Materials & Method

2.1 Chemicals and instruments

2.1.1 Chemicals.

The chemicals used in this work are listed in table (2-1) :-

Table (2-1): The chemicals used in this work

Substance	Source	Purity %
Phenol	Fluka	99.9%
3- nitro phenol	Fluka	98.5%
3- amino phenol	Fluka	98.9%
2,4- Dinitro phenol	Fluka	98.9%
Acrylamide	Fluka	99.9%
Bis Acrylamide	BDH	99.6%
Ammonium per sulfate	BDH	99.8%
Charcoal	Fluka	——
De- ionized water	Lab.	R= 16 mΩ
Sodium chloride	BDH	99.9%

Where

R= resistance

mΩ= ohm (resistance unite)

2.1.2 Zeolite.

The molecular formula of Zeolite is :-

$$Ca_{4.5}Na_3(AlO_2)_{12}(SiO_2)_{12}.30H_2O$$

As shown in table (2-2):

Constituent	**Wt.%**
SiO_2	32.52
Al_2O_3	27.64
CaO	11.38
Na_2O	4.20
L.O.I.	24.25
Total	99.99

Table (2-2): The chemical analysis for Zeolite compounds.

2.1.3. Instruments.

The instruments used in this work are listed in Table (2-3):

Instrument	Remarks
UV-Vis spectrophotometer	SHEMADZO UV-VISIBLE spectrophotometer UV-1650 PC
pH-meter	Expandable ion analyzer
Centrifuge	HARAEUS sepatech labofuga A
Magnetic stirrer with hot plate	JLASSCO (India).
Mesh	200mm DIAx50mm ASTM E11 300 micron part no. 60132000300 Serial no. 03012571
Water bath shaker	COMPENSTATE with citenco motors F.H.P. England.
F.T.I.R.	SHEMADZO spectrophotometer (8300). Japan

Table (2-3): Instruments used in research

2.2. Experimental

2.2.1. Preparation of acrylamide- Bisacrylamide) Copolymer (78) :.

- Mixture 22 gm acrylamide and 0.6gm N,N- methylene- bisacrylamide in total volume of 100 ml H_2O. Filter the solution. In 50 ml flask take 22 ml mixture of acrylamide and bisacrylamide, then add 7.9 ml of water and 0.1 ml TMED and 3.5 ml Ammonium per sulfate, , then washed with distilled water .

-Preparation of 3.5 ml Ammonium per sulfate, weight 0.35 gm of Ammonium per sulfate and diluted to 10 ml of water .

2.2.2. Determination of swelling of the (acrylamide- Bisacrylamide) Copolymer :

The swelling measurement of the polymer was done according to the ASTM procedure by placing a calculated piece of polymer sample in (water at pH=7, at pH=6, at pH=8),and (at 0.1 M of NaCl aqueous solution, at 0.2 M of NaCl aqueous solution).

The weight of the polymer was measured each(24) hour until the weight of the swelled polymer becomes constant. The degree of swelling was calculated according to equation (79).

$$\Delta m = (m_t - m_o)/m_o \times 100 \qquad (2\text{-}1)$$

Where

m_o= weight of dry sample.

m_t = weight of swelled sample

Δm =swelling percentage.

2.2.3. preparation of Sample solution

A 100 ppm stock solution of (Ph, NPh, APh and DNPh) was prepared by dissolving (0.05 gm) of each compound in 500 mL of deionized water, and add a small quantity of KOH .

Other standard solutions, with concentration of (ph 70-95, NPh 30-55, APh 20-45 and DNPh 5-30) ppm were prepared by subsequent dilution using deionized water of the stock solution.

2.2.4. Determination of λ max and calibration curve

To determine the wave length at maximum absorption, absorption spectrum for each compound by using UV-Vis has been recorded in the range (200-1100 nm) by using quartz cell (Cuvette) of 1cm thickness (path length). The spectra are shown in figures (2-1 – 2-4)

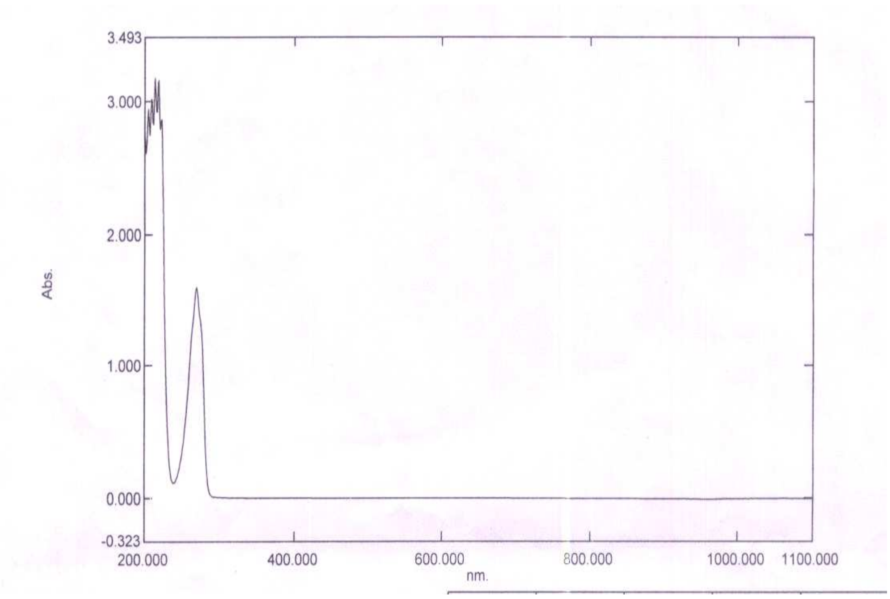


Figure (2-1) Maximum wavelength for Ph compound.

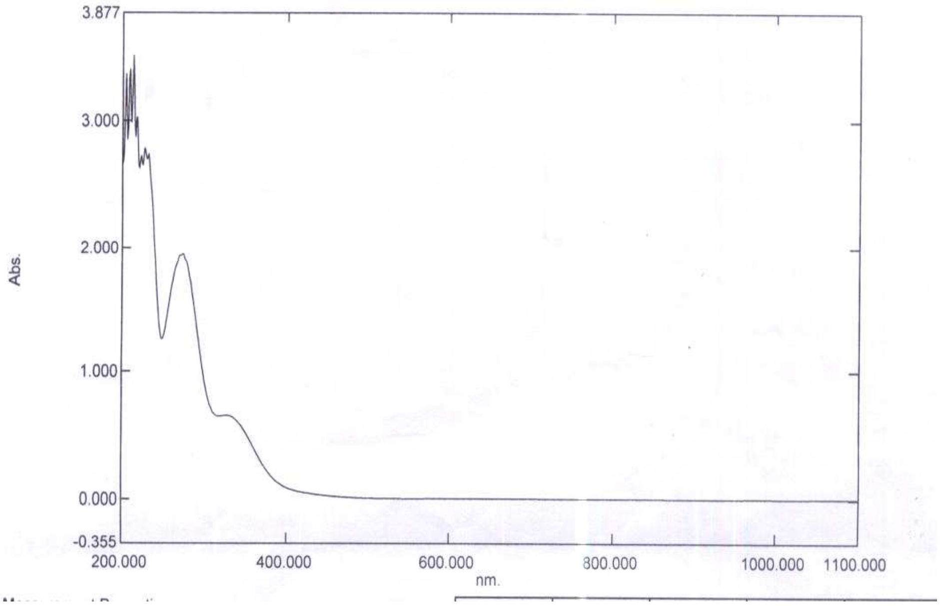


Figure (2-2) Maximum wavelength for NPh compound.

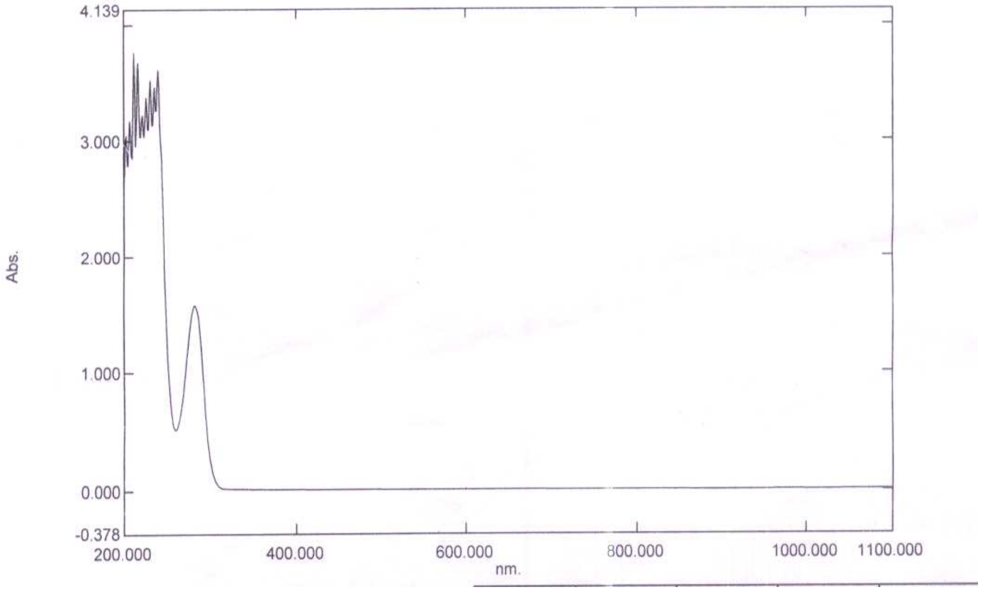


Figure (2-3) Maximum wavelength for APh compound.

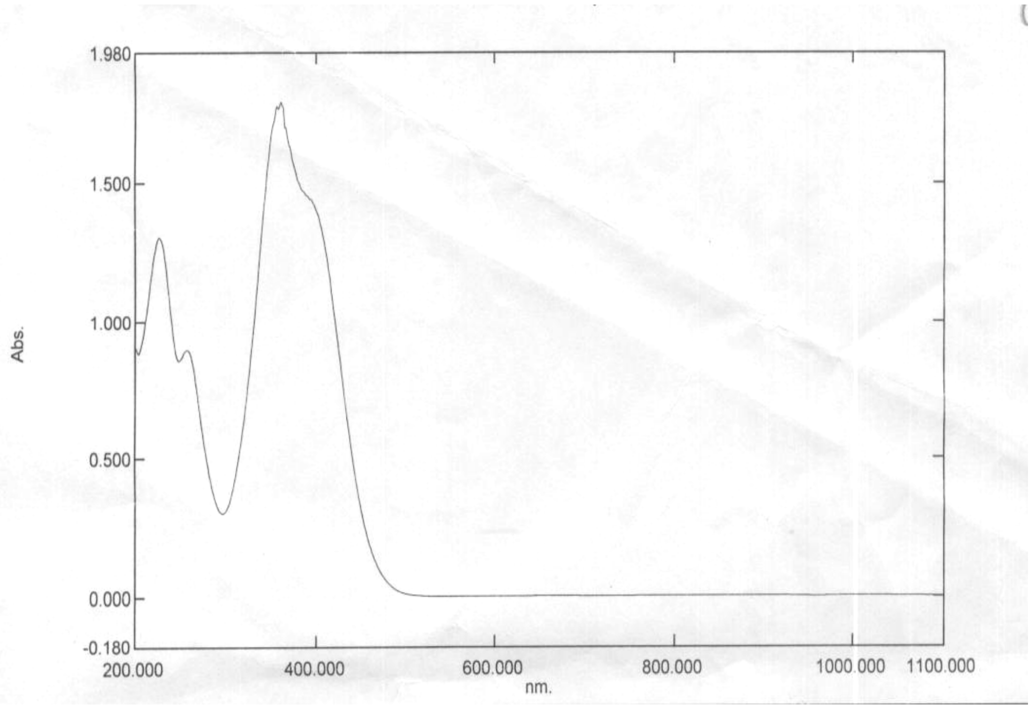


Figure (2-4) Maximum wavelength for DNPh compound.

The calibration curve was determined by fixing the λ max that obeys the (Lambert beer's law) at specific concentrations prepared for each compound, after that , the absorption has been recorded and the calibration curve plotted between absorption and concentration, the best line between points has been drawn using least square method.

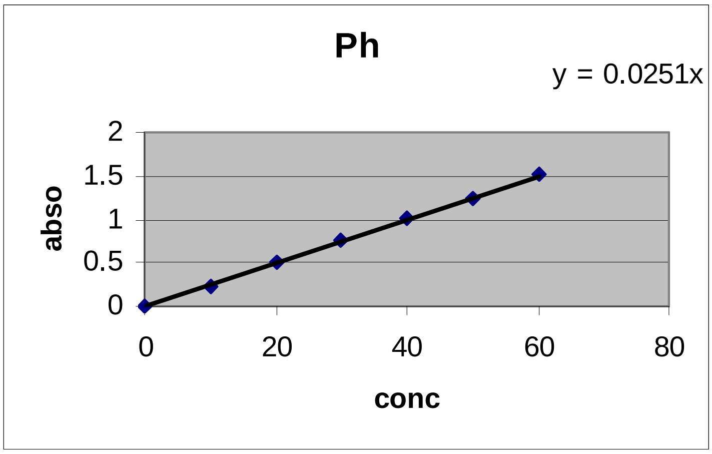


Figure (2-5) Calibration curve for Ph compound, and (r = 0.0251)

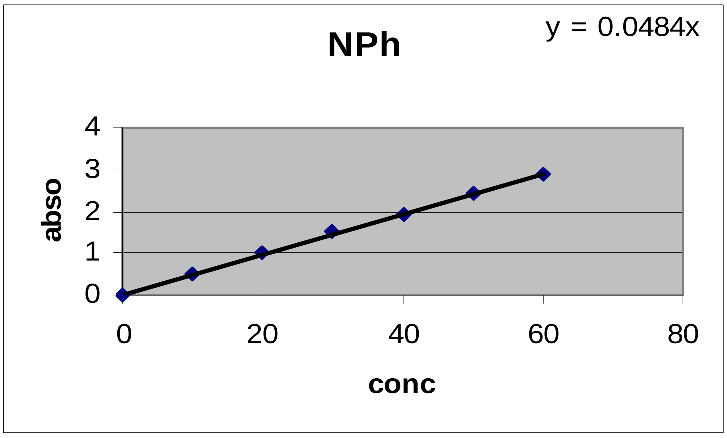


Figure (2-6) Calibration curve for NPh compound, and (r = 0.0484)

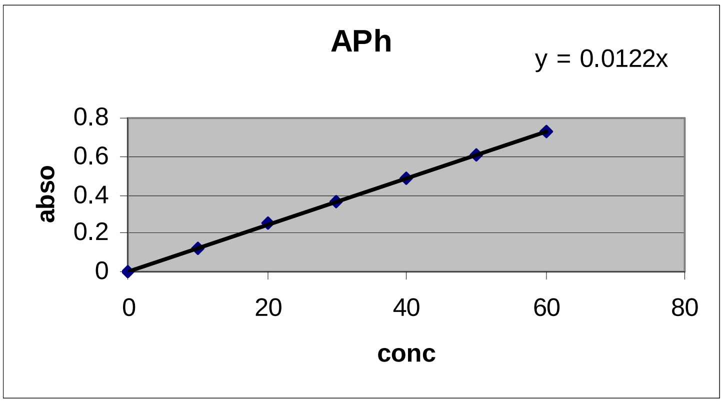


Figure (2-7) Calibration curve for APh compound, and (r = 0.0122)

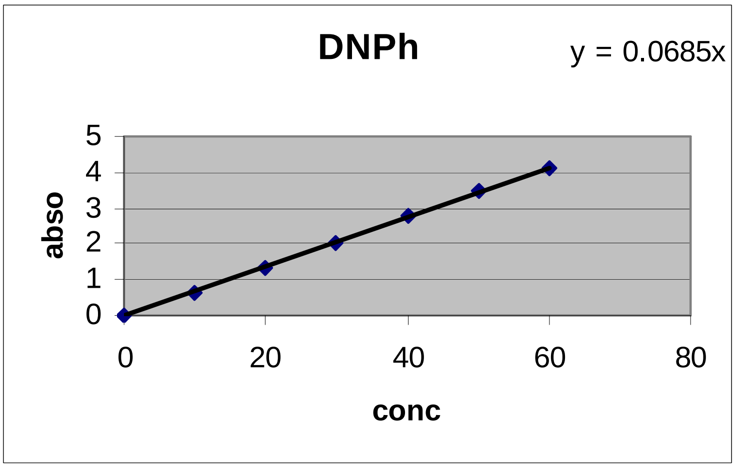


Figure (2-8) Calibration curve for DNPh compound, and (r = 0.0685)

2.2.5. Determination of equilibrium time

A (0.04gm) of the polymer less than 300 μ diameter (granules) has been placed in a 250 ml flask. Then 50 mL of adsorbed of 20 ppm adsorbate was added at constant temperature and the flask was fixed in water path shaker. Then the initial time has been recorded and after each half an hour. a sample has been piped and placed in the centrifuge for 10 minutes (at 4000 rpm) , a supernatant has been separated by decantation and adsorption of the solution has been recorded at λ max for certain sample. The process has been achieved repeatedly to the equilibrium.

2.2.6. Adsorption Isotherms of polymer:

In order to determine the adsorption isotherm for each compound , 6 conical flasks has been used, containing (0.01 gm) of polymer. Then 10 mL of adsorbate has been added into the flask which has a concentration ranged between (ph 70-95, NPh 30-55, APh 20-45 and DNPh 5-30) ppm. After closing, the flasks were shaken with water bath shaker at 25 C^o according to the equilibrium time of the reaction. After that they are centrifuged for 10 minutes.

UV-Vis spectrophotometer has been used to measure the absorbance for the solutions, at the convenient wavelength for each compound. The values obtained of absorbance have been used to determine the equilibrium concentration of calibration curve.

2.2.7. study the factors affecting adsorption

2.2.7.1. Effect of Temperature

effect of temperature has been accomplished by taking four degrees (15, 25, 35, and 45) C^o. Therefore, the adsorption isotherm for each compound has been studied in each degree, and the effect of temperature on adsorption has been recorded.

2.2.7.2. pH effect

To accomplish this study two pH values has been suggested pH=8 and pH=6, a full study of adsorption isotherms has been achieved.

2.2.7.3. Ionic strength

The effect of ionic strength , has been performed on the following compounds(Ph, DNPh, NPh and APh), at different concentrations (0.1, 0.2) M of sodium chloride solution has been used and the effect of this salt on adsorption has been recorded.

2.2.8. Adsorption Isotherms on Zeolite and charcoal:

In order to compare the adsorption between the polymer and Zeolite and charcoal the adsorption isotherm of compounds (Ph, DNPh, NPh, APh) were determined following the same procedure used in the determination of the adsorption isotherm in the polymer.

Introduction

The development of thin film chemistry over the past 15 years has enabled advances in several technologically important areas. Work in thin film materials design synthesis has benefited second harmonic generation(1-3), chemical sensing (4-7),separation(8-9). And molecular scale electronic device application.

The methods of choice for the controlled assembly of layered thin films include Langmuir Blodgeett deposition Monolayer self- assembly (10-12),and ionic (13-15), and covalent layer growth(16-18),the characterization of these materials has focused on layer thickness Morphology, Wettability, and constituent orientation. Among our reasons for interest in thin film materials is their potential for interest use in controlling chemical separators. We focus here on the thermodynamics and kinetics of interaction between vapor phase or liquid phase adsorbate and polymer interfacial layers.

1.1. Adsorption :

Adsorption is a phenomenon of material aggregation as ions or molecules or atoms on a surface of another material (19). Adsorption may be physical or chemical binding of the molecules of certain matter at the active sites for certain surface through physical or chemical forces with the active sites at the surface(20) . The adsorption also involves a removal of soluble materials in the solution or the solvent by solid surface or recovering these soluble substance by this surface (21) with process known as ″ Desorption0″ .Naturally the physical states of the matter which contain limit surface are in solid or in liquid state . Hence the adsorption phenomenon would be solid □ liquid, solid □ gas, liquid □ liquid, liquid □ gas and solid □ solid ⁽²²⁾

The substance that is adsorbed called ″Adsorbate ″ and the surface of solid material called ″Adsorbent″ such as Charcoal, Silicagel, Zeolite, and Porous Clays.

The reason for adsorption phenomenon is the existence of some unsaturated forces on the adsorbent due to the in complete coordination or insufficient material surface particles, like the liquid or solid phase adsorption which leads to saturate those forces on the adsorbent surface ·

Decreasing in surface free energy (ΔG) is occurred during the adsorption process, and decreasing in entropy (ΔS) at the surface that the adsorption take place, due to losing the degree of freedom possessed before adsorption. The decreasing of free energy (ΔG) and the entropy (ΔS) in the same time will cause decreasing in heat content (ΔH) according to the thermodynamic relation (exothermic change)(23) :

$$\mathbf{\Delta G = \Delta H - T\Delta S \qquad (1\text{-}1)}$$

So single partial layer may be formed at the adsorbed surface and in this case is called Unimoleculer adsorption. Also multilayer may be formed at the adsorbed surface and known as ″ multimolecular adsorption″ on the other hand the penetration process of a particle in the phase of adsorbent called ″absorption″ and the process of absorption and adsorption process together called ″sorption″(24) This process usually take place on the porous surface adsorbents. The enthalpy of this process is positive (endothermic process), because the distribution inside the Adsorbent needs energy (25). The incorporation process of adsorbent and Adsorbate without distribution is termed ″incorporation″ adsorption .

1.2. Types of Adsorption

The physical and chemical forces are involved in the adsorption between the adsorbate and the adsorbent, the adsorption can be divided in to two Types: -

First type: - physical adsorption (27) (physisorption)(28) : - it is a natural attraction forces between the adsorbing surface and the atoms or molecules or ions that were adsorbed at the surface. The physical adsorption is nonspecific(29)because the atom or the molecule that suffering from physical adsorption does not bonded chemically with the atoms of the adsorbent surface, but it is contained with certain area at the surface and this area depending upon the volume of the adsorbed atoms or molecules or ions with little physical adsorption heat(20) . The physical adsorption does not need an activation energy and it is an opposite way, (22,30,31) the adsorbed atom or ion at the surface has an ability to move through certain area at the surface and this adsorption is non localized, and this type of adsorption involves the formation of several layers at the surface .

Second type:- chemical adsorption (chemisorptions);chemical bonds (ionic or covalent) will form in this type of adsorption between the surface and the atoms or molecules or ions that adsorbed on the surface . The chemical adsorption is specific because it taking place in certain conditions and the adsorption does not taking place at another surface with the same conditions or does not taking place at the same surface with changing the conditions.

The chemical adsorption is exothermic with heat greater than that from the physical adsorption . the chemical adsorption needed to activation energy under going slowly forward reaction only normally, it is of strong chemical bonds(22,32,33) And it is localized because it taking place at the sites of low internal energy, and the adsorbed units need constant activation energy at the homogeneous surface , while non-constant activation energy needed at heterogeneous surface(34). One layer is forming in the chemical adsorption between the substance and the adsorbing surface normally.

1.3. Factors influencing the Adsorption process

1.3.1. Nature of Adsorbent

The properties of adsorbent that effect on quantity of adsorption include the polarity and porosity of surface. The polar surface tend to adsorb the more polar components in solution (35) while porous surface effect on the quantity as well as selectivity (36,37).

The homogenousity of the surface makes the adsorption isotherms match with theoretical interpretation proposed for adsorption in contrast to the non □homogenous surface(38) .where the adsorption capacity for a variety of materials increases as the surface area of adsorbent increases too.

1.3.2. Nature of Adsorbate

As mentioned previously, the polarized surface of absorbent tends to adsorb the high quantity of polar component in solution (39). More over the adsorption quantity increases as the molecular mass of Adsorbate increases, and it decrease, as the solubility increases (40, 41)

1.3.3. Solvent Effect

Molecules of solvent compete with solute molecules in adsorption process to occupy the distributed adsorption sites on the adsorbent. This competition depends on the interaction between solute and the adsorbent surface, and solvent □solute interaction and solvent-surface interaction .

Therefore .the resultant of these interactions is greater as the interacting group is similar in polarity.

1.3.4. PH Effect

The effect of pH on the adsorption process in being difference in adsorption, as the difference in adsorption system. The acidity change, which that lead to increase the solubility of adsorbate in solution decrease adsorption process. While the change which lead to decrease the solubility of the Adsorbate molecules increase adsorption process (42) also, in the case of surface that have polarized or charged to the adsorbing particles throughout the effect of acidity .In contrast the adsorbing quantity decrease if the surface charges are similar to charge of adsorbing particles (43).

1.3.5. Temperature Effect

It is known that adsorption process is exothermic(44).unless there is companying an absorption or distribution process inside the porous solid phase(45.46) .Hence the temperature increasing will lead to decrease in the adsorption quantity . In the molecular prospective increasing temperature the kinetic energy for adsorbing molecules on the adsorbent surface , which may increase the probability of molecules separation from surface and back to the solution again(47).

The adsorption process that accompanying an absorption or distribution inside the porosity would be endothermic process. subsequent the kinetic energy for molecules adsorbent may increasing their ability to inter inside the solid phase porous and increase the distribution. therefore, adsorption quantity increase as the temperature increase (25) .

1.3.6. Ionic Strength Effect

The effect of ionic strength on adsorption process could be summarized as below:-

For adsorbate, if it is in an ionic form increasing of ionic strength lead to increase adsorbate solubility. However, Low adsorption process would be expected unless, there are similar ions, which cause the common ion effect reducing the adsorbate solubility and increase its adsorption (48, 49).

Whereas, the non □ ionic Adsorbate, the ionic strength may lead to the occurrence of salting □ out process. Which decreases the solubility and increase the adsorption process (50)?

In addition, the formation of a coordinated complex between the Adsorbate and number of ions that are available in solution will effect on the adsorption process. This effect depends on the solubility and charge of the formed complex (51).

For the adsorbent, if it is non polar without charges, there will be no effect of ionic strength, but in the case of polarized surface, probably, the adsorbing ions will compete on adsorption sites on the adsorbent surface which decreases the adsorption.

In the case of charged adsorbent surfaces with similar charges to the adsorbate particles, increasing ionic strength will cover the adsorbent by a layer of opposite charge to the absorbate, which leads to increase adsorption process(42).while if the surface has opposite charge to the Adsorbate particles, then increasing ionic strength will decrease adsorption quantity(52,22).

1.4. Adsorption Isotherms

Generally adsorption Isotherms could be defined as the relationship between the quantity or amount of Adsorbate on the surface and their activity in the distribution phase at constant temperature(53). The adsorption isotherms can be defined also as the relation between the adsorbed substance (adsorbated) at the surface of adsorbent with the primary concentration of the solution at constant temperature(54).

The first isotherm for the adsorption between the solute and the solvent described from Van Bemmeler (1888).the isotherm depending temperature can serve in the extraction of important information about the fact of adsorption process with the availability of information in describing the adsorption process and conditions of this process. Adsorption isotherms can serve to obtain the thermodynamic quantities of the adsorption.

Giles (55) has classified ″Adsorption Isotherms″ depending on the prefixes of isotherms, and has given this classification the characters (S, L, H and C). As illustrated in figure (1□ 1)

Hence, **S** is the adsorption isotherm has s □ shape, in which the direction of the Adsorbate on the surface is vertical and the solvent may undergo sever or hard adsorption on the surface of adsorbent . The class **L** is special for Langmuir isotherm, in which the direction of adsorbate's is horizontal and in a single layer. Class **H** special for high affinity adsorption, which takes place in very dilute solution, and adsorption of large molecules like polymers.

Finally, class **C** indicates that there is constant partition between the adsorbent, and the adsorbate in the solution, and indicates that there is a high probability to chemisorptions.

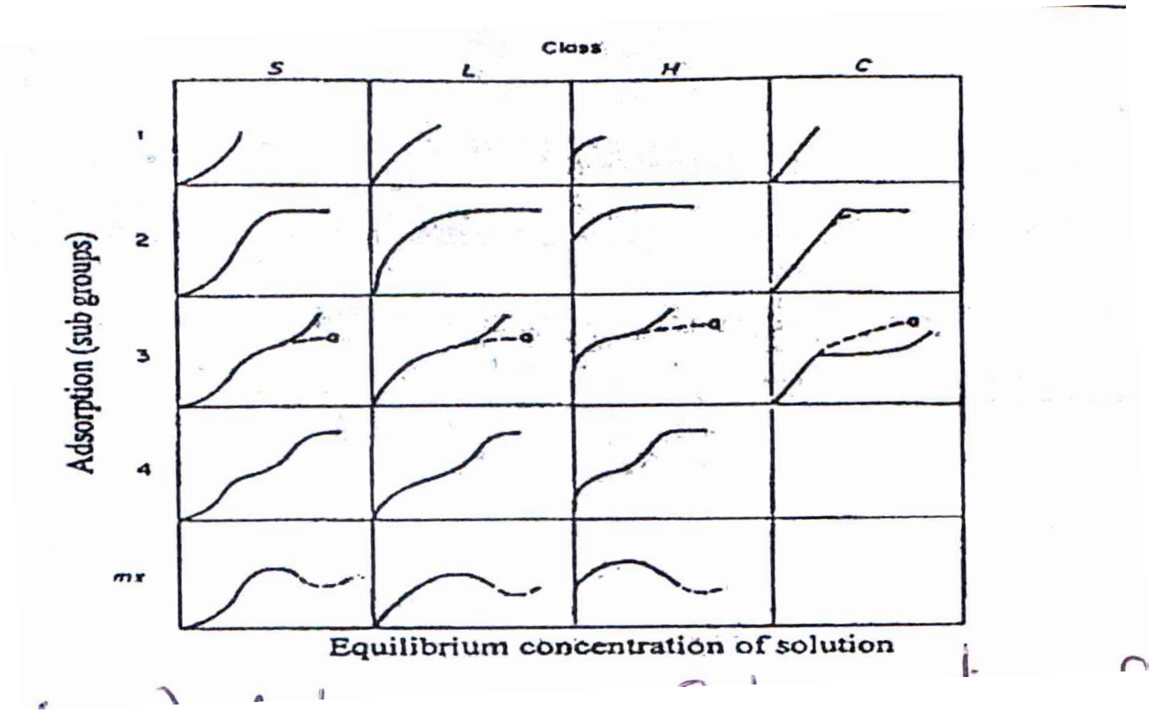


Figure (1-1) Adsorption Giles classification

1.5. Langmuir Equation for Adsorption:

Irving Langmuir in (1918) developed this equation (56) that has been proposed according to the interpretation for the adsorption of gases on the surfaces of solid materials, but the equation could be applied to the adsorption of soluble materials in liquid phase on the surface of solid materials (57).

Langmuir equation depends on the following assumptions:-

1. The surface of the solid phase has limited number of sites which adsorption process occurs on, with homogenous surface, since the area of any sites of adsorption is constant and the distribution of energy is regular.
2. The adsorption is localized, occurs between adsorbate and empty sites. The Adsorbate particle has no ability to move (mobile), and the empty sites can not adsorb more than one particle.

3. From the above 1 and 2 it is clear that the adsorption is mono □ layer, and reaches the maximum value, when all the empty sites on the adsorbent are covered by the particles of Adsorbate. Therefore, Langmuir equation could be derived as follows :-

A	+	B	$\rightarrow$	A	+	**B**	(1□ 2)
Solute in Solution		solvent in adsorption layer	$\leftarrow$	Solute in a dsorption layer		solvent in Solution	
X_2		X_1^S		X_2^S		X_1	

Where X_1,X_2 are the mole fractions for solvent and solute, respectively in solution X_1^S X_2^S are the mole fractions for adsorbed solvent, and solute respectively, on the surface of the solid phase at the equilibrium :-

$$K = X_1 X_2^S / X_2 X_1^S = a_1 X_2^S / a_2 X_1^S \qquad (1 □ 3)$$

Were a_1,a_2 are the activity of solvent and solute respectively, assuming that the activity of solvent remain constant, because of the small quantity that has been lost by adsorption, and large quantity that has been earned by dsorption, so $b = K / a_1$ then equation becomes :-

$$b = X_2^S / a_2 X_1^S \qquad (1 □ 4)$$

At equilibrium the solute activity a_2 could be approximated to the concentration at equilibrium of the solute Ce and the summation of mole fractions for solute and solvent in adsorption layer :-

$$X_2^S = b\,Ce \,/\, 1 + b\,Ce \qquad (1\ □5)$$

By considering that n_2^S is the number of moles of adsorption sites that are occupied by solute particles and n^S is the total number of adsorption sites.

$$\Theta = n_2^S / n^S = X_2^S = b\,Ce \,/\, 1 + b\,Ce \qquad (1\ □6)$$

Were Θ is part of unoccupied site by Adsorbate particles, and since the quantity of Adsorbate for each gram of adsorbent (Qe) is directly proportional with Θ then:

$$Qe = K\,\Theta \qquad (1\ □\ 7)$$

$$Qe = K\,b\,Ce / 1 + b\,Ce = a\,Ce / 1 + b\,Ce \qquad (1\ □\ 8)$$

$$Ce / Qe = 1 / a + b / a\,Ce \qquad (1\ □9)$$

Plotting Ce ⁄ Qe against Ce, straight line is obtained a slope equals b ⁄ a and an intercept equals 1 ⁄ a that in figure (2□1)

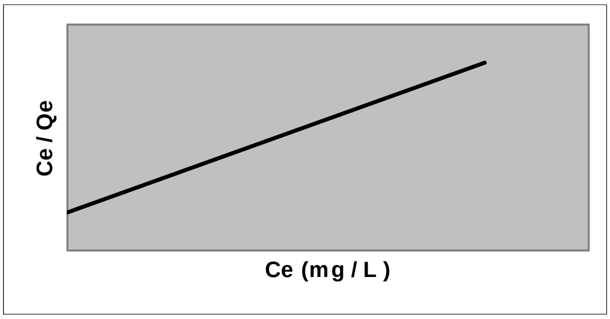


Figure (1-2) relationship of line for Langmuir isothermal

1.6. Freundlich Equation of Adsorption

It is one of the important and well known used isothermal equation in adsorption and discovered by the German scientist ″ Herbert Maxfinaly Freundlich″ the changes the internal energy is not systematic because the adsorption sites take place at different energy levels(58) and this leads to changing the adsorption isotherm so that the equation of ″ Freundlich″ was used to represent the chang in adsorbed substance quantity under the unit of area or the mass of the adsorbed substance with concentration at equilibrium .

Freundlich first use was in the describing of the adsorption of gaseous phase with the adsorption of the solute and solution.

Freundlich equation is an empirical equation has the following formula:-

$$Qe = Kf\ Ce^{1/n} \qquad (1 \square 10)$$

Were Qe is the quantity of Adsorbate on (1 gm) of adsorbent at equilibrium Ce is the concentration of Adsorbate in solution at equilibrium, Kf and n are Freundlich constants.

The most signification defect of this equation is the disability for describe the maximum value of adsorption, and its constants have no simple physical meaning (43).

The natural Logarithm of equation is in linear formula:-

$$\ln Qe = \ln Kf + \mathbf{1/n} \ln Ce \qquad (1□11\ )$$

Plotting $\ln Qe$ against $\ln Ce$, a linear straight line is obtained with slope equals $\mathbf{1/n}$ **,** and the intercept $\ln Kf$(59).

Freundlich equation, in contrast to Langmuir equation, is not linear at very low initial concentration but retain convex towards the center of adsorption quantity.

The adsorption process in solution is much more responds to Freundlich equation comparing to Langmuir equation as shown in figure (3□ 1).

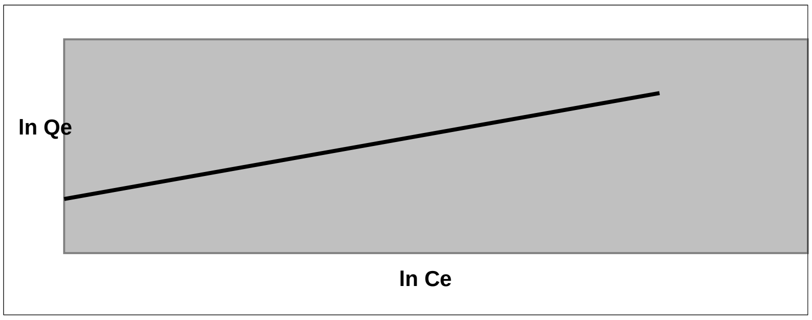


Figure (1- 3) relationship of line for Freundlich isothermal

1.7.Brunaner,Emmett and Teller (BET) equation:

An important theory about the multilayer adsorption according to Langmuir theory, it was found that the expression Isothermal (BET) which is considered the basic way to calculate the surface area for solid materials by using the data of multilayer physical adsorption (60).

In (1938) Brunaner, Emmett and Teller (61) derived by statistical ways and by Kinetic studies the following

$$\frac{p}{n(p^{o}-p)} = \frac{1}{n_m c} + \frac{(c+1)}{n_m c} \cdot \frac{p}{p^{o}} \qquad (1 - 12)$$

n: number of adsorbed moles material at equilibrium
n_m: number of adsorbed moles material at the first partial layer .
p: gas pressure at equilibrium
po: gas pressure at saturation
c: constant at constant temperature and equal to :

$$c = \frac{\exp (q_i - q_L)}{RT} \qquad (1 - 13)$$

q_i: heat of adsorption at first layer .
q_L: condensation heat of gas .

Brunaner ,Emmett and Teller(62), have classified adsorption isotherms according to five categories as illustrated in Figure (4-1):-

Class I: - is for adsorption of type L according to Giles classification.

Class II: - is as expected from BET approximation in multi – layer adsorption, which normally happens in adsorption of gas.

Class III:-takes place when interaction between first layer and adsorbate is much weaker than interaction between first and second layer.

Class IV: - is similar to class I, but there is two limits for adsorbate instead of one limit.

Class V: - was suggested as a common class of class I and II.

Class III and V are not so familiar, or common and the chemisorptions may occur in class I only, while the physisorption can occur in any class of the previous categories .

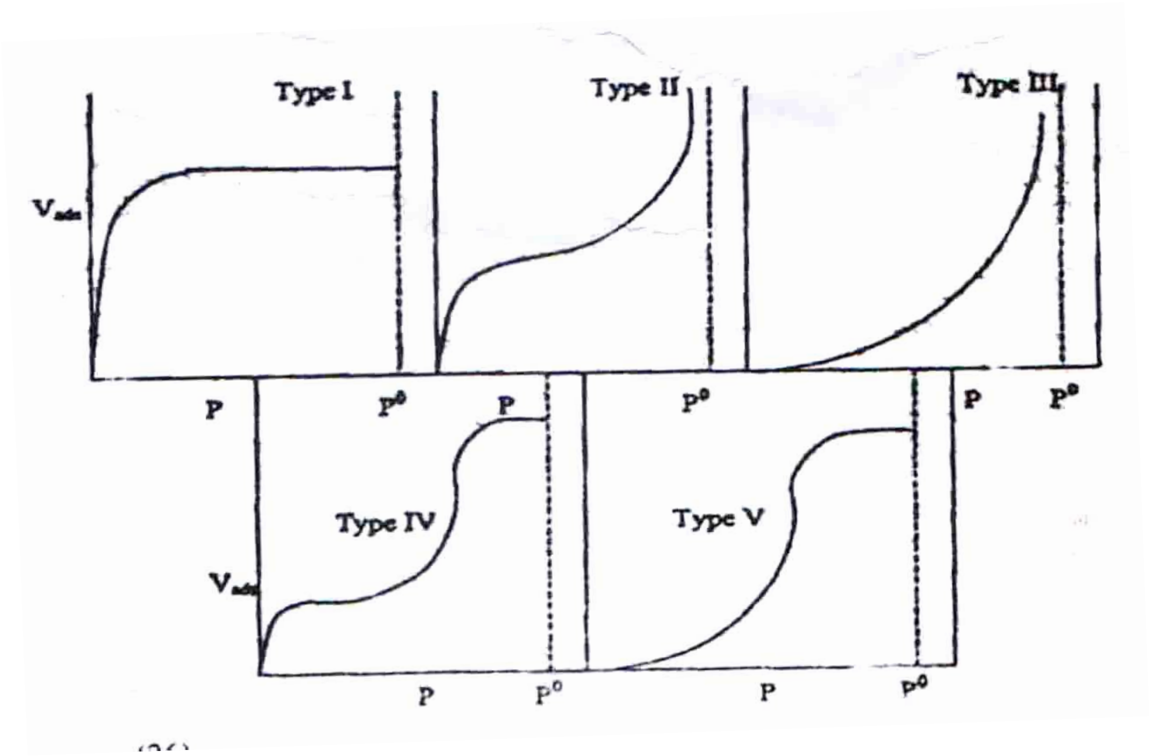


Figure (1-4) Adsorption Brunaner classification

According to the equation (12 -1) the sketching of p/ n (p^o- p) versus (p^o- p) gives straight line it is slope (c-1/ n_mc) and it is intercept equal to 1/n_mc as shown in figure (5 – 1)

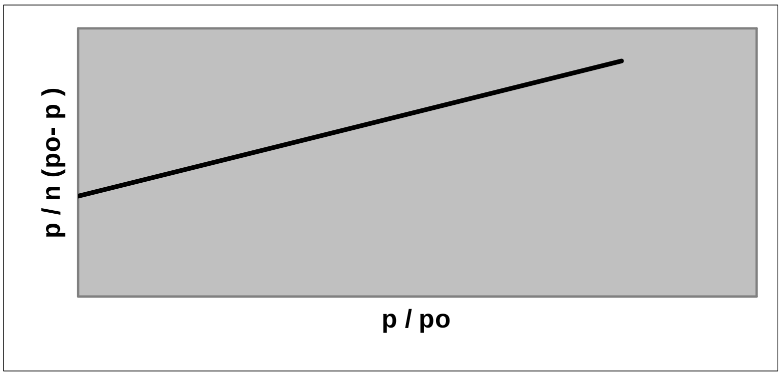


Figure (1-5) relationship to line equation (BET)

1.8. Adsorption of organic pollutant materials from solution :

The adsorption on polymers at solid – liquid interfaces has been studied extensively in recent years, (63, 64).

Mckay, Otterburn and Sweeney (65) studied the removal of color from effluent using silica as rate processes. They found that removal of basic dye from effluent by adsorption on to silica gel is mainly controlled by intraparticlre diffusion although a small boundary layer resistance was experienced. They also determined the activation energy for dye removal.

Kawaguchi et.al (66) . have studied the adsorption of ps and PMMA on to silica surface by IR and Lipatov et.al (67, 68) have studied the adsorption of a mixture of PS and PMMA on to the same surfaces.

Kumar, and Upadhyay(69)studied removal of phenols by adsorption on fly Ash, they found that the Freundlich isotherm is more suitable for all the systems investigated in their study on adsorption of phenol and cresol and their mixtures from aqueous solutions on activated carbon and fly ash, also on the effects of contact time and initial solute concentration and the isotherm parameters evaluation.

Polymer adsorption at solid surfaces is important in a variety of fields, such as material and food sciences, medical science, and stone conservation (70).

Safarik, (*et.al.*)(71) Studied the sorption of water soluble organic dyes on magnetic poly (oxy-2, 6-Dimethyl-1, 4-phenylene) (PODMP) by using Magnetic (PODMP) for sorption of water soluble organic compounds (dyes belonging to triphenylmethane, hetropolycyclic and azo dye groups) from water solutions. They found in general that the hetropolycyclic dyes exhibited the lowest sorption.

Longhinotti, (*et. al).*(72) studied the adsorption of anionic dyes on the biopolymer chitin, the adsorption of the anionic dyes orange IV, orange G, and xylenol orange on chitin, employing the Langmuir isotherm found that the adsorption capacity is dependent on pH , and the rise in the temperature reduces adsorption capacity by chitin.

Karadag, (*et.al.*)(73) Studied removal of water-soluble cationic dyes

with TriSyl Silicas, by investigating the adsorption of certain water-soluble cationic dyes, (basic blue 9, basic blue 12, basic blue 17, brilliant cresyl blue ,janus green B, basic green 4, basic violet 1, basic violet 3, and thionin) on to TriSyl Silica by batch adsorption at 25 C. They found Langmuir type adsorption.

Breidenich,(*et.al.*) (74), studied the adsorption of polymers anchored to membranes and found that if one includes the finite size of the anchor segment, the membrane bends towards the polymer for sufficiently strong adsorption.

Mohammed (75) studied synthesis and characterization of Zeolite – urea formaldehyde polymer complex and study of adsorption of some phenolic compounds from aqueous solution on its surface. Using FT.IR spectroscopy and x-ray diffraction pattern .showed that the effect of temperature, that the characterization of Zeolite –urea formaldehyde polymer complex was adsorption more than Zeolite– phenolic compounds from aqueous solution on its surface.

Al-Samarmed(76) , identified adsorption isotherms for some aldehyed compounds on the surface of the Zeolite (5A) the results followed Freundlich equation this study involved the effect of temperature, PH and ionic strength on the process of adsorption.

Pekel and Guven (77).studied the effect of solvent, temperature and concentration on the adsorption of poly (n-Butyl methacrylate) on alumina from solution by using UV. And F.T.I.R. photoacoustic spectroscopy techniques, the results obtain is in conformity with Langmuir isotherm.

1.9.THE AIM OF THE WORK

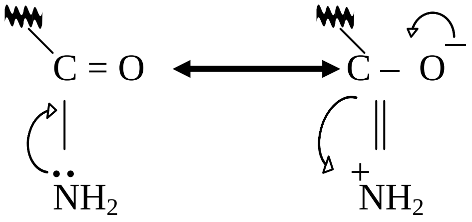
The aim of this work is to study the possibility of using across linked polymer (acrylamide- bisacrylamide) co-polymer as adsorbent for some organic phenolic compounds from aqueous solution and it is efficiency and comparing it is efficiency with Zeolite and charcoal .

Results & Discussion

3.1 Preparation of (acrylamide Bisacrylamide) Co -polymer :-

The polymer was identified by FTIR spectrophotometer the used in studies and we notice the stretching vibration of (NH_2) group with it is symmetric parts (3200 cm^{-1}) and with asymmetric about (3370 cm^{-1}) this two peaks were presence case of the hydrogen bonding or because of in pure parts of the water.

The peak in the (2930 cm^{-1}) this peak of stretching vibration of (C – H) aliphatic group and in the (1662.5 cm^{1}) that found a strong peak that retain to the stretching vibration which belongs to the amide carbonyl group .



That the stretching vibration of the amide carbonyl group decreased under the stretching vibration standard of the natural amide group this happened because of the resonance between the carbonyl drawing group and the two electron pair which consists in amine group that lead to feature oblique of carbonyl bond as double and increasing of the single this case of decreasing of the force constant of the bond that lead to decreased of the vibration frequency.

To the all above mentioned cases that the peak in (1535 cm^{-1}) that retain to the group of (C=$^{+}NH_2$) and the stretching of the peak in (1275 cm^{-1}) which belongs to the bond of C – O $^{-}$ which consist during the resonance.

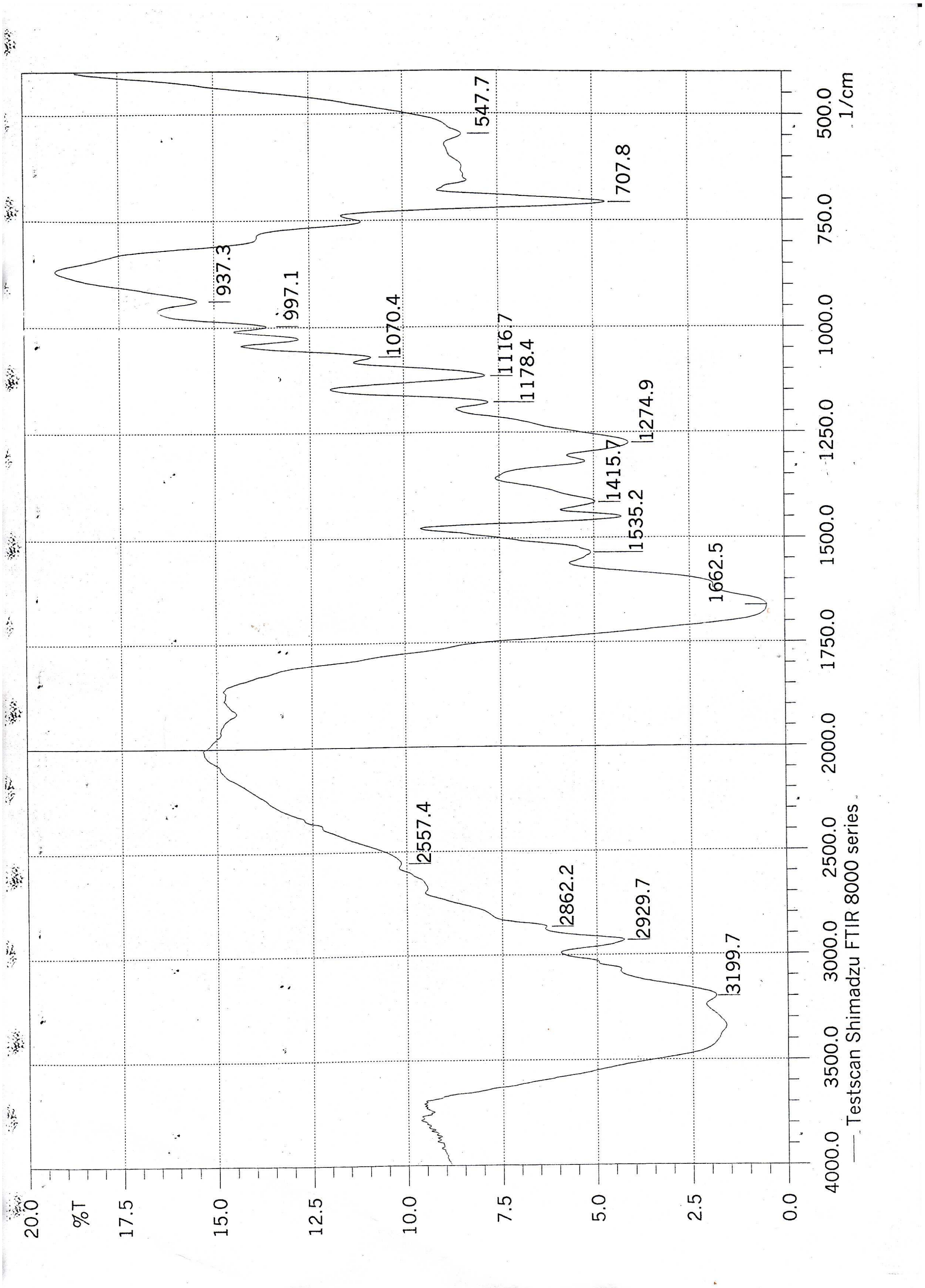
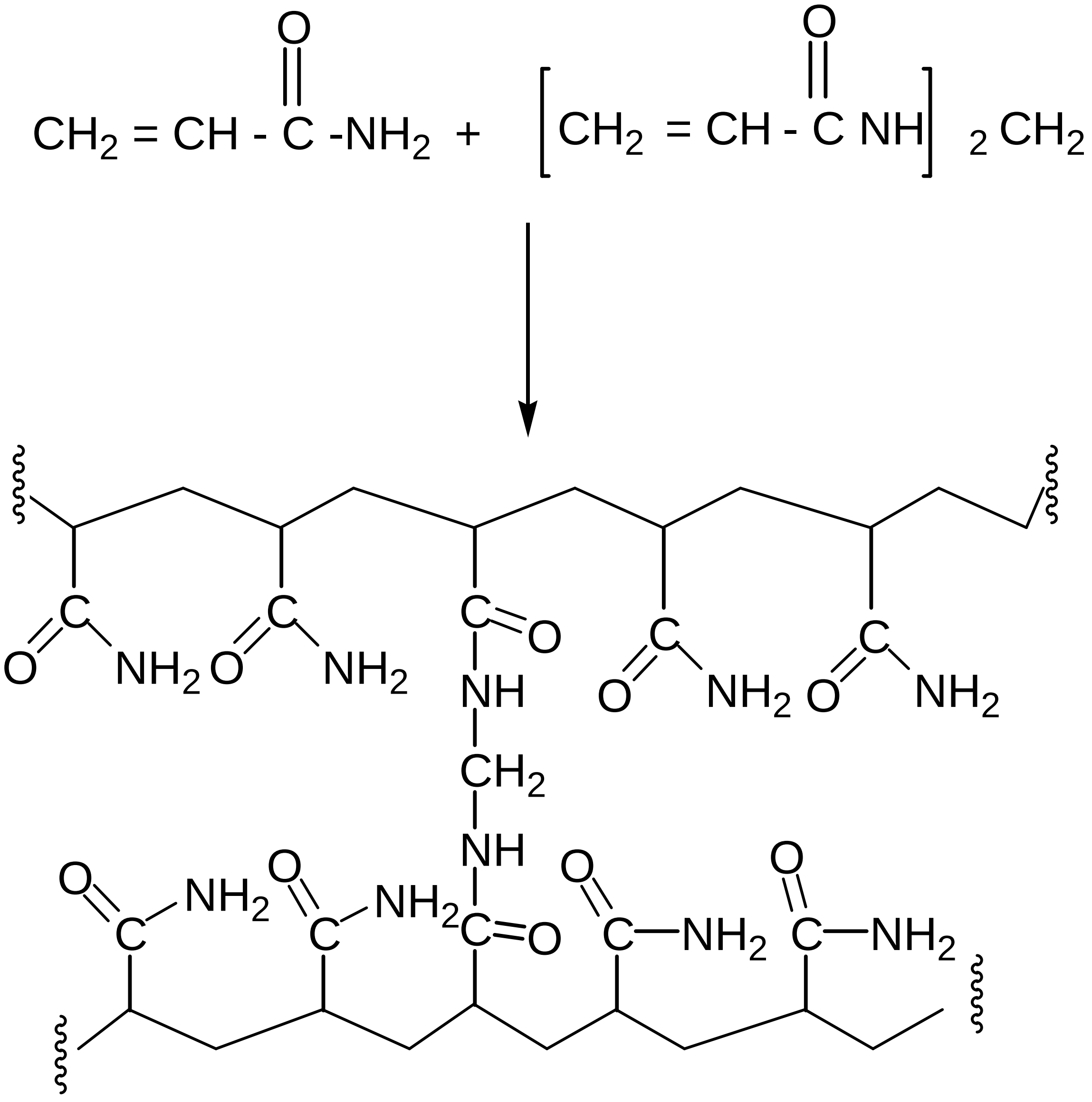


Figure (3 – 1) FTIR spectrum of the prepared polymer

And the suggestion of polymer structure is:-



$$CH_2 = CH - \overset{\overset{O}{\|}}{C} - NH_2 + \left[CH_2 = CH - \overset{\overset{O}{\|}}{C} NH \right]_2 CH_2$$

3.2 swelling of the polymer:-

Swelling test for the prepared polymer was performed according to ASTM procedure (79). The swelling have been measured in water at pH = 7, pH= 6, pH= 8, and 0.1M NaCl solution, 0.2M NaCl solution, swelling of Zeolite has been done on the same method.

The results listed in table (3 – 1):-

Table (3 – 1) swelling percentage for polymeric particles

The polymer	Solvent	Swelling percentage %
Co-Poly (acrylamide – Bisacrylamide)	Water pH=7; at 25C°	3.3%
	pH=6, at 25 C°	2.0/3%
	pH=8, at 25 C°	5.201%
	0.1M NaCl; at 25 C°	1.859%
	0.2M NaCl; at 25 C°	1.462%

3.3 Adsorption

3.3.1 Adsorption Isotherms

Adsorption of compounds (NPh, DNPh, APh, ph) in aqueous solution at 25 C°, and pH 7, and was investigated using less than 300µm diameter granules of the polymer of (0.01) gm as adsorbent, with adsorbate, of initial concentrations of each (NPh 30,35,40,45,50 and 55) (ph 70,75,80,85,90 and 95), (DNPh 5to 15,20,25 and 30)ppm and(APh 20,25,30,35,40,and45)and the total volume of adsorbate is 10ml.

The amount of adsorption has been calculated using the following equation (42):

$$Qe = \frac{Vsol\,(C_{\circ} - Ce)}{m} \qquad (3\text{-}1)$$

Where

Qe = the quantity of adsorbate in mg/g.

V = the total volume the adsorbate in L.

$C_{\circ}$ = is initial concentration of solution in mg/L

m = weight of adsorbent (gm).

The results have given the isotherms which are shown in table (3 – 2)

Table (3 – 2) illustrates the values of Ce and Qe for compounds (ph, DNPh,Ph, APh) at 25C$^{\circ}$.

Ph			DNPh			NPh			APh		
$C_{\circ}$ mg/L	Ce mg/L	Qe mg/g	$C_{\circ}$ mg/L	Ce mg/L	Qe mg/g	$C_{\circ}$ mg/L	Ce mg/L	Qe mg/g	$C_{\circ}$ mg/L	Ce mg/L	Qe mg/g
70	50.398	19.601	5	4.554	0.445	30	20.826	9.173	20	16.393	3.606
75	54.422	20.577	10	7.226	2.773	35	25.185	9.814	25	20.491	4.508
80	58.207	21.792	15	9.810	5.189	40	28.966	11.033	30	24.672	5.327
85	61.872	23.127	20	13.007	6.992	45	33.533	11.466	35	29.098	5.901
90	64.581	25.418	25	16.364	8.635	50	37.314	12.685	40	32.622	7.377
59	69.003	25.996	30	19.343	10.656	55	41.549	13.450	45	37.213	7.786

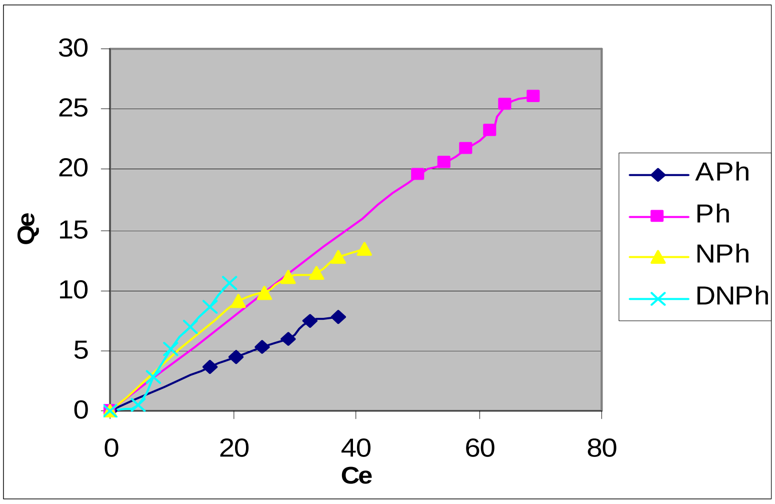


Figure (3 – 2) shows the adsorption isotherms for (ph, DNPh, APh, NPh).

From figure (3 – 2) and according to Giles classification(55,83), ph follows L_3 adsorption mode, thus molecules would be arranged parallel on the surface polymer, with three layers, and the adsorption is happened through the hydrogen bonding between the Ph and the polymer, and the adsorption isotherm for this compound is of Langmuir type.

From the same figure and according to same classification APh follows L_2, adsorption mode, and this compound have high affinity adsorption towards the surface, and its arranged parallel for adsorbent surface with two layer, and the adsorption isotherm for this compound is of Langmuir type.

Also the same figure, the adsorption of DNPh follows S_2 adsorption mode according to Giles classifications and that means the compound arrange in classes or clusters form on polymer surface also it arranged vertically on polymer surface, with two layers, and the adsorption isotherm for compound is of Freundlich type.

NPh follows L_2 adsorption mode on the polymer surface according to Giles classification and here we see some of similarity between the type of adsorption of these two compound (APh, NPh) they arranged in the same form on polymer surface and for similar reasons in both hydrogen bonding is the pushing force to adsorption of APh, and NPh, and the adsorption isotherm for this compound is of Langmuir type.

However, the adsorption value determined depending on Freundlich and Langmuir equation of the four compounds is listed in table (3 – 3) could be:-

$$\mathrm{In}\,Qe = \mathrm{In}\,Kf + \frac{I}{n}Ce$$ Freundlich equation (3-2)

$$\frac{Ce}{Qe} = \frac{1}{a} + \frac{b}{a}Ce$$ Langmuir equation (3-3)

Table (3 – 3) adsorption modes for compounds according to Freundlich and Langmuir Equation.

Ph				DNPh				NPh				APh			
Ce	Ce / Qe	In Ce	In Qe	Ce	Ce / Qe	In Ce	In Qe	Ce	Ce / Qe	In Ce	In Qe	Ce	Ce / Qe	In Ce	In Qe
50.4	2.571	3.92	2.98	4.554	10.23	1.52	-0.81	20.83	2.27	3.04	2.216	16.39	4.546	2.76	1.44
54.4	2.644	4	3.02	7.226	2.606	1.98	1.02	25.19	2.566	3.23	2.283	20.49	4.545	3.02	1.51
58.2	2.671	4.06	3.08	9.81	1.89	2.28	1.65	28.97	2.625	3.37	2.4	24.67	4.631	3.21	1.67
61.9	3.675	4.13	3.14	13.01	1.86	2.57	1.94	33.53	2.924	3.51	2.439	29.1	4.931	3.37	1.78
64.6	2.54	4.17	3.24	16.36	1.894	2.8	2.16	37.31	2.941	3.62	2.54	32.62	4.422	3.53	1.79
69	2.654	4.23	3.26	19.34	1.815	2.96	2.37	41.55	3.089	3.73	2.598	37.21	4.779	3.66	1.8

Plotting of Ce and Ce/Qe for Langmuir equation is shown in figure (3 -3)

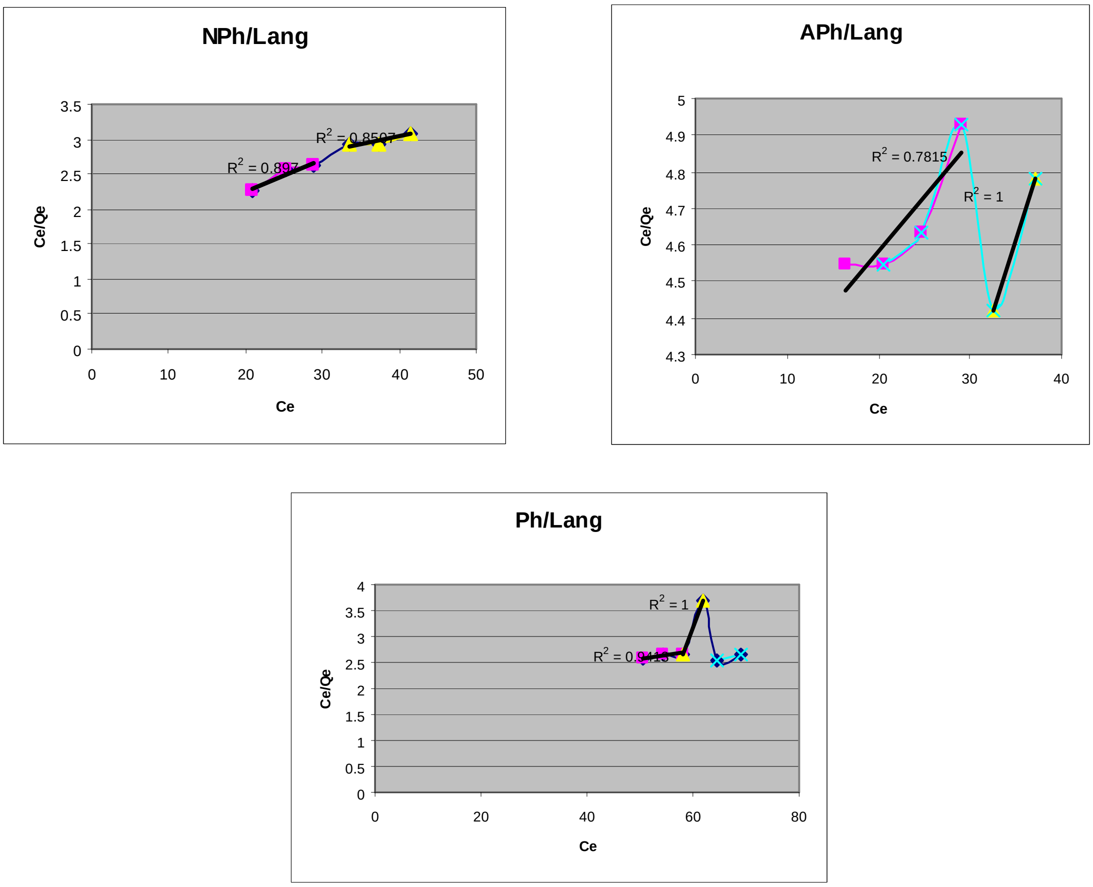


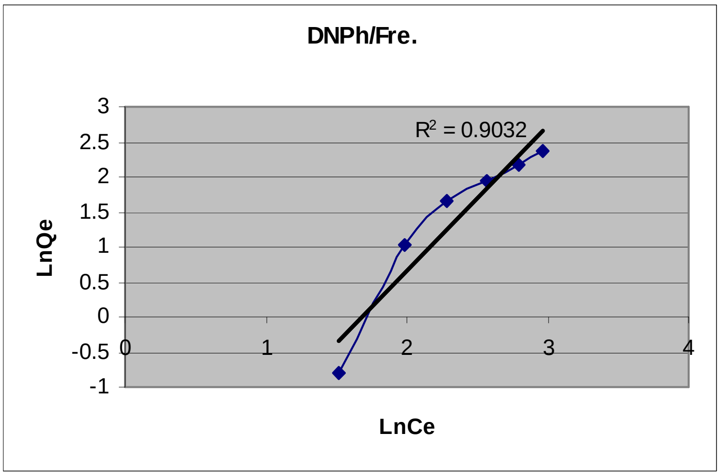
Figure (3-3)shows the Langmuir slop in Ce against Ce/Qe for compound (Ph, APh , NPh) at 25C^o

The Langmuir constants are calculated and listed in table (3-4)

Table (3-4) value of Langmuir constant for compounds (Ph, NPh, APh)at 25 C^o

compound	a	b	r
Ph	0.462	0.004	0.165
Ph_1	0.518	0.006	0.969
Ph_2	-0.076	-0.02	1
Ph_3	1.154	0.03	1
APh	0.226	0.001	0.342
APh_1	0.25	0.0075	0.883
APh_2	0.53	0.04	1
NPh	0.65	0.024	0.976
NPh_1	0.724	0.031	0.947
NPh_2	0.453	0.009	0.922

Plotting of ln Ce and ln Qe for Freundlich equation shown in figure (3- 4)



Figure(3-4) shows of Freundlich slop Ce against Ce / Qe value for the compound (DNPh).

The c Freundlich constant are calculated and listed in table (3-5) .

Table (3-5) value of Freundlich constant for the compound (DNPh)

Compound	K_f	n	r
DNPh	0.801	0.482	0.95

3.3.2 Temperature effect

The effect of temperature on the adsorption process for the compounds (Ph, DNPh, NPh, APh), on surface of the polymer, was investigated in four different temperatures (15,25,35,45) C° at the following conditions, pH = 7 with less than 300µm diameter granules of adsorbent of (0.01)gm, with adsorbate of initial concentration between (70 – 95 ppm of ph, 30 – 55 ppm NPh, 20 – 45 ppm of APh and 5 – 10 ppm of DNPh),

The results are listed in table (3 – 6) .

However, the results are listed in table (3 – 5 ……… 3 – 8), since the behavior of each compound is different from the other, hence the results for each compound discussed separately.

Table (3 – 6) Adsorption isotherm for the compounds (ph, DNPh, NPh, APh) at different temperatures (15, 25, 35, 45) C°

Ph							
15		25		35		45	
Ce	Qe	Ce	Qe	Ce	Qe	Ce	Qe
7.569	62.43	50.398	19.601	49.641	20.358	35.059	34.94
11.394	63.6	54.422	20.577	53.784	21.215	37.529	37.47
14.780	65.219	58.207	21.792	58.247	21.752	42.191	37.808
18.007	66.992	61.872	23.127	61.075	23.924	46.932	38.067
21.115	68.884	64.581	25.418	64.581	25.418	50.95	39.043
25.338	69.661	69.003	25.996	68.764	26.235	54.183	40.816

DNPh							
15		25		35		45	
Ce	Qe	Ce	Qe	Ce	Qe	Ce	Qe
4.072	0.927	4.554	0.445	3.912	1.087	4.394	0.605
7.109	2.89	7.226	2.773	4.554	5.445	6.175	3.824
10.7	4.299	9.81	5.189	8.248	6.751	9.824	5.175
14.043	5.956	13.007	6.992	11.138	8.861	13.094	6.905
17.313	7.686	16.364	8.635	14.189	10.81	14.759	10.24
20.235	9.766	19.343	10.656	19.109	10.89	19.591	10.408

NPh							
15		25		35		45	
Ce	Qe	Ce	Qe	Ce	Qe	Ce	Qe
28.698	1.301	20.826	9.173	20.103	9.896	19.855	10.144
30.33	4.669	25.185	9.814	23.615	11.384	24.318	10.681
34.938	5.061	28.966	11.033	28.822	11.177	28.264	11.735
37.024	7.975	33.533	11.466	32.086	12.913	28.719	16.28
39.028	10.971	37.314	2.685	36.776	13.223	36.095	13.904
41.157	13.842	41.549	13.45	41.095	13.904	41.033	13.966

APh							
15		25		35		45	
Ce	Qe	Ce	Qe	Ce	Qe	Ce	Qe
15.539	4.46	16.393	3.606	15.958	4.041	16.733	3.266
19.452	5.547	20.491	4.508	20.579	4.42	20.981	4.016
23.942	6.057	24.672	5.327	24.929	5.07	25.442	4.557
28.501	6.498	29.098	5.901	29.362	5.637	29.984	5.015
33.421	6.278	32.622	7.377	33.875	6.124	34.672	5.327
37.921	7.078	37.213	7.786	38.753	6.246	39.007	5.992

Figures (3-5) , (3-6) , (3-7), (3-8) show a plot of adsorbate quantity versus equilibrium concentrations for (APh ,DNPh ,NPh ,Ph), respectively, and at temperatures which have been previously mentioned. However, the results of each compound are discussed separately as follow;

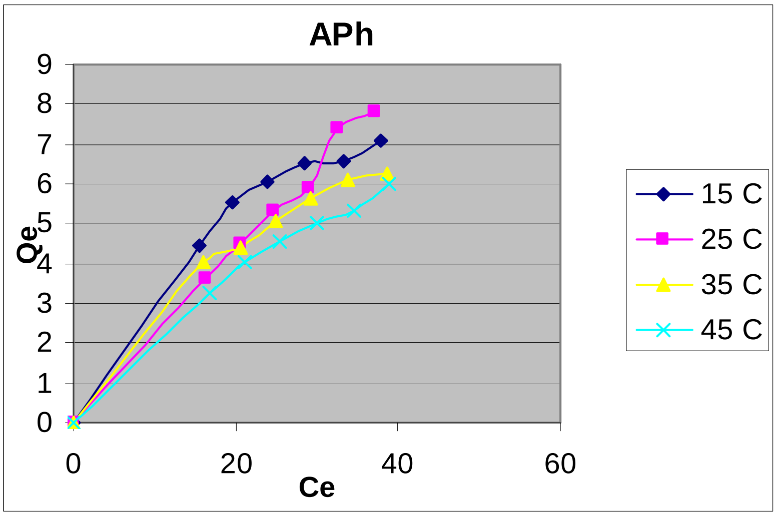


Figure (3 – 5) Adsorption isotherms of APh at (15,25,35,45) C˚

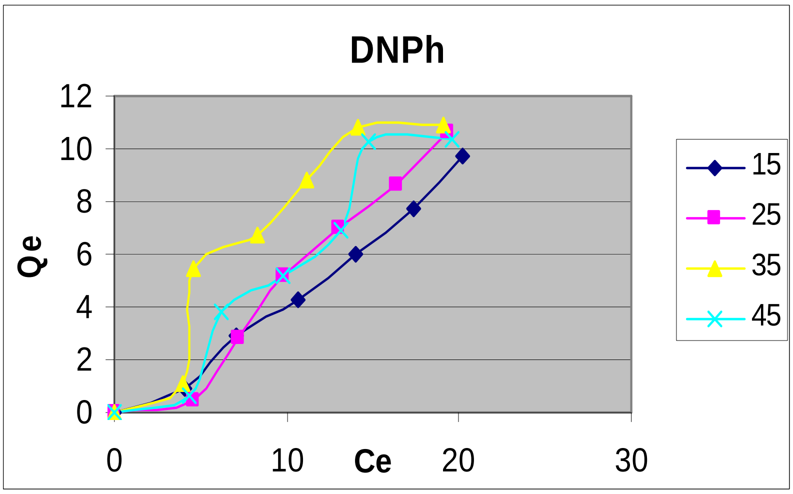


Figure (3 – 6) Adsorption isotherms of DNPh at (15,25,35,45) C˚

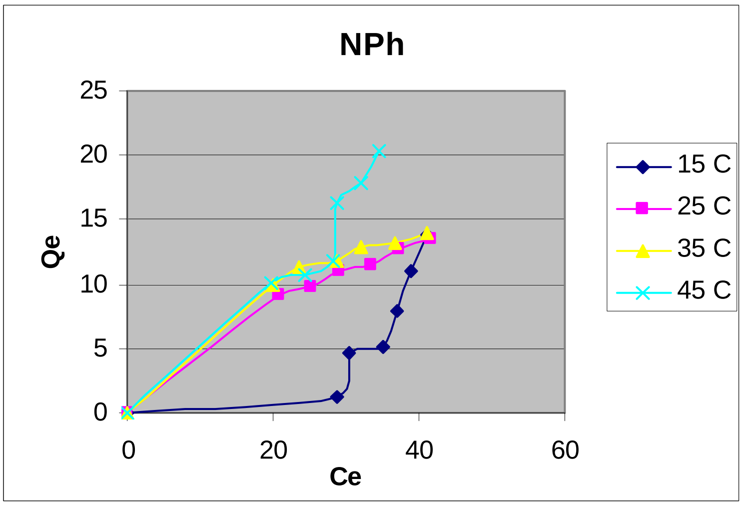


Figure (3 – 7) Adsorption isotherms of NPh at (15,25,35,45) C°

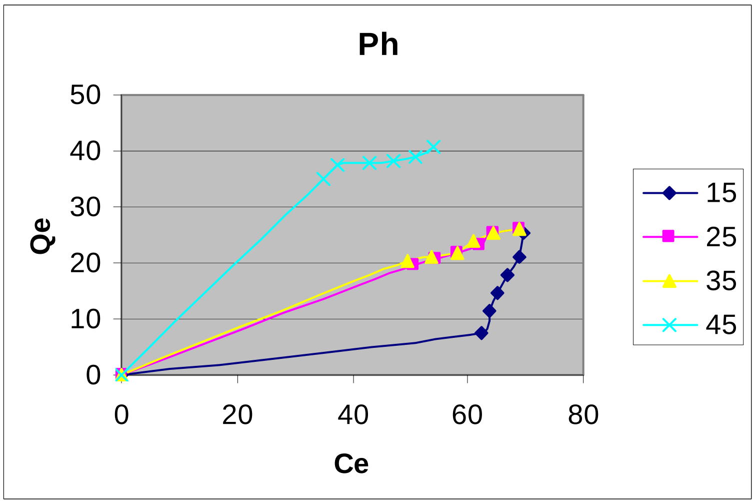


Figure (3 – 8) Adsorption isotherms of ph at (15,25,35,45) C°

In compound APh, we noticed decrease in its adsorption with increasing of temperature which means that make the dsorption more happen than adsorption process with increasing of the temperature.

From the general form for isotherms of this compound at temperatures (15,25,35,45) we found it follows L adsorption mode which explain the decreasing of adsorption with increasing of temperature because the inability of this compound to fill the holes or porous in polymer skeletal and the molecules of this compound arranged parallel to the surface at all temperatures. The absorption doesn't occur for this compound in polymer skeletal.

In DNPh compound, we notice that it takes the S adsorption mode and this mode transit with range between S_2 at (15,25)C° temperatures and S_3 at (45)C° temperature. That the bonding of DNPh with surface is through the hydrogen bonding between (OH) and (NO_2) or through the hydrogen bonding of (4 – NO_2) group from hydrogen bonding also in vertical with the surface, and because of the vertical arrangement of these molecules, it can penetrate the polymer porous, and the increasing of adsorption of this compound with increasing of temperature make this suggestion.

$$15 > 25 > 35 > 45$$

In NPh and Ph compound, the mode of adsorption at (15) C° is S_2 which means that the arrangement of its molecules is vertical, but when the temperature are increased the adsorption mode of this compound transit form to L type that between L and L_2 with increasing occurred in quantity of its adsorption which suggests occurring of hydrogen bonding between the NPh and polymer surface.

3.3.3 Thermodynamic functions

ΔH has been calculated for all adsorption processes according to equation (1)(80), via plotting logarithmic value of the maximum adsorption quantity at equilibrium concentration as (in Qe max) against the temperature as (1/T).

The results are listed in table (3 – 7) and figure (3 – 9):

$$\text{In}\,\frac{\text{Qe max}}{\text{Ce max}} = \frac{-\Delta\,\text{H}}{\text{RT}} + \text{constant} \qquad (3\text{-}4)$$

Table (3 – 7) values of 1/T and In Qe max for the compounds used in the study.

T		Ph		DNPh		NPh		APh	
T(K)	T-1 (K^{-1} 10^{-3})	Qe max	In Qe max	Qe max	In Qe max	Qe max	In Qe max	Qe max	In Qe max
288	3.472	8.102	2.092	1.856	$3.472*10^{-3}$	5.052	1.620	6.511	1.873
298	3.355	20.271	3.009	2.072	$3.356*10^{-3}$	11.326	2.427	5.925	1.762
308	3.247	20.345	3.013	2.327	$3.247*10^{-3}$	13.106	2.573	5.234	1.655
318	3.124	40.816	3.709	2.381	$3.145*10^{-3}$	20.392	3.015	4.928	1.595

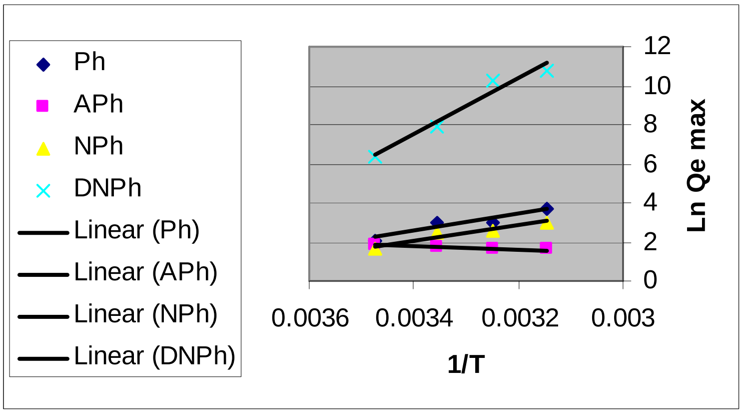


Figure (3 – 9) shows values of In Qe max against 1/T for adsorption of compound ph, DNPh, APh, NPh on the adsorbent surface.

All these data have been treated by using the least square method and ΔG was calculated. The Gibbs free energy ΔG for adsorption is associated with equilibrium constant K_{eq} according to the following equation:

$$\Delta G= -RT \ln K_{eq} \qquad (3\text{-}5)$$

Since

$$\frac{Ce}{Qe} = K_{eq} \qquad (3\text{-}6)$$

So eqnilibriu m because :

$$\Delta G = - RT \ In \frac{Qe}{Ce} \qquad (3 - 7)$$

Knowing that Qe should be in mg/kg, ΔS have been calculated Via Gibbs relation ship.

$$\Delta G = \Delta H - T\Delta S$$

Table (3 – 8) illustrates the value of thermodynamic function of compounds (ph, DNPh, NPh, APh) on the surface of the polymer.

Compound	Δ H J /mol	Δ G J /mol	Δ S J /mol.K
Ph	37109.273	- 123.88.286	166.099
DNPh	14026.134	- 15578.516	99.344
NPh	33186.22	- 14347.125	159.508
A Ph	7196.51	- 13161.37	68.315

Table (3 – 8) illustrates the thermodynamic function value for adsorption of compound (Ph, DNPh, NPh, APh) on the surface of polymer.

From table (3 – 8), the ΔH values show that the adsorption of APh compound is endothermic process in little degree of temperature, while its noticed from isothermal adsorption for this compound at (15,25,35 and 45) temperature, that decreasing in adsorption with decreasing of temperature, the adsorption in this case must be exothermic (ΔH negative value).

Therefore, it can be explained from the positive ΔS which increasing of disorder of molecules arrangement on adsorbent surface, and in spite of the evolved heat as a result of hydrogen bonding and electrostatic attraction between the compound and adsorbent surface. But it doesn't enough to overcome the entropy (or disorder) produced at adsorption, while its noticed that the moderate value for negative (ΔG) which make the adsorption process more acceptable from the thermodynamic point of view.

Also in DNPh compound the adsorption process is endothermic (positive ΔH) and this agreement with its isothermal adsorption in the range of (15,25,35 and 45) temperature – Although ΔH doesn’t high because of the presence of two forces, first electrostatic force and the second is hydrogen bonding. Here the competition is occurred between the two forces, and the electrostatic force tend to weak the bonding between the compound and the polymer where as the hydrogen bonding tend to enhance the bonding and the traces heating produced is from the overcome of repulsive electrostatic on the hydrogen bonding with increasing the temperatures. The ΔS of APh is high, and as we remembered previously that the DNPh compound in is two possibilities which mean the increasing the possibility of bonding of the compound and the polymer (increase ΔS bond), when ΔG is higher it was in APh, that's the adsorption process is more spontaneous than NPh(35).

In compound NPh and ph its found that adsorption is endothermic process. The increasing of adsorption by increasing temperatures enhance that result. Also, the ΔS for adsorption of these two compounds is more than that for APh and DNPh compounds. When, we return to adsorption isotherms, we found inflection in the arrangements of these molecules from the S mode to L mode which means that there are multi possibilities vertical and horizontal for ph and NPh arrangements on polymer surface.

In the same method from ΔG values for adsorption of these two compounds it is noticed that it is spontaneous and preferable thermodynamically(81).

3.3.4 Ionic strength

The effect of ionic strength on the adsorption process for compound (ph, DNPh, NPh, APh) on the surface of the polymer, was investigated in three different ionic strength (0.0, 0.1and 0.2) M NaCl at the following conditions, 25C°, PH = 7, and less than 300Mm diameter granules of (0.01) gm of adsorbent, with adsorbate of initial concentrations (70 – 95ph, 30 – 55 NPh, 20 – 45 APh and 5 – 10 DNPh)ppm.

However, the results are shown in figures (3 – 10………. 3 – 13)

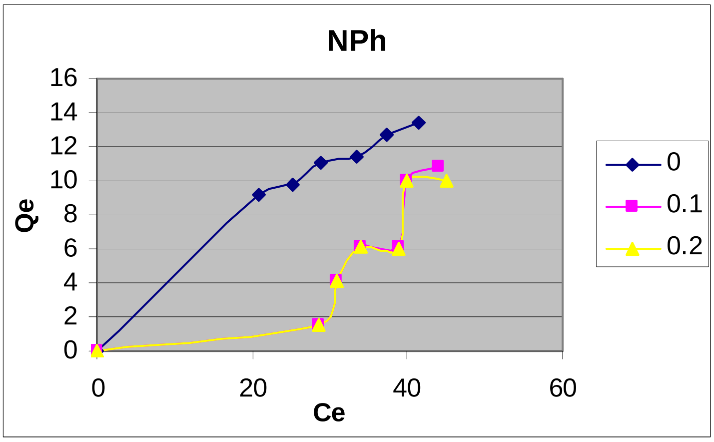


Figure (3 – 10) shows the effect of ionic strength on the adsorption isotherm of compound (NPh).

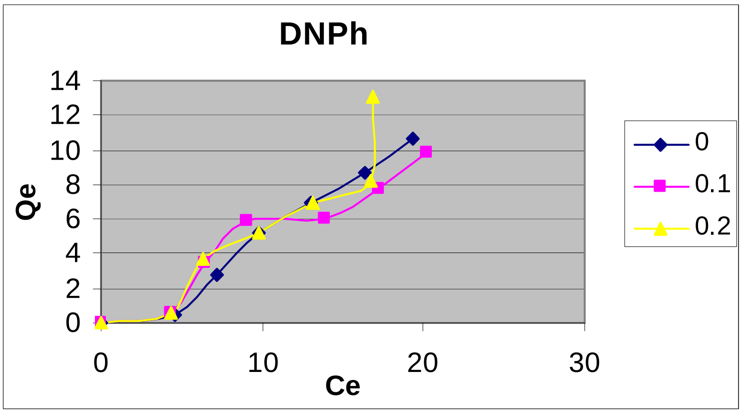


Figure (3 – 11) shows the effect of ionic strength on the adsorption isotherm of compound (DNPh).

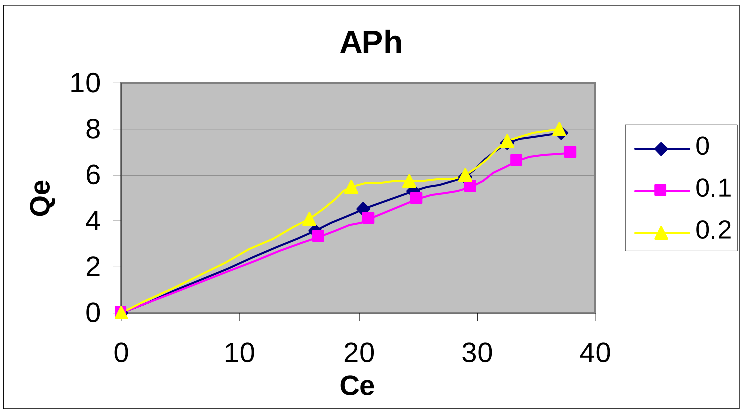


Figure (3 – 12) shows the effect of ionic strength on the adsorption isotherm of compound (APh).

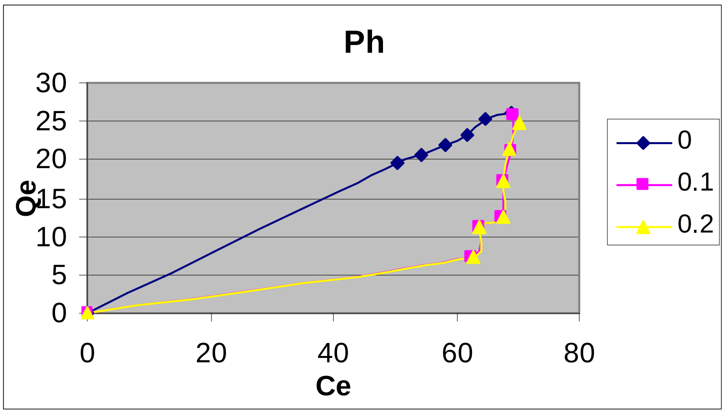


Figure (3 – 13) shows the effect of ionic strength on the adsorption isotherm of compound (Ph).

Figure (3 – 11) and (3 – 12) about compounds NPh and DNPh, its noticed that effects of ionic strength on the adsorption of this compounds on polymer surface are weak and unstable. But it follows the general type. In case of increasing of ionic strength for solution the electrostatic double layer will appear with contract (or opposite) charge for polymer surface and will reduce the appeared the negative charge, and finally reduce the repulsion occurring between the polymer surface and compound and the adsorption will increase.

While in case of compound APh, the increasing of solution ionic strength increase the interference of the solvent and solute (increasing the solubility) according to Deby – Hükel low(48,49) and also reducing the adsorption quantity according to this low (43,50) ,and then decreasing the adsorption process, when the ionic strength reaches to (0.2)M it will make salting(50), and finally reducing the solubility of the compound and increasing of its adsorption. That shown in figure (3 – 13).

Figure (3 – 14) show the increasing of ionic strength in ph compound will increase the solubility of ph according to Deby – Hükel Low and here we notice decreasing of adsorption by increasing of ionic strength as the result.

3.3.5 Effect of PH

The effect of PH on the adsorption process for compounds (Ph, DNPh, NPh, APh) on surface of polymer, three different PH (6,7and 8) at the following conditions, 25C° with less than 300µm diameter granules of adsorbent of (0.01)gm, with adsorbate of initial concentrations (70 – 95 Ph, 30 – 55 NPh, 20 – 45 APh, and 5 – 30 DNPh) ppm.

The results are shown in figures (3 – 15 …….. 3 – 18).

However, the results of each compound is discussed as follow.

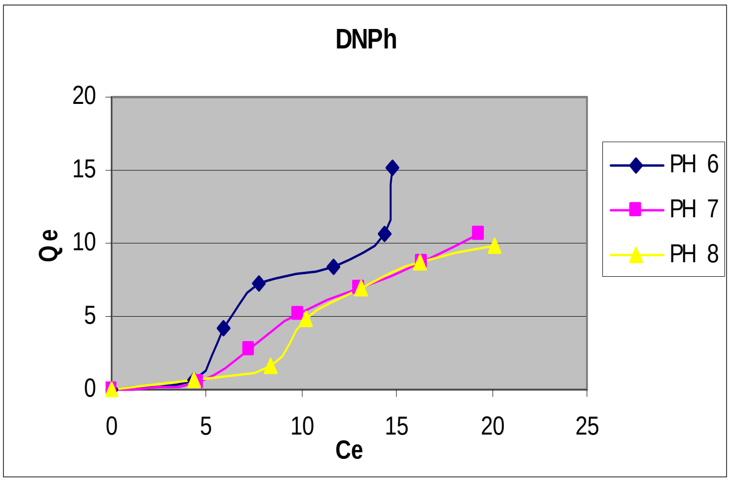


Figure (3–14) shows the effect of pH on the adsorption of compound(DNPh).

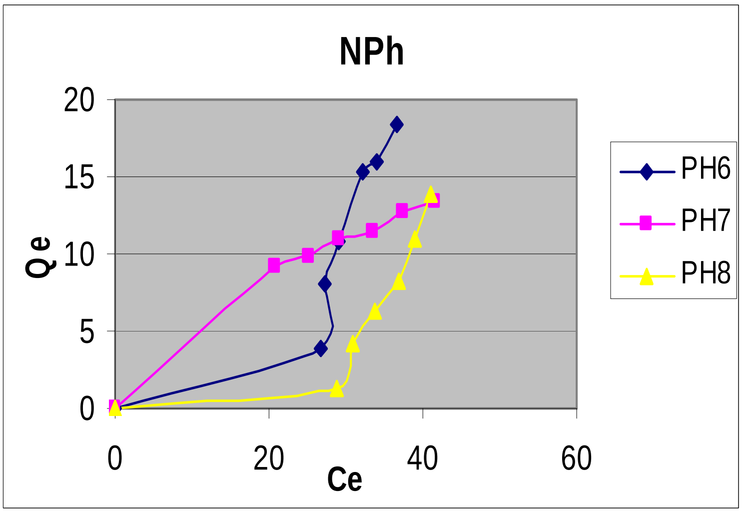


Figure (3–15) shows the effect of PH on the adsorption of compound(NPh).

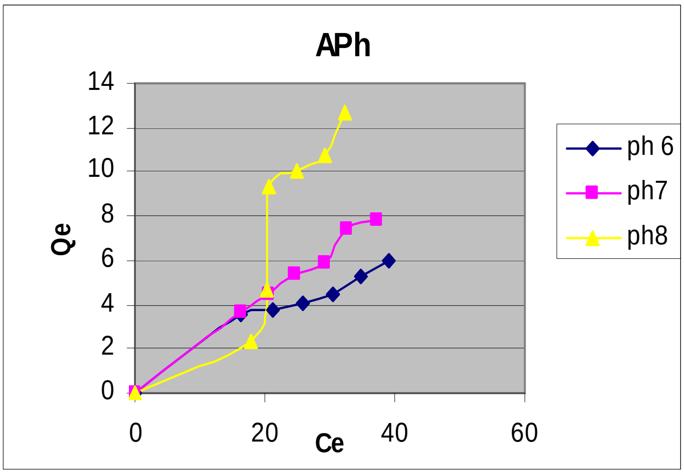


Figure (3–16) shows the effect of PH on the adsorption of compound (APh).

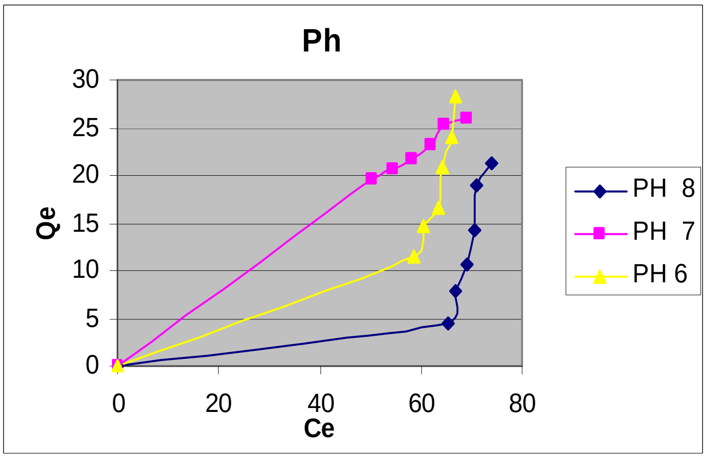


Figure (3–17) shows the effect of PH on the adsorption of compound (Ph).

The compound of DNPh which belongs to S adsorption mode, we have noticed decreasing in adsorption value with increasing of PH solution. The increasing of PH value solution will increase the stability of negative charge of 2, 4 – Di nitro phenoxide anion, also stability of DNPh and increasing of repulsive force between adsorbent surface and DNPh from the other hand, in general these two effects may reduce the adsorption. That shown in figure (3 – 15).

Also, figure (3 – 16), explain the NPh compound the adsorption decrease with increasing PH solution for the same reasons, with notice that NPh in low concentrations and PH = 6, the adsorption values will be lower than that in PH = 7 at the same concentration may due to strong bonding with the solvent (aqueous) in low concentration at PH = 6, the bonding of NPh in dissolved phase larger than its bonding with adsorption surface in adsorpance phase.

In APh compound, the adsorption of APh at PH=8 is the largest then at PH=7 and finally at PH=6

PH8 > PH7 > PH6

The reason behind that due to the presence of amino group which neutralize the acidic effect of (OH) group in APh compound at PH=6, the amino group will be in equilibrium state with aprotic from (Ammonium NH_3^+), therefore the solubility will increase in PH=6, and the adsorption of this compound in its lower values, than it will increase with in creasing of PH due to decreasing ionization of amino group and finally, decreasing of solubility of this compound with notice, it must be careful from continuance of increasing of PH which may increase the ionization of hydroxyl group and finally increasing of solubility in high range of PH, higher than 8 and decreasing of adsorption. That shown in figure (3 – 17).

In compound Ph, the largest adsorption at PH=7 and then PH=6 and the last at PH=8.

PH7 > PH6 > PH8

That we have see deviation of acidity solution from natural may make interference of Ph molecules with solvent (water) molecules more than its interferences with polymer surface. These results can be explained on the bases of decreasing of ionization of Ph compound, and this will increase its adsorption as comparable between its adsorption at PH=7, and PH=6, also the decreasing of hydrogen bonding between ph compound and water molecules make more adsorption (as comparable between adsorption of this compound at PH=6 and PH=8). This explained shown in figure (3 – 18).

3.4 Comparison phenols adsorption on prepared polymer surface with Zeolite and Charcoal.

Since most of the studies available are the adsorption on zeolite 5A and charcoal. This adsorbent was studied extensively, in order to evaluate and validate some of the result on the polymer (Acrylamide – Bisacrylamide) copolymer.

Comparison of the adsorption processes for the compounds (Ph, DNPh, NPh, APh) on the surface adsorbent of (polymer, zeolite and charcoal) at 25C° and PH=7with adsorbate of initial concentrations (70 – 75ph, 30 – 55 NPh, 20 – 45 APh, and 5 – 30 DNPh) ppm. The result shown in figures (3 -19 ……. 3-22).

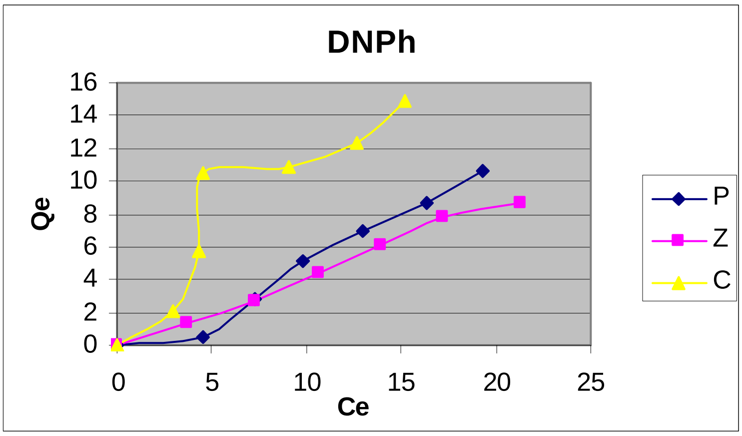


Figure (3-18) shows the adsorption isotherms on polymer, Zeolite and charcoal for compound (DNPh) at 25C˚.

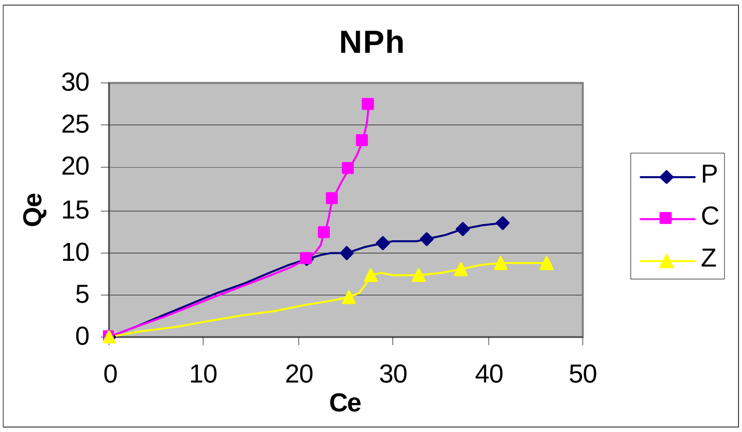


Figure (3-19) shows the adsorption isotherms on polymer, Zeolite and charcoal for compound (NPh) at 25C˚.

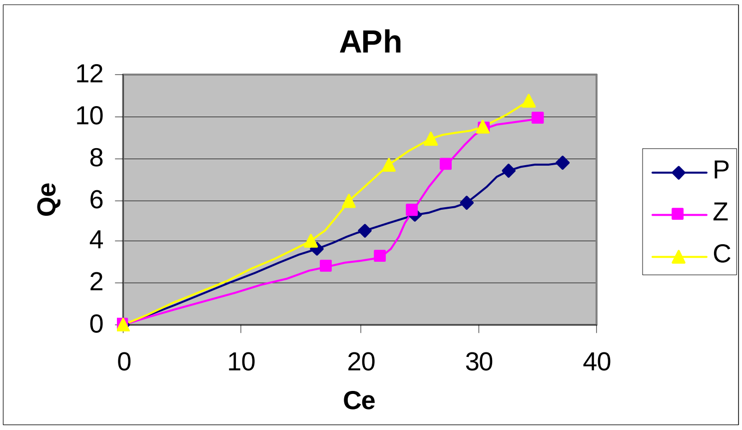


Figure (3-20) shows the adsorption isotherms on polymer ,Zeolite and charcoal for compound (APh) at 25C˚.

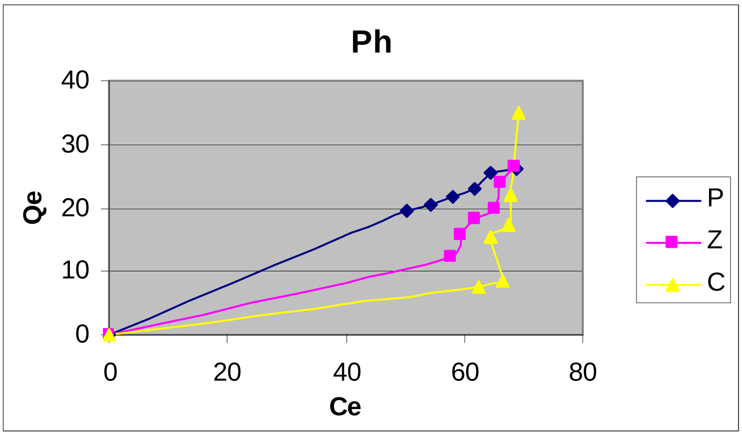


Figure (3-21) shows the adsorption isotherms on polymer, Zeolite and charcoal for compound (Ph) at 25C˚.

Figure (3 – 18) showed that the DNPh compound follows the order in adsorption:-

C > P > Z

And this explain the bonding force of DNPh with carbon surface through the complexation, and the formation of adsorption line similarity to saturation curve which explained this of Langmuir type in spite of its S adsorption mode.

That the initial concavity for adsorption curve for this compounds on carbon surface it take the S adsorption mode because of porosity of carbon surface.

But in continuous of adsorption. The adsorption will reach to the saturation state because of the correspondence of the DNPh molecules on the cyclic carbon surface that have electronic atmosphere through the charge transfer complexation.

But at the adsorption of the same compound on zeolite surface the amount of its adsorption is the lowest one because of the general skeletal for crystal lattice zeolite charged with negative charge and in general the adsorbent would be very low on its surface.

The compound NPh take the following order of adsorption :-

$$C > P > Z$$

And the same explanation on the DNPh that have the same cases and that shown in figure (3 – 20).

The compound APh follows the following order:-

$$Z > C > P$$

The negative charge on the zeolite increased the adsorption of this compound through electrostatic attraction.

The porosity and large surface area of carbon surface make it more active than the prepared polymer in adsopance of APh in its aqueous solution besides it must be considering that surface carbon doesn’t neutral absolutely because of the free electron, make the carbon surface to electronic active which prefer the adsorpance of APh compound on carbon surface in its aqueous solution(82). That shown in figure (3 – 21).

Also ,the compound Ph follows the following order in it adsorption;

$$P > C > Z$$

Also , For the same reasons remembered previously . that is large negative charge for Zeolite skeletal and π electron on carbon , these factors decrease the bonding between Ph and these surface comparable with it is bonded and the polymer surface which has the largest adsorption with phenols.

Conclusions

1. Polymer swellings were in different of PH and in Nacl in 0.1 misgreater of 0.2 M.
2. a temperature of 25C˚:-
   a – The adsorption mode was L for ph, NPh, APh, while it was S for DNPh.
   b- The adsorption quantities following the order
   APh > DNPh > NPh > Ph
3. the adsorption of all compounds was endothermic
4. there was individual variation for the adsorption of each compound in relation to its ionic strength
5. The adsorption of compounds (ph, DNPh, NPh, APh), were comparison in studies that is adsorption on the other adsorption standardization surface such zeolite and porous carbon, that found only the ph adsorption on the surface polymer that a greater the zeolite and carbon, but on the other adsorption compounds in different of adsorption ability on this adsorption surfaces.

Suggestion for future work

1. Copolymer (Acrylamide - Bisacrylamide)is for future work to be used as absorbate
2. Future work could be designed to study.
    - a- Adsorption of other organic or inorganic on the surface of this polymer to fine is ability to be used in the sanitation and purification processes.
    - b- Adsorption of a mixture of the four compound on thesis polymer
    - c- Adsorption of each of the compounds in non aqueous solution
    - d- Adsorption of each of the four compounds on other adsorb ate than Zeolite 5A and charcoal for comparison and validity
    - e- Study the specific conductivity of phenolic compound solution before and after adsorption.
3. generally it was noticed that adsorption quantities is proportionally correlated with the PH studies
4. The adsorption for all compound was endothermic
5. The adsorption of compounds (ph, DNPh, NPh, APh), were comparison in studies that is adsorption on the other adsorption standardization surface such Zeolite and porous carbon, that found only the ph adsorption on the surface polymer that a greater than the Zeolite and carbon, but on the other adsorption compounds in different of adsorption ability on this adsorption surfaces.

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List of abbreviations

Symbols and abbreviations

ΔG	Change of Gibbs free energy
ΔH	Change in enthalpy
T	Temperature
ΔS	Change in entropy
X_1	Mole fractions of solvent
$X^s{}_1$	Mole fraction for solvent in the adsorption surface
X_2	Mole fraction of solute
$X^s{}_2$	Mole fraction for solute in the adsorption surface
b,a	Langmuir constant
Ce	Concentration of solvent in the solution at equilibrium
θ	Covered part from surface
Kf ,n	Freundlich constant
ASTM	American standard for testing material
$C_\circ$	Initial concentration of solvent in solution
m	Weight of adsorbate
r	Correlation coefficient
R	Gas constant
X_m	Highly adsorbate
BET	Brunaner – Emmett – Teller
t	Time
ph	Phenol
DNPh	2,4 – Dinitro phenol
NPh	3 – nitro phenol
APh	3 – amino phenol
Z	Zeolite
P	Polymer (acrylamide Bisacrylamide)
C	Charcoal
min	Minute
M	Molar
L.O.I	Lost on ignition
TMED	N,N,N,N-Tetra Methyl Ethylene Di-amine
Ps	Poly styrene
PMMA	Poly methyl methacrylate

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Republic Of Iraq
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Department Of Chemistry

Study Of Adsorption Process For Some Phenolic Compounds On The Surface Of (Acrylamide -Bisacrylamide) Co Polymer.

A Thesis
Submitted to the College of Science
of Al-Nahrain University
In Partial Fulfillment of the Requirements
for the degree of Master of Science
in Chemistry

By

Alaa Joeid Hamad

B.Sc. in Chemistry (Al-Nahrain University, 2004)

July 2007 ***Rajab 1428***

بِسم الله الرَحمن الرَحيمِ

الله نُورُ السَّمَوَاتِ وَالأَرْ◌َضِ مَثَلُ نُورِهِ كَمِشْكَاةٍ
فِيهَا مَصْبَاحٌ المِصبَاحُ فِي زُجاجَةٍ الزُّجاجَةُ
كَأَنَّهَا كَوكَبٌ دُرِّيٌ يُوقَدُ مِن شَجَرَةٍ مُّبارَكَةٍ
زَيتوُنَةٍ لا شَرْقِيَّةٍ وَلا غَربِيّةٍ يَكَادُ زَيتُها يُضِئ
وَلَوْ لَمْ تَمسَسْهُ نَارٌ نُّورٌ عَلَى نُورٍ يَهدِي اللهُ
لِنورِهِ مَن يَشَاءُ وَيَضْرِبُ اللهُ الأَمْثَالَ لِلنَّاسِ
وَاللهُ بِكُّلِ شَيءٍ عَلِيمٌ
صَدَق اللهُ العَظِيمْ

سُورة النُور الآية (35)

Supervision Certification

I certify that this thesis was prepared by the graduate student Alla Joeid Hamad under our supervision in Al-Nahrain University, college of science as partial requirements for the degree of **Master of Science in chemistry.**

Signature:
Name: Assist. Prof. Dr. Emaad Taha Bakir Al-Takrity
Date: / / 2007

In view of the available recommendation, it forwards this thesis for debate by the examining committee.

Signature:
Name: Assist. Prof. Dr. Salman A.Ahmed

Head of chemistry Department
College of Science
Al- Nahrain University
Date: / / 2007

Committee certification

W e, the examining committee, certify that we have read this thesis and have examined the student Alaa Joeid Hamad in its content, , and that in our opinion it is adequate as a thesis for the degree of **Master of Science in chemistry.**

Chairman

Signature:

Name:

Date: **/ / 2007**

Member	**Member**
Signature:	Signature:
Name:	Name:
Date: **/ / 2007**	Date: **/ / 2007**

Member (supervisor)

Signature:

Name: **Assist. Prof. Dr. Emaad Taha Bakir Al-Takrity**

Date: / **/ 2007**

Approved for the council of the College of Science.

Signature:

Name: Assist.Prof.Dr. LAITH ABDUL AZIZ AL-ANI

Dean of the College of Science

Date: / / 2007

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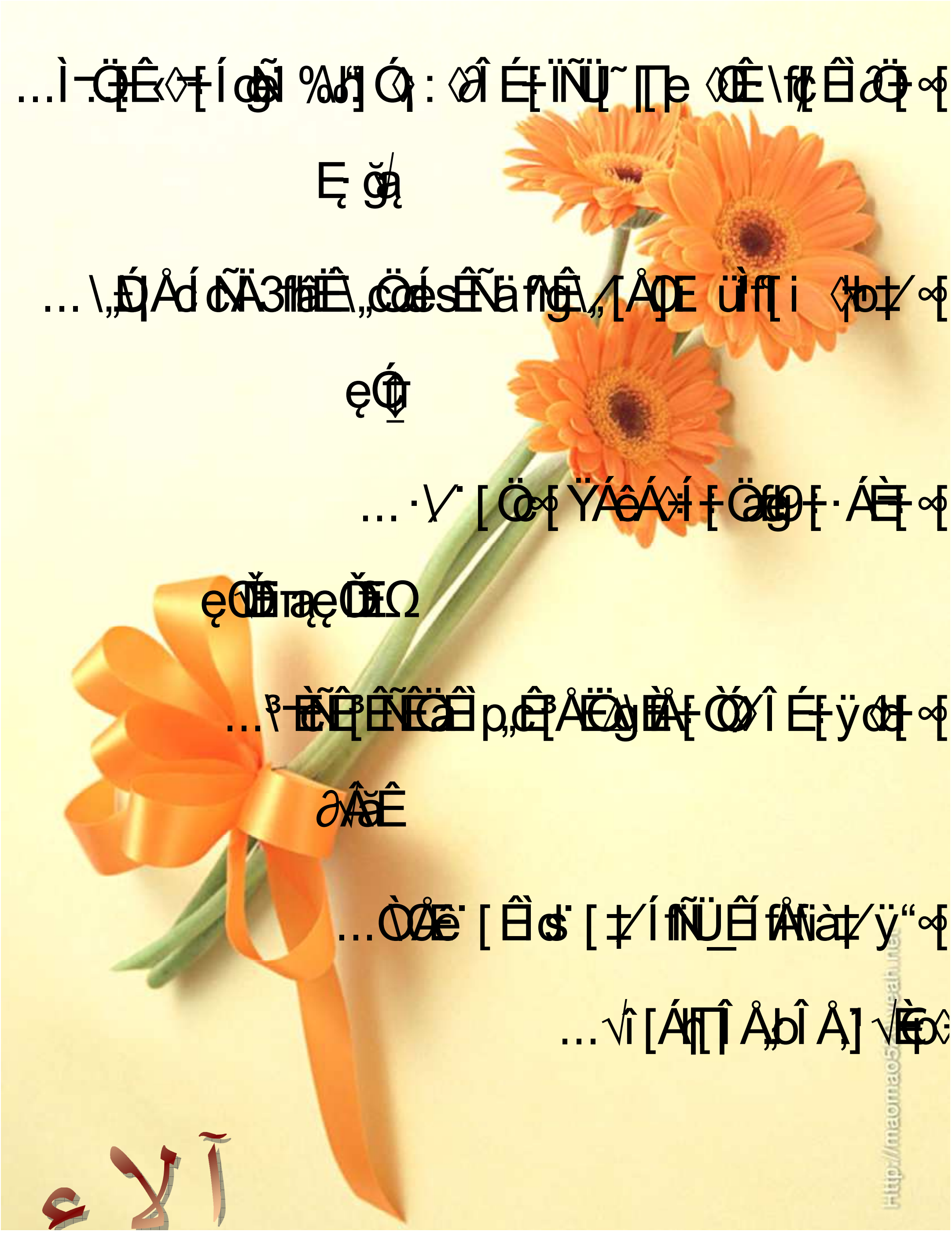

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Alaa

Summary

Copolymer(Acrylamide–Bisacrylamide),was prepared, and identified by F.T.I.R. Spectroscopy then swelling tests were performed for this polymer in different solvents.

The adsorption processes of some phenolic compounds: ph, DNPh, APh and NPh in aqueous solution on the surface of this polymer were investigated by the use of UV – visible spectrophotometer and also studied at different: PH, temperatures, and ionic strength.

Results revealed that the adsorption for compounds at temperature of $25C^{\circ}$ took: L – mode for ph, APh and NPh while it was S – mode for DNPh according to Giles classification.

1. at temperature of $25C^{\circ}$ the adsorbate arranged in the following order:-
   APh > DNPh > NPh > ph.
2. No deferent pattern was noticed with regard to the adsorption quantities according to the ionic strengths.
3. Generally it was noticed that adsorption quantities is proportionally correlated with the PH studies .
4. The adsorption for all compounds was endothermic .
5. comparison the adsorption of compounds (Ph, DNPh , NPh , APh) on other standardization adsorption surface such , Zeolite and porous carbon , showed that only Ph adsorption on polymer surface was greater than on Zeolite and Carbon, while other compounds showed different adsorption ability on this adsorption surfaces .

☎ÀÛńö√✆

تم في هذه الدراسه تحضير الكوبوليمر (Acrylamide- Bisacrylamide) وشخص البوليمر المحضر بواسطه FTIR كما تم قياس تأثير الانتفاخ لهذا البوليمر في عدد من المذيبات.

كما اجريت عملية امتزاز بأستخدام مطيافه الاشعة المرئية (فوق البنفسجية) كل من المركبات(Ph, DNPh, NPh, APh) في المحاليل المائيه لها وفي درجات حرارة (15و25و35و45)مْ وفي اوساط حامضية (PH =6) وقاعدية (PH =8) واوضحت نتائج تلك الدراسات ان الشكل العام لامتزاز تلك المركبات على سطح البوليمر بدرجة (25)م يأخذ النمط (L) µ (APh, NPh, ph) ويأخذ النمط (S) µ(DNPh) حسب تصنيف Giles

١ -ان ترتيب المادة الممتزة يأخذ الترتيب التالي بدرجة (25)مْ

APh >DNPh>NPh>ph

٢ -يكون امتزاز تلك المركبات ذو طبيعه ماصة للحرارة.

٣ -ان تأثير الشدة الايونية كان متفاوتاً من ناحية امتزاز تلك المركبات.

٤ -وبصورة عامة يقل الامتزاز بزيادة PH لهذه المركبات.

٥ -قورن امتزاز المركبات المذكورة في الدراسة بأمتزازها على سطوح ممتزة والتي هي الكاربون المسامي والزيولايت حيث وجد انه في حالة ال Ph فقط يكون امتزازه على سطح البوليمر المحضر اكبر من امتزازه من على سطحي الكاربون والزيولايت ، اما بالنسبة لمواد الممتزة الاخرى فتختلف في قابلية امتزازها على هذه السطوح الممتزة.

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قسم الكيمياء

دراسة امتزاز بعض المركبات الفينولية
على سطح الكوبوليمر
(اكريل امايد- بس اكريل امايد)

رسالة مقدمة
الى
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علوم في الكيمياء

من قبل
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