PERFORMANCE OF THE FLUIDIZED-BEDS ADSORBERS

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ABSTRACT

The aim of the present research was to study the ability of the fluidized-beds of activated carbon to adsorb isothermally pollutants from aqueous solutions. The main pollutant was phenol; pollutants like O-chlorophenol, O-nitrophenol, and O-cresol were also removed by adsorption onto activated carbon to study the effect of molecular structure of the adsorbate on the adsorption process. Adsorption isotherms have been determined and analyzed according to the Langmuir and Freundlchs' equations. The heat of adsorption was calculated using Clasius-Clapeyron correlation.

INTRODUCTION

Wastewater treatment has become one of the principal problems facing modern civilization. The ill effects of wastewater are in part economic, as in the added cost of purifying the water municipal, industrial, or agricultural use. Pollution may make natural waters unfit as an environment for fish or other wildlife. Industrial waste is one of the causes of stream pollution, it is roughly comparable, in its nationwide pollutional effect, with municipal sewage and other sanitary and domestic wastes. A major source of contamination is agriculture, which discharges both excessive quantities of silt and chemicals leached or washed from the soil.

Adsorption is probably one of the most common of the advanced wastewater treatment processes; and are finding increased used in wastewater treatment for removal of refractory organics, toxic substances, and color. It was first observed by Scheele in 1773 for gases and subsequently for solutions by Lowitz in 1785, after that adsorption was found to be one of the best commercially proven method for removing organic contaminants.

Liquid-phase adsorption processes using activated carbon have been successfully applied for removing organic molecules from domestic and industrial wastewater. Knowledge of both adsorption capacity and the rate of adsorption is required in designing adsorption equipment.

The concept of upflow fluidized-beds is relatively new, and as a result the engineering development has not progressed as far as fixed-beds and moving technology. Fluidizing the medium allows solids to pass through and overcomes the problems associated with fixed-bed systems, such as high head-losses, plugging, and frequent need to keep excessive head loss from building up. Furthermore, other problems common to fixed-beds, such as air binding and fouling with particulate matter, are usually not encountered with fluidized-beds operation. The fluidized-beds offers a high available surface area, since there is no contact between particles, intimate contact of the entire surface with the waste stream is assured. Hence, then present research has focused on this mode of operation.

Because it was desired to obtain fundamental information pertinent to the interpretation of adsorptive characteristics in various adsorbate-carbon systems, it was essential to conduct the experiments with well-defined adsorbate material. Consequently, studies of the phenol-carbon system were deemed desirable to serve as a bridge between this research and the work of other. Accordingly, an extensive program of research on the adsorption of the phenol onto granular activated carbon has been conducted in order to gain a more complete understanding of the kinetics of adsorption in columns of fluidized media and of the factors controlling rates of adsorption in this system.

EXPERIMENTAL ARRANGEMENTS

1. Materials

a. **Adsorbate:** It was desired to obtain fundamental information pertinent to the interpretation of adsorptive characteristics in various adsorbate-carbon systems. So it was essential to conduct the experiments with well-defined material, and since the characteristics of the adsorption of phenol onto activated carbon are known better than those for the adsorption of most other organic solutes, so this work has been done with the phenol-carbon system.

b. **Adsorbent:** Activated carbon (supplied by N. V. Norit Verkoop Central, Amsterdam, Holland) was used as an adsorbent in the present work. Its properties are listed in Table 1 and 2.

Table (1) Properties of Activated Carbon

Dimension	2.6 mm x 0.68 mm
Bulk Density	400 kg/m^3
Particle Density	1400 kg/m^3
Void Fraction of Bed	0.4
Surface area	950 x 10^3 m^2/kg
Internal Porosity of Particle	0.4

Table (2) Carbon Particle Size Range

Shape	Particle Size range x 10^3 (m)	Particle Diameter (dp) x 10^3 (m)
Cylindrical	2.6 x 0.68	1.22
Granular	0.9-0.7	0.8
Granular	0.7-0.57	0.63
Granular	0.57-0.4	0.48

2. Procedure

A small-scale pilot plant of fluidized-beds adsorber was constructed to determine the column characteristics of the adsorption system, Fig.(1). Four different experiments were carried out to find the minimum fluidizing velocity (U_{mf}) for different bed heights (0.10, 0.15, 0.20, and 0.25).

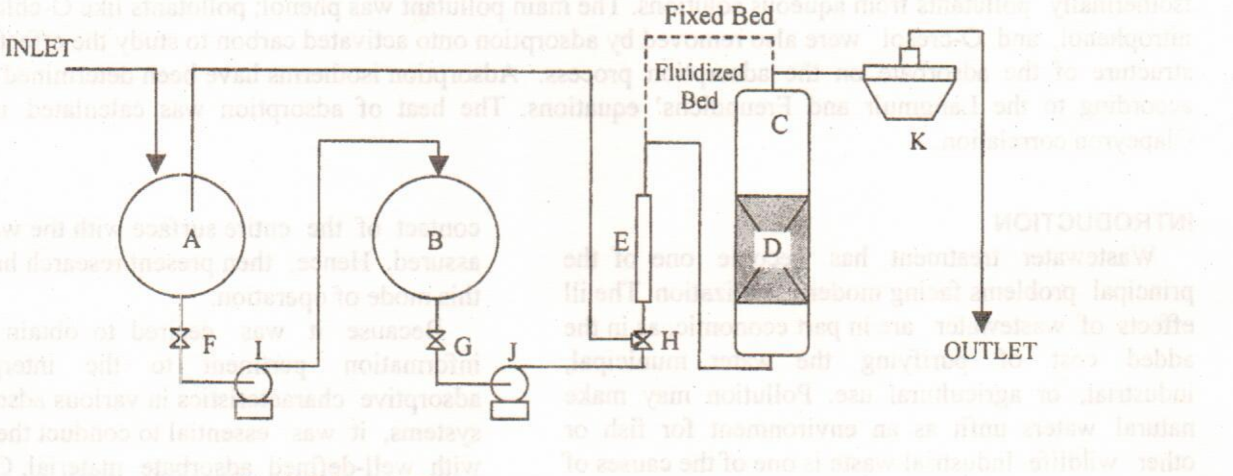


Fig.(1) Schematic Diagram of Experimental Apparatus

A&B	Two Q.V.F. Containers	H	Three-Way Valve
C	Q.V.F. Glass Column	I&J	Two Centrifugal Pumps
D	Bed of Activated Carbon	K	Cyclone
E	Calibrated Rotameter	L	U-Tube Mercury Manometer

F&G Two Q.V.F. Valves

Thirty four different column runs were conducted with activated carbon, thirty three of them were of fluidized beds adsorber at various initial conditions (concentration, bed height, flow rate, pH, particle size, adsorbate molecular structure and temperature). One run was conducted with down flow fixed bed column.

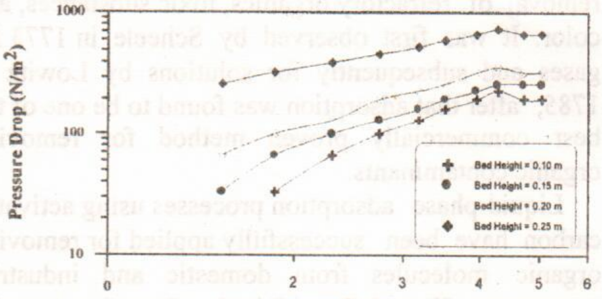
3. Analysis

A Shimadzu model UV-160 A Ultraviolet Visible Spectrophotometer was used to determine the solution concentrations.

RESULTS AND DISCUSSION

a. Prediction of Minimum Fluidizing Velocity (U_{mf})

Minimum fluidizing velocity (U_{mf}) was predicted for different carbon bed heights of 0.1, 0.15, 0.20 and 0.25 m; Fig.(2), and it was equal to 0.0038 m/s for different bed heights.

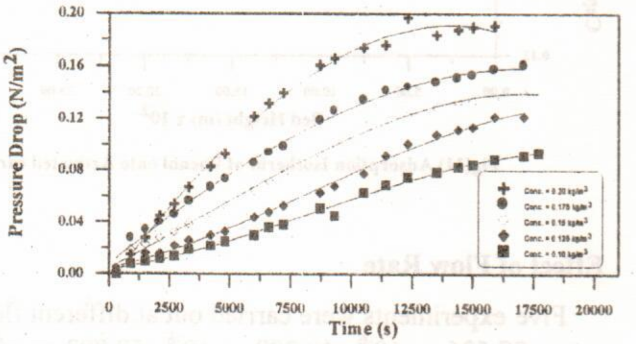


Fig(2) Plot of Pressure Drop -Velocity Curves for different Bed Heights to Determine the Minimumum Fluidizing Velocity

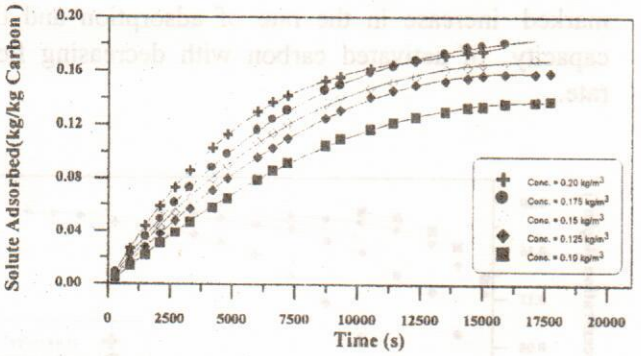
b. Parameters Affecting Adsorption Process

Effect of Solute Initial Concentration

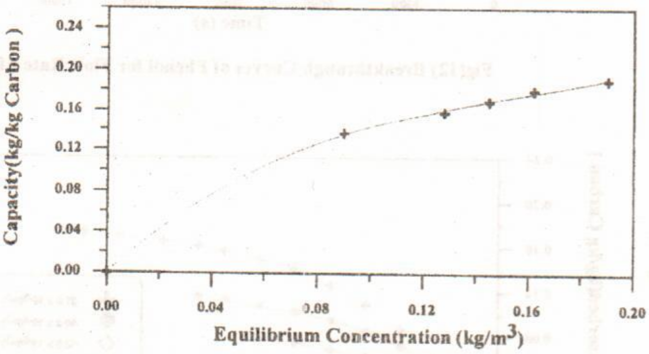
Five fluidized beds studies were carried out at different phenol concentrations; 0.10, 0.125, 0.15, 0.175 and 0.25 kg/m^3. Fig.(3) shows that the exit solution concentration increases as the solution concentration was increased. Also Fig.(4) represents that the total quantity of solute removed from the solution at any period of time increases with increasing influent concentration. So, the capacity of activated carbon increases as the influent concentration of the adsorbate increases, Fig.(5). This would be anticipated with the basis of the increased driving force of mass transfer with increased concentration of solute in solution.



Fig(3) Breakthrough Curves for Phenol for Concentration Effect



Fig(4) Cumulative Adsorption at Different Concentrations of Phenol onto Carbon



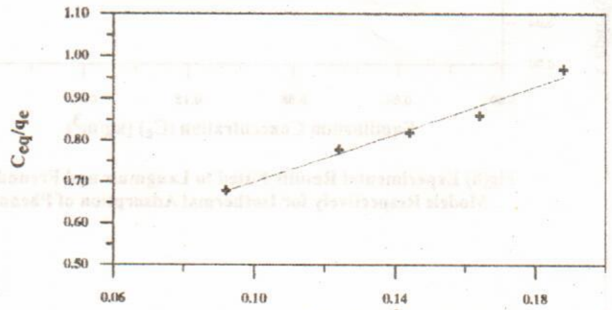
Fig(5) Adsorption Isotherm for Phenol onto Activated carbon

Langmuir and Freundlich Isotherms

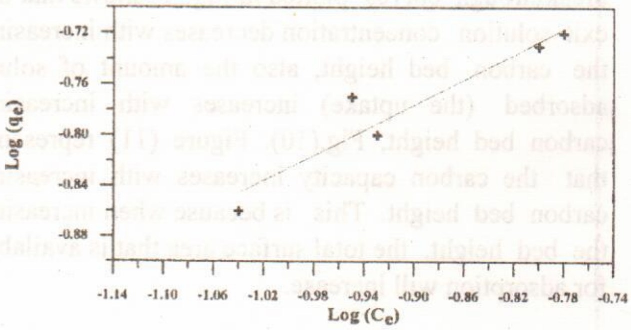
Adsorption isotherms had been determined and analyzed according to Langmuir equation, Eq.1, and Freundlich equation, Eq. 2. Figure (6) represents the applicability of the Langmuir equation, and Fig.(7) represents that the equilibrium data for adsorption also correlated well with Freundlich equation.

$$q_e = \frac{Qbc}{1+bc} \ldots(1)$$

$$q_e = KC^{1/n} \ldots(2)$$



Fig(6) Plot of C_{eq}/q_e vs. C_{eq} for Determination of Langmuir Constants of Phenol



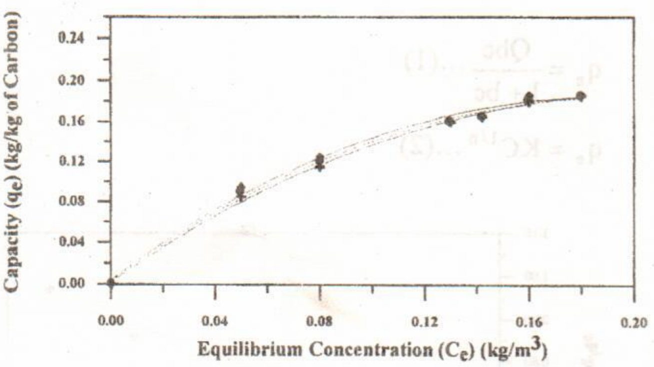
Fig(7) Plot of Log q_e vs. Log C_{eq} for determination of Freundlich Constants of Phenol

The Langmuir and Freundlich isotherm constants for the relevant adsorbate are listed in Table (3).

Table (3): Langmuir and Freundlich constants for phenol – carbon system

	Langmuir		Freundlich	
	Q (kg/kg)	b (m³/kg)	K (kg/kg)	1/n (m³/kg)
Constants	0314	8.454	0.431	0.476
Correlations	$q_e = \frac{2.653C_{eq}}{1+8.454C_{eq}}$		$q_e = 0.431C_{eq}^{0.476}$	
Correlation Coefficient	100%		98%	

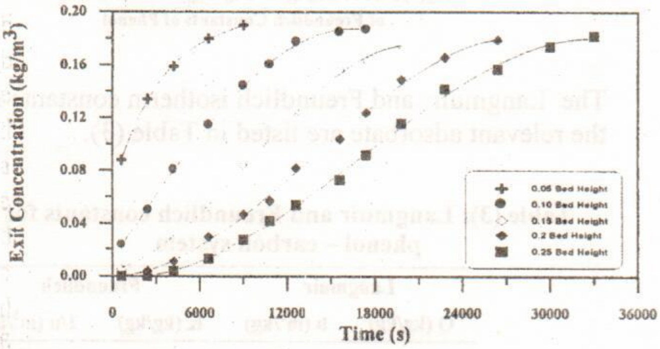
Figure (8) shows a comparison between the experimental, Langmuir, and Freundlich isotherms. It can be seen that the Langmuir isotherms gives the best agreement over the whole adsorption range since it predicts the experimentally observed monolayer better than the exponentially increasing Freundlich isotherms.



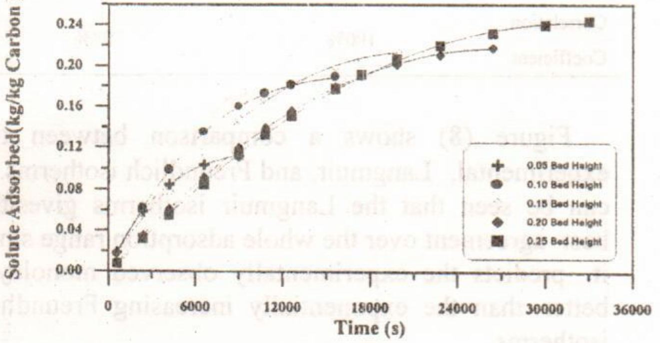
Fig(8) Experimental Results Fitted to Langmuir and Freundlich Models Respectively for Isothermal Adsorption of Phenol

Effect of Carbon Bed Height

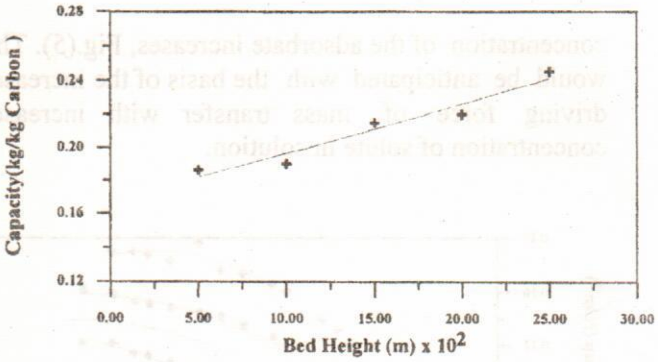
Five experiments were carried out with different bed heights; 0.05, 0.10, 0.15, 0.20, and 0.25 m. The breakthrough curves plotted in Fig.(9) shows that the exit solution concentration decreases with increasing the carbon bed height, also the amount of solute adsorbed (the uptake) increases with increasing carbon bed height, Fig.(10). Figure (11) represents that the carbon capacity increases with increasing carbon bed height. This is because when increasing the bed height, the total surface area that is available for adsorption will increase.



Fig(9) Breakthrough Curves of Phenol for Carbon Bed Height Effect



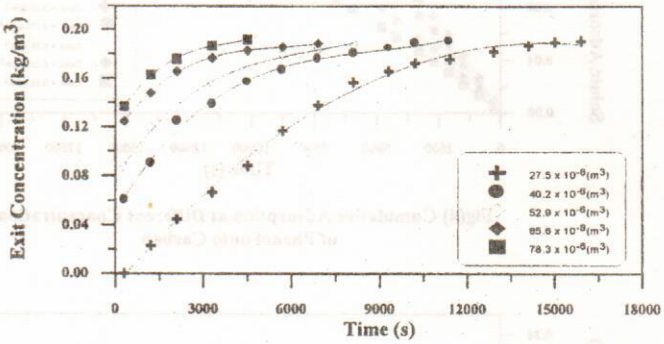
Fig(10) Cumulative Adsorption of Phenol at Different Carbon Bed Heights



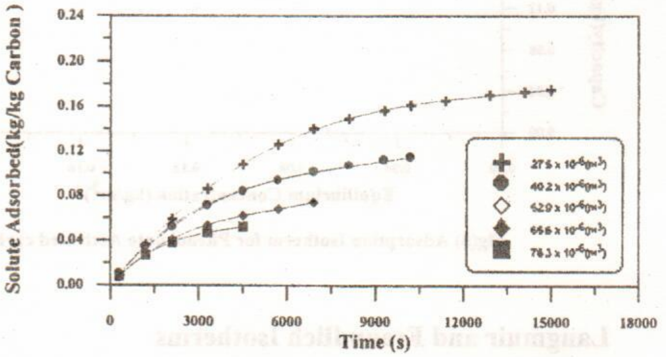
Fig(11) Adsorption Isotherm of Phenol onto Activated carbon

Effect of Flow Rate

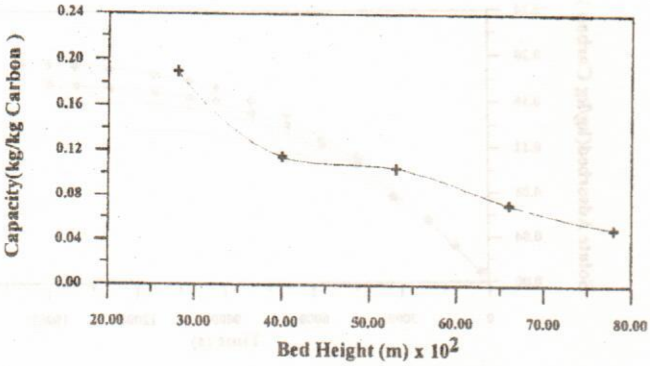
Five experiments were carried out at different flow rates; 27.526 x 10^{-6}, 40.209 x 10^{-6}, 52.893 x 10^{-6}, 65.570 x 10^{-6}, and 78.260 x 10^{-6} m^3/s. examining Figs.12, 13, and 14, it can be seen that there is a marked increase in the rate of adsorption and the capacity of activated carbon with decreasing flow rate.



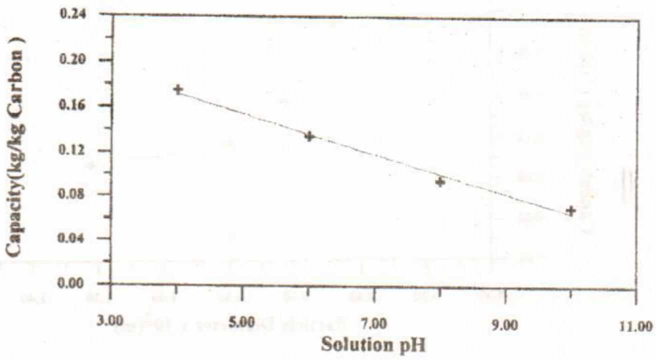
Fig(12) Breakthrough Curves of Phenol for Flow Rate Effect



Fig(13) Cumulative Adsorption of Phenol at Different Flow Rates



Fig(14) Adsorption Isotherm of Phenol onto Activated carbon



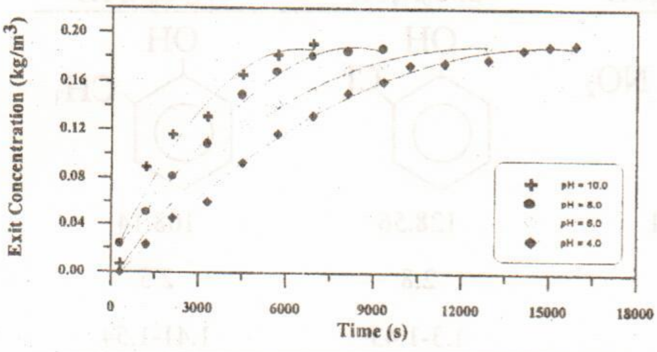
Fig(17) Adsorption Isotherm of Phenol onto Activated carbon

Effect of Solution pH

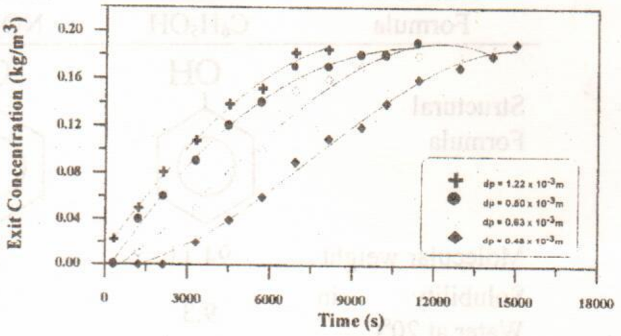
Four experiments were carried out with different solution pH; 4, 6, 8, and 10. From Figs. 15, 16, and 17, it can be seen that the total amount of solute removed from solution at any period of time and carbon capacity at equilibrium increases with decreasing pH. This is due to the fact that most carbons bear net negative charges, therefore, decreasing solution pH will cause neutralization of the negative charges at the surface of the carbon with increasing hydrogen-ion concentration, thereby, reducing hindrance of diffusion and making available more of the active surface of the carbon. Also lower pH conditions can enhance the suppression of the phenol ionization and the ionized (neutral) solute is adsorbed more readily than the ionized solute.

Effect of Particle Size

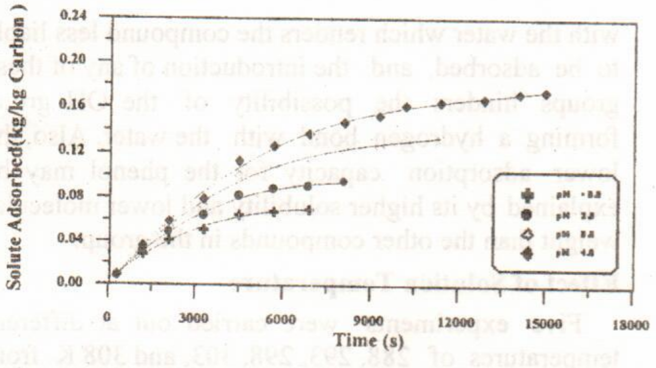
Four experiments were carried out at different particle diameters of 1.22×10^{-3}, 0.80×10^{-3}, and 0.48×10^{-3} m. Examining Figs. 18, 19, and 20, it can seen that the rate of adsorption, the total quantity of solute removed from the solution at any period of time, and carbon capacity at equilibrium increases with decreasing the particle size of the activated carbon. This is because adsorption is a surface phenomenon, as such, the extent of adsorption is proportional to specific surface area (portion of total surface area that is available for adsorption) which is larger with small particle size.



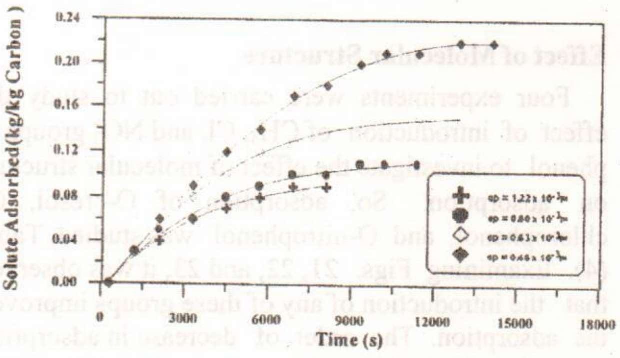
Fig(15) Breakthrough Curves of Phenol for pH Effect



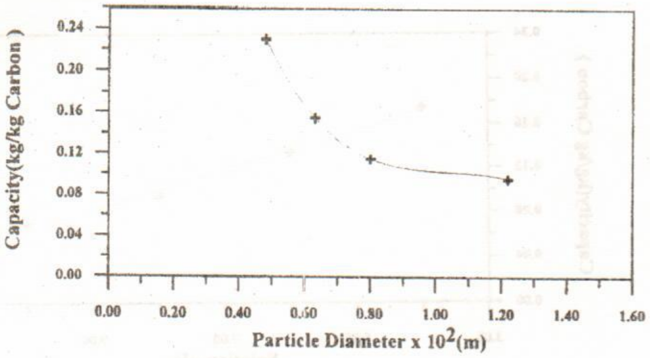
Fig(18) Breakthrough Curves of Phenol for Particle Size Effect



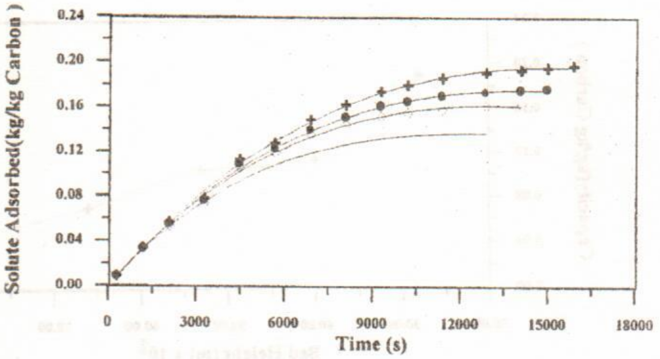
Fig(16) Cumulative Adsorption of Phenol at Different Solution pH



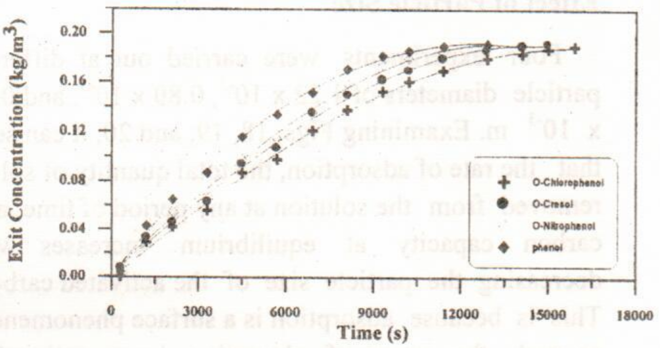
Fig(19) Cumulative Adsorption of Phenol at Different Adsorbent Particle Size



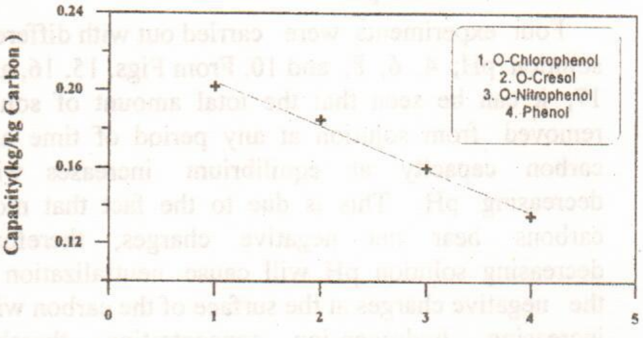
Fig(20) Adsorption Isotherm of Phenol onto Activated carbon



Fig(22) Cumulative Adsorption of Phenol at Different Molecular Structure

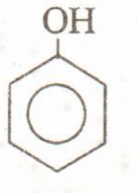
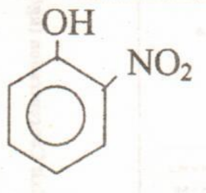
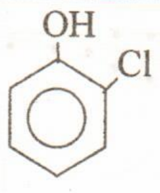
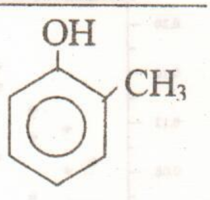


Fig(21) Breakthrough Curves of Phenol for Molecular Structure Effect



Fig(23) Adsorption Isotherm of different Pollutants onto Activated carbon

Table (4) Some Characteristics of the different adsorbates used in the present work

Molecular Formula	Phenol C_6H_5OH	O-Nitrophenol $NO_2.C_6H_4OH$	O-Chlorophenol $Cl.C_6H_4OH$	O-Cresol Cl. $CH_3.C_6H_4OH$
Structural Formula				
Molecular weight	94.11	139.11	128.56	108.14
Solubility in Water at 20°C	9.3	0.2	2.8	2.5
Dipole Moment	1.55-1.73	3.1	1.3-1.43	1.41-1.54

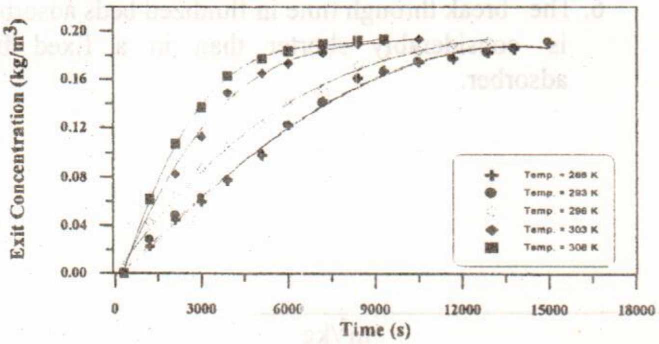
Effect of Molecular Structure

Four experiments were carried out to study the effect of introduction of CH_3, Cl, and NO_2 groups to phenol to investigate the effect of molecular structure on adsorption. So, adsorption of O-cresol, O-chlorophenol, and O-nitrophenol was studied, Table (4). Examining Figs. 21, 22, and 23, it was observed that the introduction of any of these groups improved the adsorption. The order of decrease in adsorption was: Cl > CH_3 > NO_2 > OH.

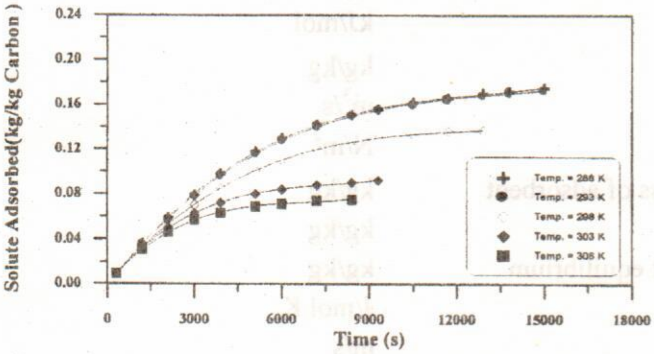
The adverse effect of the OH group on the adsorption of phenol may be attributed to the capability of this group to form hydrogen bonding with the water which renders the compound less liable to be adsorbed, and the introduction of any of these groups hinders the possibility of the OH group forming a hydrogen bond with the water. Also, the lower adsorption capacity for the phenol may be explained by its higher solubility and lower molecular weight than the other compounds in the group.

Effect of Solution Temperature

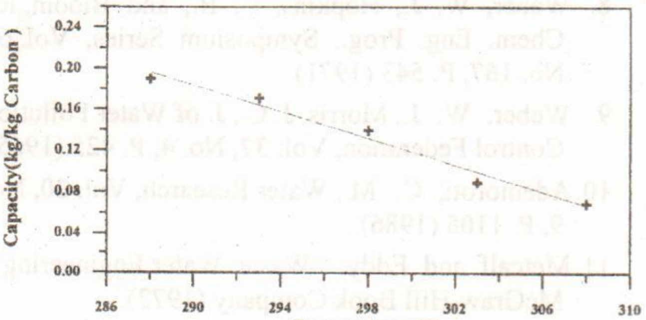
Five experiments were carried out at different temperatures of 288, 293, 298, 303, and 308 K. from Figs. 24, 25, and 26, it can be seen that the total quantity of solute removal from the solution and carbon capacity increases as the temperature decreased which is applicable for most exothermic systems.



Fig(24) Breakthrough Curves of Phenol for Temperature Effect



Fig(25) Cumulative Adsorption of Phenol at Different Temperatures



Fig(26) Adsorption Isotherm of Phenol onto Activated carbon

Equilibrium Isosters and the Isosteric Heat of Adsorption

The equilibrium isosters were obtained by plotting the concentration C against the temperature T, Fig.(27), for different values of the capacity q (0.05, 0.06, and 0.07 kg/kg carbon) of carbon.

This was achieved by obtaining c for temperature 288, 293, 298, 303, and 308 K for a given value of q. The heat of adsorption (ΔH) for the phenol-carbon system was calculated by using Clasius-Clapeyron equation, Eq.4.

$$\Delta H = -R\,\frac{(\partial \mathrm{LnC})}{\partial(1/T)_q} \quad \ldots(4)$$

This was carried out by plotting LnC against 1/T for different values of the capacity, Fig.(28). The values of ΔH were calculated from the slopes of the straight lines obtained.

Heat of adsorption of phenol was equal to 41.1 kJ/mol (9.822 kcal/mol), which indicates that the adsorption of phenol on activated carbon was of a physical nature.

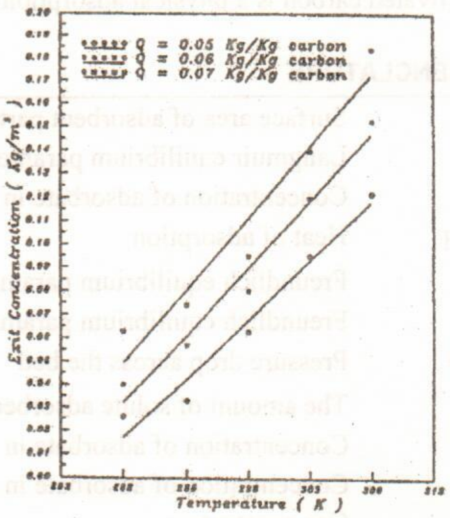


Fig.(27) Equilibrium Isosters of Phenol on Carbon

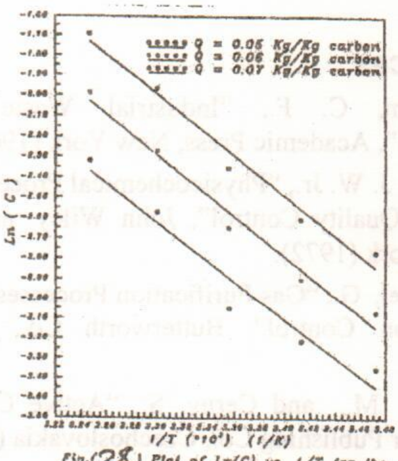


Fig.(28) Plot of Ln(C) vs. 1/T for the Determination of the Heat of Adsorption for Phenol

for temprature (288.293,303. and 308k) for a n (ΔH) for the phenol-carbon system was on. eqn.(4):

CONCLUSION

1. The equilibrium isotherm for phenol-activated carbon was of a favorable type, and was well represented bu Langmuir and Freundlich's equations.
2. The caapcity of activated carbon increased by increasing influent concentration of solute, increasing bed height, decreasing flowrate of influent, decreasing solution pH, decreasing

particle size, and decreasing temperature of influent.

3. The rate of mass transfer increased by increasing influent concentration, increaing bed heigh, increasing flowrate of influent, decreasing pH, decreasing particle size and nearly constant with increasing temperature.
4. Heat of adsorption was found to be 41.1 kJ/mol which confirms that adsorption of phenol onto activated carbon is a physical adsorption.
5. The hydrogen bonding between the solute and the water has a major effect on the adsorption by activated carbon.
6. The break through time in fluidized beds adsorber is considerably shorter than in a fixed bed adsorber.

NOMENCLATURE

a	Surface area of adsorbent particle	m^2/kg
b	Langmuir equilibrium parameter	m^3/kg
c	Concentration of adsorbate in fluid phase	kg/m^3
ΔH	Heat of adsorption	kJ/mol
k	Freundlich equilibrium parameter	kg/kg
1/n	Freundlich equilibrium parameter	m^3/s
ΔP	Pressure drop across the bed	N/m^2
Q	The amount of solute adsorbed per unit mass of adsorbent	kg/kg
q	Concentration of adsorbate in solid phase	kg/kg
q_e	Concentration of adsorbate in solid phase at equilibrium	kg/kg
R	Gas constant	J/mol K
U_{mf}	Minimum fluidizing velocity	m/s

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