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Nano -Quartz Extraction from Acidic Activated Iraqi Bentonite

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Abstract

The purpose of this study is the activation of natural Iraqi bentonite that has been obtained from Wadi Bashira region, in the Western Desert of Iraq, to obtain the Nano particle sized then Nano-Quartz was extracted. This method included bentonite nano particles preparation by purification with HCl solution, calcination, the planetary ball mill to get bentonite in nanometer size and centrifugation to obtain the Nano-quartz. Results of quartz purification process were characterized by Fourier transforms infrared spectroscopy (FTIR), energy dispersive X-ray spectroscopy (EDS) and scanning electron microscope (SEM), particle size analyzer (PSA) and the X-rays diffraction (XRD). All tests have shown almost a clear decline in the proportion of the high-calcium in crude Iraqi bentonite in conjunction with an increase in high rates of silica in Quartz phase.

Keywords: Bentonite, Acidic activation, Rheological properties, nano-quartz**.**

استخلاص النانو كوارتز من البنتونايت العراقي المنشط حامضيا

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الخلاصة

الغرض من هذه الدراسة هو تفعيل البنتونيت العراقي الطبيعي الذي تم الحصول عليه من منطقة وادي بشيرة، في الصحراء الغربية من العراق، للحصول على حجم نانوي للجسيمات ثم استخراج النانوكوارتز. تم تنفيذ هذه الطريقة في إعداد جزيئات نانو عن طريق التنقية مع محلول حمض الهيدروكلوريك ، التكليس، مطحنة الكرات الكوكبية للحصول على البنتونايت بحجم النانومتر والطرد المركزي للحصول على نانو الكوارتز. وقد تميزت نتائج عملية تنقية الكوارتز بواسطة التحليل الطيفي للأشعة تحت الحمراء (FTIR)، مطيافية الاشعة السينية المشتتة للطاقة (EDS) والمجهر الإلكتروني الماسح (SEM)، محلل حجوم الجسيمات (PSA) و جهازحيود الأشعة السينية (XRD). وقد أظهرت جميع الاختبارات تقريبا انخفاضا واضحا في نسبة الكالسيوم العالية في البنتونيت العراقي الخام بالتزامن مع زيادة في معدلات عالية من السيليكا في طور الكوارتز.

Introduction

Clay belongs to a wider group of minerals such as bentonite, attapulgite, mica, kaolinites which have different molecular structures and are used in different purposes. However, in chemistry, all clay minerals may simply be described as hydrous silicates. These materials can be found in the nature from different sources and can also be synthesized in the laboratory. In terms of their natural locations, clay minerals can be divided into two classes: residual clay and transported clay (or sedimentary clay).

Residual clays are produced from the surface weathering of rock or shale (a dark fine-grained sedimentary rock composed of layers of compressed clay, silt, or mud) through various means, and they are generally found in the place of origin [1]. Residual clays could be produced by the chemical decomposition of rocks, i.e., granite containing silica and alumina; by the solution of rocks, i.e., limestone; and by the disintegration and solution of shale [1, 2]. The transported clay, the second type,

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is removed from the original deposit through erosion and deposited to a distant place. Bentonite is an aluminium phyllosilicate, generally impure clay consisting mostly of montmorillonite.

A particular feature of this group of minerals is the substitution of Si^{4+} and Al^{3+} in the crystal structure by lower valency cations [3].

1. Structure of clay minerals

Mineralogists use the term "clay minerals" for a group of hydrous layered magnesium- or alumino-silicates (phyllosilicates). The structures of the different clay minerals are based on two structural units, an octahedral layer and a tetrahedral layer [4].

1.1 Octahedral layer

This layer consists of two parallel planes packed with oxygen or hydroxyl. Octahedral sheets consist of edge-linked octahedra with OH in the corners and cations (R) in the center [5]. In the middle, with exactly the same distance to all the oxygen (or hydroxyl) a cation is located; this makes a octahedral structure. The cations are usually Al^{3+}, Mg^{2+}, Fe^{2+}, but all other transition elements and Li are possible [6]. When Al^{3+} is in the center, only 2/3 of the positions are filled and the structure is called gibbsite with formula $Al_2(OH)_6$. With Mg^{2+} in the center all the positions are filled and the structure is called brucite with formula $Mg_3(OH)_6$. Then the octahedral sheets can be described as composed of two planes of closest-packed hydroxyls with cations occupying the octahedral sites between the two planes [5, 6].

1.2 Tetrahedral layer

This layer consists of tetrahedrons with oxygen or hydroxyl in all four corners and a silicon (Si) atom in the center.Tetrahedral sheets consist of corner-linked tetrahedra with oxygens in the corners and cations (T) in the centre. By sharing corner oxygen (or hydroxyl) several silicon tetrahedra can combine and make larger structures, like the hexagonal structure. Dominant cation is Si^{4+}, but Ae^{3+} is substituted for it frequently, up to half of the Si. Fe^{3+} is substituted for Si^{4+} occasionally; T/O ratio is T_2O_5 [6]. The tetrahedra rest on a triangular face and share all three oxygens with three other tetrahedra. The sheet of linked tetrahedra has hexagonal symmetry [7]. The fourth, apical, oxygen atoms downward from the base [6].

1.3 Montmorillonite

Montmorillonite is composed of two sheets of silica tetrahedral with an octahedral sheet in the center, the tips of the tetrahedrons point in the same direction towards the center of the structure [7]. The structures are stacked with the O layer of one tetrahedron-octahedron-tetrahedron unit facing the O layer of another unit. This result in a very weak bond and a separation between the units, the main feature of the montmorillonite structure is that water or other polar molecules can enter between the unit layers and cause the montmorillonite to expand in the vertical direction [8].

Experimental method

Collection and preparation of samples

In this work Sampling of bentonite from the western region of Iraq. High grade calcium montmorillonite claystone (calcium bentonite) sample from Wadi Bashira region, supplied by the Bentonite Grinding Mill until 75µm; obtained from the State Company for Geological Survey and Mining (Iraq). Through assays were performed and previous research, the Iraqi bentonite in that region are calcium enriched [9]. The bentonite used in this study was calcium bentonite powder.

Bentonite Sample Purification Process

In the beginning it was sieving bentonite samples taken from State Company for Geological Survey using a Sieve Shaker,of type Retsch AS 200 with (52µm) sieve. Each amount of grinding for 20 minutes was determined by the time adjuster. After that, Bentonite product from sieving was milled using planetary ball mill. The mill used type of Retsch (PM 100 cm), Balls with a diameter of 1 cm was used. The speed of rotation of the device set at 400 rpm and for four hours of grinding to get to the more finer bentonite. To eliminate impurities of iron ratios of natural bentonite magnets was used. After that it has been sieved again by Sieve Shaker with (38µm) sieve. Product of sieving and milling process was treated chemically to get activated bentonite.

Bentonite Activation Processes

This process has succeeded in getting on the size of the nano-bentonite, but failed to activate the bentonite to be used in the drilling fluid. The reason for its failure was due to the weak rheological properties of the liquid product and that compared to the properties of the American Petroleum Institute API. The slurry mud of bentonite showed low viscosity in spite of higher Particles suspension in solution.A summary of process is to identify the changes in the surface properties of bentonite after acid activation, using hydrochloric acid solutions (HCl) at room temperature. After reaching the granular size 38µm by milling and sieving, the hydrochloric acid was used to remove impurities of aluminum. Hydrochloric acid in bentonite into the mix in a bowl with the proportion of bentonite: hydrochloric acid solution, 1:10, using a magnetic stirrer for 2 hours at room temperature until homogeneous. Different concentrations where used to dilute the hydrochloric acid and the best of these ratios were 73 ml of acid per 1000 ml of distilled water. According to the above mentioned ratio 10 g of bentonite was added for every 100 ml of solution. Then separates the hydrochloric acid solution bentonite using filter paper, then do washing using distilled water and re-washing several times until neutral PH. Bentonite resulting from filtration was dried in the sun, after that calcination process for dry bentonite under the temperature of 600 C for 2 hours in high-temperature resistance furnace.

Re-grinding the resulting bentonite using planetary ball mill (PM 100) again for 10 hours intermittently to obtain natural bentonite nanometers in size as illustrated in Figure-1. The aim of reaching to this smaller size to facilitate the process of disposal of the high percentage of calcium in the natural bentonite, and to facilitate the replacement process of ionic calcium sodium bentonite to obtain active Na-Bentonite.

Figure 1- acidic activated bentonite.

Results and Discussion

Analysis morphology of nano particle natural bentonite

Particle size analyzer was used to measure the diameters of inactive natural bentonite particles obtained from the State Company for Geological Survey and Mining (Iraq). Figure-2 shows the measurements results of the particle diameters for a natural bentonite sample which illustrates magnitudes of the average diameter of the bentonite sample particles (45.6, 51.8) µm, while the particle size distribution from the smallest to largest size is 0.166 to 3080µm.

After grinding and sieving processes, the analysis results of the particle sizes of natural bentonite sample have shifted, where the magnitude of the average diameter of the particles of bentonite sample has become (18.7, 21.2) µm, while the particle size distribution from the smallest to largest size is 0.145 to 76 µm as shown in Figure-3.

The shift occurred as a result of the use of 38µm mesh sieve, and it's purpose to create a larger surface area during the activation process.

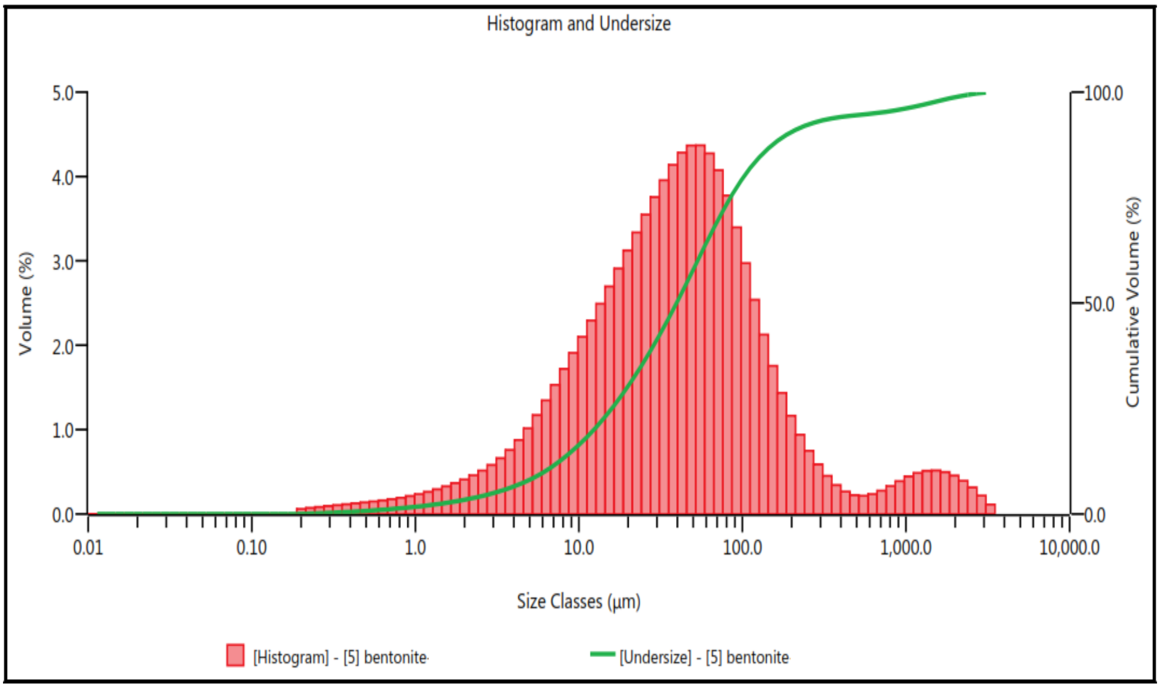


Figure 2- Size of Natural Bentonite Use Particle Size Analyzer (PSA).

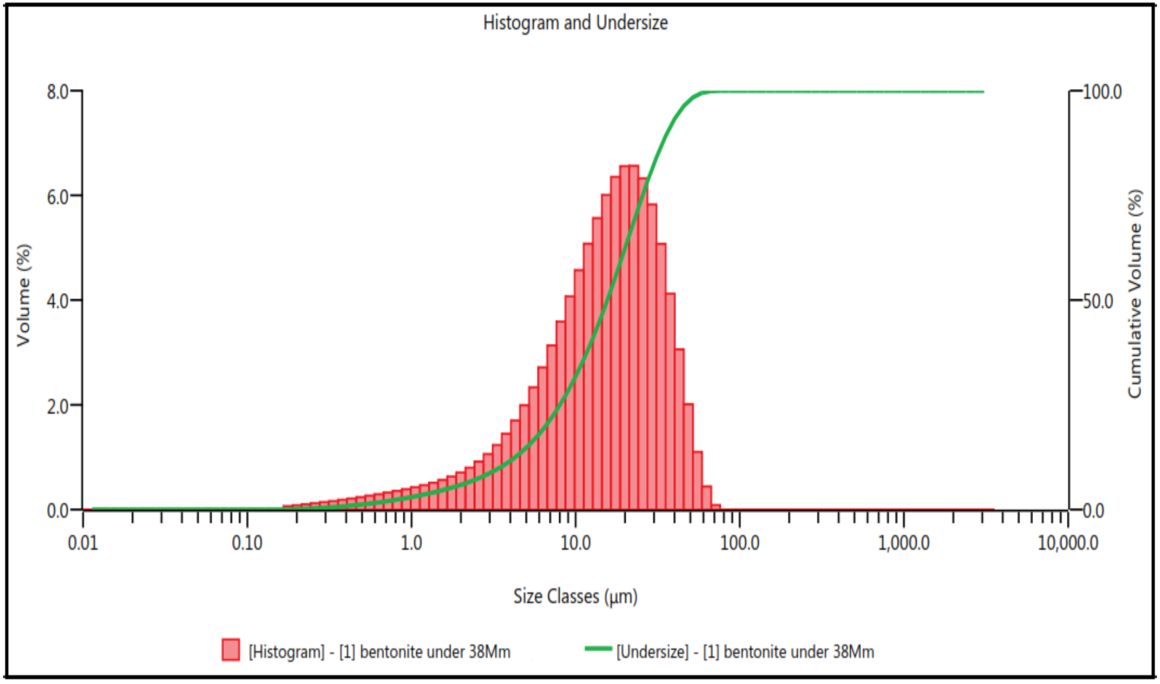


Figure 3- Size of Natural Bentonite using Particle Size Analyzer (PSA) after grinding and sieving processes**.**

X-ray Diffraction

X-ray diffraction has been studied for testing samples which explained the chemical composition befor and after activation. From the X-ray diffrograms the planes orientation; particulate size and miller indices (hkl) of bentonite samples were calculated. Figure-4 shows the results of X-ray measurements of natural Bentonite. The strongest three peaks resulted from the test observed at ($2\Theta^{\circ}$ = 22.2745, 26.7237 and 15.5144) and that correspond to (020), (101) and (001). From these results we have obtained and compared with the Standard X-ray Diffraction Powder Patterns that could be obtained a natural bentonite components in consistent with data achieved by others [2].

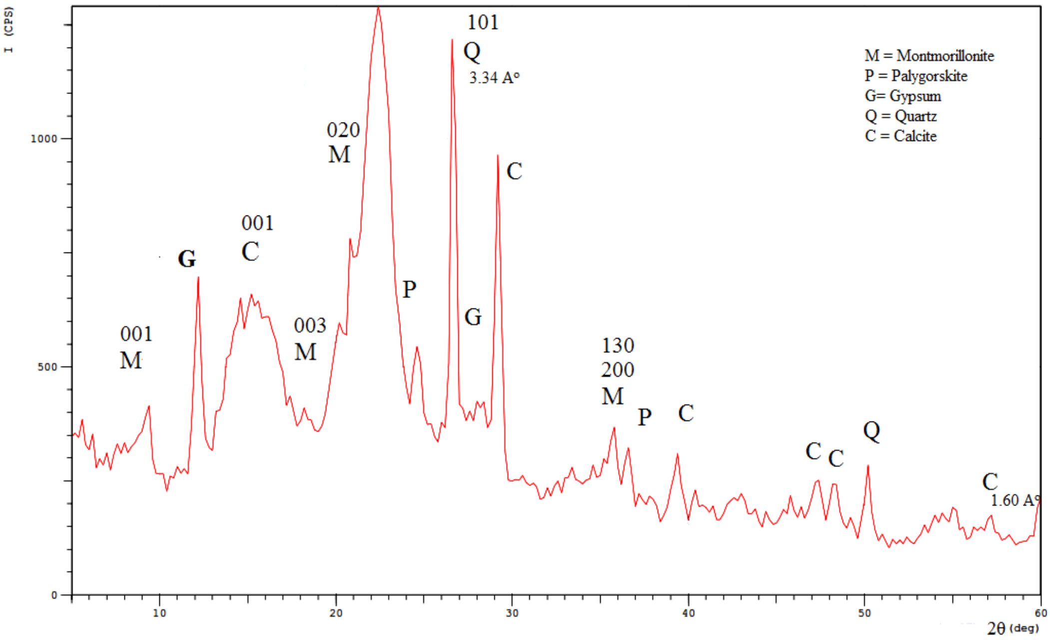


Figure 4- XRD pattern of natural bentonite sample

Table-1 summarizes the obtained values of 2θ, d, average particulate size and miller indices (hkl) for natural bentonite sample. Despite a visibly good crystallinty, many reflections are missed from their diffraction patterns, as shown in Figure-4.

Table 1- Analysis of the XRD study of natural bentonite

Sample	2θ(degree)	d (A^o)	(hkl)	Particulate size A^o	I/I_o
Natural Bentonite	22.2745	3.98789	020	2.32223x10^{-8}	100
	26.7237	3.33319	101	5.79828 x10^{-8}	40
	15.5144	5.70696	001	2.50414 x10^{-8}	36

The results of X-ray diffraction measurements of an acidic activated bentonite sample showed a significant decrease in calcium ratios which are available in natural bentonite, which were offset by High suspension of bentonite particles in the water. However, the bentonite resulting from the acidic activation process did not give the required properties to work as a drilling fluid according to the API, but it can be said that it is an excellent way to get nano-quartz as illustrated in the Figure-5.

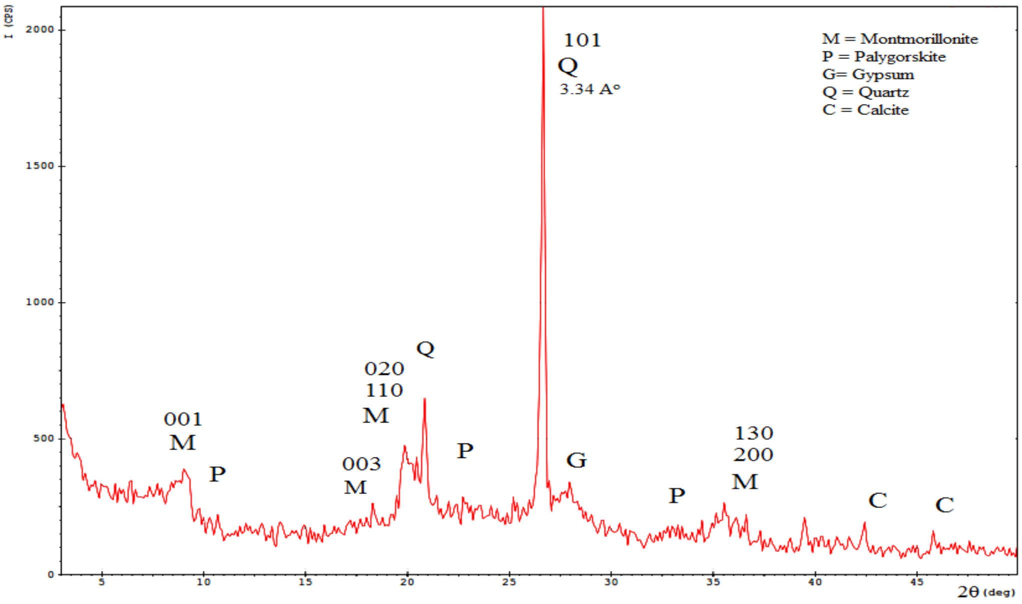


Figure 5- XRD pattern of acidic activated bentonite sample.

The strongest three peaks resulted from the test observed at ($2\Theta^\circ$ = 26.6689, 20.8749 and 19.9168) and that correspond to (101), (020,110) and (003). A comparison between Figure-4 and 5 shows that the height of the quartz became a magnitude of ($I/I_\circ$=100) in Figure-5 after it was equal to ($I/I_\circ$=40) in Figure-4, as well as calcium ratios, which was in a calcite form decreased in activated bentonite for what it was in raw bentonite. Calcite is a mineral composed of calcium carbonate, $CaCO_3$, one of the weak water-soluble salts. High rates of weak water-soluble salts like calcite and gypsum found in abundance in bentonite Iraqi natural has become a very few in the bentonite activated acidic as illustrated by Figure-5. This explains why higher suspension happened to particles of bentonite and in spite of this, it did not live up to the characteristics of the API as mentioned previously.

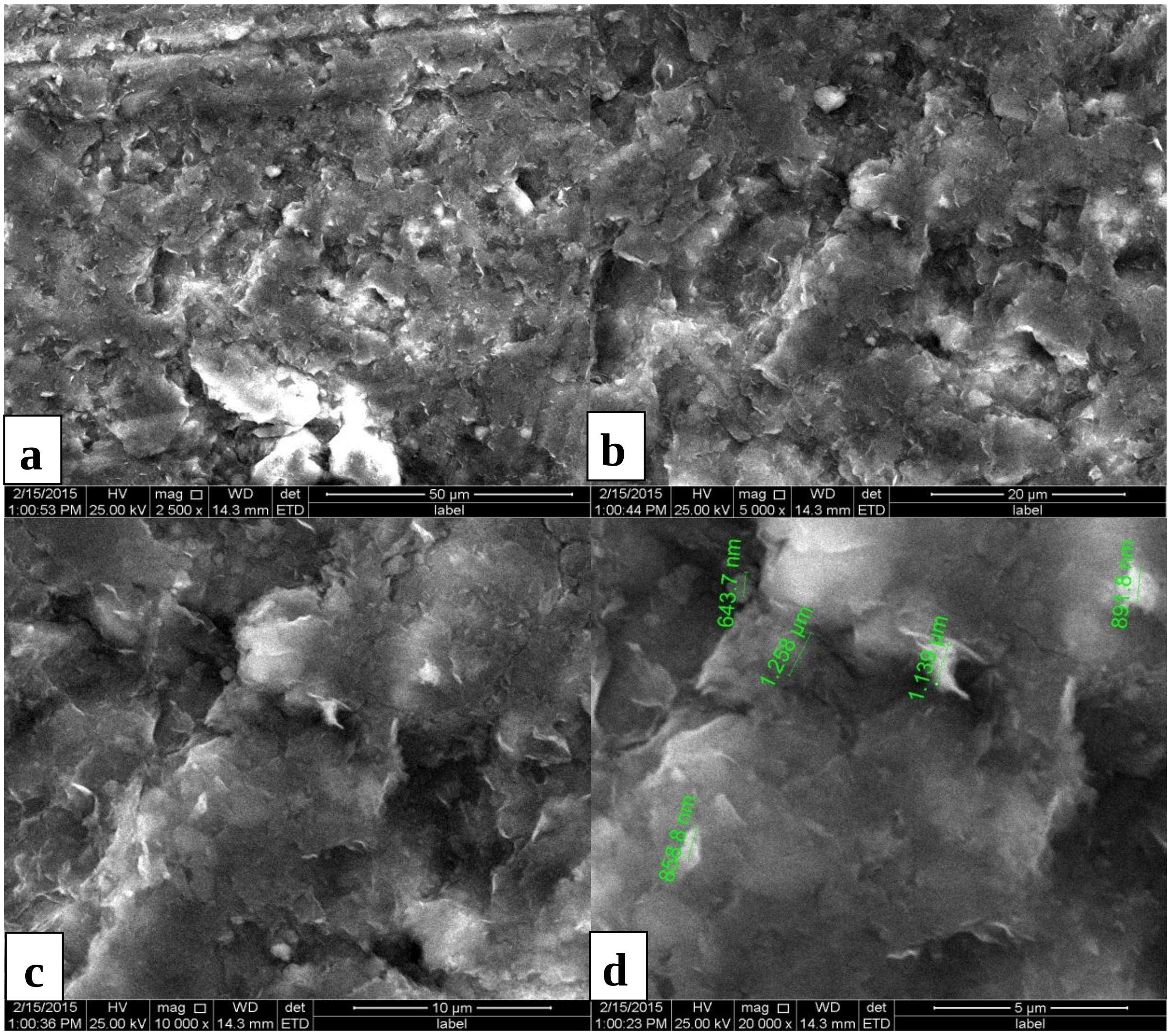
In Table-2 accurate volumes can be observed, for the bentonite by the dominated peak of ($2\Theta^\circ$ =20.8749), which corresponds to (020, 110) of Montmorillonite.

Table 2- analysis of the XRD study of acidic activated bentonite.

Sample	2θ(degree)	d (A°)	(hkl)	Particulate size A°	$I/I_\circ$
Acidic activated bentonite	26.6689	3.33991	101	3.93759×10^{-8}	100
	20.8749	4.25200	020 110	1.029762×10^{-7}	25
	19.9168	4.45432	003	2.00425×10^{-8}	17

Scanning Electron Microscope (SEM) Analysis

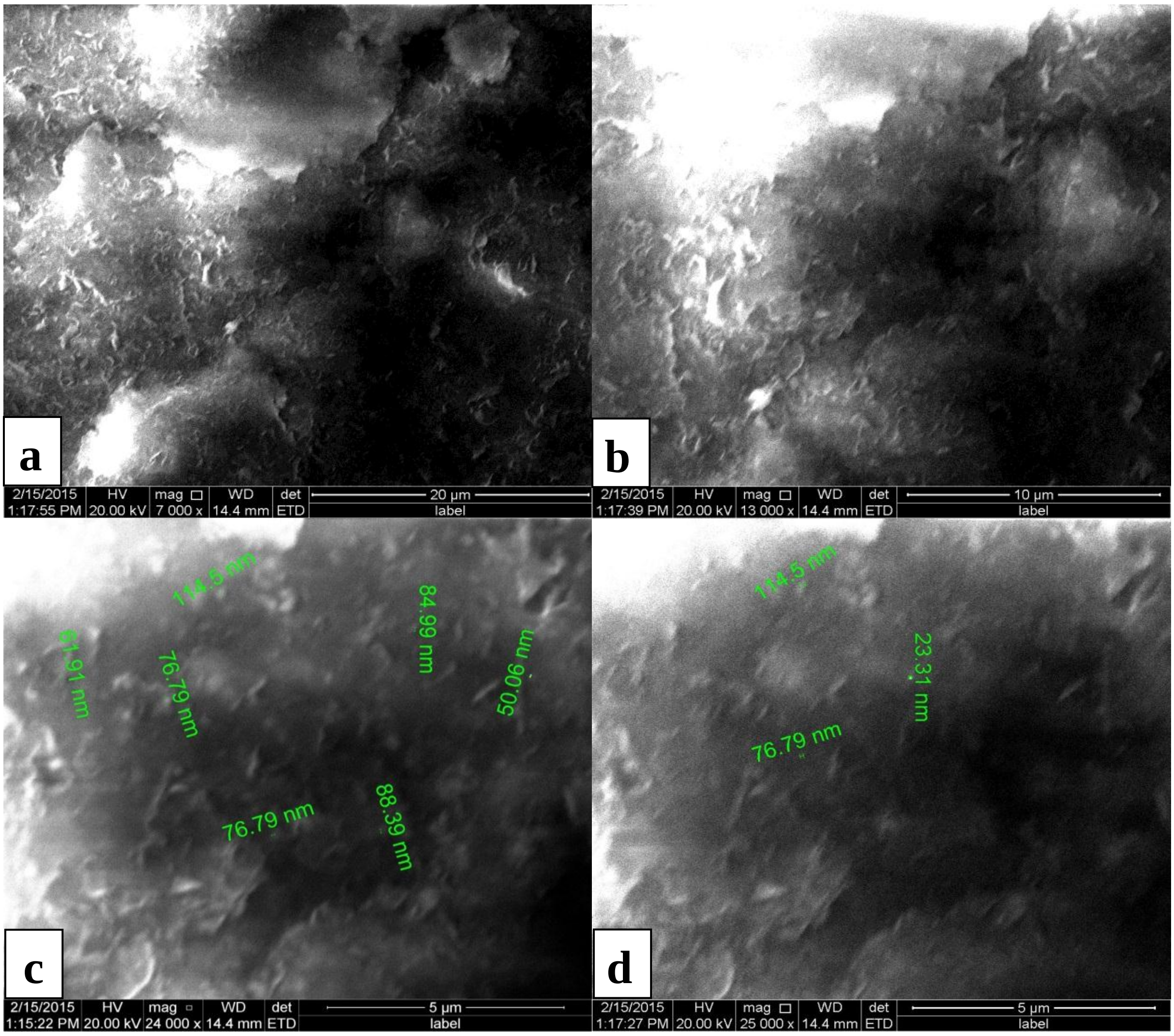
Scanning electron microscope illustrates morphological observations of natural bentonite sample surface, that was formed like alumenium silicate mineral surface morphology of bentonite particles with a magnification of 2500, 5000, 10.000 and 20.000 as shown in Figures-6(a, b, c, d) respectively.



Figures 6 (a, b, c, d) - Microstructure Particle of Natural Bentonite.

These figures can show natural bentonite sample consists of diverse phases, distributions and color contrast too. Aluminum silicate mineral has a majority element content of aluminum (Al) and silicon (Si) [3]. This is confirmed by the EDX results showed that the energy spectrum arises are Calcium (Ca), Aluminum (Al), Silicon (Si), and others as it will be mentioned later.

Acid activated bentonite morphological observations illustrated through Figures-7 (a, b, c and d) with a magnification of 7000, 13.000, 24.000 and 25.000 respectively.



Figures 7 (a, b, c, d) - Microstructure Particle of Acidic Activated Bentonite.

Through Figures-7 (c and d) it is clears the particle has become smaller size compared with the volumes in Figure-6d, This is in consistent with previous results of research with respect to Nano-sized particles of acidic activated bentonite as demonstrated by Figures-7(c and d). Results revealed by the electron scanning microscope consistent with the X-ray diffraction test results for acidic activated bentonite sample.

Analysis of Energy Dispersive Spectroscopy (EDS)

This test allowed to identify the chemical composition of natural bentonite (raw material) and activated bentonite. From Figure-8 can be seen natural bentonite that shows very high percentages of calcium components. This is in consistent with previous research notes, as instructed in earlier research for the cause of the weakness of rheological properties of natural bentonite to the high proportion of calcium.

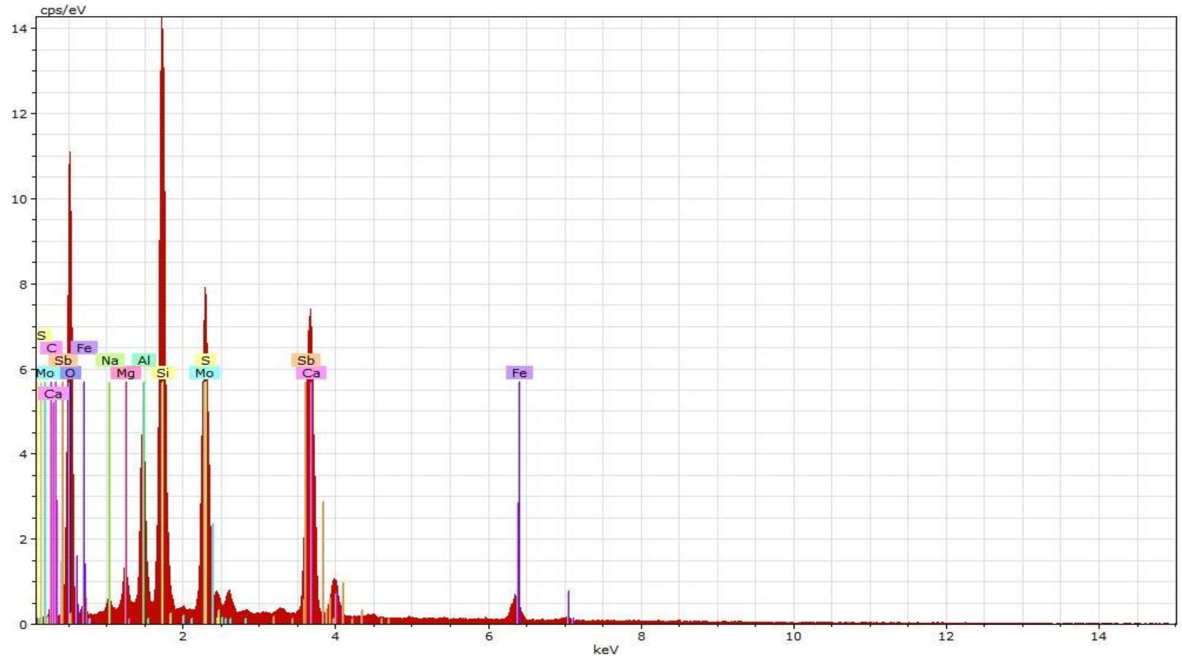
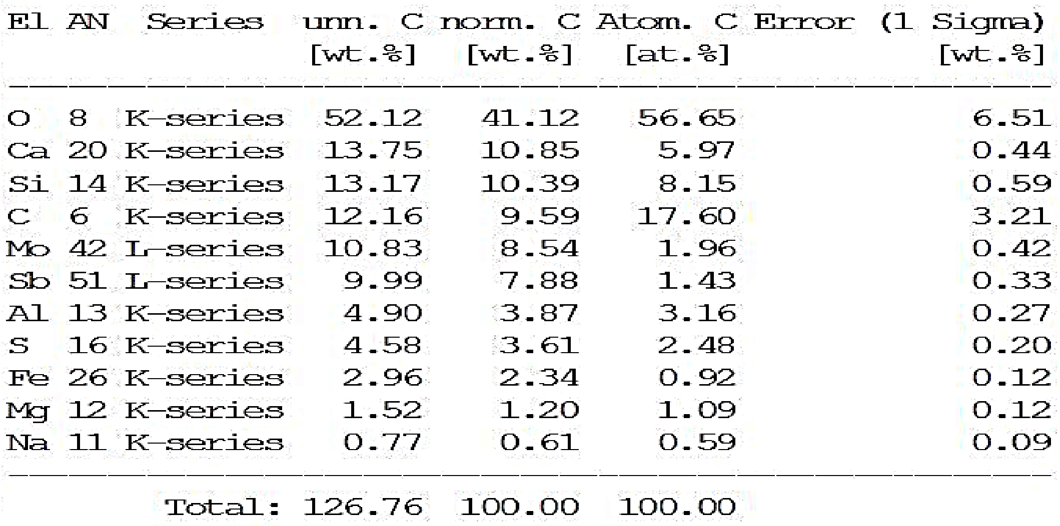


Figure 8- Energy Dispersive Spectroscopy of natural bentonite (raw material).

The most abundant element in the Iraqi natural bentonite is silicon as illustrated in Figure-8. These results are in consistent with the X-ray diffraction analysis. At least the remaining percentages are for other metals like aluminum, iron, magnesium, etc., as noted by the shape that the ratio is at least sodium and these ratios can be seen from Table-3 accurately.

Table 3- chemical composition quantitatively of natural bentonite by (EDS).



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El AN  Series   unn. C norm. C Atom. C Error (1 Sigma)
                 [wt.%]  [wt.%]   [at.%]          [wt.%]
-----------------------------------------------------
O   8  K-series  52.12   41.12   56.65            6.51
Ca 20  K-series  13.75   10.85    5.97            0.44
Si 14  K-series  13.17   10.39    8.15            0.59
C   6  K-series  12.16    9.59   17.60            3.21
Mo 42  L-series  10.83    8.54    1.96            0.42
Sb 51  L-series   9.99    7.88    1.43            0.33
Al 13  K-series   4.90    3.87    3.16            0.27
S  16  K-series   4.58    3.61    2.48            0.20
Fe 26  K-series   2.96    2.34    0.92            0.12
Mg 12  K-series   1.52    1.20    1.09            0.12
Na 11  K-series   0.77    0.61    0.59            0.09
-----------------------------------------------------
         Total: 126.76  100.00  100.00
```

EDS test results of acidic activated bentonite sample showed a decrease in the proportion of calcium than exists in the natural bentonite, which explains the longest time suspension in the water. Longer period of suspension happened for bentonite particles as a result of which the proportion of calcium decline occurred as it illustrated in Figure-9.

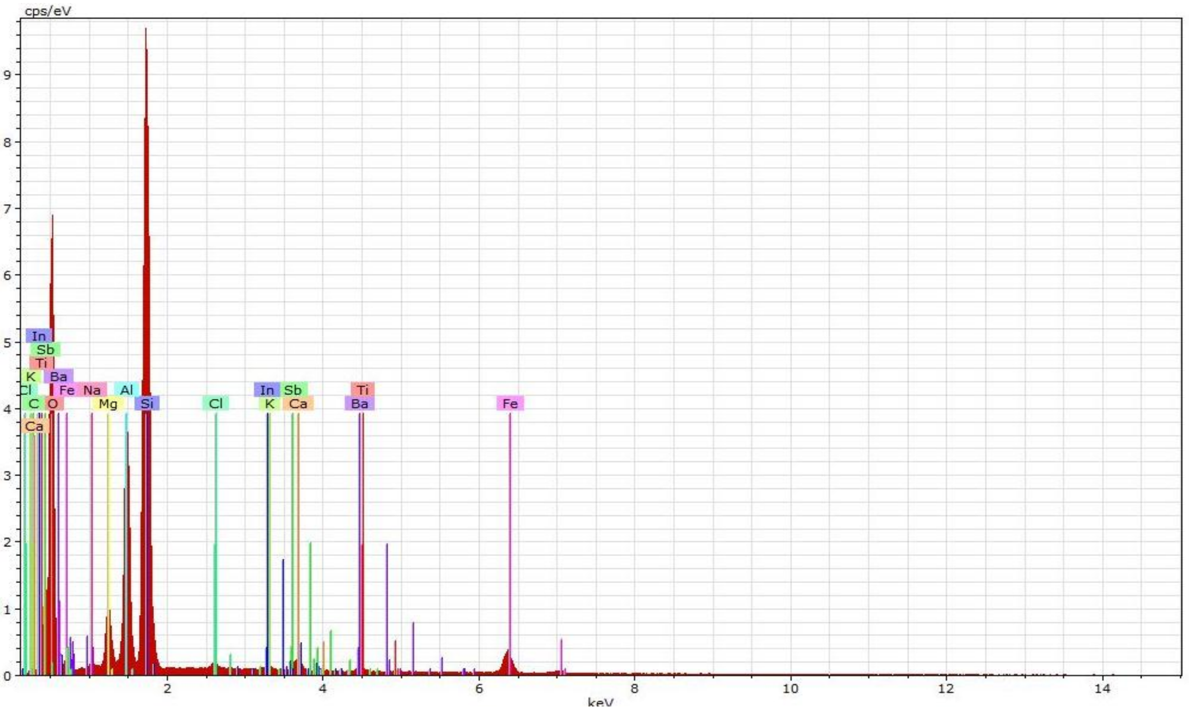
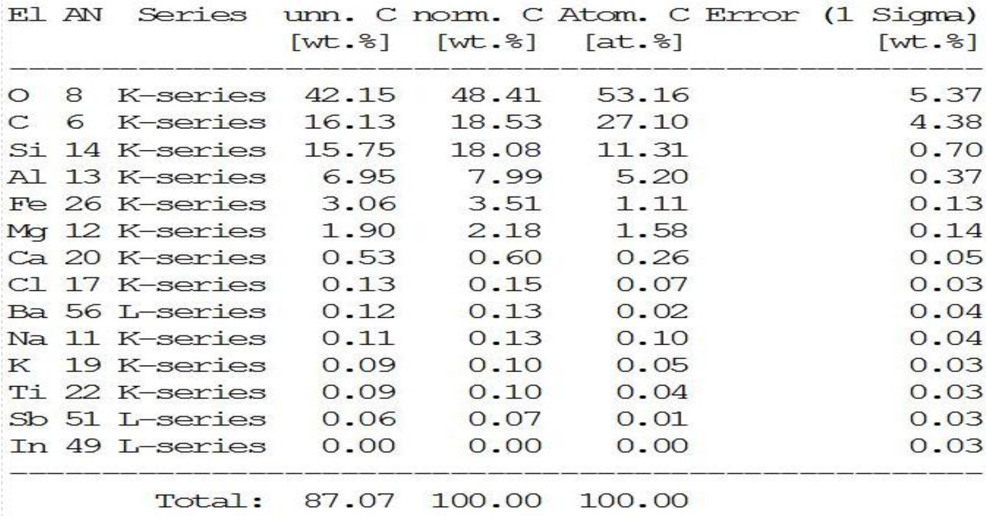


Figure 9- Energy Dispersive Spectroscopy of Acid Activated bentonite by (EDS).

In spite of the comment period has increased, but it did not give the desired results of the rheological properties. From Table-4, we find that the proportion of silicon has increased obviously compared to the rest of the elements of what makes it a successful method to extract silicon and especially after the burn where a quartz phase became very clear.

Table 4- chemical composition quantitatively of acidic activated bentonite (EDS).



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El AN  Series   unn. C norm. C Atom. C Error (1 Sigma)
                [wt.%]  [wt.%]  [at.%]           [wt.%]
-----------------------------------------------------
O   8  K-series  42.15   48.41   53.16             5.37
C   6  K-series  16.13   18.53   27.10             4.38
Si 14  K-series  15.75   18.08   11.31             0.70
Al 13  K-series   6.95    7.99    5.20             0.37
Fe 26  K-series   3.06    3.51    1.11             0.13
Mg 12  K-series   1.90    2.18    1.58             0.14
Ca 20  K-series   0.53    0.60    0.26             0.05
Cl 17  K-series   0.13    0.15    0.07             0.03
Ba 56  L-series   0.12    0.13    0.02             0.04
Na 11  K-series   0.11    0.13    0.10             0.04
K  19  K-series   0.09    0.10    0.05             0.03
Ti 22  K-series   0.09    0.10    0.04             0.03
Sb 51  L-series   0.06    0.07    0.01             0.03
In 49  L-series   0.00    0.00    0.00             0.03
-----------------------------------------------------
        Total:   87.07  100.00  100.00
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Fourier Transforms Infrared Spectroscopy (FTIR):

The absorption of infrared radiation by clays was recorded over a range of 4000 to 400 cm^{-1} as shown in Figures-10 and -11 for natural Iraqi bentonite and acidic activation bentonite samples respectively. Natural Iraqi bentonite FTIR spectrum Figure-10 showed adsorption band at 3628.22cm^{-1} (Al-Al-OH) (Mg-OH-Al) corresponding to starching vibration of structural OH groups coordinating to Al-Al pair or Mg-OH-Al. Adsorbed water gives a broad bands from 4300.29 cm^{-1} to 3533.59 cm^{-1} corresponding to H_2O-stretching vibration. Al, Mg bound water molecules gives H-O-H stretching vibration band at 1637cm^{-1}. The broad band around 1035 cm^{-1} belongs to Si-O stretching vibration. Finally the complex bands from 430.00 cm^{-1} to 528.51 cm^{-1} are related to Al-O-Si, Si-O-Si deformations [10,11].

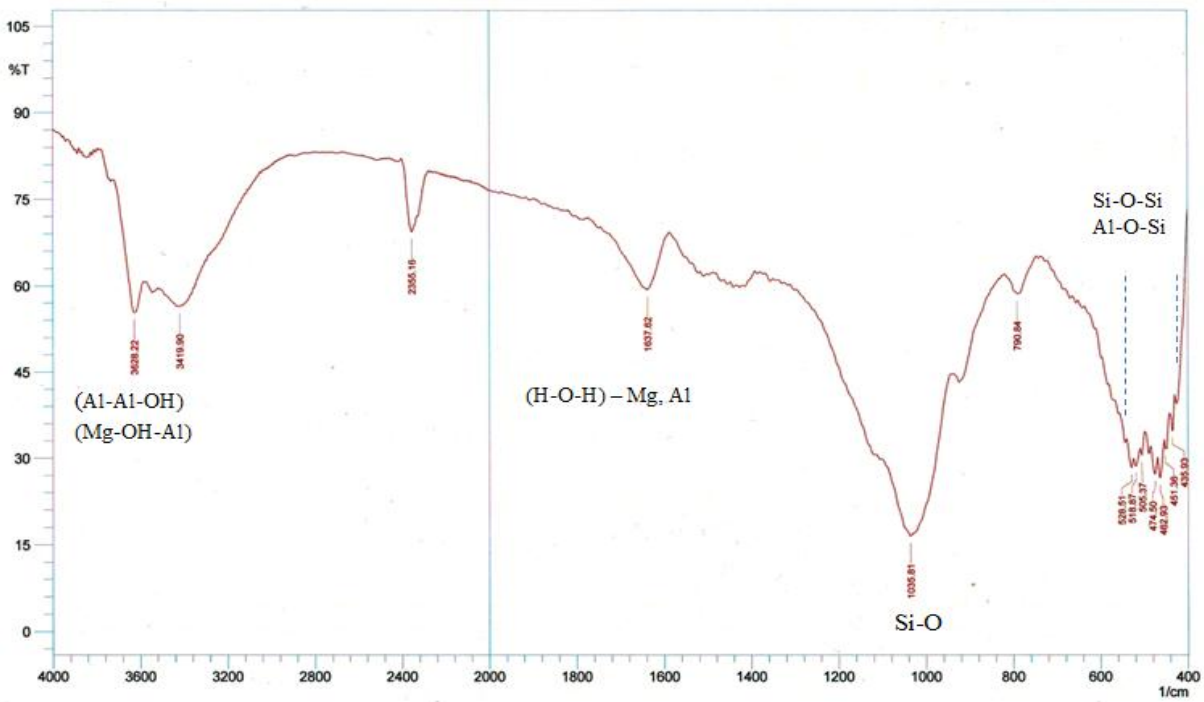

Figure 10- FTIR spectrum for naturl crude Iraqi bentonite.

Burned acidic activated Iraqi bentonite FTIR spectrum of Figure-11 showed the same bands of that in Figure-10, but sharper and with higher transmittance percent, also the band of adsorbed water become a single band at 3612.79 cm^{-1} mostly due to burning process and the same thing happen with band Al, Mg bound water molecules gives H-O-H stretching vibration band at 1637.62 cm^{-1}.

Also four bands at 1737.92, 1523.82, 1419.66 and 1317.43 cm^{-1} corresponding to H...O...H are weak. The broad band around 1026.16 cm^{-1} belongs to Si-O stretching vibration. The quartz characteristics band from 920.08 cm^{-1} to 509.22 cm^{-1} becomes boarder. Finally Al-O-Si, Si-O-Si and Si-O stretching vibration bands around 428.21 cm^{-1} are found [6,10,11].

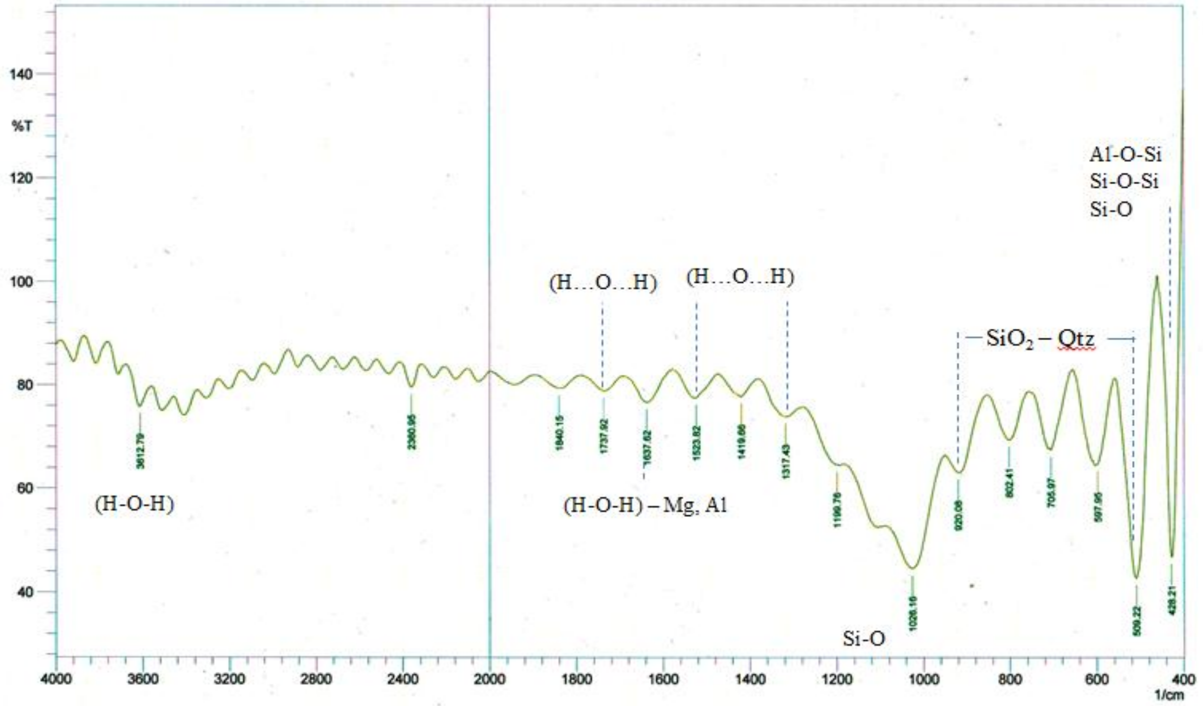

Figure 11- FTIR spectrum for acidic activated bentonite sample.

Conclusion:

The acidic activation process succeeded as a way to extract pure nano-quartz from natural Iraqi bentonite according to the results of the tests. The amount volumes produced of Nano-quartz was large, In contrast the acidic activation process led to significantly reduce in high calcium content in Iraqi bentonite. Calcination process greatly assisted to transformation of the silicon content of Iraqi bentonite to the quartz phase

References:

1. Zahra Darvishi and Ali Morsali. **2011**. Synthesis and characterization of Nano-bentonite by sonochemical method. *Ultrasonics Sono Chemistry Journal*, 18, pp:238-242.
2. Abdul Wahab A. Al-Ajeelt, Jassim M. Kshash and Saly N. Mahdi. 2013. Sodium Activation of Iraqi High Grade Montmorillonite Claystone By Dry Method. *Iraqi Bulletin of Geology and Mining*, 9, pp:65-73.
3. Nurdin Bukit, Erna Frida and Mukti Hamjah Harahap. **2013**. Preparation Natural Bentonite in Nano Particle Material as Filler Nanocomposite High Density Poliethylene (HDPE). *Chemistry and Materials Research*, 3(13).
4. Togan Uskarci. **2006.** Behaviour of Bentonite Suspensions In Non-Aqueous Media, M.Sc. Thesis, Mining Engineering, Middle East Technical University.
5. Hans Erik Tveit. **2012**. Evaluation of Bentonite as an Alternative Sealing Material in Oil and Gas Wells. M.Sc. Thesis, Department of Petroleum Engineering and Applied Geophysics Norwegian University of Science and Technology, p:77.
6. Liisa Carlson. **2004**. Bentonite Mineralogy", Working Report -02. Geological Survey of Finland. Olkiluoto, Finland.
7. S.D. Inglethorpe, D.J.Morgan, D.E.Highley and A.J.Bloodworth. **1993**. Industrial Minerals Laboratory Manual Bentonite. Technical report WG/93/20 Mineralogy and Petrology Series, British geological survey.
8. Youngsoo Jung , Matthew Barry, Jung-Kun Lee , Phuoc Tran , Yee Soong , Donald Martello, and Minking Chyu. **2011**. Effect of Nanoparticle-Additives on the Rheological Properties of Clay-Based Fluids at High Temperature and High Pressure. *The American Association of Drilling Engineers*, pp:12-14.
9. Abdul Wahab A. Al-Ajeel, Wasan A. Muslimand and Mayada S. Joodi. **2011**. Bloating characteristics of low grade ca-montmorillonite claystone and the effect of some additives. *Iraqi Bulletin of Geology and Mining*, 7(2), pp:57− 67.
10. Omar S. Alkhazrajy, Mohammed H. Abdul Latif and Maha A. Al – Abayaji. **2012**. Adsorption of Metoclopromide Hydrochloride onto Burned Initiated Iraqi Bentonite. Journal of Al-Nahrain University, 15 (2), pp:35-46.
11. Mahasneh, M. A. and Saleh, S. K. **2012**. Evaluation of Jordanian Bentonite Performance for Drilling Fluid Applications. *Contemporary Engineering Sciences*, 5, pp:149 – 170.