Adsorption of Mono Substituted Nitro Phenols From Aqueous Solution on the Zemeej Surface at Different Temperatures

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Abstract

Adsorption of o-Nitrophenol (o-Nph), m- Nitrophenol (m-Nph) and p- Nitrophenol (p-Nph) on the sedimentary sand of the Tigress River which is known locally by “Zemeej” from aqueous solution at 288, 298, 308, 318 and 328 k^0 . This study indicates that o-Nph and m-Nph take multi-layered S type according to Giles classification while p-Nph takes a multi-layered L type according to the same classification. The isotherms treated by Freundlich model and show a good response to this model because the heterogeneous nature of the surface. The adsorption for all materials was endothermic as shown from ΔH values and explained through the porous nature of the surface, the remaining thermodynamic functions ΔG and ΔS were also calculated at all temperatures for all adsorbents which indicate that the randomness, finally the results indicate that the orientation on NO_2 group to para position acts to decrease the quantity of adsorption.

Key wards: adsorption; nitrophenol; Zemeej; Freundlich isotherm

Introduction

The adsorption of phenols on agricultural soil is an important subject because the large spectrum of products, that a phenolic compound constitutes a major component forming it such as pesticides herbicides coloring materials, medical materials and even a natural product released by a living organism [1-6], its adsorption studies provide information about its stability on the soil and its distribution between soil and aqueous media. So this study is important to many fields of application in addition to the environmental field. Many researchers concerned with adsorption of various substances on the surface of soil minerals such as Kaolinite, Bentonite etc. [7-9], but there is no studies of adsorption carried on sand sediments of Tigress River that is known locally by (Zemeej) which is the best type of agricultural soil used in Baghdad. Adsorption is an important surface phenomenon usually describes the accumulation of ions, atoms or molecules on a surface [10]. It is a physicochemical process which offers great potential as a means of producing quality effluent [11]. This phenomenon of adsorption is basically due to the presence of residual forces at the surface of a liquid or a solid. Adsorption is a spontaneous process and hence is attained by a decrease in free energy change and entropy of the system [12]. The concept of adsorption equilibrium is involved deeply in the measurement and correlation of adsorption capacity, selectivity and re-generatability data. Generally, equilibrium is the constraint that limits each of these vital factors for adsorption application. However, there are many phenomena where adsorption is essential to the process such as decolorisation and dyeing of fibers, these processes occur through the adsorption process on solid surfaces [13].

Materials and Methods

Instruments:

1- Visible spectrophotometer.
2- Dunboff metabolic shaking Incubater GCA/ precision Scientific.
3- Hettich Universal (D-7200), Centrifuge tubes.
4- Electronic Balance, Sartorius Lab. L420 B, +0.0001.

Materials:

All Nitrophenols were supplied by Fluka. (Zemeej) was obtained from local markets in Baghdad.

Methodology

The (Zemeej) was washed with excessive amounts of distilled water, dried at 160°C for three hours. The (Zemeej) was ground and sieved to a particle size of 320 μm. Wavelength of maximum absorbency was recorded for each Nitrophenol dissolved in aqueous media and found to be 280nm for o-Nph, 272nm for m-Nph and 318nm for p-Nph. These values were utilized for estimation of the quantity of adsorbed material. Solutions of different concentrations were prepared by serial dilution and measured at desired λ_{max} and plotted against concentration values, the calibration curve in the concentration range that falls in the region of applicability of Beer-Lambert's law was employed.

Adsorption Isotherm

A series of solutions of Nitrophenol (5ml) of concentrations range (5-55) mg/L at pH ≈ 8 were added to stoppered flasks containing 0.1g of (Zemeej). The flasks were shaken in a thermostatically controlled water bath at a speed of 45 rpm and 298k till equilibrium is attained (300 min). This time is sufficient for the adsorption process to reach equilibrium. After the equilibrium time elapsed, the suspensions were centrifuged at 3000 rpm for 10 min. The clear supernatants were assayed for Nitrophenol spectrophotometrically. Equilibrium concentrations were obtained by comparing the experimental data with the calibration curve. The quantity of $^{\text{Nitrophe0nol}}$ adsorbed was calculated according to the following equation (1)

$$Q_e = \frac{V_{sol.}(C_0 - C_e)}{m} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Where:

Q_e: Quantity of adsorption at equilibrium (mg/g)
m : Mass of adsorbent (g).
C_0 : Initial concentration (mg/L).
C_e : Equilibrium concentration (mg/ L).
$V_{sol.}$: Volume of solution (L).

Effect of Temperature

Adsorption experiment was repeated in the same manner at temperatures of 288, 308, 318 and 328 k^0 to estimate the basic thermodynamic functions.

Results and Discussion

Figures (1,2and3) indicate the adsorption of so-Nph and m-Nph on the silica surface are multi-layered S type according to the Giles classification at all temperatures of the study while p-Nph takes a multi-layered L type according to the same classification. The multi-layered adsorption that is taking place on this surface is not strange due to the heterogeneous-porous nature of the silica surface, S type (or sigmoidal shape) means low extent of adsorption at low concentration of adsorbate then the adsorption increases rapidly with the increase of adsorbate concentration, this is because of the affinity between the adsorbent and the adsobate which is weak at the beginning but the initial amount of adsorbate that is settled on the surface of the adsorbent, it acts to provide a new active sites of adsorption which increases the adsorption extent with increase of concentration [14]. In our case, we think that the initial amounts of o-Nph and m-Nph (which carry a negative charge) that adsorbed on the silica surface (which carries a negative charge too) through hydrogen bonding among functional groups of the nitrophenols with surface polar groups letting the aromatic part of phenol directed out above the surface, with the increase of these hydrophobic aromatic groups that are covering the surface gradually become hydrophobic and this what will increase the adsorption extent rapidly, so the active sites that are covered with initial amounts of phenols will become preferred by later amounts of phenols more than empty active sites and for this reason the adsorbate molecules will aggregate as clusters on the adsorbent surface [15,16].

P-Nph isotherm takes the L type because when one of its hydrophilic groups interacts with surface polar groups through hydrogen bonding the other polar group of phenol will remain directed out the surface, therefore the surface will still hydrophilic and the decrease of the number of empty active sites that exist on the surface which will stay the more preferred positions of adsorption. The previous explanation indicates why the overall extent of adsorption of o-Nph is the largest among the other phenols. In spite of the adsorption of p-Nph takes L type of adsorption we decide to consider a Freundlich model of adsorption for all phenols because of multi-layered nature of adsorption for all phenols and the complicated nature of the surface so figures (4, 5 and 6) show the response of these adsorption isotherms to the Freundlich equation [17]:

$Qe=K_F(Ce)^{\wedge}(1/n)$…………………………… ………(2)

Where K_F is the Freundlich adsorption constant and its unit depends on n, n is unit-less constant. Correlation coefficient (R) that is shown in table (1) with K_F and n values indicate a good response of adsorption isotherms to Freundlich model at all temperatures and for isomers of Nitrophenol.

By increasing the temperature in general, all phenols showing an increase of the adsorption extent, this probability may be due to an endothermic absorption process taking place into pores and voids of the adsorbent in conjugation with a normal exothermic adsorption process that proceed on the adsorbent surface. To estimate the overall thermodynamic nature of the adsorption, we apply Vant-Hoff equation which is given by:

$\ln K^{\circ}_{ad} = (-\Delta H)/RT + C$……………….(3)

Where K°_{ad} is the thermodynamic equilibrium constant that is represented by [14]:

$K^{\circ}_{ad} = \lim_{Ce \to 0} [Qe/Ce]$ ………………….….(4)

ΔH The enthalpy change of adsorption (J/mol), or gas constant ($J.mol^{-1}.\ k^{-1}$) and C is the integration constant.

This method of calculating equilibrium constant at zero concentration is the characteristic of multi-layer adsorption isotherms specially to those obeying Freundlich isotherm and the reason is there is no characteristic maximum point of Qe such that exists in Langmiur isotherms which the $K^{\circ}ad$ is calculated on it, instead for Freundlich isotherms we plotted $K^{\circ}ad$ vs. Ce then taking the intercept of the strait line and this will be the adsorption equilibrium constant at characteristic zero equilibrium concentration of the adsorbate [18]. Figure (7) shows similarity of equilibrium constant alteration with the temperature for both o-Nph and m-Nph while p-Nph shows a different behavior; in addition the Gibbs free energy of the adsorption is calculated from the equation [19]:

$\Delta G = -RT\ln K^{\circ}_{ad}$ ……………………………………….(5)

Also the entropy change calculated from:

$\Delta G = \Delta H - T\Delta S$…………………………………………...(6)

All the thermodynamic parameters and K°_{ad} are listed in the table (2). As expected the adsorption processes were endothermic for all Nitophenols, o-Nph and m-Nph that have similar positive values of ΔH which support our previous proposition about contribution of absorption process in the porous and voids of the adsorbent beside the adsorption process that is taking place on the adsorbent surface, in addition for p-Nph the adsorption is less endothermic as a result to the seasons that are described above, ΔS valus are positive and change slightly with the change of temperature to each compound but the difference among the compounds is considerable, first ΔS values of o-Nph and m-Nph are close to each other and higher than that of p-Nph because the possibility of carrying out the adsorption process at the hydrophobic sites that are generated after the initial stage of adsorption, this process is not possible for p-Nph, also we expect the slight biggest value of ΔS for m-Nph than that of o-Nph is due to meta orientation of polar groups which when one of them is directed perpendicularly to adsorbent surface the other will stay free to orient horizontally with the surface in any direction. As a result for all of these reasons ΔG values are all negative as expected and decrease with the increase of temperatures for all Nitrophenols.

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Table(1) :Freundlich constants (K_f, n) and correlation coefficient R.

oNph			
T/k^o	K_f	n	R
288	0.163	0.950	0.968
298	0.558	1.353	0.991
308	0.777	1.336	0.923
318	0.794	1.110	0.961
328	1.093	1.171	0.929
mNph			
T/k^o	K_f	n	R
288	0.178	1.003	0.891
298	0.151	0.879	0.917
308	0.664	1.169	0.973
318	1.074	1.343	0.988
328	1.234	1.408	0.963
pNph			
T/k^o	K_f	n	R
288	0.425	1.284	0.979
298	0.375	1.051	0.970
308	0.326	0.945	0.964
318	0.438	0.999	0.915
328	0.544	1.100	0.862

Table (2): Adsorption constant (K_{ad}^0) at zero concentration with thermodynamic parameters.

oNph				
T/k^o	K_{ad}^O	ΔH(J/mol)	ΔG(J/mol)	ΔS(J/mol.k)
288	196.8891	30607.37	-12648.9	150.19548
298	346.2544	30607.37	-14486.8	151.3227
308	529.0003	30607.37	-16058.2	151.51158
318	721.9644	30607.37	-17401.8	150.97214
328	947.7332	30607.37	-18691	150.29992
mNph				
T/k^o	K_{ad}^O	ΔH(J/mol)	ΔG(J/mol)	ΔS(J/mol.k)
288	215.2087	32629.22	-12862	157.95544
298	232.4402	32629.22	-13499.4	154.79396
308	583.3441	32629.22	-16308.6	158.88904
318	819.8402	32629.22	-17737.9	158.38715
328	909.1994	32629.22	-18577.8	156.11899
pNph				
T/k^o	K_{ad}^O	ΔH(J/mol)	ΔG(J/mol)	ΔS(J/mol.k)
288	305.3952	9425.773	-13700	80.297817
298	358.1403	9425.773	-14570.4	80.524119
308	375.3758	9425.773	-15179.7	79.887949
318	471.299	9425.773	-16274.2	80.817562
328	484.7507	9425.773	-16862.7	80.147853

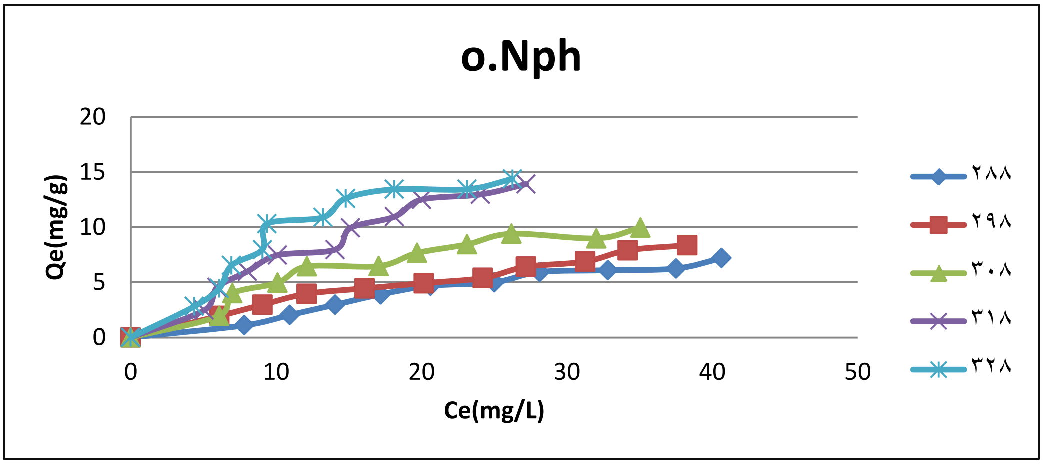

Fig. (1) Adsorption isotherm of o-Nph

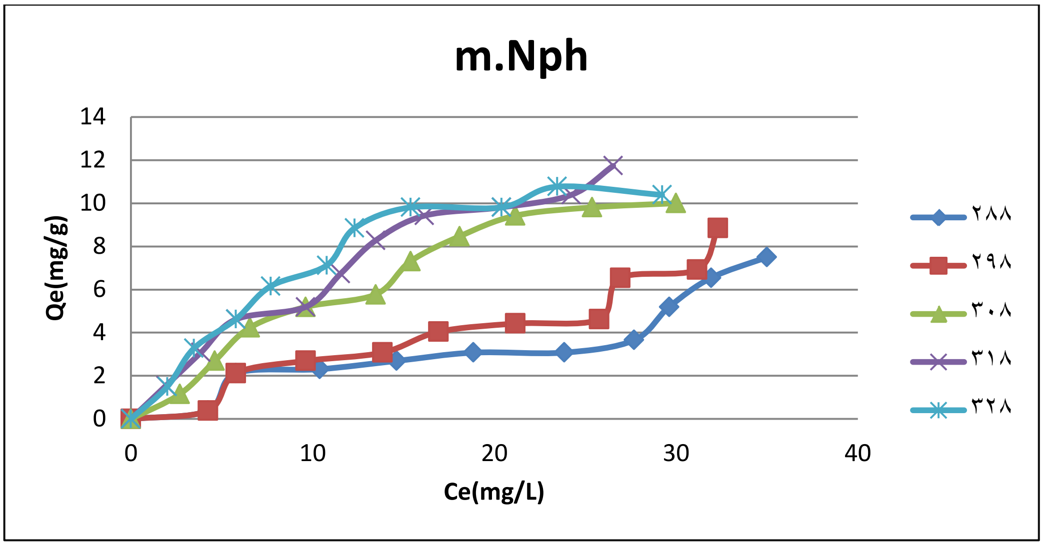

Fig. (2) Adsorption isotherm of m-Nph

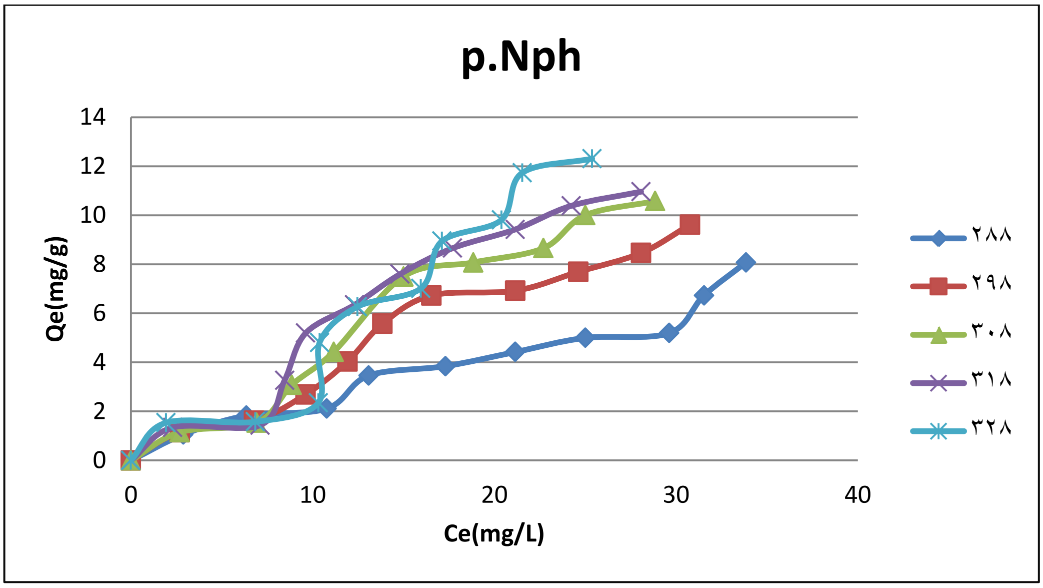

Fig. (3) Adsorption isotherm of p-Nph

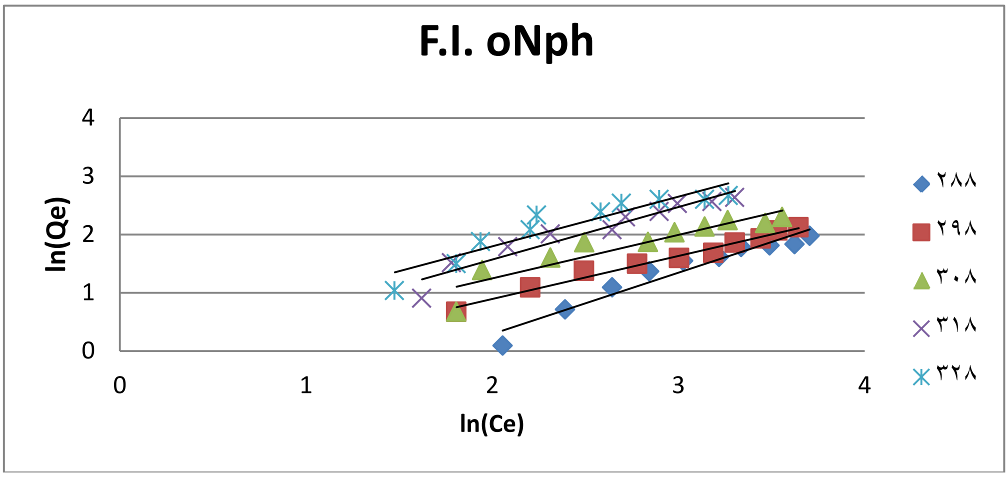

Fig. (4) Linearized Freundlich curves for o-Nph

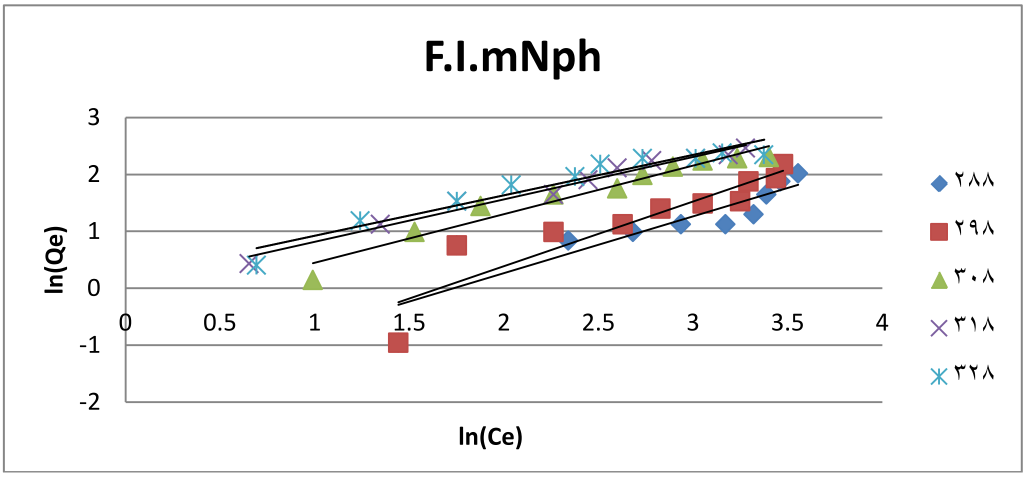

Fig. (5) Linearized Freundlich curves for m-Nph

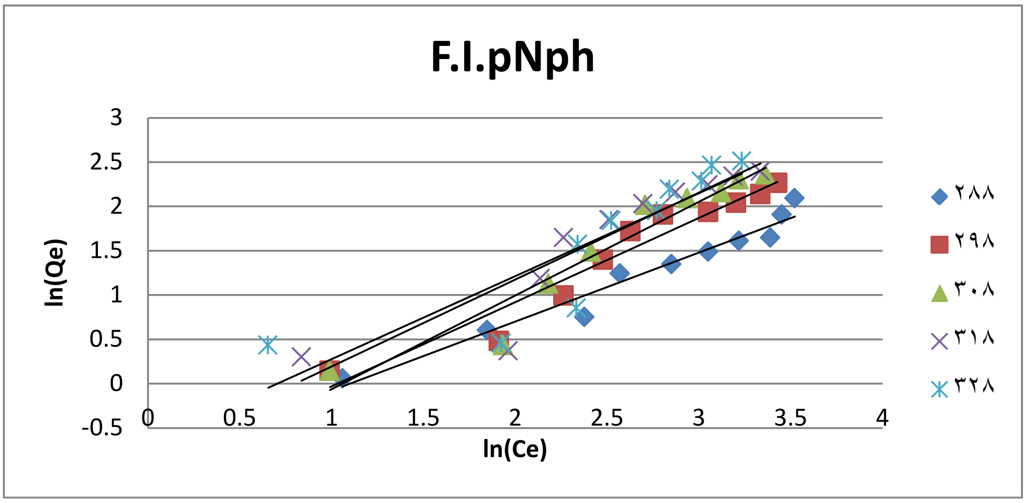

Fig. (6) Linearized Freundlich curves for p-Nph

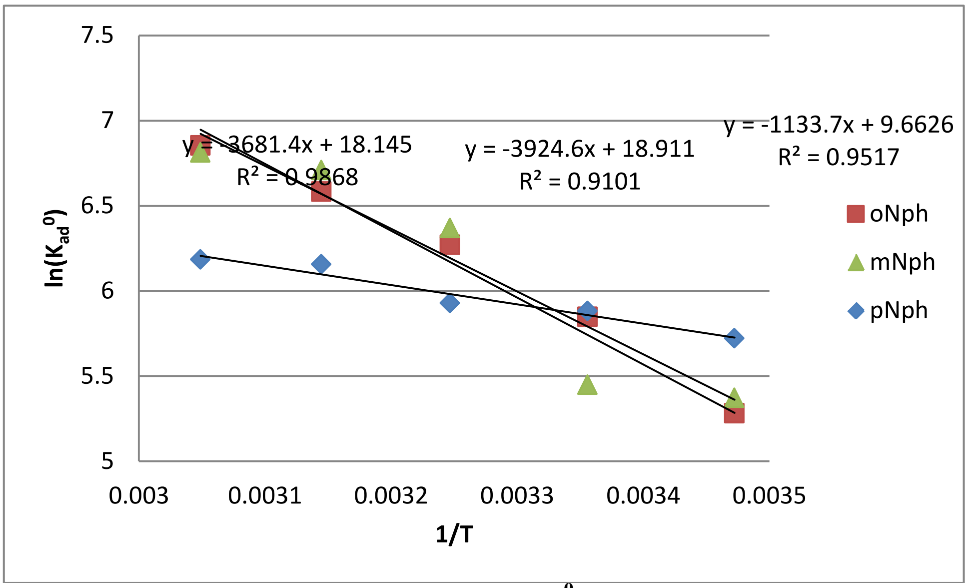

Fig. (7) Plot of $\ln(K_{ad}^{0})$ vs. 1/T

امتزاز النيترو فينولات احادية التعويض من محلولها المائي على سطح الزميج في درجات حرارة مختلفة

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الخلاصة

تم اجراء دراسة امتزاز o-Nitrophenol (o-Nph) و m- Nitrophenol (m-Nph) و p- Nitrophenol (p-Nph) من محاليلها المائية على سطح الزميج في درجات حرارة (288, 298, 308, 318, 328) k^0 و قد بينت هذه الدراسة ان امتزاز o-Nph و m-Nph تاخذ النمط S متعدد الطبقات حسب تصنيف Giles بينما ياخذ p-Nph النمط L متعدد الطبقات طبقا لنفس التصنيف، عولجت ايزوثيرمات الامتزاز لهذه المواد عند درجات الحرارة المدروسة وفق نموذج Freundlich للامتزاز نظرا لطبيعة السطح غير المتجانسة و بينت هذه الحسابات ان ايزوثرمات الامتزاز هذه تستجيب بصورة جيدة لنموذج Freundlich . بينت هذه الدراسة ان الامتزاز كان من النوع الماص للحرارة لكافة المواد الممتزة و ذلك من خلال قيم ΔH المحسوبة وقد فسرت هذه النتيجة استنادا الى الطبيعة المسامية للسطح الماز، بالاضافة الى ذلك تم حساب قيم الدوال الثرموديناميكية ΔG و ΔS عند جميع درجات الحرارة حيث يتضح ان الترتيب العشوائي للمواد الممتزة على السطح اكبر من ذلك الذي تمتلكه في المحلول المائي. واخيرا من النتائج التي تم التوصل اليها ايضا ان وجود مجموعة النايترو يعمل على تقليل كمية الامتزاز في هذا النظام.

الكلمات المفتاحية : زميج، الامتزاز، نيتروفينول، ايزوثيرم فرندليش