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Ministry of Higher Education
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College of Science
Department of Chemistry

REMOVABLE STUDY OF SOME PHENOLS AND ACIDS COMPOUNDS FROM AQUEOUS SOLUTIONS BY (TRIETHANOLAMINE-GLYCERYLMALEATE) POLYMER SURFACE

A Thesis

Submitted to the College of Science Al-Nahrain University in partial fulfillment of the requirements for the Degree of Master of Science in Chemistry

By

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بسم الله الرحمن الرحيم

ن والقلم وما يسطرون ﴿١﴾

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الاهــــــداء

اليك يا منبع الحياة وخير الدنيا وصفاتها، الى من كان دعائها

سر نجاحي وكان رضاها سر سعادتي الى ..... **(أمي)**

الى من اهداني عمره وشبابه وعلمني أصغر معاني الحياة

وجعل روحه كمنهل يستسقى من ظمأ الايام الى ..... **(أبي)**

والى فخري وسندي وعوني في هذه الحياة ومن فضلهم علي

لا يقل عن فضل أمي وأبي الى ..... **(اخوتي واخواتي)**

الى التي كان لها فضل المؤازرة في عملي ..... **(زوجتي الغالية)**

..... اليكم جميعاً اهدي جهدي المتواضع هذا .....

محمـد

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Mohammad

Summary

Triethanolamine-glycerylmaleate polymer was prepared, and identified by FTIR spectroscopy then swelling tests were performed for this polymer in different solvents.

The adsorption processes of the some phenols and acids compounds: **ph, na, nal, B, AB** and **DAB** in aqueous solutions on the surface of this polymer were investigated by the use of UV-visible spectrophotometer and also studied at different: temperatures, ionic strength, and pH.

The results revealed that the adsorption for compound at temperature of 25 °C took: **S**-mode for all compounds according to Giles classification.

1- At temperature of 25 C the adsorbate amount arrange to the following order:

ph < nal < na < B < AB < DAB

2- The adsorption for ph, na, nal, and B take the following order for ionic strength

0.1M NaCl > 0.0M NaCl >0.2M NaCl

But for AB, and DAB take

0.0M NaCl > 0.1M NaCl >0.2M NaCl

3- Generally it was noticed that adsorption quantities is proportionally correlated with the pH studies.

4- The ΔH values for all adsorbate compounds were negative, while ΔS values were negative for all compounds except for ph and B.

5- In comparison with zeolite (5A) the prepared polymer posse's higher ability to adsorb than zeolite especially for AB and DAB compounds.

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Symbols and Abbreviations

ΔG	Gibbs free energy Change
ΔH	Enthalpy Change
ΔS	Entropy Change
x_1	Mole fractions of solvent
x_1^s	Mole fraction for solvent on the adsorbent
x_2	Mole fraction of solute
x_2^s	Mole fraction for solute on the adsorbent
b , a	Langmuir constant
C_e	Concentration of solute in the solution at equilibrium
Q_e	Adsorbate Concentration of solute on the solid phase at equilibrium
θ	Surface coverage
K_f , n	Frindlich constant
ASTM	American Standard For Testing Material
C_o	Initial Solute concentration in solution
m	Weight of adsorbent
r	Correlation coefficient
X_m	maximum adsorption
BET	Brunauer- Emmett- Teller
ph	phenol
na	ß-naphthol
nal	2,7-di naphthalidol
B	benzoic acid
AB	para amino benzoic acid
DAB	2,5-diamino benzoic acid
N	Avogadro's number
S	Surface area
L.O.I.	Lost On Ignition

Chapter One

Introduction

Chapter one

1. Introduction

1.1 Review for water pollution

Pollution is one of the most important problems that facing the global, in which it becomes in a great level of dangerous due to the increase in its size and geographical aspect that pay the international and world wide attention.

The pollutants are materials affect the environmental elements "water, air, and soil" and change their natural constructions causing danger to the creative life directly or indirectly. with the developing of the industrial technology and technical aspects for the new world, the water pollution has becomes a great world wide problem that always incriminate all the governmental and populations and costs a lot of money [1,2].

The matter becomes more complicated with the variations of the pollutants and their sources according to the bad uses of industries, agricultural and water closet beside of the usage of large amount of chemical compounds as pesticides, fertilizers and cleaners in all kinds.

More over nuclear explosions under lands or in the deep seas have large effect on the aquatic ecosystems and environmental pollution. It is known that the toxic chemicals exposed during its cyclic in the environment to number of changes resolving and change in phase, e.g. photolysis, biodegradation, these changes always gives a more toxic chemical compounds (than the original once), so there is an increase in effects in the environment system.

The aromatic phenols are an example of the toxic compounds that find in the petroleum components, or in the pesticides or in the chemical materials used in the industrial process [3-5].

1.2 Types of water pollution

The water pollution can be classified according to the properties of the pollutants materials and their effects on. In general, water pollution can be classified in to four types [6]:

1- **Physical pollution**: consists of color, density, heat, solid particles, foam, and radioactive activity.
2- **Physiological pollution**: consists of mixing of the pollutants with the water which affects the human body parts.
3- **Biological pollution**: this the most important type of pollution because it effects directly the human health and it consist of bacteria, germs, viruses, warms and other ting structure.
4- **chemical pollution** :one of the most dangerous types of pollution because of its direct toxic effect on the living organisms or indirect effect due to the accumulative of these pollutant in the body of the living object.

The organic chemical pollutants of the water consist of a large amount of the components that wasted from industrial or service resources, e.g aldehydes, ketones and phenols which are considered as a toxic component that have cancer effectiveness[7].

The subject of the current research deals with pollution of water by the chemical materials, so we will present its sources and the methods of preventive from it.

1.3 Water pollution sources:

Water pollution (WP) is defined as: addition of any foreign materials to the water environment, in which these materials are chemical or biological, which reduce water quality making the water unsuitable for drinking purposes, leading to damage the human health, living sources and the environmental system [8].

Rivers: are the most important water resources so any addition of pollutants to it will change the rivers environment and affect the aquatic ecosystems. These changes are either physical change e.g. increases in river water temperature; increase the turbidity, changes on the oxygen level or biological changes like. Increase in the growth of the undesired living objects (alga) or in some times chemical changes resulting from the addition of chemical material to the water. The degree of effectiveness for this pollutant is always depending on the type and quantity of these pollutant and the properties of the receiving water [9].

However, the source can be classified in to the following:

1.3.1 Water closet (heavy water)

It consists of the waste water that produced from the different service activities human waste output (stool) cleaners, oils, and dissolved salt. These pollutants are very dangerous materials and should be treating before it goes directly to the rivers or water sources [10].

1.3.2 Agricultural waste water

It consists of the water and rains that takes the extra needing chemical (fertilizers), that are used in a large amount or the pesticides used in the preventive of the (vegetations) that passes towards the neighbor water sources [11].

1.3.3 Industrial waste water

It consists of the water resulted from the different industrial activities e.g. the chemical materials resulted from the petroleum industries ,refineries ,paint and drug industries and the biological pollutants ,bacteria ,viruses that are related to the food industries the meat packing industries the diary products industries[12].

1.4 Waste water treatment methods:

The output of the water closet and the industrial waste, are the main sources of the water pollution, so it is necessary to submit it to the treatment, in order to minimize or put the lower level from the chemical and biological pollutant before they goes to the water resources.

There for, it is very important to pass the polluted water through processing treatments, which start with, first “Primary Treatment” ,that consist of using mechanical methods to pick up the suspended solids, and floating bodies.

While second “Secondary Treatment” consist of using biological methods to pick up the residual organic materials through the biodegradation and finally stage the “Tertiary Treatment” which is vary developing process stage to pick up the resolved organic pollutants in the water [10]. The most important methods used here are:

1.4.1 oxidation:

The chemical oxidation by, using strong oxidation agent e.g. ozone [13] hydrogen peroxide[14]and the photo oxidation[15] is used to treat the polluted water with different chemical materials despite some of these methods are economically undesirable but in general they are used to remove the water pollutants [16].

1.4.2 Ion exchange:

The ion exchange system are used to remove the ions of the heavy materials and the organic materials from the polluted water this method have been used efficiently to remove some ions of heavy elements, phosphorus, NH_3 and some other organic materials [17]. The industrial resins are also used as ion exchanges as well as some natural compounds such as zeolite [18].

1.4.3 reverse osmosis:

It is physical method based on the fact says when two different concentrated solutions are separated with a semi penetrated membranes, water penetrate through the membranes from the low concentration towards the highly concentrated [19].

The reverse osmosis used as an advance technology for water purification from the pollutants where the ionizing exchange processes are happened before it, so as to get a high quality water[20], all above represent the advantageous of this method .

The disadvantageous of this method is the highly costs, because of need to change membrane, so many researchers and industries are preferring now other methods.

1.5 Adsorption

Generally adsorption could be defined as a phenomenon of a material aggregation as ions or molecules or atoms on a surface of another material [21].

Naturally the physical states of the matter which contain limit surfaces 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 surface which adsorbed material called "Adsorbent" and the material which adsorbed called "Adsorbate ". The adsorption process in solution, include attach surface between liquid phase and solid phase.

The reason for adsorption phenomenon is the existence of some unsaturated forces on the adsorbent due to the incomplete coordination or insufficient material-surface particles, like the liquid or solid phase adsorption which leads to saturate those forces on surface as well. This may cause a decrement in energy (free energy) of the surface. Hence, the adsorption is spontaneous process, with decreasing the degrees of freedom for the adsorbate; this could be thermodynamically expressed by:

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

The enthalpy of this process will take a negative value; and generally, the most of adsorption processes will be exothermic.

The adsorption could be divided into, physisorption, and chemisorption.

The major differences between them are in the field of interaction forces between the adsorbate particle and the adsorbent surface and in the energy evolved from both processes. The energy evolved in chemisorptions is greater than that in physisorption.

In addition, the chemisorptions are a uni-molecular adsorption, it occurs on single layer, while physisorption often occurs on multi-layer adsorption.

The adsorption is either be localized (the particle has no ability to move) or mobile (the particle has the ability to move) which is called "mobile adsorption". [23]

The reverse process of adsorption is called "desorption", which usually occurs at elevated temperatures enough to break the binding energy between the adsorbent and adsorbate [24].

On the other hand, the penetration process of a particle in the phase of adsorbent called "absorption", and the process of absorption and adsorption processes together called "sorption" [25]. This process usually takes place on the porous surfaces of adsorbents. The enthalpy of this process is positive (endothermic process), because the distribution inside the adsorbate needs energy [26].The interaction process of adsorbent and adsorbate without distribution is termed "interaction".

1.6 adsorption Isotherms:

Adsorption isotherm is the relationship between the quantity or amount of adsorbate on the surface and their activity in the distribution phase at equilibrium in constant temperature [27].

Giles [28] 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 an S-shape, in which the direction of the adsorbate on the surface is vertical and the solvent may undergo severe or hard adsorption on the surface of adsorbent. The class **L** is special for Langmuir isotherm, in which the direction of adsorbates is horizontal and in a single layer.

Class **H** special for high affinity adsorption, which takes place in very dilute solutions, and in adsorption of large molecules like polymers. Finally, class **C** indicates that there is a constant partition between the adsorbent, and the adsorbate in the solution, and indicates that there is a high probability to chemisorptions.

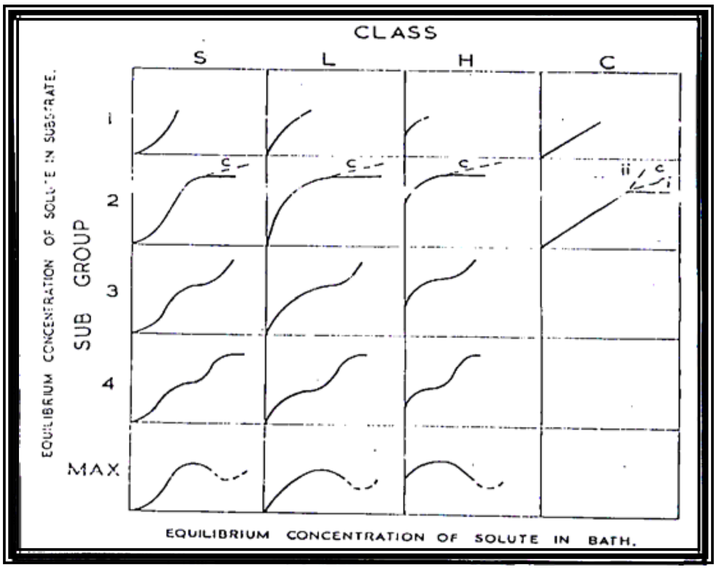


Figure (1-1) Giles classification for adsorption [28]

Brunauer –Emmett-Teller [29], have classified adsorption isotherms according to five categories as illustrated in figure (2-1):-

Class I: is for adsorption of type **L** according to Giles classification, while **class II:** is as expected from **BET** approximation in multi-layer adsorption, which normally happens in adsorption of gases.

Class III: takes place when interaction between first layer and adsorbent is much weaker than interaction between first layer and adsorbate, while **Class IV** is similar to **Class I**, but there are two limits for adsorbate instead of one limit and **Class V** was suggested as a common class of **classes I and II.** Classes **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.

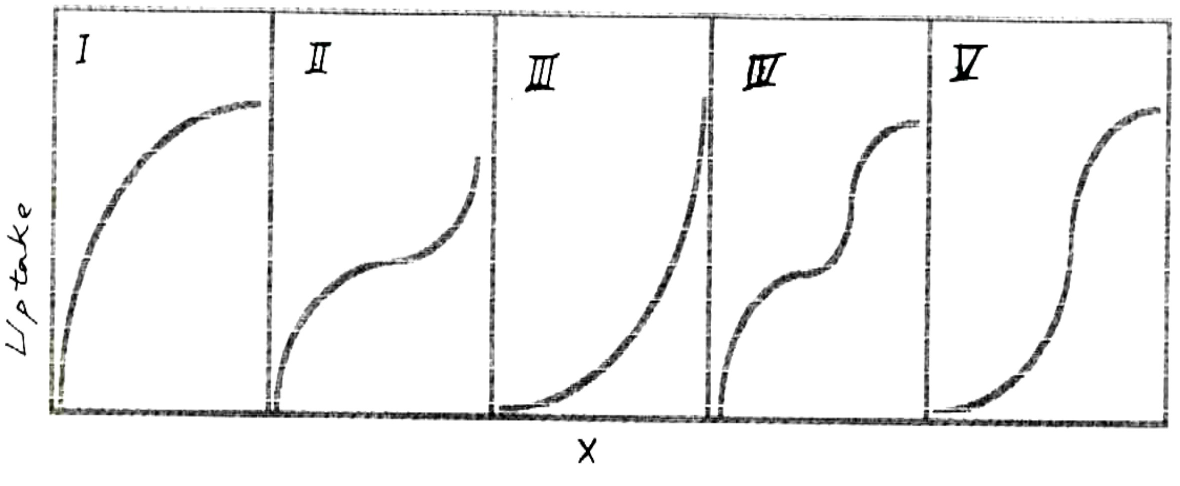


Figure (1-2) Brunauer classification for adsorption [30]

1.6.1 Langmuir equation for adsorption in Liquid

Langmuir equation 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 [31].

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 homogeneous surface, since the area of any site of adsorption is constant and the distribution of energy is regular.

2- The adsorption is localized, occurs between adsorbate and active site. The adsorbate particle has no ability to move (mobile), and the active site 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 active sites on the adsorbent are covered by the particles of adsorbate.

Therefore, Langmuir equation could be derived as follows:

$$\left(\begin{array}{ccccccc} A & + & B & \rightleftharpoons & A & + & B \\ \text{Solute} & & \text{solvent} & & \text{Solute} & & \text{solvent} \\ \text{In solution} & & \text{in adsorption Layer} & & \text{in adsorption layer} & & \text{in solution} \\ \mathbf{X_2} & & \mathbf{X_1^s} & & \mathbf{X_2^s} & & \mathbf{X_1} \end{array} \right)$$

{Equation 1.1}

Where X_1، X_2 are the mole fraction for the solvent and solute respectively in solution and X_1^s، X_2^s are the mole fraction for the adsorbed solvent and solute, respectively in the solid surface at equilibrium.

$$K = \frac{x_1 x_2^s}{x_2 x_1^s} = \frac{a_1 x_2^s}{a_2 x_1^s} \quad \text{……………………..} \ \mathbf{(1\text{-}2)}$$

Where a_1, a_2 are the activity for solvent and solute respectively assuming that the solvent activity still constant because of the smallest lose from it by adsorption and gained by desorption so $b = \frac{K}{a_1}$ then the equation be comes:

$$b = \frac{x_2^s}{a_2 x_1^s} \quad \text{……………} \ \mathbf{(1\text{-}3)}$$

At equilibrium the activity of the solute a_2 to the equilibrium concentration for the solute **Ce** and the summation of mole fraction for the solute and the solvent in the adsorption equal to one so:

$a_2 = Ce$ **………….(1-4)**

$X_1^s + X_2^s = 1$ **………(1-5)**

$$x_2^s = \frac{bc_e}{1 + bc_e} \quad \text{………...} \ \mathbf{(1\text{-}6)}$$

By considering that n_2^s is number of moles of adsorption positions which occupied by the solute particles and n^s is the total number of the adsorption positions

$$\theta = \frac{n_2^s}{n^s} = x_2^s = \frac{bc_e}{1+bc_e} \text{ .... } \mathbf{(1\text{-}7)}$$

Where θ is the part of the surface which occupied by adsorbate. The quantity of the adsorbate for each gram of the adsorption material is directly proportional with θ .

$$Q_e = K'\theta \text{ .... } \mathbf{(1\text{-}8)}$$

$$Q_e = \frac{K' bc_e}{1+bc_e} = \frac{ac_e}{1+bc_e} \text{ .... } \mathbf{(1\text{-}9)}$$

The quantity of adsorbate Q_e at equilibrium for each 1 gram of the adsorption material, (a, b) is Langmuir constants.

The linear formula for this equation:

$$\frac{C_e}{Q_e} = \frac{1}{a} + \frac{b}{a} C_e \text{ .... } \mathbf{(1\text{-}10)}$$

Plotting $\mathbf{C_e/Q_e}$ versus $\mathbf{C_e}$ we will have a straight line its slope = $\frac{b}{a}$ and the intercept at $\frac{1}{a}$.

1.6.2 Freundlich equation for adsorption

In heterogeneous surfaces, the adsorption process in solution is much more responds to Freundlich equation comparing to Langmuir equation.

Freundlich equation is an empirical equation has the following formula:

$$Q_e = K_f C_e^{1/n} \quad \ldots\ldots\ldots \ \mathbf{(1\text{-}9)}$$

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

The most significant defect of this equation is the disability for describe the maximum value of adsorption, and its constants have no simple physical meaning [32].

The natural logarithm of the equation is in linear formula:

$$\ln Q_e = \ln K_f + \frac{1}{n} \ln C_e \ \ldots\ldots\ldots \ \mathbf{(1\text{-}10)}$$

Plotting lnQe against lnCe give a linear straight line with slope equals1/n, and the intercept equals ln k_f [33]

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

1.7 Factors Influencing adsorption process

1.7.1 Nature of adsorbent

The properties of adsorbent that affect on quantity of adsorption include the polarity and porosity of surface. The polar surfaces tend to adsorb the more polar components in solution [34]. While porous surface affects on the quantity as well as selectivity [35, 36].

The homogenous of the surface makes the adsorption isotherms match with theoretical interpretation proposed for adsorption in contrast to the non-homogenous surface. [37] Where the adsorption capacity for a variety of materials increases as the surface area of adsorbent increases too.

1.7.2 Natural of adsorbate:

As mentioned previously, the polarized surfaces of adsorbent tend to adsorb the high quantity of polar component in solution [38]. More over, the adsorption quantity increases as the molecular mass of adsorbate increases, and it decrease, as the solubility increases. [39, 40]

1.7.3 Solvent effect

The 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, solvent and adsorbent surface, and solvent-solute interaction.

Therefore, the resultant of these interactions is greater as the interacting groups are similar in polarity.

This effect is clear throughout Traube's rule [22] which suggests that adsorption quantity of aliphatic carboxylic acids increased in their aqueous solutions as the hydrocarbon chain on the carbon surface increase. It is known that the surface of carbon has a low polarity so, it adsorbs large amount of less polar component from aqueous solution. In addition, the interaction between solute (carboxylic acid) and solvent (water) decreases, as the length of the hydrocarbon chain increases due to the difference in polarity and decreasing the solubility would increase the adsorption too.

In adsorption of the same carboxylic acids on silica gel surface as adsorbent in toluene solvent, the polarity of surface increases, and the solvent polarity decreases, the process is going to be completely in reverse to carbon surface and the adsorption quantity decrease as the length of hydrocarbon chain increases, and decreasing the polarity of carboxylic acid.

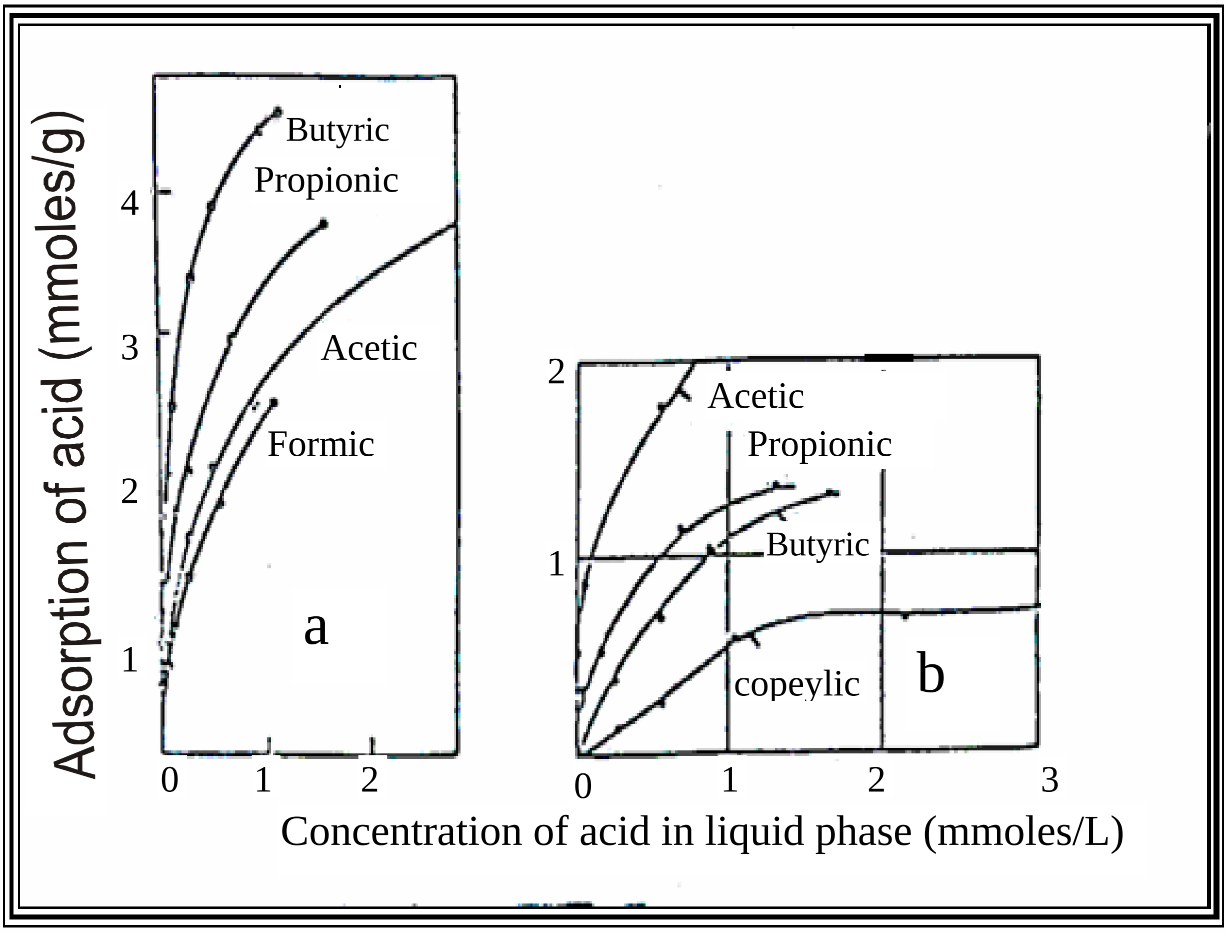


Figure (1-3) a. Adsorption of the carboxylic acid on the carbon surface in the aqueous media, b- Adsorption of carboxylic acid on silica gel surface in toluene[25]

1.7.4 pH effect

The pH of the solution has different influence on the adsorption process with the difference of the adsorption system. The acidic changes that cause to increase the adsorbate solubility in the solution and decrease the adsorption quantity. While the changes that cause to decrease solubility of the adsorbate molecules led to increase the adsorption quantity[41].

In the case of the surfaces contain polarized or charged positions the adsorption amount increase, if the surface acquired different charge from the adsorbate particles, through the acidic effect reversely the adsorbate amount decrease if the surface acquired equivalent adsorbate charge .

1.7.5 Temperature effect

It is known that adsorption process is exothermic [23] unless there is companying an absorption or distribution process inside the porous solid phase [42, 43]. Hence the temperature increment will lead to decrease in the adsorption quantity. In the molecular prospective increasing temperature leads to increasing the kinetic energy for adsorbing molecules on the adsorbent surface, which may increase the probability of molecules desorbed [44].

The adsorption process that accompanying an absorption or distribution inside the pores, would be endothermic process, subsequently the kinetic energy for molecules may induce their ability to penetrate inside the solid phase pores and increase the distribution. Therefore, sorption quantity increases as the temperature increases [26].

1.7.6 Ionic strength effect

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

For adsorbate, if it is an ionic form, so increasing ionic strength leads to increase the 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 increases its adsorption [45, 46].

Whereas, the non-ionic adsorbent, the ionic strength may lead to the occurrence of salting-out process, which decreases the solubility and increase the adsorption process [47].

In addition, the formation of a coordinated complex between the adsorbate and number of ions that are available in solution will affect on the adsorption process. This effect depends on the solubility and charge of the formed complex [48].

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

In the case of similar charges between adsorbent surface and adsorbate particles, increasing ionic strength will cover the adsorbent by a layer of opposite charge to the adsorbate, which leads to increase adsorption process [41]. While if the adsorbent surface has opposite charge to the adsorbate particles, then increasing ionic strength will decrease adsorption quantity [49, 22].

1.8 Zeolite

Zeolite is a term used to denote a group of crystallized minerals of wet salts belong to aluminosalicylic acid with metals from the first and second groups of the periodic table. These zeolites are either natural or artificial, though some of the artifices contains in the structure other than those within aluminosalicylic acid like phosphorus, gallium and germanium [50].

Zeolite as a word, is of Greek origin contains two parts, the first means (stone) and the other means (boiling) [51]. Elements of zeolite can lose part or all of the water that it contains without a change in its crystallized structure, it also has the ability to absorbed molecules from another compounds to compensate the losing of water molecules.

However, one of the most important and widely distributed characters of zeolite minerals in practical aspects is the higher ability of ions exchange. This is because of the unique molecular structure of zeolite.

Zeolite structure is a three dimensional net work and the basic units are SiO_4^{-4} and AlO_4^{-5} with the quaternary surfaces (Alumina silicate) these units bound to each other sharing what it contains of oxygen atoms, thus forming strong bonds giving the solid structure for the crystallize of zeolite.

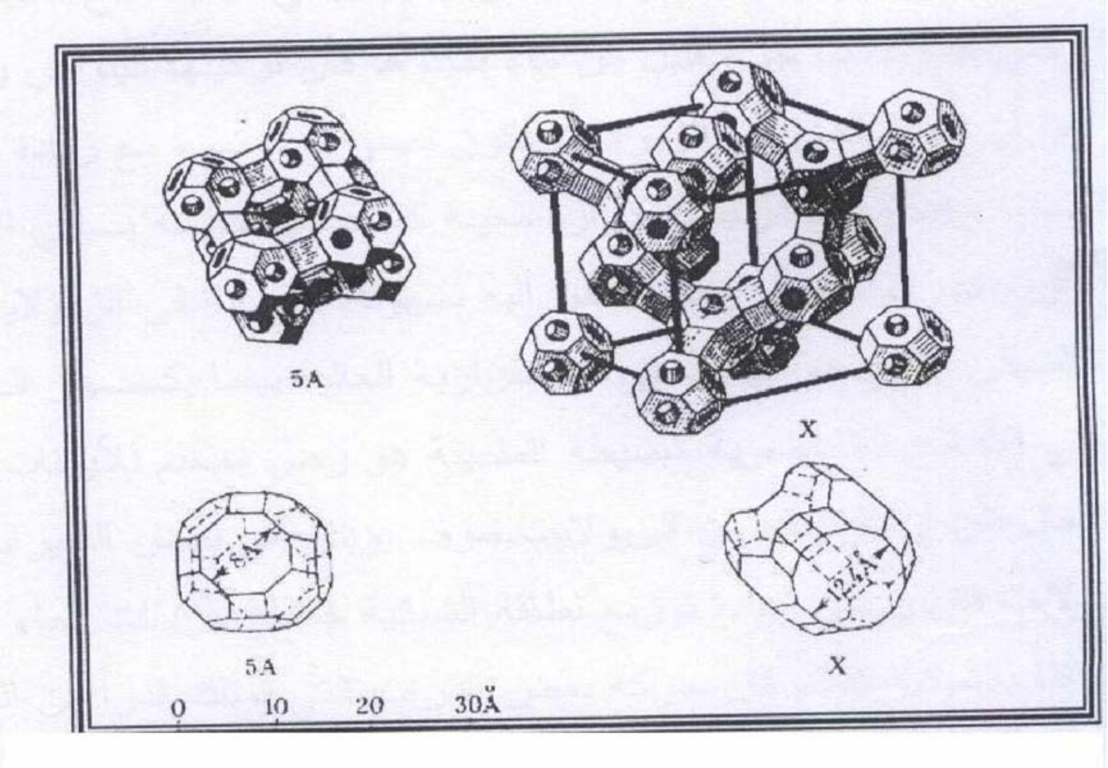


Figure (1-4) The crystallized structure of zeolite (5A) and zeolite X [14].

The molecular formula for zeolite can be shown as [52]:

$$M_{2/n}.\ Al_2O_3.\ \ x\ SiO_2\ .\ y\ H_2O$$

Where n = the metal equivalent.

The structural formula for zeolite can be representing by the structure of its crystallized cell as [50]:

$$M_{x/n}\ [(AlO_2)\ x\ (SiO_2)\ y].\ z\ H_2O$$

There are also other unique characteristics for zeolites with regards to the nature of its surface being acidic, also the similarity equal diameters of its canals. This gives to zeolites the abilities of excitation and higher selectivity.

This is why zeolite presents in the most important non homogenous assisting factor in oil industry [53] and also in miscellaneous industries for drying gases. The previously stated structure of zeolite (5A) gives the crystals of this materials their net shaped skeleton with intervening cannels and vacuoles of three dimension this let zeolite to act as molecular sieves which is a term called by the scientist Mc Bain in 1932 to denote the compounds that possess the characteristics of selective adsorption and absorption to the ions and molecules according to their size and shape [51].

1.9 What are polymers?

It is difficult to visualize civilized life without polymers or polymer products. Polymer has become the most important materials due to it's use in many fields from domestic use up to aerospace shuttles [54].

Polymers are long chain molecules consisting of repeating units called monomers. The composition of the monomer, and the way in which the monomers are linked, determine the properties of the polymer.

Polymers have existed for centuries in the form of oil and resins which called natural polymer. It was only at the end of the nineteenth century that scientists such as Charles Good-year began to manufacture artificial polymers [55] by process known as polymerization.

However, polymer is produced by two main polymerization processes:

– Step-growth polymerization.

– Chain-growth polymerization.

There are four methods for polymerization:

Bulk, solution, suspension, and emulsion polymerization.

1.9.1 The adsorption on polymer

The interrelation between solute and its porous polymer (adsorbent) is called "adsorption", taking as an example the adsorption of dye on cellulose. The validity of the theory of microspores volume filling and the possibility of calculating the adsorption parameters on its basis are substantiated. The controversial matter of analogy of the adsorption process with the volumetric dissolving is discussed.

The phenomenon of adsorption from solutions on the surface of solid adsorbents are a basis of numerous physico-chemical and biochemical processes. For a long time the interest to this phenomenon was determined by the necessity of solving purely applied problems (dyeing, catalysis, sewage purification and so forth). Recently the considerable progress has been observed in the development theory of the adsorption from solutions. However, the solution of many fundamental problems is far from completion. The purpose of this investigation is to find out some quantitative regularities of the solution properties effect on the adsorption of dissolved substances on porous polymer adsorbents [56].

1.10 Adsorption of organic pollutant materials from solution:

The adsorption on polymers at solid-liquid interfaces has been studied extensively in recent years [57, 58].

The technique of (Solid-Liquid Chromatography) (SLC) [59] was used for the determination of the characters of diffusion, adsorption and absorption of small size molecules of amino acids on large crystals of zeolite of the type KX. It was noticed that zeolite was adsorbed quickly but with marked difference in concentration at equilibrium and in diffusion velocity in between crystals. Also it was noticed that the largest amino acid molecule in size is the least concentration at equilibrium.

Adsorption isotherms [60], was identified for some aldehydes compounds on the surface of the zeolite (5A) the results followed Freundlich equation this study showed also the effect of temperature, pH and ionic strength on the process of adsorption.

To be complete study the adsorption of some ketones compounds from aqueous solutions on the surface of Iraqi zeolite 4A and export zeolite 4A[61] and the results showed the adsorption on the surface of both zeolite increased by the increase in acidity of the solution.

The synthesis and the characterization of zeolite –urea formaldehyde polymer complex and the adsorption of some phenolic compounds from aqueous solutions on its surface[62] was studied. By using FTIR spectroscopy and x-ray diffraction pattern .he studied the effect of temperature, pH, and Ionic strength on the adsorption process.

The removal of color from effluent using Silica as fast processes[63] was studied. It was found that removal of basic dye from effluent by adsorption onto Silica gel is mainly controlled by intraparticle diffusion although a small boundary layer resistance was experienced. Also the activation energy for dye removal was determined.

The removal of water-soluble cationic dyes with TriSyl Silicas was[64] studied 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) onto TriSyl Silica by batch adsorption at 25 C. They found that adsoption followed Langmuir type of adsorption.

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, they found that the adsorption capacity was depending on pH , and the rise in the temperature reduces adsorption capacity by Chitin[65] was studied.

The removal of phenols by adsorption on Fly Ash[66] was studied, it was found that the Freundlich isotherm is more suitable for all the systems investigated in the study for the adsorption of phenol and cresol and their mixtures from aqueous solutions on activated carbon and fly ash.

Polymer adsorption at solid surfaces is important in a variety of fields, such as material and food sciences, medical science, and stone conservation..[67].

The adsorption of poly styrene and polymethylmethaacrylate onto silica surfaces by I.R. spectrometer [68] was studied .And the mixture adsorption of poly styrene and polymethylmethaacrylate onto the same surfaces[69, 70] was also studied.

The effect of solvent, temperature and concentration on the adsorption of poly (n-Butyl methacrylate) on alumina from solution by using UV and FTIR photo acoustic spectroscopy techniques [71] was studied. The obtained results are in conformity with Langmuir's isotherm.

The adsorption of some phenols in aqueous solutions by using Styrene-divinylene benzene copolymer as permeable adsorbate[72] was studied. The study included also effect of pH and ionic strength.

The sorption of water soluble organic dyes on magnetic poly(oxy-2,6-Dimethyl-1,4-phenylene)(PODMP) and (dyes belonging to triphenylmethane, hetropolycyclic and azo dye groups)from water solutions[73] was studied . In general it was found that the hetropolycyclic dyes exhibited the lowest sorption.

The photo modification of polymer films [74], was studied azobenzen containing polyurethanes showed for the first time that the principal mechanism of optical recording could be the mass transfer of polymers during the cis-trans isomerization of azo dyes units on the polymers from illuminated areas to non illuminated areas. Beside this transport,some irreversible photochemical reactions involving a tmospheric oxygen are suggested as another possible origin for the holographic recording.

The adsorption of polymers anchored to membranes [75] was studied and it was found that if one includes the finite size of the anchor segment, the membrane bends towards the polymer for sufficiently strong adsorption.

1.11 Aim of the work

The polluted water must be treated before being to reduce recycled to the rivers the harmful for the environment.

Adsorption is an important method to remove the organic pollutants from water, due to its low cost, and no need for equipment and complicated techniques.

The aim of this work is to study the ability of (Triethanolamine-glycerylmaleate) polymer to adsorb some aromatic components, which are known as a toxic component on the living objects. In addition, the study would be extend to investigate the polymer efficiency as an adsorbent substance in different adsorption conditions like temperature, pH value and Ionic strength, comparing with zeolite efficiency.

Chapter Two

Expeirmetal part

Chapter two

2. Experimental part

2.1 Chemicals

The following materials and chemicals used in this work were obtained from different companies with it's purity as listed below:-

Table (2-1) Chemicals purity and molecular weight which inter in this study

Chemicals	% Purity	Molecular weight (g/mole)	Supplied from
Phenol	98 %	94.11280	Hannover
ß–Naphthol	98 %	144.1726	BDH
2,7-dinaphthalidol	97 %	160.1720	BDH
Benzoic acid	99 .9%	122.1230	Merk
Para amino benzoic acid	99.9%	137.1378	Fluka
3,5-Diaminobenzoic acid	99.9%	152.1524	Fluka
Methylene blue	99.9%	374.3983	BDH
Tri-ethanol amine	99 .9%	149.1894	BDH
Glycerol	99 .9%	92.0944	BDH
Maleaic anhydride	99 .9%	98.058	Fluka
Ethanol	99 .9%	46.0688	Fluka
Ether	99 .9%	74.1224	Fluka
De-ionized water	R = 16mΩ	18.0152	Lab.
Sodium chloride	99 .9%	58.4428	Fluka

Where
R = resistance
mΩ = mille ohm (resistance)

Zeolite:

Zeolite was obtained from the Alraia Company and the molecular formula

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

The chemical analysis for zeolite compounds have constituents: - SiO_2 (32.52 wt %), Al_2O_3 (27.64 wt %), CaO (11.38 wt %), Na_2O (4.20 wt %), L.O.I (24.25 wt %) total = (99.99 wt %) .

2.2 Instruments

1- Double – beam UV-Vis spectrophotometer (UV 1650 CP), Shimadzu / (Japan), interfaced with computer via Shimadzu UV – Vis prop data system program.

2- Shimadzu Fourier transforms infrared model FTIR 8300 (Kyoto, Japan) was used to record the IR spectra for the prepared polymers. Infrared spectra- photometer as KBr disc.

3- Sensitive balance type Mettler accurate (0.1 mg).

4- Shacker device with water both and control on it's temprature Dunboff Metabolic Shaking Incubator GCA / Precision Scientific Chicago, (USA).

5- pH-Meter, Hanna, HI 8417, (England).

6- Oven from type Vindon Scientific LTD, Oldham, (England).

7- Centerfuge device Labfuge A, Heraues Sepatech, (West Germany).

Note: - These instruments are supplied at Al-Nahrain University chemistry Department.

2.3 Preparation of poly (Triethanolamineglycerylmaleate)[76]

In a 100 ml round-bottom flask immersed in a sand bath and equiped with a thermometer and magnetic stirrer a mixture of triethanolamine and Glycerol (7.48 g, 0.05 moles) and (4.66g, 0.05 moles) were placed. The mixture is heating with magnetic stirrer for 15 min. and (14.7g, 0.15mole) of maleic anhydride was added to the mixture after the temperature 100 °C and raised gradually to 140 °C, and maintained for 3 hours. Continued heating at this temperature causes increasing in viscosity of the solution until crystalline polymer was formed.

The product was washed with warm water and methanol for several times, and then dried in vacuum oven at 50 °C over night.

2.4 Solubility and stability test for poly (Triethanolamine-glycerylmaleate)

A- The solubility of **poly (Triethanolamine-glycerylmaleate)** polymer has been examined using different types of solvents like water, methanol, ethanol, dioxane, chloroform, carbon tetrachloride, hexane and benzene and found insoluble and stable in all these solvents.

B- The stability of polymer in acidic and alkaline solutions was also examined by treating the polymer with solutions of different pH ranged from 1 to 8 for a period of two weeks, It found that the polymer stable and does not dissolved. However at pH solutions greater than 8 the polymer begins to decompose (dissolve) due to the hydrolysis of ester bond in the structure of polymer.

2.5 Polymer swelling determination

Swelling measurements of the polymers was done according to ASTM procedure by placing a calculated piece of polymer sample in solvents (acetone or hexane or water), in these of using the water at pH ranging (6-8), with 0.1 M of NaCl in aqueous solution, or 0.2 M of NaCl aqueous solution and (zeolite). The weight of polymer was measured each (24) hour until the weight of the swelled polymer became constant. The swelling of polymer was calculated according to equation [80]

$$\Delta m = \frac{m1 - mo}{mo} \quad \text{……..} \ (2\text{-}1)$$

m_0 = weight of dry sample

m1 = weight of swelled sample

Δm = swelling percentage

2.6 Surface area measurement [78]

MB compound was used to calculate the surface area of the polymer, according to the following equation:

$$S = Qe \times N \times A / 1000 \times M.Wt.of\ MB \quad \text{……}(2\text{-}2)$$

$$S = Qe \times N \times 160 \times 10^{-20} / 1000 \times M.Wt.of\ MB$$

S = surface area of the adsorbent m^2/g

Qe = quantity of adsorbate mg/g

N = Avogadro number $mole^{-1}$

A = surface area of methyleneblue molecule = $160 * 10^{-20}\ m^2$

2.7 Preparation of standard solutions:

Prepared stock solution of 1000 ppm from(ph, nal, B, AB, and DAB) compounds by dissolving (1g) of each components in (1L) deionized water.

(1g) of na added to deionized water, and insoluble particles was filtered and measured it weight, then subtracted from the total added weight (1g) of na, measuring ppm equal (164).

The concentration of all components (ph, na, nal, B, AB, and DAB) was prepared in rang (5-30) ppm from stock solution.

2.8 Determination of λ_{max} and Calibration Curves for the Compounds used in the study

To determine the wave length for the maximum absorption, the absorption spectrum have been recorded for each component using UV-Vis instrument conc. of solutions(20 ppm) for the range 200 – 800 nm using quartz cell, with cell thickness equal path length 1cm. The spectrums are shown in figures (2-1 to 2-6)

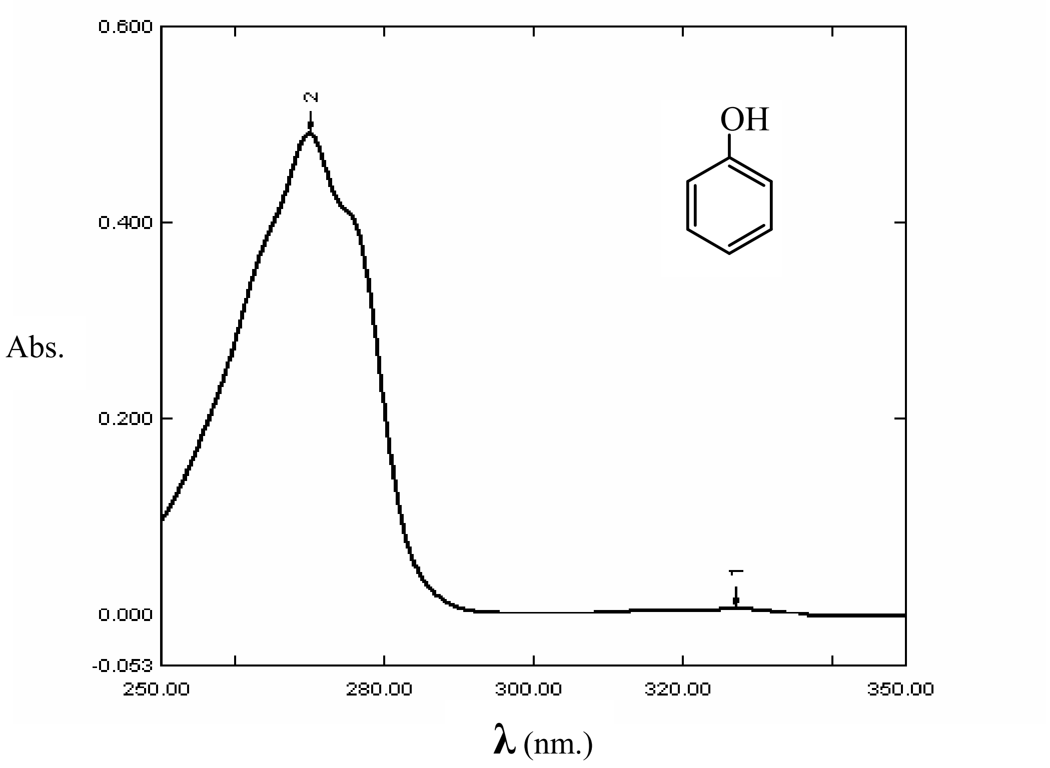


Figure (2-1) UV spectrum of phenol compound

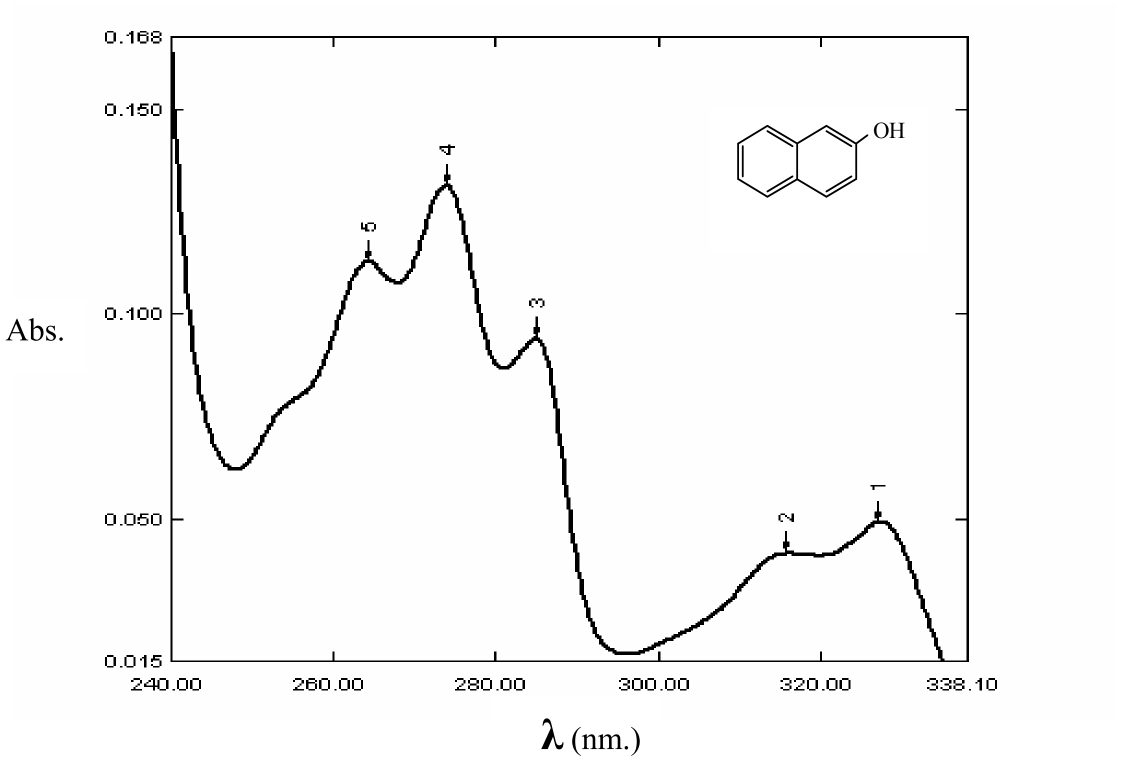


Figure (2-2) UV spectrum of ß-naphthol compound

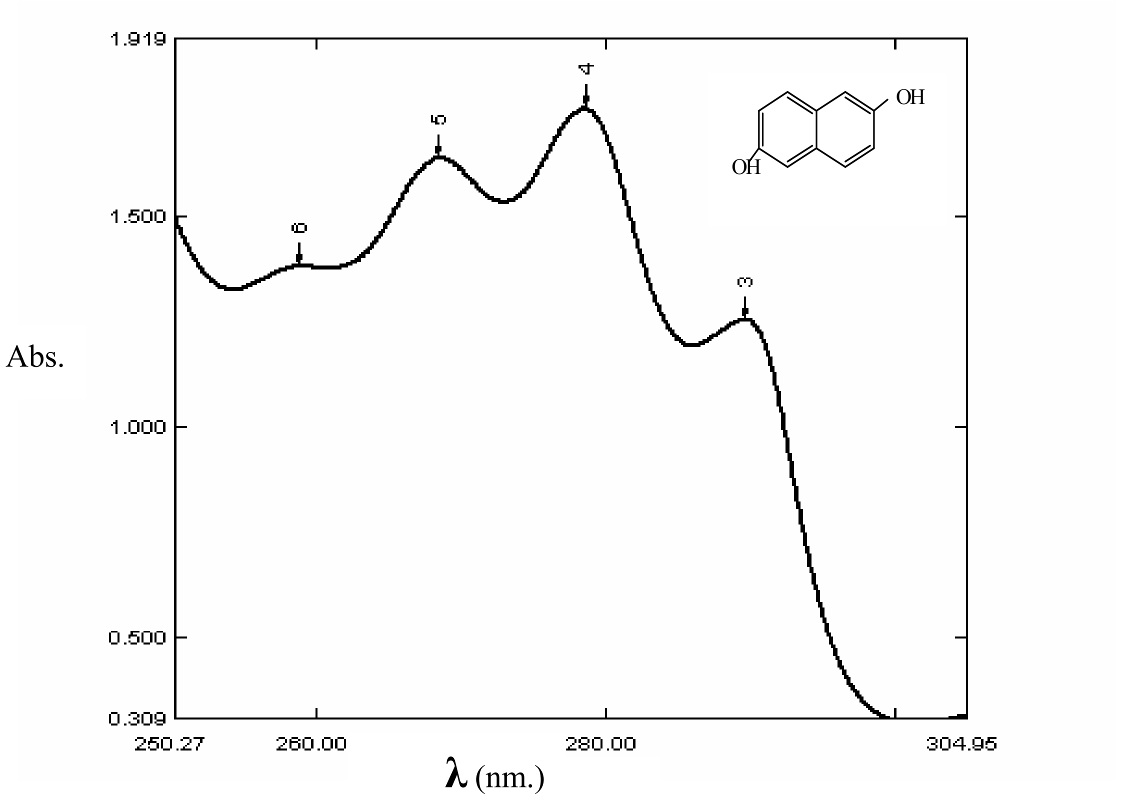


Figure (2-3) UV spectrum of 2,7-di naphthalidol compound

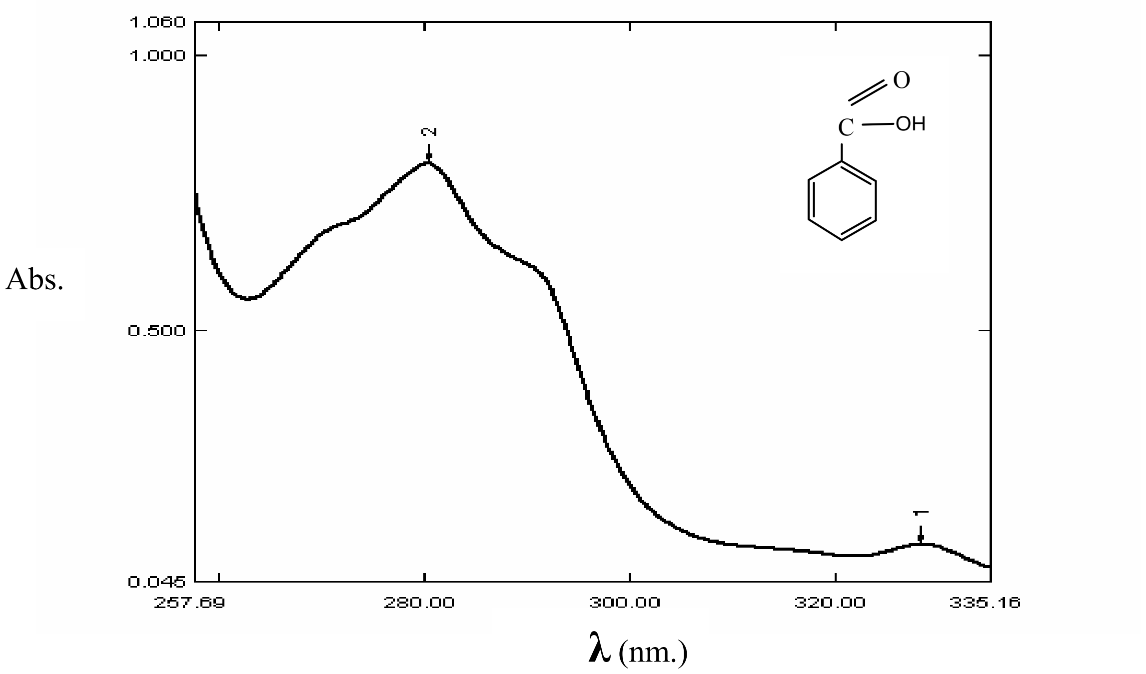


Figure (2-4) UV spectrum of benzoic acid compound

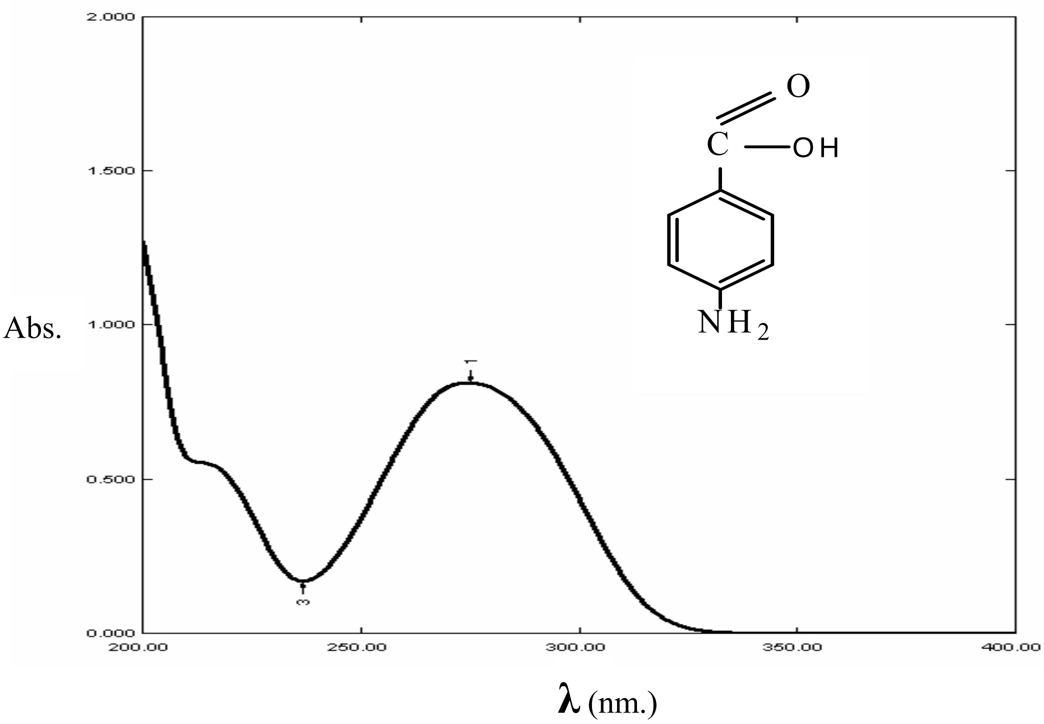


Figure (2-5) UV spectrum of para amino benzoic acid compound

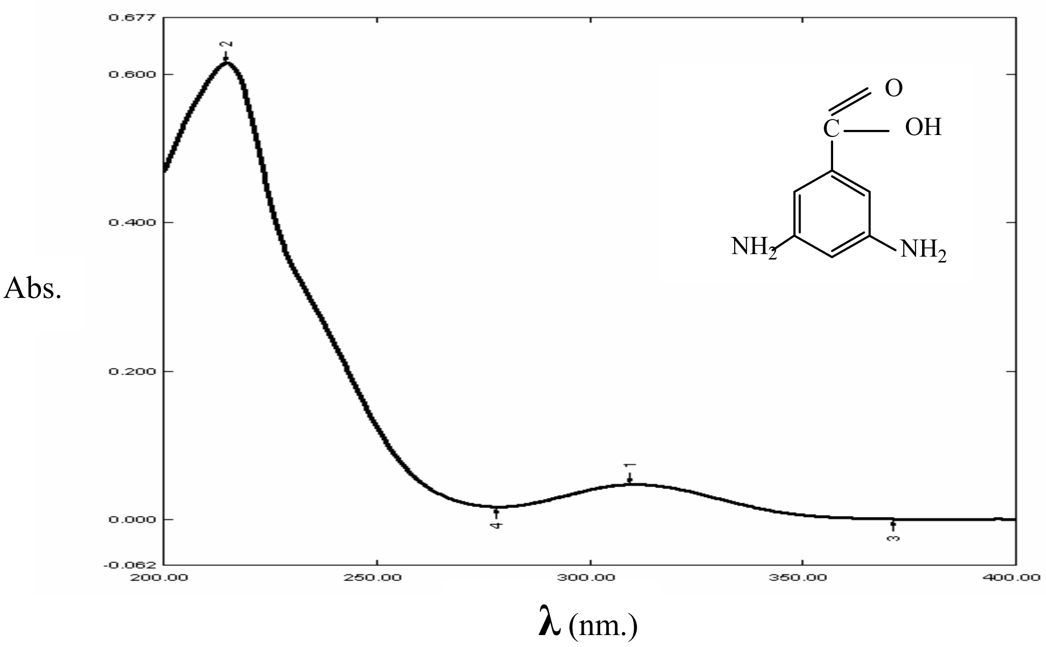


Figure (2-6) UV spectrum of 2,5-diamino benzoic acid compound

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 a calibration curve plotted between absorption and concentration, the best line between points has been drawn using least square method.

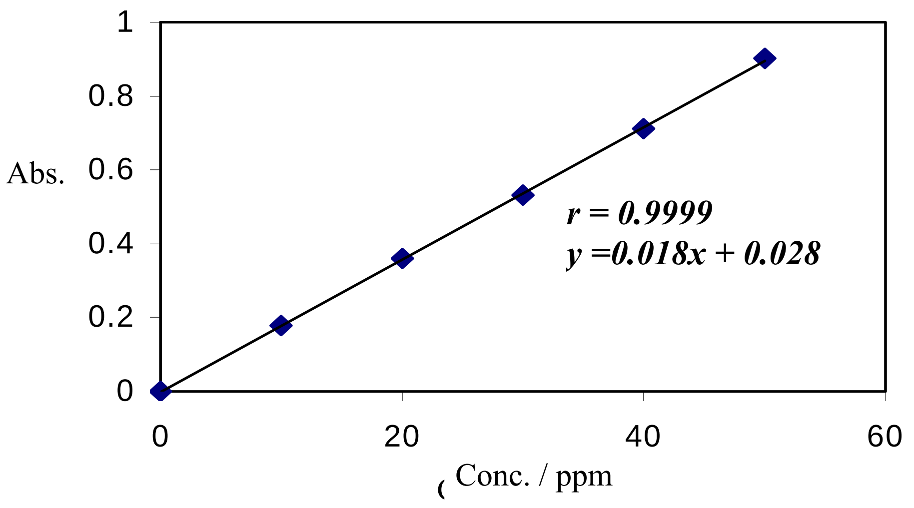


Figure (2-7) calibration curve for ph compound at λ $_{max}$ = 269.8 nm

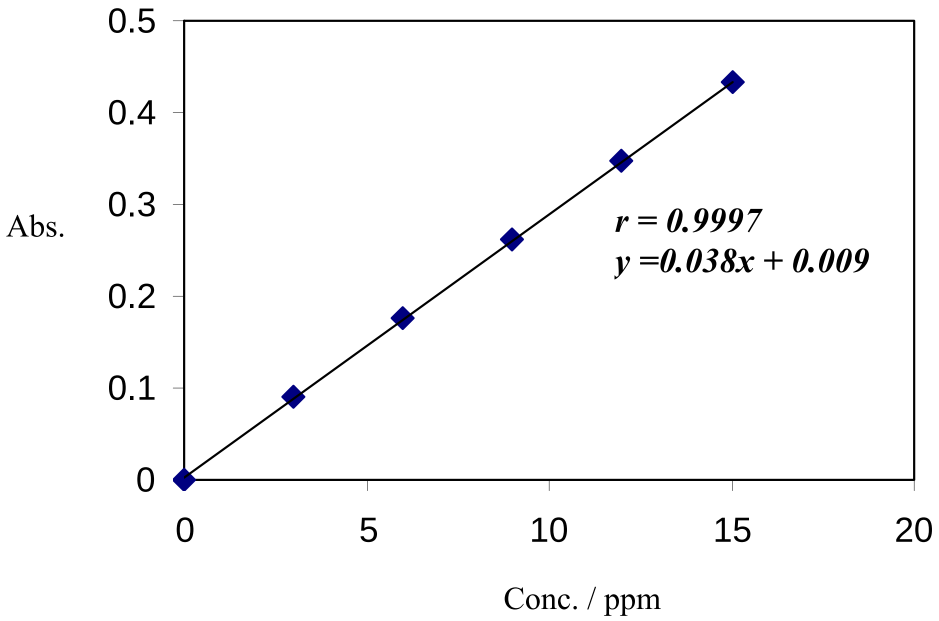


Figure (2-8) calibration curve for na compound at λ $_{max}$ = 273.8 nm

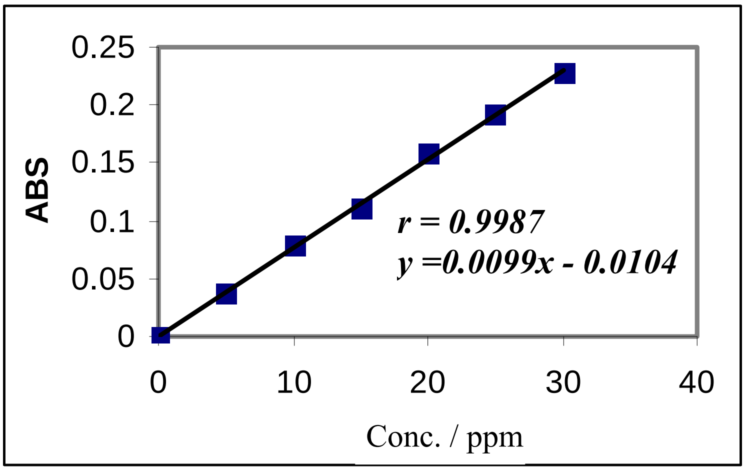


Figure (2-9) calibration curve for nal compound at λ $_{max}$ = 279.0 nm

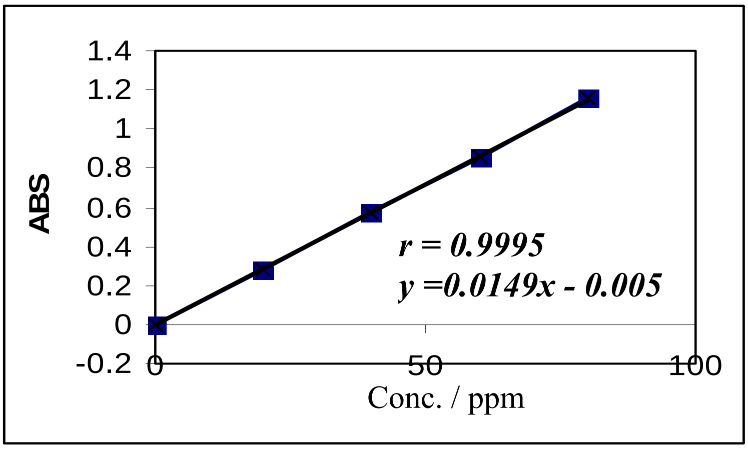


Figure (2-10) calibration curve for B compound at λ $_{max =}$ 283.0 nm

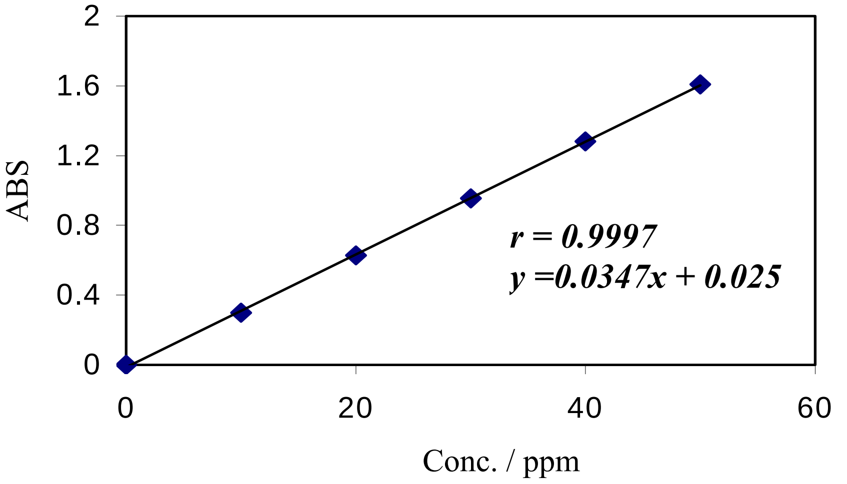


Figure (2-11) calibration curve for AB compound at λ $_{max}$ = 276.0 nm

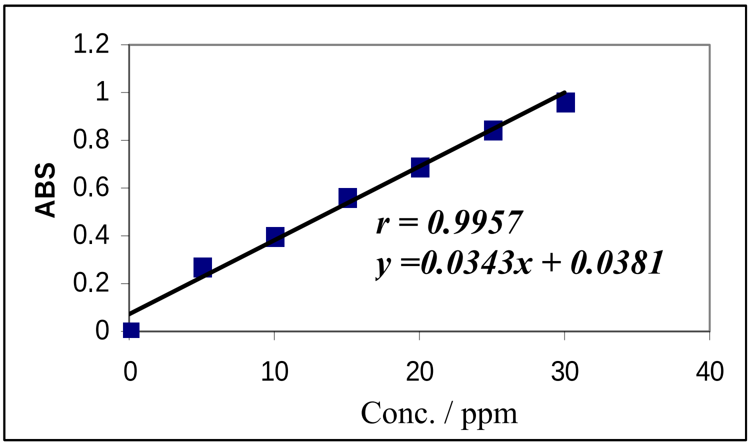


Figure (2-12) calibration curve for DAB compound at $\lambda_{max} =$ 238.0 nm

2.9 Determination of Equilibrium Time

A (0.04g) of polymer (this weight is the best between the weights used) less than 300 µm diameter (granules) has been placed in a 250 ml conical flask. Then 50 mL of adsorbate 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 taken 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.

2.10 Adsorption Isotherms:

In order to determine the adsorption isotherm for each compound, 6 conical flasks has been used, containing (0.04 g) of polymer. Then 50 mL of adsorbate has been added into the flask which has a concentration ranged between (5-30) ppm. After closing, the flasks were shaken in water bath shaker at 25 ˚C 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 each solution, at the convenient wavelength for each compound. The absorbate values obtained have been used to determine the equilibrium concentration for calibration curve.

2.11 Measuring the variable effects during adsorption process

2.11.1 Effect of temperature

The effect of temperature during the adsorption in three different temperatures (25, 35, and 45) ˚c have been studied thus the adsorption isotherm for the each compounds studied in each temperature and the effect of temperature on adsorption has been recorded.

2.11.2 pH effect

To study the pH effect on the adsorption, the adsorption isotherms for the each compound have been studied on the polymer surface in pH values (6, 7, and 8). The value of pH has been justified by pH-meter using dilute solutions from 1M sodium hydroxide and 1M hydrochloric acid.

2.11.3 Ionic strength effect

The ionic strength effect for compounds has been studied in different ionic strength, concentration and an amount of the fixed surface (0.04g).

(5, 10, 15, 20, 25, 30) ppm of adsorbate was used with different ionic strength in the range (0.0-0.2) M by using NaCl as a strong electrolyte. Plotting Qe against Ce gives the ionic strength effects for all adsorbate.

2.12 Adsorption Isotherms on Zeolite:

In order to compare between the adsorption on polymer and on zeolite, the adsorption isotherm of compounds (ph, na, nal, B, AB and DAB) were determined by following the same procedures used to determined the adsorption isotherm on polymer.

Chapter Three

Results and Discussion

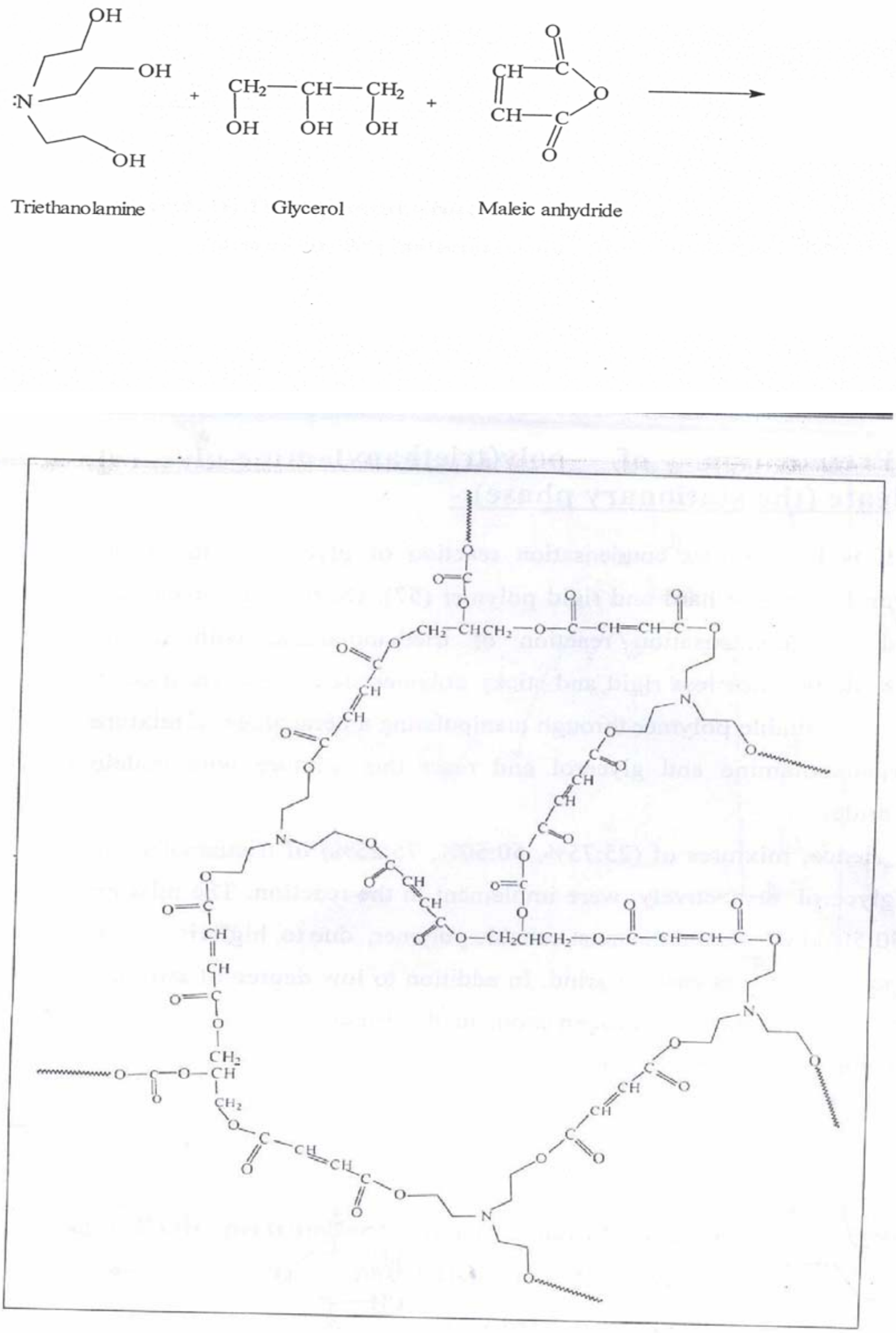
Chapter three

3. Result and Discussion

3.1 Preparation of poly (triethanolamine-glyceryl maleate) as adsorption surface:-

It is known that condensation reaction of glycerol with maleic anhydride produce hard and rigid polymer [77]. On the other hand, it found that condensation reaction of triethanolamine with maleic anhydride produce less rigid and stick polymer. Therefore, we tried to prepare a suitable polymer through manipulating a percentage of mixture with maleic anhydride.

Hence, mixtures of (0.05 mole) triethanolamine and (0.05 mole) glycerol, respectively, with (0.15 mole) maleic anhydride were implementing in the reaction. The mixture was found most suitable polymer, due to high rigidity of the polymer, and good adsorbent surface. In addition, it has low degree of swelling and a high number of nitrogen atom in the backbone of polymer, as shown in follow reaction scheme:-



The suggested structure of the prepared poly (Triethanolamine-glycerylmaleate) chains [77]

This polymer was identified by FTIR spectra as shown in the fig (3-1).

The figure indicate some distinguished peaks at {1728, 1263, 1591} cm^{-1} which also represent the carbonyl group, C-O bond in the ester group and carbon-carbon double bond, respectively.

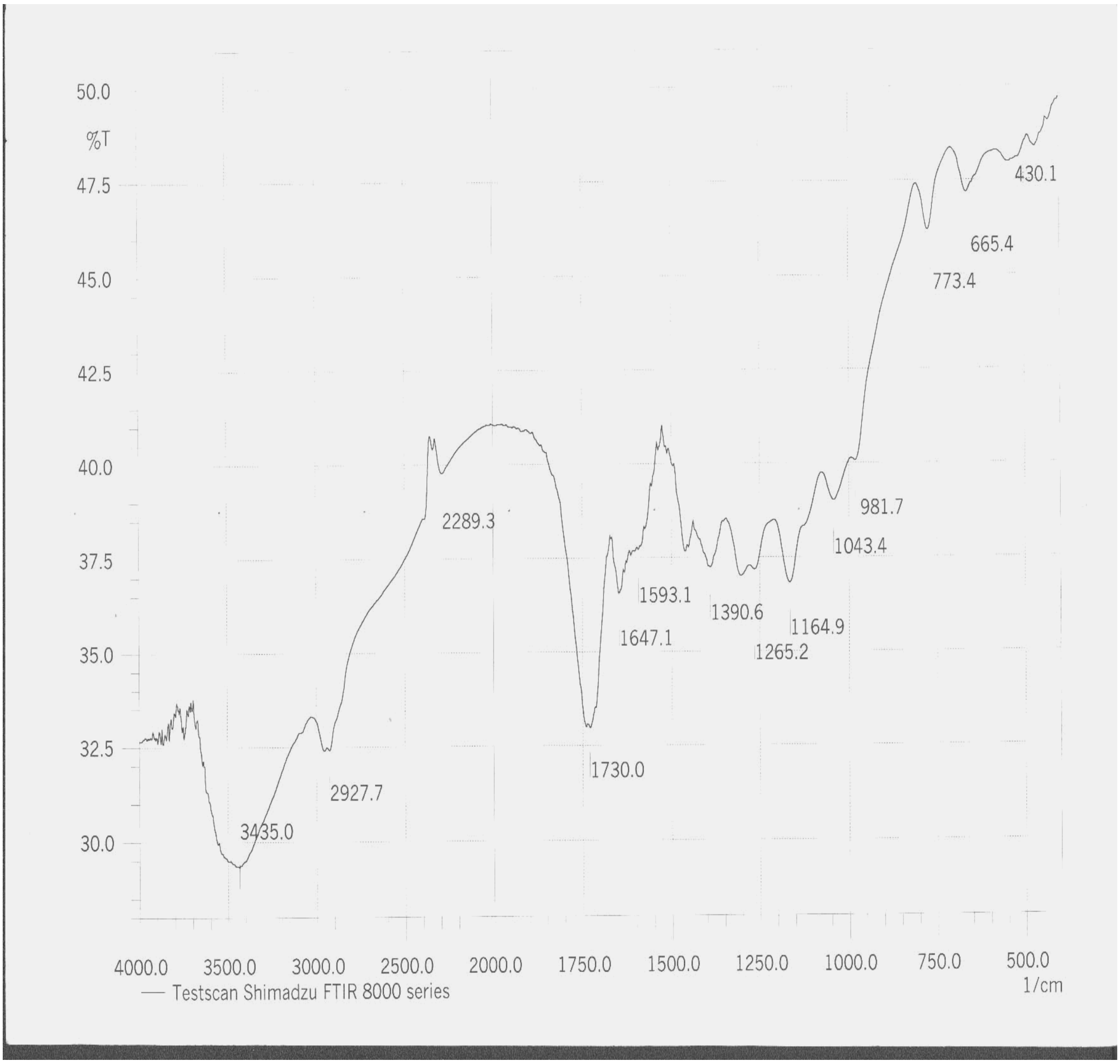


Figure (3-1) FTIR Spectrum for the prepared adsorbance.

3.2 Swelling of the polymer

Swelling test of organic polymer was performed according to ASTM procedure [77]. The degrees of cross linking have been measured in aqueous solutions at pH=7, pH=6, pH=8, and 0.1M NaCl solution, 0.2M NaCl solution, at 35°C, and at 45°C, in acetone, and hexane solvents, and swelling of zeolite has been done with the same method.

According to equation (2-1) :- $$\Delta m = \frac{m1 - mo}{mo}$$

Table (3-1) swelling percentage for polymeric particles.

The polymer	solvents		Swelling percentage (%)
Poly(Triethanolamine-glycerylmaleate)	Water	pH = 6, at 25 °C	19.85 %
		pH = 7, at 25 °C	28.6 %
		pH = 8, at 25 °C	41.848 %
		0.1 M NaCl , at 25 °C	37.335 %
		0.2 M NaCl , at 25 °C	27.695 %
		pH = 7, at 35 °C	18.185 %
		pH = 7, at 45 °C	29.487 %
	Acetone		10
	Hexane		12
Zeolite	PH = 7, at 25 °C		21.4 %

We observe the increasing of contraction of the polymer bulk by increasing the acidity of the media and simply explained by the increasing of hydrogen bonding between polymer chains due to increase the H^+ concentration and decrease the swelling.

There are two factors effect by the presence of external ions in the swelling process; the first one according to the Deby-Hukel theory, where the increase of ionic strength of the media increasing the right direction of the ionic equilibrium that present on the polymer surface such as

$$\text{Poly-COOH} \rightleftharpoons \text{poly-COO}^- + H^+$$

And this equilibrium gives the polymer chains a negative charge along the chain which make them to repulse with each other and that's led to increasing of swelling of polymer and we can see this case in the increasing of the ionic strength from (0.0 – 0.1) M NaCl.

Second by the increasing the concentration of NaCl from (0.1 to 0.2) M the phenomena of salting out process become considerable which act to remove the water molecules that surround the polymer surface and helps it to swell, as a result of this the polymer will shrink and swelling will decrease.

In the case of increasing temperature of the solution from 25°C to 35°C the polymer would be shrink due to the increase of flexibility for the polymer's chains and formation hydrogen bonding between (-OH, COOH, N-tert) groups of the polymer.

In 45°C the polymer would be swallow this is because the thermal kinetic energy of the polymer's chains is larger than the hydrogen bonding energy that made polymer expand.

The swelling of polymer is larger than the swelling of zeolite at the same conditions this may be due to the flexibility of the polymer's chains which greater than that of zeolite.

3.3 Surface area measurement [78]

According to the equation (2-2) in the page 30 surface area equal

$A = 160 \times 10^{-20}$ m^2

$N = 6.023 \times 10^{23}$ mole^{-1}

M.Wt. = 374.3983 g .mole^{-1}

Qe_{max} = 10.650 mg .g^{-1}

$\boldsymbol{S = 27.44\ m^2.g^{-1}}$

3.4 Determination of equilibrium time

This figures (3-2) and (3-3) shows equilibrium time for (ph, na, nal, B, AB, and DAB) compounds.

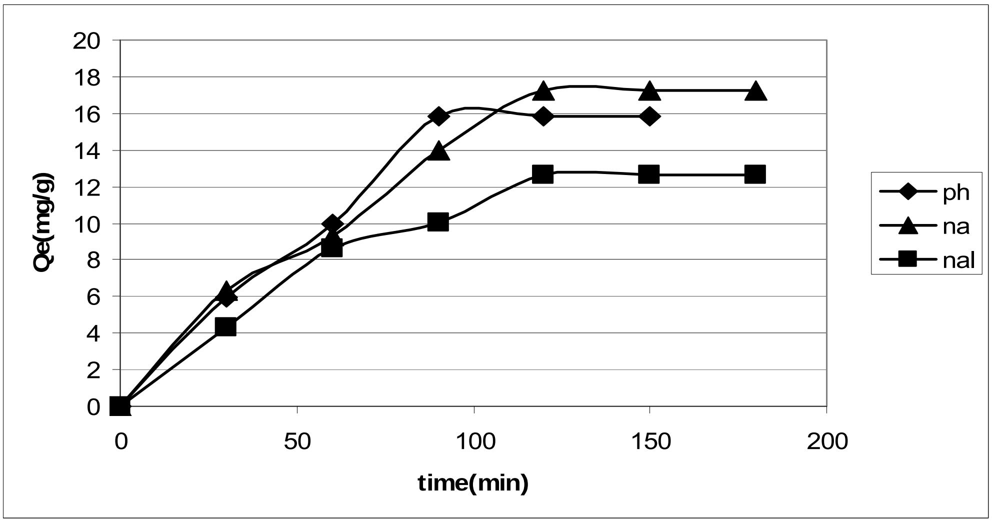


Figure (3-2) equilibrium time for ph, na, nal at 25 ºC and pH=7

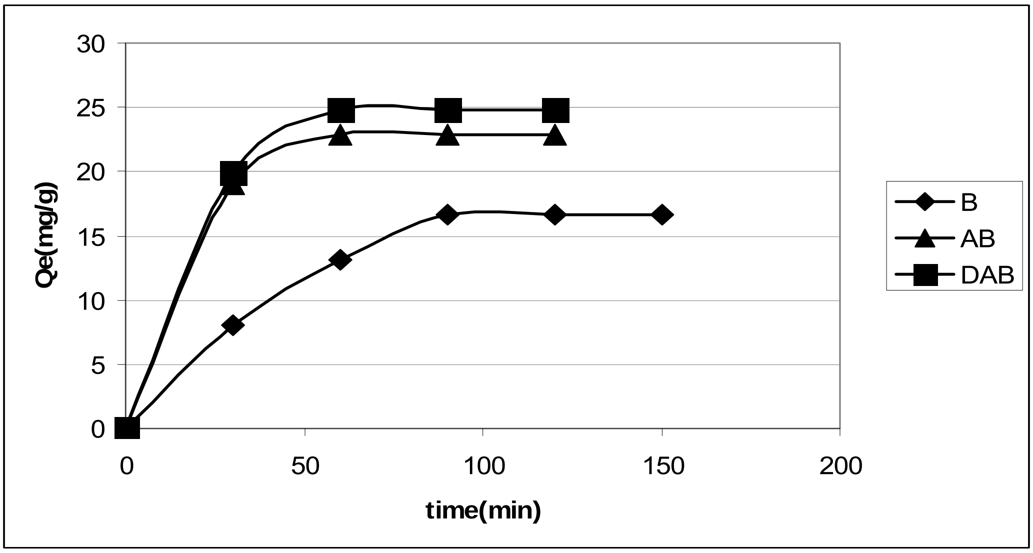


Figure (3-3) equilibrium time for B, AB, DAB at 25 ºC and pH=7

3.5 Adsorption Isotherms

Adsorption of compounds (ph, na, nal, B, AB, and DAB) in aqueous solution at 25ºC, and pH 7, was investigated using less than 300 µm diameter granules of the polymer of (0.04) gm as adsorbent, with adsorbate of initial concentrations (5, 10, 15, 20, 25, and 30) ppm.

The amount of adsorption has been calculated using the following equation [41].

$$Q_e = \frac{V_{sol}(c_o - c_e)}{m} \quad …….. (3\text{-}1)$$

$$Qe\ \% = \frac{C_o - C_e}{C_o} \quad …….. (3\text{-}2)$$

Where

Qe = quantity of adsorbate matter (mg/g)

V = volume of solution (L)

C_o = starting concentration for solution (mg/L)

Ce = concentration at equilibrium for adsorbate matter solution (mg/L)

m = weight of the adsorbent matter (g)

Qe % = percentage of adsorption quantity

The results are shown as the following table (3-2)

Table (3-2) values of Ce and Qe for ph, na, nal, B, AB, and DAB at 25 ºC and pH=7

C_o mg/L	ph		na		nal	
	Ce mg/L	Qe mg/g	Ce mg/L	Qe mg/g	Ce mg/L	Qe mg/g
5	3.231	2.211	1.873	3.908	3.321	2.098
10	4.446	6.934	2.823	8.971	4.234	7.207
15	5.843	11.446	4.467	13.166	6.010	11.237
20	7.345	15.818	6.213	17.233	7.341	12.659
25	8.934	20.082	7.432	21.960	9.010	19.987
30	11.831	22.711	10.213	24.733	11.631	22.961
C_o mg/L	B		AB		DAB	
	Ce mg/L	Qe mg/g	Ce mg/L	Qe mg/g	Ce mg/L	Qe mg/g
5	3.101	2.373	1.078	4.902	0.097	6.128
10	4.111	7.361	1.098	11.127	0.103	12.371
15	5.201	12.248	1.202	17.247	0.163	18.546
20	6.712	16.610	1.731	22.836	0.193	24.758
25	8.210	20.987	2.277	28.403	0.201	30.998
30	10.913	23.858	2.334	34.582	0.220	37.225

The results are represented in figures (3-4) and (3-5)

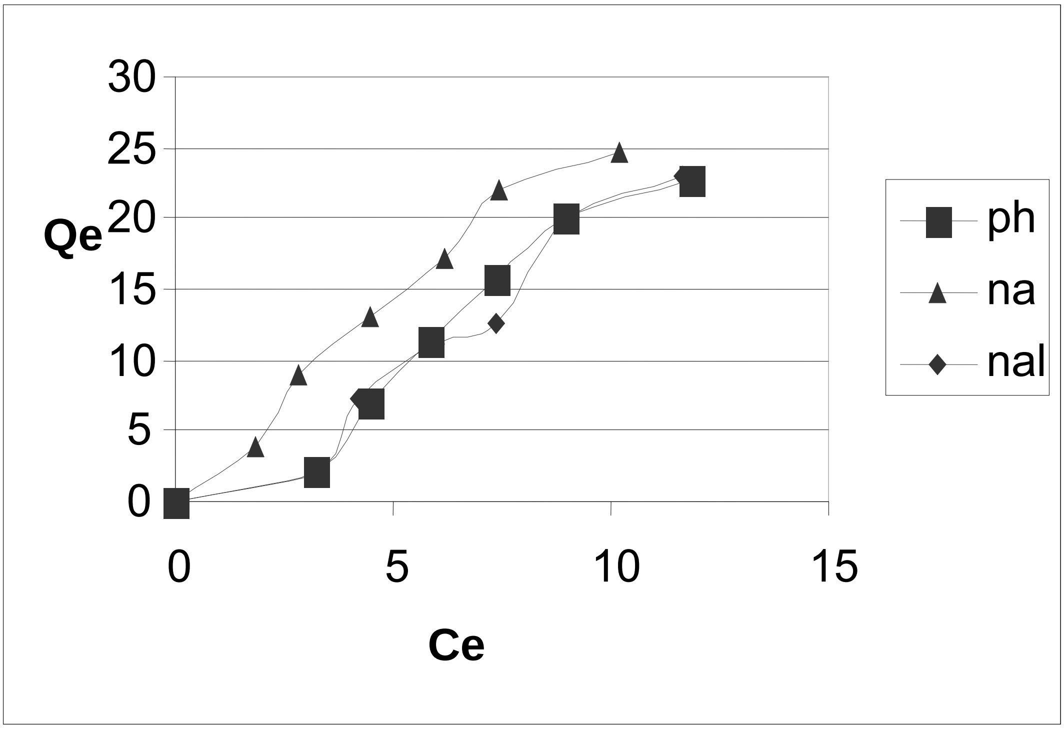


Figure (3-4) adsorption isotherms for ph, na, nal at 25 ºC and pH=7

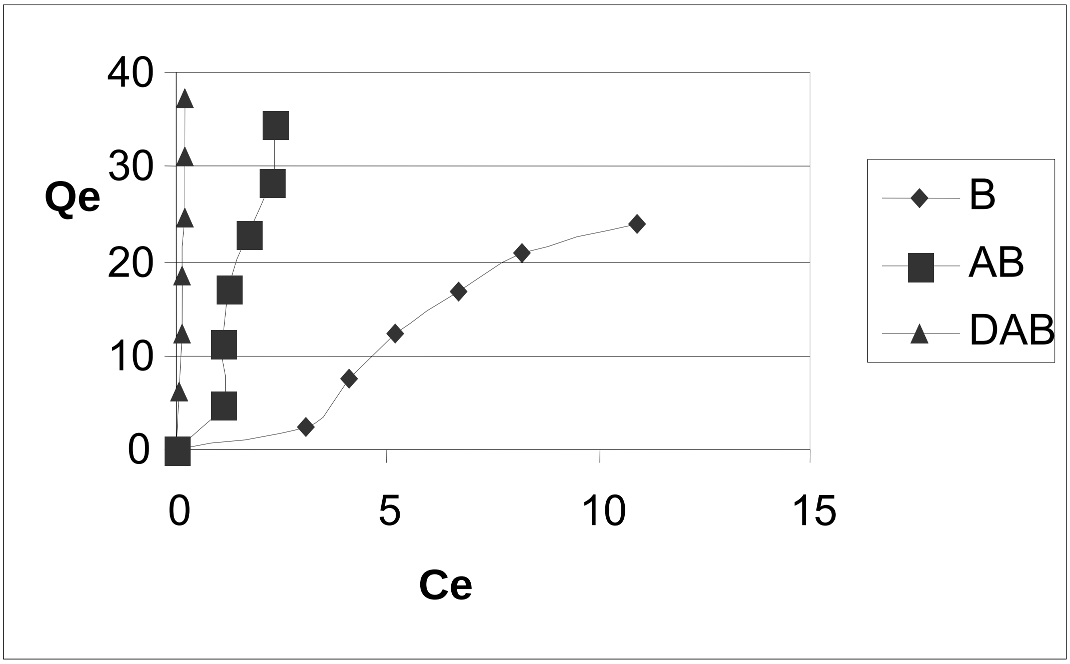
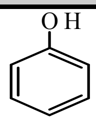
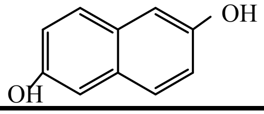
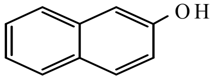
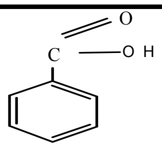
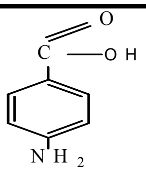
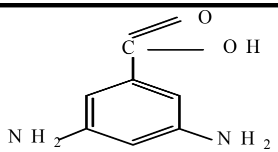


Figure (3-5) adsorption isotherms for B, AB, DAB at 25 ºC, pH =7

Table (3-3) shows structure, molecular weight and Qe% for (ph, nal, na, B, AB and DAB)

compounds	structure	Molecular weight(g/mole)	Qe %
ph		94.1128	60%
nal		160.1720	61%
na		144.1726	66%
B		122.1230	64%
AB		137.1378	92%
DAB		152.1524	99%

The general shape of adsorption for these compounds is (S) shape according to Giles classification. This indicates that the adsorbate molecules arrange in rows or clusters shapes on the polymer surface.

Since that the polymer surface is heterogeneous, and from the swelling calculations in the aqueous solutions, it seems that its surface is polarized with high degree of porosity. That may propose that the clusters which produced from the adsorption are produced in the polymer porous after the swelling.

However, the arrangement of adsorbate quantity at 25ºC were as following arrangement:

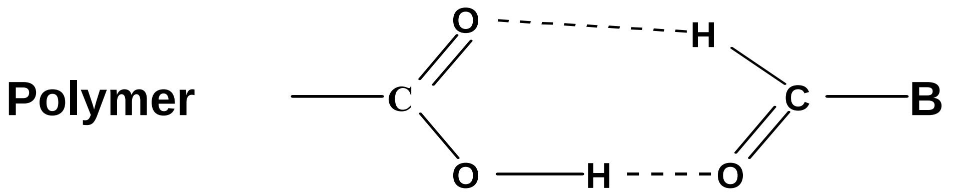
ph <nal <na <B <AB <DAB

In (ph) the adsorption type is (S2) that mean the adsorbate molecules arranged vertical in two layers or two areas separated from each other on the polymer surface. More over the molecular weight of the phenol has a low molecular weight and does not contain localized negative charge hence it decrease the ability of it's adsorption on the polymer surface.

In (na) the adsorption type is (S3), that mean the adsorbate molecules arranged vertical and in multi layers adsorption. The (na) has high molecular weight and does not has localized negative charge leading to low solubility in the aqueous solutions. That explain the increase of it's adsorption quantity on the polymer surface.

In (nal) the adsorption types is also (S3), that describe the adsorbate molecules arranged vertical and in multi layers adsorption. It is observed that the (nal) adsorption quantity is less than the (na) adsorption quantity, may due to that increase in the negative charge density for (nal) which increase the repulsion forces with the polarized polymer surface.

While in (B) the adsorption type is (S2), that mean's the adsorbate molecules to arranged in vertical layers or two areas separated from each other on the polymer surface, (B) has a highly negative charge and low molecular weight that mean the adsorption quantity estimated to it be also low, but more than phenol, that because adsorption forces which increase the quantity of adsorption addition with the (Vander walls and dipole-dipole) forces and hydrogen bonding forces. It is known that the carboxylic acids are produced dimmers and the cyclic composition of this dimmers make a very high stability.



And this leads us to propose that the (B) compound coordinate with hydrogen bonds with different carboxyl groups on the external surface of the polymer.

For (AB) compound the adsorption type is (S3) which show the adsorbate molecules arranged vertical and in multi layers adsorption, the appearance of positive charge in the adsorbate molecules increases it's attraction with negatively charge surface and this causes the increase of the adsorption.

Finally adsorption of (DAB) compound is type (S3) which mean the adsorbate molecules arranged vertical and in a multi layers adsorption. The adsorption quantity of DAB was greater than (AB) compound because found two (-NH_2) groups which increase it's ability to adsorption.

However, the adsorption values determined depending on Freundlich equation for all compounds.

The drawing values of lnQe against lnCe are shown in figure (3-6), (3-7) and reported in table (3-4).

Table (3-4) values of lnCe and lnQe for ph, na, nal, B, AB, and DAB at 25 ºC and pH=7

ph		na		nal	
lnCe	lnQe	lnCe	lnQe	lnCe	lnQe
0	0.793	0.627	1.363	1.200	0.741
1.492	1.937	1.037	2.194	1.443	1.975
1.765	2.437	1.496	2.577	1.793	2.419
1.994	2.761	1.826	2.846	1.993	2.538
2.189	2.999	2.005	3.089	2.193	2.995
2.700	3.122	2.323	3.208	2.453	3.133
B		AB		DAB	
lnCe	lnQe	lnCe	lnQe	lnCe	lnQe
1.131	0.864	0.075	1.589	-2.333	1.812
1.413	1.996	0.093	2.409	-2.273	2.515
1.648	2.505	0.184	2.847	-1.814	2.920
1.903	2.810	0.548	3.128	-1.645	3.209
2.105	3.043	0.823	3.346	-1.604	3.433
2.389	3.172	0.847	3.543	-1.514	3.616

These data has been treated according to the least square methods for Freundlich equation, and the figures (3-6) and (3-7) showing the linear Freundlich relation for all compounds.

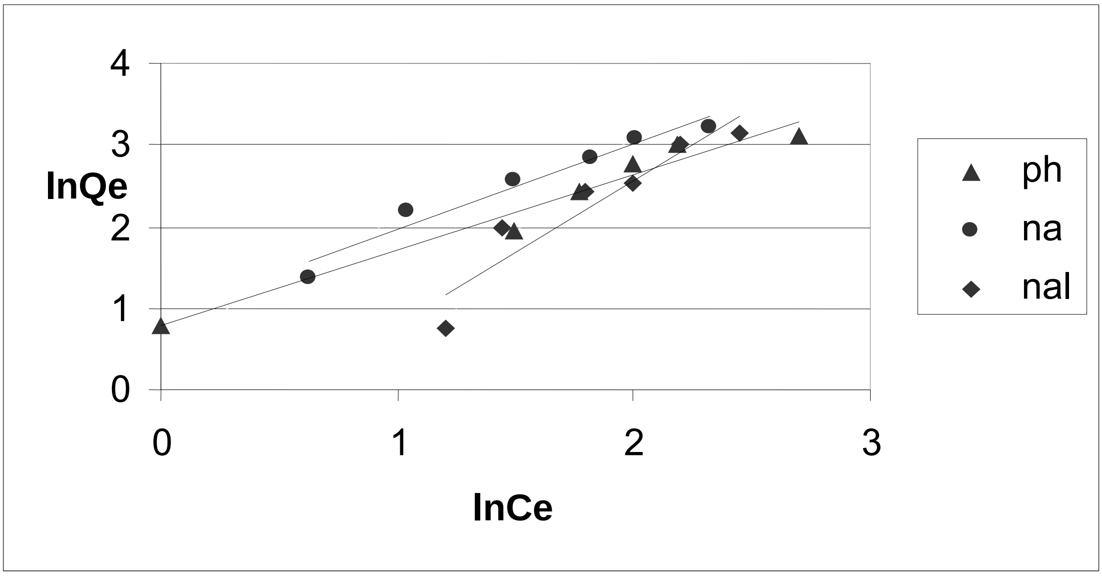


Figure (3-6) Freundlich straight lines for ph, na, nal at 25 ºC and pH=7

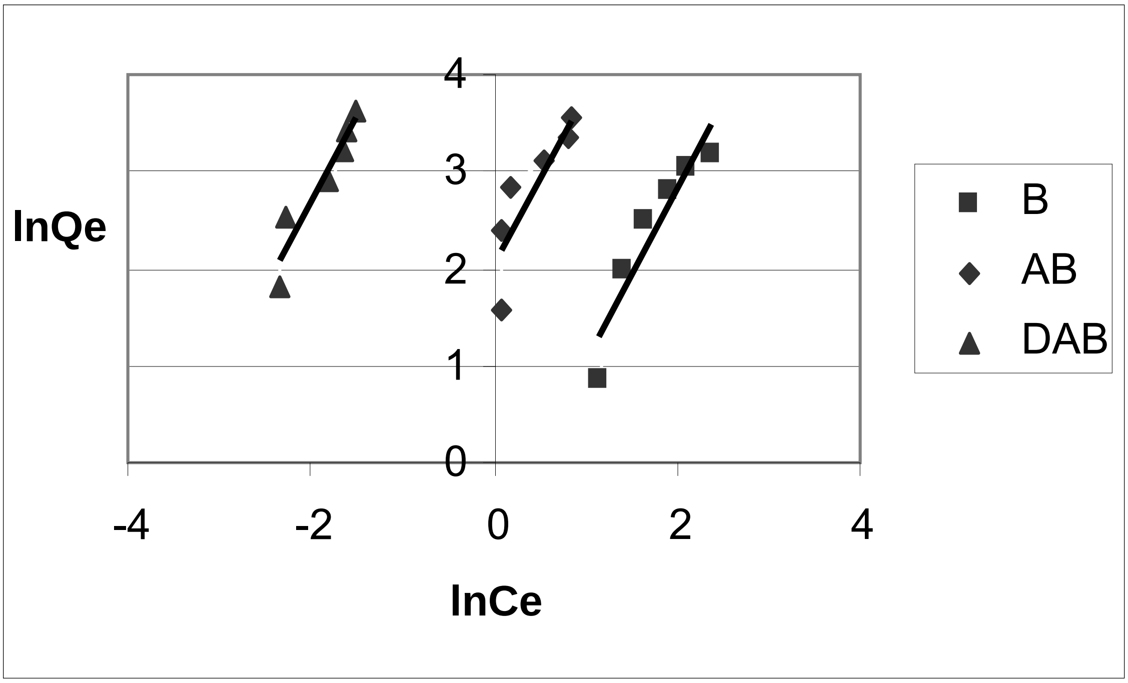


Figure (3-7) Freundlich straight lines for B, AB, DAB at 25 ºC and pH =7

Freundlich practical constants (r, k, n) has been calculated from the information of this strength after the treatment of the point by least square method and shown in the table (3-5)

Table (3-5) values of Freundlich constant for ph, na, nal, B, AB, and DAB at 25 ºC and pH =7

Compound	Kf	n	r
ph	2.172	1.079	0.982
na	2.472	0.946	0.975
nal	0.394	0.571	0.941
B	0.502	0.572	0.936
AB	7.900	0.577	0.864
DAB	522.695	0.557	0.952

3.6Temperature effect

The effect of temperature on the adsorption process for the compounds (ph, na, nal, B, AB, and DAB), on surface of the polymer, was investigated in three different temperature (25, 35,45) ºC at the following conditions, pH= 7, with less than 300 µm diameter granules of adsorbent of (0.04) g, with adsorbate of initial concentrations (5, 10, 15, 20, 25, and 30) ppm, for each compound. The results are listed in table (3-6).

However, the results are shown in figures (3-8---3-13), since the behavior of these compounds in different temperature.

Table (3-6) adsorption isotherms for ph, na, nal, B, AB, and DAB at 25 ºC35 ºC45 ºC and pH=7

ph						
25ºC			35ºC		45ºC	
C_o (mg/L)	C_e (mg/L)	Q_e (mg/g)	C_e (mg/L)	Q_e (mg/g)	C_e (mg/L)	Q_e (mg/g)
5	3.231	2.211	3.201	2.248	4.165	1.043
10	4.446	6.942	6.539	4.326	5.396	5.755
15	5.843	11.450	7.123	9.846	6.716	10.280
20	7.345	15.820	7.645	15.440	8.276	14.660
25	8.934	20.080	9.321	19.600	9.951	18.810
30	11.830	22.710	12.010	22.490	12.660	21.670

na						
25ºC			35ºC		45ºC	
C_o (mg/L)	C_e (mg/L)	Q_e (mg/g)	C_e (mg/L)	Q_e (mg/g)	C_e (mg/L)	Q_e (mg/g)
5	1.873	3.908	3.010	2.4875	4.120	1.100
10	2.823	8.971	3.521	8.098	6.165	4.793
15	4.467	13.166	5.529	11.838	7.314	9.607
20	6.213	17.233	6.987	16.266	10.558	11.802
25	7.432	21.960	8.213	20.983	11.015	17.481
30	10.213	24.733	11.897	22.627	13.421	20.723

nal						
25ºC			35ºC		45ºC	
C_o (mg/L)	C_e (mg/L)	Q_e (mg/g)	C_e (mg/L)	Q_e (mg/g)	C_e (mg/L)	Q_e (mg/g)
5	3.321	2.098	4.256	0.930	4.613	0.483
10	4.234	7.207	5.278	5.902	5.463	5.671
15	6.010	11.237	6.967	10.041	7.921	8.848
20	7.341	12.659	8.466	14.417	10.996	11.255
25	9.010	19.987	10.931	17.586	12.252	15.935
30	11.631	22.961	12.751	21.561	14.916	18.855

B						
	25°C		35°C		45°C	
C_o (mg/L)	C_e (mg/L)	Q_e (mg/g)	C_e (mg/L)	Q_e (mg/g)	C_e (mg/L)	Q_e (mg/g)
5	3.101	2.373	4.046	1.192	4.267	0.916
10	4.111	7.361	5.013	6.233	5.379	5.776
15	5.201	12.248	6.767	10.291	6.987	10.016
20	6.712	16.610	8.266	14.667	8.566	14.292
25	8.210	20.987	10.731	17.836	10.941	17.573
30	10.913	23.858	12.551	21.811	12.951	21.311
AB						
	25°C		35°C		45°C	
C_o (mg/L)	C_e (mg/L)	Q_e (mg/g)	C_e (mg/L)	Q_e (mg/g)	C_e (mg/L)	Q_e (mg/g)
5	1.078	4.902	1.719	4.101	2.661	2.923
10	1.098	11.127	1.838	10.202	3.041	8.698
15	1.202	17.247	1.868	16.415	4.807	12.741
20	1.731	22.836	2.539	21.826	4.907	18.866
25	2.277	28.403	3.119	27.351	5.873	23.908
30	2.334	34.582	3.212	33.485	6.321	29.598
DAB						
	25°C		35°C		45°C	
C_o (mg/L)	C_e (mg/L)	Q_e (mg/g)	C_e (mg/L)	Q_e (mg/g)	C_e (mg/L)	Q_e (mg/g)
5	0.097	6.128	1.178	4.777	1.819	3.976
10	0.103	12.371	1.189	11.013	1.825	10.218
15	0.163	18.546	1.229	17.213	1.852	16.435
20	0.193	24.758	1.813	22.733	2.435	21.956
25	0.201	30.998	2.810	28.273	3.017	27.478
30	0.220	37.225	2.873	34.436	3.211	33.486

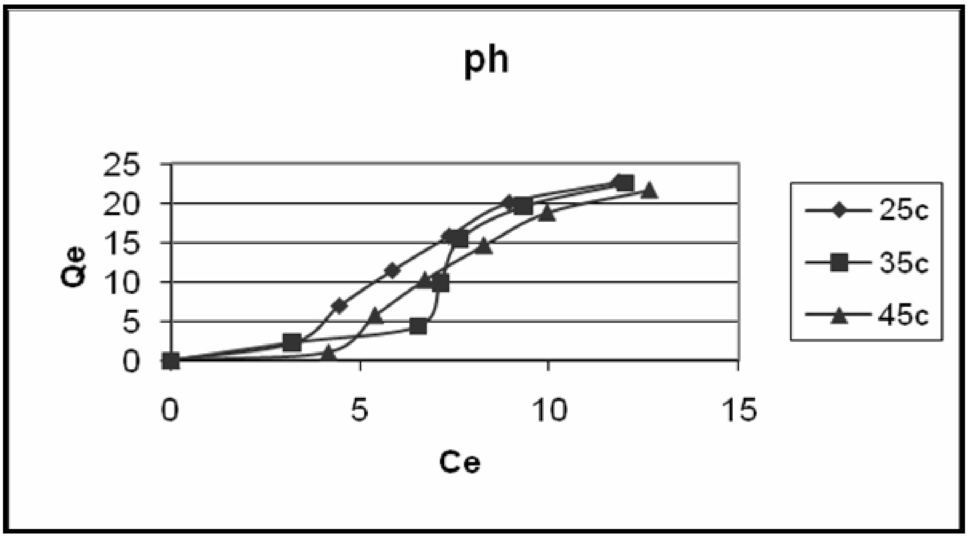


Figure (3-8) adsorption isotherms for ph at 25 ºC, 35 ºC, 45 ºCand pH=7

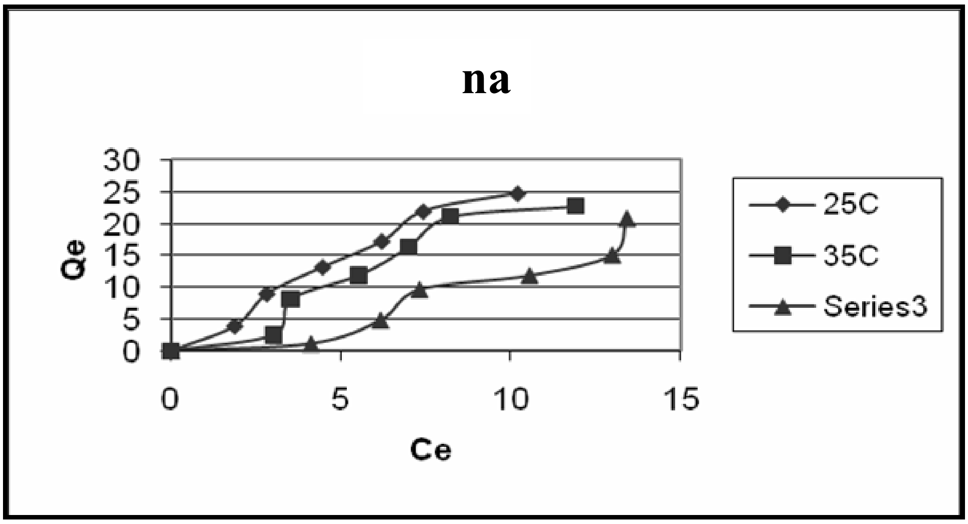


Figure (3-9) adsorption isotherms for na at 25 ºC, 35 ºC, 45 ºCand pH=7

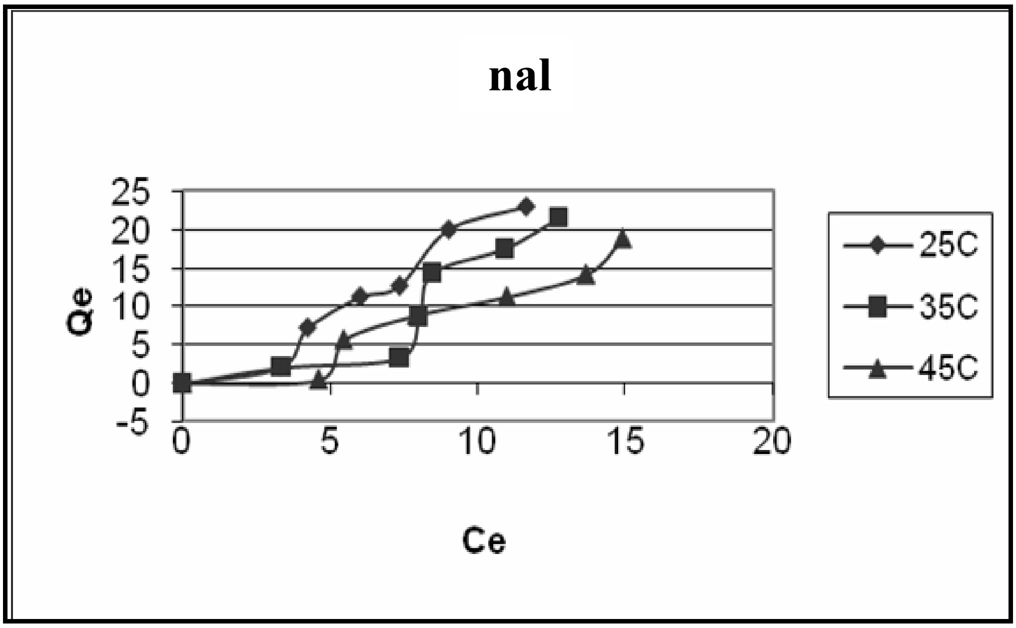


Figure (3-10) adsorption isotherms for nal at 25 ºC, 35 ºC, 45 ºC and pH=7

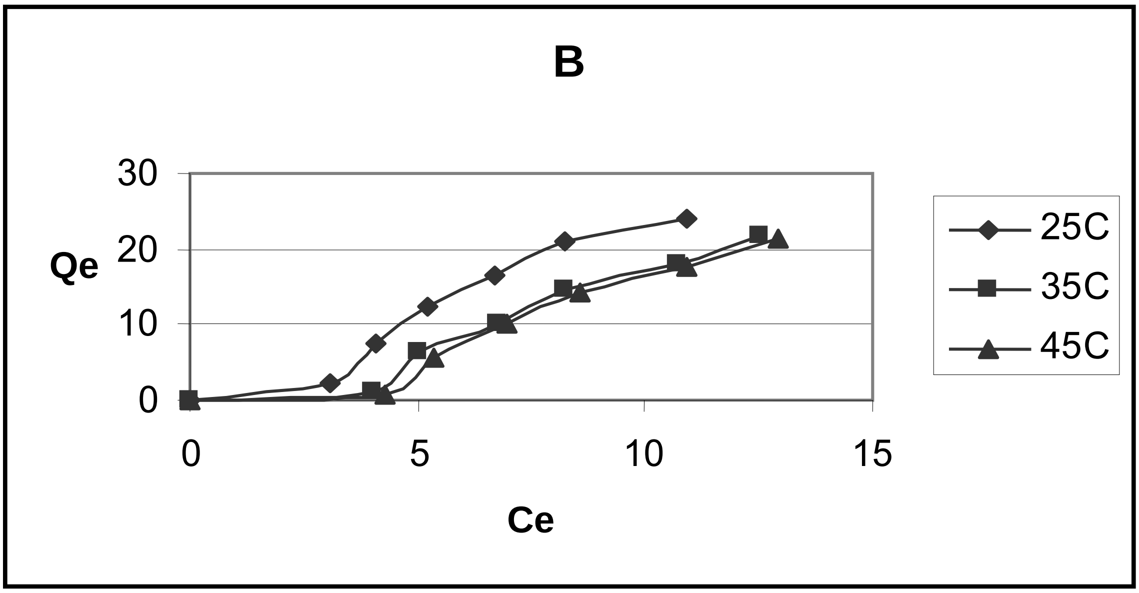


Figure (3-11) adsorption isotherms for B at 25 ºC, 35 ºC, 45 ºC and pH=7

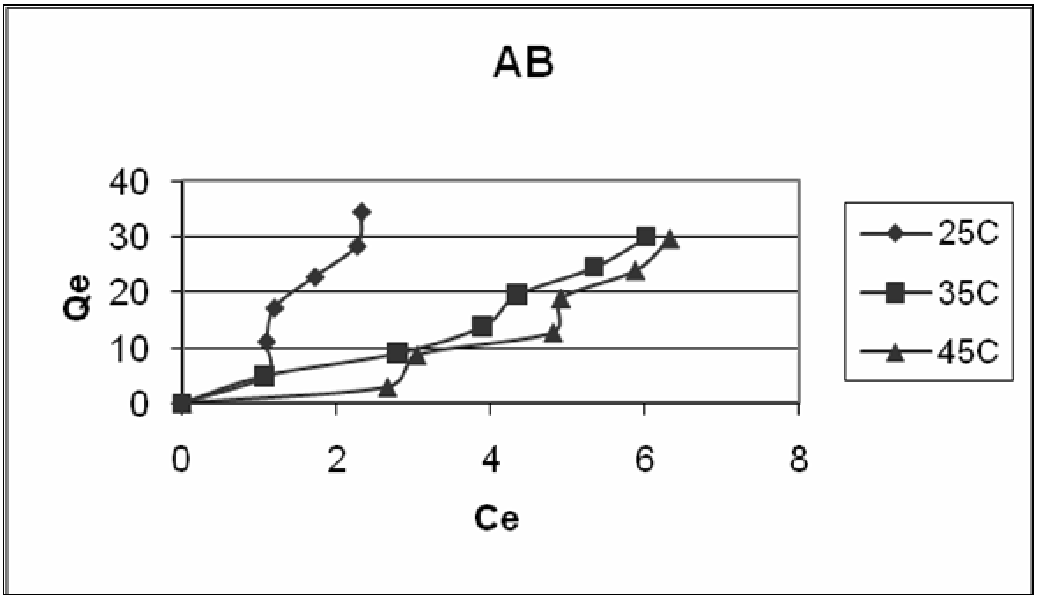


Figure (3-12) adsorption isotherms for AB at 25 ºC, 35 ºC, 45 ºC and pH=7

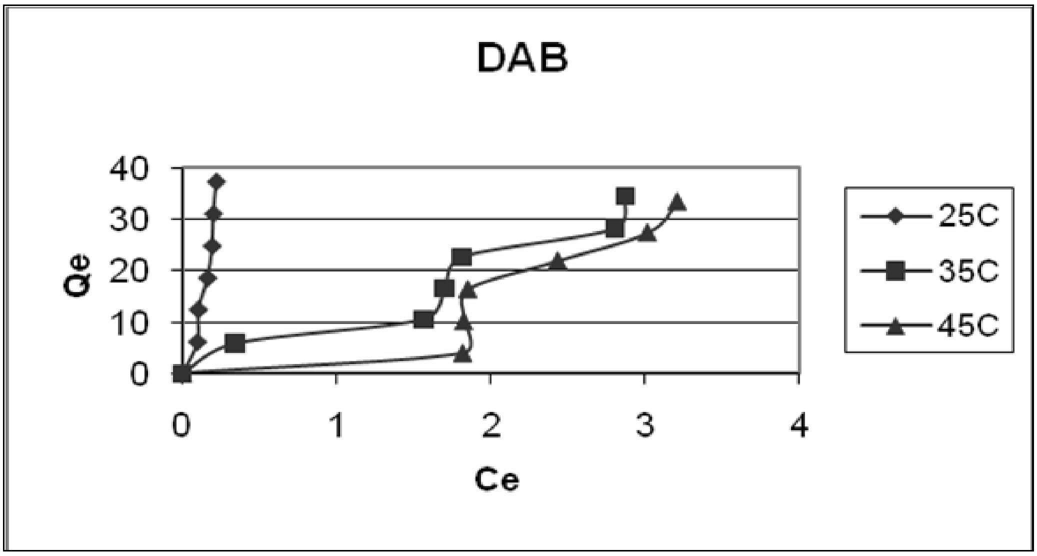


Figure (3-13) adsorption isotherms for DAB at 25 ºC, 35 ºC, 45 ºC and pH=7

For compounds ph, nal, AB, and DAB the adsorption multi layer means there are many centers on the polymer surface can contribute to the adsorption process but, these compounds show intercepting phenomena by conversion the adsorption pattern from S-mode in 25 ºC to the L-mode in 35 ºC and returning to S-mode in 45 ºC

25 ºC → 35ºC → 45 ºC
S2 → L2 → S2 ph…
S3 → L2 → S2 nal…
S3 → L2 → S3 AB…
S3 → L3 → S3 DAB…

We can explain that by return to the effect of temperature on the swelling of polymer that happen to shrink between (25 ºC - 35 ºC) and re-expand between (35 ºC - 45 ºC), it is known that S-type adsorption occurs when the adsorbate molecules precipitate vertical as a clusters on the surface but, L-type occurs when the adsorbate molecules precipitate horizontal as a layer on the surface when the polymer swell the active sits on its surface become far from each other then lead to the adsorbate molecules to be aggregate as a cluster on the polymer surface specially at (25 ºC and 45 ºC) which gives the characteristic S-shape of adsorption. While the polymer is shrinking at (35 ºC) and the active sits would be close to each other making the clusters of the adsorbate molecule close to each other too and forming continuous layers that give L-type of adsorption of Langmuir type.

In the case of na, and B the functional group carried by the molecule is the main position of bonding between the molecules and the surface, which leads to the adsorbate molecules to precipitate perpendicularly on the surface. These conformations can not form a layer in the contraction or swelling of the polymer. For this reason the adsorption shape will stay S-type of adsorption.

25 ºC → 35ºC → 45 ºC
S3 → S3 → S3 na…
S2 → S2 → S2 B…

Generally we notice increasing the temperature leads to increase the kinetic energy for the adsorbate compounds and subsequently decrease the adsorption process.

The increasing of temperature leads to also increase the solubility of all of these compounds (ph, na, nal, B, AB, DAB) in it's aqueous solutions so that decrease the adsorption process and this processes called (desorption) .

3.6.1.Thermodynamic calculations:

ΔH has been calculated for all adsorption processes, according to equation (3.1) [79], via plotting logarithmic value of the maximum adsorption quantity at equilibrium concentration as (ln Qe_{max}) against reciprocal of temperature as (1/T). The results are listed in table [3-7] and figures (3-14), and (3-15):

$$\ln\chi_m = \frac{-\Delta H}{RT} + \text{ Cons. } .... \quad [3.3]$$

Where

ΔH:- Enthalpy Change

X_m:- maximum adsorption

R:-constant

Table (3-7) values of 1/T and $\ln Q_{max}$ for ph, na, nal, B, AB, and DAB at 25 ºC and pH=7

		Ce=11.831(mg/L)		Ce=10.213(mg/L)		Ce=11.631(mg/L)	
		ph		na		nal	
T(K)	1/T(K^{-1})	Qe_{max}	$\ln Qe_{max}$	Qe_{max}	$\ln Qe_{max}$	Qe_{max}	$\ln Qe_{max}$
298	0.00335	22.710	3.120	24.730	3.200	22.960	3.130
308	0.00324	21.980	3.090	22.250	3.100	19.470	2.970
318	0.00314	21.010	3.040	10.150	2.320	12.150	2.490
		Ce=10.913(mg/L)		Ce=2.334(mg/L)		Ce=0.22(mg/L)	
		B		AB		DAB	
T(K)	1/T(K^{-1})	Qe_{max}	$\ln Qe_{max}$	Qe_{max}	$\ln Qe_{max}$	Qe_{max}	$\ln Qe_{max}$
298	0.00335	23.860	3.170	34.580	3.540	37.230	3.620
308	0.00324	18.670	2.920	8.320	2.120	4.570	1.520
318	0.00314	17.970	2.890	2.010	0.698	2.220	0.7960

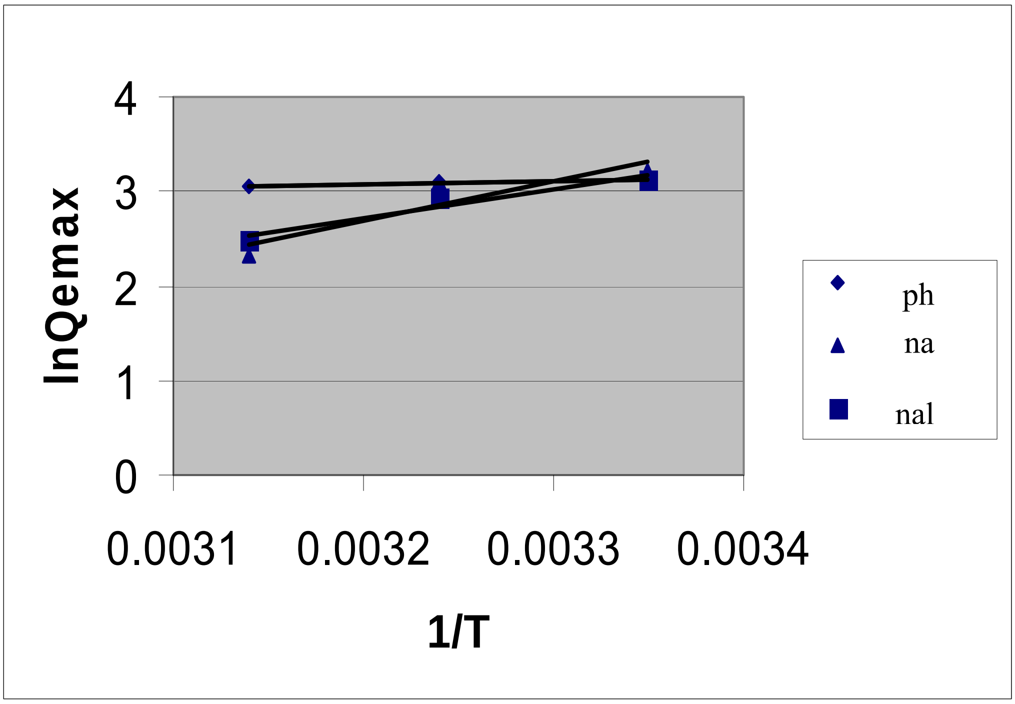


Figure (3-14) Shows values of $\ln Qe_{max}$ against 1/T for adsorption of compounds ph, na, and nal on the adsorbent surface.

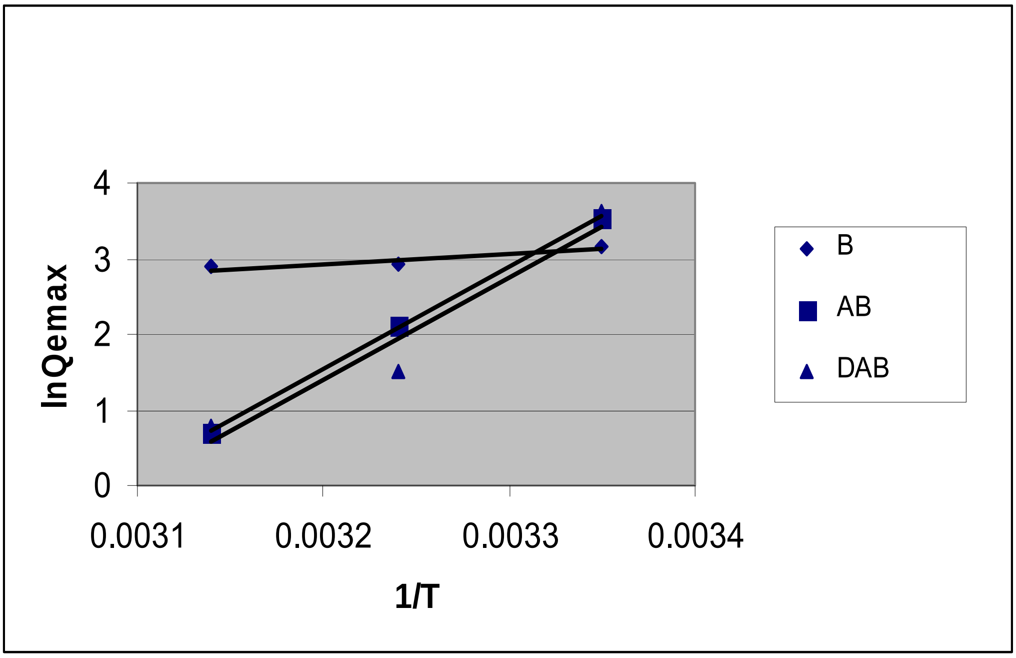


Figure (3-15) shows values of $\ln Qe_{max}$ *against 1/T for adsorption of compounds B, AB, and DAB on the adsorbent surface.*

All these data have been treated by using the (Least Square Method) and then ΔH was calculated. The Gibbs free energy ΔG for adsorption is associated with equilibrium constant K_{eq} according to the following equation:

$$\Delta G = -RT \ln K \qquad [3.4]$$

Where $K = \frac{Q_e}{C_e}$...... [3.5] Then calculate ΔG

$$\Delta G = -RT \ln \frac{Q_e}{C_e} \qquad [3.6]$$

Knowing that Qe should be in mg/g, ΔS have been calculated via Gibb's relationship

$$\Delta G = \Delta H - T\Delta S \qquad [3.7]$$

Table (3-8) illustrates the value of thermodynamic function of compounds (ph, na, nal, B, AB, and DAB) on the surface of the polymer.

Table (3-8) values of thermodynamic functions for ph, na, nal, B, AB, and DAB on the polymer surface

Compound	**ΔH** kJ/mol	**ΔG** **kJ/mol**	**ΔS** **j**/mol.**k**°
Ph	-3.077	-18.730	52.530
na	-34.822	-19.306	-52.070
nal	-25.020	-18.799	-20.870
B	-11.366	-19.053	25.790
AB	-112.555	-23.797	-297.820
DAB	-112.422	-29.827	-277.160

Table (3-8) shows the thermodynamic functions value for adsorption of (ph, na, nal, B, AB, and DAB) compounds on the polymer surface.

The low negative values of ΔH indicate that the absorption was included with of these compounds and the negative values of ΔG indicate that the adsorption is spontaneous.

The value, of ΔS [80] shows that the order of the molecules on the surface in the case of (ph, B) compounds will be less than in the liquid phase and this was due to the diffusion process including in the porous polymer but corresponding all of DAB, AB, nal, and na these order on the adsorbent surface be greater corresponding with it inside the liquid phase which arranged on the surface in limit positions and channels and take a limited order.

The adsorptions of all compounds on the polymer surface are, favorable from thermodynamics point of view with following sequence

$$\mathbf{DAB > AB > na > B > nal > ph}$$

$$\xrightarrow[\textbf{Decreasing the } \Delta G]{\hspace{10cm}}$$

To explain this result we must take two factors in considerable

1- The strength of bonding between the active sites on the surface and the adsorbate molecules, which represented by ΔH negative value.

2- The high negative value of ΔH in DAB and AB that mean chemisorptions occur on the surface.

3.7 Effect of pH on the adsorption:

The effect of pH on the adsorption process for the compounds (ph, na, nal, B, AB, DAB) on surface of the polymer were investigated in three different pH (6, 7 and 8) at the following conditions: 25ºC, with less than 300 µm diameter granules of adsorbent of (0.04) g, with adsorbate of initial concentrations (5, 10, 15, 20, 25, and 30) ppm, for each compound. The results are shown in table (3-9), and figures (3-16 to 3-21).

Table (3-9) adsorption isotherms for ph, na, nal, B, AB, and DAB at pH= 6, 7, 8 at 25ºC

ph						
	6		7		8	
C_o (mg/L)	C_e (mg/L)	Q_e (mg/g)	C_e (mg/L)	Q_e (mg/g)	C_e (mg/L)	Q_e (mg/g)
5	4.660	0.425	3.231	2.211	1.987	3.766
10	6.210	4.737	4.446	6.942	4.234	7.207
15	9.846	6.442	5.843	11.446	4.967	12.541
20	11.731	10.336	7.345	15.818	6.213	17.233
25	13.510	14.362	8.934	20.082	7.963	21.296
30	14.981	18.773	11.831	22.711	10.531	24.336
na						
	6		7		8	
C_o (mg/L)	(mg/L) C_e	Q_e (mg/g)	C_e (mg/L)	Q_e (mg/g)	C_e (mg/L)	Q_e (mg/g)
5	3.897	1.378	1.873	3.908	1.231	4.711
10	5.731	5.336	2.823	8.971	2.135	9.831
15	7.512	9.360	4.467	13.166	4.213	13.483
20	8.342	14.572	6.213	17.233	6.131	17.336
25	11.345	17.068	7.432	21.960	6.973	22.533
30	15.987	17.516	10.213	24.733	9.913	25.108
nal						
	6		7		8	
C_o (mg/L)	C_e(mg/L)	Q_e (mg/g)	C_e (mg/L)	Q_e (mg/g)	C_e (mg/L)	Q_e (mg/g)
5	4.421	0.723	3.321	2.098	1.911	3.861
10	7.213	3.483	4.234	7.207	4.298	7.150
15	8.731	7.836	6.010	11.237	5.303	12.121
20	9.987	12.516	7.341	12.659	6.431	16.961
25	12.421	15.723	9.010	19.987	8.787	20.266
30	15.754	17.807	11.631	22.961	11.012	23.735

B						
	6		7		8	
C_o (mg/L)	C_e (mg/L)	Q_e(mg/g)	C_e (mg/L)	Q_e (mg/g)	C_e (mg/L)	Q_e (mg/g)
5	4.201	0.998	3.101	2.373	1.789	4.013
10	7.521	3.098	4.111	7.361	2.912	8.860
15	9.125	7.343	5.201	12.248	3.123	14.847
20	11.973	10.033	6.712	16.610	5.987	17.516
25	15.895	11.381	8.210	20.987	6.213	23.483
30	19.875	12.656	10.913	23.858	7.971	27.536
AB						
	6		7		8	
C_o (mg/L)	C_e (mg/L)	Q_e (mg/g)	C_e (mg/L)	Q_e (mg/g)	C_e (mg/L)	Q_e (mg/g)
5	2.789	2.763	1.078	4.902	0.463	5.671
10	4.874	6.407	1.098	11.127	1.109	11.113
15	6.013	11.233	1.202	17.247	1.173	17.283
20	7.943	15.071	1.731	22.836	1.597	23.003
25	9.012	19.985	2.277	28.403	1.981	28.773
30	10.987	23.766	2.334	34.582	2.101	34.873
DAB						
	6		7		8	
C_o (mg/L)	C_e (mg/L)	Q_e (mg/g)	C_e (mg/L)	Q_e (mg/g)	(mg/L) C_e	(mg/g) Q_e
5	0.216	5.980	0.097	6.128	0.021	6.223
10	0.351	12.061	0.103	12.371	0.0931	12.383
15	0.471	18.161	0.163	18.546	0.113	18.608
20	0.512	24.360	0.193	24.758	0.151	24.811
25	0.613	30.483	0.201	30.998	0.181	31.023
30	0.741	36.573	0.220	37.225	0.197	37.253

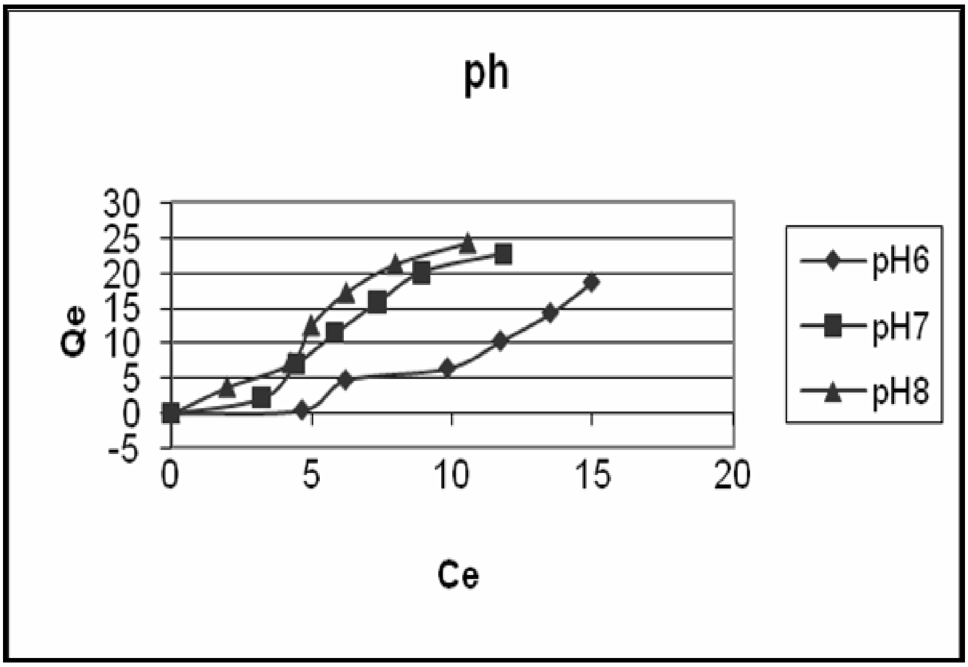


Figure (3-16) adsorption isotherms for ph at pH= 6, 7, 8 at 25ºC

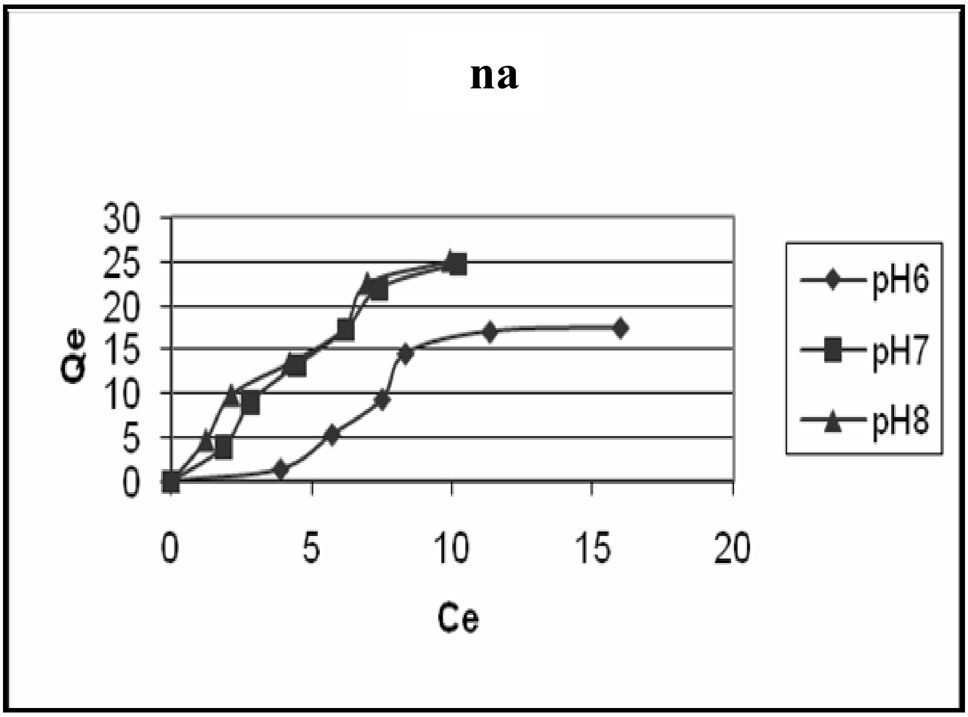


Figure (3-17) adsorption isotherms for na at pH= 6, 7, 8 at 25ºC

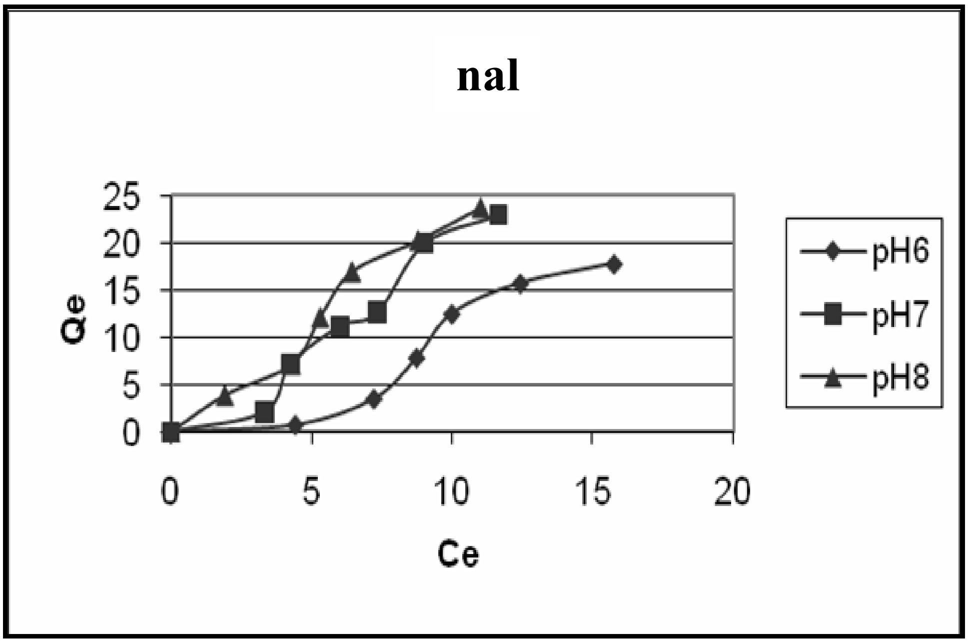


*Figure (3-18) adsorption isotherms for nal at pH= 6, 7, 8   at 25º*C

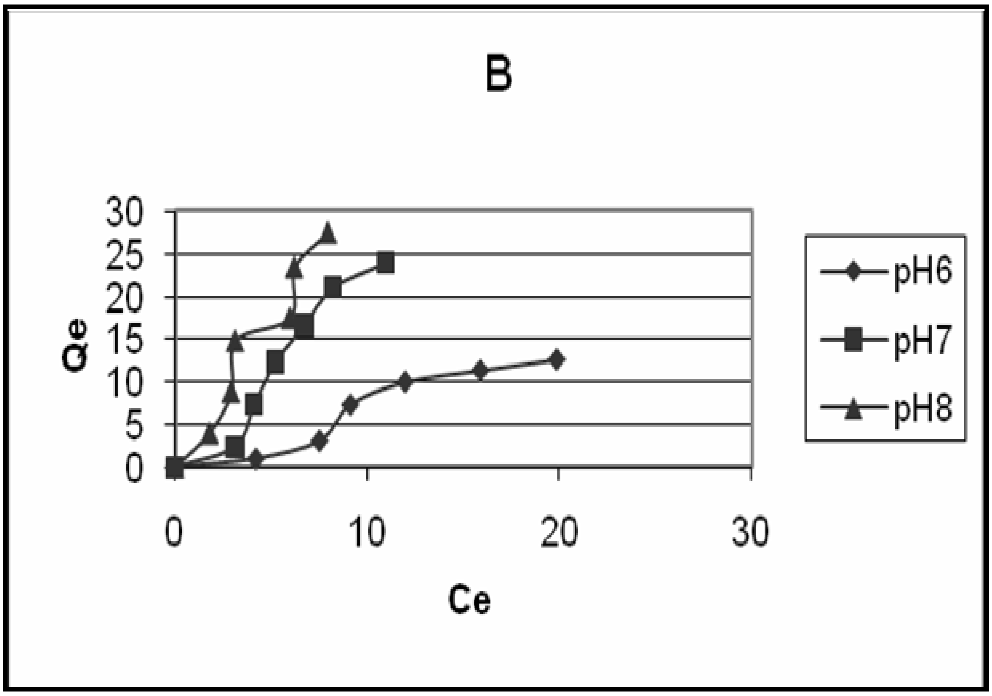


*Figure (3-19) adsorption isotherms for B at pH= 6, 7, 8   at 25º*C

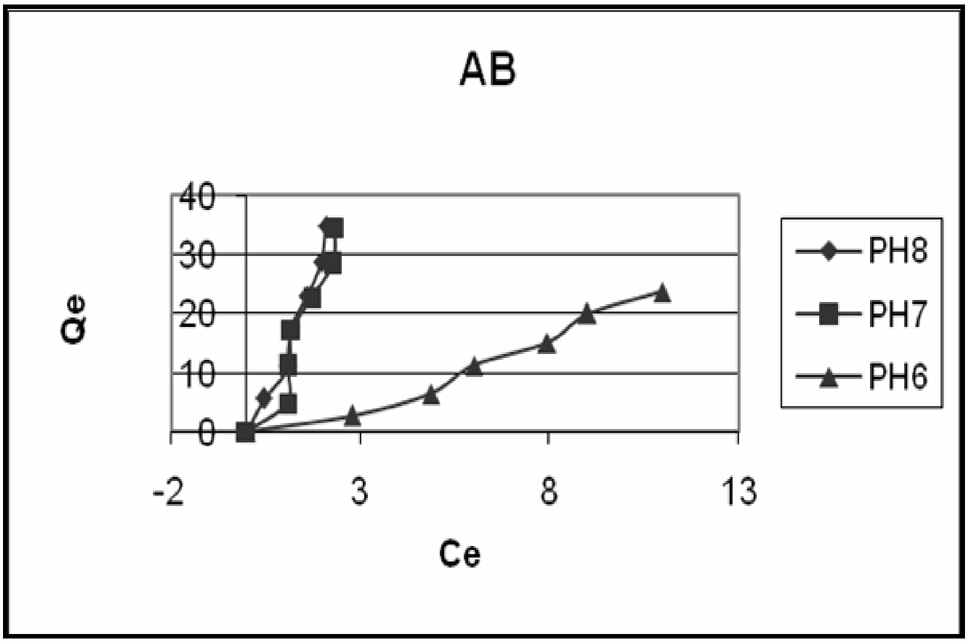


Figure (3-20) adsorption isotherms for AB at pH= 6, 7, 8   at 25ºC

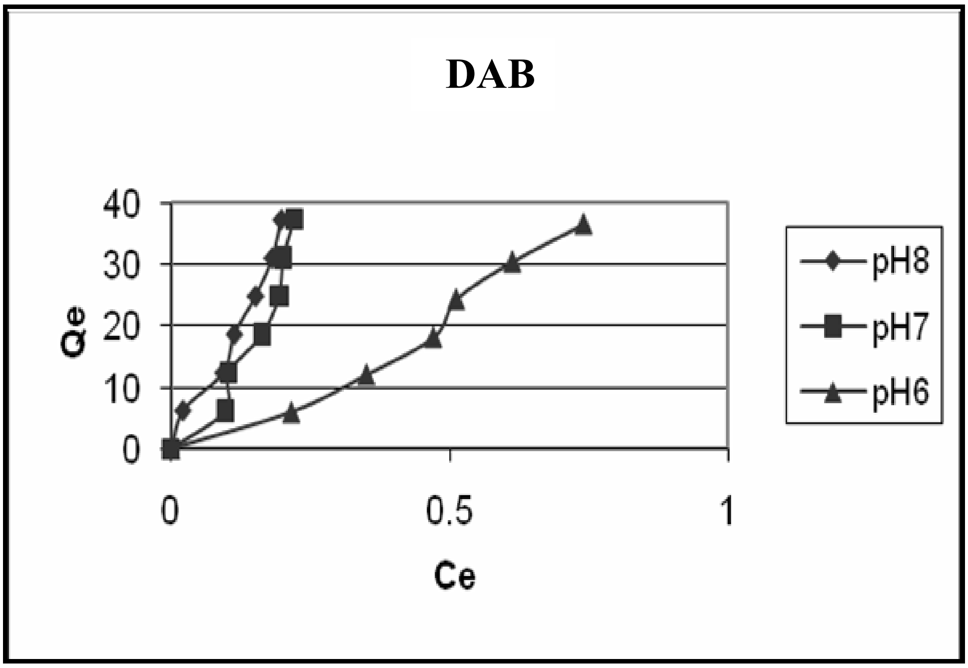


Figure (3-21) adsorption isotherms for DAB at pH= 6, 7, 8   at 25ºC

The swelling factor is the critical factor that influences on the adsorption quantity with variation of the pH of the solution, the swelling of the polymer take the sequence:-

$$\underrightarrow{\mathbf{pH = 8 > pH = 7 > pH = 6}}$$

Decreasing adsorption quantity, and swelling

This will lead to adsorb more quantity of the for all adsorbate in the media that the polymer has a largest swelling in spite of the negative charge of the adsorbent surface which be formed in the basic media and as a summary the swelling of the polymer factor will be greater than the repulsion between the negative charged adsorbate molecules and negative charge on the polymer surface.

The general adsorption type for ph is S2-shape and for na is S3-type, the active sites on the polymer surface can adsorbed these phenols without change its type of adsorption.

pH =6 → pH =7 → pH =8
S2 → S2 → S2 ph…
S3 → S3 → S3 na…

For B the pH change for the solution which cause the swelling of the polymer create more active sites with same configuration at the transition from pH=6 to pH=7 while at pH=8 a new active sites have been created with different configuration S3-shape in spit of these active sites remain far from each other and this will not allow to form L-shape.

pH =6 → pH =7 → pH =8
S2 → S2 → S3 B…

This behavior happen in nal, AB, and DAB and take S2-shape initially at pH=6 then its convert to S3-shape at pH=7 as a result of increasing the number of active sites on the polymer surface with conserving of its shape and charge but, at pH= 8 these active sites become to adsorbed the molecules closed to each other horizontally to convert the shape from S3-shape to L3-shape

pH =6 → pH =7 → pH =8
S2 → S3 → L3 nal…
S2 → S3 → L3 AB…
S2 → S3 → L3 DAB…

3.8 Effect of ionic strength

The effect of ionic strength on the adsorption process for compounds (ph, na, nal, B, AB, and DAB) on the surface of the polymer, was investigated in three different ionic strength (0.0, 0.1 and 0.2) M NaCl at the following conditions, 25ºC, pH= 7, and less than 300 μm diameter granules of (0.04) gm of adsorbent, with adsorbate of initial concentrations (5, 10, 15, 20, 25, and 30) ppm, for each compound. However, the results are shown in table (3-10) and figures (3-22---3-27).

Table (3-10) shows the effect of ionic strength on the adsorption isotherms for ph, na, nal, B, AB, and DAB at pH= 6, 7, 8 at 25ºC

Ph						
0.0 NaCl			0.1 NaCl		0.2 NaCl	
C_o (mg/L)	C_e (mg/L)	Q_e (mg/g)	C_e (mg/L)	Q_e (mg/g)	C_e (mg/L)	Q_e (mg/g)
5	3.231	2.211	3.197	2.254	3.974	1.283
10	4.446	6.942	6.541	4.323	6.845	3.943
15	5.843	11.450	4.578	13.030	8.111	8.611
20	7.345	15.820	7.297	15.880	9.879	12.650
25	8.934	20.080	8.471	20.660	10.010	18.740
30	11.830	22.710	9.741	25.320	14.350	19.560
na						
0.0 NaCl			0.1 NaCl		0.2 NaCl	
C_o (mg/L)	C_e (mg/L)	Q_e (mg/g)	C_e (mg/L)	Q_e (mg/g)	C_e (mg/L)	Q_e (mg/g)
5	1.873	3.908	1.501	4.373	4.213	0.983
10	2.823	8.971	2.749	9.063	6.214	4.732
15	4.467	13.166	4.578	13.027	7.547	9.316
20	6.213	17.233	5.874	17.657	10.324	12.095
25	7.432	21.960	7.412	21.985	12.879	15.151
30	10.213	24.733	8.417	26.978	14.879	18.901

nal						
	0.0 NaCl		0.1 NaCl		0.2 NaCl	
C_o (mg/L)	C_e (mg/L)	Q_e (mg/g)	C_e (mg/L)	Q_e (mg/g)	C_e (mg/L)	Q_e (mg/g)
5	3.321	2.098	2.120	3.600	4.712	0.360
10	4.234	7.207	4.974	6.280	6.412	4.485
15	6.010	11.237	5.010	12.487	8.741	7.823
20	7.341	12.659	6.541	16.823	11.245	10.943
25	9.010	19.987	8.210	20.987	14.587	13.016
30	11.631	22.961	9.874	25.157	17.254	12.746

B						
	0.0 NaCl		0.1 NaCl		0.2 NaCl	
C_o (mg/L)	C_e (mg/L)	Q_e (mg/g)	C_e (mg/L)	Q_e (mg/g)	C_e (mg/L)	Q_e (mg/g)
5	3.101	2.373	2.877	2.653	3.541	1.823
10	4.111	7.361	4.001	7.498	6.897	3.878
15	5.201	12.248	4.985	12.518	8.656	7.930
20	6.712	16.610	6.124	17.345	10.874	11.407
25	8.210	20.987	8.541	20.573	12.974	15.018
30	10.913	23.858	10.241	24.698	15.985	17.518

AB						
	0.0 NaCl		0.1 NaCl		0.2 NaCl	
C_o (mg/L)	C_e (mg/L)	Q_e (mg/g)	C_e (mg/L)	Q_e (mg/g)	C_e (mg/L)	Q_e (mg/g)
5	1.078	4.902	1.012	4.985	2.641	2.948
10	1.098	11.127	1.451	10.686	3.142	8.572
15	1.202	17.247	3.541	14.323	4.879	12.651
20	1.731	22.836	4.102	19.872	5.874	17.657
25	2.277	28.403	5.210	24.737	7.568	21.790
30	2.334	34.582	6.007	29.991	10.874	23.907

DAB						
	0.0 NaCl		0.1 NaCl		0.2 NaCl	
C_o (mg/L)	C_e (mg/L)	Q_e (mg/g)	C_e (mg/L)	Q_e (mg/g)	C_e (mg/L)	Q_e (mg/g)
5	0.097	6.128	0.124	6.095	1.541	4.323
10	0.103	12.371	1.541	10.570	3.541	8.073
15	0.163	18.546	1.987	16.266	4.547	13.060
20	0.193	24.758	2.012	22.485	4.879	18.901
25	0.201	30.998	2.541	28.073	5.214	24.732
30	0.220	37.225	2.987	33.766	6.214	29.732

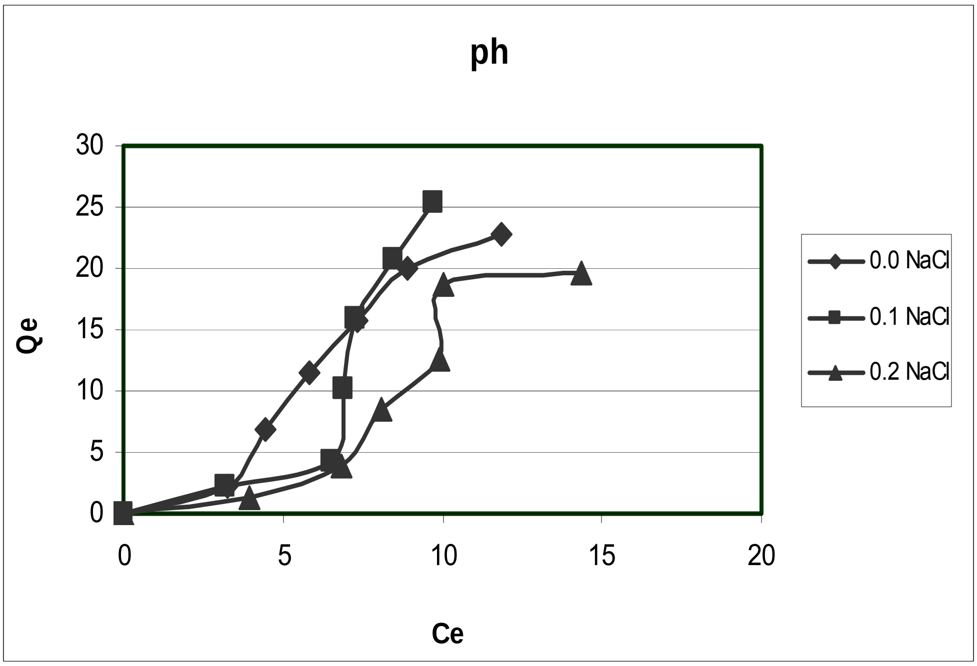


Figure (3-22) shows the effect of ionic strength on the adsorption isotherms for ph at pH= 6, 7, 8 at 25ºC

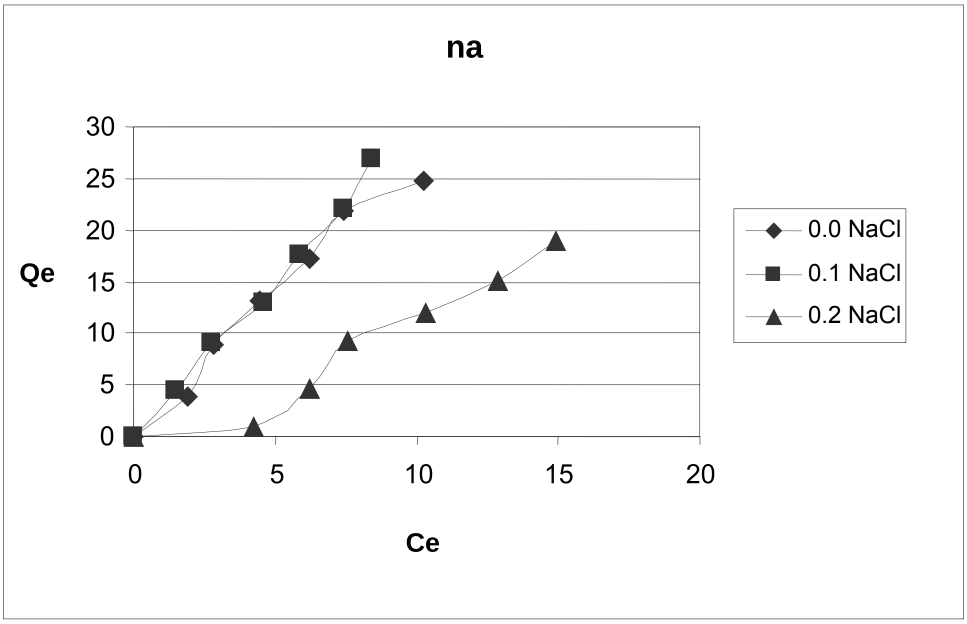


Figure (3-23) shows the effect of ionic strength on the adsorption isotherms for ph at pH= 6, 7, 8 at 25ºC

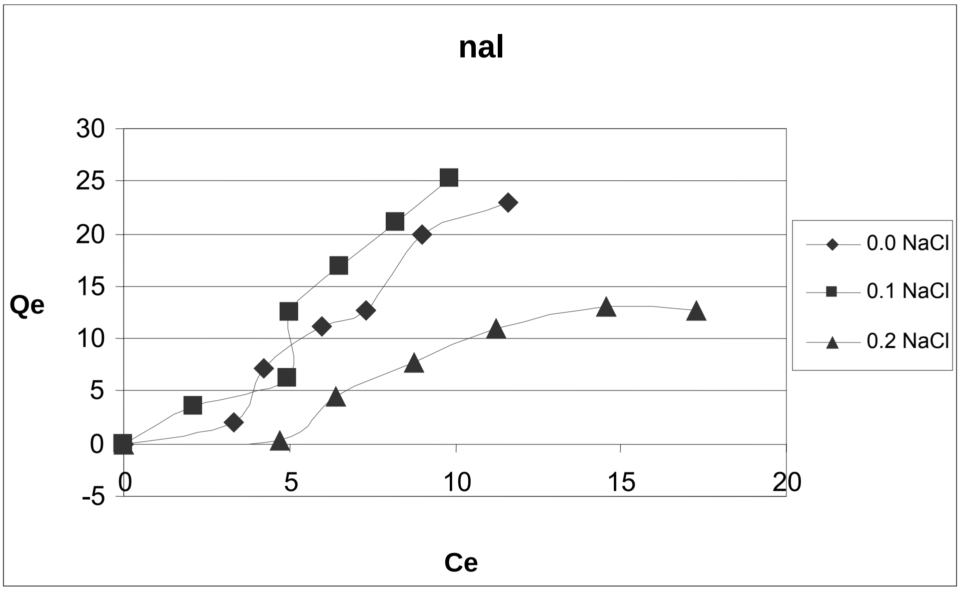


Figure (3-24) shows the effect of ionic strength on the adsorption isotherms for nal at pH= 6, 7, 8 at 25ºC

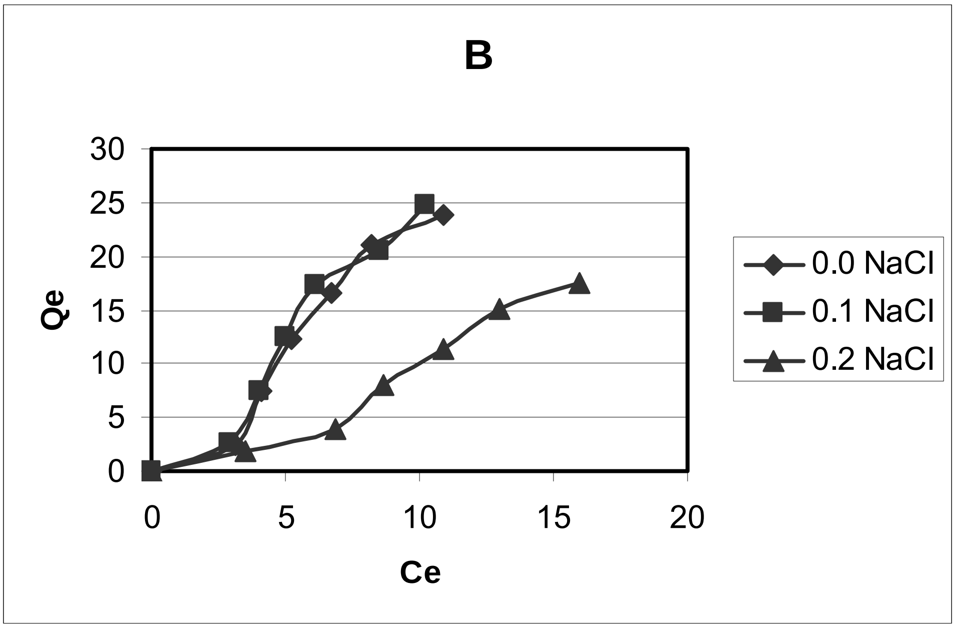


Figure (3-25) shows the effect of ionic strength on the adsorption isotherms for B at pH= 6, 7, 8 at 25ºC

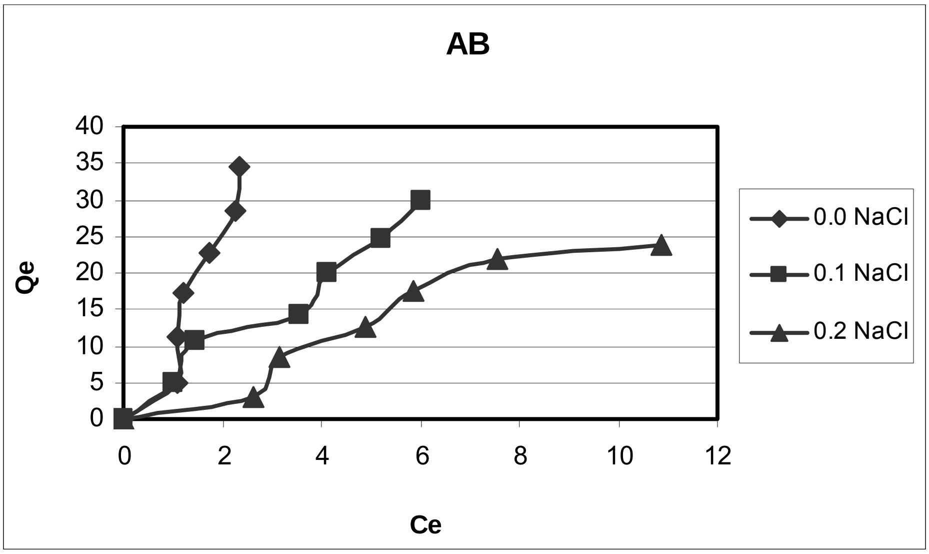


Figure (3-26) shows the effect of ionic strength on the adsorption isotherms for AB at pH= 6, 7, 8 at 25ºC

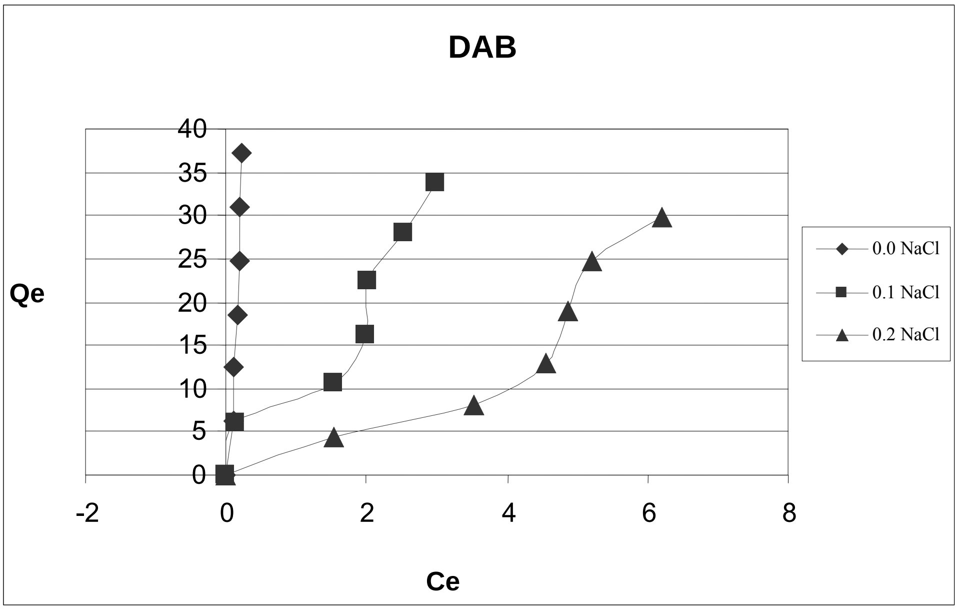


Figure (3-27) shows the effect of ionic strength on the adsorption isotherms for DAB at pH= 6, 7, 8 at 25ºC

The ionic strength factor influence on the adsorption process of the compounds as follow:

For ph, na, nal, and B take the following sequence in general:

0.1M NaCl > 0.0M NaCl > 0.2M NaCl

$\longrightarrow$

Decreasing of adsorption quantity

Especially at the final segments of the adsorption curves which can be explained by the swelling and contraction of the polymer bulk. The largest swelling occur at ionic concentration 0.1 NaCl and the minimum occur at 0.2 NaCl and these result was explained previously, this leads to increase the number of active sites that capable to adsorbed the adsorbante molecules and the contraction on the surface leads to decrease the quantity of adsorption as a result of the decreasing of available active sites on the polymer surface.

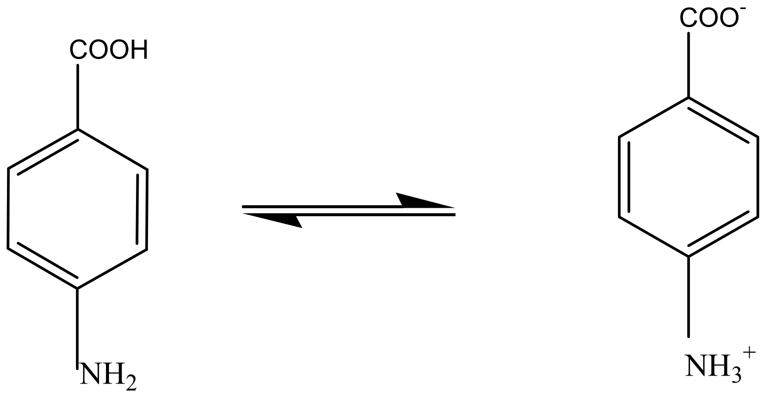
For AB, and DAB the quantity of adsorption take the sequence

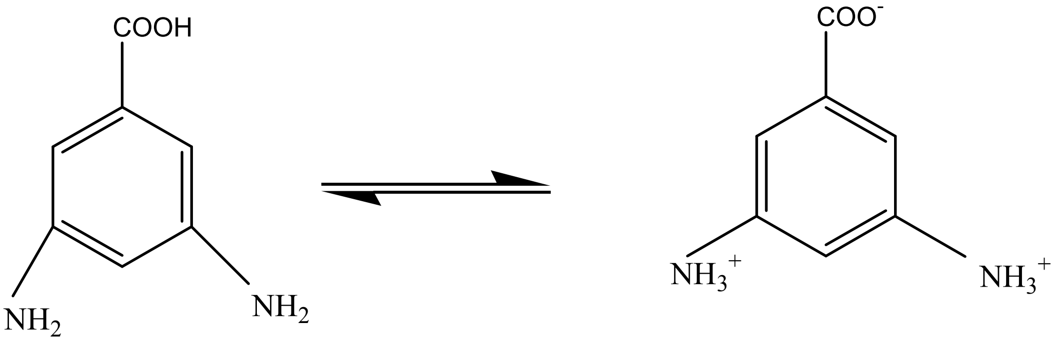
0.0M NaCl >0.1M NaCl>0.2M NaCl

$\longrightarrow$

Decreasing of adsorption quantity

From this sequence we suggest the following behavior to describe this result by increasing the ionic concentration of the solution the formation of zoitter ion of the functional groups of these two molecules will increase according to Duby-Hukl law but, because these molecules can form zoitter ion this rearrangement will be neutral as all





As a result of this equilibrium the solubility of the adsorbate molecules will increase without forming a net positive charge can contribute of increasing adsorption quantity, even when the salting out process will happen the ionic center of the zwitter ion will remain ionized and the solubility will stay high because of the short distance between the opposite ionic centers in the molecule.

For ph, na, nal, B, and DAB occur transition in the adsorption mode from S2-shape or S3-shape at ionic strength 0.0M to Sn-shape or Ln-shape where n = (1, 2, 3).

0.0M NaCl→ 0.1M NaCl→0.2M NaCl

S2	→	L2	→	S2	ph…
S3	→	L3	→	S2	na…
S3	→	L3	→	S2	nal…
S2	→	S3	→	S2	B…
S3	→	L3	→	L2	DAB…

We can describe this from the swelling of the polymer surface and from the effect of the strong salt behavior (salting-out) we mean at ionic strength 0.1M the active sites begin to change there configuration and begin to close to each other some times and far from each other times and that's lead to the change between S-shape and L-shape of adsorption by increasing ionic strength the polymer will become to shrank and the polymer chains begin to back to each other this give a rigid configuration to the active sites geometry and take a constant shape to the adsorption mode.

For AB its conserve on S3-shape of adsorption and this may be due to that AB molecules contribute to take stable configuration with increasing of the ionic strength.

0.0M NaCl→ 0.1M NaCl→0.2M NaCl
S3 → S3 → S3 AB…

3.9 Comparison between adsorption on the polymer (Triethanolamine-glycerylmaleate) with that on zeolite 5A

Since most of the studies available are the adsorption on zeolite 5A. This adsorbent was studied extensively, in order to evaluate and validate some of the results on the polymer (Triethanolamine-glycerylmaleate). Comparison of the adsorption processes for the compounds (ph, na, nal, B, AB, and DAB) on the surface adsorbents: of (the polymer, and of the zeolite) at: 25ºC, and pH=7, with adsorbate of initial concentrations (5, 10, 15, 20, 25, and 30) ppm, was investigated.

Table (3-11) adsorption isotherms for ph, na, nal, B, AB, and DAB at 25 ºC on the zeolite surface and pH=7

	ph		na		nal	
C_o (mg/L)	Ce(mg/L)	Qe(mg/g)	Ce(mg/L)	Qe(mg/g)	Ce(mg/L)	Qe(mg/g)
5	3.523	1.846	1.543	4.321	3.621	1.723
10	4.980	6.275	3.599	8.001	4.634	6.707
15	6.213	10.983	4.867	12.666	6.612	10.485
20	7.976	15.030	6.613	16.733	7.892	15.135
25	9.652	19.185	7.731	21.586	9.921	18.848
30	12.315	22.106	10.931	23.836	12.431	21.961

	B		AB		DAB	
C_o (mg/L)	Ce(mg/L)	Qe(mg/g)	Ce(mg/L)	Qe(mg/g)	Ce(mg/L)	Qe(mg/g)
5	3.401	1.998	1.532	4.335	1.631	4.211
10	4.512	6.86	4.012	7.485	4.124	7.345
15	5.701	11.623	5.776	15.811	7.712	9.11
20	7.421	15.723	8.772	21.093	8.991	13.761
25	8.973	20.033	12.578	24.037	12.542	15.572
30	11.523	23.096	14.632	29.848	13.971	20.036

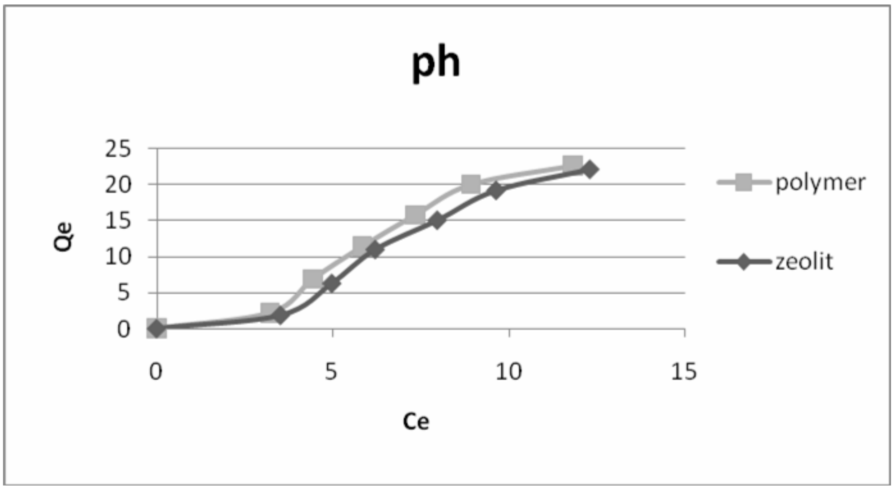


Figure (3-28) adsorption isotherms for "ph" on the polymer and zeolite at 25 ºC at pH=7

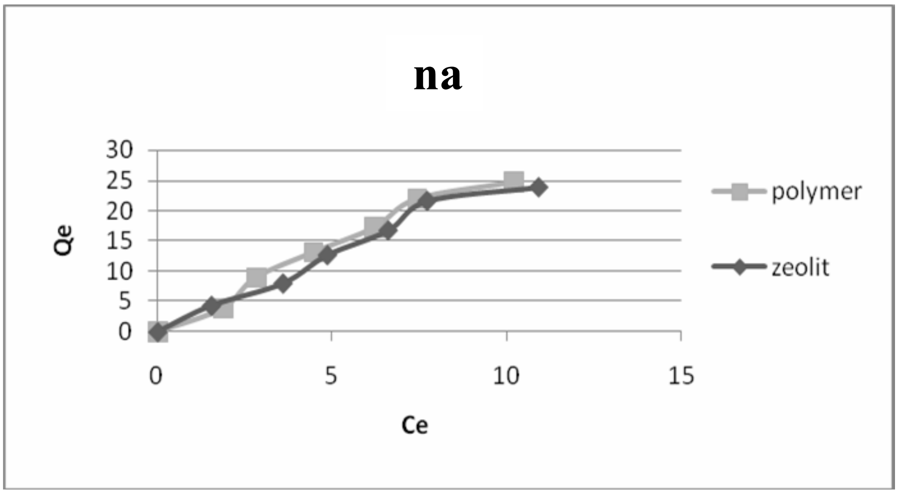


Figure (3-29) adsorption isotherms for "na" on the polymer and zeolite at 25 ºC at pH=7

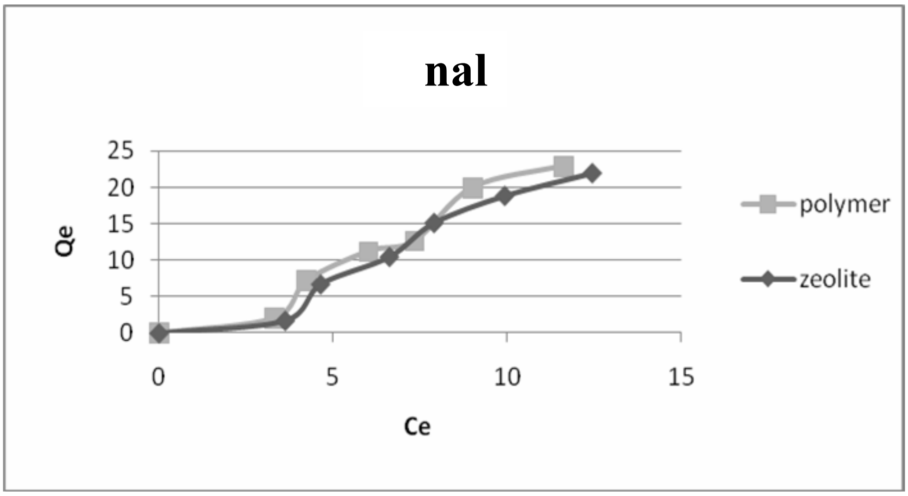


Figure (3-30) adsorption isotherms for "nal" on the polymer and zeolite at 25 ºC at pH=7

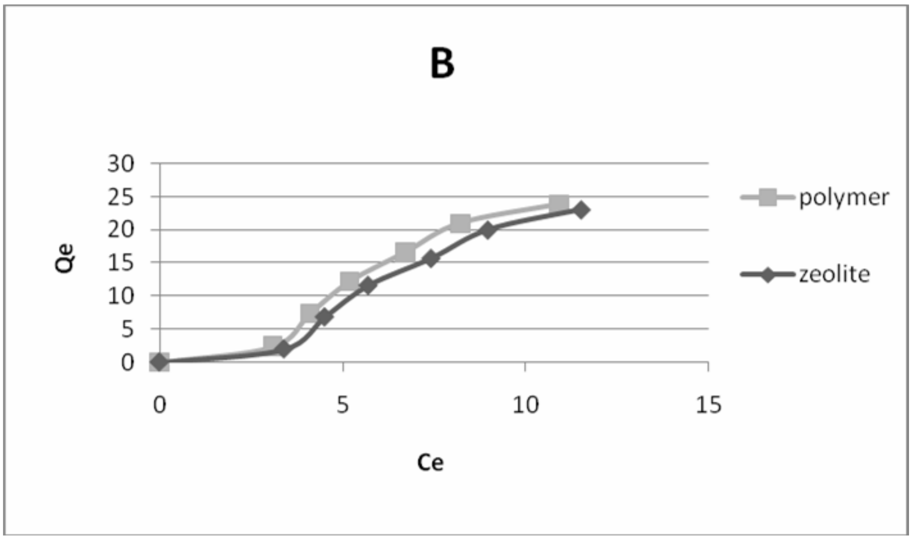


Figure (3-31) adsorption isotherms for "B" on the polymer and zeolite at 25 ºC at pH=7

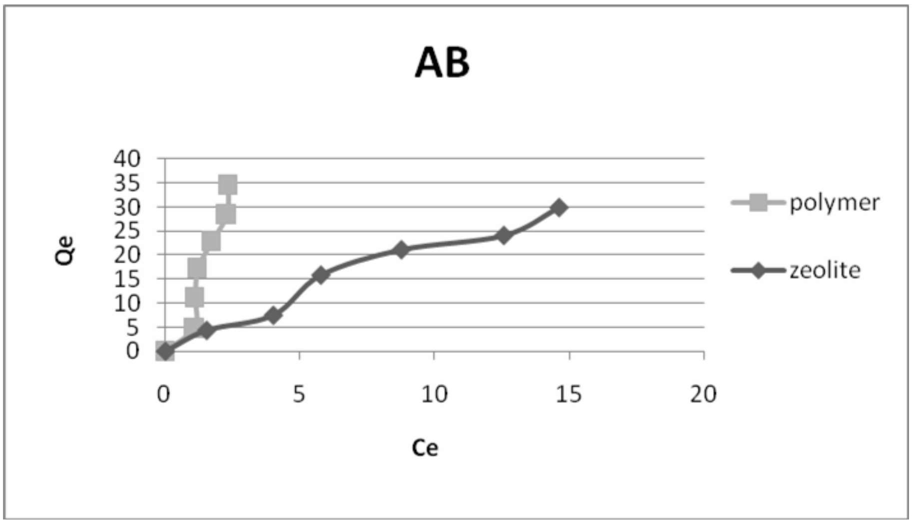


Figure (3-32) adsorption isotherms for "AB" on the polymer and zeolite at 25 ºC at pH=7

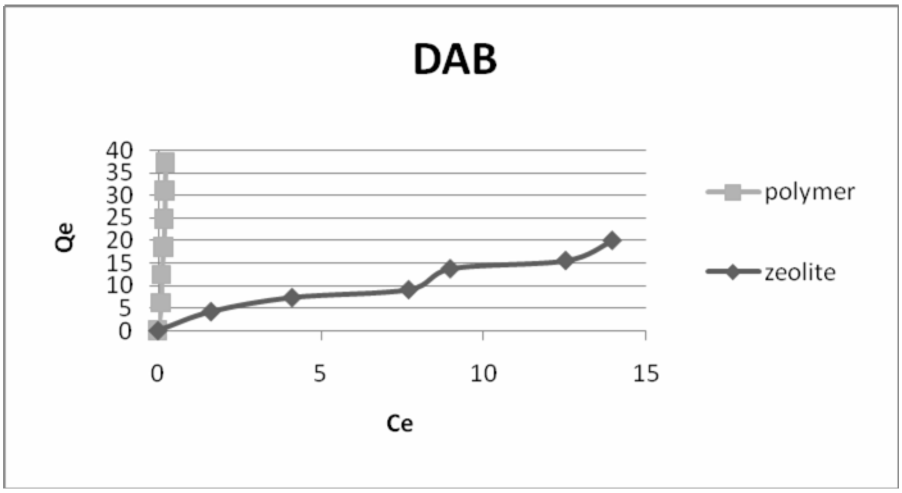


Figure (3-33) adsorption isotherms for "DAB" on the polymer and zeolite at 25 ºC at pH=7

Compare between adsorption on the polymer and zeolite for all compounds the quantity of adsorption for adsorbate molecules on the polymer is larger than that of the zeolite for three reason:

1- The swelling of the polymer is larger than zeolite.

2- The pore diameter of the zeolite 5Ǻ is regularly along the surface while the pores among the polymer net work is varying in size and diameter and generally are larger than 5Ǻ these factors leads to the following result:

A- The shape of adsorption.

Polymer	→	zeolite	
S2	→	S2	…ph
S3	→	S3	…nal
S2	→	S2	…B
S3	→	L3	…na
S3	→	L3	…AB
S3	→	L3	…DAB

B- Adsorption quantity for AB, and DAB on the polymer surface larger than adsorption quantity on zeolite surface that because found (-NH_2) groups which form positive ions in the solution and form physical forces with polymer surface also this molecules can not flow from zeolite pores while in polymer is easy to flow.

Conclusions

1. Polymer swellings were in the following orders:

   a- at pH = 8 > at pH = 7 > at pH =6

   b- With 0.1M NaCl > with 0.0M NaCl > with 0.2M NaCl

2. At temperature of 25 ºC at pH=7:-

   a- The adsorption mode was S-mode for all compounds (ph, na, nal, B, AB, and DAB)

   b- The adsorption quantities followed the following order

ph < nal < na < B < AB < DAB

3. The adsorption of all compounds was exothermic.

4. There was individual variation for the adsorption of each compound in relation to its ionic strength and pH effect.

5. The adsorption quantity of each of the compounds (ph, na, nal, B, AB, and DAB) was greater in the case of Triethanolamine-glycerylmaleate than on zeolite (5A).

Future work

a- Adsorption of other organic or inorganic compounds on the surface of this polymer to fine its ability to be used in the purification processes.

b- Adsorption of a mixture of compounds on this polymer.

c- Adsorption of each of the compounds in non aqueous solution.

d- Adsorption of each of the six compounds on other adsorbent than zeolite (5A) for comparison and validity.

e- Study the specific conductivity of the solution for all compounds before and after adsorption.

References

REFERENCES

1- H. Rachel Plattenberg "**Environmental Pollution**", Wiley, New York (2007).

2- R. D. Gupta "**Environmental Pollution**", London (2006), p.1.

3- B. J. Dutlka, Line, D. Jurkovic, A. Mcinis, R. Lee, H. B. Onuska, F. & S. S. Rao, **"Environ Toxico Water Qual"** (1998), 13, 313.

4- *D. Clifford & J. S. Thomas, **"Environ. Sci. Technol"**, (1986), 20(11), 1072.*

5- P. K.Goel, **"Water Pollution Causes, Effects and Control"** New Age International Limiter, Publishers, New Delhi (1997), p.64.

6- A. Kumar **"Industrial Pollution"**, Van Nostrand Reinhold Company, New York (2006), p.203.

7- R. K. Boutwell & D.K. Bosch, Cancer Research, (1959) ,19, 413.

8- R. vaidya & D.K. markandey **"Environmental pollution control"**, W. B. Sunders Company, London (2005), p.434.

9- B. K. Sinha & S. Choudhary **"environment Pollution & Health Hazards"**, (2008) , 249.

10- *M.A. Al-Omar, **"Environmental Pollution"**, Wail Publisher, Jordan (2000), p.171.*

11- T. H. Y. Tebutt, **"Principles of Water quality control"**, 2nd ed., Wiley,New York (1977), p.53.

12- A. C. Chris, **"Principles of Industrial Chemistry"**, Wiley, New York (1978), p.135.

13- G. R. Petyon & W. H. Glaze, Environ. Sci. Technol, (1988), 22(7), 761.

14- *J. Kochany & J. R. Bolton, Environ. Sci. Technol., (1992), 26(3), 262.*

15- *K. E. Lipczynka & Bolton, J. R. Environ. Sci. Technol., (1992), 26(3), 259.*

16- *J. W. Walter, Jr. Smith, & H. Environ. Sci. Technol., (1986) ,20(10), 970.*

17- F. G. Helfferich, chem.. Eng. Proc., (1977) ,50, 91.

18- *A. Fujishima, & M. Yasuhisa, Electro chem. J, .. Soc., (1981), 128(8), 1731.*

19- R. Kunin, chem.. Eng. Proc., (1977), 50, 95.

20- R. W. Legon, Chem. Eng., (1982), 89(2), 502.

21. A. I. Liapis, & Rippin, D.W. Chem. Eng.Sci., (1978) **,33,**593.

22. A. W. Adamson, **"Physical Chemistry of surfaces"** Wiley, New York (2001).

23. Mittal **"Physical Chemistry"**, McGraw-Hill Kogakusha, LTD., Tokyo (2009).

24. *U. Abdo, S. Nosier, & Y. Eltawil, , J. Environ. Sci. health, (1997)**, 32**, 1159.*

25. H. Kuhn , D. H. Waldck &Horst, **"Principles of Physical Chemistry",** Macmillan pulishing Co., London (2009).

26. *M. Doming, I. Fernandez, & F. G. Morals, J. Chromtog ., (1984) **,29**, 14.*

27. P. Atkins, V. walters & J. D. Paula,**" Physical Chemistry Volume 1:Thermodynamics & Kinetics",** 8th edition, Vani education books, India *(2006).*

28. *G. H. Giles, D.Smith & J. Colld. Intfc. Sci., (1982) **,47**, 755.*

29. *S.Brunauer, P. H. Emmett & J. Teller, Amer. Chem. Soc,(1938) **,66**,309.*

30. S. Brunauer, **"The Adsorption of gases and Vapours" Vol 1**, Princeton University Press, Princeton (1974).

31. *I. Langmuir, J. Amer. Chem. Soc, (1918)**, 40,** 1361.*

32. K. M. Awad, **“The Principle of Soil Chemistry”**, Basra University Press, Basrah (1986) (Arabic).

33. A.W. Adamson, **"Physical Chemistry of surface"**, Wiley, New York (1976), P.550, PP: 387, 388.

34. R. G. Mortimer, **“Physical Chemistry”**, Mir Publishers, Moscow (2008).

35. *M. D. Keith, J.Chem. Soc. Faraday Trans. I, (1973)*, ***69***, *1117.*

36. *T. Orhan , J. G. Chang & J. David, J. Phys. Chem., (1989)* ***,93***,*7294.*

37. A. Clark, **“The Theory of Adsorption and Catalysis”**, Academic Press, New York (1970).

38. *M. Thomas & P. Robert , J. Agr. Food Chem., (1965)* ***,13 (4)***, *334.*

39. *D. Barry & M. Cook , J. Phys. Chem., (1975)*, ***79(23)***, *2555.*

40. J. Williamp & L. Gary, Environ. Sci. Technol., (1995), **29(3)**, 807.

41. *S, A. Iesa, M. S. Al-Ameri & N. Y. Salman , Iraqi J. Chem., (2001),* ***27 (1)*** *, 207 (Arabic).*

42. *V. P. Ravi, R. V. Jarsa & T. S. Bhat, , J. Chem.Tech. Biotech., (1998),* ***71***, *173.*

43. K. K. Panaday , G. Prasad & V. N. Singh, *Wat. Res*., (1995)**, 19 (7)** ,869.

44. G. Mckay , M. S. Otterburn & A. G. Sweeney, *Wat. Res*., (1980) **,14, 21**.

45. Skoog, West, Holler & Crouch **“Fundamentals of Analytical Chemistry”**, 8th edition, Rinehart and Winstone, Inc., California (2004).

46. L. I. Antropov, **“Theoretical Electro Chemistry”**, Mir Publishers, 2ed edition, Moscow (1975).

47. J. C. Kuriacose & J. Rajaram, **“Chemistry in Engineering and Technology” Vol 1**, TATA McGraw-Hill Publishing Co. LTD.,

New Delhi (1984). & C. W. Frank, **"Analytical Chemistry"**, Academic Press, New York (1979).

49. *J. W. Mcginity & J. A. Hill, J. Pharm. Sci., (1975)* ***,64*** *, 1566.*
50. D.W. Break, **"Zeolite Molculer Sieves"**, John Wiley and Sons, New York (1973).
51. R. Szostack, **"Moleculer Sieves"**, 2ed edition, Blackie Academic and Professional, Atlanta (1990).
52. J. E. Huheey, **"Inorganic chemistry"**, Harper & Row, Harper International Edition, New York (1972).
53. P. A. Jacobs, **"Carboniogenic activity of Zeolites"**, Elsevier Scientific Publishing Com., Amsterdam (1977).
54. R. J. Crawford, "Plastics Engeneering", third edition, chapter one (2001).
55. I. M. Campbell, **"Introduction to Synthetic Polymers"**, Oxford University Press, second edition, (2000).

56- A.G. Zakharov & A.N.Prusov **"Theoretical and experimental peculiarities of adsorption from solutions"** Pure & Appl. Chem. 1996 , Vol. 68, No. 8, pp. 1569-1576.Printed in Great Britain. Q 1996 IUPAC

57. Y. S. (Eds.) Lipatov & L. M. Sergeva, Adsorption of polymers, Naukova Dumka, Kiev, (1972).
58. H. Sakai & Y. Imamura, Bull. Chem. Soc. Jpn**.,** (1987)**, 60**, 1261-1264.
59. C. B. Ching, K. Hidjat & M. S. Uddin, Chem. Abs.,(1989) 111, 103167z.
60. D. T. Al-Samarrmad, M.Sc. Thesis, College of Education –Ibn Al-Haitham, University of Baghdad (2002) (Arabic).
61. K. Z. Al-Eikedi, M.Sc. Thesis, College of Education- Ibn Al Haitham, University of Baghdad (2001) (Arabic).

62. A. J. Mohamed, Ph.D. Thesis, Collage of Education- Ibn Al-Haitham, University of Baghdad (2002) (Arabic).
63. G. McKay, M. S. Otterburn & A. G. Sweeney, Water Research, Pergamon Press Ltd., Britain , (1980)**, 14**: 15-20,.
64. E. Karadag, D. Saraydin & F. Aydin, J. Turk. chem..,(1998)**,22**: 227-236.
65. E. Longhinotti & et.al., Adsorption of the anionic dyes, Brazil, (1997).
66. *S. Kumar, N. Upadhya & D. Upadhya, J. chem. Tech. Biotechnol., (1987)**, 37**; 281-290.*
67. *K. Kobayashi, K. Araki, Y. Imamura & R. Endo, Bull. Chem. Soc. Jpn., (1990) ,**63**, 511-515.*
68. *M. Kawaguchi, S. Yamagiwa & A. Takahashi, J. Chem. Soc. Faraday I, (1990) ,**86**, 1383.*
69. *Y. S. Lipatov, G. M. Semenovich, L. M. Sergeeva & L. V. Dubrovina, J. Coll. Int. Sci., (1982)**, 86**,423-435.*
70. Y. S. Lipatov, L. M. Sergeeva, G. M. Semenovich, T. T. Todosiichuk, L. V. Dubrovina & V. N. Chornaya, Polym. Sci. USSR, (1981)**, 23**, 2641-2649.
71. *N. Pekel ,O. Guven & J.Turk. chem.., (2002) ,**26**:221-227.*
72. M. P. Stevens, **“Polymer chemistry on introduction”**, Oxford University press, Oxford (1999).
73. I. Safarik, M. Safarikova & V. Buricova, collect. Czech. Chem. common, (1995) ,1448- 1462.
74. *M. Itoh, J. phys. D. Appl. Phys., (1998), 31:463- 471.*
75. *M. Breidenich, R.R. Netz & R. Lipowsky, Eur. Phys. J., (2001),**5** :403-414.*
76. A. Ghazwan, M.Sc. Thesis, University of Al-Nahrain, 2004, pp.:34 39.

77. R. Wayne Sorenson, **“Preparative Methods of Polymer Chemistry”**, Second edition, (1968), p.688.

78. *R.I. Yousif, M. F. Tutunji , G. A. Derwish & S. M. Musleh, J. Colloid & Interface Sci., (1999),* ***216****, 348.*

79. I. Yousif, M.Sc. Thesis, University of Baghdad, 2004, pp.: 44-53.

80. Y. Gerasimov, **“Physical Chemistry”**, **Vol 2** Mir publishers, Mosco (1974).

الخلاصة

تم في هذه الدراسة تحضير بوليمر(محضر سابقاً) -Triethanolamine glycerylmaleate وشخص البوليمر المحضر بواسطة FTIR كما تم قياس تأثير الانتفاخ لهذا البوليمر في عدد من المذيبات .
وتم متابعة عملية الامتزاز باستخدام مطيافية الاشعة المرئية (فوق البنفسجية) لكل من المركبات (ph, na, nal, B, AB and DAB) في محاليلها المائية وفي درجات حرارة (25,35,45) مْ وفي أس هايدروجيني (pH=6) و (pH=8)
وأوضحت نتائج تلك الدراسات أن الشكل العام لامتزاز تلك المركبات على سطح البوليمر بدرجة 25 مْ يأخذ النمط (S) لجميع المركبات حسب تصنيف Giles .
أظهرت الدراسات النتائج الاتية :-

1- ان ترتيب المادة الممتزة يأخذ الترتيب التالي بدرجة 25 مْ

ph < nal < na < B < AB < DAB

2- الامتزاز ل (ph, na, nal and B) يأخذ الترتيب الاتي للشدة الايونية المختلفة

0.1M NaCl > 0.0M NaCl>0.2M NaCl

ولكن ل(AB and DAB) يأخذ

0.0M NaCl > 0.1M NaCl> 0.2M NaCl

3- يقل الامتزاز بانخفاض ال (pH) لهذه المركبات .
4- ان ΔH لجميع هذه المركبات سالبة .
5- اوضحت دراسة مقارنة الامتزاز لتلك المركبات على سطح الزيولايت أن البوليمر المحضر ذو قابلية أعلى لامتزاز المركبات وخصوصاً بالنسبة لل AB و DAB .

جمهورية العراق
وزارة التعليم العالي والبحث العلمي
جامعة النهرين
كلية العلوم
قسم الكيمياء

دراسة ازالة بعض المركبات الفينولية و الحوامض العضوية من محاليلها المائية على سطح البوليمر (ثلاثي ايثانول امين كليسيرايل ماليت)

رسالة
مقدمة إلى كلية العلوم- جامعة النهرين
وهي جزء من متطلبات نيل درجة الماجستير في الكيمياء

من قبل

محمد حسين علي
بكالوريوس 2003 (جامعة النهرين)

جمادي الثاني 1431 **حزيران 2010**