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Comparison of adsorptions of phenol,p-nitrophenol and 1-butanol on the activated carbon

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ABSTRACT

Adsorption of 1-Butanol, Phenol, and P-nitrophenol on activated carbon have been studied. The results were used to testifying the validity of different models based on thermodynamic principles: Freundlich, Langmuir and Henry isotherms. The maximum capacity of adsorbent for three compounds was determined, The constants of equilibrium were determined by Freundlich isotherm and virial isotherm expression for phenol and 1-butanol, respectively. The thermodynamic functions: $\Delta G^\circ, \Delta S^\circ, \Delta H^\circ$, were calculated from the data of adsorption of phenol on activated carbon as a function of temperature. In addition , adsorption of mixtures of phenol and p-nitrophenol under limited range of concentration were studied. Finally arrangement of carbon atoms in activated carbon and surface coverage of activated carbon by phenol and 1-butanol for different configurations of compounds has been discussed.

Keywords: Activated carbon; Adsorption; 1-butanol; Phenol; p-nitrophenol isotherms - virial expression

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INTRODUCTION

The adsorption properties of the activated carbon (A. C) for gases and liquids, being caused that applaied widely the powdered and granular A.C for separations in the chemical petroleum,and pharmaceutical industries as well as in the removal of pollutants from water and air.

A.C is procured by carbonization of raw carbonaceous materials such as wood, resin like P.V.C and etc., in an inert atmosphere. Then the products are activated by different ways until obtain various carbons which they have high surface areas($400-1500m^2/g$) and different properties. [1]

LITERATURE SURVEY

Mattson et al. [2] observed a hysteresis in studying adsorption of phenol on the activated carbon, which was attributed to reversible adsorption of phenol on carbon.

Zogorski et al [3]. have studied the kinetics of phenol adsorption on the activated carbon. They showed that the adsorption of phenols were extremely rapid, approximately 60-80% of the adsorption occurred within the first hour of contact.

Chakravorti. Ranjit.k [4] have studied adsorption of phenol on activated carbon in both batch and fixed-bed systems. Isotherms have been determined in batch experiments for C pellets in 3 mesh ranges: $\frac{4}{6},\frac{6}{8},\frac{8}{10}$.

Bethell, James Robert [5] have recoverd quantitatively the 4.87% phenol existing in the aqueous effluents from phenolic resin manufacture , by adsorption on activated carbon.

Costa, Enrique, et al. [6] have determined the effective diffusion coefficients of adsorption of phenol and p-nitrophenol in solution on the activated carbon.

Irfan Z. Shirgaonkar, et al. [7] have studied the adsorption equilibrium of substituted phenols on the activated carbon. They have developed a new model using a thermodynamic approach and also they have obtained equation which is similar to Freundlich model.

Haghseresht F.; LU, G.Q. [8] have determined the adsorption isotherms of phenol, p-nitrophenol and

P-chloropenol on the best adsorbent that was prepared by them. Their results were correlated with theoretical isotherm equations such as the Langmuir, Freundlich, Radish Peterson equations.

Abe. Ikuo. et al. [9] have determined the Freundlich adsorption constants for the isomers of butanol and pentanol in clarifying the absorbability of structural isomers of some alcohols . Their results were correlated with various physical constants such as solubility in water, b.p. and some topochemical indexes characterizing the molecule connectivity or branching.

Du, Youru, et al. [10] have H-NMR study of Me, Et, n-Pr, iso-Pr and allyl alcohol adsorbed on charcoals with various pore structures. Their studies show that the adsorption mechanism is by capillary condensation in pores with radii smaller than 30A°, and by mono/ multi layer adsorption on the solid surface of pores with larger radii. The ^{13}CNMR parameters suggest that the adsorbed alcohol are preferentially oriented in the monolayer with the Me bonded to the solid surface. Longer chain alcohols are bent in capillaries with radii smaller than 10A°.

Branton, Peter G. et al. [11] have determined adsorption isotherms of methanol, ethanol, propane-1-ol butane-1-ol and water vapor on MCM-41. model mesoporous adsorbent. The isotherms of the alcohols are all of type IV, whereas the water isotherm is of type V in the IUPAC classification. Each adsorption isotherm exhibits a sharp step, indicative of capillary condensation within a narrow distribution of mesopores. The isotherms are reversible in the monolayer-multilayer region.

THE APPLIED EQUATIONS

1- Henry equation which is applied in the from of:

$$\frac{x}{m} = kp \qquad (1)$$

2- Langmuir equation of adsorption isotherm:

$$\frac{p}{a} = \frac{1}{a_m k} + \frac{p}{a_m} \qquad (2)$$

3- Freundlich isotherm equation:

$$\frac{x}{m} = kC^{\frac{1}{n}} \qquad (3)$$

where $a = \frac{x}{m}$ gram adsorbed per gram adsorbent

a_m : monolayer capacity

$\theta = \frac{a}{a_m}$: surface coverge

p: equilibrium pressure (atm)

K and n: Constants

C: Concentration (mg/ L)

4- The virial adsorption expression:

$$p = \frac{C}{k}\exp[2A_1 C + \frac{3}{2}A_2 C^2 + \frac{4}{3}A_3 C^3 + ...] \quad (4)$$

A1.A2.A3,... Virial coefficients

C:Concentration $(\mathrm{mol/cm^3})$

5- The thermodynamic relationships:

$$-\Delta G^\circ = RT \ln K \quad (5)$$

$$\ln K = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (6)$$

The osmotic pressure relation:

$$\Pi = CRT \quad (7)$$

C:Concentration (mol/L)

E XPERIMENTAL SECTION

Three organic compounds were choosen as adsorbates for the study. Phenol is a solid ,(d= 1.06 g/ml,and solubility, 82 g/L), para-nitrophenol,a solid(d =1.48 g/ml and solubility ,16 g/L) and 1-butanol, a liquid(d =0.81 g/ml and solubility, 83 g/L) were obtained as reagent grade from Merck company, also adsorbent,i.e. activated carbon, 2.5mm size (serial number 2518).

PRETREATMENT OF A.C

Granular activated carbon was first crushed and the particle size 60-80 mesh/inch was desired. The resulting fraction was washed in boiling deionized water for 3 times, dried at 120°C for 3h and stored in a desiccator.

THE CONCENTRATION OF SOLUTIONS

The initial solutions were prepared by dissolving the determined amounts of solutes in deionized water and diluting to the mark in volumetric flasks and mixing the solution. The equilibrium concentration of the solutions have been delivered from the calibration curves which the linear calibration curves were produced from the instruments response against the concentration of standard solutions.

CAPACITY DETERMINATION OF ADSORBENT

The experiment has been carried out with 50mL of solutions of different concentration of the compound in Erlenmeyer flasks to which 1 gram activated carbon were added. The flasks were kept on a rotary shaker 250 rpm. After passing 72h at room temperature $(30 \pm 2)\ ^\circ C$ and $(25 \pm 2)\ ^\circ C$ the samples were filtered through whatman paper no.1, and the filtrates were analysed for the residual compounds in a unicam 8625 UV-vis spectrophotometer with corresponding maximum absorption wavelengths

(phenol $\lambda_{max} = 211 nm$) (p-nitrophenol $\lambda_{max} = 319$ nm) and in a Varian star 3400cx gas-chromatograph for 1-butanol. The similar experiments were carried out for determination of optimum time of adsorption (the time for 95% of the capacity). The total obtained results are listed in table 1.

Table 1. adsorption capacity and optimum times

Feature / Compound	Cin g/L	Capacity (x/m)		t_{op} (h)
		mg/g	mmol/g	
Phenol	20	450	4.79	$2\frac{1}{2}$
p-nitrophenol	6	204.45	1.47	1
1-butanol	16.2	700	2.46	1

Cin: initial concentration

EQUILIBRIUM STUDIES

Adsorption isotherm experiments were carried out similar to the earlier experiments but in the optimum time. The results obtained are given in table2. Also experiments were carried out at different temperatures to obtains the data for determination of thermodynamic parameters.

Table 2. adsorption data

phenol		p-nitrophenol		1-butanol	
C(g/L)		C(g/L)		C(g/L)	
in	eq	in	eq×1000	in	eq
0.5	0.0099	0.1	---	0.2025	0.0250
1	0.0118	0.3	---	0.405	0.078
1.5	0.025	0.5	---	0.810	0.200
2	0.179	1	---	1.0125	0.292
4	0.603	1.5	0.035	1.620	0.544
6	1.599	1.7	0.188	2.025	0.690
8	1.763	1.9	0.234	4.050	1.730
10	3.746	2	0.541	8.100	4.049
12	5.476	2.3	0.781	16.200	9.234
14	6.019	2.4	0.818		
16	8.021	2.5	0.986		
18	10.346				
20	12.013				

in: initial eq: equilibrium

DATA TREATMENT

The equilibrium data are treated following to the applied equations until obtain the necessary terms for drawing Henry, Langmuir and Freundlich isotherms. For example the results obtained for l-butanol are given in table3.

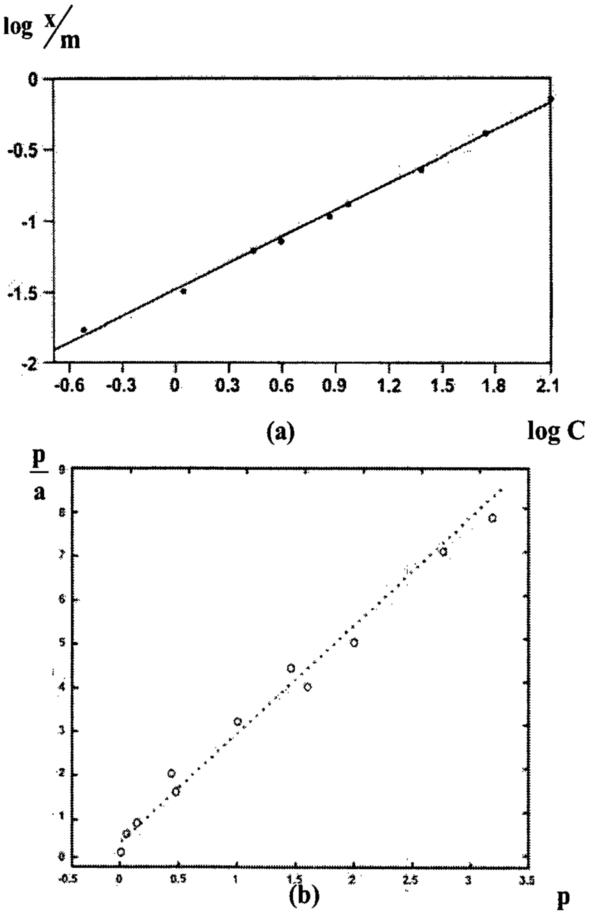

Fig 1. The Isotherms

a: Freundlich for 1-butanol b: Langmuir for phenol

The straight – lines graphs as referred to above calculations are givens in Fig.l. Other graphs were not linear.

And so the concerned data obtained for phenol at different temperatures have fitted in Langmuir equation. The results are listed in table 4.

Table 3. The treated data for l-butanol

Cin (mg/L)	Ceq		$\log C_{eq}$	$\frac{x}{m}$ (mg/g)	$\log \frac{x}{m}$	C_{ads} mmol/L	$P_{eq\,(atm)}$	$\frac{P}{a}$	$\ln \frac{C}{P}$
	(mg/L)	(mmol/L)							
202.5	25	0.3	0.25	17.8	-1.75	2.4	0.007	0.41	5.84
405	78	1.1	0.04	32.7	-1.49	4.4	0.027	0.82	5.09
810	200	2.7	0.43	61.0	-1.21	8.2	0.066	1.08	4.82
1012.5	292	3.9	0.59	72.1	-1.14	9.7	0.095	1.31	4.63
1620	544	7.3	0.86	107.6	-0.97	14.5	0.175	1.63	4.42
2025	690	9.3	0.97	133.5	-0.88	18.0	0.222	1.66	4.40
4050	1730	23.3	1.37	232.0	-0.64	31.3	0.536	2.31	4.07
8100	4049	54.6	1.74	405.1	-0.39	54.7	1.150	2.84	3.86
16200	9234	124.6	2.10	696.6	-0.16	940.	2.079	2.98	3.81

m=0.5g v=50ml B=-2.5533 (L/mol)

Table 4. The values of K_L as a function of T.

$T(^\circ C)$	$10^3 \frac{1}{T}, T(^\circ K)$	K_L	$\ln K_L$
6	3.58	22.94	3.132
25	3.35	7.12	1.962
30	3.300	2.579	0.947
35	3.24	1.27	0.239
40	3.19	0.189	-1.666

CALCULATION OF RELATED THERMODYNAMIC FUNCTIONS

For phenol, $\Delta H^\circ, \Delta S^\circ$, were delivered from slope and intercept of the straight-line obtained by plotting lnk against $\frac{1}{T}$. The isotherm constant for l-butanol was determined from the graph of $\ln\frac{C}{P} vs C$ and extrapolation by mathematica computer program.

According to the equation 4 when $C \to o,.\ \ln\frac{C}{P} \to \ln k$. The results are summarized in table 5

Table 5. The thermodynamic parameters

parameters / compound	$-\Delta G^\circ$	$-\Delta H^\circ$	$-\Delta S^\circ$
	(kJ/mol)		
Phenol	2.92	29.55	0.294
l-butanol	15.5	N.D	N.D

N.D : not determined

RESULTS

The evaluation of data showed that in the range of concentrations studied, adsorptive equilibrium of the phenol followed the Langmuir isotherm and that of l-butanol obey the Freundlich; so there is no equilibrium for p-nitrophenol. Because the concentration of the solutions under study were low (up to 2.5 g/l) and consequently, the whole of p-nitrophenol was adsorbed and insignificant amount of that remained in solution .

In the case of the mixtures of phenol and p-nitrophenol in the range of studied concentrations

(125+56 to 450+7 mg, phenol + p-nitrophenol) adsorption of two compounds were approximately complete. This signifies that adsorption of one compound in mixture has no interference with the adsorption of the other. However it is necessary to remember that, the whole quantity of two compounds do not exceeded from the capacity of A. C. for phenol.

The obtained values of the isotherms constants and maximum capacity of A.C for three studied compounds, are summarized in table 6.

Feature / compound	C g/L	$(\frac{x}{m})$ (g / g)	K
Phenol	20	0.450	K_L=7.12
p-nitrophenol	6	0.205	---
l-butanol	16.2	0.7	K_F=3.22, n=1.68

Table6

DISCUSSION

In order to compare the adsorption of three compounds on A.C. Our attention is focus on two factors , i.e. the values of ΔG° adsorption and surface coverage of A.C by the compounds studied. We know that the adsorptive capacity of an activated carbone for a solute will likewise depend on both the A.C and the solute. Investigations have shown that A.C. with high surface area has much larger adsorption capacity. The porosity of A.C. and the screening action of prores, are very importance. The adsorbability of the compounds depends on their molecular structure, solubility and the length of the chain of hydrocarbon and so constituents of their chemical groups, etc. It is cleared up that, for one type of A.C. and in the case of equal solubility of the compounds, the difference between their adsorbability intervene from the structure and the size of the molecule as well as their behavior toward the A.C.

Negative values of ΔG° for adsorption reveal that, two compounds are adsorbed spontaneously, additionally adsorption of phenol ($-\Delta G^\circ < 10 kJ/mol$) have physical nature, whereas the adsorption of l-butanol ($-\Delta G^\circ > 10\ kJ/mol$) have chemical nature. About the surface coverage of A.C. we refer to an surface area of $1000\,m^2$/g for A.C.

If we suppose that the carbon atoms are in liber –state

and having 77pm radii, thus the surface area of one gram carbon equalize to the $3736\,m^2$. By comparing this two numbers, we conclude that in the granular or powdered carbon, the atoms must be joint-up to another in the manner that the surface of three carbon atoms are equal to the surface of one of them. Now if we suppose that, all the points of the surface of A.C. are activated sites, therefore they must be covered by somehow of the molecule of adsorbents. In case of coverage by 1-butanol, according to refrence [10] l-butanol is adsorbed by methyl group. Furthermore we know that, two models are proposed for l-butanol:ship and chair configurations. The calculation present surface area of 0.6×10^4 and $1.5\times10^4\,pm^2$ for methyl group and l-butanol molecule respectively. Hence for surface area of $1000m^2/g$ of A.C. the capacity must be107or266 mmol of l-butanol per one gram of A.C. while in our experiments, it was determined 9.5 mmol/g. (i.e an coverage of 6% or 3.6%) This means that all of the site situated onto the A.C. are not actives for l-butanol. Calculation for phenol with hexagonal configuration (graphite lattice with $d_{c-c}=142$ and 335 pm), yield surface area of $2.63\times10^4 pm^2$ for each molecule of phenol. Therefore in case of complete occupation of sites, must be adsorbed 63mmol phenol per one gram of A.C. while we have find out 4.79 mmol/g (i.e an coverage of 7.6%). The great difference between the calculated and determined capacity of A.C. for two compounds may be intervened from the different sources. For example the errors in determination of surface occupied by one molecule of adsorbent or capacity maximum of adsorbate and etc., and finally the adsorbability of water toward the active sites of adsorbat in comparison to adsorbents.

The results obtained for mixtures of phenol and p-nitrophenols reveals that, the capacity of A.C. is larger than 4.79mmol/g.

In addition, existence of adsorbate,i.e. p-nitrophenol in phenolic solutions has not effect on adsorptive capacity of A.C. for phenol.

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