Research Journal of Pharmaceutical, Biological and Chemical Sciences

Removal of Cu (II) from Aqueous Solution by Using Natural Plant Material *Cynodon dactylon*

Samu Solomon J[1], Martin Devaprasath P[1], Chandramohan M[2].

[1]Department of Chemistry, Tranquebar Bishop Manickam Lutheran College, Porayar, Tamil Nadu, 609307, India
[2]Department of Chemistry, AVVM Sri Pushpam College, Poondi, Tamil Nadu, 613503, India

ABSTRACT

The studies on adsorption of Cu (II) were conducted by varying various parameters such as contact time, pH, and amount of adsorbent, concentration of adsorbate, mesh size and temperature. The kinetics of adsorption of Cu (II)) ion followed pseudo second order. Langmuir adsorption, Freundlich, Temkin, DKR, Harkin-jura, Redlich-peterson and Halsey isotherms were employed in order to evaluate the optimum adsorption capacity of the adsorbent. The adsorption capacity was found to be pH dependant. *Cynodon dactylon* was found to be very effective and reached equilibrium in 3 h (adsorbate concentration 150 mg l^{-1}). The rate constant has been calculated at 303, 313, 323 and 333K and the activation energy (Ea) was calculated using the Arrhenius equation. Thermodynamic parameters such as standard Gibbs energy (ΔG∘) and heat of adsorption (ΔH∘) were calculated. The ΔG∘ and ΔH∘ values for Cu(II) adsorption on the *Cynodon dactylon* showed the process to be endothermic in nature. The percentage of adsorption increased with decrease in pH and showed maximum removal of Cu(II)in the pH range 5 for an initial concentration of 10 mg l^{-1}.

Keywords: Adsorption; Cu(II); *Cynodon dactylon*; Kinetics; Isotherm and thermodynamics

Corresponding author
Email: samusolomon@yahoo.com.

INTRODUCTION

Pollution from heavy metals is a major concern in developing countries. The discharge of heavy metals into water-courses is a serious pollution problem which may affect the quality of water supply. Increasing concentrations of these metals in the water constitute a severe health hazard mainly due to their non degradability and toxicity. Numerous metals such as chromium Cr (III) and Cr(VI), copper (Cu), lead (Pb), manganese (Mn), mercury (Hg), cadmium (Cd), etc are known to be significantly toxic(Adsorption of Copper from Aqueous Solution , Journal of Engineering Science and Technology AUGUST 2008, Vol. 3(2)).Cu, the metal considered in this project, is a widely used material. Copper metal contamination exists in aqueous waste streams from many industries such as electronic and electrical, metal plating, mining, manufacture of computer heat sinks, Cu plumbing, as well as biostatic surface, as a component in ceramic glazing and glass colouring. Unfortunately, Cu is a persistent, bio accumulative and toxic chemical that does not readily break down in the environment and is not easily metabolized. It may accumulate in the human or ecological food chain through consumption or uptake and may be hazardous to human health or the environment. Drinking water that contains higher than normal levels of Cu may cause vomiting, diarrhea, stomach cramp and nausea. The chronic effects of consumption of high levels of copper are liver and kidney damage. The suggested safe level of Cu in drinking water for humans varies depending on the sources, but tends to be pegged at 1.5 to 2.0 mg/L. Hence, removal of copper from water and wastewater assumes important. Respectively, among the unit operations in water and wastewater treatment, adsorption occupies an important position. It is recommended that the absorbent is available in large quantities, of free or very low cost and easily regenerable. In the midst of a large variety of adsorbent available, activated carbon is the most important and cheapest adsorbent used in the current method of pollution control. In India, the plant *Cynodon dactylon* is usually used as medicinal herb and enormously available in the waste lands, parks and gardens. However, a large portion of it is destroyed. Therefore, application of *Cynodon dactylon* activated carbon as an adsorbent offers highly effective technological means in dealing with the heavy metals pollution of the aqua-environment with the minimum investment requirement.

MATERIALS AND METHOD

The pH was adjusted with a digital pH meter (Jenway Model 3320) using HCl (0.1 mol L^{-1}) and NaOH (0.1 mol L^{-1}). Copper (II) was estimated with a UV/VIS spectrophotometer (Labomed UVD 3500) at λmax   620 nm.

Preparation of adsorbent

Cynodon dactylon, collected from the Tranquebar area, was crushed with laboratory-scale crushers, powdered with a disk pulverizer, and sieved to 0-63 mesh (ASTM). The powdered adsorbent was washed, dried at 105 ◦ C for 10 h in an oven, and stored in high-density polythene (HDPE) bags. The proximate analysis of the coal was carried out by using standard methods (ASTM D 5142-90). Powdered adsorbent was soaked in HCl (0.1 mol L^{-1}) for 24 h, followed by filtering and washings with distilled water. Afterwards, it was dried in an oven

at 105 ◦ C for 10 h and stored in HDPE bags.

Chemicals

All c h e m i c a l s   used during experimental work were of analytical grade and were used as such without purification. Copper (II) (Fluka), HCl (E. Merck 11.6 M). Double distilled water was used for the preparation of all types of solution and dilution when required.

Instrumentation

Balance ER-120A (AND), Electric grinder (Kenwood), pH meter HANNA pH 211 (with glass electrode), UV/VIS s p e c t r o p h o t o m e t e r (Labomed, Inc. Spectro UV-Vis double beam UVD = 3500).

Standard Solutions

The stock Copper (II) solution was prepared by dissolving accurately analar grade of 3.9280 mg of $CuSO_4.5H_2O$ (E. Merck). in 1000 ml of Double distilled water to make it to 1000 ppm solution. Form this stock solution, 10,20,30,40, 50 and 60 ppm solutions were prepared by diluting it suitably.

Adsorption Experiments

The adsorption studies were carried out at 30 ± 1 ^{0} C. pH of the solution was adjusted with 0.1 N HCl and NaOH. A known amount of adsorbent was added to sample and allowed sufficient time for adsorption equilibrium. Then the mixture was filtered and the remaining metal ion concentration was determined in the filtrate (Spectro UV-Vis Double Beam UVD- 3500, Labomed. Inco) at λ_{max} = 620 nm. The effect of various parameters on the rate of adsorption process were observed by varying mesh size of adsorbent, contact time t, initial concentration of metal ion C_O, adsorbent amount, initial pH of solution and temperature. The solution volume (V) was kept constant 50 mL. The metal ion adsorption (%) at any instant of time was determined by the following equation:

$$\text{Metal ion adsorption (\%)} = (C_O - C_e) \times 100/ C_O$$

Where C_O is the initial concentration and C_e is the concentration of the metal ion at equilibrium. To increase the accuracy of the data, each experiment was repeated three times and average values were used to draw the graphs.

Isotherm studies

A series of experiments were carried out for isothermal and kinetic study of *Cynodon dactylon* adsorption of Copper (II) metal ion. Langmuir (eq:1), Freundlich (eq:2),

Temkin (eq:3), Harkin-Jura (eq:4), Halsey (eq:5), Redlich-peterson (eq:6) and Dubinin-Kaganer-Radushkevich (DKR) (eq:7) were plotted by using standard straight-line equations and corresponding parameters were calculated from their respective graphs.

$$Ce/X = 1/K*K_L + Ce/K \qquad \text{-----------------------} \quad (1)$$
$$\log qe = \log K_F + 1/n \log Ce \qquad \text{----------------------} \quad (2)$$
$$qe = K_T \ln Ce + b_T \qquad \text{-----------------------} \quad (3)$$
$$1/qe2 = B/A - 1/A \log Ce \qquad \text{-----------------------} \quad (4)$$
$$\ln qe = 1/n \ln K - 1/n \ln Ce \qquad \text{------------------------} \quad (5)$$
$$qe = K_R Ce / (1+b_R Ce\beta) \qquad \text{-------------------------} \quad (6)$$
$$\log qe = \log Xm - \beta\varepsilon^2/2.303 \text{ ----------------------} \quad (7)$$

$K(mg/g)$: an indicator of the adsorption capacity,$1/n$ (mg/L): adsorption intensity, ε (the Polanyi potential) = $RT \ln (1 + 1/Ce)$,qe: the amount of metal ions adsorbed per unit weight of *Cynodon dactylon*(mg/g), K': constant related to the adsorption energy (mol2/KJ2),R: gas constant (kJ/K.mol),T: temperature (K),Ce is the equilibrium concentration of the adsorbate (mg/L) and X is the amount of adsorbate adsorbed (mg/g). K_L indicates monolayer adsorption capacity (mg/g), K is the Langmuir equation constant (L/mg), K_F and $1/n$ are constants for a given adsorbate and adsorbent at a particular temperature and b_T (KJ/mol) is adsorption potential of the adsorbent. K_T is the Temkin isotherm constant and $1/A$ is the external surface area for the Harkin –Jura isotherm.K_R, b_R, β are Redlich Peterson constants. Xm is maximum sorption capacity; β is mean sorption energy and ε sorption potential in DKR isotherms

RESULTS AND DISCUSSION

Characterization of adsorbent

The adsorbent analysis revealed that it had high moisture content and volatile matter. Ash content was also appreciable. Results are illustrated in Table 1.It was determined by proximate and ultimate analysis as follows:

Proximate analysis

Moisture

About 1g of finely powdered air-dried adsorbent sample is weighed and taken in a crucible. The crucible is placed inside an electric hot-air oven and heated at 100-105'C for 1hour. It is then taken out, cooled in desiccators and weighed. From this, the percentage of moisture can be calculated as follows:

Percentage of moisture = (loss in weight of adsorbent / weight of air dried adsorbent taken)*100

Volatile matter

The crucible with moisture free adsorbent sample is covered with a lid and placed in an electric muffle furnace, heated at 905-945'C for seven minutes. It is then taken out, cooled in desiccators and weighed. From this, the percentage of volatile matter can be calculated as follows:

Percentage of volatile matter = (loss in weight of adsorbent / weight of dried adsorbent taken)*100

Ash content

The crucible with residual adsorbent sample is placed in an electric muffle furnace, heated without lid at 650-750'C for 30 minutes. It is then taken out, cooled in desiccators and weighed. From this, the percentage of ash content can be calculated as follows:

Percentage of ash = (weight of ash left / weight of dried adsorbent taken)*100

Fixed carbon

The fixed carbon content can be calculated from the following equation

Percentage of = 100- % of (moisture+ volatile matter + ash)

Ultimate analysis of Sulphur

A known quantity of adsorbent sample is burnt completely in a Bomb calorimeter. During this process sulphur is converted in sulphate, which is extracted with water. The extract is then treated with $BaCl_2$ solution so that sulphates are precipated as $BaSO_4$.The precipitate is filtered, dried and weighed. From the weight of $BaSO_4$ obtained, the sulphur present in the adsorbent was calculated as follows.

$$S \xrightarrow{2O_2} SO_4^{2-} \xrightarrow{BaCl_2} BaSO_4$$
$$(32) \qquad\qquad\qquad (233)$$

Percentage of sulphur in adsorbent = (32* weight of $BaSO_4$ obtained) / (233* weight Of dried adsorbent taken)

Results are given in table: 1

Parameters	Moisture	Volatile matter	Ash	Fixed C	S	Heating value Btu/lb
Values	2.5%	10.13%	5.5%	75.11	1.2%	5.56%

Effect of initial pH

The acidity of solution pH is one of the most important parameters controlling the uptake of heavy metals from wastewater and aqueous solutions. The uptake and percentage removal of copper from the aqueous solution are strongly affected by the pH of the solution as illustrated in Fig. 1. The adsorption of copper increases from 29% to 93.01%, when the pH increases from pH 1 to pH 5 respectively. Copper sorption is noted to increase significantly 93.01% adsorption capacity at pH 5. After that the capacity of adsorption decreases slightly in pH range of 6 to 9.The minimum adsorption observed at low pH (pH 1) may be due to the fact that the higher concentration and higher mobility of H+ ions present favoured the preferential adsorption of hydrogen ions compared to Cu (II) ions [1]. It would be plausible to suggest that at lower pH value, the surface of the adsorbent is surrounded by hydronium ions (H+), thereby preventing the metal ions from approaching the binding sites of the sorbent [2]. This means that at higher H+ concentration, the biosorbent surface becomes more positively charged such that the attraction between biomass and metal cations is reduced [3]. In contrast, as the pH increases, more negatively charged surface becomes available thus facilitating greater copper removal. It is commonly agreed that the sorption of metal cations increases with increasing pH (Fig 1) as the metal ionic species become less stable in the solution. However, at higher pH values (pH 6, pH 7, pH 8 and pH 9) there is a decrease in the adsorption capacity. This is due to the occurrence of copper precipitation. At pH6 there are three species present in solution as suggested by Elliot and Huang. [4], Cu2+ in very small quantities and Cu(OH)+ and Cu(OH)2 in large quantities. Three species are adsorbed at the surface of adsorbent by ion exchange mechanism with the functional groups present in adsorbent or by hydrogen bonding.
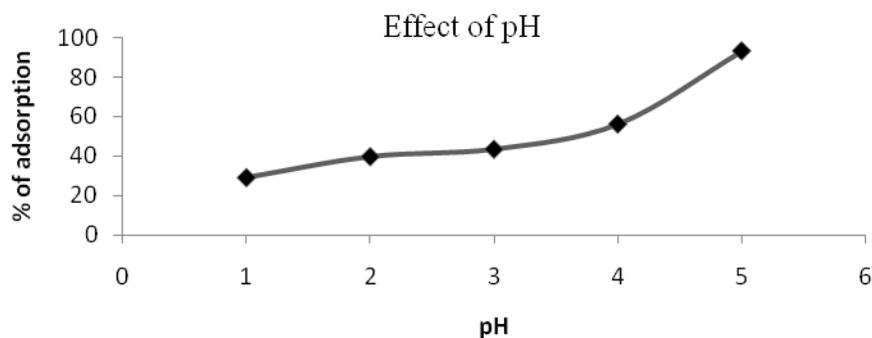

Fig 1

Effect of adsorbent dosage

The adsorbent dosage is another important parameter, which influences the extent of metal uptake from the solution and thus the effect as shown in Fig. 2. It was evident that the amount of metal uptake increases from 70.03% with 50mg adsorbent up to 96.09 % with 200mg adsorbent. Prior to that, it is apparent that the percent removal of copper increases as the adsorbent dosage increases from 50mg up to 200mg due to the limited availability of the number of adsorbing species for a relatively larger number of surface sites on the adsorbent at higher dosage of adsorbent. It is plausible that with higher dosage of adsorbent there would be greater availability of exchangeable sites from metal ions [5]. Besides, Fourest and Roux [6] suggested that the reduction in adsorbent dosage in the suspension at a given metal

concentration enhances the metal/adsorbent ratio, and thus increases the metal uptake per unit adsorbent, as long as the latter is not saturated. Similar observation has been reported by Mashitah et al [7] for the adsorption of copper ions onto Pycnoporous sanguineus biomass. However, in some cases, the adsorption capacity decreased sharply with the increasing of adsorbent dosage these results may due to the overlapping of the adsorption sites as a result of overcrowding of adsorbent particles [8]. Moreover, the high adsorbent dosage could impose a screening effect of the dense outer layer of the cells, thereby shielding the binding sites from metal [9].
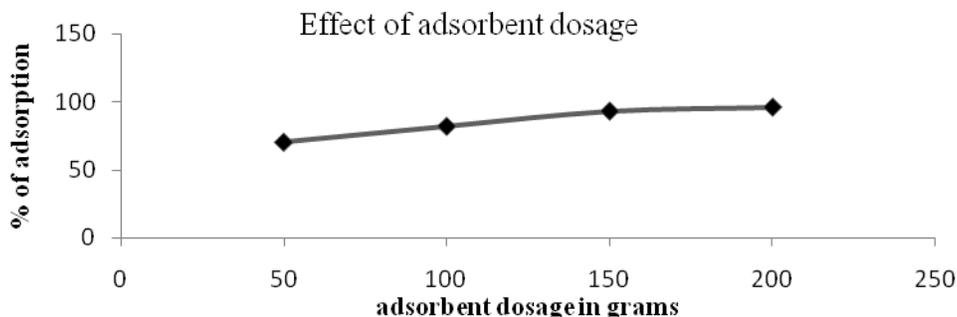
Fig 2

Effect of initial adsorbate concentration

Figure 3 show that adsorption capacity decreases from 96.11% to 63.35 % as the metal concentration increases from 10 to 60 mg/L. The trend is that of the result of the progressive decrease in the electrostatic interaction between the copper ions and the absorbent active sites. Moreover, this can be explained by the fact that less adsorption sites were being covered as the metal ions concentration decreases [10]. Besides, lower initial concentrations lead to an increase in the affinity of the copper ions towards the active sites [11]. The decline in the adsorption capacity is due to the availability of smaller number of surface sites on the adsorbent for a relatively larger number of adsorbing species at lower concentrations [12]. Similar results were observed by Han et al. [13] for the adsorption of copper (II) and lead (II) on chaff.
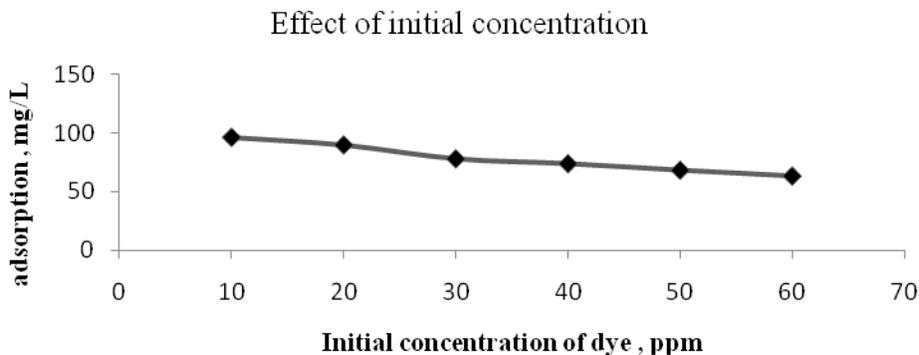

Fig 3

Effect of Mesh Size

The effect of adsorbent's mesh size was studied in the range of 0-200 microns mesh size (0-63, 63-125, 125-200) for checking the maximum adsorption of Copper(II), and the smallest mesh size (0-63) was shown to be best for adsorption, as particles with smallest size presents a larger surface area and the results are shown in Fig. 4. Mesh size is inversely related with particle size. As the mesh size is larger, the size of particle is accordingly decreased which results in more surface area available for adsorption.
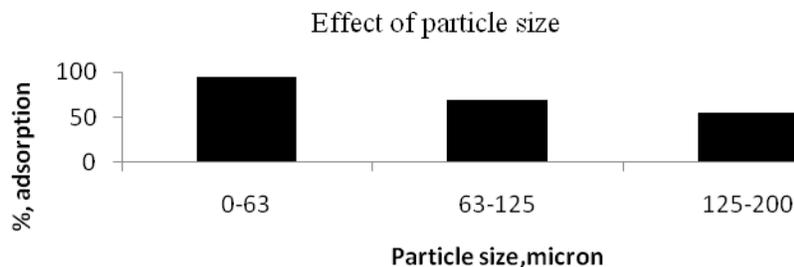
Fig 4

Effect of Temperature

Temperature has an important effect on the rate of adsorption. The percentage of Copper (II) adsorption was studied as a function of temperature in the range of 30-60 $^{\circ}$C. The results obtained were present in Fig. 5. It was observed that adsorption yield increase with increase in temperature. The minimum adsorption w a s   96.21 % a t 30 ° C a n d maximum adsorption was 99.82 % at 60 $^{\circ}$C for 25 ppm initial concentration of metal ion solution. The increase in adsorption at high temperature because molecules move with great speed and strong interaction was available for metal ion anions with adsorbent material.


Fig 5

Adsorption isotherm

Isotherm parameters, evaluated from the linear plots of equations (1-7) are
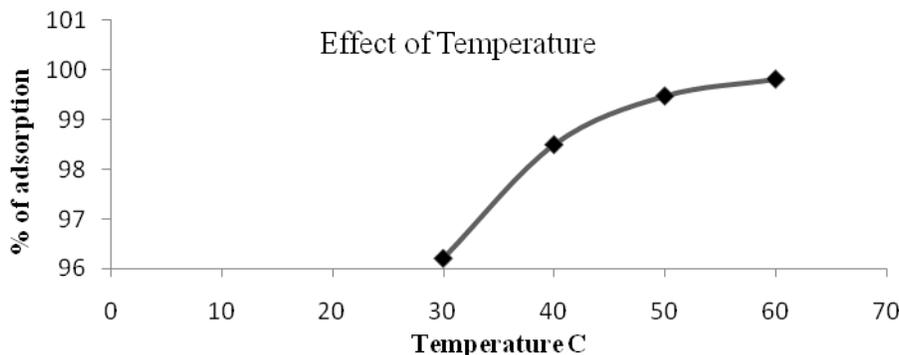
illustrated in Table 2a,2b and 2c,(Fig:6-12).The K_L value for the Langmuir isotherm, i.e. 4.5454mg/g, indicated the high adsorption capacity of biosorbent toward chromium adsorption. The R^2 (correlation coefficient) value 0.972 indicated that the Langmuir isotherm is good for explaining the Copper (II) adsorption. The R^2 value calculated for the Freundlich isotherm was found to be 0.993, indicating that the experimental data can be explained by the Freundlich isotherm. The Kf (ultimate adsorption capacity) value as calculated from the Freundlich isotherm was 4.4463.The Temkin equation was also good to explain the experimental data ,with an R^2 value 0.950.bT (heat of sorption) was calculated from the Tempkin plot as 4.731 KJ/mol ,indicating moderately strong cohesive forces between Copper (II)and biosorbent. A value less than 8 indicates a weak interaction between the adsorbent and adsorbate .The Harkin –Jura expression of the value of the correlation coefficient was 0.984, providing good suitability for the experimental data of Copper (II) on *Cynodon dactylon* Halsey's expression of the value of the correlation coefficient was 0.993, providing a better fit for the experimental data of Copper (II) on *Cynodon dactylon*. The Harkin-Jura and Halsey equations were more suitable to explain the multi layer adsorption of the adsorbate on adsorbent [14]. The R^2 value calculated for the Redlich-peterson isotherm was found to be 0.997, indicating that the experimental data can be explained by the Redlich-peterson isotherm. The β value as calculated from this isotherm was 0.664. The R^2 value calculated for the DKR isotherm was found to be 0.965, indicating that the experimental data can be explained by the DKR isotherm poorly. The β value as calculated from this isotherm was 1.264.

c0	%	ce	c0-ce	qe	ka	Ka C0	ce/qe	logce
10	96.11	0.389	9.61	3.20	8.2356	82.3565	0.1214	-0.4101
20	89.66	2.068	17.93	5.98	2.8904	57.8079	0.3460	0.3156
30	77.96	6.612	23.39	7.80	1.1791	35.3721	0.8481	0.8203
40	73.84	10.46	29.54	9.85	0.9409	37.6351	1.0628	1.0197
50	68.29	15.86	34.15	11.38	0.7179	35.8930	1.3930	1.2002
60	63.35	21.99	38.01	12.67	0.5762	34.5703	1.7356	1.3422

Table 2a

log qe	log ce/qe*-1	Ceβ	1/ce+1	ε2	1/qe2
0.5056	0.9157	0.534228	3.5707	10.2903	0.097433
0.7765	0.4610	1.620039	1.4836	0.9883	0.027989
0.8919	0.0715	3.505105	1.1512	0.1260	0.016453
0.9932	-0.0265	4.75422	1.0956	0.0529	0.010317
1.0562	-0.1440	6.264846	1.0631	0.0238	0.007719
1.1028	-0.2394	7.784622	1.0455	0.0126	0.006229

Table 2b

Langmuir parameters		K_L = 4.5454	q0 = 13.888	b_L = 0.3272	R^2 =0.972

Freundlich parameter	K_F = 4.4463	n =2.985		R^2 = 0.993
Dubinin-kaganer-Radushkevich parameters	β = 1.2644	b = 0.609	q0 =4.0644	R^2 = 0.965
Redlich peterson parameters	β= 0.664	K_R = 100	b_R = 22.2	R^2 = 0.997
Temkin parameters	k_T = 5.243	b_T = 4.731		R^2 = 0.950
Harkin-jura parameters	A= 45.45	B = 15.45		R^2 = 0.984
Halsey parameters	n= 2.985	K = 6.9193		R^2 = 0.993

Table 2c

y = 0.072x + 0.220
R^2 = 0.972

Fig 6

y = 0.335x + 0.648
R^2 = 0.993

Fig 7

y = -0.549x + 0.609
R^2 = 0.965

Fig 8

Halsey isotherm

$y = 0.335x + 0.648$
$R^2 = 0.993$

Fig 9

Temkin isotherm

$y = 5.243x + 4.731$
$R^2 = 0.950$

Fig 10

Harkin-jura isotherm

$y = -0.022x + 0.034$
$R^2 = 0.984$

Fig 11

Redlich-peterson isotherm

$y = 0.222x + 0.010$
$R^2 = 0.997$
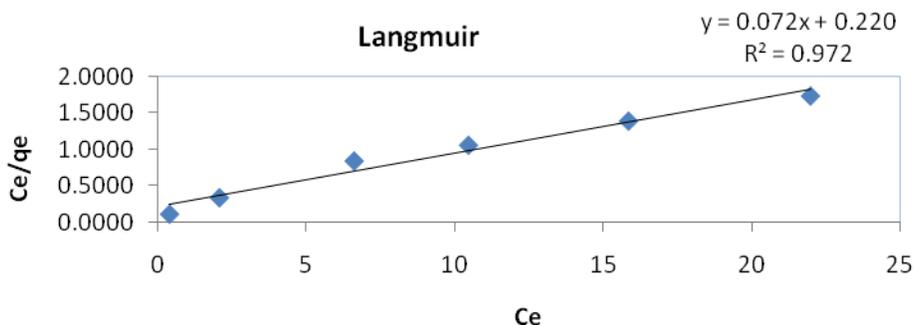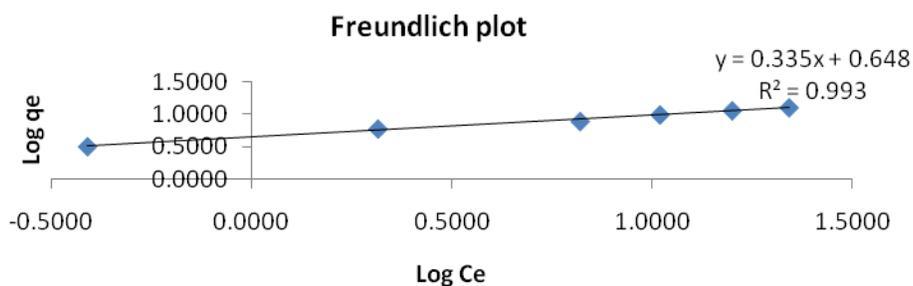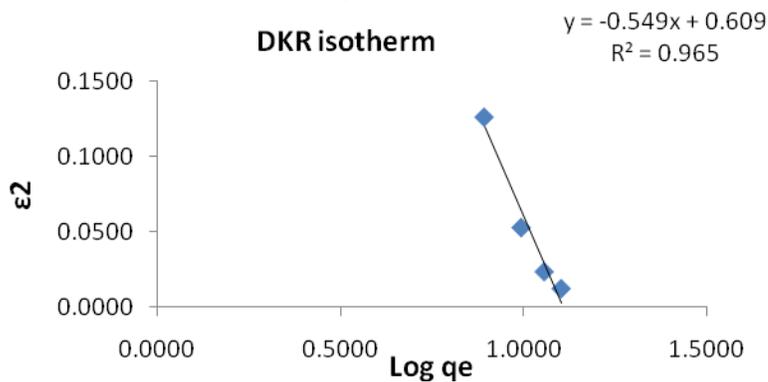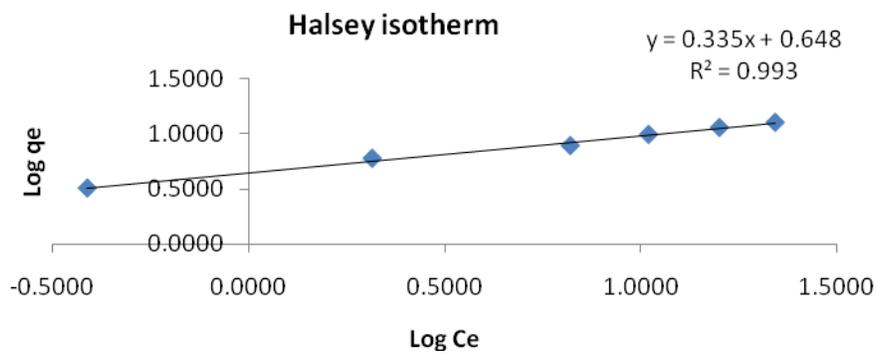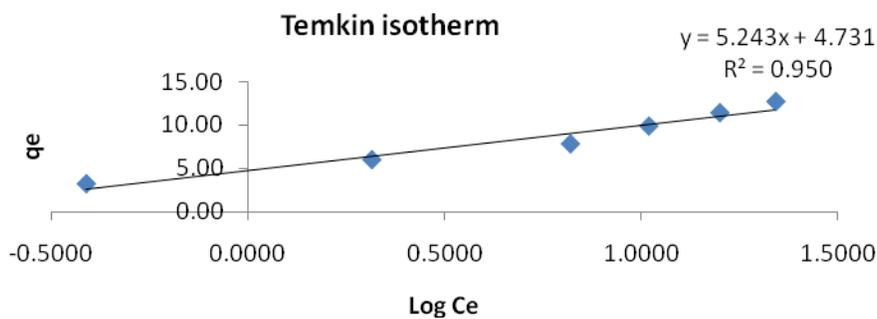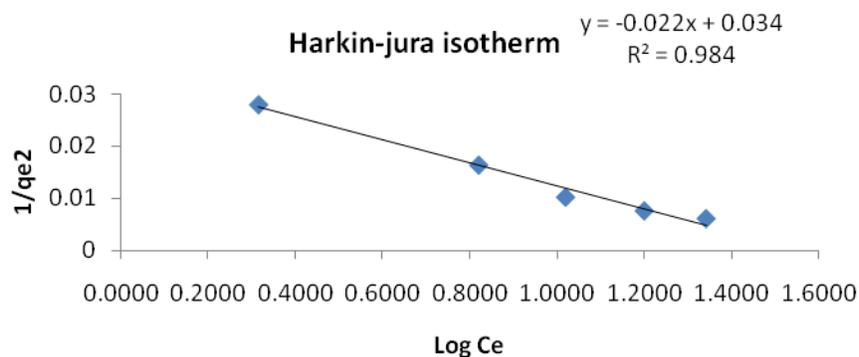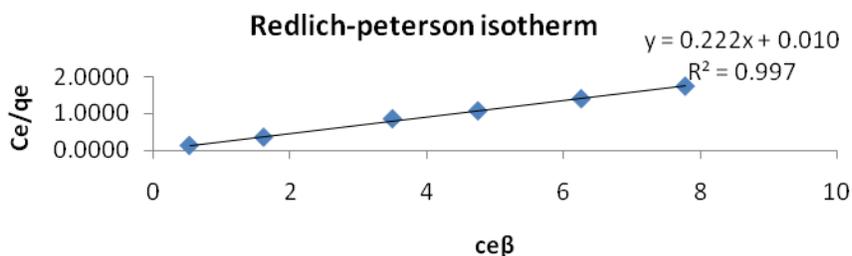
Fig 12

Thermodynamic parameters

Thermodynamic parameters such as standard Gibbs free energy (ΔG^0),Enthalpy (ΔH^0) and entropy (ΔS^0) were also calculated using equations 8 and 9 and the results obtained are illustrated in table-3a,3b (Fig:13).

$$\Delta G^0 = -RTlnK \qquad \text{----------------------------8}$$

$$lnKc = (\Delta S^0/R)-(\Delta H^0/RT) \qquad \text{----------------------------9}$$

Here, K denotes the distribution coefficient for the adsorption. R is the universal constant and T is the absolute temperature in Kelvin. The negative value of the ΔG^0 at the studied temperature range indicated that the sorption of Copper (II) on sorbent was thermodynamically feasible and spontaneous. The increase in the value of ΔG^0 with temperature further showed the increase in feasibility of sorption at the elevated temperature for *Cynodon dactylon*. In other words, sorption is endothermic in nature .The positive value of ΔH^0 for *Cynodon dactylon* showed that the sorption was endothermic. The positive value of ΔS^0 showed an increased randomness at the solid Copper (II) solution interface during the adsorption of Copper (II), reflecting the affinity of *Cynodon dactylon* for Copper (II).

T,K	c0	%	ce	c0-ce	ka
303.15	50	96.21	1.895	48.105	8.461741
313.15	50	98.5	0.75	49.25	21.88889
323.15	50	99.48	0.26	49.74	63.76923
333.15	50	99.82	0.09	49.91	184.8519

Table 3a

| ΔG0	ΔH0	ΔS0	Log 10 Ka	1/T
-5382.43	16.0836	67.78088	0.92746	0.003299
-8034.44			1.340224	0.003193
-11163.8			1.804611	0.003095
-14457.2			2.266824	0.003002

Table 3b
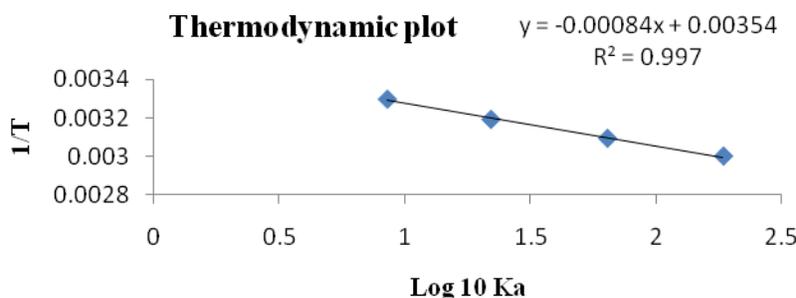
Fig 13

Arrhenius equation

Activation energies for adsorption of Copper (II)on adsorbent was calculated using the Arrhenius equation (eq10),plotted in Fig 14 and tabulated in table 4.The activation energy obtained(Table 4) in this case ,indicate that physical forces are involved in the sorption mechanism and sorption feasibility.

Arrhenius equation
$Log K = Log A - (E_A / 2.303 \ RT)$ ------------------ 10

Ea	Log A	R2
86.56	15.81	0.997

Table 4

$y = -4521.x + 15.81$
$R^2 = 0.997$
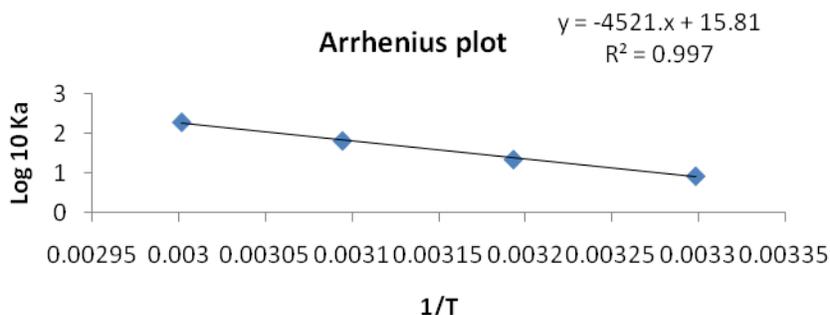
Fig 14

Kinetic study

A linear trace for the plot of log (qe-q) Vs time (Fig:15-18) shows that the adsorption kinetics follow pseudo second order kinetics' additionally pseudo first order,intra particle diffusion and Elovich model of kinetics were verified. (Tables 5a, 5b, 5c)

First order equation
$Log (q_e-q_t) = log q_e - (K1t / 2.303)$ ------------------ 11

Second order equation
$t/qt=1/n+t/qe^2$ ---12

Intra particle diffusion equation
$qt= Kpt1/2+C$ ---------------------------------------13

Elovich model equation
$qt=\alpha+\beta Lnt$ ---------------------------------------14

Time,min	%	C0	Ce	ct=C0-Ce	qt	t/qt
30	63.89	10	3.6	6.389	2.130	14.087
60	69	10	3.1	6.9	2.300	26.087
90	74.21	10	2.6	7.421	2.474	36.383
120	78	10	2.2	7.8	2.600	46.154
150	90.14	10	1.0	9.014	3.005	49.922
180	95.9	10	0.4	9.59	3.197	56.309

Table 5a

qe-qt	Log (qe-qt)	t1/2	1/qt	1/t	Ln t
1.370	0.1368262	5.477226	0.469557	0.033333	3.401197
1.200	0.0791812	7.745967	0.434783	0.016667	4.094345
1.026	0.0112884	9.486833	0.404258	0.011111	4.49981
0.900	-0.0457575	10.95445	0.384615	0.008333	4.787492
0.495	-0.3051024	12.24745	0.332816	0.006667	5.010635
0.303	-0.5180799	13.41641	0.312826	0.005556	5.192957

Table 5b

I Order	K1 = 0.00691	qe = 1.3703	R2=0.897
II Order	K2 = 0.006795	qe = 3.6363	R2=0.969
Intra particle diffusion	Kp = 0.148	C = 1.022	R2=0.926
Elovich model	β = 0.383	α = 0.951	R2=0.977

Table 5c

I order kinetics

$y = -0.004x + 0.341$
$R^2 = 0.897$

Fig 15

II order kinetics

$y = 0.278x + 8.918$
$R^2 = 0.969$

Fig 16

Elovich plot

$y = 0.337x + 0.960$
$R^2 = 0.977$

Fig 17

**Intra particle diffusion**

$y = 0.134x + 1.288$
$R^2 = 0.926$
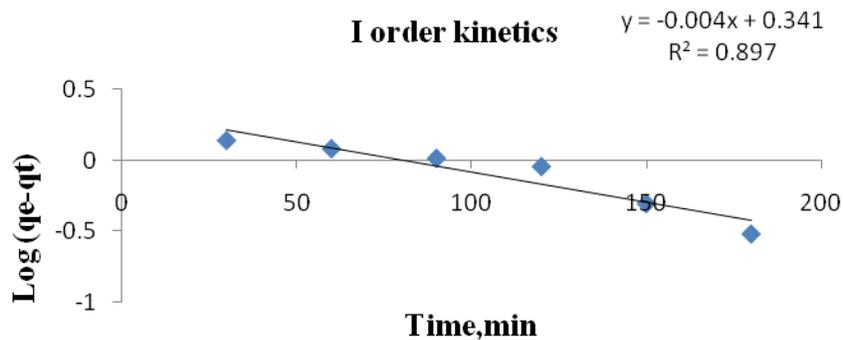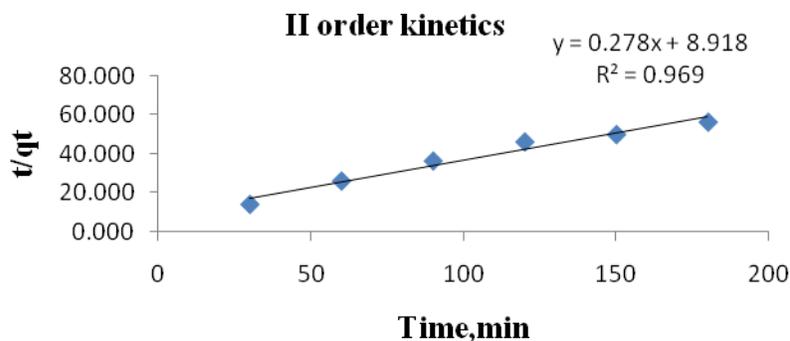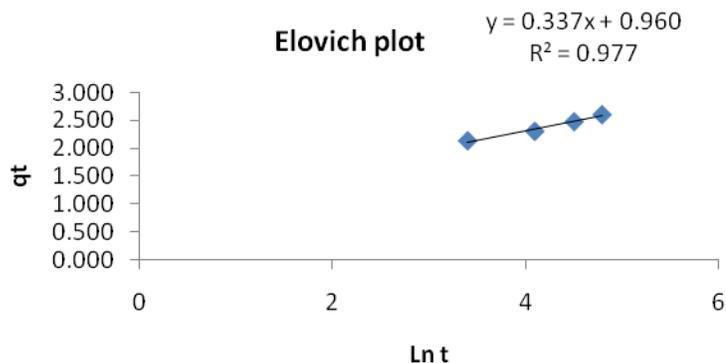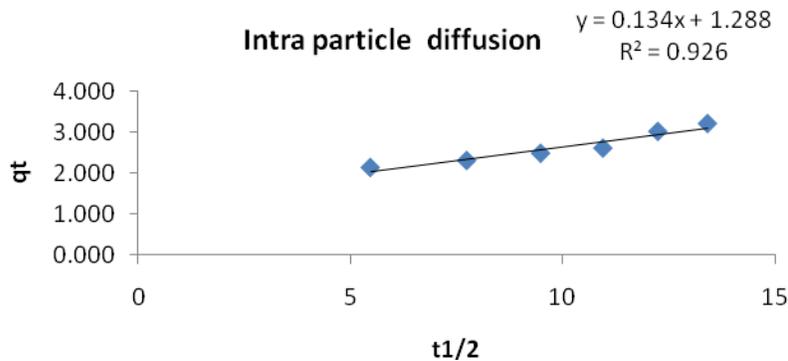
Fig 18

FT-IR studies

The action of oxidizing Oxygen on the surface of the carbonaceous precursor causes formation of surface oxides .Their structure have not been investigated completely because of the greater number of possible surface groups .The most common Oxygen groups on the surface are carboxylic, lactonic and phenolic .These groups have acidic character, which can be relatively easily determined by titration methods that are based on titrations using bases of different strengths. The method of Boehm has been followed to find the density of functional groups present on the carbon surface. FT-IR (JASCO FTIR-3500)spectra of the activated carbon

samples before and after adsorptions are shown in the figures(19 &20) respectively. The spectra provide the evidences for the presence of surface groups on the adsorbent's surface as established by Boehm titrations. Notable differences among them are the peak intensities .The carbons have marked differences in the intensities of nearly all the absorption bands , reflecting that the density of corresponding functional groups differ a lot. The intense broad band between 3100 and 3500 cm-1 are connected with v(O-H).The O-H groups are likely associated by means of hydrogen bonds. The band of non bonded hydroxyl groupings ,besides being a sharp band is usually located above 3500 cm-1 .The band in the range below 3849.96 and3962 cm-1 were assigned by Zawadzki to Hydrogen bonds of type (H2O—H—OH2)+ with protons of acidic groups. Intense bands at 2285 cm-1 indicates C-H stretching from CH2 groups. The bands around 1620 cm-1 are ascribable to v(C=O) vibration in configurations such as lactones, quinone and COOH groups .their intensity denotes a low concentration of surface C=O groups in adsorbent. According to correlation charts, Band at 1620 cm-1 are due to asymmetric and symmetric v (COO-) vibrations are skeletal C=C aromatic vibrations .The band at 1200cm-1 is associated with phenolic OH groups and to OH groups in aliphatic carbons respectively. It could also be due to –SO3H groups because of sulphuric acid treatment. The bands at 875.95 and 588.76 cm-1 are due to COO and C-O-H groups respectively. After adsorption some peaks is vanished due to desorption in to adsorbate and few peaks are slightly shifted to higher or lower wave numbers due to electrostatic forces. There are no new peaks after adsorption confirmed absence of formation of new compounds shown in the table 6.
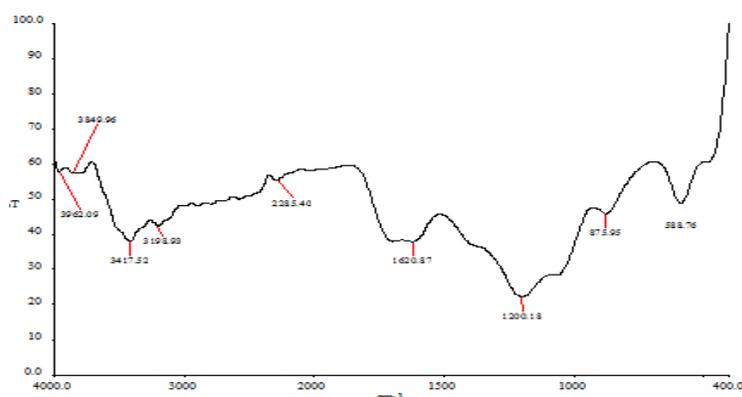

Fig 19

Wave number,cm-1 Before ads	Functional group
588.76	COO
875.95	C_O_H
1200.18	Lactonic groups
1620.87	Skeletal C=C aromatic
2285.40	C-H &CH2
3198.93	V(O-H) vibrations, Hydrogen bonds
3417.52	V(O-H) vibrations, Hydrogen bonds

| 3849.96 | V(O-H) vibrations, Hydrogen bonds |
| 3962.09 | V(O-H) vibrations, Hydrogen bonds |

Table 6
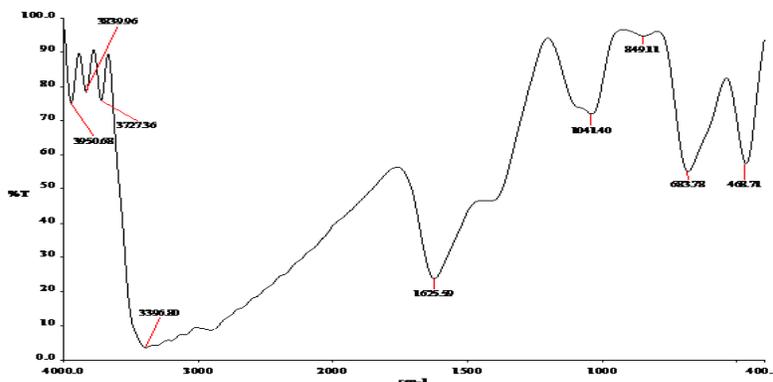
Fig 20

CONCLUSION

The study indicates that activated carbon prepared from *Cynodon dactylon* could be used as an effective adsorbent material for the treatment of copper in aqueous wastewater. The adsorption of copper on activated carbon is found to be pH, initial concentration and dose dependent. The optimum conditions of copper uptake obtained from this study are: pH 5.0, initial concentration 10 mg/L and biomass loading of 150mg. In addition, the correlation of Langmuir adsorption isotherm fits the experimental data most accurately. It was determined that the maximum adsorption capacity is 96 %. The material is not only economical, but also is an agricultural waste product. Hence activated carbon derived from *Cynodon dactylon* would be useful for the economic treatment of wastewater containing copper metal ions. There are one or two new peaks after adsorption confirmed the presence of copper on adsorbent surface.

REFERENCES

[1]   Ajmal M Rao, Ahmad RAK and Ahmad R. Hazardous Materials 2000; 79:117-131.
[2]   Wong KK, Lee CK, Low KS and Haron MJ. Chemosphere 2003; 50:23-28.
[3]   Saeed A, Muhammed Iqbal and Waheed Akhtar M. Hazardous Materials 2004; 117:65-73.
[4]   Elliot HA and Huang CP. Water Resources 1981; 15:849.
[5]   Babel S and Kurniawan TA. Chemosphere 2004; 54:951-967.
[6]   Fourest E and Roux JC. Appl Microbiol Biotech 1992; 37:399-403.
[7]   Mashitah MD, Zulfadhly Z and Bhatia S. Artificial Cells, Blood Substitues and Immobilized Biotech 1999; 27(5&6):429-433.
[8]   Garg VK, Gupta R, Yadav AB and Kumar R. Bioresource Tech 2003; 89:121-124.

[9]   Pons MP and Fuste CM. Appl Microbiol Biotech 1993; 39:661-665.
[10]   Laraous S, Meniai AH and Bencheikh Lehocine M. J Eng Sci and Tech 2008; 3(2): 185, 483-490.
[11]   Al-Asheh R, Banat Z, Al-Omari and Duvnjak. Cleaner Production 2003; 11:321-326.
[12]   Khalid N, Ahmad S, Toheed A and Ahmed J. Appl Radiation and Isotopes 2000; 52:31-38.
[13]   Han R, Zhang J, Zou W, Xiao H, Shi J and Liu H. Hazardous Materials 2005; 133:262-268.
[14]   Oladoja NA, Asia IO, Aboluwoye CO, Oladimeji YB and Ashogbon AO. Turkish J Eng Env Sci 2008; 32:143-152.