Kinetics, Isotherms and Thermodynamics Study of Copper Adsorption On To Activated Carbon from African Bush Mango Seed Shells (Irvingia)

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ABSTRACT

The isotherms, kinetics and thermodynamics of bath sorption of copper (Cu) on activated carbon from African bush mango seed shell (ABMSS) have been investigated. The effects of initial concentration, dosage contact time, and pH were examined. The results showed that adsorption capacities of the activated carbons decreased with increase in initial concentration of copper. The process sorption followed a pseudo second order kinetics. It could be best fitted by Langmuir isotherms with R^2 value of O.99. The thermodynamic parameters such as ΔH, ΔS and ΔG were computed from experimental data. These values show that adsorption is endothermic and non-spontaneous. Moreover the relative weak values of ΔH (207.85 kcal/mol) confirm a physical adsorption. The maximum adsorption of copper onto ABMSS activated carbon were obtained at contact time of 70 minutes, p^H of 8, adsorbent dosage of 10g/l, with Copper initial concentration of 50mg/l .

Keywords:*African Bush Mango Seed Shells, Adsorption, Activated Carbon, Isotherms ,Thermodynamics, Kinetics.*

1. INTRODUCTION

Heavy metal pollution of waste water is a common environmental hazard since the toxic metal ions can ultimately reach the top of the food chain and thus become a risk factor for human health one of such heavy metal of concern is copper. It is present in the waste water of several industries such as paper and pulp, fertilizer pharmaceuticals and wood preservatives (Periasanry and Namaswayam, 1996). The excessive intake of copper by man leads to severe mucosal irritation, widespread capillary damage, hepatic and renal damage central nervous problems followed by depression, gastrointestinal urination and possible necrotic changes in the liver and kidney (Kalavalhy et al, 2005). Effective methods for copper ion removal that have been used include ion exchange, reverse osmosis, electrochemical treatment, evaporative recovery and adsorption. The application of such processes are often limited because of technical or economic constraints (Kumar et al, 2006).

Biosorption is a proven technology for the removal of copper from synthetic and real industrial effluents. The high cost of activated carbon has motivated scientists into the search for new low cost adsorption means. In recent years considerable attention has been focused on the removal of copper from aqueous solution using adsorbents derived from low-cost material. Several adsorbents such as saw dust, wheat shell (Basci et al, 2004), Bagasse fly ash (Gupta and Ali, 2000), fly ash (Bois et al, 2003) and spent activated clay (Weng et al, 2007) have been used for treatment of copper rich effluents at the solid, liquid interface.

In the present investigation African bush mango seed shell activated carbon has been used as adsorbent for the removal of copper. The aim of this work is to explore the possibility of utilizing ABMSS activated carbon for the adsorptive removal of copper from effluents. The effects of initial concentration p^H, adsorbent dose and contact time were

investigated. The kinetics of copper adsorption onto the adsorbent was analysed by the pseudo first and pseudo second order model. The equilibrium data were fitted to the Langmuir and Freudlich isotherm equations to determine the best fit isotherm equation. In order to determine the thermodynamic feasibility and the thermal effects of the sorption, the Gibbs free energy (ΔG^o) the entropy ΔS^o and enthalpy were calculated. The ΔG^o is the fundamental criterion to determine if a process occurs spontaneously.

2. MATERIALS AND METHODS

2.1 Preparation of Adsorbent

The dried African bush mango seed shell was washed dried and crushed to desired mesh size (2mm). It was carbonized at 800ºC for 2hrs in a stainless steel vertical tabular reactor placed in a tubular furnace. The char produced was crushed and sieved with 600μm sieve size. The char was soaked in 6m KOH solution with 1:1.5 char to KOH ratio. The mixture was then dehydrated in an oven at 105ºC to remove moisture and then was activated under the same condition as carbonization, but to a final temperature of 850ºC for 1hr. The activated product was then cooled to room temperature and washed with hot deionized water and 0.1NHcl until pH of the washing solution reached 6.7.

2.2 Chemicals

Stock solutions of copper II was prepared by dissolving accurately weighted amount of copper II sulphate in 1000ml distilled water various concentrations of test solution of copper II ranging from 50mg/l to 150mg/l were prepared by subsequent dilution of stock each experimental solution was adjusted to the required initial p^H value using 1m HCl or 1m NaOH before mixing the adsorbent. The concentration of residual copper was determined.

2.3 BATCH EXPERIMENTS

The effect of various parameters on the removal of copper II onto ABMSS activated carbon was studied. Batch adsorption experiments were conducted at 25±1°C for each experimental run. 50ml of stock solution of known initial concentration and p^H were taken in a 250ml plugged flask. 2g of adsorbent is added to the solution and the mixture was shaken at a constant agitation speed of 200rpm) samples are drawn at appropriate intervals and the adsorbent was separated by centrifugation at 5000rpm for 10 minutes. Analysis was carried out for the residual copper concentration. The effect of dose of adsorbent on the removal of copper was measured by contacting 50ml of Copper solution with different amounts of ABMSS activated carbon (2.0-10.0)g/L till equilibrium was attained. Adsorption equilibrium isotherms were studied using ABMSS AC dosages from (2-10g/L) per 50ml of Copper solution.

Copper solution with Initial concentrations which ranged from 50-150mg/L were also used with initial p^H of 6. In all sets of experiments the plugged conical flasks were shaken at a speed of 200rpm for 2hours. The solution was separated from the mixture, analyzed for copper concentration. The adsorption capacity was obtained by using a mass equilibrium equation below.

$$qe = \frac{(Co-Ce)V}{W}$$

Co = Initial concentration of copper II (mg/L)

Ce = Equilibrium concentration

W = Weight of activated carbon

V = Volume of adsorbate in litres (L) = 0.05L

2.4 ADSORPTION KINETIC MODEL

The kinetic experiments were performed using a procedure similar to the equilibrium studies. 50mls of known concentration of copper (II) solution in a flask. Then the flask was mixed with 2g of adsorbent agitated for a contact time e varied in range 0-60 minutes at a speed of 200rpm under room temperature the adsorbent was separated from the solution by centrifugation and filtrate was analyzed by the same procedure as batch equilibrium studies. The amount of copper adsorbed at each time interval per unit mass of the adsorbent qt (mg/g) was calculated using the equation.

$$qt= \frac{(Co-Ct)V}{W} \quad ....(1)$$

Where Co (mg/L is the initial copper solution, ct (mg/L) is its concentration at time t V(L) is the volume of the solution and W(g) is the mass of the adsorbent.

3. RESULTS AND DISCUSSION

Analysis of adsorption data is vital for developing equilibrium and kinetic equations that can be used for design purposes.

3.1 EFFECT OF P^H

P^H is an important factor that influences heavy metal adsorption from aqueous solutions. It affects both the surface charge of the adsorbent and the degree of ionization of the heavy metal in solution (Aksu 2005) Fig 1 represents the effect of initial p^H of solution on the adsorption of copper onto ABMSS AC. using 50mg/L initial copper concentration and 2g/L adsorbent concentration optimum p^H was found to be pH 8.0 for the adsorbent studied. The maximum removal efficiency was 72% this may be as a result of the competition between the hydrogen and the copper ions, on the sorption sites. However at increased initial concentration of the solution percentage removal reduced as shown in fig 1.

Table 1 effect of Time on Percentage Removal of Cu Using Abmss Ac

Time in mins	Ct	% Removal	Co 50mg/l
20	12.3	54.3	
30	10.4	61.3	Co = Initial Copper
40	6.0	77.7	
50	3.0	89.0	Ct = Final Copper Concentration
60	2.3	91.4	
70	1.8	93.3	
80	1.8	93.3	

Table 2 Effect Of Dosage On Percentage Cu Removal Using Abmss Ac

Dosage	Ct	% Removal	Co 50mg/l
2	10.8	59.8	
4	7.2	73.2	
6	5.0	81.4	
8	2.4	91.0	
10	1.6	94.0	
12	1.6	94.0	

Table 3 Effect Of P^h On Percentage Removal Of Cu Using Abmss Ac

p^H	Ct(Cu)	% Removal	Co 50mg/l
2	43.5	13	
4	31.0	38	
6	19.5	38	
8	14.0	72	
10	15.0	70	

571

Table 4 Effect of P^h on Percentage Removal at Different Initial Concentrations Using Abmss A/C

p^H	Co mg/l	Ce mg/l	% Removal	Co mg/l	Ce mg/l	% Removal	Co mg/l	Ce mg/l	% Removal
2	50	43.5	13	1.00	890	11	150	134.7	10
4		31.0	38		680	32		105.0	30
6		19.5	61		49.0	51		87.5	42
8		14.0	72		42.0	58		82.5	45
10		15.0	70		37.0	63		90.5	40

Table 5 Adsorption Isotherm

Temp	Ce	qe	ce/qe	Log qe	Log ce	Ln ce
30	12.5	9.38	1.33	0.97	1.10	2.52
40	11.5	9.62	1.19	0.98	1.06	2.44
50	10.5	9.88	1.06	0.99	1.02	2.35
60	9.0	10.25	0.88	1.01	0.95	2.20

Table 6 Adsorption Kinetic Model

Time (m)	ct	qt	log ct	qe – qt	log qe-qt	1/ct	t/qt
10	27.0	5.75	1.43	4.50	0.15	0.037	1.74
20	16.0	8.50	1.20	1.75	0.24	0.062	2.35
30	14.0	9.00	1.15	1.25	0.096	0.071	3.33
40	12.5	9.38	1.10	0.87	-0.06	0.080	4.26
50	12.5	9.38	1.10	0.87	-0.06	0.080	5.33
60	12.5	9.38	1.10	0.87	-0.06	0.080	6.40

Table 7 Thermodynamic Studies

Temperature t	qe	Kd	ln kd	$\frac{1}{T}$
30	10.50	0.21	-1.56	0.033
40	10.63	0.21	-1.53	-0.025
50	10.88	0.22	-1.52	0.020
60	11.25	0.23	-1.47	0.016

3.2 Effect of Adsorbent Dosage

The effect of varying doses of ABMSS AC was investigated using 50mg/L of initial copper concentration at initial p^H of 5.0. Table 2 shows an increase in percentage removal of copper with the increase in dose of adsorbent up to a certain limit and then it remains almost constant. Increase in adsorption with increasing dose of adsorbent is expected due to the increase in adsorbent surface area and the availability of more adsorption sites (Mall et al 2006) the adsorption capacity of copper onto ABMSS AC increased with increase in dosage up till 10g/L the percentage removal remained constant at 94%.

3.3 Effect of Contact Time

Effect of contact time for the removal of copper by ABMSS AC at 2g/L biomass concentration shows increase in adsorption of copper with increase in time. At a certain time, the percentage removal remained constant as time increased.

The maximum removal was 93.3% and it was attained in about 70 minutes.Fig 2 shows the effect of time on Cu removal at different concentrations using ABMSS AC

3.4 Adsorption Kinetic Study

Kinetic models have been used to investigate the mechanism of sorption and potential rate controlling steps which is helpful for selecting optimum operating conditions for the full scale batch process (Kalavathy et al, 2005). Pseudo first order, and Pseudo second order in models were used.

3.4.1 Pseudo First Order

The Pseudo first order rate expression based on solid capacity is generally expressed as follows.

$$\frac{dq}{dt} = k_{1ad}(q_e - q) \quad \text{...(2)}$$

Where qe is the amount of copper adsorbed at equilibrium (m/g). q is the amount of adsorbent at time t (mg/g), k1ad is the rate constant of first order adsorption (L/min). After integration and applying boundary conditions, t=0 to t and q=0 to qe the integrated form of equation (2) becomes

$$\log(q_e - q) = \log(q_e) - \frac{k_{1ad}}{2.303}t \quad \text{......................................(3)}$$

Values of adsorption rate constant (k1ad) for copper adsorption onto ABMSS AC were determined from the straight line plot of log(qe-q) against t. The data were filled with a poor correlation coefficient table 2 indicating that the rate of removal of copper onto ABMSS does not follow the Pseudo first order equation.

3.4.2 Pseudo Second Order Model

The Pseudo second order equation is also based on sorption capacity of the solid phase. It predicts the behaviour over the whole range of data. Furthermore, it is in agreement with chemisorption being the rate controlling step and is expressed as (Ho et al, 2000).

$$\frac{dq}{dt} = k_{2ad}(q_e - q)^2 \quad \text{..(4)}$$

Where k_2ad is the rate constant of second order adsorption (g/mg/min for the same boundary conditions the integrated form of the above equation now becomes

$$\frac{t}{q} = \frac{1}{k_2qe^2} + \frac{1t}{q}$$

.…………………………………….………(5)

The initial sorption rate h (mg/g.mm) at t = 0 is given as

h = k_2ad q^2e

………………………………………………(6)

Where k_2ad and h values were determined from slope and intercept of plots of t/qt against t, fig3. The values of the parameter k_2 and R^2 are presented in table 8, the correlation coefficients of data examined were all high $R^2 > 0.98$ this shows that the model can be applied for the entire adsorption process hence the sorption of copper onto ABMSS AC follows the Pseudo second order kinetic model same behavior have been observed in biosoprtion of copper onto agricultural waste sugar beet pulp (Aksu and Isoglu, 2005) and adsorption of copper onto H_3PO_4 activated rubber wood saw dust (Kalavathy et al, 2005).

Table 8 Adsorption Kinetic Model Rate Constants For Abmss At Different Initial Concentration

Adsorbent	Dose of Adsorbent g/L	Initial Cu conc. mg/L	K2	R2
ABMSS/AC	2	50	0.097	0.994
ABMSS/AC	2	100	0.072	0.998
ABMSS/AC	2	150	0.067	0.998

3.5 Adsorption Equilibrium Study

It is important to evaluate the most appropriate correlations for equilibrium curves, to optimize the design of a sorption system Langmuir Freundlich and Tempkin isotherm models were used to describe the adsorption equilibrium. Experimental isotherm data were conducted at an equilibrium time of 8O minutes for different dosages of adsorbent. The Langmuir adsorption isotherm is based on the assumption that all sites possess equal affinity for the adsorbate. It may be represented in the linear form as follows (Langmuir 1916).

$$\frac{Ce}{qe} = \frac{1}{kLQm} + \frac{ce}{Qm}$$ ....(7)

Where Qm is maximum copper uptake mg/g, KL the Langmuir adsorption constant, L/mg. The values of KL were increased with increasing dosage. High KL values are used to calculate dimensionless separation parameter RL. The essential characteristics of Langmuir isotherm model can be expressed in terms of a dimensionless separation factor (RL) which is defined by

$R_L = {}^1/1 + K_LC_o$ where KL is the Langmuir constant and Co is the initial solute concentration mg/L. The value of RL indicates the type of the isotherm to be either unfavourable if (RL>1) linear (RL = 1) favourable (0<RL<1 or irreversible RL = 0.From the plot of t/qt vs t, in copper adsorption onto ABMSS AC, fig4 the dimensionless factor RL was 0.5 which is less than 1. Langmuir isotherm can be used to correlate the equilibrium data. The Langmuir predicts monolayer adsorption for the adsorbate assuming constant heat of adsorption for all sites on the active sites of the adsorbent.

FREUNDLICH ISOTHERM

The empirical Freundlich isotherm is based on the equilibrium relationship between heterogeneous surfaces. This isotherm is derived from the assumption that the adsorption sites are distributed exponentially with respect to the heat of adsorption. The logarithmic linear form of

Freundlich isotherm may be represented as follows (Freundlich, 1906).

$$\log qe = \log K_F + \frac{1}{nf}\log ce$$ ....(8)

Where K_F (L/g) and $^1/n_F$ are Freundlich constants indicating the sorption capacity and sorption intensity respectively. The magnitude of K_F sorption capacity was obtained as 0.088, the value of n, sorption intensity was less than unity, 0.55 for ABMSS removal of Cu hence the Freundlich isotherm could not correlate the equilibrium data.

Tempken Isotherm

Tempken isotherm assumes that the heat of adsorption decreases linearly with the coverage due to adsorbent-adsorbate interaction (Vijayaraghavan et al, 2006). The Tempkin isotherm has generally been applied in the following linear form (Temken and Pyozhez, 1940).

qe = BlnA + Blnce

$$B = \frac{RT}{b}$$ ....(9)

Where A(L/g) is Tempken isotherm constant b (J/mol) is a constant related to heat of sorption, R is the gas constant (8.314 J/mol k) and T the absolute temperature (k). A plot of qe versus In ce enables the determination of isotherm constants A, b from the slope as 1.75 and 126.77 for dosage of 2g/L and concentration of 50mg/L.

3.6 Thermodynamics Study

In order to fully understand the nature of adsorption the thermodynamic parameters such as free energy change (ΔGᵒ) enthalpy change (ΔHᵒ) and entropy were calculated, it was possible to estimate these thermodynamic parameters for the

adsorption by considering the equilibrium constants under the several experimental conditions. The following equations were used.

$$\Delta G = Ttlnkd(T) \quad ....(10)$$

$$\ln kd = \frac{\Delta S}{R} - \Delta H/RT \quad ....(11)$$

The kd value is the adsorption coefficient obtained from Langmuir equation which is equal to the ratio of amount adsorbed (q_e in mg/g) to the adsorptive concentration in mg/L. These values were obtained from experiments at various temperatures , with the above equations the values of ΔH^o and ΔS^o were determined from the slope and intercept of linear plots of lnkd vs $\frac{1}{T}$.

Slope and intercept obtained from plot of lnkd vs $\frac{1}{T}$ fig 5, for Cu sorption onto ABMSS AC at initial concentration 50mg/L were used to calculate ΔH ΔS and ΔG at different temperatures using the relation

Intercept = $\frac{\Delta S}{R}$

Slope = $\frac{\Delta H}{R}$

$\Delta G^o = \Delta H - T\Delta S$

Initial concentration 50mg/L

ΔH (J/mol)	ΔS (J/mol k)
136.49	-9.98
TEMP K	**ΔG^o (J/mol k)**
303	3.04×10^3
313	3.20×10^3
323	$3 \times 31 \times 10^3$
333	$3 \times 39 \times 10^3$

The positive ΔH^o values shows that the adsorption of Cu onto ABMSS AC was endothermic in nature which supported the results obtained earlier where the Cu uptake increase with increase in solution temperature. The negative ΔS^o describes decreasing degree of freedom and randomness during the adsorption process at the solid liquid interface. This phenomenon had also been observed in the adsorption of azodye orange II by titania aerogel Abramian, 2009 and direct dyes by carbon nanotubes (Kuo et al, 2008). For standard free energy ΔG^o values were positive which describe the condition of non-spontaneous nature of adsorption process at the range of temperature studied.

4. CONCLUSION

The study showed the ability of ABMSS A/C to sorb copper from aqueous solution. The adsorption was found to be initial concentration, pH dosage and time dependent. Sorption data can be adequately modelled by Langmuir isotherm. The kinetic study allowed the validation of a Pseudo second order mechanism. Negative values of ΔS^o indicate the increasing randomness of the system, (Seedhar et al, 1999).
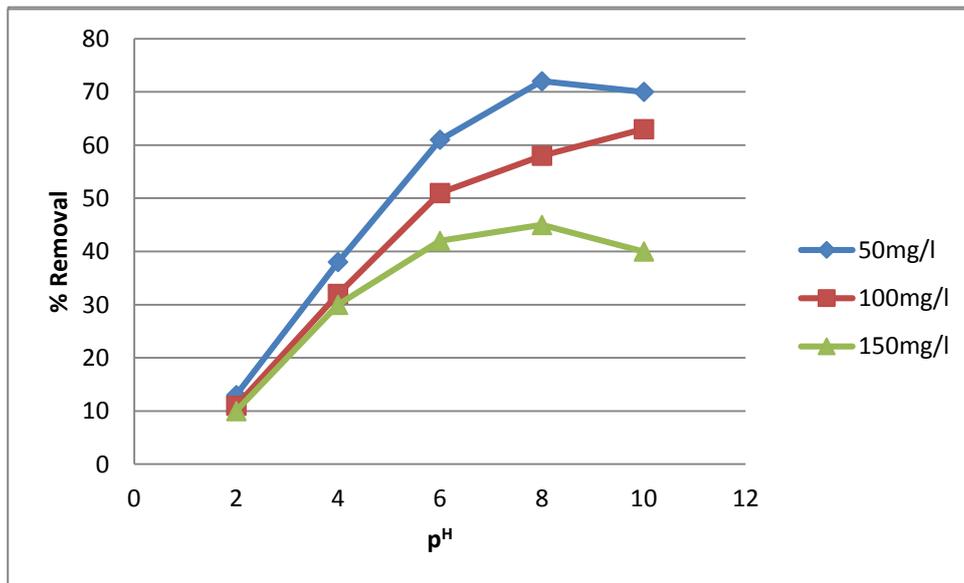

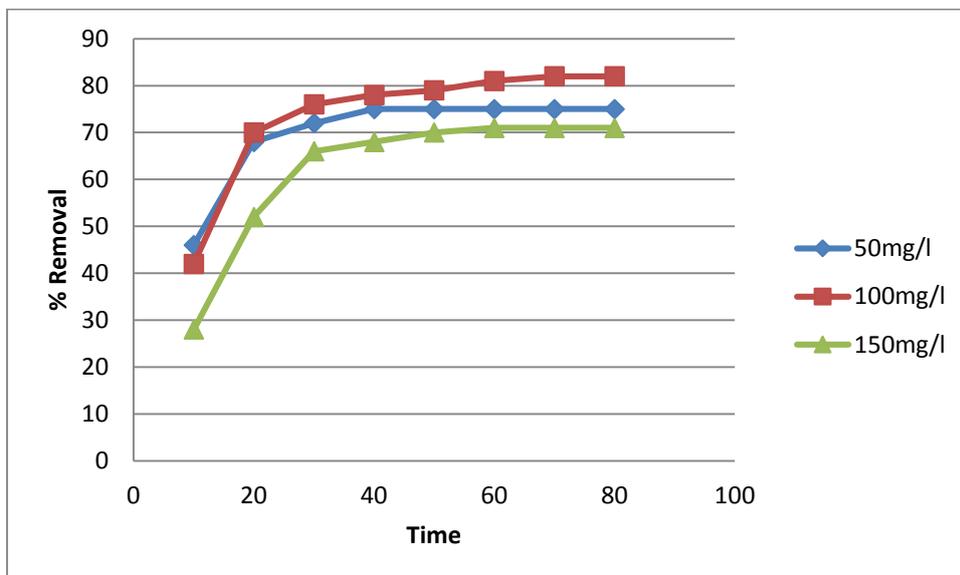**Fig 1: Percentage Removal Of Copper Vs P^h At Different Concentrations**

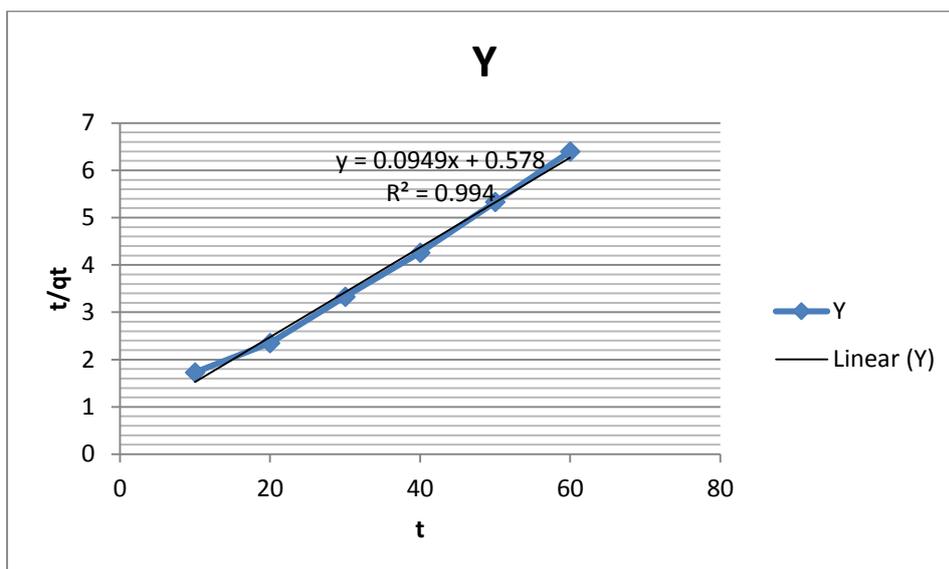**Fig 2: Percentage Removal Of Copper Vs Time At Different Concentrations**

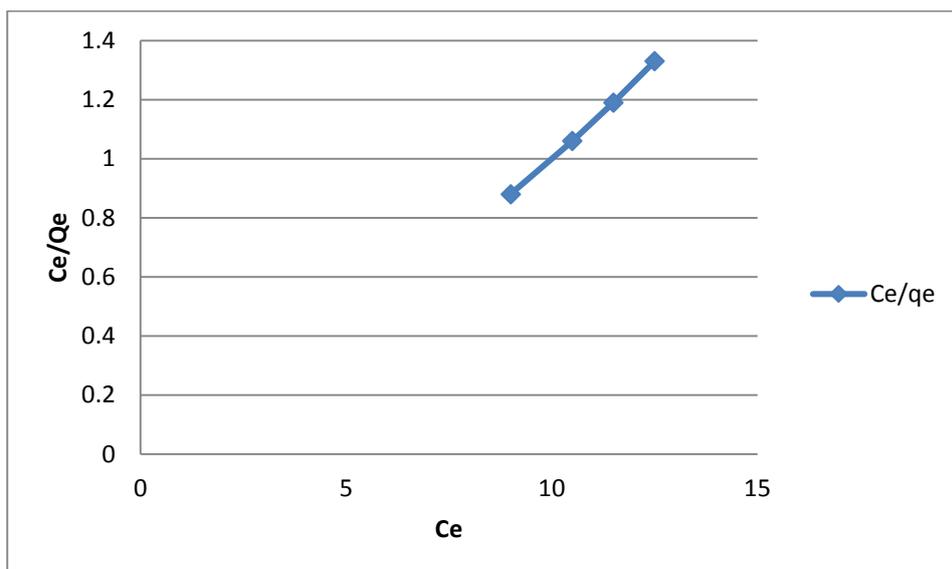**Fig 3: Pseudo Second Order Plot For Copper Removal Using Abmss Ac**

Fig 4: Langmuir Plot For Copper Adsorption Onto Abmss Ac
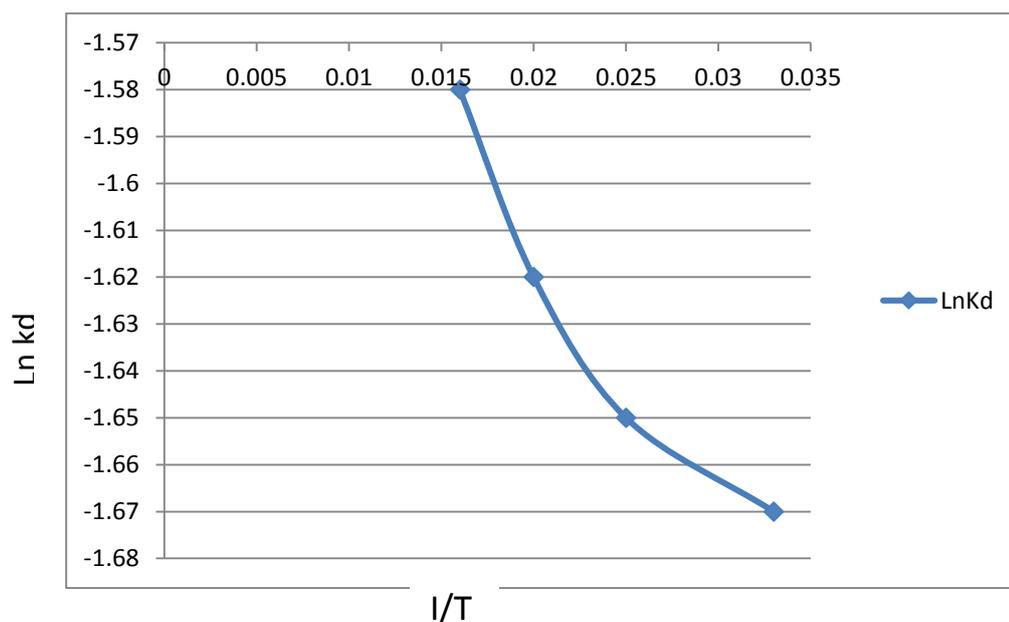

Fig 5: Thermodynamics Studies For Cu Adsorption Onto Abmss A/C

REFERENCES

Abramian, and Hel Rassey, (2009) "Adsorption Kinetics and Thermodynamics of Axo-dye Orange II onto Highly Porous Titania Aerogel" Chemical Engineering Journal Vol. 150 No. 2-3 Pp 403-410.

Aksu, Z. Isoglu I. A. 2005, "Removalof copper [11] ions from aqeous solution by biosorption onto agricultural waste sugar beet pulp ," J process Biochemistry. 40 3031-3044.

Basi, N., Kocadagistan E., Kocadagistan B. (2004) "Biosorption of Copper (II) from Aqueous Solutions by Wheat Shell", Desalination. 164: 135-140.

Bois, L., Bonhomme, A. Ribes, A. Pais, B, Raffin, G, Tessier, F. (2003) "Functionalized Silica for Heavy Metal Ions Adsorption Colloids Surf Physiochem. Eng. Aspects 221:221-230.

C. Kuo, C.H. Wu and J.Y. Wu. (2008) "Adsorption of Direct Dyes from Aqueous Solutions by Carbon Nanotubes: Determination of Equilibrium Kinetics and Thermodynamic Parameters, "Journal of Colloid and Interface Science, Vol. 327 No. 2 Pp. 308-315.

Freundlich, H.M.F (1906), "U ber die Adsorption in lo Sungen, Zeitschrift Fur Physiklische Chemie 57, 385-470.

Gupta, V.K, Ali, I. (2000), "Utilization of Bagasse Flyash (A Sugar Industry Waste for the Removal of Copper and Zinc from Waste Water" Sep Purif Technol 18: 131-140.

Ho, Y.S., Mckay, G, Wase, D.A.J Foster, C.F. (2000), "Study of the Sorption Divalent Metal Ions onto Peat" Adsorp Sci. Technol 18: 639-650.

Kalavathy, M.H., Karthikeyan, T., Rajgopal S., Muranda L.R. (2005) "Kinetic and Isotherm Studies of Cu(II) Adsorption unto H_3PO_4 Activated Rubber Wood Sawdust". Journal of Colloid and Interface Science 292: 354-362.

Kumar, I.P, King, P. And Prasad V.S.R.K (2006) "Removal of Copper from Aqueous Solution using Ulva Fasciata Sp-A Marine Green Algae" Journal of Hazardous. Materials B 137, 367-373.

Langmuir, I. (1916) "The Constitution and Fundamental Properties of Solids and Liquids" J.A.M. Chem. Soc. 38: 2221-2295.

Mall, D. I, Srivastava V.C. and Agarwal N.K. (2006), "Removal of Orange G and Methyl Violet Dyes by Adsorption onto Bagassefly Kinetic Study and Equilibrium Isotherm Analysis" Dyes and Pigments 69:210-223.

Periasamy, K., Namaswayan (1996) "Removal of Copper (II) by Adsorption onto Peanut Hull Carbon from Water and Copper Plating Water Industry" Chemosphere 32: 769-789.

Seedhar, M.K. Madhukumar, A., Anirudhan T.S. (1999), Evaluation of an Adsorbent Prepared by Treating Coconut Husk with Polysulphide for the Removal of Mercury from Waste Water. Indian J. Eng Mater Sci, 6(5) 279-285.

Temken, M.J. and Pyozhev, V. (1940) "Actaphysicochim USSR 12: 327-352.

Vijayaraghavan, K., Padmesh, T.V.N., Palanivelu, K., Velan M. (2006), "Biosorption of Nickel(II) ions onto sargassum Wightii.

Weng, C.H., Tsai, C.Z., Chu, S.H., Sharma, Y.C. (2007) "Adsorption Characteristics of Copper (II) Onto Spent Activated Clay". Separation and Purification Technology, 54:187-197.

577