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Adsorption of Phenols from Aqueous Phase on Activated Carbon-Comparative Study

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The most hazard which humanity faces today is environmental pollution. The three natural media water, air and soil are receiving pollutants in ever increasing volume. Increasing environmental and scientific awareness and concern are bound to expand the role of granular activated carbon as the most efficient, broad spectrum and economical technology at tertiary level for scavenging refractory organics from potable and waste water. In the present work adsorption of some priority pollutants from their single and multi-component aqueous solutions on to various grades of granular activated carbons are studied. SEM and FTIR studies indicate the presence of various surface groups. The effect of physico-chemical parameters associated with the adsorbent on the adsorption equilibrium and adsorbate removal rate was also studied. Adsorption equilibrium and kinetic experiments are carried out in a batch reactor.

Key Words: Activated carbon, Adsorption, Wastewater treatment, Batch system adsorption isotherm.

INTRODUCTION

The environmental awareness and concern has bound to expand the role of granular activated carbon adsorption as a highly advantageous process for scavenging soluble, chemically stable and biologically non degradable pollutants from potable and waste water. Further activated carbon can be efficiently and economically regenerated for multiple reuse applications. The availability of a wide variety of granular activated carbon (GAC) samples in several countries has further boosted its application as an efficient and economically feasible domestic and industrial waste water treatment[1].

In the present investigation single and multi-solute adsorption equilibrium and kinetic studies have been carried out using *ortho*-chloro phenol, *meta*-nitro phenol, *para*-nitro phenol, classified as priority pollutants by environmental protection agency[2,3] as adsorbates. The influence of physico-chemical parameters associated with adsorbent such as source of GAC, surface area, particle size, pore structure and presence of surface groups on the adsorbent surface, adsorbate solubility, effect of dissolved oxygen on adsorption, carbon surface characteristics, on adsorption equilibria and kinetics were evaluated A batch reactor was employed for the evaluation of equilibrium and kinetic data.

Adsorption equilibrium data were analyzed by the Langmuir and B.E.T. isotherm equations where as the kinetic data was expressed by using a simplified rate expression based on Langmuir theory[4].

EXPERIMENTAL

The commercially available GAC filtrasorb-300 (f 300) was used as adsorbent in this work. It was first sieved to (12 × 16) mesh (B.S. standard) sample and then processed for its use as an adsorbent in the following manner. The adsorbent granules were first washed several times with distilled water. After 7-8 washings the clear leachate was obtained. After this the adsorbent sample was boiled with distilled water for about 5 min, the water was decanted off and the carbon slurry was further washed with distilled water till the leachate was visibly clear. The sample was then dried in an oven at 100-110 ºC and stored in a calcium chloride dessicator until use. The physical properties of the sample are reported in Table-1.

p-Nitrophenol (PNP), *o*-chlorophonol (OCP), *m*-nitrophenol (MNP) were selected as adsorbates in the present investigation. These compounds are frequently encountered in water and wastewater and impart objectionable taste and odour to drinking water. They are hence classified as priority pollutants by the environmental protection agency (EPA) USA. These adsorbates were obtained commercially in the purest form available, subjected to purification tests as and when necessary. The aqueous solutions of these adsorbates were used for equilibrium and kinetic studies[5]. Measurement of concentration of adsorbate in the solution was made by direct ultra violet absorption spectroscopy by measuring the optical density of the components at their respective maximum absorbance wavelengths on a GBC 911A UV spectrophotometer. The physico-chemical properties of these adsorbates, their wavelength of maximum absorption and the molar extinction coefficient (e) values are reported in Tables 2 and 3.

Adsorption isotherm and kinetics: The adsorption equilibrium data was obtained by stirring 0.25 g of GAC with 0.5 L of adsorbate solution taken in 1 L round bottom flask maintained at 30 ºC. (in the concentration range of $1\text{-}22 \times 10^{-4}$ mol/L). Stirring was continued for 5 h at a stirring speed of 800 ± 50 rpm. Some of the experimental were run for several days where no significant change in the equilibrium concentration value could be observed.

An alternative method was also used for the determination of the adsorption equilibrium data. The adsorption equilibrium experiments were carried out in 100 mL of adsorbate solution of desired concentration (in the concentration range of $1\text{-}22 \times 10^{-4}$ mol/L) were taken in 125 mL clean and dried BOD bottles. The BOD bottles were preferred over normal reagent bottles as they are provided with round glass stoppers which are air tight and the evaporation losses are avoided. After about 10-15 min of stirring on an electric shaking machine, known quantity of the adsorbate solution was withdrawn from the bottle for UV analysis. The withdrawal of the adsorbate solution was so adjusted that the initial adsorbate volume of 0.100 L was maintained 0.100 ± 0.001 g of accurately weighed GAC sample was then introduced in each bottle. Adsorbate solution without GAC addition was used as a control.

Five days were required to reach equilibrium. As a precaution any measure, the bottles were shaken for 7 days at room temperature. The adsorbate solution was again withdrawn from the system and analyzed to determine the equilibrium concentration. Some of the points on the isotherm were also tested for their reproducibility.

The method offered an advantage as the shaking machine had capacity of holding 60 bottles at a time and hence multiple isotherms could be evaluated simultaneously. All the equilibrium studies were conducted at room temperature and the fluctuations in the temperature of the adsorbate solution were not more than ± 2 ºC.

For evaluating the competitive or preferential adsorption of one solute over the other, the initial concentration of the different solutes were kept nearly same by mixing the required amount stock solutions of various solutes so as to compare their competitive adsorption on the adsorbent.

Adsorption rate studies were carried out in a 5 L cylindrical vessel fitted with baffles. 2 g of accurately weighed GAC sample was introduced into 4 L of adsorbate solution with constant stirring. Samples were withdrawn at selected intervals of time for analysis. Adsorbate solution without GAC addition was used as a control. The initial concentration of each adsorbate was kept same for multi-component adsorption equilibrium and kinetic studies.

Measurement of adsorbate concentration in single and multisolute solution was made by direct UV absorption spectrophotometry[6,7] by measuring the optical density of the components at their respective maximum absorbance wavelength.

Interpretation of kinetic data: A simplified interpretation of the kinetic data based on Langmuir theory[8] has been used. Rate was expressed as a function of directly measurable system variable, the fluid phase adsorbate concentration. It is assumed that the various solutes diffuse independently of one another and the competitive effects are taken into account only through the adsorption isotherm. Rate constant found in this manner are purely phenomenological depending upon the rate of adsorption and are useful only in comparisons between various adsorbates. The individual processes like adsorption, desorption and molecular diffusion are all coupled together and represented by the overall rate constant.

Langmuir theory assumes that the rate of adsorption is proportional to the product of adsorbate concentration in the fluid phase and the fraction of the vacant adsorbent surface. The fraction of the surface covered by the adsorbate, θ, is proportional to the decrease in fluid phase adsorbate concentration, thus

$$d\theta/dt = k_aC(1 - \theta) - K_d\theta \quad (1)$$

and

$$\theta = f(C_0 - C) \quad (2)$$

where, k_a and K_d are adsorption and desorption rate constants, C_0, C and C_e are the fluid phase adsorbate concentrations at zero, time t and at equilibrium, respectively, f is a constant. Substituting eqn. 2 in eqn. 1 and solving the resultant equation by applying the concept of steady state gives the final rate expression.

$$\text{In } [(C - C_e)/(C + \alpha) = -k_aC_et + \text{In } [C_0 - C_e)/(C_0 + \alpha) \qquad (3)$$

where, $\alpha = (C_0/KC_e)$ and $K = K_a/K_d$, the Langmuir constant.

The adsorption and desorption rate constants were thus evaluated by plotting In $[(C - C_e)/(C + \alpha)]$ against t, the linear regression analysis of the data gave very high correlation coefficients in the range 0.976-0.995.

RESULTS AND DISCUSSION

Adsorption isotherm plots for all the adsorbent-adsorbate systems indicated the typical isotherm plot for single solute system. The equilibrium data fitted well into Langmuir equation expressed as.

$$Q_e = Q^0bC_e/(1 + bC_e)$$

Competitive adsorption is closer to the bisolute system.

$$Qe_1 = \frac{Q_1^0 b_1 ce_1}{1 + b_1 C_{e_1} + b_2 C_{e_2}} \quad Qe_2 = \frac{Q_2^0 b_2 Ce_2}{1 + b_1 C_{e_1} + b_2 C_{e_2}}$$

where Q_{e_1} and Q_{e_2} = amount of solutes 1 and 2 adsorbed per unit weight or per unit surface area of adsorbent at equilibrium concentrations. $Q_{e_1}C_{e_2}$. Q^0_1 and $Q^0_{2\text{obtained}}$ = monolayer capacity of the soluted Nos. 1 and 2, respectively that are obtained from single solute systems. b_1 and b_2 = constants that are a function of the energy of adsorption of solutes 1 and 2, respectively and that are obtained form single solute systems.

The Langmuir treatment for competitive adsorption satisfactorily predicts the extent of adsorption from a bisolute system when Q^0_1 and Q^0_2 are unequal.

The BET isotherm was developed for the generalization of the ideal localized monolayer treatment (Langmuir model to account for the multilayer adsorption.

The BET equation is

$$\frac{C_e}{Q_e(C_s + C_e)} = \frac{1}{Q^0Z} + \frac{(Z-1)}{Q^0Z}\frac{C_e}{C_s}$$

where C_s = saturation concentration of the adsorbate, Z = constant.

A plot of $C_e/[Q_e(C_s - C_e)]$ against $[(C_e/C_s)]$ should give a straight line having slope $[(Z - 1)/Q^0_Z]$ and intercept $[1/Q^0_Z]$.

A glance at Q^0 value for *para*-substituted phenols show that adsorption capacity of adsorbates follow the trend OCP > PNP > MNP monolayer capacity seems to increase with increasing molecular weight and decreasing solubility of the adsorbate. These observations are supported by literature that adsorption increases with decreasing solubility of the adsorbate in the solvent[9,10]. The adsorbate solubility in water for the compounds studied is in the order.

MNP < PNP < OCP

The obtained data for bisolute -GAC system are summarized in Table-1 to 10.

TABLE-1
PROPERTIES OF GAC: FILTRASORB 300

N_2-BET surface area* (m^2/g)	970
Particle density* (g/cm^3)	0.7303
Pore volume* (g/cm^3)	0.850
Moisture content (wt %)	5.3
Ash content (wt %)	5.4
Volatile matter (wt %)	1.7
Carbon content (wt %)	87.6

*: Information supplied by the manufacturer.

TABLE-2
PHYSICO-CHEMICAL PROPERTIES OF ADSORBATES

Adsorbate	Symbol used	m.w.	Water solubility mol/L at 30 ºC	λ_{max}	ε cm^{-1}, mol^{-1} (observed value)
p-Nitrophenol	PNP	139.11	0.1294	316	8199
o-Chlorophenol	OCP	128.56	0.1724	273	1916
m-Nitrophenol	MNP	–	–	272	5526

TABLE-3
MOLAR EXTINCTION COEFFICIENT "ε" VALUES
AT DIFFERENT WAVELENGTHS FOR ADSORBATES

λ (nm)	PNP	OCP	MNP
272	2347	–	5526
273	2347	1916	–
277	2998	–	–
316	8199	3	1980

TABLE-4
PROPERTIES OF ADSORBATE

System	M. wt. (1)	M. wt. (2)	Solubility (1)	Solubility (2)	Slope (1)	Intercept (1)	Slope (2)
OCP-PNP-F300	128.56	139.11	0.1724	0.1294	0990.83	1.5996	1231.80
MNP-PNP-F300	139.11	139.11	0.0970	0.1294	1344.70	13.6470	1098.20

TABLE-5
B.E.T. MONOLAYER CAPACITY DATA FOR F300-BISOLUTE SYSTEMS

System 1-2-GAC	b (1)	Q^0 (1) (mol/g)	Q^0 (1) (ppm)	b (2)	Q^0 (2) (mol/g)	Q^0 (2) (ppm)	Q^0 (1) + Q^0 (2) (mol/g)
OCP-PNP-F300	619.42	10.09	129.75	557.43	8.12	112.93	18.21
MNP-PNP-F300	98.53	7.44	103.45	749.06	9.11	126.67	16.54

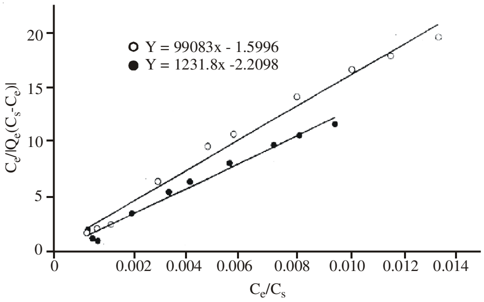

Fig. 1. B.E.T. isotherm plot for bisolute OCP-PNP F-3000 system

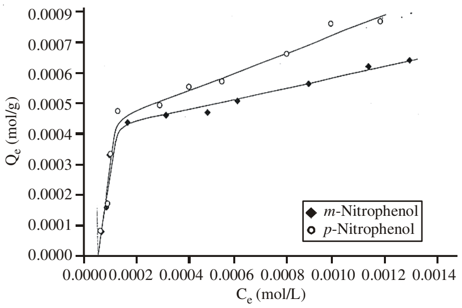

Fig. 2. Competitive adsorption isotherm of MNP-PNP-F300 system

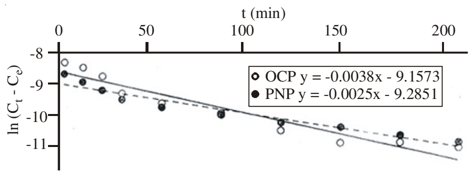

Fig. 3. Competitive adsorption kinetics of OCP-PNP F- 300 system

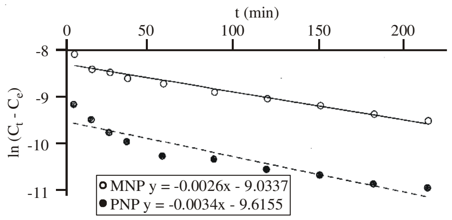

Fig. 4. Competitive adsorption kinetics of MNP-PNP-F300 system

TABLE-6
COMPARISON OF MONOLAYER CAPACITY OF AN ADSORBATE FROM SINGLE AND MULTISOLUTE SYSTEMS

System 1-2-GAC	Solubility (1) (mol/L)	Solubility (2) (mol/g)	Q^0 (1*) (ppm/g)	Q^0 (2*) (ppm/g)	Q^0 (1) (ppm)	Q^0 (2) (ppm)	Q^0 (1) + Q^0 (2) (ppm)
OCP-PNP-F300	0.1724	0.1294	190.45	166.00	129.75	112.93	242.68
MNP-PNP-F300	0.0970	0.1294	145.50	166.00	103.45	126.67	203.12

Q^0 (1*) and Q^0 (2*) are monolayer capacity values obtained from single solute adsorption equilibrium data. Q^0 (1) and Q^0 (2) are monolayer capacity values obtained from single bisolute adsorption equilibrium data.

The more hydrophobic compound MNP is adsorbed to much lesser extent. This indicates that along with the molecular weight and aqueous phase solubility of the adsorbate, other physical and chemical properties of the adsorbates like molecular size and branching, nature and position of the substituent group, possibility of intermolecular or inter molecular hydrogen bonding with the solvent and dipole moment *etc*., are playing a decisive role in overall adsorption process.

Conclusion

The source material used for preparation of GAC has a significant effect on its adsorption capacity, pore structure and surface characteristics. Bituminous coal based samples Filtrasorb-300 shows a loosely packed rough surface with lot of cracks, crevices and cavities. They high pore volume and widely dispersed pores.

Para substituted isomers of phenols are more preferably to be adsorbed as compared to *ortho* and *meta* isomers.

TABLE-7
BISOLUTE ADSORPTION EQUILIBRIUM DATA OF OCP-PNP-F300 SYSTEM
Adsorbate 1 = *o*-chlorophenol, adsrobate 2 = *p*-nitrophenol

Co1	Co2	Ce1	Ce2	Qe1	Qe2	CE/Cs(1)	Ce/[QE(CE-Cs)]	CE/Cs (2)	Ce/[QE(CE-Cs)]
0.000160	0.000133	0.000046	0.000028	0.000114	0.000105	0.000267	2.3453	0.000216	2.0534
0.000349	0.000337	0.000074	0.000080	0.000275	0.000257	0.000429	1.5617	0.000618	2.4076
0.000589	0.000568	0.000109	0.000148	0.000480	0.000420	0.000632	1.3189	0.001144	2.7257
0.000885	0.000861	0.000341	0.000389	0.000544	0.000472	0.001978	3.6447	0.003006	6.3835
0.001220	0.001175	0.000588	0.000640	0.000632	0.000535	0.003411	5.4181	0.004946	9.2854
0.001406	0.001355	0.000728	0.000771	0.000678	0.000584	0.042230	6.2503	0.005958	10.2689
0.001746	0.001724	0.000995	0.001089	0.000751	0.000635	0.005771	7.7291	0.008416	13.3688
0.002108	0.002048	0.001288	0.001365	0.000820	0.000683	0.007471	9.1801	0.010549	15.6059
0.002321	0.002286	0.001459	0.001556	0.000862	0.000730	0.008463	9.9058	0.012025	16.6682
0.002623	0.002573	0.001697	0.001798	0.000926	0.000775	0.009843	10.7403	0.013895	18.1921

TABLE-8
BISOLUTE ADSORPTION EQUILIBRIUM DATA OF MNP-PNP-F300 SYSTEM
Adsorbate 1 = *m*-nitrophenol, adsorbate 2 = *p*-nitrophenol

Co1	Co2	Ce1	Ce2	Qe1	Qe2	CE/Cs(1)	Ce/[QE(CE-Cs)]	CE/Cs (2)	Ce/[QE(CE-Cs)]
0.000104	0.000100	0.000019	0.000014	0.000085	0.000086	0.001358	16.0832	0.000104	1.2073
0.000210	0.000230	0.000043	0.000051	0.000167	0.000179	0.002976	17.8227	0.000395	2.2107
0.000403	0.000414	0.000059	0.000069	0.000344	0.000345	0.004140	12.0915	0.000529	1.5334
0.000604	0.000595	0.000145	0.000106	0.000459	0.000489	0.010156	22.3634	0.000820	1.6794
0.000812	0.000816	0.000316	0.000302	0.000496	0.000514	0.22122	45.6428	0.002334	4.5523
0.001018	0.001018	0.000500	0.000438	0.000519	0.000580	0.034930	69.8059	0.003386	5.8584
0.001199	0.001192	0.000633	0.000590	0.000566	0.000602	0.044245	81.7464	0.004557	7.5988
0.001598	0.001596	0.000951	0.000894	0.000647	0.000702	0.066497	110.0808	0.006906	9.8997
0.001953	0.001916	0.001228	0.001108	0.000725	0.000808	0.085902	129.6919	0.008561	10.6847
0.002171	0.002165	0.0001412	0.001342	0.000759	0.000823	0.098774	144.4912	0.010373	12.7413

TABLE-9
BISOLUTE ADSORPTION KINETIC DATA OF OCP-PNP-F300 SYSTEM
Particle size 12 × 16 mesh, T = 35 ºC, pH = 7.2, W = 2.0003 g, V = 400 L
adsorbate 1 = *o*-chlorophenol, adsorbate 2 = *p*-nitrophenol

Time (min)	Ct1 (mol/L)	Ct2 (mol/L)	Qtl (mol/g)	Qt1 (mol/g)	Ct1/Co	Ct1/Co
0	0.000148	0.000132	0.000000	0.000000	1.000000	1.000000
5	0.000144	0.000112	0.000008	0.000040	0.972973	0.848485
10	0.000128	0.000100	0.000040	0.000064	0.864865	0.757576
20	0.000114	0.000093	0.000068	0.000078	0.770270	0.704545
30	0.000100	0.000086	0.000096	0.000092	0.675676	0.651515
40	0.000084	0.000079	0.000128	0.000106	0.567568	0.598485
60	0.000077	0.000074	0.000142	0.000116	0.520270	0.560606
90	0.000071	0.000070	0.000154	0.000124	0.479730	0.530303
120	0.000061	0.000066	0.000174	0.000132	0.412162	0.500000
150	0.000055	0.000064	0.000186	0.000136	0.371622	0.484848
180	0.000056	0.000060	0.000184	0.000144	0.378378	0.454545
210	0.000054	0.000057	0.000188	0.000150	0.364865	0.431818
240	0.000053	0.000057	0.000190	0.000150	0.358108	0.431818
270	0.000052	0.000056	0.000192	0.000152	0.351351	0.424242
300	0.000052	0.000056	0.000192	0.000152	0.351351	0.424242

TABLE-10
BISOLUTE ADSORPTION KINETIC DATA OF MNP-PNP-F300 SYSTEM
Particle size 12 × 16 mesh, T = 35 ºC, pH = 7.2, W = 2.0003 g, V = 400 L
adsorbate 1 = *o*-chlorophenol, adsorbate 2 = *p*-nitrophenol

Time (min)	Ct1 (mol/L)	Ct2 (mol/L)	Qtl (mol/g)	Qt1 (mol/g)	Ct1/Co	Ct1/Co
0	0.000168	0.000132	0.000000	0.000000	1.000000	1.000000
5	0.000148	0.000095	0.000040	0.000072	0.880952	0.725191
10	0.000130	0.000078	0.000076	0.000106	0.773810	0.595420
20	0.000112	0.000067	0.000112	0.000128	0.666667	0.511450
30	0.000109	0.000059	0.000118	0.000144	0.648810	0.450382
40	0.000103	0.000054	0.000130	0.000154	0.613095	0.412214
60	0.000098	0.000047	0.000140	0.000168	0.583333	0.358779
90	0.000091	0.000046	0.000154	0.000170	0.541667	0.351145
120	0.000086	0.000042	0.000164	0.000178	0.511905	0.320611
150	0.000086	0.000040	0.000174	0.000182	0.482143	0.305344
180	0.000075	0.000037	0.000186	0.000188	0.446429	0.282443
210	0.000071	0.000036	0.000194	0.000190	0.422619	0.274809
240	0.000069	0.000033	0.000198	0.000196	0.410714	0.251908
270	0.000068	0.000034	0.000200	0.000194	0.404762	0. 259542
300	0.000068	0.000034	0.000200	0.000194	0.404762	0. 259542

Monolayer capacity and removal rate of the adsorbate increases with its hydrophobic nature and molecular weight. *ortho*-Chloro phenol is adsorbed to greater extent as compared to *para*-nitro phenol because of the electron-withdrawing inductive effect of chlorine.

The adsorption capacity for each adsorbate in the bisolute system gets reduced relative to its value in the single solute system but the cumulative adsorption capacities for multisolute systems were higher than those for single solute systems. In the mixture the competitive effects are more pronounced as the number of solutes increases and the total adsorption capacity is thus enhanced due to the increased cumulative adsorbate concentration.

Adsorption kinetic studies show that the hydrophobic solutes namely PNP and OCP were removed more rapidly as compared to MNP. From multisolute system the more hydrophobic solute was removed at a faster rate. The removal rate of individual components decreased as compared of their removal rate from single solute systems but the sum of the removal rate for the all the components was much higher for bisolute system.

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