KINETIC AND ISOTHERM STUDIES OF COPPER (II) REMOVAL FROM WASTE WATER USING ACTIVATED ACANTHACEAE

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ABSTRACT

The present investigation deals with the utilization of Acanthaceae and an activated Acanthaceae prepared from Acanthaceae Leaves adsorbents for the removal of copper from waste water. A series of experiments were conducted in batch system to evaluate the effect of the variables. The effect of pH, initial copper concentration dose of adsorbents and contact time were considered. Adsorption kinetic data were tested using pseudo- second- order Elovich model and intra-particle diffusion models. Studies revealed that intra- particle diffusion played an important role in the mechanism of copper (II) adsorption. The equilibrium data were analyzed using Langmuir, freundlich isotherm models at different doses of AAC. Thermodynamic parameters such as ΔH^o, ΔS^o, and ΔG^o were evaluated. The positive ΔH^o value, pH dependent results and desorption of copper suggest that adsorption of Cu(II) on AAC involves physisorption mechanism. The equilibrium data were analyzed using different error analysis equations. The freundlich model describes the data of AAC.

Keywords: Adsorption, Activated Acanthaceae, Thermodynamics, Kinetics.

INTRODUCTION

Heavy metal pollution of wastewater is a common environmental hazard, since the toxic metal, metal ion dissolved can ultimately reach the top of the food chain and thus become a risk factor for human health. One of such heavy metals of concern is copper. It is present in the wastewater of several industries, such as metal cleaning and planning baths, refineries, paper and pulp, fertilizer and wood preservatives [1]. 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 irritation and possible necrotic changes in the liver and kidney [2]. 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 is often limited because of technical or economic constraints [3]. Biosorption is a proven technology for the removal of copper (II) ions from synthetic and real industrial effluents. The high cost of activated carbon has motivated scientists to 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 materials. Several adsorbents, such as sawdust, silica and iron oxide [4], wheat shell [5]. Baggasse fly ash [6], fly ash [7] and spent activated clay[8] have been used for the treatment of copper(II) rich effluents at the solids – liquid interface. The present investigations activated Acanthaceae prepared from Acanthaceae Leaves have been

used as adsorbents for the removal of copper (II). The aim of present work is to explore the possibilities of utilizing activated Acanthaceae for the adsorptive removal of copper from wastewater.

ADSORBENT

The Acanthaceae leaves were collected from Villages around Thiruvarur district. The Acanthaceae leaves were washed with distilled water to remove the impurities and ground with a grinder. After the grinding the Acanthaceae leaves were carbonized with sulphuric acid and washed with distilled water and dried and activated for 4 hours at 400°C in a furnace. The AAC particles were sieved and stored into plastic bags and ready for use.

ADSORBATE

All reagents used in this study were of analytical grade. Stock solution of copper (II) was prepared by dissolving accurately weighed amount of copper sulphate in 1000 ml distilled water. All experimental solutions were prepared by diluting the stock solution to the required concentrations. A known weight of AAC was added to 50 ml of the Cu(II) ions solutions with an initial concentration of 50 mg L^{-1} to 250 mg L^{-1}. The contents were shaken thoroughly using a mechanical shaker rotating with a speed of 120 rpm. The solution was then filtered at preset intervals of time and the residual Cu(II) ions concentration was determined by colorimetry. The experiments were also conducted in order to evaluate the effect of different variables such as dose of the adsorbent, initial Cu(II) ion concentrations, contact time, pH and the effect of the presence of other ions such as chloride ions on adsorption process under a given set of optimal conditions.

ADSORPTION EXPERIMENT

The batch adsorption experiments were performed by contacting 25 g of the selected AAC with 50 ml of the aqueous solution of different initial concentrations (50 to 250 mg/L) at different solutions pH. The experiments were performed in wrist action shaker for a period of 1 hour at 120 rpm using 250 ml Erlenmeyer flasks containing 100 ml of different copper ion concentrations at room temperature (30°C). Continuous mixing was provided during the experimental period with a constant agitation speed of 120 rpm for better mass transfer with high interfacial area of contact. The remaining concentration of copper in each sample after adsorption at different time intervals was determined by AAC after filtering the adsorbent with Whatman GF/A filter paper to make it adsorbent free. The copper concentration retained in the adsorbent phase was calculated according to

$$q_e = (C_i – C_e) \, V/ \, W \, ….. \, (1)$$

where C_i and C_e are the initial and equilibrium concentrations (mg/L) of copper solution respectively; V is the volume(L); and W is the weight (g) of the adsorbent. The ions removal percentage can be calculated as follows :

$$\%R = \frac{(C_0 – C_t) \times 100}{C_0} \, …(2)$$

Batch kinetic studies

The batch kinetic [9] experiments were basically identical to those of the adsorption equilibrium method. The aqueous samples were taken at present time intervals and the concentrations of Cu(II) ions were similarly measured. All the kinetic experiments were carried out at 30, 40, 50 and 60°C at initial concentrations of 50, 100, 150, 200, and 250 mg/L. The amount of adsorption at time t, q_t (mg/g) was calculated by

$$q_t = (C_0 – C_t) \, V/W \, ……….....(3)$$

Where C_t (mg/L) is the liquid phase concentration of Cu(II) ions at any time.

Dosage of adsorbent

The various doses of the adsorbents were mixed with the Cu (II) ions solutions and the mixture was agitated in a mechanical shaker. The adsorption capacities for different doses were determined at definite time intervals by keeping all other factors constant.

Initial concentration of Cu (II) ions

In order to determine the rate of adsorption, experiments were conducted with different initial concentrations of Cu (II) ions ranging from 50 to 250 mg/L. All other factors were kept constant.

Contact time

The effect of period of contact on the removal of the Cu(II) ions on adsorbent in a single cycle was determined by keeping the particle size, initial concentration, dosage, pH and concentration of other ions constant.

pH

Adsorption experiments were carried out at pH 2, 3, 4, 5, 6, 7, 8, 9 and 10. The acidic and alkaline pH of the media was maintained by adding the required amounts of dilute hydrochloric acid and sodium hydroxide solutions. The parameters like particle size of the adsorbents, Cu(II) ions concentration, dosage of the adsorbent and concentration of other ions have been kept constant while carrying out the experiments. The pH of the samples was determined using a portable pH meter, Systronics make. The pH meter was calibrated with 4.0 and 9.2 buffers.

Chloride

The experiments were done in the presence of varying chloride environments using various sodium chloride solutions. While doing the experiments, the absence of other ions has been ensured.

Temperature

The adsorption experiments were performed at four different temperatures viz., 30, 40, 50 and 60°C in a thermostat attached with a shaker, Remi make. The constancy of the temperature was maintained with an accuracy of ± 0.5 °C.

Zero Point Charge

The pH at the potential of zero charge of the AAC (pHzpc) 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 °C to remove the dissolved carbon dioxide. 50 mg of the activated AAC was added to 50 ml of the solution. After stabilization, the final pH was recorded. The plot of final pH versus initial pH was used to determine the zero point charge of the AAC.

Titration Studies

Literature survey has revealed that , only strong acidic carboxylic acid groups are neutralized by sodium bicarbonate, and neutralized by sodium carbonate are thought to be lactones, lactol and carboxyl group. Only the weak acidic phenolic groups react with sodium hydroxide. Therefore, by selective neutralization using bases of different strengths, the surface acidic functional groups in AAC 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 AAC 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.

Desorption Studies

Desorption studies help to elucidate the nature of adsorption and recycling of the spent adsorbent and the Cu(II) ions. The effect of various reagents used for desorption was studied.

RESULTS AND DISCUSSION

Characterization of the Adsorbent

The physico-chemical properties of the chosen adsorbent, AAC, were carried out by standard methods [10] and are listed in the following Table-1.

Effect of contact time and initial Cu(II) ions concentration

The experimental results for the adsorption at various concentrations (50 to 250 mg L^{-1}) with contact time are shown in Figure 1. The respective data are presented in Table-2, revealing that, percent adsorption decreased with increase in initial Cu(II) ions concentration, but the actual amount of Cu(II) ions adsorbed per unit mass of AAC increased with an increase in Cu(II) ions concentration. It means that the adsorption is highly dependent on initial concentration of Cu(II) ions. It is because of the reason that at lower concentration, the ratio of the initial number of Cu(II) ions molecules to the available surface area is low. Subsequently the fractional adsorption becomes independent of initial concentration. However, at higher concentrations, the available

sites of adsorption become fewer and hence the percentage removal of Cu(II) ions is dependent upon initial concentration [10,11]. Equilibrium has been established at 60 minutes for all concentrations. Figure-2 reveals that the curve is single, smooth, and continuous, leading to saturation, suggesting the possibility of monolayer coverage of the Cu(II) ions on the AAC adsorbent surface.

Effect of Dosage of AAC

The adsorption of Cu(II) ions on AAC was studied by varying the concentration (50 - 250 mg / 50ml) for 30 mg L^{-1} of Cu(II) ions concentration. The percent adsorption increased with an increase in the AAC concentration (Figure 2). This may be due to the increased AAC surface area and availability of more adsorption sites [10, 11]. Hence the remaining parts of the experiments were carried out with an optimum dose of the adsorbent (25 mg/50 ml).

Theory of Adsorption isotherm

To quantify the sorption capacity of the absorbent for the removal of Cu(II) ions, the most commonly used isotherms, namely Freundlich and Langmuir have been adopted.

Freundlich isotherm

The linear form of Freundlich isotherm [12] is represented by the equation

$$\text{Log } q_e = \log K_f + (1/n)\log C_e \quad \text{................}(4)$$

Where q_e is the amount of Cu(II) ions adsorbed per unit weight of the sorbent (mg/L), K_f is (mg/g(L/mg)) the measure of adsorption capacity and $1/n$ is the adsorption Intensity. The value of K_f and n are calculated from the intercept and slope of the plot of log q_e vs log C_e respectively. The constant K_f and n values are given in table 3. In general K_f value increases the adsorption capacity for a given adsorbate increases. The magnitude of the exponent $1/n$ gives an indication of the favorability of adsorption. The value of n > 1 represents favorable adsorption condition (or) the value of $1/n$ is lying in the range of 1 to 10 confirms the favorable condition for adsorption. This is further supported by Langmuir isotherm.

Langmuir isotherm

The Langmuir isotherm model [13] is based on the assumption that the maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface. The linear form of the Langmuir isotherm equation can be described by

$$C_e/q_e = (1/Q_m b) + (C_e/Q_m) \quad \text{...............}(5)$$

Where C_e (mg/L) is the equilibrium concentration of the adsorbate, q_e (mg/g) is the amount of adsorbate per unit mass of adsorbent, Q_m and b are Langmuir constants related to adsorption capacity and rate of adsorption respectively. Q_m is the amount of adsorbate at complete monolayer coverage (mg/g) which gives the maximum adsorption capacity of the adsorbent and b (L/mg) is the Langmuir isotherm constant that relates to the energy of adsorption (or rate of adsorption). The linear plot of specific adsorption capacity C_e/q_e against the equilibrium concentration (C_e) shows that the adsorption obeys the Langmuir model. The Langmuir constant Q_m and b were determined from the slope and intercept of the plot and are presented in table (3) In order to find out the feasibility of the isotherm, the essential characteristics of the Langmuir isotherm can be expressed in terms of dimensionless constant separation factor R_L [14,15] by the equation

$$R_L = (1/(1+bC_o)) \quad \text{.....}(6)$$

Where C_o (mg/L) is the highest initial concentration of adsorbent and b(L/mg) is Langmuir isotherm constant. The parameter R_L indicates the nature of the shape of the isotherm accordingly.

$R_L > 1$ Unfavorable adsorption

$0 < R_L < 1$ Favorable adsorption

$R_L = 0$ Irreversible adsorption

$R_L = 1$ Linear adsorption

The R_L values between 0 and 1 indicate the favorable adsorption for all initial concentration (C_o) and temperatures studied. The calculated R_L value is given in Table. 4.

Thermodynamic treatment of the adsorption process

Thermodynamic parameters associated with the adsorption, via standard free energy change (ΔG^0),

standard enthalpy change (ΔH^0), and standard entropy change (ΔS^0) were calculated as follows. The free energy of adsorption process considering the adsorption equilibrium constant K_0 is given by the equation

$\Delta G° = \square - RT \ln K_0$ ………. (7)

Where $\Delta G°$ is the free energy of adsorption (kJ/mol), T is the temperature in Kelvin and R is the universal gas constant(8.314 J $mol^{-1}K^{-1}$).The adsorption distribution coefficient K_0 for the sorption reaction was determined from the slope of the plot of ln (q_e/C_e) against C_e at different temperatures and extrapolating to zero C_e according to the method suggested by Khan and Singh [16] The adsorption distribution coefficient may be expressed in terms of enthalpy change ($\Delta H°$) and entropy change ($\Delta S°$) as a function of temperature,

$\ln K_o = (\Delta H°/RT) + (\Delta S°/R)$ ……(6)

Where $\Delta H°$ is the standard heat change of sorption (kJ/mol) and $\Delta S°$ is standard entropy change (kJ/mol), the value of $\Delta H°$ and $\Delta S°$ can be obtained from the slope and intercept of plot of ln K_0 against 1/T. The values of thermodynamic parameter calculated from equations 5 and 6 are shown in table (5). The thermodynamic treatment of the sorption data indicates that $\Delta G°$ values were negative at all temperatures.

From the results it can be made out that physisorption is much more favorable for the adsorption of Cu(II) ions. The positive values of $\Delta H°$ show the endothermic nature of adsorption and they governs the possibility of physical adsorption for in the case of physical adsorption, while increasing the temperature of the system, the extent of Cu(II) ions adsorption increases, this rules out the possibility of chemisorptions. The low $\Delta H°$ value depicts that Cu(II) ions is physisorbed on to the adsorbent AAC [17,18,19,20].

The negative values of $\Delta G°$ (Table-5) shows the adsorption is highly favorable and spontaneous. The positive value of $\Delta S°$ (Table-5) show the increased disorder and randomness at the solid solution interface of Cu(II) dyes with AAC adsorbent.

Adsorption kinetics

The study of adsorption dynamics describes the solute uptake rate and evidently this rate controls the residence time of adsorbate uptake at the solid-solution interface .The kinetics of Cu(II) ions adsorption on the AAC were analyzed using pseudo-second-order [21] Elovich [22,23] and intra-particle diffusion [24] kinetic models.

The conformity between experimental data and the model predicted values was expressed by the correlation co efficient (γ), (γ values close or equal to 1).A relatively high correlation coefficient (γ) value indicates that the model successfully describes the kinetics of Cu(II) ions adsorption on AAC adsorbent.

The pseudo-second- order equation

The pseudo - second-order adsorption kinetic rate equation is expressed as

$dq_t / d_t = k_2(q_e - q_t)^2$ …..(8)

Where: k_2 is the rate constant of pseudo- second-order adsorption (g $mg^{-1}min^{-1}$). For the boundary conditions t = 0 to t= t and q_t = 0 to q_t = q_t the integrated form of Eq. (8) becomes: $1/(q_e - q_t) = 1/q_e + k_2t$ …. (9)

This is the integrated rate law for a pseudo second-order reaction. Equation (9) can be rearranged to obtain

Eq.(9),which has a linear form:

$t/q_t = (1/k_2q_e^2) + ((1/q_e)t$ ……….(10)

If the initial adsorption rate (h)(mg $g^{-1}min^{-1}$) is :

$h = k_2q_e^2$ …………. (11)

equation (10) and (11) becomes,

$t / q_t = 1 / h + 1 / q_e t$ …(12)

The plot of (t/q_t) and t of Eq.(12) should give a linear relationship from which q_e and k_2 can be determined from the slope and intercept of the plot, respectively. The pseudo-second order rate constants k_2, the calculated h values, and the correlation coefficients (γ) are summarized in Table 6.

The Elovich equation

The Elovich model equation is generally expressed as $dq_t / d_t = \alpha \exp(-\beta q_t)$ ……..(13)

Where; α is the initial adsorption rate (mg g^{-1} min^{-1}) and β is the desorption constant (g mg^{-1}) during any one experiment. To simplify the Elovich equation. Chien and Clayton (1980) assumed $\alpha\beta t \gg t$ and by AAC lying boundary conditions $q_t = 0$ at t= 0 and $q_t = q_t$ at t = t Eq.(13) becomes:

$$q_t = 1/\beta \ln (\alpha\beta) + 1/\beta \ln t \ldots (14)$$

If Cu(II) ions adsorption fits the Elovich model, a plot of q_t vs. ln(t) should yield a linear relationship with a slope of $(1/\beta)$ and an intercept of $(1/\beta)$ln $(\alpha\beta)$. The Elovich model parameters α, β, and correlation coefficient (γ) are summarized in table 6.

The intra particle diffusion model

The intra -particle diffusion model used here refers to the theory proposed by Weber and Morris [22] based on the following equation for the rate constant:

$$q_t = k_{id} t^{(1/2)} + C \ldots (15)$$

Where k_{id} is the intra -particle diffusion rate constant (mg g^{-1}min^{-1}) and C is the constant. If the rate limiting step is intra -particle diffusion, the graphical representation of (q_t) absorbent Cu(II) ions (mg g^{-1}) depending on the square root of the contact time ($t^{1/2}$) should yield a straight line passing through the origin [22].The slope of the plot of qt vs. $t^{1/2}$ will give the value of the intra -particle diffusion coefficient (k_{id}) and correlation coefficient (γ) indicate the fitness of this model. The intercept value indicates that the curve is not passing through the origin, so the intra- particle diffusion is not only a rate controlling step .The intra-particle parameters are summarized in table 6.

Effect of pH

One of the most important parameters controlling the adsorption process is pH. The effect of pH of the solution on the adsorption of Cu(II) ions on AAC was determined. The result is shown in Figure. 3. The pH of the solution was controlled by the addition of HCl or NaOH. The uptake of CuII) ions at pH 7.5 was the minimum and a maximum uptake was obtained at pH 3.0 – 6.7. However, when the pH of the solution was increased (more than 7.5), the uptake of Cu(II) ions was increased. It appears that a change in pH of the solution results in the formation of different ionic species and different AAC surface charge. As pH values are lower than, 6 the Cu(II) ions can enter the pore structure. As pH values are higher than 6.7, the zwitterions form of Cu(II) ions in water may increase the aggregation of Cu(II) ions to form a bigger molecular form (dimer) and become unable to enter the pore structure of the AAC surface.

Effect of the Ionic Strength on the Adsorption of Cu(II) ions on AAC

The effect of sodium chloride on the adsorption of Cu(II) ions on AAC is shows that the low solution concentration of NaCl had little influence on the adsorption capacity. At higher ionic strength the adsorption of Cu(II) ions will be increased due to the partial neutralization of the positive charge on the AAC surface and a consequent compression of the electrical double layer by the chloride anion. The chloride ion can also enhance adsorption of Cu(II) ions onto AAC by pairing of their charges and hence reducing the repulsion between the Cu(II) ions molecules adsorbed on the surface. This initiates AAC to absorb more of positive Cu(II) ions.

Desorption studies

Desorption studies help to elucidate the nature of adsorption and recycling of the spent adsorbent and the Cu(II) ions. If the adsorbed Cu(II) ions can be desorbed using neutral pH water, then the attachment of the Cu(II) ions of the adsorbent is by weak bonds. If sulphuric acid or alkaline water desorbs the Cu(II) ions, then the adsorption is by ion exchange. If organic acids, like acetic acid can desorb the Cu(II) ions, then the Cu(II) ions has been 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 more than 68 % removal of adsorbed Cu(II) ions could be got . The reversibility of adsorbed Cu(II) ions in mineral acid or base is in agreement with the pH dependent results obtained. The desorption of Cu(II) ions by mineral acids and alkaline medium

indicates that the Cu(II) ions were adsorbed onto the AAC through physisorption [25,26].

REFERENCES

1. Periasamy . K , Namasivayam . C , Removal of copper(II) by adsorption onto peanut hull carbon from water and copper plating industry wastewater. Chemosphere 32 : 769 – 789 (1996).

2. Kalavathy.M.H , Karthikeyan .T Rajgopal. S and Miranda.L.R , Kinetics and isotherm studies of Cu(II) adsorption onto H_3PO_4- activated rubber wood sawdust . Journal of colloid and Interface Science. 292 : 354 – 362 (2005).

3. Kumar . Y.P, King.P and Prasad. V.S.R.K, Removal of copper from aqueous solution using Ulva fasciata sp. A marine green algae , journal of Hazardous Materials B137 : 367 – 373 (2006).

4. Ajmal .M, Khan, A.H ., Ahmad. S, Ahmad.A , Role of sawdust in the removal of copper (II) from industrial wastes , Water Res. 32(10) : 3085 – 3091.(1998).

5. Basic. N, Kocadagisten .E , Kocadagisten .B , Biosorption of copper (II) from aqueous solutions by wheat shell , Desalination . 6: 174 – 184 (2004).

6. Bois.L, Bonhomme. A, Ribes.A ,Pais.B , Raffin . G. Tessier.F, Functioalized silica for heavy metal ions adsorption Colloids Surf . Physicochem .Eng .aspects. 221 : 221 – 230. (2003).

7. Weng . C.H , Tsai . C.Z, Chu . S.H and Sharama.Y.C, Adsorption characteristics of copper(II) onto spent activated clay, separation and purification Technology, 54 : 187 – 197 (2007).

8. Li .W.Zhang.S and Shan . X.Q , Surface modification of goethite by phosphate for enhancement of Cu and Cd adsorption ,colloids and surface A: Physicochem Eng . Aspects. 293 : 13 – 19. (2007).

9. Hameed.B.H. et al., A novel agricultural waste adsorbent for the removal of cationic dye from aqueous solution., Journal of hazardous materials, 162 (2009) 305-311.

10. Namasivayam C, Muniasamy N, Gayathri K, Rani M and Renganathan K, Removal of dyes from aqueous solution by cellulosic waste orange peel, Biores Technol, 1996, 57, 37.

11. Namasivayam C and Yamuna R T, Adsorption of direct red by biogas residual slurry, Environ Pollut, 1995, 89, 1.

12. Frendlich.H., The dye adsorption is losungen (Adsorption in Solution)., Z Phys. Chem.,57 (1906) 385 – 470.

13. Langmuir.I., The adsorption of gases plane surfaces of glass, mica and platinum., J. Am. Soc., 579 (1918) 1361 – 1403.

14. Weber.T.W. Chakravorti.R.K, Pore and Solid diffusion models for fixed bed adsorbers., J. Am. Inst. Chem. Eng.20 (1974) 228.

15. McKay.G., Blair.H. S., Gardner. J. R., Adsorption of dyes on chitin. I. Equilibrium Studies., J. Appl. Polym. Sci. 27 (1982) 3043 – 3057.

16. Khan.A.A. and Singh.R.P., "Adsorption Thermodynamics of Carbafuran on Sn (IV) arsenosilicate in Li^+, Na^+ and Ca^{2+} forms," J. Colliod and Surface., 24 (1987) 33 – 42. 1987.

17. Arivoli S and Hema M, Comparative study on the adsorption kinetics and thermodynamics of dyes onto acid activated low cost carbon, Intern J Phys Sci., 2007, 2, 10 – 17.

18. Arivoli S, Venkatraman B R, Rajachandrasekar T and Hema M, Adsorption of ferrous ion from aqueous solution by low cost activated carbon obtained from natural plant material, Res J Chem Environ 2007, 17, 70-78.

19. Arivoli S, Kalpana K, Sudha R and Rajachandrasekar T, Comparitive study on the adsorption kinetics and thermodynamics of metal ions onto acid activated low cost carbon, E J Chem, 2007, 4, 238 – 254.

20. Renmin Gong, Yingzhi Sun, Jian Chen, Huijun Liu, Chao yang, Effect of chemical modification on dye adsorption capacity of peanut hull, Dyes and Pigments, 2005,67, 179.

21. Ho.Y.S. McKay.G., The kinetic of sorption of divalent metal ions on to Sphagnum moss peat, Water Res. 34 (2000) 735 – 742.

22. Chien.S.H. Clayton.W.R., Application of Elovich Equation to the kinetics of Phosphate release and sorption on soil. Soil Sci. Sco. Am. J. 44 (1980) 265 – 268.

23. Spark.D.L., Kinetics of Reaction in pure and mixed system in soil physical chemistry. (1986) CRC. Press, Boca Raton.

24. Weber.W. J., Morris.J.C., Kinetics of adsorption on Carbon from solution J. Sanitary Eng. Div. 90 (1964) 79.

25. Yupeng Guo, Jingzhu Zhao, Hui Zhang, Shaofeng Yang, Zichen Wang and Hongding Xu, Use of rice husk based porous carbon for the absorption Rhodamine B from aqueous solution, Dyes and Pigments, 2005, 66, 123-128.

26. Sreedhar M K and Anirudhan T S, Mercury (II) adsorption of desorption characteristics of oconut husk based carbon – Kinetics and self diffusion, Indian J Environ Protect, 1999,19, 8.

Table-1 Characteristics of the adsorbent

Properties	AAC
Particle size (mm)	0.044
Density (g/cc)	0.2856
Moisture content (%)	1.55
Loss on ignition (%)	85
Acid insoluble matter (%)	3.5
Water soluble matter (%)	0.52

pH of aqueous solution 6.75
pHzpc 6.55
Surface groups (m equiv/g)
i) Carboxylic acid 0.428
ii) Lactone, lactol 0.065
iii) Phenolic 0.039
iv) Basic (pyrones and chromenes) 0.028

TABLE .2. EQUILIBRIUM PARAMETERS FOR
ADSORPTION OF Cu(II) ON AAC

M_o	Ce (Mg / L)				Qe (Mg / g)				Removed (%)			
	30° C	40° C	50° C	60° C	30° C	40° C	50° C	60° C	30° C	40° C	50° C	60° C
50	3.0920	2.7024	2.3696	2.1632	93.816	95.5952	95.2608	95.6736	93.816	94.5952	95.6736	95.2608
100	12.1896	10.5400	8.3176	6.7248	175.6208	178.92	183.3648	186.5504	87.8104	89.460	93.2752	91.6824
150	25.9992	22.3232	18.7928	15.6752	248.0016	255.3536	262.4144	264.6496	82.6672	85.1178	89.5498	87.4714
200	48.9568	44.2968	39.3992	34.5392	302.0864	311.4064	321.2016	330.9216	75.5216	77.8516	82.7304	80.3004
250	70.0760	64.1776	58.2480	52.8680	359.848	371.6448	383.504	394.264	71.9696	74.3289	78.8528	76.7008

TABLE .3. LANGMUIR AND FREUNDLICH ISOTHERM

TEMP. (C°)	LANGUMUIR PARAMETER		FRUENDLICH PARAMETER	
	Q_m	b	K_f	n
30°	418.57088	0.06599	5.88260	2.34119
40°	430.27605	0.074937	6.07267	2.3344
50°	439.1691	0.0897	6.319878	2.34042
60°	450.8325	0.10354	6.51430	2.3159

PARAMETER FOR Cu (II) ON AAC

TABLE .4. DIMENSIONLESS SEPERATION FACTOR
(R_L) FOR Cu(II) ON AAC

(C_i)	TEMPERATURE °C			
	30°C	40°C	50°C	60°C
50	0.23256	0.21066	0.18231	0.16188
100	0.13158	0.11773	0.10030	0.08807
150	0.09174	0.08169	0.06918	0.06048
200	0.07042	0.06254	0.05279	0.04606
250	0.05714	0.05067	0.04268	0.03719

TABLE .5. THERMODYNAMIC PARAMETERS FOR THE ADSORPTION OF Cu(II) ON AAC

C_o	$\Delta G°$				$\Delta H°$	$\Delta S°$
	30° C	40° C	50° C	60° C		
50	-6850.48	-7448.56	-8058.28	-8572.04	10.6633	57.8481
100	-4974.29	-5565.28	-6444.90	-7280.63	18.6336	77.6724
150	-3935.46	-4538.06	-5218.59	-5947.37	16.3972	67.0034
200	-2838.13	-3271.17	-3773.49	-4337.34	12.2924	49.8346
250	-2375.44	-2766.58	-3199.66	-3643.64	10.45820	42.3098

TABLE 6. THE KINETIC PARAMETERS FOR ADSORPTION OF Cu(II) ON AAC

| C_o	Temp °C	PSEUDO –SECOND- ORDER				ELOVICH MODEL			INTRAPARTICLE DIFFUSION		
		q_e	K_2	γ	h	α	β	γ	K_{id}	γ	C
50	30	103.6646	0.00131	0.9962	14.0793	143.3599	0.06918	0.9921	1.65553	0.9912	0.17486
	40	103.8083	0.00138	0.9963	14.8771	192.7565	0.07242	0.9924	1.6760	0.9914	0.16467
	50	103.87751	0.001469	0.9961	15.8619	264.6251	0.07580	0.9930	1.6956	0.9915	0.15527
	60	104.4696	0.00144	0.9960	15.8159	248.1254	0.07455	0.9915	1.69420	0.9917	0.15737
100	30	193.8828	0.000693	0.9964	26.0717	258.0513	0.03677	0.9940	1.62333	0.9918	0.176249
	40	197.0107	0.0006964	0.9951	27.0307	306.1686	0.03718	0.9923	1.6410	0.9919	0.17037
	50	200.6737	0.000737	0.9952	29.7013	413.153	0.03796	0.9928	1.66820	0.9921	0.16173
	60	204.4193	0.000728	0.9953	30.4534	407.400	0.03700	0.9927	1.67463	0.9923	0.163025
150	30	276.3919	0.000446	0.9942	34.0729	274.0236	0.0248	0.9926	1.57714	0.9925	0.18718
	40	282.4223	0.0004691	0.9951	37.4187	358.3784	0.02507	0.9933	1.60688	0.9928	0.17788
	50	289.6318	0.000484	0.9956	40.6742	444.3900	0.02511	0.9935	1.63233	0.9938	0.17144
	60	294.1242	0.00039	0.9944	34.5373	569.9083	0.02680	0.9936	1.6468	0.9945	0.15794
200	30	341.97033	0.00031	0.9941	36.8557	209.2315	0.01838	0.9939	1.49777	0.9961	0.209591
	40	349.9902	0.000324	0.9944	39.7764	261.9943	0.01862	0.9940	1.52862	0.9967	0.19940
	50	359.1229	0.00033	0.9922	42.8424	316.001	0.01863	0.9941	1.5555	0.9969	0.19219
	60	367.2266	0.00035	0.9932	48.3123	431.5385	0.01900	0.9943	1.59035	0.9968	0.18109
250	30	409.3547	0.000253	0.9933	42.4012	223.1823	0.01506	0.9937	1.4658	0.9977	0.21561
	40	421.3301	0.000250	0.9935	44.4047	244.8973	0.01481	0.9928	1.48564	0.9975	0.21201
	50	435.9824	0.000234	0.9936	44.6258	237.7719	0.01481	0.9920	1.49300	0.9974	0.215051
	60	443.2708	0.000254	0.9939	50.0952	313.0525	0.01418	0.9919	1.5288	0.9978	0.20259
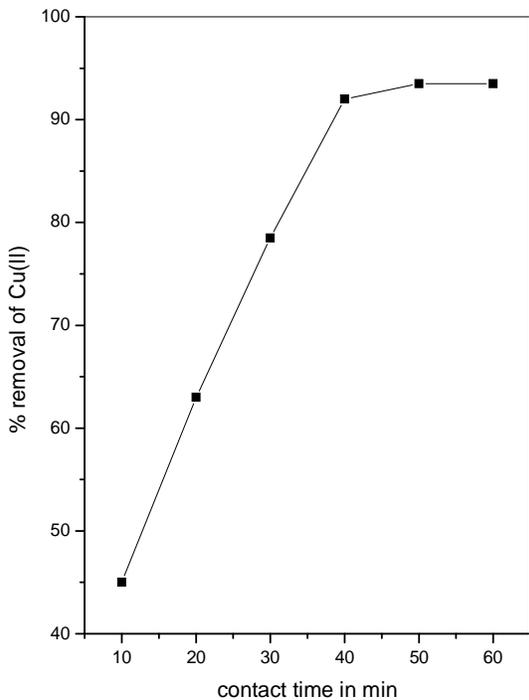
Fig.1-Effect of adsorbent dose on the removal of Cu(II) ion
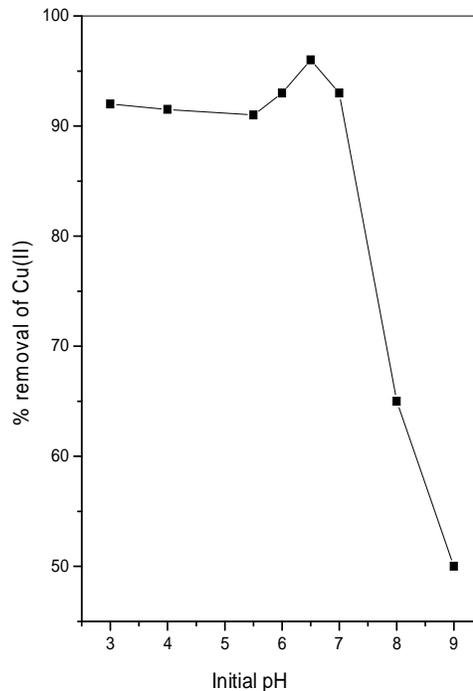[Cu(II)]=50 mg/L:Adsorbent dose=25mg/50ml:Temp=30^{0}C

Fig.3-Effect of initial pH on the removal of Cu(II)
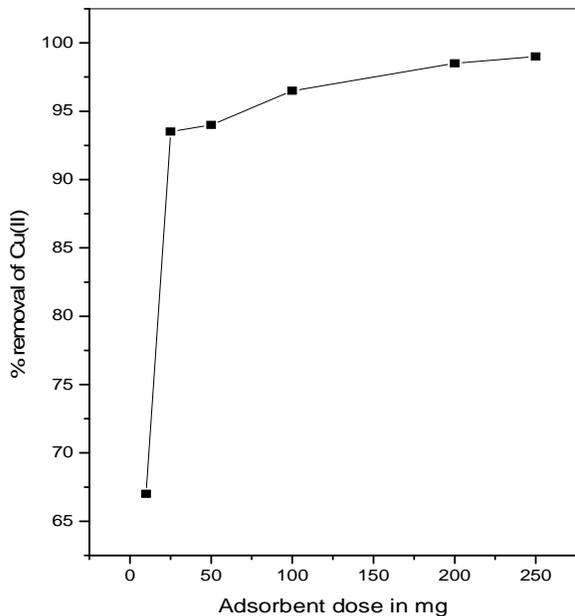[Cu]=50 mg/L:Adsorbent dose=25mg/50ml:Temp=30^{0}C:Cotact time=60 min

Fig.2-Effect of adsorbent dose on the removal of Cu(II)
[Cu(II)]=50 mg/L:Contact time=60 min:Temp=30^{0}C