BIOSORPTION STUDIES ON CU(II) IONS USING POWDERED LEAVES OF HIBISCUS ROSA-SINENSIS AND TABERNAEMONTANA DIVARICATA AS ADSORBENTS

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Abstract

The commonly used process of heavy metal removal is chemical precipitation, electro winnowing etc., in this study low-cost biosorbents such as the leaf powders of Hibiscus rosa-sinensis and Tabernaemontana divaricata were used for the study of Cu(II) metal ions removal. The experiment was performed by using batch experiments. The effect of concentration, dosage, and time variations was checked. According to the results highest percentage of adsorption attained by Hibiscus rosa-sinensis was 95% at 750mg dosage of adsorbent and time of contact at 30 min. The regression value is indicating that the order of all used isotherm models such as Freundlich, Langmuir and Temkin. The characterization of adsorbents was done by using FT-IR spectral analysis.

Keywords: *Biosorption, Biosorbent, Batch experiment, characterization, isotherm*

INTRODUCTION

Water contamination by trace metals is rapidly growing due to increasing human activities in the mining, agriculture and manufacturing industries. The trace metals are non-biodegradable, highly toxic and cannot be detoxified biologically [1]. Biologically copper is an essential trace element for the terrestrial green plants and algae under the concerned limits and involves in photosynthesis, it is a cofactor of oxidase, oxygenase and enzymes such as superoxide dismutase and acrobat oxidase [2]. Researchers have reported that water discharged from copper electroplating industries, textile industries or washing effluents may contain up to 500mg^{-1} copper [3]. Therefore it is necessary to remove Cu ions from industrial wastewater before discharging them into natural water bodies. The conventional methods used for the removal of heavy metals include chemical precipitation, lime coagulation, ion exchange etc.., [4]. Biosorption is an alternative process for the uptake of heavy metals from aqueous solutions by biological materials. The biosorption of metals by biomass has been much explored in recent years. Different forms of inexpensive, non-living plant materials such as agricultural waste materials and seaweeds, molds, yeasts and other dead microbial biomass have been widely investigated as a potential biosorbents for heavy metals [5,6]. In this study, we used the leaf powders of *Hibiscus rosa-sinensis* and *Tabernaemontana divaricata* are used as the biosorbent. It is considered economic and eco-friendly due to its unique chemical composition, availability in abundance, renewable, low in cost and more efficient for heavy metal remediation.

MATERIALS AND METHODS
Preparation of adsorbent

Hibiscus rosa-sinensis and *Tabernaemontana divaricata* leaves were selected as adsorbents for the removal of Cu(II) ions in this study. The leaves were obtained from the concerned plants located in

nearby areas of Nagercoil. *Hibiscus rosa-sinensis* and *Tabernaemontana divaricata* leaves were collected and each leaf was washed thoroughly under running tap water to remove dust and any adhering particles. The leaves were then dried under sunlight for a few days and then in an oven at 80 ºC until they become crisp. The dried leaves were crushed and blended to powder form using a blender. The *Hibiscus rosa-sinensis* and *Tabernaemontana divaricata* leaves powder were boiled and washed several times until it was free of color and turbidity. Then the powder was dried in an oven at 80 ºC overnight and stored in airtight plastic for further use to avoid contact with moisture in the atmosphere.

Fig: 2.1.1 leaves of *Hibiscus rosa-sinesis*

Fig: 2.1.2 Powdered leaves of *Hibiscus rosa-sinesis*

Fig: 2.1.3leaves of *Tabernaemontana divaricata*

Fig: 2.1.4 Powdered leaves of *Tabernaemontana divaricata*

Preparation of adsorbate
A stock solution of Cu (II) ions was prepared from the salts of Copper sulfate ($CuSO_4.5H_2O$) in double distilled water. The amount of 3.921 g of $CuSO_4.5H_2O$ is making up to 1000 mg/L. The amount of copper sulfate before and after biosorption is estimated by using Iodometric titration.

Adsorption experiment
Batch experiments were carried out by shaking a series of bottles containing various amounts of the different adsorbents such as *Hibiscus rosa-sinensis* and *Tabernaemontana divaricata* in heavy metal ion solutions like Cu(II) and separately. The experiment is varied with the effect of initial concentration, the effect of adsorbent dosage and the effect of contact time. The solution bottles were agitated for one hour until equilibrium was attained, at the end of the mixing of the adsorbent particles with the adsorbate, the whole mixture was separated from the suspension by filtration through a Whatman filter paper. The percentage of metal removal was calculated by using the formula,

% Biosorption = ($Co - Ce$ **)/$Co \times 100$**

Where, C_o =Initial concentration of metal ion; C_e = Concentration of metal ion at equilibrium state. Freundlich, Langmuir and Temkin isotherms were also applied to explain the relationship between adsorbent and adsorbate. The characterization of the adsorbent was studied by using FT-IR analysis.

RESULT AND DISCUSSION
Effect of initial concentration
The effect of the initial concentration of adsorbate ion is studied by taking 20mg, 40mg, 60mg, 80mg & 100mg with an adsorbent dosage of 150mg, constant room temperature (27.5 C), Constant time (60mins) and constant rotation per minute (150rpm). The adsorption percentage of Cu(II) ion on *Hibiscus rosa-sinensis* leaves was decreased by 55%, 37.5%, 33%, 18.75% & 14% and *Tabernaemontana*

divaricata leaves were also decreased by 45%, 32.5%, 25%, 15% & 12% while the initial concentration increased were depict in Fig: 3.1.1 & 3.1.2.

The percentage of adsorption of the metal ion by *Tabernaemontana divaricata* leaves was lower by comparing the adsorption percentages of *Hibiscus rosa-sinensis* leaves and the adsorption percentage of Cu(II) ion on *Hibiscus rosa-sinensis* leaves were higher than *Tabernaemontana divaricata* leaves in every varying concentration of metal ion this is because at lower concentration the number of Cu(II) ion is low when compared to the available adsorbent active sites, therefore, adsorption is more frequent.
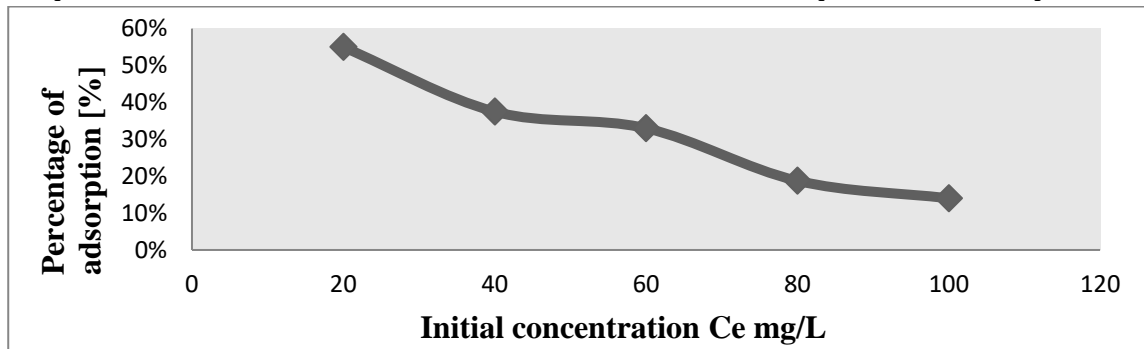
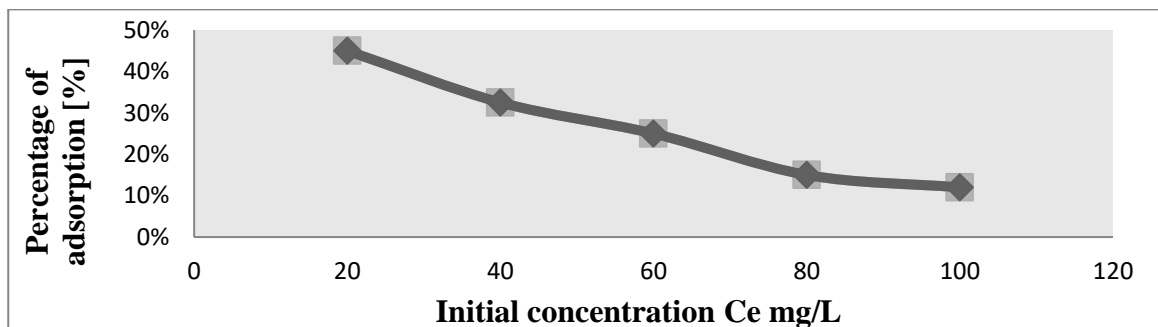**Fig:3.1.1 plot of percentage of adsorption Vs initial concentration for *Hibiscus rosa-sinesis leaves***

Fig:3.1.2 plot of percentage of adsorption Vs initial concentration for *Tabernaemontana divaricata* leaves

Effect of adsorbent dosage

In this study, five different dosages were recommended 150mg, 300mg, 450mg, 600mg, and 750mg respectively. The process of adsorption was carried out under the identical initial metal ion concentration condition (20mg), constant room temperature (27.6°), constant contact time (60 min) and constant rotation per minute (150 rpm). The adsorption percentage of Cu(II) ions on Hibiscus Rosasinesis leaves increased by 55%, 75%, 80%, 85% & 95% and Tabernaemontana divaricata leaves were also increased by 45%, 60%, 65%, 70%, & 75% at beginning adsorption increases rapidly after a particular dosage 300mg the percentage of adsorption increases in a gradual manner is depicted in Fig: 3.2.1 & 3.2.2

The above results concluded that the adsorbent dosage increase and the adsorption of Cu(II) ions in *Hibiscus rosa-sinensis* and *Tabernaemontana divaricata* leaves as adsorbent. The equilibrium value of the amount adsorbed (q_e) also decreases. This is because of the increase in the amount of adsorbent and also there is an increase in the number of available adsorption sites which directly increases the rate of adsorption. The number of metal ions adsorbed to the adsorbent unit mass decreases and causes q_e

value to decrease as the adsorbent dosage increases. The maximum percentage removal of Cu(II) ion was 95% by Hibiscus rosa-sinensis leaves as adsorbent.
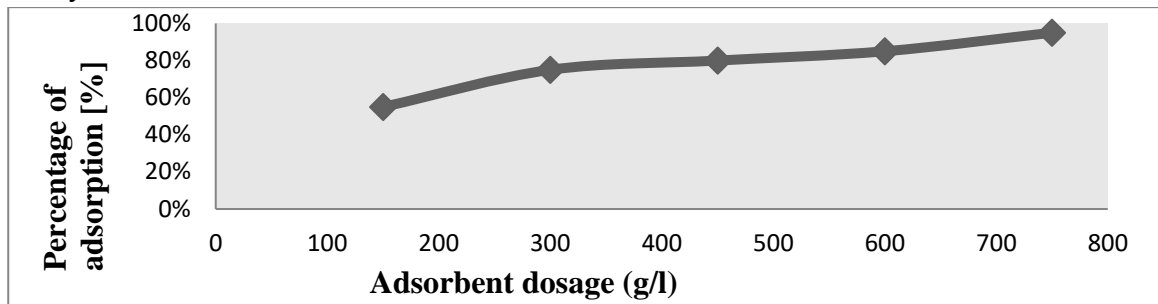

Fig:3.2.1 plot of percentage of adsorption Vs adsorbent dosage
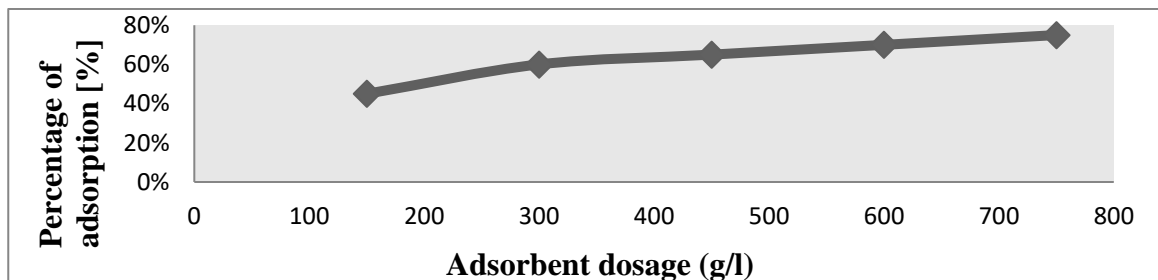**for *Hibiscus rosa-sinensis leaves***

Fig:3.2.2 plot of percentage of adsorption Vs adsorbent dosage for
***Tabernaemontana divaricata* leaves**

Effect of contact time

The recommended contact time for this study ranged from 30-150 minutes, at time intervals of 30 minutes. In this study, the effect of the contact time of the adsorption of Cu(II) ions was carried out at identical initial metal concentration conditions (20mg), constant temperature (27,6 C), constant rotation per minute (150rpm) and constant adsorbent dosage (150mg).

The percentage of adsorption on *Hibiscus rosa-sinensis* leaves is maximum at 30min is 75% after that the adsorption percentage remains constant at 67% and *Tabernaemontana divaricata* leaves are maximum at 90min at 60% but from the initial time at 30min adsorption is only 55% after that its tends to decrease till 35% this may be due to the availability of the active sites and uncovered surface on the adsorbent (Here dosage keeps constant as 300mg). After 60minutes adsorption was not rapid and become about constant due to the saturation of available binding sites with the metal ions depict in Fig: 3.3.1 & 3.3.2   From the above results, the contact time increase there is a variable percentage of adsorption is observed that it reaches the saturation the variation occurs after the maximum percentage of adsorption it remains constant by decreasing or increasing manner the highest percentage of adsorption is achieved by *Hibiscus rosa-sinensis* leaves as 75% at 30min contact time which may due to availability of saturation sites and higher dosage.
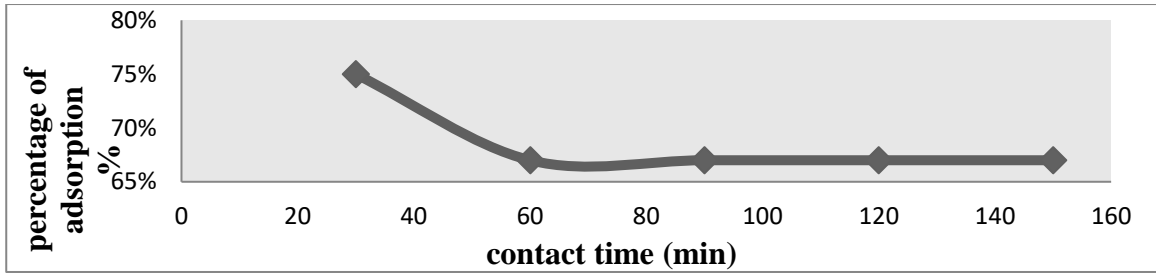
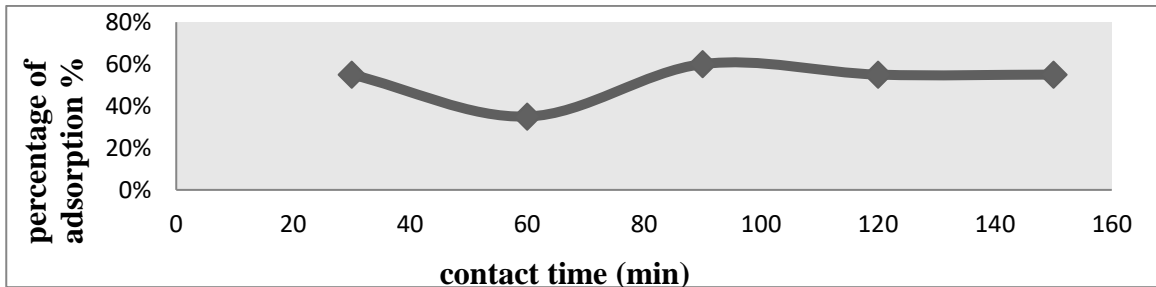**Fig:3.3.1 plot of percentage of adsorption Vs contact time for *Hibiscus rosa-sinensis* leaves**

Fig:3.3.2 plot of percentage of adsorption Vs contact time for *Tabernaemontana divaricata* leaves

Freundlich Isotherm

The mathematical form of the Freundlich equation is given by the following equation,

$$\log qe = \log kf + \left(\frac{1}{n}\right) \log Ce$$

Where, C_o =Initial concentration of metal ion; C_e = Concentration of metal ion at equilibrium state; K_f = Freundlich constant; n = order of reaction; qe = amount of adsorbate adsorbed per unit mass of adsorbent. The value of K_F is 3.7584 and 1/n is 0.061 for *Hibiscus rosa-sinensis* leaves and K_F is 2.4434 and 1/n is 0.135 for *Tabernaemontana divaricata* leaves is calculated from slope and intercept of the plot log q_e vs log C_e in Fig 7&8. The value of 1/n is less than 1 and R^2 = 0.046 shows favorable adsorption by *Hibiscus rosa-sinensis* leaves and 1/n is less than 1 and R^2 = 0.364 shows favorable adsorption by *Tabernaemontana divaricata* leaves.
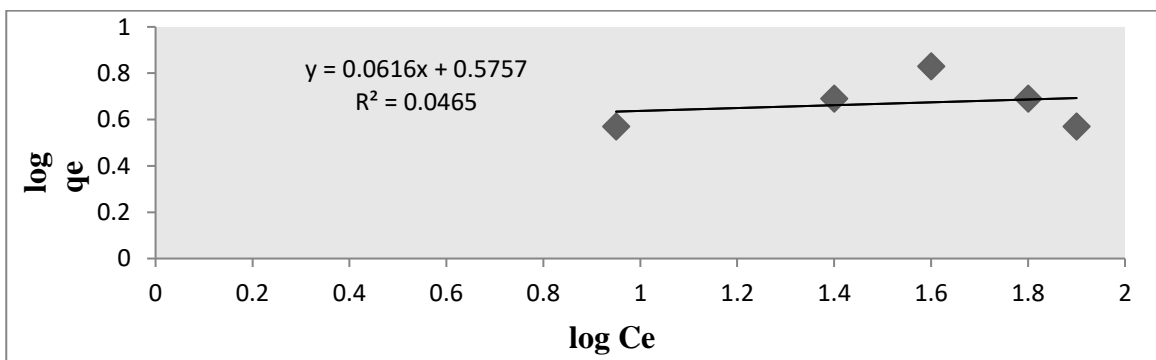

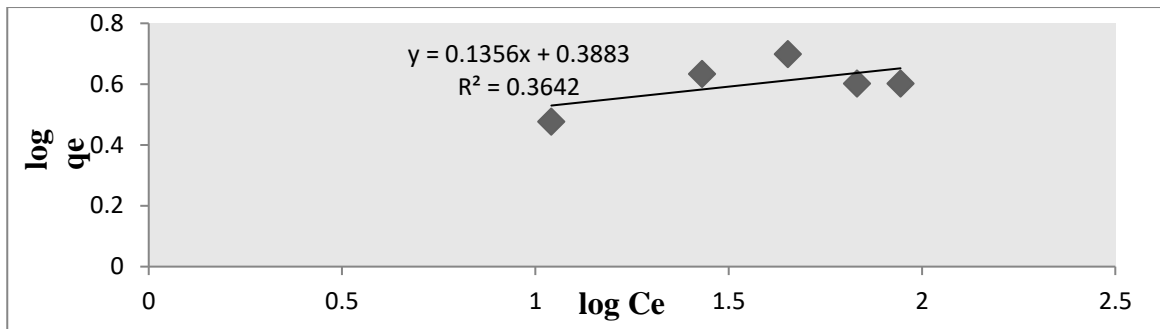**Fig 3.4.1 : Freundlich plot for Cu(II) loaded *Hibiscus rosa-sinesis* leaves**

Fig 3.4.2 : Freundlich plot for Cu(II) loaded *Tabernaemontana divaricata* leaves

Langmuir Isotherm

Mathematically the linear form of the Langmuir equation is given below.

$$\frac{Ce}{qe} = \frac{1}{aKL} + \frac{Ce}{KL}$$

Where, C_o =Initial concentration of metal ion; C_e = Concentration of metal ion at equilibrium state; qe = amount of adsorbate adsorbed per unit mass of adsorbent;

a, K_L= adsorption capacity and rate of adsorption.

When C_e/q_e plot against C_e a straight line with a slope of $1/K_L$ was obtained. The characteristics of the Langmuir isotherm model are expressed in terms of the dimensionless parameter (RL). This parameter is mathematically defined as R_L = 1+ aCo where, a = Langmuir constant, C_o = initial concentration of copper ions the value of R_L indicates the type of isotherm is either favorable (0<R_L<1), unfavorable (R_L>1), linear (R_L = 1) or irreversible (R_L = 0).

The value of K_L and a for *Hibiscus rosa-sinensis* leaves were found to be 3.8314 and -1.408 and for *Tabernaemontana divaricata* leaves are 4.0816 and -1.75. The value of R_L was found to be less than one and this confirms that Langmuir isotherm model is fitted for the adsorption of Cu (II) onto *Hibiscus rosa-sinensis* leaves and *Tabernaemontana divaricata* leaves. The value of regression R^2 is found as 0.921, 0.977 and indicating the copper favors the Langmuir isotherm model and monolayer adsorption onto the surface of *Hibiscus rosa-sinesis* and *Tabernaemontana divaricata* leaves depict in Fig: 3.5.1 & 3.5.2
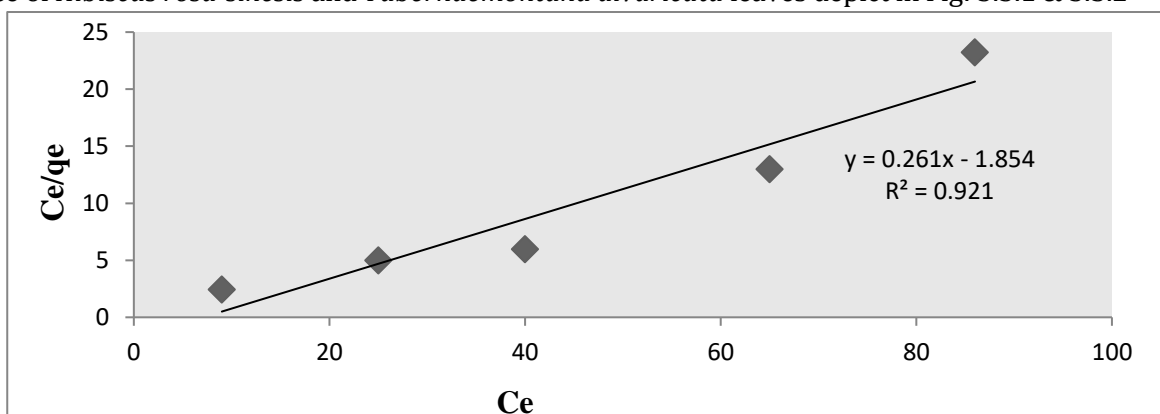

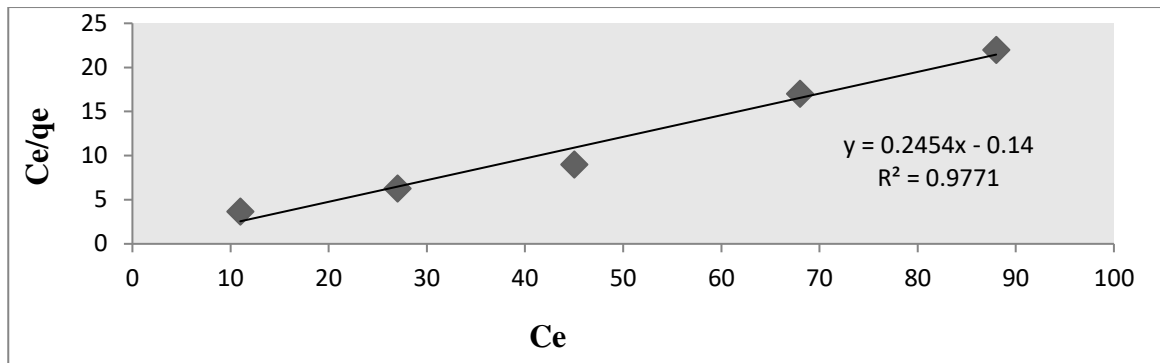**Fig 3.5.1: Langmuir plot for Cu(II) loaded *Hibiscus rosa-sinensis* leaves**

Fig 3.5.2 : Langmuir plot for Cu(II) loaded *Tabernaemontana divaricata* leaves

Temkin Isotherm

The Temkin isotherm model explains the influence of metal-metal interaction on the surface of biosorbent. Therefore, the heat of biosorption of metal sorbate on the surface decreases linearly with the occupation due to metal-metal interactions. This linear form of Temkin isotherm is given by the following expression:

$$q_e = a + b \ln C_e$$

Where, C_e = Concentration of metal ion at equilibrium state; q_e = amount of adsorbate adsorbed per unit mass of adsorbent; a,b = isothermal constants related to binding capacity and Temkin constant. The value of 'a' and 'b' can be obtained from the plot of qe vs ln Ce.
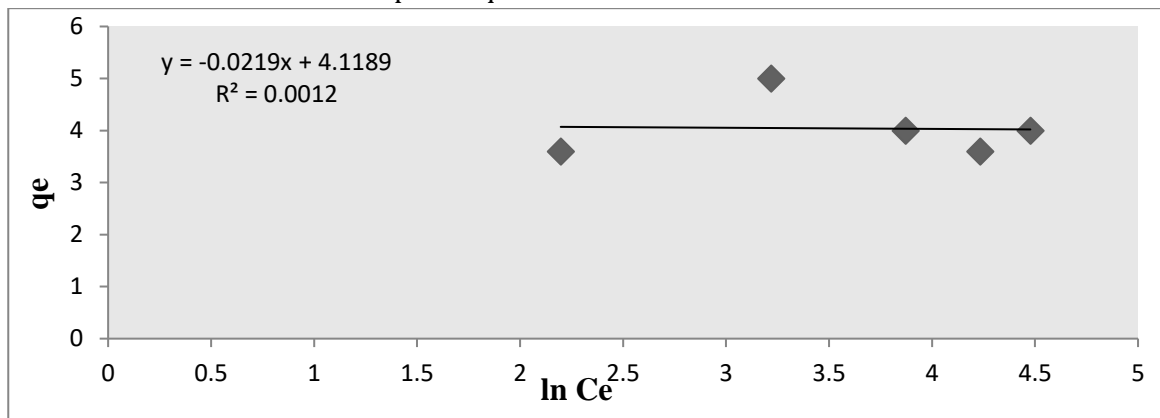

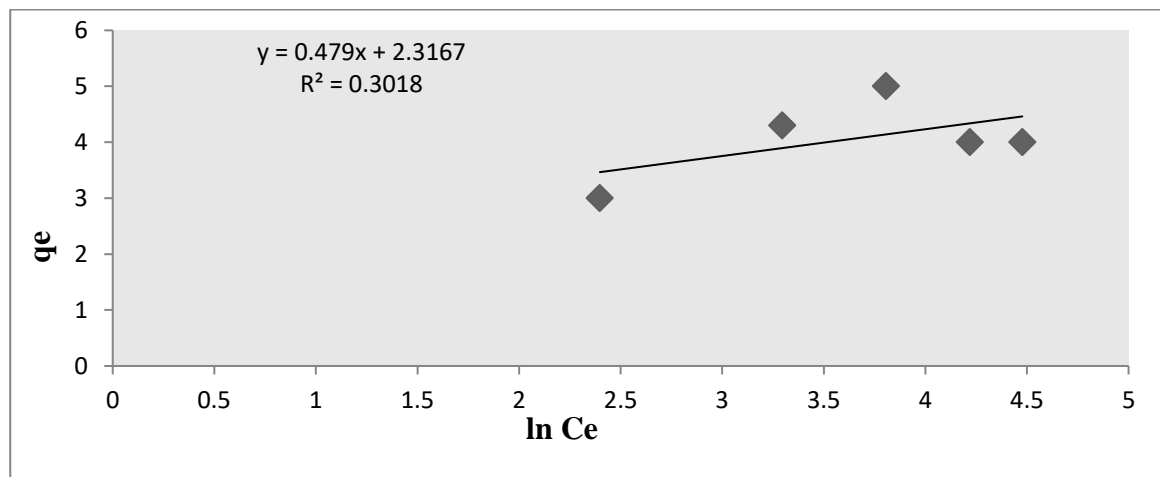**Fig: 3.6.1 Temkin isotherm plot for Cu(II) loaded Hibiscus rosa-sinensis**

Fig: 3.6.2 Temkin isotherm plot for Cu (II) loaded *Tabernaemontana divaricata* leaves

CHARACTERIZATION OF ADSORBENT

FT-IR spectral analysis is used to study the charactrestic functional group which is responsible for adsorbing metal ions. The FT-IR spectra of *Hibiscus rosa-sinensis* and Tabernaemontana *divaricata* before and after adsorption on Cu(II) ions were studied below.

According to Figure 3.7.1 before the biosorption of Cu(II)ions on *Hibiscus rosa-sinensis* leave shows the broadband near 3412 cm^{-1} due to O-H vibration in the hydroxyl group. The peak at 2855 cm^{-1} and 2924 cm^{-1} is assigned to C-H stretching. The band at 1644 cm^{-1} represents N-H stretching. The peak at 1383 cm^{-1} and 1321 cm^{-1} is due to the deformation of CH_3 and the stretching of C=O. The band at 1245 cm^{-1} and 1053.61 cm^{-1} is due to C-O stretching and C-OH stretching and bending. After the biosorption of Cu(II) ions variation of the FT-IR spectrum is observed in Fig 3.7.2 broad intense band near 3419 cm^{-1} due to O-H vibration in the hydroxyl group the peak becomes more intense due to the presence of copper ions in salt used for the analysis. C-H stretching peak shifted and become intense at 2922 cm^{-1} and 2852 cm^{-1}. The N-H stretching band shifted at 1632 cm^{-1} represents. The deformation of CH_3 and stretching of the C=O peak shifted to 1384 cm^{-1} and 1318 cm^{-1}. C-O stretching and C-OH stretching and bending bands shifted at 1241 cm^{-1} and 1156 cm^{-1}.
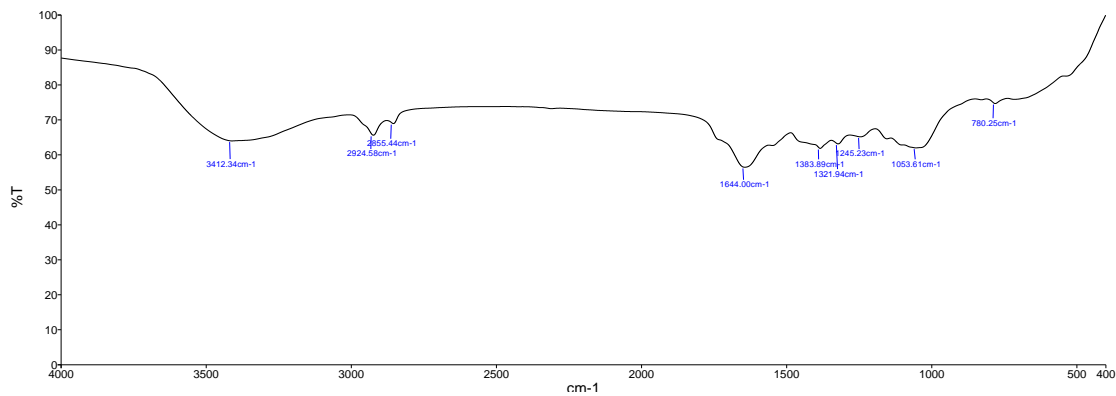

Fig: 3.7.1 FT-IR spectrum of *Hibiscus rosa-sinesis* before biosorption of Cu (II) ions
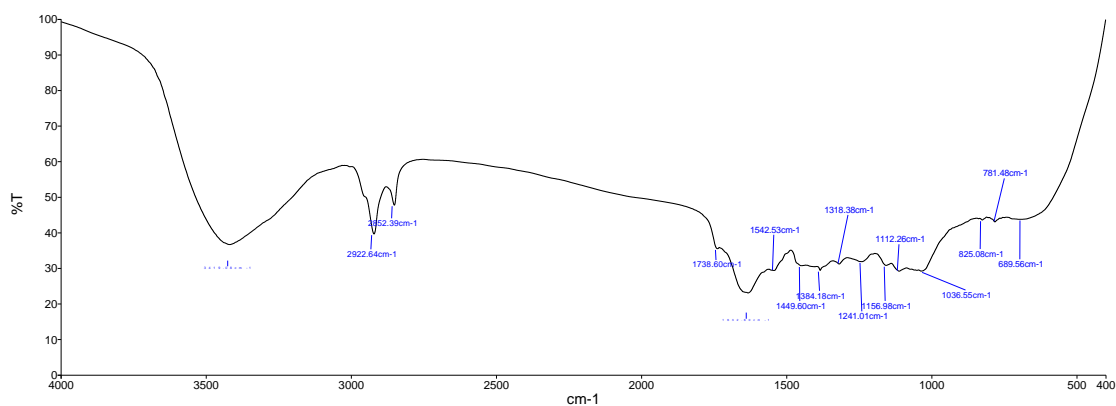

Fig: 3.7.2 FT-IR spectrum of *Hibiscus rosa-sinesis* after biosorption of Cu(II) ions

According to Figure 3.7.3 before biosorption of Cu (II) ions on *Tabernaemontana divaricata* leaves shows a broad band near 3406 cm^{-1} due to O-H vibration in the hydroxyl group. The peak at 2921 cm^{-1} and 2851 cm^{-1} are assigned to C-H stretching. The band at 1619 cm^{-1} represents N-H stretching. The peak at 1374 cm^{-1} and 1318 cm^{-1} is due to the deformation of CH_3 and the stretching of C=O. The band at 1248 cm^{-1} and 1062 cm^{-1} is due to C-O stretching & bending and C-OH stretching & bending. After the biosorption of Cu (II) ions a variation of the FT-IR spectrum is observed in Fig 3.7.4 broad intense band

near 3416 cm⁻¹ due to O-H vibration in the hydroxyl group the peak becomes more intense due to the presence of copper ions in salt used for the analysis. C-H stretching peak shifted and become intense at 2923 cm⁻¹ and 2854 cm⁻¹. The N-H stretching band shifted at 1640 cm⁻¹ represents. The deformation of CH_3 and stretching of the C=O peak shifted to 1383 cm⁻¹ and 1318 cm⁻¹. C-O stretching and C-OH stretching and bending bands shifted at 1239 cm⁻¹ and 1105 cm⁻¹.
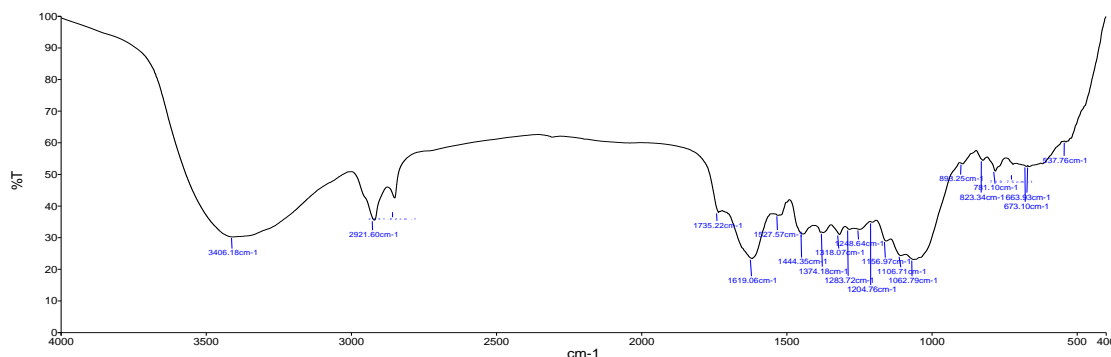

Fig: 3.7.3 FT-IR spectrum of *Tabernaemontana divaricata* leaves before biosorption of Cu (II) ions
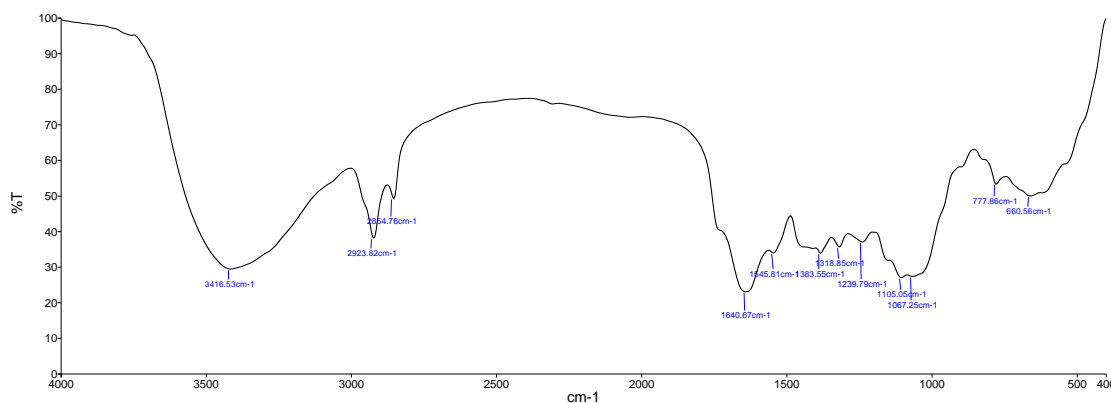

Fig: 3.7.4 FT-IR spectrum of *Tabernaemontana divaricata* after biosorption of Cu(II) ions

CONCLUSION

This work aim is to find the possible use of *Hibiscus rosa-sinensis* and *Tabermontana divaricata* leaves powder as adsorbent for biosorption of Cu(II) ions from an aqueous solution. All the equilibrium concentrations perfectly fitted with Langmuir, Freundlich and Temkin adsorption isotherms the highest percentage of adsorption attained by *Hibiscus rosa-sinensis* was 95% at constant time and a high adsorbent dosage of 750mg. According to the variation in the FT-IR spectra before and after adsorption considered that ion-exchange was a major adsorption mechanism and a certain amount of surface complexation mechanism coexisted. The overall results indicate that both *Hibiscus rosa-sinensis* and *Tabermontana divaricata* leaves are an effective, low cost and renewable biosorbents for the biosorption of Cu(II) ions from aqueous solution. However *Hibiscus rosa-sinensis* leaves were much efficient adsorbent than *Tabermontana divaricata* leaves.

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