# MODIFICATION OF MOLECULAR SIEVES 13X AND THEIR POSSIBLE USES IN REMOVAL OF PHENOL POLLUTANTS

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**Requirements for the Degree of Master of Science**
**in Chemical Engineering**

**by**

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# *CERTIFICATION*

We certify that the preparation of this thesis titled "**Modification of Molecular Sieves 13X and Their Possible Uses in Removal of Phenol Pollutants**" was made by **Laith Salim Sabri Al-Kuffi** under our supervision at Al-Nahrain University, College of Engineering, in partial fulfillment of the requirement for the degree of Master of Science in Chemical engineering.

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# ABSTRACT

The removal of phenol pollutant from water was studied using continuous adsorption process onto MS type 13X. This adsorbent was treated with urea and thiourea to enhance its adsorption ability towards phenol.

The preparation step was made by mixing of saturated solution of urea or thiourea, with powder molecular sieve 13X and adding sodium silicat as binder to give homogenous mixture in approximate weight percent, 20 wt% urea or thiourea, 30 wt% binder, 50 wt% MS13X. The molecular sieve samples were dried and shaped in cylindrical particles of about 5 mm diameter and 4-8 mm length. The samples ware characterized by X-ray diffraction pattern, FTIR (Infrared Diffraction) Spectroscopy and surface area measurements.

The urea and thiourea treatment, under the experimental conditions employed in the present work, has affected partial their silica and alumina constitution, as shown by their XRD results. Further more, the treatment caused a marked increase in surface area of adsorbents, particularly for urea sample.

The FTIR studies show some interesting interactions between the added urea and thiourea with the original substrates, these are mainly hydrogen band type interactions of the urea and thiourea molecules through their –$NH_2$ moiety with the –OH group of framework oxygen in the mineral or with the adsorbed water. The urea displayed more significant interaction with molecular sieve 13X than thiourea.

Experiments were carried out to investigate the possible use of MS13X and its modified samples for removal of minor amount of phenol from water. Although the investigation was included investigation the effect of the main operating conditions (high of bed, flow rate, inlet concentration of phenol, and Temperatures) on the ability of such adsorbents on the adsorption performance.

Molecular sieve 13X and its admixtures with urea and thiourea showed good ability to remove phenol from water. The urea modified sample, which has the largest surface area, was the best adsorbent for phenol followed by thiourea treated sample.

The results showed also that high percentage removal was achieved by low phenolic solution flow rate, high bed length and low temperatures, as it's expected for the adsorption processes.

The increasing of inlet phenol concentration in water affected largely the driving force and the rate of adsorption, resulted also in higher capacities. While the percentage removal of phenol was decreased by fixed other operating conditions.

Excellent degree of phenol removal, greater than 98% was achieved using 0.2 l/h flow rate of 10 ppm phenolic solution and 56 cm bed length at 30ºC, within the present experiments.

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# LIST OF SYMBOLES

| | | |
|---|---|---|
| **$^{o}$A** | Angstrom, standard unit for measuring small distances equal $1\times10^{-10}$ | |
| **A** | Zeolite type A | |
| **3A** | Potassium exchange Zeolite A | |
| **4A** | Zeolite type A in the sodium from, also referred as A | |
| **5A** | Calcium exchange Zeolite A | |
| **BET** | Brunauer, Emmett, and Teller | |
| **b** | Langmuir equilibrium parameter | **m$^3$/kg** |
| **C** | Concentration of adsorbate in fluid at any time | **g/cm$^3$** |
| **$C_o$** | Concentration of adsorbate in feed phase | **g/cm$^3$** |
| **FTIR** | Infrared Diffraction | |
| **HPLC** | High Performance Liquid Chromatography | |
| **$K_f$** | Freundlich equilibrium parameter | **Kg/kg** |
| **MB** | Molecular Weight of solvent | **g/g mol** |
| **Me** | The positive ion | |
| **MTZ** | Mass Transfer Zone | |
| **MTZL** | Mass Transfer Zone Length | **m** |
| **MS** | Molecular sieve | |
| **1/n** | Freundlich equilibrium parameter | **m$^3$/kg** |
| **ppm** | Part Per million | |
| **Q** | Flow rate | **Cm$^3$/min** |
| **$q_e$** | Concentration of adsorbate in solid phase at equilibrium | **Kg/kg** |
| **X** | Zeolite type X, also referred as 13X | |
| **13X** | Zeolite type X, the number referred to sodium as the main Cation | |
| **XRD** | X-Ray Diffraction | |
| **$\lambda_{max}$** | Maximum Wave Length | |
| **WHO** | World Health Organization | |

# CHAPTER ONE

# INTRODUCTION

Adsorption is a process used to separate materials or to remove trace amounts of undesired components by entrapping them on a solid material. This solid material should have a large internal surface area and have the property of preferentially concentrating the adsorbed material on its surface. Molecular sieves, silica gel and alumina are common solid adsorbents used in the petroleum and petrochemical industries and in the removal of pollutants from environment (1). The fluid phase may be either gas or liquid (2).

As the gas or liquid enters a dry desiccant bed, all of the adsorbable components are adsorbed at different rates. After the process has proceeded for a very short period of time, a series of adsorption zones will appear. These zones represent the length of tower involved on the bed. Moreover, they form and move down through the desiccant bed. When the back of the zone reaches the outlet of the bed, no more adsorption of that component will occur.

The unique combination of physical and chemical properties of zeolites makes them suitable for wide applications in industry, agriculture, medicine (3), and in the removal of pollutants from the environment (4).

Molecular sieves are ordered, porous crystalline aluminosilicates (zeolites) having a definite crystalline structure as determined by X-ray diffraction, within which there are large number of smaller cavities which may be interconnected by a number of still smaller channels or pores. Since the dimensions of these pores are, such that accept for adsorption molecules of certain dimensions while rejecting those of large dimensions.

N-paraffins are separated to this day in large scales by gas or liquid phase adsorption from petroleum fractions, on fixed bed of molecular sieves type 5A. The use of long chain n-paraffins in the production of biodegradable detergents has provided incentive for the extraction of n-paraffins from kerosene (5). Molecular sieves types X and Y are suitable for adsorption of large molecules, such as p-xylene from mixtures with its isomers in liquid phase (6) (7).

Phenol and its derivatives are serious pollutants of water and soils. Contact with large amount leads to death through paralyzing the central nervous system it has been reported that the presence of phenols in drinking water as 0.001 $mg.L^{-1}$(8). Phenols are present in wastewater from oil refineries, coke plants, agricultural pesticides, and phenolic resin plants (9).

Wide informations are available about the removal of phenolic pollutants from water and wastewater. It is possible to remove phenol and chlorinated phenols from aqueous solutions by adsorption on zeolites (10). The concentration of phenol in water could be reduced greater than 99% by chemical precipitation method using lime (9).

The main objective of present project was the removal of phenol pollutant in from water using a fixed bed adsorber. Molecular sieve type 13X was chosen as adsorbent due to its greater ability to accept molecules such as organic phenolic pollutants, into their internal structure.

Attempts were also made to enhance the adsorption capabilities of MS 13X towards phenol, by its modification with strong adduct forming molecules, such as urea and thiourea, since these materials has strong affinity toward phenolics (10). This includes preparation, characterization and adsorptive properties of the modified adsorbents.

The purpose of this investigation is also the evaluation at varying different conditions, in the adsorption of phenol traces.

# CHAPTER TWO
# LITERATURE SURVEY

## 2.1 Fundamentals of Adsorption

### 2.1.1 Principles of Adsorption

Adsorption describes any process wherein molecules from the gas or the liquid are held on the surface of a solid by surface forces.

A porous solid material of large surface area per unit mass in which adsorption of gases or liquids occurs on its surface is called as adsorbent the material to be adsorbed on the adsorbent is known as adsorbate. (11)

Adsorption from solution on a solid occurs as the result of two characteristic properties for a given solvent-solute-solid system, or a combination thereof. The primary driving force for adsorption may be a consequence of lyophobic (solvent-disliking) character of solute relative to the particular solvent, or of a high affinity of the solute for the solid. For the majority of system encountered in water and waste water treatment practice, adsorption results from the combined action of two forces.

The degree of solubility of a dissolved substance is by far the most significant factor in determining the intensity of the first of two forces. The more the substance likes the solvent system (the more hydrophilic in the case of an aqueous solution) the less likely is to move toward an interface to be adsorbed. The second primary driving force for adsorption results from a specific affinity of solute for the solid. In this context, it is desirable to distinguish between three principals' type of adsorption, the affinity may be predominantly:-

**1**- Electrical attraction of the solute to the adsorbent. This kind of adsorption falls within the realm of ion-exchange, and is often referred to as exchange adsorption.

**2-** Van der waals attraction, here when a molecule approaches the solid surface, electrons may take up a new equilibrium distribution but they maintain their respective association in the interacting forces (12). The result from the action of van der waals forces is physical adsorption.

**3-** Chemical force, in adsorption such as a surface will tend to form chemical bonds with a near by phase and this process is called chemusorption, or is the result of chemical interaction between the solid and the adsorbed substance. (13)

The difference between chemical and physical adsorption is that electron transfer takes place between adsorbent and adsorbate in chemisorption but do not take place in physical adsorption. (14)

Physical adsorption is usually weaker than chemisorption and often to distinguish between the two types of adsorption, the heat of physical adsorption is less than about 10 kcal/mol while the heat of adsorption for chemisorption is usually in the range of 10 to 100 kcal/mol (15). Physical adsorption forces are similar to these, which cause condensation of gases into liquids or solids. When adsorbing molecule approaches the surface of the solid, there is an interaction between that molecule and the molecule in the surface which tend to concentrate the adsorbing molecules on the surface as much as that a gas molecule is condensed on the surface of bulk liquid, the molar heats of adsorption are of the same magnitude as molar heat of vaporization (15).

H.M.Barry defines the adsorption as a physical phenomenon which occurs when gas or liquid molecules are brought into contact with a solid surface the process of adsorption involves separation of a substance from one phase accompanied by its accumulation or concentration at the surface of another (16).

### 2.1.2 Adsorption mechanism

Adsorbents may be divided into two classes. Those which owe their activity to surface adsorption and capillary condensation and another type which react chemically.

The basis of distinction is the nature of the bonding between the molecules and the surface. With physical adsorption the only bonding is weak Van der Waals type forces. There is no significant redistribution of electron density in either the molecules or at the substrate surface. The nature of this bond may lie any where between the extremes of vitally complete ionic chemisorption is a chemical bond, involving substantial rearrangement of electron density, formed between the adsorbate and substrate. The nature of this bond may lie any where between the extremes of vitally complete ionic or complete covalent character (17). The difference between the two processes is shown in Table (2-1). The physical adsorption finds wide application in natural gas processes and in separation of petrochemicals.

**Table 2-1** Typical Characteristics of Adsorption Processes

| Parameter | Chemisorption | Physisorption |
|---|---|---|
| Temperature range | Virtually unlimited given molecule may effectively adsorb only over a small range | Near or below the condensation point of the gas |
| Adsorption enthalpy | Wide range related to the chemical bond strength typically 40-800 KJ/mole | Related to factor like molecular mass and polarity 5-40 KJ/mole |
| Nature of adsorption | Often dissocative may be irreversible | Non-dissocative reversible |
| Saturation up take | Limited to one monolayer | Multiple uptake possible |
| Kinetics of adsorption | Very variable often an activated process | Fast since it is a non-activated process |

### 2.1.3 Adsorption Isotherms

Giles (18) made a classification for adsorption isotherm depends on the primary section of isotherms. This classification gives the symbols S, L, H, C, when S class take the shape adsorption in which the adsorbed particules directed on the surface vertically or oblique, as well as the solvent may undergo a great adsorption on the adsorbed surface, while class L is specialized for bisotherm adsorption of Langmiur type (19). And the adsorbed particules directed horizontally on the surface and the adsorption is unilayer.

Class H is specialized for the high affinity adsorption and seen the highly diluted solutions and during adsorption of large molecules like polymers and finally, class C refers to the presence of constant partition between the adsorbed material and the adsorption surface on the other hand, also it refers to high possibility of chemical adsorption as shown in Fig (2-1).

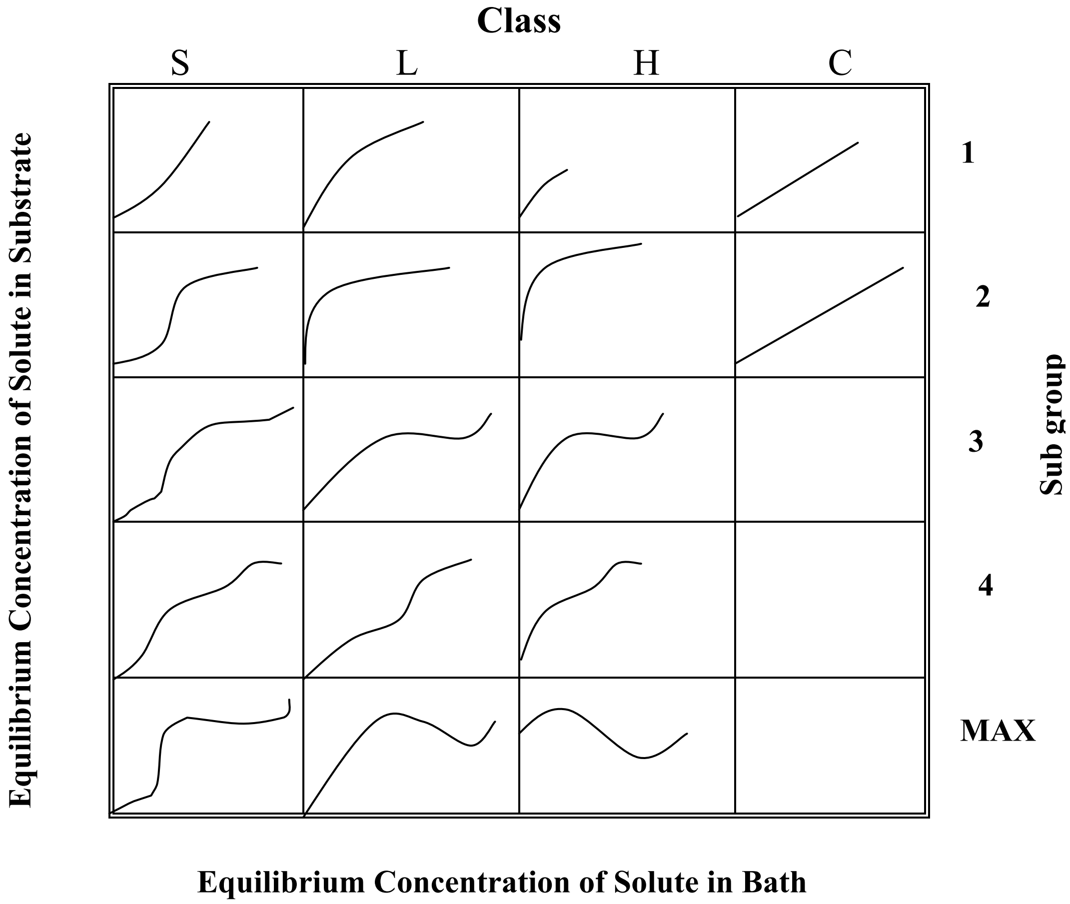


**Figure 2-1** Giles Classification of Adsorption (18)

Brunauer and his group made another classification of adsorption isotherm according to five classes ;(20)(21) Class I is the L type according to Giles, while class II is nearly expected from BET at multilayer adsorption and mostly occurs gases adsorption starts in which it refers that adsorption about infinity when start gas condensation. In class III is seen when the interference between the first layer and the adsorbed material is weaker than interference between second layer and first layer.

Class IV is similar to class I except that there are two limitations for the quantity of adsorbed material instead of one. Class V is suggested as combination between I and II. The classes III and V are not widely distributed. The chemical adsorptions occur within class I only while physical adsorptions occur in any one of the five classes as shown in Fig (2-2).

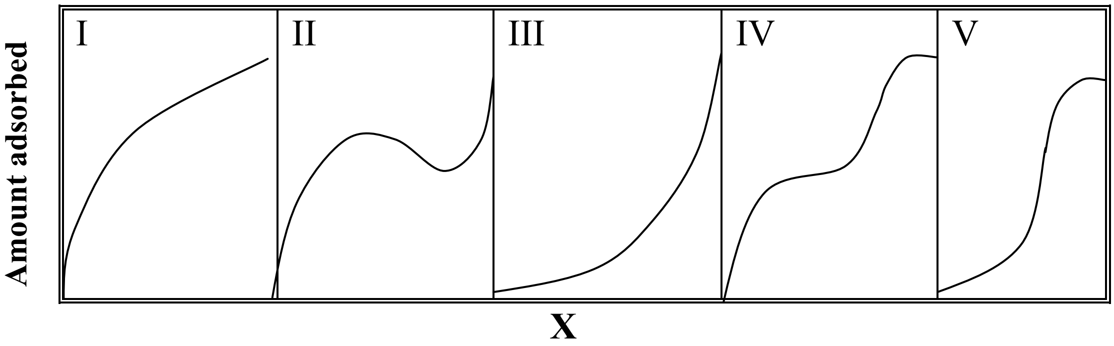


**Figure 2-2** Brunauer Classification of Adsorption (22) (20)

## 2.2 Liquid Phase Adsorption

The liquid is a homogeneous mixture; it is customary to designate one component the solute and the other the solvent. The assumption is then made that the change in composition of the bulk liquid in contact with the porous solid is due entirely to adsorption of the solute. That is, adsorption of the solvent is tacitly assumed not to occur (21).

The adsorption in a liquid-solid system results in the removal of solute from solution and their concentration at the surface of the solid , to such time as the concentration of the solute remaining in solution is in a dynamic equilibrium with that at the surface.

At this position of equilibrium, there is a defined distribution of solute between the liquid and solid phases. The distribution ratio is a measure of the position of equilibrium in the adsorption process; it may be a function of the concentration of the solute, the concentration and nature of competing solutes, and the nature of the solution. For practical applications, the classical equations of Freundlich and Langmuir are still dominant because of their simplicity and ability to correlate isotherm (21).

The Langmuir's equation is :( 21) (23)

$$\mathbf{q_e = QbC/ (1+bC)} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \textbf{(2-1)}$$

**$q_e$**= the amount of solute adsorbed per unit mass of adsorbent at concentration C (Kg/kg).

**Q**= the amount of solute adsorbed per unit mass of adsorbent informing a complete monolayer on the adsorbent surface Kg/kg.

**b**= Langmuir equilibrium parameter $m^3/kg$

**C**= Concentration of adsorbate in solid phase at equilibrium $Kg/cm^3$

The Freundlich equation is: (23) (21)

$$\mathbf{q_e = K_f\ C^{1/n}} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \textbf{(2-2)}$$

**$q_e$**= The amount of adsorbate in solid phase at equilibrium Kg/Kg.

**$K_f$**= Freundlich equilibrium parameter Kg/kg.

**1/n**= Freundlich equilibrium parameter $m^3/kg$.

The preferred form for depicting this distribution is to express the quantity ($q_e$) as a function of (C) at a fixed temperature, the quantity ($q_e$) being the amount of solution adsorbed per unit weight of solid adsorbent, and (C) the concentration of solute is remaining in solution at equilibrium.

In binary and multicomponent mixtures competition varies. Simple competitions involes large number of organic compounds where any increase in concentration of one solute decrease concentration of others. However, this effect varies with many variables such as the range of concentration. Sometimes the adsorption of one substance is not influenced by the presence of another because the second is not appreciably adsorbed. For example the production of pure p-xylene by separation from m-xylene, o-xylene and ethylbenzene plays a prominent part in the petrochemical industry (6). And other example adsorption kinetics of straight chain paraffins in liquid phase by fixed beds of molecular sieves (7).

The factor effecting on dynamic liquid adsorption are Type of adsorbent(24), Particle size(24), Depth of adsorbent bed(24), Fluid velocity(24)(25), Adsorbate concentration(24), Nature of adsorbate(26)(24), Temperature(24), The presence and concentration contaminant(27)(24), decomposition and polymerization of the adsorbate(24)(27), and Ionic strength effect(28)(29).

## 2.3 Adsorbents

### 2.3.1 Properties of Adsorbent

Adsorbents are generally used as fixed bed through which the streams to be treated are passed (25), therefore the adsorbents must have good mechanical properties such as strength and resistance to attrition and it must have good kinetic properties. The adsorbents ought to be capable to transfer adsorbing molecule rapidly to the adsorption sites.

In most application the adsorbent ought to be regenerated after use, therefore, it is desirable that regeneration can be carried out efficiently and without damage to mechanical and adsorptive properties.

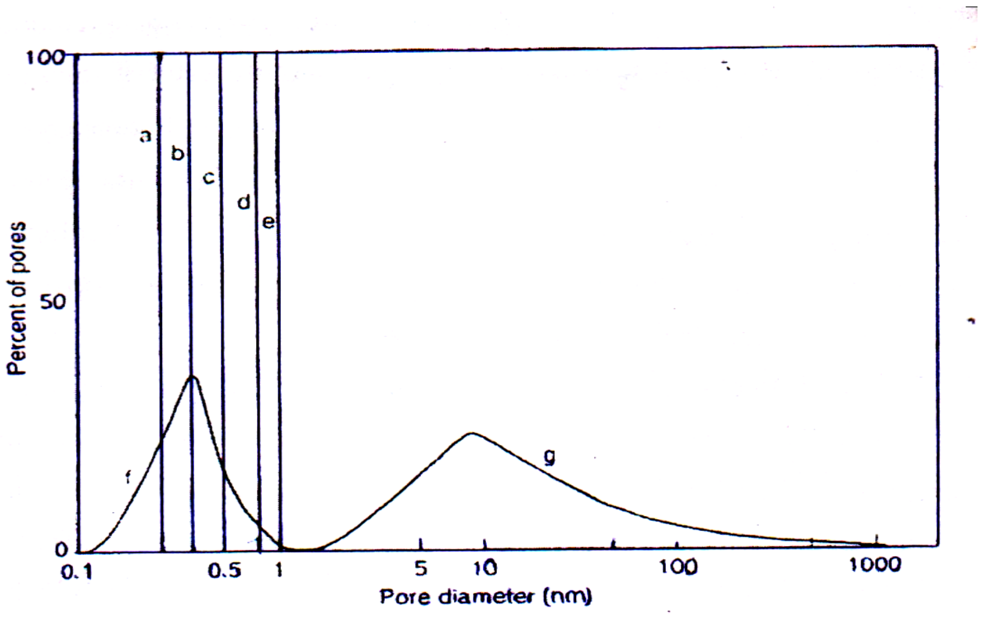
The raw materials and methods for production adsorbents have to be ultimately be inexpensive for adsorption to complete successfully on economic grounds with alternative separation processes (30). Since adsorption is a surface related phenomenon, the useful adsorbents are all characterized by a large surface area per unit weight; the high internal surface area of an adsorbent creates, and the high capacity needed for a successful separation or purification process. Adsorbents can be made with internal surface areas, which range from about 100 $m^2/g$ to over 3000 $m^2/g$. For practical applications, the range is normally restricted to about 300-1200 $m^2/g$. (30)

A large specific surface area is preferable for providing large adsorption capacity, but the creation of a large internal surface area in a limited volume inevitably gives rise to large numbers of small sized pores between adsorption surfaces (31). Some of the qualities that make a solid commercially important adsorbent are available in a large quantity, high capacity for the gases and liquids to be adsorbed, high selectivity, ability to reduce the materials to be adsorbed to a low concentration, ability to be regenerated and used again, mechanical strength, and chemical inertness (16).

Pore sizes may be distributed throughout the solids as in the case of an activated carbon, or take very precise values as in the case of zeolite crystal. Pore sizes are classified generally into three ranges, macropores with diameter in excess of 50 nm, mesopores (known also as transitional pores) with diameters in the range 2-50 nm, and micropores with diameters smaller than 2nm.

The largest pores within an adsorbent are generally in the submicron size range and they account for only a small fraction of the total pore volume (30). Pore size distributions for adsorbents are shown in Fig (2-3) (30). Many adsorbent materials such as carbons, silica gels and alumina are amorphous and contain complex networks of interconnected micropores, mesopores and macropores.

In contrast, in zeolitic adsorbents, the pores or channels have precise dimensions although a macroporous structure. They are created when pellets are manufactured from the zeolite crystals by the addition of binder (30).



a, b, c, d, e and f for molecular sieves, type 3A, 4A, 5A, 10X, 13X and Ms-carbon respectively and g for carbon.

**Figure 2-3** Micropores Size Distribution for Different Adsorbent (30)

## 2.3.2 Classification of Adsorbents

The common used adsorbents are as follows:

1. Bauxite naturally occurring mineral composed primarily of $Al_2O_3$.
2. Alumina, a purer manufactured version of bauxite.
3. Gels, composed largely of $SiO_2$ or alumina gel, manufactured by chemical reaction.
4. Molecular sieves, a calcium sodium alumina silicate (Zeolite).
5. Carbon (Charcoal), a carbon product treated and activated to have adsorptive capacity.

Adsorbent material must have a high internal volume, which is accessible to the components being removed from the fluid. Such a highly porous solid may be carbonaceous or inorganic in nature, synthetic or naturally occurring, and in certain circumstance may have true molecular sieving properties (30). Adsorbents have been developed for a wide range of separation commercial materials. Adsorbents are providing usually as pellets, granules, beads and powders (25). Commercial adsorbents which exhibit ultra porosity and which are generally used for the separation of gas and liquid mixtures include the molecular sieve zeolite, activated alumina silica gel and activated carbon .(32)

The application for these adsorbents depends on their particular adsorptive properties. The surface selectivity can be broadly classed as hydrophilic or hydrophobic (25). Polar adsorbents are thus called "hydrophilic" and alumina silicates such as zeolite, porous alumina, silica gel, or silica-alumina are examples of adsorbents of this type (33). On the other hand, non-polar adsorbents are generally "hydrophobic”. Carbonaceous adsorbent polymer adsorbent and silicates are typical non-polar adsorbents. These adsorbents have more affinity with oil or hydrocarbons than water. (34)

The polar or hydrophilic types are generally employed when the materials to be removed are more polar than the process liquid. Specific applications include dehydration of organic liquid, decolorization and removal of peroxides from vegetable oils and animal fats and oils, and the treatment of spent lubes and petroleum waxes.

The non-polar or hydrophobic adsorbents are generally employed to remove less polar contaminants from polar bulk streams (35). Specific application includes, decolorization of sugar syrups, removal of sulfurous, phenolic compounds and various aqueous solution of acids, alkalis, amines, glycols, salts and gelatin, removal of grease from dry cleaning solvents and from electroplating solution and removal of protein wastes, aniline, benzene, phenol, and camphor from water(36).

## 2.4 Molecular Sieves

### 2.4.1 Structure and Types

Molecular sieves are crystal compounds of alumina silicat with alkaline metal, and look like the natural Zeolite, and prepared with several groups according to the metal type and its proportion to alumina and silicone oxide, as they are used for industrial purposes after mixing with about 20% of natural clay as a binder (39).

The structure of crystal molecular sieve contains voids of diameter (11.4 ºA), and these voids unit to form smaller voids of different diameter according to metal type and its proportion to aluminum and silicon oxide. Therefore, the molecular sieve are of many classes and used in the separation of the compounds according to their molecular diameter (39).

Famous industrial groups are referred to as according to the diameter of voids in to (3A, 4A, 5A, 10 X, 13 X) in addition to, (Y) groups. While the general chemical structure of molecular sieve is (39):

$$\mathbf{Me_{12/n}\,(AlO_2)_{12}.\,(SiO_2)_{12}.X\,H_2O}$$

In which (Me) is the positive ion of change (n), therefore, the known group (4A) is composed of:

**$0.96\ Na_2O.1.00\ Al_2O_3.1.02\ SiO_2$**

It contains, voids of (4°A) diameter, this group is used to adsorb the molecules of molecular diameter less than (4°A). When (75%) of sodium ions are replaced with potassium ions of large size in the crystal compound, we obtain the group (3A) of voids with (3°A) diameter and when we replace (75%) of sodium ions of group 4A with calcium ions of smaller size, we obtain the group (5A) of (5°A) diameter which have the ability to adsorb the molecules of diameter less than (5°A) as in the linear paraffins. In addition to group, (A) molecular sieve. There are other types known as (Y) and (X) contain voids of (8-10) °A. While the general structure of the group known as (13X) is (39):

**$Na_2O.Al_2O_3.2.0\text{-}3.0\ SiO_2$**

And when (75%) of sodium ions in this group is replaced with calcium we obtain the known group (10X), which used to separate large molecules like non-branched paraffins, aromatic compounds, while the (Y) groups consist of

**$Na_2O.Al_2O_3.3.0\text{-}6.0\ SiO_2$**

Used mostly as catalyst in cracking operation and others. All the previous sieves have pH of about (10) and it is considered stable at pH (5-12).

The positive ions of molecular sieves can be replaced with others of specific catalyst properties of some chemical reactions. And the replacements occur by (Ion Exchange) (39).

The frameworks consist of tetrahedral arrangement of sodalite units linked by hexagonal faces with six bridge oxygen ions (41). The crystalline molecular sieves have a very high internal surface area, or equivalent surface area, and up to 50 vol. % in terms of internal porosity. This is due to a system uniform interpenetrating channels and cavities (38) (37). This result in series of wide, nearly spherical cavities (super cages), each of which opens by common windows (distorted 12-rings of 8-9A° diameter (40)) into four identical tetrahedral distributed cavities. The overall view of the faujasite lattice is that of a tightly packed aggregate of oxygen atoms interlaced with large voids at least for a highly ionic model where the aluminum and silicon ions are small enough to occupy the center of the tetrahedron of four oxygen ions (41). The unit cell of Lind 13X is: (42) (43) (44)

$$\mathbf{Na_{86}.\ (AlO_2)_{86}.\ (SiO_2)_{106}.264H_2O}$$

The water of hydration that fills the cavities is loosely bound and is removed by heat treatment. The voids that formerly were occupied by this water can be refilled by adsorbing a variety of gases and liquids. The numbers of water molecules in the unit cell are 246. The 13X sieve has even larger channels and adsorbs most ordinary hydrocarbon (45).

### 2.4.2 Adsorption Properties of Molecular Sieve

Various terms have been used to describe the penetration and containment of molecules in dehydrated crystalline zeolite. These include occlusion, imbibitions, and intercalation per sorption, sorption and adsorption. Adsorption is used because it is best describing the interaction between a molecule and a surface, where there it is external surface of a solid or the internal convoluted surface of a dehydrated, microporous zeolite crystal (32).

The molecular sieve zeolite is distinct from other three major adsorbents (silica gel, activated carbon, and activated alumina) in that they are crystalline and the adsorption takes place inside the crystals (25). Zeolite adsorbent is not only the most important adsorbents today, but their importance is increasing, mainly because of the following unique adsorptive property (46). These materials have high capacity, and selectivity adsorbents, because of the following reasons:

**1-** They can separate molecules based upon the molecular size and shape of the particular molecular species relative to the uniform apertures in the zeolite crystal. (37)

**2-** They can separate molecules based upon selectivity effects. This is caused by the interaction of the zeolite with certain molecular parameters such as bipole moments and the like. (37)

**3-** Highly hydrophilic surface. (46)

**4-** Variation of properties by ion-exchange. (46)

Molecular sieves selectively adsorb or reject molecules based upon difference in molecular size, shape, and other properties such as polarity. The sieve effect may be total or partial (47). So, separation may be achivied in one of two ways through the molecular sieve effect or dominant cation present (48). During the adsorption of various molecules, their micropores fill and empty reversibly.

Adsorption in molecular sieves is a matter of pore filling, and the usual surface area concepts are not applicable (25). Molecular sieves have a sorption area available on the inside of a large number of uniformly sized pores of molecular dimensions (49). With such an arrangement molecules of a certain size and shape enter the pores and are adsorbed while larger or differently shaped molecules are excluded (50).

Molecular sieves may be activated by heating to affect the loss of the water of hydration. The dehydration results in crystals interlaced with channels of molecular dimensions that offer very high surface area for the adsorption of foreign molecule (50). The molecular sieves is porous crystals the pore system of which consisted only of channels of molecular dimensions(43), these dimensions being quite precise and controlled as accurately as the position of the lattice atoms surrounding them(51) (52). Zeolite 13X (NaX) is the largest known pore size in zeolite. Some of physical properties of 13X are shown in Table (2-2) (16) (53).

**Table 2-2** Physical Properties of Molecular Sieves 13X

| Specification | Value |
|---|---|
| Internal porosity (%) | 38 |
| Bulk dry density (g/cm$^3$) | 0.58-0.64 |
| Average pore diameter (nm) | 0.8-1.0 |
| Surface area (Km$^2$/g)(54) | 0.6-0.7 |
| Sorptive capacity (Kg/Kg) | 0.25-0.36 |
| Crushing strength (N) | 30 |
| Atteition loss (Wt. %) | 0.3 |

### 2.4.3 Application of Molecular Sieve

Molecular sieve adsorbents have become a powerful tool in the hands of the process engineer and are being utilized today in virtually all the major process industries. (60)

Silica gels, alumina, activated carbons, carbon molecular sieves, and organic resin zeolite are important industrial adsorbent with a wide range of uses. Their diversity is due to the fact that molecular sieves have high adsorption capacity and show great selectivity (56). Major industrial adsorption process using zeolite adsorbents may be classified as hydrocarbon separation processes, drying of gases and liquids, separation and purification of industrial streams, pollution control applications, and non-regenerative application.(46)

These adsorption phenomena are commercially exploited in a number of applications such as the drying of refrigerant, the recovery of normal paraffin hydrocarbons from various hydrocarbon feedstock for the manufacture of biodegradable detergent (57), the removal of nitrogen from air to produce oxygen enriched gas for use in the treatment of secondary sewage effluent, the removal of water, carbon dioxide (58) and sulfur containing components from natural gas (48), the selective adsorption of aromatics from hydrocarbon mixture(37), and the separation of straight chain paraffins from petroleum fraction. Furthermore, molecular sieves are used widely as catalyst, such as cracking processes.

Molecular sieves 13X used in separation, purification and drying (59). Some of these applications are purification of air before liquefaction (32), natural gas purification (32), and separation of substance (32). Separation of certain aromatic hydrocarbon, drying and mercaptan separation from natural gas and LPG (60), $NH_3$ and $CO_2$ removal from gas streams (54) (60). Adsorption of aromatic hydrocarbon and organic sulfur compounds, and petrochemical industry and catalysis of hydrocarbon processing (55).

Other applications…….Natural molecular sieves zeolites are being used to treat low and intermediate aqueous waste (Radioactive Waste Treatment). Current users are British Nuclear Fuels in Great Britain, West Valley Nuclear and Data Ridge National Laboratory. Natural molecular sieves zeolite has been used in the clean-up at Three Mile Island and Chernobyl (62).

## 2.5 Mass Transfer Zone

### 2.5.1 Definition

Adsorption takes place from the inlet of the column and proceeds to the exit. In the course of adsorption, a saturated zone is formed near the inlet of the column and a zone with increasing concentration is observed at the frontal part. Mass transfer from fluid to adsorbent occurs in this region, called the "mass transfer zone"(31).

The mass transfer zone or adsorption zone is defined as the portion of the bed in which adsorption is occurring. It is the distance between the layer of the exhausted adsorbent at the top of the zone and the layer of unused adsorbent at the bottom of the zone (63). Fig (2-4) shows the mass transfer zone inside the bed. When a fluid containing a constant concentration (C) of adsorbate enters a fixed bed, the concentration in the fluid falls to a low value in equilibrium with the fresh adsorbent over a finite length of column. That length is termed the MTZ (Mass Transfer Zone) and shown as 0a. As the adsorbent at the plane (0), C becomes saturated in equilibrium with (C.a) at time (t1), moves to the position (eb) at (t2). After a time (t3), when the low concentration end of the adsorption wave has reached the exit of the bed (64).

In practice, it is difficult to follow the progress of the MTZ inside a column packed with adsorbent, because it is difficult to make meaning measurement of parameter other than temperature (30). But the movement and the breakthrough of this mass transfer zone completely described the adsorption process of a packed bed (65).

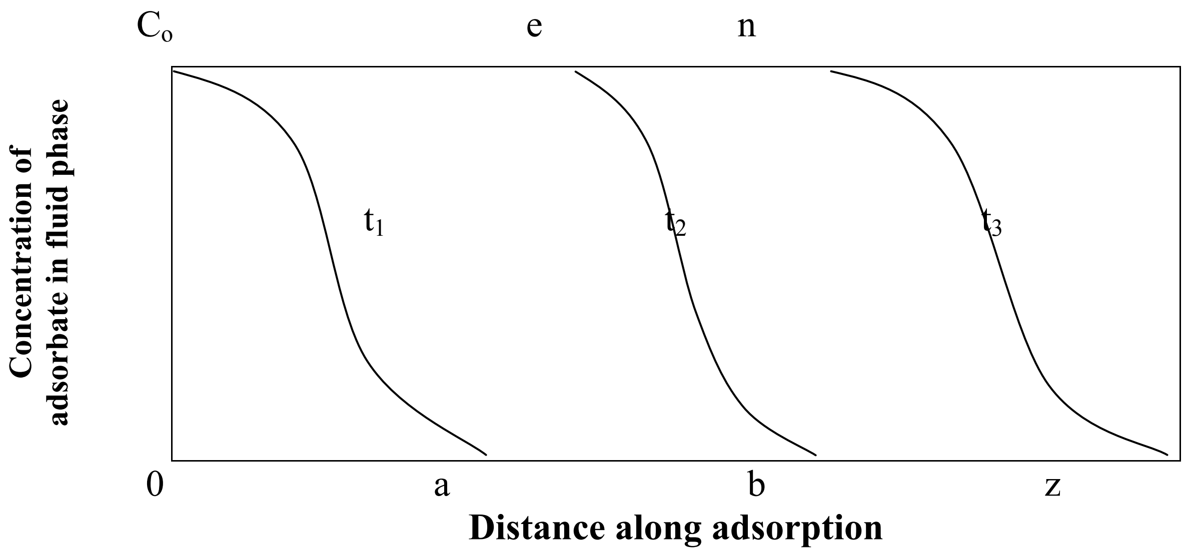


**Figure 2-4** Mass Transfer Zone (MTZ) at Various Positions

### 2.5.2 Mass Transfer Zone Length

The height of the adsorption zone can be calculated from experimental breakthrough data. This height can be calculated from equation (2-3).

$$Z_a=Z\,(t_e-t_b)/[t_e-(1-f)(t_e-t_b)] \qquad \textbf{2-3}$$

Where:

**$Z_a$**= the mass transfer zone length, cm

**Z**= the height of adsorbent bed, cm

**$t_e$**= time required to exhaustion, minutes

**$t_b$**= time required to break point, minutes

**f**= Exploitation grade of mass transfer zone

Actually, f is often approximately 0.5 but may vary from abut 0.35 to 0.65 depending on the shape of the breakthrough curve. It is obtained from the surface under and above the S-curve(66) (17).

The MTZL is independent of the bed length .Its function as a type of adsorbent, adsorbent particle size, fluid velocity, fluid properties, adsorbate concentration in entering fluid, adsorbate concentration in the adsorbent (if the latter has not been fully reactivated), temperature of the adsorbent bed, and pressure (66) (17).

### 2.5.3 Breakthrough Curve

The performance of a fixed bed adsorption column is characterized by the variation of the effluent concentration with time (breakthrough curve)(35). The theoretical derivation of this curve is very important step in the design of any fixed bed adsorption system (67). For explaining the breakthrough curve it considered that an adsorbent bed with feed entering at one end and product leaving at other end. Fig (2-5) shows the adsorbate concentration in the stream leaving bed as a function of time.

The distribution of adsorbate in the solid bed is indicated in the sketch at (a), where the relative density of the horizontal lines in the bed is meant to indicate the relative concentration of adsorbate. The uppermost layer of the bed is practically saturated and the bulk of adsorption takes place over a relatively narrow adsorption zone in which the concentration changes more rapidly.

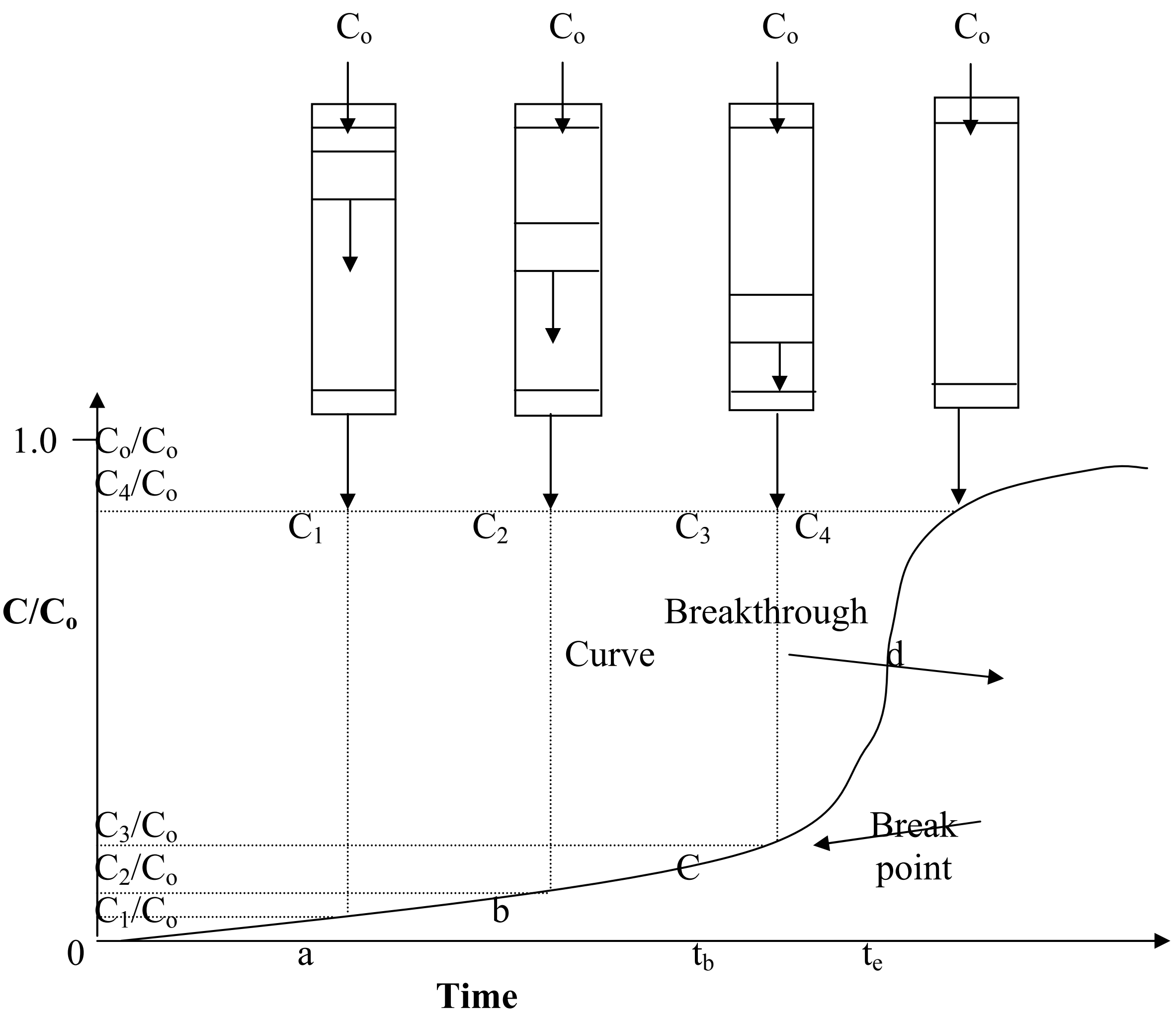


**Figure 2-5** Breakthrough Curve Development in a Column

As flow continues, the adsorption zone moves downward as a wave, at a rate ordinarily very much slower than the linear velocity of the fluid through the bed. At a later time, as at (b) in the figure, roughly half of the bed is saturated with solute, but the effluent concentration (C2) is still substantially zero. At (C), in the figure, the lower portion in the adsorption zone has just reached the bottom of the bed, and the concentration of solute in the effluent has suddenly risen to an appreciable value (C3) for the first time.

The system is said to have reached the "break point”. The solute concentration in effluent rises rapidly as the adsorption zone passes through the bottom of the bed and at (d) has substantially reached the initial value (C), the portion of effluent concentration curve between positions (C) and (d) is termed the "breakthrough curve”. The shape and the time of appearance of the breakthrough curve influence greatly the method of operating a fixed adsorbed. The curves generally have an S shape, but they may be steep or relatively flat and in some cases considerably distorted (13).

The break point is often taken about as a relative concentration of 0.05 or 0.1 and since only the last portion of fluid processed has this high concentration, the average fraction of solute removed from the start to the break point is often 0.99 or higher(68). If adsorption continued beyond the break point, the concentration would rise rapidly to about 0.5 and then more slowly approach 1.0(69). The time at which the trailing edge of the mass transfer wave reaches the affluent end of the bed is called the equilibrium time, and designated ($t_e$). At time ($t_e$) all of the adsorbent in the bed is at equilibrium with the concentration of sorbable component in the feed. The adsorbent capacity is completely spent and the bed is said to be at equilibrium(70).

## 2.6 Applications of Adsorption

The major economic uses of adsorption indicate the widespread applicability of the method and also suggest the areas in which new uses are most likely to develop.

The unit operation of adsorption provides for the separation of fluid system into two or more components. The use of solid for removing substance from either gases or liquid solution has been widely used since biblical times, this process known as adsorption. From the early days of using bone Chan for decolorization of sugar solutions and foods, to the later implementation of activated carbon for removing nerve gases from the battlefield, to days many of applications. The adsorption phenomenon has become a useful tool for purification and separation purposes. There are several definitions of adsorption such as the preferential partitioning of substances from the gases or liquid phase onto the surface of a solid substance (34). The applications of adsorption can be classified into two types:

1. Drying and purification:

This includes the application in which contaminants at concentration have about 3% or less is removed from a carrier fluid. The removal of water, odorants and colorants represent typical examples. Purification refers to removal of up to a few percent of an impurity from a carrier stream. Natural gas dehydration and sweetening are widely carried out by adsorption processes.

2. Bulk Separation:

This involves the application in which the sorbable component represents a significant fraction of a bulk fluid, generally on the order of 3% to 50%. Bulk separation process recovers both the carrier fluid and the adsorbate. The separation of normal paraffin's from kerosene is a common example (71).Table (2-3) shows the major application of adsorption:

**Table 2-3** Shows the Major Application of Adsorption $^{(25)}$

| Separation | Adsorbent |
|---|---|
| **Gas bulk separation** | |
| Normal Paraffin's, Isoparaffine, Aromatics | Molecular sieves |
| $N_2/O_2$ | Zeolite |
| $O_2/N_2$ | Carbon molecular sieve |
| $CO, CH_4, CO_2, N_2, A, NH_3/H_2$ | Zeolite, activated carbon |
| Acetone/vent streams | Activated carbon |
| $C_2H_4$/Vent streams | Activated carbon |
| $H_2O$/ethanol | Zeolite |
| **Gas purification** | |
| $H_2O$/olefin-containing cracked gas, natural gas, air, synthesis gas, etc. | Silica , alumina , zeolite , molecular sieves |
| $CO_2/C_2H_4$, natural gas, etc. | Molecular sieves, Zeolite |
| organic/vent streams | Activated carbon , other |
| Sulfur compounds /natural gas , hydrogen ,liquefied petroleum gas (LPG),etc | Zeolite |
| Solvent/air | Activated carbon |
| Odors/air | Activated carbon |
| $NO_X/N_2$ | Zeolite |
| $SO_2$/vent streams | Zeolite |
| **Liquid bulk separation** | |
| Normal paraffin ,isoparaffine , aromatic | Zeolite |
| p-xylene/o-xylene , m-xylene | Zeolite |
| detergent-rang olefins/paraffin's | Zeolite |
| p-diethyl benzene / isomer mixture | Zeolite |

| | |
|---|---|
| fructose/glucose | Zeolite |
| **Liquid purification** | |
| $H_2O$/organic, oxygenated organic, Chlorinated organic, etc | Silica , alumina , zeolite |
| Organic ,oxygenated organic, chlorinated organic,etc./$H_2O$ | Activated carbon |
| Odor ,taste bodies/drinking $H_2O$ | Activated carbon |
| Sulfur compounds/organic | Zeolite , other |
| Various fermentation products/ fermentor effluent | Activated carbon |
| Decolororizing petroleum fraction, sugar syrups, vegetable oils, etc. | Activated carbon |

## 2.7 Phenolics Pollutants

### 2.7.1 Hazard Effect

Phenols are protein degenerating and highly toxic (72). Contact with large amount leads to death through paralyzing the central nervous system (73). If phenol is inhaled or swallowed, local cauterizing occurs with headaches, dizziness, vomiting, irregular breathing, respiratory arrest, and finally heart failure (74). Phenols are toxic to fish as well as human at levels above (2) mg/L and can cause bad test in fish at concentration for below the toxic level (74). Sufficient concentration of phenol can deplete the oxygen in a receiving body of water since it has a relatively high oxygen demand (theoretically, 2.4 mg O/mg phenol) (74).

The pollution of natural water resources supplied by phenolic-bearing wastes is becoming an increasingly serious problem in recent years. Phenols are present in wastewater from oil refineries, coke plants and phenolic resin plants for example of industrial phenolic waste water from phenolformaldeyde (novolac) resin plant(74) (10).

Phenols, particularly chlorophenol, whether from the chlorination of water or from industrial and agricultural sources, are serious pollutants of water and soils (10). It has been reported that concentrations of phenols in unpolluted water are usually less than 0.02 $mg.L^{-1}$ (75). However, WHO's Guidelines for Drinking Water Quality gives the level of phenols for drinking water as 0.001 $mg.L^{-1}$ (8).

### 2.7.2 Removal

Phenols pollutants can be removed either chemically or by adsorption. Phenol can be removed from water and wastewater by chemical precipitation with Iraqi manufactured lime using Calcium hydroxide $Ca(OH)_2$ slurry (milk of lime) of (10%) concentration prepared by dissolving powdered lime in distilled water(74).

Jordanian zeolitic tuffs was used to remove phenol, p-chlorophenol, o-chlorophenol, and 3,5-dichlorophenol from aqueous solution (10). It was reported, that both urea and thiourea admixtures were more effective than the free zeolitic tuff in the removal of phenol and chlorinated phenols from water (10).

Iraq zeolite type 5A was used to remove of phenol, o-nitro phenol, and o-amino phenol from aqueous solutions. It was reported, that urea admixture to obtain zeolite-urea complex, and the complex was then polymerized with formaldehyde to obtain zeolite-polyurea formaldehyde resin (75).

Nedelchra and Iranva studied the adsorption of some phenols form watery solutions on the surface of cotton treated with NOCl shell cellulose used in paper industry which find that the quantity of adsorbed material increase with increase OH groups of phenols (76).

Miskarli studied the phenol adsorption on treated pentonate. The modification was done to increase its hydrophobic property in both hydrocarbon and watery media. Phenols from water solution could be faster adsorbet than from hydrocarbons media (77).

Anand, Dasare studied the adsorption of some phenols from water solutions by using styrene –divinylene benzene copolymers. The investigation was included the effect of pH and present of ions on the adsorption ability (78).

# CHAPTER THREE
# EXPERIMENTAL WORK

## 3.1 Materials

Synthetic crystalline molecular sieve type 13X as adsorbent was supplied by Fluka AG. Urea and Thiourea were used for adsorbent modification, which were obtained from local market as chemical grade materials. Sodium silicate obtained from AL-Basil Company was used as binder for the adsorbent. Phenol (99.95%pure) was used as adsorbent material and supplied from (BDH) laboratory reagents.

## 3.2 Preparation of Adsorbent

Molecular sieve 13X for adsorption and modification purposes was dried in oven type of (HERAEUS) at 120ºC for 2hours, then cooled in a discater contains silica gel to avoid the humidity from the environment in which it is kept during the storage period to be used in the adsorption column.

The molecular sieve 13X for modification process was crushed gently by hammer and hand ground by a glass rod. The ground material was sieved to get powder of particules size less than 45 micrometer. Saturated solution of urea or thiourea was prepared by dissolving of 50g of each in 70 ml distilled water. The required amounts of pulverized MS13X and sodium silicate as binder were added to the saturated solution of urea or thiourea room temperature. The mixture was mixed manually to get homogenous slurry. The blend was shaped into cylindrical parts of 5mm and 4-8mm length by meet machine. The cylindrical pellets were dried at room temperature for 72hr and then at 120ºC for 2hr in an oven and finally cooled in a discater. The final proportion of material for molecular sieve modification was as follows:

| | |
|---|---|
| Molecular sieve 13X, as powders | 50% |
| Urea or Thiourea | 20% |
| Sodium silicate, as binder | 30% |

## 3.3 Characterization of Adsorbents

The crystallinity of the original and modified molecular sieve 13X was determined by means of X-Ray diffraction type (X-RD 1390 PHILIPS). The XRD patterns of the samples are shown in Appendix (A) and (B). This test was made in the College of Science, the Geology Department, University of Baghdad.

The bands and structures of the original and modified molecular sieve 13X was determined by means of INFR-RED type (SHIMADZU FTIR 8400S). The IR patterns of the samples are shown in Appendix (C) and (D). This test was made in the College of Science, the Chemistry Department, University of Baghdad.

The surface area measurements for some selected samples of the original and modified MS13X were conducted by Ibn-Sina Company by adsorption of $N_2$ using Carlo-Erba sorptomatic.

## 3.4 Adsorption of Phenol

### 3.4.1 Apparatus

The adsorption of phenolic pollutants was performed in a conventional continuous flow packed column. The adsorption column was made from Q.V.F glass of internal diameter 1.5cm and length 80cm. It was included four distributers (aluminum) located in 14 cm intervals to get the best diffusion. The bottom of adsorption column is fitted with a valve connected with a 50ml receiver for collection of effluent. A 15 liters glass container for feed, connected with dosing pump (SEYBERT AND RAHIER) type R308 W24e, for pumping the feed at desired flow rate to the top of adsorption column.

The heating of aqueous phenolic solution at desired temperatures was done by water bath, type memmert, to evaluate the effect of temperature on the adsorption. The insulation was by fiber glass, and controlled automatically. The temperature measurement was done by a thermocouple.
A schematic diagram of the apparatus employed throughout the investigation is show in Fig 3-1.

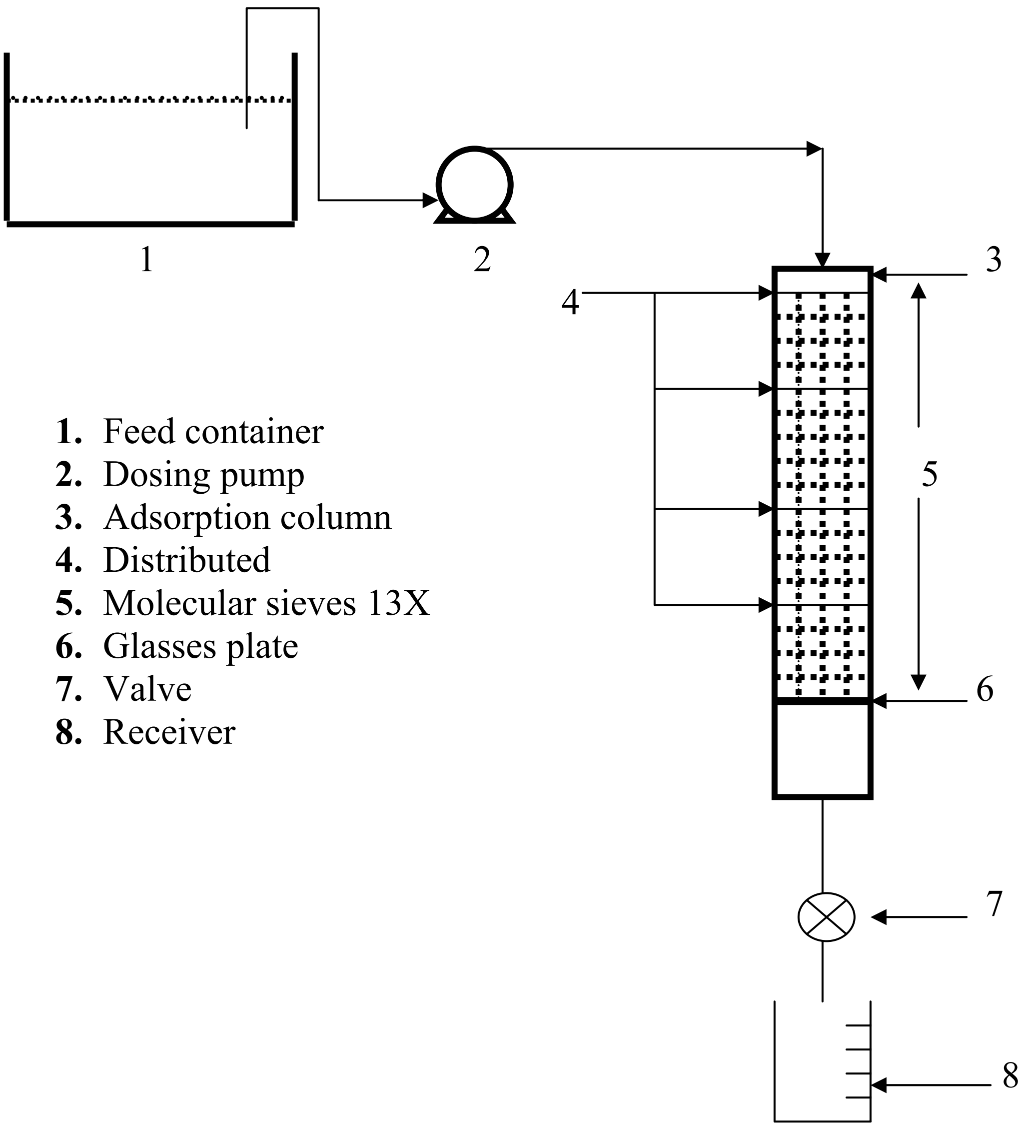
### 3.4.2 Operating Procedure

The adsorption column was packed for each experiment with the desired hight of the adsorbent, original and modified MS13X. Aqueous solution of desired amount of phenol (i.e. 10ppm) was pumped in for each run, at constant flow rate. Samples of effluent were taken every 30 min for analysis of phenol content. Each experiment was carried out for 2hr. the different parameters were studied on the adsorption performance. Those were, phenolic flow rate, hight of bed, phenol concentration and temperature.

### 3.4.3 Analytical Method

High Performance Liquid Chromatograph (HPLC) type SHIMADZU LC-4A, was used to determine the concentration of phenol in aqueous solutions, as shown in Fig 3-2. the adsorption fixed bed type Hypersil BDS-C18 Tunr, consisted of 250 mm hight and 4.6 mm diameter column, packed with 5% carbowax 20M on Chromosorb WAW. The mobile phase composed of 70% deionized water and 30% Acetone niteral.

50 μl sample was supplied through the injection device, type CTO-2AS, while the mobile phase was introduced to the column by a pump, type LC-4A, with 1.0 ml/min. the phenolic sample was transferred by the mobile phase downward the column, at 300 bars pressure. The effluent of separation column is conjected with a detector, type SPD-2AS. The results were displayed by a monitor, type C-R4A, as area of absorption. The actual concentration of phenol determined by the calibration curve given in Fig 4-2. The operating condition of HPLC was fixed by knowing the maximum absorption photo of phenol ($\lambda_{max}$) determined by uv-spectroscopy, as shown in Fig 4-1.



1. Feed container
2. Dosing pump
3. Adsorption column
4. Distributed
5. Molecular sieves 13X
6. Glasses plate
7. Valve
8. Receiver

**Figure 3-1** Flow Sheet Diagram of Experimental Equipment

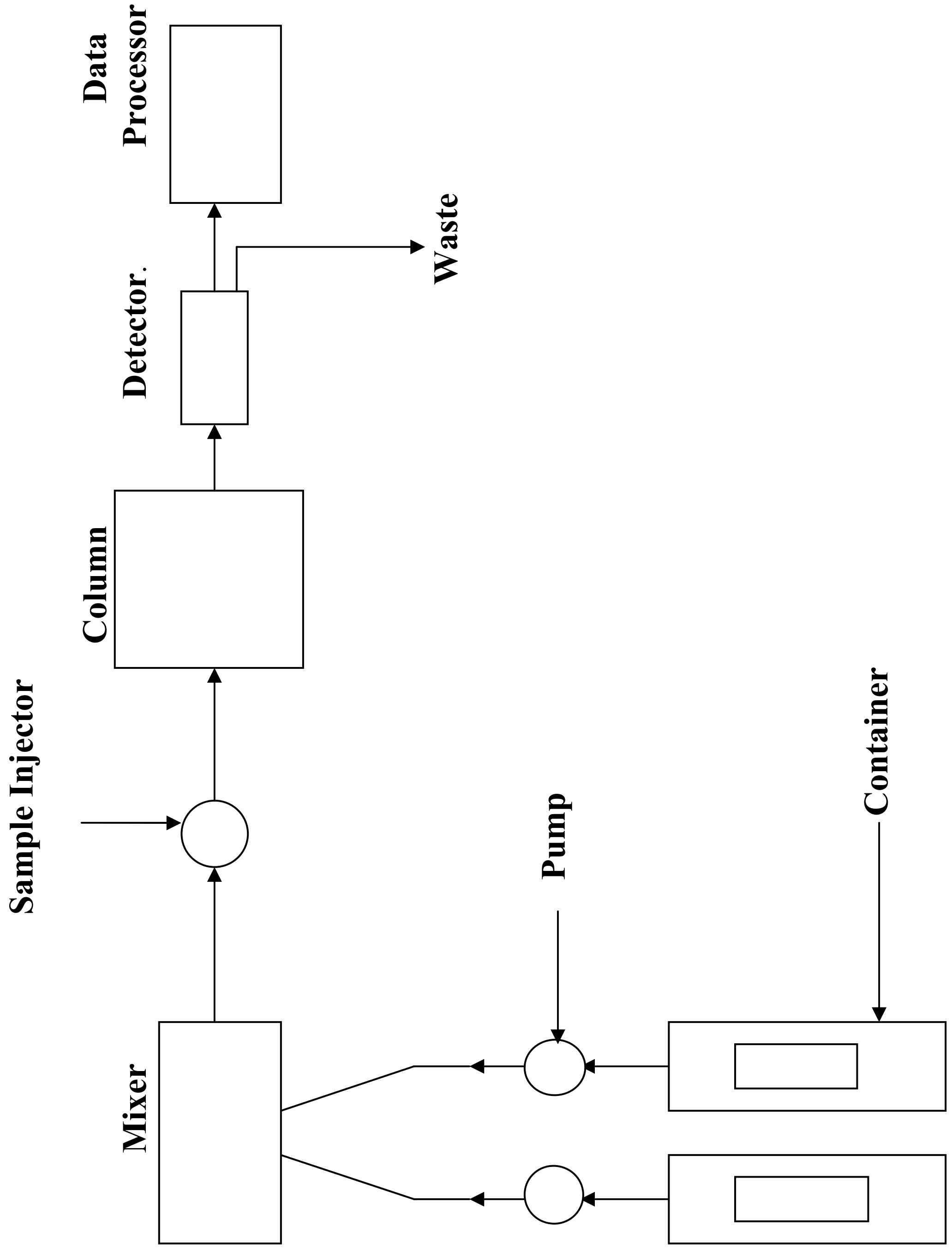


**Figure 3-2** Schematic Diagram of HPLC System

# CHAPTER FOUR
# RESULTS AND DISCUSSIONS

## 4.1 Characterization of MS Samples

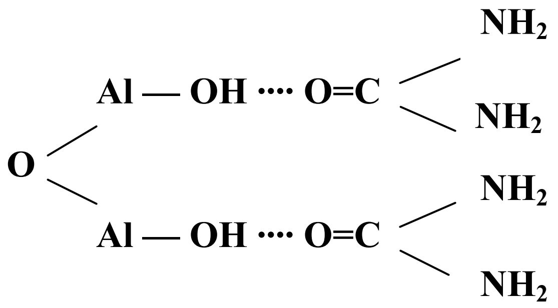
### 4.1.1 X-Ray Diffraction Crystallization

The X-ray diffraction pattern is a plot of intensity versus 2θ. The intensity is the heights of the main diffraction peaks and the 2θ is the angle at which the peaks occur. The identification of the structure is achieved by comparing its X-ray diffraction pattern with that of a standard type.

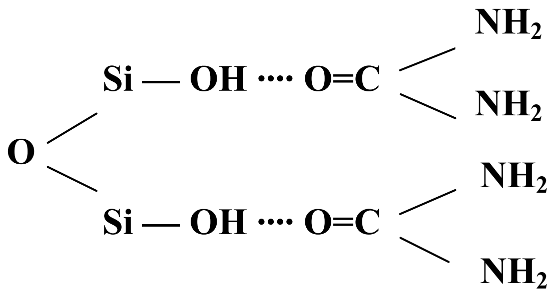
Fig A-1 shows X-ray diffraction of molecular sieve 13X which seems to have high degree of crystallization, and it is seen when the angle 2θ was equal to 6.2, 23.4, 26.7, and 31.1 high intensities of peaks appeared in the X-ray diffraction pattern (81), the value of XRD for original MS13X, $MS_U$, and $MS_T$ listed in tables B-1, B-2 and B-3 respectively.

The XRD for the samples of molecular sieve 13X treated with urea and thiourea, presented in Figs A-2 and A-3, show that both urea and thiourea have affected the structure of MS13X.The characteristics tops of MS13X, remain in position.

The main changes in urea admixture is the great difference in the intensity of crystalline level 6.2 (14.255°A), and the appearance of a new levels at 7.0 (12.628°A), 9.8 (9.025°A), 9.95 (9.303°A), 12.3 (7.196°A), and 23.8 (3.7386°A); Thus, the interance of urea molecules in the crystalline level which lead to partial closure to decrease the diffraction X-ray intensity and the width of this level is as great as it allows to urea molecules inter freely and formation a new group [C=O]$^{(10)}$ at limiting 5.8290ºA to 3.9690ºA,and silicate Hydroxyl group, and alumina Hydroxyl group at 7.6286ºA and 5.829ºA respectively, as illustrated in structure **A** and **B;**

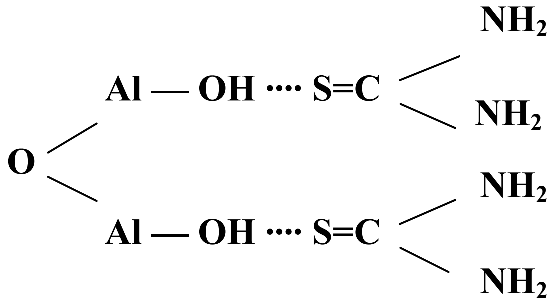


**Structure A**

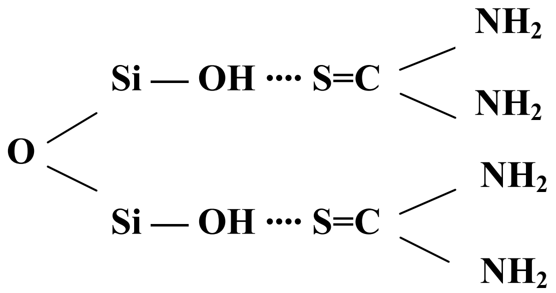


**Structure B**

Fig A-3 shows the X-Ray pattern of MS13X modified by thiourea. The standard peaks in MS13X structure of thiourea admixture remain in there position, also and appearance new peaks at 7.2 (12.278ºA), 11.8 (7.500ºA), 24.0 (3.708ºA), 27.1 (3.290ºA), 29.98 (2.980ºA), and 34.2 (2.622ºA). Thus indicate that the interance of thiourea molecules in the crystalline level formation resulted in a [C=S], [N-C-N] $^{(84)}$, Alumina Hydroxyl, and silicate Hydroxyl groups, as shown in structure **C** and **D**, respectively.



**Structure C**



**Structure D**

### 4.1.2 Infrared Spectral Characteristic

FTIR-absorption bands of original MS13X are given in table D-1, and are illustrated in Fig C-1. The bands in the region 3460-3950cm$^{-1}$ can be assigned to [O-H] vibration in different environments. Thus, the band at 3750 cm$^{-1}$ is assigned to terminal silanol –OH, the band at 3600 cm$^{-1}$ to bridge [Si-OH-Si(Al)], and the bands at 3570 cm$^{-1}$ and 3450 cm$^{-1}$ are due to hydrogen bonded [Si(Al)-OH](83)(85).

The bonded water absorption broad bands are found at 3400 cm$^{-1}$, 3200 cm$^{-1}$, and 3000 cm$^{-1}$ which indicate the different types of bandings and locations for the water molecules. Thus, the high frequency band at 3400 cm$^{-1}$ could be attributed to trapped water within the MS13X structure. The bending vibration of $H_2O$ is found at region 1650 to 1750 $cm^{-1}$, which has as expected suffered shift to higher frequency as compared to molecular water(79)(80)(85).

The spectrum clearly shows the three characteristic MS13X spectral bands, from asymmetric stretching vibrations, which appear as strong band at 977.8 $cm^{-1}$ due to phillipsite, faujasite, and chabasite, and a prominent shoulder at 1150 $cm^{-1}$ due to the latter two MS13X symmetric stretching vibration at 900 $cm^{-1}$ for chabasite, 656 $cm^{-1}$ for faujasite and 550 $cm^{-1}$, 565 $cm^{-1}$, and 453 $cm^{-1}$ for faujasite, and 410 $cm^{-1}$ for phillipsite (82).

For the latter the bands at 1629 $cm^{-1}$ and 977.8 $cm^{-1}$ can be characterized as due to asymmetric and symmetric stretching vibrations of the carbonate group respectively. As for [Si-O-Si] open chain at region 1030 to 1080 $cm^{-1}$ and [Si-O-Si] cyclic chain at region 1033 to 1076 $cm^{-1}$, to the bending vibration of the silicate group (83).

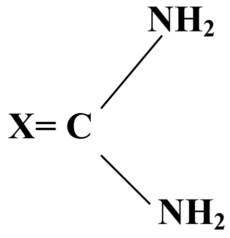
The spectra of MS13X modified by Urea gives asymmetric stretching and symmetric for [–$NH_2$] group at region 3450 and 3344 $cm^{-1}$ respectively, and Hydrogen bond at 3259 $cm^{-1}$. The bands in the region 1750, 1730, and 1685 $cm^{-1}$ can be assigned to [C=O] vibration in different environments. While the bands of [C=N] are at region 1690 and 1640 $cm^{-1}$ and [$C=N^+H$] strong band at 1606 $cm^{-1}$. The asymmetric band of [N-C-N] at 1465 $cm^{-1}$, are given in table D-2 and illustrated in Fig C-2. The spectra of MS13X treated by Thiourea gives [–$NH_2$] bands at region 3365, 3393 and 3270 $cm^{-1}$. The [N-C-N] bond at 1470 $cm^{-1}$, and [C=S] at 1410 $cm^{-1}$, are given in table D-3 and illustrated in Fig C-3. Few [–OH] bands of MS13X, as detected the original MS13X, were observed in the MS13X-Urea ($MS_U$) and MS13X-Thiourea ($MS_T$) admixtures.

The medium strong vibration of the band [–OH] of MS13X appearing at 3570 $cm^{-1}$ has shifted to 3550 and 3560 $cm^{-1}$ in $MS_U$ and $MS_T$ , respectively. The band at 3689 $cm^{-1}$ in $MS_T$ has as a nearest counter part the band at 3600 $cm^{-1}$ due to the bridge [–OH] group. The band at 3485 $cm^{-1}$ in MS13X showed a very slight shift to a higher frequency, appearing at 3527 $cm^{-1}$ in $MS_U$.The trapped water band at 3400 $cm^{-1}$ in original MS13X appeared at 3430 $cm^{-1}$ in $MS_T$ only. The broad water bands at 3200 $cm^{-1}$ and 3000 $cm^{-1}$ in MS13X appeared as broad undistinguished bands in $MS_U$ and $MS_T$.

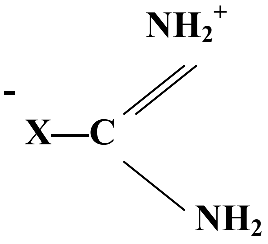
Three distinct shoulders appeared in $MS_U$ at region 3420, 2927, and 2736 $cm^{-1}$, which appear shifted to lower frequencies, could be attributed to water acting as a bridge between MS13X and Urea through hydrogen bonding. The water bending vibration appearing at 1650 $cm^{-1}$ in MS13X and $MS_T$ has shifted to a higher frequency of 1670 $cm^{-1}$ in $MS_U$. When considering the [–$NH_2$] vibrations, it is interesting to observe that in the spectra of Urea and Thiourea shown in Fig C-4 and C-5, the asymmetric vibration ($NH_2$) appears to have given rise to strong bands 3450 $cm^{-1}$ for Urea and 3393 $cm^{-1}$ for Thiourea where the spectra are measured in KBr matrix. These bands appear as medium strong and medium bands at 3380 and 3313 $cm^{-1}$, In $MS_U$ and $MS_T$ respectively.

The symmetric vibration ($NH_2$) which appeared at 3344 $cm^{-1}$ in Urea has no correspondingly observed band in $MS_U$, but in $MS_T$. The similar vibration, which appeared at 3270 $cm^{-1}$ in Thiourea, seems to have shifted to 3250 $cm^{-1}$. Interestingly the bonded [–$NH_2$] which gave a band at 3259 $cm^{-1}$ in urea has suffered a significant shift to 3100 $cm^{-1}$ in $MS_U$, no similar band was observed in $MS_T$

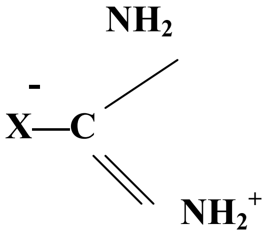
The changes observed in the ($NH_2$) and asymmetric vibration [N-C-N] bands are of special interest. The asymmetric vibration [N-C-N] appearing as strong bands at 1465 and 1472 cm$^{-1}$ in Urea and Thiourea respectively, has in both cases showed marked low frequency shifts to 1400 and 1413 cm$^{-1}$, respectively. On the other hand. The ($NH_2$) bands that appear at 1627 cm$^{-1}$ in Urea have suffered high frequency shifts in MS$_U$ to 1637 cm$^{-1}$, no similar band was observed in MS$_T$. This behavior indicates two tautomeric structures, as follows (10)



I



II A



II B

Structure I seems to predominate over structure II in the MS$_U$ admixture. Smaller shift in asymmetric vibration (NCN) MS$_T$ comes to only two thirds of that in MS$_U$, which may suggest that structure II still has a somewhat significant contribution. Furthermore, the band at 1606 cm$^{-1}$ in urea, which is usually attributed to vibration [C=O] with a contribution from ($NH_2$), showed in MS$_U$ a considerable shift to 1629 cm$^{-1}$,thus supporting the views of the predominance of structure I. However, the corresponding vibration [C=S] of thiourea with a value of 1413 cm$^{-1}$ has only suffered a slight shift to 1395 cm$^{-1}$, indicating that an interaction with MS13X has not affected the character of the carbon-sulfur bond(86)(85).

The characteristic MS13X bands in the region 1250 to 400 cm$^{-1}$ seem to have hardly been affected by the presence of Urea and Thiourea. Thus, the very strong vibration [Si-O-Si (Al)] band at 978 $cm^{-1}$ in MS13X appeared at almost shift to 990 $cm^{-1}$ in $MS_U$, but only slightly shift to 985 $cm^{-1}$ in $MS_T$ . Taken together with the observed shifts in ($NH_2$) vibration, it seems that the interaction is among the Urea and Thiourea molecules and with the matrix is mainly through [$–NH_2$] moiety.

### 4.1.3 Surface Area

The results of surface area measurements for MS13X modified by urea and thiourea relative to MS13X (original) are summarized in table 4-1. These results indicate an expansion in the estimated surface area for the urea and thiourea admixtures. Urea modified MS13X has the largest surface area, of about 730 $m^2/g$ followed by $MS_T$ of about 675 $m^2/g$, compared with 600 $m^2/g$ for the untreated MS13X.

The smaller size urea molecules may have enhanced the adsorption capacity through more extensive binding of molecules and thus caused a marked increase in surface area of the modified MS13X.

**Table 4-1 Surface Area of Adsorbent Samples**
T= 30ºC

| Adsorbent | Surface Area $m^2/g$ |
|---|---|
| MS13X (original) | 600 |
| $MS_U$ | 730 |
| $MS_T$ | 675 |

## 4.2 Adsorption of Phenol

Experiments were carried out to investigate the possible use of the molecular sieve 13X for the removal of phenol traces from aqueous solutions. Modifying of molecular sieve with urea and thiourea was done, to study their ability to removal of phenol pollutant, and possible enhancement of adsorption capacity of molecular sieve. The experiments were done continuously using fixed bed adsorbents, to study the adsorption performance of phenol from water, and to evaluate the effect of various parameters that affected its removal. Table 4-2 summarizes the selected experimental operating condition for each adsorbents.

**Table 4-2 Summary of Experimental Operating Conditions for Adsorption of Phenol**

| Exp.No. | Flow rate (Q), l/h | Bed length (H) , cm | Temper. ($^{o}$ K) | Bed weight (M), g | Inlet Con. ($C_o$), g/cm$^3$ |
|---|---|---|---|---|---|
| 1 | 0.2 | 56 | 303 | 77 | 10 |
| 2 | 1.0 | 56 | 303 | 77 | 10 |
| 3 | 0.2 | 30 | 303 | 44 | 10 |
| 4 | 0.2 | 56 | 303 | 77 | 50 |
| 5 | 0.2 | 56 | 303 | 77 | 100 |
| 6 | 0.2 | 56 | 303 | 77 | 150 |
| 7 | 0.2 | 56 | 313 | 77 | 10 |
| 8 | 0.2 | 56 | 323 | 77 | 10 |

The effluents of adsorption system were collected each 30 min. during the continuous operation, to determine the phenol content by HPLC. Fig 4-1, gives the wave length on which higher absorption will occur absorption photo of phenol ($\lambda_{mix}$), and it is found equal 210 nm, and this value will fixed in HPLC.

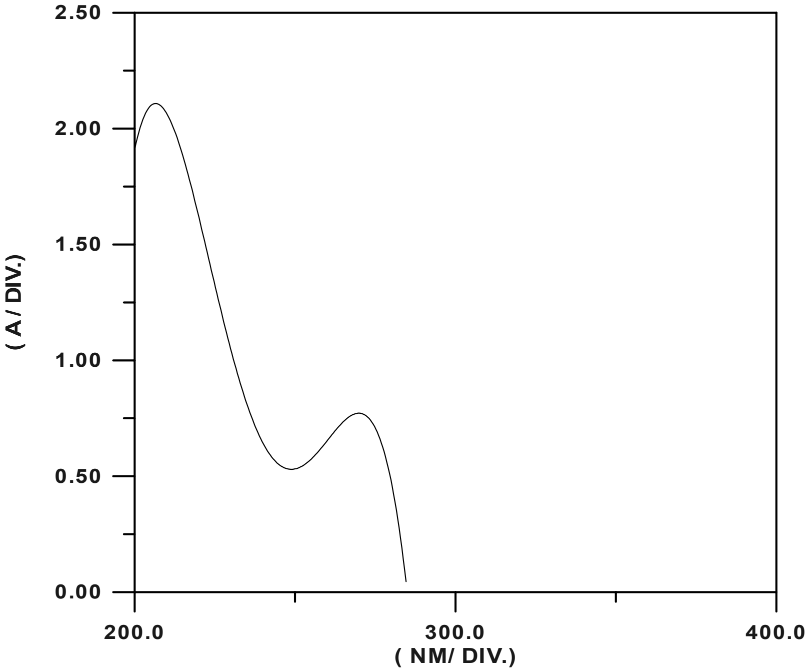


**Figure 4-1 Wavelength Absorption of Phenol by U.V. Spectrophotometer**

To determine the outlet concentration it should evaluate the standard curve by taking the U.V absorption of different phenol concentrations in water. The selected concentrations of phenol were 0.2, 1.0, 1.3, 1.5, 2.5, 5, 7, and 10 ppm. A straight line represents the correlation between area of absorbance and concentrations, as in the Fig 4-2. A linear equation for this straight line is:

**C = 9.0333 * A + 0.0019**………………………..4-1

Where, C is phenol concentrations in ppm and A is area of absorbance.

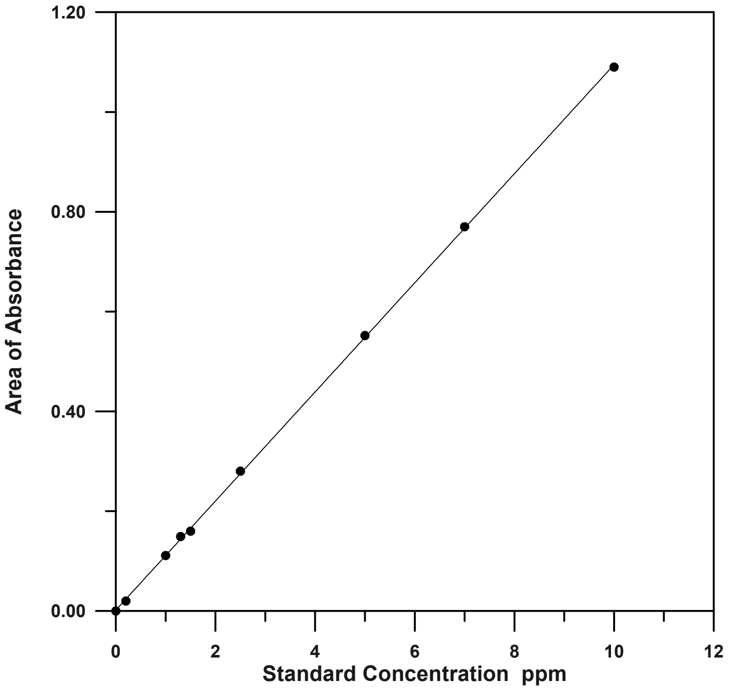


**Figure 4-2 Standard Curve for Aqueous Phenol Solutions**

For determination the accumulative of molecular sieve samples toward the adsorption was determined by equation 4-2.

$$\mathbf{q_i = [(C_o - C_t)/M] \times Q \times t} \text{ ……………………….4-2}$$

**$q_i$** = the quantity of the solute adsorbed per unit mass of adsorbent at any given time, g/g of adsorbent.

**$C_o$**= Initial concentration of adsorbate, g/cm$^3$.

**$C_t$**= Effluent concentration of adsorbate, g/cm$^3$.

**M**= Mass of adsorbent, g

**Q=** Volumetric flow rate of solution, cm$^3$/min.

**t=** adsorption time, min.

A sample of calculation given is listed in Appendix F. while the experimental results, were listed in Appendix E.

## 4-3 Time Effect

The breakthrough curves for phenol adsorption experiments were obtained by plotting effluent concentration against time, as shown in Figs 4-3, 4-4, and 4-5. See tables E-1, E-2, and E-3. The results show a gradual increase of phenol concentration in effluent with time, until reachs nearly the initial concentration in influent. This observation indicates that the adsorption rate decreases with time increase, due to gradually saturation of adsorbent with operating time.

The figures show also a linear portion exists for each curve at early period of experiments. Deviations from linearity occurred because of increasing influence of intra particle transport on the overall rate of mass transfer with time progress. The time dependence adsorption experiments indicated that MS13X-Urea admixture, which displayed the largest surface area, showed the greatest ability to remove phenol from water, followed by thiourea admixture.

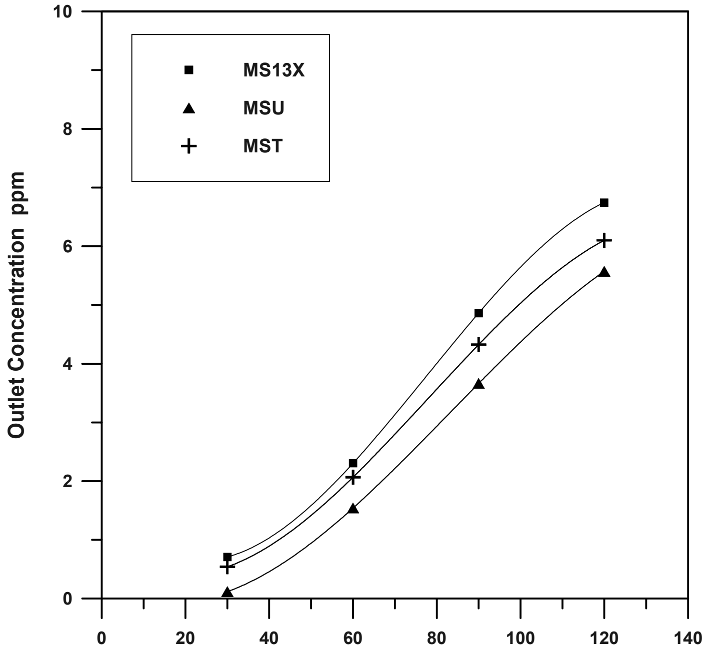


**Figure 4-3 Breakthrough Curves for Adsorption of Phenol**
Q= 0.2 l/h, h= 56 cm, and T= 30ºC

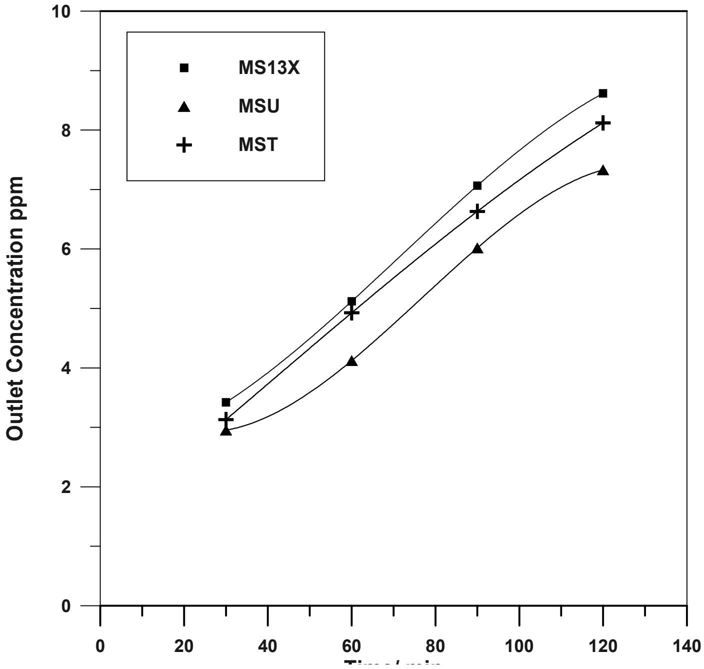


**Figure 4-4 Breakthrough Curves for Adsorption of Phenol**
Q= 0.2 l/h, h= 30 cm, and T= 30ºC

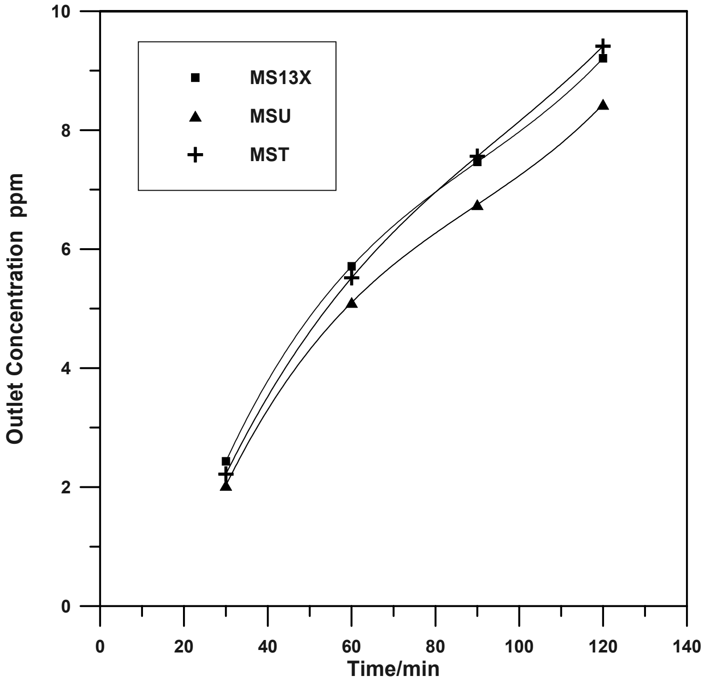


**Figure 4-5 Breakthrough Curves for Adsorption of Phenol**
Q= 1.0 l/h, h= 56 cm, and T= 30ºC

Tables 4-8, E-10 and E-11 listed the calculated of accumulative adsorption of phenol. To show the adsorption rate at different time, the accumulative adsorptions versus time are plotted in Figs 4-6, 4-7, and 4-8. The results indicate a gradual increase of accumulative phenol with increasing the contact time (23).

It must be observed that urea modified samples has the largest accumulative adsorption, followed by thiourea samples. Also, low influent flow rate and high bed length causes in higher amount of adsorbed phenol.

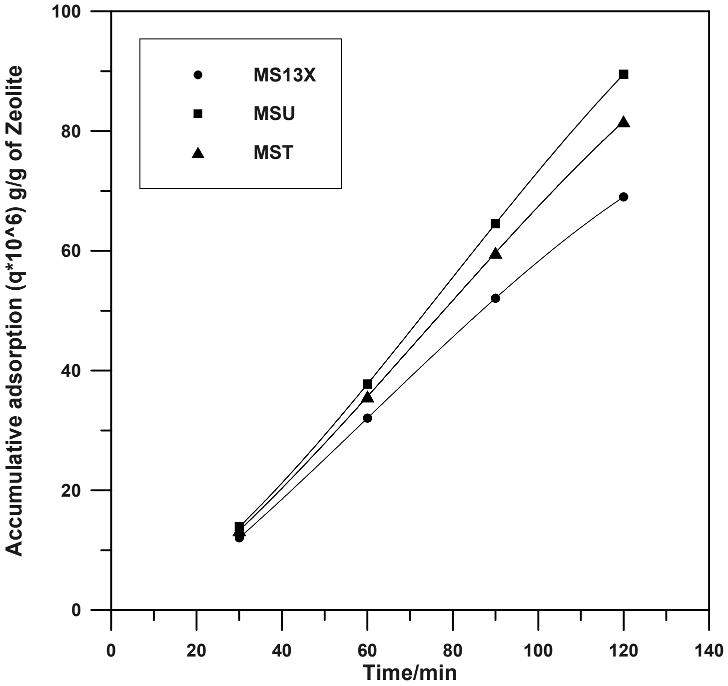


**Figure 4-6 Accumulative Adsorption of Phenol at Different Time**

Q= 0.2 l/h, h= 56 cm, and T= 30ºC

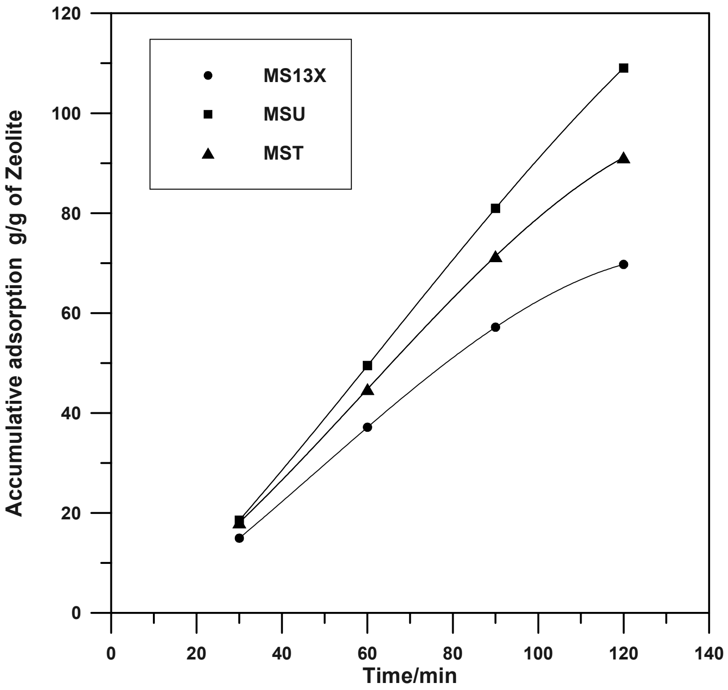


**Figure 4-7 Accumulative Adsorption of Phenol at Different Time**
Q= 0.2 l/h, h= 30cm, and T=30ºC

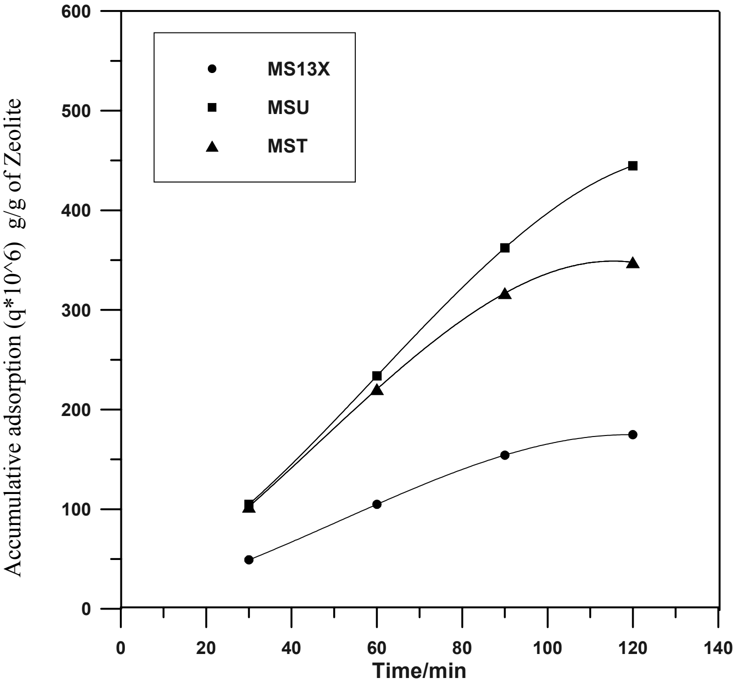


**Figure 4-8 Accumulative Adsorption of Phenol at Different Time**
Q= 1.0 l/h, h= 56 cm, and, T= 30ºC

## 4.4 Effect of Bed Depth

The adsorbent useful capacity is usually fixed by the actual amount available to hold phenol and its required outlet concentration. Therefore, the total weight of adsorbent influences the amount of phenol load for the cycle at a given other operating conditions.

Two bed lengths were chosen to investigate the effect of adsorbent weight on adsorption behavior of minor amount of phenol. Those were 30 cm and 56 cm, value of tables E-4, E-5 and E-6, as illustrated in Figs. 4-9, 4-10 and 4-11 for original and modified molecular sieves 13X respectively. Further results are given also in Figs.4-3 and 4-4 of breakthrough curves by using the above mentioned bed lengths.

The results show, that the amount of phenol adsorbed from water increases with increases of bed length, due to increase the actual amount of surface available to hold phenol. The urea modified molecular sieve is here again more effective for phenol removal, followed by thiourea modification, as shown in Figs.4-10 and 4-11 respectively. While the original MS13X has less efficiency for adsorption of phenol as shown in Fig.4-9.

Fig.4-10 illustrate clearly, that about a complete removal of phenol is achieved by using 56 cm bed length of urea modified sample at the mentioned conditions. This indicates that the amount of adsorbent has a predominate roll on removal of phenol from aqueous media (31).

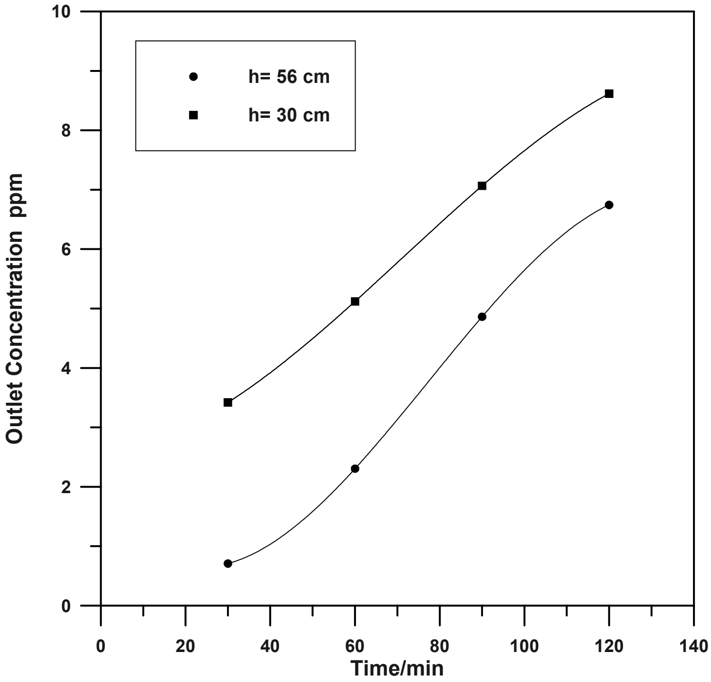


**Figure 4-9 Adsorption of Phenol at Different Bed Hight of MS13X**

Q=0.2l/h, T=30ºC

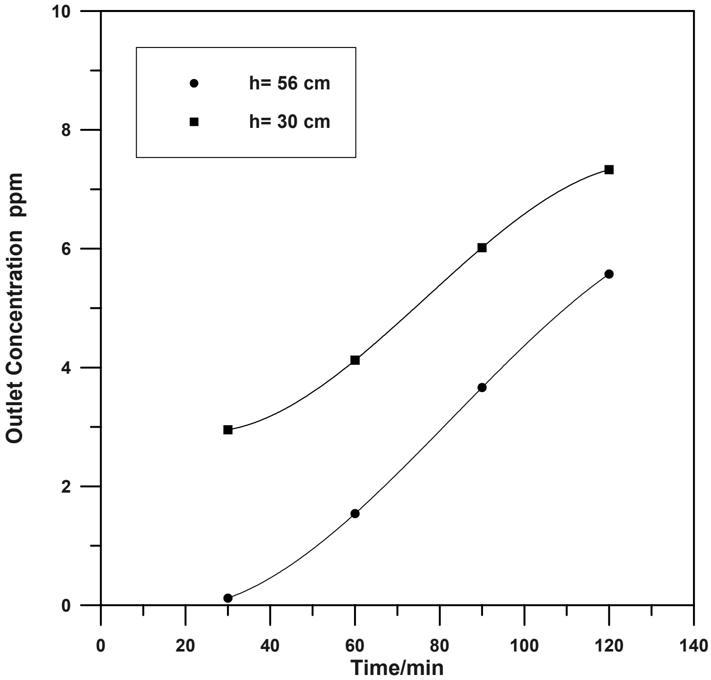


**Figure 4-10 Adsorption of Phenol at Different Bed Hight of $Z_{UREA}$ modified**

Q=0.2l/h, T=30ºC

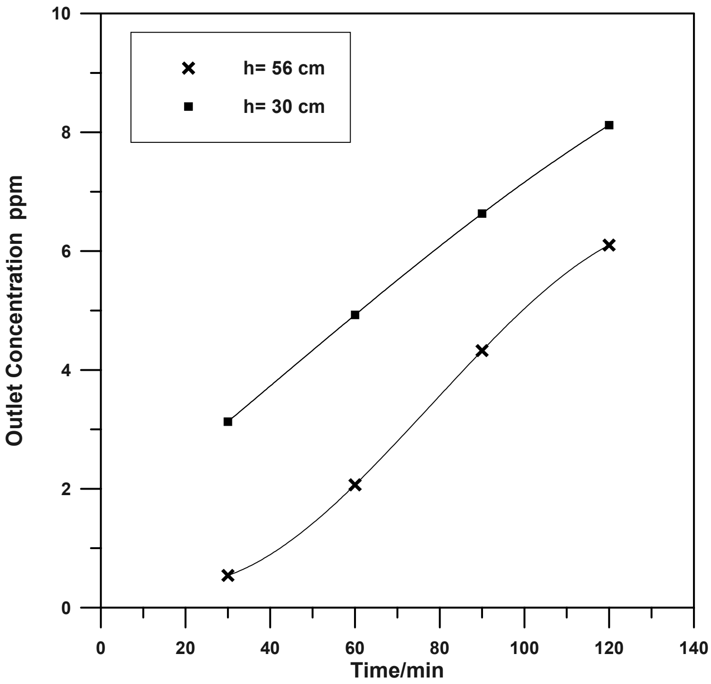


**Figure 4-11 Adsorption of Phenol at Different Bed Hight of $Z_{THIOUREA}$ Modified**
Q=0.2l/h, T=30ºC

### 4.5 Phenolic Solution Flow Rate

The effect of solution flow rate for adsorption of phenol on original and by urea and thiourea modified MS13X adsorbents are shown in Figs. 4-12, 4-13 and 4-14. These figures are plotted from tables E-7, E-8 and E-9 respectively.

The results give a comparison for phenol outlet concentrations by using a low flow rate, 0.2 l/h phenolic solution and a high flow rate, 1.0 l/h at constant other conditions. It is noticed that the removal of phenol from aqueous solutions decreases as flow rate increases, as it's expected. This is attributed to the fact that the high flow rate increases the contact time of phenol within the bed, leading to more adsorption affinity than high flow rate of low contact time (23). This effect is clearly demonstrated for urea modified bed in Fig.4-12 as an example. The results show that at flow rate 1.0 l/h, the outlet aqueous solution contains less than 0.5 ppm phenol, while it is about 2 ppm at 0.2 l/h, both are for the first sample collection at 30 min.

It is also noticed, that the solution inlet flow rate has a noticeable effect on the accumulative adsorption of phenol by proceeding the time, as shown later in Figs.4-6 and 4-8. Thus, rapid increase was observed with low flow rate, mainly for urea modified MS13X adsorbent. This phenomenon is discussed in details in part 4-8.

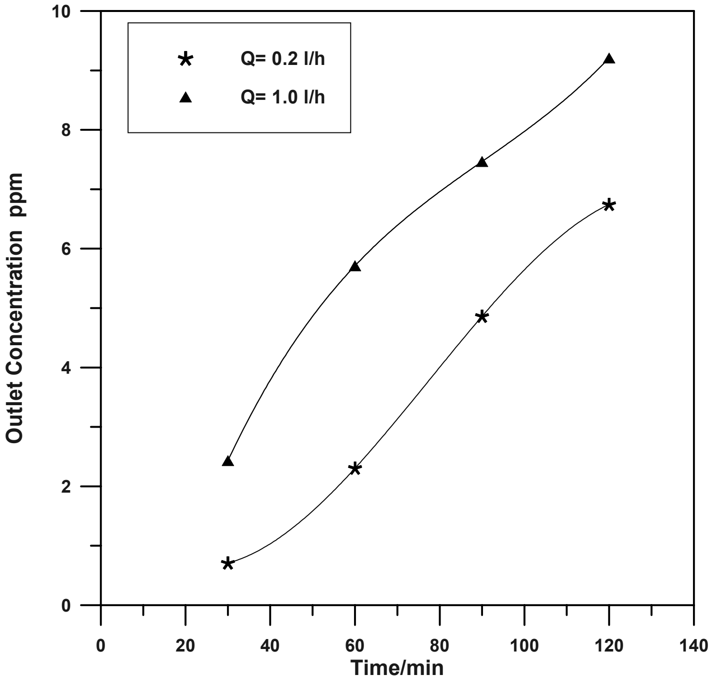


**Figure 4-12 Effect of Flow Rate on Adsorption Phenol by Using Original MS13X**
h= 56 cm, T=30ºC

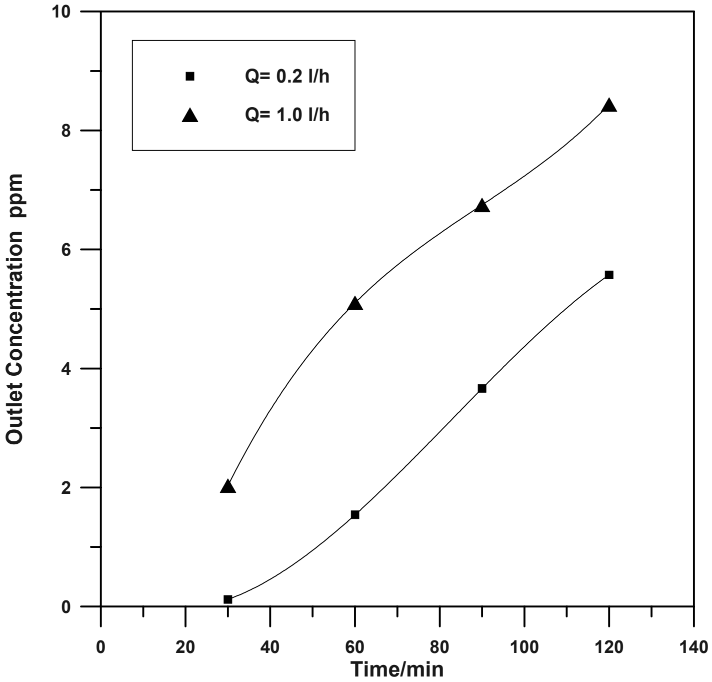


**Figure 4-13 Effect of Flow Rate on Adsorption Phenol by Using Urea MS13X**
h= 56cm, T=30ºC

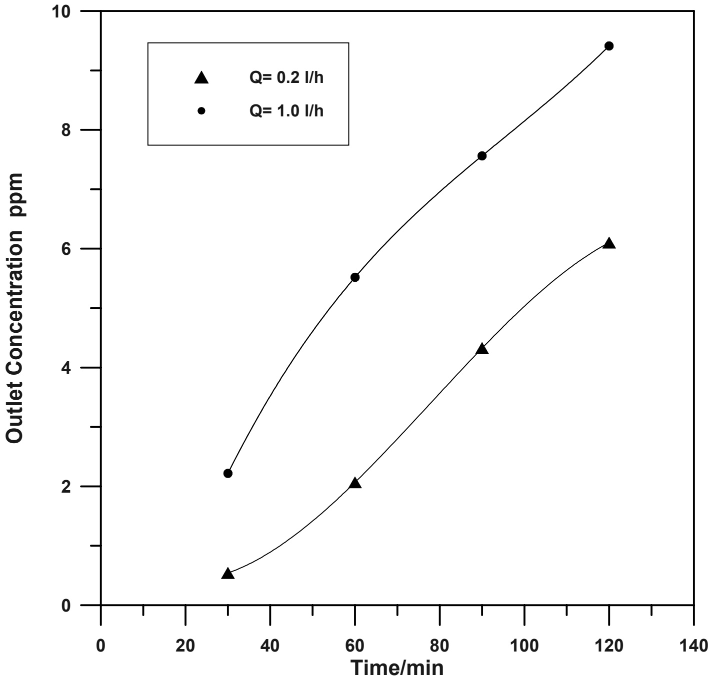


**Figure 4-14 Effect of Flow Rate on Adsorption Phenol by Using Thiourea MS13X**
h= 56cm, T=30ºC

### 4.6 Effect of Inlet Phenol Concentrations

Experiments were conducted to investigate the inlet concentration dependent on removal of phenol by adsorption. The remaining concentration of phenol in effluent should give an indication about the adsorption ability of adsorbents toward phenol, as shown in Fig.4-15. From this figure, it can be noticed a progressive increase of phenol concentration in outlet of adsorption, as the inlet concentration increases. This may be attributed to the fact that the driving force is affected noticeably the adsorption rate at the increasing of phenol in the inlet solutions (31).

It must also be observed that high removal of phenol for high inlet concentrations required more amount of adsorbent (higher bed lengths) or low flow rates.

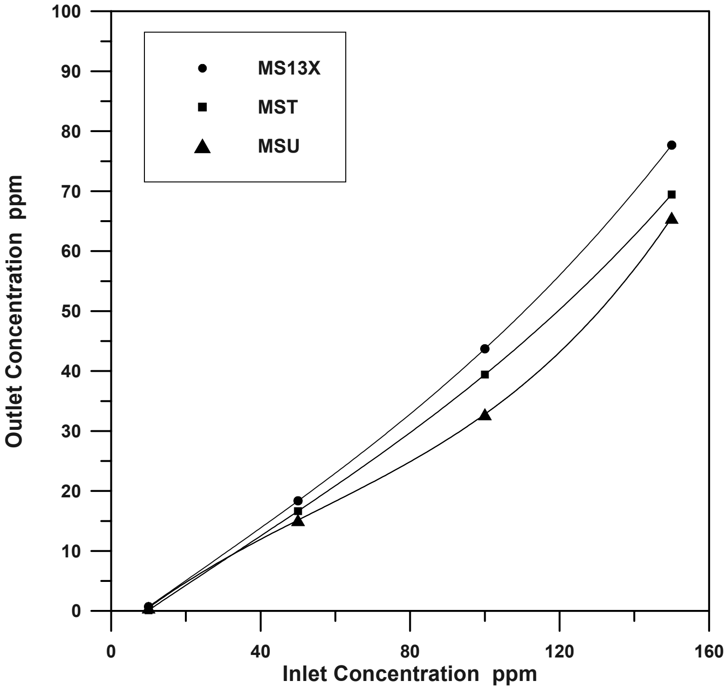


**Figure 4-15 Adsorption of Phenol at Different Inlet Concentrations**
Q= 0.2 l/h, h= 56 cm, and T= 30ºC

### 4.7 Effect of Temperature

Experiments were conducted to determine the effect of temperatures on adsorption of phenol from aqueous media using original and modified MS13X as adsorbents. Three temperatures were chosen for this purpose. Those were 303, 313 and 323ºK. The results in table E-12 are illustrated in Fig.4-16 for removal of phenol.

The results show that the temperature increase leads in a noticeable decrease in the ability of phenol adsorption for all studied adsorbents. This can be attributed to the fact that the adsorption is usually a reversible and exothermic process (75). Thus, the extent of phenol adsorption is increased with decreasing the temperature. It is noticed also the temperature dependence is fast, the same for all adsorbents considered in present investigation.

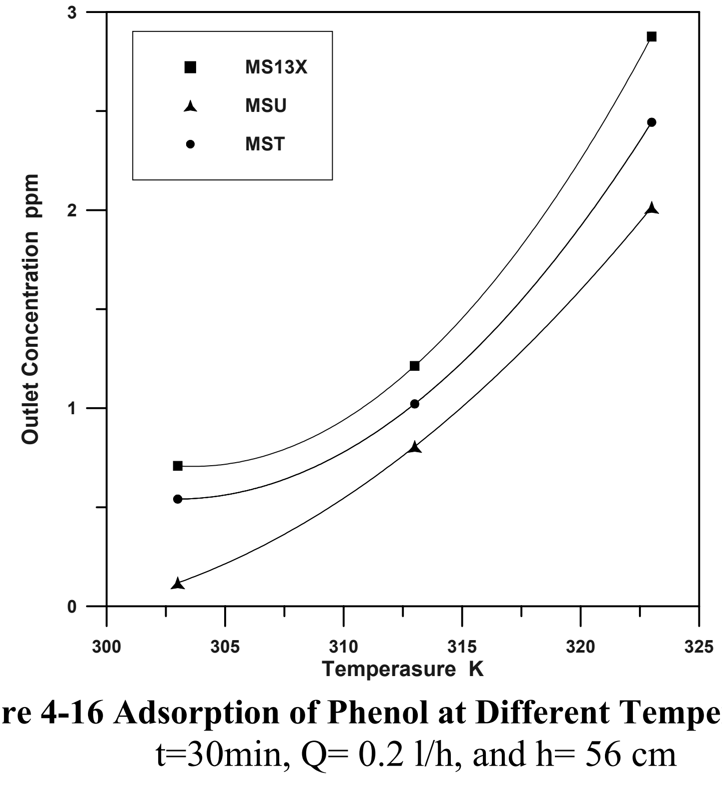


**Figure 4-16 Adsorption of Phenol at Different Temperature**
t=30min, Q= 0.2 l/h, and h= 56 cm

## 4.8 Percentage Removal of Phenol

The experiments were conducted to investigate the ability of molecular sieve 13X to remove traces of phenol from water. Therefore percentage removal of phenol should be a good indication for this purpose. Figs.4-17, 4-18 and 4-19 show the percentage removal at different time of continuous operation. The experiments were carried out for 10 ppm phenol initial concentration and at different other conditions.

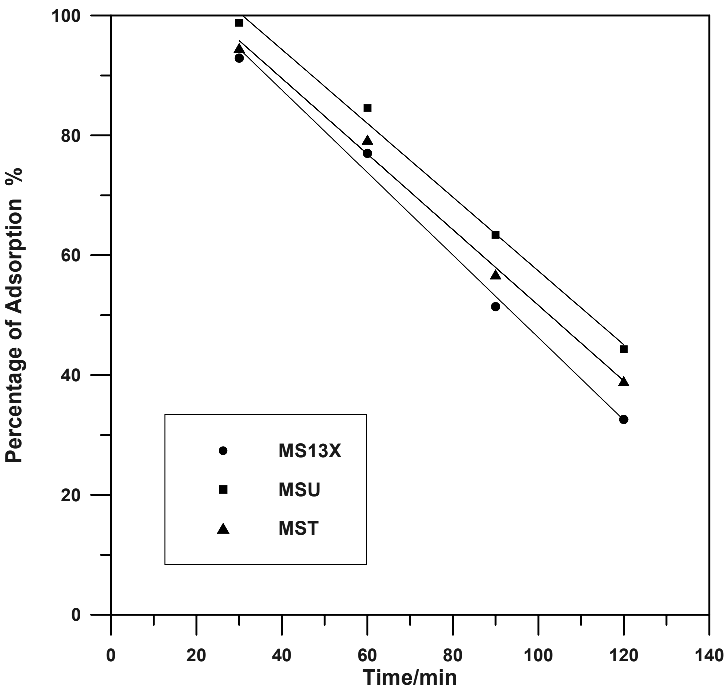


**Figure 4-17 Percentage of Adsorption Phenol**
Q= 0.2 l/h, h= 56 cm, and T= 30ºC

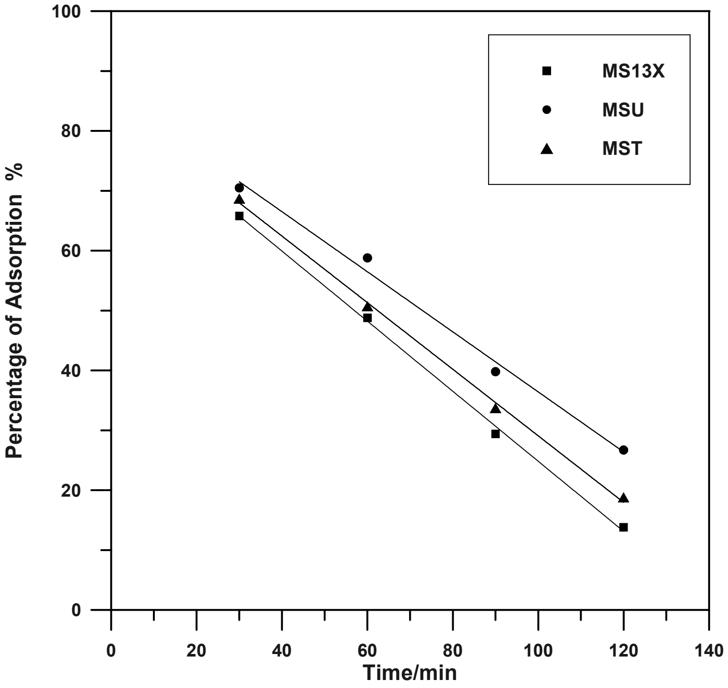


**Figure 4-18 Percentage of Phenol Adsorption**
Q= 0.2 l/h, h= 30 cm, and T= 30ºC

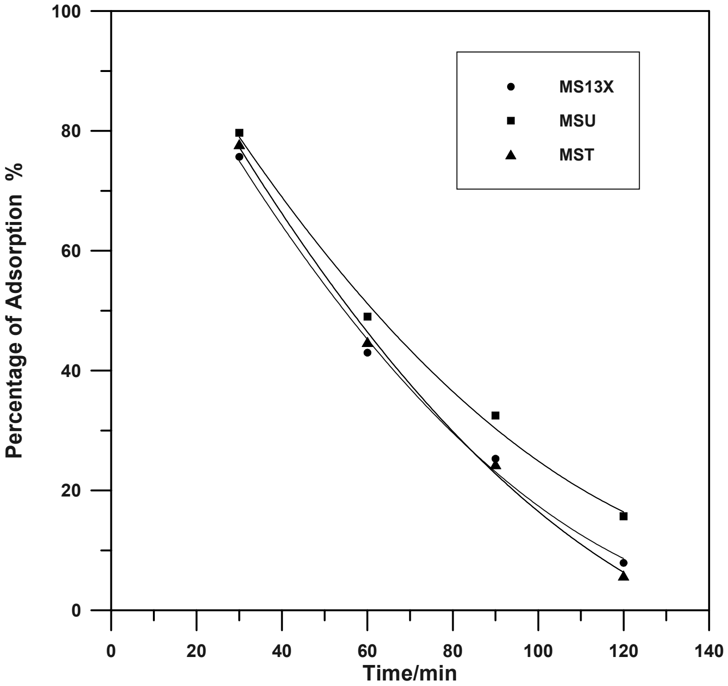


**Figure 4-19 Percentage of Adsorption Phenol**
Q= 1.0 l/h, h= 56 cm, and T= 30ºC

Further results are also illustrated in tables 4-3, 4-4 and 4-5. The results show that significant removal of phenol can be obtained, more than 90% at low operating time for all adsorbents. While the degree of phenol reduction decreases gradually with time increase values lower than 20% at 120 min for high flow rate as shown in Fig.4-17.

**Table 4-3 Effect of Time on Percentage Removal of Phenol**
Q= 0.2 l/h, h= 56 cm, $C_o$= 10 ppm, and T= 30ºC

| Sample. No | Time/min | MS13X | $MS_U$ | $MS_T$ |
|---|---|---|---|---|
| 1 | 30 | 92.9 | 98.8 | 94.6 |
| 2 | 60 | 77 | 84.6 | 79.3 |
| 3 | 90 | 51.4 | 63.4 | 56.8 |
| 4 | 120 | 32.6 | 44.3 | 39 |

**Table 4-4 Effect of Time on Percentage Removal of Phenol**
Q= 0.2 l/h, h= 30 cm, $C_o$= 10 ppm, and T= 30ºC

| Sample. No | Time/min | MS13X | $MS_U$ | $MS_T$ |
|---|---|---|---|---|
| 1 | 30 | 65.8 | 70.5 | 68.7 |
| 2 | 60 | 48.8 | 58.8 | 50.7 |
| 3 | 90 | 29.4 | 39.8 | 33.7 |
| 4 | 120 | 13.8 | 26.7 | 18.8 |

**Table 4-5 Effect of Time on Percentage Removal of Phenol**

Q= 1.0 l/h, h= 56 cm, $C_o$= 10 ppm, and T= 30ºC

s

| Sample. No | Time/min | MS13X | $MS_U$ | $MS_T$ |
|---|---|---|---|---|
| 1 | 30 | 75.7 | 79.7 | 77.8 |
| 2 | 60 | 43 | 49 | 44.8 |
| 3 | 90 | 25.3 | 32.5 | 24.4 |
| 4 | 120 | 7.9 | 15.7 | 5.8 |

water containing 10 ppm phenol on its percentage reduction. High bed length and low flow rate insured an excellent degree of phenol removal. As it is expected, low flow rate is resulted in increasing the contact time, which means increasing the interface accumulation or concentration of phenol at the surface. Thus, the percentage removals of about 93-99% are achieved by 0.2 l/h flow rate on 56 cm bed length. While those are between about 76-80% by using 1.0 l/h flow rate on the same bed length for the considered adsorbent.

Data of phenol removal, as given in table 4-6, indicate that the phenol level is expected for unpolluted water. Since phenols are toxic to fish as well as human at levels above (2) ppm (2 mg/l) and can cause bad taste in fish at concentrations for below the toxic level (74).

The bed hight is more affected the degree of phenol removal than the flow rate. The values for 30 cm bed high are reduced to approximately 66-70.5% at 0.2 l/h flow rate, as shown in table 4-6.

**Table 4-6 Percentage Removal of Phenol Different Flow Rate and Bed Hight**

Time = 30 min, $C_o$= 10 ppm, and T= 30ºC

| Adsorbent | Q (l/h) | h (cm) | % removal | ppm phenol in effluent |
|---|---|---|---|---|
| MS13X | 0.2 | 56 | 92.9 | 0.71 |
| $MS_T$ | 0.2 | 56 | 94.6 | 0.54 |
| $MS_U$ | 0.2 | 56 | 98.8 | 0.12 |
| MS13X | 1.0 | 56 | 75.7 | 2.43 |
| $MS_T$ | 1.0 | 56 | 77.8 | 2.22 |
| $MS_U$ | 1.0 | 56 | 79.7 | 2.03 |
| MS13X | 0.2 | 30 | 65.8 | 3.42 |
| $MS_T$ | 0.2 | 30 | 68.7 | 3.13 |
| $MS_U$ | 0.2 | 30 | 70.5 | 2.95 |

The urea modified sample showed an overall distinction as the best adsorbent for phenol. This may be attributed to its having the largest surface area about 730 $m^2$/g, and to ability of urea to form a strong hydrogen bond with phenol either directly or through the adsorbed water (10). Untreated MS13X, although having lower surface about too 730 $m^2$/g area than modified samples showed lower removal of phenol, as illustrated in table 4-7. While the data for the thiourea treated sample with 675 $m^2$/g surface lie in between.

### Table 4-7 Effect of Surface Area on Removal of Phenol

| Adsorbents | Surface area | % removal | Accumulative g/g of adsorbent |
|---|---|---|---|
| MS13 | 600 | 92.9 | 12.1 |
| $MS_T$ | 675 | 94.6 | 13.3 |
| $MS_U$ | 730 | 98.8 | 13.9 |

It must be noticed, that the accumulative amounts of phenol are higher on urea, and thiourea modified adsorbent than the original MS13X, as given in table 4-8, at different operating times. This can be also attributed to increasing ability of the modified samples towards the phenol removal. Those are about 89.5, 81.6 and 69 ppm/g for $MS_U$, $MS_T$ and original MS respectively.

### Table 4-8 Effect of Time on Accumulative ($10^{-6}$g/g) Adsorption of Phenol

Q= 0.2 l/h, h= 56 cm, T= 30ºC, and $C_o$= 10 ppm

| Time/min | MS13X | $MS_U$ | $MS_T$ |
|---|---|---|---|
| 30 | 12.0675 | 13.9188 | 13.3232 |
| 60 | 32.0564 | 37.7496 | 35.6718 |
| 90 | 52.0804 | 64.5308 | 59.6558 |
| 120 | 68.9987 | 89.4738 | 81.6208 |

The effect of solute concentration for percentage removal of phenol on original and by urea and thiourea modified MS13X as adsorbents, are illustrated in table 4-9. The experimental results show that the removal is variable with the initial concentration. The percentage removal decreases sharply as the solute concentration increases, as presented in table 4-9 value for urea modified adsorbent is about 99% for 10 ppm initial concentration, lowered to about 63, 56 and 48% for 50, 100 and 150 ppm concentrations. This can be attributed to the increasing saturation of adsorbent particles, as solute concentration increases. Increasing phenol removal at high initial concentration required higher bed length and / or low flow rates. It must be mentioned, that the rate of adsorption is lowered by increasing the saturation of adsorbents. Then, the driving force governing rate is the concentration difference between the phenol in solution and that on the adsorbent (23).

**Table 4-9 Effect of Inlet Concentration on Percentage Removal of Phenol in First Sample at 30 min**

Q= 0.2 l/h, h= 56 cm, and T= 30ºC

| Inlet Conce. ppm | MS13X | $MS_T$ | $MS_U$ |
|---|---|---|---|
| 10 | 92.9 | 94.6 | 98.8 |
| 50 | 63.3 | 66.7 | 69.7 |
| 100 | 56.3 | 60.6 | 67.2 |
| 150 | 48.2 | 53.7 | 56.3 |

# CHAPTER FIVE
# CONCLUSIONS AND RECOMMENDATIONS

## 5.1 CONCLUSIONS

According to the results obtained from this study, the following conclusions are deduced:

1. Modified MS13X with urea and thiourea resulted in an increase of surface area.
2. The XRD patterns obtained showed that the modified of MS13X had resulted in some changes in the silica and alumina structure which may be attributed to the solubilization of both silica and alumina in the presence of urea and thiourea.
3. The FTIR studies showed some interesting interactions between the added urea and thiourea with the mineral substrate, these are mainly hydrogen-bond type interactions of the urea and thiourea molecules through their $-NH_2$ moiety with the –OH groups or framework oxygen in the mineral or with the adsorbed water, the urea displayed more significant interaction with MS13X than thiourea.
4. The largest surface area $MS_U$ sample showed the greatest ability to remove phenol from water, than $MS_T$ sample, and the latter is greater than the original MS13X.

5. The percentage removal of phenol onto MS13X, $MS_U$ and $MS_T$ increased with the increasing bed depths, and will increase with low flow rate, and decreasing with temperature increases.

## 5.2 Recommendations

1. This study can be extended to modify other molecular sieve types such as 10X, 5A and 4A, and comparison between all these types with results of this research.

2. This study can be extended to prepare the $MS_U$ and $MS_T$ complex with certain some polymers such as of Formaldehyde or with other substances contain a higher surface area.

3. Study the effect of particle size and shape on the isothermal accomplishment of adsorber working under isotherm working.

4. Study the effect of the presence of other pollutant with phenol in water on the performance of MS13X.

5. Study the removal of phenol derivatives onto modified Zeolites.

6. This study can be extended to show the capacity of MS13X under non-isothermal condition, on variable pressure.

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# Appendix A
# X-Ray Diffraction

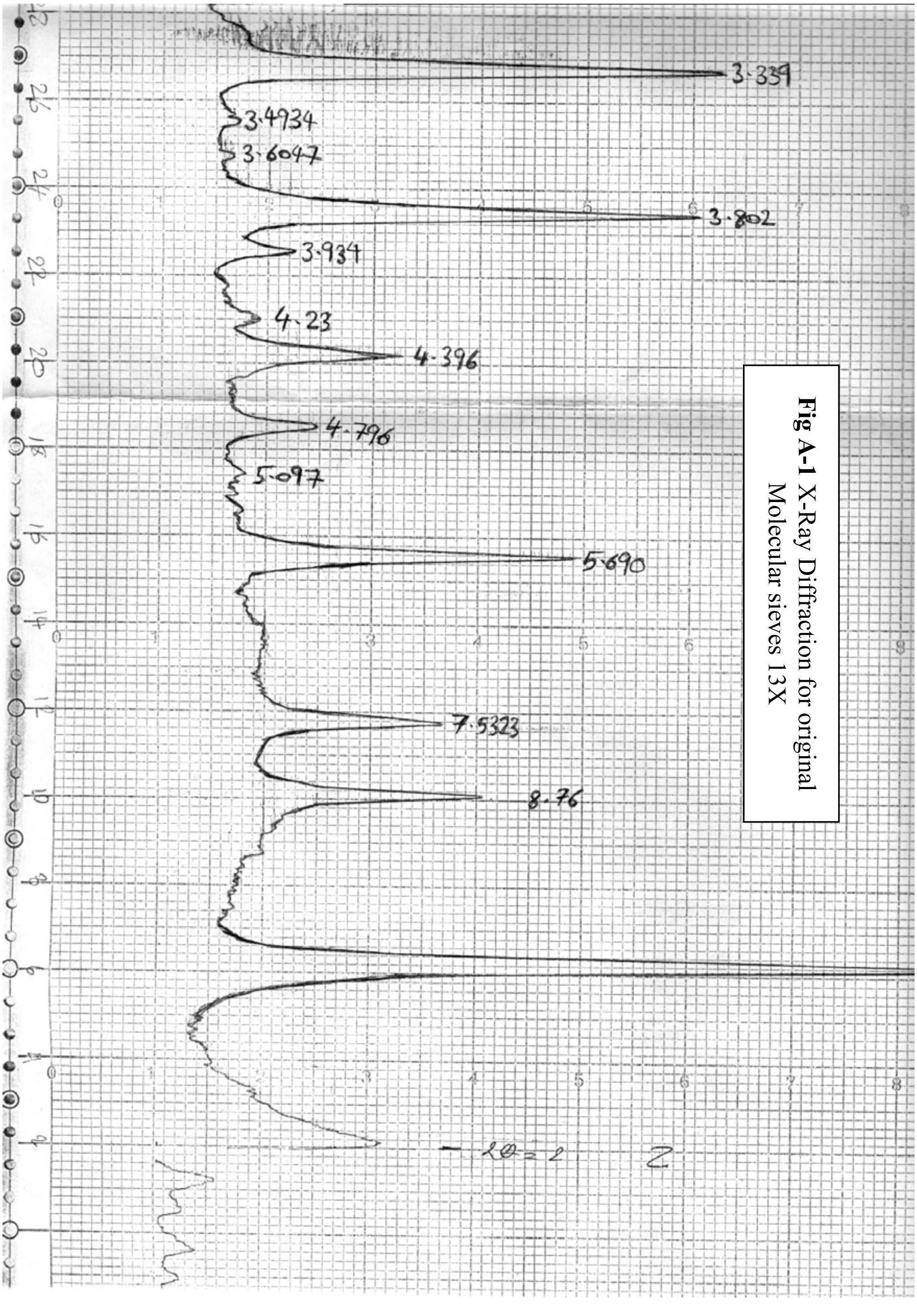

**Fig A-1** X-Ray Diffraction for original Molecular sieves 13X

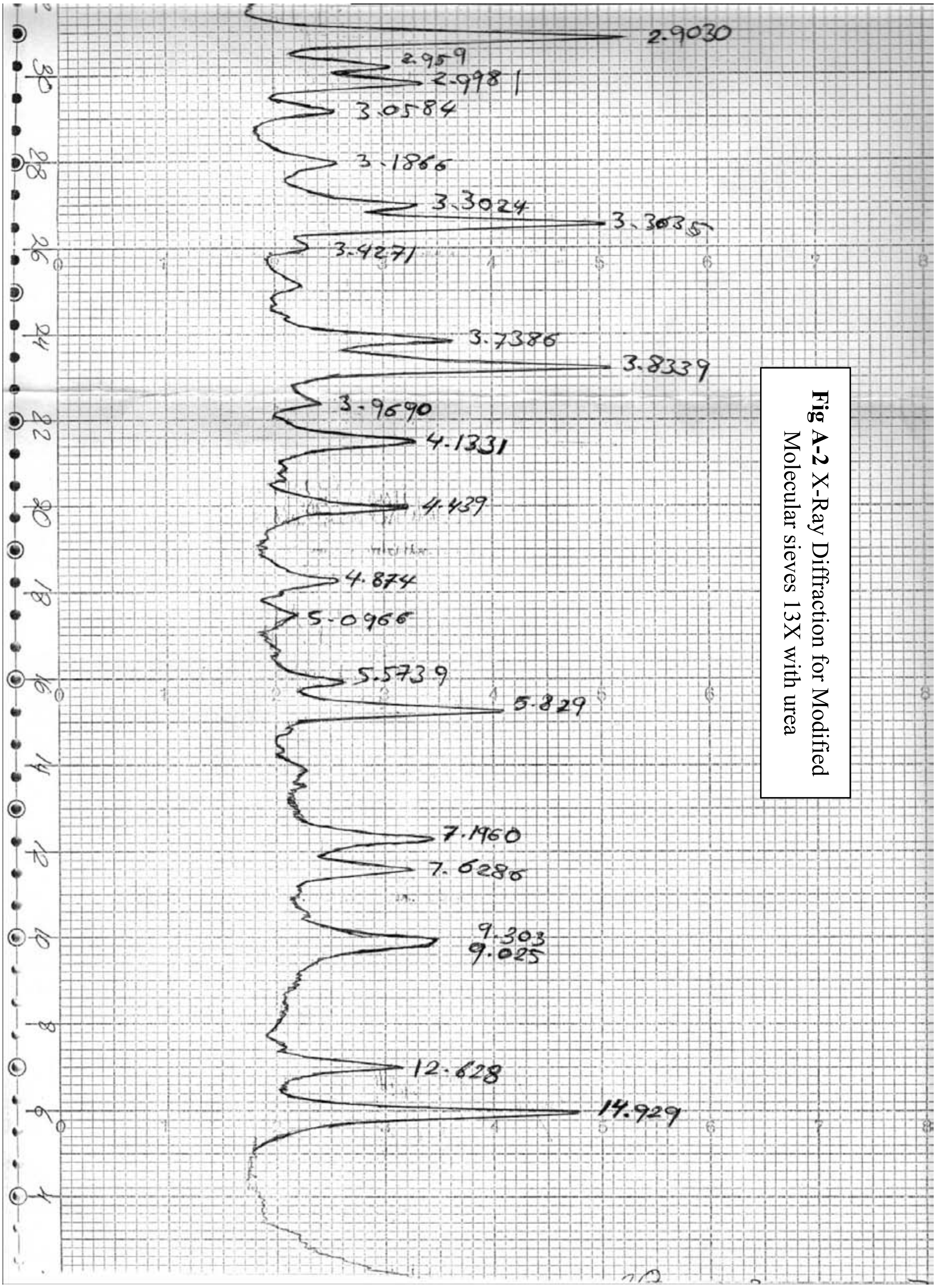

**Fig A-2** X-Ray Diffraction for Modified Molecular sieves 13X with urea

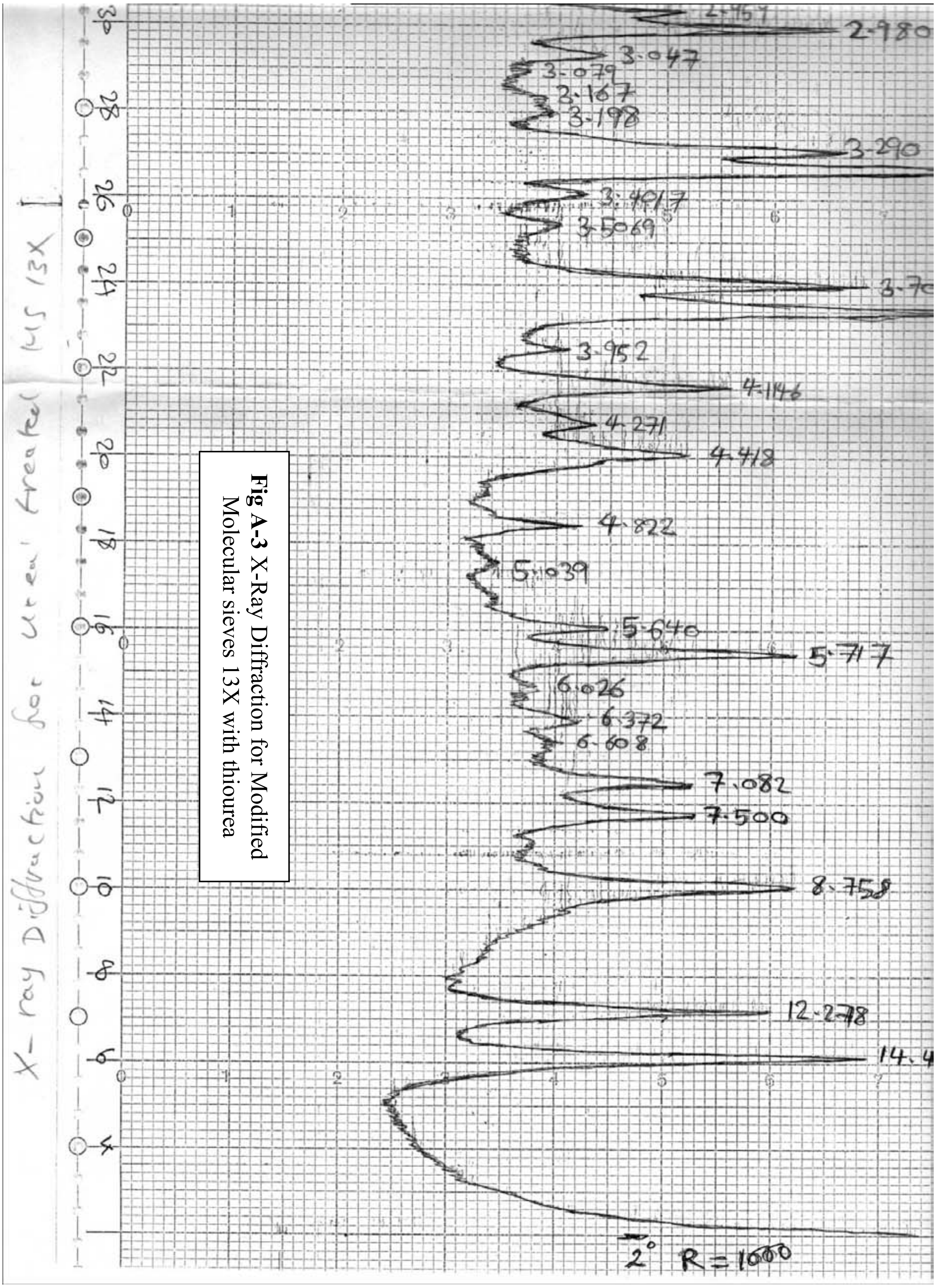

**Fig A-3** X-Ray Diffraction for Modified Molecular sieves 13X with thiourea

# Appendix B

# X-Ray Diffraction Value

**Table B-1 X-ray diffraction of original molecular sieve 13X**

| 2θ | d/ ºA |
|---|---|
| 6.2 | 14.256 |
| 10.1 | 8.7588 |
| 11.75 | 7.5323 |
| 15.575 | 5.6900 |
| 18.5 | 4.7964 |
| 20.2 | 4.3965 |
| 21.0 | 4.2307 |
| 22.6 | 3.9347 |
| 23.4 | 3.8020 |
| 24.7 | 3.6047 |
| 25.5 | 3.4934 |
| 26.7 | 3.3391 |
| 29.3 | 3.0485 |
| 30.4 | 2.9406 |
| 31.1 | 2.8760 |
| 32.1 | 2.7880 |
| 32.7 | 2.7388 |
| 33.71 | 2.6590 |
| 34.3 | 2.6140 |
| 35.0 | 2.5640 |
| 37.4 | 2.4050 |
| 38.3 | 2.3500 |

## Table B-2 X-Ray diffraction of Modified MS13X by Urea

| 2θ | d/ $^{o}$A |
|---|---|
| 6.0 | 14.929 |
| 7.0 | 12.628 |
| 9.8 | 9.025 |
| 9.95 | 9.303 |
| 11.6 | 7.6286 |
| 12.3 | 7.1960 |
| 15.3 | 5.829 |
| 15.9 | 5.5739 |
| 17.5 | 5.0966 |
| 18.2 | 4.874 |
| 19.9 | 4.439 |
| 21.5 | 4.1335 |
| 22.4 | 3.9690 |
| 23.2 | 3.8339 |
| 23.8 | 3.7386 |
| 25.1 | 3.548 |
| 26.0 | 3.4271 |
| 26.5 | 3.3635 |
| 27.0 | 3.3024 |
| 27.9 | 3.1866 |
| 29.2 | 3.0584 |
| 29.8 | 2.9981 |
| 30.2 | 2.959 |
| 30.4 | 2.9030 |
| 31.9 | 2.814 |
| 32.5 | 2.7632 |
| 33.5 | 2.675 |
| 34.1 | 2.6368 |
| 35.0 | 2.5637 |
| 50.09 | 1.821 |
| 50.6 | 1.804 |
| 51.1 | 1.774 |
| 51.8 | 1.765 |
| 52.6 | 1.740 |
| 53.4 | 1.716 |

### Table B-3 X-Ray diffraction of Modified MS13X by Thiourea

| 2θ | d/ °A |
|---|---|
| 6.1 | 14.490 |
| 7.2 | 12.278 |
| 10.1 | 8.758 |
| 11.8 | 7.500 |
| 12.5 | 7.082 |
| 13.4 | 6.608 |
| 13.9 | 6.372 |
| 14.7 | 6.026 |
| 15.5 | 5.717 |
| 16.0 | 5.540 |
| 17.6 | 5.039 |
| 18.4 | 4.822 |
| 20.1 | 4.418 |
| 20.8 | 4.271 |
| 21.6 | 4.1146 |
| 22.5 | 3.952 |
| 23.4 | 3.802 |
| 24.0 | 3.708 |
| 25.4 | 3.5069 |
| 26.2 | 3.4017 |
| 26.7 | 3.339 |
| 27.1 | 3.290 |
| 27.9 | 3.198 |
| 28.18 | 3.167 |
| 29.0 | 3.079 |
| 29.31 | 3.047 |
| 30.2 | 2.959 |
| 31.0 | 2.885 |
| 32.1 | 2.788 |
| 33.2 | 2.698 |
| 34.2 | 2.667 |
| 35.0 | 2.622 |
| 36.6 | 2.564 |
| 37.5 | 2.398 |
| 38.0 | 2.368 |
| 39.5 | 2.2816 |

# Appendix C

# FTIR Pattern

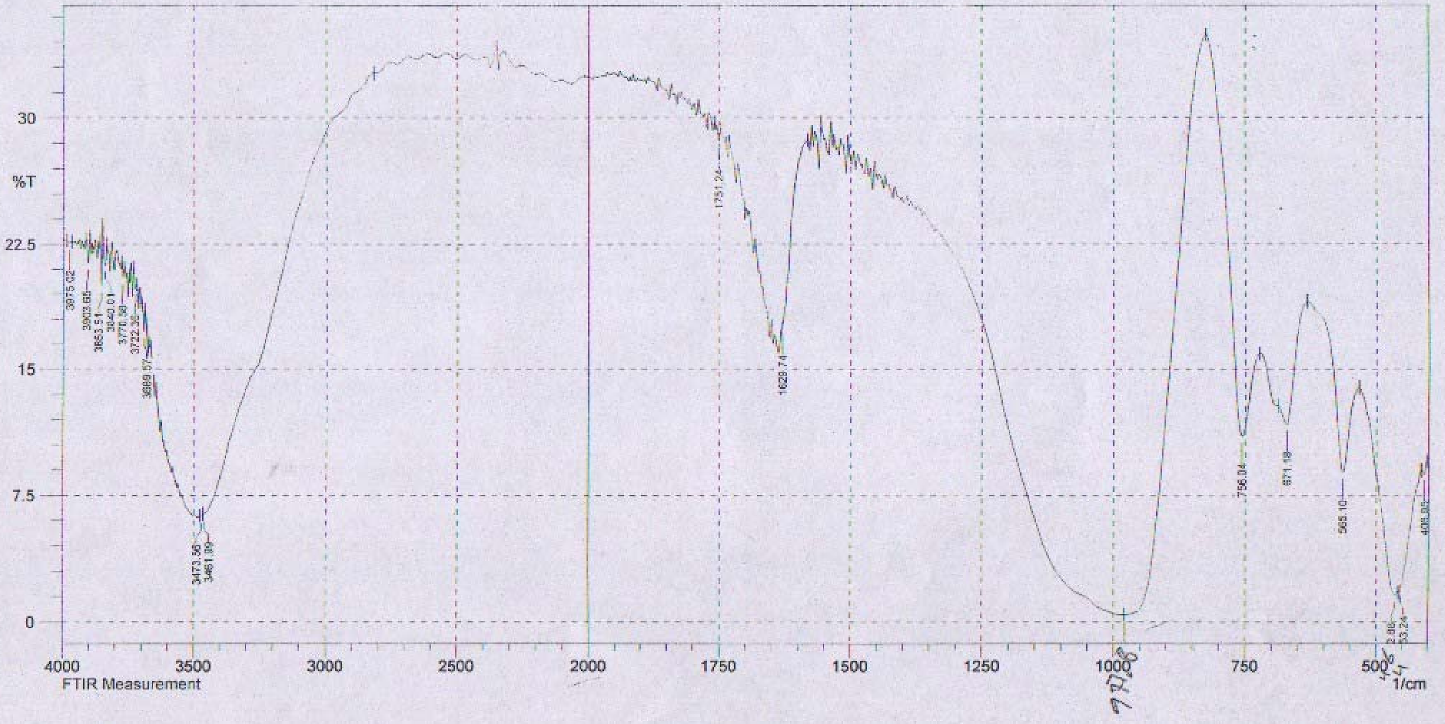

Fig C-1 Infrared spectra for the molecular sieve 13X

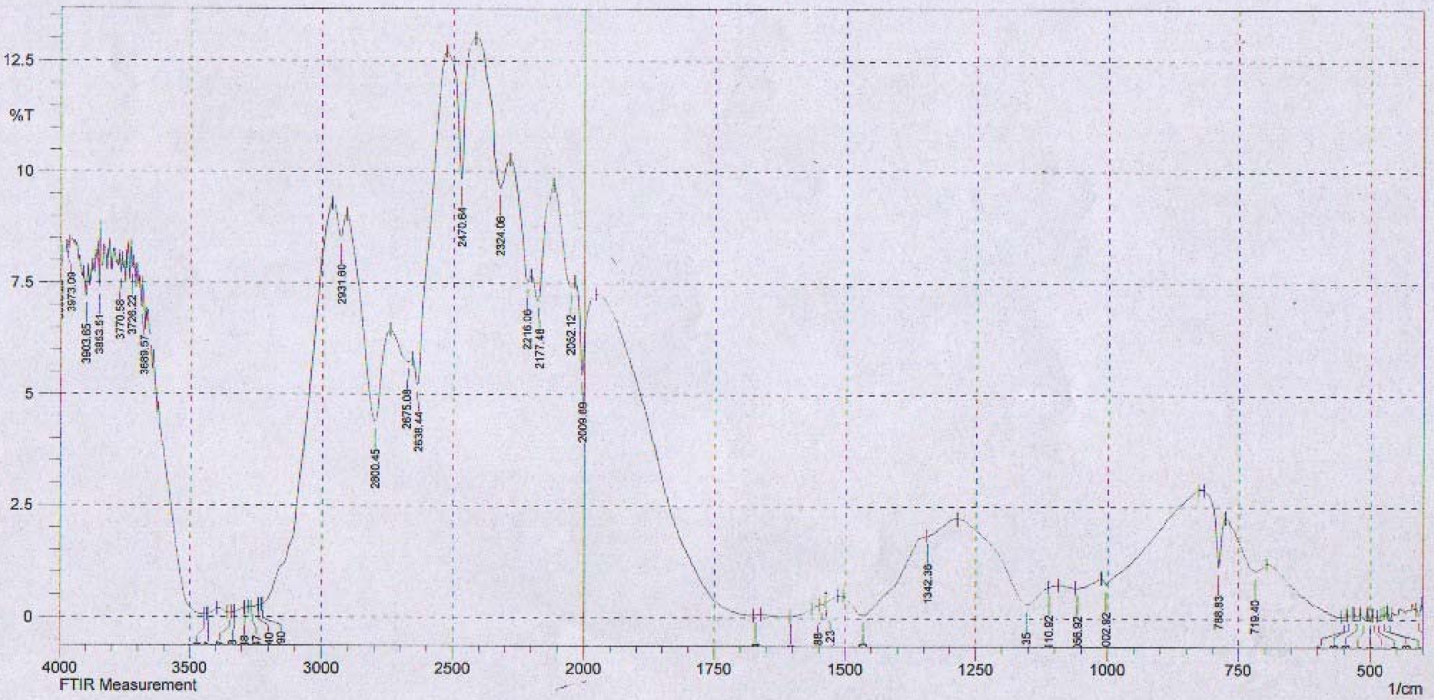

Fig C-2 Infrared spectra for urea treated molecular sieve 13X

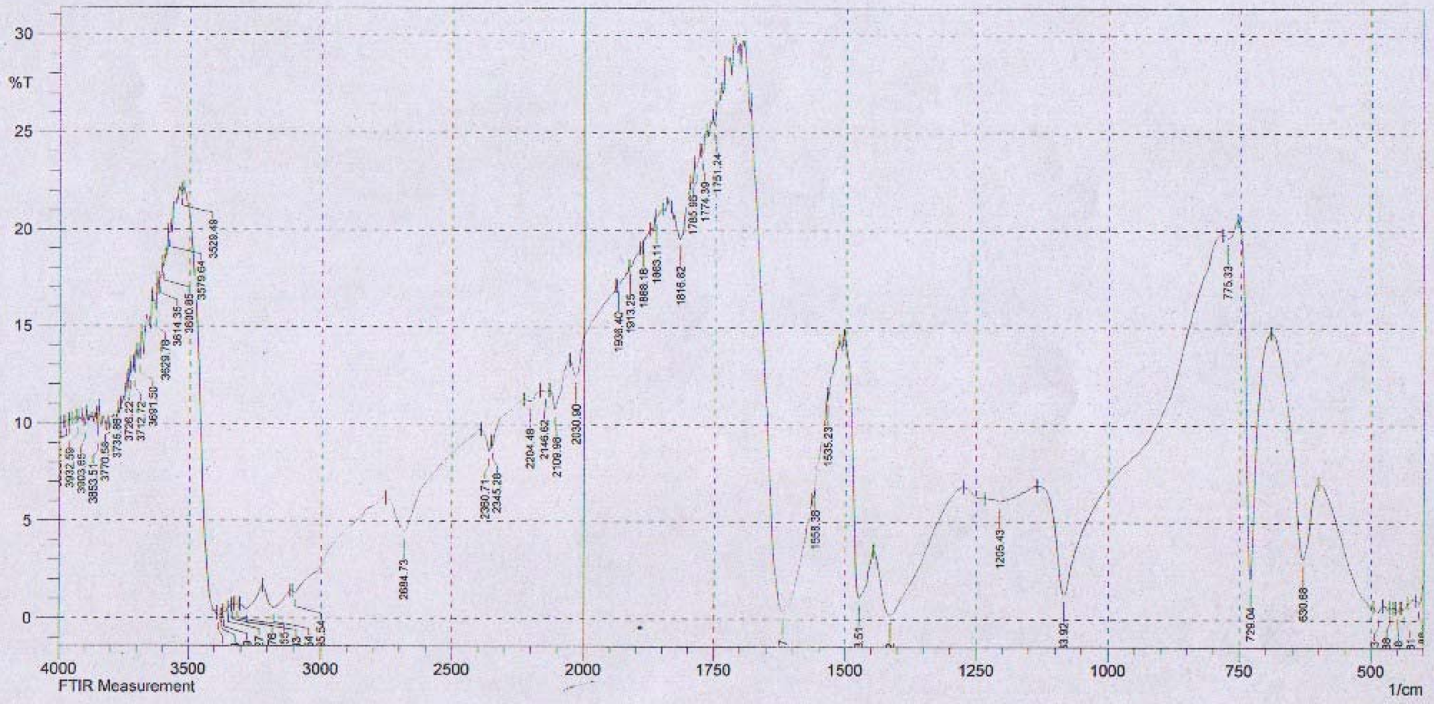

Fig C-3 Infrared spectra for thiourea treated molecular sieve13X

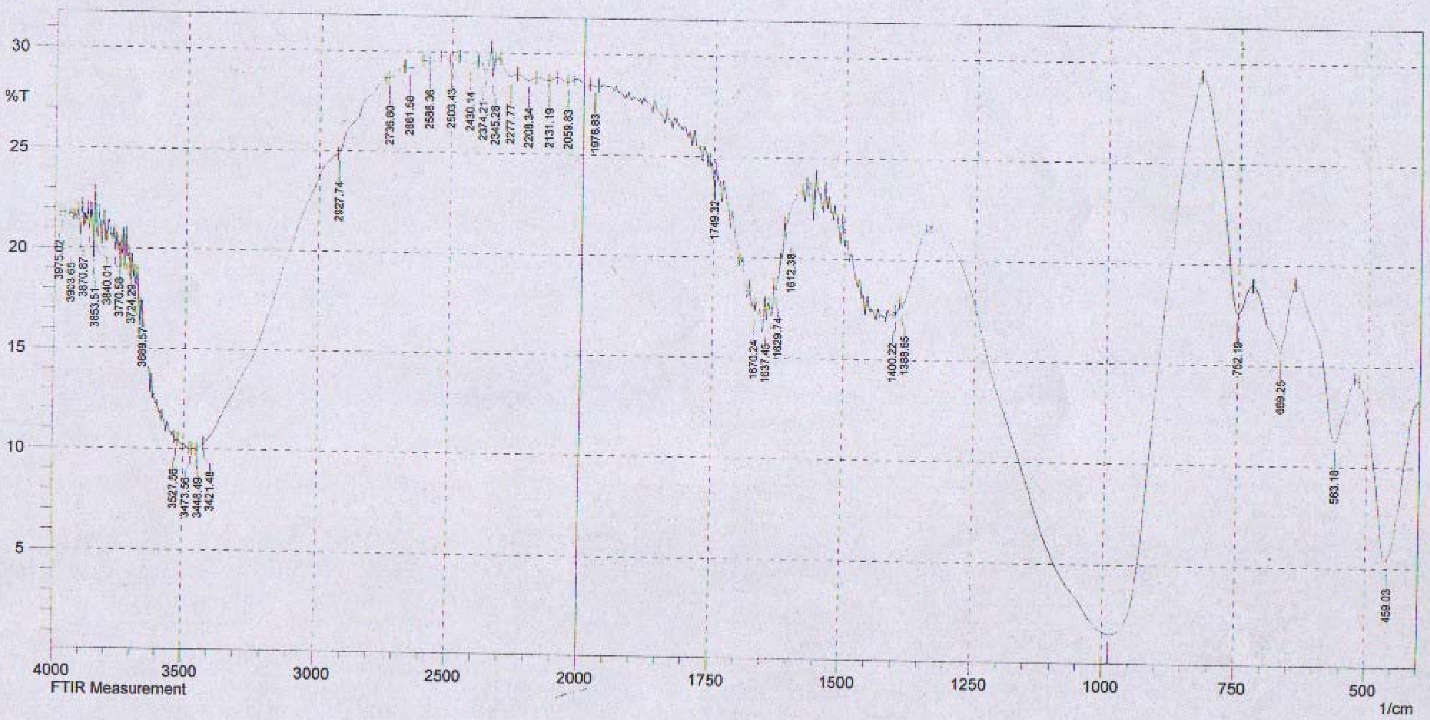

**Fig C-4** Infrared spectra for the molecular sieve13X modified with urea

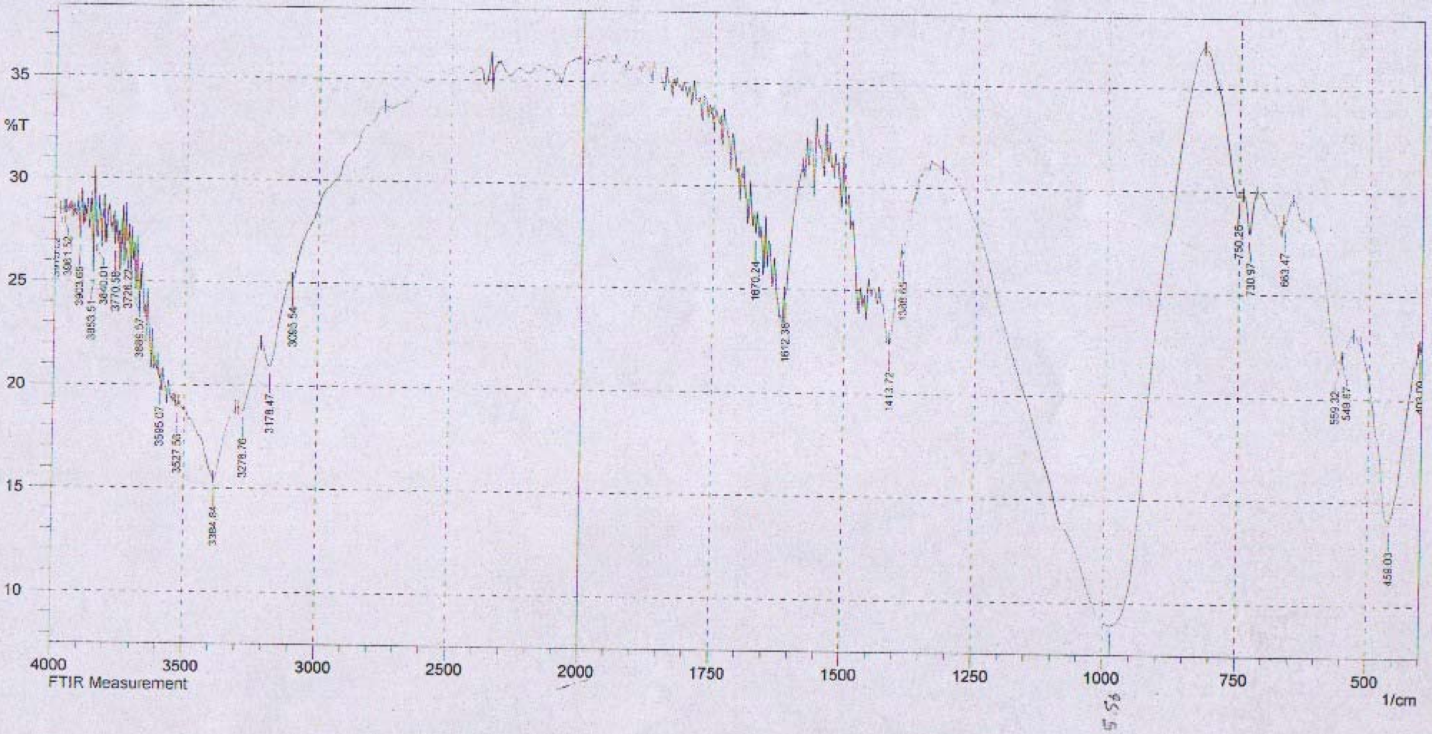

Fig C-5 Infrared spectra for the molecular sieve13X modified with thiourea

# Appendix D

# FTIR Value

## Table D-1 Infrared Absorption Bands ($cm^{-1}$) of Sample MS13X

| Assignment | MS13X |
|---|---|
| [Si-OH] | 3750 (w)- 3950(w) (80)(82) |
| [Si-OH-Si(Al)] | 3600 (ms) (10) |
| [Si(Al)-OH] (H-bond) | 3570 (ms) (80) |
| [Si(Al)-OH] (H-bond) | 3450 (ms) (80) |
| [-OH] stretching vibration of water | 3400 (ms) (80) |
| [-OH] stretching vibration of water | 3200 (sh.m) (80) |
| [-OH] stretching vibration of water | 3000 (80) |
| [$H_2O$] vibration | 1650 (m)-1750 (m) (10) |
| [Si-O-Si] open chain | 1030-1080 (s) (80) |
| [Si-O-Si] cyclic chain | 1033-1076 (s) (80) |
| [Si-O-Si(Al)] asymmetric vibration | 1001 (s) (82) |
| [Si-O-Si(Al)] | 772.1 (w) (10) |
| [Si-O-Si(Al)] | 656 (m) (83) |
| [Si-O-Si(Al)] | 550 (s) (82) |

**Table D-2 Infrared absorption bands ($cm^{-1}$) of sample Urea**

| Assignment | Bands |
|---|---|
| [$NH_2$] asymmetric vibration | 3450 (s)$^{(80)(79)}$ |
| [$NH_2$] symmetric vibration | 3344 (s)$^{(80)}$ |
| [$NH_2$] ( H-bond) | 3259 (s)$^{(80)}$ |
| [C=O] | 1750-1730-1685 (s)$^{(80)}$ |
| [C=N] | 1690-1640 (v)$^{(80)}$ |
| [$C=N^+H_2$] | 1606 (s)$^{(10)}$ |
| [N-C-N] asymmetric vibration | 1465 (s)$^{(10)}$ |

**Table D-3 Infrared absorption bands ($cm^{-1}$) of sample Thiourea**

| Assignment | Bands |
|---|---|
| [$NH_2$] asymmetric vibration | 3393 (S)$^{(80)(79)}$ |
| [$NH_2$] symmetric vibration | 3365 (S)$^{(80)(83)}$ |
| [$NH_2$] (H-bond) | 3270 (S)$^{(80)}$ |
| [C=S] | 1413 (S)$^{(80)}$ |
| [C=N] | 1410 (S)$^{(80)(83)}$ |
| [N-C-N] | 1472 (S)$^{(80)}$ |

# Appendix E

# Experimental Data

**Table E-1 Concentrations (ppm) of phenol in effluent stream**
Q= 0.2 l/h, h= 56 cm, $C_o$ =10 ppm and T= 30ºC

| Samples. NO | Time/min | MS13X | $MS_U$ | $MS_T$ |
|---|---|---|---|---|
| 1. | 30 | 0.7082 | 0.1178 | 0.5407 |
| 2. | 60 | 2.3044 | 1.5402 | 2.0664 |
| 3. | 90 | 4.8606 | 3.6619 | 4.3239 |
| 4. | 120 | 6.7433 | 5.5727 | 6.1013 |

**Table E-2 Concentrations (ppm) of phenol in effluent stream**
Q= 0.2 l/h, h= 30 cm, $C_o$ =10 ppm and T= 30ºC

| Samples. NO | Time/min | MS13X | $MS_U$ | $MS_T$ |
|---|---|---|---|---|
| 1. | 30 | 3.4184 | 2.9513 | 3.1291 |
| 2. | 60 | 5.1195 | 4.1217 | 4.9258 |
| 3. | 90 | 7.0642 | 6.0162 | 6.6313 |
| 4. | 120 | 8.6168 | 7.3293 | 8.1212 |

### Table E-3 Concentrations (ppm) of phenol in effluent stream

Q= 1.0 l/h, h= 56 cm, $C_o$ =10 ppm and T= 30ºC

| Samples. NO | Time/min | MS13X | $MS_U$ | $MS_T$ |
|---|---|---|---|---|
| 1. | 30 | 2.4321 | 2.0292 | 2.2170 |
| 2. | 60 | 5.7113 | 5.1021 | 5.5178 |
| 3. | 90 | 7.4662 | 6.7483 | 7.5621 |
| 4. | 120 | 9.2094 | 8.4361 | 9.4130 |

### Table E-4 Effect of bed high on outlet phenol concentration (ppm), by using MS13X adsorbent

Q= 0.2 l/h, $C_o$ =10 ppm and T= 30ºC

| Samples. NO | Time/min | MS (56 cm) | MS (30 cm) |
|---|---|---|---|
| 1. | 30 | 0.7082 | 3.4184 |
| 2. | 60 | 2.3044 | 5.1195 |
| 3. | 90 | 4.8606 | 7.0642 |
| 4. | 120 | 6.7433 | 8.6168 |

### Table E-5 Effect of bed high on outlet phenol concentration (ppm), by using $MS_U$ adsorbent

Q= 0.2 l/h, $C_o$ =10 ppm and T= 30ºC

| Samples. NO | Time/min | $MS_U$ (56 cm) | $MS_U$ (30 cm) |
|---|---|---|---|
| 1. | 30 | 0.1178 | 2.9513 |
| 2. | 60 | 1.5402 | 4.1217 |
| 3. | 90 | 3.6619 | 6.0162 |
| 4. | 120 | 5.5727 | 7.3293 |

### Table E-6 Effect of bed high on outlet phenol concentration (ppm), by using $MS_T$ adsorbent

Q= 0.2 l/h, $C_o$=10 ppm and T= 30ºC

| Samples. NO | Time/min | $MS_T$ (56 cm) | $MS_T$ (30cm) |
|---|---|---|---|
| 1. | 30 | 0.5407 | 3.1291 |
| 2. | 60 | 2.0664 | 4.9258 |
| 3. | 90 | 4.3239 | 6.6313 |
| 4. | 120 | 6.1013 | 8.1212 |

### Table E-7 Effect of flow rate on outlet phenol concentration (ppm), by using MS13x adsorbent

h=56 cm, l/h, $C_o$=10 ppm and T= 30ºC

| Samples. NO | Time/min | MS (0.2 l/h) | MS (1.0 l/h) |
|---|---|---|---|
| 1. | 30 | 0.7082 | 2.4321 |
| 2. | 60 | 2.3044 | 5.7113 |
| 3. | 90 | 4.8606 | 7.4662 |
| 4. | 120 | 6.7433 | 9.2094 |

### Table E-8 Effect of flow rate on outlet phenol concentration (ppm), by using $MS_U$ adsorbent

h=56 cm, l/h, $C_o$=10 ppm and T= 30ºC

| Samples. NO | Time/min | $MS_U$ (0.2 l/h) | $MS_U$ (1.0 l/h) |
|---|---|---|---|
| 1. | 30 | 0.1178 | 2.0292 |
| 2. | 60 | 1.5402 | 5.1021 |
| 3. | 90 | 3.6619 | 6.7483 |
| 4. | 120 | 5.5727 | 8.4361 |

### Table E-9 Effect of flow rate on outlet phenol concentration (ppm), by using $MS_T$ adsorbent

h=56 cm, l/h, $C_o$ =10 ppm and T= 30ºC

| Samples. NO | Time/min | $MS_T$ (0.2 l/h) | $MS_T$ (1.0 l/h) |
|---|---|---|---|
| 1. | 30 | 0.5407 | 2.2170 |
| 2. | 60 | 2.0664 | 5.5178 |
| 3. | 90 | 4.3239 | 7.5621 |
| 4. | 120 | 6.1013 | 9.4130 |

### Table E-10 Effect of time on accumulative ($10^{-6}$g/g) adsorption of phenol

Q= 0.2 l/h, h= 30 cm, T= 30ºC, and $C_o$= 10 ppm

| Samples. No | Time/min | MS13X | $MS_U$ | $MS_T$ |
|---|---|---|---|---|
| 1 | 30 | 14.9585 | 18.5496 | 18.0817 |
| 2 | 60 | 37.143 | 49.4886 | 44.7885 |
| 3 | 90 | 57.1602 | 80.9402 | 71.384 |
| 4 | 120 | 69.7352 | 109.0534 | 91.1618 |

### Table E-11 Effect of time on accumulative ($10^{-6}$g/g) adsorption of phenol

Q= 1.0 l/h, h= 56 cm, T= 30ºC, and $C_o$= 10 ppm

| Samples. No | Time/min | MS13X | $MS_U$ | $MS_T$ |
|---|---|---|---|---|
| 1 | 30 | 49.1423 | 104.8791 | 102.4313 |
| 2 | 60 | 104.8398 | 233.7846 | 220.432 |
| 3 | 90 | 154.1996 | 362.2164 | 316.7384 |
| 4 | 120 | 174.7347 | 444.6271 | 347.7327 |

**Table E-12 Effect of Temperature on adsorption of phenol**

Q= 0.2 l/h, h= 56 cm, T= 30ºC, and $C_o$= 10 ppm

| Samples. No | T/ K | MS13X | $MS_U$ | $MS_T$ |
|---|---|---|---|---|
| 1. | 303 | 0.7082 | 0.1178 | 0.5407 |
| 2. | 313 | 1.2132 | 0.8061 | 1.0214 |
| 3. | 323 | 2.8761 | 2.0132 | 2.4437 |

# APPENDIX F
# SAMPLE OF CALCULATION

Equation 4-2 was used for calculation of accumulative adsorption of phenol.

$$\mathbf{q_i = [(C_o\text{-}C_t)/M] \times Q \times t}$$

A sample of calculation is taken at the following conditions.

at Q= 0.2 l/h or Q= 3.3334 $cm^3$ /min, variables time from 30 to 120 min, for MS13X M= 77g and $C_o$ =10 ppm or $10\times10^{-6}$ $g/cm^3$:

$q_i = [(10- 0.7082)\times10^{-6} /77]\times3.3334\times30$
$= 12.0675 \times10^{-6}$ g/g of zeolite (solute adsorbed)

$q_i =[(10- 2.3044)\times10^{-6} /77]\times3.3334\times60$
$= 19.9889 \times10^{-6}$ g/g of zeolite (solute adsorbed)

$q = 12.0675 \times10^{-6} + 19.9889 \times10^{-6}$
$= 32.0564 \times10^{-6}$ (Accumulation of Adsorption)

$q_i = [(10- 4.8606)\times10^{-6} /77]\times3.3334\times90$
$= 20.0240 \times10^{-6}$ g/g of zeolite (solute adsorbed)

$q = 32.0564 \times10^{-6} \times 20.0240 \times10^{-6}$
$= 50.0804 \times10^{-6}$ (Accumulation of Adsorption)

# الخلاصة

تم دراسة امكانية ازالة ملوثات الفينول من الماء بطريقة الامتزاز المستمرة بوجود المناخل الجزيئية نوع 13X. كما تم تطوير المادة وسط الامتزاز بالمعاملة مع محاليل مشبعة من اليوريا والثايويوريا لتعزيز قابلية على امتزاز الفينول.

تضمنت مرحلة تحضير نماذج الامتزاز عند هزج هسحوق الماخل الجزيئية مع محاليل مائية مركزة من اليوريا او الثايويوريا ، ثم اضافة سليكات الصوديوم كمادة رابطة ، يتكون خليط متجانس بالنسب الوزنية، ٥٠% مناخل جزيئية، ٣٠% مادة رابطة، ٢٠% مادة التحوير، يوريا او ثايويوريا . تم تشكيل النماذج على شكل اسطواني بقطر ٥ ملم متجفيفها.

معاملة الماخل الجزيئية باليوريا او الثايويوريا تحت الظروف المدروسة ،ادى الى التاثير الجزيئي على التركيب السيليكا والالومينا فيها ، كما تبين تحاليل تقنية حيود الاشعة السينية . االمعاملة ادت الى زيادة ملحوظة في المساحة السطحية للمادة ، خاصة النماذج المعززة باليوريا. كما ان تحاليل مطياف الاشعة تحت الحمراء اعطت حصول تاثيرات ملحوظة لليوريا او الثايويوريا على المادة الاساس. انعكا س ذلك بصورة رتيسية باتجاة ربط الهايدروجين في المادة المعززة من خلال مجاميع $NH_2$- مع مجاميع OH- لتركيب الاوكسجين في الماخل الجزيئية او من خلال الماء الممتز. لوحظ ان اليوريا ادت الى تاثير اكثر مع المادة الاساس مقارنة بالثايويوريا.

تم اجراء تجارب عملية لدراسة امكانية ازالة الفينول من المحاليل المائية باستخدام المناخل الجزيئية نوع 13X. والنماذج المحسنة. التجارب شملت كذلك تاثير العوامل الرئيسية على قابلية مواد المتزاز لامتزاز الفينول.

تتمتع المناخل الجزيئية نوع 13X وتحويراتها مع اليوريا او الثايويوريا بقابلية جيدة لامتزاز بقايا الفينول من الماء. حيث تعد النماذج المجسنة باليوريا والتي تتمتع بدورها باكبر مساحة سطحية ، افضل النماذج يليها تلك المعاملة بالثايويوريا.

اظهرت النتائج ان اعلى نسب الازالة حصلت باستخدام تراكيز واطئة للفينول في المحاليل المائية، سرع واطئة للمحاليل طول اكبر لوسط الامتزاز ، ودرجة حرارة واطئة ، كما نتوقع ذلك لعمليات الامتزاز التقليدية.

يؤثر زيادة تركيز الفينول في الماء بشدة على القوة الدافعة وبالتالى على سرعة الامتزاز وتعطي ايضا سعة اكبر. بينما تنخفض نسبة الازالة للفينول عند ثبوت ظروف التشغيل الاخرى.

تم تحقيق ازالة عالية للفينول اكثر من ٩٨% باستخدام ٠,٢ لتر/ساعة سرعة جريان المحلول الحاوي على ١٠ جزء بالمليون فينول، ٥٦ سم طول وسط الامتزاز عند ٣٠م ضمن التجارب المستخدة في البحث.

# شكر و تقدير

اودُ أن أعبر عن خالص شكري وتقديري وَ امتناني العميق للمشرف الدكتور محمد نصيف لطيف لما بذله من جهد كبير و ارشادات سديدة و قيمة طوال فترة اعداد الرسالة.

أودُ أيضاً أن أشكر السيد رئيس القسم و موظفي قسم الهندسة الكيماوية لإبدائهم المساعدة اللازمة أثناء فترة البحث.

ولا أنسى أن أتقدم بالشكر و الامتنان إلى من لازمني طوال فترة البحث وخلال أصعب الظروف إلى أعز من في الوجود إلى أبي و أمي و جميع أفراد عائلتي فلهم جزيل الشكر و التقدير.
وخالص شكري وتقديري الى الست منيرة في قسم علوم الكيماء (المختبر الخدمي) لما بذلته من جهد كبير اثناء فترة البحث.
االى من احببت طوال عمري................

**م..ليث سالم صبري**

# تحسين المناخل الجزيئية 13X واستخداماتها المحتملة في ازالة ملوثات الفينول

رسالة
مقدمة الى كلية الهندسة في جامعة النهرين و هي جزء من متطلبات نيل
درجة ماجستير علوم في الهندسة الكيمياوية

من قبل
**ليث سالم صبري الكوفي**
(بكالوريوس في الهندسة الكيمياوية٢٠٠٢ )

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