Kinetic and Equilibrium study of Adsorbent Prepared from Potato Peels for removal of solute CD from wastewater

Prof Dr K N Sheth[1], Dr S A Puranik[2]
[1] Dean (Interdisciplinary Research), Gujarat Technological University,
[2] Former Director, Atmiya Institute of Science & Technology
Email - profdrknsheth@gmail.com

Abstract: *Amongst various isotherm models, the most commonly utilized isotherm model is Langmuir isotherm. BET isotherm models being relatively complex in nature have not been utilized by researchers. Attempts have been made in this investigation to utilize both these adsorption isotherm models. Four low cost adsorbents which have been prepared on lab scale having four different grades, for each adsorbent depending on the activation temperature used during the manufacture have been selected for kinetic and equilibrium study. This paper focuses on adsorbent Potato Peels Activated Carbon (PPAC). Effect of variation of doses (d) of the adsorbents and its contact time (Ct) have been considered as the major variables for this isotherm studies. The value of constants obtained for Langmuir and BET adsorption isotherm are expected to be very useful in designing of a suitable adsorption system for removal of metals from wastewater. It has been found that at elevated temperature and at higher values of initial concentration of solute, adsorption becomes more favorable.*

Key Words: *adsorbents, isotherm, Potato Peels Activated Carbon (PPAC),*

1. INTRODUCTION:

Adsorption is mass transfer process wherein a substance is transferred from the liquid phase to the surface of the solid where it is bound by chemical or physical forces (1)

Adsorption process is usually described by the equilibrium isotherm they follow. These isotherms are simply relationships between the moles of sorbate adsorbed per unit mass of adsorbent and the concentration of sorbate remaining in solution at equilibrium at constant temperature (2). Two important physicochemical aspects for the evaluation of the adsorption process as a unit operation are the equilibrium of the adsorption and the kinetics. Equilibrium studies give the capacity of the Absorbent. (3) Adsorption isotherms describe the equilibrium conditions for an adsorbate that which is adsorbing on to the surface of an adsorbent (4)

The preferred form for depicting this distribution is to express the quantity q_e as a function of Ce at fixed temperature, solute adsorbed per unit weight of solid adsorbent, and Ce the concentration of solute remaining in solution at equilibrium. An expression of this type is termed an adsorption isotherm. (5) The adsorption isotherm is a functional expression for the variation of adsorption with concentration of adsorbate in bulk solution at constant temperature. (6)

2. LANGMUIR ISOTHERM:

Irving Langmuir an American chemist who was awarded the Nobel Prize for chemistry in 1932, for "his discoveries and research in the realm of surface chemistry" gave the concept of isotherm (7)

The Langmuir isotherm equation assumes that fixed individual sites exists on the surface of the adsorbent, each of these sites being capable of adsorbing one molecule, resulting in a layer one molecule thick over the entire carbon surface. **The Langmuir model also assumes that all sites adsorb the adsorbate equally.** The number of molecule adsorbed soon increase to the point at which further adsorption is hindered by lack of space on the adsorbent surface. The rate of adsorption then becomes proportional to the empty surface available, as well as to the fluid concentration. At the same time as molecules are adsorbing, other molecules will be desorbing if they have sufficient activation energy. At a fixed temperature, the rate of desorption will be proportional to the surface area occupied by the adsorbate. **When the rate of adsorption and desorption are equal, a dynamic equilibrium exists** (8)

The Langmuir adsorption isotherm is often used for adsorption of a solute from a liquid solution. The Langmuir adsorption isotherm is perhaps the best known of all isotherms describing adsorption and is often expressed as: (9)

$$\frac{X}{m} = \frac{X_m b.Ce}{1+b.Ce} \qquad OR$$

$$q_e = \frac{X_m b.C_e}{1+b.C_e} \qquad (3.1)$$

Where,

C_e = the equilibrium concentration of chromium is aqueous Solution, (mg/L)

q_e = the amount of chromium adsorbed by unit weight of Adsorbent at equilibrium, (mg/L)

X_m = the maximum adsorption capacity corresponding to Complete monolayer coverage. (mg of solute adsorbed per g of adsorbent)

Equation (3.1) can be rearranging to the following linear form,

$$\frac{Ce}{qe} = \frac{1}{Xm.b} + \frac{Ce}{Xm} \qquad (3.2)$$

The linear form can be used for linearization of experimental data by plotting C_e/q_e against C_e the Langmuir constant X_m & K can be evaluated from the slope and intercept of linear equation.

The essential characteristics of a Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter R_L,(142) which is defined by,

$$R_L = \frac{1}{1 + b.Co} \qquad (3.3)$$

Where,

Co = the initial concentration (mg/L)

b = the Langmuir constant

The parameter indicates that the shape of isotherm as follows:

If $R_L > 1$ the nature of Adsorption is unfavorable.

$R_L = 1$ the nature of Adsorption is linear.

$0 < R_L > 1$; the nature of adsorption is favorable.

$R_L = 0$; the nature of Adsorption is irreversible.

The limitation of Langmuir isotherm includes (2),(10)

- The assumption that the energy of adsorption is independent of degree of coverage.
- Reversibility of bonding
- Allow only one monolayer.

Since most waste waters contain more than one substance which will be adsorbed, direct application of Langmuir equation is not possible. Morris and Weber have developed from the Langmuir relationship from competitive adsorption of two substances. More complex relationship could similarly be developed for multi component mixtures. (11)

BET ISOTHERM [12]

In 1938, Brunauer, Emmett, and Teller, developed equilibrium Isotherm, which is now known as the BET Isotherm or theory. As in the case in Langmuir's isotherm, the theory is based on the concept of adsorbed molecules, which is not free to move the surface, and which exerts no lateral forces on adjacent molecules of adsorbate. [19] The BET theory does, however, allow multi layers of adsorbed to be building up on different parts of the surface but assumes that the net amount of surface which is empty or which is associated with monolayer, bi-layer, etc is constant for any particular equilibrium condition.

Their assumptions are: [13]

(1) The adsorbed surface is composed of fixed individual sites.
(2) Enthalpy of Adsorption is the same for any layer
(3) Energy of Adsorption is the same for layer other than first.
(4) A new layer can start before another is finished.
(5) Molecules can be adsorbed more than one layer thick on the surface of Adsorbent.

The adsorbate exceeds a monolayer the Brunauer - Teller (BET) equation is:-

$$\frac{q}{qe} = \frac{b.Ce}{(Cs - Ce)[1 + (b-1)Ce/Cs]} \qquad or \qquad (3.6)$$

$$\frac{Ce}{qe(Cs - Ce)} = \frac{1}{b.q} + \frac{(b-1)}{b.q} - \frac{Ce}{Cs}$$

Where,

q_e = is the amount of metal ions adsorbed by unit weight of adsorbent at equilibrium, (mg/g)

q = is the amount of ions adsorbed by unit weight of adsorbent in forming a complete monolayer on the surface, mg/g

C_s= the saturation concentration of the adsorbate in solution, mg/L
C_e = the concentration of adsorbate in solution, mg/L.
b = BET constant
With this equation, q_e and b can be obtained from the slop and intercept of the straight-line best fitting of the plot of

Ce/ [qe (Cs-Ce)] Vs Ce/Cs

2. MATERIALS AND METHODS:

The particulars of producing and activating adsorbent from agro-waste potato-peels have been published. Readers may refer to research papers as shown in References- specific references no. 14, 15

3. RESULTS AND DISCUSSIONS:

LANGMUIR ADSORPTION ISOTHERM: ADSORBENT PPAC, ADSORPTION OF Cd UNDER OPTIMUM DOSE CONDITIONS

Data obtained under different sets of conditions, variation of contact time from 5 min. to 70 min., variation of temperature from 400 ^{0} C to 700 ^{0} C and Cdi variation from 2.5 mg/L to 5.5 mg/L have been processed for construction of Langmuir adsorption isotherm. Data processed have been plotted in Fig. (1.1.0) consisting of 16 straight lines which is a plot of Ce/qe versus Ce with concentration Cdi as a parameter for a fixed value of temperature.

The values of Langmuir adsorption isotherm constants q_0, b & R_L which have been determined from the slope and the intercept of the straight line plots are reported in Table. (1).

BET ADSORPTION ISOTHERM: ADSORBENT PPAC, ADSORPTION OF Cd UNDER OPTIMUM DOSE CONDITIONS

Data obtained under different sets of conditions, variation of contact time from 5 min. to 70 min., variation of temperature from 400 ^{0} C to 700 ^{0} C and Cdi variation from 2.5 mg/L to 5.5 mg/L have been processed for construction of BET adsorption isotherm. Data have been plotted in Fig. (2.0.0) consisting of 16 straight lines which is a plot of Ce/Cs versus Ce/ (Cs-Ce)*qe with concentration Cdi as a parameter for a fixed value of temperature.
The values of BET adsorption isotherm constants 1/b*q, b-1/b*q and b which have been determined from the slope and the intercept of the straight line plots are also reported in Table (2)

3. CONCLUSIONS:

From Fig. (1.1.0) following conclusions can be drawn:
(i) For four different values of Cdi, varied from 2.5 mg/L to 5.5 mg/L, four different values of intercepts, with increasing trend are obtained for a fixed value of temperature.
(ii) Similar trend is observed for all the four values of the activation temperatures under consideration.
(iii) With an increase in temperature from 400 0 C to 700 0 C, for a fixed values of Cdi, the slope of these four lines appear to be practically the same.
From Table (1) which is a summary table for various values of Langmuir constants for the case under the consideration following conclusions can be drawn:
(i) Under otherwise identical conditions for a fixed value of Cdi = 2.5 mg/L, as temperature is increased from 400 0 C to 700 0 C, the value of q0 increases from 0.965 to 1.229. Similar conclusions can be derived for other fixed values of Cdi namely 3.5 mg/L, 4.5 mg/L and 5.5 mg/L.
(ii) Under otherwise identical conditions of temperature 600 0 C, with an increase in concentration of Cdi from 2.5mg/L to 5.5 mg/L , the value of q0 increases from 1.194 to 3.073 respectively. Similar observations can be derived for other values of activation temperatures like 400 0 C, 500 0 C and 700 0 C.
(iii) Thus, the constant of Langmuir isotherm q0 appears to be a strong function of initial concentration of solute and a weak function of activation temperature.
(iv) The essential characteristics of Langmuir isotherm can be expressed in terms of dimensional less constant separation factor RL (equilibrium parameter). The values of RL decrease with an increase in temperature as well as with an increase in initial concentration of solute.

Thus, at elevated temperature and at higher values of initial concentration of solute, adsorption becomes more favorable.

From Fig. (2.0.0) following conclusions can be drawn:

(i) For four different values of Cdi, varied from 2.5 mg/L to 5.5 mg/L, four different values of intercepts, with increasing trend are obtained for a fixed value of temperature.
(ii) Similar trend is observed for all the four values of the activation temperatures under consideration.
(iii) With an increase in temperature from 400 ^{0} C to 700 ^{0} C, for a fixed values of Cdi, the slope of these four lines appear to be practically the same.

From Table (2) which is a summary table for various values of BET constants for the case under the consideration following conclusions can be drawn:

(i) Under otherwise identical conditions for a fixed value of Cdi = 2.5 mg/L, as temperature is increased from 400 ^{0} C to 700 ^{0} C, the value of 1/b*q increases from -2.486 to -0.562 Similar conclusions can be derived for other fixed values of Cdi namely 3.5 mg/L, 4.5 mg/L and 5.5 mg/L.

(ii) Under otherwise identical conditions of temperature 600 ^{0} C, with an increase in concentration of Cdi from 2.5mg/L to 5.5 mg/L, the value of 1/b*q increases from -0.672 to -0.261 respectively. Similar observations can be derived for other values of activation temperatures like 400 ^{0} C, 500 ^{0} C and 700 ^{0} C.

(iii) Thus, the constant of BET isotherm 1/b*q appears to be a strong function of initial concentration of solute and a weak function of activation temperature.

(iv) The essential characteristics of BET isotherm can be expressed in terms of dimensional less constant b (BET constant). The values of b decrease with an increase in temperature as well as with an increase in initial concentration of solute.

Thus, at elevated temperature and at higher values of initial concentration of solute, adsorption becomes more favorable.

Table-1 Isotherm Studies: Removal of Cd using PPAC
Value of Langmuir Constants- Optimum dose d = 50mg/50mL

Sr. No.	Adsorbent	Cdi	Value of Langmuir constants			
		mg/L	qo	b	R_L	Type
1	PPAC-400C	2.5	0.965	-2.801	-0.167	Favourable
2	PPAC-500C	2.5	1.074	-3.395	-0.134	Favourable
3	PPAC-600C	2.5	1.194	-4.262	-0.104	Favourable
4	PPAC-700C	2.5	1.229	-4.527	-0.097	Favourable
5	PPAC-400C	3.5	1.577	-2.667	-0.120	Favourable
6	PPAC-500C	3.5	1.665	-2.990	-0.106	Favourable
7	PPAC-600C	3.5	1.801	-3.641	-0.085	Favourable
8	PPAC-700C	3.5	1.594	-2.702	-0.118	Favourable
9	PPAC-400C	4.5	2.078	-2.179	-0.114	Favourable
10	PPAC-500C	4.5	1.933	-1.886	-0.134	Favourable
11	PPAC-600C	4.5	2.149	-2.368	-0.104	Favourable
12	PPAC-700C	4.5	2.139	-2.350	-0.104	Favourable
13	PPAC-400C	5.5	2.634	-1.926	-0.104	Favourable
14	PPAC-500C	5.5	2.815	-2.253	-0.088	Favourable
15	PPAC-600C	5.5	3.073	-2.911	-0.067	Favourable
16	PPAC-700C	5.5	2.893	-2.426	-0.081	Favourable

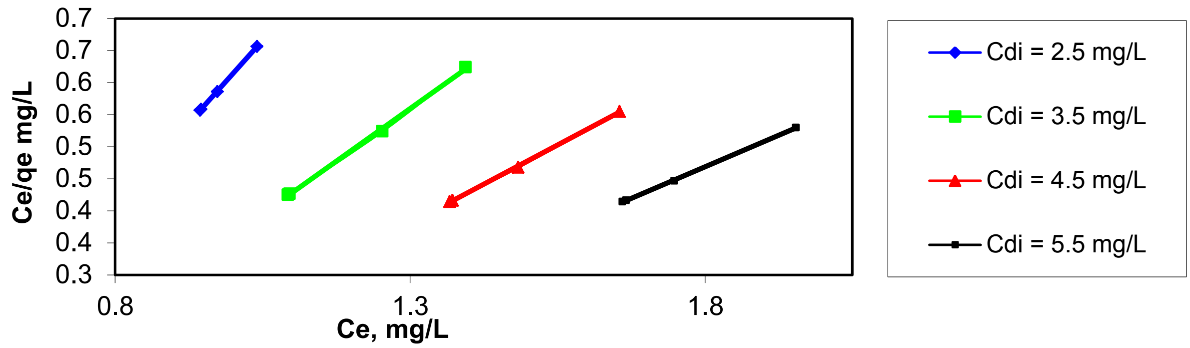
Table-2 Isotherm Studies: Removal of Cd using PPAC
Value of BET Constants- Optimum dose d = 50mg/50mL

Sr. No.	Adsorbent	Cdi	Value of BET Constants			
		mg/L	1/b*q	b-1/b*q	b	Type
1	PPAC-400C	2.5	-2.486	6.702	-1.695	Favourable
2	PPAC-500C	2.5	-1.264	4.575	-2.618	Favourable
3	PPAC-600C	2.5	-0.672	3.380	-4.027	Favourable
4	PPAC-700C	2.5	-0.562	3.100	-4.518	Favourable
1	PPAC-400C	3.5	-0.940	3.934	-3.185	Favourable
2	PPAC-500C	3.5	-0.677	3.351	-3.951	Favourable
3	PPAC-600C	3.5	-0.429	2.783	-5.492	Favourable
4	PPAC-700C	3.5	-0.867	3.730	-4.303	Favourable
1	PPAC-400C	4.5	-0.810	3.643	-3.498	Favourable

2	PPAC-500C	4.5	-1.264	4.575	-2.618	Favourable
3	PPAC-600C	4.5	-0.672	3.380	-4.027	Favourable
4	PPAC-700C	4.5	-0.693	3.443	-3.968	Favourable
1	PPAC-400C	5.5	-0.648	3.275	-4.058	Favourable
2	PPAC-500C	5.5	-0.438	2.772	-5.325	Favourable
3	PPAC-600C	5.5	-0.261	2.314	-7.872	Favourable
4	PPAC-700C	5.5	-0.374	2.613	-5.988	Favourable

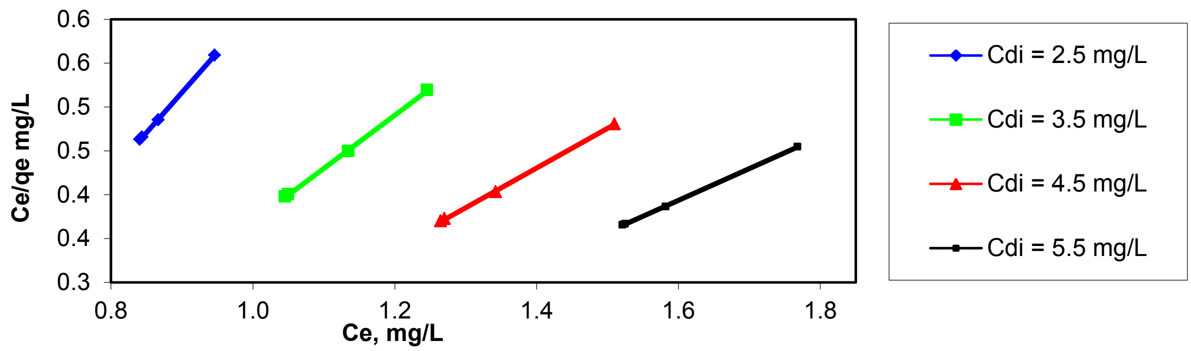
Fig. 1.0.0 Isotherm Studies: Variation of Dosages of Adsorbent PPAC

Fig. 1.1.0 Langmuir Isotherm PPAC 400 C



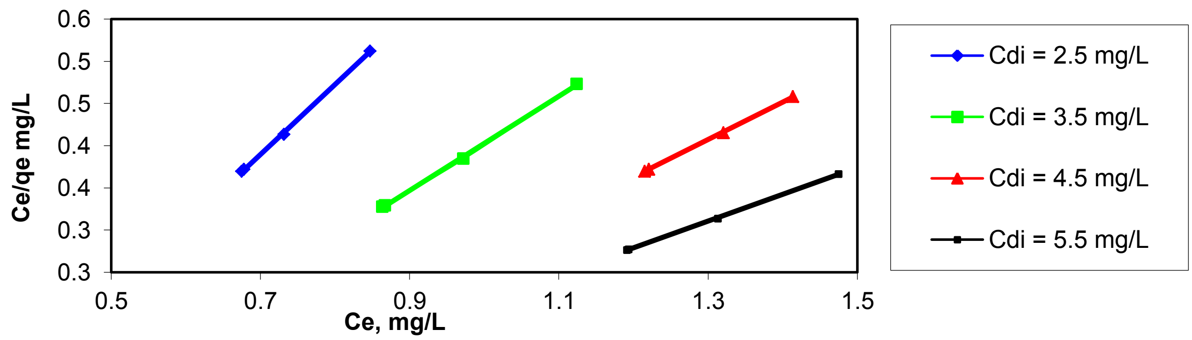
y1 = 1.0321x - 0.3664 R2 = 0.9998 y2 = 0.6567x - 0.2617 R2 = 0.9989 y3 = 0.488x - 0.2297 R2 = 0.9994 y4 = 0.3938x - 0.2206 R2 = 0.9997

Fig. 1.2.0 Langmuir Isotherm PPAC 500 C



y1 = 0.9139x - 0.2604 R^2 = 0.9999 y2 = 0.6056x - 0.206 R^2 = 0.9995 y3 = 0.4512x - 0.1789 R^2 = 0.9997 y4 = 0.3616x - 0.1671 R^2 = 0.9999

Fig. 1.3.0 Langmuir Isotherm PPAC 600 C



y1 = 0.8295x - 0.1909 R^2 = 0.9995 y2 = 0.5579x - 0.1551 R^2 = 0.9993 y3 = 0.4428x - 0.1684 R^2 = 0.9998 y4 = 0.3167x - 0.1011 R^2 = 0.9997

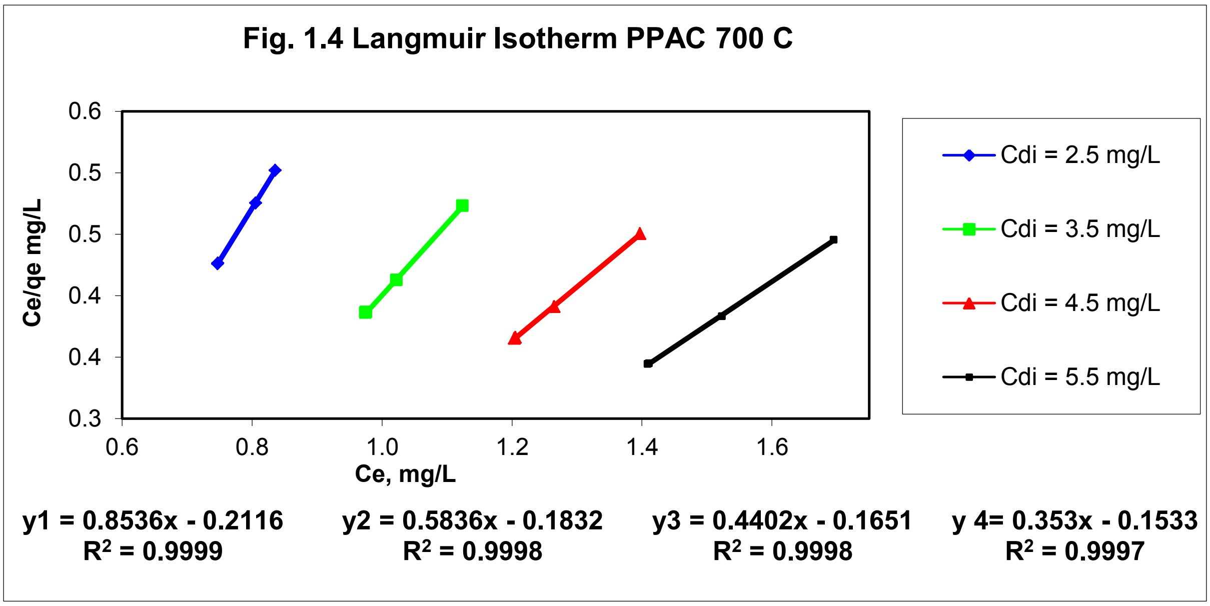
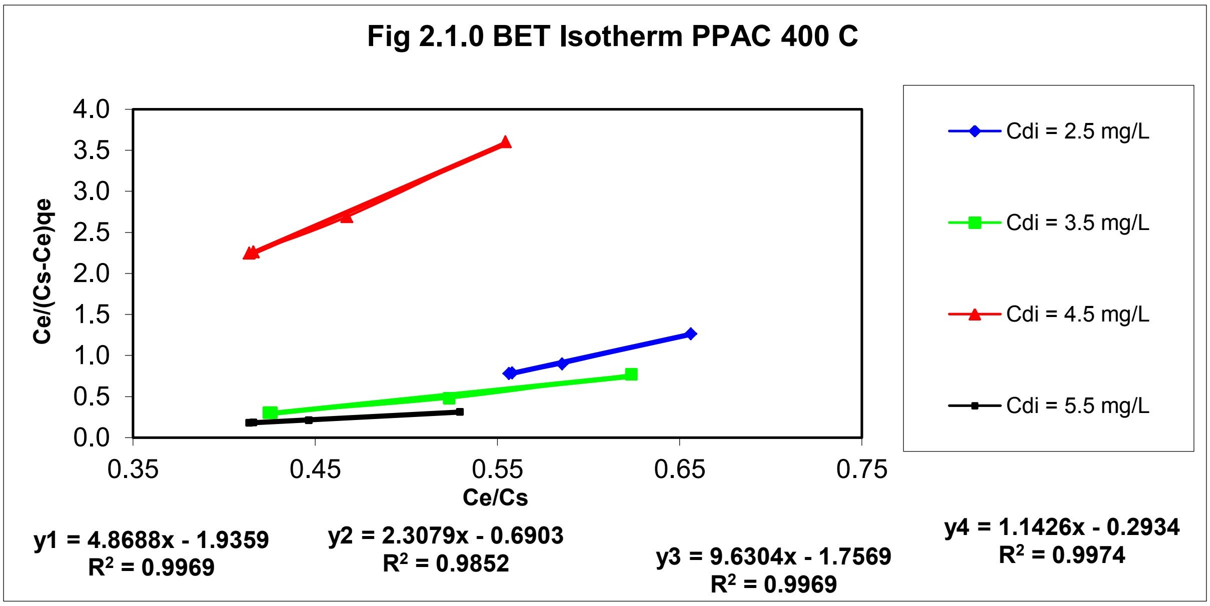


Fig.2.0.0. Isotherm Studies: Effect of Variation of Dosages of Adsorbent PPAC



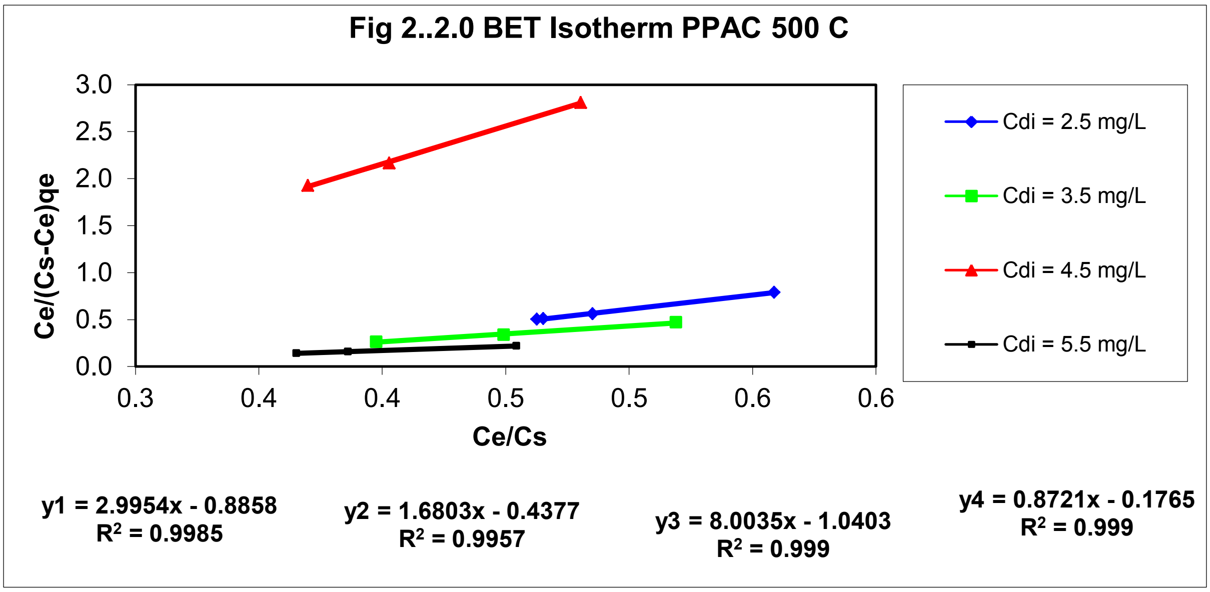


Fig 2.3.0 BET Isotherm PPAC 600 C

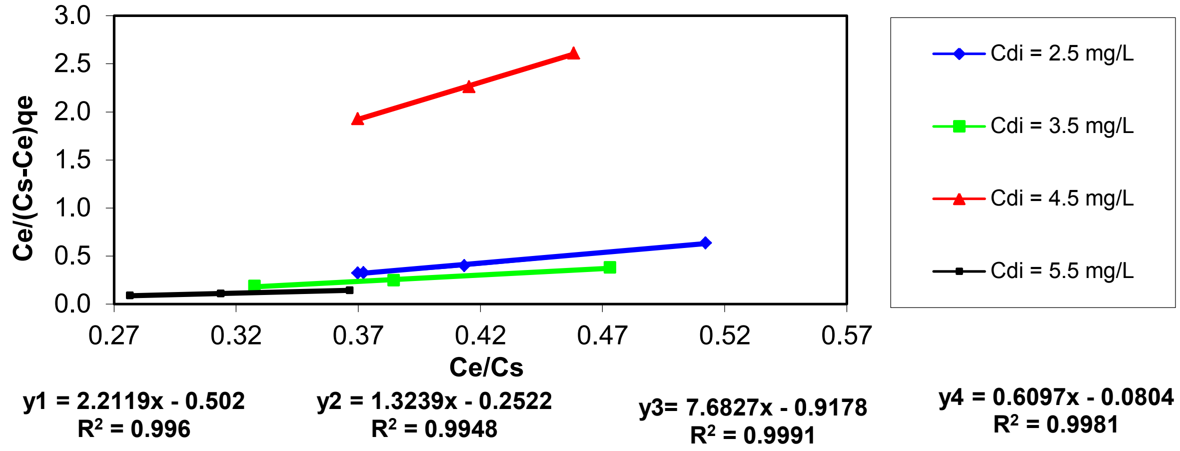
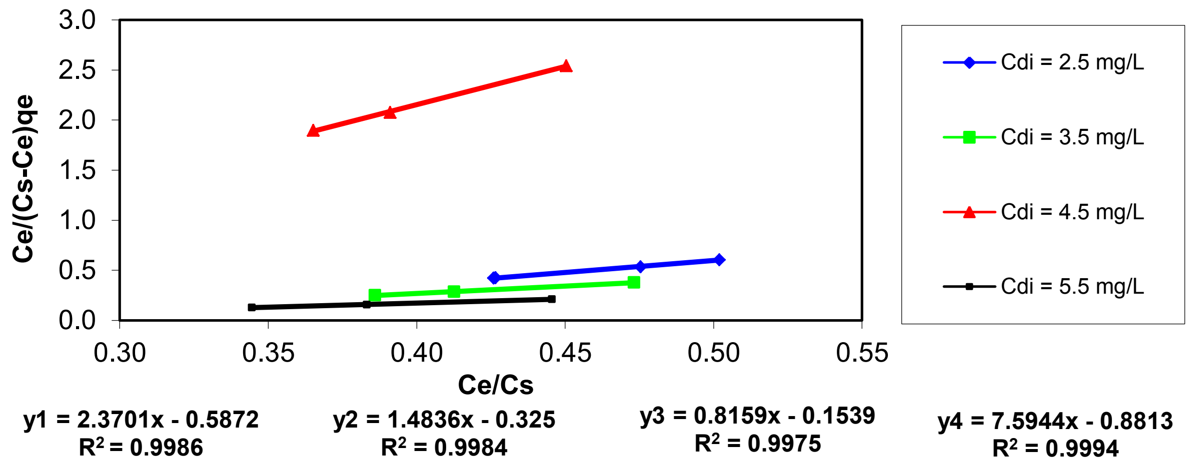


Fig 2.4.0 BET Isotherm PPAC 700 C



REFERENCES:

1. PROF.K.N.SHETH, VIRAL M .SONI,(July 2005) Comparative Study of Removal of Cr(VI) with PAC,GAC and adsorbent prepared from Tobacco Roots, Journal of Environmental Science & Engineering , NEERI, Nagpur, 47 No.3ISSN 0970-3500.pp 218-221
2. Dedrick, Robert L, Beckmann, Robbert B, (1967)" Kinetic Adsorption By Activated Carbon From Dilute Aqueous Solution" Chemical engineering progress symposium series no. 74. (Physical adsorption processes and principles Volume. 63, , pp 68-78.
3. D. Popovski, V. Mitrevski, (2005) "A Method For Generating Water Sorption Isotherm Models", Electronic Journal of Environmental, Agricultural and Food Chemistry, 4(3),
4. K.N.SHETH, F.S UMRIGAR,(2005) Sorption Studies for Removal of Cadmium from wastewater using Corncob Activated Carbon, Environmental Pollution Control Journal , Kanuj Enviro Tech New Delhi, 8No.4,May-June, ,ISSN 0970-3497.pp 37-41
5. N M Gajjar, DR.K.N.Sheth ,(Dec, 2013), "A comparative study of removal of Fluoride from water using GSAC, GAC & PAC," International Journal of Innovative research and Studies, (UGC approved, Sr. no 7279 newly added ISSN-23199725) pp 464-476
6. K N SHETH and F.S.UMRIGAR,(2006) "Transport Mechanism of Cadmium using CCAC as Adsorbent" Pollution Research, 25(3), Enviro Media, Karad ISSN: 0970-3527. (UGC approved, Sr. no 38004 newly added ISSN-02578050), SCOPUS & ISI Journal , pp 481-484
7. Irving Langmuir, "Surface Chemistry" Nobel Lecture, Dec ,14 1932 pp 287-325
8. PROF.K.N.SHETH, (9 Mar-Apr 2006)Study on Langmuir Isotherms in Treatment of Metallic Effluents using Mung Husk, Environmental Pollution Control Journal , Kanuj Enviro Tech New Delhi, ,ISSN: 0970-3497. pp 52-56.

9. J M Coulson and J F Richardson,(1998) "Chemical Engineering "vol. 2 , 5 th edition , Asian Publisher, , pp 745-817.
10. PROF.K.N.SHETH, F.S UMRIGAR,(Dec 2005) The effect of Activation Temperature on removal of Cadmium using activated Carbon made from potato peels ,Journal of Engineering and Technology Sardar Patel University (UGC approved, Sr. no 2748 newly added ISSN-007625), Vallabh Vidyanagar, ,ISSN: 0970-3500.pp 1-9
11. Dharmesh K Patel (Nov. 2003) " Comparative Study of Low Cost Adsorbents CCAC and MHAC in Removal of Chromium with Commercially Available PAC and GAC," M. E. (Environment Engineering) Thesis guided by Prof K N Sheth and submitted to S. P. University,
12. Edward D. Schroeder,(1977) "Water and Waste water treatment," International student edition, , pp 53-71.
13. Walter J Weber,Jr. (1972), "Physico-Chemical Processes For Water Quality Control" John Wiley & sons Inc, USA , pp 199-242.
14. PROF.K.N.SHETH, S.A PURANIC, F.S.UMRIGAR, J.H PATEL,(9, Sept-Oct 2006) Production and Characterization of Adsorbents from Agro wastes, Journal of Environmental Pollution Control, New Delhi, , ISSN: 0970-3527. pp 20-31
15. B. V. Thacker, Dr. K. N. Sheth,(2015) "Comparative Study Of Low Cost Adsorbent MSAC In Removal Of Chromium (Vi) With Commercially Available PAC And GAC, National Conference on Research Trends in Civil Engineering, April 22-24, Department of Civil Engineering, HJD Institute- Kera ISBN: 978-81-907055-4-1