Phenol and Parachlorophenol Removal Using Granular Activated Carbon

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Abstract: The main goal of the present work is to remove phenol and parachlorophenol from synthetic solution using granular activated carbon (GAC). Two carbon types are used, the first is commercial supplied to Iraqi market by Spanish company (referred to as CGAC) and the second is manufactured using Iraqi waste material, referred to as MGAC. The experiments are performed according to batch and continuous mode (granular activated carbon adsorption column). The results show that both pollutants can be removed and the breakthrough and exhaustion times are proportional with the thickness of GAC and inversely proportional with the inlet pollutants concentration and surface over flow rate (SOR). The results also indicated that adsorption capacity is inversely proportional with SOR and it is directly proportional with the thickness of GAC column and pollutants concentration. MGAC gives better performance as compared with CGAC. In the present work, it is proved that adsorption capacity is a function of the operating conditions, carbon and adsorbent type and it is not pure carbon property. The results indicated also that Langmuir model fit the experimental data fairly.

Keywords: Phenol, Parachlorophenol, Adsorption, Granular Activated Carbon.

INTRODUCTION

Industrial wastewater, especially waste water of chemical and petrochemical industries contain slow or non biodegradable organic compounds which can't be removed by conventional treatment methods [1]. Phenolic compounds have dangerous effects on the environmental system as well as on human being [2].

Thus it is considered as a priority pollutants according to US EPA and EU EPA [3]. These two agencies recommended reducing the concentration of these compounds in drinking water to 0.001mg/l [4]. These compounds, if present in river water will react with chlorine, which is used in drinking water treatment units, producing chlorinated hydrocarbon compounds. These compounds are carcinogenic [5]. Drinking water treatment units are not capable in removing these compounds while adsorption units using activated carbon can remove them effectively. EPA considered this treatment method as the most efficient one in removing such compounds [6,7]. Tigris River suffers greatly from throwing wastewater of Baiji Oil Rrefineries, Fertilizer Company, Electric power Generation Company, as well as the petroleum leaks from petroleum pipe lines [8].

Al-An and Al-Baldawi [9] compared the performance of single and dual filtration pilot units operated under same condition to treat Tigris river water. They found that dual filters give better performance, lower pressure losses, and higher operating times, about three times of the single filter media.

Latif [10] used activated carbon as a filtration and adsorption medium and he compared the performance with that of sand filter. He stated that the result of filter used activated carbon gives better results than that of sand filter and of lower pressure losses and back wash water.

Al-Ani [11] used three types of filters, the first is sand filter, the second is activated carbon, and the third is dual media filter of sand and activated carbon. He concluded that the second filter is the best concerning adsorption, turbidity removal, length of operating time, and lower pressure losses.

Al-Najjar [12] used Ninvite local rock as an adsorbent and filtration medium. He compared th results with that obtained from activated carbon and anthracite coal. He concluded that activated carbon has greater adsorption capacity, however Ninvite proved its ability to give good organic compounds removal.

Thiel *et al*. [13] studied four dual media filters and they found that the filter of sand and activated carbon gives better results than the others concerning organic compounds removal.

Al-Rawi [14] compared the results obtained from different filters using different arrangements of sand anthracite coal. They found that anthracite coal gives little improvement of the filter performance.

Al-Raw [15] tried to replace rapid sand filter by dual media filter. He employed sand and anthracite as a filtration medium. The results show that the dual filter gives double production rate and reducing the required water for back wash.

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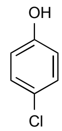
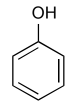
Table 1: Some Properties of Phenol and Parachlorophenol

Parachlorophenol	Phenol	Property
PCP	Ph	Symbole
C_6H_5OCl	C_6H_5OH	Chemical formula
		Structural formula
129	94.11	Atomic weight, gr/mole
28	66.7	Solubility in water at 20°C, gr/liter

2. EXPERIMENTAL PROCEDURE

Adsorption experiments are performed according to two schemes, the first is batch while the second is continuous using adsorption column (Figure **1**). In batch experiments, specific GAC dose is added to the previously prepared solutions of Phenol and Parachlorophenol. The solution is continuously stirred and the samples are taken at various time intervals to measure the concentration of the pollutants. This process is continued until the steady state is reached (pollutant concentration remains unchanged with time).

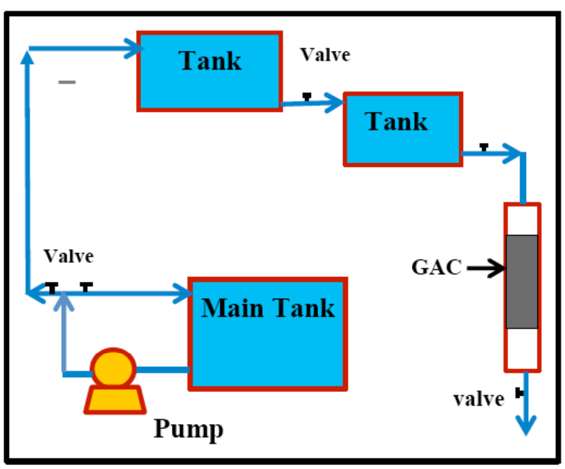


Figure 1: Schematic diagram of the unit.

Table **1** includes some properties of the pollutants. In adsorption column experiments, the prepared polluted water sample is allowed to flow at a predetermined flow rate and the outlet concentration is measured with time until its value is equal to the inlet concentration. Table **2** includes some properties of CGAC. The operating variables are inlet pollutants concentration, GAC thickness, and surface over flow rate (SOR). The ranges of the operating variables are listed in Table **3**. To cover these variables, 125 experiments are required. Thus Box-Wilson method is used to reduce the number of experiments.

Table 2: Some Properties of CGAC

Value	Property
383.2	Surface area
0.78	Effective size
1.372	Uniformity Coefficient

Table 3: Ranges of the Operating Variables

Range	Variable
5-25	Surface over floe rate, $m^3/m^2/hr$
1-25	Inlet concentration, mg/l
12-48	GAC thickness, cm

RESULTS AND DISCUSSION

The results of continuous adsorption scheme are listed in Table **4** and represented graphically on Figures **2** –[14].

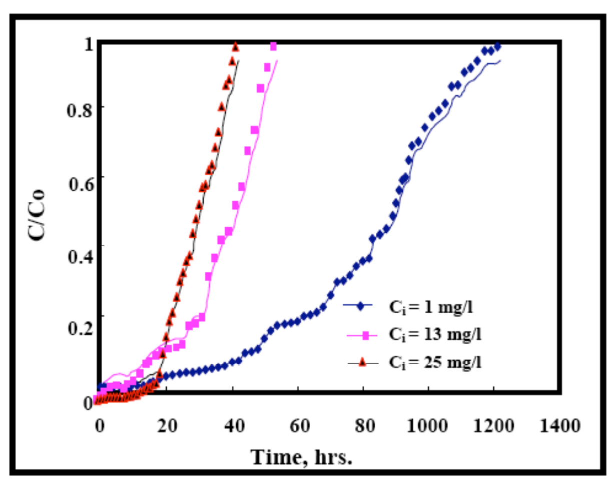


Figure 2: Phenol adsorption isotherm.

Figure **2** and **3** represent sample of the adsorption isotherms obtained from this study.

Table 4: Experimental Results Parachlorophenol

		Phenol		GAC thickness, cm	Inlet concentration, mg/l	SOR, $m^3/m^2/hr$	Run No.
TE, hr	TB, hr	TE, hr	TB, hr				
575	155	405	95	40.392	19.93	4.4717	1
405	32	265	20	19.608	19.93	4.4717	2
710	160	610	118	40.392	6.072	4.4717	3
525	180	470	70	19.608	6.072	4.4717	4
600	280	435	118	40.392	19.93	3.0283	5
412	65	355	32	19.608	19.93	3.0283	6
830	200	650	105	40.392	6.072	3.0283	7
610	140	510	100	19.608	6.072	3.0283	8
805	170	650	50	30	13	2.5	9
485	95	390	10	30	13	5	10
1155	320	1045	250	30	1	3.75	11
405	183	383	100	30	25	3.75	12
365	85	305	10	12	13	3.75	13
770	170	650	98	48	13	3.75	14
528	100	445	30	30	13	3.75	15

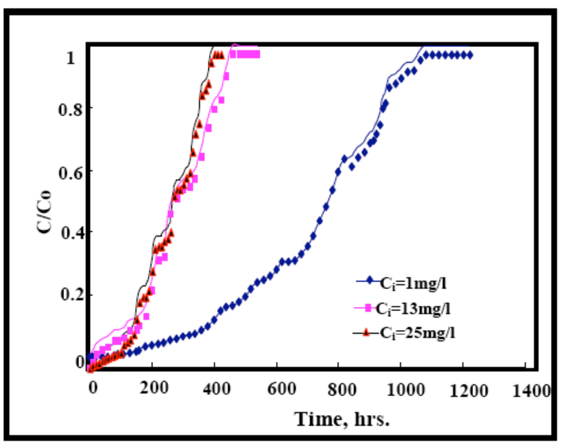


Figure 3: Parachlorophenol adsorption isotherm.

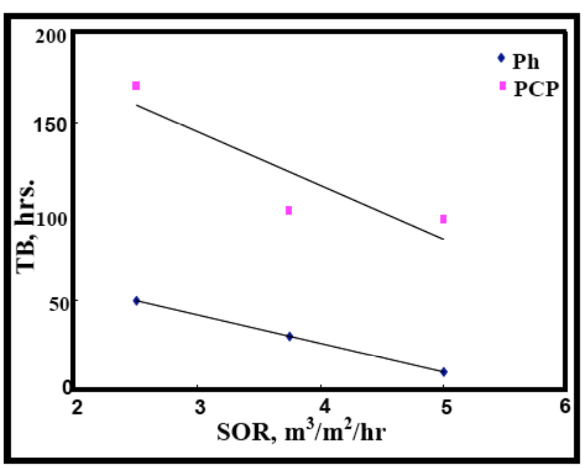


Figure 4: Relation between TB and SOR.

The Effect of SOR on TB

Figures **4** and **5** show that breakthrough (TB) and exhaustion time (TE) for phenol and parachlorophenol are inversely proportional with surface over flow rate (SOR). This is the same trend obtained by [16-18]. The required time to occupy all adsorption sites is not enough at high SOR. This leads to a reduction of both TB and TB with the increase of SOR. Figures **6** and **7** show that TB and TE at various SOR for parachlorophenol are higher than the corresponding values of phenol. This is due to the following reasons:

- The affinity of parachlorophenol with GAC is more than that of phenol i.e. it is more competence [19].
- The molecule of parachlorophenol is larger than that of phenol, this will lead to a more difficulty in transporting from the outer surface of GAC to the final inner adsorption sites (needs more time). This is results in leaving more adsorption sites empty as compared with that for phenol.
- The adsorption capacity for parachlorophenol is higher than that of phenol leading to adsorption of larger quantity.
- Parachlorophenol, as a result of its lower solubility in water as compared with phenol has higher affinity and more competence. Thus, the adsorption isotherm of parachlorophenol is more flat than that of phenol as it is clear from Figures **2** and **3**.

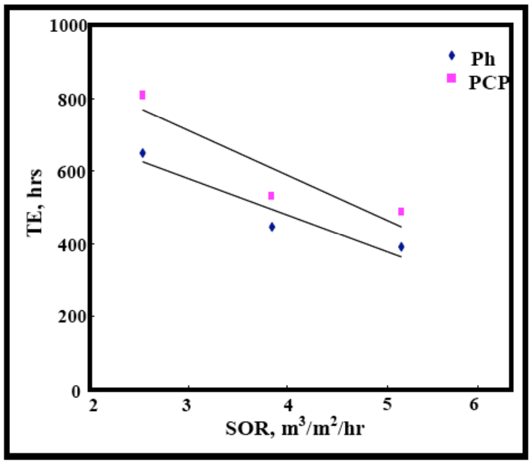


Figure 5: Relation between TE and SOR.

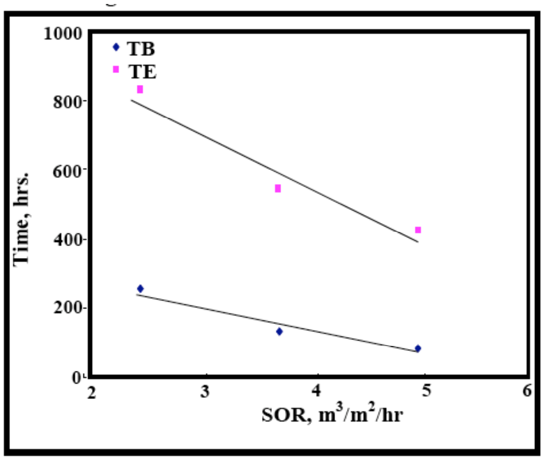


Figure 6: The effect of SOR on TB and TE of phenol.

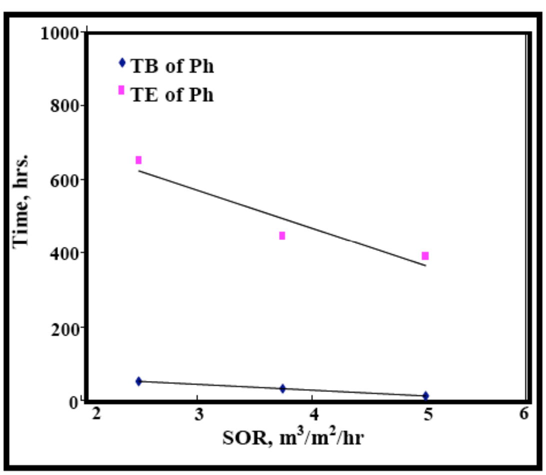


Figure 7: The effect of SOR on TB and TE of parachlorophenol.

Effect of Inlet Concentration on TB and TE

Figures **8** and **9** show that both TB and TE are decreased when the inlet concentration of phenol and parachlorophenol are increased. This is the same trend obtained by [8,20,21]. This is due to the fact that lower concentration gives more chance for the three adsorption mechanisms to work. Moreover, higher concentration will lead to a more driving force for the adsorption process according to:

$$\frac{dC}{dt} = \mathbf{k}(\mathbf{C}_\mathrm{i} - \mathbf{C}_\mathrm{t}) \tag{1}$$

Where:

C = pollutant concentration, mg/l

C_i = inlet pollutant concentration, mg/l

C_t = pollutant concentration at any time, mg/l

k = mass transfer coefficient

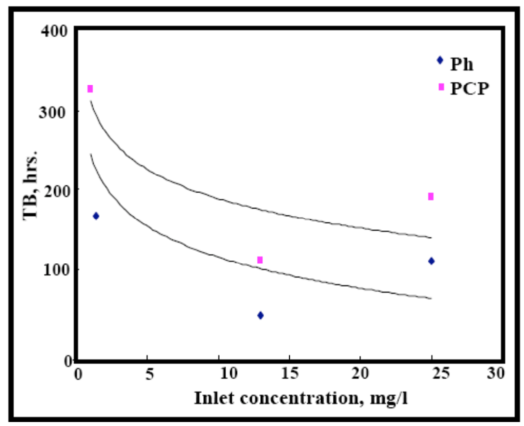


Figure 8: Effect of inlet pollutant concentration on TB.

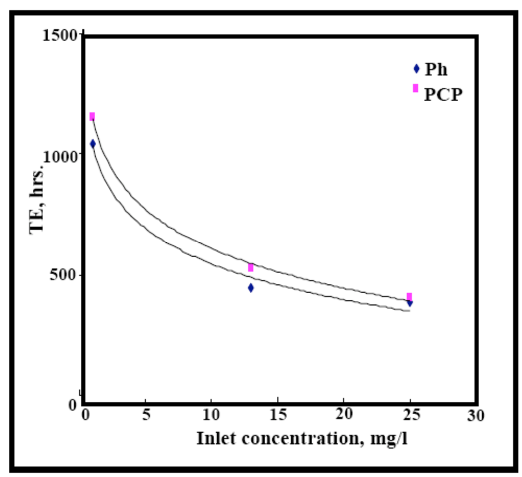


Figure 9: Effect of inlet pollutant concentration on TE.

This leads to the adsorption of greater quantities at shorter time for higher inlet pollutants concentration and thus, faster saturation of adsorption sites giving shorter TB and TE. Higher inlet pollutant concentrations results in a lower difference between TE and TB giving steeper adsorption isotherm (Figures **2** and **3**). This is because of the available time to occupy the adsorption sites becomes shorter for higher inlet pollutant concentration.

Effect of GAC Thickness on TB and TE

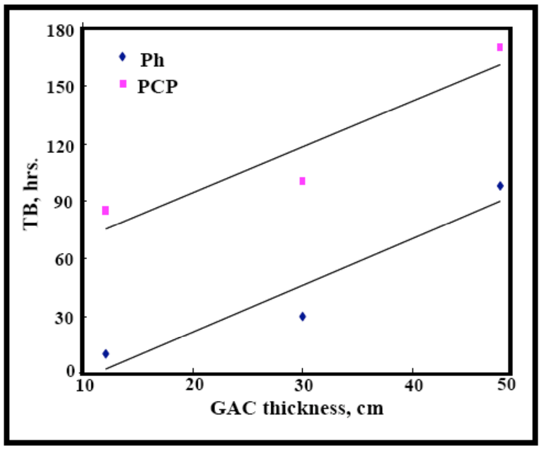


Figure 10: Effect of GAC thickness on TB.

Figures **10** and **11** indicate that TB and TE are increased as the GAC thickness is increased. This is in good agreement with the results obtained [18,21,22]. This is due to two reasons. The first is the increase of the available adsorption sites as the GAC thickness increased. The second is the mass transfer zone (adsorption zone, MTZ) moves from the top of the column to the bottom of the column, as GAC thickness increased the required time for this zone to reach the bottom of the column is increased giving more contact time and hence allow more chance for the adsorption mechanisms to work. This will make the adsorption isotherm steeper for lower GAC thickness.

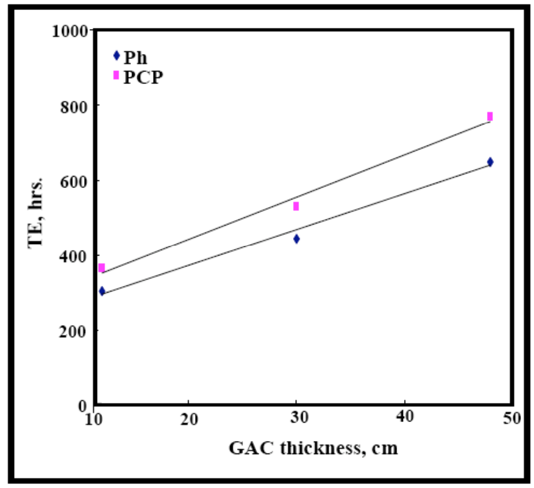


Figure 11: Effect of GAC thickness on TE.

Adsorption Capacity

The experimental results are fitted with the two famous adsorption models, namely Freundlich and

Table 5: Adsorption Capacities for Phenol and Parachlorophenol with the Correlation Coefficient (R^2)

Parachlorophenol		Phenol		GAC thickness, cm	Inlet concentration, mg/l	SOR, $m^3/m^2/hr$	Run No.
R^2	Adsorption Capacity, mg/gr	R^2	Adsorption Capacity, mg/gr				
0.767	227.2727	0.942	88.49558	40.392	19.93	4.4717	1
0.923	161.2903	0.878	64.93506	19.608	19.93	4.4717	2
0.8571	65.35948	0.8	42.55319	40.392	6.072	4.4717	3
0.8968	62.89308	0.833	37.17472	19.608	6.072	4.4717	4
0.8817	178.5714	0.9425	109.8901	40.392	19.93	3.0283	5
0.7654	169.4915	0.968	103.0928	19.608	19.93	3.0283	6
0.9599	36.23188	0.9122	26.45503	40.392	6.072	3.0283	7
0.8185	71.94245	0.837	53.76344	19.608	6.072	3.0283	8
0.8538	133.3333	0.9018	109.8901	30	13	2.5	9
0.867	113.6364	0.915	83.33333	30	13	5	10
0.844	25.90674	0.862	22.72727	30	1	3.75	11
0.9429	196.0784	0.8808	129.8701	30	25	3.75	12
0.7876	113.6364	0.9192	78.74016	12	13	3.75	13
0.881	140.8451	0.935	112.3596	48	13	3.75	14
0.8304	125	0.9438	86.95652	30	13	3.75	15

Langmuir. The results show that Langmuir model gives better fit. The adsorption capacity is calculated for each experiment and the results are listed on Table **5**. The results show that the adsorption capacity range for phenol is 22.7 – 129.87 mg/gr. The corresponding range for parachlorophenol is 25.9 -227.27 mg/gr. These results indicate that adsorption capacity is not a pure property for the adsorbent but it is a function of the operating conditions as well as adsorbent type. Thus, comparing adsorbent materials on the basis of adsorption capacity alone will give erroneous conclusion unless the operating variables are the same.

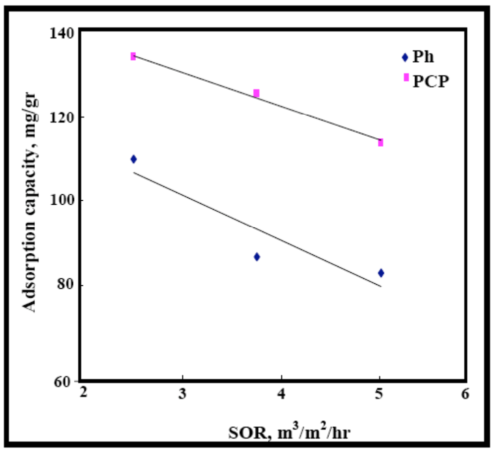


Figure 12: The effect of SOR on the adsorption capacity, [C_i=13mg/l, H=30cm].

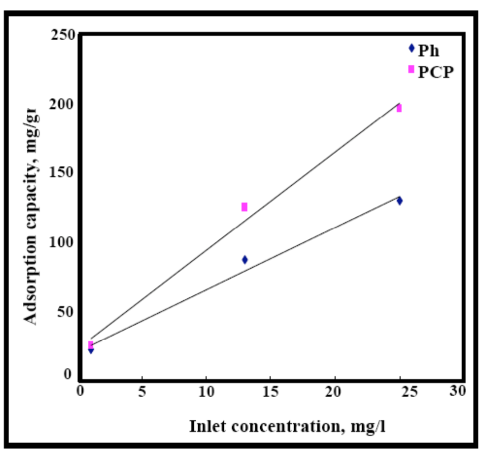


Figure 13: The effect of inlet concentration on the adsorption capacity, [SOR=3.75m^3/m^2/hr, H=30cm].

Table **5** indicates that adsorption capacities for parachlophenol are higher than that for phenol due to higher affinity and lower solubility in water. The results show that the adsorption capacity is inversely proportional with SOR and directly proportional with GAC thickness and inlet concentration for both phenol and parachlorophenol (Figures **12**-**14**). The increase of SOR leads to a shorter contact time between the pollutants and GAC which leads to lower adsorbed quantity. On the other hand, increasing GAV thickness will give more contact time for adsorption and hence more pollutant is adsorbed. The increase of inlet concentration will increase the adsorption driving force (C_i-C_t) according to Equation 1, forcing more pollutants to be adsorbed at shorter time.

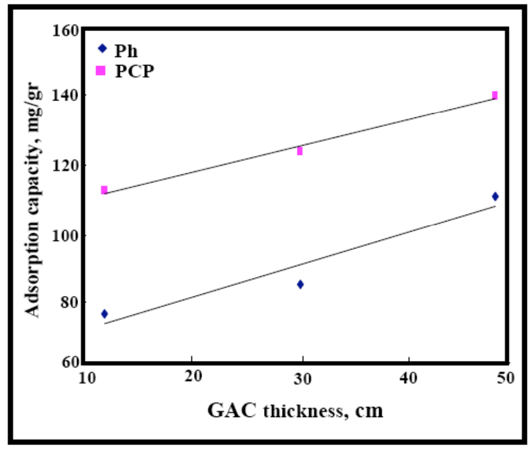


Figure 14: The effect of GAC thickness on the adsorption capacity, [C_i=13mg/l, SOR=3.75m^3/m^2/hr].

Mass Transfer Zone, MTZ [δ]

The values of adsorption velocities and mass transfer zones [MTZ] for phenol and parachlorophenol are calculated using Equations 2 and 3 respectively. These values are listed in Table **6**.

$$V_{ads} = \frac{H}{TE} \quad (2)$$

$$\delta = H - TB * V_{ads} \quad (3)$$

Where

H = GAC thickness, m

TB = breakthrough time, sec.

TE = exhaustion time, sec.

V_{ads} = adsorption velocity, m/sec

δ = mass transfer zone (MTZ), m

Table **6** indicated that the adsorption velocities and MTZ for parachlorophenol are lower than the corresponding values of phenol. This means that the required time for MTZ of parachlorophenol to reach the adsorption column bottom is higher than that of phenol. This will give more contact time, higher amount of adsorbed parachlorophenol, more flatness for the

Table 6: Adsorption Velocities and Mass Transfer Zone for Phenol and Parachlorophenol

Parachlorophenol		Phenol		GAC thickness, cm	C_i, mg/l	SOR, $m^3/m^2/hr$	Run No.
MTZ, m	Adsorption velocity, m/sec	MTZ, m	Adsorption velocity, m/sec				
0.29504	1.95E-07	0.30917	2.77E-07	40.392	19.93	4.4717	1
0.18059	1.34E-07	0.18128	2.06E-07	19.608	19.93	4.4717	2
0.3129	1.58E-07	0.32578	1.84E-07	40.392	6.072	4.4717	3
0.12885	1.04E-07	0.16688	1.16E-07	19.608	6.072	4.4717	4
0.21542	1.87E-07	0.29435	2.58E-07	40.392	19.93	3.0283	5
0.16515	1.32E-07	0.17841	1.53E-07	19.608	19.93	3.0283	6
0.30659	1.35E-07	0.33867	1.73E-07	40.392	6.072	3.0283	7
0.15108	8.93E-08	0.15763	1.07E-07	19.608	6.072	3.0283	8
0.23665	1.04E-07	0.27692	1.28E-07	30	13	2.5	9
0.24124	1.72E-07	0.29231	2.14E-07	30	13	5	10
0.21688	7.22E-08	0.22823	7.97E-08	30	1	3.75	11
0.16444	2.06E-07	0.22167	2.18E-07	30	25	3.75	12
0.09205	9.13E-08	0.11607	1.09E-07	12	13	3.75	13
0.37403	1.73E-07	0.40763	2.05E-07	48	13	3.75	14
0.24318	1.58E-07	0.27978	1.87E-07	30	13	3.75	15

adsorption isotherm, and higher TB & TE. Figures **15** and **16** show the relation between MTZ and SOR for both pollutants respectively. These Figures indicated that MTZ is increased with the increase of SOR. This is due lower contact time for higher SOR which lead to an empty adsorption sites left behind resulting in a reduction of TB & TE. It is also noticed from these Figures that the degree to which SOR affect MTZ is higher for phenol. This is due to the higher affinity of parachlorophenol. These finding assure the results listed in Table **5**, which indicate that the adsorption capacities of parachlorophenol are higher than the corresponding of phenol.

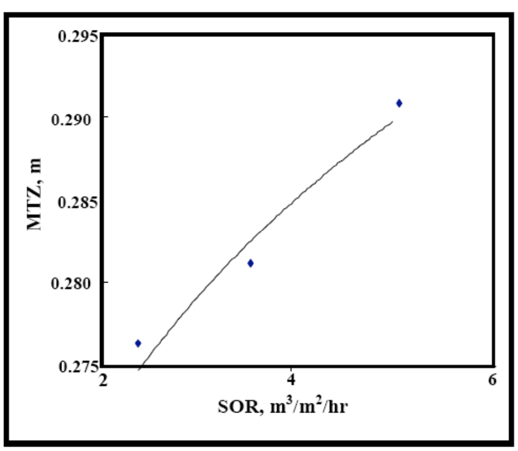


Figure 15: Relation between MTZ for phenol and SOR, [H=30cm].

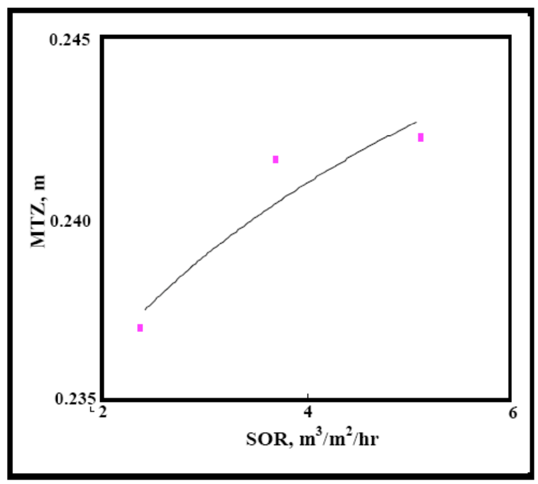


Figure 16: Relation between MTZ for parachlorophenol and SOR, [H=30cm].

Performance of Manufactured GAC (MGAC)

Activated carbon is produced from local Iraqi waste material (Date stone) using chemical activation method. Activation unit (Figure **17**) of University Malaya (UM), Malaysia is employed to manufacture the activated carbon using $ZnCl_2$ as a chemical reagent with an impregnation ratio of 1. In order to compare the performance of MGAC with that of CGAC, the operating variables of run number 13 is used to conduct a continuous mode adsorption experiment.

Figure **18** represents the adsorption isotherm for phenol and parachlorophenol when using CGAC and MGAC. This Figure indicated that TB and TE for parachlorophenol and phenol when using MGAC are

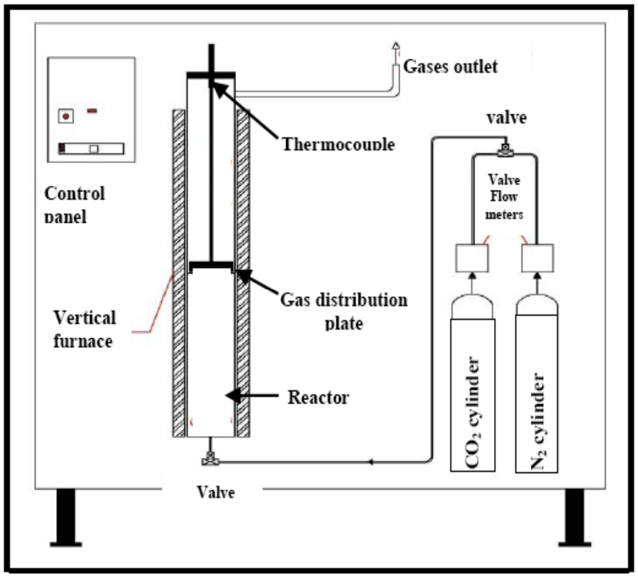
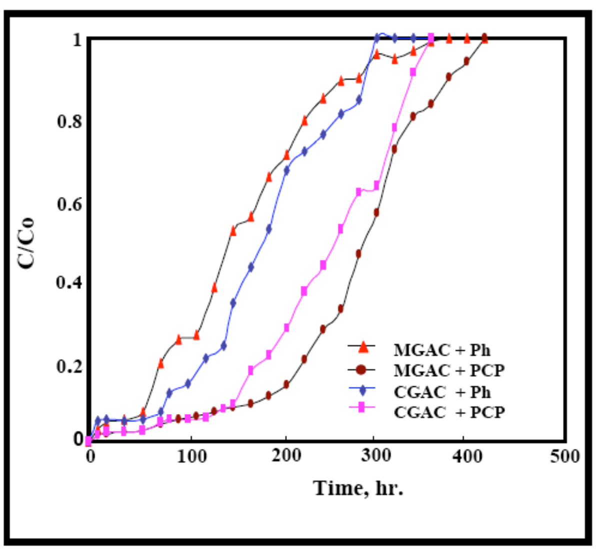


Figure 17: Schematic diagram of the Activation unit.



Figrue 18: Comparison of adsorption isotherms for CGAC &MGAC.

Higher than the corresponding values when using CGAC. It is found that TB for phenol and parachloro-phenol when using MGAC are 30 and 95 hours respectively while the corresponding values for CGAC are 10 and 85 hours. It is also found that TE for phenol and parachlorophenol when using MGAC are 345 and 430 hours respectively while the corresponding values for CGAC are 305 and 365 hours. This is due high surface area for MGAC (1610m^2/gr) as compared with that of CGAC (383.2 m^2/gr). The ratio of surface area of CGAC to that of MGAC is 0.238. This great difference in surface area did not mean that the difference in TB's and TE's is in the same degree. This is good agreement with the results of [23]. Adsorption process affected by many parameters other than surface area such as: the functional groups, types of functional groups (acidic or basic), and pores volume. It is well known that most of adsorption process takes place within small pores and part of intermediate pores while large pores play as a passage for the entry of the adsorbed molecules [23-25].

The experimental data are fitted using Freundlich and Langmuir models and the results show that Langmuir model gives better fit (R^2 is 0.984 and 0.8846 for phenol and parachlorophenol respectively). The constants of Langmuir model are calculated and listed in Table **7** which indicates that the adsorption capacities for phenol and parachlorophenol with MGAC are higher than the corresponding values with CGAC. MGAC gives an increase in the adsorption capacity of phenol is 67.1% while the corresponding increase for parachlorophenol is 250.88%.

The adsorption velocity and MTZ are calculated for both pollutants when adsorbed on MGAC and CGAC. The results are listed in Table **8** which shows that the adsorption velocity and MTZ for both pollutants when adsorbed on MGAC are lower than the corresponding values for adsorption on CGAC. This will gives higher TB & TE, higher adsorption capacity due to higher surface area.

Table 7: Langmuir Model Constants for Phenol and Parachlorophenol Using MGAC and CGAC

Adsorbent and Adsorbate	Adsorption Capacity, mg/gr	b,L/mg	R^2
MGAC + phenol	131.5789	0.184466	0.9847
MGAC + parachlorophenol	294.1176	0.10794	0.8846
CGAC + phenol	78.74016	2.015873	0.9192
CGAC + parachlorophenol	113.6364	0.76522	0.7876

Table 8: Adsorption Velocity and MTZ for Phenol and Parachlorophenol Using MGAC and CGAC

Activated Carbon type	SOR, $m^3/m^2/hr$	Inlet Concentration, mg/l	GAC thickness, cm	Phenol		Parachlorophenol	
				Adsorption Velocity, m/sec.	MTZ, m	Adsorption Velocity, m/sec.	MTZ, m
MGAC	3.75	13	12	9.66E-08	0.10957	7.75E-08	0.09349
MGAC	3.75	13	12	1.09E-07	0.11607	9.13E-08	0.09205

Batch Adsorption Experiments

Batch adsorption experiments are conducted at 25 °C for phenol and parachlorophenol using MGAC and CGAC. The results are shown on Figures **19** and **20**. The experimental results are fitted using Langmuir and Freundlich models. More agreement is obtained with Langmuir model [Figures **21** and **22**] (R^2 is 0.952 – 0.9958, while R^2 is 0.8158 – 0.9432 for Freundlich model). Langmuir model can be represented as a linear equation as follows:

$$\frac{C_e}{q_e} = \frac{C_t}{a} + \frac{1}{a * b} \quad (4)$$

Where:

a = maximum adsorption capacity

b = adsorption energy which is a ratio between the adsorption rate and desorption rate(Lua and Jia, 2009)

q_e = adsorbed pollutants per unit mass of adsorbate

These constants (a & b) as well as the dimensionless Langmuir adsorption coefficient (R_L) according to Equation 5 [26] are calculated and listed in Table **9**.

$$R_L = \frac{1}{1 + b * C_i} \quad (5)$$

R_L represents a description for the adsorption curve type

R_L>1, the adsorption curve is unfavorable

R_L>1, the adsorption curve is unfavorable

R_L=0,, the adsorption curve is linear

R_L=1, the adsorption curve is irreversible

< R_L< 1, the adsorption curve is favorable

Table **9** indicates that the adsorption capacity for parachlorophenol on MGAC and CGAC are 102.204 and 100 mg/gr respectively. The corresponding values for phenol are 83.3 and 74.07 respectively. This is due to larger surface area of MGAC as compared with that of CGAC. Moreover, parachlorophenol has greater affinity than phenol [24] Jung, MW. Ahn, KH. Lee, Y. Kim KP. Rhee JS. Park JT. and Paeng, KJ.]; and [19] [Termoul M. Bestani B. Benderdouche N. Belhakem M. and Naffrechoux, E. 2006]

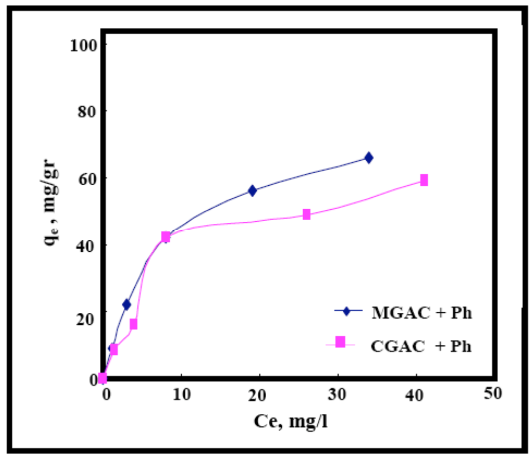


Figure 19: Adsorption isotherm for phenol on MGAC and CGAC.

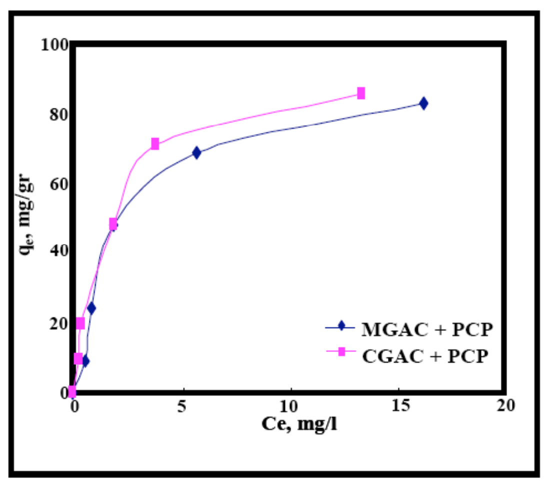


Figure 20: Adsorption isotherm for parachlorophenol on MGAC and CGAC.

From the results of continuous mode adsorption experiments it is noticed that the range of adsorption capacity for parachlorophenol when using CGAV is 25.9-227.7mg/g (Table **5**) while it is 100 mg/l for batch

Table 9: Langmuir Model Constants

Adsorbent and Adsorbate	Adsorption Capacity, mg/gr	b, L/mg	R_L	R^2
MGAC + phenol	83.33333	0.111732	0.082148	0.9958
MGAC + parachlorophenol	102.0408	0.276056	0.034958	0.9552
CGAC + phenol	74.07407	0.089582	0.10042	0.9647
CGAC + parachlorophenol	100	0.4629	0.0211	0.9908

experiment. Same trend is noticed for phenol. It is expected that different values for adsorption capacity will be obtained when the operating variables such as the pollutant concentration and granular active carbon dose are changed. This Figure assures that the adsorption capacity is not a pure characteristic of activated carbon only but it is a function of the operating parameters as well as adsorbent type. Using laboratory data will give a misleading Figure unless using the same operating parameter values for the laboratory and field unit.

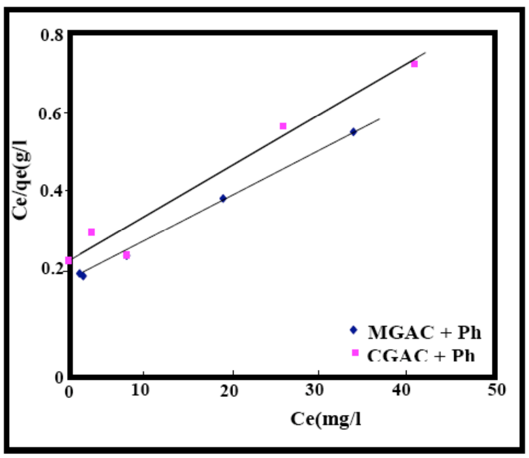


Figure 21: Relation between Ce/qe and Ce for phenol on MGAC and MGAC.

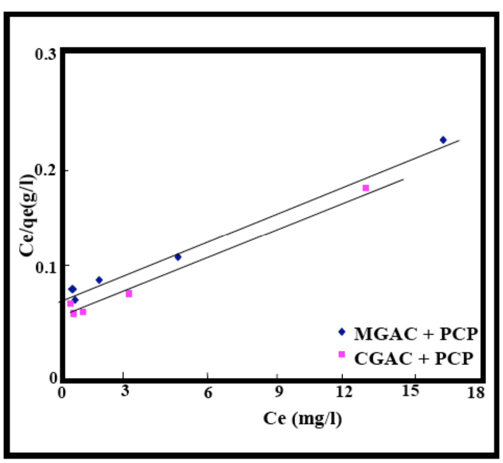


Figure 22: Relation between Ce/qe and Ce for parachlorophenol on MGAC and MGAC.

Continuous Adsorption Model

One of the main objectives for using Box-Wilson method is to reduce the number of experiment and hence the cost of the required study. Other goal is to represent the operating variables into a mathematical equation that enables the determination of the depending variable (in this work TB and TE) with the independent variables (SOR, GAC thickness{H}, and the inlet pollutant concentration. This is done to enable forecasting of TE and TB depending on the known operating conditions of the field unit. Box - Wilson model can be represented by Equation 6.

$$Y = b_o + b_1X_1 + b_2X_2 + b_3X_3 + b_{11}X_1^2 + b_{22}X_2^2 + b_{33}X_3^2 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{23}X_2X_3 \quad (6)$$

Where:

Y dependent variable, (TB or TE)

b_o, b_1, b_3…. constants

X_1, X_2, X_3 are independent variables (SOR, Ci, and H respectively.

Employing statistica v5.5 program with the experimental data listed in Table **4** as an input data into Equation 6 enables the constants b_o, b_1, b_2…. to be determined. These constants are determined for phenol and parachlorophenol and listed in Table **10**. Once these constants are determined, TB or TE can be found for the field unit for any set of operating variables (SOR, Ci, H) using Equation 6. The calculated values of TB and TE are determined using the constants listed in Table **10** and the operating variables listed in Table **4**. The results are listed in Table **11**. The experimental values of TB and TE are compared with the calculated values by Equation 6 and represented graphically on Figures **23-26**. These figures show that acceptable agreement between experimental and calculated values is obtained.

Table 10: Constants for Phenol and Parachlorophenol

Parachlorophenol		Phenol		b
Constants for TE	Constants for TB	Constants for TE	Constants for TB	
545.011143	104.4447	467.087595	31.4305	b_o
-56.759842	-20.80428	-46.661914	-8.7332	b_1
-142.36819	-27.7074	-138.63301	-27.844	b_2
105.739038	38.14322	79.0943319	26.5053	b_3
17.7484538	5.319584	-4.1419437	-1.9852	b_{11}
65.4664047	47.38207	64.430519	49.2674	b_{22}
-9.6451846	3.552252	-19.164262	6.49795	b_{33}
21.625	-19.75	-5	-2.25	b_{12}
-6.625	-21.5	7.5	4	b_{13}
-5.875	37.25	-7.5	13.5	b_{23}

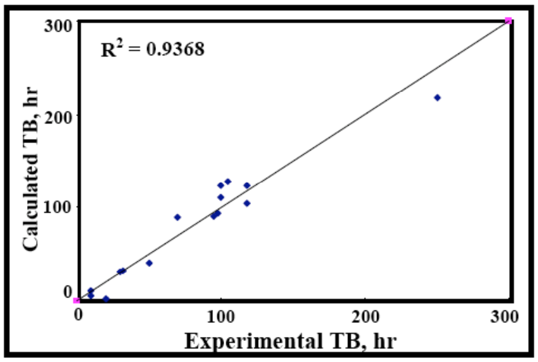


Figure 23: Calculated versus experimental TB for phenol.

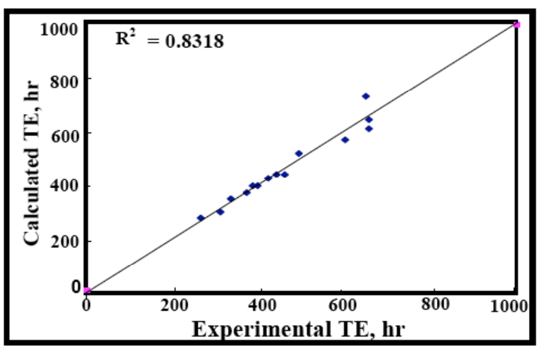


Figure 24: Calculated versus experimental TE for phenol.

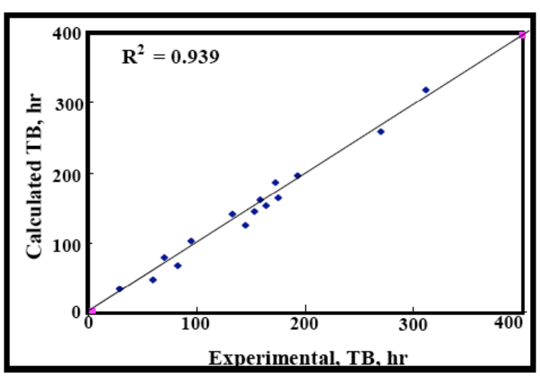


Figure 25: Calculated versus experimental TB for parachlorophenol.

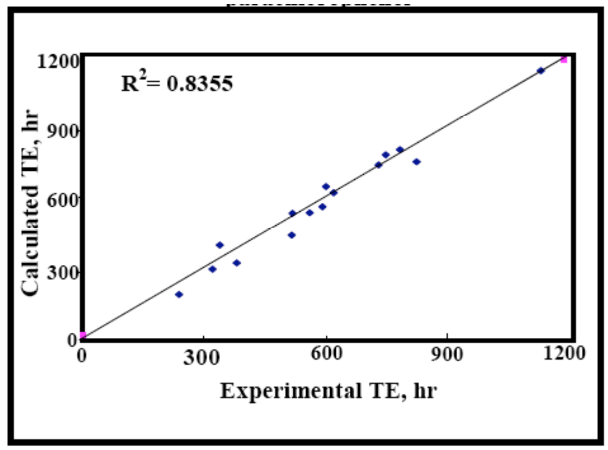


Figure 26: Calculated versus experimental TE for parachlorophenol.

CONCLUSIONS

Breakthrough and exhaustion times for Phenol and parachlorophenol are inversely proportional with surface over flow rate and inlet pollutants concentration while it is directly proportional with GAC thickness.

- Breakthrough and exhaustion times for parachlorophenol are higher than the corresponding values of phenol.
- Adsorption capacity is directly proportional with the inlet pollutants concentration and GAC thickness while it is inversely proportional with surface over flow rate.
- Manufactured activated carbon has better performance than commercial activated carbon
- Adsorption capacity is a function of the operating variables and it is not a pure property of activated carbon.

Table 11: Experimental and Calculated Values of TB and TE

Parachlorophenol				Phenol				Run No.
Calculated TE, hr	Experimental TE, hr	Calculated TB, hr	Experimental TB, hr	Calculated TE, hr	Experimental TE, hr	Calculated TB, hr	Experimental TB, hr	
534.32	575	146.33	155	397.011	405	90.39	95	1
347.84	405	38.544	32	238.823	265	23.78	20	2
787.55	710	166.74	160	699.277	610	123.6	118	3
577.58	525	207.96	180	511.089	470	89.57	70	4
617.84	600	270.44	280	485.335	435	104.4	118	5
404.86	412	76.652	65	357.146	355	32.34	32	6
957.57	830	211.85	200	767.601	650	128.5	105	7
721.09	610	167.07	140	609.412	510	110.5	100	8
690.69	805	154.49	170	533.855	650	40.5	50	9
499.75	485	84.502	95	376.884	390	11.12	10	10
969.69	1155	285.1	320	882.55	1045	217.6	250	11
490.76	405	191.89	183	416.189	383	124	100	12
339.87	365	50.337	85	279.833	305	5.232	10	13
695.58	770	178.65	170	545.906	650	94.4	98	14
545.01	528	104.44	100	467.088	445	31.43	30	15

NOMENCLATURE

A — Langmuir constant, adsorption capacity, Mg/L

$b, b_o, b_1, \ldots$ — Langmuir constant

C — Pollutant concentration, mg/L

C_e — Equilibrium pollutant concentration, mg/L

C_i — Inlet pollutant concentration, mg/L

C_t — Pollutant concentration at any time, mg/L

H — Granular activated carbon thickness, cm

K — Mass transfer coefficient

q_e — Mass adsorbed per unit mass of adsorbate, mg/gr

R_L — description for the adsorption curve type

R^2 — Coefficient of correlation

SOR — Surface over flow rate, $m^3/m^2/hr$

t — Time, sec.

TB — Breakthrough time, hours

TE — exhaustion time, hours

V_{ads} — Adsorption velocity, m/sec.

$X_1, X_2 \ldots$ — Independent variables of Box- Wilson model

Y — Dependent variable of Box – Wilson model

Greek letters

δ — Mass transfer zone thickness, MTZ, m

ABBREVIATIONS

CGAC — Commercial granular activated carbon

MGAC — Manufactured granular activated carbon

MTZ — Mass transfer zone

PCP — Parachlorophenol

Ph — phenol

REFERENCES

[1] Crawford HB, Cline G. Water treatment plant design. American Society of Civil Engineers. American water Works Association. McGraw- Hill Inc. New York 1990; 457.

[2] Besselievre EB, Schwartz M. The treatment of industrial wastes. McGraw–Hill kogakusha Ltd. Tokyo Japan 1976; 151-226.

[3] Hameed BH, Rahman AA. Removal of phenol from aqueous solutions by adsorption onto activated carbon prepared from biomass material. J of Hazardous Materials 2008; 160: 576-581. http://dx.doi.org/10.1016/j.jhazmat.2008.03.028

[4] WHO Guidelines for Drinking Water Quality. 3rd edition 2004; 1: Geneva.

[5] Daifullah AA, Girgis BS. Removal of some substituted phenols by activated carbon obtained from agricultural waste. Water Research 1998; 32(4): 1169-1177. http://dx.doi.org/10.1016/S0043-1354(97)00310-2

[6] Mukherjee S, Kumar S. Misra AK. Fan M. Removal of phenols from water environment by activated carbon, bagasse ash and wood charcoal. Chemical Engineering Journal 2007; 129: 133-142. http://dx.doi.org/10.1016/j.cej.2006.10.030

[7] Beker U, Ganbold B. Dertli H. Gülbayir DD. Adsorption of phenol by activated carbon: Influence of activation methods and solution pH. Energy Conversion and Management 2010; 51: 235-240. http://dx.doi.org/10.1016/j.enconman.2009.08.035

[8] Al-Qaysi IA. Using granular activated carbon for the removal of phenol, parachlorophenol and benzene from Baiji Oil Refineries wastewater. MSc Thesis College of Engineering. Tikrit University 2010.

[9] Al-Ani MY. Al-Baldawi MF. The effectiveness of using single and dual media filtration. Proceeding 4th Scientific Conference SRC 1986.

[10] Latif IH. Activated carbon as a combined filtration and adsorption medium in water treatment. PhD Thesis University of Birmingham 1990.

[11] Al-Ani FH. An Investigation into the use of locally produced granular activated carbon in treatment of water supplies. PhD Thesis University of Technology 1998.

[12] Al-Najjar QA. Study of the fasibility of using local Iraqi ninvite rock in treating drinking water. MSc Thesis University of Mousil 2000.

[13] Thiel P, Zappia L, Franzmann P, Warton B, Alessandrino M, Heitz A, Nolan P, Scott D, Hiller B, Masters D. Activated carbon VS. anthracite as primary dual media filters- pilot plant study, 69th Annual water industry engineers and operators Conference. Bendigo Exhibition Centre 2006; 5-7 September.

[14] Al-Rawi SM, Shihab AS, Ameen AZ. Behavior assessment of various filters configuration in removing water low turbidity: A statistical treatment. Al-Rafidain Engineering 2007; 15(1): 72-83.

[15] Al-Rawi SM. Introducing sand filter capping for turbidity removal for potable water treatment plants of Mosul/Iraq. Int J of Water Resour and Enviro Engin 2009; 1: 1.

[16] Babu BV, Gupta S. Modeling and simulation for dynamics of packed bed adsorption. Chemical Conference. Mumbai 2004.

[17] Ebrahim SE. Evaluation of heterogeneous adsorbents bed for the removal of organic materials from water. PhD Thesis. University of Baghdad 2008; 4-39.

[18] Alhamed YA. Adsorption kinetics and performance of packed bed adsorber for phenol removal using activated carbon from dates. stones J of Hazardous Materials 2009; 170: 763-770. http://dx.doi.org/10.1016/j.jhazmat.2009.05.002

[19] Termoul M, Bestani B, Benderdouche N, Belhakem M, Naffrechoux E. Removal of phenol and 4-chlorophenol by chemically activated olive stones. Adsorption Science Technology 2006; 24: 375. http://dx.doi.org/10.1260/026361706779849780

[20] Wa'adalla K. Removal of multi-pollutant from wastewater by adsorption method. PhD Thesis university of Baghdad 2006; 3-122.

[21] Lua AC, Jia Q. Adsorption of phenol by oil–palm-shell activated carbons in a fixed bed. Chemical Engineering Journal 2009; 150: 455-461. http://dx.doi.org/10.1016/j.cej.2009.01.034

[22] Gupta A, Nanoti O, Goswami AN. The removalof furfural from water y adsorption with polymeric resin. Separation Science and Technology 2001; 36(13): 2835-2844. http://dx.doi.org/10.1081/SS-100107632

[23] Hsieh C-T, Teng H. Liquid-phase adsorption of phenol onto activated carbons prepared with different activation levels. J of Colloid and Interface Science 2000; 230: 171-175. http://dx.doi.org/10.1006/jcis.2000.7052

[24] Jung MW, Ahn KH, Lee Y, Kim KP, Rhee JS, Park JT, Paeng KJ. Adsorption characteristics of phenol and chlorophenols on granular activated carbons (GAC). Microchemical J 2001; 70: 123-131. http://dx.doi.org/10.1016/S0026-265X(01)00109-6

[25] Fierro V, Torne´-Ferna´ndez V, Montane D, Celzard A. Adsorption of phenol onto activated carbons having different textural and surface properties. Micro porous and mesoporous Materials 2008; 111: 276-284. http://dx.doi.org/10.1016/j.micromeso.2007.08.002

[26] Park KH, Balathanigaimani MS, Shim WG, Lee JW, Moon H. Adsorption characteristics of phenol on novel corn grain-based activated carbons. Microporous and Mesoporous Materials 2010; 127: 1-8. http://dx.doi.org/10.1016/j.micromeso.2009.06.032

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