a major role in removing the copper (II) ion. The findings of the present study also showed that as the contact time increased, the metal ion's primary concentration as well as the dose of the intended adsorbate of the adsorption efficiency increased, as well. Adsorption equilibrium data follows Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherm models. The equilibrium data's were fitted very well in the Langmuir and BET isotherm equation. The kinetic study of copper (II) ion on to ASTNCwas performed based on pseudo-first-order, pseudo-second-order and intra-particle diffusion equations. The data's indicate that the adsorption kinetics follow the pseudo-second-order rate. This study concludes that the ASTNCcould be employed as an appropriate, inexpensive, accessible and low-cost adsorbent for the removal of copper (II) ion from aquatic environments.

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