

## Beneficiation Pretreatment and Chemical Activation Method For Preparation and Characterization of Nano Structure Bentonite

The 5<sup>th</sup> International Scientific Conference for Nanotechnology and Advanced Materials and Their Applications ICNAMA 2015 (3-4) Nov.2015

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### ABSTRACT

Bentonite has widely been employed in many industrial applications due to their physicochemical properties and availability at low cost. The aim of this work was conducted to submit the Iraqi natural bentonite clay to beneficiation pretreatment and chemical acidification using 60% sulfuric acid under mechanical agitation for 2 hours at atmospheric temperature and pressure condition. The resulting bentonite was washed several times with distilled water and modified with ethanol under ultrasonic mixing. An experimental study was conducted to study the chemical composition, grain size, structural characterization and morphology of nano particle bentonite obtained using techniques of AFM microscopy, X-ray fluorescence XRF, X-ray diffraction XRD, scanning electron microscopy SEM, surface area by BET method, and FT-IR spectra.

The calculated surface area of nano bentonite was 161.842 m<sup>2</sup>/gm, and total pore volume of 0.2196 cm<sup>3</sup>/gm. The nanoscale bentonite particles diameter in the range of 52 nm at maximum intensity of AFM. The FITR spectra assigned peaks; at 3392.22 and 1635.69 cm<sup>-1</sup> is attributed to OH stretching (Al-OH and Si-OH) for bentonite, at 1159, 798.20 and 677.46cm<sup>-1</sup> are assigned to characteristic bands of silicates; and peak at 500.08 cm<sup>-1</sup> is responsible for Al-O-Si group deformation. SEM analysis show that nano bentonite structure due to beneficiation and activation conditions. The results of X-ray diffraction after activation observed that the intensity of the reflections of the characteristic peak of the gypsum and calcite belonging to the other minerals change due to destruction of the structure in the bentonite phases.

**Keywords:** Bentonite, Beneficiation, Acid Activation, Nano Bentonite

### استخدام المعالجة والتنشيط الكيماوي لتحضير ودراسة خصائص بينتونيت نانوي

#### الخلاصة

يستخدم البنتونيت في تطبيقات صناعية عديدة نتيجة لخواصه الكيميائية والفيزيائية ولتوفره بكميات كبيرة وتكاليف منخفضة. ان الغرض من هذه الدراسة هو تحضير بنتونيت نانوي من خام البنتونيت العراقي باستخدام معالجة رفع الجودة والتنشيط الكيماوي بحامض الكبريتيك ذو تركيز 60% ولفترة ساعتين عند درجة الحرارة

الاعتيادية والضغط الجوي. لقد تم غسل البنتونايت الناتج عدة مرات بالماء المقطر وتم معاملته مع الايثانول باستخدام الخلاط الفوق صوتي. اجريت دراسة مختبرية للتركيب الكيميائي، حجم الدقائق، خصائص التركيب الداخلي والمورفولوجي للدقائق النانوية باستخدام تقنيات ميكروسكوب القوى الذري، تفلور بالاشعة السينية، حيود الاشعة السينية، المجهر الماسح الالكتروني، المساحة السطحية، قياس طيف الاشعة الحمراء. لقد كانت المساحة السطحية  $161.842 \text{ m}^2/\text{gm}$  وحجم المسامات الكلي  $0.2196 \text{ cm}^3/\text{gm}$ . القطر النانوي لدقائق البنتونايت عند اقصى شدة لل AFM هو  $52 \text{ nm}$ . لقد اشر طيف FITR عند  $392.22$  و  $1635.69 \text{ cm}^{-1}$  لل OH (Al-OH and Si-OH) وعند  $1159, 798.20$  و  $677.46 \text{ cm}^{-1}$  اشترت لاصرة السيلكات وعند  $500.08 \text{ cm}^{-1}$  للمجموعة Al-O-Si. لقد بينت صور الماسح الالكتروني SEM الشكل النانوي للبنتونايت نتيجة عملية رفع الجودة والتفاعلات الكيماوية. حيود الاشعة السينية X-ray diffraction ايضا بينت التغيرات في اطوار البنتونايت بعد المعالجة.

## INTRODUCTION

Recently, the nano clay materials application developers a new capabilities across many fields of science, engineering and medicine. Nano scale materials have a relatively larger surface area per mass. This can make materials more chemically reactive, and affect their strength or surface properties. Bentonite due to their unique enhanced physical, mechanical, chemical, and thermal properties are expected to offer better solutions for changing the structure and properties of many materials and tend to designing active composite materials for many applications ie. asphalt emulsifiers, ceramics, construction and civil engineering, household cleaners, industrial coatings, oil and gas drilling, wastewater treatment, etc. [1].

The demand for good quality bentonite clay were attributed to the variation of particle size, shape and their composition from montmorillonite clay [2]. The presence of clay minerals in appreciable amounts, such as elites, clients, chlorites and non-clay components such as quartz and feldspar will have an adverse effect on bentonite quality. Beneficiation of bentonite is an important process to remove impurities and to improve their properties to desired quality [3]. The chemical acidification method is widely used in preparation of bentonite for bleaching or as a catalytic material in the oil industry[4,5]. Acidification mechanism takes place by cation exchange with H ions and reject Al and other cations outside of the sites and at the same time leaving the  $\text{SiO}_4$  groups largely unchangeable [6,7,8].

The aim of this study was done to prepare and characterize nano scale bentonite.

## Experimental Method

### Sample Collection And Preparation:

Bulk samples of the bentonite clay were supplied from National Company for Iraqi geological and mining. The bentonite beneficiation were carried out in two stages [9]; samples were milled, screened, washed with distilled water and dried at  $105 \text{ }^\circ\text{C}$  for 3 hr to remove moisture and volatile organics from the clay. The resulting material was then dispersed in deionised water, agitated and allowed to settle for one day. The clear liquid was decanted and the clay re-suspended into reaction flask with 60% concentration sulfuric acid in weight ratio bentonite/acid equal to 0.5 for a time of 2 hr at ambient temperature with magnetic stirrer. The suspension was filtered and washed from excess acid using distilled water. For modifying bentonite, 20 g was dispersed in 200 mL of ethanol under ultrasonic mixer for 32 hr and  $40^\circ\text{C}$ . The clay produced was dried in oven at  $105 \text{ }^\circ\text{C}$  for 3 hr and kept at room condition for milling for a period of 15 hr using Ball Miller Retsch PM 400 to size nano scale particles[10].

**Chemical Analysis:**

Chemical composition of bentonite was expressed as mass percentages of different components of its total mass. Shimadzu X-ray fluorescence was carried out to determine the chemical analysis. Since the results shown in Table (1).

**BET Surface Area Analysis:**

The specific surface area of the bentonite particles were analyzed by BET N<sub>2</sub> method using Micomeritics ASAP 2020 analyzer.

**Scanning Electron Microscopy (SEM):**

The morphology and particle size of the bentonite was examined by using Angstrm Advanced Com scanning electron microscope (SEM). Micrographs were taken at 16 kV with a working distance in range 6.541-6.591 mm.

**X-ray diffraction (XRD):**

X-ray diffractometry was used to identify crystalline mineral phases of bentonite. Mineralogical composition for bentonite before and after beneficiation pretreatment was determined by X-ray diffraction (XRD) using shimadzu x-ray diffraction with CuK $\alpha$  radiation ( $\lambda=1.54060$  A).

**FTIR spectra**

Infrared spectroscopy is a best suitable method for measurement based on the absorption of FTIR in the chemical bonds related to the mineral composition. This method gives some information of the amorphous compounds present [11]. FTIR spectroscopy was used to obtain qualitative group for bentonite. The spectra were recorded on Bruker model working with the requirements of EMC Directive 2004/108/EC and low voltage Directive 2006/95/EC. Figures (4) shows spectra were recorded in the range of 400-4000 cm<sup>-1</sup> with resolution of 4 cm<sup>-1</sup>.

**RESULTS AND DISCUSSION****Chemical composition**

Bentonite is the one of the smectite group, composed of layers (called 2:1 layer) made up of two silica tetrahedral sheets with a center alumina octahedral sheet [12]. In acid activation, the acid attacked the smectite flakes and releasing octahedral cation such as Ca<sup>2+</sup>, Mg<sup>2+</sup>, Fe<sup>3+</sup>, Al<sup>3+</sup> and these cation dissolve in the solution [13, 14]. From table 1, the acid activation induced a significant decreasing of the octahedral cation whereas, SiO<sub>4</sub> increase after activation.

From Tabel (1), it can be seen that the natural bentonite has a mass ratio SiO<sub>2</sub>:Al<sub>2</sub>O<sub>3</sub> = 3.37 less than nano bentonite (10.99). The higher percent of SiO<sub>2</sub> and lower percent of Al<sub>2</sub>O<sub>3</sub> gives an indication of this sample having less amount of Montmorillonite and may be declared as poor quality Bentonite [15]. The acid activation induced a significant decrease of Fe<sub>2</sub>O<sub>3</sub> content from 6.56 to 5.68%; also the SiO<sub>2</sub>, MgO, Al<sub>2</sub>O<sub>3</sub> contents decreased.

**Table 1: Chemical Composition of Natural and Nano Bentonite**

material	MgO	SO <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	LOI
Natural bentonite	3.81	0.54	15.21	6.47	51.33	6.56	14.2
Nano bentonite	2.24	0.03	6.79	1.50	74.44	5.68	18.9

**BET analysis**

The surface area and pore volume of natural and nano bentonite are reported in Table (2). The calculated surface area nano bentonite was 161.842 m<sup>2</sup>/gm, total pore volume of 0.2196

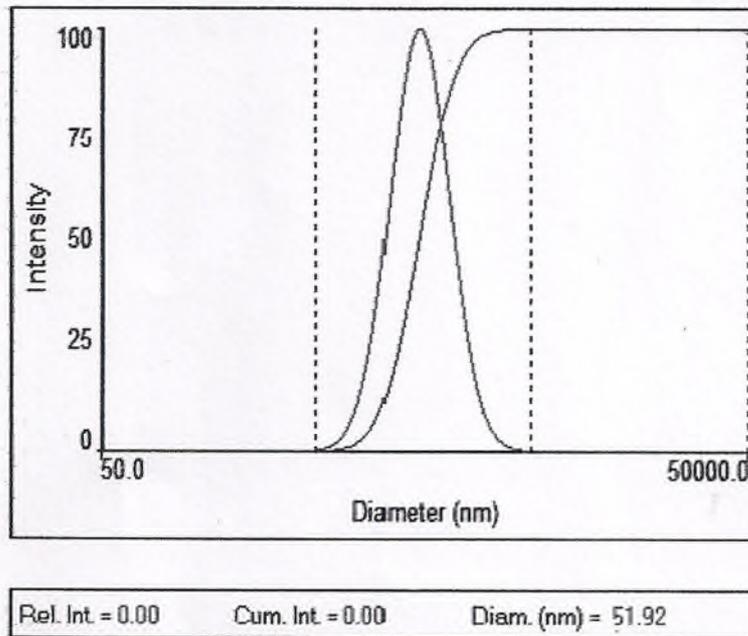
cm<sup>3</sup>/gm. The nanoscale bentonite particle diameter in the range of 52 nm at maximum intensity of AFM as shown in Figure (1). BET analysis shows that the surface area of nano bentonite increased to 161.842 m<sup>2</sup>/gm comparing with that of natural bentonite, 52.2 m<sup>2</sup>/gm. Because of the depletion of the cation from interlayer also, the dissolution of cation such as (Ca<sup>2+</sup>, Mg<sup>2+</sup>, Fe<sup>3+</sup>, Al<sup>3+</sup>), led to the structural deformation and then increase surface area [13, 14]. Also the pore volume of nano bentonite increased to 0.2196 cm<sup>3</sup>/gm comparing with that of natural bentonite, 0.0593 cm<sup>3</sup>/gm because of the partial dissolution of exchangeable cation such as Ca<sup>2+</sup>, Fe<sup>3+</sup>, Al<sup>3+</sup> from 2:1 layer of the smectite mineral [13]. The high surface area and pore volume arise from the conversion of layer structure to porous product.[16]

**Table 2: Surface Area and Pore Volume of Natural and Nano Bentonite**

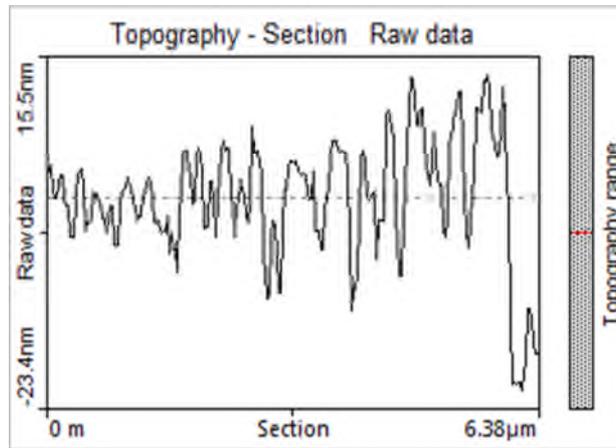
Material	Surface area m <sup>2</sup> /GM	Pore volume cm <sup>3</sup> /GM
Natural bentonite	52.2	0.0593
Nano bentonite	161.842	0.2196

**Atomic Force Microscopy AFM:**

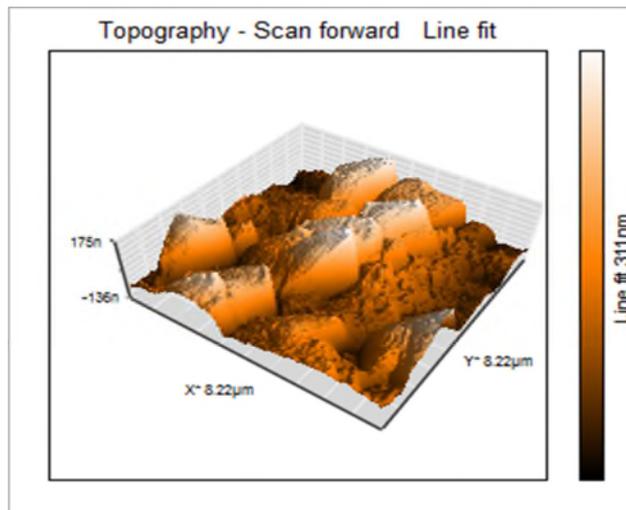
AFM is one of the important parameter to characterize clay size, and shape of single layer [17,18]. An investigation of three-dimensional structure of nanoscale bentonite by AFM detected differences in their structure. Many layer have an irregular shape. The largest layer in Figure (2) is ~5µm. The highest of the monolayer along a horizontal line in the AFM images are shown in figure (2). Over the length of the line (6.38 µm), the top of the magnolia is at ~15 nm and bottoms at ~0 nm. The latter corresponds to the dark spots in the Figure (3), which are a parts of the substrate not being covered with bentonite layer. While the white particles in the AFM image have a highest of ~175 nm.



**Figure (1) Intensity The Nanoscale Bentonite vs Particles Diameter.**



Figure(2): Topography Section of Nano Bentonite Use AFM



Figure(3): AFM micrograph from the Surface Structure of Nanoscale Bentonite

### FTIR Spectrum of Bentonite Clay

The spectra of the clays were measured in the range of 650 to 4000  $\text{cm}^{-1}$ . Fig.4 is the spectrum of bentonite clay used in this research. The peaks marked are assigned as follows: The peaks at 3392.22 and 1635.69  $\text{cm}^{-1}$  is attributed to OH stretching (Al-OH and Si-OH) for bentonite respectively[19,20]. The peaks at 1159, 798.20 and 677.46 $\text{cm}^{-1}$  are assigned to characteristic bands of silicates which are mostly related to stretching vibrations of M -O (where M = Si, Al) [19,21] respectively. The peak at 500.08  $\text{cm}^{-1}$  is responsible for Al-O-Si group deformation.

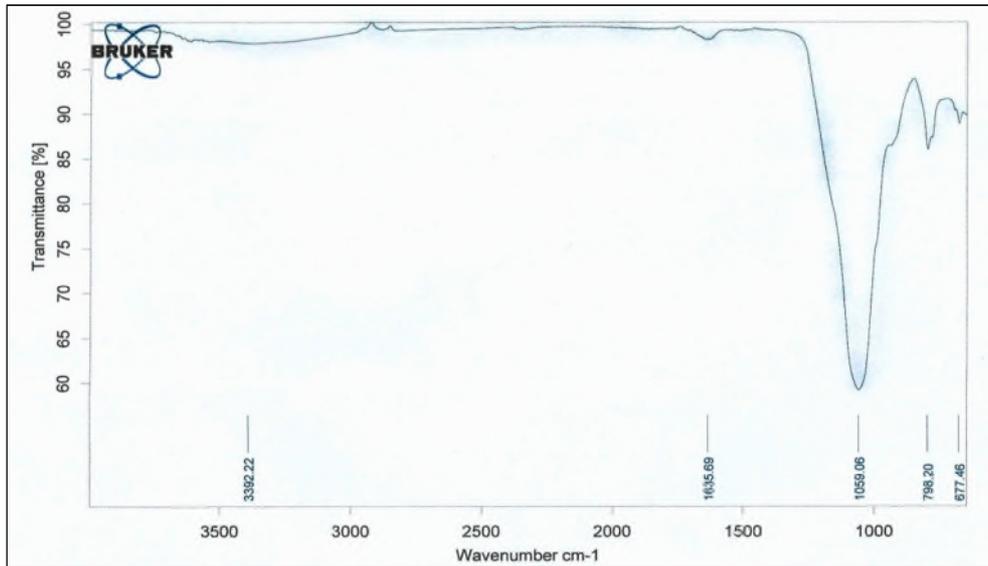
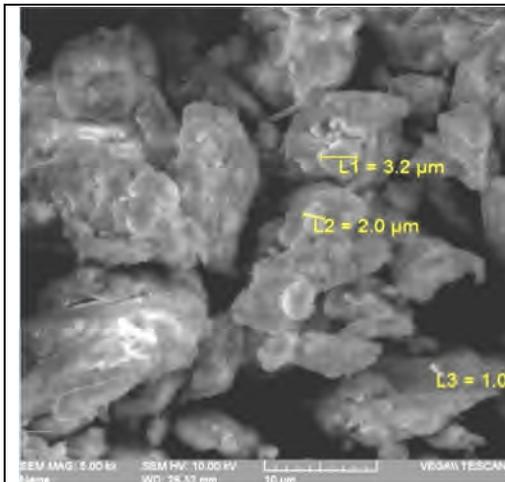


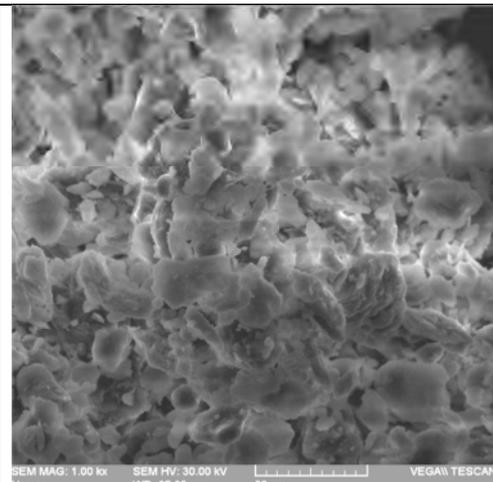
Figure (4) Spectrum of Bentonite

#### Scanning Electron Microscopy (SEM)

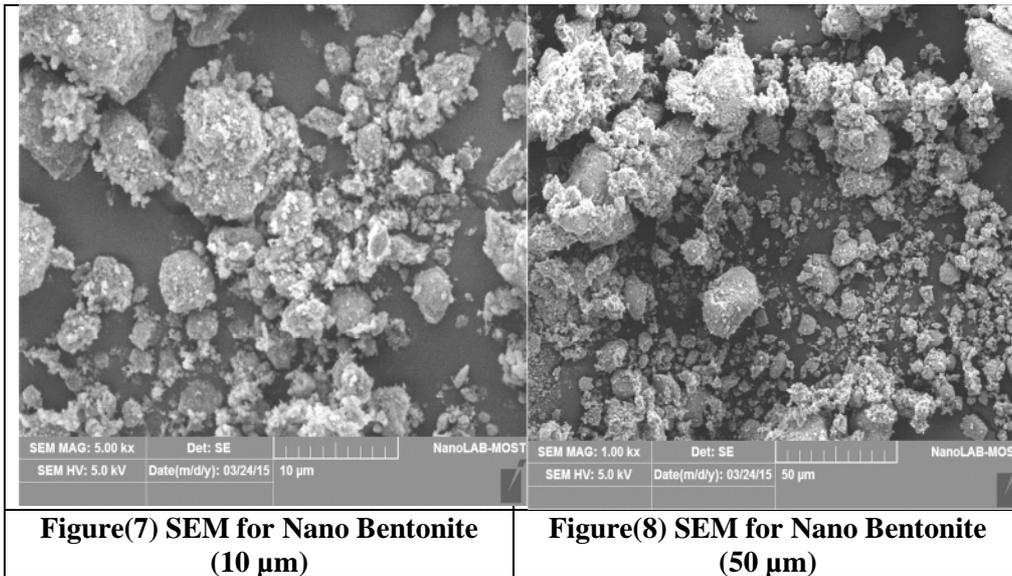
Figure (5-8) shows that the comparison of SEM micrographs which represent the shape and surface morphology of natural and nano bentonite in the range of 10 and 50  $\mu\text{m}$ . According to the figures it can be indicates that the micro scale of bentonite particles with irregular clusters and non uniform in nano structure. A high percentage showed semispherical particles appeared to be greater than size. The results show that the most particles size with different form, since micro and nano scale particles due to beneficiation and activation conditions



Figure(5) SEM for Bentonite (10  $\mu\text{m}$ )

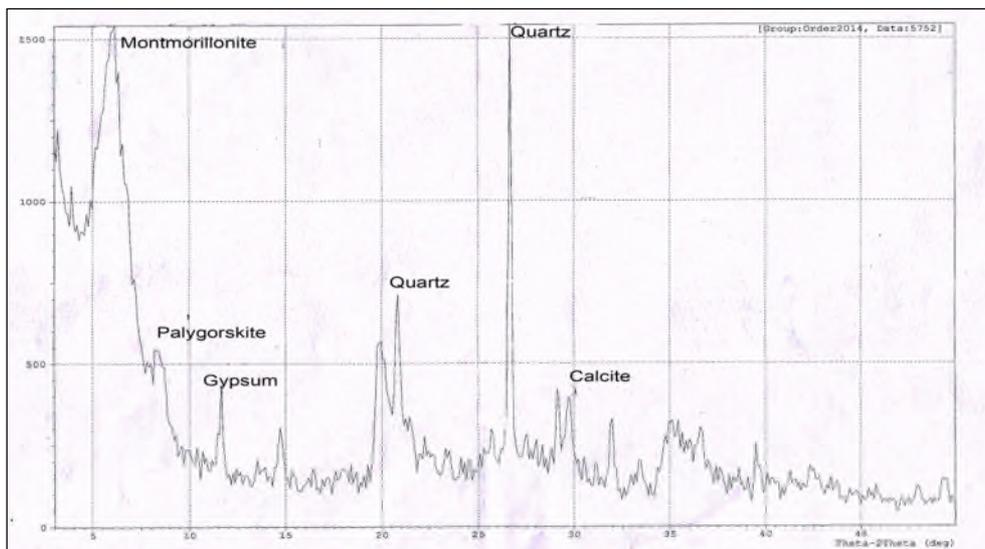


Figure(6) SEM for Bentonite (50  $\mu\text{m}$ )

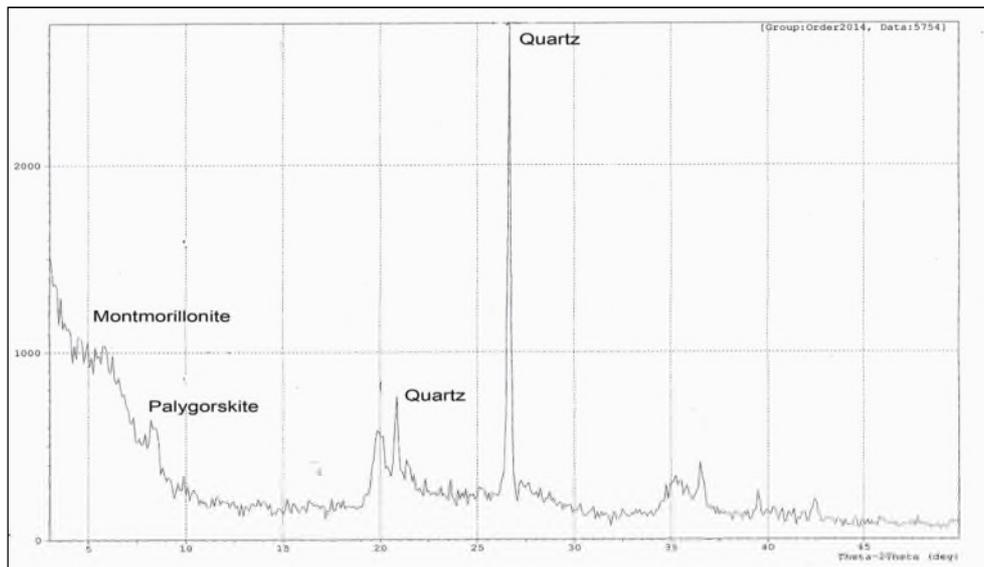


**X-ray diffraction (XRD)**

The X-ray diffractogram of the natural, untreated bentonite is shown in Figure (9). The reflections observed in 6 Å is a montmorillonite characteristic. Other reflections are observed at 9, 11.5, 26.5 and 29.5 Å which correspond to palygorskite, gypsum, quartz and calcite respectively. The qualitative result by XRD of natural bentonite shows that the quartz is the general phase. Figure (10) shows that the X-ray diffraction after acid treatment, which it can be observed that the intensity of the reflections of the characteristic peak of the gypsum and calcite disappeared after acid treatment due to the destruction of the bentonite structure and dissolution of Ca<sup>2+</sup> cation [22, 14]. Activation and treatments have a main step in preparation of nano scale crystal materials as catalysts which depending on activated sites, crystalline structure and particle size.



**Figure (9): X-Ray Diffractogram of The Natural, Untreated Bentonite**



**Figure (10): X-ray Diffractogram of The Natural, Treated Bentonite**

## CONCLUSIONS

In the present work it was prepared nano scale bentonite from Iraqi natural bentonite. The nano structure was characterized with modern analytical equipment. The nano bentonite has a mass ratio  $\text{SiO}_2:\text{Al}_2\text{O}_3 = 2.32$  less than natural bentonite (10.99). The calculated surface area for nano bentonite was  $161.842 \text{ m}^2/\text{gm}$  and total pore volume of  $0.2196 \text{ cm}^3/\text{gm}$ . The nanoscale bentonite particle diameter in the range of 52 nm at maximum intensity of AFM.

AFM revealed differences in their structure, indicated that the nanoscale surface was increased because of the nano particles size decrease, quantity increase, and random distribution.

The FTIR spectra of the clays were measured in the range of  $650$  to  $4000 \text{ cm}^{-1}$  assigned peaks; at  $3392.22$  and  $1635.69 \text{ cm}^{-1}$  is attributed to OH stretching (Al-OH and Si-OH) for bentonite, at  $1159$ ,  $798.20$  and  $677.46 \text{ cm}^{-1}$  are assigned to characteristic bands of silicates; and peak at  $500.08 \text{ cm}^{-1}$  is responsible for Al-O-Si group deformation

SEM analysis indicates the micro scale of particles with irregular clusters and non-uniform in nano structure, since these micro and nano scale particles due to beneficiation and activation conditions.

The X-ray diffractogram of the natural, untreated bentonite observed in  $6 \text{ \AA}$  is a montmorillonite characteristic, and at  $9$ ,  $11.5$ ,  $26.5$  and  $29.5 \text{ \AA}$  correspond to palygorskite, gypsum, quartz and calcite respectively. The X-ray diffraction after activation observed that the intensity of the reflections of the characteristic peak of the gypsum and calcite belonging to the other minerals changes due to destruction of the structure in the bentonite phases.

## Acknowledgment

Financial support from Ministry of Industry and Minerals, Chemical And Petrochemical Research Center in Baghdad, Iraq is gratefully appreciated.

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