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Removal of Some Hydrocarbon Pollutants from Baiji Oil Refinery Wastewater Using Granular Activated Carbon Column

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ABSTRACT

Petrochemical industry, specially oil refineries produces large quantities of wastewater that is strongly polluted with hydrocarbon compounds. Although Baiji oil refinery has wastewater treatment plant, it discharges water to Tigris river that is strongly polluted with hydrocarbon compounds that exceed the Iraqi permissible limits. Thus the aim of the present work is to remove phenol, parachlorophenol, and benzene from the wastewater of Baiji oil refinery using granular activated carbon(GAC)column. A laboratory scale apparatus is designed and constructed in order to perform this study taking into account the ability to control the most important parameters affecting adsorption process. Actual wastewater samples taken from the final discharge point of wastewater treatment unit of Baiji oil refinery are used to conduct all experiments.

The results indicated that these pollutants could be removed completely. Moreover, it indicates that breakthrough and exhaustion time are directly proportional with GAC thickness and inversely proportional with pollutants concentration and liquid hourly space velocity (LHSV). The results show that maximum breakthrough time is 39.26, 21.35, and 16.58 hours at LHSV of 0.5 hr^{-1} and 35cm of GAC thickness for phenol, parachlorophenol, and benzene respectively. The corresponding minimum breakthrough time is 9.24, 5.23, and 6.08 hours at LHSV of 129 hr^{-1}. However, the corresponding maximum exhaustion time is 49.6, 48.7, and 43.84 hours, while the minimum exhaustion time are 27.5, 16.54, and 10.89 hours. The results show that breakthrough time for phenol is 27.23 hours when the phenol inlet concentration is 5.212 mg/l, it decreased to 13.83 hours at inlet phenol concentration of 19.31 mg/l. The corresponding exhaustion time is 68.83 and 37.22 hours. Other two pollutants have similar trend. Based on the experimental data, dynamic adsorption capacities are calculated and found to be increased with the increase of pollutants concentration and LHSV. It is also found that calculated adsorption zone thickness is proportional with LHSV. The calculated maximum dynamic carbon adsorption capacity are 115.4, 67.62, and 12.628 mg/g for phenol, parachlorophenol, and benzene respectively at LHSV of 129 hr^{-1}. The corresponding minimum capacity at LHSV of 0.5 hr^{-1} are found to be 1, 0.99, and 0.257 mg/g. Calculated values of minimum and maximum adsorption zone thickness for the three pollutants at LHSV of 0.5 and 129 hr^{-1} are (0.0729, 0.1965, and 0.2176) and (0.2324, 0.2118,and 0.1545)cm respectively.

Application of the most famous the adsorption models shows that only Freundlich model gives excellent agreement with experimental data. Finally, new three models are developed. The first and second relate breakthrough and exhaustion time with LHSV, wastewater pollutants

concentration, and GAC thickness while the third relates adsorption velocity with LHSV and inlet pollutant concentration.

Keywords: Adsorption, Hydrocarbon pollutants, GAC, Oil refinery wastewater.

NOMENCLATURES

LHSV Liquid hourly space velocity, hr^{-1}
C Outlet pollutant concentration at any time, mg/lit.
C_{Br} Breakthrough pollutant concentration mg/lit.
C_{EX} Exhaustion pollutant concentration, mg/lit.
C_o Initial inlet concentration, mg/lit.
$K_{L.a}$ Mass transfer constant, sec^{-1}
T_B Breakthrough time, hours
T_E Exhaustion time
H Thickness of activated carbon, cm
n,K Constants of Freundlich model, dimensionless
x Mass of adsorbed pollutants, mg
M Mass of activated carbon, gram
V_{ads} Adsorption velocity, cm/min.
σ Adsorption zone thickness, cm

INTRODUCTION

Adsorption is defined as the transfer of a material from liquid or gas phase onto solid surface [2, 7,9,10]. This phenomenon is used extensively to separate different pollutants from gas and liquid phases [6, 26]. Adsorption phenomenon takes place into three steps. In the first step, the adsorbate is transferred to the outer surface of the adsorbent while in the second step the adsorbate is transferred into the pores of the adsorbent. In the final step, the adsorbate is transferred onto the inner surface of the adsorbent[22]. Powdered activated carbon (PAC) and (GAC) had been used extensively to remove different types of pollutants from water and wastewater [4].

Esmail 2008 used GAC and imperlyte XAD4 with glass beeds in order to remove phenol and methylene dye blue from water. She stated that using 5% of glass beeds improved the results significantly (increased operating time by 80%). She also stated that Langmuir model gives acceptable agreement with experimental data.

Waadalla 2006 performed a study to remove phenol, furfural, and parachlorophenol from Dura oil refinery wastewater using GAC. She found that breakthrough time increased with GAC thickness and decreased with the increase of pollutants concentration and flow rate.

GAC has been used by Wen His.Cheng 2008 to remove toluene. He found that adsorption capacity is directly proportional with contact time.

Hameed and Rahman 2008 used GAC to remove phenol at 30°C, pH of 3-10 and phenol concentration of 25-300 mg/l. They found that Langmuir, Dublinin, Temkin, Radushevich, and Freundlich models represent experimental data acceptably. They found that maximum adsorption capacity is about 150 mg/g.

Pananicolaou et al. 2007 stated that adsorption is more efficient for adsorption of higher surface area and long chain hydrocarbons adsorbed more efficiently than shorter chain hydrocarbons.

Rajoriya et al. 2007 tried to remove Benzyldedyde from water using GAC. They found that the removal efficiency increased with contact time and quantity of GAC. They stated that adsorption capacity increased with temperature decrease and Temkin model represent experimental data fairly.

Paual et al. 2007 performed a study on water containing 113 organic pollutants include pharmaceutical, hydrocarbons, and pesticides. They used GAC to treat this water which is found to be capable of removing 53% of these pollutants.

Jae Kwang Lee et al. 2003 used different types of activated carbon to remove certain heavy metals such as lead, cadmium, and chromium. They found that 98% removal

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efficiency could be obtained. The most important parameters affecting adsorption and used in the design of full scale adsorption units are investigated by different authors [1,8,16,9,12,17,24,25]. These parameters are LHSV, GAC thickness, and inlet pollutant concentration. Breakthrough and exhaustion time are found to increase with the increase of GAC thickness [9,17]. They are found to be increased with the decrease of LHSV [8,9,25] and decrease of inlet pollutant concentration [1,12,16,24]. Kwan-Yeop et.al. 2009 found that micro filtration could not remove color and certain organic compounds, thus he used micro filtration-Granular Activated Carbon to remove these pollutants. Although Baiji oil refinery has wastewater treatment plant, however, it discharges water to Tigris river that still contain hydrocarbon pollutants above the Iraqi permissible limits. Thus, the main target of this work is to reduce these pollutants level below the permissible limits.

Experimental Apparatus and Procedure

Fig.(1) represents a schematic diagram of the laboratory apparatus which is designed and constructed to perform the present work. It consists of the following parts:

- Wastewater tank: it is used to store the actual wastewater samples taken from the effluent point of wastewater treatment plant of Baiji oil refinery. It is of 60× 60 ×50 cm dimensions made of galvanized steel.
- Pump: it used to pump the wastewater to be treated to the GAC column which gives maximum flow rate of 30 liter/min.
- Flow meter: It is made by cryotek srl company type10C used to measure the flow rate.
- Column: It is of 120cm length and 4cm^2 cross sectional area provided with many sampling valves
- Inlet and outlet valves .
- Treated water storage with the same dimensions and characteristics of the wastewater storage tank.

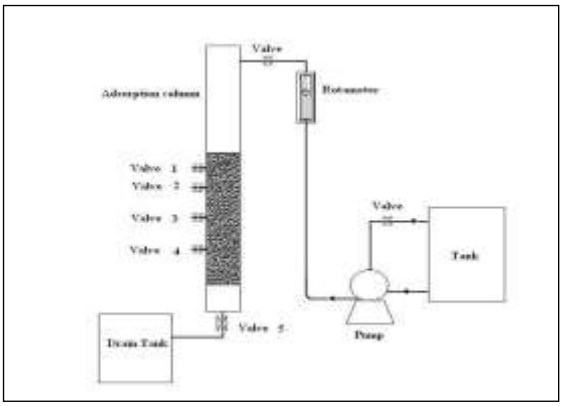

Fig.1 Schematic Diagram of the Experimental Apparatus

GAC: supplied from Unicarbon company (Table.1 shows the characteristics of this GAC). It is rested on a plate made of Perspex. Thickness of GAC is 35cm and sampling valves are located at 5, 10, 20, and 30 cm from the top of GAC surface.

Table(1) Physical Properties of GAC

Value	Property
482.025 Kg/m^3	Density
0.41	Porosity
(2-3)mm	Particle Size
1175.62 m^2/gm	Surface Area

UV Spectrephometer used to measure the pollutant concentration according to ASTM standard is supplied by Thermo orion company. The laboratory apparatus is designed to enable certain parameters to be controlled such as liquid hourly space velocity (LHSV), inlet pollutants concentration and GAC thickness. Table (2) includes operating parameters for the three pollutants (phenol, parachlorophenol, and benzene) that are

Table (2) Operating Conditions for Adsorption Experiments

Run No.	Inlet concentration(mg/l)			Liquid hourly space velocity(hr^{-1})
	Phenol	parachloro phenol	Benzene	
1	23.100	22.300	5	0.5
2	23.245	19.675	6	1.5
3	22.775	20.897	6.765	3.0
4	19.310	18.540	5.765	25.0
5	10.324	9.879	3.022	25.0
6	5.212	5	2.657	25.0
7	18.543	17.665	5.698	75.0
8	21.124	21.345	4.594	129.0

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used in this study. All experiments are performed under room temperature and pH of 7. Eight experiments are conducted in this work. However, and since the GAC column is provided with 5 sampling ports located at different locations of the column, therefore, in each experiment, five samples are taken at each time interval that enable us to study the effect of GAC thickness. Thus, the number of experiments are 40.

At the beginning, GAC had been washed and cleaned using distilled water then dried before being packed into the column. Actual wastewater sample is put into the storage after treated with alum to allow suspended solids to be removed, then pH is adjusted to 7.0 before being pumped at desired flow rate into the column. Samples are taken continuously at a predesigned time intervals from the side and outlet valves. Then after, the concentration of phenol, parachlorophenol, and benzene are measured.

RESULTS AND DISCUSSION

The adsorption curves are given in Figs. (2-4). The effluent concentration (C) is zero for all pollutants up to certain point then the outlet concentration is increased with time until it is equal to the initial inlet pollutant concentration (C_o). Breakthrough and exhaustion pollutants concentration (C_{BT}, C_{Ex}) are equal to 5% and 95% of initial pollutant concentration respectively. C_{BT} and C_{EX} are calculated to find breakthrough and exhaustion time (T_B and T_E).

T_B and T_E are plotted as a function of LHSV for the three pollutants on Figures (5 and 6) respectively. These two Figures indicate that these times are increased with the decrease of LHSV. Same trend is obtained by Walker, Weatherley1998, Gupta Nanoti and Goswami2001, Waadalla 2006 and Gupta and Babu 2006, Rajoriya et al. 2007. Moreover, the effects of LHSV above 15 -20 hr^{-1} on T_B and T_E are small. This is due to the fact that higher LHSV gives lower contact time between GAC and pollutants allowing only smaller quantities of pollutants to be adsorbed. For high LHSV (above 15-20 $hr^{-1)}$, the available time for adsorption becomes smaller. The third mechanism of mass transfer is the slowest

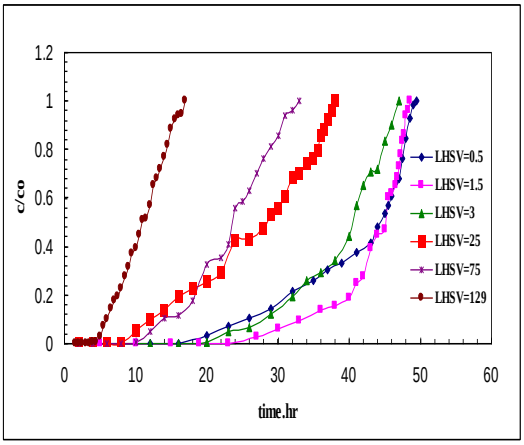

Fig2. Adsorption Curves of Phenol on GAC, GAC thickness

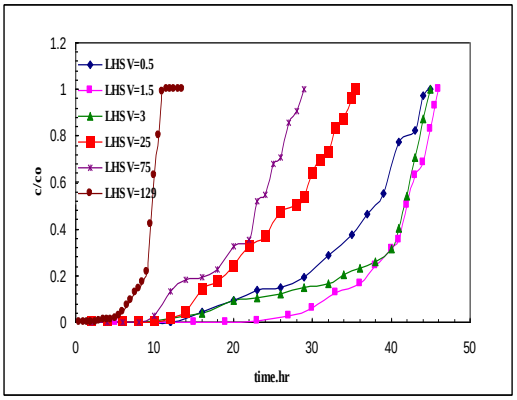

Fig. 3 Adsorption Curves of Parachlorophenol on GAC, GAC Thickness Equal 35 cm

and governing mechanism, thus, at this region (high LHSV), the adsorption mechanism have no enough time allowing more and more pollutants to escape. On the contrary, for low LHSV there is enough contact time enabling the three mechanisms to work allowing more pollutants to be adsorbed. Figs. (2-4) show that for LHSV of 0.5 hr^{-1} for phenol, parachlorophenol, and benzene needs about 50, 50, and 45 hours

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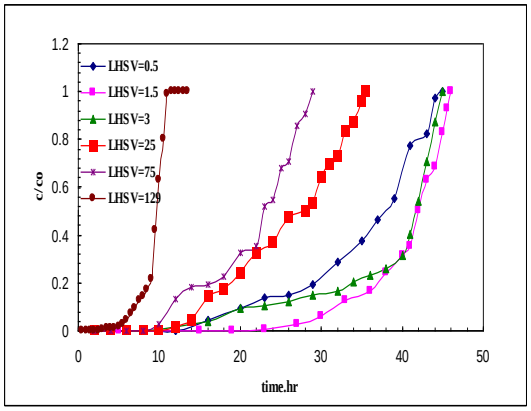

Fig.4 Adsorption Curves of Benzene on GAC, GAC Thickness Equal 35 cm

respectively to reach exhaustion point. On the other hand, at LHSV of 129 hr^{-1} they need about 30, 15, and 10 hours respectively to reach exhaustion point. This means that the higher LHSV is the faster to reach exhaustion point. At high LHSV some of the adsorption sites are left unsaturated allowing pollutants to go out. Figs.(2-4) also show that the exhaustion time of phenol is the largest followed by parachlorophenol and benzene. This is due to two reasons, the first is the molecule size of phenol is smaller than that of parachlorophenol. The other reason is the adsorption ability of benzene is less than that of the other two compounds.

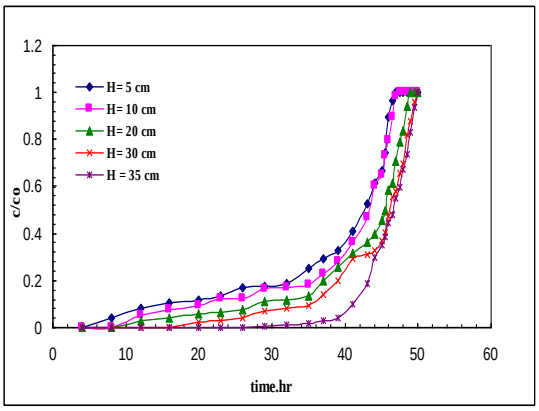

Fig.5 Relation Between Breakthrough Time and LHSV(Thickness=35 cm)

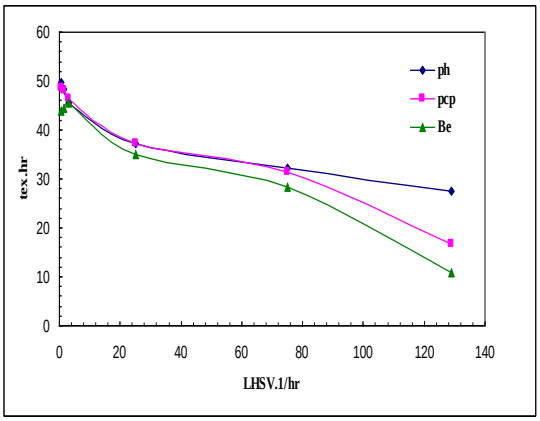

Fig.6 Relation Between Exhaustion Time and LHSV, Thickness=35 cm

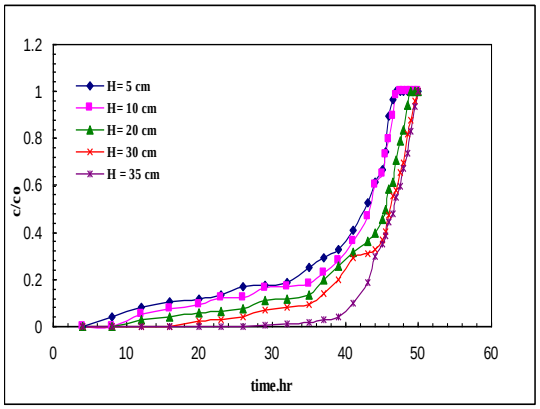

Fig.7 Adsorption Curves of Phenol at LHSV Equal 0.5 hr^{-1}

Figs. (7-9) represent the relation between the outlet pollutants concentration with GAC thickness at LHSV of 0.5 hr^{-1}. Data for other LHSV are of similar trend. The required time to reach breakthrough and exhaustion are found and plotted as a function of GAC thickness on Figures (10-12) for LHSV of 0.5 hr^{-1}. Data for other LHSV are of similar trend. These figures show that breakthrough and exhaustion time are increased with increasing GAC thickness since the available adsorption sites are increased as the GAC thickness increased. Moreover, as the thickness is increased, the contact time is increased allowing more pollutants to be adsorbed. This trend is confirmed by the results of Gupta Nanoti and Goswami 2001, Malkoc and Nuhoglu 2006, Waadalla 2006, and Rajoriya et al. 2007. It is obvious from Figs. (7-9) that the adsorption curves for

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phenol is the steepest followed by parachlorophenol and phenol i.e. the outlet concentration of phenol is low till about 40 hours then it increased sharply. This indicates that phenol is more favorable to be adsorbed than parachlorophenol and benzene.

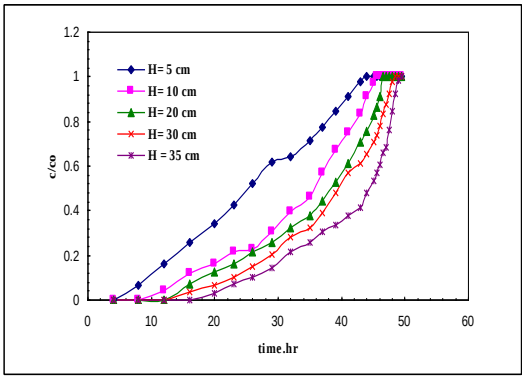

Fig.8 Adsorption Curves of Parachlorophenol at LHSV Equal 0.5hr^{-1}

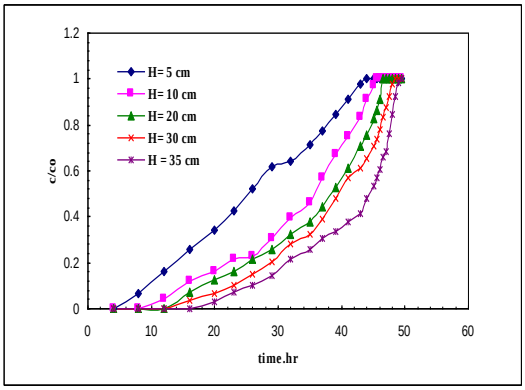

Fig.9 Adsorption Curves of Benzene at LHSV Equal 0.5hr^{-1}

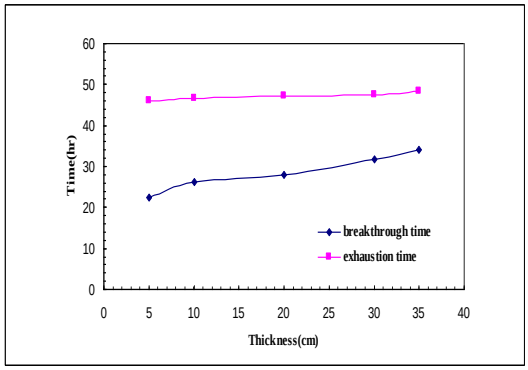

Fig.10 Relation Between Breakthrough and Exhaustion Time for Phenol And GAC Thickness, (LHSV=1.5hr^{-1})

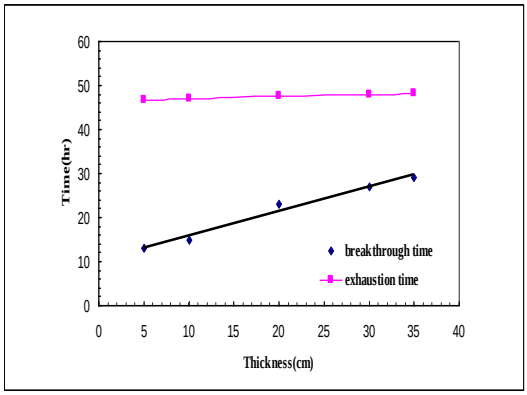

Fig.11 Relation between Breakthrough and Exhaustion Time for Parachlorophenol and GAC Thickness, (LHSV=1.5hr^{-1})

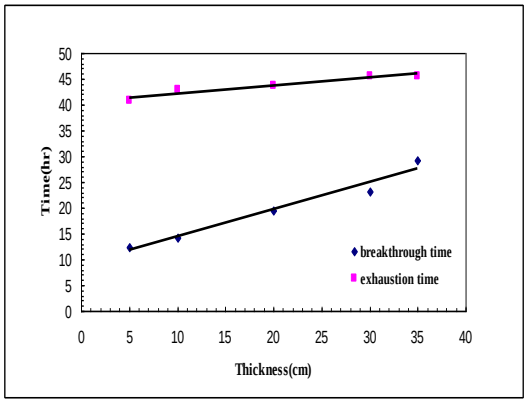

Fig.12 Relation Between Breakthrough and Exhaustion Time for Benzene and GAC Thickness, (LHSV=1.5hr^{-1})

Figs. (13-15) show that increasing pollutants concentration will reduce the breakthrough and exhaustion time. As the inlet pollutant concentration increased, GAC is saturated faster and faster due to the increase of the driving force (C_o-C).

$$dc/dt = K_{La}(C_o - C) \quad \text{.....(1)}$$

Same trend is found by Ivars, N., 1976, Lin, S. H., Wang, C.S. 2002, Babu 2004, Waleed 2004 Babu, B.V. and Ramakrishna, 2004, and Waadalla 2006.

From the above discussion, it is obvious that breakthrough and exhaustion time are both directly proportional with GAC thickness and inversely proportional with the inlet pollutant concentration and LHSV.

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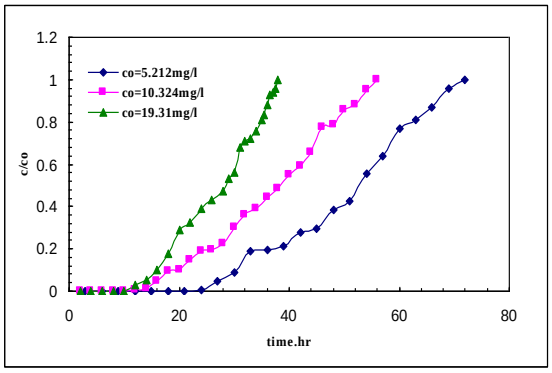

Fig.13 Adsorption Curves of Phenol on Activated Carbon(Thickness=35 cm)

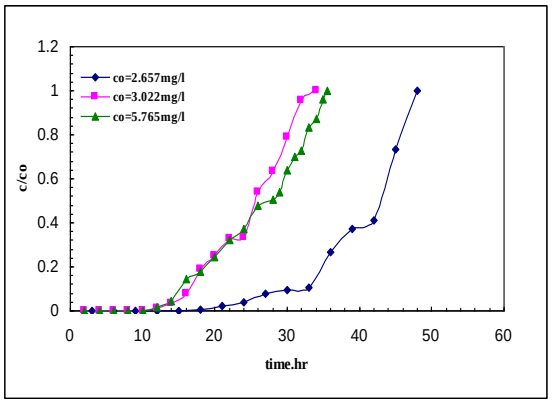

Fig.14 Adsorption Curves of Parachlorophenol on Activated Carbon(Thickness=35 cm)

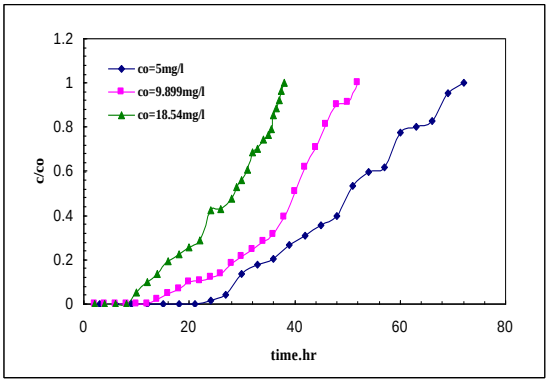

Fig.15 Adsorption Curves of Benzene on GAC, (GAC Thickness Equal 35 cm)

Since T_B and T_E have great practical importance for engineers and there is no simple model that enable the engineers to determine them from operational parameters, a multivariable non linear regression computer program (Statistica-Software Windows 5.5, 1999) is used to develop such relation (Equations 2 and 3).

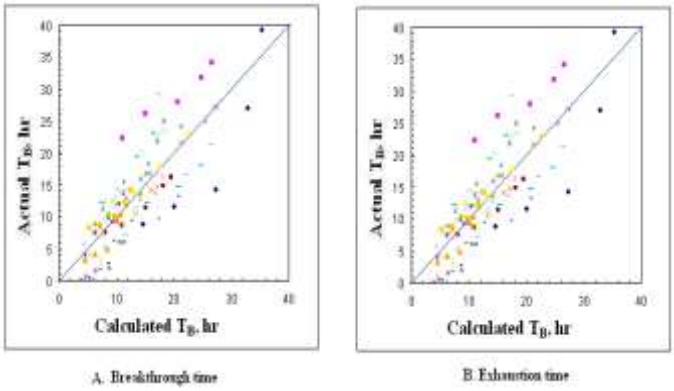

Fig.16 Relation Between Actual and Calculated Breakthrough and Exhaustion Time

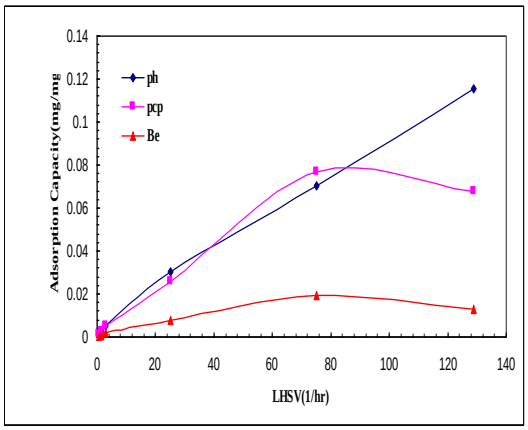

Fig.17 Relation Between Adsorption Capacity and LHSV for Phenol, Parachlorophenol, and Benzene

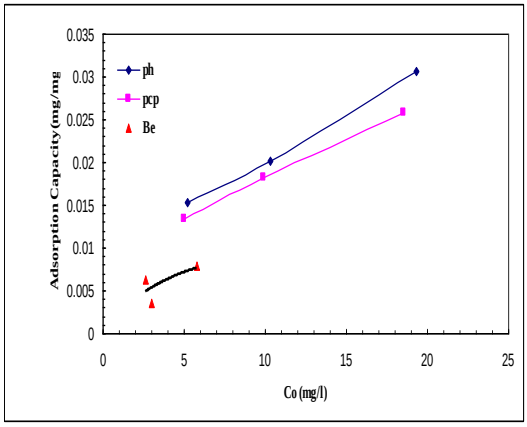

Fig.18 Relation Between Adsorption Capacity and C_O for Phenol, Parachlorophenol, and Benzene

The following procedure is followed to obtain this model.

Since T_B α LHSV, T_B α $1/C_o$, and T_B α 1/H and T_E α LHSV, T_E α $1/C_o$, and T_E α 1/H, moreover, there is no linear relation

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between these variables, thus, each independent variable is raised to certain exponent and lumped together to get Equations 2 and 3. The physical feasibility for the variables is checked and found to be right since the exponent for C_o and LHSV have negative sign, which means inverse proportionality and the exponent of H has positive sign which means direct proportionality.

$T_B = A\ H^M\ Co^N\ LHSV^S$ .....(2)

$T_E = A\ H^M\ Co^N\ LHSV^S$ .....(3)

Where

T_B, T_E = breakthrough and exhaustion time respectively, hrs.

A, M, N, and S = constants.

H = GAC thickness, (cm)

C_o = inlet pollutant concentration, (mg/l)

LHSV = Liquid hourly space velocity (hr^{-1})

Values of A, M, N, and S in addition to coefficient of correlation (R^2) for Equations (2 and 3) are listed in Tables (3 and 4) respectively. The calculated values for T_B and T_E are plotted against actual values on Figure (16) that indicates acceptable agreement. These two models can be used in designing full scale units acceptably and enable the engineers to determine the anticipated T_B and T_E depending on the practical operating conditions.

The most famous adsorption models (Freundlich, Langmuir[15], BET[3], Radke–PrauSnitz[20], Redlich – Peterson[23]) are used to find which of these models can represent the experimental data acceptably. None of them give acceptable agreement except Langmuir $\left[R^2 = 0.407 - 0.8405\right]$ and Freundlich model $\left[R^2 = 0.9028 - 1.0\right]$. Table (5) includes the constants for Freundlich model for phenol, parachlorophenol, and benzene. These models are designed to represent adsorption isotherms under equilibrium conditions while our data are taken under dynamic conditions.

Adsorption Capacity

Since it is found that only Freundlich model gives acceptable agreement with experimental data, it is used to find the adsorption capacity of GAC for these pollutants under different operating conditions. According to this model,

$$\log x/M = \log k + 1/n \log c \quad \text{.....(4)}$$

Where

x/M= mass of adsorbed pollutants to the mass of activated carbon.

$k, n =$ constants.

Plots of x/M versus c on log-log paper will give k and n. Entering C= C_o on X-axis, going vertically to the straight line, then read on Y-axis the adsorption capacity. Fig.(17) represents the relation between adsorption capacity with LHSV. This Figure show that adsorption capacity increased as LHSV is increased for the three pollutants. This is because as LHSV increased, the adsorbed pollutants is decreased and thus more adsorption sites are left empty. These adsorption sites are included in finding adsorption capacity. The above Figure also exhibit fast increase of adsorption capacity up to LHSV of about 20 hr^{-1}, then the increase becomes slower with LHSV. This means that the three adsorption mechanisms work together acceptably up to LHSV of 20hr^{-1} beyond this value, the third adsorption step (the governing step) has no enough time to work properly resulting in reducing the quantity of adsorbed pollutants. The above Figure clarifies that maximum and minimum adsorption capacity for phenol, parachlorophenol, and benzene are about 115, 67, and 12 mg/gr and 1, 1, 0.2 mg/gr respectively. This is also indicates that phenol is the most competent compound.

Fig.(18) represents the relation between adsorption capacity with the inlet pollutant concentration. It is found that adsorption capacity increased with the increase of inlet pollutant concentration. This is due to two reasons. The first is the increased of driving

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force as the inlet concentration is increased (Equation 1). The second reason is the increase of x/m with the increase of C according to Freundlich model (Equation 4).

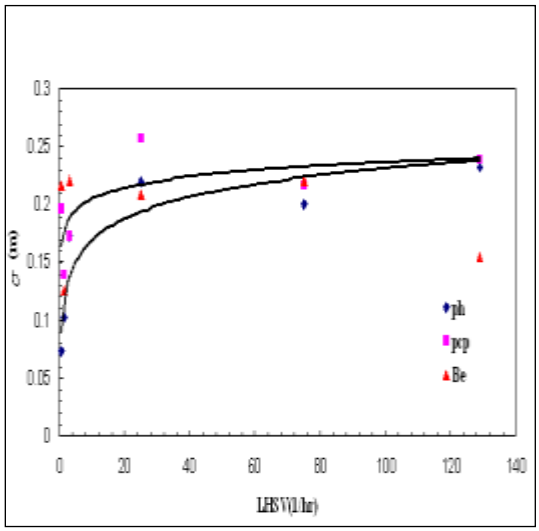

Fig.19 Relation Between Adsorption Zone Thickness and LHSV for Phenol, Parachlorophenol, and Benzene

Adsorption Zone Thickness(σ)

To find out σ, first we calculated adsorption velocity using Equation (5)[5] at different operating conditions.

$$V_{ads.} = H / T_E \qquad \text{.....(5)}$$

Then using Equation (6)[5], σ can be found

$$T_B = [H - \sigma]/V_{ads} \qquad \text{.....(6)}$$

The calculated values of σ are plotted against LHSV on Fig.(19). This figure shows that σ increased sharply with the increase of LHSV up to about 20 hr^{-1}, then it trends to level out . As σ increased, the breakthrough time is decreased according to Equation (6). On the other hand increasing σ will increase the left empty adsorption site. Smaller σ (at lower LHSV) means most of the available adsorption sites are occupied, i.e. more efficient adsorption.

Adsorption Velocity (V_{ads}) Model

Wark K. (1981) and Crawford M.(1976) gave similar models for adsorption velocity which are derived analytically. These models relate adsorption velocity with many parameters such as mass flow rate and inlet pollutant concentration. However, in order to use these models, it is required to perform many experiments to determine α and β (constants that characterize the shape of equilibrium curve). Non-linear regression analysis technique is used to develop new model for adsorption velocity (Equation 7) for the three studied pollutants. This model is also similar to the previously mentioned models of Kenneth Wark (1981) and Martin Crawford (1976)

$$V_{ads}=B\ LHSV^{d}C_o^{\ f} \qquad \text{.....(7)}$$

Values of B,d, and f for the three pollutants are listed in Table (6). Calculated values of V_{ads} using Equations 5 and 7 are drawn on Fig.(20) which gives acceptable agreement.

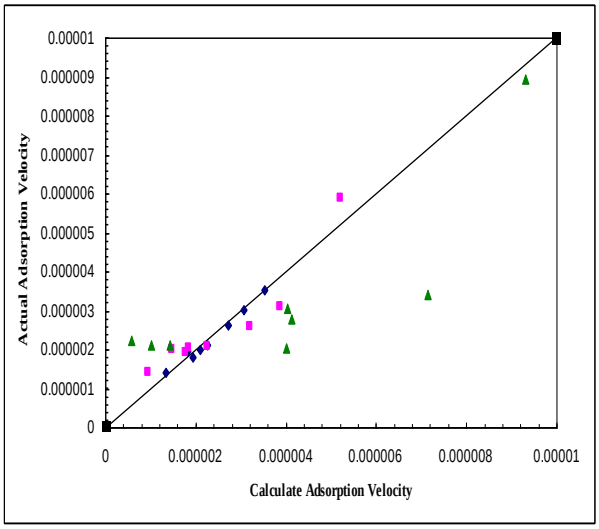

Fig.20 Relation Between Actual and Calculated Adsorption Velocityfor Phenol, Parachlorophenol, and Benzene

CONCLUSIONS

1. Breakthrough and exhaustion times are directly proportional with GAC thickness and inversely proportional with LHSV and inlet concentration.
2. Adsorption capacity is directly proportional with LHSV and inlet concentration.

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3. Adsorption zone thickness is increased with the increase of LHSV.
4. Phenol is more favorable to be adsorbed than parachlorophenol and benzene.
5. Freundlich model represents the experimental data acceptably.
6. New models are developed to relate T_B , T_E , and V_{ads} with the most important operating parameters.

REFERENCES

1. Babu, B.V., and Ramakrishna, "Dominant Design Variables and Modeling Parameters for Adsorption in Batch Studies", chem. conf., Mumbai, 2004.
2. Bhatia ,S. C., "Environment Pollution and Control in Chemical Process Industries", Khanna publisher, PP.(250- 260), 2001.
3. Brunaur, S. Emmett , P. H. and Teller , E.,(BET), "Adsorption of Gases in Multimolecular Layers", J. Amer, Chem. Soc., vol.(60), P.(309), 1938.
4. Cotruvo, .A. and Wu,C., "Environmental Protection Agency's view on the use of activated carbon to remove trace organic chemicals from drinking water, Activated Carbon Adsorption of Organic from the Aqueous Phase",Vol.(1) ,edited by Suffet ,I.H. and McGuire ,M.J.,Ann Arbor Science ,Michigan ,PP.(1-11),1981.
5. Crawford,M.,"Air Pollution Control Theory"**,** McGraw –Hill Inc., New York**,**US,PP.(514-517),March,1976.
6. Crittenden, T. C. Truss ell, R. R. Hand, D. W., Howe, K. J. and Techobanoglous, G., "Water Treatment Principles and Design", 2nd edition, John Wiley and sons, Inc., 2005.
7. Esmail, Sh., "Evaluation of Heterogeneous Adsorbents Bed for the Removal of Organic Materials from Water", Ph. D. Thesis, university of Baghdad PP.(4-39), Iraq, 2008.
8. Gupta, S. and Babu ,B.V., "Modelling and Simulation of Fixed Adsorption Column: Effect of Operating Variables", Department of Chemical Engineering Birla Institute of Technology and science pilani (Rajasthan), India,2006.
9. Gupta,A.,Nanoti ,O., and Goswami,A.N., "The Removal of Furfural From Water by Adsorption with Polymeric Resin", Separation Science and Technology,Vol(36),No.13,PP.(2835-2844),2001.
10. Hameed, B. H., and Rahman, A.A., "Removal of phenol from aqueous Solution by Adsorption onto Activated Carbon Prepared from Biomass Material", Applied science publishers LTD, Essex, chapter 3, PP.(49-84), 2008.
11. Hines A., Maddox R., "Mass Transfer Fundamentals and Applications", Prentice-Hall. Ins., 1985.
12. Ivars, N., "Analysis of Some Adsorption Experiments with Activated Carbon", chem. Eng. Sci. , 31, PP. (1029-1035), 1976.
13. Jae Kwang Lee, Geunpark, Seung kon Ryu and Joon Hyung kim, "Effect of Two-step Surface Modification of Activated Carbon of The Adsorption Characteristics of Metal Ions in Waste Water II. Dynamic Adsorption "Dept. of chemical engineering, Chungnam National university, Dee jean, 305-7649, Korea, vol.(4), No.1 PP.(14-20), March, 2003.
14. Kwan – Yeop Kim, Hyung- Soo Kim, Jihoon Kim, Jongss-woo Nam, Jin-Mo Kim and Sukil Son, "A hybrid Microfiltration –Granular Activated carbon System for Water Purification and Waste Water Reclamation Reuse", Department of civil, Archite ctural and Environmental system Engineering, Sunglcyunkwan university, suwon, Korea, 2009.
15. Langmuir, I. J., "The Adsorption of Gases on Plane Surfaces of Glass, Mica. and Platinum",Amer, chem. soc., vol.(40), PP.(1361), 1918**.**
16. Lin, S. H., Wang, C.S., "Treatment of High-Strenth Phenolic Waste Water by a New Two-Step Method" Journal of Hazardous materials,B90,PP. (205-216), 2002.
17. Malkoc, E., and Nuhoglu,Y., "Fixed Bed Studies for The Adsorption of Chromium (VI) onto Tea Factory Waste", Chemical Engineering Science,Vol.(61) ,PP.(4363-4372),2006.
18. Pananicolaou, C., Pasadakis, N., Dimon, D., Kalaitzidis, S., "Adsorption of No, SO_2, and Light Hydrocarbons on Activated Carbon Greek Brown Coals", Jour Environmental Engineering, ASCE,120, PP.(190-201), 2007.

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19. Paual E. Stacke lberg, Jacob Gibs, Edward T. Furlong, Michael T. Meyer , Steven D. Zaugg, R. Lee lippincoth, "Efficiency Convertional Drinking Water – Treatment Process in Removal of Pharmaceuticals and other Organic Compounds", science of the total Environmental 377, PP.(255-272), 2007.
20. Radke, C. J. and Prausnitz , J. M., "Adsorption of Organic Compounds from Dilute Aqueous Solution on Activated Carbon", Ind. Eng. Chemi. Fund., 11. PP.(445-451), 1972.
21. Rajoriya, R. K., Prasad, B., Mishrq. I. M., And wase war, K. L. , "Adsorption of Benzaldehyde on Granular Activated Carbon Kinetics, Equilibrium, Thermodynamic", Chemical Engineering Department, Indian , Institute of Technology(III), Q.21.(3), PP.(219-226), (2007).
22. Ramalho, R. S., "Tertiary Treatment of Waste Waters, introduction to waste Water treatment process", Academic press, Chapter8, PP.-(485-502), 1983
23. Waadalla, K., "Removal of Multi-pollutant from Waste water by Adsorption Method"), Ph. D. Thesis, university of Baghdad PP.(3-122), Iraq. 2006.
24. Waleed, M. A., "Designing of Pilot for Treatment of Waste Water Contaminated by Furfural", M.sc Thesis, University of Baghdad, 2004.
25. Walker, G.M, Weatherley, L.R., "Fixed Bed Adsorption of Acid Dyes onto Activated Carbon", Environmental Pollution,Vol.(99), PP. (133-136),1998.
26. Wark, K. and Warner, C. F., "Air Pollution, Its Origin and Control" Vol. (2), PP.(221-229), New York, (1976).
27. Wen-His cheng, "Adsorption Characteristics of Granular Activated Carbon and SPME Indication of Vocs Breakthrough", Department of occupational safety and Hygiene, fooyin university, kaohslung country, Taiwan, Republic of china., cheng . Aerosol, and Air Quality Research, vol.(8), No.2 , PP.(178-187), 2008.

Table1. Physical Properties of GAC

Property	Value
Density	482.025 Kg/m^3
Porosity	0.41
Particle Size	(2-3)mm
Surface Area	1175.62 m^2/gm

Table 2. Operating Conditions for Adsorption Experiments

Run No.	Inlet concentration(mg/l)			Liquid hourly space velocity(hr^{-1})
	Phenol	parachlorophenol	Benzene	
1	23.100	22.300	5	0.5
2	23.245	19.675	6	1.5
3	22.775	20.897	6.765	3.0
4	19.310	18.540	5.765	25.0
5	10.324	9.879	3.022	25.0
6	5.212	5	2.657	25.0
7	18.543	17.665	5.698	75.0
8	21.124	21.345	4.594	129.0

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Table 3. Constant for Breakthrough Model, Equqtion 2

Pollutants	A	M	N	S	R^2
Phenol	28.2880	0.4510	-0.4971	-0.2535	0.737937
Parachlorophenol	31.9161	0.4305	-0.6041	-0.2238	0.777510
Benzene	9.2514	0.4445	-0.4973	-0.1283	0.538435

Table 4. Constant for Exhaustion Model, Equation 3

Pollutants	A	M	N	S	R^2
Phenol	104.3746	0.13588	-0.3750	-0.12286	0.844162
Parachlorophenol	122.4362	0.14269	-0.4493	-0.15048	0.806403
Benzene	25.8845	0.17990	-0.04282	-0.10980	0.523414

Table 5. Constant for Freundlich Model

Run No.	n for			K for			R^2 for		
	Ph	Pcp	Be	Ph	pcp	Be	ph	pcp	Be
1	0.9032	0.9514	0.9917	0.000032011	0.000037983	0.00005078	0.9997	0.9905	0.9586
2	0.9058	0.8958	1.1294	0.000092363	0.000088961	0.00015	0.9999	0.9989	0.9926
3	0.8989	0.8560	0.7428	0.00015	0.00014	0.00014	0.9983	0.9983	0.9947
4	0.7541	0.8195	0.8259	0.00057	0.00073	0.00095	0.9974	0.9921	0.9958
5	0.8329	1	0.8107	0.0021	0.0043	0.0022	0.9988	1	0.9951
6	0.8032	0.9886	1.2484	0.0011	0.0018	0.0014	0.9945	0.9589	0.9644
7	0.7474	1.2599	1.0203	0.0016	0.0037	0.0024	0.9975	0.9028	0.9482
8	0.7776	0.7732	0.8025	0.0022	0.0012	0.0018	0.9978	0.9917	0.9992

Table 6. Constant for Adsorption Velocity Model

Pollutants	B	D	F	R^2
Phenol	0.000015	0.127458	0.536709	0.9792
Parachlorophenol	0.000066	0.216532	0.933881	0.8656
Benzene	0.000001	0.5008	0.0379	0.6072

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