

Purification, Beneficiation and Activation of Iraqi Attapulgite Clay Mineral

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Abstract

This study aimed to obtain a pure activated Attapulgite mineral to use it as adsorption surface in our search, because of its importance in removing impurities, desulfurization, decolorizing, neutralizing, and deodorizing of petroleum fuel. The large specific surface area and high cation exchange capacity of Attapulgite make it suitable in our work. However, the adsorption capacity of natural Attapulgite is limited, new activated pure Attapulgite clay was synthesized by purification and beneficiation Attapulgite to increase its ability to use in our search and other various fields, particularly in the petroleum refining. The pure activated calcined Attapulgite characterized by FT-IR spectroscopy, X-ray diffraction (XRD), and scanning electron microscopy (SEM). Attapulgite mineral was purified by floatation with the dispersed swelled sodium methyl acrylate granules leaving other impurities of clay mineral and sand in the bottom of the vessel. Therefore many peaks in FT-IR spectrum were disappeared comparing with the FT-IR spectrum of crud material. The disappearance of calcium carbonate peaks at $(29.3556) 2 \theta$ was observed due to the purification of Attapulgite from other mineral impurities using sodium methyl acrylate, while the peaks of the Attapulgite remained clear. SEM images of pure activated Attapulgite show a high resolution with an accurate vision of needle- shaped structure.

Keywords: *Desulfurization; Beneficiation; Attapulgite; Adsorption; Surface.*

Introduction

Attapulgite or Polygorskite is needle-like natural clay mineral Figure 1; consist of magnesium-aluminum silicate mineral. Polygorskite is salt gel, fuller's earth, and activated natural clay. Attapulgite of a molecular formula is: $[(OH)_4 (Mg, Al)_5 (OH)_2 Si_8 O_{20}] 4H_2O$ Figure 2, exhibit a good dispersion colloidal properties, high adsorbing capacities, alkaline resistant, de

coloring abilities, temperature resistant and Possesses plastic & adhesive characteristics. Attapulgite is of a laminated chain structure as seen in Figure 3, [1] where significant substitution of Mg^{+2} by Al^{+3} and Fe^{+3} take place in the octahedral position and Ca^{+2} , Na^{+} and K^{+} take place as interlayer cations [2, 3].

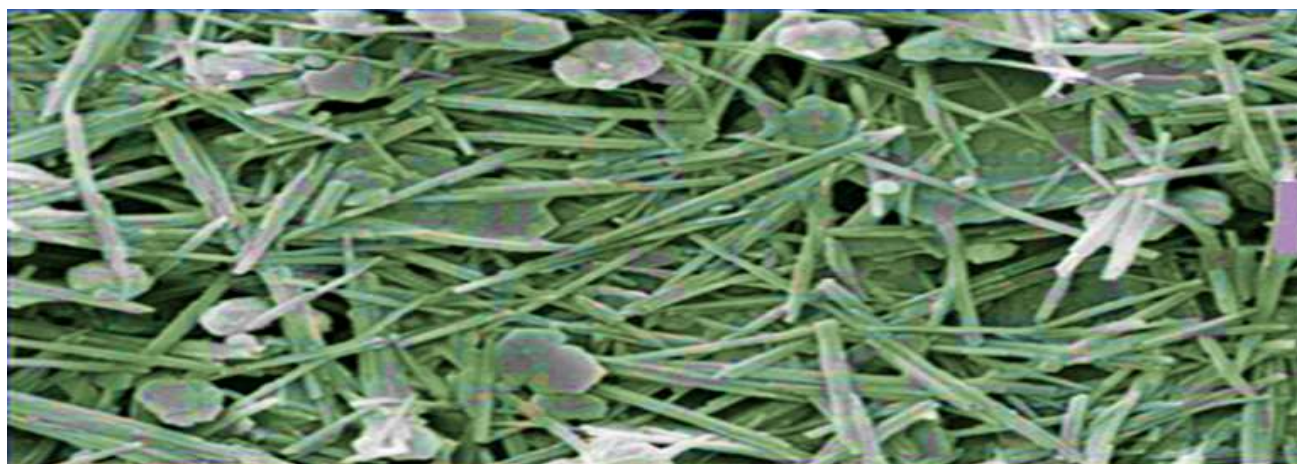


Figure 1: Attapulgite Image under high resolution SEM

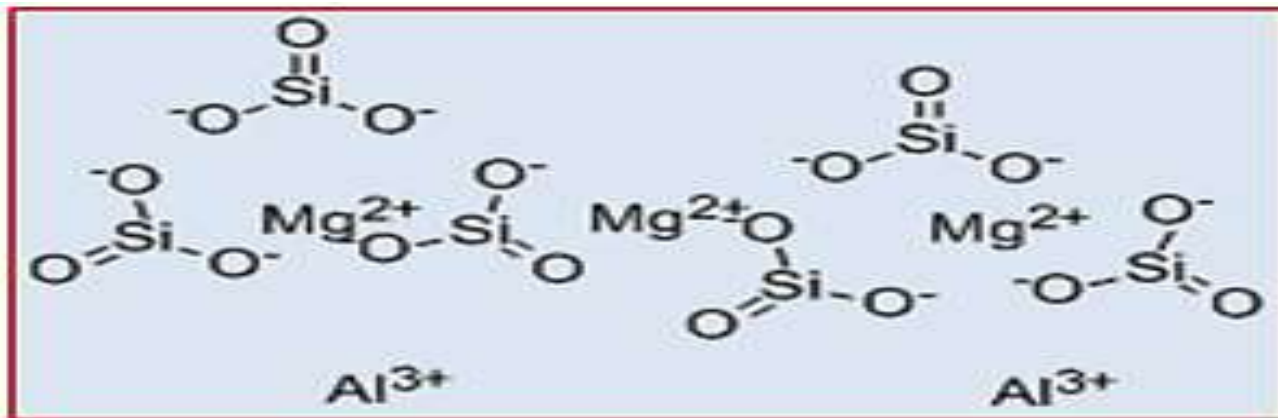


Figure 2: Structure of Attapulgite Clay

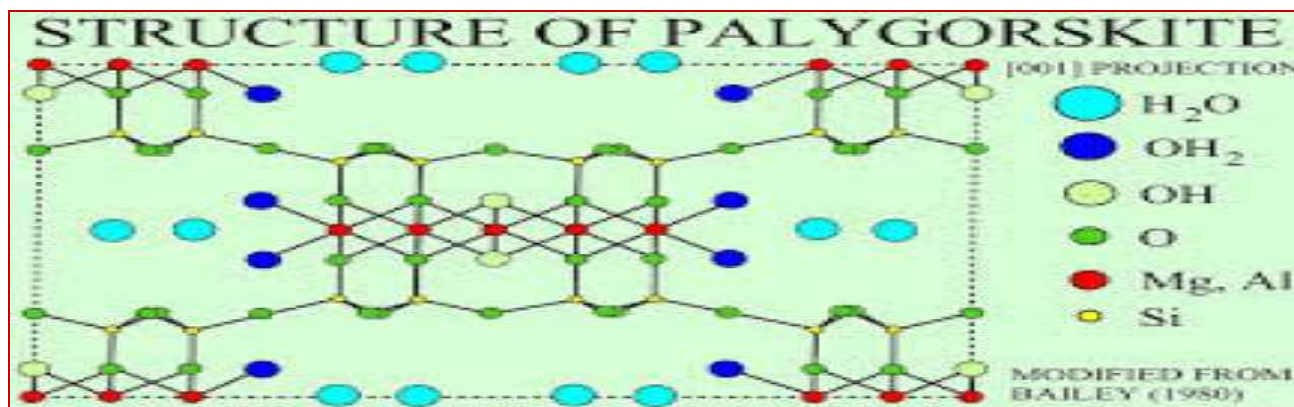


Figure 3: Attapulgite chain structure

Attapulgite uses divided into two broad categories:

colloidal and non-colloidal, table 1 represents these uses [4].

Table 1: Uses of Attapulgite clay mineral

Colloidal		Non Colloidal	
1	Oil-base and water-base foundry sand binders	1	Petroleum refining, decolorizing, neutralizing, brightening, desulfurization, deodorizing
2	Adhesive viscosity control	2	Vegetable oils and animal fats neutralizing, decolorizing, deodorizing
3	Oil well drilling mud	3	Carrier for granular and powdered agricultural chemicals (insecticides, herbicides, etc.)
4	Latex paint thickener and gelling agent	4	Pharmaceutical intestinal absorbent
5	Pharmaceutical thickener and adsorbent	5	Floor absorbents
6	Liquid suspension fertilizers	6	Animal bedding, pet litter
7	Polishes— suspending agent for abrasives	7	Flow ability additive to dry fire extinguisher powders
8	Wax emulsion stabilizer	8	Catalytic applications (no carbon required papers, olefin polymerization, etc.)
9	Metal drawing lubricants— suspending agent	9	Anti-caking agent
10	Laundry washing powders	10	Chromatographic adsorbent
11	Bonding agent for granulation of powders	11	Drying of oils

Attapulgite is widely distributed in Iraq, take place in many rock units, like Digma Formation (Akashat area) which is one of the important Attapulgite-rich Formations in Iraq, [5] also Attapulgite clays from Tar AL-Najaf (Injana) region in AL- Najaf

governorate was used to produce high reactivity Attapulgite [6]. The origin of Attapulgite, in these formations, is of marine sedimentary and almost always correlating with Montmorillonite clay mineral [7].

The montmorillonite correlating with the Attapulgite-bearing rocks of these Formations is of Calcium base which is non-swelling clay therefore our study is important to prepare a pure and active Attapulgite clay mineral free of Ca- Montmorillonite by creating a new and easy method for Purification, Beneficiation and Activation of Iraqi Attapulgite clay mineral.

Experimental

Materials

Najaf Iraqi Attapulgite-montmorillonite clay stone used in the present work was obtained from the General Company for Geological

Survey and Mining in Baghdad, Iraq. This crude Attapulgite-Montmorillonite claystone is gray italics to green in color; Table 2 shows chemical analysis of crude Attapulgite-Montmorillonite claystone sample.

Table 2: Chemical analysis of crude Attapulgite – Montmorillonite claystone sample

Compound	SiO ₂	Al ₂ O ₃	Fe ₂ O 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

Clay Sample was sieved to yield particle size equal to 75 μm and 250 μm, dried in an electric oven at 100 °C for 24 h., and stored in a desiccator for use. Chemicals were purchased from Fluka-BDH Chemicals. Distilled and deionized water with a conductivity value of 1.5 x 10⁻⁵ S Cm⁻¹ was used.

Instruments

FT-IR instrument (Shimadzu FT-IR Spectrometer-30000:1/IRAFF); Thermostatic Shaker Bath [GFL (D-3006), Fed – Rep. of Germany]; Centrifuge (JANETZI-T5, Germany, 3000 rpm); X-ray diffraction (Shimadzu X-ray Diffraction meter 04-XRD-6000); Scanning Electron Microscope, (SEM Micrographs VEGA3 TESCAN); Electric Balance; (Sartorius Lab-BL 210 S, Germany ± 0.0001g); Oven Equipment LTD, Green Field, NR OLDJAM, (20-360 C°) furnace; Forth Flotation cell; and Granulating Machine (GK Dry Granulating Machine).

Preparation of activated and Pure Attapulgite

Aqueous slurry containing 15% solid raw claystone was initially prepared using Najaf Iraqi Attapulgite-montmorillonite raw claystone sample. Homogenized clay slurry was prepared using high impeller speed 2500 rpm for 1 h. and was advantaged to increase its Attapulgite – montmorillonite content and cation exchange capacity (CEC) by attrition-scrubbing using Flotation Cell. The resulting solid was separated by centrifugation, washed five times with deionized water and dried at 100 °C for 24 hour.

The second step involves activation of 15% Attapulgite-montmorillonite slurry in distilled water (prepared from the first step dried clay), by treatment with H- form Amber light orange ion exchange at the molar ratio of 1:1, followed by agitation for 24 h. at 150 rpm and 60 °C using thermo- stated shaker bath (Alba Tch.). Clay suspension was separated from Amber light orange ion exchange granules using 75 μm sieve.

The resulting solid was separated by centrifugation washed five times with deionized water and dried at 100 °C for 24 hour. The third step involves the separation of the Attapulgite clay mineral from the associated Montmorillonite clay by addition of sodium methyl acrylate as a chemical dispersant to 15 % Attapulgite-montmorillonite slurry in distilled water (prepared from the second step dried clay), selectively disperse discrete, individual particles of Attapulgite while liberating other non-Attapulgite minerals such as Montmorillonite, Sepiolite, Bentonite, Calcium Carbonate, Silica and Kaolin, from in between the Attapulgite Bundles [8].

Then resulting solid was separated by centrifugation washed five times with deionized water and dried at 100 °C for 24 hour after shaping by a granulating Machin to 1 and 2 mm diameter granules. Finally, the dried pure H-Form Attapulgite granule was calcined at 900 °C using Muffle Furnace to be converted into non-dissoluble granules in aqueous and organic solutions [9].

Result and Discussion

FT-IR Characterization of Attapulgite Clay Samples

FT-IR spectrums of Attapulgite samples were shown in Figure 4.

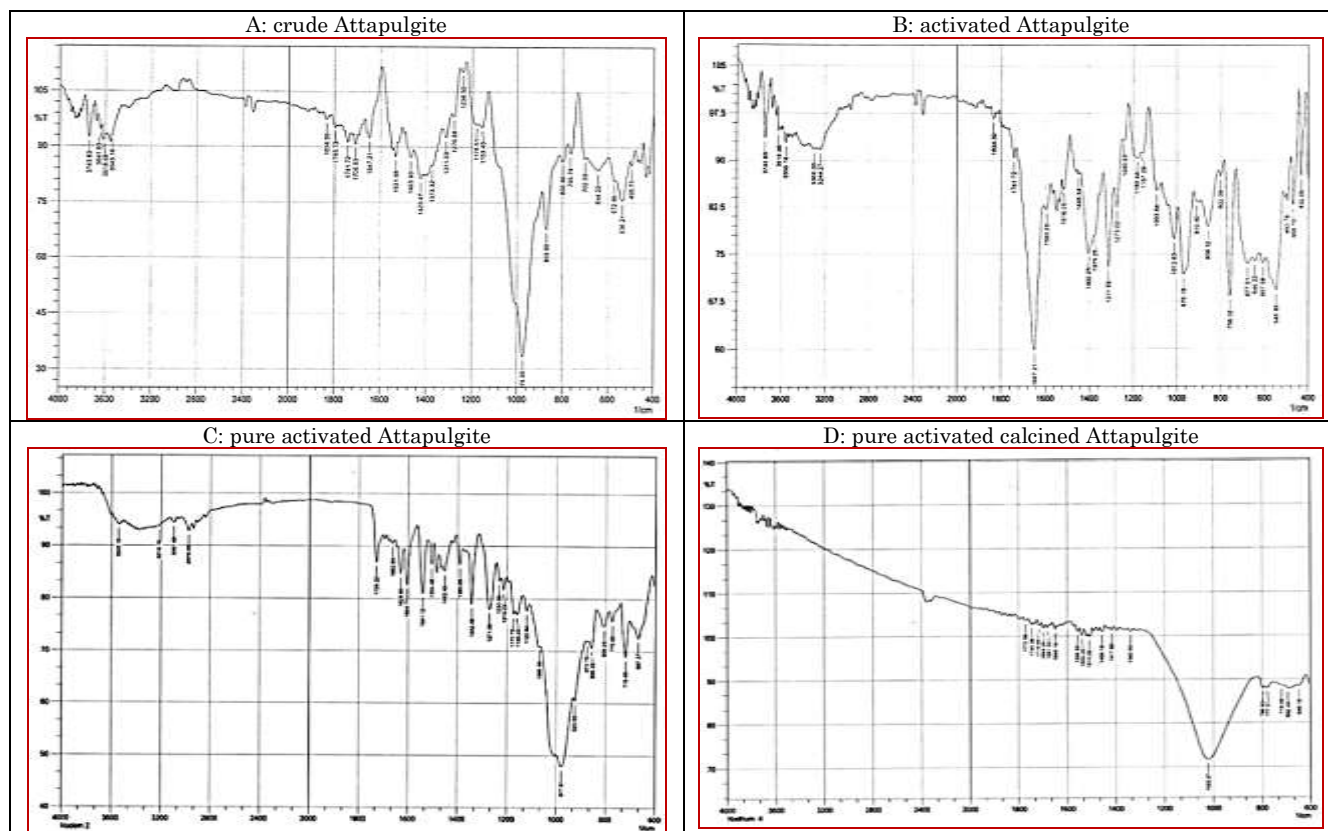


Figure 4: FT-IR of Attapulgite crude (A); activated Attapulgite (B); pure activated Attapulgite (C); and pure activated calcined Attapulgite

FT-IR Analysis of Crude Attapulgite Sample

The important peaks of active groups in Attapulgite crude FT-IR spectrum was involved in table 3, represent (3743 cm^{-1}), & (3641 cm^{-1}) peaks that refer to O-H bonded with H stretching; (3618 cm^{-1}) refer to O-H bonded with metal stretching (metal: Al, Fe,

& Mg); (3545 cm^{-1}) refer to H₂O coordinated; (1647 cm^{-1}) refer to H₂O adsorbed 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; and (702 cm^{-1}) refer to metal with O as oxide.

Table 3: 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 ₂ O coordinated	3545
H-O-H	H-O-H adsorbed	1647
Al ₂ O 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

FT-IR Analysis of Activated Attapulgite Sample

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; (3300 cm^{-1}) refer to O-H (H_2O) normal polymeric (stretching) as evidence of

entrance the water. Mg-O appears because of Montmorillonite prefund with Attapulgite M-O at (719cm^{-1}) like Al^{+3} , Fe^{+3} & Mg^{+2} .

Table 4: FT-IR spectrum of activated Attapulgite

Group	Mode of Vibration	vcm-1
-OH	Stretching (str.)	3743
-OH	Stretching (str.)	3618
-OH	Stretching(str.)	3641
H-O-H	H_2O coordinated(m)	3545
O-H	Normal polymeric(stretching)(str.)	3300
-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

FT-IR Analysis of Pure activated Attapulgite Samples

Due to addition of sodium methyl acrylate Attapulgite mineral was purified by floatation with the dispersed swelled sodium methyl acrylate granules leaving other impurities of clay mineral and sand in the bottom of the vessel. Therefore many peaks in FT-IR spectrum were disappeared comparing with the FT-IR spectrum of crud

material. Some peaks become strong because the structural composition of mineral did not change. (923 cm^{-1}) due to SiH_3 ; ($806, 820$ & 873cm^{-1}) for Si-O; (3545 cm^{-1}) due to Coordinated water stretching O-H (H_2O); (3219cm^{-1}) for H-O-H; bonded(stretching,($1662, 1650$ & 1629cm^{-1}) for Coordinated and absorbed water H -O-H.(1541cm^{-1}) due to Al_2O_3 bending; (1068cm^{-1}) for Mg-O bending; (719cm^{-1}) due to M-O bending.

Table 5: FT-IR-spectrum for 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	3097
H-O-H	Coordinated and absorbed water	1629,1650,1662
Al_2O_3	bending	1541
Si	Silicon	1604
O-SiO ₃	Asymmetric (Bending)	1120
Si-O-Si	Stretching	1159
Mg-O	bending	1068
-OH	bending	1020
O-SiO ₃	bending	977
SiH_3	bending	923
Si-OH	bending	806 ,820 ,873
M-O	bending	719

FT-IR Analysis of Pure activated calcine Attapulgite Samples

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° ; (1022.27cm^{-1}) for (Si-O) group become stronger and bordered due to calcining operation. (1539cm^{-1}) of Al_2O_3 bending was small because of water loos due to calcining. The above explanations indicate that a pure activated calcined Attapulgite was obtained as shown in Table 6.

Table 6: FT-IR spectrum of pure activated calcine Attapulgite

Group	Mode of Vibration	vcm ⁻¹
Al_2O_3	Bending (m)	1539
Si-O-Si	Stretching (str.)	1022.27
SiH_3	Twisting (m)	692

Powder X-ray diffraction Characterization of Attapulgite clay Samples

Powder X-Ray Diffraction of Attapulgite crude

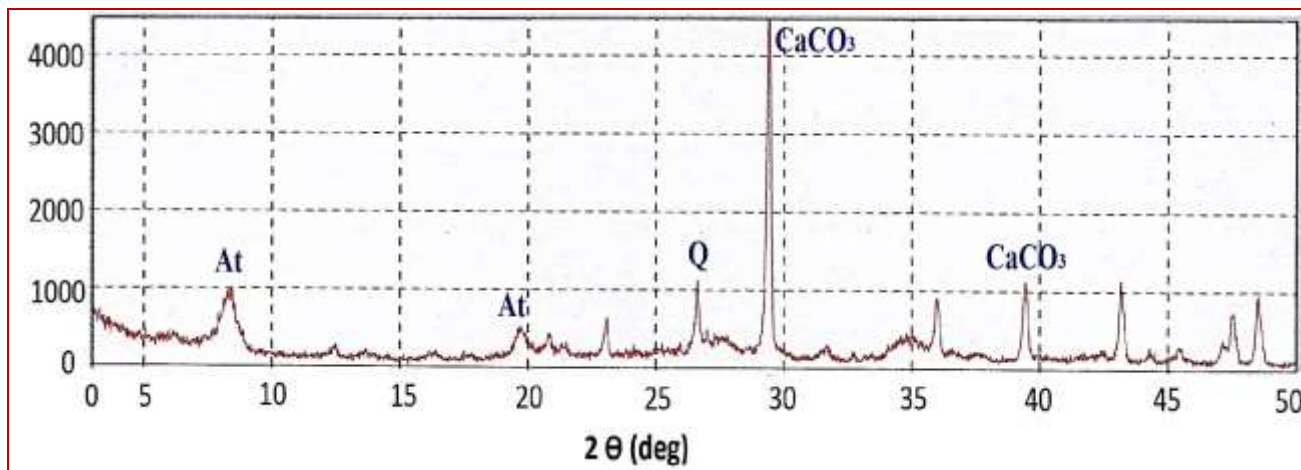


Figure 5: X-ray of Attapulgite crude

Table 7: X - ray diffraction peaks of Attapulgite crud

Compound or group	2θ (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

The peaks of Attapulgite appear at (8.5138, 20.8896)2θ (deg.); Quartz at (26.6684 2θ (deg.); Calcite at (29.4448)2θ (deg.). X- Ray diffraction spectrum shown in Figure5. Peaks in Table (7) with location and severity, [91, 127-128].The peaks explain presence of Attapulgite, quartz and calcite.

The comparison between the crude and the activated acetylate shows an increase in the absorption intensity of Attapulgite at (8.28819; & 6977) 2θ in X-ray diffraction spectra, due to the removal of impurities and high band gap due to high swelling, as shown in table 8, and Figure 6.

Powder X-ray Diffraction of activated Attapulgite

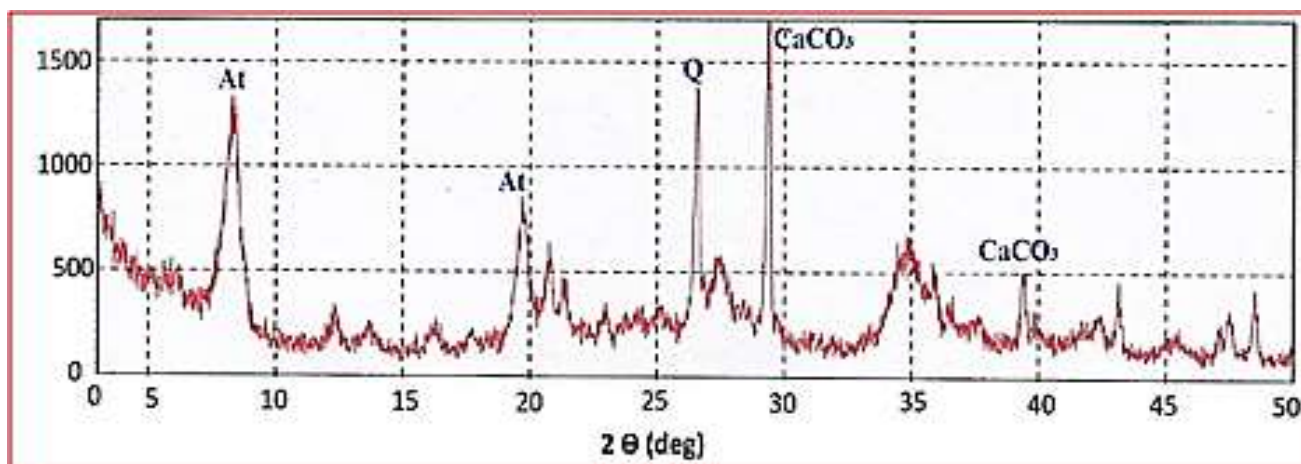


Figure 6: X-ray of pure activated Attapulgite

Table 8: x- ray diffraction spectrum peaks of activated Attapulgite

Compound or group	2θ (deg)	d(A)	I (C/Sec.)
Attapulgite	8.2880	10.65961	153
Attapulgite	19.6977	4.50337	91
Quartz	26.5660	3.35261	174
Calcite	29.3556	3.04006	235

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 7, and Table 9.

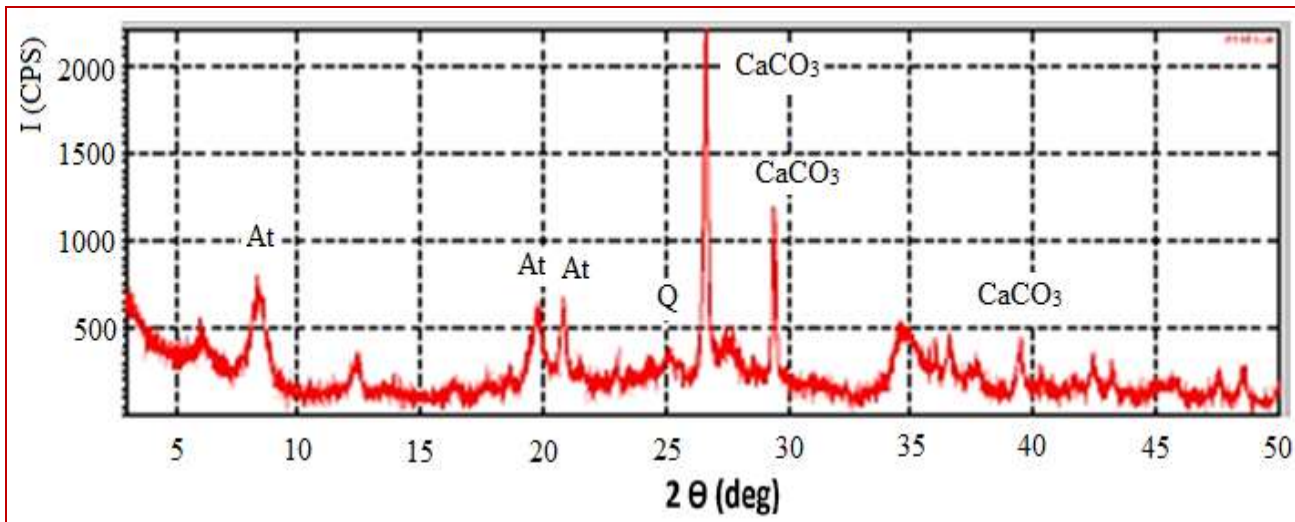


Figure 7: X-ray of pure activated Attapulgite

Table 9: x-ray diffraction spectrum peaks of pure activated Attapulgite

Compound or group	2θ (deg)	d(A)	I (C/Sec.)
Attapulgite	8.4347	10.47454	24
Attapulgite	8.6720	10.18844	19
Quartz	26.5584	3.35356	100

PXRD of a pure activated calcined Attapulgite

The Attapulgite peaks at (8.4347; 19.3471; & 20.7722) 2θ have a low intensity absorption

due to calcining process to high temperatures range 850-950 C° that leads to shrinking of the band gape of Attapulgite clay mineral, as shown in Figure 8 and Table 10.

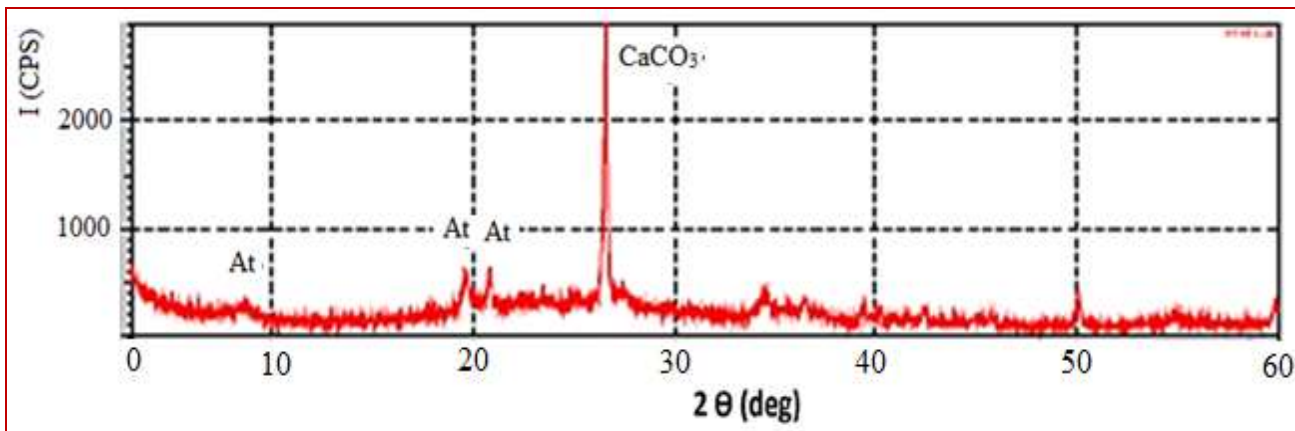


Figure 8: X-ray of pure activated calcine Attapulgite

Table 10: x-ray diffraction spectrum peaks of pure activated calcined Attapulgite

Compound or group	2θ (deg)	d(A)	I (C/Sec.)
Attapulgite	8.4347	10.47454	24
Attapulgite	19.3471	3.04092	50
Attapulgite	20.7722	4.27279	24
Quartz	26.5584	3.35356	100

Scanning Electron Microscopy (SEM) Characterization of Attapulgite clay Samples

SEM images of low and high magnification Figure 12 (1a, 1b, 1c, & 1d) of initiated H - form Attapulgite show a normal characteristic needle-shaped structure of Attapulgite Clay mineral, while in Figure 12 (2a, 2b, 2c, & 2d) 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. The calcined pure activated Attapulgite SEM images Figure 12 (3a, 3b, 3c, & 3d) show that the sharpness of needle-shaped structure was diminished due to the losing of the water of crystal lattice.

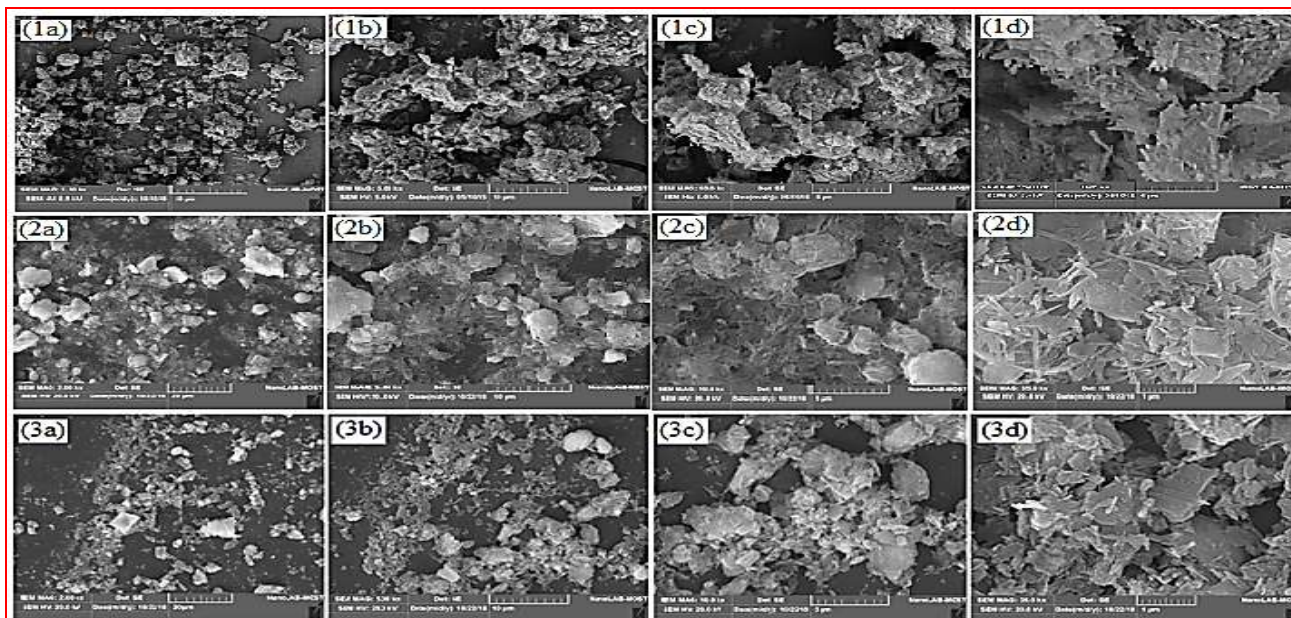


Figure 12: SEM images 1a, 1b, 1c, &1d of initiated H - form Attapulgite; 2a, 2b, 2c, 2d SEM images of pure activated Attapulgite; 3a,3b,3c, 3d SEM images of calcined pure activated Attapulgite

Conclusion

A new and efficient method was applied in our search lead to having high percent active H-form clay mineral and low percent of sand and impurities. Also applying a good published method of purification of attapulgite clay mineral [8] using sodium methyl acrylate increases the purity of Attapulgite clay mineral, and this is our goal in beneficiation of Attapulgite to increase its efficiency in removing impurities,

desulfurization, decolorizing, neutralizing, and deodorizing of petroleum fuel and other uses.

Acknowledgement

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