REMOVAL OF PHENOL FROM WATER BY ADSORPTION

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ABSTRACT

Gas-liquid chromatography (GLC) with a flame ionization detector system using the direct injection of aqueous solutions was used to monitor the adsorption of phenol dissolved in water onto activated carbon.

The effect of various initial conditions concentration, flow rate, temperature, bed depth and different linear velocity on the performance of the activated carbon to remove phenol from water were studied.

INTRODUCTION

With the increase in use of surface water as a source for potable water, the presence of trace organic contaminants in surface water continues to a reuse great interest and concern, particularly because the surface water resources are receiving unprecedented organic loads from both municipal and industrial wastes, and little is known of their long term effects on the human body.

Adsorption using activated carbon has developed as an important unit process for the removal of organic from water and waste water[1].

Liquid-solid adsorption onto activated carbon is characterized by slow rates and long period between actions. The liquid flowing through an adsorber may be in contact with the carbon for minutes, such as when removing taste from water or for several hours as in the case of decolorizing sugar solution. The granular carbon bed life may extend from a few days for sugar solutions to several years for taste removal[2].

Active carbon is a porous carbonaceous material prepared by carbonizing and activating organic substances of mainly biological organic. The most important of activated carbon is very large adsorptive power, which is primarily due to a high developed porous structure[3].

There are basically three types of carbon system:

1. Fixed beds.
2. Pulse beds.
3. Fluidized beds.

These beds can be arranged in series, in parallel or in combination of both.

In the present research phenol was chosen as a pollutants because of its harmful effect in water and its industrial importance.

According to the National Institute for Occupational Safety and Health (NIOSH), expouser to phenol should be controlled so that no employees are exposed to phenol concentration > 20 mg/m^3 which is time-weighted average concentration for up to a 10-h work/day, 40-h work/week[4].

EXPERIMENTAL PROCEDURE

A glass Q. V. F. column was used (1.53×10^{-2} m) internal diameter. The activated carbon bed was confined in the column by fin stainless steel screens. Two Q. V. F. spherical containers were used. The first one as feed container with a capacity of 0.05 m^3 and the second one as receiver with capacity of 0.025 m^3. Two calibrated rotameters were used to measure the flow rates. The solution pumped from the feed container through the carbon bed by means of centrifugal pump. Recycle method used to reduce the flow rate to desired quantities.

After preparing the solution with the desired concentration of phenol, the three-way valve was opened in the vent direction, the solution was pumped through the rotameter the vent opening for few minutes to allow all bubbles to be moved out. During this time adjustment of the flow rate to be desired value can be obtained by means of needle valves, the direction of the three-way valve was converted to the column. Every 10 minutes, (50 ml) sample was taken from the outlet of the column until steady state was reached.

The concentration of the solute (phenol) in solution was determined by the use of GLC with a flame ionization detection system using direct injection of the aqueous solution.

A 1.5 m long, 4 mm diameter glass column packed with 5% carbowax. 20 M on chromosorbe WAW was used. The following operating condition for G. L. C. system were employed.

Hydrogen flow 6.7×10^{-7} m^3/s.

Nitrogen flow 6.7×10^{-7} m^3/s.

Air flow 6.7×10^{-7} m^3/s.

Column temperature 190 °C.

Injection temperature 220 °C.

Detector temperature 220 °C.

For all experiments, demineralized water was used for preparing the required solutions. The pH of solution was between 6.5-6.8 due to acidic action of phenol.

RESULTS AND DISCUSSION
Effect of Solute Concentration

To show the activity of carbon for adsorbing phenol at different concentration (100×10^{-3}, 200×10^{-3}, 300×10^{-3}, 405×10^{-3} and 500×10^{-3} kg/m^3) respectively, the solute adsorbed versus time were plotted in Fig.(1) and from this figure the following indication were obtained:

a. A linear portion exists for each curve at the early period of the experiments, with increasing influent concentration, the linear segment of the curves extent over a shorter period of time.

Deviation from linearity occurred because of increasing influence of intraparticle transport on the overall rate of mass transfer as each run progress[5].

b. Equilibrium time is inversely related to the initial concentration and this explained by the fact that since the rate of diffusion is controlled by the concentration gradient, it takes a longer contact time to reach adsorption equilibrium for the case of low values of initial solute concentration[6].
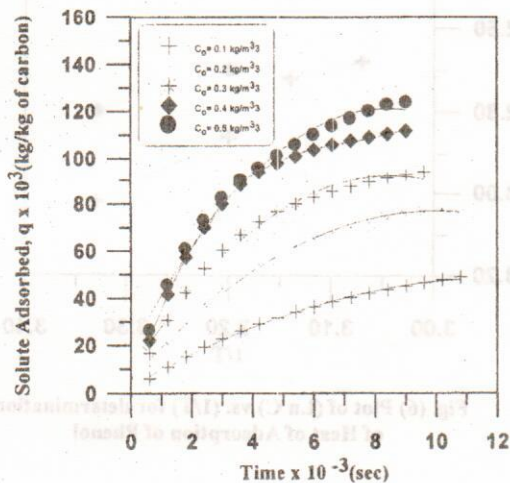

Fig. (1) Cumulative Adsorption at Different Concentrations
Z=0.06 m, Q=$8.3 \times 10^{-7} m^3/sec$, T=316 K

The equilibrium data for adsorption were found to correlate well with both Langmuir and Freundlich equations for the adsorption isotherm in the range of concentration studied. Plotting of C_{eq}/qe versus C_{eq} shows a straight line Fig.(2) and this means that the equilibrium data correlated well with Langmuir equation.
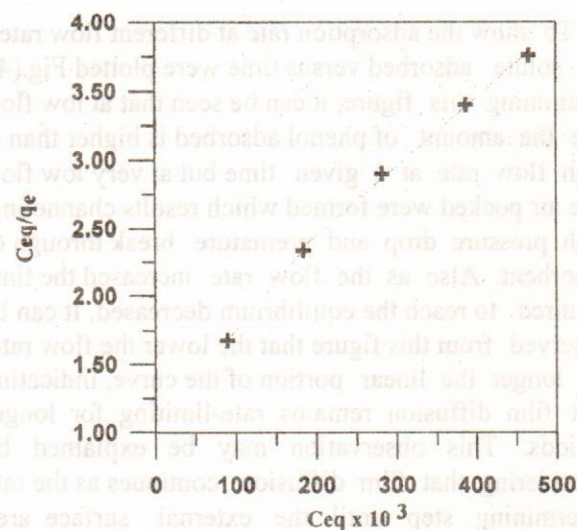

Fig. (2) Plot of Ceq/q_e vs. Ceq for determination of Langmuir Constants for Phenol

$$C/q = (1/Qb) + (C/Q)$$

The monolayer capacity (Q) and the Langmuir equation constant (b) were calculated from the slope and the intercept of the straight line, their values were tabulated in Table (1). Also plotting log (C_{eq}) against (qe) Fig.(3) shows the straight line and this means that the equilibrium data for adsorption also correlated well with Freundlich equation. The values of (k) and (1/n) were calculated from the intercept and the slope of the straight line, their values were tabulated in Table (1).
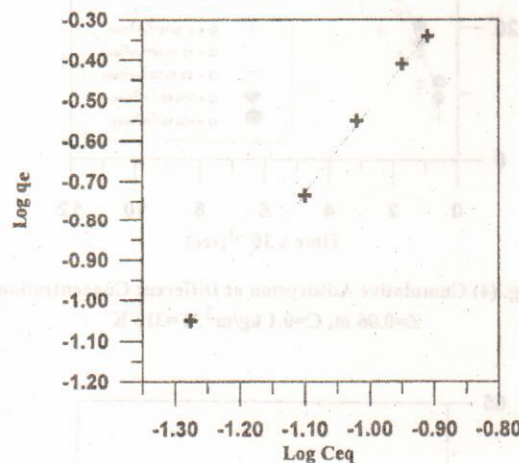

Fig. (3) Plot of Log (Ceq) vs. Log (Ceq) for determination of Freundlich Constants for Phenol

Table (1)

Equation	Q (kg/kg)	B (m³/kg)	k (kg/kg)	1/n (m³/kg)
Langmuir	0.17	5.602		
Freundlich			0.182	0.507

Effect of Flow Rates

Five experiments were carried out at different flow rates 8.5×10^{-7}, 12.5×10^{-7}, 19.4×10^{-7}, 25×10^{-7} and 40×10^{-7} m^3/s respectively.

To show the adsorption rate at different flow rates, the solute adsorbed versus time were plotted Fig.(4). Examining this figure, it can be seen that at low flow rate the amount of phenol adsorbed is higher than at high flow rate at a given time but at very low flow rate air pocked were formed which results channeling, high pressure drop and premature break through of adsorbent. Also as the flow rate increased the time required to reach the equilibrium decreased. It can be observed from this figure that the lower the flow rate, the longer the linear portion of the curve, indicating that film diffusion remains rate-limiting for longer periods. This observation may be explained by considering that film diffusion continues as the rate determining step until the external surface area becomes essentially saturated with solute[7].

The mass transfer rate increased as the flow rate increased. Increased flow rate in this region may be expected to give a compression or reduction of the surface film, there by decreasing resistance to mass transfer and increasing the mass transfer rate[7].
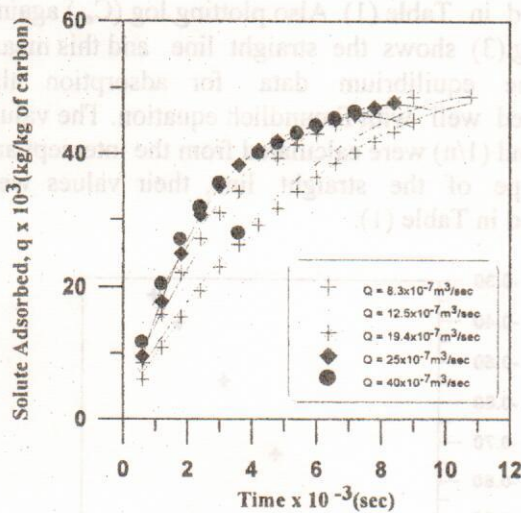

Fig. (4) Cumulative Adsorption at Different Concentrations
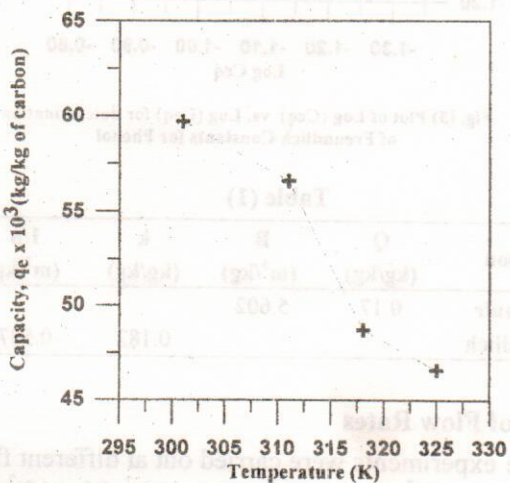$Z=0.06$ m, $C=0.1$ kg/m^3, $T=316$ K

Fig. (5) Effect of Temperature on the Capacity of Activated Carbon for Isothermal Adsorption of Phenol

Effect of Temperature

Four experiments were carried out at different temperatures (301, 311, 318 and 325 K) respectively to study the effect of temperature on the activity of carbon for adsorbing phenol. Fig.(5) shows that as the temperature increased the adsorption decreased and this due to that adsorption are normally exothermic, thus the extent for adsorption generally increased with decreasing temperature.

The heat of adsorption (ΔH) for the system phenol-activated carbon was calculated by using Clausious-Clapeyron equation[8].

$$\Delta H = -R \left(\frac{d \ln (c)}{d (1/T) q} \right)$$

This was carried out by plotting (ln) against (1/T) for different values of the capacity (q) (35×10^{-3} and 45×10^{-3} kg/kg of carbon, Fig.(6). The values of (ΔH) were calculated from slopes ($-\Delta H / R$) of the straight lines represented in Fig.(6). This was found to be equal to (5.28 kj/mole). Which is in good agreement with the latent heat of vaporization (i.e. physical adsorption).
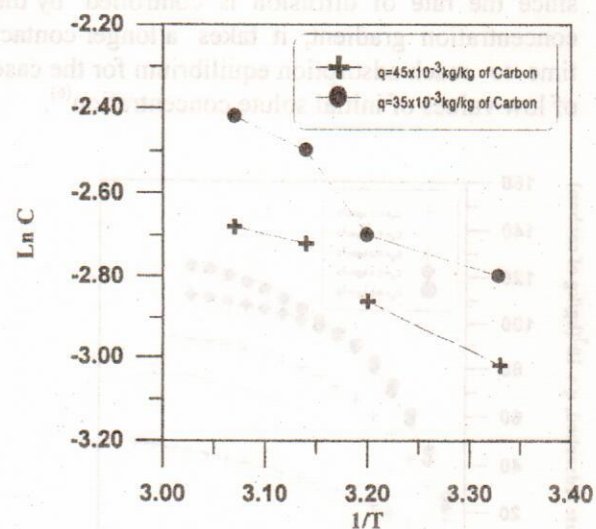

Fig. (6) Plot of (Ln C) vs. (1/T) for determination of Heat of Adsorption of Phenol

Effect of Bed Depth

The effect of bed depth on the adsorption capacity of activated carbon were studied at (0.02, 0.04, 0.06, 0.08 and 0.1 m) respectively, plotting the capacity against bed depth, Fig.(7) shows that the capacity of activated carbon increased with increasing bed depth, i.e. the adsorption increase with increasing bed depth and this is due to an increased in the contact time.
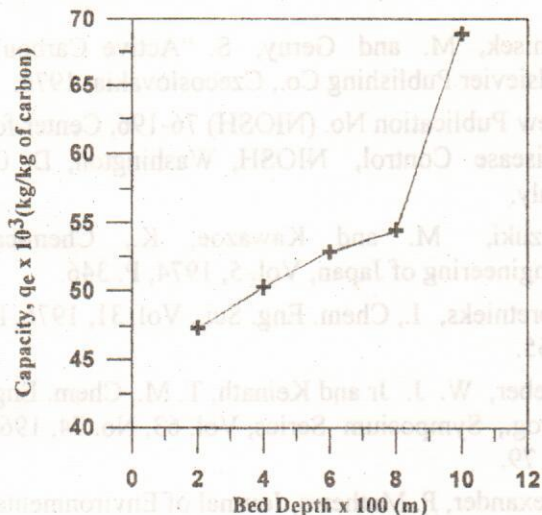
Fig. (7) Effect of Bed Depth on the Capacity of Activated
Carbon for Isothermal Adsorption of Phenol

Effect of Linear Velocity

The effect of linear velocity on the activity of activated carbon for removing phenol were studied at 1.98×10^{-3}, 3.1×10^{-3} and 4.7×10^{-3} m³/s respectively.

These values were obtained by varying the column diameter 0.025, 0.02 and 0.015 m respectively. Plotting the linear velocity against the capacity showed that the rate of adsorption and the capacity of activated carbon were increased as the linear velocity increased.
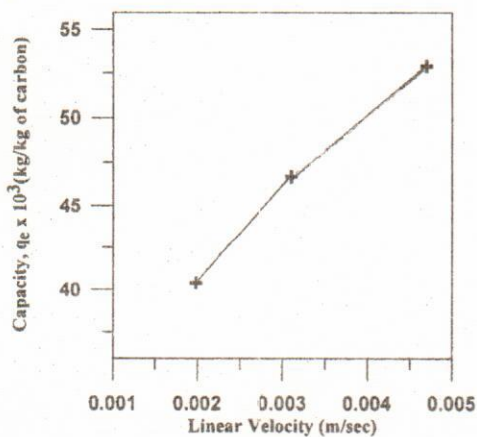
Fig. (8) Effect of Linear Velocity on the Capacity of Activated
Carbon for Isothermal Adsorption of Phenol

Effect of Concentration, Flow Rate, Bed Depth, Temperature and Linear Velocity on the Capacity of Activated Carbon

Applying multiple correlation to the experimental data the following correlation were obtained and listed below:

$q = 12\,C^{0.23}\,Z^{0.18}\,T^{-0.7}$	± 6.1	1.91 A
$q = 0.45\,C^{0.29}\,D^{0.17}\,Z^{0.28}$	± 5.8	1.93 B
$q = 0.7\,C^{0.76}\,T^{-0.5}\,Q^{-0.08}$	± 5.3	0.95 C
$q = 0.06\,C^{0.32}\,Q^{-0.09}\,Z^{0.21}$	± 4.6	0.966 D
$q = 0.06\,C^{0.36}\,Q^{-0.9}\,Z^{0.25}\,T^{-0.41}\,D^{013}$	± 4.1	1.97 E
$q = 1.6\,C^{0.33}\,Z^{0.24}\,D^{0.15}\,Q^{-0.09}$	± 3.1	0.98 F

From the above correlation the following indications were obtained:

1. Equations (A and C) showed that the effect of flow rate was more than the effect of bed depth on the capacity of activated carbon.

2. Equations (E and F) showed that the presence of temperature will decrease the correlation coefficient.

3. Equation (F) represents the best fitting for the experimental data (i.e. high value of correlation coefficient).

CONCLUSIONS

The following points can be concluded from the present research

1. The equilibrium isotherm for the system phenol-activated carbon was favorable type, and was well represented by Langmuir and Freundlich equations. The equation constants (Q, b, 1/n, k) were calculated and tabulated in Table (1).

2. The capacity of activated carbon increased with increasing inlet solute concentration. This can be explained by increasing the concentration will lead to increase driving force and consequently increasing the adsorption rate.

3. The influence of temperature had a small effect on the capacity of the activated carbon for the present conditions.

4. The capacity of the activated carbon increased with increasing bed depths, linear velocity and will increase with decreased flow rates.

5. The rate of mass transfer for initial stage adsorption increased with increasing influent concentration, flow rate, and will be nearly constant with increasing influent concentration, flow rate, and will be nearly constant with increasing temperature and bed depth.

6. Heat of adsorption was found to be 5.28 kJ/mole, this confirm that the adsorption of phenol on activated carbon is a physical adsorption.

NOMENCLATURE

C: Adsorbate Concentration in the bulk of the solution.

q: Amount of solute adsorbed per unit mass adsorbent at concentration C.

Q: Amount of solute adsorbed per unit mass adsorbent in forming a complete monolayer on the adsorbent surface.
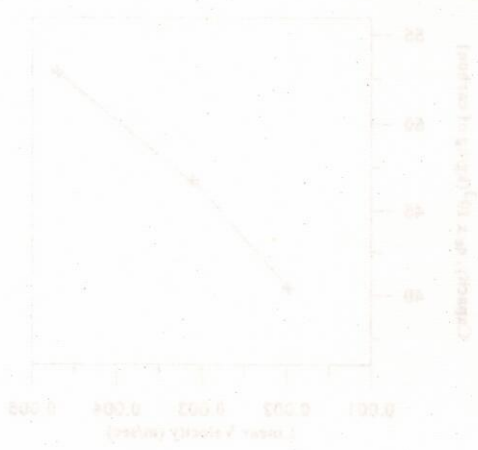
b: constant.

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