Republic of Iraq
Ministry of Higher Education and Scientific Research
University of Baghdad
College of Education for Pure Science
(Ibn Al-Haitham)
Department of Chemistry

# Beneficiation and Purification of Iraqi Attapulgite Clay Minerals to Remove Mercaptance Contents from Iraqi Fuels

A Thesis

Submitted to the Council of the College of Education for Pure Sciences (Ibn Al-Haitham) University of Baghdad, in partial fulfillment of the Requirements for Obtaining a Master Degree in Analytical Chemistry

By

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2019 AD 1440 AH

بِسۡمِ ٱللَّهِ ٱلرَّحۡمَٰنِ ٱلرَّحِيمِ

{ قال ربِّ أشَرْحْ لِي صَدري * ويسر لي أَمري *و أُحُللْ عقدةً مِنْ لِساني *يَفقُهواْ قَولِي *}

صدق الله العلي العظيم

سورة طه (25_٢٨)

# Confirmation message supervisor

Acknowledged that preparing this message tagged (purify and improve Iraqi Attapulgite clays specifications to remove sulfur content and dewaxing fuel) for the student (Nadhem Tahir Gharab ) under my supervision in the Chemistry Department, college of Education Sciences (Ibn-Al-Haithem) – University of Baghdad and is part of the requirements of the master of Science degree in chemistry

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# Certification

We,the examining committee,after reading this thesis “**Benefication and purification of Iraqi Attapulgite Clay Minerals to Remove Mercaptance Content from Iraqi Fuels**”**and examining the student** “ Nadhem Gharab Taher” in its content s,find that it is qualifiedfor the degree of master of science in analytical chemistry with grade of ( **excellent)** on (    / 7 / 2019 ).

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*I dedicate this research*
*source of tenderness and mercy,*
*my mother and father mercy of*
*Allah on them*
*And for*
*my family*

*Nadhem*

# Acknowledgment

Praise is to Allah who guided us to this and we did not find without that guided of Allah, and peace and blessings are upon the Prophet Mohamed and his family and companions.

To my family who provided me all the amenities, help and urged me to climb the ladder of science my supervisor who lend a hand in everything, the source of knowledge Assistant Professor Mohamed Hassan Abdul latif.

To all teachers and all who contributed to the moral and material Support in the Chemistry Department, to everyone meet me with a smile lift her off me all worried and distressed**.**

To the deanship of the college of education-Ibn Al- Haithem and the dean Prof .Dr. Hassan Ahmed Hassan.

To Ahmed Qasim and Mohammed Hassan (Al- Dora refinery lab's)

Finally, thanks and appreciation is to my second family (friends), which gave me all the love and support during my studies (Nazar, Mohammed, Hashim, Younis, Munjid, Mahmood, Alaa, Sahar, Saba, Zakya, Athra ... etc)

# Abstract

Due to high costs for imported the enhanced gasoline was impact of thinking to use alternatives local for removing sulfur contents of Iraqi gasoline and produce-enhanced gasoline. This work include an analogue to purification and beneficiation of an Attapulgite Iraqi clay specification to use as adsorption agent of Sulphur compounds from Iraqi gasoline by activated the clay to reduce Sulphur content in gasoline and kerosene.

Crude Iraqi Attapulgite clay mineral was imported from Iraqi Geological survey. Purification process was based on American means (Ser. No 09/, 190, 528, filed Nov.12, 1980, now US Pat .No. 6130, 179) developed by adding sodium methyl acrylate. The clay was activated after removing of sand and other impurities using H-form ion exchange (dewax 50) format where the metal interfacial cations was replaced by protons $H^+$ and then adding sodium acrylate to isolate pure Attapulgite from other contaminated clay minerals such as Montmorillonite by floatation using floatation cell for use as adsorption agent for mercaptance. Different analytical techniques were used in this work, which include FT –IR spectrum, X- ray diffraction spectrum, X-ray fluorescent, SEM, X-ray diffraction and EDX. All the results of this work Purification and activation process managed to remove impurities and increase the proportion of metal Montmorillonite and Attapulgite, next step increasing proportions of Attapulgite mineral by add methyl sodium acrylate.

Some of peaks disappeared from FT-IR spectrum of crude were observed due to the impurities and other type of clay where removed from Attapulgite and obtained activated Attapulgite clay such as (977.9 $cm^{-1}$), (923 $cm^{-1}$) due to (O-H) (bending).

The difference in the intensity peaks were observed in x- ray diffraction spectrum due to the activation Attapulgite clay, when compared with x- ray diffraction spectrum of Attapulgite crude and led to the low percentage of calcite which removing the largest proportion of impurities and increase the proportion of the Attapulgitte.

Electron microscope image proved a clear change in crystalline structures that appeared on the surface of the clay showing the purification and beneficiation Attapulgite to use as adsorption agent.

Metal cation concentrations decreased indicated in figure of EDX test shows success replacing metal cation by $H^+$ and form H-Form when adding amber light orange were acidified diluted HCl.

Low concentration of Sulphur content in units of ppm concentration in crude oil in the table shows the amount of Sulphur in gasoline before and after removing of Sulphur content.

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# CHAPTER ONE

## INTRODUCTION

# 1. Introduction

## 1.1. Clays

At the beginning of the 20th century, Iowenstein hypothesis that "clay matter consists of very small granules dating to a certain number of crystallized minerals." [1]. Clay minerals are the most common minerals. Clay material may consist of one mineral or may contain on varying amounts of non-clay minerals such as quartz and other minerals. The plains are widespread because of the abundance of mineral materials in them, so they are of great importance to industry and to many enormous uses [2]. Clays are also defined as sediments that occur naturally and consist of one or more metals and other compounds [3]. The chemical analysis of the various types has shown that it is an aluminum silicate and contains amounts of iron, magnesium and other elements. Water is one of the main components of the linens. It plays the role of Lubricant. It acquires clay as plasticity [4].

Many types of clay contain organic compounds and salts are soluble in water. Thus, crystallized clay minerals are the basic components of clay materials, i.e., their components determine the properties of clay materials. Many clay materials have similar chemical structures, the crystalline structure i revealed by X-ray diffraction as the best diagnostic method [5]. An idea gave about the nature and behavior of clay within the solution. According to Grouy-Chapnan theory, this theory assumes two layers, the result of Ions ($OH^-$) or ($O^{-2}$) in the grille clay and an outer layer containing positive ions [6]. The general principle of the regularity of elements in clay minerals is the two-dimensional arrangement of tetrachloride oxygen and a two-dimensional arrangement of aluminum iron or octane hydrogen peroxide. Quadrilateral plates and eight surfaces in different positions linked together with ionic bonds, figure below [7].

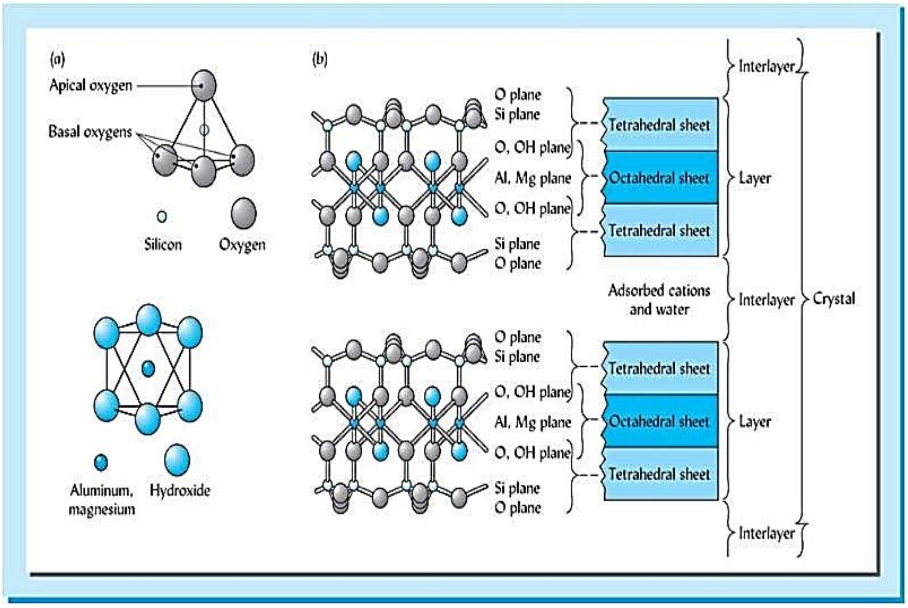


Figure (1-1) Molecular and structural components of silicate spectra

Figure (1-1) shows; (a) A four-tiered four-sided shape surrounded by silicon ion with four oxygen atoms, eight-sided octagonal shapes surrounded by aluminum or magnesium ions, six hydroxyl groups or oxygen atoms.

(b) A large number of clay crystals consisting of eight quadrilateral shapes.

Clay has a plasticity when the powder is wet enough [8]. The porosity of the mud gives it a high surface area which gives it high efficiency (higher activity) in adsorption [9].

### 1.1.1Structure of Clays

The layers constructed from four-plate sheets surrounded by a silicon atom with four oxygen atoms and eight-sheet plates surrounded by a metal such as aluminum or magnesium with eight atoms of oxygen. The tetrahedral and octahedral molecules combined by the exchange of oxygen atoms, and the non-common oxygen is present in the hydroxyl structure. Two of the main arrangements for the four-surface and eight-surface plates are combined to form a single layer of clay, As shown in the following figure(1-2) ;

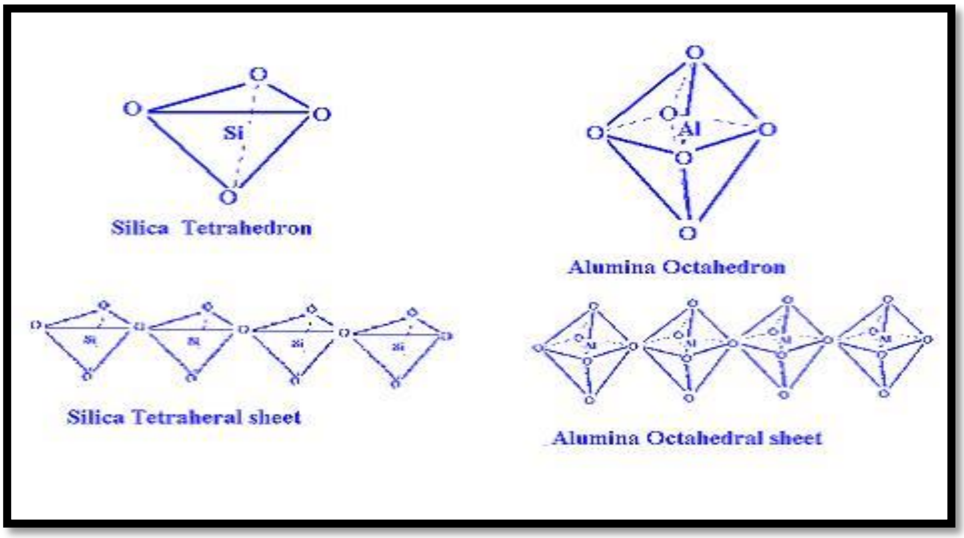


Figure (1-2) Four-layer silicon sheets and aluminum plates Eight sheets.

If one sheet of four surfaces combined with one plate of eight surfaces, the clay is known as 1: 1, such as the Kaolin group, whose general composition is $Al_2Si_2O_5\ (OH)_5$, where the thickness of the layer is about 0.7nm. If the crystalline lattice is composed of one plate, the eight surfaces are located between two four-plate plates. It is of type 2: 1, known as phyllosilicates. The thickness of the layer is about 0.94nm. This layer is electrically neutral. The type (2: 1) called mica figure (1-3), when the silicon substituted in the aluminum quaternary [10].

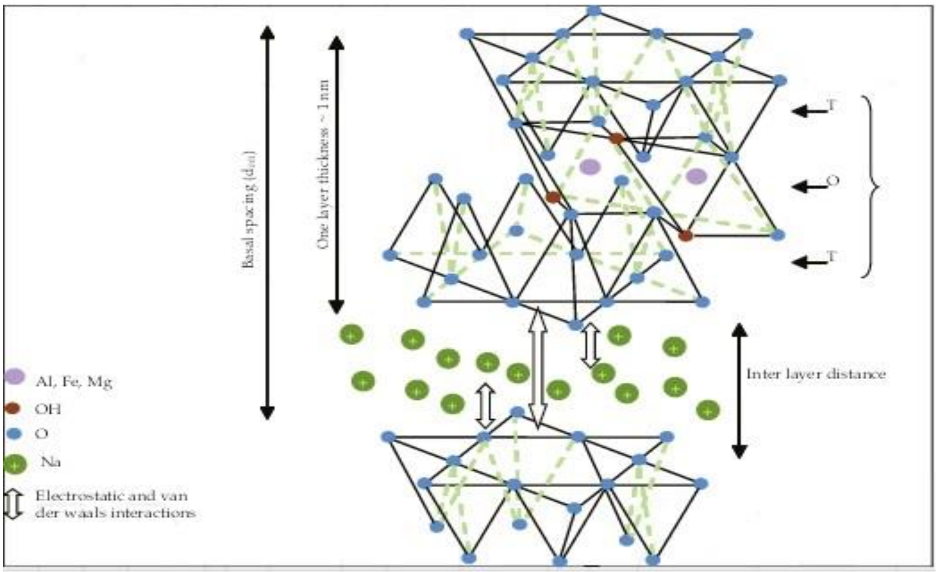


Fig (1-3) shows the structure of Smectite clays type (2:1) [11]

## 1.1.2.Clay mineral properties

The clay minerals are characterized by the following characteristics:

1. The composition of the one-dimensional layer at the nanometer rate, the thickness of the layer (1: 1) (TO) be about 0.7nm and the layer (TOT) is about 1nm.
2. Variation in layers or particles.
3. The existence of several types of surfaces.
4. The ease with which the external and sometimes internal surface can be modified by adsorption, ion exchange, grafting
5. Plasticity.
6. Hardening; drying and burning.

But these qualities do not apply to all metals many scientists associate or bind clay minerals with the samples that have the following characteristics:

a. The particle size of particles that is, the size of their nanoparticles from (1-100) nm.

b. Large surface area.

c. Large cation exchange capacity depends slightly on the acidity of the surrounding media.

d. The capacity of the anion exchange does not depend on the PH.

e. Separation of layers is subject to change and this depends on the moisture of the ocean.

f. The tendency of foreign substances insertion; including organic compounds and molecules.

g. The ability of some elements such as $Na^{+}$ and $Li^{+}$ on the exchange to show the expansion between the layers in the water [12].

### 1.1.3 Smectite Clays

Is a group of clay minerals that have the ability to bulge and shrink because of the change in the moisture content, characterized by the composition of the class and the existence of a wide space between the layers , the most important clay minerals belonging to Smectites are shown in the following table:

Table (1-1) Common clay minerals belonging to the group of smectite [11].

| Smectites | Chemical formula |
|---|---|
| Montmorillonite | $M_x(Al_{4-x}Mg_x)Si_8O_{20}(OH)_4$ |
| Hectorite | $M_x(Mg_{6-x}Li_x)Si_8O_{20}(OH)_4$ |
| Saponite | $M_xMg_6(Si_{8-x}Al_x)O_{20}(OH)_4$ |

The class structure of the swollen surfaces carries a small negative charge and therefore attracts the water molecules or other polar molecules between the two layers of the Interlayer, causing the expansion of the distance in this region. The water molecules are generally lined around positive ions such as sodium or calcium between the clay layers and then into the outer layer. As shown in the following figure(1-4);

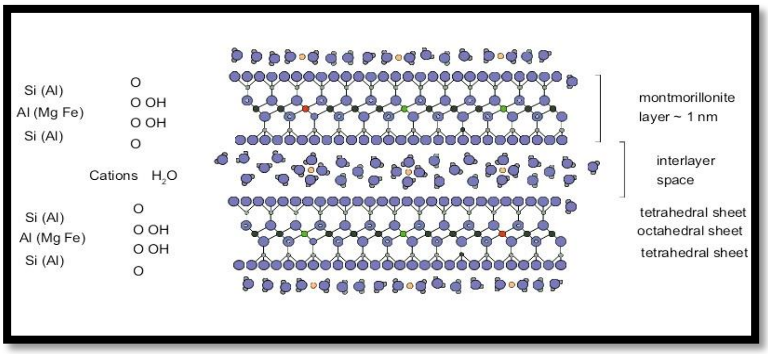


Figure (1-4) the alignment of water molecules and positive ions between two layers of Montmorillonite.

Figure (1-4) shows if a large amount of water molecules inserts the space between the two layers of clay, these extra particles do not line up in the same way that the water between the two layers aligns.

The swelling rate dependent on the type of cation found between the two layers, as the sodium-rich is more bulging than Smectite containing calcium. Sodium characterized by high exchange of positive ions, the removal of toxins and impurities from liquids, adsorption of oil, and bulging clay can adsorb the urea and prevent it from forming ammonia [13].

## (1.1.4) Bentonite

Bentonite It is a naturally slimy substance consisting mainly of hydrolytic silicate, containing magnesium, iron and calcium carbonate, and is mainly composed of Montmorillonite, which belongs to the group of sulfate [14]. In (1890) Bentonite was found in the earth's crust in the Benton region. It is a volcanic origin, characterized by soft grains and grayish yellowish color, consisting primarily of silica (60-70%), aluminum (15-20%) and a low proportion of iron. The bond between bentonite particles is very weak, Water molecules enter easily between its molecules and this leads to their separation from each other and this is why Bentonite has a high capacity to bloom up to eight times its original size [15].

The name Montmorillonite derived from the Mont Mellon region of France [2]. The Montmorillonite contains an eight layer between two quadrilateral layers. The water between these three layers removed without the internal atomic structure of the metal being destroyed when heated to a temperature not exceeding 100$^{o}$ C [16, 17]. It expressed in the chemical formula: [Ca, Na, K (Al, Mg, Fe $^{+3}$) (Si, Al)$_4$O$_{10}$ (OH$_2$).nH$_2$O].

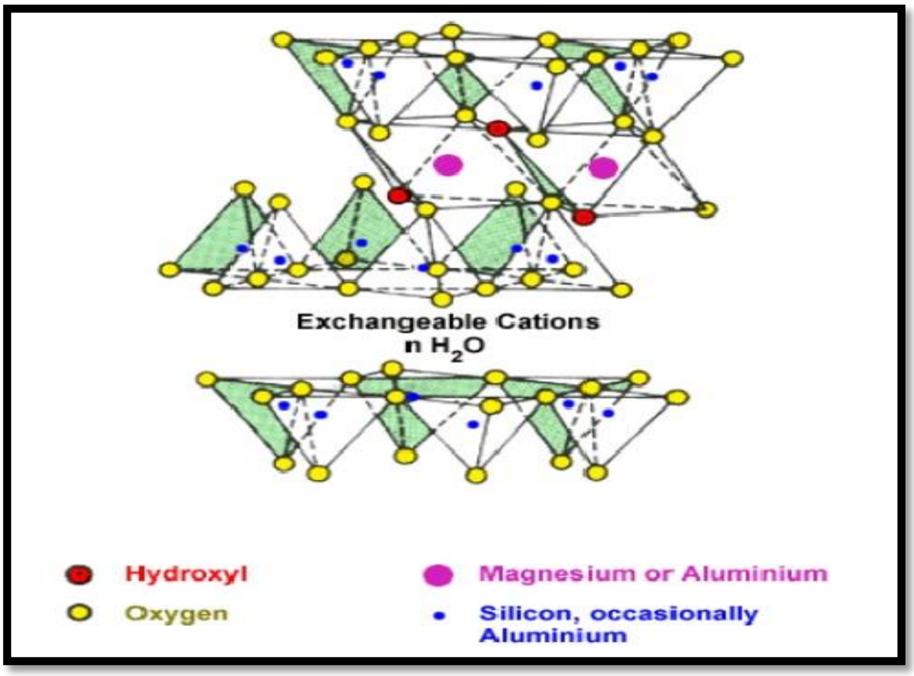


Figure (1-5) Synthesis of Montmorillonite group [20]

Bentonite also contains iron, volcanic and other compounds, which are impurities, which removed during the process of mineral processing. Montmorillonite Bentonite gives its typical properties include high absorption capacity; high ability to exchange positive ions (the ability to obtain some cations of solution) and the ability to bulge when placed with water. Some types of Bentonite are not swelling with water but have a high capacity for absorption as in Minced clay (used for bleaching), especially when activated [21]. The properties of Bentonite has made it important in many industrial applications, as it is used in various fields, including the purification of vegetable oils, industrial oils, cosmetics, pharmaceuticals and coatings [22]. In the production of ceramic materials, Bentonite used as an additive to bind granules of carbide silica and was first used as a base material in the production of a ceramic body with the effect of magnesia and alumina [23,24]. It used in alloys and in the ceramic industry because it has high plastic properties when placed in water as well as iron ore and may be exposed to high temperatures when used in these applications [25]. Used in the preparation of drilling fluids and sulfur filtering [16]. It used in the manufacture of sand molds used in metal mining. Bentonite, saturated with sodium ions, used in this process and used in the manufacture of pesticides [2]. In Iraq Bentonite discovered firstly in the Hamrin mountain ranges in the 1970s [26], Bentonite divided to;

1. High swelling Bentonite (sodium Bentonite), mineral deposits found in the United States and check republic. .
2. Slow swelling Bentonite (calcium Bentonite, potassium Bentonite or magnesium Bentonite) [21, 27].

## (1.1.5) Attapulgite - Palygorskit

It is an aluminum-magnesium silicate, containing magnesium and iron with different percent [28]. It is one of clay minerals that belong to the genus silicates derived from the Attapuligus region of Florida, USA. Its chemical formula is $[(H_2O)_4 (Mg.\ Al)_5 (OH)_2Si_8O_{20}].4H_2O$. The mineral clay series of the Attapulgite contains a small group. The composition of the mineral is composed of quadrilateral contacts on a double chain structure. The chains in this structure linked by magnesium or aluminum atoms, if six atoms of oxygen [2] surround each of these atoms. The Attapulgite mineral has a needle structure with channels that extend along the crystal installation axis and is usually a water container in the normal state of the ore. The draining of the content of these channels of water done when the raw material treated thermally as it is ready to receive new particles. This property allows the Attapulgite metal to be highly absorbable [29]. It is a natural mineral with high surface area and porous structure [30, 31].

Attapulgite consists of multiple environmental conditions ranging from salty Lakes environment and intense evaporation or marine sediments. Attapulgite used in the industry for more than forty years before they knew about mineral clay clearly. The chemical composition has some similar characteristics Montmorillonite in 1940 composition discovered by Pradley who showed that needle-like particles form later by electro-microscope [ 32 ], as shown in the following figure(1-6);

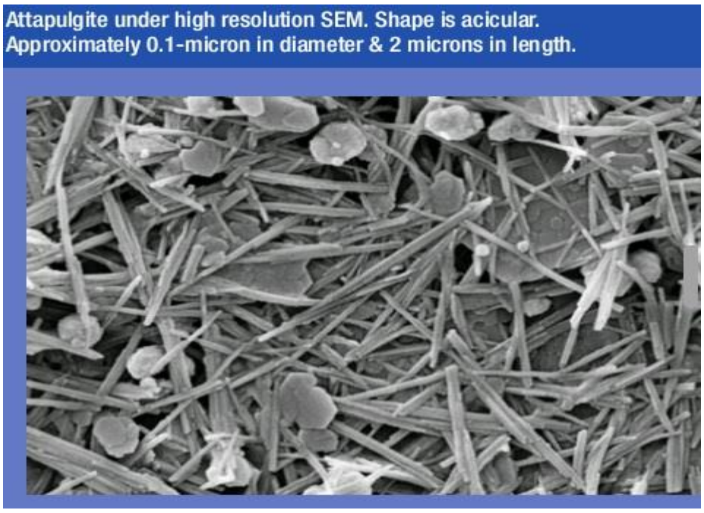


Figure (1-6) Image of the electron microscopy scanner for the Attapulgite clay.

The Attapulgite found in Iraq in the Western Desert and Najaf. they were characterized as yellow color slanted to orange. It did not dissolve in water; organic acid, inorganic acid and hydroxyl bases solutions. The tests proved the validity of the Iraqi Attapulgite in the bleaching color paraffin wax [33]. As well as used for adsorption of dyes, bacteria and alkali. It used in the manufacture of fertilizers and pesticides as used in the field of pharmacy [2].

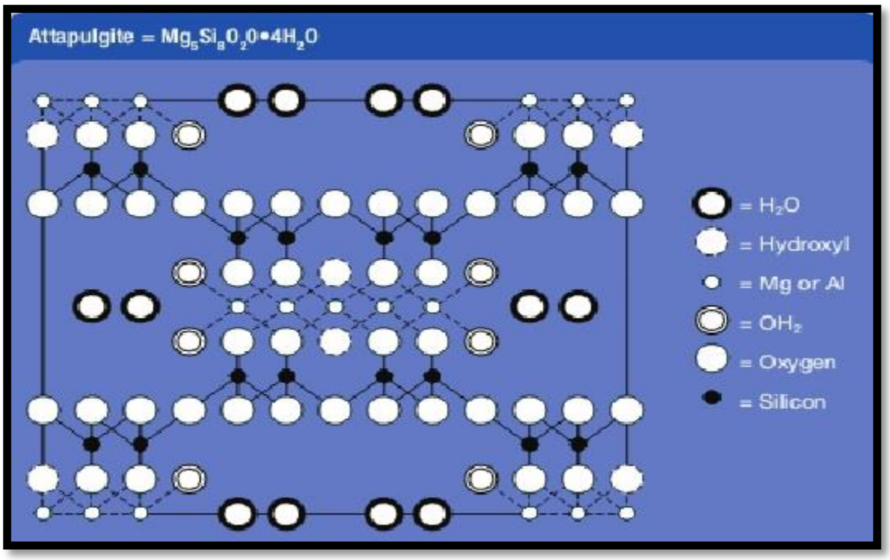


Figure (1-7) crystalline lattice in the Attapulgite

Figure (1-7) shows crystalline lattice of Attapulgite and the layers components; Hydroxyl; H2O; Mg or Al and silicon.

## (1.1.6) Interjection

In chemistry is the inclusion of the molecule or ion in the layered structures of compounds. Many of the host molecules can penetrate into the solid layers. There are many examples such as the addition of the potassium atom to the graphite (figure 1-8) is a physical process in which molecules like pigments or polymers can enter the class structure of compounds or other substances. This achieved through either adsorption or ion exchange, and can defined as the introduction of guest species within the interstellar zone while preserving the structure these layers are exposed to the resulting materials of this intercalation compound [34].

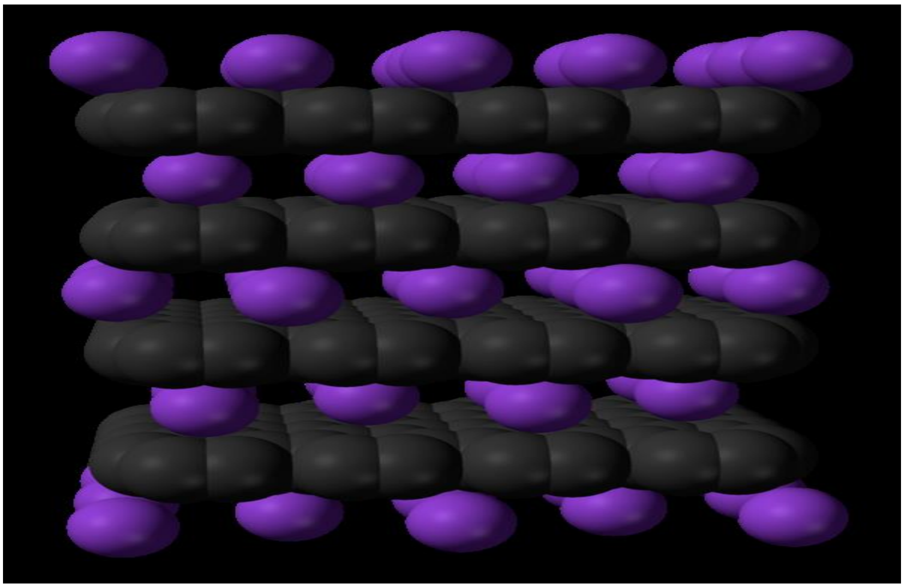


Figure (1-8) shows the absorption of potassium in the graphite

## (1.1.7) Insertion of Clays

The purpose of the process Insertion in the clay is the formation of a new type hybrid clay has new qualities that differ from the characteristics of the original clay has been used in this process organic compounds and inorganic polymers to produce this type of clay and as previously studied in the previous research [35-36]. The clay minerals of the Smectite group are featured by the presence of interchangeable ions in the space between layers [27]. Organic and inorganic molecules are not only applied to surfaces in interchangeable or exchangeable surface sites but also overlap between layers because the space between the clay layers of the type (2: 1) helps this process.

Insertion of molecules or ions into the space among the layers is through ion exchange or through the interference process, as the molecules enters either as cations or as neutral particles. The original cations remain an integral structure between the layers of the smectite [37, 40].

Polar organic molecules can remove the molecules of water among the layers of the smectite[41]. The adsorption of neutral molecules on the smectite by: hydrogen bonds, dipolar reactions, base-acid reactions, coordinate bonds, transmission of charge, forces Vanderwalls, polar molecules such as alcohol, amides, ketones, amines and phenols form complexities with sphincters.

The acid can be inserted among the layers of the smectite and these compounds as vapor, liquid or solid.

Solvent molecules are generally involved in adsorption in the space among layers. Moreover, that these compounds can enter among layers of clay and replace the water molecules in the Smectite.

Interference achieved by three methods:

1. The reaction between the Smectite (solid- phase) and the solution, which included with organic or inorganic substance called solid- liquid reaction.
2. The interaction between the secretite (solid phase) and the vapor of organic substance or inorganic and called this reaction solid-gas.
3. The interaction between the Smectite (solid phase) with organic matter or solid-state membership and this reaction is called solid -solid [42].

## (1.1.8) Ion Exchange

It is a chemical reaction in which a free ion is exchanged in aqueous solution with an element associated with a solid material that has the ability to conduct such exchange.

The first part is the solid material, which in its chemical composition contains sites that are editable to the water solution in exchange for other free ions in the solution occupy its positions in solid material.

The second part is free ions that dissolved in water and are not suspensions with the chemical ability to expel solids linked to solid matter and convert them to ions and occupy their positions. [43]

Ion exchange defined as a reverse exchange of ions between aqueous solution and a solid permeable material. The Thomson and Way ion exchange technique, which worked in soil chemistry, discovered when they extracted the soil with $NH_4Cl$ solution and found that:

1- $Ca^{+2}$; $Mg^{+2}$; $K^{+}$and $Na^{+}$ transfer from soil to solution extracted.

2- Take (retention) equivalent amount of ammonium ion $NH_4^+$ by soil.

Soil [$Na^{+}$, $K^{+}$, $Mg^{++}$, $Ca^{++}$] + $NH_4$ + → Soil [$NH_4^{+}$] + [$Na^{+}$, $K^{+}$, $Mg^{++}$, $Ca^{++}$] [44, 45] .

To ensure this exchange process, the solutions must be water capable of dissolving ions, and the solids must have properties that enable them to carry out the ion exchange process, such as containing easy-to-release atoms during the exchange process. These solid materials called ion exchangers.

Types of ion exchangers;

Ion exchange divided into the type of ions involved in the exchange process to two parts:

1. Cation exchange

It called acidic exchange, which occurs when the positive ion replaces the slushy in aqueous solution with a positive ion in a solid material. In the water, most important positive ions are calcium, magnesium, iron, manganese, sodium and hydrogen.

2. Anion exchange

The basic exchange called when a negative ion dissolved in the water solution with a negative ion in the solids. The most important negative ion dissolved in water is chloride, sulphate, nitrate, carbonate, hydroxide and fluoride [43].

## (1.1.9) clay minerals and ion exchange property

Clays are a class of minerals that characterized by the softness of their granules (less than 2 microns) and their installation of water silicate aluminum, which is the product of other metals, mainly in sediments.

The clay minerals characterized by the adsorption of certain positive and negative ions and their retention in an ion exchangeable state with other ions with a greater advantage for adsorption and then re-release into the water medium. The exchangeable ions are bonded to the surface of the ocean to construct alumina silica, the ion exchange capacity is measured in milligrams per 100 g (100 meq /gm). The main positive ions in this field are: $Ca^{2+}$, $Mg^{2+}$, $H^{+}$, $K^{+}$, $NH^{4+}$ and $Na^{+}$. The main common negative ions are; $SO_4^{2-}$, $Cl^{-}$, $PO_4^{3-}$ and $NO_3^{-}$.

The ion exchange property in the titans is due to several predetermined causes:

1. Broken bonds around the edges of alumina silica unitsIs unstable, because it needs ions (positive or negative) to reward the electric charge of the clay metal.

2. Inhalations within the crystalline clay metal cell, especially when $Al^{3+}$ replaces $Si^{4+}$ in the tetrahedral sheet, or two-valent ion, such as $Mg^{2+}$ replace trivalent aluminum in the eight layer of crystalline structure (octahedral sheet), resulting in such a total negative charge resulting in an unstable electrical charge, which requires the adsorption of positive ions to neutralize the difference in charge and reach stability.

3-Replacement within the Crystalline clay minerals cell, especially when $Al^{3+}$ replaces $Si^{4+}$ in the tetrahedral sheet, or two-valent ion, such as $Mg^{2+}$ replace the trivalent aluminum in the eight layer of the crystalline structure octahedral sheet. Such results in the presence of a negative total charge resulting in an unstable electrical charge, which requires positive ion adsorption to neutralize the charge difference and reach stability.

4. Ion exchange may be due to the hydrogen ions associated with the hydroxyl root and are exposed to exchange with other ions, when they are on the edges of the crystalline unit of the clayes.

Concentration ion exchange capacity (CEC) is varied in clay metals and montmorlonite is characterized by high capacity. There is a wide range of this capacity for each clay metal. The pH function of the ion exchange environment is an important factor in determining the ion exchange capacity of the clay as well as particle size For example, Montmorillonite is characterized by a high ion exchange capacity in each precipitant and sometimes in each layer within a single precipitator with a specific ion exchange capacity and it is not permissible to generalize in this area. Sodiumic Montmorillonite features higher capacity ion exchange of calcium Montmorillonite e due to the higher amplification of the first species [2,46].

Low ion exchange is due to the lack of swell ability of these metals. Hofmann and Endell (1939) explained that heating the clay leads to the penetration of ion exchangeable into the crystalline structure of Montmorillonite. The smaller these ions have smaller crystalline diameters, the easier it is to move into the crystalline structure, The ion exchange capacity of the calcium calcite Montmorillonite at heating compared to the sodium Montmorillonite indicates that the calcium ion is smaller than the sodium ion.

In modern studies there is a different interpretation of this phenomenon as between [Sarikaya 47].The low concentration ion exchange capacity (CEC) is due to the deformation of the crystalline layers of the Montmorillonite structure by heat resulting from the loss of different forms of water between the layers and within the crystalline construction of the metal. In the above source, heating up to 500C°results in a slight decrease in ion exchangeability. This is justified by the fact that the water displacement of Montmorillonite at this temperature is reversible progress, as the metal's ability to restore the water remains, while the higher temperatures It creates a final (gradual) expulsion of crystalline water, resulting in deformation in crystalline layers.

The importance of ion exchange in the fields is high lighted in several fields, most importantly in the agricultural field. This property provides the possibility of retaining the beneficial elements of the plant and providing it as food when re-released by ion exchange in the soil environment. In the industrial field, the importance of this feature lies in the use of coatings in the filtration and purification processes for their ability to exchange ion and absorb unwanted ions from the filtration environment at interchangeable sites. The ion exchange property can also be used to improve the specifications of some industrial ions by reacting with ions that increase their efficiency and thermal properties, such as in the activation of sodium calcite Montmorillonite [48].

## (1.1.10)Activation of Clays by Exchange method

The clay is activated to improve the smectite(Montmorillonite) by grinding (Attrition - Scrubbing) of the clay solution containing 50% of the hard clay and at high continuous speed (2500 rpm) for one hour using the flotation cell and the conversion of (Ca- montmorillonite) to the hydrogen form (H- Montmorillonite). This process is done by mixing the clay produced by the float cell after it is concentrated with the hydrolytic ion-activated exchangers (H-Form with 1 hour and speed) (150 rpm) Then the clay is separated from the mixture by a medium filtration process and wash the resulting slurry five times distilled water followed by the separation process using a centrifuge to remove the floating then the process of drying in the degree of clay. Figure (1-9) shows a- Ca- Montmorillonite b -H-form.

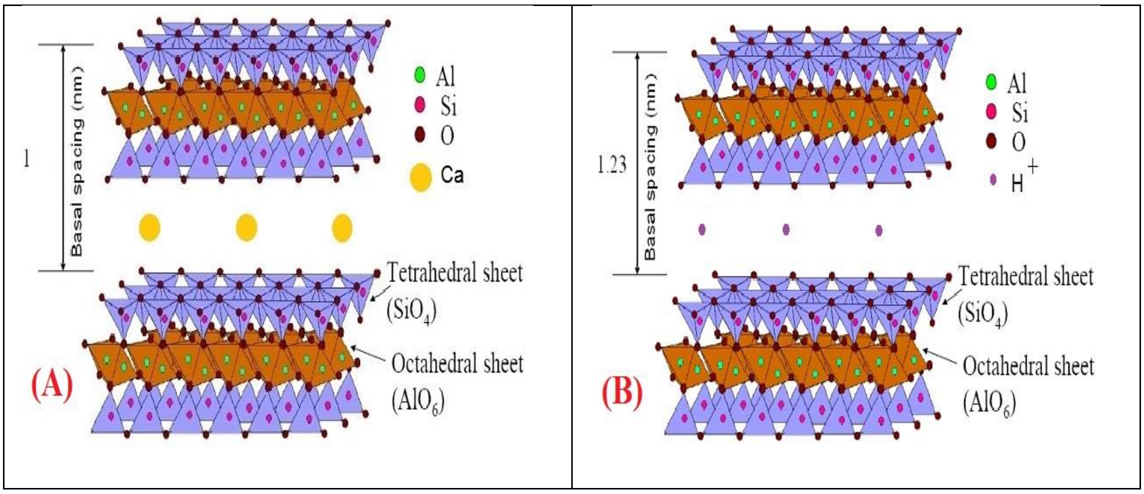


Figure (1-9) a-shows calcium Montmorillonite ;b-shows activated Montmorillonite ($110^{o}$C) for a period of three hours [49].

## (1.2) Adsorption

Adsorption is a process which collects adsorbent (liquid or gas) (adsorbate, adsorbent material (solid surface (adsorbent, these surfaces because it's unsaturated or militiamen like activated charcoal (Charcoal, Activated clays (porosity (Porous Clays), (Zeolite) And others. The particular type of correlation may occur a chemist or physicist between surface active sites adsorbet and adsorbent molecules, this process leads to the formation of atomic or molecular layer one stationed on the roof, then the phenomenon called adsorbet adsorption Mono-molecular Adsorption Unimolecular)).Desorption includes several layers composition sometimes molecular adsorption surface centered at zerihao, then the process is called multi- adsorption (Adsorption molecular particles , as in figure( 1-10) ,(1-11)[50].

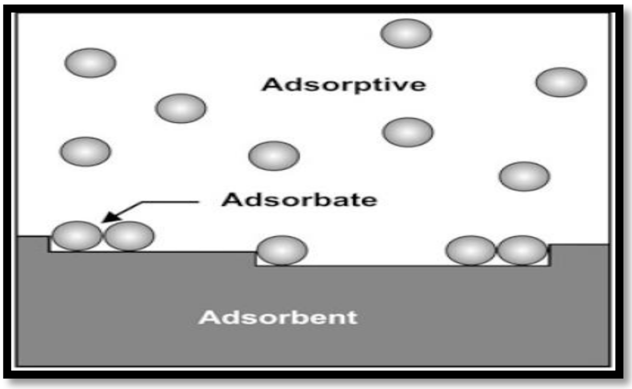


Figure (1-10) adsorption prosses

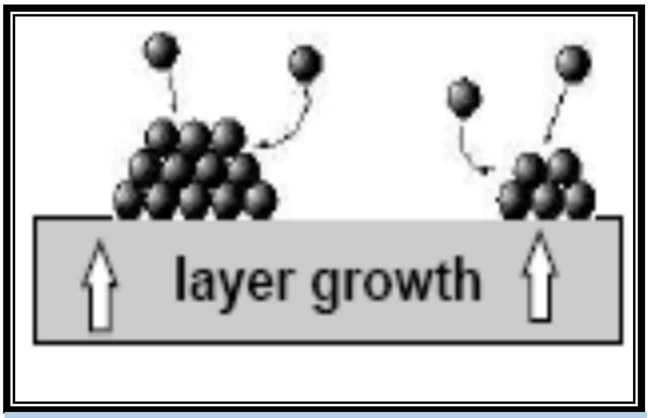


Figure (1-11) configure adsorption

Desorption process vary ((adsorption process of absorption (absorption) containing penetrate adsorbent (liquid or gas) to the surface of the solid, absorbent material and spread within them as well as their concentration on the surface as a result, an increase in the concentration of solute in the bilateral area, often occur Adsorption and absorption processes on the same surface, then called the process of absorption (Sorption), where is the change in enthalpy is positive because the process absorbs energy during propagation within the developed surface absorbent either reverse the process of adsorption is a process of blackmail or departure or areas sometimes (Desorption Aggregate, ears on a hard surface after interaction leave, returning to the stage by adsorption, influenced by the process of black mail in aqueous solution by several factors including the nature of adsorbents, adsorbent surface, temperature, and pH of the solution, and the nature of the solvent if using a better solvent or adsorbent materials, the process of black mail can be fast and complete [51, 56, 57, 58, 59].

## (1.2.1) Type of Adsorption

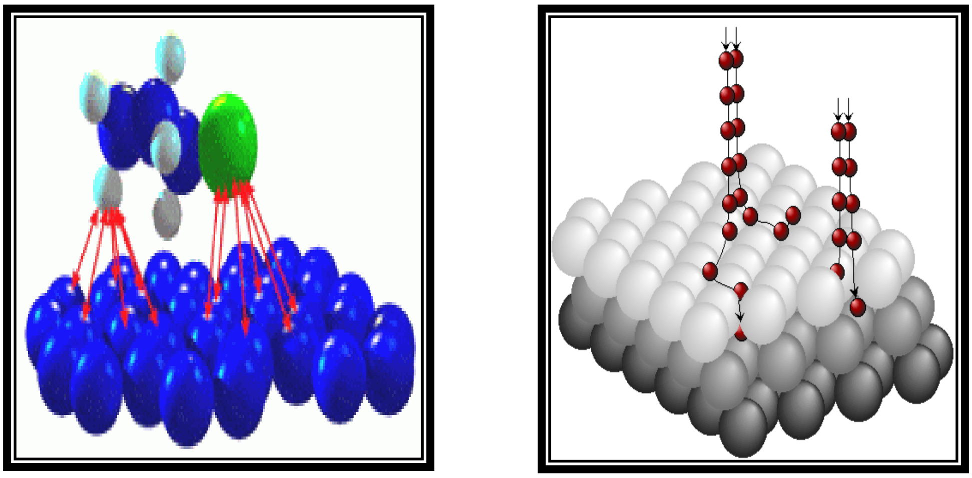
Adsorption can be classified into two types of Raesinovka interactions and link type and strength between adsorbed molecules and surface physical adsorption, desorption chemical adsorbent, as in figure (1-12):

### **(1.2.1.1)** Physical Adsorption

Adsorption physical Colloquially called the ion (Phys sorption), forces that cause physical adsorption is strong physical attraction, strong type are themselves that cause condensation of gases to form a fluid, usually referred to as van der Waals forces (Vander Waal Forces), relatively weak [60]. Physical adsorption usually can be reversed easily in low temperatures, which he quickly balance and this balance process effect with temperature degrees. Generally high temperature to decrease the amount of adsorbent, moreover, type of adsorption bye privacy (Non-Specific), because the atom or molecule that suffer physically and chemically linked adsorption of surface atoms adsorbent, but running a specific area of Surface, according to the number of atoms or molecules adsorbed .

### (1.2.1.2) Chemical Adsorption

Colloquially called the (chemisorption) , in addition to the bonds formed between atoms on the surface the latent powers; adsorbed in chemical adsorption due to partial or total transfer of electrons between molecules adsorption and surface adsorption the surface electronically polyunsaturated, and as a result the bonding between Have substantially lower non-process is invertible, which no State of balance, high temperature leads to an increased amount of adsorbent. Chemical adsorption process characterized by Specific specificity)), may be fast or slow, adsorption temperature is greater than 80kj.mol-1 (61, 60, 62) is much greater than the physical adsorption, this site type, any particle that does not have the ability to move from place adsorbed chemical adsorption. Normally on the surface monolayer diamond and access additional adsorption theory made up another layer above the first layer but kind of difficult and special circumstances.



**(a)** **(b)**

Figure (1-12) adsorption occurs on the surface a- chemical b- physical

The temperature has a big role in adsorption, physical adsorption may occurs at Low temperature and turns into a chemical adsorption when raising temperatures (63) as in hydrogen adsorption on the nickel in surface (Figure 1-13).

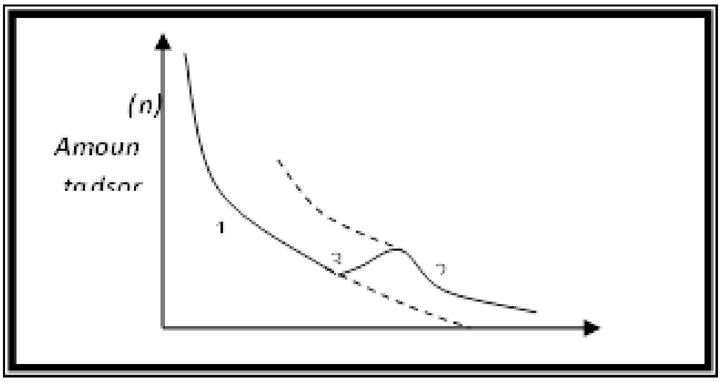


Figure (1-13) transmission of physical adsorption to the chemist with increasing temperature**.**

As: curve (1): decrease of physical adsorption with temperature. The curve (2): chemical adsorption. Curve (3): illustrates transformation from physical adsorption area to the chemist.

### (1.2.1.3)Adsorption from solution

Characteristic of adsorption of aqueous solutions is that the solution contains more than one article (at least two thawed and solvent) compete for the effective surface sites, adsorbent competing surface adsorbent and solvent and solute and solvent to bind particles. The components of the solution displaces each other when concentrations were changed (64), and may accompany eddies adsorption on the surface of the adsorbent adsorption solvent itself and that the various distractions abound about the usual format isotherm. Can imagine non-material electrolytic adsorption on the surface interval between lotion and solid matter from two perspectives:

The first perspective: the adsorption on single molecular layer, and be in contact with the surface of the solid material, either post this layer layers are present within the solution and weak link adsorbed layer. This figure is largely similar to the chemical adsorption of gases on solids. In addition, relies on already declining between solute and solid (adsorbent) increases with the number of minutes the solute on the surface of a solid material, and the heat of adsorption in aqueous solution and the solution temperature value approach and this other than adsorption.

The first perspective: the adsorption on single molecular layer, and be in contact with the surface of the solid material, either post this layer layers are present within the solution and weak link adsorbed layer. This figure is largely similar to the chemical adsorption of gases on solids. And relies on already declining between solute and solid (adsorbent) increases with the number of minutes the solute on the surface of a solid material, and the heat of adsorption in aqueous solution and the solution temperature value approach and this other than adsorption.

The second perspective: based on the adsorption layer thickness of several molecules, and that mutual respect between solute and less solid surface to bypass such fish, and the decrease is gradual, and that the shape similar to the physical adsorption of vapors on surfaces of solids, adsorption becomes multi-molecules Upon reaching the saturated steam pressure. In addition, according to this perception is adsorption solute distribution between the size of the solution and phase interface and is influenced by temperature and concentration, and that the amount of adsorption generally diminishes with increasing temperature and increases with increasing concentration (53).

## (1.2.3)Factors Influencing the Adsorption Process

### (1.2.3.1)Nature of Adsorbate

Adsorption process depends on the nature of the material and physical properties and adsorbent chemicals, of these properties: molecular weight adsorbent adsorption increases with increasing frequently. As well as having effective aggregates and adsorption polarized effect in the process of adsorption, thus polar adsorption surface adsorption larger part in solution for example ringed vehicles adsorption mechanistic aspects have been more likely than adsorption the compounds. And the size of the molecule sorbet, that control the ability of the particles to be adsorbed on the surface, for example in certain circumstances be lead ion adsorption of cadmium ion adsorption weakness because of the large size of the ion (64), besides, adsorption process is affected by the concentration of adsorbent as adsorption capacity increases Upward [65].

## (1.2.3.2)Nature of Adsorbent

Adsorption depends on the characteristics of the surface chemical nature as adsorbent surface, surface area, and volume of particles adsorbent distributed on the surface [66]. The chemical composition in terms of functional aggregates, hard surface adsorption increases with a lower volume of particles and increase the surface area, which is available More active sites, and thus be greater adsorption capacity [67].Porous on surface with volume characterized from quantity and selectivity of progress [56] Adsorption depends on the characteristics of the surface chemical nature as adsorbent surface, surface area, and volume of minutes mezza, and distributed on the surface [66], and the chemical composition in terms of functional aggregates, hard surface adsorption increases with a lower volume of minutes and increase the surface area, which is available more active sites, and thus be greater adsorption capacity [67].

### (1.2.3.3) Initial Concentration of the Adsorbate

The amount of adsorbent of solution to increase its focus on balance, and that the shape that represents the relationship between capacitance acid adsorbent and adsorption isotherm called equilibrium concentration [64].

### (1.2.3.4)Temperature Effect

In accordance with the principle of le chatelier (Le Chatelier's principle), the high temperatures of adsorption exothermal processes (Exothermic), reduces the adsorption of solute (unless accompanied by absorption process or spread within the pore hard surface adsorbent). Working temperature increase the kinetic energy of molecules Facilitates separation of adsorbed surface adsorbent and return within the solution, heat-absorbent desorption processes (Endothermic), high temperature increase solute adsorption, increased temperature adsorbed molecules to penetrate the larger proportion of solid phase, thus increasing velocity It followed an increase in adsorption [68] .

### (1.2.3.5) PH effect

To change the pH of the solution (effective hydrogen ion) to great effect in the phenomenon of adsorption from aqueous solution by its effect on the chemical status of surface adsorbent, and adsorbent and solvent, and this effect can be observed by its rival hydrogen ions and hydroxyl ions and their correlation with Surface adsorbent or adsorbent or solvent. As a result, the effect of changing the pH increases or reduces the adsorption capacity [69]. Ratio between the quantity of adsorbent in units of (mg) weight article adsorbent Unity (g)) of adsorbents due to change in load surface with change of pH value of the solution, and the impact of changing acidity function Will change the behavior of isotherms adsorption. [70]

## (1.3) Gasoline

Gasoline is well define as a blend consist of more than four hundred volatile and flammable liquid hydrocarbons has from 4 to 12 carbon atoms per molecule. The gasoline burns when convert to vapors. The flash point of Gasoline is (- 7 °C) and its ignition temperature auto is (307 °C) [71]. It is a blend of paraffin, naphtha, olefins, and aromatic hydrocarbons. Gasoline also, has small amounts of sulfur In addition to hydrocarbons, atmospheric oxygen, and nitrogen traces. This petroleum fraction distils within the temperature range of (30– 220 °C) .Gasoline is produced by mixing various fuel streams coming from different production methods.

The hugest and most broadly used basis of energy in the world is Crude oil. Main portions of the crude oils are used as vehicle fuels such as gasoline, diesel and jet fuel. However, such crudes have sulfur, naturally in the formula of organic sulfur compounds. The properties ,which have a great effect on the value of the crude oil are two, sulfur content and the API gravity. The sulfur content is expressed as a percentage of sulfur by weight and differs from less than 0.1% to greater than 5% dependent on the kind and source of crude oils. Sulfur compounds exist in numerous forms and can be ordered into four main groups: mercaptans, sulfides, disulfides and thiophenes. It is famous that the sulfur compounds are not desired in refining process since they tend to deactivate some catalysts used in crude oil treating. Sulfur compounds reason of several decay problems in pipeline, pumping, and refining apparatus, as well as the premature breakdown of combustion machines and polluting of the catalytic converters, which are used in automotive engines. Today, the strongest motivation for the reduction of sulfur in fuels is due to environmental regulation, which is imposing stringent limits for sulfur levels in transference fuels. Sulfur is the responsible of the production of sulfur oxides ($SO_x$) caused by the combustion of fuels that is used in moving. Large sulfur content is also responsible for the producing of particulate from vehicles. With such great sulfur amount, it also prevents the use of advanced after treatment systems, which cannot work.

## (1.3.1) Physical and chemical properties

Information regarding the physical and chemical properties for the gasoline mixture is located in Physical properties of gasoline; surface tension; the force of attraction between the surface molecules of a liquid surface tension together with viscosity affects the rate of spread over water or ground. The lower the surface tension, the greater capacity-spreading rate. Low surface tensions characteristic of low specific gravity oils as temperature increases; surface tension decreases. Physical properties of oil such as Viscosity (the viscosity of oil is a measure of the oil's resistance to shear), Viscosity is more commonly known as resistance to flow. High viscosity implies a high resistance to flow while a low viscosity indicates a low resistance to flow. Changes temperature, decreasing temperature increases viscosity. Viscosity is determined by the amount of light. Viscosity effects on oil spill clean ups Influences. Oil, which has a low surface tension; low specific gravity and low viscosity, has been spilled implications. Same concerns on High API crude oil. Low Point temperature, which the oil becomes "plastic" and will not flow. Overrides the effects of viscosity and surface tension light oils with low viscosities have lower points. Heavy oils may become solid on cold water, and may become fluid while in the sunny places, penetrating into the shoreline. Flash Point Temperature at which an oils vapors will ignite must know for safety lighter, volatile oils, once spilled, will gradually lose their lighter components to evaporation and dispersion. Solubility of oil in water

generally is very low ~ 5 ppm. Solubility can have important consequences for the potential toxicity of hydrocarbons to aquatic organisms Physical and Chemical properties affect, the physical and biological effects of an oil spill. The behavior of the oil slick. The efficiency of various clean up methods. The physical and chemical properties of the oil largely determine the thickness and spreading rate of the slick, the formation of emulsions .Physical and Chemical Properties affect Spreading of the oil slick Subsequent breakup of the oil slick . Rates
; Extent of emulsification; evaporation and biodegradation.

## (1.3.2)Specifications & Standards

The basic understanding of gasoline is important to realize fuel quality standards and how they effect on the vehicle, how and why quality standards are set, and what importance they have on the ability of driving , presentation and strength of a vehicle engine and associated systems. Gasoline is not a single substance. It is a complicated blend of components which different broadly in their physical and chemical properties. The pure gasoline has no such thing. Gasoline should cover a varied range of effective situations, for example difference in fuel systems, engine temperatures; fuel pumps and fuel pressure. It must also cover a variety of environments; altitudes and driving designs. The gasoline properties must be equalized to give desired presentation for engine over a very wide variety of circumstances. In some relations, the main quality standards represent compromises, so that all the numerous performance requests and environmental principles may be satisfied. Atmospheric straight run cuts together with products from catalytic reforming and cracking isomerization, etc. The most commonly are units used feeds to produce the gasoline finally. Gasoline segments are these fractions were referred to the mixture procedures are determined such that the properties requirements of the final gasoline are met .Gasoline is blended mainly to achieve physical specifications for boiling range; vapor pressure; oxidation stability and octane with the aim being desired engine presentation, namely cold/hot starts; acceleration, knock and resistance to vapor lock, etc. A number of analytical techniques are available to detect gasoline pollution as flash point, refractive index and density but in this thesis, we are interested in fractional distillation.

## (1.4) Kerosene

### (1.4.1)Composition

It is oil-derived, flammable and odorless hydrocarbon. Kerosene is used as fuel in aircraft jet engines and some of the less purified types used in baking ovens and used as fuel for heating. Kerosene obtained by partial distillation of oil at (250 ° C). Kerosene used as fuel for several purposes such as: Heating and lighting

- Where it much in lanterns and kerosene lamps instead of whale oil. In 1880, fake kerosene lamps were the source of 39% of fires in New York City. The uses of the kerosene lamp subsequently replaced by an electric lamp and battery-operated flashlight.
- It used as fuel for heating when power failures caused by kerosene heaters that are not recommended for indoor use because of the risk of carbon monoxide. Transportation the kerosene used as fuel for jet engines, kerosene added to diesel to prevent it from switching to wax at low temperatures. It used to treat stagnant water ponds to prevent mosquitoes from hatching. It used to remove lice from hair, but this practice is painful and very serious. This destroys natural fat in the hair and scalp. It also used as fuel for aircraft.

### (1.4.2)Properties

Kerosene is a low viscosity, clear liquid consist of hydrocarbons obtained as products of the fractional distillation of petroleum between ($150^{o}$C and (275 °C) (300 and 525 °F), resulting in a mixture with a density of (0.78–0.81 g/cm3) composed of carbon chains that typically contain between 10 and 16 carbon atoms per molecule. It is miscible in petroleum solvents but immiscible in water.

The standard specification D-3699-78 recognizes two grades of kerosene: grades 1-K (less than 0.04% sulfur by weight) and 2-K (0.3% sulfur by weight). 1-K grade kerosene burns cleaner with fewer deposits, fewer toxins, and less frequent maintenance than 2-K grade kerosene, and is the preferred grade of kerosene for indoor kerosene heaters and stoves.[71]

Regardless of crude oil source or processing history, kerosene's major components are branched and straight chain alkanes and naphthenes (cycloalkanes), which normally account for at least 70% by volume. Aromatic hydrocarbons in this boiling range, such as alkyl benzenes (single ring) and alkyl naphthalenes (double ring), do not normally exceed 25% by volume of kerosene streams. Olefins are usually not present at more than 5% by volume. [72]

The kerosene flash point is between 37 and 65 °C (100 and 150 °F), and its auto ignition temperature is 220 °C (428 °F) [73] .The pour point of kerosene depends on grade, with commercial aviation fuel standardized at (−47 °C ,−53 °F).
١-K grade kerosene freezes around( −40 °C) (−40 °F, 233 K) [74] .
Heat of combustion of kerosene is similar to that of diesel fuel; its lower heating value is (43.1 MJ/kg) (around 18,500 Btu/lb.), and its higher heating value is 46.2 MJ/kg (19,900 Btu/lb.) [75].

## (1.5)Desulfurization

Desulfurization is the removal of sulfur to prevent contamination. Desulfurization has variants, including:

- Hydrodesulphurization
- Desulfurization extractive
- Desulfurization oxidation
- Bio desulfurization
- Desulfurization occurs by alkylation, chlorinolysis and by using adsorption surfaces ,such as activated clays particles

For a number of years there has been an ever-growing body of governmental regulations to address concerns about the environment and energy security. Many of these regulations have been aimed at reducing the environmental effect of the vehicle. Most systems initially focused on the automobile and have resulted in automotive technology, which significantly decreases vehicle releases compared to pre-control stages. This kind of progress already achieved via automotive technology, it was apparent that if further gains were to be made, it would be essential to focus on cleaning up the fuels that these vehicles use. Many attempts to change Compositional of gasoline were carried out. Refiners have over the years, altered the structure of gasoline in response to technical progresses and variations in demand for finale use yields. But, recent structural variations have been, and will continue to be, driven by environmental considerations. The sulfur content is expressed as a percentage of sulfur by weight and differs from less than 0.1% to greater than 5% dependent on the kind and source of crude oils. Sulfur compounds exist in numerous forms and can be ordered into four chief groups: mercaptans, sulfides, disulfides and thiophenes.

The sulfur compounds are not desired in refining process due to they tend to deactivate some catalysts used in crude oil treating. Sulfur compounds caused several decay problems in pipeline; pumping and refining apparatus, as well as the premature breakdown of combustion machines and polluting of the catalytic converters, which used in automotive engines. Great content of sulfur, it prevents the use of advanced after treatment systems, which cannot work. Removing organic sulfur from hydrocarbon fuels is becoming an increasingly challenging task for refineries. This is due to the stringent environmental regulations, which are placing considerable pressure on refinery operators to reduce sulfur below 10 ppm by the year 2010. The current specification in Europe and the USA calls for a maximum sulfur content of 50 ppm in gasoline and diesel by 2005. Sulfur compounds are present in crude oil in a wide range of both aliphatic and aromatic forms and mainly concentrated in the heavy part of the crude oil. To meet the demand for gasoline, catalytic cracking processes are employed industrially to convert these long chains hydrocarbons to shorter chains to products of high quantities of gasoline. During these processes, conventional hydro desulphurization (HDS) catalytic processes remove major sulfur compounds.

## (1.6)-Aim of studying

The presence of Sulphur in fuel such as gasoline caused economic problems and larger financial losses especially in Iraq, because it leads to big problems in engines working by gasoline. For all these reasons, looking for studies to improve properties of Iraqi fuel to save high costs by using local replacement to reduce importation of gasoline.one of replacement is Attapulgite by purification and beneficiation to prepare pure activated calcined Attapulgite for this purpose.

# CHAPTER

# TWO

# EXPERMENTAL

# 2. Experimental

## 2.1. Chemical Compounds:

The materials used in this study are shown in the following table (2-1) as well as the sources and percentage of purity.

Table (2-1) names, formula and sources of chemicals used and the degree of purity

| **No** | **Chemicals** | **Supplied from** |
|---|---|---|
| **1** | Hydrochloric acid (37%) | BDH |
| **2** | Sodium Methyl acrylate 65% Analar | Fluka |
| **3** | Ion-exchanger Amberlight orange | China |

## 2.2. Instruments

1. Thermostatic Shaker Bath. GFL (D – 3006), Fed – Rep. of Germany. Performed at chemistry dep./College of Education for Pure Science / Ibn Al-Haitham / University of Baghdad.
2. Fourier transforms infrared spectrophotometer type. SHIMADZU (8400)was used in this study. Samples were prepared as KBr disc and the spectra were recorded in a range of (400-4000) $cm^{-1}$ performed at College of Education for Pure Science / Ibn Al-Haitham / University of Baghdad (The Central Service Laboratory)
3. Centrifuge . JANETZI – T5, Germany, 3000 rpm. Performed at chemistry dep. lab /College of Education for Pure Science / Ibn Al-Haitham / University of Baghdad.)
4. X-ray diffraction. Shimadzu X-ray Diffraction meter 04 – XRD-6000. performed at College of Education for Pure Science / Ibn Al-Haitham / University of Baghdad (The Central Service Laborator)
5. Scanning Electron Microscope. (SEM Micrographs VEGA3 – TESCAN)(Ministry of Science and Technology Laboratories)

6. Oven (Equipment LTD, Green Field. NR OLDJAM, (20–360 $C^0$) Performed at chemistry dep. Lab /College of Education for Pure Science / Ibn Al-Haitham / University of Baghdad.)
7. X-ray fluorescence. (Oxford-ASTM-D-4294, LAB.X3000)(Ministry of Oil /Al-Dora refinery Lab.).
8. Furnace . Performed at chemistry dep. Lab /College of Education for Pure Science / Ibn Al-Haitham / University of Baghdad.).

## 2.3. Clays

### Attapulgite clay

Attapulgite clay was obtained from the State company for geological survey and mining in Baghdad in below some information about it. There is an Attapulgite in Iraq (in Al-Anbar governorate, Okashat location area, Najaf sea area) also features color gray italics to green and that clay do not melt in the water. The following table shows the chemical analysis of the proportions of ingredients for Attapulgite clay.

Table (2-2) the percentages of the components of attapulgite

| **Compound** | **$SiO_2$** | **$Al_2O_3$** | **$Fe_2O_3$** | **CaO** | **MgO** | **$SO_3$** | **L.O.I %** | **Total** |
|---|---|---|---|---|---|---|---|---|
| Wt. % | 49.0 | 12.6 | 6.2 | 6.2 | 6.0 | 1.5 | 11.6 | 93.1 |

## 2.4. Used solutions

### 2.4.1. Preparation of solutions

1- Preparation of hydrochloric acid 20% by solving 20 ml of HCl (12 N) in 100ml of distilled water.
2- Preparation dewaxes 50 by solving 100 g of dewax crystals in 1 liter of distilled water.

### 2.4.2. Preparation of Clay Powder

Creating clay powder is prepared by washing with sufficient amount of distilled water for a number of times. Remove soluble foreign substances; sands and materials in water. Clay is separated from impurities by weight difference principle as separating layer floating clay and leaves the impurities thereby ensures obtain the highest metal Montmorillonite up to 90% , then got drying clay in an oven at (110 °C) for five hours and frying dried clay by furnace at ( 850-900$^o$ C) and get fresh activated Attapulgite.

Grinding the calcination clay for the purpose of getting mini particles then sieve them by mesh to select suitable Size. (75 µm) and (250 µm) sieve mesh (2004- Test Sieves (Retsch Gmb, Co.KG, Germany) were selected in all processes concerning in this work.

### 2.5. Activation of Attapulgite Clays

### 2.5.1. Prepare pure Attapulgite clay:

1- Crush Attapulgiti clay crude into small pieces then washed numbers of times by deionized water to remove the sands, impurities which sticking with it , then washed with deionized water.

2- Collection the floatation clay then dehydrated it by oven at 100$^o$ C.

3- Treatment Attapulgite clay (other types of clays may companied Attapukgite) with dewax 50 exchanger (Amber light Orange) and diluted HCl acid for activating conver clay to the H-Form.

4- Add sodium polymethyl acrylate to floating pure Attapulgite only using flotation cell.

5- Filtering of attapulgite and dehydrated it by oven at 100 °C.

6- Frying dried clay by furnace at (850-900 $^o$C) to obtain activated pure Attapulgite.

7- Crush the activated pure clay by ceramic mortar and put it through a sieve by 250µm and 75 µm -size sieves, and the resulting Attapulgite is ready for use desulphurization of fuel (gasoline and kerosene).

### 2.2.2. Column Method

1. Fill the glass columns with Attapulgite clay( each column has 1 g ).

2. Add 20 ml of gasoline into the first column then let the gasoline pass through the column as drops for 1 hour.

3. For 2hours for the second column, let the gasoline pass through as drops.
4. Add 20 ml of gasoline into the third one for 3 hour, and let the gasoline pass as drops two.
**5.** Rebate the steps (2, 3, 4) using Kerosene instead of gasoline**.**

### 2.2.3. Batch Method

1. Mix 20 ml of gasoline with 1 g of Attapulgite powder using three conical flask at 25 °C ; first for one hour ,second for two hours, third for three hours ..
2. Mix 10ml of gasoline (4 samples )first with 1g of Attapulgite ,second with 1.1g of Attapulgite, third with1.2g of Attapulgite ,forth with 1.3g of Attapulgite (constant volumes of gasoline with different amount of Attapulgite )
3. Mix 5ml, 10ml, 15ml and 20 ml of gasoline (4 samples) with 1g of Attapulgite for each volume at 25 °C by using shaker (different volumes of gasoline with constant amount of Attapulgite).
4. Rebate the steps (1, 2, 3) using Kerosene instead of gasoline.

# CHAPTER three

# Results and discution

# 3. RESULTS AND DISCUTION

This chapter includes a discussion of all results obtained from the implementation of this study, the use of of fuel ( gasoline). studying of purification by using Attapulgitee to desulfurize the fuel by a pure activated clay for this purpose .

Some different analysis methods were done on the clays and fuel to explain adsorption such as X-rays diffraction , FTIR( Fourier transform Infrared spectroscopy),SEM (scanning electronic microscope), EDX(Energy Depressive Detection X-ray), X-ray fluoresces .

## (3.1)FT-IR spectroscopy analysis

### (3.1.1)FT-IR spectroscopy analysis of crude attapulgite

IR spectrum shows clay attapulgite crude in figure (3-1) having vertices shown in the table (3-1)[ 87,124,125,126 ].

The peaks (3743 cm$^{-1}$), (3641 cm$^{-1}$) refer to O-H bonded with H (stretching); (3618 cm$^{-1}$ ) refer to O-H bonded with metal (stretching) (metal: Al, Fe, & Mg) ; (1647 cm$^{-1}$) refer to H2O coordinated and absorbed water (bending ) ; (1531 cm$^{-1}$ ) refer to Al2O3 ( stretching ) ; (1100 cm$^{-1}$) refer to Si-O-Si ( bending) ,(974 cm$^{-1}$ ) refer to (O-SiO3) ( stretching ) (,(910 cm$^{-1}$ ) refer to (M-OH; M; metal (bending ) ,( 860 ,820 cm$^{-1}$ ) refer to Si-OH.(702cm$^{-1}$) refer to metal with O as oxide.as showen in figure (3-1) **[**102] .

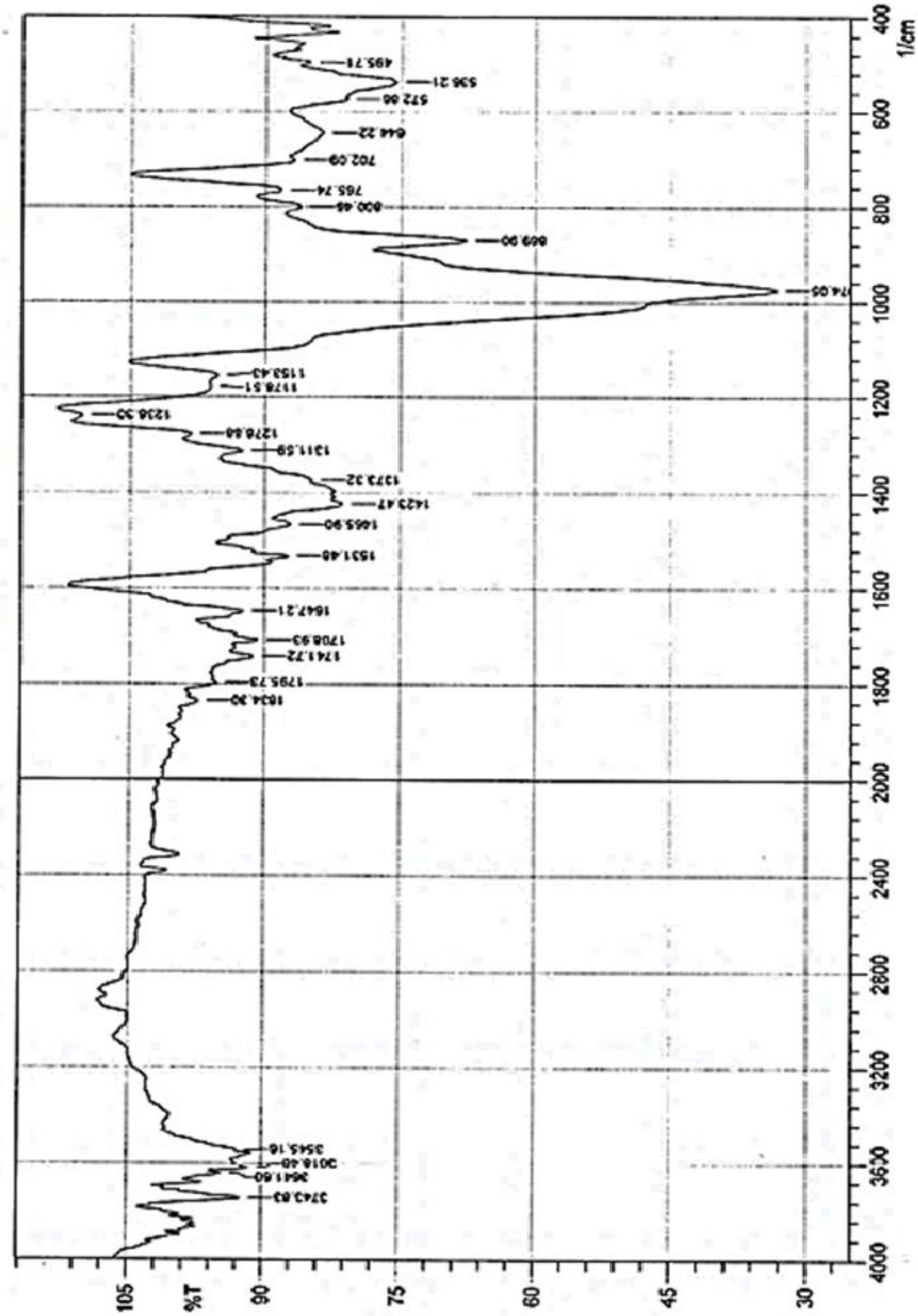


Figure (3-1) FT-IR spectrum of crude attapulgite

Table (3-1) peaks of FT-IR spectrum of Attapulgite crude

| **Group** | **Mode of Vibration** | **vcm-1** |
|---|---|---|
| -OH | Stretching | 3743 |
| -OH | Stretching | 3618 |
| -OH | Stretching | 3641 |
| H-O-H | $H_2O$ coordinated | ٣٥٤٥ |
| -OH | $H_2O$ coordinated adsorbed water (bending) | 1647 |
| $Al_2O_3$ | Stretching | 1531 |
| Si-O-Si (Al) | Bending | 1100 |
| Si-O-Si (Al) | Bending | 974 |
| M-OH | Stretching | 910 |
| Si-OH | Bending | 860,820 |
| M-O | Stretching | 702 |

## **(3.1.2)** FT-IR spectroscopy analysis of activated Attapulgitte

The peaks (3747, 3641, 3618, 1531, 1100, 974, 910, 860 & 820 cm$^{-1}$) bands appears again due to presence them in structure of mineral, but more strong and sharp because the purification removed the impurities and sands from minerals. Due to increase of space among layers and replaced cations by H+ ions, make the account of water increases because of swelling; (3300cm$^{-1}$) refer to O-H (H2O) normal polymeric (stretching) as evidence of entrance the water. Mg-O appears because of montrmonolite prefund with Attapulite M-O at (719cm$^{-1}$) like Al$^{+3}$, Fe$^{+3}$&Mg$^{+2}$.as shown in figure (3-2).

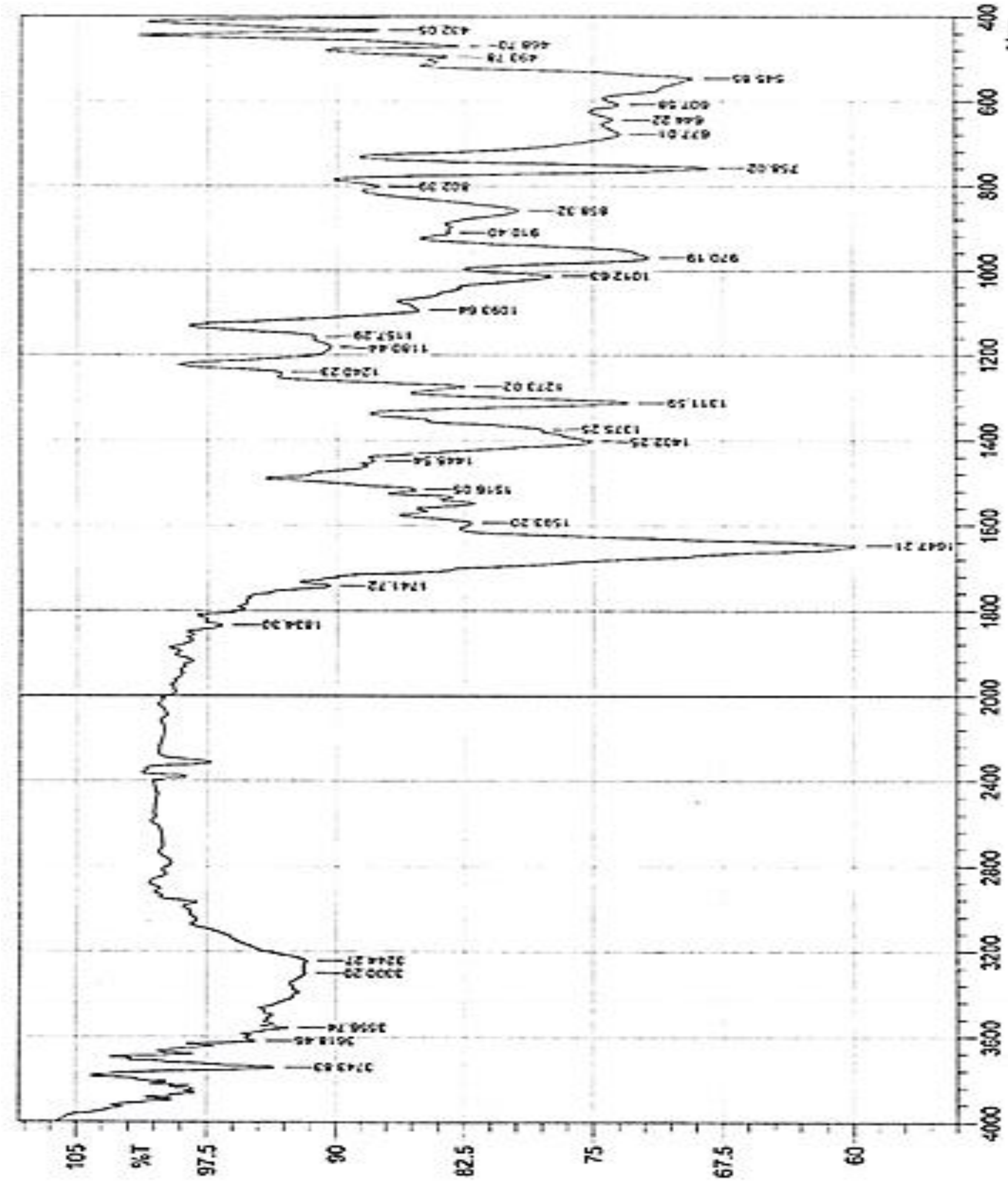


Figure (3-2) FT-IR spectrum for activated Attapulgite

Table (3-2) FT-IR spectrum peaks activated Attapulgite

| Group | Mode of Vibration | νcm-1 |
|---|---|---|
| -OH | Stretching (str.) | 3743 |
| -OH | Stretching (str.) | 3618 |
| -OH | Stretching(str.) | 3641 |
| H-O-H | $H_2O$ coordinated(m) | ٣٥٤٥ |
| O-H | Normal polymeric(stretching)(str.) | ٣٣٠٠ |
| -OH | $H_2O$ coordinated water(bending)( str.) | 1647 |
| $Al_2O_3$ | Stretching(m) | 1531 |
| Si-O-Si(Al) | Bending (m) | 1100 |
| Si-O-Si(Al) | Bending(str.) | 974 |
| M-OH | Stretching(w,) | 910 |
| Si-OH | Bending (m) | 860,820 |
| M-O | Stretching (w) | 702 |

## (3.1.3 ) FT-IR spectroscopy analysis of a pure activated Ataapulgite

Due to addition of sodium methyl acrylate, the most of Montmorillonite mineral removed, and their peaks disappeared. Some peaks become strong because the structural composition of mineral did not change. (923cm$^{-1}$)due to SiH$_3$,( 806,820,873cm$^{-1}$ )for Si-O.( 3545 cm$^{-1}$)due to Coordinated water ( stretching) O-H(H2O); (3219cm$^{-1}$)for H-O-H;

bonded( stretching),( 1662,1650,1629cm$^{-1}$)for Coordinated and absorbed water H -O-H.( 1541cm$^{-1}$)due toAl2O3 bending. (1068cm$^{-1}$) for Mg-O bending.(719cm$^{-1}$) due to M-O bending**.**

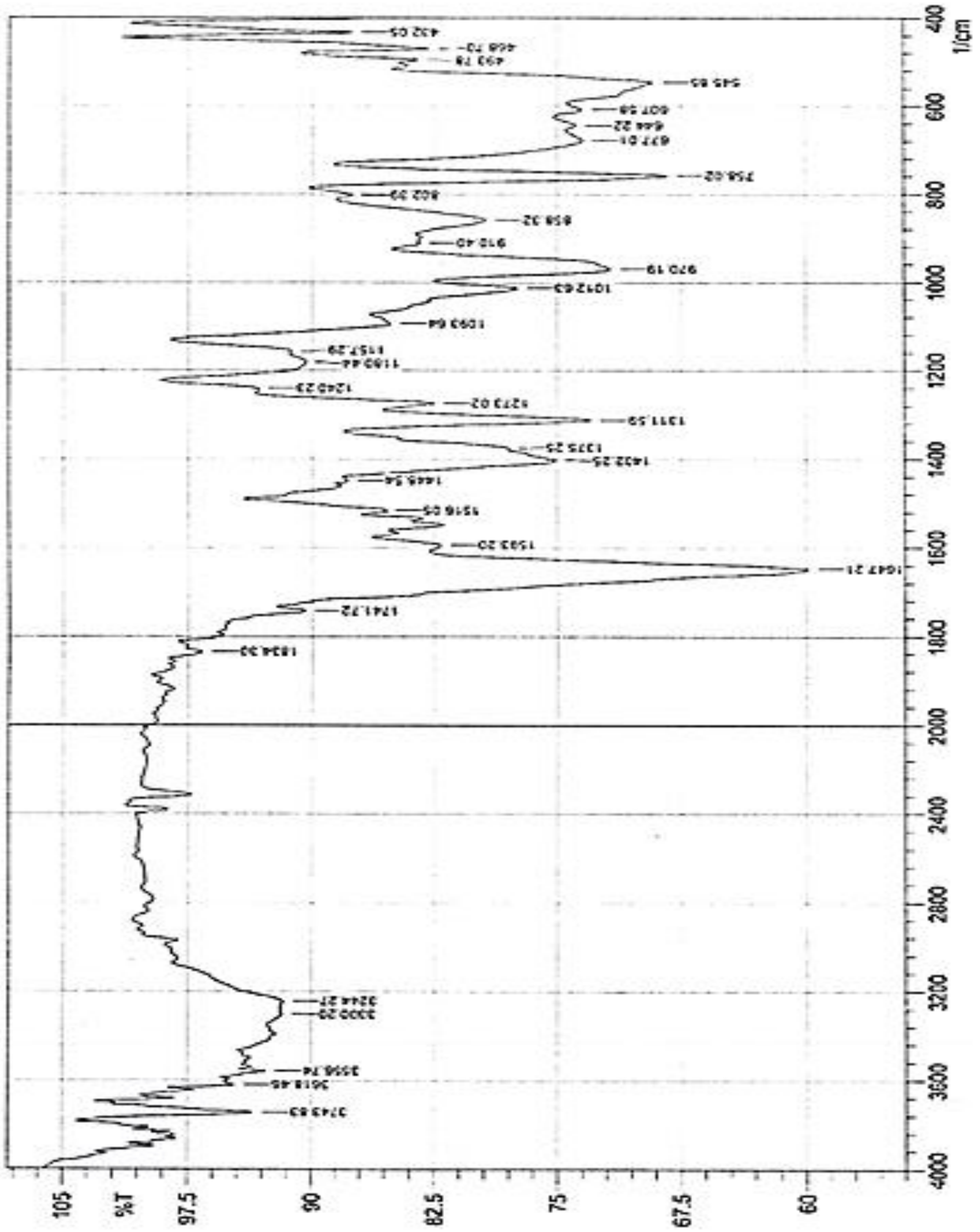


Figure (3-3) FT-IR spectrum of pure activated Attapulgite

Table (3-3) infrared spectrum peaks pure activated Attapulgite

| **Group** | **Mode of Vibration** | **vcm-1** |
|---|---|---|
| O-H( $H_2O$) | Coordinated water ( stretching) | 3545 |
| H-O-H | Stretching | 3219 |
| H.O-H | crystalation lattice water | ٣٠٩٧ |
| O-H-H | Coordinated and absorbed water | ١٦٦٢,١٦٥٠,١٦٢٩ |
| $Al_2O_3$ | bending | 1541 |
| Si | Silicon | 1604 |
| O-$SiO_3$ | Bending0 (Asymmetric | ١١٢٠ |
| Si-O-Si | Stretching | ١١٥٩ |
| Mg-O | bending | ١٠٦٨ |
| -OH | bending | 1020 |
| O-$SiO_3$ | bending | ٩٧٧ |
| $SiH_3$ | bending | ٩٢٣ |
| Si-OH | bending | ٨٧٣,٨٢٠ ,٨٠٦ |
| M-O | bending | ٧١٩ |

### (3.1.4) Infrared spectroscopy analysis of a pure activated calcine Ataapulgite

Peaks appeared in FT-IR chart due to calcining. Most of compounds specially hydroxides of metals converted to oxides, coordinated and adsorbed water disappeared because of calcining at high temperature 850-900° C , (1022.27$cm^{-1}$) for (Si-O) group become stronger and bordered due to calcining operation. (1539$cm^{-1}$) of $Al_2O_3$ bending was small because of water loss due to calcining. The above explanations indicate that a pure activated calcined Attapulgite was obtained as shown in table (3-4).

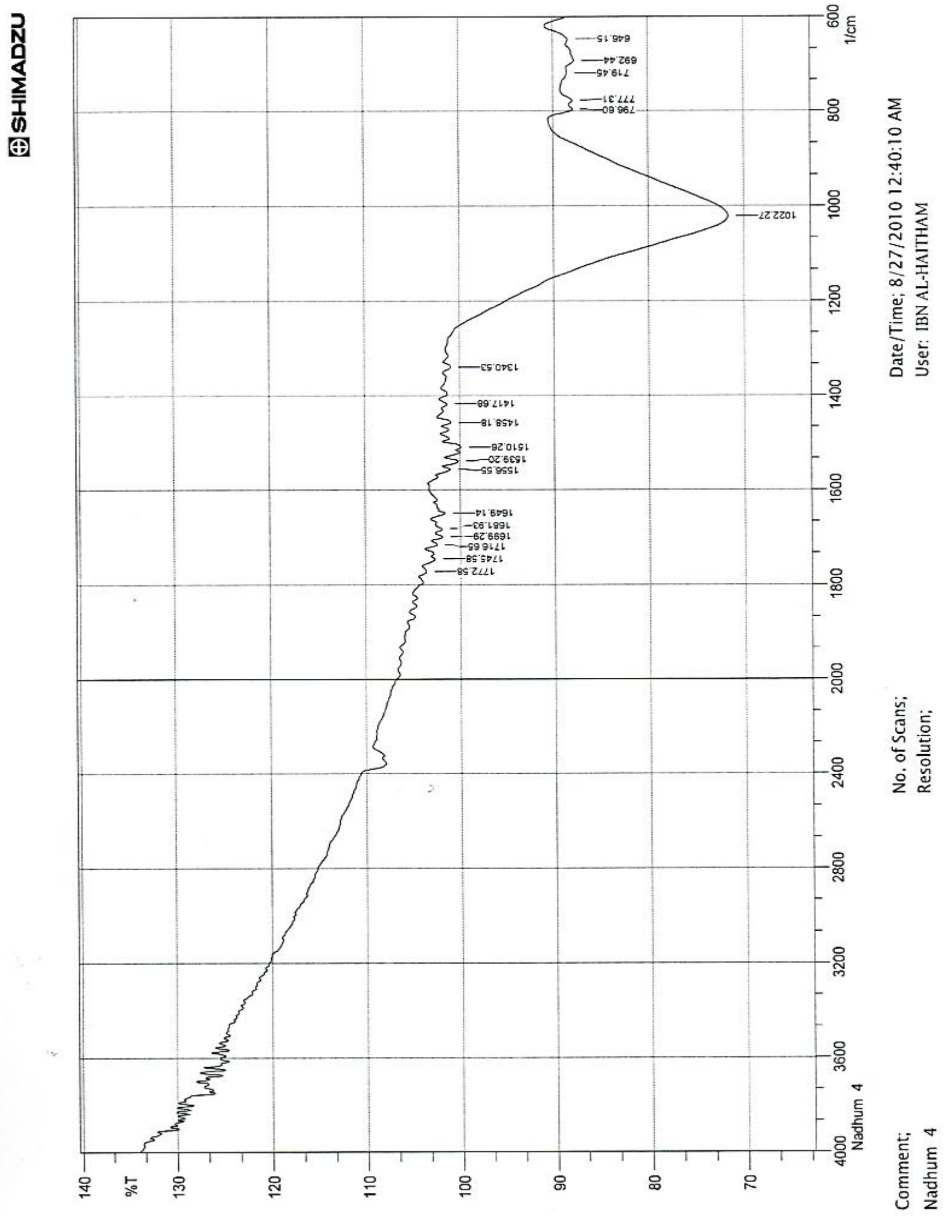


Figure (3-4) FT-IR spectrum of pure activated calcined Attapulgite

Table (3-4) FT-IR spectroscopy analysis of a pure activated calcine Attapulgite peaks

| Group | Mode of Vibration | vcm$^{-1}$ |
|---|---|---|
| $Al_2O_3$ | Bending (m) | 1539 |
| Si-O-Si | Stretching (str.) | 1022.27 |
| $SiH_3$ | Twisting (m) | 692 |

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## (3.2)Powder X-Ray Diffraction

### (3.2.1) Powder X-Ray Diffraction of Attapulgit Crude

X- ray diffraction spectrum shown in figure (3-5) peaks shown in table (3-5) with location and severity [91, 127,128].

The peaks of Attapulgite appear at(8.5138,20.8896 )2Ɵ (deg) ); Quartz at (26.6684 2Ɵ(deg)); Calcite at (29.4448)2Ɵ (deg). X- ray diffraction spectrum shown in figure(3-5). Peaks in table (3-5) with location and severity. [91, 127,128]. The peaks explain presence of Attapulgite, quartz and calcite.

Table (3-5) X-ray diffraction peaks of Attapulgite crude

| **Compound or group** | **2Ɵ (deg)** | **d(A)** | **I (C/Sec.)** |
|---|---|---|---|
| Attapulgite | 8.5138 | 10.37740 | 109 |
| Attapulgite | 20.8896 | 4.24958 | 36 |
| Quartz | 26.6684 | 3.33997 | 136 |
| Calcite | 29.4448 | 3.03105 | 742 |

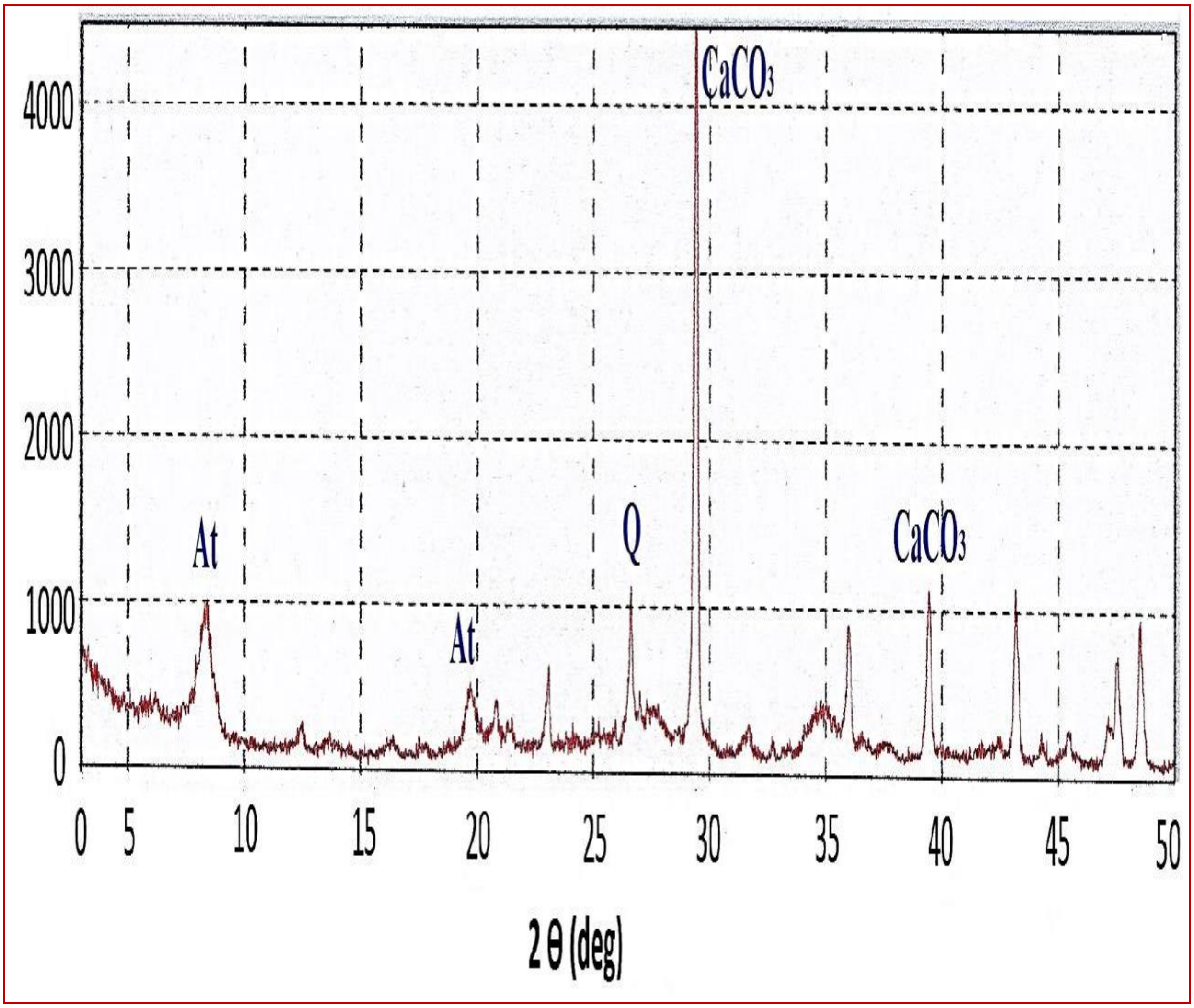

Figure (3-5) x-ray diffraction spectrum Attapulgite (Attapulgite At: quartz: Q)

## (3.2.2) PXRD of activated Attapulgite

The comparison between the crude and the activated attapulgite shows an increase in the absorption intensity in the X-ray diffraction spectra due to the removal of impurities and the inflow of the water-permeable layers, as shown below.the table of absorption peaks of activated Attapulgite., as shown in figure (3-6) and table (3-6) shows the most important these peaks with intensity.

Table (3-6) X-ray diffraction peaks Activated Attapulge

| Compound / group | 2Ө (deg) | d(A) | I (C/Sec.) |
|---|---|---|---|
| **Attapulgite** | **8.2880** | **10.65961** | **153** |
| **Attapulgite** | **19.6977** | **4.50337** | **91** |
| **Quartize** | **26.5660** | **3.35261** | **174** |
| **Calcite** | **29.3556** | **3.04006** | **235** |

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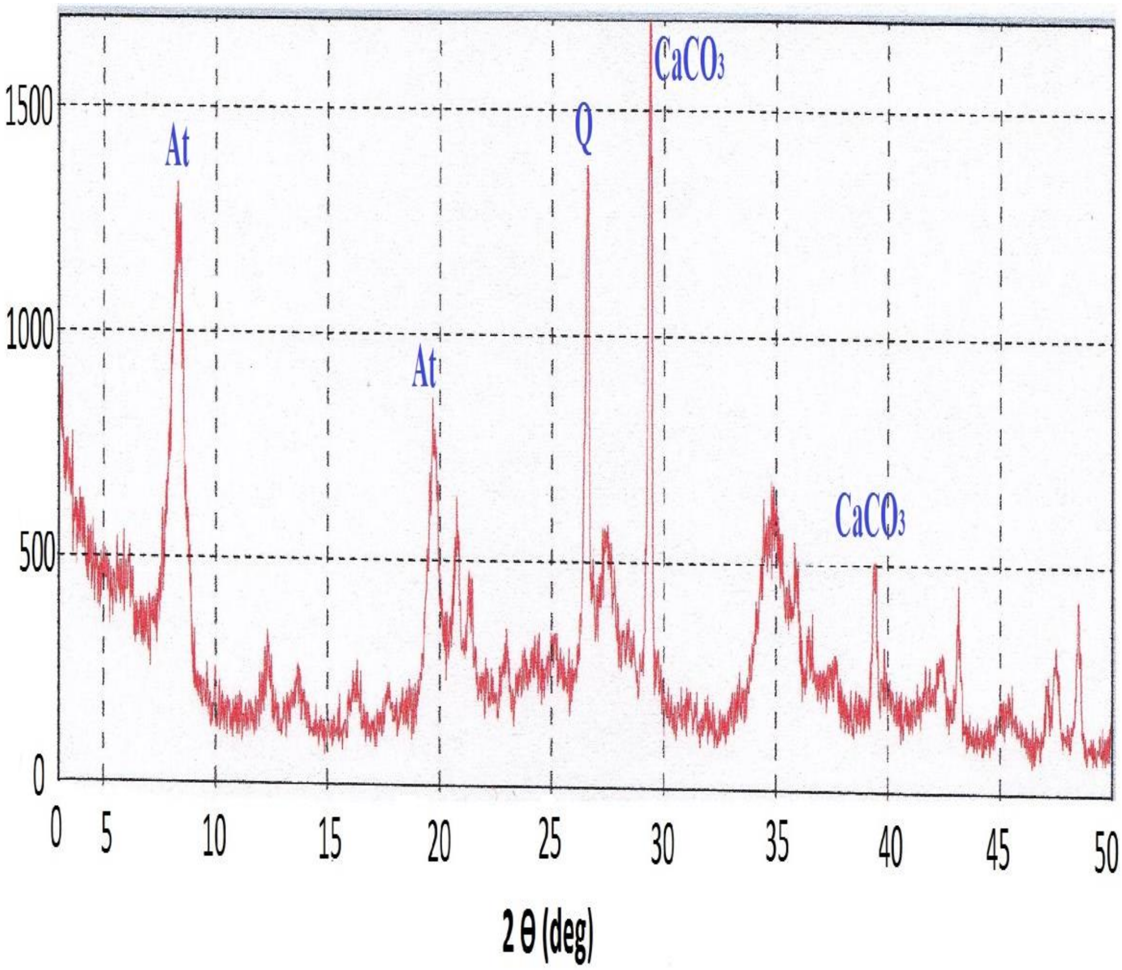

Figure (3-6) x-ray diffraction spectrum Activated attapulgite (Attapulgite At:, quartz: Q) shows the most important these peaks with intensity.

## (3.2.3) PXRD of a pure activated Attapulgite

The disappearance of calcium carbonate peaks at (29.3556) 2 ϴ was observed due to the purification of Attapulgite from other mineral impurities using sodium methyl acrylate, while the peaks of the Attapulgite remained clear, as shown figure (3-7) and table(3-7).

Table (3-7) X-ray diffraction peaks for pure activated Attapulgite

| **Compound / group** | **2ϴ (deg)** | **d(A)** | **I (C/Sec.)** |
|---|---|---|---|
| **Attapulgite** | **8.4347** | **10.47454** | **24** |
| **Attapulgite** | **8.6720** | **10.18844** | **19** |
| **Quartize** | **26.5584** | **3.35356** | **100** |

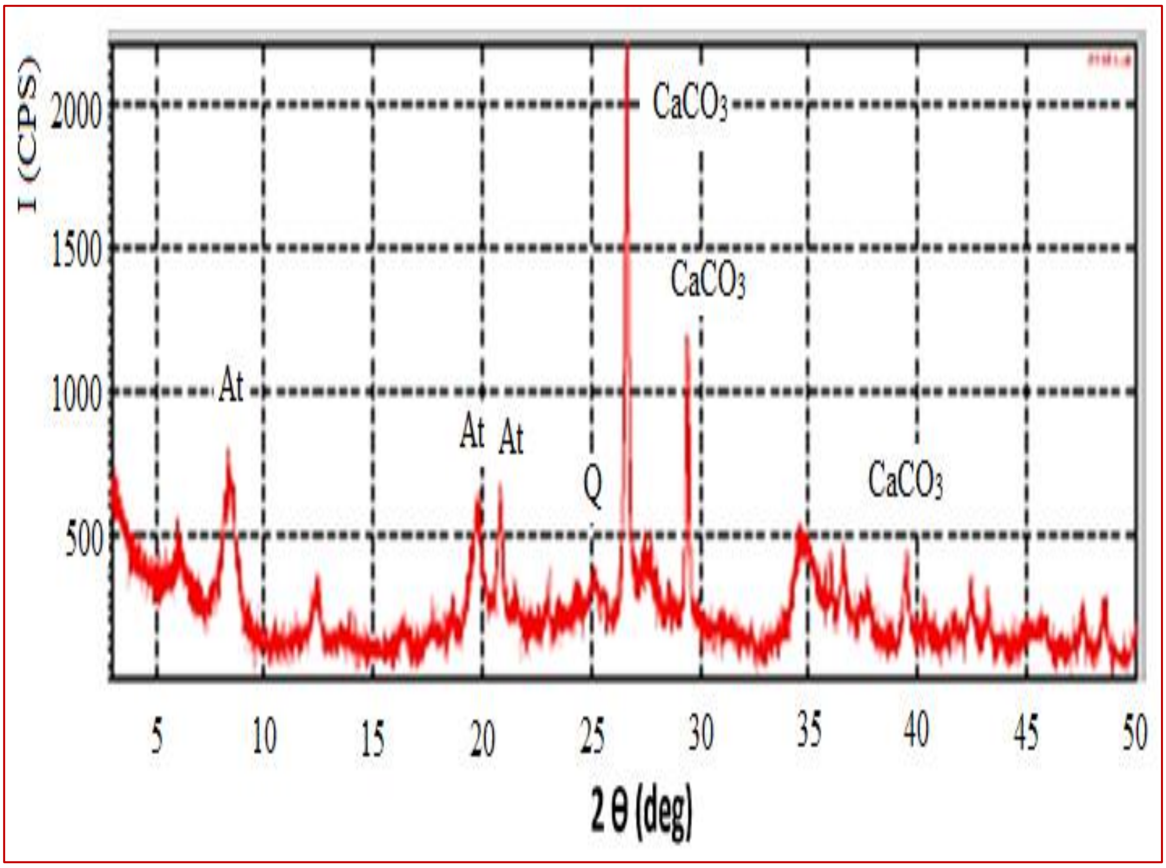

Figure (3-7) x-ray diffraction spectrum pure Activated attapulgite

## (3.3.4) PXRD of a pure activated calcine Attapulgite

The Attapulgite peaks at (8.4347; 19.3471; & 20. 7722) 2ϴ have a low intensity absorption due to calcing process to high temperatures range 850 – 950 C$^o$ that leds to shrinking of the band gape of Attapulgite clay mineral, as shown in figure (3-8) and table (3-8).

Table (3-8) peaks of strongest intensity of x-ray diffraction

| **Compound / group** | **2ϴ (deg)** | **d(A)** | **I (C/Sec.)** |
|---|---|---|---|
| **Attapulgite** | **29.3471** | **3.04092** | **50** |
| **Attapulgite** | **20. 7722** | **4.27279** | **24** |
| **Quartize** | **26.5584** | **3.35356** | **100** |

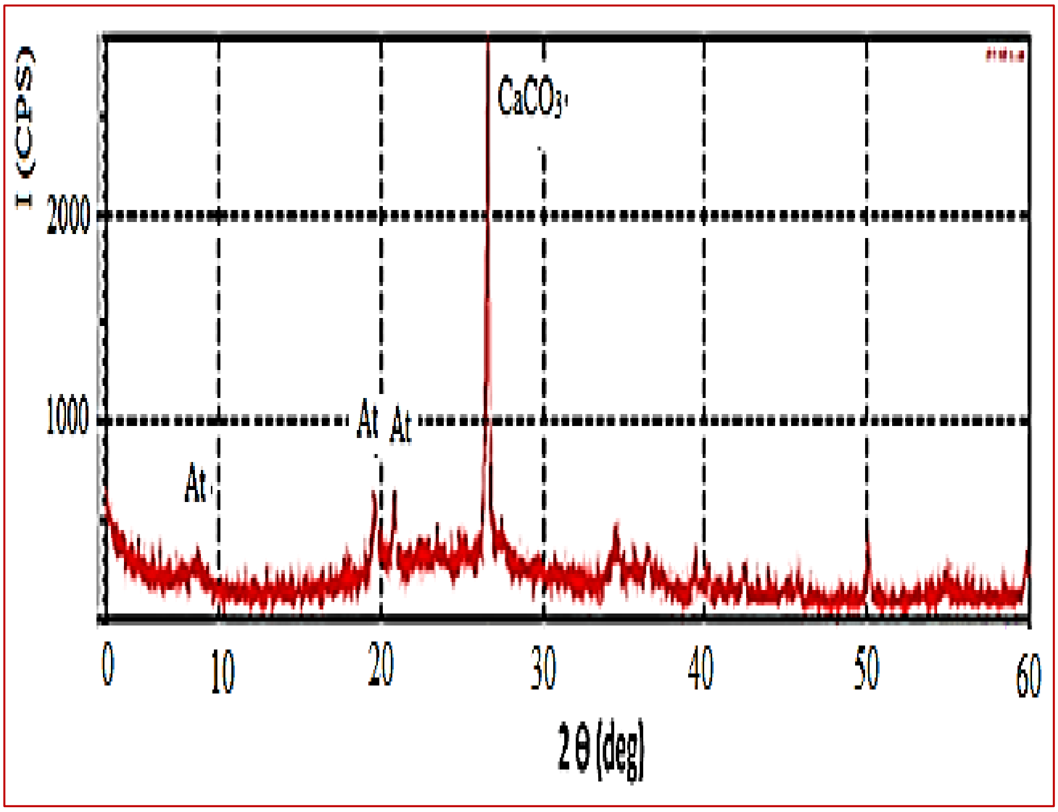

Figure (3-8) x-ray diffraction spectrum of calcine pure Activated Attapulgite

## (3.3)Scanning Electron Microscope

### ( 3.3.1) SEM image of Crude Attapulgite

Electron microscope image appears structure for Attapulgite clay powder consists of crystals of different needle lengths and diameter of about 500 nanometers as show in figure (3-٩) [129].

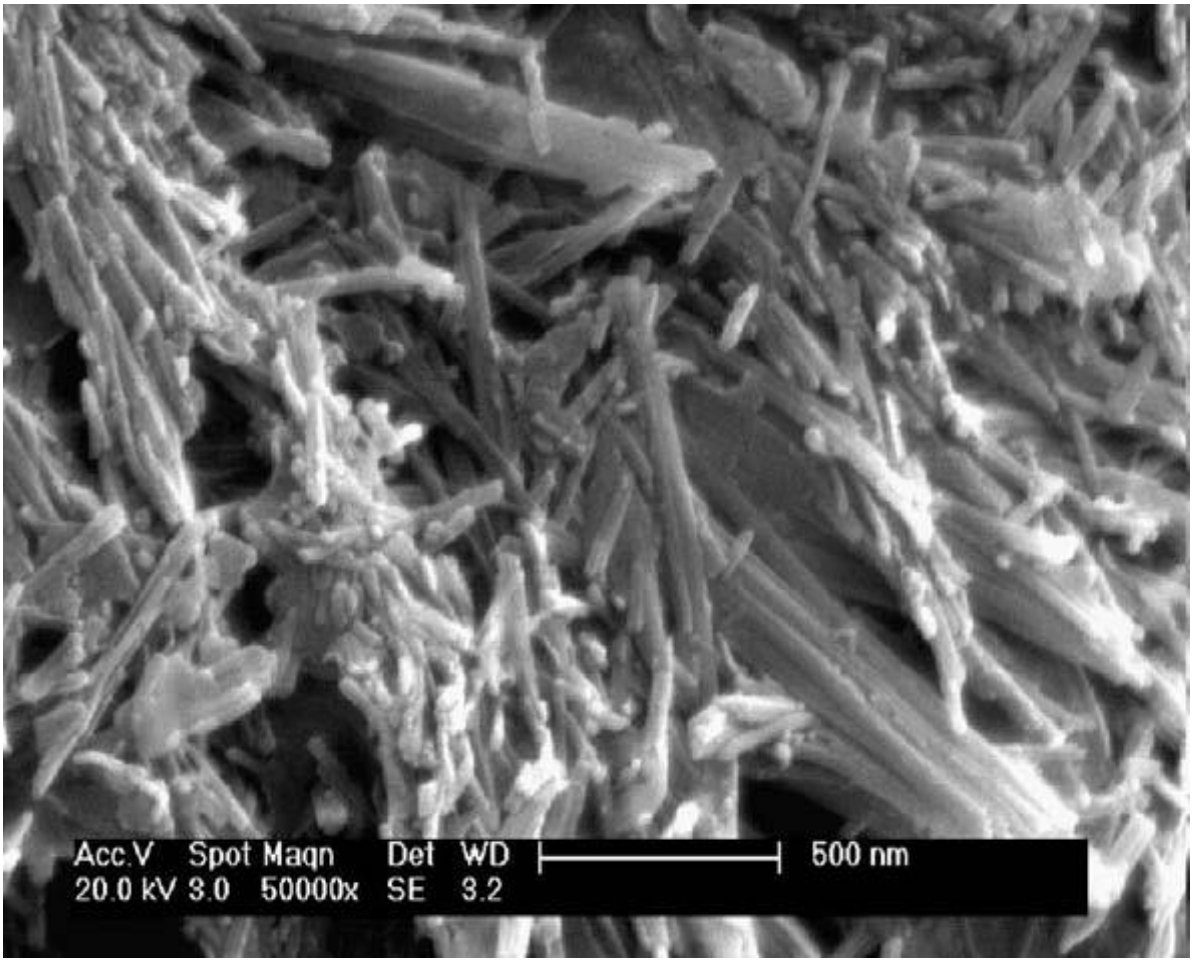

Figure (3-9) SEM image for Attapulgite crude

## (3.3.2) SEM image of activated Attapulgite

SEM images of low and high magnification figure (3-10) (1a, 1b, 1c, &1d) of initiated H - form Attapulgite show a normal characteristic needle-shaped structure of Attapulgite clay mineral as shows figure (3-10).

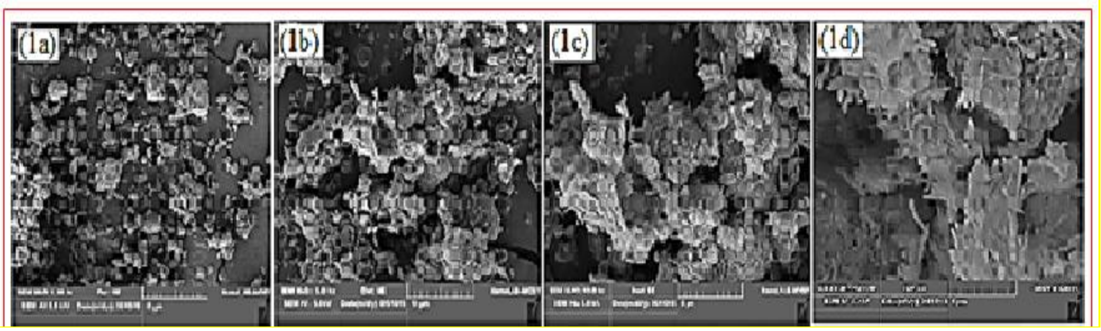

Figure (3-10) SEM image of activated Attapulgite

## (3.3.3) SEM of a pure activated Attapulgite

The SEM images of pure activated Attapulgite show a high resolution with an accurate vision of needle- shaped structure, due to the active purification method using sodium methyl acrylate. As shown in figure (3-11) (2a, 2b, 2c, &2d).

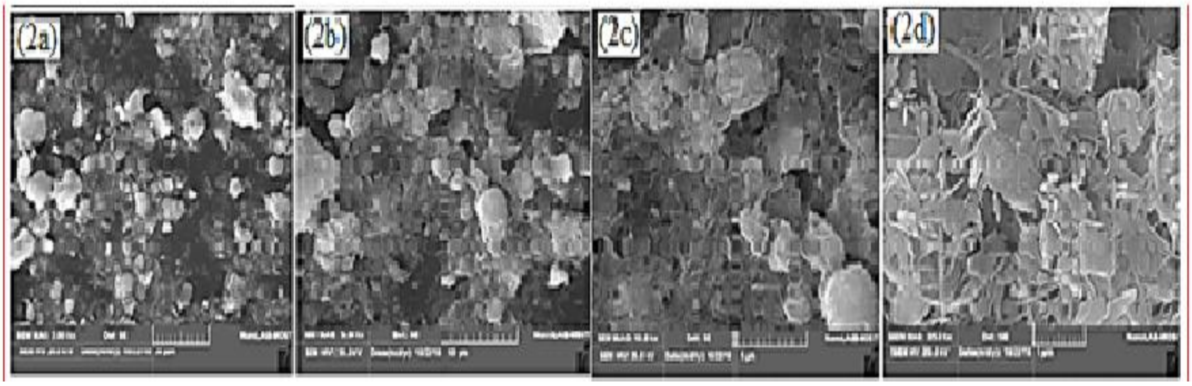

Figure (3-11) SEM image of pure activated Attapulgite with different scale of resolution.

## (3 .3.4) SEM of pure activated calcine Attapulgite

The calcined pure activated Attapulgite SEM images figure(3-12) (3a, 3b, 3c, &3d) show that the sharpness of needle- shaped structure diminished due to the loosing of the water of crystal lattice.

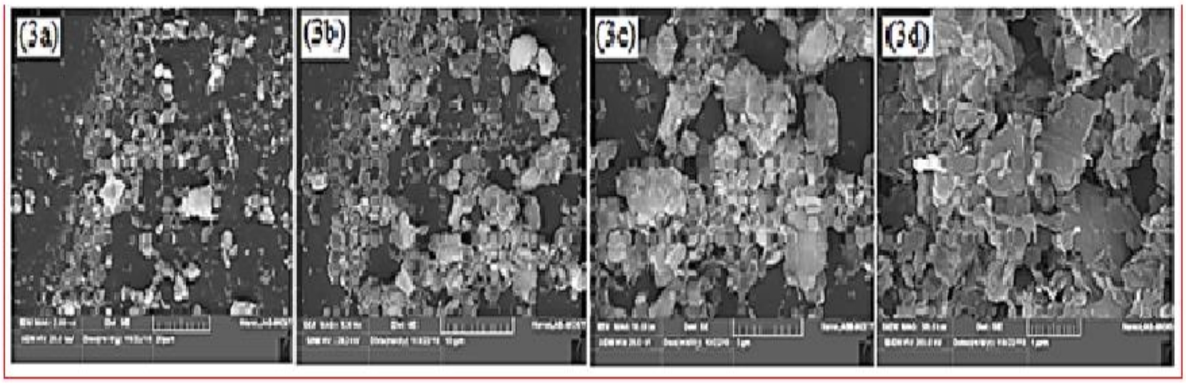

Figure (3-12) SEM of pure activated calcine Attapulgite

## (3.4) EDX(Energy DiffractionX-ray Detection) of pure activated calcine Attapulgite

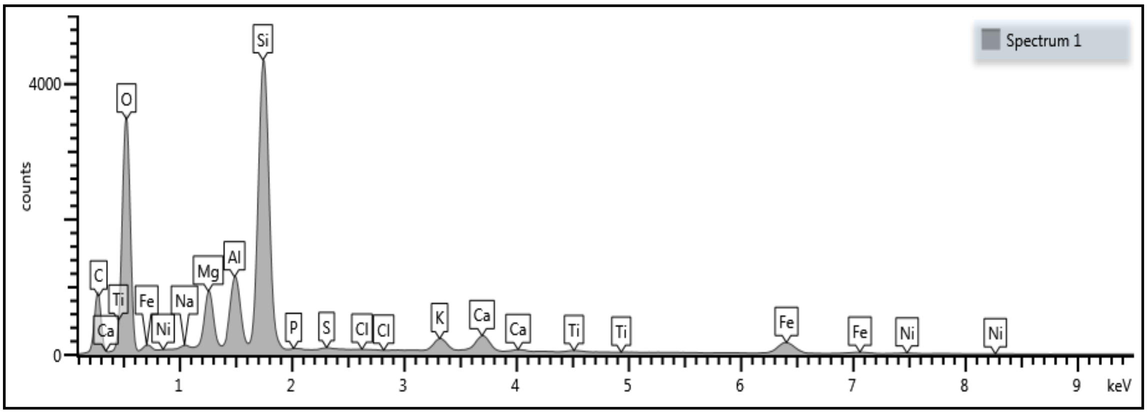

Figure (3-13) shows contains of a pure activated calcine Attapulgite

The percentage of Ca decreased to smallest percentage because of activated , pure and calcinations processes which remove all impurities( such as calcium carbonate $CaCO_3$ ) and other types of clays as following table (3-9 ).

Table (3-9) percentage of elements in pure, activated calcine Attapulgitte

| Element | Wt% | Wt% Sigma |
|---|---|---|
| O | 50.64 | 0.33 |
| Na | 0.48 | 0.08 |
| Mg | 5.32 | 0.12 |
| Al | 6.64 | 0.12 |
| Si | 26.96 | 0.23 |
| P | 0.16 | 0.06 |
| S | 0.19 | 0.06 |
| Cl | 0.02 | 0.05 |
| K | 1.72 | 0.08 |
| Ca | 2.43 | 0.09 |
| Ti | 0.38 | 0.07 |
| Fe | 4.64 | 0.17 |
| Ni | 0,42 | 0.12 |
| Total | 100 | |

## (3.5) Desulfurization of gasoline and kerosene by Attapugite

### (3.5.1) FT-IR spectrum of gasoline crude:

From the following spectrum we observe appearance of absorption area refer to sulfide as merceptance has wave length ($cm^{-1}$) in addition there are many peaks of different of carbon , hydrogen bonds indicate that gasoline consist of a mixture of hydrocarbons. The relationship between IR peaks and oil composition is some how blurred by overlapping absorption peaks. yet, a quick visual inspection of the spectra would reveal some differences/trends in the 1750-650$cm^{-1}$ region. These are observed in the peak areas of the C=O absorption at about 1700$cm^{-1}$ ; the C=C absorption at about 1608.60$cm^{-1}$ ; the aromatic ring peaks between 890-730$cm^{-1}$.The long chain aliphatic hydrocarbon vibration at about 721.4$cm^{-1}$ , all of which tend to either increase or decrease depending on the composition of the crude oil involved.

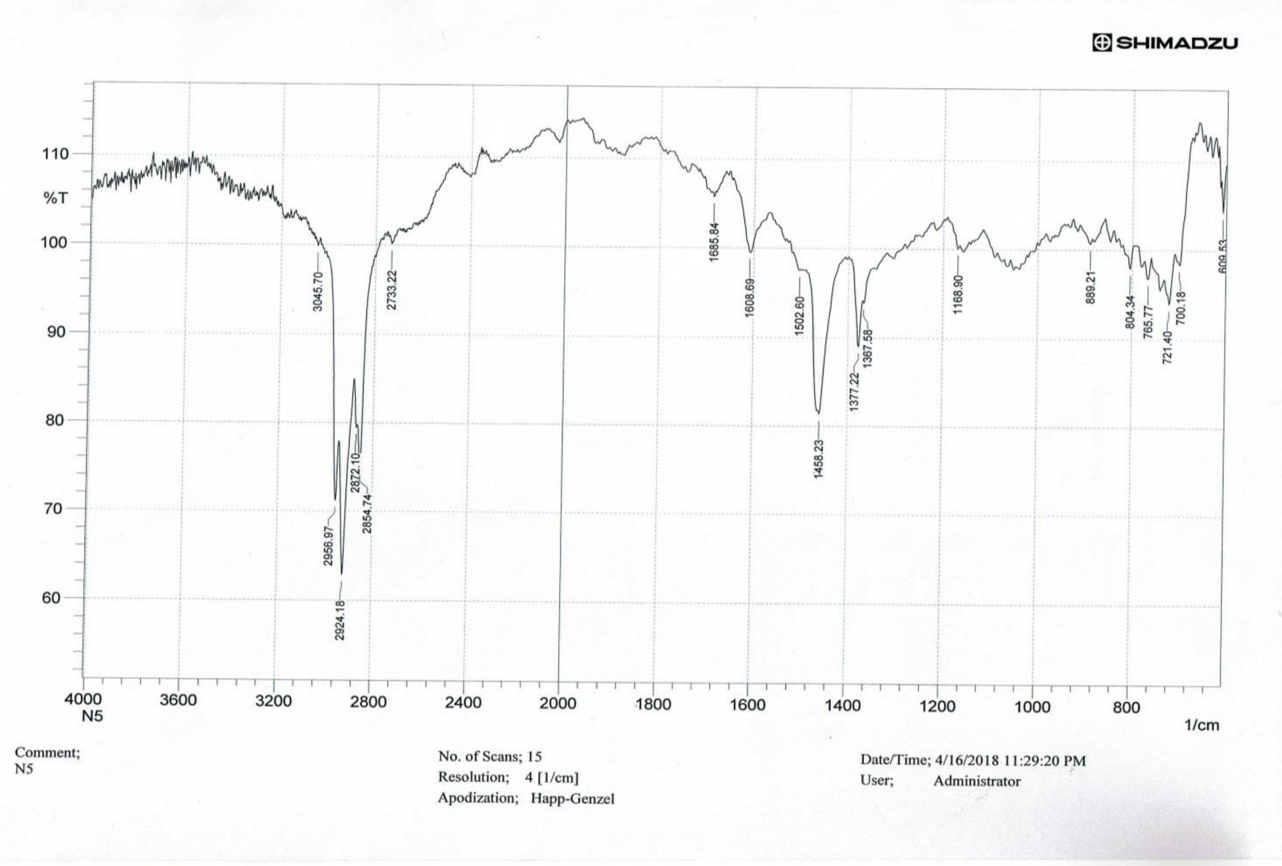

Figure (3-14) shows peaks of groups of gasoline

Through tests operated for gasoline by two methods;

1-**column method**: gasoline passed through a column contains a pure activated calcine particles of Attapulgite clay which are packaged in three columns(each one has 2 g of Attapulgite ), we obtained the following results(in ppm ) for Sulphur ions as shown in table (3-12).

Table (٣-10) shows time of contact ( hrs.) against conc. of Sulphur in samples constant volumes ( 20 ml)at constant temperature (25C$^0$).

| SAMPLES | Time contact | S (ppm) |
|---|---|---|
| Gasoline Crude | | 195.9 |
| Gasoline 1 | 1hr | 65.1 |
| Gasoline 2 | 2hr | 65.1 |
| Gasoline 3 | 3hr | 62.1 |

I form and decreasing in Sulphur concentration compared to the crude and removing a large amounts of Sulphur from the samples due to adsorption amount by pure activated Attapulgite where (H $^+$) ions bonding with the Sulphur as merciptan (HS$^-$) these tests were operated in central laboratories for use of (Ministry of Oil /Daura Refinery / Quality Control Laboratories Department ).

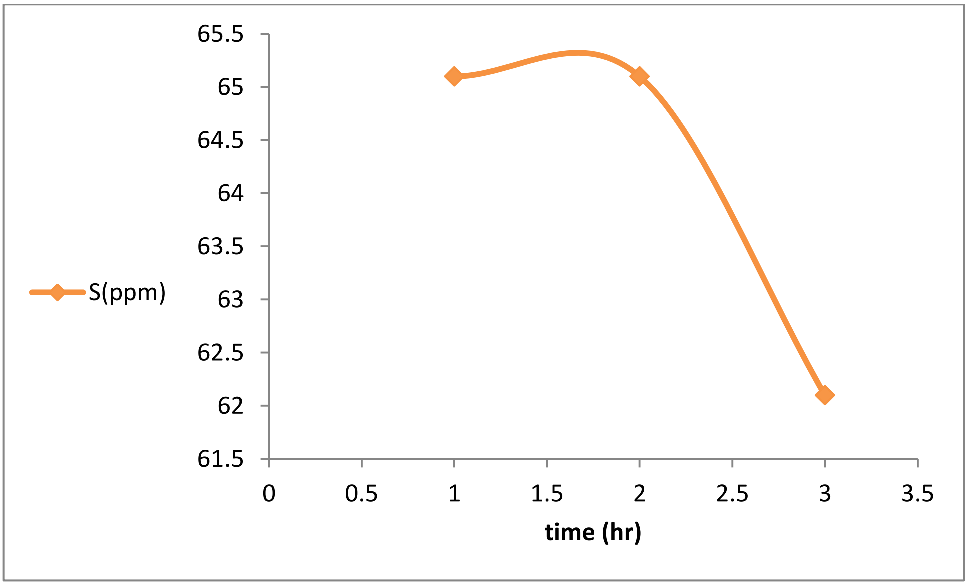

Figure (3-15) shows relationship between contact time and Sulphur (ppm)

(Column method)

2-**Batch method**:20 ml of gasoline mixed with 1g of pure activated calcined Attapulgite for 1 hr.; 2hr ; 3hr; 4hr with continues shaking at 25 C°. The results obtained in table (3-11).

Table (3-11) shows time of contact (hrs.) against conc. of Sulphur in samples.

| SAMPLES | Time contact | S (ppm) |
|---|---|---|
| Gasoline Crude | | 195.9 |
| Gasoline 1 | 1hr | 37.5 |
| Gasoline 2 | 2hr | 37.5 |
| Gasoline 3 | 3hr | 39.0 |
| Gasoline 4 | 4hr | 35.6 |

The comparison between two methods, the batch method is better to use in our study because the amount of removal Sulphur larger than column method.

Through select best results which obtained through results has removed the large amount of Sulphur and selected by choosing the best volume of gasoline to use with the perfect amount of activated clay and best time to contact between the gasoline and the activated Attapulgite and following chart shows, figure (3-16) that:

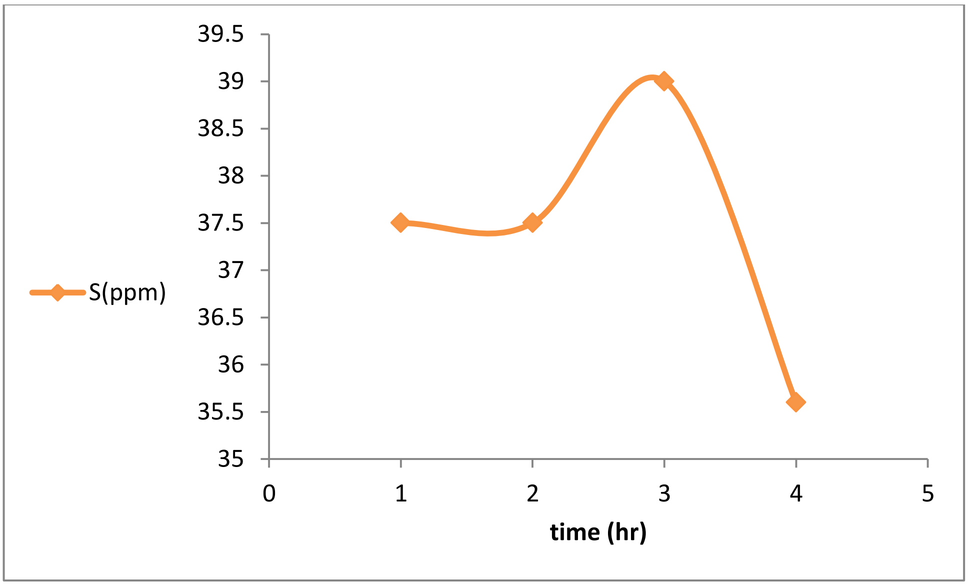

Figure (3-16) shows relationship between contact time and Sulphur (ppm)(batch method)

The best time have to remove larger content of sulfide is one hour so we complete the work depending on this truth by taking:

1- Different volumes of gasoline with constant amount of clay (1 g ) at constant time (1 hr. ) and temperature(25 $C^0$) to choose best volume of gasoline .

Table (3-12) shows values of volume of gasoline samples against conc. of Sulphur in samples.

| No | V mL | S (ppm ) |
|---|---|---|
| 1 | 5 | 102.93 |
| 2 | 10 | 94.9 |
| 3 | 15 | 94.0 |
| 4 | 20 | 96.9 |

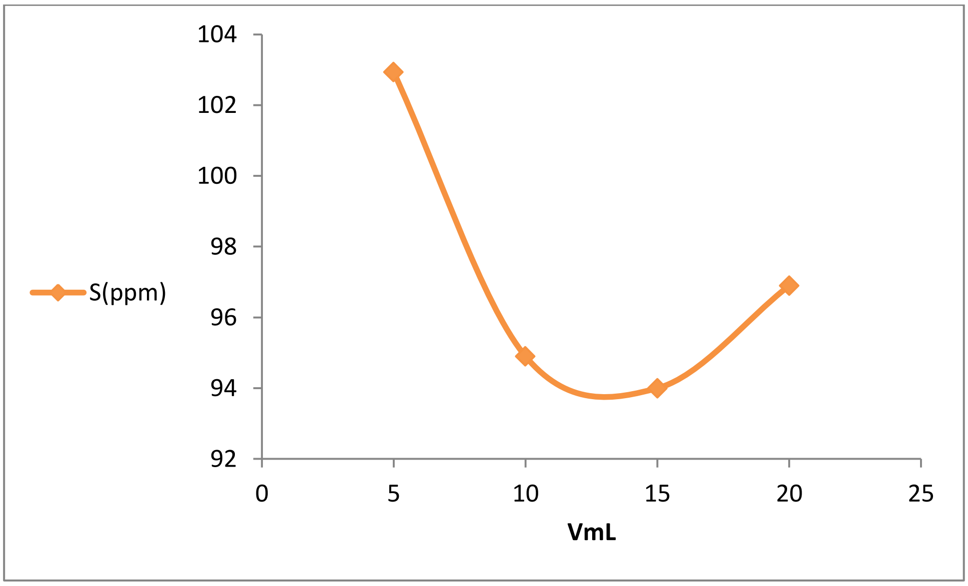

Figure (3-17) shows relationship between volumes of gasoline and Sulphur (ppm)

2- Different amounts of clays with constant volume (10ml) of gasoline at constant time (1hr.) to choose best amount of clay.

Table (3-13) include determination of Sulphur conc. in gasoline crude samples after contact with pure activated calcine Attapulgite

| No | Clay (g) | S( ppm ) |
|---|---|---|
| 1 | 1 | 94.9 |
| 2 | 1.1 | 100.01 |
| 3 | 1.2 | 94.9 |
| 4 | 1.3 | 89.79 |

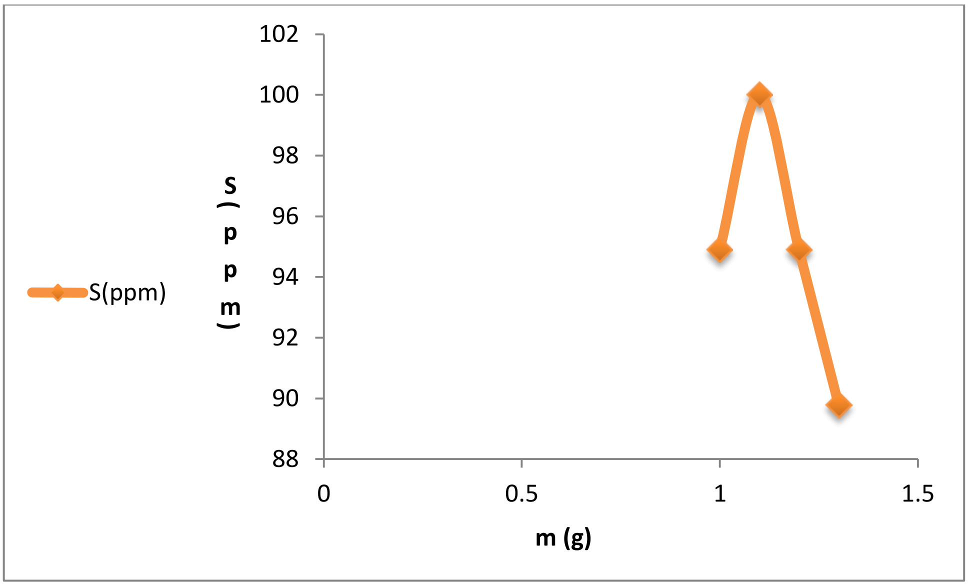

Figure (3-18) shows relationship between mass of pure activated calcine Attapulgite against conc. of Sulphur (ppm) in gasoline crude samples at constant temperature.

From results in above proved that is best quantity of Attapulgite is ( 1 .3 g ) to use it for best volume of gasoline ( 15 ml) in best time of contact (1 hr. ) to remove larger amount of Sulphur from gasoline .

All of processes which were operated on gasoline crude samples to remove a larger possible amount of Sulphur from it by using pure activated calcine Attapulgite as adsorbed surface to adsorption of Sulphide ions from gasoline .

## (3.5.2 ) FT_IR for kerosene crude

The relationship between IR peaks and oil composition somehow blurred by overlapping absorption peaks. Yet, a quick visual inspection of the spectra would reveal some differences/trends in the 1750-650cm$^{-1}$ region. These are observed in the peak areas of the C=O absorption at about 1700cm$^{-1}$ ; the C=C absorption at about 1608.60cm$^{-1}$ ; the aromatic ring peaks between 890-730cm-1and; the long chain aliphatic hydrocarbon vibration at about 721.4cm$^{-1}$ , all of which tend to either increase or decrease depending on the composition/type of the crude oil involved.

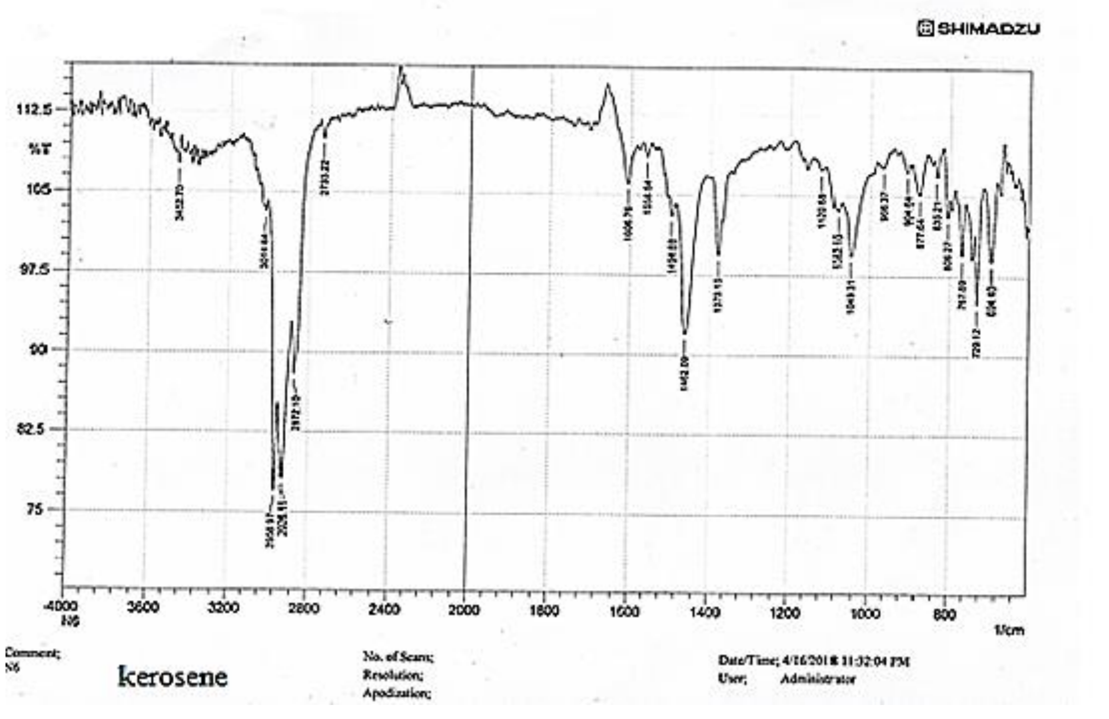

Figure (3-19) FT_IR for kerosene crude

Through tests operated for gasoline by two methods;

1-**column method**: kerosene passed through a column contains a pure activated calcine particles of Attapulgite clay which are packaged in three columns(each one has 2 g of Attapulgite ), we obtained the following results(in ppm ) for Sulphur ions as shown in table (3-1).

Table (3-14) include determination of Sulphur conc. in kerosene crude samples after contact with pure activated calcine Attapulgite (column method)

| SAMPLES | Time contact | S (ppm) |
|---|---|---|
| kerosene Crude | | 37.6 |
| kerosene 1 | 1hr | 36.5 |
| kerosene 2 | 2hr | 32.7 |
| kerosene 3 | 3hr | 34.9 |

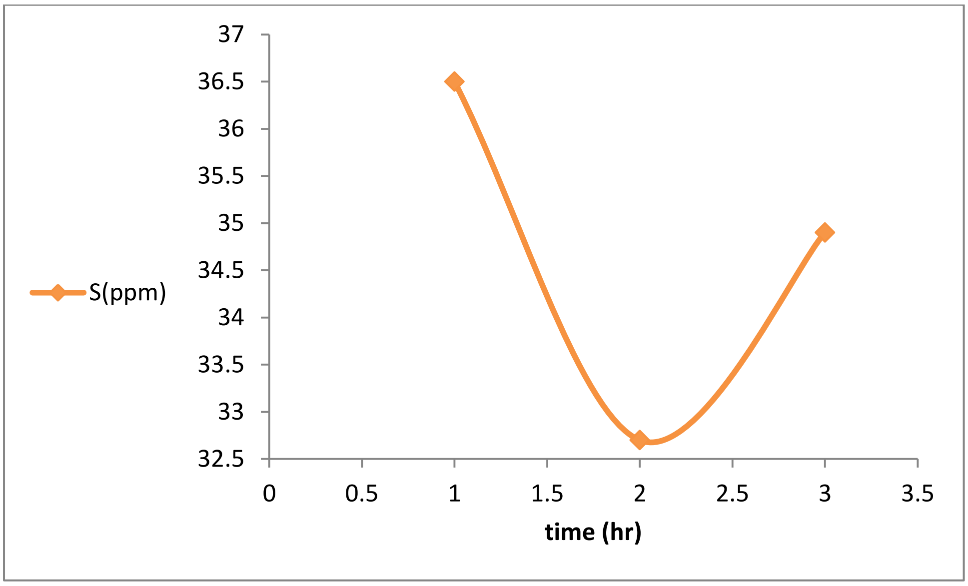

Figure (3-19) shows relationship between contact time and Sulphur (ppm)(column method)

2-**Batch method**:20 ml of kerosene mixed with 1g of pure activated calcined Attapulgite for 1 hr.; 2hr ; 3hr; 4hr with continues shaking at 25 C°. The results obtained in table (3-20).

Table (3-15) include determination of Sulphur conc. in kerosene crude samples after contact with pure activated calcine Attapulgite(batch method).

| SAMPLES | Time contact | S (ppm) |
|---|---|---|
| kerosene Crude | | 37.6 |
| kerosene 1 | 1hr | 34.3 |
| kerosene 2 | 2hr | 34.5 |
| kerosene 3 | 3hr | 35.6 |
| kerosene 4 | 4hr | 35.6 |

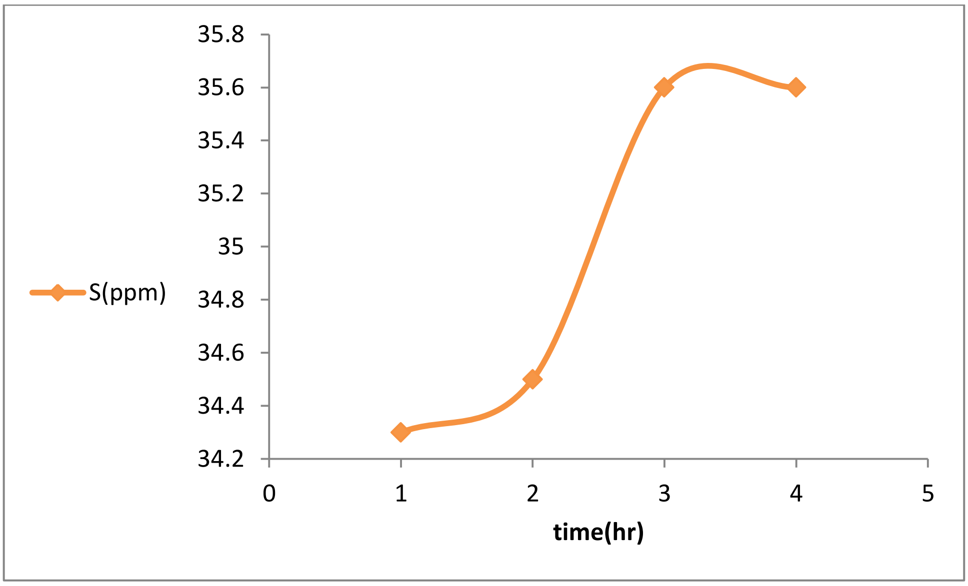

Figure (3-20) shows relationship between contact time and Sulphur (ppm) (Batch method)

The difference between gasoline and kerosene is the gasoline has more aromatic compounds make it able to react with adsorption surface, which has H- form while the kerosene has long carbon chain make in active with H- form because it has an aliphatic groups.

## (3.7)Conclusions

**1-**Iraqi Attapulgite minerals are more suitable to use as an active adsorption agent specially when activated.

2- The activation process led to remove impurities and increase the proportion of montmorillonite and Attapulitgite metal reaches over (90%) in the clay.

3-using sodium methyl acrylate increased purity of Attapulgite without of other types of clays.

4-Ability of pure activated Attapulgite to reduce Sulphur content from gasoline increased.

## (3-8) suggestions

1- Using another types of clays for same purpose.
2- Using another types of fuel such as kerosene.
3- This work extended to other examinations such as Atomic Force Microscopy (AFM).

# CHAPTER four

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# الخلاصة

نظرا للمبالغ الطائلة التي تصرفها الحكومة العراقية على استيراد الجازولين المحسن وهدر العملات الصعبة للبلد كان له الاثر البالغ في البحث عن بدائل محلية للتخلص من المحتوى الكبريتي للجازولين العراقي العادي وتحويله اتلى جازولين محسن ومن خلال الاستفادة من براءة الاختراع الامريكية (Ser. No 09/, 190, 528, filed Nov.12, 1980, now US Pat .No. 6130, 179) ويتضمن هذا العمل طريقة لتنقية وتحسين مواصفات اطيان الاتابلكايت العراقية لاستعمالها كعامل امتزاز لمركبات الكبريت (الميركبتان ) من الجازولين العراقي من خلال تنشيط الطين لخفض كمية الكبريت الى اقل ما يمكن في الجازولين . وتعتمد خطوات تنقية الاتابلكايت العراقي والذي تم الحصول عليه من الهيأة العامة للمسح الجيولوجي وبالاعتماد على براءة الاختراع الامريكية المذكورة في اعلاه والتي تم تطويرها بإضافة مادة بولي مثيل اكريلات الصوديوم .حيث تم تنشيط الطين بعد ازالة الرمل والشوائب باستعمال المبادل الايوني ديواكس ٥٠ مغ حامض الهيدروكلوريك المخفف لتحويل الطين الى صيغة حامضية (H –form) حيث تستبدل الايونات الموجبة في المعدن بأيونات $H^+$ ثم تضاف مادة المثيل اكريلات الصوديوم لتطويف الاتابلكايت حصريا دون غيره من الاطيان الاخرى لاستعماله كمادة ممتزة للميركبتان .

استعمل في هذا العمل مختلف التقنيات التحليلية مثل طيف الاشعة تحت الحمراء واشعة اكس والمجهر الالكتروني وجهاز الفلورة بأشعة اكس واي دي اكس ، حيث اظهرت كل النتائج الحصول على اطيان الاتابلكايت النقية والمنشطة من خلال التخلص من الشوائب وزيادة نسبة معدن الاتابلكايت والذي يعود الى اضافة مثيل اكريلات الصوديوم .

لوحظ ايضا اختفاء بعض قيم القمم في جهاز مطيافية الاشعة تخت الحمراء من شكل مخطط الاشعة تجت الحمراء للات تابلكايت الخام بسبب ازالة الشوائب والتخلص من الاطيان المتعلقة بالاتابلكايت وبالتالي زيادة نسبة الاتابلكايت كمعدن والقمم هي (997.9 9. و ٩٢٣) سم $^{-1}$ و والتي الى اصرة (O-H).

لوحظ ايضا الاختلاف في شدة الامتصاص في فحوصات حيود الاشعة السينية الاتابيكايت اذا ما قورن بالاتابلكايت الخام بسبب تنشيط طين الاتابالكايت وتقليل نسبة الكالسايت بسبب ازالة الشوائب .

وكذلك يظهر المجهر الالكتروني تعوذ للاتابلكايت صور ذات دقة عالية توضح مراحل الحصول على اتابلكيت العالي النقاوة وهذ يتضح من خلال ظهور الاتابلكايت ذات اشكال ابرية ويثبت الطبيعة التركيبية للاتابلكايت وجاهزيته للاستخدام ام كسطح ماز فعال .

يوضح فحص EDX انخفاض تراكيز الايونات الموجبة بسبب استبدالها بأيونات +H عند اضافة المبادل الايوني المنشط بحامض الهيدروكلوريك المخفف .

وكذلك لوحظ انخفاض في المحتوى الكبريتي للكازولين المار خلال الاتابلكايت المنشط عن تركيزه قبل معاملته بالاتابلكايت المنشط .

**جمهورية العراق**
**وزارة التعليم العالي والبحث العلمي**
**جامعة بغداد**
**كلية التربية للعلوم الصرفة / أبن الهيثم**
**قسم الكيمياء**

# تنقية وتحسين مواصفات اطيان الاتابلكايت العراقية لإزالة المحتوى الكبريتي من الوقود العراقي

**رسالة مقدمة إلى**

**مجلس كلية التربية للعلوم الصرفة –ابن الهيثم– جامعة بغداد وهي جزء من متطلبات نيل درجة الماجستير في علوم الكيمياء التحليلية**

**من قبل**

## ناظم غرب طاهر عراض

**بكالوريوس علوم كيمياء / الجامعة المستنصرية ١٩٩٤**

**بأشراف**

## أ.م.محمد حسن عبد اللطيف

**١٤٤٠ هـ ٢٠١٩ م**