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Adsorption Studies of Phenol Removal on Activated Carbon Derived from Phoenix Dactylifera (Date Palm) Seeds

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***Abstract*: Locally available material such as date palm seeds were tested as an adsorbent for the removal of phenol from synthetic sample have been carried out at room temperature 32°c. Batch, kinetic and isotherm studies were carried out under varying experimental conditions of optimum contact time, adsorbent dosage and pH .The Freundlich and Langmuir adsorption models were used for the mathematical description of adsorption equilibrium. Batch sorption experiments were applied to examine the kinetics of the adsorption of phenol. The rate of adsorption of phenol obeys first order rate equation.**

Key Words: phenol, date palm seeds, contact time, dosage, pH, kinetics, adsorption isotherms

I. Introduction

Many wastewaters contain significant level of organic contaminants; which are toxic or otherwise undesirable because they create odour, unsightly color, foaming, etc. Among the different organic pollutants of aquatic ecosystems, phenols, especially the chlorinated ones, .are considered as priority pollutants since they are harmful to plants, animals and human, even at low concentrations. Phenol toxicity in wastewater, largely contributed by the pharmaceutical, coke-oven, textile and leather industries can be objectionable even up to 0.001ppm in water (WHO).Also it causes several dreaded acute and chronic toxic effects on human health (inducing a wide range of symptoms: headache. vomiting, fainting, liver and kidney damage and other mental disorders) .A wide range of various treatment methods namely "ion exchange, biodegradation, oxidation, solvent extraction and adsorption) have been reported to be used for removal of organic pollutants, in general phenol, in particular ,from industrial effluent (kojima et aI., 1995).Yet, adsorption has been universally accepted as one of the most effective pollutant move process, with low cost, ease in handling, low consumption of reagents, as well as scope for recovery of value added components through desorption and regeneration adsorbents.

In the present study adsorbents used are date palm seeds used for the removal of phenol. The effect of various parameters such as contact time, adsorbent dosage and pH has been studied to identify adsorption capacity of adsorbents. The adsorption kinetics using first order was applied to determine the rate equation. The batch experiments have been performed to determine the adsorption of phenol on date palm seeds. The adsorption data were moulded with the Langmuir and Freundlich isotherms.

II. Materials and Methods

The Phoenix dactylifera (date palm) seeds used as adsorbent. The scientific name was derived from "Phoenix', the legendary bird of ancient Greece. The specific name dactylifera came from the shape of the fruit, 'dactylos' being the ancient Greek word for finger. It is believed to have originated in the lands around the Persian Gulf. The seed of date palm as an agro waste have potential to be a very good and cheap source for a carbonaceous raw material. So in present work phoenix dactylifera (date palm) seeds are used to prepare low cost activated carbon.

Preparation of Phoenix Dactylifera (Date Plam) seeds Activated Carbon:

Date Seed Carbon was used for adsorption study. Date seeds were dried and grounded into small particles. The samples were thoroughly washed in hot distilled water so as to remove all dirt and impurity, dried for one day, at 105±5°C in an electric oven, followed by crushing and sieving, to obtain the practical by an average diameter of 150µ. The final sample were dried, desiccated and preserved in air tight chamber for subsequent analysis and experiments were studied.

A. Physical Activation

The stored material was filled in small container in three layers, by compacting each layer without any air space to avoid the loss in weight of the powder; otherwise it would result in burning of the material directly leaving behind only the ash. Small hole has been placed on the lids of both the containers. The small container was then placed into a bigger container, such that sand surrounded the small container completely, the lid of the bigger container was tightly fitted. .Then the setup was kept in muffle furnace and heated at steady rate to attain the temperature of 800°. After attaining the 800°C temperature the furnace was allowed to cool for about 10 hours and then the container is taken out. The sketch furnished in figure 1 shows the set-up of the containers.

The Activated Carbons are collected passing through 300 micron sieve size and retained on 150 micron sieve size, then packed in polythene bags and stored in desiccator.

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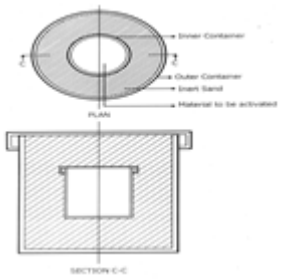

Fig. 1. Practical setup of the containers for the preparation of activated carbon

B. Chemical Activation

The known quantity of washed and dried Phoenix dactylifera (Date Palm) seed powder was mixed with the activating agents (NaCl and $CaCl_2$), in required quantity, depending upon the impregnation ratio (I.R)

$$Impregnation\ ratio\ (IR) = \frac{Weight\ of\ the\ active\ agent\ added}{Weight\ of\ carbonizing\ material}$$

In this mixture, required quantity of distilled water was added and boiled on hot plate till most of the water evaporated and slurry like mixture was retained. After that the mixture was oven dried in a clean tray for 24 hours maintained at 105 ± 5°C which helps in evaporation of moisture from the mixture. Preheated carbonizing material was filled in the small container for carbonizing according to the above said procedure.

The activated carbon was washed with 0.1N HCl followed by hot distilled water for about 8 times to remove the activating agents and HCl respectively. Washed carbon was dried at 105° C and then sieved for required size (i.e., 300 micron passing and 150 micron retained) and packed in polythene bags.

Characteristics of Phoenix dactylifera (Date Palm) seed:

Before using Phoenix dactylifera (Date Palm) seed carbon as an adsorbent, it is essential to know some of the characteristics such as moisture content, ash content, pH, decolorizing power and surface area of the prepared carbon using standard methods. The results are shown in Table-I.

TABLE I
CHARACTERISTICS OF PREPARED ACTIVATED CARBONS

S. No.	Characteristics	Physically activated carbon	Chemically activated					
			NaCl (I.R.)			$CaCl_2$ (I.R.)		
			0.25	0.50	0.75	0.25	0.50	0.75
1	Moisture content (%)	4.00	4.0	4.0	4.0	4.0	4.0	5.00
2	Ash content (%)	11.77	14.00	13.25	11.67	15.26	15.05	13.10
3	Decolorizing power (mg/g)	3.00	3.00	6.00	7.5	6.00	9.00	10.50
4	Surface area (m^2/g)	503.31	513.44	528.61	564.02	541.26	576.67	588.05
5	pH	9.50	7.24	7.10	6.94	6.80	6.64	6.44
6	Specific gravity	1.218	1.086	1.543	0.946	0.994	1.040	1.001
7	Bulk Density (g/cm^3)	0.45	0.405	0.459	0.385	0.416	0.256	0.285

1. Preparation of synthetic phenol solution

a) Stock phenol solution:

Dissolve 1.0gm phenol in freshly boiled and cooled distilled water and dilute to 1litre. Standardize the stock phenol solution. 1ml=1mg phenol

b) Intermediate phenol solution

Take 10ml volume of stock phenol solution in 1litre of volumetric flask and dilute to the mark with freshly boiled and cooled distilled water so as to get. 1ml=10µg phenol

2. Estimation of phenol by Bromination method

Chemicals used are0.1N sodium thiosulphate, brominating mixture (KBr + KBrO3), conc.Hcl, 10% KI solution and starch.

Procedure:

For blank titration pipette out 25ml of brominating mixture in a conical flask add 25ml of distilled water, add 5ml of conc.Hcl and one test tube 10% KI solution. Immediately titrate the liberated iodine against 0.1N Na2S2O3.5H2O till the colour of solution changes to pale yellow. Add 1ml of freshly prepared starch solution, the solution changes to blue and continue the titration drop wise till the blue colour of solution changes to colourless.

For main titration take 25ml of diluted phenol solution in a conical flask , add 25ml of brominating mixture, 25ml of distilled water, 5ml of conc.Hcl shake well and keep it for about 10mins for occasional shaking, now add one test tube 10% KI solution. Immediately titrate the librated iodine against 0.1N Na2S2O3.5H2O till the colour of the solution changes to pale yellow. Add 1ml freshly prepared starch solution and continue the titration drop wise till blue colour of the solution changes to colourless.

Batch sorption experiment

In batch sorption, a predetermined amount of adsorbent is mixed with a sample, stirred for a given contact time and subsequently separated by filtration. Powdered adsorbent is more suitable for the batch type of contact process.

Phenol removal affinity of activated carbon of Date Palm seed was determined from batch experiments as a function of contact time, dose of adsorbent and pH. Removal isotherms were drawn to these results.

Contact time:

The adsorption is strongly influenced by the contact time. To study the effect of contact time, 100mL of 10mg/L phenol solution was mixed with 700mg of activated carbon, stirred at different contact times varying from (10mins, 20mins, 30mins up to 120mins). Then filtrate was analyzed for residual phenol concentration.

Adsorbent dosage:

To determine the optimum dosage of activated carbon, the different dosages were added to the conical flasks varying from (100mg, 200mg, and 300mg up to 1200mg), containing 100ml of 10 mg/L of phenol solution. The solution in the conical flasks was subjected to stirring for optimum contact time then filtered and analyzed for residual phenol concentration.

In the beginning the rate of adsorption was high and attains equilibrium and corresponding dosages taken as optimum dosage.

pH:

The extent of adsorption is strongly influenced by the pH at which adsorption is carried out. The effect of pH on phenol

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adsorption was studied by performing equilibrium adsorption tests at different initial pH values. i.e., from 4.0 to 10.0. The pH of solution was adjusted by using 0.1N H_2SO_4 or 0.1N NaOH. The activated carbon were mixed and stirred to optimum contact time, filtered and analyzed for residual phenol concentration. The pH at which maximum phenol removal forms optimum pH.

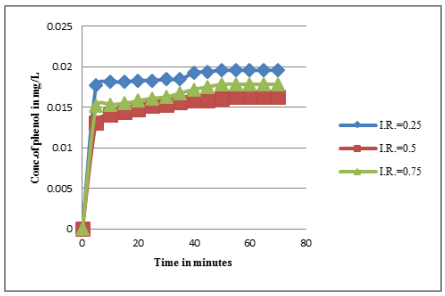

Fig. 2. pH- Time vs. Conc. Of phenol

Sorption kinetics:

The beakers containing 100mL of phenol solution of concentration 10mg/L and known amount of activated carbon were stirred. The samples were withdrawn at different time intervals and filtered and analyzed.

Sorption equilibrium:

To the stoppered bottles containing 100mL of 10mg/L phenol solution, different doses of prepared carbon were added and stirred for optimum contact time, the filtered supernatant solution was analyzed for phenol concentration.

III. Results and Discussion

A. Effect of Contact Time

Contact time has greater influence on the adsorption process. The effect of contact time on removal of phenol from synthetic sample is shown in Fig. 3, 4 and 5 .It is observed that the extent of phenol adsorption increases with increase in time and attain equilibrium at particular time and it remains almost constant. Hence optimum contact time for all prepared carbons is listed in Table-II.

TABLE II
Optimum time, dosage and maximum pH for prepared carbon

S. No.	Types of carbon	I.R.	Optimum time (min)	Optimum dosage in (mg)	Optimum pH
1.	Physically activated	--	65	700	6.5
2.	Chemically activated				
3.	Sodium chloride (NaCl)	0.25	60	1100	6.5
		0.50	55	1000	6.5
		0.75	50	900	6.5
4.	Calcium chloride ($CaCl_2$)	0.25	55	1000	6.5
		0.50	50	900	6.5
		0.75	45	800	6.5

Initial conc. of phenol = 0.02178 mg/L Temperature =32^O C, Volume of sample = 100mL

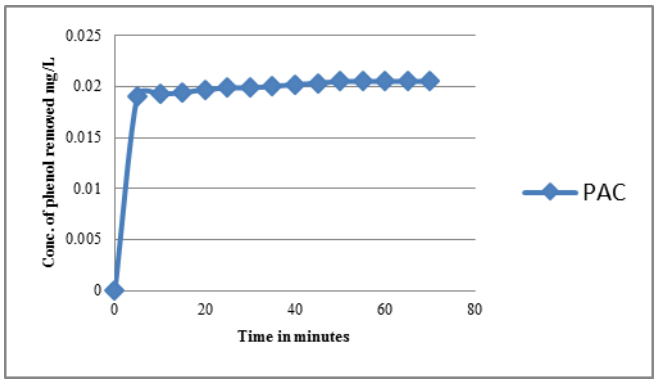

Fig. 3. Effect of contact time on phenol removal by physically activated carbon

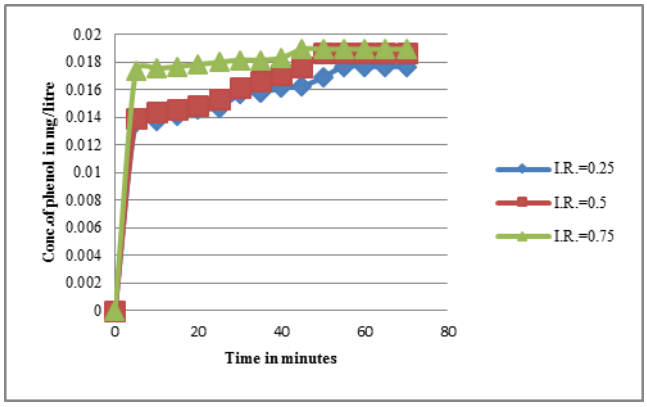

Fig. 4. Effect of contact time on phenol removal by chemically (NaCl) activated carbon

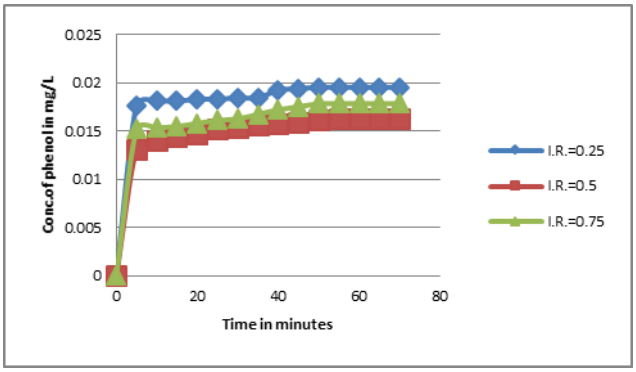

Fig. 5. Effect of contact time on phenol removal by chemically ($CaCl_2$) activated carbon

B. Effect of Adsorbent Dosage

Effect of adsorbent dosage is studied and conc. of phenol removal versus dosage is plotted as shown in Fig. 6, 7 and 8. From the graph it is observed that, as the dosage of carbon increases, amount of residual phenol decreases sharply and attains minimum. The dosage, at which maximum removal is attained, is taken as optimum dosage. Hence optimum dosages for all prepared carbon are listed in Table-II

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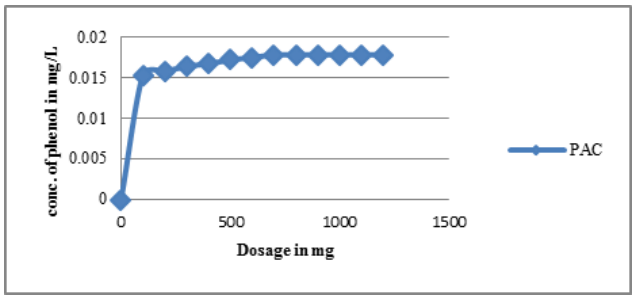

Fig. 6. Effect of contact dosage on phenol removal by physically activated carbon

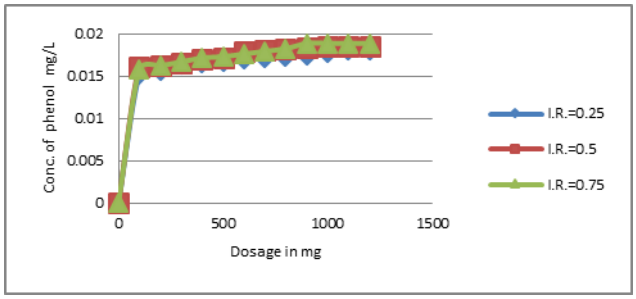

Fig. 7. Effect of contact dosage on phenol removal by chemically (NaCl) activated carbon

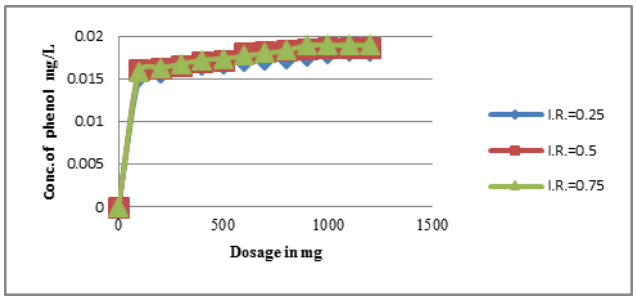

Fig 8. Effect of contact dosage on phenol removal by chemically ($CaCl_2$) activated carbon

C. *Effect of pH on phenol Removal*

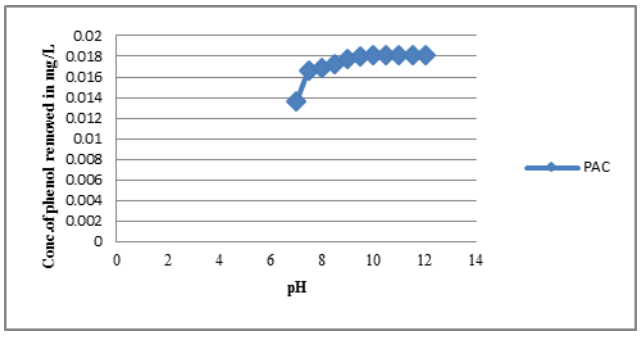

Fig. 9. Effect of pH on phenol removal by physically activated carbon

The extent of adsorption is strongly influenced by pH at which adsorption is carried out. The pH of the solution as influenced on extent of adsorption removal efficiencies of phenol by prepared activated carbon at different pH values as shown as in Fig. 9, 10 and 11. Hence optimum pH for all prepared carbon are listed in Table-II.

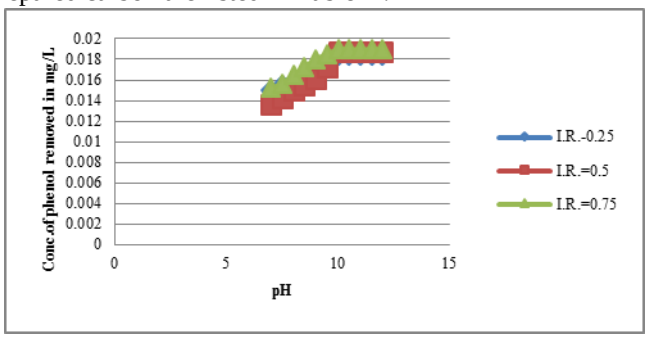

Fig. 10. . Effect of pH on phenol removal by chemically (NaCl) activated carbon

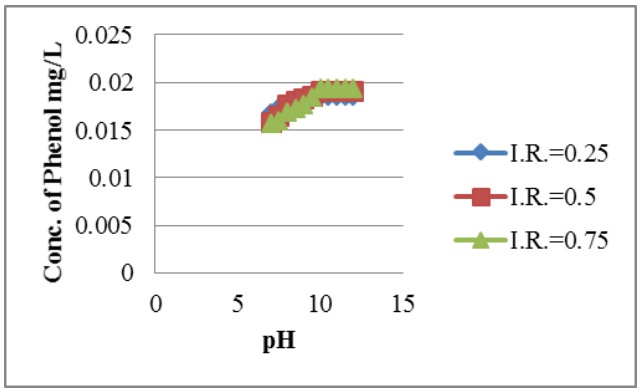

Fig. 11. Effect of pH on phenol removal by chemically ($CaCl_2$) activated carbon

D. *Sorption Kinetics*

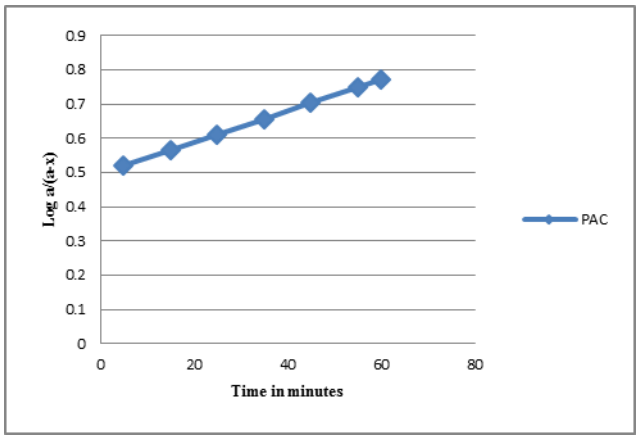

Fig. 12. Reaction rate constant for physically activated carbon

The sorption Kinetics study has been carried out at room temperature for activated. The batch kinetics data for the adsorption of the phenol was tested for the first order reaction. The $\log_{10}$ a/ (a-x) Vs 't' for activated carbon were drawn in Fig. 12, 13 and 14. This produces a straight line graph with slope = k / 2.303. From the values of graphical and calculated "K" values, it is observed that adsorption of phenol follows first order rate equations and both the values differs slightly.

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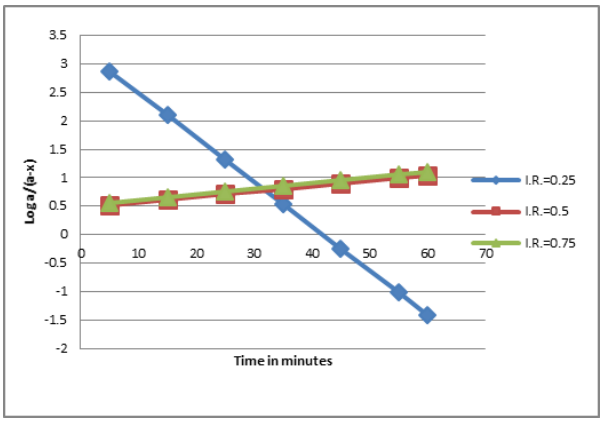

Fig. 13. Reaction rate constant for chemically (NaCl) activated carbon

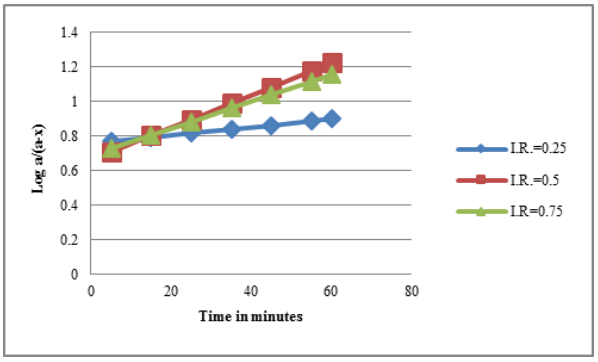

Fig. 14. Reaction rate constant for chemically ($CaCl_2$) activated carbon

E. *Pore Diffusion (Webber and Morries)*

Further, the rate of pore diffusion can be determined by,

$C / C_0 = K_P \times t^{½}$

Where,
C = Concentration of sorbate at any time "t" (min) in mg/L
C_0 = Initial concentration of sorbate in mg/L.
t = time taken for sorption
K_P = rate of pore diffusion

The plot of C / C_0 Vs $t^{1/2}$ for phenol is shown in Figure 15, 16 and 17 which is straight line graph. It shows that, as time passes, pore diffusion decreases and hence adsorption increases.

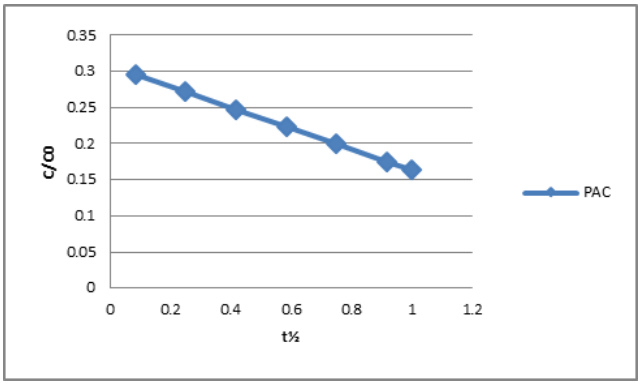

Fig. 15. Webber and Morris plot of physically activated carbon

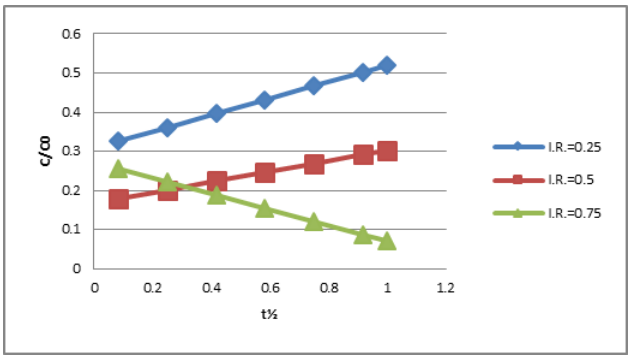

Fig. 16. Webber and Morris plot of chemically (NaCl) activated carbon

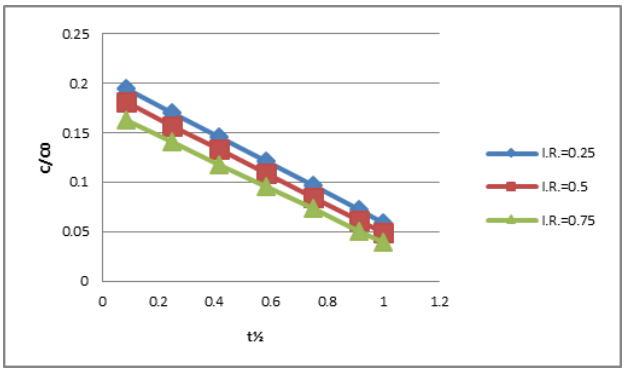

Fig. 17. Webber and Morris plot of chemically ($CaCl_2$) activated carbon

F. *Adsorption Isotherm*

In the present study, various adsorption isotherm models have been used to study the capacity and equilibrium co-efficients for adsorption of phenol by activated carbon. Equations that are often used to describe the experimental isotherm data were developed by Freundlich and Langmuir isotherms.

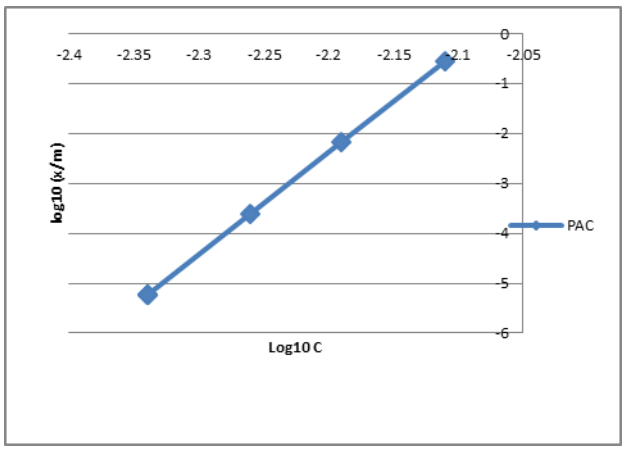

Fig. 18. Plots of Freundlich isotherm for physically activated carbon

The Freundlich isotherm is as below. $q=x/m=KC^{1/n}$
The Langmuir isotherm is as below:
$q=x/m= abc / (a + bc)$
Where
q= x/m= Amount of solute adsorbed per unit weight of adsorbent in mg/g.

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C= Equilibrium concentration of adsorbate in solution after adsorption in mg/L
'K' and '1/n' are Freundlich constants.
'a' and 'b' are Langmuir constants.

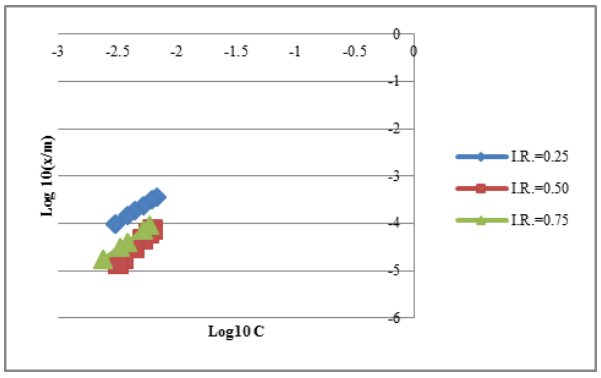

Fig. 19. Plots of Freundlich isotherm for chemically (NaCl) activated carbon

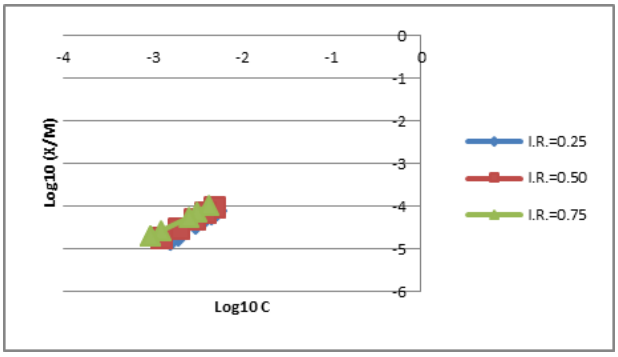

Fig. 20. Plots of Freundlich isotherm for chemically ($CaCl_2$) activated carbon

G. Langmuir Isotherm

The Langmuir isotherm is used to describe the single layer adsorption and the linear form of the Langmuir's isotherm is,
X/M = abc / (a + bc)
$C / (X/M) = 1/ab + c / a$ (1)
Where,
X/M = Amount of adsorbate adsorbed per unit weight of adsorbent.
C= Equilibrium concentration of adsorbent in solution after adsorption or saturated concentration. 'a' and 'b' are emperical constants.
The equation (1) is of the type y = c+mx, where c = 1/ab and m=1/a, x = c the plot of C/(X/M) Versus C produces a straight-line graph. The value of constants 1/b and 1/ab are calculated by intercept and slope.
1 / ab = intercept; slope = 1/a
Intercept = 1/b X slope; b = slope / intercept.

The plot of linearized Langmuir isotherm (C / X/M versus C) for different adsorbents is shown in Fig. 21, 22 and 23.
From the above graphs 'a' and 'b' are evaluated by knowing slope and intercept. This can further be authenticated by least square analysis and graphical values are the important characteristics of Langmuir isotherm can be expressed in terms of dimensionless constants. A dimensional less equilibrium parameter called separation factor, 'R' is used to study the applicability of Langmuir adsorption isotherm. This is defined by Webber and Chakravarthi as follows.

$R = 1 / [(1 + a) Co]$ (2)

Where,
a = Langmuir constant and
C_0=Initial concentration in mg/L
From the above equation Webber and Chakravarthi has given parameter indicating the shape of the isotherm as follows:

TABLE I
SHAPE OF THE ISOTHERM

Values of R	Type of Isotherm
R > 1	unfavorable
R = 1	Linear
0 < R < 1	Favorable
R = 0	Irreversible

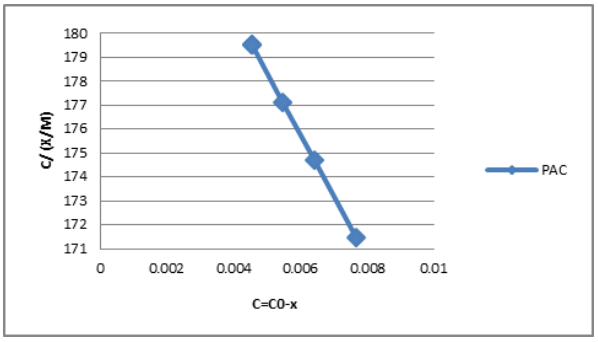

Fig. 21. Plot of Langmuir isotherm for physically activated carbon

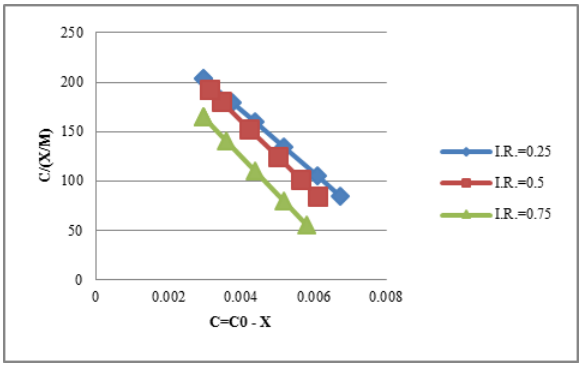

Fig. 22. Plot of Langmuir isotherm for chemically (NaCl) activated carbon

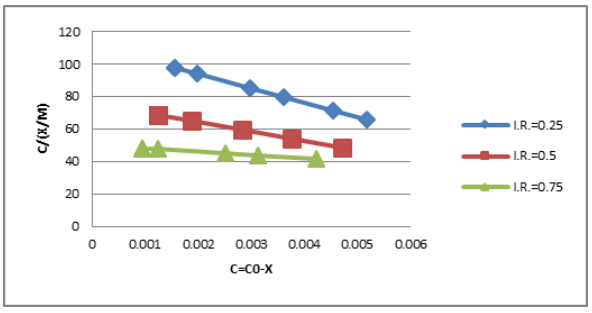

Fig. 23. Plot of Langmuir isotherm for chemically ($CaCl_2$) activated carbon

IV. Conclusion

Based on the experimental study the following conclusions are drawn

1. It's evident from the characteristic properties that prepared activated carbon is good adsorbent for removing phenol and these adsorbents are easily and cheaply available.
2. The extent of phenol adsorption increases with increase in time and attain equilibrium at a particular time. Hence the optimum contact time for physically activated carbon is 65 minutes with removal efficiency of 94.44% and for chemically activated carbon i.e. NaCl activated carbons of I.R. 0.25, 0.50 and 0.75 are 60, 55, 50 minutes with removal efficiency of 84.89%, 87.76% and 89.88% respectively and for $CaCl_2$ activated carbons of I.R. 0.25, 0.50 and 0.75 are 55, 50, 45 minutes with removal efficiency of 91.36%, 93.52, 94.96% respectively.
3. As the dosage increases, amount of residual phenol decreases sharply and attains minimum. This decrease is mainly due to enhanced total surface area of the adsorbent. The point where maximum removal is attained is taken as optimum dosage. Hence optimum dosage for optimum dosage for physically activated carbon is 700mg with removal efficiency of 82.73% and for chemically activated carbon i.e. NaCl activated carbons of I.R. 0.25, 0.50 and 0.75 are 1100mg, 1000mg, 900mg with removal efficiency of 83.45%, 86.33% and 87.04% respectively and for $CaCl_2$ activated carbons of I.R. 0.25, 0.50 and 0.75 are1000mg, 900mg, 800mg with removal efficiency of 85.61 %, 86.33% and 87.76% respectively.
4. The impact of phenol removal is dependent on pH of the medium. The optimum pH for removal of phenol was found to be 6.5 for both physically activated and chemically activated carbon. Removal efficiency of physically activated carbon is 83.45% and for chemically activated carbon i.e. NaCl activated carbons of I.R. 0.25, 0.50 and 0.75 with removal efficiency of 80.57%, 82.01% and 84.17% respectively and for $CaCl_2$ activated carbons of I.R. 0.25, 0.50 and 0.75 with removal efficiency of 84.89%, 86.33% and 87.76% respectively.
5. The rate of adsorption of phenol obeys first order reaction equation. It also follows Webber and Morris equation for pore diffusion. .
6. The result of the batch experiments follows Freundlich (1/n>1) isotherms but Langmuir isotherms (R<1) and (R>1) proves to be an unfavourable adsorption.

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