



Research Article

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Adsorption of the copper ion by *Phoenix sylvestris* leaves

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ABSTRACT

A Carbonaceous adsorbent prepared from an indigenous waste by acid treatment was tested for its efficiency in removing copper ion. The parameters studied include agitation time, initial copper ion concentration, carbon dose, pH and temperature. The adsorption followed first order equation and the rate is mainly controlled by intra-particle diffusion. Freundlich and Langmuir isotherm models were applied to the equilibrium data. The adsorption capacity (Q_m) obtained from the Langmuir isotherm plots were 25.062, 26.737, 28.248 and 29.761 mg/g respectively at an initial pH of 7.0 at 30, 40, 50 and 60 °C. The temperature variation study showed that the copper ion 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 copper ion solutions. Almost 80 % removal of copper ion was observed at 60 °C. The Freundlich and Langmuir isotherms obtained, positive ΔH^0 value, pH dependent results and desorption of metal ion in mineral acid suggest that the adsorption of copper ion on PSC involves physisorption mechanism.

Key words: Activated carbon (PSC), copper ion, Adsorption isotherms, Equilibrium, Kinetic and Thermodynamic parameters, Intra particle diffusion and regeneration pattern.

INTRODUCTION

The discharge of highly colored effluents into natural water bodies is not only aesthetically displeasing, but it also impedes light penetration, thus upsetting biological processes within a stream. In addition, many metal ions are toxic to some organisms causing direct destruction of aquatic communities. Some metal ions can cause allergic dermatitis, skin irritation, cancer and mutation in man. Wastewaters from metal industries released into nearby land or rivers without any treatment because the conventional treatment methods are not cost effective in the Indian context. 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 [1-3].

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, almond shells, pine bark, wool waste, coconut shell etc., as carbonaceous precursors for the removal of dyes from water and wastewater [1-3].

The present study undertaken to evaluate the efficiency of a carbon adsorbent prepared from acid activated *Phoenix sylvestris* leaves carbon for the removal of metal ion in aqueous solution. In order to design adsorption treatment systems, knowledge of kinetic and mass transfer processes is essential. In this paper, the applicability of kinetic and mass transfer models for the adsorption of copper ion onto acid activated carbon was reported.

EXPERIMENTAL SECTION

Phoenix sylvestris Leaves collection and adsorbent development was collected from local agricultural farms. It was oven dried at 1100°C overnight then it is added with conc. sulphuric acid in a weight/volume ratio of 1:1. The resulting black product was washed with water until free from excess acid and dried at $150 \pm 5^\circ\text{C}$. The resulting black mass was kept in a furnace maintained at 400°C for 12 hours for activation. The carbon product obtained was ground well to fine powder which is used for all experiments.

Adsorption dynamic experiments

Batch equilibration method

The adsorption experiments were carried out in a batch process at 30, 40, 50 and 60°C temperatures. The known weight of adsorbent material was added to 50 ml of the copper solutions with an initial concentration of 10 mg/L to 60 mg/L. The contents were shaken thoroughly using a mechanical shaker (Remi Model) rotating with a speed of 120 rpm. The solution was then filtered at preset time intervals and the residual dye concentration was measured by double beam UV-Visible spectrophotometer using 620 nm filters.

Effect of variable parameters

Dosage of adsorbents

The various doses of the adsorbent were mixed with the metal ion solutions and the mixture was agitated in a mechanical shaker. The adsorption capacities for different doses were determined at definite time intervals by keeping all other factors constant.

Initial concentration of metal ion

In order to determine the rate of adsorption, experiments were conducted with different initial concentrations of dyes ranging from 10 to 60 mg/L. All other factors were kept constant.

Contact time

The effect of contact time on the removal of copper by the adsorbent in a single cycle was determined by keeping particle size, initial concentration, dosage, pH and concentration of other ions as constant. pH Adsorption experiments were carried out at pH 3, 4, 5, 6, 7, 8, 9 and 10. The acidic and alkaline pH of the media was maintained by adding the required amounts of 0.1 ml/L hydrochloric acid and sodium hydroxide solutions. The parameters like particle size of the adsorbents, metal ion concentration, dosage of the adsorbent and concentration of other ions are kept constant while carrying out the experiments. The pH of the samples was determined using a portable pH meter (Systronics Model). The pH meter was calibrated with 4.0 and 9.2 buffers.

Chloride

The experiments were done in the presence of varying chloride environments using sodium chloride solutions. While doing the experiments, the absence of other anions was ensured.

Temperature

The adsorption experiments were performed at 30, 40, 50 and 60 °C in a thermostat attached water bath shaker (Remi Model). The constancy of the temperature was maintained with an accuracy of $\pm 0.5^\circ\text{C}$.

Zero point charge

The zero point charge of the carbon (pH_{zpc}) was measured using the pH drift method [4]. The pH of the solution was adjusted by using 0.01 mol/L sodium hydroxide or hydrochloric acid. Nitrogen was bubbled through the solution at 25°C to remove the dissolved carbon dioxide. 50 mg of the activated carbon was added to 50 ml of the solution. After stabilization, the final pH was recorded. The graph of final pH versus initial pH was used to determine the zero point charge of the activated carbon.

Titration studies

According to Boehm [4] only strong acidic carboxylic acid groups are neutralized by sodium bicarbonate, where as those neutralized by sodium carbonate are thought to be lactones, lactol and carboxyl group. The weakly acidic phenolic groups only react with strong alkali, sodium hydroxide. Therefore, by selective neutralization using bases of different strength, the surface acidic functional group in carbon can be characterized both quantitatively and qualitatively. Neutralization with hydrochloric acid characterizes the amount of surface basic groups that are, for example, pyrones and chromenes. The basic properties have described to surface basic groups and the pi electron system of carbon basal planes. The results indicate that the activated carbon used may possess acidic oxygen functional group on their surface and this is supported well by their respective zeropoint charge values. The results obtained from the above characterization studies are given in the Table.1.

Desorption studies

Desorption study was used to elucidate the nature of adsorption and recycling of the spent adsorbent. The effect of various reagents used for desorption were studied.

RESULTS AND DISCUSSION

Characterization of the adsorbent:

Activated carbons are a widely used adsorbent due to its high adsorption capacity, high surface area, micro porous structure and high degree of surface respectively. The wide usefulness of carbon is a result of their specific surface area, high chemical and mechanical stability. The chemical nature and pore structure usually determines the sorption factivity [4]. The physico chemical properties of the chosen adsorbent are listed in following Table.1

Table.1 Characteristics of the adsorbent

Properties	PSC
Particle size(mm)	0.045
Density (g/cc)	0.030
Moisture content (%)	1.65
Loss on ignition (%)	92.0
Acid insoluble matter (%)	2.20
Water-soluble matter (%)	0.48
PH of aqueous solution	6.95
pHzpc	6.15

Effect of contact time and initial copper ion concentration:

The experimental results of adsorptions of copper ion on the activated carbon at various concentrations (5, 10, 15, 20 and 25 mg/L) with contact time are shown in Figure 1. The equilibrium data were collected in Table. 2 reveals that, percent adsorption decreased with increase in initial copper ion concentration the actual amount of copper ion adsorbed per unit mass of carbon increased with increase in metal ion concentration. It means that the adsorption is highly dependent on initial concentration of copper ion. It is because of that at lower concentration, the ratio of the initial number of copper ion to the available surface area is low subsequently the fractional adsorption becomes independent of initial concentration. However, at high concentration the available sites of adsorption becomes fewer and hence the percentage removal of copper ion is dependent upon initial concentration. Equilibrium have established at 40 minutes for all concentrations. Figure 1 reveals that the curves are single, smooth, and continuous, leading to saturation, suggesting the possible monolayer coverage of the copper ion on the carbon surface [5,6].

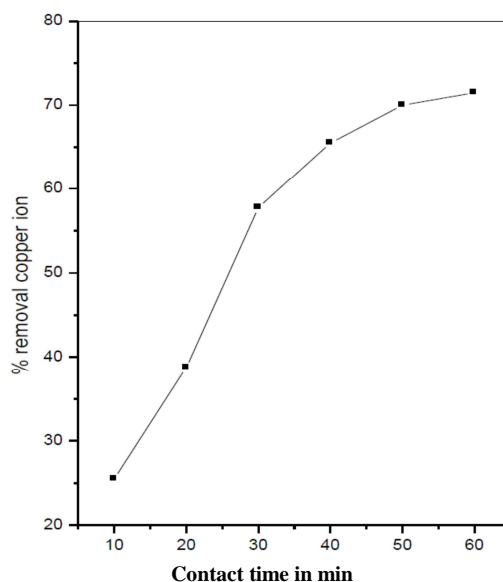


Fig.1. Effect of contact time on the removal of Copper ion
[M]=20mg/L; Adsorbent dose =25mg/50ml; Temp=30° C

Table. 2 Equilibrium Parameters for the adsorption copper ion

Copper ion	C _e (mg /L)				Q _e (mg/g)				Metal ions Removed (%)			
	30°	40°	50°	60°	30°	40°	50°	60°	30°	40°	50°	60°
5	0.5215	0.4728	0.4312	0.4054	8.957	9.0544	9.1376	9.1892	89.57	90.544	91.376	91.892
10	1.9587	1.7525	1.4747	1.2756	16.0826	16.495	17.0506	17.4488	80.413	82.475	85.253	87.244
15	4.2849	3.8254	3.3841	2.9944	21.4302	22.3492	23.2318	24.0112	71.434	74.49733	77.43933	80.03733
20	8.3546	7.7721	7.1599	6.5529	23.2908	24.4558	25.6802	26.8942	58.227	61.1395	64.2005	67.2355
25	13.3945	12.6572	11.9160	11.2435	23.211	24.6856	26.168	27.513	46.422	49.3712	52.336	55.026

Effect of carbon concentration:

The adsorption of the copper ion on carbon was studied by varying the carbon concentration (10-250mg/50ml) for copper ion concentration of 15 mg/L. The percentage of adsorption increased with increase in the carbon concentration (Figure 2). This was attributed to increased carbon surface area and availability of more adsorption sites [5,6].

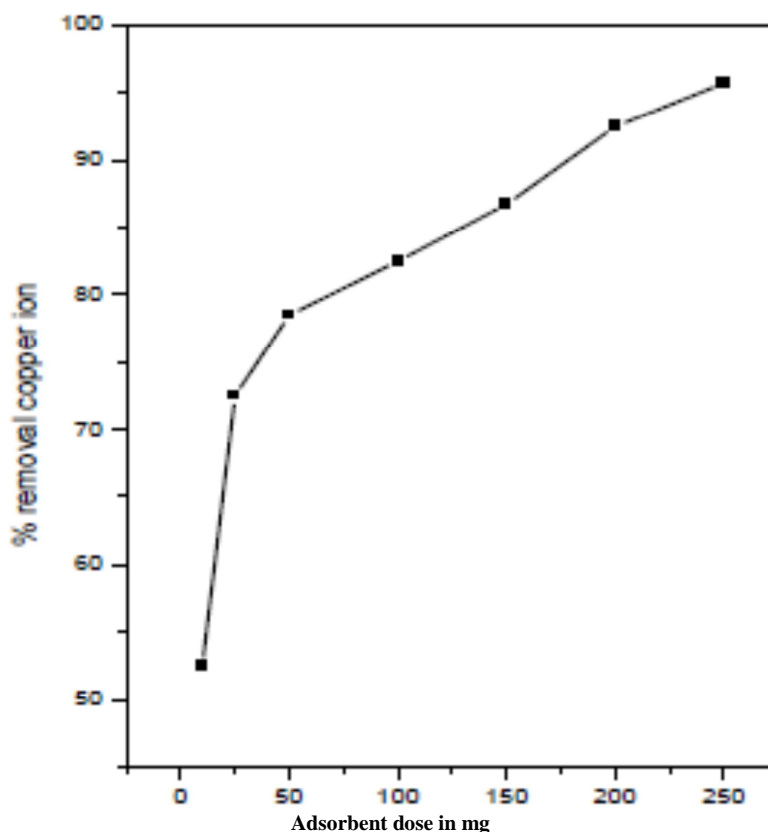


Fig.2. Effect of adsorbent dose on the Adsorption of copper ion
[M]=15mg/L; Contact time =60min; Temp=30° C

Adsorptin isotherm:

The experimental data analyzed according to the linear form of the Langmuir[7] and Freundlich[8] isotherms.

The Langmuir isotherm represented by the following equation

$$C_e/Q_e = 1/Q_m b + C_e/Q_m \dots \dots \dots (1)$$

Where C_e is the equilibrium concentration (mg/L), Q_e is the amount adsorbed at equilibrium (mg /g) and Q_m and b is Langmuir constants related to adsorption efficiency and energy of adsorption, respectively. The linear plots of C_e/Q_e versus C_e suggest the applicability of the Langmuir isotherms. Values of Q_m and b were determined from slope and intercepts of the plots (Fig.3) and are presented in Table 3. 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[9,10]. 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. To confirm the adorability of the adsorption process, the separation factor (RL) has calculated and presented in Table 4. The values were found to be between 0 and 1 and confirm that the ongoing adsorption process is favourable[1,11] The Freundlich equation have also employed for the adsorption of copper ion on the adsorbent.

The Freundlich isotherm have represented as

$$\log Q_e = \log K_f + \frac{1}{n} \log C_e \dots \dots \dots (2)$$

Where Q_e is the amount of copper ion adsorbed (mg/ g), C_e is the equilibrium concentration of metal ion in solution (mg/L) and K_f and n are constants incorporating all factors affecting the adsorption capacity and intensity of adsorption, respectively. Linear plot of $\log Q_e$ versus $\log C_e$ shows that the adsorption of copper ion follows the Freundlich isotherm. Values of K_f and n were found and given in the Table 5, shows the increase of negative charge on the surface that enhances the electrostatic force like Vanderwaal's between the carbon surface and metal ion,

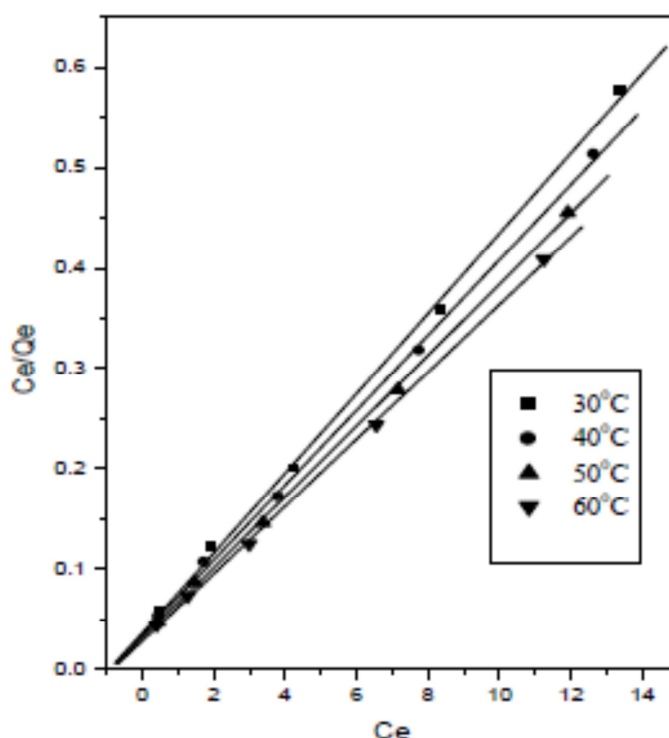


Fig.3. Linear Langmuir isotherm for the adsorption of copper ion

The values clearly show that dominance in adsorption capacity. The intensity of adsorption is an indicative of the bond energies between copper ion and adsorbent and the possibility of slight chemisorptions rather than physisorption [10,11]. The possibility of multilayer adsorption of metal ion percolation process cannot be ruled out. However, the values of n is greater than one indicating the adsorption is much more favourable[12,13].

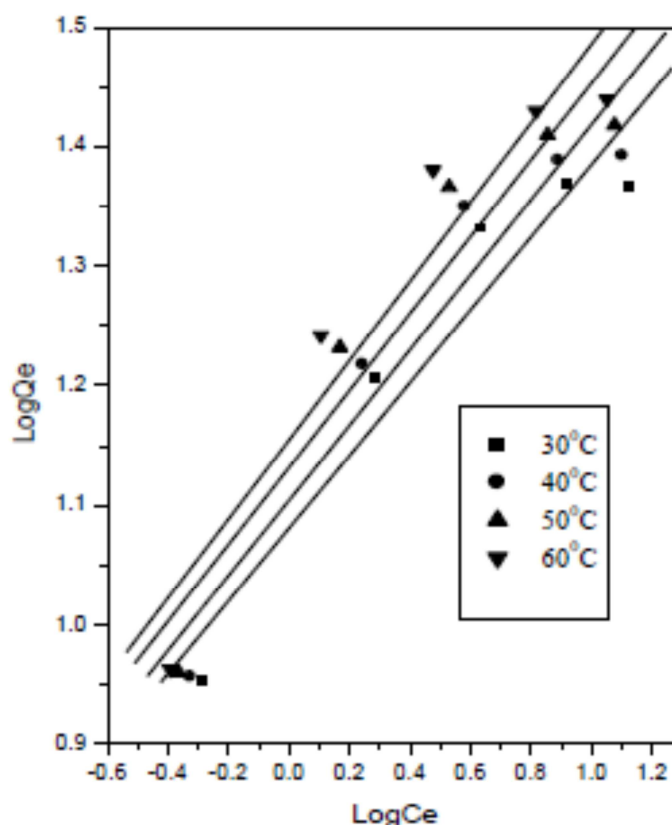


Fig.4. Linear Freundlich isotherm for the adsorption of Copper ion onto PSC

Table.3 Langmuir isotherm Results

(metal ion)	Temp (°C)	Statistical parameters / Constants		
		r^2	Q_m	B
Copper ion adsorption	30°	0.9955	25.062	1.1145
	40°	0.9962	26.737	1.1098
	50°	0.9999	28.248	1.1683
	60°	0.9998	29.761	1.2043

Table.4 Freundlich isotherm Results

(metal ion)	Temp (°C)	Statistical Parameters/ Constants		
		r^2	k_f	N
Copper ion adsorption	30°	0.9680	2.9476	3.2916
	40°	0.9718	3.0171	3.1847
	50°	0.9770	3.1012	3.1142
	60°	0.9850	3.1737	3.0238

Table.5 Dimensionless separation factor (R_L)

Copper ion (mg/L)	Temperature (°C)			
	30°	40°	50°	60°
5	0.152	0.153	0.145	0.142
10	0.082	0.083	0.078	0.076
15	0.056	0.057	0.054	0.052
20	0.042	0.043	0.041	0.039
25	0.034	0.035	0.033	0.032

Kinetics of adsorption:

Kinetics of sorption describes the solute uptake rate, which in turn governs the residence time of sorption reaction. It is one of the important characteristics in defining the efficiency of sorption. In the present study, the kinetics of the copper ion removal has carried out to understand the behaviour of this low cost carbon adsorbent. The adsorption of copper ion from an aqueous solution follows reversible first order kinetics, when a single species considered on a

heterogeneous surface. The heterogeneous equilibrium between the copper ion solution and the activated carbon have expressed as $A \rightleftharpoons B$ Where k_1 is the forward rate constant and k_2 is the backward rate constant. A represents copper ion remaining in the aqueous solution and B represents copper ion adsorbed on the surface of activated carbon. The rate constants calculated as earlier [11,12,13]. The data furnished in Table 7, is evident that the forward rate constant is much higher than the backward rate constant suggesting that the rate of adsorption is clearly dominant. At equilibrium, the rate is the ratio of the concentration of adsorbate in adsorbent and concentration of adsorbate in aqueous solution given by K_0 . The calculated values presented in the Table 6. The results indicates that K_0 values decreases with increase in the concentration of the copper ion and increases with increase in temperature. A clear examination of the effect of copper ion concentrations on the rate constant K_{ad} , the values help to describe the mechanism of metal ion removal taking place. In cases of strict surface adsorption a variation of rate should be proportional to the first power of concentration. However, when pore diffusion limits the adsorption process, the relationship between initial copper ion concentration and rate of reaction will not be linear. It shows that pore diffusion limits the overall rate of copper ion adsorption [12,13]. The contact-time experimental results can be used to study the rate-limiting step in the adsorption process, as shown by Weber and Morris [13,14]. Since the particles are vigorously agitated during the adsorption period, it is probably reasonable to assume that the rate is not limited by mass transfer from the bulk liquid to the particle external surface, one might then postulate that the rate-limiting step may be either film or intraparticle diffusion. As they act in series, the slower of the two will be the rate-determining step [13].

The rate constant for intraparticle diffusion is obtained using the equation

$$Q = K_p t^{1/2} + C \dots \dots \dots (3)$$

Here, K_p (mg/g/min) is the intraparticle diffusion rate constant. The K_p values obtained from the slope of the linear portions of the curves at metal ion concentration (Fig.5). The K_p values increased with increase in the copper ion concentration, which reveals that the rate of adsorption is governed by the diffusion of adsorbed copper ion within the pores of the adsorbent [1,14].

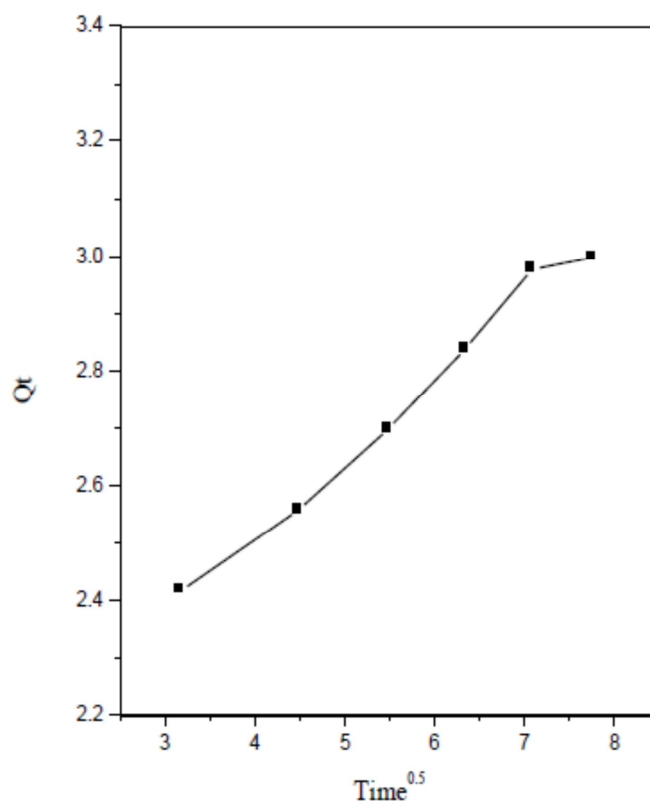


Fig.5. Effect of intra particle diffusion on the adsorption of copper ion
[Cu]=20mg/L; Adsorbent dose=25mg/50 ml; Temp=30° C

Effect of temperature: The adsorption capacity of the carbon increased with increase in the temperature of the system from 30°- 60°C. Thermodynamic parameters such as change in free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were determined using the following equations [11,12,15,16]

$$K_0 = C_{\text{solid}}/C_{\text{liquid}} \dots\dots\dots(4)$$

$$\Delta G^\circ = -RT \ln K_0 \dots\dots\dots(5)$$

$$\log K_0 = \Delta S^\circ / (2.303RT) - \Delta H^\circ / (2.303RT) \dots\dots(6)$$

Where K_0 is the equilibrium constant, C solid is the solid phase concentration at equilibrium (mg/ L), C_{liquid} is the liquid phase concentration at equilibrium (mg/L), T is the temperature in The positive values of ΔH° show the endothermic nature of adsorption and it governs the possibility of physical adsorption. Because in the case of physical adsorption, while increasing the temperature of the system, the extent of copper ion adsorption increases, this rules out the possibility of chemisorptions. However, the very low ΔH° value depicts copper ion is physisorbed onto adsorbent [12,13,15] The negative values of ΔG° (Table 6) shows the adsorption is highly favourable for copper ion. However, it indicates that the copper ion adsorption was spontaneous. The positive values of ΔS° (Table 6) shows the increased disorder and randomness at the solid solution interface of with adsorbent. While the adsorption there are some structural changes in the copper ion and the adsorbent occur. The adsorbed water molecules, which have displaced by the adsorbate species, gain more translational entropy than is lost by the adsorbate molecules, thus allowing the prevalence of randomness in the system [5,12,18]. The results show that more efficient physisorption. Enhancement of adsorption capacity of the activated carbon at higher temperatures has attributed to the enlargement of pore size and activation of the adsorbent surface [11,12,13].

Table.6 Equilibrium constant and thermodynamic parameters for the adsorption of metal ions onto acid activated carbon Temperature (°C)

Copper ion(mg/L)	K_0	ΔG°								
		30°	40°	50°	60°	30°	40°	50°	60°	ΔH° ΔS°
5	8.58	9.57	10.59	11.33	-5.417	-5.879	-6.338	-6.721	5.27	43.82
10	4.10	4.70	5.78	6.83	-3.557	-4.030	-4.711	-5.323	7.16	59.59
15	2.50	2.92	3.43	4.00	-2.308	-2.789	-3.311	-3.844	6.16	51.22
20	1.39	1.57	1.79	2.05	-0.836	-1.179	-1.568	-1.990	4.61	38.40
25	0.86	0.97	1.09	1.22	-0.361	-0.650	-0.851	-0.958	3.69	30.73

ΔH° (kJ/mol), ΔS° (J/K/mol), ΔG° (J/mol)

Table. 7 Rate constants for the adsorption of copper ions ($10^3 k_{\text{ad}}$, min^{-1}) and the constants for forward ($10^3 K_1$, min^{-1}) and reverse ($10^3 K_2$, min^{-1}) process

Copper ion (mg/L)	Temperature (°C)											
	k_{ad}				k_1		k_2					
	30°	40°	50°	60°	30°	40°	30°	40°	30°	40°	30°	40°
5	41.60	42.27	43.35	45.21	36.77	4.28	38.27	3.99	39.61	3.73	41.54	3.66
10	26.57	28.56	31.46	35.01	21.36	5.20	23.55	5.00	26.82	4.64	30.54	4.46
15	20.31	21.75	23.82	25.66	14.51	5.80	16.20	5.54	18.44	5.37	20.53	5.12
20	15.20	15.96	17.01	17.88	8.85	6.35	9.76	6.20	10.92	6.09	12.02	5.86
25	12.17	12.94	14.11	14.42	5.65	6.52	6.38	6.55	7.38	6.73	7.94	6.48

Effect of pH: The solution pH plays a major role in determining the amount of copper ions absorbed. Adsorption was studied over the range of pH ~ 3-10 and the results are shown in Fig.6. The initial metal ion concentrations were kept constant. Adsorption of copper ions increased appreciably (1-2 times) with increase of pH from 3 to 10 and consistent with results obtained by others. The increase is partly attributed to the formation of different hydroxo species with rise in solution pH. Based on the hydrolysis constants of metal ions as defined in $M^{2+} + nH_2O \rightleftharpoons M(OH)_n^{2-n} + nH^+$ and taking only primary metal species expected to be formed in the working pH range into consideration, the species distribution diagrams for copper ion is constructed and given in Fig. 4. It is evident that Cu^{2+} and its monohydroxo species are the predominating species up to pH ~ 9, while dihydroxo species are also formed to a significant extent above pH ~ 7.5 for copper ion. Since maximum adsorption copper ion was achieved at pH ~ 6.25, it may safely be stated that the removal of copper ion was mostly due to adsorption and not precipitation. However, precipitation of small fractions of Cu^{2+} even at pH ~ 6.25 on the surface by nucleation cannot be neglected. At still higher pH (>7), however, part of Cu^{2+} may be precipitated as dihydroxo species, which also depend upon the initial metal ion concentration. The other important factor, which might contribute to the higher adsorption of metal ions with increased pH, is the pH_{zpc} of PSC. At any pH below pH_{zpc} the surface of metal oxides/ oxyhydroxides is positively charged and at pH above pH_{zpc} the surface is negative. When the solution pH exceeded pH_{zpc}, the metal species are more easily attracted by the negatively charged surface of adsorbent, favoring accumulation of metal species on the surface and thus promoting adsorption [17,19].

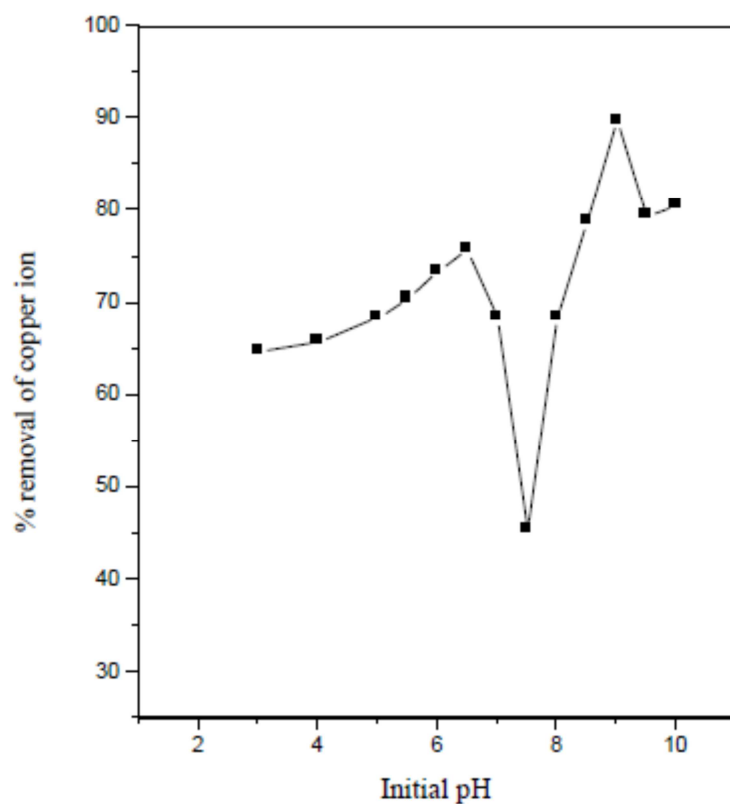


Fig.6 Effect of initial pH on the adsorption of Copper ion
[Cu]=20mg/L; Adsorbent dose=25mg/50ml; Contact time=60 min

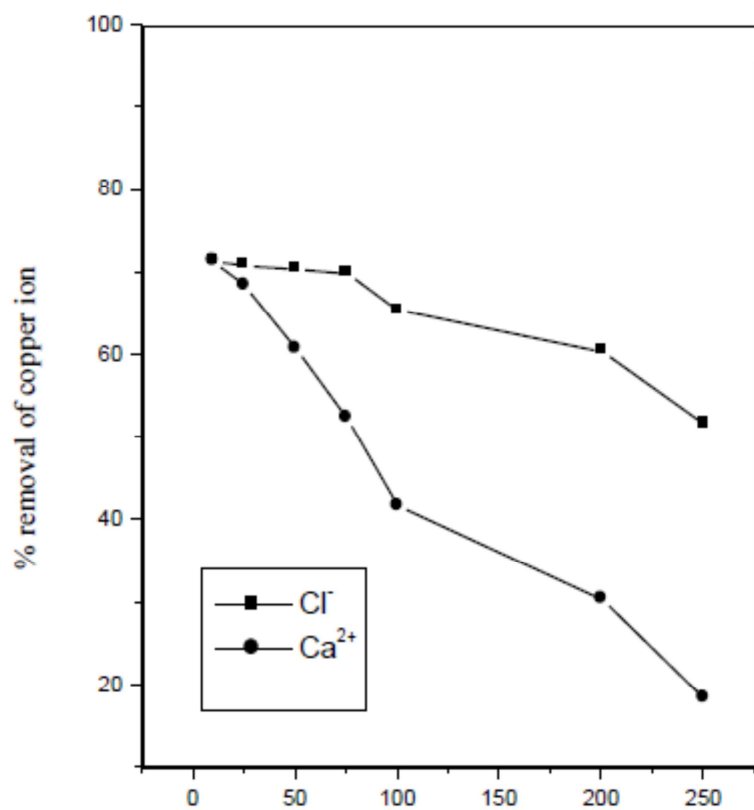


Fig.7. Effect of other ions on the adsorption of copper ion
[Cu]=20mg/L; Adsorbent dose=25mg/50ml; Contact time=60 min

Effect of other ions: Till now all the adsorption results discussed above were obtained by taking a single cation as adsorbate (e.g. Cu^{2+}) however, in reality the contaminated water contains several other ions (both cations and anions), which can affect the adsorption of heavy metals. Therefore, it was thought worthwhile to study the effect of some commonly occurring ions on adsorption behavior of copper ion under present study. A typical water sample containing Chloride ions and Calcium ions was doped with known quantities of adsorbate metal ions and they were used as the simulated water matrix for adsorption. A fixed amount PSC was dispersed in this water matrix containing adsorbate. The other adsorption parameters were kept constant, as stated earlier. The results are collected in Fig.7. It is evident that the presence of the abovementioned ions in the adsorbate solution practically did not affect the extent of adsorption. It may be noted that almost the whole iron content in the adsorbate solution is removed after adsorption. The concentration of other ions, however, marginally decreased (within 10% of initial concentration) after adsorption. A higher concentration level of interfering ions may, however, adversely affect the adsorption capacity of PSC. Adsorption of different heavy metal from a simulated water matrix containing a high background level of different ions is being carried out to assess its future applicability to removal of toxic metals from industrial effluents [16,17,19].

Desorption studies: Desorption studies help to elucidate the nature of adsorption and recycling of the spent adsorbent and the copper ion. If the adsorbed copper ion can be desorbed using neutral pH water, then the attachment of the copper ion of the adsorbent is by weak bonds. If sulphuric acid or alkaline water desorb the copper ion, then the adsorption is by ion exchange. If organic acids, like acetic acid can desorb the copper ion, then the metal ion has held by the adsorbent through chemisorption. 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 85% removal of adsorbed copper 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 copper ion was adsorbed onto the activated carbon through by physisorption mechanisms[11,12,17,18].

CONCLUSION

The experimental data are correlated reasonably well by the Langmuir and Freundlich adsorption isotherms. The low as well high pH value shows the optimum amount of adsorption of copper ion by the adsorbent. The amount of copper ion adsorbed by the adsorbent was increased with increasing ionic strength and temperature. The dimensionless separation factor (RL) shows that the chosen activated carbon can be used for the removal of copper ion from aqueous solution. The values of ΔH° , ΔS° and ΔG° results shows that *Phoenix sylvestris* leaves carbon has the potential for use as an adsorbent for the removal copper ion from wastewater.

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