A COMPARISON STUDY BETWEEN ACTIVATED CARBON AND COKE FOR PHENOLIC WASTEWATER TREATMENT

F. Abdelrasoul

Sanitary Engineering Department, Alexandria University, 21544 Alexandria, Egypt

ABSTRACT

A simple experimental set-up was used to study the treatability aspect of phenolic wastewater. Two types of systems: i) granular activated carbon (A.C) and ii) coke were experimented under different phenol loadings (100, 200 and 300 mg/l) and different flow rates (21.6 and 43.2 l/d) with initial COD concentration 500 mg/l. The A.C system gave the higher COD and phenol % removal in comparison with coke system. An application of a adsorption packed-bed reactor model was used to study the efficiency of the removal of phenolic wastes. The model equations are a combination of Particle Kinetics and Transport Kinetics. The model was verified for Coke as sorbent and phenol as sorbate. Experiments were conducted to determine the Langmuir equilibrium coefficients (α and Xm) and to determine the bulk sorbate solution concentration versus different adsorption column depths and at different times as well. The model can predict any data, which cannot be known from laboratory work. Moreover, the model can answer any questions asked by engineers or column designers to help develop better and an economic design. The results of the model showed good agreement with the laboratory data.

Keywords: Activated carbon, Coke, Phenol, Adsorption packed-bed model.

INTRODUCTION

Phenol is a toxic material that may be found in domestic wastewater from some industries such as petrochemicals, coal cooking, petroleum refining and pharmaceutical plants. It is important to remove such material from the wastewater to eliminate its danger to the environmental. A tertiary treatment may be needed to meet the effluent concentration required by law when such effluents discharged into streams (Suschaka, [1]).

Adsorption is the process of collecting substances that are in solution on a suitable interface. The interface can be between liquid and a gas or another liquid or solid and liquid (Belkin, [2]). The demands for a better quality of treated wastewater effluent have led to an intensive examination and use of the process of adsorption on active carbon. Complete treatment of phenolic wastewater with active carbon was studied by Sorour [3].

A fixed-bed column is commonly used for contacting wastewater with carbon. Fixed-bed column can be operated singly, in series, or in parallel. The water to be treated is applied to the top of the column and withdraw at the bottom. The advantage of a downflow design is that adsorption of organic and filtration of suspended solids are accomplished in a single step (Metcalf and Eddy, [4]).

The model which will be used in this research work was developed by Vagliasindi [5]. The model equations are a combination of particle kinetics and transport kinetics.

This research will focus on studying the removal of phenol and organic matter in wastewater by using coke instead of active carbon. Coke is manufactured in El-Naser Co. for Coke and Chemicals from a blend of different coals. The specifications of the coke are shown in Appendix A (El-Gohary [6]). A comparison study between active carbon and coke will be done too. Coke is cheaper than active carbon so the use of coke may be useful. It may be necessary in some cases to meet regulations to use more than one stage of carbon column; here comes the importance of cost of course as well as the importance of effluent quality. The model will be verified against the lab data for coke as sorbent and phenol as sorbate. The model can predict any data which is hard or cannot be known from the laboratory work and help engineers or column designers for better and economic design.

MATERIALS AND METHODS

1. Experimental Work

1.1 Synthetic Sewage

According to Battistoni [7], the activated sludge process utilizing a synthetic sewage as prepared by diluting with tap water (1-100) a concentrated stock solution containing 48.6 g/l of glucose, 11.65 g/l of $Na_3PO_4.12H_2O$ and 8.8 g/l of $(NH_4)_2SO_4$. The synthetic sewage was daily prepared fresh. The diluted solution has average COD concentration equals to 500 mg/l.

1.2 Determination of Langmuir Equilibrium Coefficients (α and Xm) for Coke

The set of experiments was done on a bench scale for part I to determine the Langmuir equilibrium coefficients (α and Xm). To determine the equilibrium coefficient α and Xm, phenol with concentration (20, 50, 100, 150, 200, 250, 300 mg/l) as sorbate for the set. One gram Coke for each 1 litter flask for the system as sorbent. Samples were taken at time zero then after each hour until equilibrium was reached in all flasks. All flasks were stirred continuously. For adsorption from a solution by solid adsorbent, the Langmuir adsorption isotherm is expressed as:

$$\frac{\overline{X}^*}{X_m} = \frac{\alpha C^*}{1 + \alpha C^*} \qquad (1)$$

The linearized form of the Langmuir isotherm is:

$$\frac{C^*}{\overline{X}^*} = \frac{1}{\alpha X_m} + \frac{1}{X_m} C^* \qquad (2)$$

in which,

X_m = maximum solid phase concentration used as a Langmuir isotherm coefficient (µg adsorbate/gm adsorbent);
$\overline{X}^*$ = concentration of adsorbate in solid phase at equilibrium with aqueous phase adsorbate concentration, C*, determined in accordance with Langmuir isothermexpression (µg adsorbate / gm adsorbent);
C^* = equilibrium concentration of adsorbate (µg adsorbate/mL solution);
α = equilibrium coefficient (mL solution/µg adsorbate).

1.3 Coke System

To achieve the objectives of this work a perspex column with internal diameter 5 cm and 100 cm long were used. The column was packed with coke with a size of 0.2 mm. Feed tank was made from plastic with capacity of 100 litters. The feed tank was filled with synthetic sewage of 500 mg/l COD and different phenol concentration (see Table 1). The system was provided with a peristaltic pump which was designed for research purpose. The peristaltic pump was (Master flex L/S Easy-Load) and the pump was used as feeding pump. Collecting tanks were made from plastic with capacity of 50 litters as shown in Fig.1.

Table 1. Different flow rates and different phenol concentrations used in experimental work

Flow Rate (l/d)	**Phenol Concentration (mg/l)**		
21.6	100	200	300
43.2	--	--	300

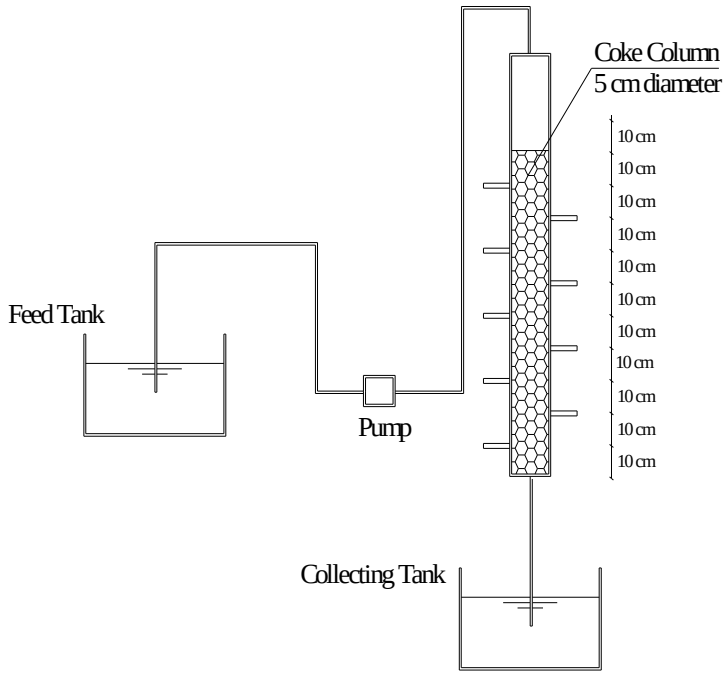

Figure 1. Coke column system

1.4 Granular Activated Carbon System

The experimental work and data for Granular active carbon [AquaSorb^{TM}2000] were taken from Sorour [3].

1.5 Analytical Techniques

Parameters monitored during this study were chosen to determine the system performance due to phenol loadings. Phenol concentrations were determined with 4-aminoantipyrine method. COD was measured by colorimetric method using spectrophotometers (DR 100 colorimeter Hach). All parameters were measured according to the Standard Methods for Examination of Water and Wastewater [8].

2. Model Verification

2.1 Adsorption Packed-Bed Reactor Model

The model equations, numerical solution and FORTRAN program were taken from Vagliasindi [6]. The packed-bed model used here is based on particle kinetics shown in equation (3) and transport kinetics shown in equation (4).

$$(\delta\overline{X}/\delta t)_P = \overline{D}.C.(\overline{X} - \overline{X}^*) \qquad (3)$$

$$(\delta\overline{X}/\delta t)_T = (1/\rho)(P/(1-P))(V + D\lambda)\,\lambda.\, C_o \exp[-\lambda(Z - Z'_o)] \qquad (4)$$

in which,

- C = concentration of adsorbate species in aqueous phase (µg adsorbate/ml solution).
- C^* = equilibrium concentration of adsorbate (µg adsorbate/ml solution).
- $C(Z)$ = concentration in column as a function of distance, Z (µg adsorbate/ml solution);
- $\overline{D}$ = kinetic coefficient in solid phase (ml solution /µg adsorbate /min).
- P = porosity of the packed bed.
- $\overline{X}$ = average concentration of adsorbate within adsorbent particle (µg adsorbate/gm adsorbent).
- $\overline{X}^*$ = concentration of adsorbate in solid phase at equilibrium with aqueous phase adsorbate concentration, C*, determined in accordance with Langmuir isotherm expression (µg adsorbate/gm adsorbent).
- $(\delta\overline{X}/\delta t)_P$ = kinetic term when splid phase diffusion is rate controlling (µg adsorbate/gm adsorbent/min)
- $(\delta\overline{X}/\delta t)_T$ = kinetic term when advection-dispersion transport is rate controlling (µg adsorbate/gm adsorbent/min).
- V = interstitial flow velocity (cm/min).
- Z'_o = distance from top of the column to the inflection point (cm).
- λ = collision probability coefficient (cm^{-1}).
- ρ = dry density of the granular adsorbent particles (gm/ml).

RESULTS AND DISCUSSION

1. Comparison between the A.C and Coke Using Experimental Data

A comparison between the two systems regarding COD% removal is shown in Fig. 2. For all cases, it is obvious that A.C system gave the higher COD% removal than coke system. The adverse effect of phenol loading on COD removal can be recognized for all cases. For example, from Fig. 2, the average COD% removal was 14 % in A.C system after 14 days of operation with 100 mg/l phenol, adding 200 mg/l of phenol decreased the COD% removal to 12 %, while adding 300 mg/l of phenol decreased it to 2 %.

Figure 3 shows a comparison between the two systems regarding phenol removal efficiency. From this figure, it is obvious that A.C system gave the highest % phenol removal. Increasing phenol loading has an adverse effect on its removal efficiency. For example, after 14 days of operation the average phenol % removal decreased from 88 % in A.C system at 100 mg/l phenol to 82 % at phenol loading of 200 mg/l, and to 77 % at phenol loading 300 mg/l for the same conditions. For more details, see Appendix B.

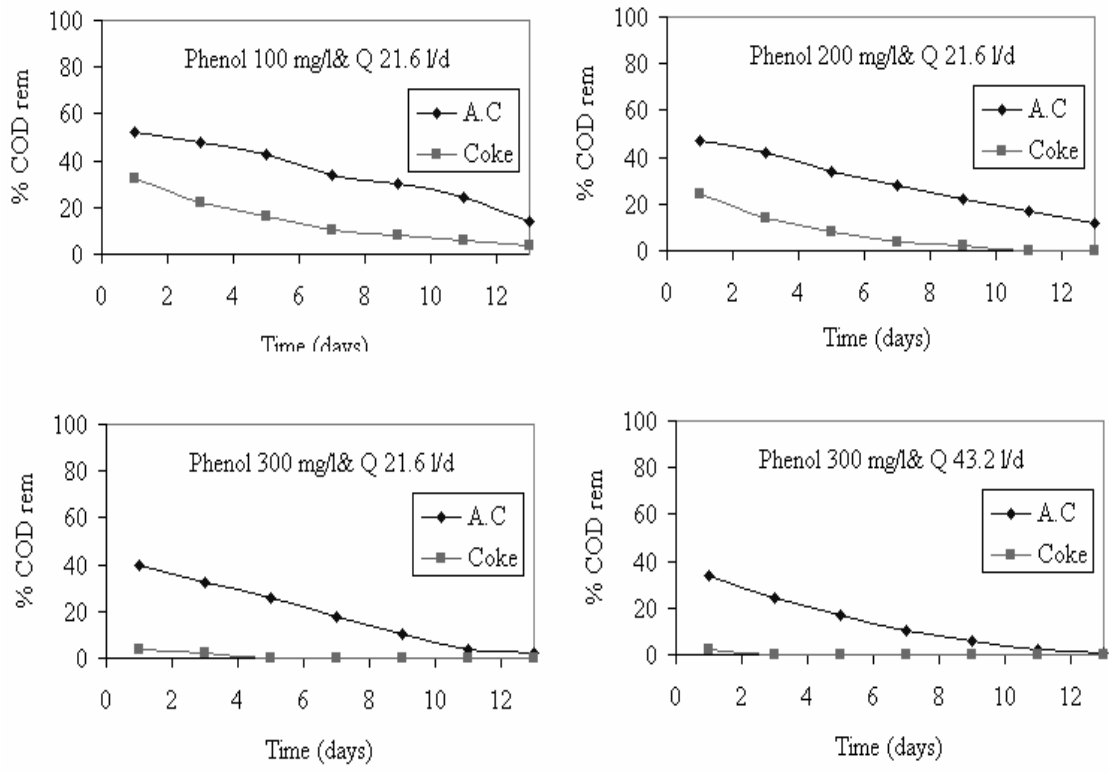

Figure 2. Comparison between A.C and coke for the removal of COD with different phenol concentrations (lad data)

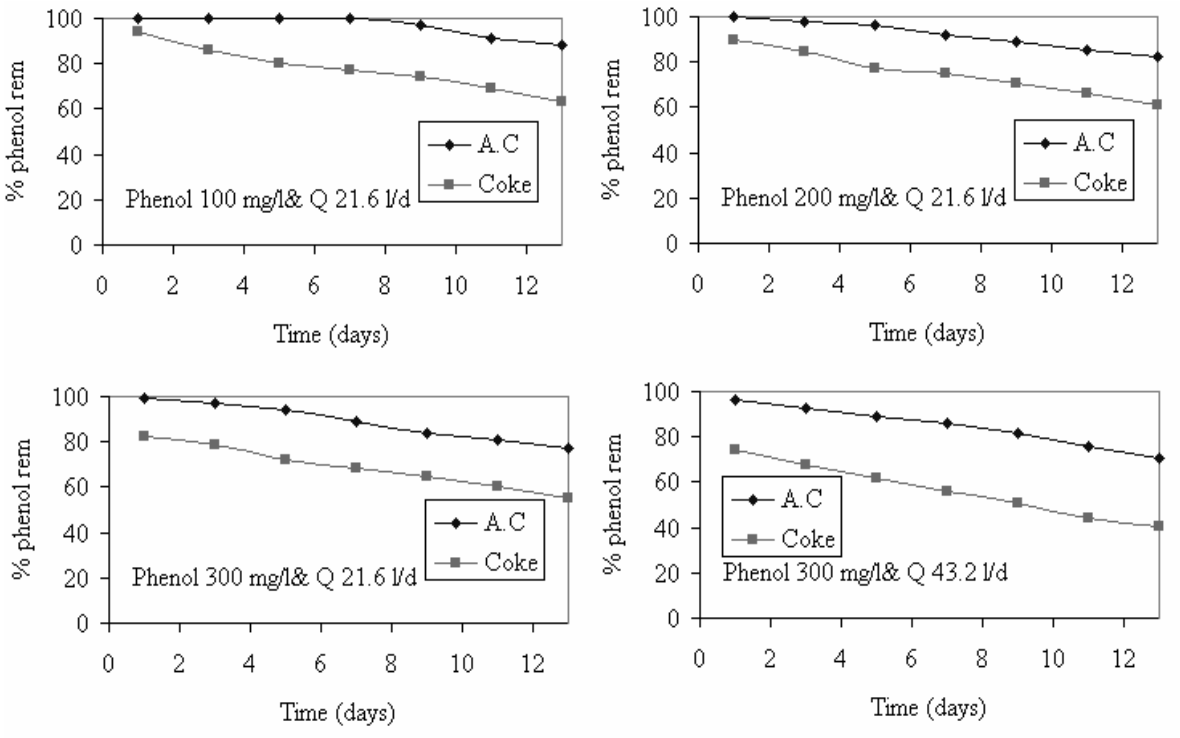

Figure 3. Comparison between A.C and coke for the removal of phenol with different phenol concentrations (lad data)

2. Langmuir Constants, α and Xm for Coke

The kinetics and equilibrium data were generated for different initial sorbate concentration. The system data were used to determine the sorbate-sorbent isotherm. Coincident with the isotherm generation, the corresponding uptake curves were determined for different initial adsorbate concentration.

Figure (4) shows the isotherm, while Figure (5) shows the linearized form of the isotherm for Coke as sorbent and phenol as sorbate. From linearized form the Langmuir constants, α and X_m, were determined using the slope and intercept.

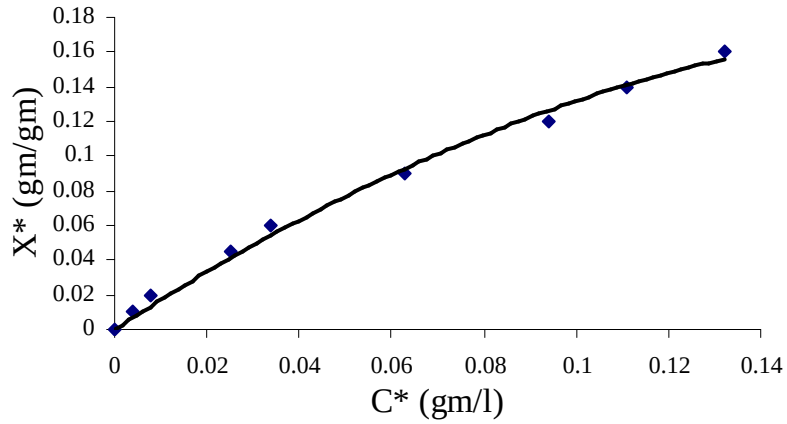

Figure 4. Langmuir isotherm for Coke

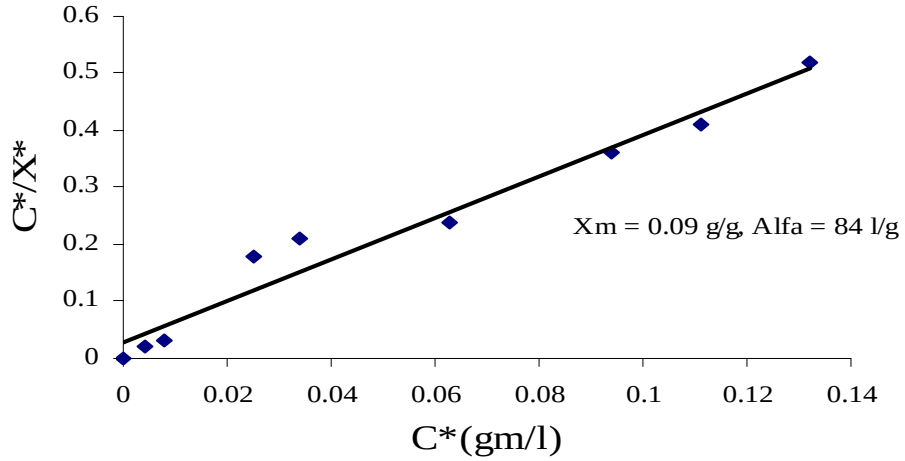

Figure 5. Linearized isotherm for Coke

The model was verified by simulating laboratory conditions for 8 lab runs. The model results were compared with those from laboratory.

3. Model Verification for Coke System

The model was verified against the laboratory data points. Figure (6) shows the measured and simulated data for Coke as sorbent and phenol as sorbate. The results of the model showed good agreement with the laboratory data.

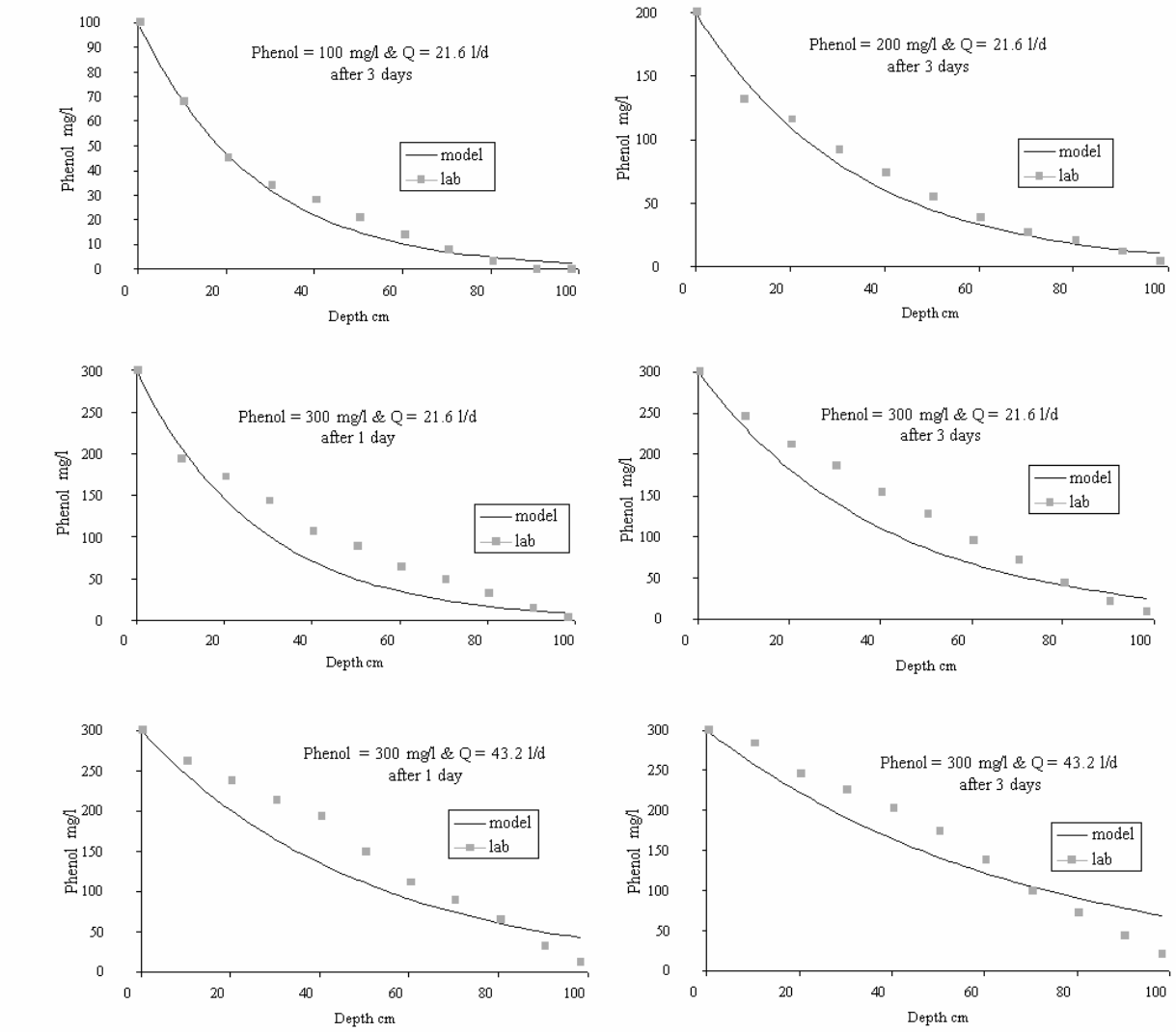

Figure 6. The laboratory data points with calibrated simulations Coke

4. Comparison between the A.C and Coke Using Model Data

Figure 7 shows a comparison between the two systems regarding phenol removal efficiency. From this figure, it is obvious that A.C system gave the highest % phenol removal. Increasing phenol loading has an adverse effect on its removal efficiency. For example, after 14 days of operation the phenol % removal was 33 % in A.C system at 500 mg/l phenol and flow rate 40 l/d and for the same conditions the phenol removal was zero % for coke system.

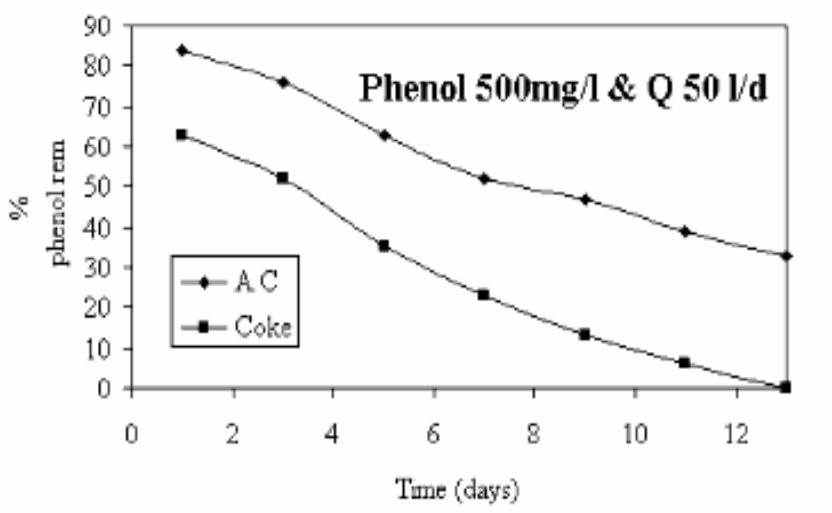

Figure 7. Comparison between A.C and coke for the removal of phenol with different phenol concentrations (model data)

5. Exercise with the Model

Simulation with the model could be used to answer questions which may not be answered from lab work or may take long time and effort. For example a quick exercise with the model showed that the break through will happen after 61 days for A.C system and after 23 days for coke system for flow rate 21.6 l/d and initial phenol concentration of 100 mg/l at 100 cm adsorption column depth.

Conclusions

(1) The A.C system gave the higher COD and phenol % removal than coke system.

(2) Increasing the influent phenol concentration decreased the COD and phenol removal efficiency.

(3) Increasing flow rate decreased the COD and phenol removal efficiency for the systems.

(4) The adsorption packed-bed reactor model was verified for Coke as sorbents and phenol as sorbate through testing over a range of phenol concentrations (100-300 mg/l).the results of the model showed good agreement with the laboratory measurements.

RECOMMENDATION

1- It is recommended to conduct further studies with coke using other pollutants. Also an economic comparative study with other coals will be helpful.

2- It is recommended using biological treatment before coal columns for removing organic matter

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APPENDIX A

Table (A.1) The specification of the coke

Loading Port	**Alexandria**			
Proximate Analysis		**TYP**	**MIN**	**MAX**
Total Moisture (ISO 579) **AR**	%	5	3	5
Ash (ISO 1171) **DB**	%	10	9	10.5
Volatile Matter (ISO 351) **DB**	%	1	0.85	1
Sulpher (ISO 351) **DB**	%	0.9	0.75	1
G.C.V (ISO 1928)	Kcal/Kg	7150	7000	7200
N.C.V (ISO 1928)	Kcal/Kg	7050	6800	7150
MICUM 40 (ISO 7517)	%	78	82	84
MICUM 10)ISO 7517)	%	7	6.5	7
Bulk Density (ISO 567)	Kg/m^3	550	480	560
Porosity (ISO 1014)	%	50	45	52
CSR(ASTM D 5341)	%	61	58	64
CRI (ASTM D 5341)	%	25	23	27
Size (Round Holes) 20-90 mm(ISO 728) < 20 mm > 90 mm	%	 90 5 5	 92 4 4	 88 6 6
Or 40-90 mm(ISO 728) < 40 mm > 90 mm	%	90 5 5	92 4 4	88 6 6
ASH Analysis				
SiO_2	%	46.7	45	48
Al_2O_3	%	27	25	28
TiO_2	%	1.15	1.1	1.2
Fe_2O_3	%	14.5	13	16
CaO	%	4.5	4.3	5
NaO	%	0.8	0.8	0.9
MgO	%	1.95	1.9	2.1
K_2O	%	1.33	1.3	1.4
Mn_3O_4	%	0.04	0.03	0.05
P_2O_5	%	0.64	0.4	1.2

APPENDIX B

Table (B.1) Phenol removal for A.C and coke systems for influent phenol = 100 mg/l, influent COD concentration 500 mg/l and flow rate 21.6 l/d

Time (days)	A.C system		Coke system	
	eff phenol mg/l	% phenol rem	eff phenol mg/l	% phenol rem
1	0	100	6	94
3	0	100	14	86
5	0	100	20	80
7	0	100	23	77
9	3	97	26	74
11	9	91	31	69
13	12	88	37	63

Table (B.2) Phenol removal for A.C and coke systems for influent phenol = 200 mg/l, influent COD concentration 500 mg/l and flow rate 21.6 l/d

Time (days)	A.C system		Coke system	
	eff phenol mg/l	% phenol rem	eff phenol mg/l	% phenol rem
1	0	100	20	90
3	4	98	32	84
5	8	96	46	77
7	16	92	50	75
9	22	89	58	71
11	29	85.5	68	66
13	36	82	79	61

Table (B.3) Phenol removal for A.C and coke systems for influent phenol = 300 mg/l, influent COD concentration 500 mg/l and flow rate 21.6 l/d

Time (days)	A.C system		Coke system	
	eff phenol mg/l	% phenol rem	eff phenol mg/l	% phenol rem
1	3	99	54	82
3	9	97	63	79
5	18	94	83	72.3
7	33	89	94	68.6
9	48	84	105	65
11	57	81	120	60
13	69	77	135	55

Table (B.4) Phenol removal for A.C and coke systems for influent phenol = 300 mg/l, influent COD concentration 500 mg/l and flow rate 43.2 l/d

Time (days)	A.C system		Coke system	
	eff phenol mg/l	% phenol rem	eff phenol mg/l	% phenol rem
1	12	96	72	76
3	21	93	87	71
5	34	88.7	99	67
7	42	86	114	62
9	56	81.3	135	55
11	72	76	156	48
13	89	70.3	177	41