ADSORPTION OF COPPER IONS BY ACID ACTIVATED LOW COST CARBON-KINETIC, THERMODYNAMIC AND EQUILIBRIUM STUDIES

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ABSTRACT

A carbonaceous adsorbent prepared from an indigenous waste, by acid treatment was tested for its efficiency in removing metal ions. The process parameters studied include agitation time, initial metal ions concentration, carbon dose, pH and temperature. Freundlich and Langmuir isotherm models were applied to the equilibrium data. The adsorption capacity (Q_m) obtained from the Langmuir isotherm plot were found to around 10 mg/g at an initial pH of 7.0. The temperature variation study showed that the metal ions adsorption is endothermic and spontaneous with increased randomness at the solid solution interface. Significant effect on adsorption was observed on varying the pH of the metal ion solutions. The Langmuir and Freundlich adsorption isotherms obtained, positive $\triangle H^0$ value, pH dependent results and desorption of metal ions in mineral acid suggest that the adsorption of metal ions on Phoenix Sylvestris carbon involves physisorption mechanism.

Key words: *Activated carbon, Metal ions, Adsorption isotherm, Equilibrium, Kinetic and Thermodynamic parameters, Intraparticle diffusion, Regeneration pattern.*

INTRODUCTION

The problems of the ecosystem are increasing with developing technology. Heavy metal pollution is one of the main problems. Toxic metal compounds coming to the earth's surface not only reach the earth's waters (seas, lakes, ponds and reservoirs) but can also contaminate ground water in trace amounts by leaching from the soil. Therefore, the earth's waters may contain various toxic metals.

Drinking water is obtained from springs, which may be contaminated, by various toxic metals. Over the past few decades the huge increase in the use of heavy metals has resulted in an increased flux of metallic substances in aquatic environment. The most important characteristics of these metals are that they are toxic to living organisms. One of the most important problems is the accumulation of metals can be more than those in water and air. The contaminated food can cause poisoning in humans and animals[1]. Although some heavy metals are necessary for the growth of plants, after certain concentrations heavy metals become poisonous for both plants and microorganisms. Another important risk concerning contamination is the accumulation of these substances in the soil in the long term. Heavy metals have an effect on the enzymes. It has been determined that various metal ions hinder various enzymes responsible for mineralization of organic compounds in the earth. According to the world health organization, the metals of most immediate concern are chromium, iron, nickel, cadmium, mercury, lead, aluminum, manganese, cobalt, copper and zinc. These metals cause direct toxicity, both to humans and living beings, due to their presence beyond specified limits. Several past disasters are due to the contamination of heavy metals in aquatic environment. Among these are, "minamita tragedy"(Metallic mercury from the laboratories and chlorine manufacturing industries was capable of being converted to concentrated methyl mercury by aquatic life). "Itai-Itai" disease was reported during 1953-1960 due to water containing cadmium form the Jintsu river in Japan (1947)[1,2].

Metal ion such chromium produces undesirable effects on human and animal life even in low concentrations. In recent years many researchers have studied the removal of different heavy metal ions including chromium, nickel, iron and copper from the water. Wastewaters from industries released in to nearby land or rivers without any treatment because the conventional treatment methods are not cost effective in the Indian context. On the other hand, low cost technologies never allow a wishful metal ion removal and it has certain disadvantages. Adsorption is one of the most effective methods and activated carbon is the preferred adsorbent widely employed to treat wastewater containing different classes of metal ions recognizing the economic drawback of commercial activated carbon. Many investigators have studied the feasibility of using inexpensive alternative materials like pearl millet husk, date pits, saw dust buffing dust of leather industry, coir pith, crude oil residue tropical grass, olive stone and almond shells, pine bark, wool waste, coconut shell etc., as carbonaceous precursors for the removal of metal ion from water and wastewater[3,4]. The present study undertaken to evaluate the efficiency of a carbon adsorbent prepared form acid activated *Phoenix Sylvestris* carbon for the removal of metal ion aqueous solution. In order to design adsorption treatment systems, knowledge of kinetic and mass transfer process is essential. In this paper, we have reported the applicability of kinetic and mass-transfer models for the adsorption of copper ion onto activated carbon.

EXPERIMENTAL

Carbon was prepared by treating air-dried *Phoenix Sylvestris* leaves with con sulphuric acid in a weight ratio of 1:1. The resulting black product was kept in a furnace maintained at 500°C for 12 hours followed by washing with water until free from excess acid and dried at 150 ± 5°C. The carbon product obtained from *Phoenix Sylvestris* carbon was ground and the portion retained between 30 and 50 μm sieves was used in all the experiments. All chemicals supplied by S.d. fine chemicals with high purity.

Batch equilibration method: All experiments were carried out at 30,40 and 50ºC temperature in batch mode. Batch mode was selected because of its simplicity and reliability. The experiments were done in different Erlenmeyer glass flasks of 100 ml capacity. Prior to each experiment, a predetermined amount of absorbent was added to each flask. The stirring was kept constant (120 rpm) for each run throughout the experiment to ensure equal mixing. Each flask was filled with a known volume of sample before commencing stirring such as metal solutions with an initial concentration of 5 mg/L to 25 mg/L. The flask containing the sample was withdrawn from the shaker at the predetermined time interval, filtered and the residual concentration of the metal ion was measured.

Effect of variable parameters

Dosage of adsorbents: Different doses consisting of 100 to 300 mg/50 ml of the adsorbent is mixed with the metal ion and the mixture was agitated in a mechanical shaker. The percentage of adsorption for different doses was determined by keeping all other factors constant.

Initial concentration: In order to determine the rate of adsorption, experiments were conducted with different initial concentrations of metal ion ranging from 5 to 25 mg/l. All other factors were kept constant.

Contact time: The effect of period of contact between the adsorbent and adsorbate on the removal of the metal ion in a single cycle was determined by keeping particle size, initial concentration, dosage, pH, and temperature constant.

Initial pH: Adsorption experiments were carried out at a range of pH of the solution i.e. 3-11. The acidic and alkaline pH of the medium was maintained by adding the required amounts of hydrochloric acid and sodium hydroxide solutions. The parameters like particle size of the adsorbents, and temperature were kept constant while carrying out the experiments.

Other ions: Adsorption studies of a specific metal ion in the presence of magnesium, calcium, sulphate and chloride ions were experimentally verified using the adsorbents. This involved the determination of the percentage of metal ion adsorbed from 20 mg/L of initial concentration of the metal ion solution with varying concentration of the added ion keeping all other factors constant.

Temperature: The adsorption experiments were performed at four different temperatures viz., 30, 40 and 50ºC in a thermostated shaker machine (Remi, India). The constancy of the temperature was maintained with an accuracy of ± 0.5º C.

Regeneration studies: The regeneration of the adsorbed carbon is done by using 0.2 M Mineral acids and sodium chloride solutions.

RESULT AND DISCUSSION

Effect of contact time: The percentage of adsorption of Cu(II) at the fifth minute is 86 while it increased to 93 at fifteenth minute and to 95 at twenty fifth minute. Beyond this stage there was no further increase in the amount of Cu(II) adsorbed by the adsorbent. This means that a minimum of 25 minutes is required by the adsorbent material to adsorb the maximum amount of Cu(II). Figure 1 explains the relationship between the percentage of copper adsorbed by the material against the contact time. Hence it is considered that the adsorption increases in the beginning and after 25 minutes it reaches an equilibrium state. Therefore 25 minutes is taken as the optimum period of contact required for the maximum removal of the metal ion by the Phoenix Sylvestris carbon. Hence all the remaining experiments related to the determination of other parameters of the adsorption studies are conducted for a minimum period of 25 minutes**.** Figure 1 reveals that the curves are single, smooth, and continuous, leading to saturation, suggesting the possible monolayer coverage of the metal ions on the carbon surface[5].

Effect of initial concentration: The influence of concentration of Cu(II) ion on the amount adsorbed has been studied at various concentration levels of Cu(II) gives the percentage of Cu(II) removed at varying concentrations. It is observed that at 10 mg/l of Cu(II) concentration the amount of Cu(II) adsorbed is about 80%. The percentage of Cu(II) ions removed at 5, 10, 15, 20, 25, and 30 mg/l levels are 83, 80, 78, 76 and 73 respectively. The trend in the adsorption of metal ions adsorbed over the surface of the Phoenix Sylvestris leaves carbon is shown in Figure 2. It is therefore evident that at low concentration ranges the percentage of adsorption is high because of the availability of more active sites on the surface of the adsorbent. As the concentration of metal ion increases, more and more surface sites are covered and hence at higher concentrations of metal ions the capacity of the adsorbent get exhausted due to non-availability of the surface sites[6]. Therefore a fall in the percentage of adsorption of Cu(II) ions observed at higher concentrations of metal ion.

Effect of Dose: The effect of the amount of adsorbent at 10 mg/l of initial copper concentration was studied. The results show that as the dosage increases from 100 to 300 mg there is an increase in adsorption from 67 to 84 %. Maximum adsorption efficiency of 84 % was attained at 200 mg of dosage itself. Beyond that there is no marked increase in adsorption with increase in dosage. This was attributed to increased carbon surface area and availability of more adsorption sites[5 , 6]. Hence 200 mg of adsorbent was chosen for further studies. The results are shown in the Figure 3.

Effect of pH: The pH of the aqueous solution is a controlling factor in the adsorption process. Thus the role of hydrogen ion concentration was examined at pH values of 2, 3, 4, 5, 7, 9 and 11. This was adjusted by adding 0.5 N HNO_3 or 0.1M NaOH with 50 ml of standard solution of 10 mg/l of Cu(II) for a contact time of 25 minutes with a dose of 200 mg of treated adsorbent. The effect of pH on the percentage of adsorption is significant It was observed that the Cu(II) ions adsorbed at a faster rate at low pH ranges compared to alkaline ranges**.** The percentage of Cu(II) ion adsorbed at pH 2 is 83 while that at pH 3 is 90. However a maximum of 92% of Cu(II) ion adsorption occurred at pH 4. At higher pH ranges, for example, at 7 and beyond, the amount of the metal ion adsorbed remains almost constant at 90%. This indicates the strong force of interaction between the metal ion and the activated carbon that, either H^+ or OH^- ions could influence the adsorption capacity. Here the interaction is more at below pH 6, the competence of acidic H+ ion with metal cation for the sorption sites. The percentage of sorption increased at the above pH value is due to the presence of ionic COOH groups. The adsorption of metal ions on the activated carbon does involve ion exchange mechanism. Due to the adsorption of metal ions through ion exchange mechanism by the adsorbent, there should be an influence on the metal ion adsorption while varying the pH. This observation is in line with the Langmuir and Freundlich isotherms. The positive $\Delta H°$ value obtained, which indicates irreversible adsorption probably due to polar interaction.[7,8]. It is, therefore, concluded that Phoenix Sylvestris carbon behaves as an efficient adsorbent of metal ion at all pH ranges.

Effect of co-ions: The influence of two cations namely calcium and magnesium and two anions chloride and sulphate on the adsorption of Cu(II) ions by the Phoenix Sylvestris carbon was studied experimentally [8,9,10] and the results are shown in Figure 5.

Effect of magnesium: The effect of concentration of Mg(II) ions on the adsorption of Cu(II) by banana bark carbon was studied by performing the experiment in the presence of excess of magnesium ions. The concentrations of Mg(II) ion chosen ranged between 100 to 1000 mg/l. The percentage of adsorption of Cu(II) ions at 200, 400, 600, 800 and 1000 mg/l are 89, 88, 88, 90 and 91 respectively. The adsorption of Cu(II) ions remained uniformly unchanged irrespective of the concentrations of the Mg(II) ion. This trend of absence of any inhibitory effect of Mg(II) ions on the adsorption of metal ions by the adsorbent is evident from Figure 5.

Effect of calcium: The effect of concentration of Ca(II) ions on the adsorption of Cu(II) ions over the Phoenix Sylvestris carbon was also verified and no appreciable change in the percentage of metal removed was noticed. The amount of Cu(II) adsorbed by the bark carbon in the presence of 200, 400, 600, 800, and 1000 mg/l of Ca(II) solution were respectively 86, 87, 86, 87, and 86%. The influence of excess of Ca (II) ions over the adsorption of Cu(II) by the adsorbent material is shown in the Figure 5.

Effect of chloride ion: The influence of concentration of chloride ion on the removal of Cu(II) ion by Phoenix Sylvestris carbon was studied in presence of chloride ions ranging between 0 to 1000 mg/l. The percentage of Cu(II) ions adsorbed by the material in presence of 200, 400, 600, 800 and 1000 mg/l of Cl^- ions are 81.6, 82.4, 82.2, 81.2 and 82.1 respectively. A look on the Figure 5 indicates that the adsorption of Cu(II) ions by the adsorbent remains unchanged irrespective of the concentrations of Cl^- ions.

Effect of sulphate ion: The percentage of adsorption of Cu(II) ions by the Phoenix Sylvestris carbon in presence of excess concentrations of sulphate ions are given in Figure 5. No appreciable change in the percentage of desorption of metal ion is evident in the presence of excess concentration of sulphate ions. This means sulphate ion do not influence in the removal of metal ions by the adsorbent species.

To conclude, the experimental results revealed the absence of any significant influence of calcium, magnesium, sulphate and chloride ions in the adsorption of Cu(II) ions by Phoenix Sylvestris carbon

Adsorption isotherms:

Langmuir[10] and Freundlich[11] adsorption isotherm models were applied to the system in order to ascertain the nature of adsorption of the metal ion by Phoenix Sylvestris carbon. The adsorption experiments were conducted at three different temperatures 30, 40 and 50ºC.

Langmuir adsorption isotherm:

The values of C_e - equilibrium concentration of Cu(II) ions and C_e/Q_e the ratio of equilibrium concentration to the amount of Cu(II) adsorbed are utilized for determining the isothermal behaviors of the adsorption process.

The Langmuir equation is expressed as follows

$$C_e / Q_e = C_e/X_{max} + 1/ X_{max}\, b \qquad \text{------------} \qquad (1)$$

Where C_e is the equilibrium or final concentration of Cu(II) ion in mg/l, Q_e is the amount of Cu(II) ion adsorbed per unit weight of activated carbon at equilibrium, Xmax is the maximum adsorption at monolayer converage and b is the adsorption equilibrium constant. From equation 1 the plot of C_e/Q_e versus C_e should give a straight line of slope $1/X_{max}$ and intercept of $1/X_{max}$ b on the C_e/Q_e axis. The linear plots of C_e/Q_e versus C_e ($0.827 < r < 0.997$) at the three temperatures indicate the applicability of Langmuir adsorption isotherm and the adsorption process occurring through monolayer coverage. The Langmuir plots showing the increase in the rate of adsorption at higher temperatures are presented in Figure 6. The C_e values of adsorbate in solution are higher at lower temperatures and they decrease with increasing temperature indicating greater adsorption at higher temperatures. The enhanced sorptive nature of the adsorbent at higher temperature is due to the swelling in the internal pores of the adsorbent to trap in more Cu(II) ions on its surface[12]. The values of Q_m and b were determined from slope and intercepts of the plots and are presented in Table 2. From the results, it is clear that the value of adsorption efficiency Q_m and adsorption energy b of the carbon increases on increasing the temperature. From the values we can conclude that the maximum adsorption corresponds to a saturated monolayer of adsorbate molecules on adsorbent surface with constant energy and no transmission of adsorbate in the plane of the adsorbent surface. The trend shows that the adsorbent prefers to bind acidic ions and that speciation predominates on sorbent characteristics, when ion exchange is the predominant mechanism. Further, it confirms the endothermic nature of the processes involved in the system[10,12].

Freundlich isotherm:

Batch adsorption isothermal data, fitted in to the linear form of the Freundlich isotherm is shown in Figure 7(log Q_e versus log C_e). The adsorption capacity, K and the adsorption intensity, 1/n are directly obtained from the slopes and the intercepts of the linear plot respectively and the data are provided in Table 1. The plot of log Q_e versus log C_e for various initial concentrations is linear indicating the applicability of Freundlich adsorption isotherm ($0.957 < r < 0.998$). The values of K_f and n were found and given in the Table 3, shows the increase of negative charge on the surface that enhances the electrostatic force like Vanderwaal's between the carbon surface and metal ions, which increases the adsorption of metal ions. The values clearly show that dominance in adsorption capacity. The intensity of adsorption is an indicative of the bond energies between metal ions and adsorbent and the possibility of slight chemisorptions rather than physisorption. The possibility of multilayer adsorption of metal ion through the percolation process cannot be ruled out. However, the values of n is greater than one indicating the adsorption is much more favourable[13]. The fit of the data to the Freundlich model indicate that the forces of adsorption by the Phoenix Sylvestris carbon adsorbent are governed by physisorption.

Effect of temperature on adsorption:

The temperature dependence of Cu(II) adsorption on banana bark carbon was examined. The adsorption experiments were conducted at three different temperatures, viz., 30, 40 and 50° C:

k_{ads} values for each of the reactions were calculated using relationship.

$$k_{ads} = \text{Amount adsorbed} / C_e$$

Where the amount of Cu(II) ions adsorbed [is the difference between the initial concentration (C_i) and is the concentration at equilibrium (C_e)] and C_e is the equilibrium concentration. From the values of equilibrium constant, the standard free energy, ΔG^o for the reaction at different temperatures were calculated using the equation,

$$\Delta G^o = - RT \ln k_{ads}.$$

The values of k_{ads} are ΔG^o are given in Table 4. The endothermic nature of the adsorption is indicated by an increase in the k_{ads} values with rise in temperature. The standard free energy, ΔG^o values were negative and this indicates the feasibility and spontaneity of the process. ΔH^o, ΔS^o values were derived using the relationship:

$$\ln k_{ads} = (\Delta S^o/R) - (\Delta H^o/RT)$$

A plot of $\ln k_{ads}$ versus 1/T was found to be linear. The values of ΔH^o and ΔS^o were determined from the slope and intercept and the values are presented in Table 4. The positive values of ΔH^o indicate that the adsorption process is endothermic. The positive value of ΔS^o shows the increased randomness at the solid / solution interface during the adsorption of metal ion by the Phoenix Sylvestris carbon [13,14,15].

Desorption studies: Desorption studies help to elucidate the nature of adsorption and recycling of the spent adsorbent and the metal ion. If the adsorbed metal ion can be desorbed using neutral pH water, then the attachment of the metal ion of the adsorbent is by weak bonds. If sulphuric acid or alkaline water desorp the metal ion, then the adsorption is by ion exchange. If organic acids, like acetic acid can desorp the metal ion, then the metal ion has held by the adsorbent through chemisorption[19]. The effect of various reagents used for desorption studies indicate that hydrochloric acid is a better reagent for desorption, because we could get more than 90% removal of adsorbed metal ion. The reversibility of adsorbed metal ion in mineral acid or base is in agreement with the pH dependent results obtained. The desorption of metal ion by mineral acids and alkaline medium indicates that the metal ion was adsorbed onto the activated carbon through by physisorption mechanisms[16].

CONCLUSION

The *Phoenix Sylvestris* carbon is found to have appreciable capacity to adsorb Cu(II) ions. The Cu(II) removal was found to occur through the process of adsorption which is basically a surface phenomenon. The material required a contact time of 25 minutes for optimum adsorption of Cu(II) ions. The adsorption process was found to depend on the initial concentration of Cu(II) ions, dosage of the material, pH and temperature. However the presence of common cations like calcium and magnesium and anions like chloride and sulphate did not have any direct influence on the metal removal efficiency of the adsorbent. The adsorption process obeyed Langmuir and Freundlich isotherms indicating a monolayer formation over the surface of the material. Temperature studies lead to the conclusion that the adsorption process is endothermic and spontaneous.

Table 1:Equilibrium Parameters for the adsorption of metal ion onto *Phoenix Sylvestris* carbon

Metal ion	C_e (mg /l)				Q_e (mg/g)				Metal ion Removed (%)			
	30°	**40°**	**50°**		**30°**	**40°**	**50°**		**30°**	**40°**	**50°**	
5	0.85	0.57	0.21		1.14	1.11	1.20		83	88	89	
10	1.99	1.22	1.02		2.00	2.20	2.25		80	87	89	
15	3.29	1.78	1.78		2.93	3.30	3.31		78	88	88	
20	4.68	3.93	3.07		3.83	4.02	4.23		76	80	84	
25	6.57	5.56	3.15		4.61	4.86	5.46		73	77	87	

Table - 2 Langmuir isotherm Results

(metal ion)	Temp	Statistical para meters		Constants
	(°C)	r2	Q_m	b
Copper ion adsorption	30°	0. 9970	10.8280	0.1140
	40°	0.9495	7.8583	0.3550
	50°	0.9000	11.0680	0.2442

Table - 3 Freundlich isotherm Results

(metal ion)	Temp	Statistical para meters		Constants
	(°C)	r^2	k_f	n
Copper ion adsorption	30°	0.9981	2.0397	1.4028
	40°	0.9547	1.5940	2.1445
	50°	0.9666	1.9854	1.4580

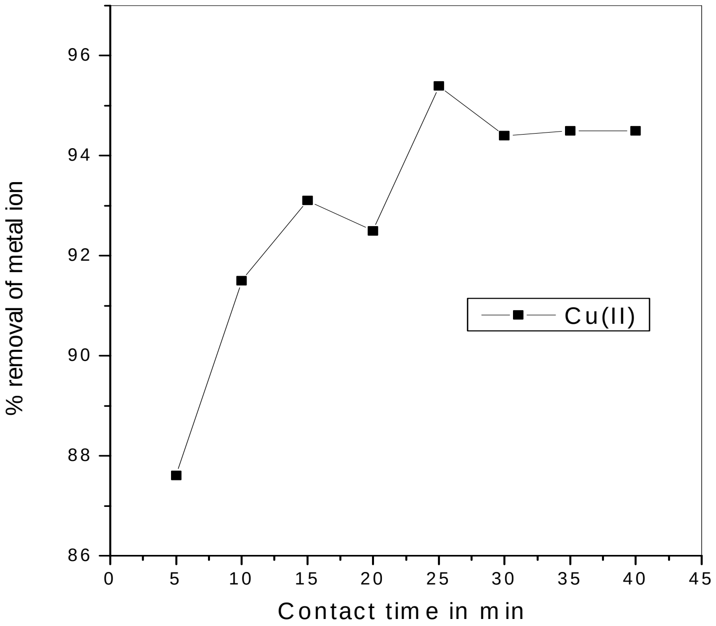

Figure 1-Effect contact time on the adsorption of copper ion

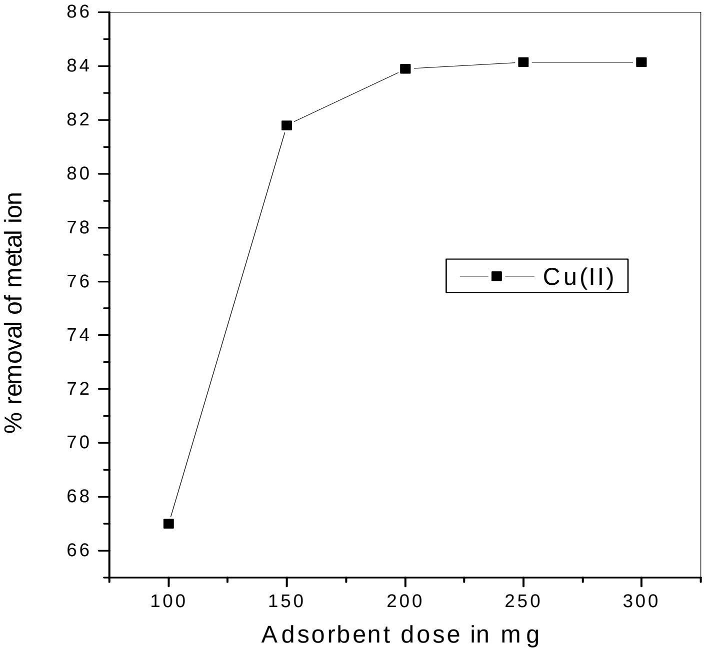

Figure 2-Effect of adsorbent dosage on the adsorption of cvopper ion

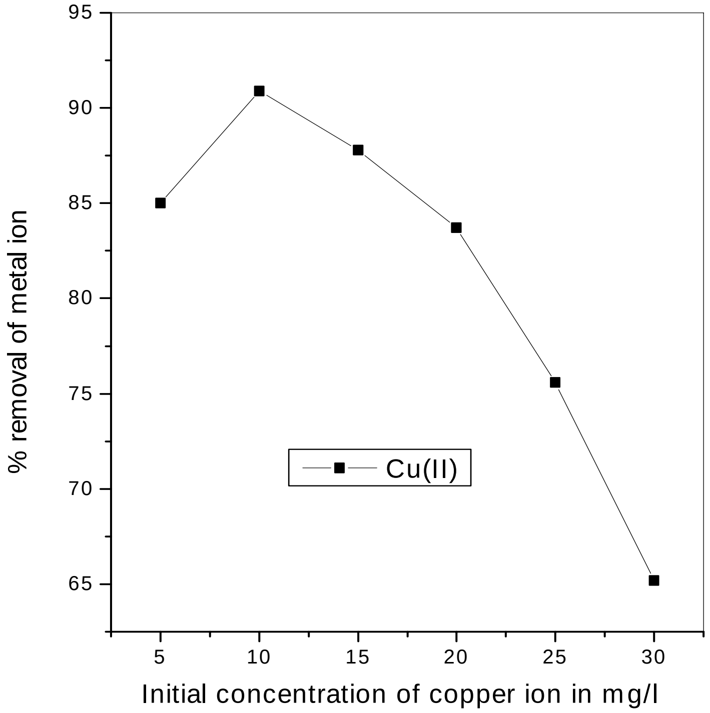

Figure 3-Effect of initial concentration of copper ion

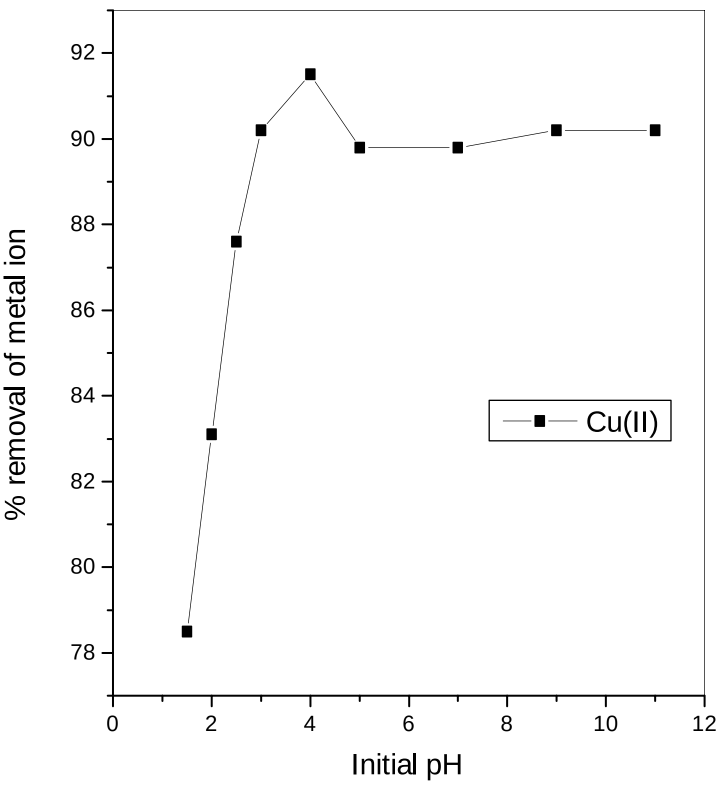

Figure 4-Effect of pH on the adsorption of copper ion

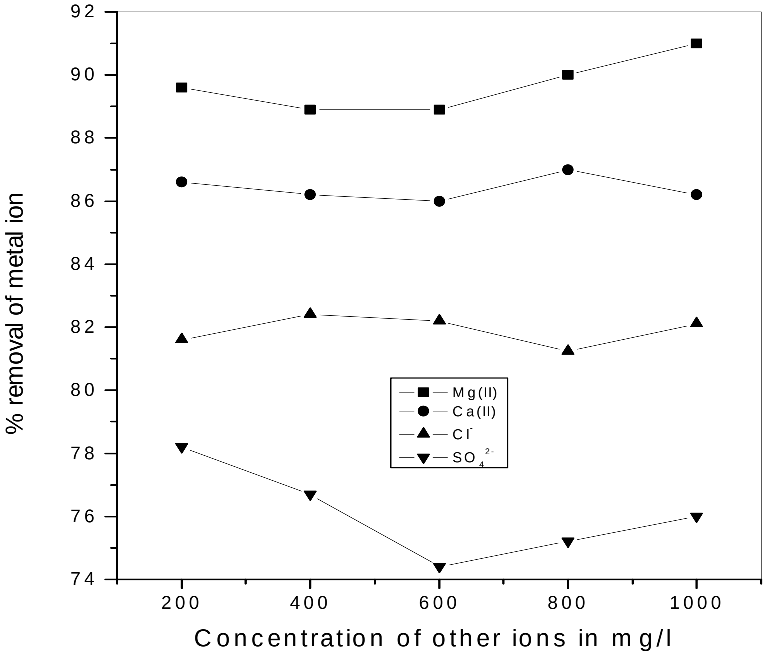

Figure 5-Effect of other ions on the removal of copper ion

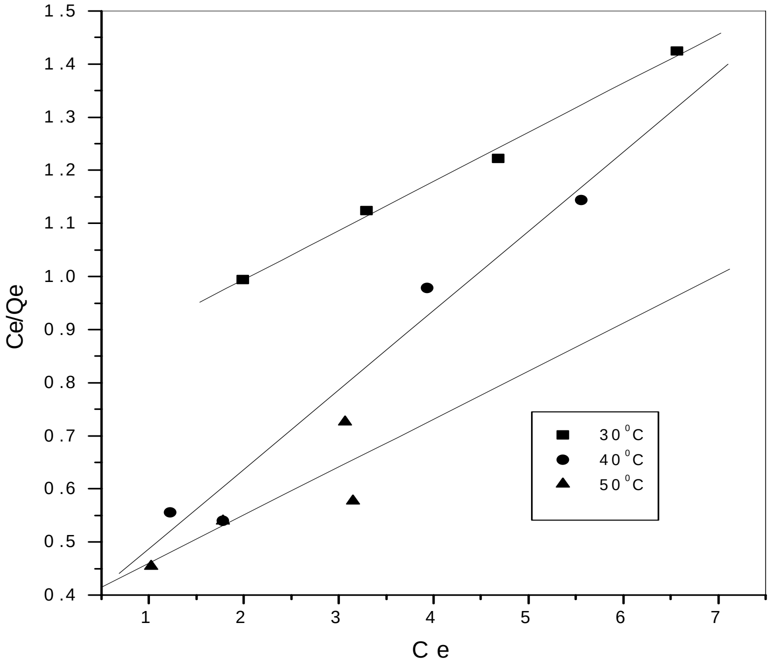

Figure 6-Langmuir adsorption isotherm for the adsorption of copper ion

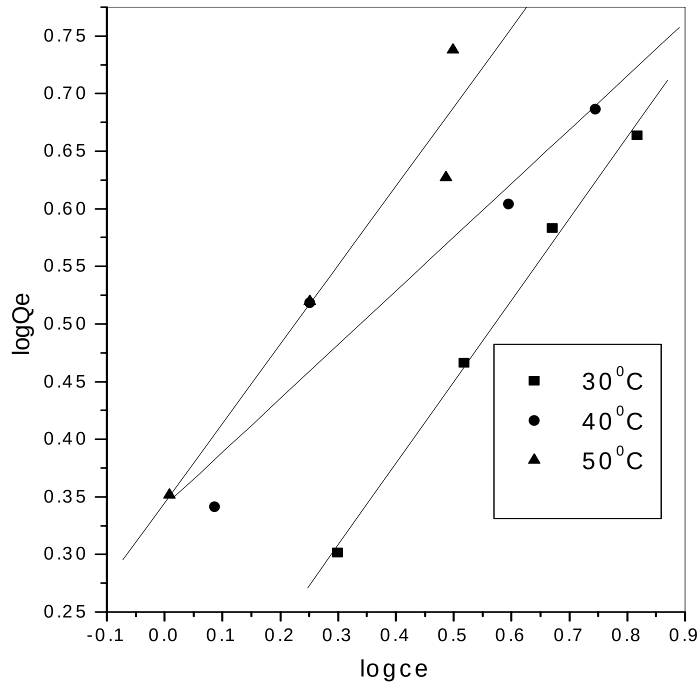

Figure 7-Freundlich adsorption isotherm for the adsorption of copper ion

Table 4 Thermodynamic parameters for the adsorption of metal ion onto *Phoenix Sylvestris* carbon

Initial concentration of Cu(II) mg/l	30° C		40° C		50° C		ΔH° (kJ/mol)	ΔS° (kJ/mol)
	K_{ads}	ΔG° (kJ/mol)	K_{ads}	ΔG° (kJ/mol)	K_{ads}	ΔG° (kJ/mol)		
5	2.5461	-2.354	4.8134	-4.089	7.1967	-5.299	43.19	359.08
10	4.0251	-3.507	7.1967	-5.135	8.8039	-5.841	32.53	119.47
15	3.559	-3.198	7.4228	-5.216	7.4228	-5.383	30.55	112.41
20	3.2735	-2.987	4.0890	-3.664	5.5147	-4.585	21.67	81.23
25	2.8025	-2.598	3.4958	-3.256	7.1587	-5.285	38.94	323.75

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