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A Comparative Study of Effect of pH and Phosphate Buffer on Adsorption of Phenols on Filtrasorb-300

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Increasing environmental awareness and concern are bound to expand the role of activated carbon as a highly efficient and broad spectrum technology for the removal of organic pollutants from aqueous waste. Adsorption equilibrium and kinetics of some priority pollutants were studied on Filtrasorbs-300 at 30°C. The effect of various physico-chemical parameters associated with both absorbent and adsorbate on the adsorption rate and equilibrium were investigated. A batch reactor was selected for the evaluation and kinetic data. The adsorption data were analysed by Langmuir and B.E.T. isotherm equation and the rate of removal of adsorbate was calculated from the kinetic data by using a simplified rate expression based on Langmuir theory. All the adsorbates were analysed by UV absorption spectrophotometry.

Key words: Activated carbon, Adsorption, Buffer solution, Batch system, Organic pollutants, Waste water, Langmuir adsorption, Adsorption kinetics.

INTRODUCTION

Complete removal or reduction of dissolved organic compounds of permissible concentration levels has become a major concern of advanced waste water treatment technology. Adsorption on granular activated carbon is a highly advantageous process for removal of soluble, chemically stable and biologically non-degradable pollutants.

Experiments were carried out to study the adsorption equilibrium of hazardous organic pollutants namely *o*-nitrophenol, *p*-nitrophenol and 2,4-dichloro phenol on granular activated carbon sample namely Filtrasorb 300 (bituminous coal based) was used to evaluate the adsorption equilibria and removal rates. These compounds are frequently encountered in water and waste water, hence are classified as priority pollutants by the Environmental Protection Agency, USA.[1,2]. The optical densities of the components were measured at their respective wavelengths of maximum absorbance.

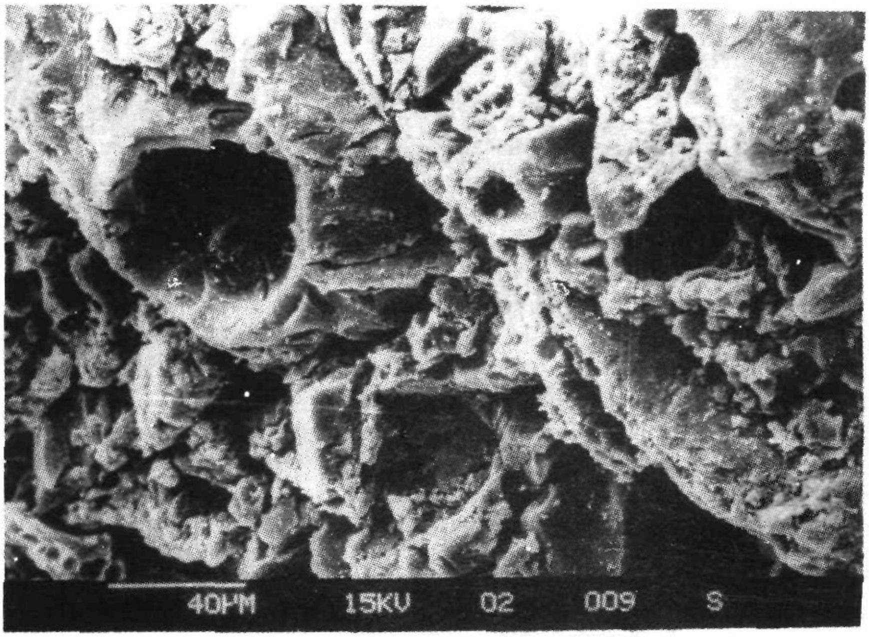
EXPERIMENTAL

Adsorbent: GAC sample of Filtrasorb-300 gifted by Calgon Corporation, A.C. Division, Pittsburgh, Pennsylvania, USA was used. The carbon was first sieved to obtain three fractions of 12 × 16 m.s., 25 × 44 m.s. and 72 × 100 m.s., washed several times with distilled water until the leachate was free from any suspended impurities and finally dried in an oven at 100–110°C for 24 h. The GAC sample was studied by scanning electron microscopy and FTIR spectroscopy to analyse the pore structure and surface characteristics.[3] The physical properties of Filtrasorb-300 (F-300) sample are reported in Table-1.

TABLE-1
PHYSICAL PROPERTIES OF FILTRASORB-300 (F-300)

Shape of GAC Filtrasorb-300	irregular
N2-BET surface area* (m^2/g)	970
Particle density* (g/cm^3)	0.7303
Pore volume* (g/cm^3)	0.850
Porosity	0.64
Moisture content (wt %)	5.3
Ash content (wt %)	5.4
Volatic matter (wt %)	1.7
Carbon content (wt %)	97.63
Mineral matter (%)	5.94
Hydrogen	0.18

*Information supplied by the manufacturer.



SEM micrograph of GAC-filtrasorb 300.

Adsorbate: These adsorbates were obtained commercially in the purest form available, subjected to purification tests as and when needed. All the stock and working solutions were prepared in boiled and cooled distilled water.

For the evaluation of adsorption equilibria the adsorbate solution ranges (1.0×10^4 to 22.0×10^{-4} mol/L) were prepared in distilled water and in the phosphate buffer having different pH 7.12 ($KH_2PO_4 + Na_2HPO_4$) 4.6 (KH_2PO_4) and 9.2 (Na_2HPO_4).

TABLE-2
PHYSICO-CHEMICAL PROPERTIES OF ADSORBATE

Adsorbate	Symbol	m.w.	m.p. (°C)	b.p. (°C)	Water solubility mol/L at 30°C	λ_{max}	e L mol^{-1}
o-Nitro-phenol	ONP	139.11	46	214	0.0143	277	5792
p-Nitro-phenol	PNP	139.11	114	279	0.1294	316	8199
2,4-Dichloro-phenol	DCP	163.01	45	210	0.0385	284	1800

For equilibrium studies experiments were performed using 125 mL borosil glass bottles at room temperature on electrical shaker. In 125 mL borosil glass bottles which were cleaned and dried previously 100 mL each of the prepared solutions were taken. The solutions were prepared in the range of 1.0×10^{-4} mol/L to 22×10^{-4} mol/L. A 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 not disturbed. Then 0.100 ± 0.0001 g of acurately weighed GAC samples were introduced in each bottle. The bottles were placed on shaker for 7 days. It was found that the time of 5 days was sufficient to reach the equilibrium for the compounds used in the study. As a precautionary measure experiments were continued for 7 days. Some of the points on the isotherm were also tested for their reproducibility.

The kinetic studies of the same absorbent/adsorbate systems were carried out in the aforesaid assembly of 8 L capacity. The initial adsorbate volume was maintained to be 4 L after the first withdrawal of the required quantity of solution for UV analysis showing initial concentration of the adsorbates. Then 2.000 g of accurately weighed GAC sample was introduced into the constantly stirred reactor. Known quantities of samples were withdrawn from the system at intervals of 5, 10, 20, 30, 40, 60, 90, 120, 150, 180, 210, 240, 270 and 300 minutes and their respective concentrations were determined in order to evaluate the fractional approach to equilibrium.

RESULTS AND DISCUSSION

Since the concentrations of interest in water and waste water are micromolar, it appears desirable to examine the Langmuir and B.E.T. isotherm equations in the very low adsorbate concentration range such as those studied in this investigation. The B.E.T. eq. is

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

In the present work ($C_s \gg C_e$) and $(Z-1) = Z$, therefore

$$\frac{C_e}{Q_e C_s} = \frac{1}{Q^0 Z} + \frac{C_e}{Q^0 C_s} \qquad \ldots (2)$$

which reduces to the Langmuir expression,

$$\frac{C_e}{Q_e} = \frac{1}{Q^0 b} + \frac{C_e}{Q^0} \quad \text{where } b = (Z/C_s) \qquad \ldots (3)$$

Thus at micromolar concentration range of solute the two isotherms give same results. B.E.T. isotherm plots were therefore carried out for all the adsorbate–adsorbent systems. The isotherms are depicted in Figs. 1 to 3. These plots also

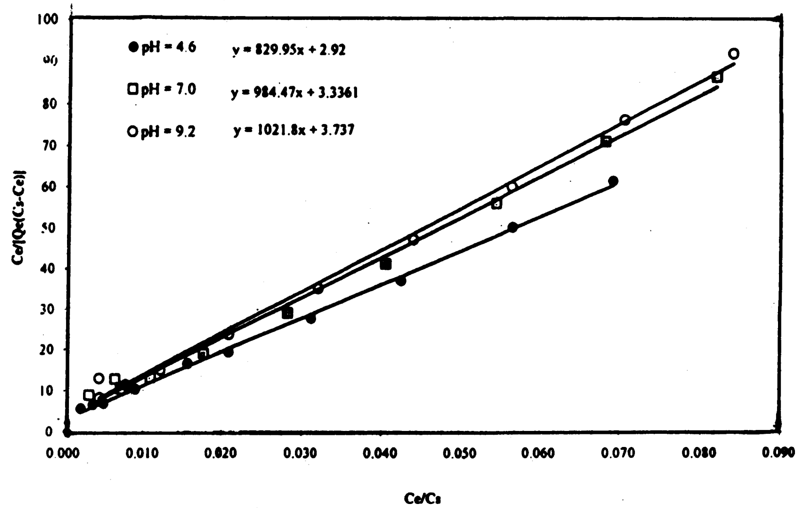


Fig. 1. B.E.T. isotherm of F300-*o*-Nitrophenol system at different pH.

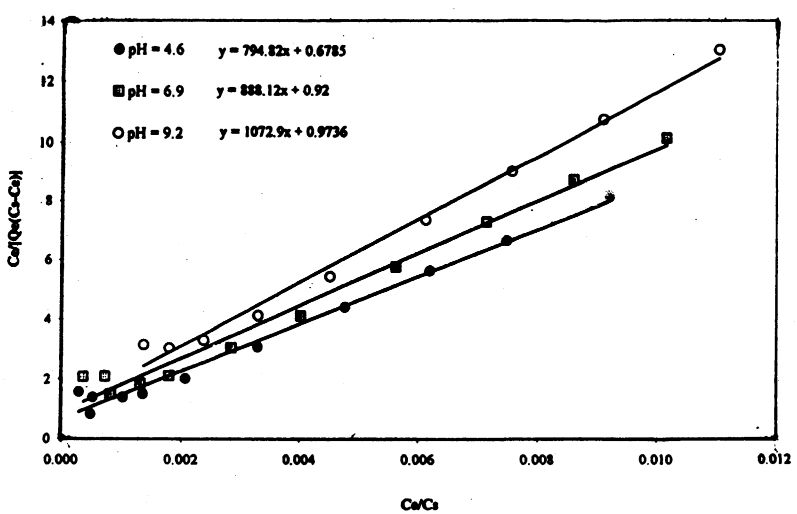


Fig. 2. B.E.T. isotherm of F300-*p*-Nitrorophenol system at different pH.

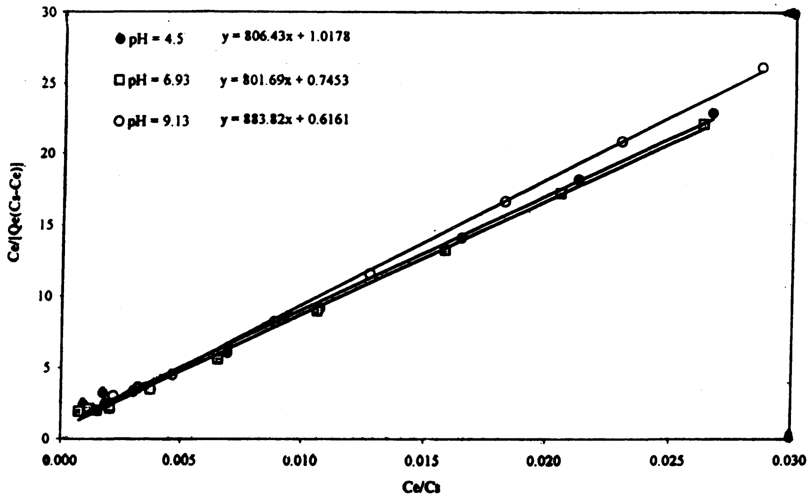


Fig. 3. B.E.T. isotherm of F300-2,4 Dichlorophenol system at different pH.

show the B.E.T. equation obtained by linear regression of the data. The regression coefficient values were above 0.98 indicating a good linear fit in all the cases.

By applying the concept of steady state we get the final rate expression

$$(\ln [(C_t - C_e)/(C_t + \alpha)] = K_a C_e + \ln (C_o - C_e)/(C_o + \alpha)] \quad (4)$$

The adsorption and desorption rate constants were thus evaluated by plotting $[(C_t - C_e)/(C_t + \alpha)]$ against time T. The linear regression analysis of the data gave very high correlation coefficient in the range 0.977–0.995.

TABLE-3

EFFECT OF pH ON ADSORPTION OF *o*-NITROPHENOL ON F300 GAC

Particle size: 12 × 16 mesh, T = 33°C, W = 0.100 g, V = 100 mL

pH = 4.6			pH = 7.0			pH = 9.2		
C_0, mol/L	C_e, mol/L	Q_e, mol/g	C_0, mol/L	C_e, mol/L	Q_e, mol/g	C_0, mol/L	C_e, mol/L	Q_e, mol/g
0.000100	0.000021	0.000079	0.000099	0.000021	0.000078	0.000099	0.000021	0.000078
0.000209	0.000025	0.000184	0.000035	0.000035	0.000161	0.000206	0.000036	0.000170
0.000407	0.000030	0.000377	0.000045	0.000045	0.000357	0.000399	0.000062	0.000337
0.000607	0.000052	0.000555	0.000092	0.000092	0.000510	0.000602	0.000063	0.000539
0.000805	0.000071	0.000734	0.000102	0.000102	0.000699	0.000802	0.000111	0.000691
0.001007	0.000128	0.000879	0.000156	0.000156	0.000848	0.001001	0.000174	0.000827
0.001186	0.000223	0.000963	0.000252	0.000252	0.000946	0.001200	0.000299	0.000901
0.001408	0.000299	0.001109	0.000403	0.000403	0.001002	0.001403	0.000458	0.000945
0.001605	0.000445	0.001160	0.000578	0.000578	0.001028	0.001603	0.000627	0.000976
0.001800	0.000605	0.001195	0.000777	0.000777	0.001029	0.001801	0.000805	0.000996
0.002003	0.000807	0.001196	0.000973	0.000973	0.001032	0.002003	0.001007	0.000996
0.002197	0.000987	0.001210	0.001170	0.001170	0.001034	0.002197	0.001199	0.000998

TABLE-4

EFFECT OF pH ON ADSORPTION OF *p*-NITROPHENOL ON F300 GAC

Particle size : 12 × 16 mesh, T = 33°C, W = 0.100 g, V = 100 mL

pH = 4.6			pH = 6.9			pH = 9.2		
C_0, mol/L	C_e, mol/L	Q_e, mol/g	C_0, mol/L	C_e, mol/L	Q_e, mol/g	C_0, mol/L	C_e, mol/L	Q_e, mol/g
0.000100	0.000023	0.000077	0.000100	0.000025	0.000075	0.000101	0.000032	0.000069
0.000204	0.000037	0.000167	0.000035	0.000047	0.000158	0.000203	0.000069	0.000134
0.000408	0.000067	0.000341	0.000045	0.000094	0.000314	0.000406	0.000137	0.000269
0.000607	0.000063	0.000544	0.000092	0.000106	0.000499	0.000602	0.000177	0.000425
0.000819	0.0000133	0.000686	0.000102	0.000170	0.000647	0.000812	0.000233	0.000579
0.001012	0.000176	0.000836	0.000156	0.000233	0.000776	0.001005	0.000305	0.000700
0.001214	0.000267	0.000947	0.000252	0.000366	0.000843	0.001204	0.000425	0.000779
0.001409	0.000424	0.000985	0.000403	0.000519	0.000882	0.001393	0.000582	0.000811
0.001613	0.000615	0.000998	0.000578	0.000726	0.000883	0.001604	0.000790	0.000814
0.001817	0.000800	0.001017	0.000777	0.000923	0.000888	0.001799	0.000977	0.000822
0.002009	0.000967	0.001042	0.000973	0.001110	0.000893	0.002003	0.001174	0.000829
0.002238	0.001189	0.001049	0.001170	0.001312	0.000908	0.002255	0.001424	0.000831

TABLE-5

EFFECT OF pH ON ADSORPTION OF 2,4-DICHLOROPHENOL ON F300 GAC

Particle size : 12 × 16 mesh, T = 33°C, W = 0.100 g, V = 100 mL

pH = 4.5			pH = 6.9			pH = 9.13		
C_0, mol/L	C_e, mol/L	Q_e, mol/g	C_0, mol/L	C_e, mol/L	Q_e, mol/g	C_0, mol/L	C_e, mol/L	Q_e, mol/g
0.000107	0.000022	0.000085	0.000103	0.000020	0.000083	0.000106	0.000023	0.000083
0.000202	0.000025	0.000177	0.000021	0.000021	0.000181	0.000201	0.000026	0.000175
0.000410	0.000035	0.000375	0.000028	0.000024	0.000380	0.000409	0.000067	0.000342
0.000602	0.000066	0.000536	0.000045	0.000045	0.000560	0.000600	0.000067	0.000533
0.000805	0.000070	0.000735	0.000057	0.000057	0.000749	0.000603	0.000083	0.000720
0.001029	0.000115	0.000914	0.000078	0.000078	0.000954	0.001030	0.000123	0.000907
0.001226	0.000144	0.001082	0.000143	0.000143	0.001083	0.001223	0.000179	0.001044
0.001421	0.000267	0.001154	0.000251	0.000251	0.001177	0.001424	0.000340	0.001084
0.001597	0.000412	0.001185	0.000408	0.000408	0.001198	0.001602	0.000490	0.001112
0.001821	0.000634	0.001187	0.000608	0.000608	0.001213	0.001816	0.000702	0.001114
0.002008	0.000817	0.001191	0.000789	0.000789	0.001216	0.002008	0.000883	0.001125
0.002217	0.001024	0.001193	0.001010	0.001010	0.001219	0.002229	0.001102	0.001127

TABLE-6
EFFECT OF pH ON REMOVAL RATE OF *o*-NITROPHENOL

GAC : F 300, T = 30°C, 12 × 16 mesh, W = 2.0001 g, V = 4.00 L

Time (min)	pH = 4.4		pH = 7.0		pH = 9.0	
	C_t, mol/L	C_t/C_0	C_t, mol/L	C_t/C_0	C_t, mol/L	C_t/C_0
0	0.000171	1.0000	0.000171	1.0000	0.000169	1.0000
5	0.000143	0.8363	0.000147	0.8596	0.000157	0.9290
10	0.000114	0.6667	0.000131	0.7661	0.000137	0.8107
20	0.000091	0.5322	0.000112	0.6550	0.000123	0.7278
30	0.000074	0.4327	0.000092	0.5380	0.000113	0.6686
40	0.000062	0.3626	0.000078	0.4561	0.000097	0.5740
60	0.000049	0.2865	0.000062	0.3626	0.000078	0.4615
90	0.000038	0.2222	0.000050	0.2924	0.000061	0.3609
120	0.000028	0.1637	0.000042	0.2456	0.000048	0.2840
150	0.000023	0.1345	0.000033	0.1930	0.000043	0.2544
180	0.000023	0.1345	0.000032	0.1871	0.000043	0.2544
210	0.000023	0.1345	0.000032	0.1871	0.000042	0.2485
240	0.000022	0.1287	0.000031	0.1813	0.000042	0.2485
270	0.000022	0.1287	0.000031	0.1813	0.000042	0.2485

TABLE-7
EFFECT OF pH ON REMOVAL RATE OF *p*-NITROPHENOL

GAC : F 300, T = 30 C, 12 × 16 mesh, W = 2.0003 g, V = 4.00 L

Time (min)	pH = 4.6		pH = 7.0		pH = 9.0	
	C_t, mol/L	C_t/C_0	C_t, mol/L	C_t/C_0	C_t, mol/L	C_t/C_0
0	0.000145	1.0000	0.000144	1.0000	0.000142	1.0000
5	0.000111	0.7655	0.000119	0.8264	0.000131	0.9225
10	0.000094	0.6483	0.000107	0.7431	0.000116	0.8169
20	0.000084	0.5793	0.000088	0.6111	0.000102	0.7183
30	0.000073	0.5034	0.000080	0.5556	0.000089	0.6268
40	0.000064	0.4414	0.000073	0.5069	0.000083	0.5845
60	0.000052	0.3586	0.000065	0.4514	0.000074	0.5211
90	0.000043	0.2966	0.000053	0.3681	0.000064	0.4507
120	0.000034	0.2345	0.000044	0.3056	0.000057	0.4014
150	0.000028	0.1931	0.000041	0.2847	0.000052	0.3662
180	0.000024	0.1655	0.000037	0.2569	0.000047	0.3310
210	0.000022	0.1517	0.000035	0.2431	0.000045	0.3169
240	0.000021	0.1448	0.000035	0.2431	0.000045	0.3169
270	0.000021	0.1448	0.000035	0.2431	0.000045	0.3169

TABLE-8
EFFECT OF pH ON REMOVAL RATE OF 2,4-DICHLOROPHENOL

GAC : F 300, T = 30°C, 12 × 16 mesh, W = 2.0002 g, V = 4.00 L

Time (min)	pH = 4.4		pH = 7.0		pH = 9.0	
	C_t, mol/L	C_t/C_0	C_t, mol/L	C_t/C_0	C_t, mol/L	C_t/C_0
0	0.000251	1.0000	0.000253	1.0000	0.000249	1.0000
5	0.000206	0.8207	0.000220	0.8696	0.000232	0.9317
10	0.000169	0.6733	0.000196	0.7747	0.000218	0.8755
20	0.000138	0.5498	0.000175	0.6917	0.000192	0.7711
30	0.000117	0.4661	0.000143	0.5652	0.000168	0.6747
40	0.000099	0.3944	0.000117	0.4625	0.000153	0.6145
60	0.000078	0.3108	0.000098	0.3874	0.000127	0.5100
90	0.000054	0.2151	0.000074	0.2925	0.000099	0.3976
120	0.000034	0.1355	0.000053	0.2095	0.000075	0.3012
150	0.000024	0.0956	0.000033	0.1304	0.000053	0.2129
180	0.000021	0.0837	0.000025	0.0988	0.000043	0.1727
210	0.000019	0.0757	0.000022	0.0870	0.000039	0.1566
240	0.000018	0.0717	0.000022	0.0870	0.000038	0.1526
270	0.000018	0.0717	0.000021	0.0830	0.000038	0.1526

TABLE-9
EFFECT OF ADSORBATE pH ON MONOLAYER CAPACITY (12 × 16 m.s.)

No.	Adsorbent/Adsorbate	pH	$Q^0 \times 10^4$ (mol/g)	Z
1.	F 300-ONP	in DW*	10.12	296
2.	F 300-ONP	4.6	12.01	285
3.	F 300-ONP	7	10.12	296
4.	F 300-ONP	9.2	9.75	274
5.	F 300-PNP	in DW*	11.93	2543
6.	F 300-PNP	4.5	12.57	1172
7.	F 300-PNP	6.9	11.25	966
8.	F 300-PNP	9.2	9.31	1103
9.	F 300-2,4-DCP	in DW*	11.81	1178
10.	F 300-2,4-DCP	4.5	12.38	793
11.	F 300-2,4-DCP	6.93	12.46	1077
12.	F 300-2,4-DCP	9.13	11.31	1436

DW*—Adsorbate solution prepared in boiled and cooled distilled water;
ONP— o^--nitrophenol; PNP—p^--nitrophenol; 2,4-DCP— 2,4-dichlorophenol.

TABLE-10
EFFECT OF ADSORBATE pH ON ADSORPTION REMOVAL RATE

No.	Adsorbent/Adsorbate	pH	b	Ka/min	kd/min
1.	F 300-ONP	in DW*	296	593.5484	2.0052
2.	F 300-ONP	4.6	285	1131.8182	3.9713
3.	F 300-ONP	7.0	296	674.1935	2.2777
4.	F 300-ONP	9.2	274	569.0476	2.0768
5.	F 300-PNP	in DW*	2543	188.5714	0.0742
6.	F 300-PNP	4.5	1172	847.6190	0.7232
7.	F 300-PNP	6.9	966	525.7143	0.5442
8.	F 300-PNP	9.2	1103	371.1111	0.3365
9.	F 300-2,4 DCP	in DW*	1178	910.0000	0.7725
10.	F 300-2,4 DCP	4.5	793	1138.8889	1.4362
11.	F 300-2,4 DCP	6.93	1077	757.1429	0.7030
12.	F 300-2,4 DCP	9.13	1436	371.0526	0.2584

DW*—Adsorbate solution prepared in boiled and cooled distilled water.

Effect of pH on adsorption capacity and adsorption rate

The adsorbate pH was adjusted to required value by adding the phosphate buffer for the adsorbent-adsorbate systems F300-ONP, F300-DCP. The isotherm data is given in Tables 3–5 and the isotherm plots are shown in Figs. 1–3. The adsorption rate plots are shown in Figs. 4–6. The pH values selected for the present work were 4.5, 7.0 and 9.2 so as to cover the acidic, neutral and basic range. The monolayer capacity values are reported in Table-3 the effect of pH on adsorption from the solution must be considered to result from the combined

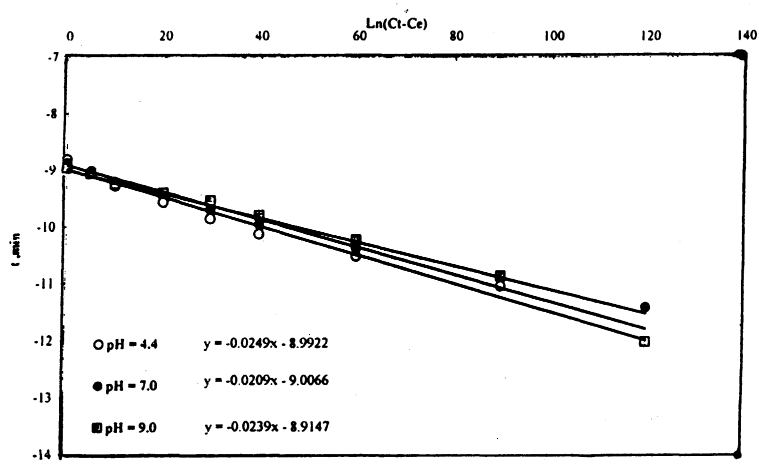


Fig. 4. Effect of pH on removal rate of o^{-}-nitrophenol.

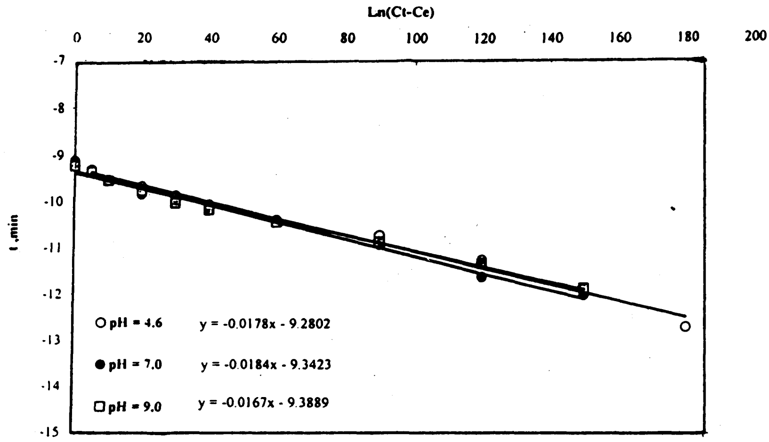


Fig. 5. Effect of pH on removal rate of p^{-}-nitrophenol

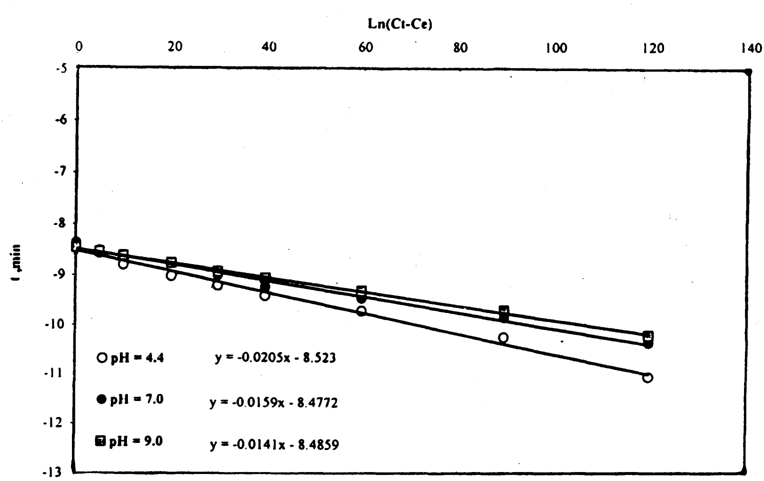


Fig. 6. Effect of pH on removal rate of 2,4-dichlorophenol

effects of pH on the nature of the adsorbate molecule, the adsorbent surface and the inorganic acids, bases and salts used to prepare the buffer for adjusting the pH.[5] The effect of pH may alter the chemical nature of the adsorbent surface. The adsorption capacity was observed to increase as the pH of the adsorbate solution decreased from 9.2 to 4.6 in case of all the three adsorbates, namely o^{-}-nitrophenol, p^{-}-nitrophenol and 2,4-dichlorophenol. The pK_a value of p^{-}-nitrophenol and o^{-}-nitrophenol is around 7.15 and that for 2,4-dichlorophenol is 7.8. The adsorption capacity for these adsorbates was observed to decrease sharply (as shown in the isotherm plots) as the pH increased above the pK_a value. The phenolic —OH ion concentration affects the associated or dissociated state of the absorbate which in turn will affect the extent of the absorption. Phenols being acidic in nature might be getting dissociated at higher pH above their pK_a value forming ionic species which are absorbed to a lesser extent by the covalent activated carbon surface. Similarly the slope of the adsorption rate plot shows that the absorbates are removed slightly at a faster rate at lower pH of 4.6. However, the difference in slopes of the kinetic plot is not much. The report by other workers[6, 7] suggests no significant difference in the absorbate uptake rate or isotherms when the adsoption was carried out from tap water, distilled water or of weak phosphate buffers.

Conclusion

The adsorbate pH influences the overall adsorption capacity and adsorbate removal rate significantly. Adsorption capacity and removal rate were found to be higher at pH 4.6 and pH 7.0 and decreased at pH 9.2.

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