CHAPTER 5

ACTIVATED CARBON ADSORPTION STUDIES IN BASAL SALT MEDIUM

CHAPTER 5

ACTIVATED CARBON ADSORPTION STUDIES IN BASAL SALT MEDIUM

5.1 INTRODUCTION

This chapter deals with removal of phenolic compounds using granular activated carbon used in biosorption experiments. The optimum temperature and pH for the bacteria *Pseudomonas aeruginosa* have been reported as 30°C and 7.0 respectively. Therefore, the adsorption equilibrium and kinetic studies have been performed for adsorption on activated carbon in presence of minimal nutrient medium (Basal Salt Medium) at 30°C and pH 7.0.

5.2 THEORETICAL BACKGROUND

5. 2.1 General Description

As discussed in Chapter 3, both the rate and extent of adsorption are influenced by the properties of the adsorbate, adsorbent, and the system parameters such as concentration of phenol, temperature and pH of the phenolic solution. The important adsorbent characteristics include surface area, pore size and their distribution, particle size of the adsorbent, etc. Nature of the adsorbate, the type and position of functional groups present on the parent molecule of the adsorbate, influence the process of adsorption.

5.2.2 Surface area, Pore sizes and their distribution

It is desirable for any adsorbent such as activated carbon to have a high surface area per unit weight. This is possible only through highly developed porous structure on adsorbents. The high surface area in the range 200-1500 m^2/g of activated carbon makes an adsorbent of practical utility. However, high surface area carbons may lack physical strength, thus limiting their usefulness in some practical applications. Also, most of the surface area resides in very small pores, thus making them unsuitable for removal of large molecules. Thus, the pore sizes as well as their distribution are both important. Typical amorphous adsorbent may contain pores of varying sizes from a few nanometers to perhaps one micrometer. The pores have been classified in three categories according to the size namely micropore, mesopore and macropores. Micropores generally make a dominant contribution to the adsorptive capacity of small molecules, which can penetrate these pores. However transport within these pores can be severely limited by steric effects, resembling molecular sieve behavior. Though mesopores do make some contribution to the adsorptive capacity, yet their main role lies in providing conduits to the smaller micro pores. Macro pores provide very little in terms of adsorptive capacity however, they contribute a lot in the kinetic behavior. The activated carbon is prepared from carbonaceous materials such as coal, lignite, and coconut shells by controlled burning. Structurally, activated carbon is an amorphous type of adsorbent.

5.2.3 Adsorption Kinetics

Adsorption is time-dependent process and as such the knowledge of the rate of uptake is essential for selecting and designing a process. The rate of uptake on a porous adsorbent such as granular activated carbon (GAC) is described in terms of mass transport resistances (Seader and Henley 1998). The slowest of these steps determine the adsorption kinetics as described in theoretical section 3.2.4 on kinetics in Chapter 3.

5.3 EXPERIMENTAL

Batch studies were carried out to determine the adsorption equilibrium and kinetics of various phenolic compounds on activated carbon in presence of basal salt medium at 30°C.

5.3.1 Materials

The materials used and the procedure adopted for these studies are as described in Chapter 3, unless or other wise mentioned.

5.3.1.1 Adsorbent

The granular activated carbon (IC 25) obtained from Gujarat Industrial Carbon Ltd., Ankleshwar, was used.

5.3.2 Methods

5.3.2.1 Analytical Procedure

All the phenols were analyzed using the standard 4-aminoantipyrene method (APHA 1989). To study the effect of the presence of Basal Salt Medium (BSM) on the calibration curves (absorbance versus concentration) were prepared for phenolic solutions containing BSM. However, no change due to the presence of BSM in the solutions of phenols was observed in the calibration curves. Hence the same calibration curve that was used in Chapter 3 was also used here.

5.3.2.2 Characterization

The activated carbon used in this study was characterized for BET-surface Area, porosity and pore-size distribution. This was got done at Postgraduate Department of Material Science, S.P. University, V.V. Nagar, India. Sample was degassed at 150°C for about 1 hour to remove moisture and unwanted adsorbed species on the carbon surface. Nitrogen was introduced at pressure slightly below atmospheric pressure and at boiling point, i.e. 77.2 K. Amount of nitrogen adsorbed at equilibrium was measured for different nitrogen pressures. Thus, with the knowledge of amount of Nitrogen at monolayer adsorption, surface area can be determined. BET surface area analyzer of Micormeritices was used in this study.

Mercury porosity meter was used for determination of porosity and pore-size distribution at SICART, V.V. Nagar. Pressure required for intrusion of mercury is inversely proportional to the diameter. Total volume of mercury introduced gives the apparent density and thus porosity of the material. Size analysis has been done using Laser particle size analyzer also at SICART.

5.3.2.3 Adsorption Equilibrium Studies

The equilibrium studies were conducted at 30±1°C for 48 h. The working solution (200 ml) at 800 mg/l concentration was obtained by adding the required amount of stock solution to the BSM. The preweighed quantities of activated carbon were contacted in a 250 ml stoppered conical flask with 200 ml of working solution for 48 h. The optimum dosage of activated carbon with different initial concentration of phenols was used for experiments. In trial run, 48 h were found sufficient to attain equilibrium. In some of the trial runs having higher dosage of activated carbon, bacterial growth was observed that affected the equilibrium concentrations. After 24 h, due to low concentration of the phenolic compounds in the solution with BSM, a favorable environment for bacterial growth was created. Therefore, it was decided to add $HgCl_2$ of 6 mg/l as bactericidal agent so that it will not affect the equilibrium of the phenolic compound. It was also tested that the presence of this agent does not interfere with any analytical procedure. After 48 h the flasks were taken out of the shaker for analysis.

5.3.2.4 Adsorption Kinetics

The required quantity of BSM was poured into 250 ml stoppered conical glass flasks. The activated carbon at 2.5 g/l was added to each flask and these flasks were kept in incubator-cum-shaker at 30°C. The kinetics of adsorption of the phenolic compounds was followed for 24 h.

5.4 RESULTS AND DISCUSSION

5.4.1 Adsorbent Properties

The physical properties of the activated carbon used in this study are given in Table 5.1 and size fraction analysis is given in Table 5.2. The surface area of the activated carbon used in the work is comparable to that used by Streat et al. (1995). The pore size distribution analysis shows that this activated carbon has pore structure as given below:

59 percent with diameter < 5 μm, 41 percent > 5 μm and 18 percent < 0.01 μm.

Table 5.1. Physical properties of activated carbon used in the study

BET Surface Area-N_2	1274.09 m^2/g
Porosity	42.74 %
Average pore diameter	1.66 μ
Bulk density	0.736 g/ml
Apparent(skeletal) density	1.29 g/ml
Pores with diameter less than 5 μm	59 %
Pores with diameter greater than 5 μm	41 %
Very small pores (less than 0.01 μm)	18 %

Table 5.2. Size analysis of activated carbon

Adsorbent	**<10%**	**<50%**	**<90%**	**Volume mean diameter**
Coconut based Activated carbon	257.01μm	438.69μm	643.25μm	446μm

5.4.2 Adsorption Equilibrium Isotherms

The adsorption equilibrium data were correlated using the same six isotherm models and the windows based statistical software, SPSS version 8.0 as described in Chapter 3. The results obtained are comparable to that reported in the literature by Streat et al. (1995). Using a coconut origin based activated carbon 208C having surface area of 1114 m^2/g and equilibrium phenol concentration range up to 600 mg/l, they collected the data and fitted in Freundlich model. The isotherm reported by them is:

$$Qe = 84.6C_e^{0.238}$$

Table 5.3. List of parameter values of the six adsorption isotherms for different systems investigated

		Freundlich	Langmuir	Redlich Peterson	Toth	Radke-Prausnitz	Fritz-Schlunder
Phenol/ Activated carbon	Parameter Values	$K_f=74.58$ $n=4.25$	$Q=277.77$ $b=0.042$	$K_1=0.11$ $K_2=-1.11$ $m=-0.3$	$T=0.91$ $a=0.259$ $th=569.68$	$K=40502$ $k=75.18$ $p=4.28$	$a_1=1.01$ $a_2=0.01$ $b_1=2.23$ $b_2=2.01$
	Max. % Dev.	0.57	3	1.85	1.45	0.69	-1.41
	% Std. Dev.	0.24	1.11	0.61	0.44	0.2	0.43
	R^2	0.99	0.97	0.99	0.99	0.99	0.99
Catechol/ Activated carbon	Parameter Values	$K_f=89.21$ $n=5.37$	$Q=236.46$ $b=0.0966$	$K_1=15.47$ $K_2=0.05$ $m=1.02$	$T=445.1$ $a=0.607$ $th=0.24$	$K=6809.5$ $k=89.61$ $p=5.39$	$a_1=1.87$ $a_2=0.02$ $b_1=4.87$ $b_2=4.68$
	Max. % Dev.	-1.99	6.3	2.6	-3.11	-1.98	-1.89
	% Std. Dev.	0.48	1.98	0.56	0.74	0.48	0.48
	R^2	0.99	0.94	0.99	0.99	0.99	0.99
3-aminophenol/ Activated carbon	Parameter Values	$K_f=67.55$ $n=4.366$	$Q=218.34$ $b=0.0968$	$K_1=140.4$ $K_2=1.84$ $m=0.79$	$T=482.7$ $a=0.74$ $th=0.24$	$K=113.19$ $k=78.85$ $p=4.98$	$a_1=1.87$ $a_2=0.02$ $b_1=4.87$ $b_2=4.68$
	Max. % Dev.	1.49	9.9	0.6	2.89	0.48	-0.17
	% Std. Dev.	0.3	2.59	0.52	0.54	0.13	0.05
	R^2	0.99	0.94	0.99	0.99	0.99	0.99

The data obtained in the present study have almost similar equilibrium concentration range and Freundlich isotherm obtained is:

$Qe = 74.58Ce^{0.235}$

Though the surface area is marginally less in their work, the high values of K_f may be due to the fact that Streat et al. (1995) have taken 30 days time whereas time taken in the present work was only 48 h.

Comparison of the six isotherm models to correlate the experimental data obtained for all the phenolic compounds is shown in Fig. 5.1. Whereas Fig. 5.2 depicts the comparison of experimental and predicted amounts of phenol adsorbed on activated carbon. The values of isotherm constants obtained by fitting the experimental data to six isotherms are enlisted in Table 5.3. Amongst six isotherm used, Langmuir gave the poorest fit with correlation coefficient (R^2) of 0.94-0.97, average % standard deviation (σ) of 5.8% and maximum percentage deviation of 9.9%. All other isotherms correlate data very well. The R^2 values for rest the models were more than 0.99. The σ values for Freundlich, Redlich Peterson, Toth, Radke Prausnitz and Fritz Schlunder were 1.02%, 1.69%, 1.72%, 0.81% and 0.96% respectively.

The relative adsorbability of three phenolic compounds is in the order (Table 5.4):

Catechol > phenol > 3-aminophenol

The difference in adsorption behavior of these three phenols has been explained and discussed earlier in Chapter 3.

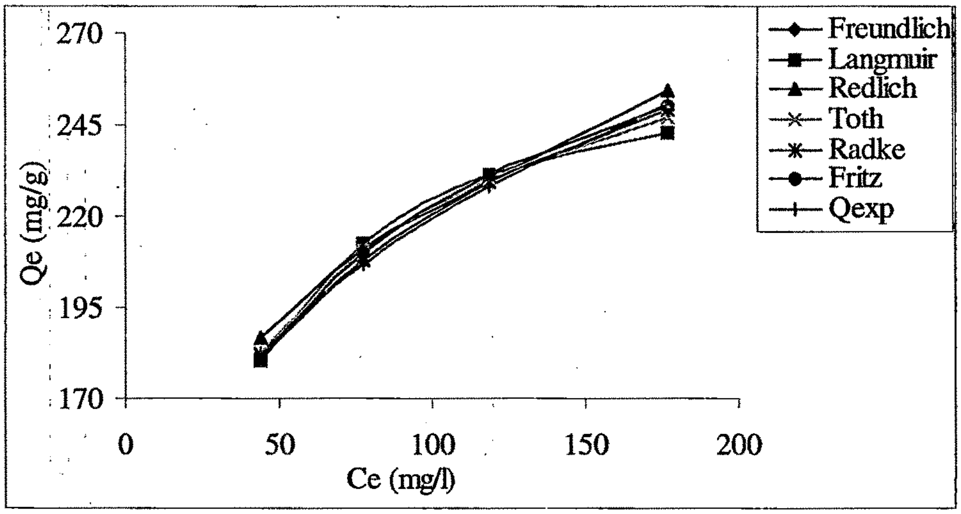

Figure 5.1. Comparison of different isotherm models for phenol adsorption on activated carbon with experimental results

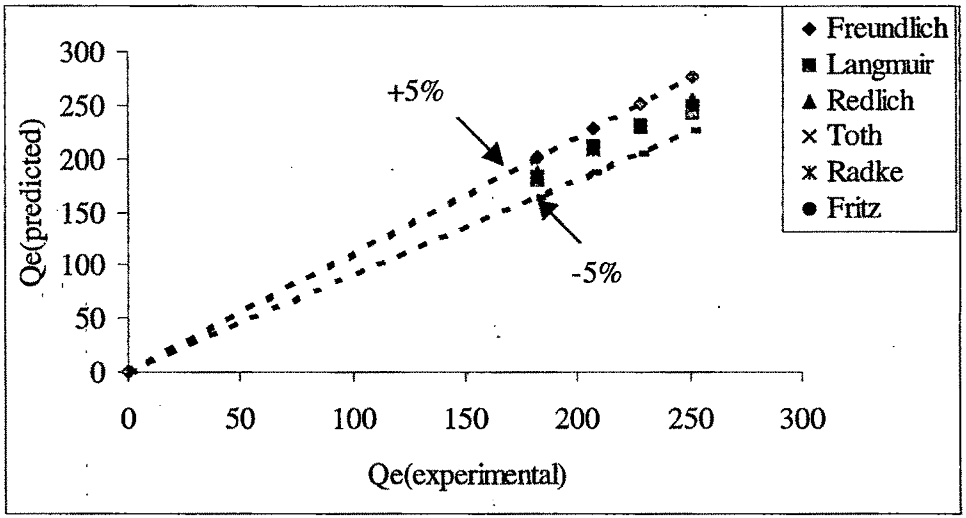

Figure 5.2. Comparison of experimental and predicted amount of phenol adsorbed on activated carbon

5.4.3 Kinetics

Lagergren's pseudo first order equation and pseudo second order rate equation given by Ho and Mckay(1998) have been used to determine kinetic parameters. Figs. 5.4 and 5.6 show the appropriate plot for pseudo first order and pseudo second order kinetics for different initial concentration of phenol adsorbed on activated carbon in BSM. The rate constants determined with these kinetic equations are listed in Table 5.5. Pseudo second order kinetics could fit the data well. Similar trend was observed in adsorption of catechol and 3-aminophenol, therefore, their plots are not shown here.

Experiments to determine the rate controlling mechanism were conducted in batch reactor at maximum 800 mg/l concentration i.e. the maximum biodegradable concentration. The rate of the uptake is controlled by the intraparticle diffusive transport. This has been discussed in Chapter 3. For intraparticle diffusion controlled process, fractional uptake curve has been plotted in Fig. 5.3. In this plot, there are regions of different rates of uptake, namely: fast, medium and slow. It is likely that adsorbate initially diffuses to the macro and then into the micro pores. This has been explained by Allen el al. (1989) in their adsorption studies of dyes, at different initial concentration on the peat in batch contactor. They observed the porous adsorbents have tree like structure wherein large diameter macro pores extended into particle body and subsequently branch out to meso pores and then to micro pores. In the present study, highly porous activated carbon has been used as an adsorbent, hence similar behavior showing different rates of uptake has been observed for adsorption of all the three phenols.

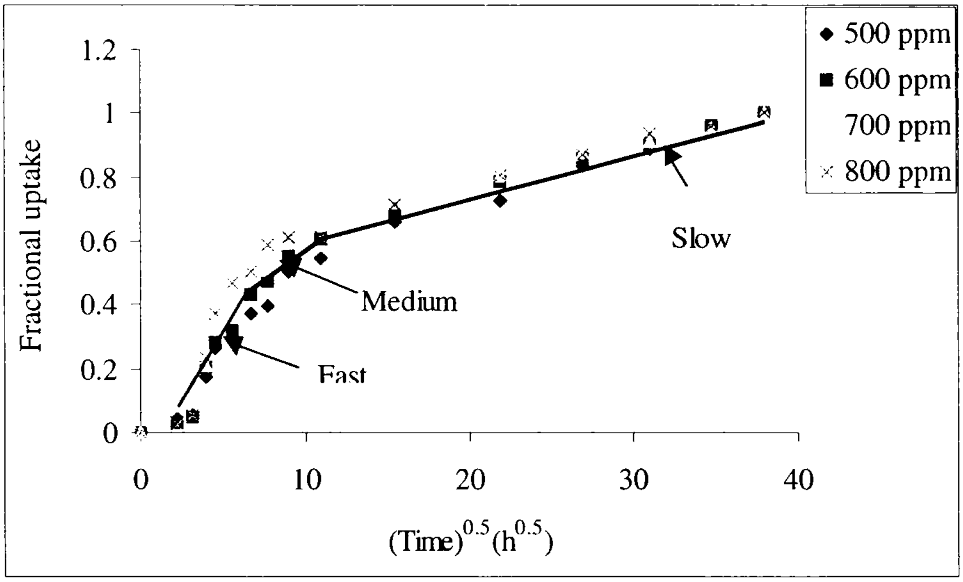

Figure. 5.3 Typical Fractional up take curve (Weber-Morris plot) for phenol adsorption on activated carbon using different initial concentration

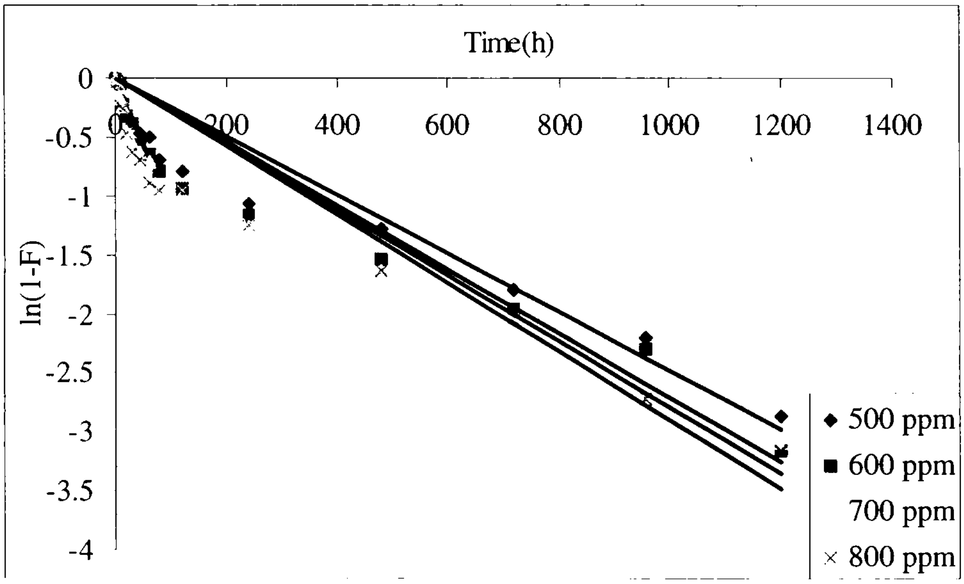

Figure 5.4. Plot to determine first order kinetics (Lagregren equation) for phenol adsorption on activated carbon

Trendline equation and correlation coefficient values for Fig. 5.4				
	500 ppm	600 ppm	700 ppm	800 ppm
y=	-0.0026x	-0.0027x	-0.0028x	-0.0029x
R^2=	0.8995	0.8546	0.7824	0.7458

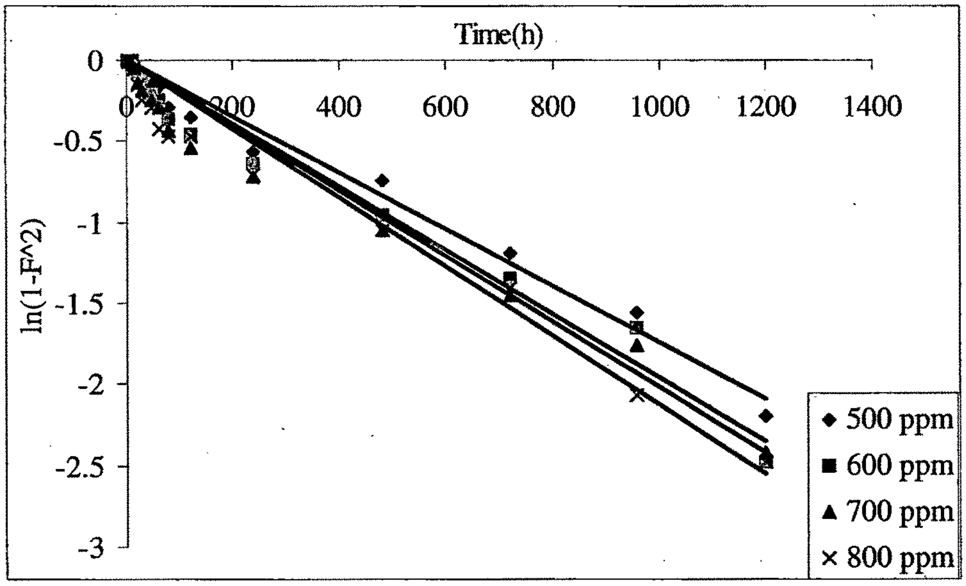

Figure 5.5. Plot to calculate effective Diffusion coefficient using Vermeulen or Urano approximations [Activated carbon / Phenol system]

Trendline equation and correlation coefficient values for Fig. 5.5				
	500 ppm	600 ppm	700 ppm	800 ppm
y=	-0.0019x	-0.002x	-0.002x	-0.0021x
R^2=	0.9861	0.9693	0.9542	0.9289

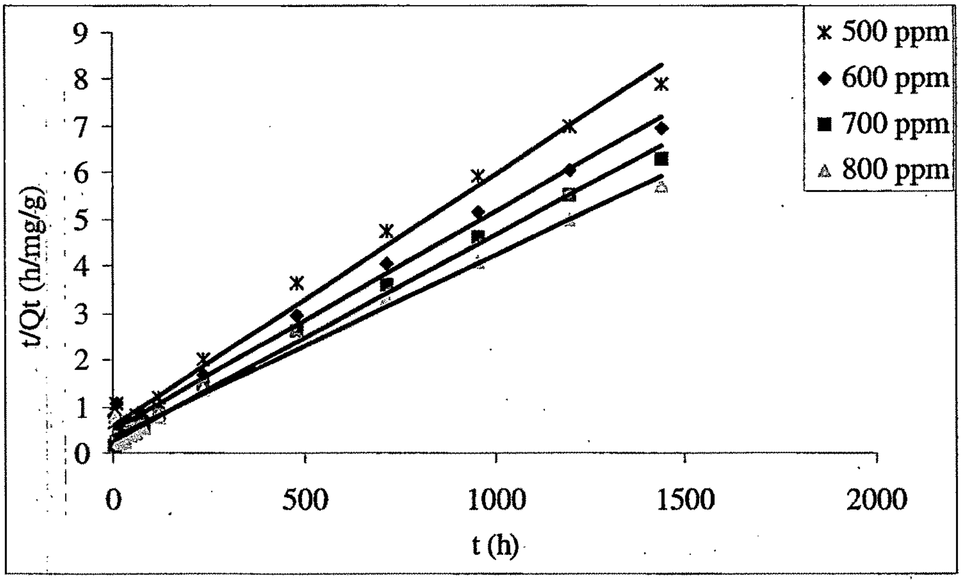

Figure 5.6. Plot to determine pseudo second order kinetics for adsorption of Phenol on Activated carbon

Trendline equation and correlation coefficient values for Fig. 5.6				
Co	500 ppm	600 ppm	700 ppm	800 ppm
y=	0.0054x + 0.5888	0.0047x + 0.4919	0.0044x + 0.265	0.0039x + 0.347
R^2=	0.9903	0.989	0.9962	0.9885

Table 5.4 Kinetic parameters for adsorption on activated carbon in presence of minimal nutrient medium

	Co (ppm)	K_1	R^2	K_2x10^5	h	R^2	$D_i x10^{13}$ (m^2/s)	R^2
Phenol	500	0.0026	0.90	4.95	1.70	0.99	95.7	0.99
	600	0.0027	0.85	4.49	2.03	0.99	100.1	0.97
	700	0.0028	0.78	7.31	3.77	0.99	101	0.95
	800	0.0029	0.75	4.38	2.88	0.99	106	0.93
Catechol	400	0.0044	0.87	13.7	3.33	0.99	181	0.96
	500	0.0047	0.87	12.8	4.55	0.99	191	0.96
	600	0.0036	0.83	10.7	4.45	0.99	141	0.96
	700	0.0036	0.87	3.36	2.00	0.97	141	0.96
	800	0.0039	0.83	6.43	4.02	0.99	156	0.95
3-Aminophenol	400	0.0038	0.98	3.21	0.9235	0.99	151	0.97
	500	0.0042	0.97	5.07	1.8044	0.99	171	0.99
	600	0.0056	0.97	4.51	2.04	0.97	241.8	0.99
	700	0.0049	0.95	8.31	3.9277	0.99	206	0.97
	800	0.0042	0.89	5.24	3.1192	0.99	171	0.96

It is evident from the discussion in the preceding section that the rates of adsorption of all the three phenolic compounds are controlled by diffusion mechanism. Hence, as given in Chapter 3, the rates of transport in this regime may be characterized by effective diffusion coefficients. Fig. 5.5 shows the typical plots to calculate effective diffusion coefficient using Vermeulen or Urano approximations. The diffusivity of the phenolic compounds based on this approach is comparable to that obtained by Streat et al. (1995) with correlation coefficient more than 0.93 in all the cases. Kumar et al.(2003) have also used the same approach for determining the rate controlling mechanism of adsorption studies.

Table 5.5 shows the diffusivities of different phenolic compounds from BSM in to activated carbon. The slight variation in the values of effective diffusion coefficient at different initial concentrations may be due to the assumption that particles are spherical whereas the particles are not fully spherical. The kinetics of adsorption show the similar type of behavior for phenol, catechol and 3-aminophenol. Kinetic behavior nay also be explained in terms of the mass transfer resistance of liquid film surrounding the adsorbent particle, intraparticle diffusion and finally adsorption on the pores of the surface of the adsorbent. The kinetics of the adsorbate is affected by its intrinsic properties such as solubility, presence and position of functional groups, molecular weight, etc. to the extent that they have impact on the mass transfer coefficient. Thus, the kinetics of the three phenolic compounds seems to be characterized by intra-particle diffusion.

5.4.4 Effect of Concentration and Contact Time

The studies were started with 800 mg/l as initial concentration of phenolic compound and decreased in the steps of 100 mg/l to concentration of 400 mg/l, when more than 95% of the initially present compound was removed from the solution. The change in concentration of phenolic solution due to adsorption was studied upto equilibrium time of 24 h. In the case of phenol, catechol and 3-aminophenol, final concentration values were 169, 200 and 221 mg/l. In all the above cases other parameters such as temperature, pH, and weight of adsorbent were kept constant. Table 5.4 shows the reduction in concentration with time for phenol, catechol and 3-aminophenol respectively. It is clear from data in this table that the equilibrium time is slightly concentration dependent. At higher concentration, it takes more time to reach equilibrium.

This is also obvious from the data that most of the adsorption takes place in the initial period, of approximately one hour, at all the concentrations for all the three phenols. Initially the number of adsorption sites available is higher and the driving force for the mass transfer is greater, therefore, the adsorbate reaches the adsorption site with ease. With the number of active sites becoming less and the adsorbent becoming crowded from the inside, thus impeding the adsorbate from reaching the adsorption site.

Table 5.5. Effect of time and initial concentration on % removal of phenols by activated carbon

	Phenol				**Catechol**					**3-Aminophenol**				
Time(h)	**500 ppm**	**600 ppm**	**700 ppm**	**800 ppm**	**400 ppm**	**500 ppm**	**600 ppm**	**700 ppm**	**800 ppm**	**400 ppm**	**500 ppm**	**600 ppm**	**700 ppm**	**800 ppm**
0	0.0	0.0	0.0	0.0	0	0	0	0	0.0	0.0	0.0	0.1	0.0	0.0
5	3.8	2.5	10.1	1.9	3.8	3.9	1.1	7.2	2.0	4.7	8.7	8.5	2.7	2.3
10	4.7	3.9	13.7	4.3	5.1	4.1	5.8	10.8	4.0	17.2	14.3	18.6	2.2	7.8
15	16.1	17.7	17.4	18.2	6.3	15.1	16.9	15.9	16.9	27.3	24.2	32.3	5.8	21.1
20	23.9	24.3	30.4	29.5	7.3	22.1	21.4	29.8	28.2	42.2	30.4	36.0	23.7	30.1
30	28.0	27.7	34.7	37.0	14.6	25.9	25.3	33.3	35.5	47.7	49.7	45.0	28.1	36.3
45	34.0	37.7	39.1	39.6	18.8	31.1	34.9	37.0	38.3	57.8	58.4	46.6	37.1	43.8
60	36.1	41.1	42.0	46.3	27.6	35.1	45.3	40.6	44.5	60.2	59.6	49.2	45.5	48.8
80	46.0	47.9	49.1	48.3	32.6	41.9	49.8	47.2	48.7	64.5	62.1	50.3	50.0	51.2
120	49.9	52.9	53.7	48.4	44.3	46.0	57.2	52.4	54.5	75.0	71.4	59.3	54.5	52.3
240	60.0	59.6	59.4	56.0	68.7	71.7	69.8	60.8	57.3	80.1	77.0	66.2	60.3	56.3
480	66.0	68.1	66.7	63.6	80.3	77.9	74.6	67.7	62.5	85.2	84.2	76.2	73.7	70.3
720	76.1	74.7	72.5	68.5	85.0	82.7	81.2	74.7	66.2	90.0	88.2	78.1	75.0	70.3
960	81.0	78.2	75.4	73.7	88.8	85.5	81.7	75.1	71.3	93.8	89.1	81.5	77.2	73.0
1200	86.0	83.2	79.0	75.4	92.0	87.0	81.9	76.5	71.9	95.0	90.7	83.9	78.6	73.8
1440	91.2	86.9	82.8	78.8	92.8	87.6	82.0	76.7	72.4	95.5	91.1	85.2	80.4	75.0

5.4.5 Effect of Mass of Adsorbent

Varying amount of activated carbon was contacted with the basal salt medium contacting 800mg/l of phenolic compound for 48 h to optimize the dose of adsorbent. Fig. 5.7 shows the presence of phenolic compound removed with the change in dose of activated carbon. For initial increase in the dose of activated carbon the increase in percentage removal is higher, but afterwards increase in dose does not affect the adsorption capacity. As discussed in Chapter 3, it may be suggested that two stage batch adsorption or column configuration may be used, where adsorbent is always in contact with approximately constant concentration of solution of phenol.

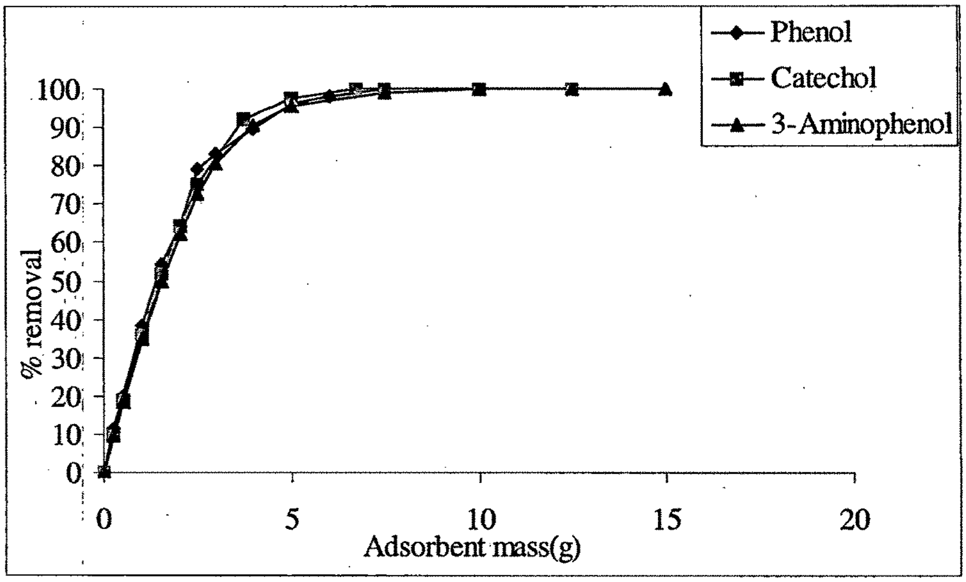

Figure 5.7. Effect of ACTIVATED CARBON dose on percentage removal of phenols [Temp.= 30 ±1 °C, pH= 7.0 Initial phenol conc.= 800 mg/l, contact time= 48 h]

5.5 Concluding Remarks

Studies on adsorption isotherm models and kinetics for three phenolic compounds phenol, catechol and 3-aminopheol on activated carbon in Basal salt medium at 30°C were carried out in batch contactors.

Six isotherm models, generally used in liquid systems, were tried to correlate the data collected. The goodness of fit of these models was tested using statistical analysis. The data were within 10% maximum deviation and correlation coefficient was always more than or equal to 0.94. Of all the isotherms studied, Langmuir gave the poorest representation. The adsorption capacity of the three phenolic compounds was found in the order:

Catechol> phenol>3-aminophenol.

The presence and position of functional group on the aromatic benzene ring and molecular weight affected the adsorption capacity of adsorbate on adsorbent.

The adsorption of all the three phenolic compounds shows three phases –rapid, medium, and slow. The initial rapid phase extends up to approximately 1 h and around 35 to 60% of the ultimate capacity is realized in this period. In the concentration range studied the film and intra-particle diffusion step was found to be rate controlling. The effective diffusivity of these compounds into activated carbon was determined by using a simple Vermeulen (1953) and Urano (1991) approximation. The values of the diffusivity coefficient were approximately of same order at all concentrations and for all the phenolic compounds.

The percentage removal of compounds increases with the decrease in initial concentration; however, the uptake decreases with decrease in initial concentration. This implies that at low concentrations, the capacity of the adsorbent cannot be utilized fully in batch contactors.

REFERENCES

Allen, S.J., Mckay, G., and Khader, K.Y. 1989. Intra-particle diffusion of a basic dye during adsorption onto sphagnum peat. Environm. Poll. 56:39-50.

Kumar, A., Kumar, S. and Kumar, S. 2003. Adsorption of resorcinol and catechol on granular activated carbon. Equilibrium and kinetics. Carbon. 41:3015-3025.

Seader, J.D., and Henley, E.J. 1998. Separation process principles. John Wiley & Sons, Inc. New York.

Standard methods of analysis: water and waste water examination. 1989. ed. 19 APHA/AWWA., Washington D.C.

Streat, M., Patrick, J. W. and Camporro Perez, M.J. 1995. Sorption of phenol and para-chlorophenol from water using conventional and novel activated carbons. Water Res. 29 (2): 467-475.

Urano, K. and Tachikawa, H. 1991. Process development for removal and recovery of phosphorus from wastewater by a new adsorbent.:Adsorption rates and breakthrough curves. Indian Eng. Chem. Res. 30: 1897-1899.

Vermeulan T. 1953. Theory for irreversible and constant pattern solid diffusion. Ind. Eng. Chem. 45(8): 1664-1670.

-*-*-*-*-*-