Republic Of Iraq
The Ministry Of Higher Education
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Al-Nahrain University
College Of Science
Department Of Chemistry

Study Of Adsorption Process For Some Dyes Compounds On The Surface Of (Triethanolamineglycerolmaleate) Polymer.

A Thesis
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in Chemistry

By

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June 2006 Jam’ady Al-Thany 1427

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الإهـــــــــــــــداء

الى معلمي الأول وقدوتي في الحياة أبي...

الى سيدة العاطفة ومنبع الحنان أمي...

الى الذي كان له فضل المؤازرة في عملي زوجي الغالي ...

الى روافد الوفاء أخواني الأعزاء...

الى قرة عيني وفلذة كبدي ابني مهند...

إليكم جميعا اهدي هذا الجهد المتواضع

نهى

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Nuha

Symbols and Abbreviations

ΔG	**Change of Gibbs free energy**
ΔH	**Change in enthalpy**
T	**Temperature**
ΔS	**Change in entropy**
X_1	**Mole fractions of solvent**
X_1^s	Mole fraction for solvent in the adsorption surface
X_2	**Mole fraction of solute**
X_2^s	**Mole fraction for solute in the adsorption surface**
b,a	**Langmuir constant**
C_e	**Concentration of solvent in the solution at equilibrium**
Q_e	**Concentration of solvent in the solid phase at equilibrium**
Θ	**Covered part from surface**
K_f, n	**Frindlich constant**
ASTM	**American Standard for Testing Material**
C_o	**Initial concentration from solvent in solution**
m	**Weight of adsorbate**
r	**Correlation coefficient**
R	**Gas constant**
Xm	**highly adsorbate**

BET	**Brunauer- Emmett-Teller**
t	**time**
PS	**Poly styrene**
PMMA	**Polymethylmethaacrylate**
MO	**Methyl orange**
SO	**Sudan orange**
MV	**Methyl violet**
MB	**Methylene blue**
min.	**minute**
N	**Avogadro’s number**
M.Wt	**Molecular weight**
S	**Surface area**
M	**Molar**
L.O.I.	**Lost On Ignition**

Summary

Triethanolamine – glycerol maleate polymer was prepared, and identified by F.T.I.R. spectroscopy then swelling tests were performed for this polymer in different solvents.

The adsorption processes of the some dyes compounds: **MO, MB, MV** and **SO** in aqueous solutions on the surface of this polymer were investigated by the use of UV–visible spectrophotometry and also studied at different: temperatures, ionic strength, and pH.

Results revealed that the adsorption for compound at temperature of 25 ^{o}C took: **S**- mode for **MO, MB** and **MV** while it was **L**-mode for **SO** according to Giles classification.

1- At temperature of 25 ^{o}C the adsorbate arrange to the following order:

MV>MB>SO>MO

2- No deferent pattern was noticed with regard to the adsorption quantities according to the ionic strengths.

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

4- The adsorption for all compounds was exothermic with distinction **MB, MV** there was absorption process too.

5- In comparison with zeolite (5A) the prepared polymer posse's higher ability to adsorbed **MV, MO** and **SO** while it was lower to **MB**.

Contents

Chapter two: Materials and Methods

Chapter three: Results and Discussions

List of Tables

Chapter Two

Chapter Three

List of Figures

Chapter one

Chapter Two

Chapter Three

Chapter *1*

Introduction

Chapter One: Introduction

Chapter One: Introduction

1.1. Adsorption from Solution

Generally adsorption could be defined as a phenomenon of a material aggregation as ions or molecules or atoms on a surface of another material [1]. 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 [2].

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:

$$\Delta G = \Delta H - T\Delta S \quad \text{(at isothermal conditions)}$$

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 chemisorptions. The major differences between them are in the field of interaction forces between the adsorbate particle 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". [3]

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 [4].

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" [5]. 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 [6].The incorporation process of adsorbent and adsorbate without distribution is termed "incorporation".

1.2. 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 [7].

Giles [8] 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 adsorbate's 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.

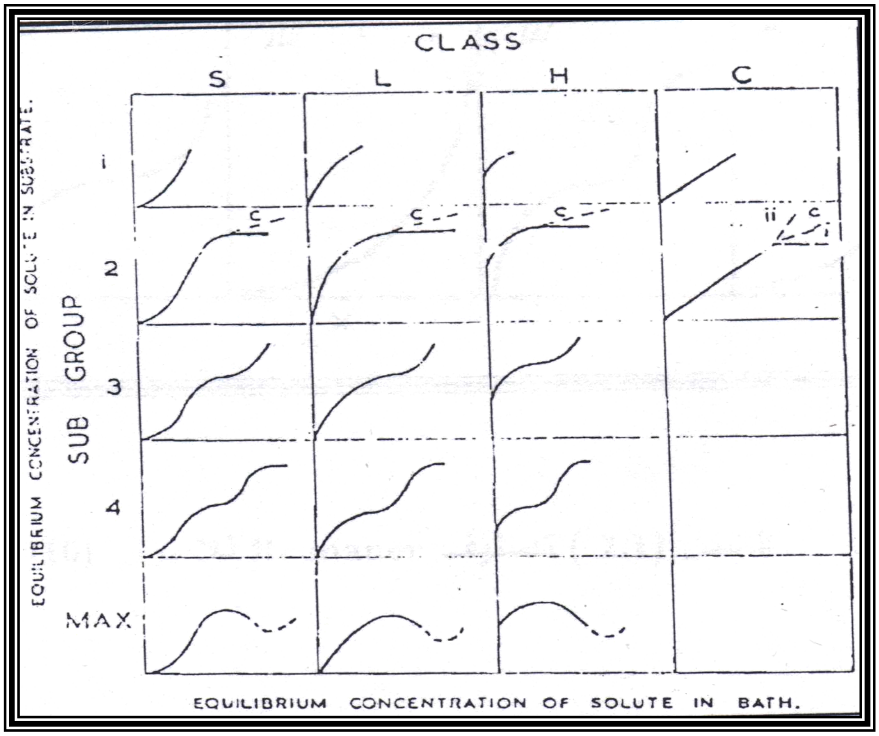

Figure (1-1) Adsorption Giles classification [8].

Brunauer –Emmett-Teller [9], 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 and adsorbate, while **Class IV** is similar to **Class I**, but there is 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.

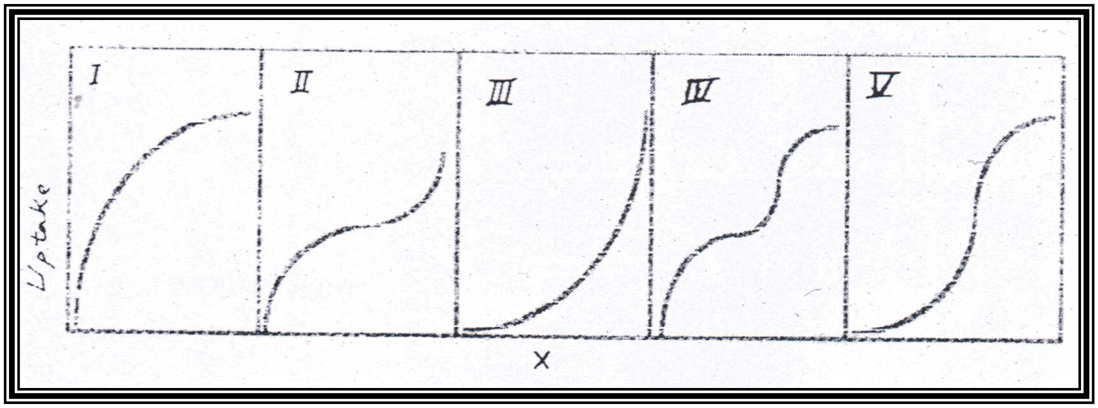

Figure (2-1) Adsorption Brunauer classification [10].

1.2.1. Langmuir Equation for Adsorption

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 [11].

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:

$$A + B \rightleftharpoons A + B \qquad (1\text{-}1)$$

solute in solution	solvent in adsorption layer	solute in adsorption layer	solvent in solution
X_2	X_1^s	X_2^s	X_1

Where x_1, x_2 are the mole fractions for solvent and solute, respectively in solution, X_1^s X_2^s are the mole fractions for adsorbed solvent, and solute respectively, on the surface of the solid phase at the equilibrium.

$$\mathbf{K} = X_1 X_2^s / X_2 X_1^s = a_1 X_2^s / a_2 X_1^s \qquad (1\text{-}2)$$

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

$$b = X_2^s / a_2 X_1^s \qquad (1\text{-}3)$$

At equilibrium, the solute activity a_2 could be approximated to the concentration at equilibrium of the solute Ce, and the summation of mole fractions for solute and solvent in adsorption layer will be equal to 1, so:

$$X_2^s = {}^{bCe}\!\diagup_{1+bCe} \qquad (1\text{-}4)$$

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

$$\theta = {}^{n_2^s}\!\diagup_{n^s} = X_2^s = {}^{bCe}\!\diagup_{1+bCe} \qquad (1\text{-}5)$$

Where θ is part of unoccupied site by adsorbate particles, and since the quantity of adsorbate for each gram of adsorbent is directly proportional with θ then:

$$Q_e = K\,\theta \qquad (1\text{-}6)$$

$$Q_e = {}^{KbCe}\!/_{1+bCe} = {}^{aCe}\!/_{1+bCe} \qquad (1\text{-}7)$$

$$Ce/Qe = 1/a + b/a\; Ce \qquad (1\text{-}8)$$

Plotting Ce/Qe against Ce, straight line is obtained with a slope equals b/a, and an intercept equals $1/a$.

1.2.2. Freundlich Equation of 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:

$$Q_e=K_fC_e^{1/n} \qquad (1\text{-}9)$$

Where Q_e is the quantity of adsorbate on (1 gm) of adsorbent at equilibrium, C_e 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 [12].

The natural logarithm of the equation is in linear formula:

$$\ln Q_e = \ln K_f + {}^{1}\!/_{n} \ln C_e \qquad (1\text{-}10)$$

Plotting lnQe against lnCe, a linear straight line is obtained with slope equals1/n, and the intercept equals ln k_f [13]

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

1.3. Factors Influencing the Adsorption process

1.3.1. 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 [14]. While porous surface affects on the quantity as well as selectivity [15, 16].

The homogenousity of the surface makes the adsorption isotherms match with theoretical interpretation proposed for adsorption in contrast to the non-homogenous surface. [17] Where the adsorption capacity for a variety of materials increases as the surface area of adsorbent increases too.

1.3.2. Nature of Adsorbate

As mentioned previously, the polarized surfaces of adsorbent tend to adsorb the high quantity of polar component in solution [18]. More over, the adsorption quantity increases as the molecular mass of adsorbate increases, and it decrease, as the solubility increases. [19, 20].

1.3.3. 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 [2] which suggests that adsorption quantity of aliphatic carboxylic acids increases 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) with 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.

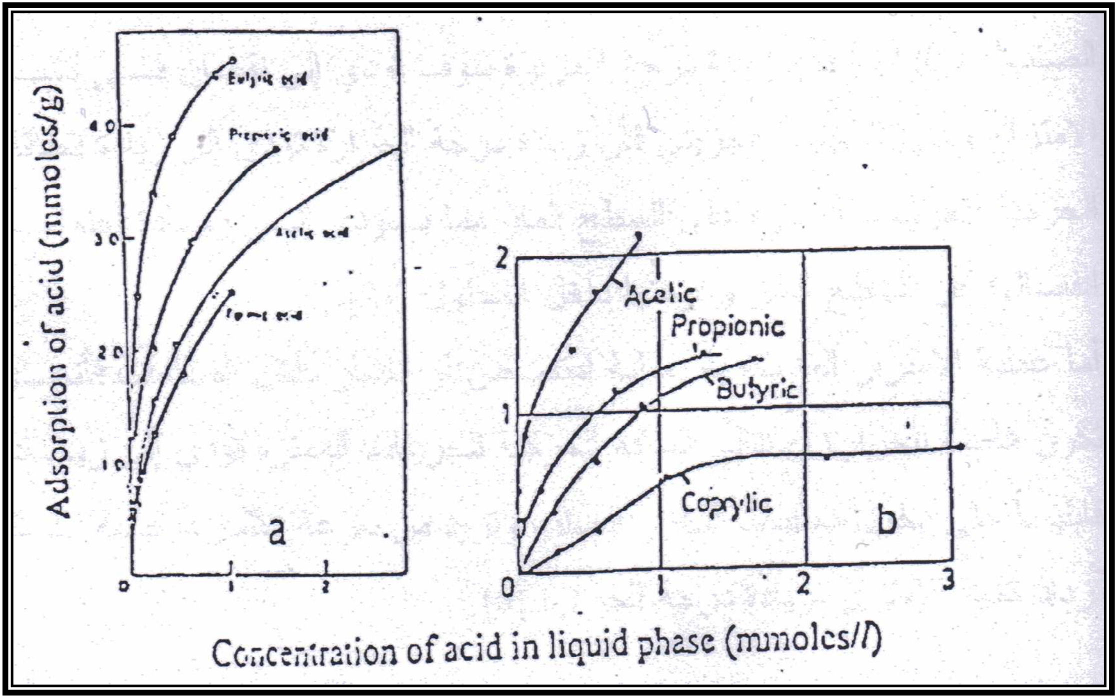

Figure (3.1) Adsorption of carboxylic acid.

a. Adsorption of carboxylic acid on the carbon surface from aqueous solution.

b. Adsorption of carboxylic acid on the silica gel surface from toluene [2].

1.3.4. pH effect

The effect of solution pH on the adsorption process is being different, as the difference in adsorption system. The acidity change, which that lead to increase the solubility of adsorbate in solution, decrease adsorption process. While the changes which lead to decrease the solubility of the adsorbate molecules increase adsorption process [21]. Also, in the case of surfaces that have polarized or charged sites, the adsorption will increase if the surface has opposite charged to the adsorbing particles throughout the effect of acidity.

In contrast the adsorbing quantity decreases if the surface charges are similar to charge the adsorbing particles [12].

1.3.5. Temperature Effect

It is known that adsorption process is exothermic [3] unless there is companying an absorption or distribution process inside the porous solid phase [22, 23]. 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 [24].

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, adsorption quantity increases as the temperature increases [6].

$Rate = \sqrt{T}$ Rate adsorption $= Ae^{-\frac{Ea}{RT}}$

1-3-6. Ionic strength Effect

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

For adsorbate, if it is in an ionic form increasing ionic strength lead 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 [25, 26].

Whereas, the non-ionic adsorbate, the ionic strength may lead to the occurrence of salting-out process, which decreases the solubility and increase the adsorption process [27].

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 [28].

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 charged adsorbent surfaces with similar charges to the adsorbate particles, increasing ionic strength will cover the adsorbent by a layer of opposite charge to the adsorbate, which leads to increase adsorption process [21]. While if the surface has opposite charge to the adsorbate particles, then increasing ionic strength will decrease adsorption quantity [29, 2].

1.4. Zeolites

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 artificids contains in the structure other than those within aluminosalicylic acid like phosphorus, gallium and germanium [30].

Zeolite as a word, is of Greek origin contains two parts, the first means (stone) and the other means (boiling) [31]. 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 are 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 and AlO_4 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.

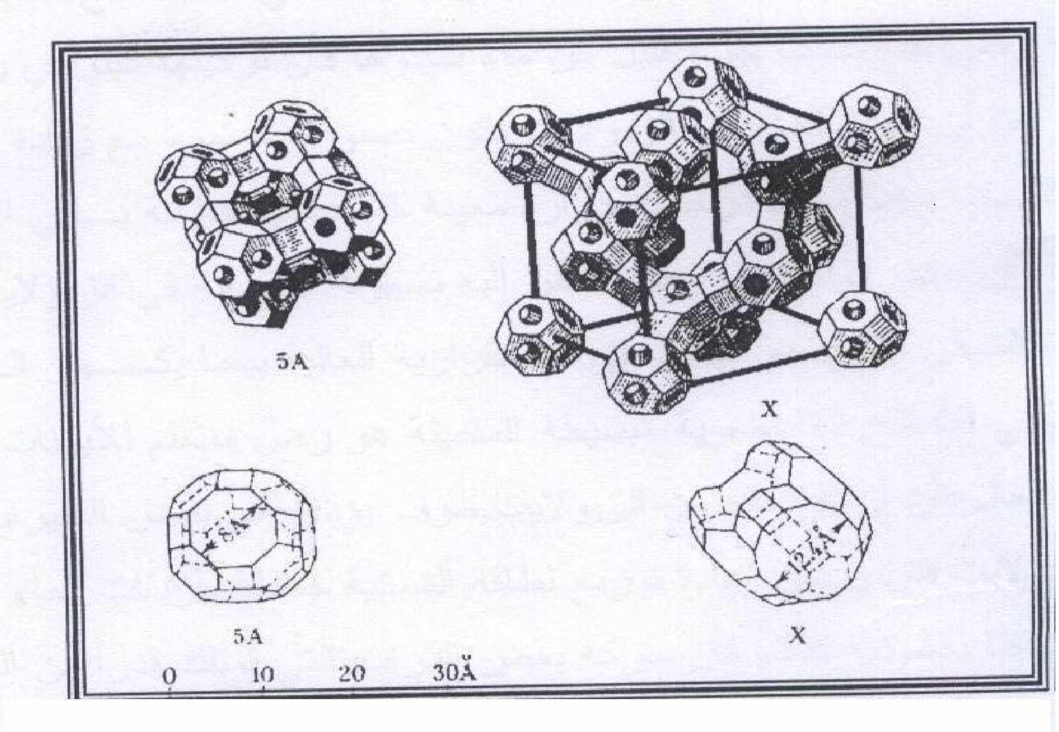

Figure (4-1) The crystallized structure of zeolite (5A) and zeolite X [14].

The molecular formula for zeolite can be shown as [32]:

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

Where n = the metal equivalent.

The structural formula for zeolite can be representing by the structure of its crystallized cell as [30]:

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

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 [33] and also in miscellaneous industries for drying gases. The previously stated structure of zeolite (5A) gives the crystals of this compound their net shaped skeleton with intervening cannals 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 moleculars according to their size and shape [31].

1.5. Adsorption of organic pollutant materials from solution:

The adsorption on polymers at solid-liquid interfaces has been studied extensively in recent years [34, 35].

Ching and Collages [36] used the technique of (Solid-Liquid Chromatography) (SLC) 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. They are noticed that zeolite adsorbed quickly but with marked difference in concentration at equilibrium also in diffusion velocity in between crystals also them is noticed that the largest amino acid molecule in size is the least concentration at equilibrium.

Al-Samarmed [37], identified adsorption isotherms for some aldehyde compounds on the surface of the zeolite (5A) the results followed Freundlich equation this study insect also the effect of temperature, PH and ionic strength on the process of adsorption.

AL-Eikedi [38] and the results elucidated that the adsorption on the surface of both zeolite increased by the increase in acidity of the solution.

Mohammed [39] studied synthesis and characterization of zeolit –urea formaldehyde polymer complex and study of adsorption of some phenolic compounds from aqueous solution on its surface. Using FT.IR spectroscopy and x-ray diffraction pattern .showed that the effect of temperature, pH, and Ionic strength on the adsorption process.

McKay, Otterburn and Sweeney [40] studied the removal of color from effluent using Silica as rate processes. They 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. They also determined the activation energy for dye removal.

Karadag, (*et.al*.)[41] studied removal of water-soluble cationic dyes with TriSyl Silicas , by investigating the adsorption of certain water-soluble cationic dyes , (basic blue 9, basic blue 12, basic blue 17, brilliant cresyl blue , janus green B, basic green 4, basic violet 1, basic violet 3, and thionin) onto TriSyl Silica by batch adsorption at 25 C. They found Langmuir type adsorption.

Longhinotti, (*et. al)*. [42] studied the adsorption of anionic dyes on the biopolymer chitin, the adsorption of the anionic dyes orange IV, orange G ,and xylenol orange on chitin, employing the Langmuir isotherm found that the adsorption capacity is dependent on pH , and the rise in the temperature reduces adsorption capacity by chitin.

Kumar, and Upadhyay [43] studied removal of Phenols by adsorption on Fly Ash, them found that the Freundlich isotherm is more suitable for all the systems investigated in their study on adsorption of phenol and cresol and their mixtures from aqueous solutions on activated carbon and fly ash, also on the effects of contact time and initial solute concentration and the isotherm parameters evaluation.

Polymer adsorption at solid surfaces is important in a variety of fields, such as material and food sciences, medical science, and stone conservation [44].

Kawaguchi *et.al*. [45]. Have studied the adsorption of PS and PMMA onto silica surfaces by I.R. .and Lipatov (*et.al*.) [46, 47] have studied the adsorption of a mixture of PS and PMMA onto the same surfaces.

Pekel and Guven [48].studied the effect of solvent, temperature and concentration on the adsorption of poly (n-Butyl methacrylate) on alumina from solution by using UV. And F.T.I.R. photoacoustic spectroscopy techniques, the results obtain are in conformity with Langmuir's isotherm.

Dasare and Anand[49] studied the adsorption of some phenols in aqueous solutions by using Styrene-divinylene benzene copolymer as permeable adsorbate their study includes also effect of pH and Ionic streagth.

Safarik, (*et.al*.)[50] studied the sorption of water soluble organic dyes on magnetic poly(oxy-2,6-Dimethyl-1,4-phenylene)(PODMP)by using magnetic(PODMP) for sorption of water soluble organic compounds (dyes belonging to triphenylmethane, hetropolycyclic and azo dye groups)from water solutions . The found in general that the hetropolycyclic dyes exhibited the lowest sorption.

Itoh (*et.al.)* [51], studied photo modification of polymer films: 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 atmospheric oxygen are suggested as another possible origin for the holographic recording.

Breidenich, (*et.al*.)[52], studied the adsorption of polymers anchored to membranes and found that if one includes the finite size of the anchor segment, the membrane bends towards the polymer for sufficiently strong adsorption

1.6. THE AIM OF THE WORK

The aim of this work is to study the possibility of using a cross linked polymer (Triethanolamineglycerolmaleate) as adsorbent for some organic dyes from aqueous solution and its efficiency and comparing its efficiency with zeolite.

The molecular formula for polymer can be shown as:

$$-[---C_{13}H_{25}O_{9}N--]-\ n$$

Chapter 2

Materials & Methods

Materials & methods

2.1. Chemicals and instruments

2.1.1. Chemicals

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

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

Substance	Source	Purity %
Tri-ethanol amine	BDH	99.9%
Glycerol	BDH	99.9%
Maleaic anhydride	Fluka	99.9%
Ethanol	Fluka	99.9%
Ether	Fluka	99.9%
De-ionized water	Lab.	R= 16 mΩ
Methyl orange	Fluka	99.9%
Methyl violet	HW	99.9%
Methylene blue	BDH	99.9%
Sudan orange	Fluka	99.9%
Sodium chloride	BDH	99.9%

Where

R= resistance

mΩ= ohm (resistance unite)

2.1.2. Zeolite

Zeolite can be obtained from the Alraia Company and the molecular formula:

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

As shown in table (2-2):

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

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

2.1.3. Instruments

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

Table (2-3): Instruments used in research

Instrument	Remarks
UV-Vis	SHEMADZO spectrophotometer
pH-meter	Expandable ion analyzer
Oven	MEMRERT 854 Schwabach
Balance	SARTORIUS portable
Centrifuge	HARAEUS sepatech labofuga A
Millipore filter paper	WHATMAN sterile membrane filter paper (size 11.0 cm)
Magnetic stirrer with hot plate	JLASSCO (India).
Water bath	PRECISTERM-TAFESA-W .Germany (0-100).
Mesh	200mm DIAx50mm ASTM E11 300 micron part no. 60132000300 Serial no. 03012571
Water bath shaker	COMPENSTATE with citenco motors F.H.P. England.
F.T.I.R.	SHEMADZO spectrophotometer (8300).Japan.
Sand bath	locally

2.2. Methods

2.2.1. Preparation of poly (triethanolamine-glyceryl maleate)[53]

In a 100 ml round-bottom flask immersed in a sand bath and equipped with a thermometer and magnetic stirrer a mixture of triethanolamine and Glycerol (7.48 gm, 0.05 moles) and (4.66gm, 0.05 moles) were placed. The mixture is heating with magnetic stirrer for 15 min. and (14.7gm, 0.15mole) of maleic an-hydride was added to the mixture after the temperature 100 ^{o}C and raised gradually to 140 ^{o}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 ^{o}C over night.

2.2.2. Determination swelling of the poly (triethanolamine-glyceryl maleate)

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

The weight of the polymer was measured each (24) hour until the weight of the swelled polymer becomes constant. The degree of swelling was calculated according to equation [54].

$$\Delta m = (m_t - m_o)/m_o \times 100$$

Where

m_o= weight of dry sample.

m_t = weight of swelled sample

Δm =swelling percentage.

2.2.3. Surface area calculation [55]

Surface area can be calculated in this work (for MB) according to the following equation:

$$S = Q_e \times N \times A \;/\; 1000 \times M.Wt.\ of\ MB$$

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

2.2.4. Sample solution preparation

A 100 ppm stock solution of (MB, MV, MO and SO) was prepared by dissolving (0.05 gm) of each compound in 500 mL of deionized water.

Other standard solutions, with concentration of (5-30) ppm, were prepared by subsequent dilution using deionized water of the stock solution.

2.2.5. Determination of λ max and calibration curve

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

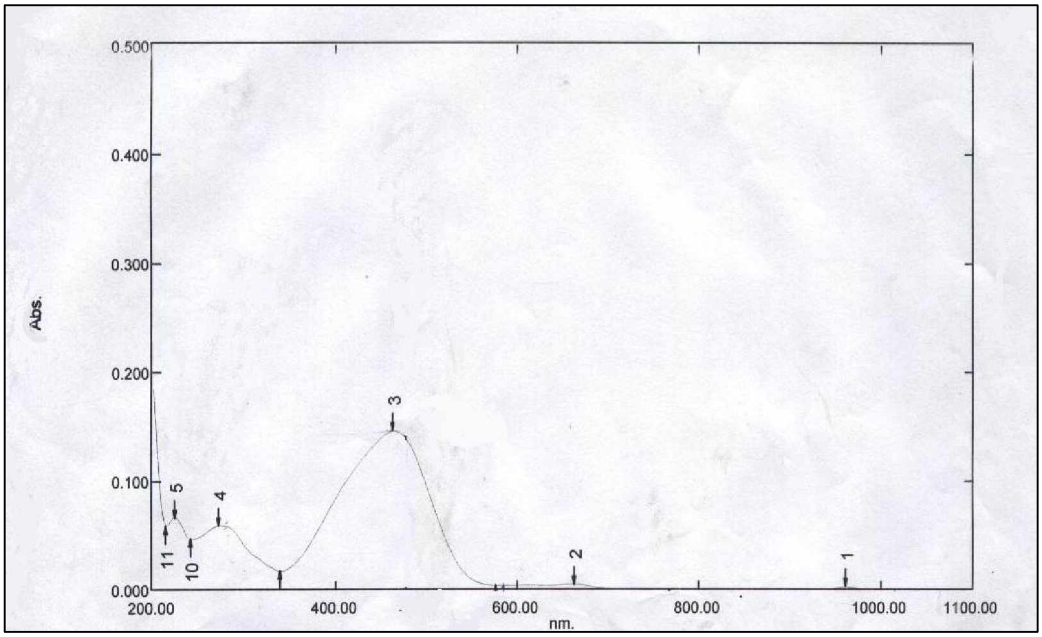

Figure (2-1) Maximum wavelength for MO compound.

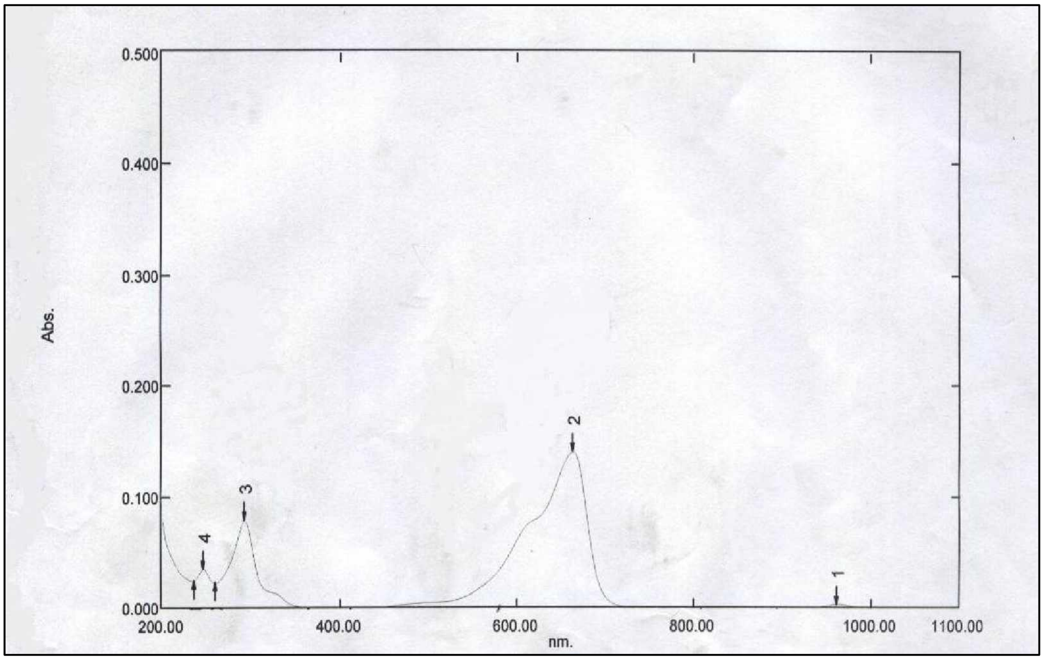

Figure (2-2) Maximum wavelength for MB compound.

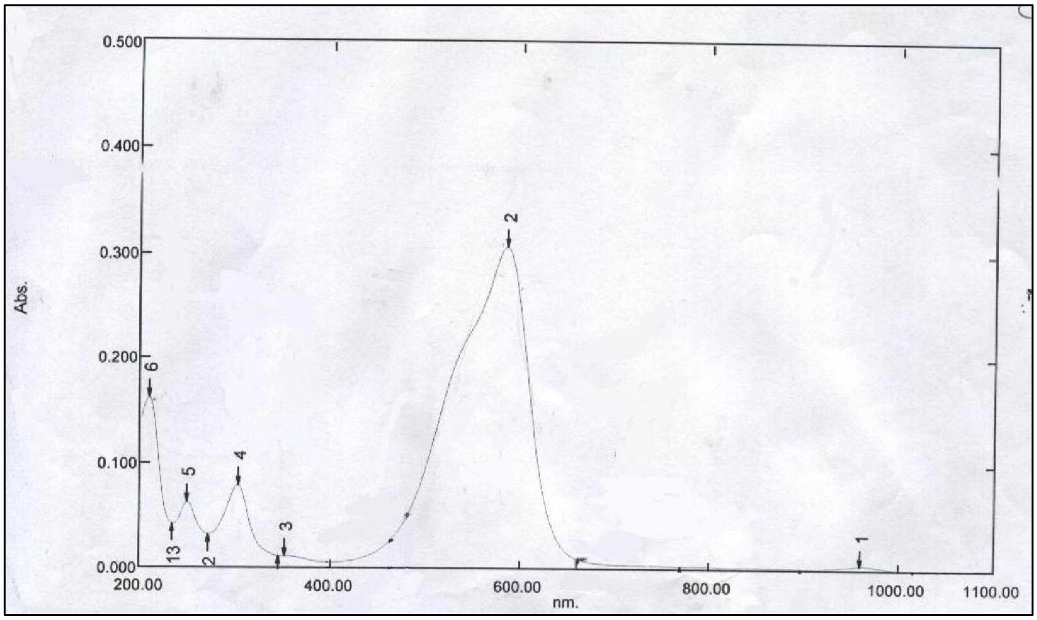

Figure (2-3) Maximum wavelength for MV compound.

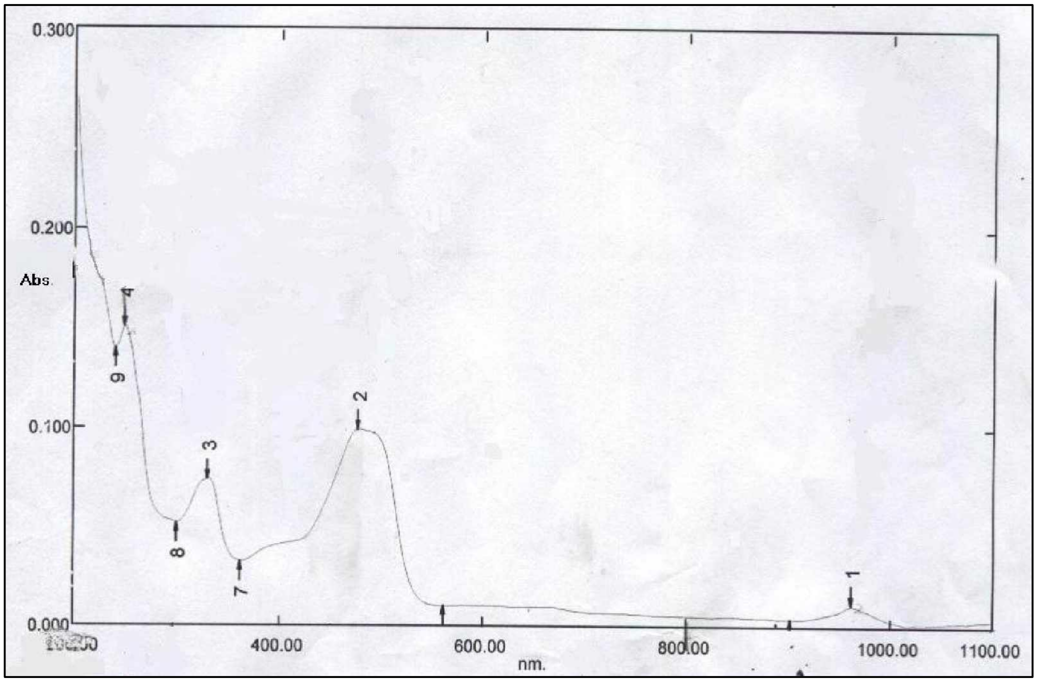

Figure (2-4) Maximum wavelength for SO compound.

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.

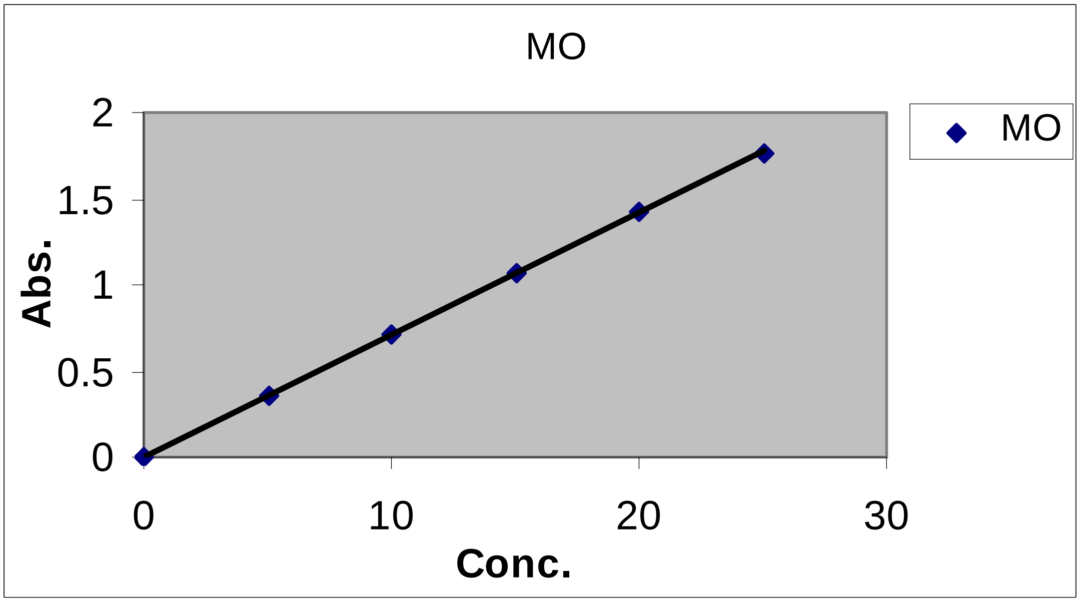

Figure (2-5) Calibration curve for MO compound, and (r = 0.9999).

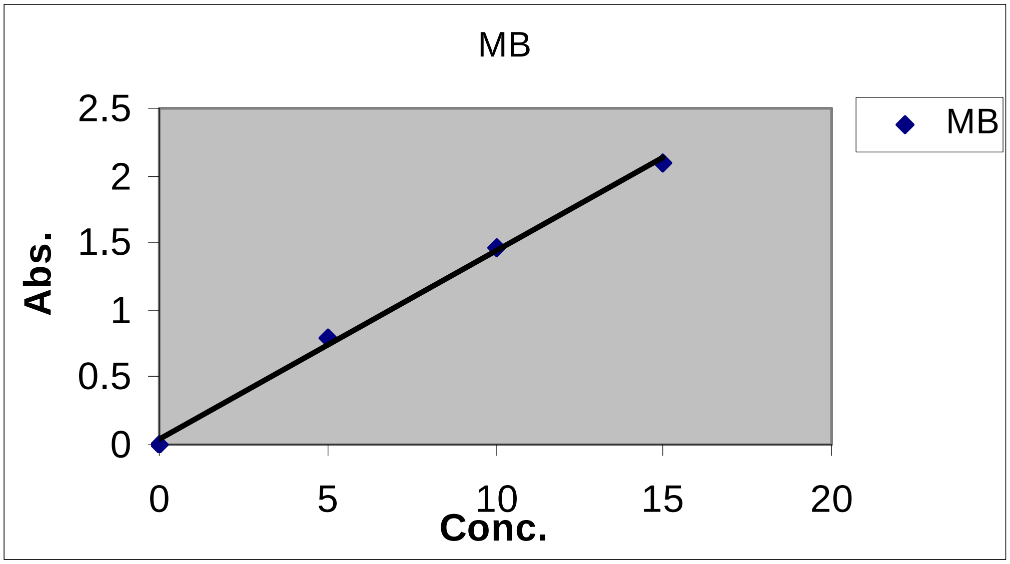

Figure (2-6) Calibration curve for MB compound, and (r = 0.9987).

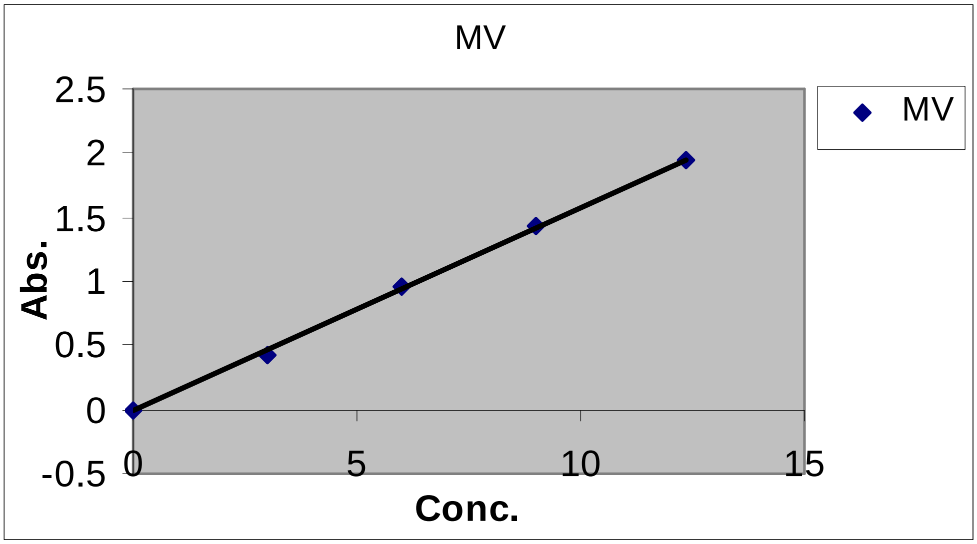

Figure (2-7) Calibration curve for MV compound, and (r = 0.9995)

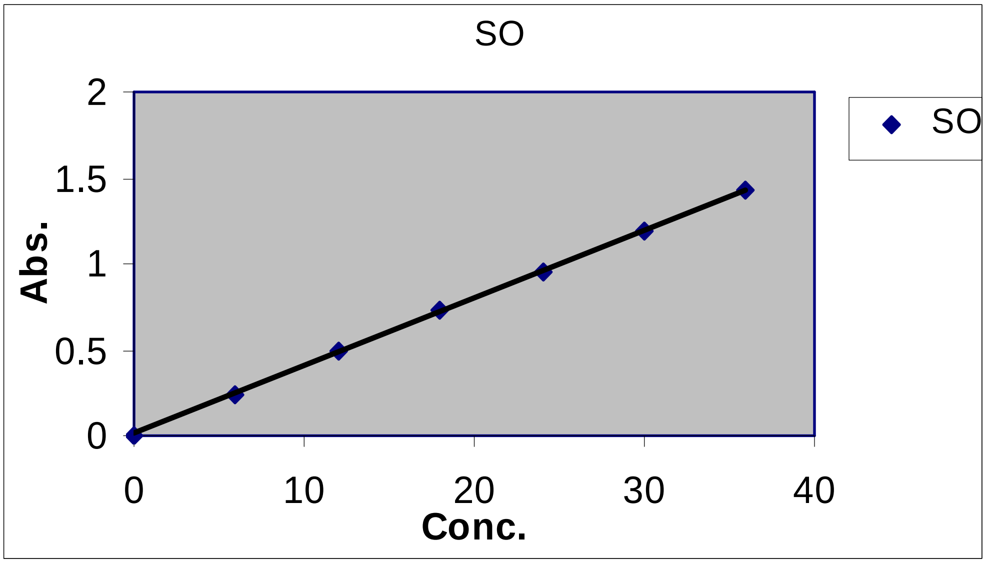

Figure (2-8) Calibration curve for SO compound, and (r = 0.9997).

2.2.6. Determination of equilibrium time

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

2.2.7. Adsorption Isotherms on polymer:

In order to determine the adsorption isotherm for each compound, 6 conical flasks has been used, containing (0.01 gm) of polymer. Then 10 mL of absorbent has been added into the flask which has a concentration ranged between (5-30) ppm. After closing, the flasks were shaken with water bath shaker at 25 ^{o}C according to the equlibrium time of the reaction. After that they are centrifuged for 10 minutes. UV-Vis spectrophotometer has been used to measure the absorbance for the solutions, at the convenient wavelength for each compound. The values obtained of absorbance have been used to determine the equilibrium concentration of calibration curve.

2.2.8. Study the factors affecting adsorption

2.2.8.1. Effect of Temperature

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

2.2.8.2. pH effect

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

2.2.8.3. Ionic strength

The effect of ionic strength effect has been performed on the following compounds (MO, MB, MV, SO), at different ionic strength values. With fixed amount of adsorbent i.e. (0.01gm), sodium chloride solution of concentration (0.1, 0.2) M has been used and the effect of this salt on adsorption has been recorded.

2.2.9. Adsorption Isotherms on Zeolite:

In order to compare the adsorption between the polymer and zeolite, the adsorption isotherm of compounds (MO, MB, MV, SO) were determined following the same procedure used in the determination of the adsorption isotherm in the polymer.

Chapter 3

Results & Discussion

Chapter Three: Results & Discussion

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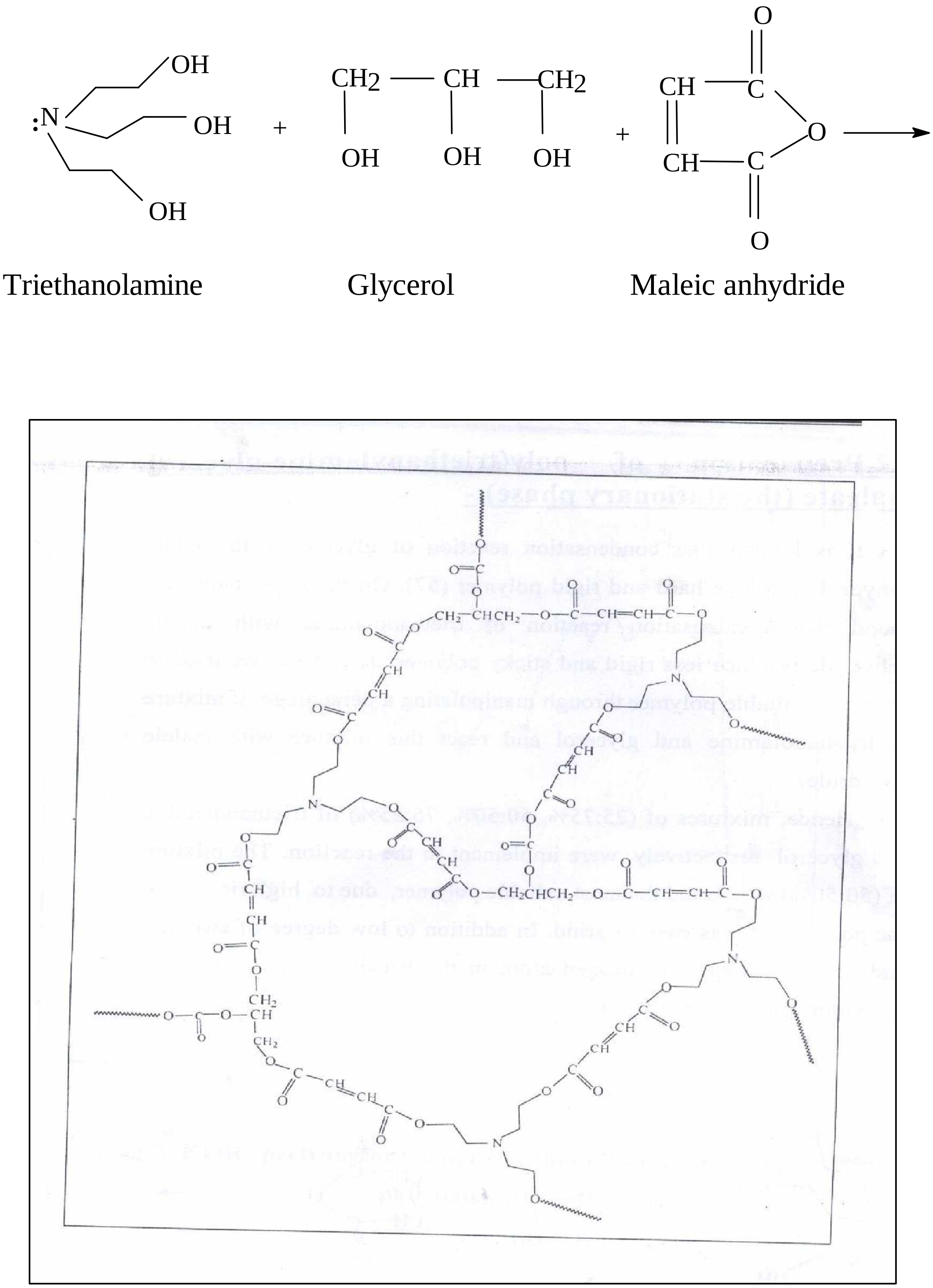
1. Preparation of Poly (triethanolamine-glycerylmaleate):

It is known that condensation reaction of glycerol with maleic anhydride produced hard and rigid polymer [54].On the other hand; we found that condensation reaction of triethanolamine with maleic anhydride produce less rigid and less sticky polymer. Therefore, we tried to prepare a suitable polymer through manipulating a percentage of mixture of triethanolamine and glycerol and react this mixture with maleic anhydride.

Hence, mixtures of (25:75%, 50:50%, 75:25%) of triethanolamine and glycerol, respectively, were implementing in the reaction. The mixture of (50:50 %) was found the most suitable polymer, due to high rigidity, and easy to grind. In addition, the polymer has low degree of swelling and a number of nitrogen atoms in its structure, as shown in reaction scheme (3-1):-



Scheme (3-1) The suggested structure of the prepared poly (triethanolamine-glycerylmaleate) chains.

This polymer was identified by F.T.I.R. spectra as shown in the figure (3-1).The figure indicate some distinguished peaks at {1728, 1263, 1591} 1/cm which represent the carbonyl group, C-O bond in the ester group and carbon-carbon double bound, respectively.

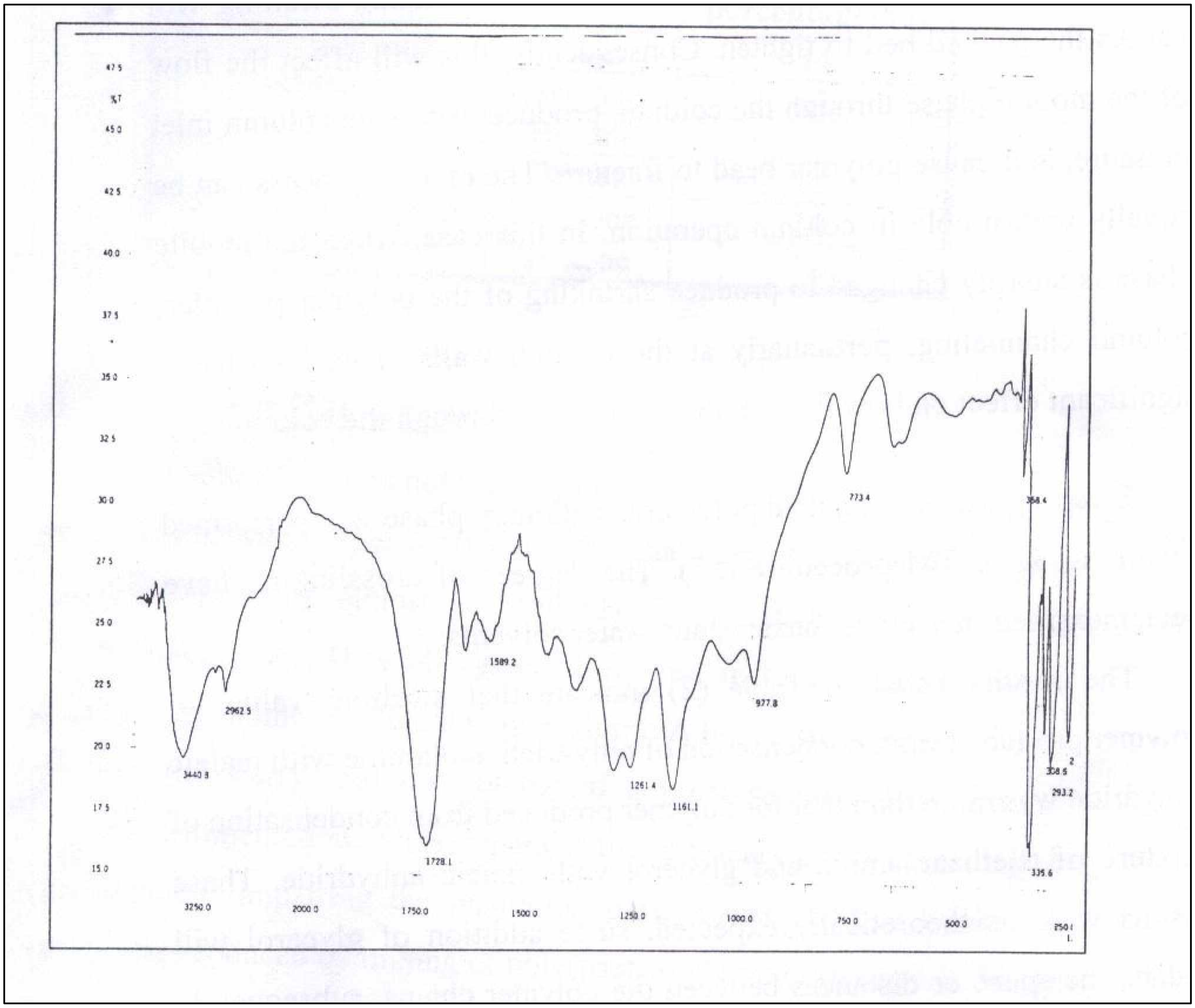


Figure (3-1) F.T.I.R. spectrum of the prepared polymer.

3.2. Swelling Of The Polymer:-

Swelling test for the prepared polymer was performed according to ASTM procedure [54]. The degrees of cross linking have been measured in water at pH=7, pH=6, pH=8, and 0.1M NaCl solution, 0.2M NaCl solution, at 35 °C , and at 45 °C. Swelling of zeolite has been done on the same method.

The results listed in table (3-1):-

The polymer	Solvent	Swelling percentage %
Poly(triethanylamine glyceryl malate)	Water pH=7,at 25 °C	28.4
	pH=6, at 25 °C	19.82%
	pH=8 ,at 25 °C	41.846%
	0.1M NaCl ,at 25 °C	37.313%
	0.2 M NaCl , at 25 °C	27.692%
	35 °C	18.181%
	45 °C	29.411%
zeolite	pH =7,at 25 °C	21.4%

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

3.3 Surface area measurement [55]

MB compound can be used to calculate the surface area of the polymer, then the results shown as below in the following equation:

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

$$S = Qe_{max} \times 160 \times 6.023 / 374$$

$$S = 27.44 \quad m^2/gm$$

3.4. Adsorption

3.4.1. Adsorption Isotherms:

Adsorption of compounds (MO, MB,MV and SO) in aqueous solution at 25°C, and pH 7, was investigated using less than 300 μm diameter granules of the polymer of (0.01) 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 [21]:

$$Qe = \frac{Vsol\,(Co - Ce)}{m}$$

Where:

Qe= the quantity of adsorbate in mg/g

V= the total volume of the adsorbate in L

Co= is initial concentration of solution in mg/ L

Ce= is concentration at equilibrium of adsorbate in mg/L

m= weight of adsorbent in (gm)

The results of the adsorption are listed in table (3-2)

C_O mg/L	MO		MB		MV		SO	
	C_e mg/L	Q_e mg/g	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	3.985	1.015	4.77	0.23	3.9614	1.0386	3.8345	1.1655
10	7.7532	2.2468	9.9662	0.0338	8.2221	1.7779	8.596	1.404
15	12.216	2.784	14.079	0.921	11.6335	3.3665	10.125	4.875
20	16.4073	3.5927	16.8184	3.1816	16.597	3.403	13.659	6.341
25	19.656	5.344	17.978	7.022	21.5342	3.4658	18.045	6.955
30	24.654	5.346	19.352	10.648	24.9716	5.0284	23.9598	6.0402

Table (3-2) Illustrates the values of Ce, and Qe for compounds (MO, MB, MV, SO) at 25°C.

The results have given the isotherms which are shown in figure (3-2)

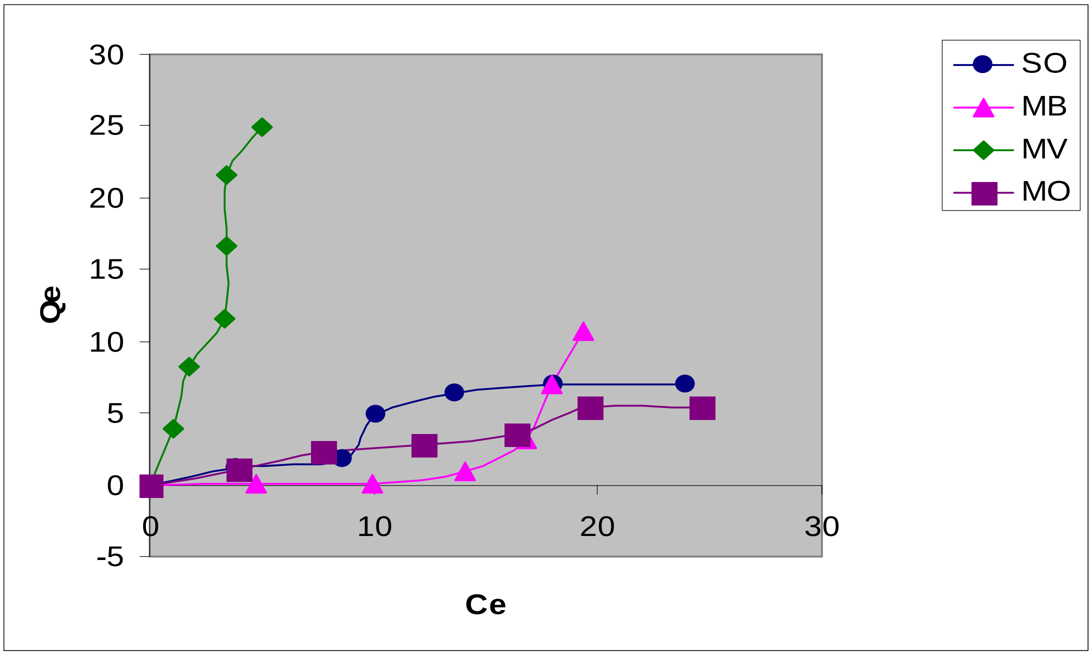


Figure (3-2) Shows the adsorption isotherms for MO, MB, MV, SO at 25^{o}C.

From figure (3-2) and according to Giles classification [8, 56], the adsorption mode for MB is **S_1** which indicates that the configuration of molecules on the surface of polymer is a vertical and a monolayer adsorption. For MV and MO the adsorption follow **S_3** mode, thus the molecules for both would be arranged also vertically on the surface of polymer but with a multilayer adsorption. Therefore, these results suggest that the adsorption isotherm for compound MB, MV and MO are of Freundlich type.

From the same figure and according to same classification SO follows **L_3** adsorption mode. Thus its molecules would be arranged horizontally on the surface of the polymer with a layer adsorption, and the adsorption isotherm for this compound is of Langmuir type.

As previously mentioned, the general form of adsorption isotherms for compounds (MO, MB, and MV) are of type (**S**) according to Giles's classification [56].

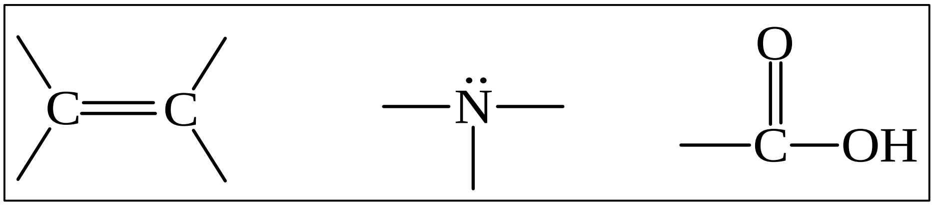
The theoretical treatment for the **S** adsorption mode [57] illustrates that the desorption activation energy depends upon the concentration of adsorbate on the adsorbent, and the process of solvent adsorption may contribute to the decrease in value of this activation energy.

The **S** mode is often indicated produced from adsorption process in which the molecules of the solvent and the solute were on the adsorbent. The adsorbed molecules of the solute were arranged by clusters vertically on the adsorbent [58]

Figure (3-2) shows also, that the amounts of the adsorbate compounds adsorbed are arranged as:

MV>MB>SO>MO

At the mentioned condition. This could be explained on the basis of the functional groups of the used polymer as adsorbent. This polymer contains alkene, amine and carboxyl groups [53]



These groups are of high or moderate electron density, so the polymer may be considered as a negatively charged species, thus the interaction between the polymer and adsorbate, which carries a positive charge, will be strong. This explains why the adsorbed quantity of each of the positive charge MV and MB, is very high. It is much higher than that of the negative charge (SO and MO compounds) [59].

The adsorbed quantity of MV is higher than that of MB, and for SO is higher than MO. This result could be attributed to the differences in the molecular weight of each compound. The molecular weight of MV is higher than that of MB, hence the solubility of MV is less than that of MB, and since that adsorption quantity is inversely proportional with its solubility [2].

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

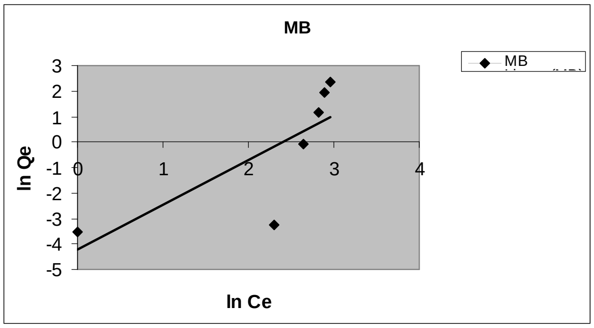
$$\ln Qe = \ln Kf + \frac{1}{n}\ln Ce \qquad \text{Freundlich equation}$$

$$\frac{Ce}{Qe} = \frac{1}{a} + \frac{b}{a}Ce \qquad \text{Langmuir equation}$$

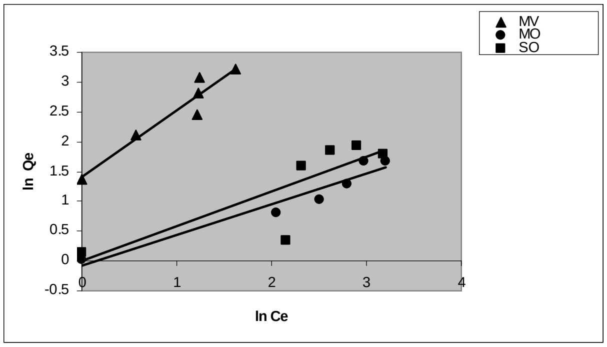
MO				MB				MV				SO			
C_e	C_e/Q_e	$\ln C_e$	$\ln Q_e$	C_e	C_e/Q_e	$\ln C_e$	$\ln Q_e$	C_e	C_e/Q_e	$\ln C_e$	$\ln Q_e$	C_e	C_e/Q_e	$\ln C_e$	$\ln Q_e$
3.985	3.926	1.383	0.015	4.77	159	1.562	-3.52	1.039	0.262	0.038	1.376	3.835	3.29	1.344	0.153
7.753	3.451	2.048	0.809	9.966	256.8	2.299	-3.249	1.778	0.216	0.5754	2.107	8.596	6.123	2.151	0.339
12.216	4.3879	2.503	1.024	14.079	15.286	2.644	-0.082	3.367	0.289	1.2138	2.454	10.125	2.078	2.315	1.584
16.407	4.5668	2.798	1.279	16.818	5.286	2.822	1.1573	3.403	0.205	1.225	2.809	13.659	2.154	2.6143	1.847
19.656	3.678	2.978	1.676	17.978	2.560	2.889	1.949	3.466	0.161	1.243	3.069	18.045	2.594	2.893	1.939
24.654	4.6116	3.205	1.677	19.352	1.8174	2.963	2.365	5.028	0.201	1.615	3.217	23.959	3.967	3.176	1.798

Table (3-3) Adsorption modes for compounds according to Freundlich and Langmuir Equations.

Plotting of lnCe and ln Qe for Freundlich equation is shown in figure (3-3) .



For MO compound



For (MB, MV, SO) compounds

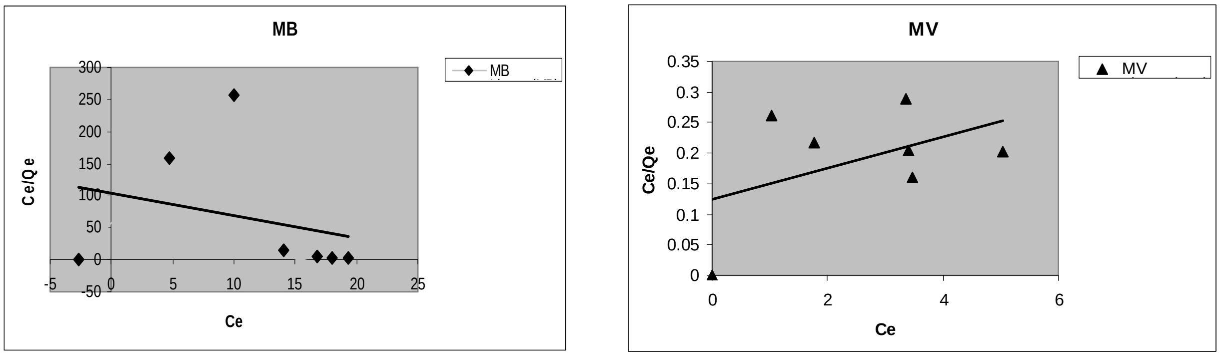
Figures (3-3) Shows the slope Freundlich in lnCe against lnQe for compounds (MO, MV, MB, SO) at 25 °C

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

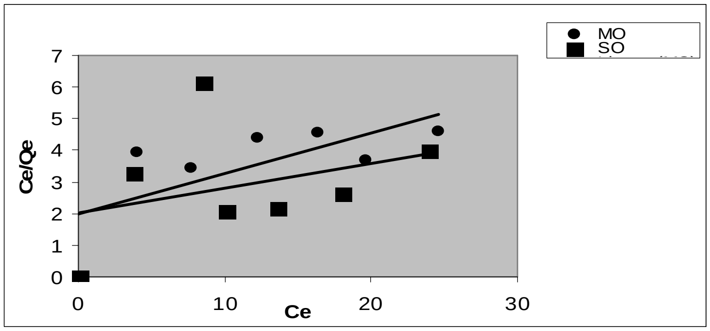
Compound	Kf	n	r
MO	0.9243	1.95	0.9911
MB	0.0149	0.226	0.906
MV	4.0609	0.87	0.96135
SO	1.002	0.923	0.8626

Table (3-4) Values of Freundlich constant for the compounds (MO, MB, MV, SO) at 25 ^{o}C

Plotting of Ce and Ce/Qe for Langmuir equation is shown in figure (3-4).



For MB compound **For MV compound**



For (MO, SO) compounds

Figures (3-4) Shows of Langmuir slope Ce against Ce/Qe values for the compounds (MO, MB, MV, SO) at 25^{o}C.

The Langmuir constant are calculated in list in table (3-5).

Compound	a	b	r
MO	31.026	0.99996	0.694
MB	119.727	573.329	-0.3379
MV	3.944	-0.04898	0.4645
SO	2.005	0.157994	0.3420
SO1	4.864	3.453	0.9945
SO2	2.404	0.33356	0.945

Table (3-5) Values of Langmuir constants for compounds (MO, MB, MV, SO) at 25^{o}C,

From the results in table (3-4) and(3-5) we can conclude the "**r** " values for each compounds approaches to one which mean that the compounds follow Freundlich or Langmuir equation.

3.4.2. Temperature Effect

The effect of temperature on the adsorption process for the compounds (MO, MB, MV, SO), on surface of the polymer, was investigated in three different temperature (25, 35,45)^{o}C at the Following conditions, pH= 7, with less than 300 μm diameter granules of adsorbent of (0.01) gm, 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 (3-5---3-8), since the behavior of these compound is different from the other, hence the results for each compound discussed separately.

Table (3-6) Adsorption isotherm for the compounds (MO, MB, MV, SO) at different temperatures (25, 35, 45) ^oC.

MO					
25°C		35°C		45°C	
Ce	Qe	Ce	Qe	Ce	Qe
3.985	1.015	4.054	0.946	4.2042	0.7958
7.7532	2.2468	8.504	1.496	6.7977	3.2023
12.216	2.784	12.548	2.452	11.5206	3.4794
16.4073	3.5927	17.2804	2.7191	16.5	3.500
19.656	5.3927	20.131	4.869	21.485	3.515
24.654	5.346	24.5154	5.4846	24.938	5.062
MB					
25°C		35°C		45°C	
Ce	Qe	Ce	Qe	Ce	Qe
4.77	0.03	4.98678	0.01322	4.9765	0.0235
9.9662	0.0338	9.3698	0.6302	7.829	2.171
14.079	0.921	14.15247	0.84753	11.6186	3.3814
16.8184	3.5927	17.49412	2.506	16.103	3.897
17.978	5.344	18.603	6.397	19.0878	5.9122
19.352	5.346	19.896	10.104	19.8957	10.1043

MV					
25°C		35°C		45°C	
Ce	Qe	Ce	Qe	Ce	Qe
3.9614	1.0386	3.2892	1.7108	4.5333	0.4667
8.2221	1.7779	6.8962	3.1038	9.218	0.785
11.6335	3.3665	10.1	4.9001	14.0225	0.9775
16.597	3.403	13.6641	6.3359	18.39922	1.60078
21.5342	3.4658	17.4055	7.5945	19.4829	5.903
24.9716	5.0284	20.5786	9.4214	24.097	5.903
SO					
25°C		35°C		45°C	
Ce	Qe	Ce	Qe	Ce	Qe
3.8345	1.1655	4.26065	0.73935	4.7744	0.2256
8.596	1.404	9.04762	0.95238	9.4737	0.5263
10.125	4.875	13.8346	1.1541	14.060	0.94
13.659	6.341	18.564	1.4362	18.6595	1.3405
18.045	6.955	23.4336	1.5664	23.51	1.4900
23.9598	6.0402	28.346	1.654	28.496	1.504

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

Compound MO:

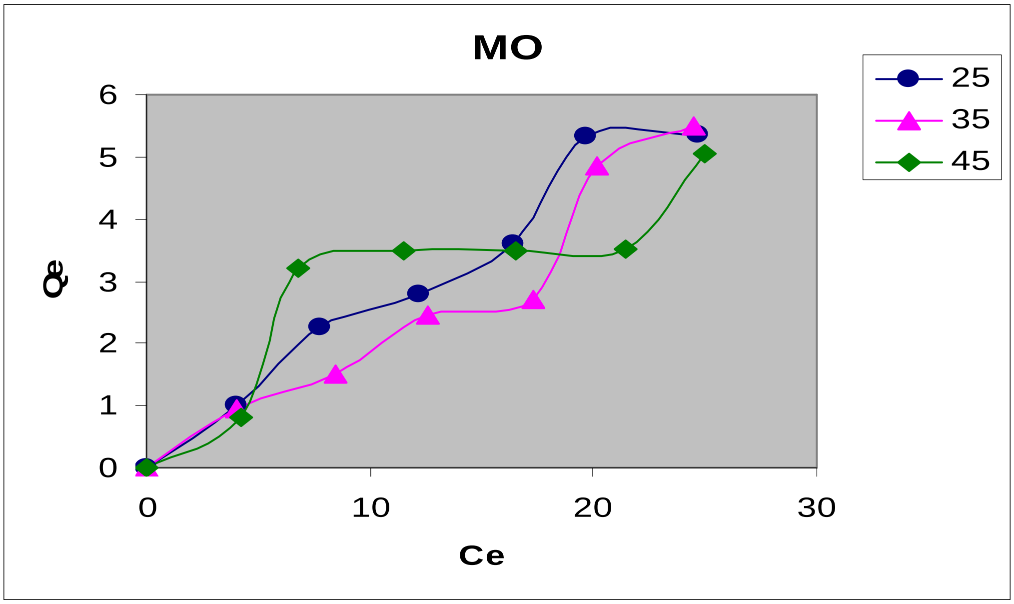


Figure (3-5) Adsorption isotherms of MO at, (25, 35, and 45) ^{o}C.

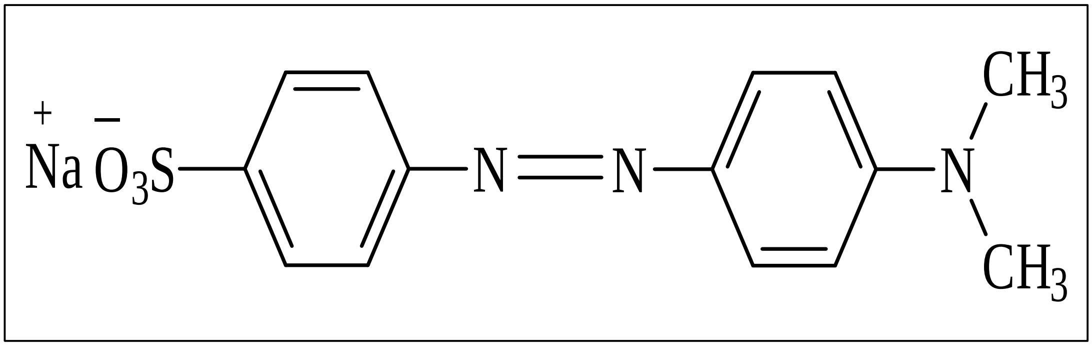
For MO compound, figure (3-5) show, the adsorption quantity, and the decreases as the temperature increases, but with a change in mode of the adsorption from **S_3** at 25^{o}C to **L_3** at 35^{o}C. The **L_3** mode, of the adsorption sites on the polymer approaching each other in energy and homogenousity during the elevation of temperature in this range. The change from **S_3** mode to **L_3** mode could be explain as the clusters of the **S_3** mode are spreading by the increase in temperature and to be distributed regularly on the surface area of the polymer around these sites resulting the **L_3** mode adsorption[8].

When the temperature reached 45 ^{o}C , the adsorption mode changed again but from **L_3** to **S_2** mode .

In this case there will be an increment in pore's diameter of the surface of the polymer which enables the MO adsorbate molecules to cross over into the cavities and absorption process may occur. The formation of $\mathbf{S_2}$ adsorption mode inside the cavities is due to that these cavities neither of the same geometry nor of the same energy content.

However, the adsorbate molecules will be arranged in clusters on certain specific areas inside the cavities, and when these cavities are fully occupied, then the adsorption on the surface of the polymer is not a homogenous the adsorption of $\mathbf{S_2}$-mode was appear.

Moreover, we notice from figure (3-5), that when temperature increases, the adsorption process will occur, despite of the increase in the surface area of the polymer due to swelling, and increasing porosity. This could be attributed to the negatively charged MO compound which repelled from polymer structure that bears high electron density centers.



This is MO structure

Compound MB:

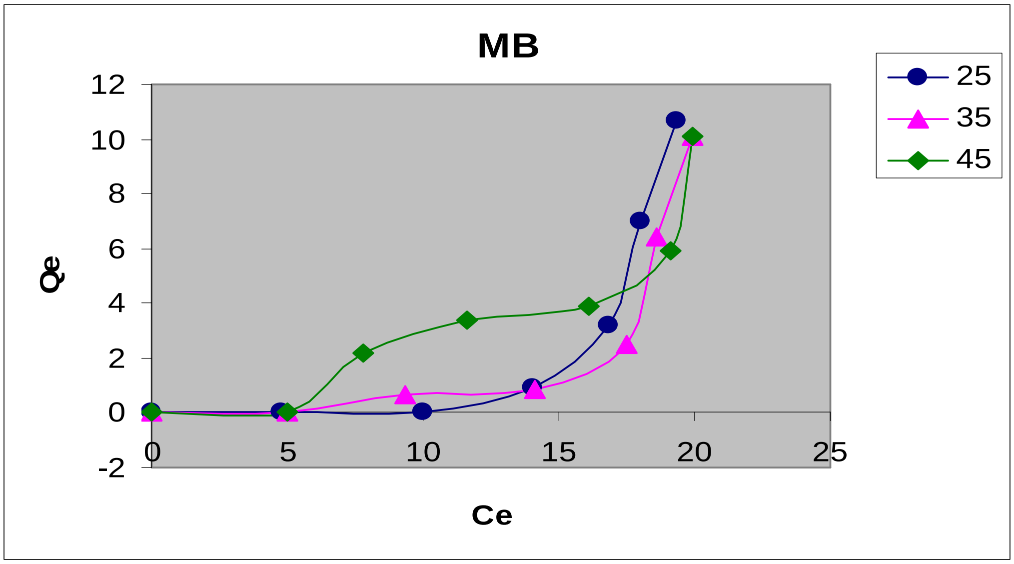
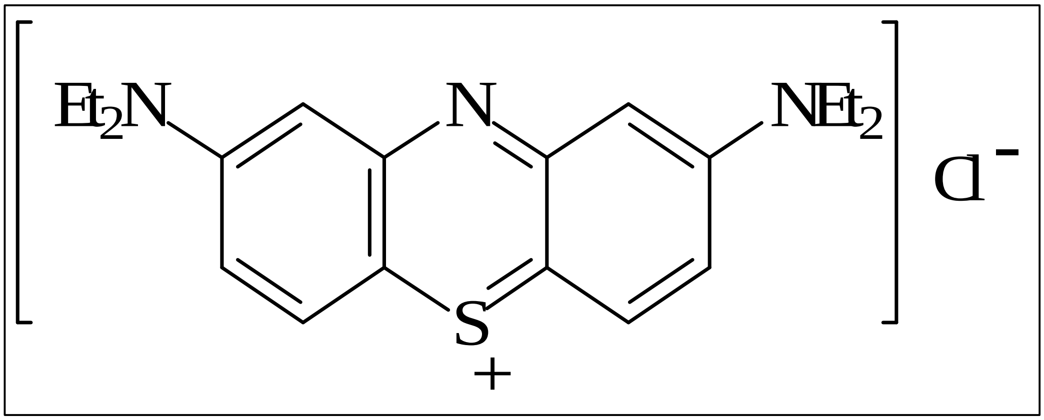


Figure (3-6) Adsorption isotherms of MB at (25, 35, and 45) °C.

Figure (3-6) indicate that there is a very slight increase in the adsorption quantity by increasing the temperature. The general mode of adsorption remains of **S**-mode, but with gradually conversion from **S_1** to **S_2** when the temperature increases.

These results indicate that the compound MB may have undergone an absorption process, which share natural adsorption process in order to balance the desorption effect which increase as the temperature increase [24].

The absorption is probably occurred, because the polymer has been swollen, so the surface area increased and the porosity diameter increased too, by temperature increment. This was appeared during the formation of a second adsorption layer, and during the conversion from **S_1** to **S_2** form.



This is MB structure

Compound MV:

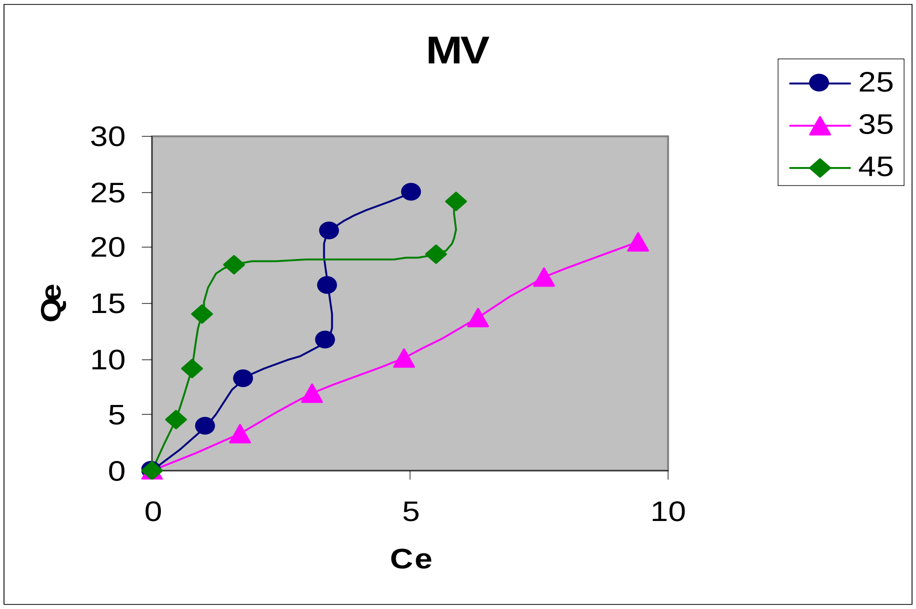
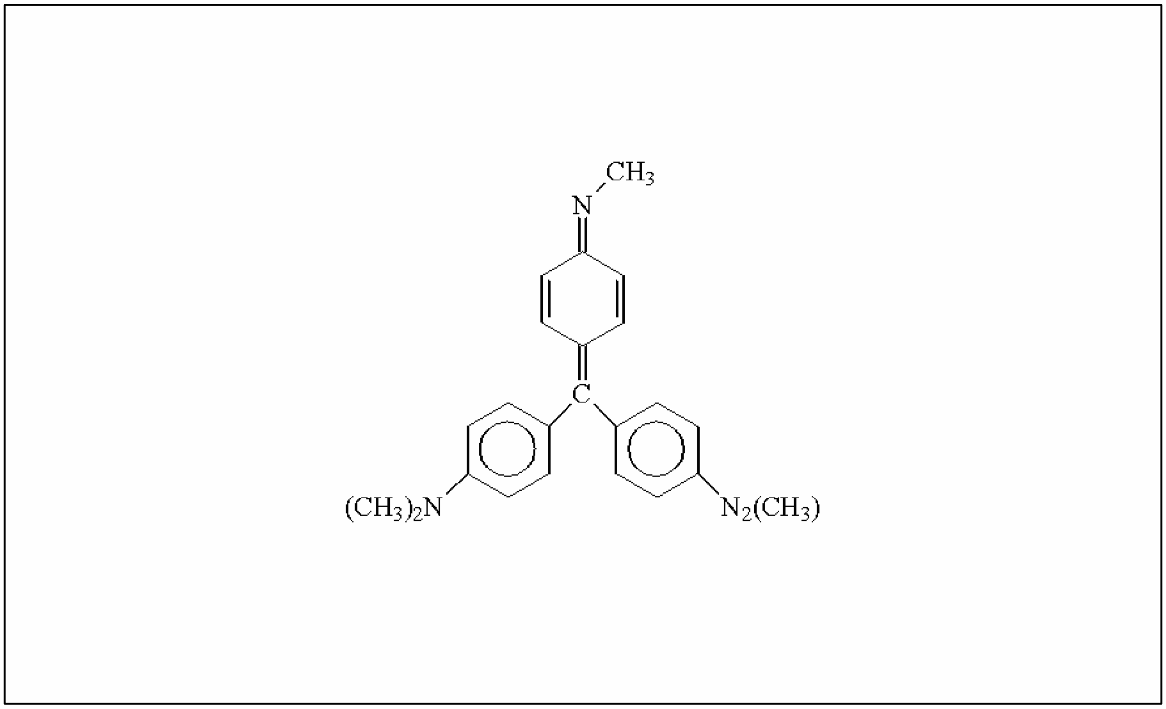


Figure (3-7) Adsorption isotherms of MV at, (25, 35, and 45) °C.

Figure (3-7) show, the adsorption quantity decreases as the temperature increases from 25 °C to 35 °C, that may be due to the dominating of desorption on the other processes, absorption and adsorption [6].

Layers formation boundaries has been decreased with keeping adsorption mode of (**S_3**), and this means that the energy barrier between these layers falls less sharply [10], which is attributed to the swollen polymer that makes the adsorption sites on the surface of polymer nearer to each other in energy by MV molecules.

When the temperature is elevated to 45°C, there will be a great change in the general mode of adsorption, from **$S_3 \rightarrow S_2$**, with large increment in adsorption quantity. This could be due to the polymer swelling leading to, the increment in pore's diameter on its surface and enabled MV molecules to pass through into the cavities of the polymer. Thus during the adsorption process, two layers have been recognized: the layer of cavities and the outer surface layer.



This is MV structure

Compound SO:

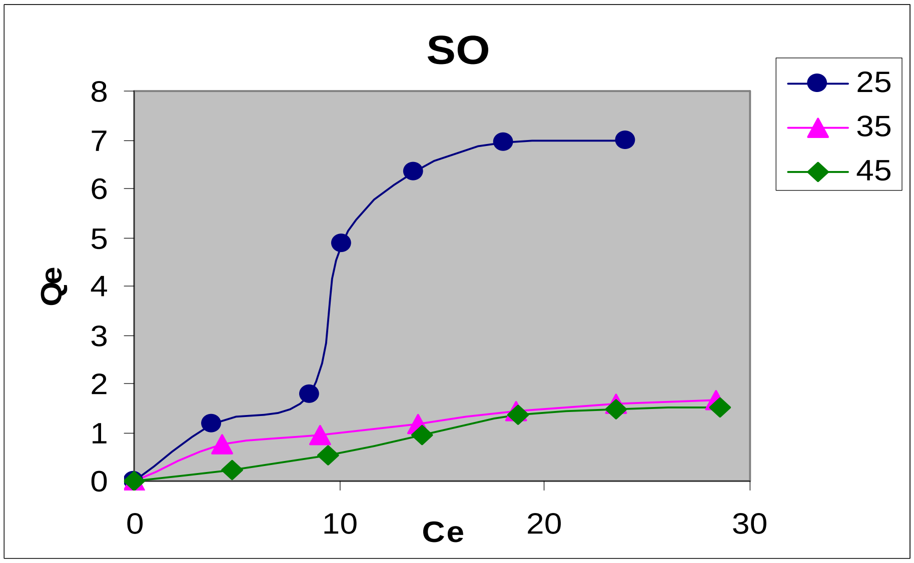
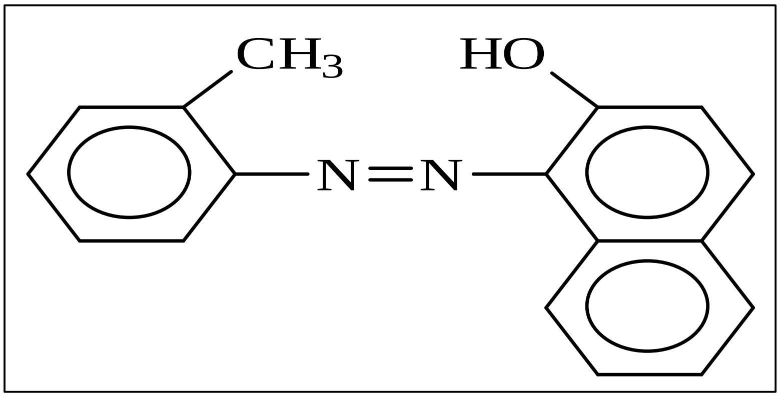


Figure (3-8) Adsorption isotherms of SO at, (25, 35, and 45) ^{o}C.

For SO compound, figure (3-8) exhibits that the adsorption quantity, generally, decreases as the temperature increases. As the temperature increases, the effect of desorption process would be favored on the other two processes (adsorption and absorption). At temperature of 25 ^{o}C the adsorption is of **L_2** mode which obeys Langmuir equation within one layer.

This means that the distribution of SO molecules in each layer of adsorption and will remain homogenous. As the temperature rise to 35^{o}C the adsorption mode will remain as **L_2**, with reduce in the decline of adsorption isotherm between the two layers of the SO compound. This means that these layers will have the same energy content as it is one layer and will be homogenous, this results is attributed to the swelling of the polymer, which makes the two layers to be merged together as they appear and behave as one layer during the adsorption process.

At 45°C the adsorption mode changed from **L_2** to **S_1**,, and as previously mentioned it is also attributed to the increasing in the porosity and of the polymer adsorption occurs inside the cavities which are non-homogeneous.



This is SO structure

3.4.3. Thermodynamic calculations:

ΔH has been calculated for all adsorption processes, according to equation (1) [60], via plotting logarithmic value of the maximum adsorption quantity at equilibrium concentration as (ln Qe max) against the temperature as (1/T). The results are listed in Table [3-7] and figure [3-9]:

$$\ln \frac{Qe\,\mathrm{max}}{Ce\,\mathrm{max}} = \frac{-\Delta H}{RT} + \mathrm{constant} \qquad [1]$$

T(K)	* 10^{-3}	C_e=19.656 mg/L		C_e=19.352 mg/L		C_e=5.0284 mg/L		C_e=23.9598mg/L	
	T^{-1} $(k)^{-1}$	MO		MB		MV		SO	
		$Q_{e\ max}$	ln $Q_{e\ max}$	$Q_{e\ max}$	ln $Q_{e\ max}$	$Q_{e\ max}$	ln$Q_{e\ max}$	$Q_{e\ max}$	ln$Q_{e\ max}$
298	3.355	5.344	1.6759	10.648	2.3653	24.98	3.22	6.955	1.93946
308	3.247	4.250	1.4469	8.532	2.1438	12.13	2.496	1.499	0.40479
318	3.1245	3.5	1.2527	7.686	2.0394	19.02	2.95	1.490	0.39877

Table (3-7) Values of 1/T & ln Qe_{max} for the compounds used in the study.

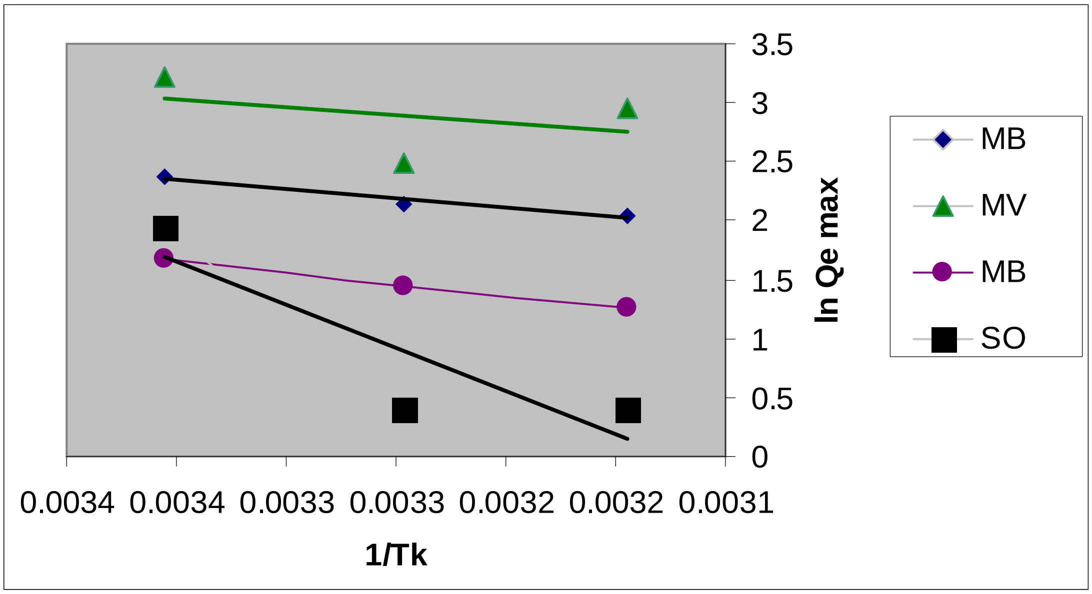


Figure (3-10) Shows values of ln Qe_{max} against 1/T for adsorption of compounds MO, MB, MV, and SO on the adsorbent surface.

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:

$$\Delta G = -RT \ln K_{eq} \qquad [2]$$

Since

$$\frac{Qe}{Ce} = K_{eq} \qquad [3]$$

So equilibrium becomes:

$$\Delta G = -RT \ln \frac{Qe}{Ce} \qquad [4]$$

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

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

Table (3-8) illustrates the value of thermodynamic function of compounds (SO, MO, MV, MB) on the surface of the polymer.

Table (3-8) illustrates the thermodynamic function values for adsorption of compounds (SO, MO, MV, MB) on the surface of polymer.

compound	ΔH J/mol	ΔG J/mol	ΔS J/mol.K
SO	$-6.14562*10^{4}$	$-1.4062347*10^{4}$	$-1.5904*10^{2}$
MO	$-1.673151*10^{4}$	$-1.388765*10^{7}$	$4.1*10^{2}$
MV	$-1.121943*10^{4}$	$-2.1085*10^{4}$	33.10630689
MB	$-1.2919718*10^{4}$	$-1.56343*10^{4}$	9.109338423

From the values of ΔH for these compounds in table (3-8), we noticed that adsorption is exothermic for all compounds, since the quantity adsorption decreases as the temperature increases.

For the compound MB, there was a small increase in the adsorption quantity with increase the temperature, that is in contrast to SO and MO compound. This could be attributed to an absorption process that taking place because compound MB possess a positive charge and interact electrostatistically with polymer surface and liberate a large amount of energy.

This is a clear evidence of the strong attraction that was formed as a result of this adsorption, and this amount of energy supplies the same energy needed or more for an endothermic absorption to occur. The same behavior occurs in adsorption of compound MV, but the energy evolved from MB is larger than energy evolved from MV molecules. This is probably because MB molecules is a planner (two dimensional) which

Enable the molecule to overlap with the lone pair of electrons on the surface of polymer and facilitates the charge transfer from the surface of the polymer to the MB molecule [61].

From the value of ΔG we noticed that adsorption processes for the four compounds were thermodynamically favored.

Then adsorbability of the compound are arrange in the following order.

MV > MB > SO > MO

Less soluble more soluble less soluble more soluble

Positively charge negatively charge

The binding energy of MB is greater on the surface of the polymer than that of MV, despite of what we found that according to ΔG values.

The adsorption of MV is more thermodynamically favored than that of MB, this ability dose not depend only on the binding energy but no the solubility as well. This is because MB more soluble than MV.

For MO and SO compounds, the SO is adsorbed much easier than MO, because it is less soluble in the solution.

From the ΔS value [62] we noticed that these results may follow the following sequence:

MV > MB > MO > SO

$$\xrightarrow[\text{Decreasing entropy}]{\hspace{6cm}}$$

This means that the disorder of MV molecules increases much highly when they transfer from solution into the surface of the polymer and arranged randomly on the surface.

For MB molecules; when they transfer from solution into polymer surface, they appear to be less disorder on the surface of polymer than that of MV molecules. These are because of the planarity of MB molecule and have less freedom in the movement than for MV which has three dimensions.

For MO molecule; it appears to be less disorder than that of MV and MB, when MO molecules transfer from solution into the surface of the polymer. The freedom for the MO molecules is less than that of MB and MV.

SO molecules are the only one with the less disorder on the surface of polymer than in solution; though it is three dimensional structures, it is rigid with less freedom of movement. The sites that are occupied by SO molecules on the surface of polymer are near to be ordered and specific which justifies the odd mode of adsorption it has taken $\mathbf{L_2}$.

3.4.4. Ionic Strength

The effect of ionic strength on the adsorption process for compounds (MO, MB, MV, SO) 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, 25°C, pH= 7, and less than 300 μm diameter granules of (0.01) 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 figures (3-11---3-14).

Compound MO:

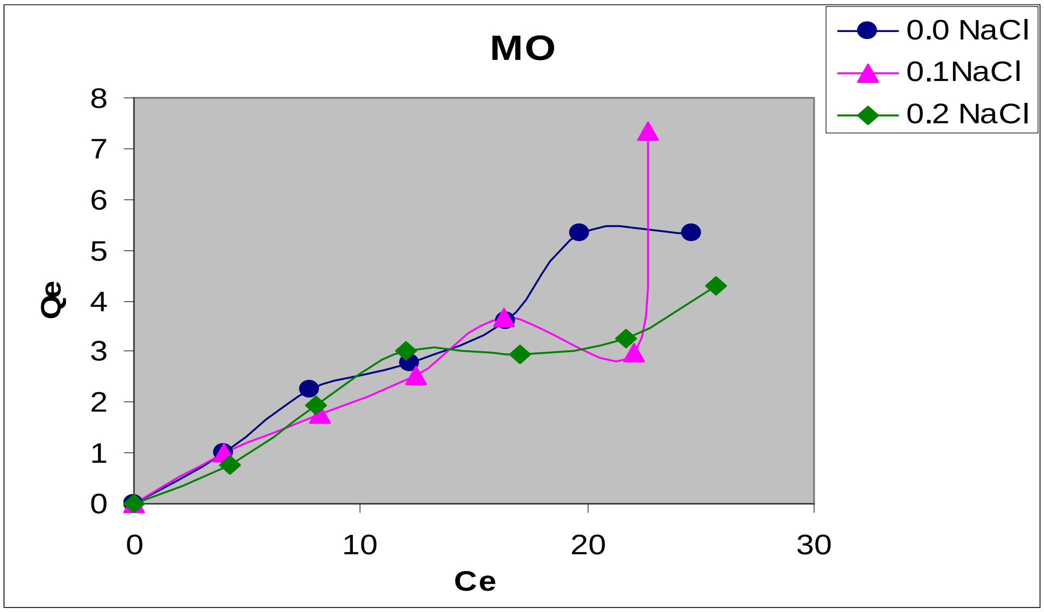


Figure (3-11) Shows the effect of ionic strength on the adsorption isotherm of compound (MO)

Figure (3-11) exhibits that the adsorption isotherm for MO compound follows the **S_3**-mode in a solution free of salts, while in solution of 0.1M NaCl, the mode change to **L_3** accompanied with slight increase in adsorption quantity.

The increment in adsorption appears at high equilibrium concentration of MO (higher than 20 ppm), but at a lower than 20 ppm, there is no big difference in adsorption quantity .The change the mode to **L_3** indicate that the adsorption on the polymer surface is homogenous, while at concentration more than 20 ppm the adsorption quantity increases due to the formation of sodium ions on the third layer leading to decreases the electrostatic repulsion between MO and surface of polymer.
At 0.2 M NaCl solution, the mode of adsorption changes from **L_3** to **S_2** with a decrease in adsorption quantity. The adsorption profile in figure (3-11) reveals that the first and second adsorption layers at 0.2 M NaCl are equivalent in shape to that curves of **L_1** and **L_2** at 0.1 NaCl and equivalent to **S_1** and **S_2** as well in solution free of salts. The unoccupied sites of adsorption retain unchanged at concentrations lower than 20 ppm and have a high affinity to be saturated by adsorbing MO molecules at different ionic strength with a change in mode between **L** to **S** may be due to a changed in regularity or homogeneous of these sites in different solutions of different ionic strength.

In solution of 0.2 M NaCl there is a competition between the factors decreasing adsorption quantity(solubility)[25,26] with those increasing factors(electrostatic double layer)[12,27].

Compound MB:

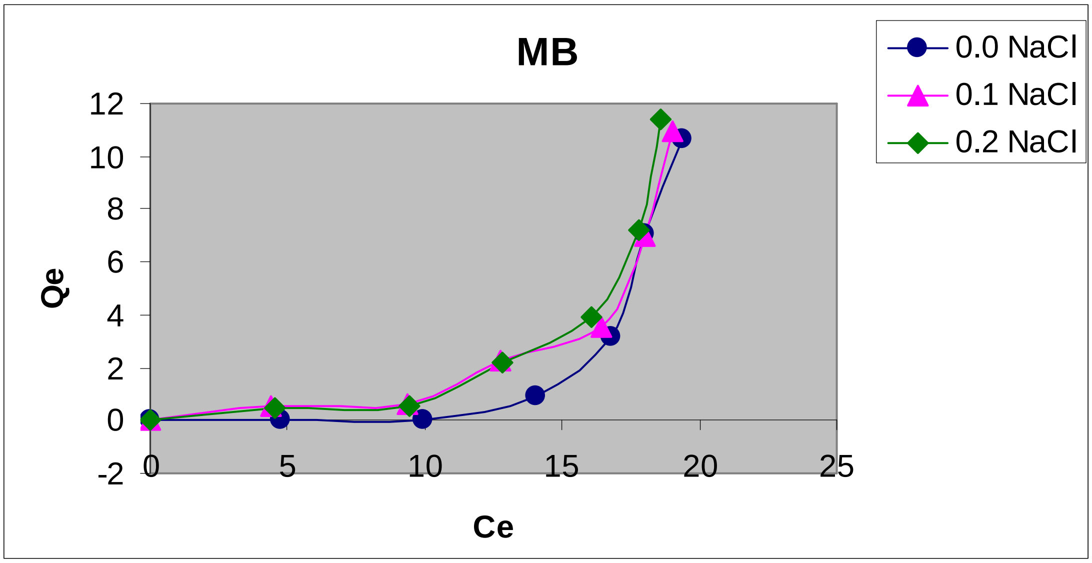


Figure (3-12) Shows the effect of ionic strength on the adsorption of compound (MB)

The adsorption of MB in solution free of salts follows the mode $\mathbf{S_1}$.

From figure (3-12) there is no change in adsorption quantity of MB whether in 0.1M NaCl solutions or in solution free of salts, but adsorption mode changed from $\mathbf{S_1}$ to $\mathbf{S_2}$. The first adsorption layer is completed at 14 ppm, and the second adsorption layer is formed after at 14ppm. The competition in adsorption of NaCl salts with MB molecules on the surface of polymer, electrostatic double layer will be formed then inhibits the attraction between MB (positively charged) with surface of polymer (negatively charged), which in turn decreases the adsorption quantity as shown below:

$$\left.\begin{array}{lcl} \text{MBCl} & \rightleftharpoons & \text{MB}^{+} + \text{Cl}^{-} \\ \text{NaCl} & \rightleftharpoons & \text{Na}^{+} + \text{Cl}^{-} \end{array}\right\}$$

From the equation it seems that the common ion effect [25, 26] play rules in reducing the solubility of MB compound subsequently increase the adsorption quantity. The common ion effect will balance the effect of electrostatic double layer; hence there is no change in adsorption.

In solution of 0.2 M NaCl, the adsorption mode is remain **S_2** unchanged which may be attributed to the competition between electrostatic double layer factor in (decreasing adsorption)and on the common ion effect factor.

Compound MV :

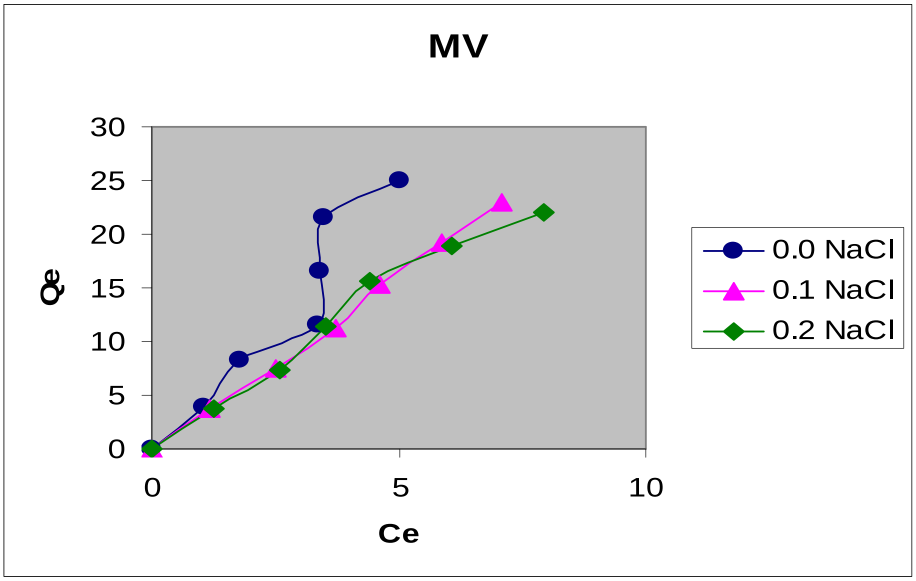


Figure (3-13) Shows the effect of ionic strength on the adsorption of compound (MV)

From figure (3-13) it seems that MV compound follows the **S_3**-mode in salt free solution, but in solution of 0.1M NaCl it is of **L_2**-mode and the adsorption quantity is large , but to a lower extent than in salt free solution.

This could be due to the increase in solubility of MV as the ionic strength increases. The adsorption mode change from **S_3-** to **L_2-**mode by the presence of salt in solution indicates that the adsorption of MV is homogenous on the surface of the polymer by adsorption of some of these salts which occurred with out swelling of the polymer. This mechanism inhibits the formation of a second layer inside pores and the outer surface of the polymer.

Despite that the adsorption of **L_2** mode, the decline in the curve more homogenous and regular in 0.1 M NaCl solution than in salt free solution, i.e. the adsorption sites in both layer would be of the same free energy needed for this adsorption.

In solution of 0.2 M NaCl the adsorption mode is of **S_2**.

The decline in curves for both solutions (0.1 and 0.2) M NaCl is nearly similar, though there is a change from **L_2** to **S_2**.

However, that indicates the change of the polymer surface from homogenous for MV compound to non-homogenous surface. The factors that influence on the adsorption as; electrostatic double layer, ionic strength and common ion effect are kept normal.

Compound SO:

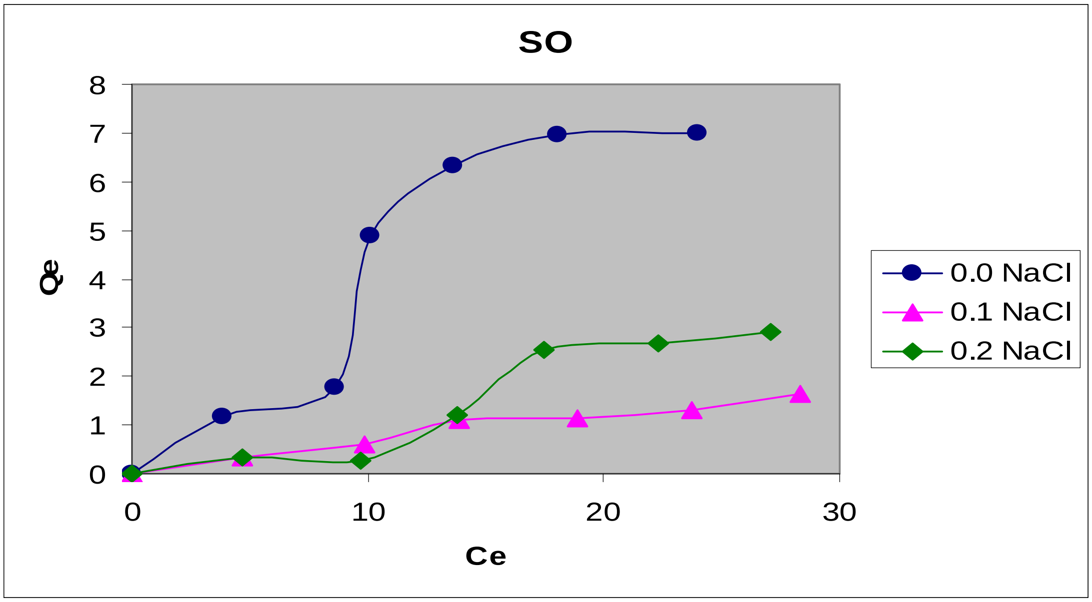


Figure (3-14) Shows the effect of ionic strength on the adsorption of compound (SO)

From figure (3-14) it is evident that adsorption of SO is **L_2** mode whether in salt free solution or in a solution of 0.1M NaCl but with a less adsorption quantity in the second solution.

This could be explained according to Deby Hükel law [25, 26]: (as the ionic strength of the solution increases, the solubility increases too). Therefore, when the solubility of SO increases, the adsorbability decreases, and the presence of salt may increase the effect of salting-out [27] of the polymer which decreases the swelling of polymer, subsequently the surface area will not increase. Hence the formed charge on the polymer surface would be highly concentrated then leads to a repulsion between polymer surface and negatively charged SO molecules.

In a solution of 0.2 M NaCl, the mode remains **L_2** with little increment in adsorption quantity than in solution of 0.1M NaCl but still less than in salt free solution. This is more likely to be due to the formation of electrostatic double layer [12, 27] than increasing the solubility with increasing ionic strength alone.

3.2.5. Effect of pH:

The effect of pH on the adsorption process for the compounds (MO, MV, MB, SO) , surface of the polymer, three different pH (6, 7 and 8) at the Following conditions, 25^{o}C, with less than 300 μm diameter granules of adsorbent of (0.01) gm, with adsorbate of initial concentrations (5, 10, 15, 20, 25, and 30) ppm, for each compound. The results are shown in figures (3-15---3-18).

However, the results of each compound are discussed separately as follow.

Compound MO:

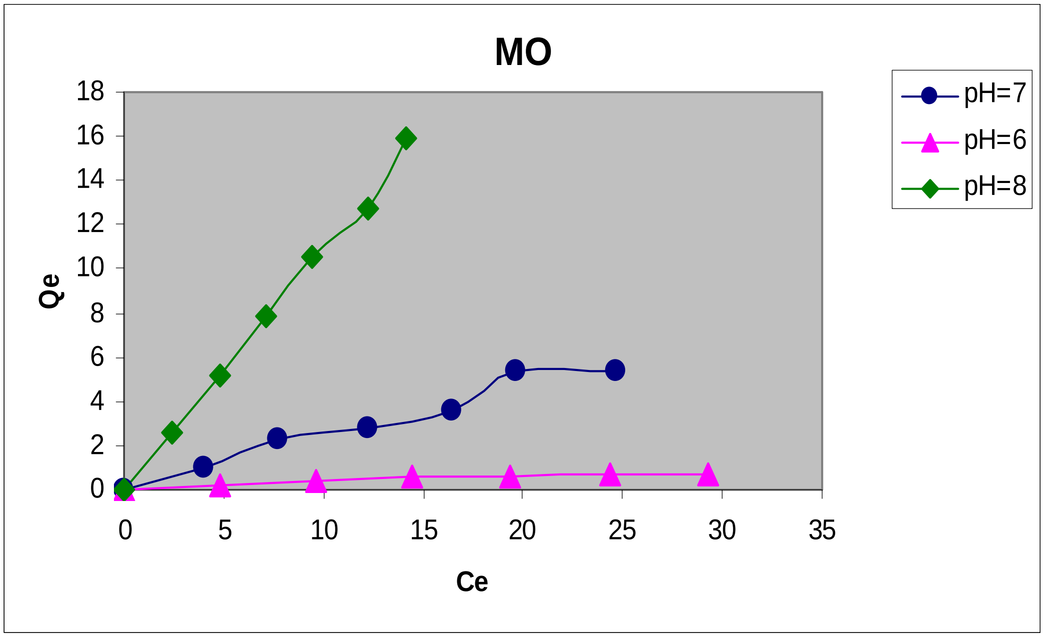


Figure (3-15) Shows the effect of pH on the adsorption of compound (MO)

The adsorption of MO it follows the $\mathbf{S_3}$-mode in aqueous solution at pH=7. From figure (3-15) exhibit that this mode is changed to from $\mathbf{S_3}$ at pH=7 to $\mathbf{L_2}$ at pH = 6, thought it could be considered as $\mathbf{L_1}$ mode, because the formation layer at Qe = 0.7ppm is more stable than that formed at Qe = 0.4 ppm.

The presence of the polymer in a week acidic medium may reduce the swelling of the polymer in this medium.

This leads to a decrease in the surface area and plugging the pores of the polymer. This explains why adsorption quantity at pH=6 is less than at pH=7, and the absence of absorption process.

On the other hand, pH = 8 we observed an increment in adsorption quantity, besides, the mode is converted to **S,** the basic medium increases the swelling of polymer, due to the high electron density in its structure, which in turn increases the repulsive forces between its chains, and decreases the hydrogen bonding between polymer chains.

These factors increase the surface area of polymer and the pores size, leading to increase the ability of the polymer to adsorb MO molecules; MO is anionic species, and by increasing the negative charge of the polymer the diffusion between the surface of the polymer and MO molecules will increase. This observation appears despite the increasing of surface area is dominating, rather than the repulsive forces between polymer and MO molecules.

This suggestion is enhanced by MO molecules to be converted toward **S-**mode in adsorption; it is they start to arrange themselves as clusters on specific sites on the surface of the polymer.

Compound MB:

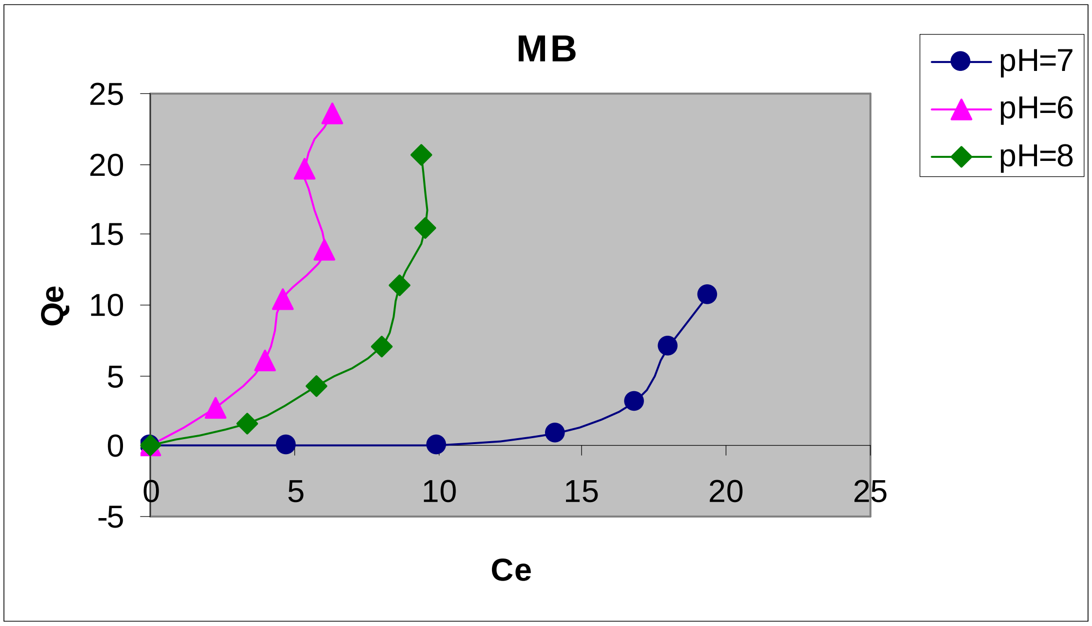


Figure (3-16) Shows the effect of pH on the adsorption of compound (MB)

For adsorption of MB in solution with pH = 7 adsorption isotherm follows the mode **S_1**.

However, in solutions of pH=6 and of pH=8 the adsorption quantity at each pH approaches each other due to the lowered solubility of the compound though the quantity at pH=8 is a little higher than at pH =6. Due to the swelling of polymer and increased surface area, but adsorption mode retain unchanged **S_2.**

Compound MV:

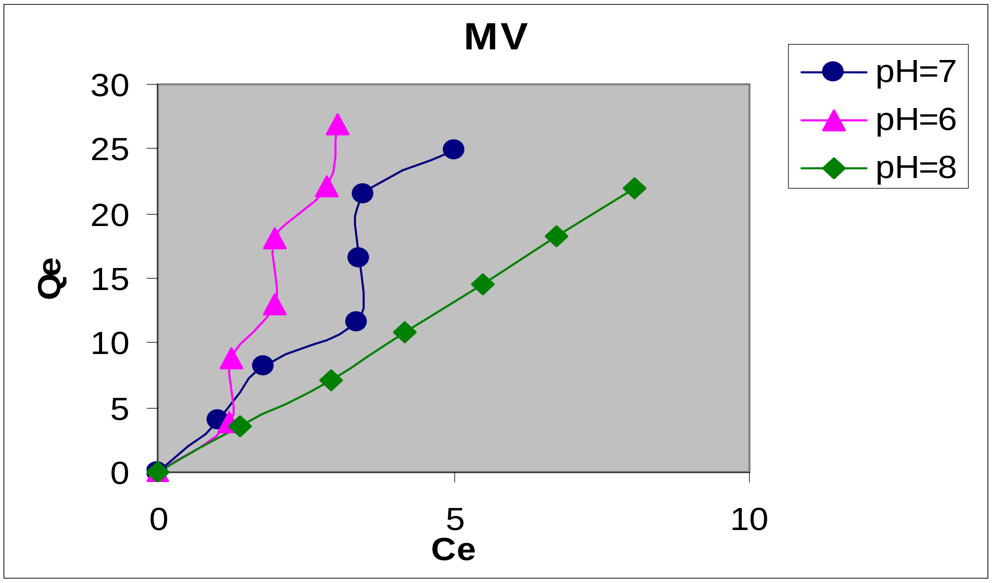


Figure (3-17) Shows the effect of pH on the adsorption of compound (MV)

For adsorption of MV compound which follows the **S₃**-mode in solution with a pH = 7 from figure (3-17).

In acidic medium pH=6, the polymer is with less swelling at pH =7 and all pores are plugged, this explains that the adsorption quantity of MV compound is low and general adsorption isotherm is of the mode **S_2**. At pH = 8 we noticed that there was an increment in adsorption quantity, due to an increase in the surface area of the polymer, due to the swelling, and the increase in the electrostatic attraction between MV that bears a positive charge with the surface of polymer which bears negative charge. The adsorption mode at pH=8 is **S_3**, due to absorption that occurs, and adsorption sites are centered inside the big pores of the polymer that bears a negative charge and then MV molecules will be as clusters.

Compound SO:

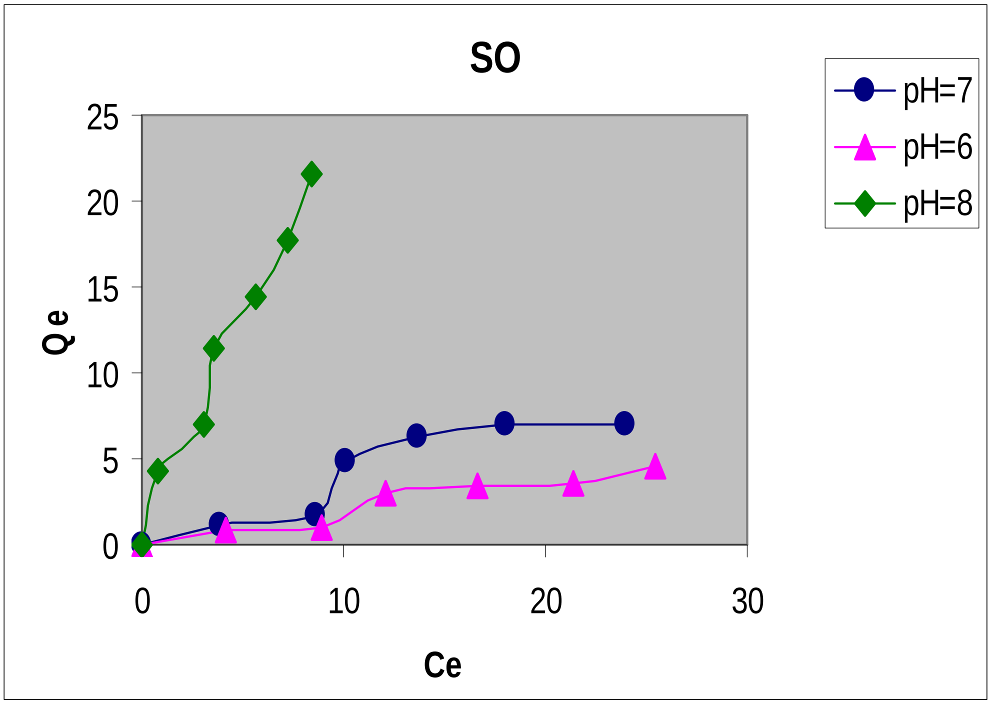


Figure (3-18) Shows the effect of pH on the adsorption of compound (SO)

The adsorption of SO in a solution of pH=7, follows the mode **L_2** .figure (3-19) show that the behavior of SO is similar to that of MO compound, in solutions of pH=6 and at pH=8 taking the considerations that adsorption quantity in both cases is greater than in MO compound. Also, we noticed that the adsorption mode is kept unchanged as **L_2**, but the adsorption quantity increases when the medium changes from acidic to basic. May be due to the swelling of the polymer at pH=8.

L_2 mode is kept unchanged because the SO molecules are of high molecular weight and do not pass into pores of polymer even when swelling takes place. Thus, adsorption occurs only on the outer surface of the polymer.

3.3. Comparison Between Adsorption On The Polymer (Triethanolamineglyceralmalate) 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 glycerol maleate). Comparison of the adsorption processes for the compounds (MO, MB, MV, SO) on the surface adsorbents: of (the polymer, and of the zeolite) at: 25^{o}C, and pH=7, with adsorbate of initial concentrations (5, 10, 15, 20, 25, and 30) ppm, was investigated.

Compound MO:

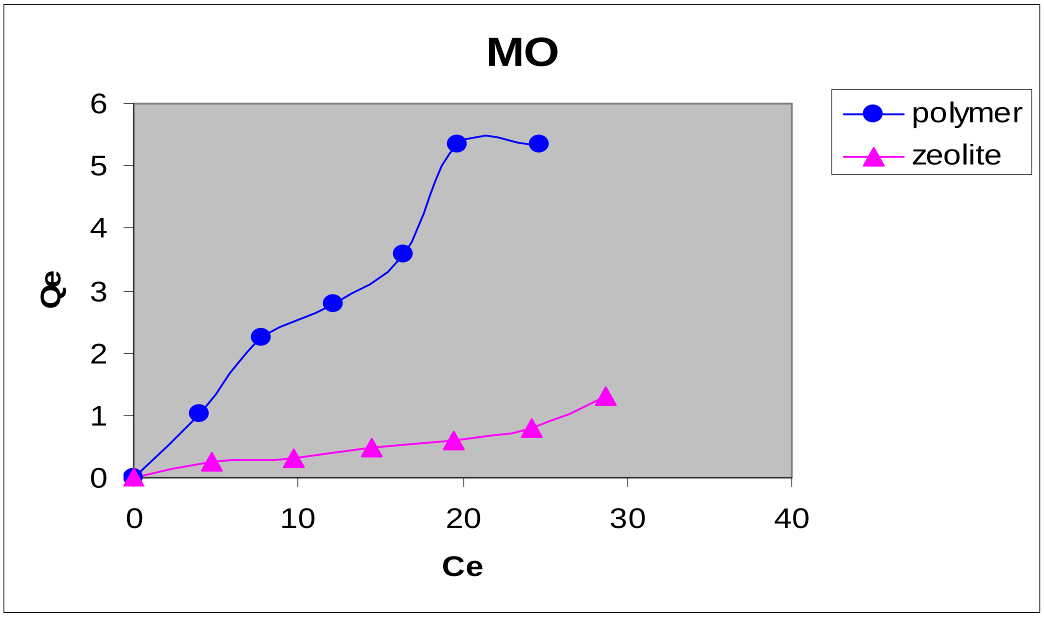


Figure (3-19) Shows the adsorption isotherms on the polymer and zeolite for compound (MO) at 25°C.

The adsorption of MO compound on the surface of the zeolite is **L** mode, while it is of **S** mode on the surface of the polymer as shown in Figure (3-19). The adsorption quantity of MO is much higher on the polymer than that on the zeolite. This results are due to that the MO molecules diffuses the pores during swelling of the polymer, the diffusion can not take place in case of zeolite, because of the negative charge being centered in zeolite lattice which leads to a repulsion between MO and zeolite much more higher than that of MO with the prepared polymer.

Compound MB:

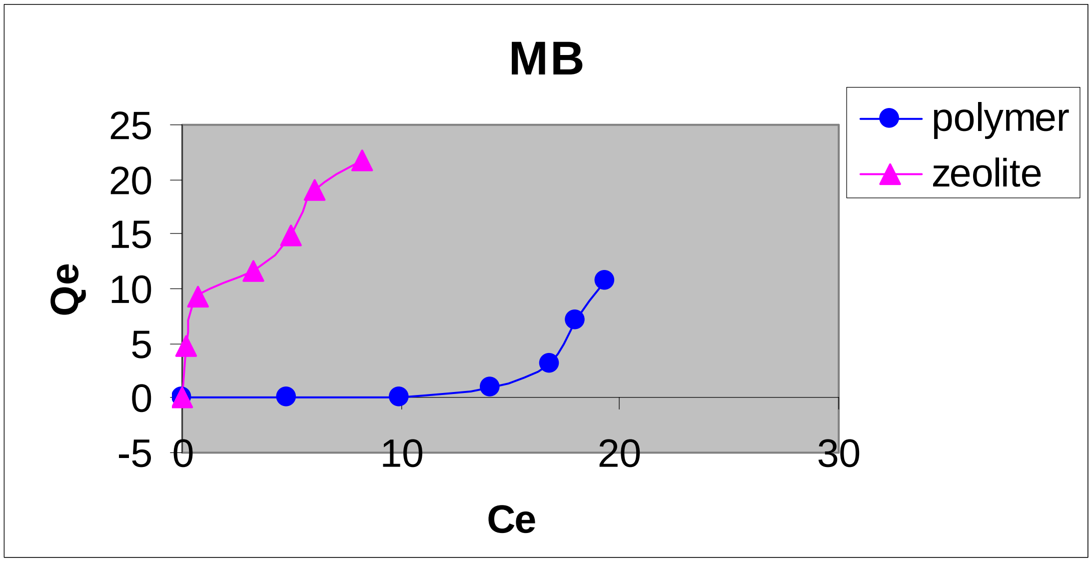


Figure (3-20)) Shows the adsorption isotherms on the polymer and zeolite for compound (MB) at 25^{o}C.

The adsorption of MB on the surface of zeolite is of **L_2** mode while it follows **S_1** on the surface of the polymer as shown in figure (3-20). These results may interrupted because absorption process that not occur inside zeolite lattice, but occurred in the polymer due to the diameters of the pores of the swollen polymer are greater than that pores formed during swelling of zeolite. The adsorption quantity on zeolite for this compound is greater than the adsorption quantity on polymer, this could be explained by the negative charge of the zeolite lattice [30] is higher than that in the polymer ,hence, MB would be attracted to the zeolite surface more than the polymer surface[31,63].

Compound MV:

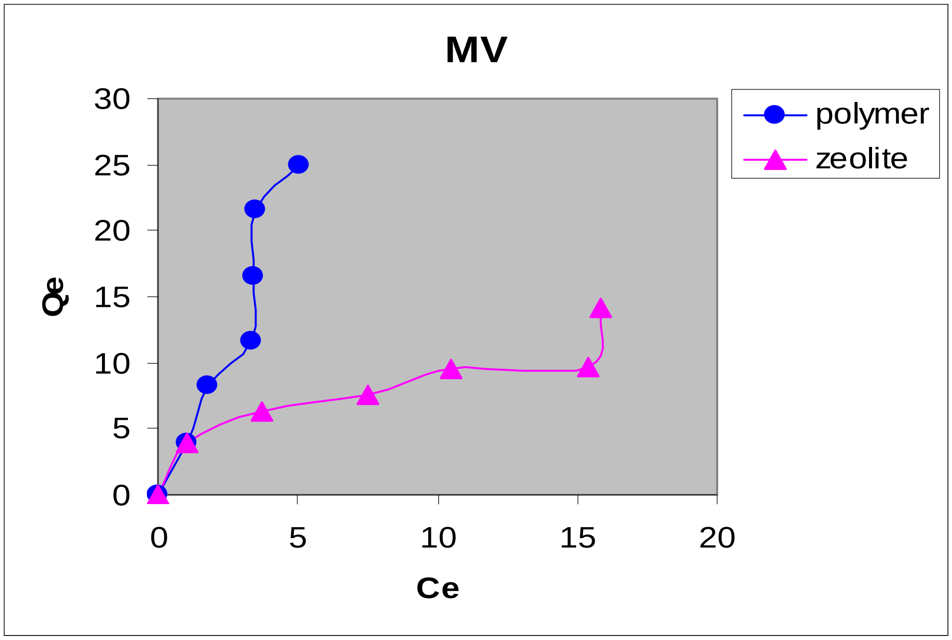


Figure (3-21) Shows the adsorption isotherms on the polymer and zeolite for compound (MV) at 25°C.

The adsorption isotherm of MV compound on the surface of zeolite is **L_3** while it is of **S_3** on the surface of the polymer as shown in figure (3-21). The adsorption quantity of MV is higher on the polymer than that on the zeolite, because MV molecules could not pass through the small pores of zeolite lattice.

Compound SO:

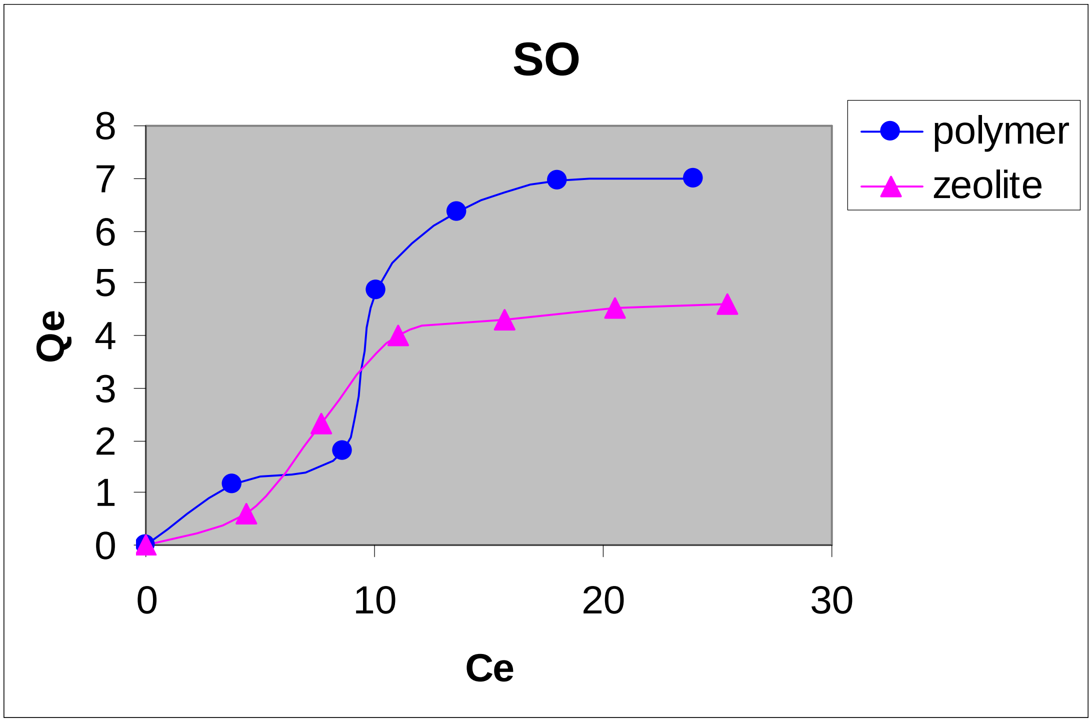


Figure (3-22) Shows the adsorption isotherms on the polymer and zeolite for compound (SO) at 25°C.

The adsorption isotherm of SO compound is of $\mathbf{S_1}$ on the surface of the zeolite, while it is of $\mathbf{L_2}$ on the surface of the polymer as shown in figure (3-22). The adsorption quantity on the surface of polymer for the compound SO is greater than the adsorption quantity on the zeolite. This could explain by the surface area of adsorption in case of the polymer being larger than the surface in case of zeolite (because of the higher ability of the polymer for swelling). In addition, the charge will be highly centered in the zeolite than in the polymer [37], so, the repulsion of SO on zeolite surface is more than the repulsion on surface of the polymer.

Conclusions

1. Polymer swellings were in the following orders :
    - a- at pH = 8 > at pH = 7 > at pH =6
    - b- with 0.1 M NaCl > with 0.0 M NaCl > with 0.2M NaCl

2. At temperature of 25 ºC :-
    - a- The adsorption mode was S for MO, MB and MV while it was L for SO.
    - b- The adsorption quantities followed the following order

MV > MB > SO > MO

3. The adsorption of all compounds was exothermic, even though there was adsorption of MB and MV compound.

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 MO, MV and SO was greater in the case of triethanolamine –glycerolmaleate than in the case of zeolite (5A), while it was the reverse for MB compound.

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 sanitation and purification processes.

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

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

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

e- Study the specific conductivity of the dyes solution before and after adsorption.

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الخـــــلاصة

تم في هذه الدراسة تحضير بوليمر (triethanolamine- glycerolmaleate) وشخص البوليمر المحضر بواسطة .F.T.I.R كما تم قياس تأثير الانتفاخ لهذا البوليمر في عدد من المذيبات .

وأجريت عملية الامتزاز باستخدام مطياف ية الأشعة المرئية (فوق البنفسجية) لكل من المركبات (MB,MV,SO,MO) في محاليلها المائية وفي درجات حرارة (25 ، 35 ، 45) م° وفي اوساط حامضية (pH=6) وقاعدية (pH=8) واوضحت نتائج تلك الدراسات ان الشكل العام لامتزاز تلك المركبات على سطح البوليمر بدرجة (25) م° يأخذ النمط (S) للـ (MV,MB,MO) وياخذ النمط (L) للـ (SO) حسب تصنيف Giles.

أظهرت الدراسة النتائج الآتية:

1. ان ترتيب المادة الممتزه يأخذ الترتيب التالي بدرجة 25 م° :

   MV> MB> SO> MO
2. ان تاثير الشدة الايونية كان متفاوتا من ناحية امتزاز تلك المركبات .
3. يقل الامتزاز بانخفاض pH لهذه المركبات .
4. ان امتزاز هذه المركبات هو باعث للحرارة مع حصول عملية امتصاص للمركبات .
5. اوضحت دراسة مقارنة لامتزاز تلك المركبات على سطح الزيولات ان البوليمر المحضر ذو قابلية اعلى لأمتزاز المركبات قيد الدراسة عدا المركب MB .

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قسم الكيمياء

دراسة أمتزاز بعض ألمركبات ألصبغية على سطح ألبوليمر (تراي أيثانول أمين كليسيرول ماليت)

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من قبل
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