

Removal of Cadmium (II) from Aqueous Solution on Activated Carbon Prepared from Typha Angustata. L: Equilibrium and Kinetic Studies

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Abstract- Activated carbon prepared from Typha Angustata.L was used as adsorbent for the removal of Cd (II) ions from aqueous solutions. The effect of operating as a function of contact time, initial pH, initial adsorbent dosage and metal ion concentration and temperature also investigated, were the equilibrium adsorption data were fitted to Langmuir and freundlich adsorption isotherm models. The kinetic study indicated that the pseudo second order rate equation better described the adsorption process. The values of the separation factors are in the range of 0-1 which indicates favourable biosorption. The results indicated that the prepared activated carbon is an efficient, alternative low- cost adsorbent for the removed of cd (II) from aqueous solutions.

Index Terms- Activated carbon, isotherms, kinetics, Cd(II), removal adsorption.

I. INTRODUCTION

Heavy metals are present in the soil, natural water and all in various forms and may become contaminates in food and drinking water (Forsther, 1977). Some of them are constituents of herbicides, paints and fertilizers applications. Hazards associated with the contamination of water have led to the development of various technologies for water purification namely filtration and ion exchange, precipitation with carbonate or hydroxide (Arowolo, 2004)

Man's exposure to heavy metals comes from mining, smelting, refining and manufacturing processes (Nriagu, 1996). Heavy metals constitute an important part of environmental pollutants which can be detrimental to a variety of living species. Excessive ingestion of these metals by humans can cause accumulative poisoning, cancer, nervous system damage and ultimately death (Issabayeva et al., 2007). Examples of these metals are Cadmium, Chromium, Copper, lead, Mercury, Nickel, Selenium, Silver, Vanadium, Cobalt and Zinc.

Heavy metals are non-biodegradable and they tend to accumulate in living organisms, causing various diseases and disorder e.g cadmium causes serious renal damage, anemia and hypertension. Cadmium occurs naturally in the environment and the main anthropogenic pathway through which cadmium enters environment is through waste from industrial processes such as electroplating, smelting, alloy manufacturing, Cadmium-nickel

batteries, pesticides, mining, cement and phosphate, fertilizers, textile operations and refining (Cheung et al, 2000; Wu et al, 2010).

This makes the process of treating waste waters or effluents with agricultural by product adsorbents more cost effective than the use of conventional adsorbents like activated carbon (Lgwe and Abia, 2005). In the present work, the removal of cadmium (II) ion from water and waste water by using activated carbon produced from Typha Angustata.L was investigated. The adsorption capacity of adsorbent was investigated using batch experiments. The influence of pH, contact time, metal ions and adsorbent concentrations were investigated. The experimental data obtained were evaluated and fitted using adsorbent equilibrium isotherms, and kinetic models.

II. MATERIALS AND METHODS

2.1 preparation of activated carbon

In the present study, Typha Angustata L flowers was collected from the perundurai, at Erode (Dt) in Tamilnadu. They were cut into small pieces and dried for 25 days. The flowers were dried and burnt the muffle furnace at 450-500°C and kept it for half an hour. To collect the carbonized material was ground well and sieved to a smaller particles size. Activated carbon have been stored in a plastic vessels for the further experiment. The sample was sieved into a smaller particle size of 0.15 to 0.25mm was used.

2.2 Adsorbate solution:

A stock solution of Cd (II) was prepared in 1000ml deionised water using 1.1416g of Cadmium sulphate. The Working solution was obtained by diluting the stock solution with deionised water, and P^H was adjusted to the desired values according to the following experimental design with 1M HCl and 1M NaOH solution. Cadmium ions concentrations were determined at characteristic wave length ($\lambda_{max} = 470 \text{ nm}$) with an double beam UV- visible spectrophotometer.

2.3 Characterization of adsorbent

Physico-chemical characteristics of the adsorbents were studied as per the standard testing methods. The XRD pattern of pure activated carbon Fig 1. Show characteristics peak at 28°.

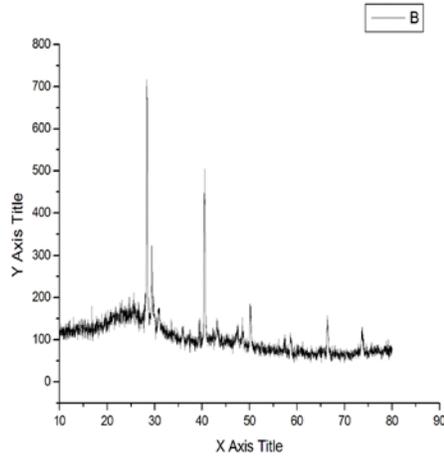


Figure 1. Activated carbon .

The result of SEM analysis are shown in the micrographs fig. 2

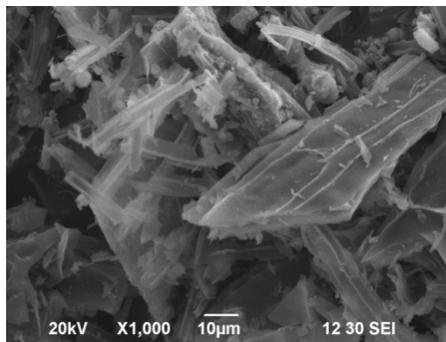


Figure 2 .Activated Carbon

FT IR spectroscopy:-

The absorption bands are due to the stretching and bending vibration of the group. The frequency of carbon peak 617.22cm^{-1}

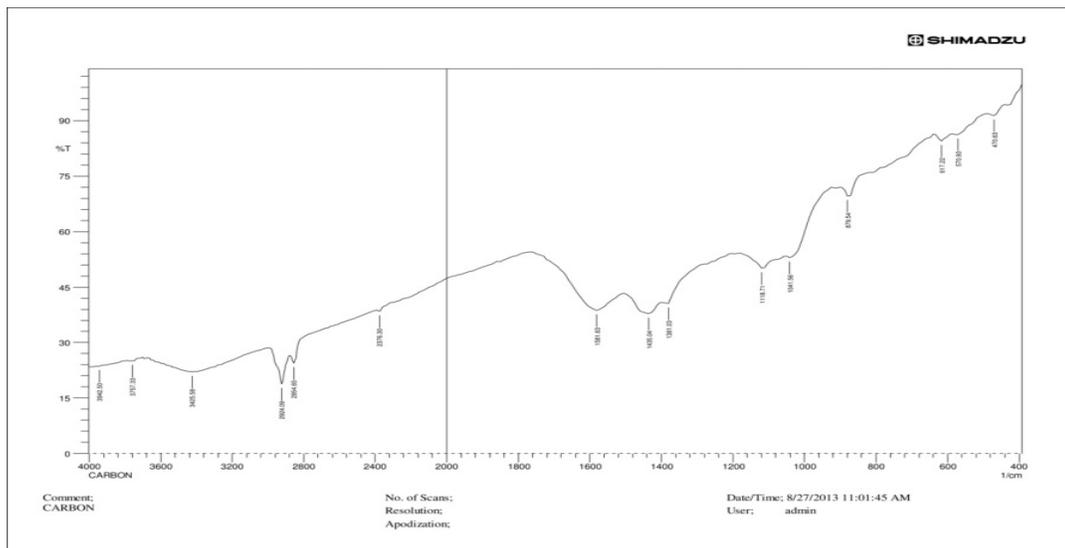


Figure 3 Carbon

III. BATCH ADSORPTION STUDIES

Batch adsorption experiments were also performed by agitation 0.1g of the adsorbent with 50ml of cadmium solution the P^H containing different initial concentration from 10 to 40mg/L at 30°C. After the established contact time (2h) was attained, the suspension was filtered, and supernatant was analyzed for the metal concentration of 10 to 40mg/L and the adsorbent dosage of 0.1g. The pH values was adjusted in the range of 4-9 by using dil. HCl and NaOH solution. Experiments were carried out by varying the adsorbent amount from 0.1 to 1.0g with Cd(II) concentration ranging from 10 to 40mg/L. The concentration of Cd(II) in the solution was determined and spectrophotometrically by developing a purple-violet colour with 2.5ml each of citrate buffer, 58.8g ammonium citrate and 38.4g citric acid in 500ml distilled water, 10% KI and pyrogene G solution mixed as complexing agent. The absorbance of the purple-violet colored solution is read at 470nm. The percentage removal of metal and amount of metal adsorbed on AC was calculated by equation (1) and (2) respectively.

$$\% \text{ removal} = \frac{100[C_0 - C_e]}{C_e} \text{-----(1)}$$

$$q_e = \frac{[C_0 - C_e]V}{W} \text{----- (2)}$$

Where q_e is the quantity of metal adsorbed on the adsorbent at the time of equilibrium (mg/g), C₀ and C_e are the initial and equilibrium concentration (mg/l). V is the volume of solution, W is the weight of adsorbent(g).

IV. RESULTS AND DISCUSSION

4.1 Effect of contact time and initial metal concentration:

The effect of contact time shows that equilibrium is achieved faster 10 to 210 min .It is observed that in both cases the percentage removal of Cd (II) ion increase with increase in metal ion concentration Fig (4). The rate of adsorption is very fast initially with about 97% of the total cadmium being removal within few minutes followed by a increased rate with the approach of equilibrium. The removal rate is high initially due to the presence of the binding sited which gradually become saturated with time resulting in increases rate of adsorption as equilibrium approached finally attain.

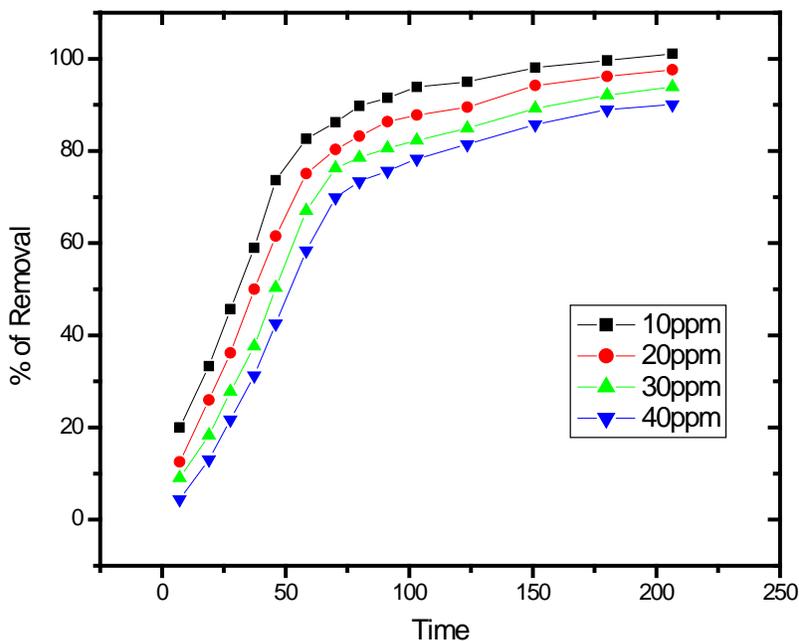


Figure 4: contact time

4.2 Effect of adsorbent dose:

Figure(2) shown the effect of adsorbent dose on the removal of cadmium.It is clear from the figure that as the adsorbent

dosage increase, the adsorption also increase. The maximum percentage removal of 95% of Cd(II) was observed at 1g.

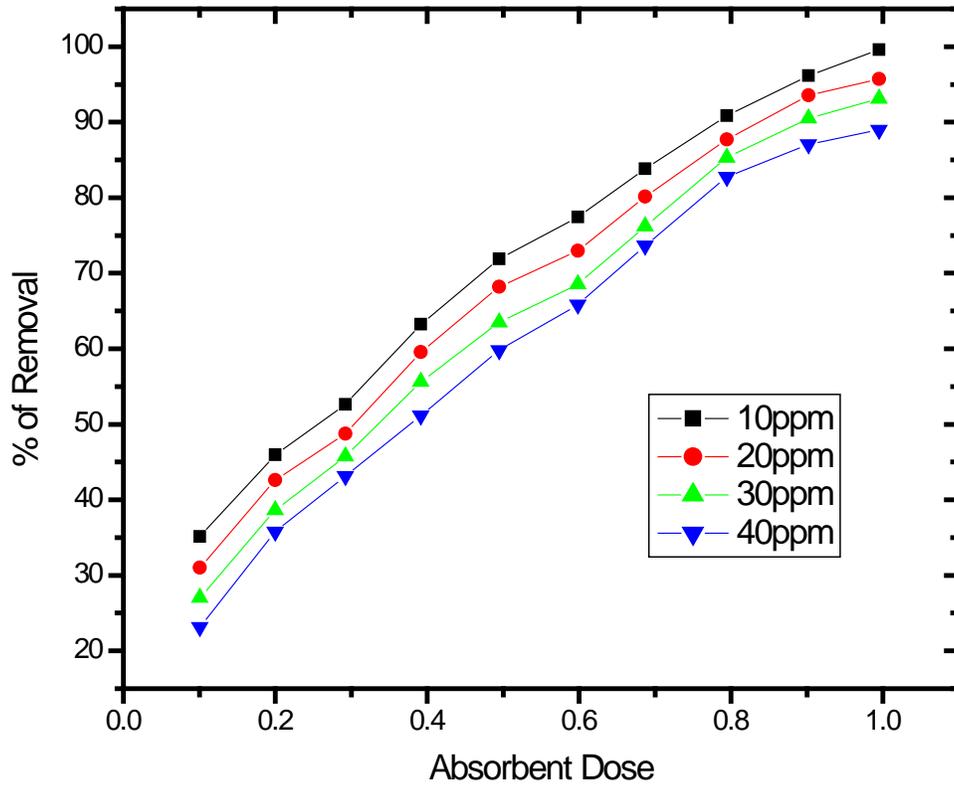


Figure 5: Adsorbent dose

4.3 Effect of temperature:

The effect of temperature on biosorption of cd(II) on activated carbon was investigated under temperature range of 30°, 34°, 38°, 42°C. The temperature dependence of cd(II) adsorption a show is figure(6).

The extent of adsorption the metals was found to increase with increase in temperature indicating that the process to be endothermic in nature.

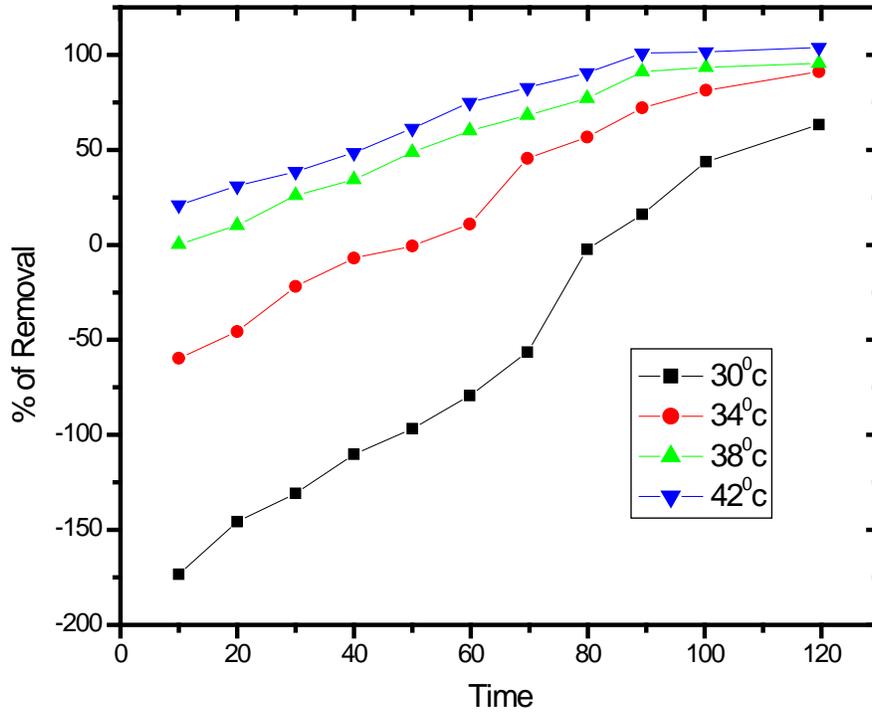


Figure 6: Effect of Temperature

4.4 Effect of pH:

The effect of initial solution pH on the adsorption capacity at equilibrium condition was studied. The result for the adsorption of Cd(II) is shown in figure 7 using 100 mg/L as initial metal

concentration. It could be seen that the removal concentration and percentage removal is P^H dependent. From the figure it is clear that cadmium adsorption efficiency is highest at P^H 6-8

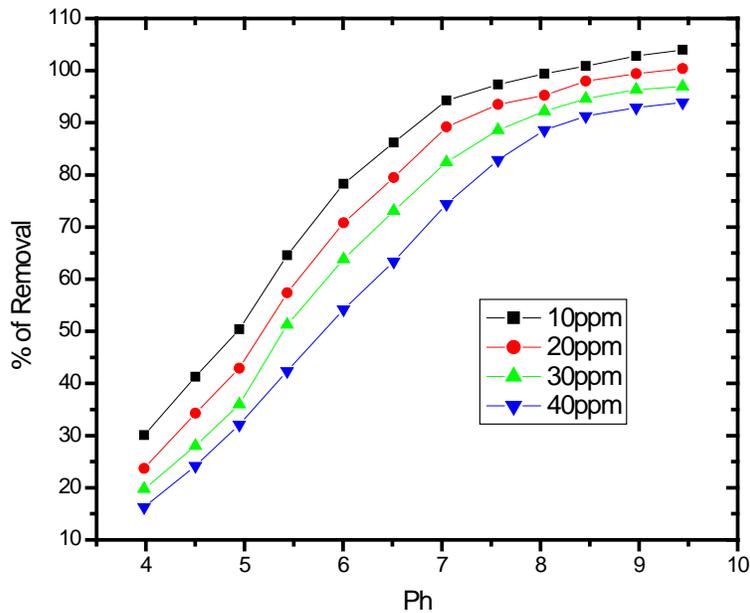


Figure 7: Effect of pH

4.5 Adsorption Isotherm

The adsorption isotherm were analyzed using Langmuir, Freundlich, and Tempkin isotherm

4.5.1 Langmuir adsorption isotherm:

The theoretical Langmuir adsorption isotherm is often used for adsorption of the solute from a liquid solution. The Langmuir adsorption isotherm is perhaps the best known of all the isotherms describing adsorption, and it is often expressed as

$$q_e = \frac{Q^0 R_L C_e}{1 + K_L C_e}$$

The above equation can be rearranged to create the following linear form

$$\frac{c_e}{q_e} = \frac{1}{Q_0 K_L} + \frac{C_e}{Q_0}$$

Where q_e is the amount of metal adsorbed per unit mass of adsorbent (mg/L) and C_e is the equilibrium concentration of the adsorbate (mg/L), and q_0 and 'b' are Langmuir constants related to adsorption capacity and rate of adsorption respectively. As required by equation (3), plotting C_e/q_e against C_e gave a straight line,

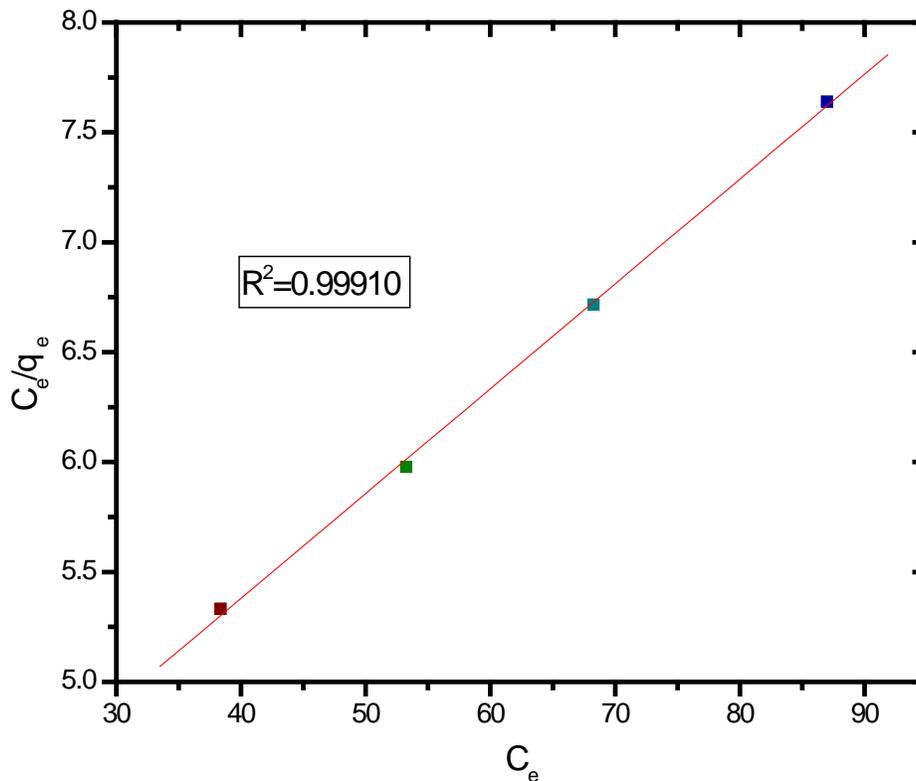


Figure 8: Langmuir adsorption isotherm

The essential characteristics of the Langmuir equation can be expressed in terms of dimensionless separation factor, R_L defined by

$$R_L = \frac{1}{1 + K_L C_0}$$

Where ' c_0 ' is the initial solute concentration of adsorbate [mg/L].

' K_L ' is the Langmuir adsorption constant (L/mg). R_L value lies between 0 and 1 indicates favourable adsorption (Norrozi B, serial, G.A, Arami M(2007)).

4.5.2 Freundlich Isotherm:

The Freundlich sorption isotherm using the log transformed form

$$\log q_e = \log k_f + 1/n \log C_e$$

Where q_e is the amount of metal adsorbed in mgL^{-1} ,

C_e is the equilibrium concentration (mgL^{-1}), K_f and n were Freundlich constant. (mg/g , L/mg) related to adsorption capacity and adsorption intensity of the sorbent respectively. The plot of $\log q_e$ vs $\log C_e$ yields a straight line which indicates the confirmation of the Freundlich isotherm for adsorption (Fig. 9). The values indicate that the nature of the adsorption is favourable.

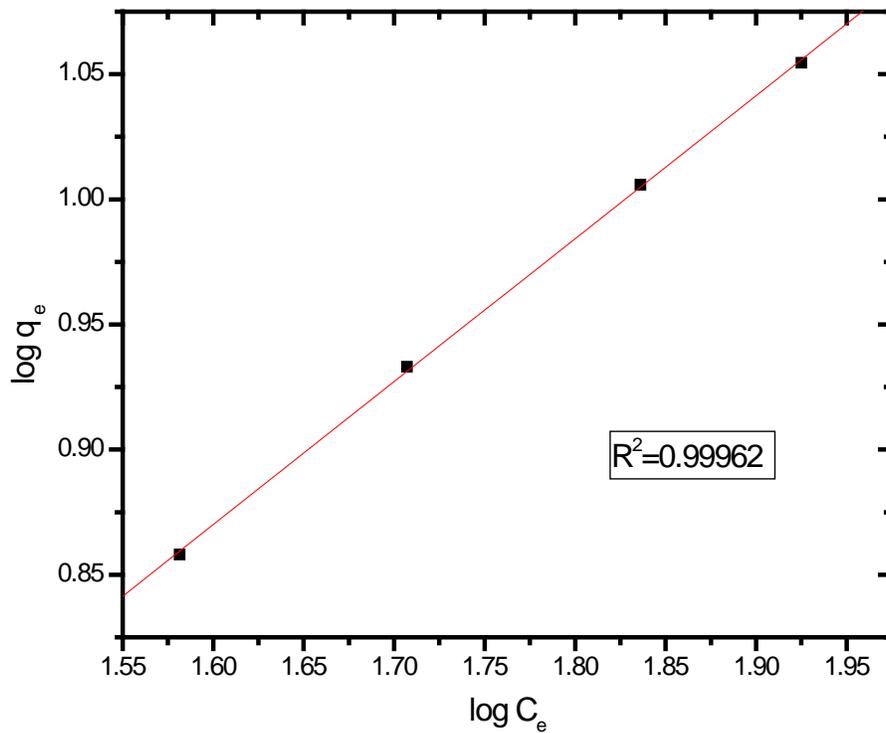


Figure 9: Freundlich isotherm

4.5.3 Tempkin isotherm

Tempkin isotherm is represented by the following equation

$$q_e = \frac{RT}{b} \ln[AC_e]$$

Equation can be expressed in its linear form as

$$q_e = B \ln A + B \ln C_e$$

Where B is a constant related to the heat of adsorption (J/mol) and A is the Tempkin isotherm constant, corresponding to the maximum binding energy (L/mg). A plot of q_e vs $\ln C_e$ is shown in Figure(10). The values of A and B calculated from the slope and intercept of the graph are given in Table 1.

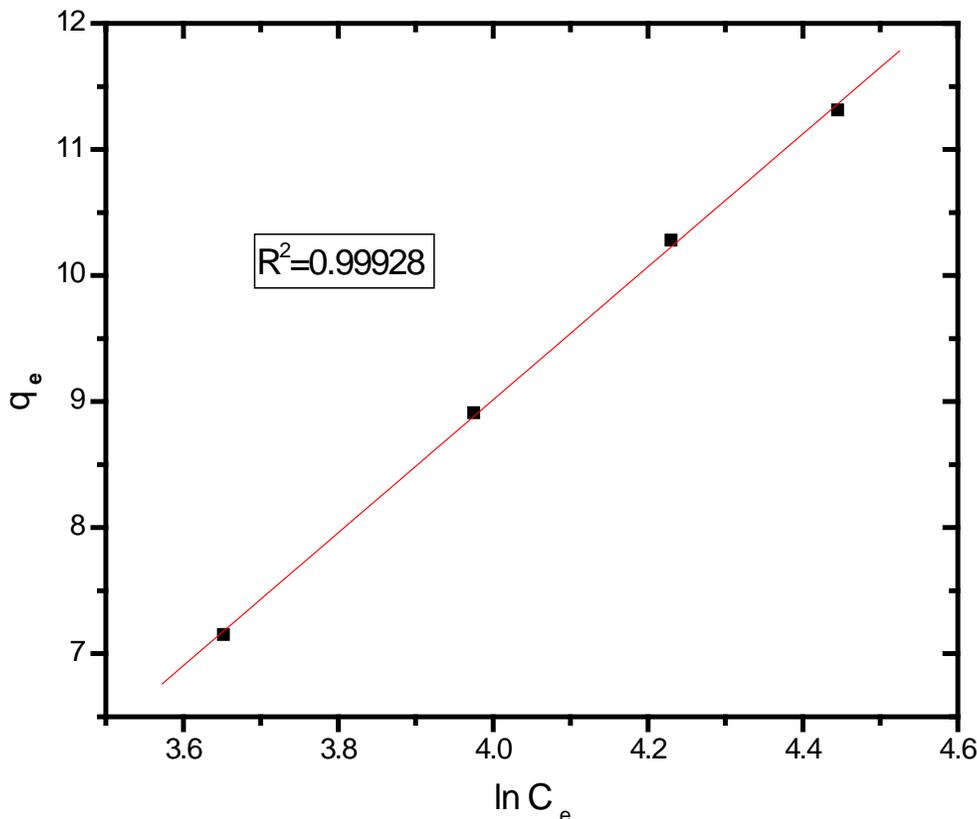


Figure10: Tempkin isotherm

Table 1: Results of isotherm plots for the adsorption of Cadmium on AC

| Initial metal Concentration Mg/L | Langmuir isotherm | | | | Freundlich isotherm | | | Tempkin isotherm | | |
|----------------------------------|-------------------|------------|--------|--------|---------------------|--------|--------|------------------|-------------|--------|
| | Q_0 (mg/g) | b (L/mg) | R^2 | R_L | K_f mg/g | N | R^2 | A (L/mg) | B (J/mol) | R^2 |
| 60 | 20.973 | 0.013 | 0.9991 | 0.5617 | 1.107 | 1.7495 | 0.9996 | 12.0784 | 5.2732 | 0.9992 |
| 80 | | | | 0.4919 | | | | | | |
| 100 | | | | 0.4347 | | | | | | |
| 120 | | | | 0.3906 | | | | | | |

4.6 Adsorption: Kinetics:

The kinetics of adsorption of Cadmium and the kinetic models of pseudo first order, pseudo second order, and Intra particles diffusion model were considered.

4.6.1 pseudo First order kinetics

In integrated from of the pseudo first order kinetics model can be represented as

$$\log(q_e - q_t) = \log q_e - (K_1/2.303)t$$

Where q_e is the amount of metal adsorbed at equilibrium(g/mg). q_t is the amount of metal adsorbed at time (mg/g) and k_1 is the pseudo first order rate constant k_1 and q_e (ther) can be calculated from the slope and intercept of the graph. The q_e (ther) and q_e (exp) value are shown in table. The adsorption process does not follow first order kinetics.

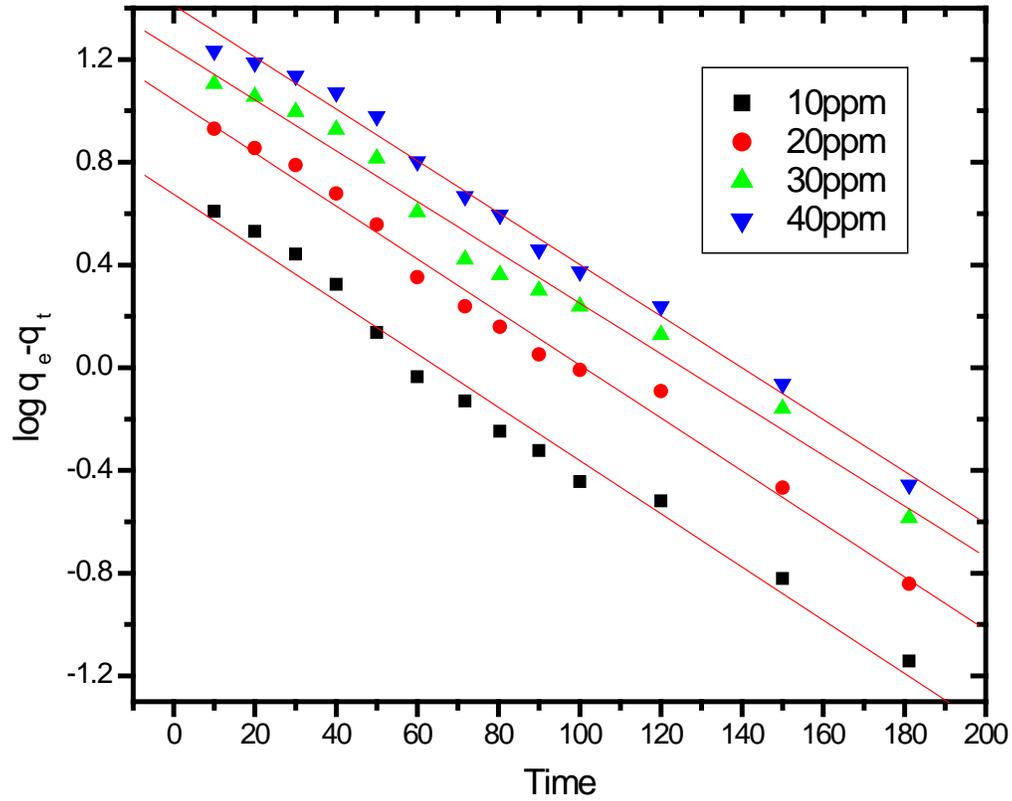


Figure 11: pseudo first order

4.6.2 Pseudo-second order kinetic model

The Pseudo-second order model has been based on assumption that sorption follows second order mechanism

$$1/q_e + q_t = 1/q_2 + K_2t$$

The linear pseudo second order kinetic equation is given as

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

where k_2 is the Pseudo-second of second order rate constant ($g\ mg^{-1}\ min^{-1}$). As expected the plot of t/q_t vs t Figure (12) was linear. The values of q_e and k_2 can be calculated from the slope and intercept. The q_e (the) and q_e (exp) values are shown in Table 2. The calculated q_e (the) values are in consonance with q_e (exp) with high correlation coefficient values. The adsorption of followed pseudo-second order kinetics.

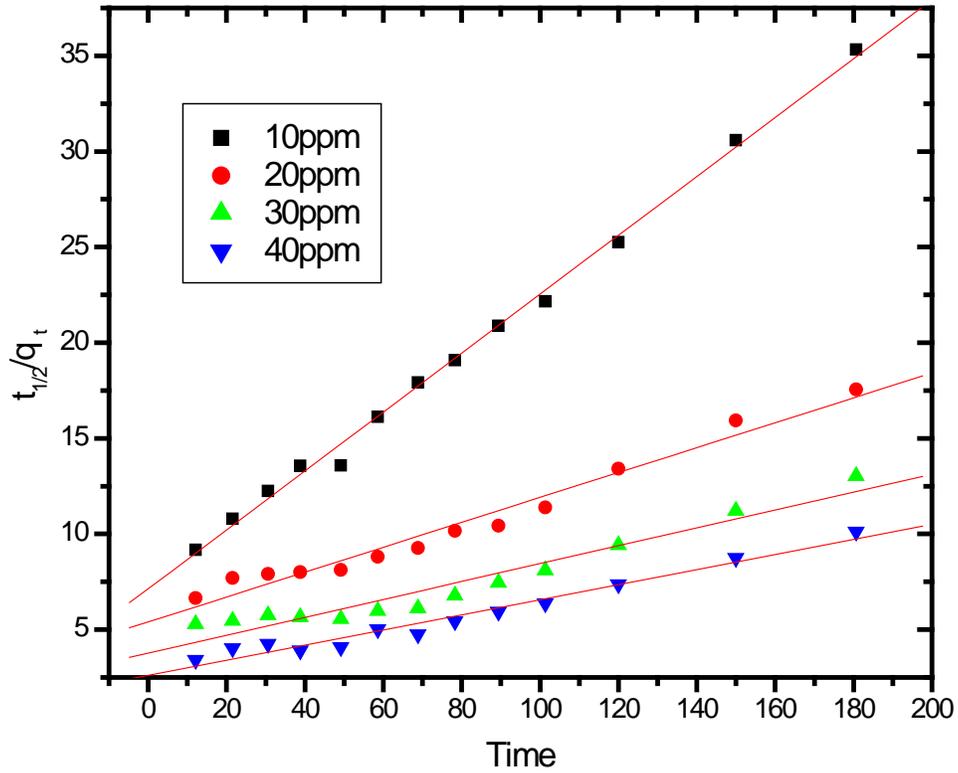


Figure 12: Pseudo second order

4.6.3 Intraparticle diffusion

The intraparticle diffusion model used here refers to the theory proposed by Weber and Morris based an intraparticle diffusion coefficient K_{id} is defined by the equation,

$$q_t = k_{id} t^{1/2} + C$$

Where K_{id} is the intraparticle diffusion rate constant ($mg/gmin^{1/2}$), C is the intercept (mg /g) can be calculated by plotting q_t vs $t^{1/2}$ and the results are given in Figure (13) and Table 2. The linear portion of the plot does not pass through the origin. Such a deviation from the origin indicates that pore diffusion is the only controlling step and not the film diffusion .

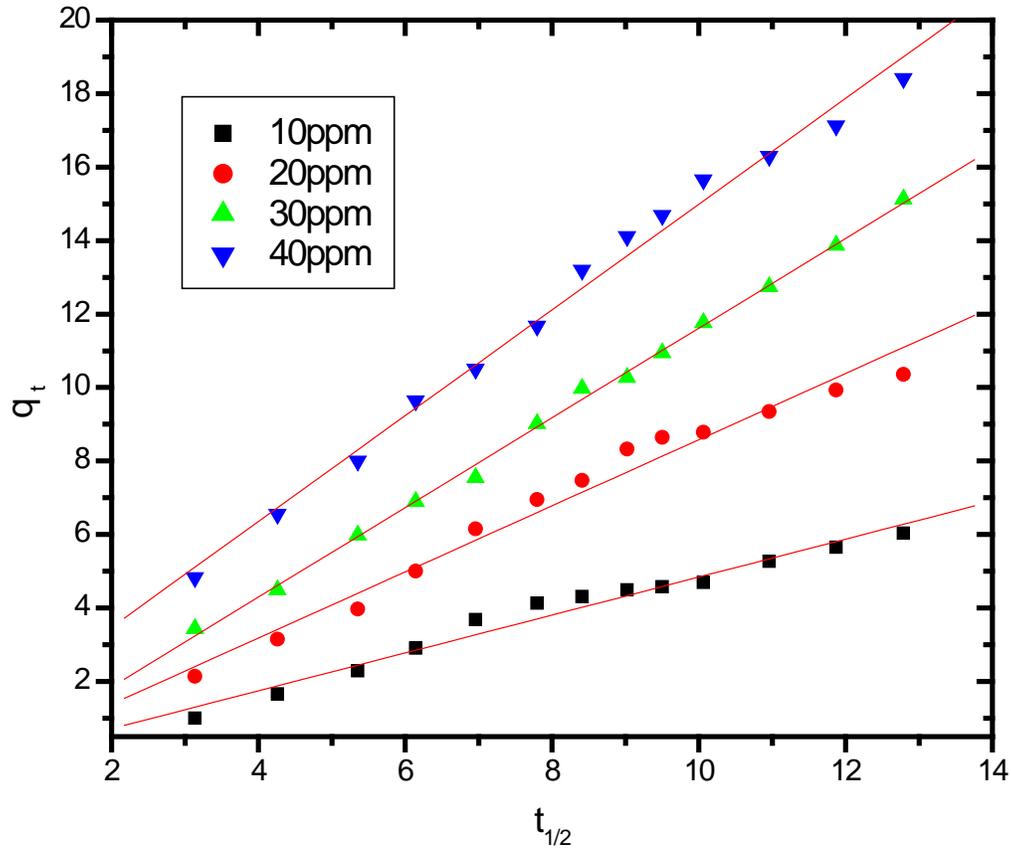


Figure13: Intraparticle diffusion

Table 2: The Kinetic Parameter for the adsorption of Chromium by Activated carbon Adsorbent

| Initial metal concentration | Pseudo first order | | | | Pseudo second order | | | | Intraparticle diffusion | | |
|-----------------------------|--------------------|-------------------|-------------------|--------|---------------------|-------------------|-------------------|--------|-------------------------|--------|--------|
| | K_1 | $q_e \text{ exp}$ | $q_e \text{ cal}$ | R^2 | K_2 | $q_e \text{ exp}$ | $q_e \text{ cal}$ | R^2 | K_{id} | C | R^2 |
| 10 | 0.0238 | 5.054 | 4.734 | 0.9935 | 0.0033 | 5.054 | 6.497 | 0.9965 | 0.5156 | 0.0629 | 0.9935 |
| 20 | 0.0237 | 9.762 | 11.017 | 0.9892 | 0.0007 | 9.762 | 15.384 | 0.9705 | 0.8999 | 0.6452 | 0.9967 |
| 30 | 0.0227 | 10.082 | 17.382 | 0.9928 | 0.0005 | 10.082 | 21.367 | 0.9352 | 1.2201 | 1.2132 | 0.9978 |
| 40 | 0.0232 | 18.023 | 25.775 | 0.9925 | 0.0005 | 18.023 | 25.380 | 0.9685 | 1.4387 | 0.4348 | 0.9909 |

V. DESORPTION STUDIES

Desorption studies with acetic acid revealed that the regeneration of adsorbent was not satisfactory, which confirm the chemisorptive nature of adsorption.

VI. CONCLUSION

The adsorption of cd(II) onto activated carbon is found be contact time and initial metal concentration, adsorbent dose, pH and temperature dependent. The maximum percentage removal occurs between the pH range of 5.0 to 9.0. The removal of cadmium by this activated carbon data can be adequately modeled by the Langmuir adsorption isotherm.

REFERENCES

- [1] Nriagu (1996). Toxic metal Pollution in africa.Science. 223:272-273.
- [2] Issabayeva G, Aruva MK, Suleiman NM(2007). Continuous adsorption of lead ions in a column packed with palm shell activated carbon. J. hazard. Mater., 155(1-2), 109-113 (5 pages). Production of granular activated carbon from waste walnut shell and its adsorption characteristics for copper (II) ions.J.Hazard. Mater. B., 85:301-315.
- [3] Cheung CW, potter JF, McKay G (2000). Elovich equation and modified second-order equation for adsorption of cadmium ions onto bone Char.J. Chem.technol.Boitechnol., Vol. 75,pp.963-970.
- [4] Lgwe JC, Abia AA (2005). Sorption kinetics and intra- particulate diffusivities of Cd, Pb, and Zn ions On Maize Cob. Afr. J. Biotech. 4(6): 509-512.
- [5] Teker M., Mustafa I. "Adsorption of Copper and Cadmium Ions by Activated Carbon From Rice Hulls". Turk J Chem., Vol.23, p.185-191,1999
- [6] Suganthi .N,Srinivasan.k, "Phosphorylated tamarind nut carbon for the removal of cadmium ions from aqueous solution", Indian Journal of Engineering and Materials Sciences, Vol. 17 p. 382-388,2010.
- [7] Kumar,P.E., Studies on characteristics and fluoride removal capacity of jambonut carbon M.Phil, Disseration: Bharathiar university, Coimbatore,1991,tamilnadu, india.
- [8] Kumar,P.E, Perumal V,OST novel adsorbent derived from the inflorescence of palmyra male flowers. Nature environment & pollution, Vol 9[3], PP 513-518,2010.
- [9] Forstner U (1977). Metal concentration in fresh water sediments, Natural Background And Cultural Effect. In: Intervention between sediment and fresh water, Golterman,H.L.(Ed).Junk publisher, the Hauge, pp.94-103.
- [10] Boparai H.K., Meera J ., Carroll D.O. "Kinetics and thermodynamics of cadmium iron removal by adsorption onto nano zerovalent iron particles", J Hazardous Mater, vol.15,p.1-8,2010.
- [11] Yavuz O ., Guzel R ., Aydin F., Tegin I., Ziyadanogullari R., "Removal of Cadmium and Lead from Aqueous Solution by Calcite", Polish J. of Environ. Stud., Vol. 16,p.467-471,2007.
- [12] Arowolo TA (2004). Heavy metals and health. West Indian med. J., 53: 63-65.

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