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Removal of Copper Ion from Aqueous solutions by low cost Activated Carbon from Thespesia Populnea Bark

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ABSTRACT

Activated carbon was prepared from low cost material like Thespesia Populnea Bark copper adsorption from industrial waste water was studied with the aim of detoxifying industrial effluents before the safe onto land or into river. In this study, removal of copper (II) from aqueous solution by adsorption on TPC (Thespesia Populnea Bark Carbon) has been investigated in batch experiments. The effect of various parameters such as adsorbent dose, contact time, pH, agitation speed, particle size and initial copper ion concentration for the adsorption of Cu (II) on TPC was determined. The adsorption isotherms were described by means of Langmuir and Freundlich isotherm models. The rate of adsorption was found that the adsorption mechanisms in the copper / adsorbent system fallow pseudo –first- order kinetics with a significant contribution from film diffusion. The various thermodynamic parameters such as $\Delta G°$, ΔH^o, and $\Delta S°$ were calculated. The percentage removal of copper ion on to TPC was very significant.

Key words: Thespesia Populnea (TPC), Copper, Adsorption, kinetics, activated carbon, pseudo-first – order equation and Aqueous solutions.

INTRODUCTION

The increased level of environmental contamination as a result of industrial development is pretentiousness a very serious problem to the global environment. Among the heavy metals like cadmium, cobalt, zinc, copper, and iron ignition beyond permissible quantities causes psychological disorder in human beings. Environmental Protection Agency (EPA) standards, the permissible limit of copper discharge in industrial effluents into water bodies is limited to 0.25 mg l^{-1}. Copper contamination of the environment is primarily due to man made (anthropogenic) activities, making it the most everywhere toxic metal in the environment. Copper is one of most common toxic metals that find its way to water sources from various industries, i.e. electroplating, mining, electrical and electronics iron and steel production, non ferrous metal industry, printing and photographic industries. Copper concentrations in humans have increased to toxic to toxic levels causes various diseases and disorders such as liver damage [1, 2]. Now days, development of surface modified activated carbon has produced a diversity of activated carbon with far superior adsorption capacity. The use of Thespesia Populnea bark with surface modification to improve its metal removal performance would add to its economic value, help reduce the cost of waste disposal and most importantly, provide a potentially inexpensive alternative to existing commercial activated carbon. The research study is to investigate the possible use of Thespesia Populnea Bark as an alternative biosorbent material for removal of Cu^{2+} ions from aqueous solutions. The effect of adsorbent dose, contact time initial metal ion concentration, temperature of solution and pH on the removal of Cu^{2+} ions were calculated and discussed.

EXPERIMENTAL SECTION

Adsorption Experiments

Adsorbent

Adsorbent like TPC solids were collected and washed to be completely free from dirt and inherent pulp. Then it is treated with conc. Sulphuric acid at a weight of ratio 1:1.The resulting products were grounded and sieved into different particle sizes ranges between 0.5 to 3.15 mm.

Batch equilibration method

Batch experiments were carried out in a batch process at 30°, 40°, 50° and 60°C temperature in batch mode. Batch mode was selected due to its simplicity and reliability. The experiments were done in different Erlenmeyer flasks of 100ml capacity. Prior to each experiment, a predetermined amount of adsorbent was added to each flask. The stirring was kept constant (120 rpm) for each run throughout the experiment to ensure and equal mixing. Each flask was filled with known volume of sample before connecting stirring, such as metal solutions with an initial concentration of 25, 50, 75, 100, and 125 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.

RESULTS AND DISCUSSION

Characteristics of the adsorbent

Activated carbon has been used as an adsorbent for the toxic substances from water due to its high adsorption capacity, micro porous structure and surface and special surface reactivity. The chemical nature and pore structure usually determines the sorption activity. The physico chemical properties are given the table 1.

Table 1.Charecteristics of the adsorbent

Sl No.	Properties	TPC
1	Particle size (mm)	0.041
2	Density (g/cc)	0.3243
3	Moisture content (%)	0.32550
4	Loss in ignition (%)	0.273
5	pH of aqueous solution	6.5

Effect of adsorbent (Thespesia Populnea Bark carbon) Dosage

The experimental results showed that TPC has high efficiency of removal of copper ions from aqueous solution. The absorption of copper ion on carbon was calculated by varying the carbon dose (10-250 mg/ 50 ml) for 30 mg / litre copper ion concentration. From fig (1), it is_observed that the percentage of adsorption increased with increases in the carbon concentration. This was attributed to increased carbon surface area and the availability of more adsorption sites [2, 3]. Hence all studies were carried out with 0.025mg of adsorbent / 50 ml of the varying adsorbate solutions of 25, 50, 75, 100 and 125. The equilibrium values obtained from the studies are tabulated in Table.2.

Table 2 – Equilibrium parameters for the adsorption of Copper ion onto TPC

Copper ion	C_e (mg/L)				Q_e (mg/g)				Metal ions removed (%)			
	Temperature ° C											
	30	40	50	60	30	40	50	60	30	40	50	60
25	2.557	2.314	2.106	1.977	44.88	45.37	45.78	46.04	89.77	90.74	91.57	92.09
50	9.693	8.662	7.273	6.278	80.61	82.67	85.45	87.44	80.61	82.67	85.45	87.44
75	20.77	18.47	16.27	14.32	108.4	113.0	117.4	121.3	72.30	75.36	78.30	80.90
100	38.67	36.66	16.27	30.56	120.8	126.6	167.4	138.8	60.42	63.33	83.72	69.43
125	61.22	57.53	33.59	50.46	127.5	134.9	182.8	149.0	51.02	53.97	73.12	59.62

Effect of contact time and Initial Copper ion Concentration

Adsorption of copper ion governs the rate, which determines the residence time and it is one of the important characteristics defining the efficiency of an adsorbent [4]. The effect of contact time on the amount of copper ion adsorbed was investigated at various concentrations (25, 50, 75, 100, and 125 mg/ l) and contact times are shown in fig.2.The equilibrium data was given in Table (2).It is observed that the percentage of adsorption decreased which increase in initial copper ion concentration, but the actual amount of copper ion adsorbed per unit mass of carbon increased with increase in metal ion concentration. This means that the adsorption is highly dependent on the initial copper ion concentration. This is because 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 site of adsorption becomes fever, and hence percentage of removal of copper ion is independent upon initial concentration. Equilibrium has been established at 60 minutes at all concentrations. Figure (2) reveals that the curves are single, smooth, and continuous, leading to saturation, suggesting the monolayer coverage of the copper ion on the carbon surface [5, 6].

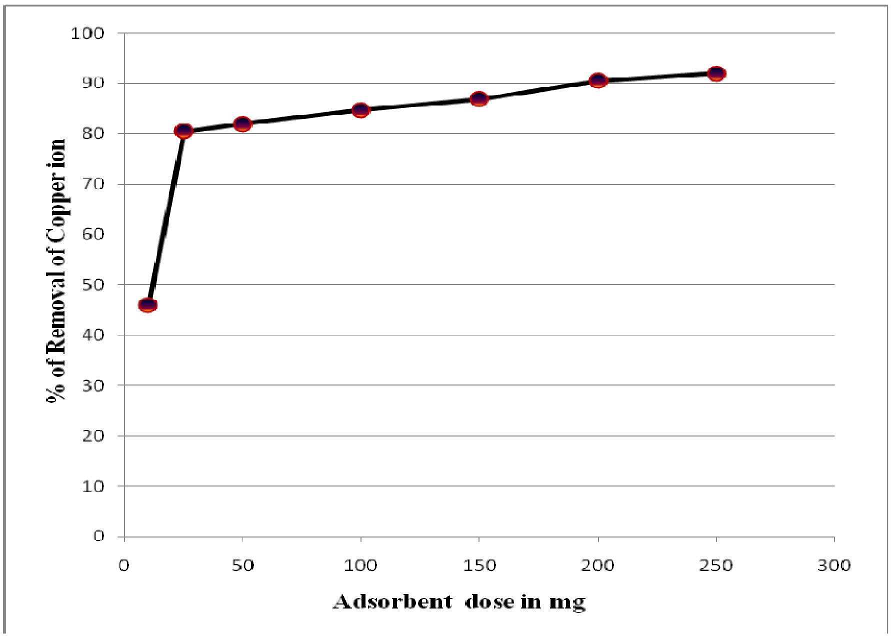

Fig. 1- Effect of adsorbent dose on the adsorption of copper ion onto TPC
[Cu] = 25mg/L: contact time = 60min: pH=6.5

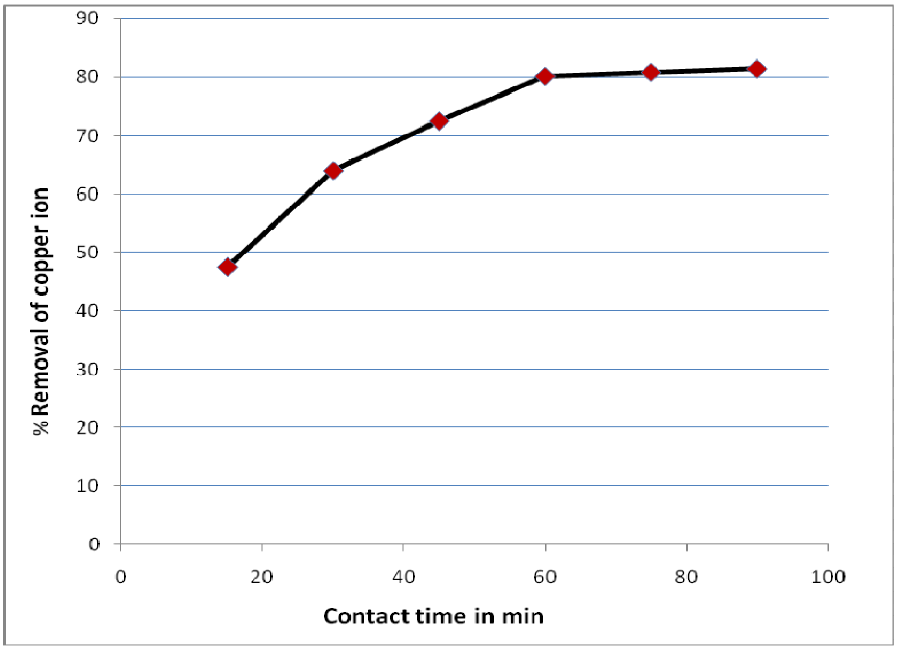

Fig. 2- Effect of contact time on the adsorption of copper ion onto TPC
[Cu]= 75 mg/L: Adsorbent dose = 25mg/ 50ml: pH=6.5

Equilibrium studies

The isotherm analysis of the data is essential to develop an equation which accurately represents the results and could be used for design purposes. In order to find out the sorption isotherm, two equilibrium models were employed: the Langmuir and Freundlich isotherm equations. The Langmuir sorption isotherm is perhaps the best known of all isotherms describing sorption [7].

Langmuir isotherm

Langmuir isotherm is applicable for monolayer sorption on to the surface of finite number of identical sites, which is based on the assumption that point of valence exists on the surface of the adsorbent and that each of these sites is capable of adsorbing one molecule. Thus, the adsorbed layer will be one molecule thick. It is represented as:

$$C_{eq}/Q_{eq} = 1/Q_m b + Ceq/Q_m \qquad (1)$$

Where C_{eq} is the equilibrium concentration of adsorbate in the solution (mg/l), Q_{eq} is the amount adsorbed at equilibrium (mg/g), Q_m and b are Langmuir constants related to adsorption efficiency and energy of adsorption, respectively. The linear plots of Ceq/ Q_{eq} vs. C_{eq} suggest the applicability of the Langmuir isotherms fig (3). The values of Q_m and *b* were calculated from slope and intercepts of the plots and are depicted 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. The values can conclude that the maximum adsorption corresponds to a saturated monolayer of adsorbate molecules on adsorbent surface with constant energy and no dispersion of adsorbate in plane of the adsorbent surface [8, 9]. To prove the favourability of the adsorption process, the separation factor (R_L) was determined and listed in Table 3.The values were found to be between 0 and 1 and confirm that the adsorption process is more favorable [8, 10].

The Freundlich isotherm

The Freundlich isotherm is most often used to describe the adsorption of inorganic and organic components in solution [11, 12]. The analysis of Freundlich isotherm is based on adsorption on heterogeneous surface using the same equilibrium data of Cu (II) adsorption on TPC. Freundlich constants Kf and n were obtained plotting the graph between log q_e versus log C_e. The Freundlich adsorption isotherm equation was analysed for the adsorption of copper ion on the adsorbent. The linear form of Freundlich isotherm is represented as by the fallowing equation.

$$\log Q_e = \log K_f + 1/n \log C_e \qquad (2)$$

Where Q_e is the amount of copper ion adsorbed (mg/g), C_e is the equilibrium concentration of copper ion in solution (mg/L), and K_f *and n* are constants incorporating the factors affecting the adsorption capacity and intensity of adsorption, respectively. Linear plots of log Q_e versus log C_e shows that the adsorption of copper ion obeys the Freundlich adsorption isotherm.

Figure 4 show the Freundlich adsorption isotherm obtained by plotting C_e/ q_e versus C_e for the adsorption of Cu (II) on TPC at the different temperatures investigated, respectively. The K_f and *n* values are given in Table 3 show that the increase of negative charges on the adsorbent surface makes electrostatic force like Vanderwaal’s between the carbon surface and copper ion. The values clearly show the dominance in adsorption capacity.

Table.3 Langmuir Isotherm, Freundlich Isotherm results and Dimensionless separation factor (R_L)

Copper ion adsorption	**Temperature C°**	**Langmuir Isotherm Results**			**Freundlich Isotherm Results**			**Dimensionless Separation Factor(R_L)**				
		Statistical parameters/constants			Statistical parameters/constants			Copper ion (mg/L)				
		r^2	**Q_m**	**b**	**r^2**	**K_f**	**n**	**25**	**50**	**75**	**100**	**125**
	30	0.9983	140.195	0.1608	0.9154	4.7735	2.9788	0.1991	0.1105	0.0765	0.0585	0.0473
	40	0.9994	148.481	0.1664	0.9167	4.8705	2.8988	0.1937	0.1072	0.0741	0.0566	0.0458
	50	0.9967	238.606	0.0895	0.9138	4.6043	1.9303	0.3088	0.1826	0.1296	0.1004	0.0820
	60	0.9932	164.176	0.1899	0.9127	5.098	2.7660	0.1739	0.0952	0.0655	0.0500	0.0404

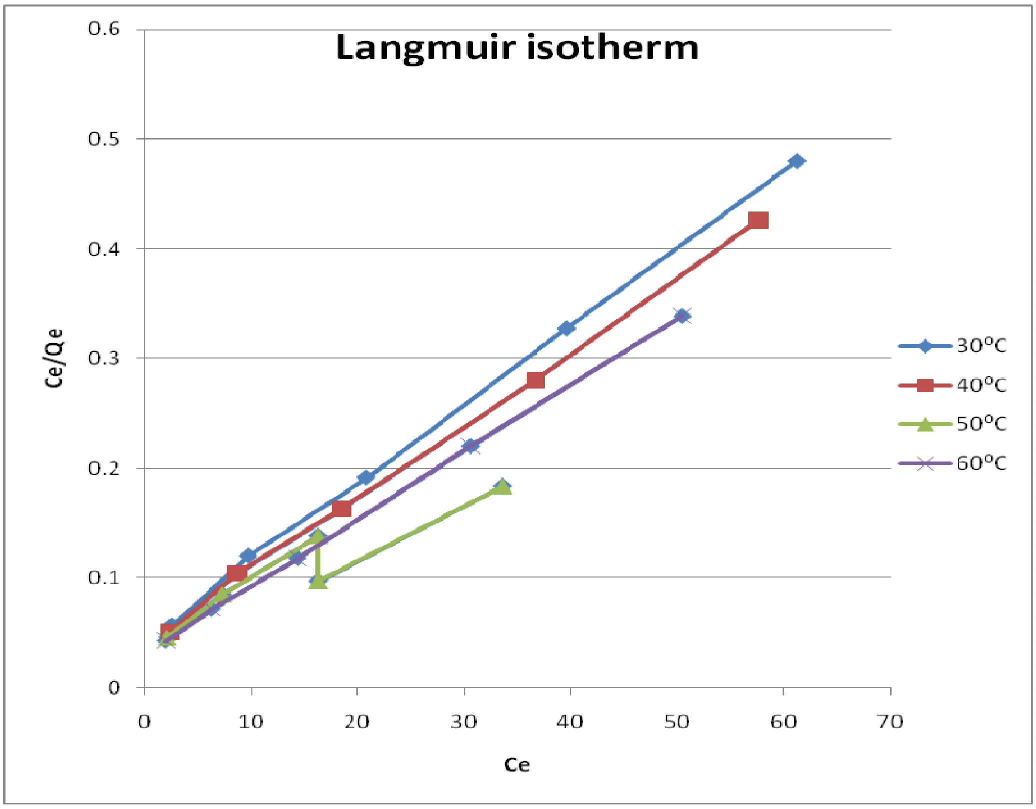

Fig. 3- Langmuir Isotherm for the adsorption of copper ion onto TPC

The intensity of adsorption is an indication of the bond energies between metal ion and adsorbent, and the possibility of slight chemisorptions rather than physisorption [9, 13]. However, the multilayer adsorption of copper ion through the percolation process may be possible. The values of *n* are less than one, indicating the physisorption is much more favorable [14].

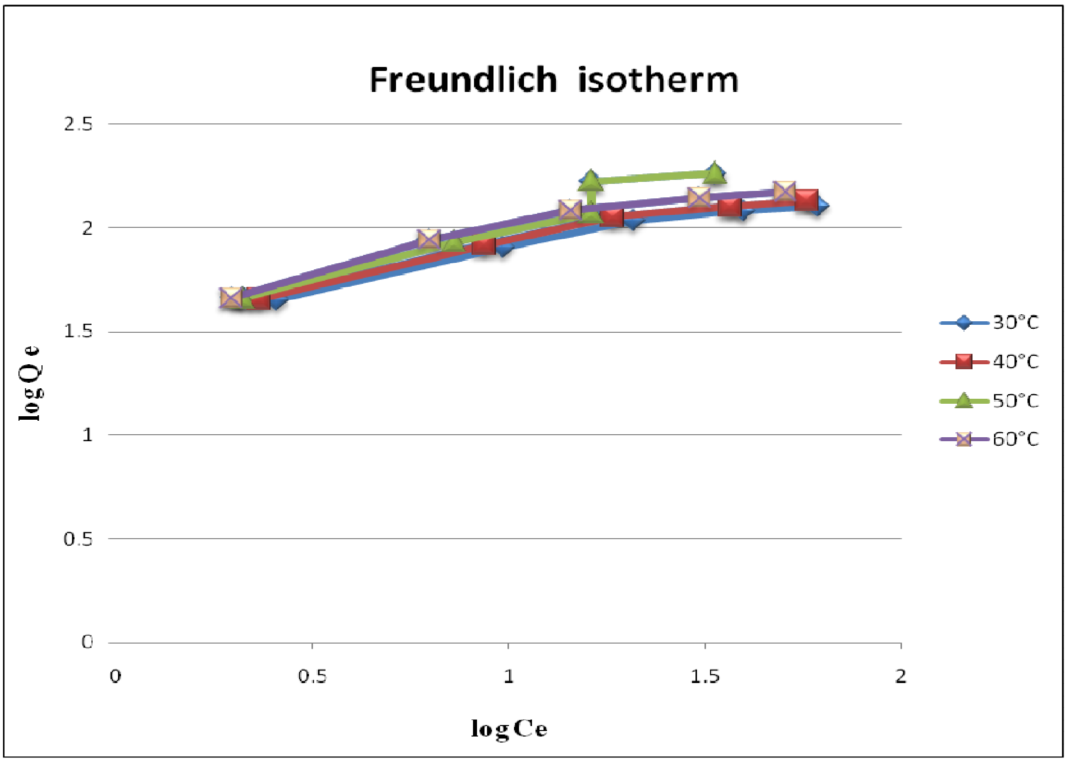

Fig 4- Freundlich Isotherm for the adsorption of copper ion onto TPC

Effect of temperature

The adsorption experiments were conducted at different temperatures such as 30°, 40°, 50° and 60°C by keeping the rest parameters and adsorbent concentration at 25 mg in 50 ml. Adsorption capacity of the carbon increased with increase of the temperature in the system from 30° to 60°C. Thermodynamic parameters such as change in free energy ($\Delta G°$) (kJ/mol), enthalpy *($\Delta H°$)* (kJ/mol) and entropy ($\Delta S°$*)* (J/K/'mol) were calculated by the following equations.

$$K_0 = C_{solid}/C_{liquid}$$

$$\Delta G° = -RT \ln K_O$$

$$\log K_0 = \Delta S°/ (2.303R) - \Delta H°/(2.303RT)$$

Where K_o 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 Kelvin, and R is the gas constant. The $\Delta H°$ and $\Delta S°$ values obtained from the slope and intercept of Van't Hoff plots are given in Table 4.The values $\Delta H°$ is the range of 1 to 93 kJ/mol shows the favorability of physisorption. It is clear that from results that physisorption is much more favorable for the adsorption for copper ion. The positive values of $\Delta H°$ indicate the endothermic nature of adsorption and it governs the possibility of physical adsorption [10, 14]. Because in the case of physical adsorption, while increasing the temperature of the system, the extent of dye adsorption increases, there is no possibility of chemisorption. The negative values of $\Delta G°$ (Table

4) indicate that the adsorption is greatly favorable of copper ion. The positive values of ΔS° (Table 4) show the increased disorder and randomness at the solid solution interface of copper ion with TPC adsorbent. The results indicate that more efficient physisorption [5, 13, and 15].

Table 4 – Equilibrium constant and thermodynamic parameters for the adsorption of copper ions onto activated carbon

Copper ion (mg/l)	K。				ΔG° Temperature (C)					
	30°	**40°**	**50°**	**60°**	**30°**	**40°**	**50°**	**60°**	**ΔH°**	**ΔS**
25	8.775	9.803	10.87	11.64	-5471.3	-5940.4	-6407.6	-6796.5	-8.0050	44.527
50	4.158	4.772	5.874	6.964	-3589.9	-4066.7	-4754.7	-5373.2	-14.696	60.195
75	2.610	3.059	3.609	4.236	-2416.9	-2909.6	-3446.9	-3997.2	-13.568	52.708
100	1.526	1.727	5.146	2.272	-1066.3	-1422.9	-4399.3	-2272.0	-19.627	68.924
125	1.041	1.172	2.720	1.476	-102.99	-414.23	-2687.4	-1079.4	-16.207	54.336

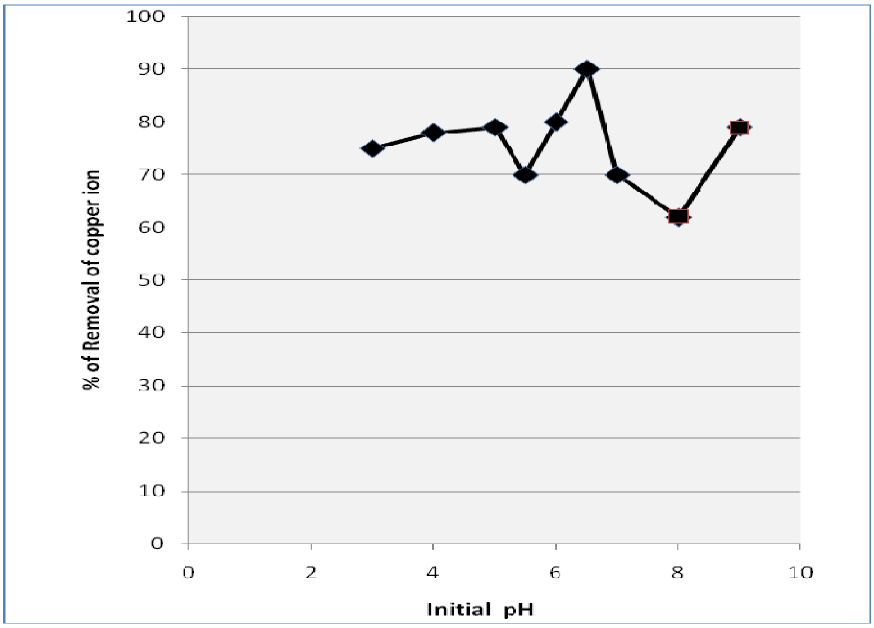

Fig. 5- Effect of pH on the adsorption of copper onto TPC
[Cu]= 75mg/L: adsorbent dose
= 25 mg / 50ml: contact time = 60min

Effect of pH

The pH is an important parameter for adsorption of metal ions from aqueous solution because its affects the solubility of metal ions. For this the role of hydrogen ion concentration was examined at different pH. In the present work, effect of pH on the adsorption of copper ion using TPC as an adsorbent is studied in the initial pH range from 1-10.The relation between the initial pH of the solution and percentage removal of copper is shown in Figure 5.it was observed that the percentage adsorption copper ions was increased appreciably (1-2 times) with increase of pH from 3 to 6.5 and consistent with results obtained by others.

Effect of the Ionic Strength

The effect of sodium chloride on the adsorption of copper ion on TPC is shown in Figure 6. The low concentrate NaCl solution had little influence on the adsorption capacity. When the concentration of NaCl increases, the ionic strength is raised. At higher ionic strength, the adsorption of copper ion will be high owing to the partial neutralization of the positive charge on the carbon surface and a consequent compression of the electrical double layer by the Cl^- anion. The chloride ion also enhances adsorption of copper ion by pairing their charges, and hence reducing the repulsion between the copper ions adsorbed on the surface. This initiates carbon to adsorb more positive copper ions [1, 16].

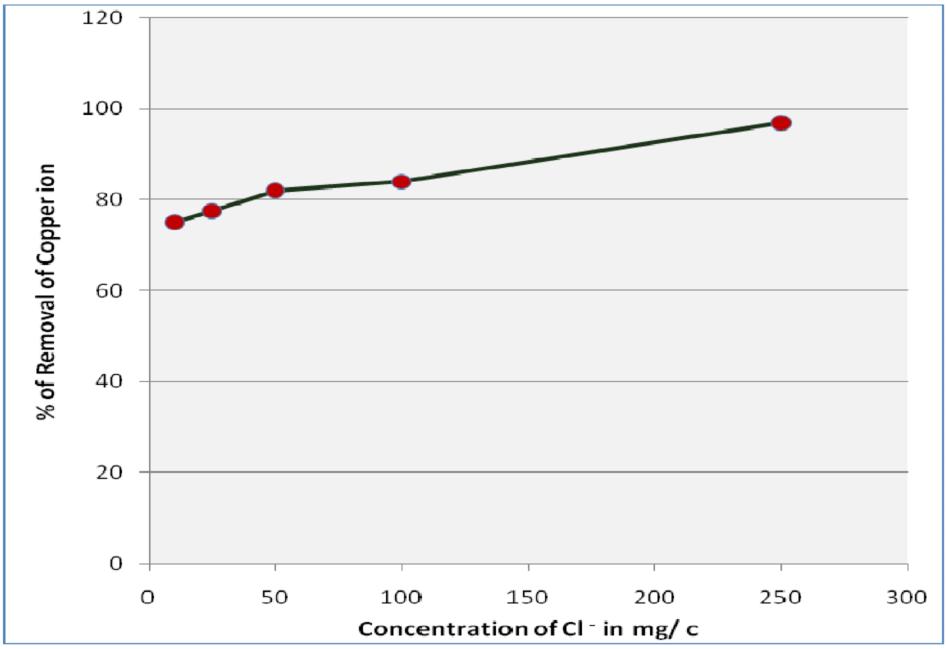

Fig. 6- Effect of other ions on the removal of copper ion
[MG]= 100mg/L: adsorbent dose
= 25 mg / 50ml: contact time = 60min

Adsorption Kinetics

In order to understand the kinetics of removal of Copper ions using TPC as an adsorbent, pseudo first-order, second-order kinetic models are tested with the experimental data. Adsorption Kinetics 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 research work, the kinetics of the adsorption copper ion has carried out to understand the behavior 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

$$A \underset{k_2}{\overset{k_1}{\leftrightarrows}} B$$

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 [9, 13, and 17]. The data are given in Table 5, shows 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 are listed given in the following Table 5. The results indicate 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 Kad (Table 5), 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 [14, 18]

The contact-time experimental results can be used to study the rate-limiting step in the adsorption process is indicated by Weber and Morris 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 [10, 17, and 19].

Table 5- Rate constants for the adsorption of copper ion (k_{ad}, min $^{-1}$) and the constants for forward (k_1, min $^{-1}$) and reverse (k_2,min^{-1}) process.

	Temperature (C)											
Copper ion	k_{ad}				**k_1**	**k_2**	**k_1**	**k_2**	**k_1**	**k_2**	**k_1**	**k_2**
	30°	**40°**	**50°**	**60°**	**30°**		**40°**		**50°**		**60°**	
25	0.0276	0.0285	0.0292	0.0305	0.024	0.002	0.025	0.002	0.026	0.026	0.002	0.002
50	0.0178	0.0191	0.0211	0.0235	0.014	0.003	0.015	0.003	0.018	0.003	0.020	0.002
75	0.0138	0.0148	0.0163	0.0176	0.010	0.003	0.011	0.003	0.012	0.003	0.014	0.003
100	0.0105	0.0111	0.0119	0.0125	0.006	0.004	0.007	0.004	0.009	0.001	0.008	0.003
125	0.0087	0.0093	0.0102	0.0104	0.004	0.004	0.005	0.004	0.007	0.002	0.006	0.004

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 sulfuric acid or alkaline water desorp the copper ion, then the adsorption is by ion exchange. If organic acids, like acetic acid can desorp 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. 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 [14, 20, 21, and 22].

CONCLUSION

TPC has been effectively used to generate high quality activated carbon because of its inherent high densities and highly carbon content. The removal of copper ion from waste water by TPC activated carbon is strongly affected by parameters like initial concentration, pH, adsorbent dosage and Temperature. The kinetics of the adsorption of copper (II) on Thespesia Populnea bark carbon powder could be described by first -order kinetic model. The equilibrium uptake increased and percentage absorption decreased with increasing of the initial concentration. Both Langmuir and Freundlich equilibrium models proved to be good fits for the experimental data for Thespesia Populnea bark activated carbon. The dimensionless separation factor (R_L), values of $\Delta H°$ $\Delta S°$ and $\Delta G°$ indicates that the carbon employed has considerable potential to adsorb metal ions from aqueous solution.

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