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# Studies on the adsorption mechanism of Cu(II) ions by a new activated carbon

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#### **ABSTRACT**

The efficiency of activated carbon prepared from Azadiracta indica bark [AIC] for the adsorption of  $Cu^{2+}$  ions from aqueous solutions has been studied as a function of agitation time, adsorbent dosage, initial metal ion concentration, temperature and pH of adsorbate solution. The optimal conditions for the adsorption have been arrived at and experiments were conducted to determine the Langmuir constants, Freundlich parameters and thermodynamic parameters such as  $\Delta G^{\circ}$ ,  $\Delta H^{\circ}$  and  $\Delta S^{\circ}$ . Desorption studies were also carried out for the recovery of both adsorbent and the metal ions. The adsorption of  $Cu^{2+}$  ions on to the surface of AIC has been confirmed by the analysis of IR spectra, XRD and SEM images before and after  $Cu^{2+}$  adsorption.

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

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#### INTRODUCTION

Heavy metal pollution represents an important environmental problem due to its toxic effects and accumulation throughout the food chain. The main sources of heavy metal pollution include electroplating, painting and surface treatment industries. The inorganic effluent from the industries contains toxic metals. The heavy metals are of special concern because they are non-degradable and therefore persistent. Commonly encountered metals of concern include Pb<sup>2+</sup>,

Cu<sup>2+</sup>, Zn<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup> etc. These metals are toxic in both their chemically combined forms as well as the elemental form. Exposure to these contaminants present even in low concentrations in the environment is proved to be harmful to the human health. In order to solve heavy metal pollution in the environment, it is important to bring applicable solutions. Many techniques have been followed for the removal of heavy metals and among them adsorption process is preferred because of its high efficiency, easy handling, cost effectiveness as well as availability of different adsorbents [1-3].

In the present investigation, the efficacy of the activated carbon prepared from *Azadiracta indica* bark (AIC) for the removal of Cu(II) ions from its aqueous solution has been studied and the applicability of the kinetic and equilibrium models for the Cu(II)-AIC system has also been discussed.

#### **EXPERIMENTAL SECTION**

#### Adsorbent

Carbon was prepared by treating air-dried *Azadiracta indica* bark with concentrated sulphuric acid in a weight ratio of 1:1. The resulting black product was kept in a furnace, maintained at  $500\,^{\circ}$ C for 12 h followed by washing with water until free from excess acid and dried at  $150\pm5\,^{\circ}$ C. The carbon thus obtained was ground well and the portion retained between 0.030 and 0.035 mm sieves was used in all the experiments. All the chemicals used were of Analytical Grade.

## Batch equilibration method

Batch mode experiments were carried out at different temperatures namely 35, 40, 45 and 50 °C. A known weight of absorbent was agitated in a temperature controlled mechanical shaker with a known volume and concentration of the adsorbate with a pH of 6.5. The initial concentration was varied from 5 mg/L to 30 mg/L. The flask containing the sample was withdrawn from the shaker at a predetermined time interval, filtered and the residual concentration of the metal ion was estimated by photoelectric colorimeter using 5 % K<sub>4</sub>[Fe<sub>3</sub>(CN)<sub>6</sub>] reagent and 620 nm filter.

## Effect of variable parameters

Experiments were carried out to determine the effect of dosage of the adsorbent (10 to 100 mg/50 ml of the adsorbate), effect of different initial concentrations of Cu(II) ions (ranging from 5 to 30 mg/L), effect of contact time on the removal of the copper ions, effect of initial pH of the adsorbate solution (pH 3-9), effect of other ions such as  $Ca^{2+}$  (using  $CaSO_4$ ) and  $Cl^-$  (using NaCl) ions during the adsorption of Cu(II) and the effect of solution temperature (35 – 50 °C) at 5 °C intervals with an accuracy of  $\pm 0.5$  °C.

## Zero point charge

The pH at the potential of zero charge of the carbon (pH<sub>zpc</sub>) was measured using the pH drift method. The pH of the solution was adjusted by using 0.01 M sodium hydroxide or hydrochloric acid. Nitrogen was bubbled through the solution at 25  $^{\circ}$ 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 plots of final pH against initial pH were used to determine the zero point charge of the activated carbon [4].

#### Titration studies

Literature survey has revealed that [4], only strong acidic carboxylic acid groups are neutralized by sodium bicarbonate, whereas those neutralized by sodium carbonate are thought to be lactones, lactol and carboxyl group. Only the weakly acidic phenolic groups react with sodium hydroxide. Therefore, by selective neutralization using bases of different strength, the surface acidic functional groups in AIC can be characterized both quantitatively and qualitatively. Neutralization with hydrochloric acid characterizes the amount of surface basic groups such as pyrones and chromenes. 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 zero point charge values. The results obtained from the above characterization studies are given in the Table-1.

#### Regeneration studies

The regeneration of the adsorbed carbon was done by using 0.2 M mineral acids and sodium chloride solutions.

#### **Analytical Measurements**

The IR spectra, SEM images and XRD diagrams of the adsorbents before and after adsorption were recorded at the CECRI, Karaikudi, South India.

#### **RESULTS AND DISCUSSION**

## Characterization of the adsorbent

The physico-chemical properties of the chosen adsorbent, AIC, were carried out by standard methods [5-7] and are listed in the following Table-1.

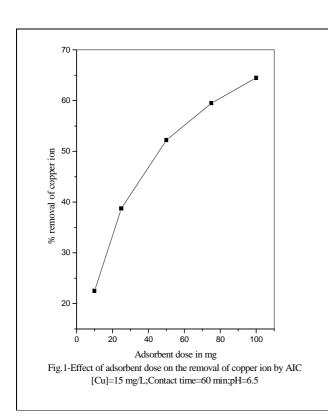
TABLE 1: CHARACTERISTICS OF THE ADSORBENT							
Properties	AIC						
Particle size (mm)	0.030-0.035						
Density (g/cc)	0.2856						
Moisture content (%)	1.55						
Loss on ignition (%)	78						
Acid insoluble matter (%)	2.5						
Water soluble matter (%)	0.52						
pH of aqueous solution	6.5						
$pH_{zpc}$	5.75						
Surface groups (m equiv/g)							
i) Carboxylic acid	0.528						
ii) Lactone, lactol	0.085						
iii) Phenolic	0.079						
iv) Basic (pyrones and chromenes)	0.018						

## Effect of dosage of AIC

The adsorption of the Cu<sup>2+</sup> ions on AIC was studied by varying the carbon concentration (10-100 mg/50 ml) for the copper ion concentration of 10 mg/L. The percentage of adsorption increased with increase in the carbon concentration (Figure 1). This may be due to the increased carbon surface area and availability of more adsorption sites [8,9].

## Effect of contact time and initial metal ion concentration

The experimental results for the adsorption of Cu<sup>2+</sup> ions on the activated carbon at various concentrations (5, 10, 15, 20, 25 and 30 mg/L) with contact time presented in Table 2 which reveals that, the percent adsorption decreased with increase in initial metal ion concentration, but the actual amount of Cu<sup>2+</sup> ion adsorbed per unit mass of carbon is found to be increased with increase in metal ion concentration. It means that the adsorption is highly dependent on initial concentration of metal ion. It is because of the reason that at lower concentration, the ratio of the initial number of metal ion to the available surface area is low, subsequently the fractional adsorption becomes independent of initial concentration. However, at high concentration, the available sites for adsorption become fewer and hence the percentage removal of metal ion is dependent upon initial concentration. Equilibrium is established at 40 minutes for all concentrations. The plot of percent Cu(II) adsorbed against contact time for the initial Cu<sup>2+</sup> ion concentration of 10 mg/L, 6.5 pH and a temperature of 35 °C is given in Figure 2 which reveals that the curve is single, smooth, and continuous, leading to saturation, suggesting the possible monolayer coverage of the metal ion on AIC [8,9].



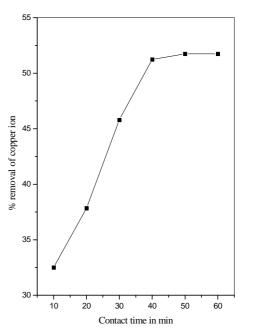
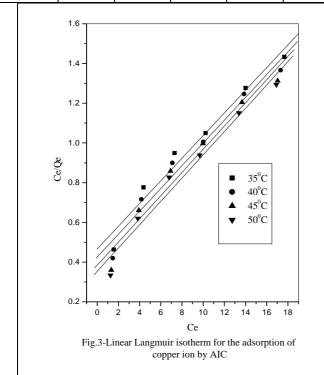
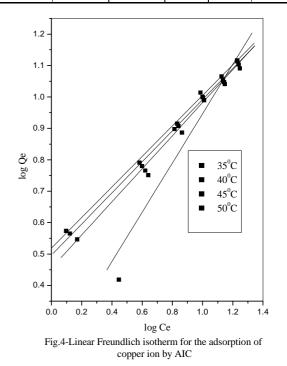


Fig.2-Effect of contact time on the adsorption of copper ion by AIC [Cu]=15 mg/L;Adsorbent dose=50 mg/50 ml;pH=6.5

TAI	TABLE 2: EQUILIBRIUM PARAMETERS FOR THE ADSORPTION OF COPPER IONS ONTO AIC													
[Cu(II)] <sub>initial</sub> ,	$[Cu(II)]_{initial}, \qquad \qquad C_e (mg/L)$					$Q_e (mg/g)$					Metal ions Removed (%)			
(mg/L)	35°	40°	45°	50°	35°	40°	45°	50°	35°	40°	45°	50°		
5	1.5820	1.4781	1.3230	1.2523	3.4180	3.5219	3.6770	3.7477	68.36	70.43	73.54	74.95		
10	4.3721	4.1738	3.9787	3.8295	5.6279	5.8262	6.0213	6.1705	56.27	58.26	60.21	61.70		
15	7.3026	7.1027	6.9281	6.7892	7.6974	7.8973	8.0710	8.2108	51.31	52.64	53.81	54.73		
20	10.2437	10.0275	7.9875	9.6825	9.7563	9.9725	10.0215	10.3175	48.78	49.86	50.06	51.58		
25	14.0215	13.8724	13.6578	13.3782	10.9785	11.1276	11.3422	11.6218	43.91	44.51	45.36	46.48		
30	17.6721	17.3226	17.0283	16.9210	12.3279	12.6774	12.9717	13.0790	41.09	42.25	43.23	43.59		





## Adsorption isotherm

The experimental data were analyzed in the light of Langmuir [10] and Freundlich adsorption isotherms [11].

The Langmuir [10] isotherm is

$$C_e/Q_e = 1/Q_m b + C_e/Q_m$$

Where  $C_e$  is the equilibrium concentration (mg/L),  $Q_e$  is the amount adsorbed at equilibrium (mg/g) and  $Q_m$  and b are Langmuir constants related to adsorption efficiency and energy of adsorption, respectively.

The plots of  $C_e/Q_e$  versus  $C_e$  suggest linearity and the applicability of the Langmuir isotherm to the  $Cu^{2+}$ - AIC adsorption system (Figure 3). Values of  $Q_m$  and b were determined from slope and intercepts of the plots 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 [12,13]. Further, it confirms the endothermic nature of the adsorption process involved in the system. To confirm the favorability of the adsorption process, the separation factor  $(R_L)$  was calculated and presented in Table 4. The values lie between 0 and 1 which confirm the ongoing adsorption process is favourable [14].

The Freundlich isotherm [11] is

$$\log Q_e = \log K_F + 1/n \log C_e$$

Where  $Q_e$  is the amount of ferrous 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 ferrous ion follows the Freundlich isotherm (Figure 4). Values of  $K_F$  and n were determined and are given in the Table 5, which reveals that an increase in the negative charge on the surface that enhances the electrostatic force like van der Waal's force between the carbon surface and metal ion, thereby increases the adsorption of copper ions. The values clearly indicate that there is dominance in adsorption capacity. The intensity of adsorption is an indicative of the bond energies between metal ion 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 are greater than one indicating the adsorption is much more favourable [13-15].

TABLE 3-L	TABLE 3-LANGMUIR CONSTANTS AND STATISTICAL PARAMETER									
S.No.	Temp., °C	$\mathbf{Q}_{\mathbf{m}}$	b	$\mathbb{R}^2$						
1	35°	0.9846	17.53	0.1089						
2	40°	0.9843	17.36	0.1190						
3	45°	0.9813	17.12	0.1319						
4	50°	0.9898	17.09	0.1416						

[Cu(II)] <sub>initial</sub> ,	TABLE 4-DIMENSIONLESS SEPARATION FACTOR, R <sub>L</sub> Temp., °C							
[Cu(II)] <sub>initial</sub> , mg/L	35	40	45	50				
5	0.647	0.626	0.602	0.584				
10	0.478	0.456	0.431	0.413				
15	0.379	0.359	0.335	0.320				
20	0.314	0.295	0.274	0.261				
25	0.268	0.257	0.232	0.220				
30	0.234	0.218	0.201	0.190				

TABLE 5-F	TABLE 5-FREUNDLICH CONSTANTS AND STATISTICAL PARAMETER									
S.No.	Temp., °C	$\mathbf{K}_{\mathbf{F}}$	n	$\mathbb{R}^2$						
1	35	2.1919	1.2742	0.9630						
2	40	1.6923	1.9007	0.9980						
3	45	1.6402	2.0210	0.9989						
4	50	1.6254	2.0584	0.9987						

#### 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 Cu<sup>2+</sup> ion removal by AIC has been carried out to understand the behavior of this low cost carbonaceous adsorbent. The adsorption of copper ions from an aqueous solution follows reversible first order kinetics, when a single species is considered on a heterogeneous surface. The heterogeneous equilibrium between the copper ion solution and the activated carbon has been expressed as:

$$A \xrightarrow{k_1} B$$

Where  $k_1$  = forward rate constant;  $k_2$  = backward rate constant;  $A = Cu^{2+}$  ions remaining in the aqueous solution and  $B = Cu^{2+}$  ions adsorbed on the surface of activated carbon.

The rate constants  $k_1$  and  $k_2$  [14-16] are presented in Table 6. From the values, it 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 of adsorption is the ratio of the concentration of adsorbate in adsorbent and concentration of adsorbate in aqueous solution given by  $K_o$  (Table 7). The results indicates that  $K_o$  values decrease with increase in the concentration of the  $Cu^{2+}$  ions and increases with increase in temperature.

TABLE 6-RATE CONSTANTS FOR THE ADSORPTION OF COPPER IONS (10 <sup>3</sup> k <sub>ad</sub> , min <sup>-1</sup> ) AND THE RATE CONSTANTS FOR FORWARD (10 <sup>3</sup> k <sub>1</sub> , min <sup>-1</sup> ) AND REVERSE (10 <sup>3</sup> k <sub>2</sub> , min <sup>-1</sup> ) PROCESS												
[C <sub>22</sub> (II)]		k,	ad		$\mathbf{k_1}$	$\mathbf{k_2}$	$\mathbf{k_1}$	$\mathbf{k_2}$	$\mathbf{k_1}$	$\mathbf{k_2}$	$\mathbf{k_1}$	$\mathbf{k}_2$
[Cu(II)] <sub>initial</sub> ,	Temp., °C											
mg/L	35°	40°	45°	50°	3.5	5°	40	)°	4:	5°	50	0°
5	4.58	4.97	5.38	5.82	2.68	1.90	3.00	1.97	3.42	1.96	3.78	2.04
10	4.35	4.60	4.92	5.21	2.44	1.91	2.68	1.92	2.96	1.96	3.22	1.99
15	4.03	4.12	4.24	4.39	2.07	1.96	2.05	2.07	2.12	2.12	2.26	2.13
20	3.79	3.91	4.05	4.19	1.85	1.94	1.96	3.55	2.03	2.02	2.15	2.02
25	3.50	3.54	3.61	3.72	1.54	1.96	1.57	1.97	1.64	1.97	1.72	2.00
30	3.33	3.40	3.49	3.58	1.36	1.97	1.44	1.96	1.51	1.98	1.56	2.02

TABLE	TABLE 7-EQUILIBRIUM CONSTANT AND THERMODYNAMIC PARAMETERS FOR THE ADSORPTION OF METAL IONS ONTO AIC									
IC (II)		Temp., °C								
[Cu(II)] <sub>initial</sub> , mg/L	35°	40°	45°	50°	35°	40°	45°	50°		
IIIg/L		]	$\zeta_{0}$			Δ	G°		$\Delta H^{\circ}$	$\Delta S^{\circ}$
5	2.16	2.38	2.77	2.99	-1.97	-2.25	-2.70	-2.94	20.93	74.23
10	1.28	1.39	1.51	1.61	-0.64	-0.86	-1.09	-1.28	12.57	42.78
15	1.05	1.11	1.16	1.21	-0.13	-0.27	-0.40	-0.51	7.64	25.24
20	0.95	0.99	1.01	1.06	+0.12	+0.01	-0.006	-0.17	5.72	18.13
25	0.78	0.80	0.83	0.86	+0.62	+0.57	+0.49	+0.37	4.91	13.85
30	0.69	0.73	0.76	0.77	+0.92	+0.81	+0.71	+0.69	4.53	11.88

 $\Delta H^{\circ}$  (kJ/mol),  $\Delta S^{\circ}$  (J/K/mol),  $\Delta G^{\circ}$  (kJ/mol)

A clear examination of the effect of copper ion concentrations on the rate constant  $k_{ad}$  (Table 6) helps to describe the mechanism of metal ion removal. 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 [14].

The contact-time experimental results can be used to study the rate-limiting step in the adsorption process, as shown by Weber and Morris [16,17]. 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's external surface and one might then postulate that the rate-limiting step may be either film or intra-particle diffusion. As they act in series, the slower of the two will be the rate-determining step [16].

The rate constant for intra-particle diffusion is obtained using the equation

$$Q = K_p t^{1/2} + C$$

Where,  $K_p$  (mg/g/min) is the intra-particle diffusion rate constant.

The  $K_p$  values obtained from the slope of the linear portions of the curves for different metal ion concentrations at 35 °C are given in Table 8. 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.

TABLE 8-INTRA-PARTICLE DIFFUSION, Kp							
[Cu(II)] <sub>initial</sub> , mg/L	K <sub>p</sub>						
5	0.117						
10	0.235						
15	0.352						
20	0.470						
25	0.588						
30	0.705						

#### Effect of temperature

The adsorption capacity of the carbon increased with increase in the temperature of the system from 35 -50 °C. Thermodynamic parameters such as change in free energy ( $\Delta G^{\circ}$ ), enthalpy ( $\Delta H^{\circ}$ ) and entropy ( $\Delta S^{\circ}$ ) were determined using the following equations [12]

$$\begin{split} &K_o &= C_{solid}/C_{liquid} \\ &\Delta G^\circ = -RT \; ln \; K_o \\ &\log \; K_o = \Delta S^\circ/\; (2.303RT) \; \text{--} \; \Delta H^\circ/(2.303RT) \end{split}$$

Where  $K_o$  =equilibrium constant;  $C_{solid}$  = solid phase concentration at equilibrium (mg/L);  $C_{liquid}$  = liquid phase concentration at equilibrium (mg/L), T = temperature in Kelvin and R = gas constant.

The  $\Delta H^{\circ}$  and  $\Delta S^{\circ}$  values obtained from the slope and intercept of van't Hoff plots are presented in Table 7. The values are with in the range of 1 to 93 kJ/mol indicating the favorability of physisorption. From the results, we could confine our self that physisorption is much more

favorable for the adsorption of copper ions. The positive values of  $\Delta H^{\circ}$  confirm the endothermic nature of adsorption and it governs the possibility of physical adsorption. The low  $\Delta H^{\circ}$  values also depict the metal ion is physisorbed onto the adsorbent [15-18].

The negative values of  $\Delta G^{\circ}$  (Table 7) indicate the adsorption is highly favorable for  $Cu^{2+}$  ions. The positive values of  $\Delta S^{\circ}$  (Table 7) shows the increased disorder and randomness at the solid (AIC)-solution ( $Cu^{2+}$ ) interface. During adsorption process, there are some structural changes in the metal ion and the adsorbent occur [17]. The adsorbed water molecules, which were 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 [17]. From the results, we can confirm that more efficient physisorption rather than chemisorption. Also 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 [14-17].

## 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  $\sim$  3-9 and the results are shown in Fig.5. The initial metal ion concentrations were kept constant. Adsorption of copper ions increased appreciably ( $\approx$ 2 times) with increase of pH from 3 to 9 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 and taking only primary metal species expected to be formed in the working pH range into consideration, the species distribution diagram for copper ion is constructed and are given in Fig. 5.

$$M^{2+} + nH_2O \rightarrow M (OH)_n^{2-n} + nH^+$$

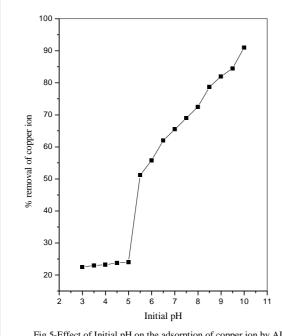


Fig.5-Effect of Initial pH on the adsorption of copper ion by AIC [Cu]=15 mg/L;Adsorbent dose=50 mg/50 ml;Contact time=60 min

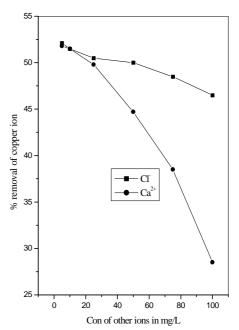


Fig.6-Effect of other ions on the adsorption of copper ion [Cu]=15 mg/L;Adsorbent dose=50 mg/50 ml;Contact time=60 min

It is evident that  $Cu^{2+}$  and its monohydroxo species are the predominating species up to pH ~ 7, while dihydroxo species are also formed to a significant extent above pH ~ 7 for copper ion. Since maximum adsorption of copper ions was achieved at pH ~ 6.5, it may safely be stated that the removal of copper ion was mostly due to adsorption and not precipitation. 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<sub>pzc</sub> of AIC. At any pH below pH<sub>pzc</sub> the surface of metal oxides/ oxyhydroxides is positively charged and at pH above pH<sub>pzc</sub> the surface is negative. When the solution pH exceeded pH<sub>zpc</sub>, 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 [19-21].

## Effect of other ions

The effect of other ions like Ca<sup>2+</sup> (using CaSO<sub>4</sub> solution) and Cl<sup>-</sup> (using NaCl solution)on the adsorption process were studied at different concentrations. The ions were added to 15 mg/L of metal ion solutions and the contents were agitated for 60 min at 35 °C. The results are shown in the Figure 6, which reveal that low concentration of Cl<sup>-</sup> does not affect the percentage of adsorption of metal ion on activated carbon, because the interaction of Cl<sup>-</sup> at available sites of adsorbent through competitive adsorption is not so effective. While the concentration of other ion Ca<sup>2+</sup> increases, the interference of these ions at available surface sites of the sorbent through competitive adsorption increases and hence decreases the percentage adsorption. The interference was more in the presence of Ca<sup>2+</sup> compared with Cl<sup>-</sup> ion. This is so because, ions with smaller hydrated radii decrease the swelling pressure with in the sorbent and increase the affinity of the sorbent for such ions [2,20,22].

#### 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 are 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 81 % 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 physisorption mechanism [14-16, 21].

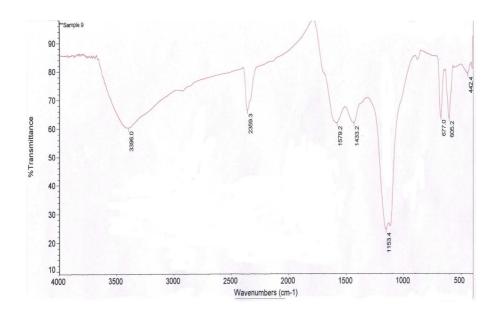
## Evidences for adsorption

The IR spectra of the raw activated carbon and after adsorption of metal ion are shown in Figures 7a and 7b respectively. The slight reduction of stretching vibration bands clearly indicate the adsorption of metal ion on the adsorbent by physical forces [2,16]. The band at around 3400 cm<sup>-1</sup> is due to the stretching of O-H group. The band at around 2400 cm<sup>-1</sup> indicate the position of asymmetrical and symmetrical stretching of methylene groups in the aliphatic and cyclic hydrocarbons. The band at around 2360 cm<sup>-1</sup> show the presence of carboxylate ion. The bands at 1579 and 1591 cm<sup>-1</sup> are assigned to C=C stretching vibration of cycloalkenes. The (S=O) symmetric stretching frequency of organic sulphates occurs in the region of 1430 cm<sup>-1</sup>. The band

at 1111 cm<sup>-1</sup> shows the alcoholic C-O stretching vibration and at around 610 cm<sup>-1</sup> likely result from  $NO_2$  bending vibrations. The C-C bending vibrations of normal alkenes occur in the region of 460 cm<sup>-1</sup>. Thus the IR results have confirmed the presence of functional groups such as OH<sup>-</sup>, COO<sup>-</sup>, CO,  $NO_2$ ,  $S_2$  on the surface of AIC that could be the potential adsorption sites for interaction with the Cu(II) ions [20].

The XRD diagrams of activated carbon and metal ion-adsorbed carbon are shown in Figures 8a and 8b respectively. The intense main peak shows the presence of highly organized crystalline structure of raw activated carbon [2,16]. After the adsorption of metal ion, the intensity of the highly organized peaks are slightly diminished. This has attributed to the adsorption of metal ion on the upper layer of the crystalline structure of the carbon surface by means of physisorption [2,16].

The SEM diagrams of raw activated carbon and metal ion-adsorbed activated carbon are shown in Figures 9a and 9b respectively. The bright spots show the presence of tiny holes on the crystalline structure of raw activated carbon. After treatment with metal ion the bright spots became black indicating the adsorption of the metal ion on the surface of the carbon by means of physisorption [2,16,17]. SEM images of AIC also show that the adsorbent has a rough surface with almost non-compact structure. It is obvious that the sorbent has considerable number of pore spaces, where appropriate conditions exist for Cu(II) ions to be trapped and adsorbed into these pores. The SEM photos also illustrate that the metals can be homogeneously adsorbed on the surface of adsorbent. It is revealed from the SEM figures that the surface of AIC is found to be not so random but rough in such a way to adhere the solute species on to the surface of the adsorbent. Therefore the adsorptive characteristics of AIC are expected to be highly effective [15,23].



## FIG. 7a IR SPECTRUM OF RAW AIC

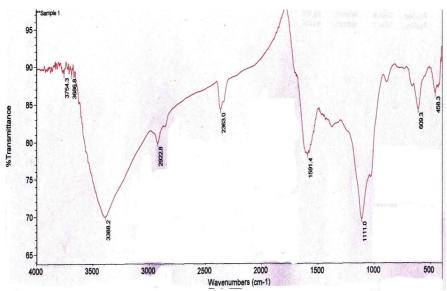


FIG. 7b IR SPECTRUM OF AIC AFTER Cu(II) ION ADSORPTION

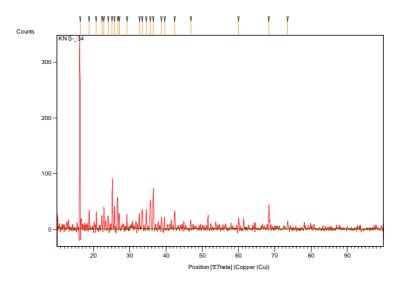


FIG. 8a XRD DIAGRAM OF RAW AIC

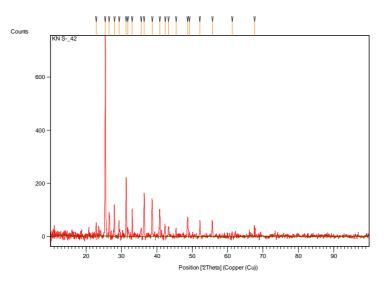


FIG. 8b XRD DIAGRAM OF AIC AFTER Cu(II) ION ADSORPTION

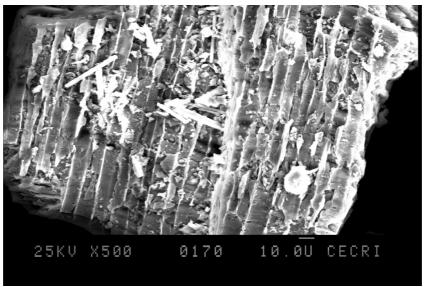


FIG. 9a SEM PHOTOGRAPH OF RAW AIC

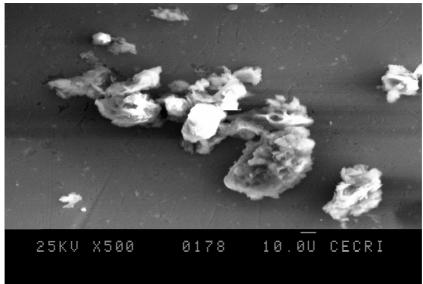


FIG. 9b SEM PHOTOGRAPH OF AIC AFTER Cu(II) ION ADSORPTION

#### **CONCLUSION**

The experimental data correlated reasonably well by the Langmuir and Freundlich adsorption isotherms and the isotherm parameters were calculated. The amount of metal ion adsorbed increased with increase in pH of the medium. The amount of metal ion adsorbed slightly decreased with increasing ionic strength and increased with increase in temperature. The dimensionless separation factor ( $R_L$ ) showed that the activated carbon can be used for the removal of metal ion from aqueous solution. The values of  $\Delta H^{\circ}$ ,  $\Delta S^{\circ}$  and  $\Delta G^{\circ}$  results show that the carbon employed has a considerable potential as an adsorbent for the removal of metal ions.

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#### **REFERENCES**

- [1] Sekaran, G.; Shanmugasundaram, K.A.; Mariappan, M.; Raghavan, K.V. *Ind. J. Chem. Tech.*, **1995**, 2, 311.
- [2] Arivoli, S. Kinetic and thermodynamic studies on the adsorption of some metal ions and dyes onto low cost activated carbons, Ph D., Thesis, Gandhigram Rural University, Gandhigram, **2007.**
- [3] Jain, C. K.; Daya Ram, Wat. Res., 1997, 31(1), 154.
- [4] Hassler, J.W. *Purification of Water With Activated Carbon*, 2<sup>nd</sup> Edition, Chemical Publishing Co. Inc., New York, **1974.**
- [5] ISI, Activated Carbon, Powdered and Granular-Methods of Sampling and Tests, 2<sup>nd</sup> Revision, First Print, Bureau of Indian Standards, IS 877:-Feb **1992.**
- [6] Rengaraj, S.; Banumathi Arabindoo; Murugesan, V. Ind. J. Chem. Tech., 1999, 6, 1-4, 1999.
- [7] Jia, Y.F.; Thomas, K.K. Langmuir, 2002, 18, 470.

- [8] Namasivayam, C.; Muniasamy, N.; Gayathri, K.; Rani, M.; Renganathan, K. *Biores. Technol.*, **1996**, 57, 37.
- [9] C Namasivayam, C.; Yamuna, R.T. Environ. Poll., 1995, 89, 1.
- [10] Langmuir, I. J. Am. Chem. Soc., 1918, 40, 1361.
- [11] Freundlich, H. Phy. Chemie., 1906, 57, 384.
- [12] Krishna, D.G.; Bhattacharyya, G. Appl. Clay Sci., 2002, 20, 295.
- [13] Balasubramanian, N.; Jafar Aahmed, A. J. Ind. Coun. Chem., 2003, 20 (2), 7-12,.
- [14] Jafar Ahamed, A.; Suganthana, B. J.Ind. Chem. Soc., August 2006, 83, 792-795,..
- [15] B.Y.M.Bueno, B.Y.M.; Torem, M.L.; .Molina, F.; .Mesquita, L.M.S. *Bio and Hydrometallurgy*, **2008**, **21(1)**, 65-75.
- [16] Jafrar Ahamed, A.; Balakrishnan, V. J. Chem. Pharm. Res., 2010, 2(3), 733-745...
- [17] Weber, W.J. Principle and Application of Water Chemistry, Edited by Faust S D and Hunter J V Wiley, New York, **1967**.
- [18] Renmin Gong; Yingzhi Sun; Jian Chen; Huijun Liu; Chao Yang, *Dyes and Pigments*, **2005**, 67, 179.
- [19] Vadivelan, V.; Vasanthkumar, K. J. Colloid Inter. Sci., 2005, 286, 91.
- [20] Yupeng Guo; Jingzhu Zhao; Hui Zhang; Shaofeng Yang; Zichen Wang; Hongding Xu. *Dyes and Pigments*, **2005**, 66, 123.
- [21] Sreedhar; M.K.; Anirudhan, T.S. Ind. J. Environ. Prot., 1999, 19, 8.
- [22] Nigamananda Das; Ranjit Kumar Jana, J. Colloid Inter. Sci., 2006, 293, 253.
- [23] Aravind, K.; Prasad, B.; Mishra, I.M. J. Haz. Mat., 2008, 150, 174.