

**Adsorption study of some derivatives of phenols on activated alumina
in aqueous solution**

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Abstract

The adsorption isotherms for five derivatives of phenol from aqueous solution onto a surface of activated Al_2O_3 has been determined at 22° , 35° and 45° . The calculation showed that these isotherms adopting langmuir equation rather than freundlich. Increasing temperature lead to an effect on reducing amount of adsorbate without changing the pattern of the isotherms.

This means that the mechanism is exothermic for all Investigated phenols. In this work the values of ΔG was determined at $22^\circ C$ and $35^\circ C$ except for n-Nitro phenol at temperature 45° was used.

الخلاصة

لقد تمت دراسة امتزاز مشتقات بعض الفينولات على سطح الالومينا الفعال بدرجات حرارة $22^\circ M$ ، $35^\circ M$ ، $45^\circ M$ في محلولها المائي، ومن خلال هذه الدراسة وجد إن ايزوثرمات الامتزاز في تلك الدرجات الحرارية من نوع ايزوثرم لانكماير ولا علاقة بايزوثرم فرنديش في الامتزاز .

عند زيادة درجة الحرارة نجد إن كمية المادة الممتزة تقل ولا تؤثر على نمط الايزوثرم، وهذا يعني ميكانيكية الامتزاز تكون هي نفسها لجميع الفينولات، وقد تم تعيين قيم ΔG عند الدرجات الحرارية $22^\circ M$ ، $35^\circ M$.

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Introduction:

The last ten years have been witnessed an increased interest on the adsorption of organic compound from their aqueous solution because of its ability to remove the pollutant from air and water. The first work in this field was published by Bohem (1) and Coughlin (2). Their study was concentrated on the adsorption of carboxylic acid on activated carbon. Theoretical and experimental attempts were made by Manes and other (3-5) and lately Manes (4) attempted to describe the process of adsorption theoretically using Hansen-Fakler modification of polany theory (6). The process of adsorption from its aqueous solution on heterogeneous alumina surface is mainly due to chemical potential and to the number of adsorption sites that processing specific chemical potential. Hence the solute molecules adsorbed on these sites. It is also possible to obtain a relation between the amount of adsorbate and the potential of adsorption by the following equation(7. 8)

$$E_{eq} = RT \ln \left(\frac{C_s}{C} \right)$$

Where E_{eq} is potential of adsorption.

R gas constant.

T absolute temperature.

C_s is amount of adsorbate mg/gm.

C concentration of phenolate at equilibrium mg/L.

Where the adsorption potential made by adsorption forces is to bring the number of molecules to point neighboring to the adsorbate, at this stage where the sticking occurs.

Several other papers (9, 10) concerning (similar compound used in this work) the adsorption on activated carbon revealed that their isotherms confine to the freundlich equation. In this work although it is possible to apply the equation, coefficient is less than that of the langmuir are confining to langmuir equation on the surface of AL_2O_3 (11).

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Material and Method:

In this work five derivative of phenols have been used. These are m-nitrophenol, m-aminophenol, m-hydroxyphenol, m-cresol, m-hydroxybenzoic acid and phenol. All of them purchased from the BDH company with purity of more than 98%. The activated $\gamma - \text{Al}_2\text{O}_3$ was supplied by BDH with purity higher than 98%. Ten ml of phenol solution and 1 gram of $\gamma - \text{Al}_2\text{O}_3$ transferred to stoppered test tube, and shaken by spinning shaker in which the tubes were rotating head to head about 3 hours. After equilibrium has been established, the solid is separated from the solution by centrifugation (4000 rpm) for 10 min. the difference in concentrations before and after adsorption gives the amount of substance adsorbed for given mass (m) of $\gamma - \text{Al}_2\text{O}_3$. The adsorption isotherms were established by measuring the concentration of solution before and after adsorption. Determinations were carried out by UV absorption using (model LKB), wavelength 276 nm. It is possible to calculate the amount of solute adsorbed per gram of adsorbent by the following equation:

$$\Gamma = \frac{V\Delta c}{m}$$

Γ = (mg) of solute per one gram of adsorbent (mg/gm).

ΔC = (mg/ml) is the solute concentration decrease due to adsorption.

V = (ml) volume of solution added to 1 gram of Al_2O_3 .

In view of the importance of knowing the dipole moment of phenol derivatives and because these were discrepancies between the published values recalculations have been carried and employing equation depending on a new measured dielectric constant and refractive index.

Dipole meter DM 01 was used for measuring dielectric constant. These data are shown in table (1).

Results and Discussion:

The study of adsorption isotherms of phenol (as an adsorbate) differs from other organic compounds with hydrocarbon chain, since adsorption in last one occurs via side chain. For instance, the presence of polar site means that the adsorption occur via polar site (12,13) on the other hand, the adsorbent play an important role in adsorption despite the difference in

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number of adsorption sites which possessing chemical potential and surface area different from one surface to another.

In this paper, adsorption isotherms for the studied phenols have been obtained at different temperature upon application of Langmuir and Freundlich equation it was found that the Langmuir has the higher correlation coefficient value 0.996.

It is evident, from the results reported have, that for those compounds in which the adsorption isotherms were determined at different temperature doesn't show any change in pattern of these isotherms; while a reducing in the amount of adsorbate was obtained. This can be interpreted in terms of comparable mechanism between phenols and alumina surfaces. Furthermore, the comparisons have been extended to include the isotherms of these phenols at 22° which have shown that (Γ) for m nitro phenol is higher than that of the others. This situation remains as it is at 35°C and 45°C (fig. 1, 2, and 3).

The increasing in (Γ) was explained by the presence of two sites of adsorption in m-nitro phenol (NO_2 and OH groups). This causes in re-arranging of these molecules onto surface initially as monomer, then when the concentration of the solution increases over $10 \times 10^{-3} \text{ mg/L}$ the saturation of the surface will began. So any additional increases go to the bulk of the solution. The substitute group plays an important role in increasing or decreasing the amount of adsorbate (14, 15) for instance this work shows that the amount of adsorbate on the surface of Alumina according to the substitute group on phenol follow the trend $\text{NO}_2 > \text{NH}_2 > \text{OH}$ this trend can be explained by the presence of Hydrogen bonding between substitute group and the surface. On the other hand, the surface itself is having a remarkable role in the adsorption. This is in agreement with the result of Anderson et al(16) who showed that the presence of OH group as a part adsorbate silica structure contribute in the adsorption process and the strength of adsorption depends upon the type of OH group. This confirmed by studying the interaction of series of monosubstituted and disubstituted benzene with silica using infrared and UV-spectroscopy (17) this work was restricted to study the adsorbate only.

It is worthwhile to mention that the solubility has significant effect on the adsorption (18) whenever the solubility increased the amount of adsorbate decreased. This will appear in the phenol isotherm (fig. 1).

From the calculated values of dipole moment it was found that the dipole moment plays an important role in the adsorption processes, for example the dipole moment of m-Nitro phenol

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is a highest value of (Γ). For the remaining phenols, the trend of (Γ) was analog to their corresponding dipole moments. The only deviation was found in the value of m-Hydroxybenzoic acid. This suggest that the presence of solute-solute interaction between two carboxylic groups might be the reason in reducing the value of (Γ) (19-21).

The effect of the temperature was clear for instance an increase in temperature between 22° and 45° the amount of adsorbate decreases as in fig (3).

Consequently, this shows a quite stability at concentration onto the adsorbent surface was occupied. for example the isotherms of 22° shows a quite stability at concentration of $10 \times 10^{-3} \text{ mgL}^{-1}$ in which the surface is at saturation and plateau is being prevailed. At highest temperature, the isotherms start to curve down and strictly beyond the $15 \times 10^{-3} \text{ mgL}^{-1}$. The slope speeding and when the temperature is 45°, the isotherms changed its pattern fig(3,4). This case is more pronounce in m-Nitro phenol where the adsorption goes to its maximum value at $15 \times 10^{-3} \text{ mgL}^{-1}$.

Analysis of the data obtained for ΔH and ΔG table suggest the presence of two type of interaction:

- 1- The adsorption of organic compound.
- 2- The hydrogen bond formation between the water molecule and the surface. Furthermore, research show that the value of ΔG and ΔH of disubstitute phenol were higher than phenol. This support the suggested mechanism which will be discussed later. It is worth to mention, that the trend of dipole moments analog to the trend of enthalpies except a deviation in the ΔH of m-Hydroxybenzoic acid. This confirm conclusion that the effective key parameter on the properties of the materials was achieved by the addition of carboxylate functional group (19, 20).

$$\Gamma = \Gamma^{\infty} \frac{KC_s}{1 + KC_s} \quad [1]$$

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After transformation

$$\frac{C_s}{\Gamma} = \frac{1}{\Gamma^\infty K} + \frac{C_s}{\Gamma^\infty} \quad [2]$$

The values of Γ and K were calculated from Eq (2), after which the equations.

$$\Delta G = -R T \ln K \quad \text{where used to calculated } \Delta G \quad [3]$$

Suggested mechanism

The isotherms for a particular temperature on the surface of alumina show no change in the pattern of these isotherms. If there is a change in these isotherms this might be a possibility for a variation in the mechanism from one concentration to another where the surface potential and the dipole moment play an important role in the adsorption process too.

All the experiments undoubtedly confirmed that the type of the surface is important in the process of the accumulation on to surface (21, 22) additional reasons might be responsible for accumulation of molecules at surface, such as the substituting group which is capable of attracting towards the surface. (23-25).

Where hydrogen bonding play an important role in departing number of molecules from the surface. Furthermore surface activity also has a direct effect in the accumulation as well as the type of substituent group, for instance the effect of $\text{NH}_2 > \text{NO}_2 > \text{OH}$.

Giles (26) showed that the adsorption of phenol at surface of carbon not occur via hydroxyl group but through aromatic ring, this, overlap between the electrons and surface. Since the surface used in heterogeneous, this means the number of pores increased consequently that according to the suggested mechanism. (27).

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Table (1)

The experimental result $\Gamma_{\text{mg/g}}$ and C_{eq} on the surface of alumina. with some physical properties of studied compound. dipole moment, solubility, molecular weight and pK_a

Compounds	$C_{\text{eq mg/L}}$	$\Gamma_{\text{mg/g}}$	Dipol moment	M. Wt. g/mol	Solubility	pK_a
m-Aminophenol	0.021	0.680	1.66	109.13	2.6	8.16
m-Nitro phenol	0.016	0.720	3.85	139.11	1.35	8.301
m-Hydroxyphenol	0.022	0.600	2.64	110.10	1.23	9.523
m-Hydroxyphenol Acid	0.022	0.370	3.06	138.12	1.06	4.08
m-Cresol	0.017	0.700	1.52	108.15	0.60	10.008
phenol	0.025	0.496	1.55	94	6.7	9.958

A= Dipol moment were premeasured using Dipol meter DM 01.

B= pK_a values were taken from reference (24).

C= solubility values were taken from reference (12, 20).

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Table (2)

Thermodynamics Parameter of adsorption of some derivatives of phenol on alumina surfaces

Compounds	a - $\Delta G(22^\circ)$ kJ/mol	a - $\Delta G(35^\circ)$ kJ/mol	b - $\Delta H(22^\circ)$ kJ/mol
m- Aminophenol	9. 286	8. 525	18. 949
m- Nitrophenol	9. 979	9. 658	18. 230
m- Hydroxyphenol	8. 051	7. 922	17. 531
m- Hydroxybenzoic acid	7. 125	6. 349	15. 976
m- Cresol	9. 328	8. 608	16. 178
Phenol	7. 025	7. 324	15. 729

a= ΔG were calculated using $\Delta G = RT \ln \Gamma_{\max}$.

b= ΔH calculated using Vant Hoff equation.

Table (3)

Results of linear regression analysis using freundlich equation

Compounds	$\Gamma_{\max}$	r	b
m-Aminophenol	0. 680	0. 9982	352. 87
m- Nitrophenol	0. 720	0. 9925	310. 2
m- Hydroxyphenol	0. 600	0. 9775	370. 8
m- Hydroxybenzoic acid	0. 370	0. 9971	433. 36
m- Cresol	0. 600	0. 9874	325. 8
Phenol	0. 496	0. 9995	423. 08

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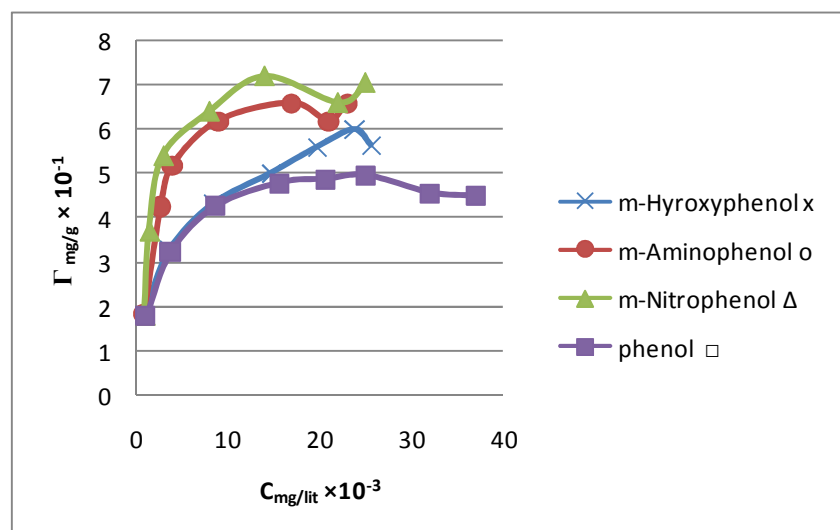


Fig (1)

Adsorption isotherms of m-Nitrophenol, m-Aminophenol, m-Hydroxyphenol and phenol at 22°C

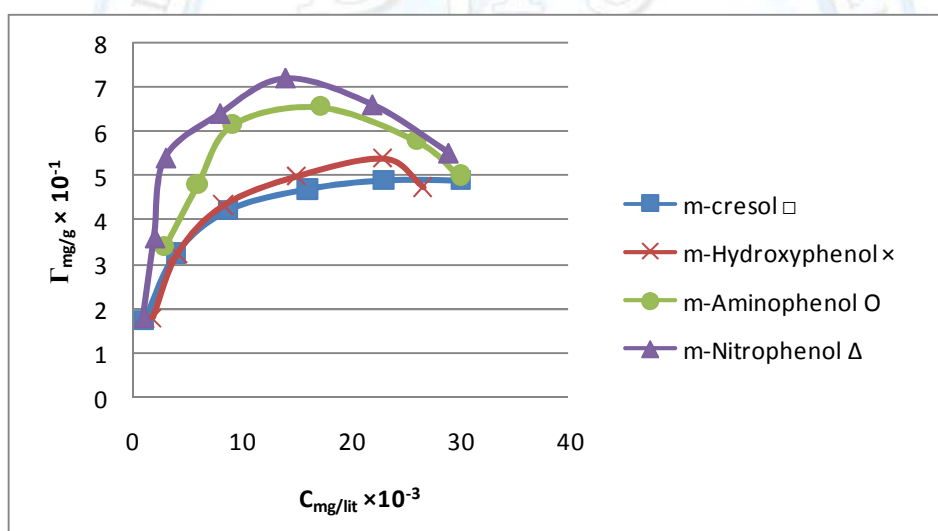


Fig (2)

Adsorption isotherms of m-Nitrophenol, m-Aminophenol, m-Hydroxyphenol, m-cresol at 35°C

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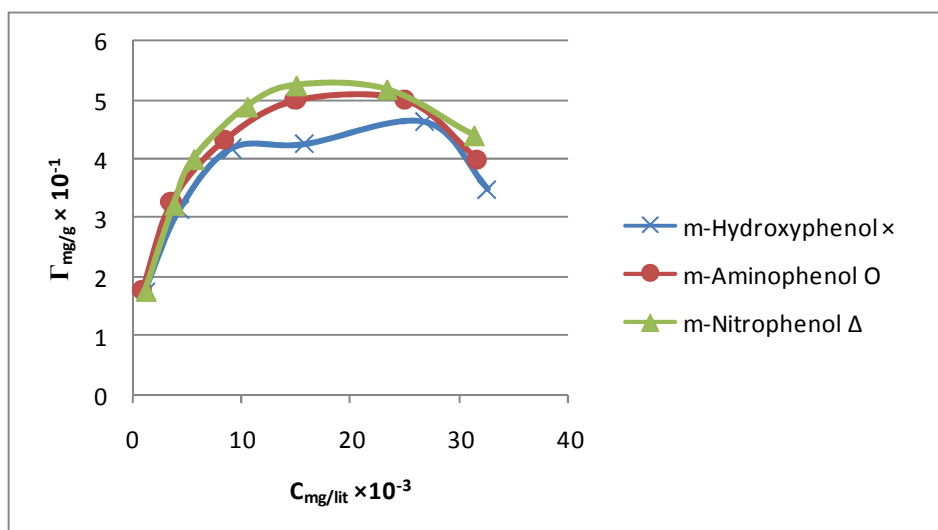


Fig (3)

Adsorption isotherms of m-Nitrophenol, m-Aminophenol, m-Hydroxyphenol at 45°C

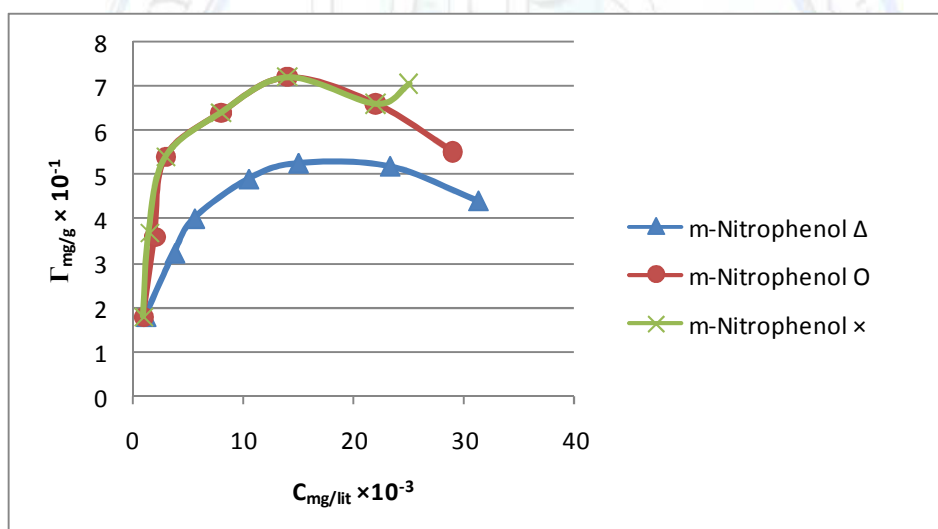


Fig (4)

Adsorption isotherms of m-Nitrophenol at 45°C

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