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Batch Adsorption Study for the Removal of Copper (II) Ion From Aqueous Solution Using *Ficus Bengalensis Leaf Powder*

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Abstract

Presence of copper in the water used for various activities affects living beings in its own way depending on its concentration. Considering the effects of high dose of copper concentration on humans and animals, it is important to remove this metal ion from industrial effluent before discharge to environmental stream. Adsorption of Copper (II) ions from aqueous solution onto a low cost adsorbent- Ficus bengalensis leaf powder was investigated to evaluate the effects of pH, effect of contact time, initial copper ion concentration, effect of temperature and adsorbent dose on the removal of Cu(II) systematically. Adsorption data was modeled using the Langmuir and Freundlich adsorption isotherm. The adsorption kinetics was found to follow pseudo-second-order rate kinetic model, with a good correlation (R^2 > 0.981). Thermodynamic parameters (ΔG°, ΔS° and ΔH°) for sorption system were determined at 30^0C.

Key words: Ficus bengalensis, heavy metal ion, adsorption, isotherms, kinetics.

Introduction

The release of heavy metals into our environment is still large. In certain areas of the world it is even increasing. The pollution of water resources due to the disposal of heavy metals has been an increasing worldwide concern for the last few decades. It is well known that some metals can have poisonous or otherwise toxic to human beings and ecological environments, include chromium, antimony, copper, lead, mercury, cadmium, manganese , etc [1-3].

Since copper is a widely used material, there are many actual or potential sources of copper pollution. Copper may be found as contaminant in food, especially shellfish, liver, mushrooms, nuts, and chocolate. Briefly, any processing or container using copper material may contaminate the product such as food, water or drink. Copper is essential to human life and health but, like all heavy metals, is potentially toxic as well. For example, continued inhalation of copper-containing spray is linked with an increase in lung cancer among exposed workers.

There are various methods for removing heavy metals including chemical precipitation, membrane filtration, ion exchange, liquid extraction or electrodialysis [4, 5]. However, these methods are not widely used due to their high cost and low feasibility for small-scale industries [6]. In contrast, the adsorption technique is one of the preferred methods for removal of heavy metals because of its efficiency and low cost. Conventional adsorbents such as granular or powdered activated carbon are not always popular as they are not economically viable and technically efficient [7]. Nonconventional materials have been tested in a large scale for this purpose, such as fly ash [8], lignite [9], tree fern [10], orange peel [11], saw dust ,bagasse [12] etc. In this paper, - Ficus bengalensis leaf powder have been used as adsorbents to remove Cu (II) form aqueous solution. Efforts have been made to use the cheapest and unconventional adsorbent to adsorb heavy metals such as Cu (II) ion form aqueous solution.

Materials and Methods

Preparation of the adsorbent

Ficus bengalensis (leaves) was collected from the local area. The leaves were washing with running tap water to remove dirt and other particulate matter. Then the leaves were dried naturally (by sun rays). After complete drying the leaves was grinded into powder, that grinded powder is sieving by using 300 micron sieve. Then sieved leaves powder was taken in 500 ml borosil beaker and treated in microwave (900 MW) for 30 minutes.

Acid treatment: This microwave assisted carbonized Ficus bengalensis leaves powder was added in one liter beaker, to this 500ml of 0.5 N sulfuric acid solution was added and the solution was shake for 5 hours in shaking machine. After complete shaking, it was filter and wash with water till it get neutralized which is checked by pH meter. It was dried in oven.

Base treatment: After acid treatment, it is treated with 0.5 N NaOH solutions. Similarly a dried leaf powder was added in 1liter beaker, to this 500 ml of 0.5 N NaOH solution was added and the solution was shake for 5 hours in shaking machine. After complete shaking, it was filter and wash with water till it get neutralized which is checked by pH meter. It was dried in oven and packed in air tight bottle.

Chemicals

Cu(II) solutions were prepared by diluting 1000 ppm of $CuSO4.5H_2O$ (Merck) stock solution with deionized water to a desired concentration range between 10 and 200 mg/L. Before mixing the adsorbent, the pH of each test solution was adjusted to the required value with 0.5 N HCl and 0.5 N NaOH solutions, respectively.

Adsorption Experiment

Batch adsorption experiments of copper were carry out to determined the adsorption capacity of Ficus bengalensis leaves powder at different metal concentrations ranging from 20 to 140 ppm and a fixed amount 0.5 gm. of Ficus bengalensis leaves activated carbon as bio - adsorbent in order to calculate the adsorption constant using different isotherms. 100ml of different concentration of copper (II) solutions ranging from 20–140 ppm were used. The microwave assisted activated carbon of Ficus bengalensis leaves was added to flasks and agitated at 30^0C and 180 rpm for 120 min for copper. The initial and final concentrations of the solutions were measured and determined by AAS at the maximum adsorption wavelength and the adsorption capacities of the adsorbent were calculated. After equilibrium was attained, the metal uptake capacity for each sample was calculated according to a mass balance on the metal ion using equation (1): $q_e = \frac{(c_o - c_e)v}{m}$ (1)

Where m is the mass of adsorbent (g), V is the volume of the solution (L), C_0 is the initial concentration of metal (mg L^{-1}), C_e is the equilibrium metal concentration (mg L^{-1}) and q_e is the metal quantity adsorbed at equilibrium (mg/g). Experiments were carried out at different initial pH values. The initial pH of the solution was adjusted with either HCl or NaOH. The percent removal of metals from the solution was calculated by the following equation (2)

$$: \% \text{ Removal } = \frac{(c_o - c_e)}{c_o} \times 100 \quad (2)$$

Where C_0 (mg/L) is the initial metal ion concentration and C_e (mg/L) is the equilibrium metal ion concentration in the solution.

Results and Discussion

Effect of pH on Cu (II) adsorption

Figure 1.1 illustrated that pH obviously influenced the removal efficiency of the copper ions in the aqueous solution. The results indicated that Cu (II) removal was increased to maximum and then decreased with pH variation from 2 to 10 at temperature 30^0C and agitation speed of 180 rpm. The maximum % removal of Cu (II) was about 89% at pH 8. Increases in metal removal with increased pH can be explained on the basis of the decrease in competition between proton and metal cations for same functional groups and by decrease in positive surface charge, which results in a lower electrostatic repulsion between surface and metal ions. Decrease in adsorption at higher pH (>pH 5) is due to formation of soluble hydroxy complexes [13]. The adsorption of Cu (II) ion was found mainly to be influenced by solution pH.

Effect of Contact time on Cu(II) adsorption

Figure 1.2 indicated that metal ions removal was increased with an increase in contact time before equilibrium was reached. All parameters such as dose of adsorbent and pH of solution were kept constant. The results indicated that Cu (II) removal was increased from 58 to 89% with the contact time variation from 120 minutes. At 120 minutes, the percentage removal of Cu (II) remains constant (89%), which showed that equilibrium was reached at 120 minutes itself. Thus the results illustrated that the optimum contact time for maximum removal (89%) of Cu (II) was 120 minutes. This result is important because equilibrium time is one of the important parameters for an economical wastewater treatment system.

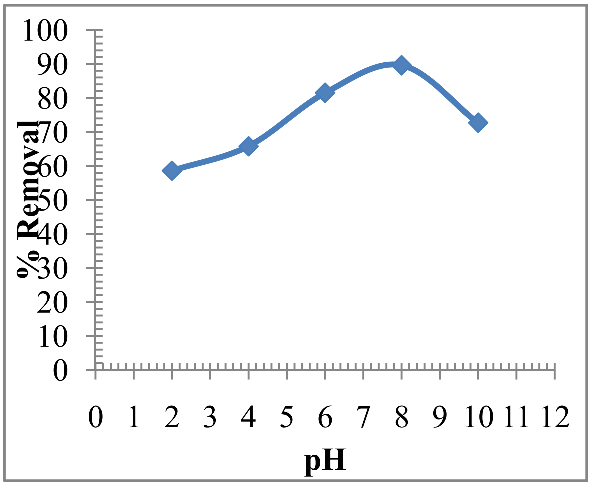

Figure 1.1 – Effect of pH on adsorption of Cu(II) of Ficus bengalensis Leaf powder. (Temp: 30^0C, C_0: 100 ppm, Adsorbent Dose : 0.5 g, Contact time: 120 minutes, Agitation speed: 180 rpm)

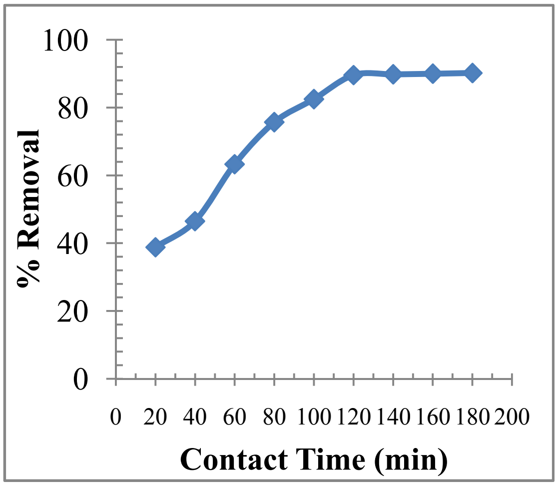

Figure 1.2 – Effect of contact time on adsorption of Cu(II) of Ficus bengalensis Leaf powder(Temp: 30^0C, pH:8 C_0: 100 ppm, Adsorbent Dose : 0.5 g, Agitation speed: 180 rpm)

Effect of adsorbent dose on Cu(II) adsorption

Adsorption efficiency of Cu (II) adsorption was studied by varying the amount of adsorbents from 0.1-1gm keeping other parameters constant. Figure 1.3 shows that removal efficiency of the copper usually improved on increasing adsorbent doses and then decreases. This may occur due to the fact that the higher dose of adsorbents in the solution provides the greater availability of exchangeable sites for the ions. From the figure 4.3 it is clear that the no further increase in adsorption after a certain amount of adsorbent was added (0.5gm). The maximum % removal of Cu (II) was about 89% at the dosage of 0.5 gm. This result also suggest that after a certain dose of adsorbent, the equilibrium conditions reached and hencethe amount of ions bound to the adsorbent and the amount of free ions in the solution remain constant even with further addition of the dose of adsorbent [14].

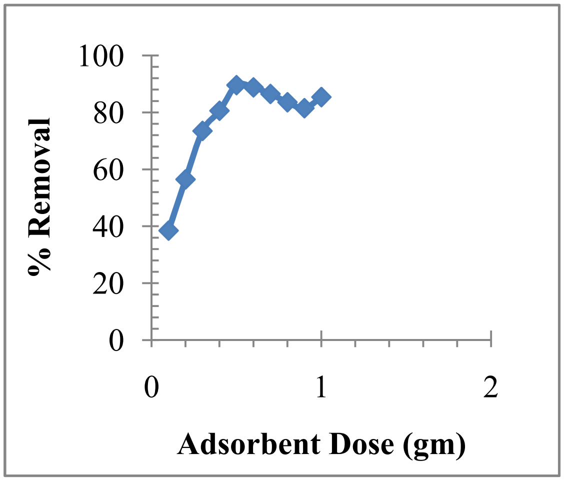

Figure 1.3 – Effect of pH on adsorption of Cu(II) of Ficus bengalensis Leaf powder (Temp: 30^{0}C, C0: 100 ppm, Adsorbent Dose : 0.5 g, Contact time: 120 minutes, Agitation speed: 180 rpm)

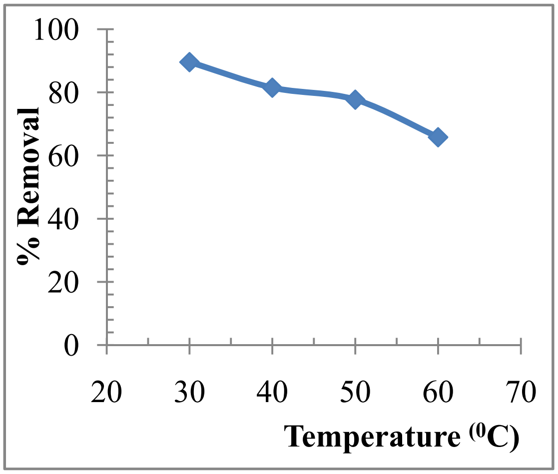

Figure 1.4 – Effect of temperature on adsorption of Cu(II) of Ficus bengalensis Leaf powder. (pH:8 C_0: 100 ppm, Adsorbent Dose : 0.5 g, contact time: 120 minutes, Agitation speed : 180 rpm)

Effect of temperature on Cu (II) adsorption

The temperature dependence of the adsorption process is related with several thermodynamic parameters. The temperature showed the negative effect on adsorption of copper onto activated carbon of Ficus bengalensis leaves as bio-adsorbent. The temperature effect on removal of copper ion using was studied within the range of 30^{0}C. Other parameters such as dose of adsorbent and pH of solution were kept constant. With increase in temperature from 30^{0}C the percent removal of copper ions was decreased from 90% to 66%. From the figure1.4, it is clear that the low temperatures are in favors of copper ion removal. This may be due to a tendency for the Copper ions to escape from the solid phase to the bulk phase with an increase in temperature of the solution. The result shows that adsorption mechanism related with removal of Copper is physical in nature. The adsorption process takes place from the electrostatic interaction, which is in general related with low adsorption heat. This implies that the adsorption process was exothermic in nature [14].

Effect of initial metal ion concentration on adsorption

The effect of initial copper concentration on the copper adsorption rate was studied in the rage 20 – 140 ppm at pH 8, temperature 30ºC, and 120 min contact time. The results presented in the figure 1.5, it was observed that the percentage of removal decreased with increasing in initial copper concentration. The poorer uptake at higher metal concentration was resulted due to the increased ratio of initial number of moles of copper to the vacant sites available. For a given adsorbent dose the total number of adsorbent sites available was fixed thus adsorbing almost the equal amount of adsorbate, which resulting in a decrease in the removal of adsorbate, consequent to an increase in initial copper concentration. Therefore it was evident from the results that copper adsorption was dependent on the initial metal concentration [14].

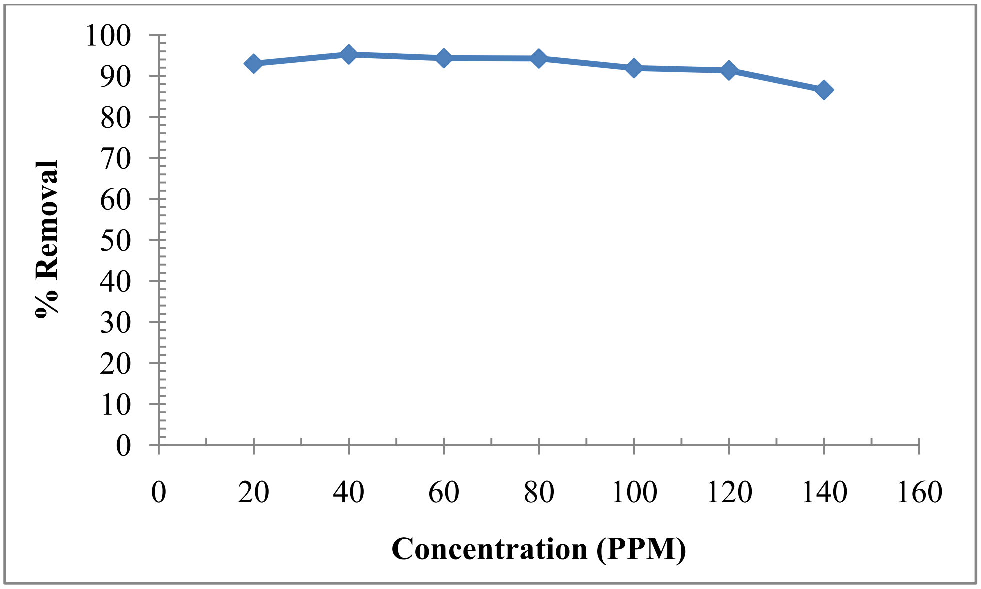

Figure 1.5 – Effect of initial metal ion concentration on adsorption of Cu(II) of Ficus bengalensis Leaf powder (pH:8, Adsorbent Dose : 0.5 g, contact time: 120 minutes, Agitation speed: 180 rpm)

Adsorption Isotherms

The Freundlich and Langmuir models are the most frequently used models to describe the experimental data of adsorption isotherms. Here, both models were used to investigate how Cu (II) ions interact with adsorbents, the Langmuir and Freundlich models were applied to describe the isotherm data obtained at 30^0C temperatures. The Freundlich isotherm is an empirical equation based on an exponential distribution of adsorption sites and energies. It is represented as:

$$\ln q_e = \ln K_F + (1/n)\ln C_e \qquad (3)$$

Where, K_F (Lg-1) and n are Freundlich constants related to adsorption capacity and adsorption intensity, respectively. The Langmuir isotherm assumes a surface with homogeneous binding sites, equivalent sorption energies, and no interaction between adsorbed species. Its mathematical form is written as: $$\frac{c_e}{q_e} = \frac{1}{K_L q_m} + \frac{c_e}{q_m} \qquad (4)$$

where, q_m and K_L represent the maximum adsorption capacity for the solid phase loading and the energy constant related to the heat of adsorption respectively.

Langmuir and Freundlich adsorption isotherms for copper from aqueous solution are presented in Figures 1.6 and 1.7 as shown below. It indicates that the experimental data fitted well to all the isotherm models. By comparing the correlation coefficients, it was observed that Langmuir isotherm gives a good model for the adsorption system, which is based on monolayer sorption on to the surface restraining finite number of identical sorption sites. The values of various constants of the two models were calculated and were represented in the Table-1.

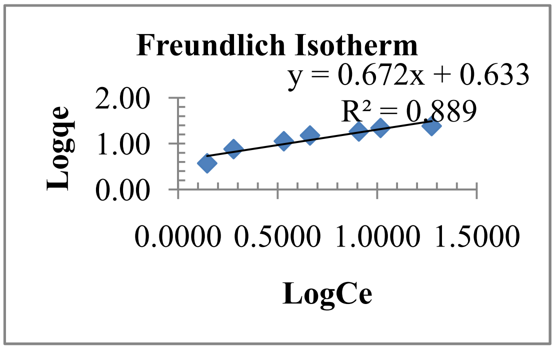

Figure 1.6 – Freundlich adsorption isotherm.

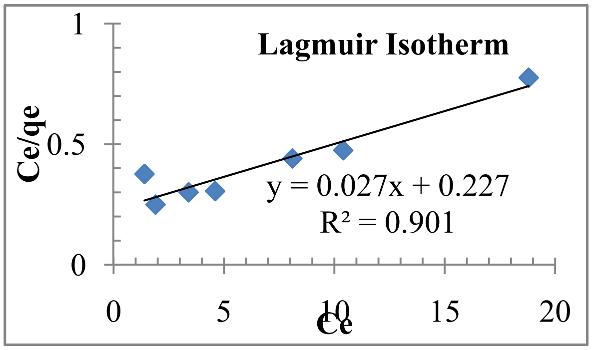

Figure 1.7 – Langmuir adsorption isotherm.

Table-1. : Parameters of Freundlich and Langmuir adsorption isotherms for Cu (II)at 30^{0}C.

Langmuir Isotherm			**Freundlich Isotherm**		
q_m (mg/g)	K_L (L/mg)	R^2	K_F (mg/Kg)	n	R^2
36.6300	160.7283	0.9018	4.2983	1.4867	0.8891

Adsorption Kinetic Study

The kinetic study of adsorption in wastewater plays an important role because it affords important insight into the reaction pathways and into the mechanism of the reaction. Pseudo first order kinetic model and Pseudo second order kinetic model have been proposed to explain the mechanism of a solute sorption from aqueous solution onto an adsorbent.

The pseudo first-order kinetic model has been widely used to predict the metal adsorption kinetics. The metal adsorption kinetics following the pseudo first-order model [15] is

$$\frac{d_q}{d_t} = K_1 + (q_e - q_t) \quad (5)$$

Where k_1 (min^{-1}) is the rate constant of the pseudo-first-order adsorption, q_t (mg/g) denotes the amount of adsorption at time t (min) and q_e (mg/g) is the amount of adsorption at equilibrium.

After definite integration by application of the conditions q_t =0 at t = 0 and q_t = q_t at t = t, Eq. (5) becomes,

$$\log(q_e - q_t) = \log q_e - \frac{k}{2.303}(t) \quad (6)$$

By plotting *log* $(q_e - q_t)$ versus *t*, the adsorption rate can be calculated.

The adsorption kinetic data can be further analyzed using Ho's pseudo second-order kinetics [15]. This is represented by

$$\frac{d_q}{d_t} = K_2 + (q_e - q_t)^2 \qquad (7)$$

Integration of Eq. (7) and application of the conditions $q_t=0$ *at* $t = 0$ and q_t gives,

$$\left(\frac{t}{q_t}\right) = \left(\frac{1}{k_2 q_e^{\,2}}\right) + \left(\frac{1}{q_e}\right)t \qquad (8)$$

Where k_2 (g/(mg min)) is the rate constant, k_2 and q_e can be obtained from intercept and slope.

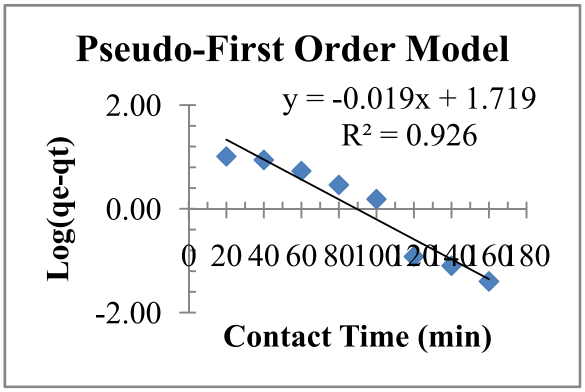

Figure 1.8 – Pseudo first order model.

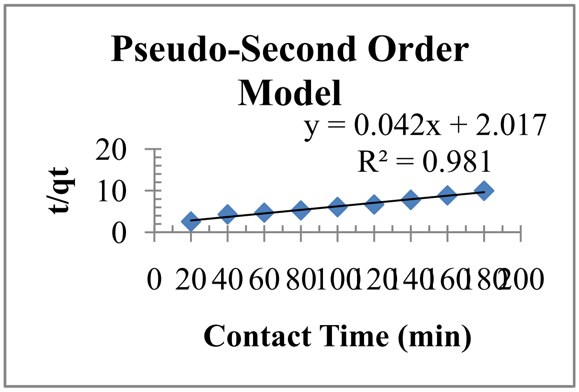

Figure 1.9 – Pseudo second order model.

The kinetics of adsorption was studied for a contact time ranging 20 –140 min. The experimental data was fitted to the pseudo first order and pseudo second order kinetic model (Figure 1.8 and 1.9). The reported R^2 value indicates that the experimental results shows better fit to pseudo-second order model. Hence, the copper adsorption seems to be more pseudo-second order.

Thermodynamic Parameters:

Thermodynamic analysis provides valuable information on the mechanism of adsorption. The thermodynamics of Cu (II) adsorption Ficus bengalensis leaf powder were studied using the free energy change, ΔG°, according to Equation (9):

$$\Delta G^\circ = -\mathrm{RT}\ln \mathrm{K} \qquad (9)$$

The plot of logK vs. 1/T (Figure 2.0**)** gives a straight line and the values of ΔS° and ΔH° can be obtained from its intercept and slope, respectively. The calculated values of ΔG°, ΔH°, and ΔS° are presented in Table 2. The negative value of ΔG^0 at all temperatures indicates that the copper adsorption reaction was spontaneous in nature. As the ΔG^0 ranges from -1.812 to -5.426 kJ/mol, the adsorption process is predominantly a physical adsorption process.

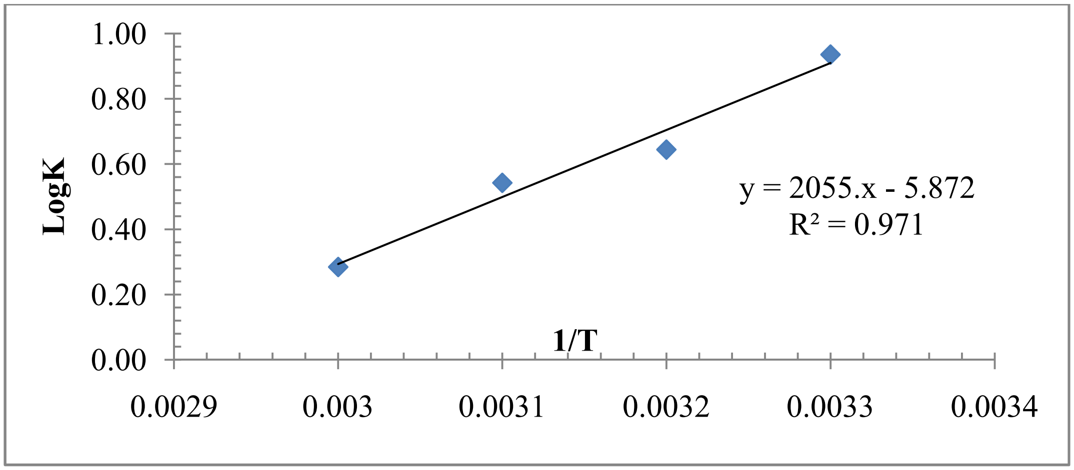

Figure 2.0 - The plot of logK vs. 1/T

Table 2 Thermodynamic Parameters Of Copper Adsorption.

T(K)	ΔG(kJ/mole)	ΔH (kJ/mole)	ΔS(kJ mol^{-1} K^1)
303	-5.426	- 39.34	0.112
313	-3.859		
323	-3.352		
333	-1.812		

Conclusion

Based on the results of this study following conclusions could be drawn:

i. The present investigation is carried out to study the suitability of a novel indigenous adsorbent; microwave assisted carbonized Ficus bengalensis leaves powder for the removal of heavy metal such as Cu (II) from the aqueous solution.
ii. Influence of process parameters such as pH, adsorbent dosage, temperature, contact time, initial metal ion concentration were at moderate levels such that they can affect the removal efficiencies of the Cu(II) were concerned.
iii. The optimum pH of solution for Cu removal was found to be 8.
iv. Within the scope of the experimental investigation the optimum temperature was found to be 30^0C.
v. The optimum time for adsorption of copper was found to be 120 min.
vi. Initial metal ion concentration showed the negative effect on adsorption efficiency i.e. at lower levels the adsorption was higher.
vii. Kinetic studies of adsorption revealed that the adsorption process followed a pseudo second order kinetic model for copper.
viii. The adsorption data were fitted to different isotherm model equation and the Langmuir model was found to be the best model for removal of Cu(II). (R^2 value 0.9018).
ix. Thermodynamic parameter of adsorption studies revealed that the adsorption of Cu(II) using microwave assisted carbonized Ficus bengalensis leaves powder is a physical adsorption phenomenon.

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