International Journal of
Nanotechnology and Allied Sciences
2017 │Volume 1│Issue 1│Pages 16-29
ISSN: 2523-9252 (Online)
www.psmpublishers.org
Research Article **Open Access**

Synthesis and Characterization of Bentonite Nanocomposites from Egyptian Bentonite Clay

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Received: 31.Aug.2017; Accepted: 17.Oct.2017; Published: 23.Oct.2017
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Abstract
The aim of this paper was synthesis of bentonite Nano-composites from Egyptian bentonite clay. Calcium bentonite clay obtained from El Barqan area northern Egypt activated by Na_2CO_3 and purified. Both raw and purified bentonite clay characterized by XRD, XRF, SEM and TGA\ DTA in addition to the study of the mineralogical composition of non-clay mineral under polarizing microscope. Physio-chemical and geotechnical properties such as Cation Exchange Capacity (CEC), Specific Surface Area (SSA), free swelling, Atterberge limits, GSD, OMC and MC were determined. Purification of raw Egyptian bentonite clay used for preparation of bentonite clay nanocomposites as its high content of montmorillonite. Purification was done by four steps; eliminate the impurity levels of non-clay minerals, eliminate the impurity levels of Fe, eliminate the impurity levels of AL and concentrate montmorillonite in the sample using centrifuge. The grain size analysis using SEM and XRD of purified bentonite clay showed the average grain size 200- 300 nm with one dimension less than 100 nm.
Keywords: Bentonite clay, Barqan, Nano-bentonite, geotechnical properties, Purification, XRD, XRF, SEM, TGA\ DTA and TM.

Cite this article: Sameh, H.I., Mabrouk, M.S., Ali, A.A., Elwalead, A.A., 2017. Synthesis and Characterization of Bentonite Nanocomposites from Egyptian Bentonite Clay. Int. J. Nanotechnol. Allied. Sci., 1(1): 16-29.

INTRODUCTION

The nanocomposite material is composed of two or more solid phases and the powder size has at last one dimension less than 100 nm (Zhang, 1994). The nanocomposites materials have unique properties. So it can be widely used as a new high performance material in aviation, automobile, shipbuilding, electronics, construction, petroleum chemical industry. Bentonite is a kind of natural Nano-clay (Shao *et al.,* 2013). The weathering of volcanic ash or glass forms bentonite but common use of the term often extended to include a material of primarily montmorillonite composition. The main factors of weathering are climate, topography, vegetation, and time of exposure (Bergaya and Lagaly, 2013; Carrado *et al.,* 2006; Christidis *et al.,* 2006). The name bentonite was applied as early as 1848 by Knight to a highly plastic clay material occurring near Fort Benton, Wyoming (Grim, 1953). Bentonite is 2:1 layer silicate structure, also referred to as T–O–T clay. Bentonite is a highly plastic and swelling clay containing small quantities of inert mineral grains with relatively high specific surface and cation exchange capacities that range from 80 meq/100 g to 150 meq/100 g (Grim and Güven, 1978; Mitchell James, 1993).

Many national and international researchers (Bukit *et al.,* 2013; Shah *et al.,* 2013; Shao *et al.,* 2013) reviewed purification of bentonite. The purification methods of bentonite generally classified into mechanical purification methods and chemical purification methods. In this paper, bentonite clay from El Barqan area Northern Western Desert, Egypt was the raw materials and both chemical and mechanical purification of bentonite carried out. Bentonite deposits distributed throughout Egypt in different locations such as Northern Western Desert and Sinai. Most industrial applications program depend on the swelling properties of bentonite to form viscous water suspensions. Depending on the relative symmetry of clay and water, these mixtures are used as bonding, plasticizing, and suspending agents in drilling clay and for pelletizing iron ores, paint, composition, makeweight, ceramic, earthen dams, landfill liners, construction (Lang, 1971), pharmaceutical (Abdel-Motelib *et al.,* 2011).

Egyptian bentonite clay mineralogical consider low grade of Ca–Mg smectite and without any beneficiation cannot using as drilling mud (Hassan and Abdel-Khalek, 1998). A study reported the Egyptian bentonite unsuitable for pharmacology (Abdel-Motelib *et al.,* 2011), and another study considered most Egyptian clays without beneficiation were unsuitable for the majority of industrial applications (El-Mahllawy *et al.,* 2013). The aim of the current study was the synthesis of bentonite Nano-composites from Egyptian bentonite clay.

MATERIALS AND METHODS

Raw material

Bentonite clay collected from a quarry in El Barqan area Northern Western Desert, Egypt. This bentonite clay is ca-bentonite type, which collected, crushed and activated by alkaline activation using sodium carbonate (Na_2CO_3).the bentonite bed is about 5 to 6 meters thick.

Sample preparation and Na-activation

The samples collected along the bentonite bed at an interval of one sample for each ½ meter. The sample crushed using 1MZ-400W tungsten type sample pulverize and activated by sodium carbonate (Na_2CO_3).

Purification of bentonite clay

Purification was done by four steps:

A- Eliminate the impurity levels of non-clay minerals:

In this steps the non-clay minerals such as quartz, feldspar and gypsum was separated from bentonite clay using sieves No. 200 (less than 63.5 um) as shown in Fig (2)

B- Eliminate the impurity levels of Fe:

In this step, ferromagnetic mineral such as hematite or magnetite separated using magnetic separation device.

C- Eliminate the impurity levels of AL :

In this step the impurity levels of AL by chemical process using HCL solution with 2 M levels. The HCl solution in bentonite with a ratio of Bentonite: HCl, 1:10, then stir until homogeneous by using a magnetic stirrer for 2 hours, using filter paper separates the bentonite HCl solution and washing again using with distilled water until a neutral of pH and concentration of montmorillonite.

D- Concentration of montmorillonite :

In this step, the high content of montmorillonite done using bentonite slurry concentration of 7%, stirring time of 20min, centrifugal time of 30min, none dispersant agent requested as shown in Figure (3).

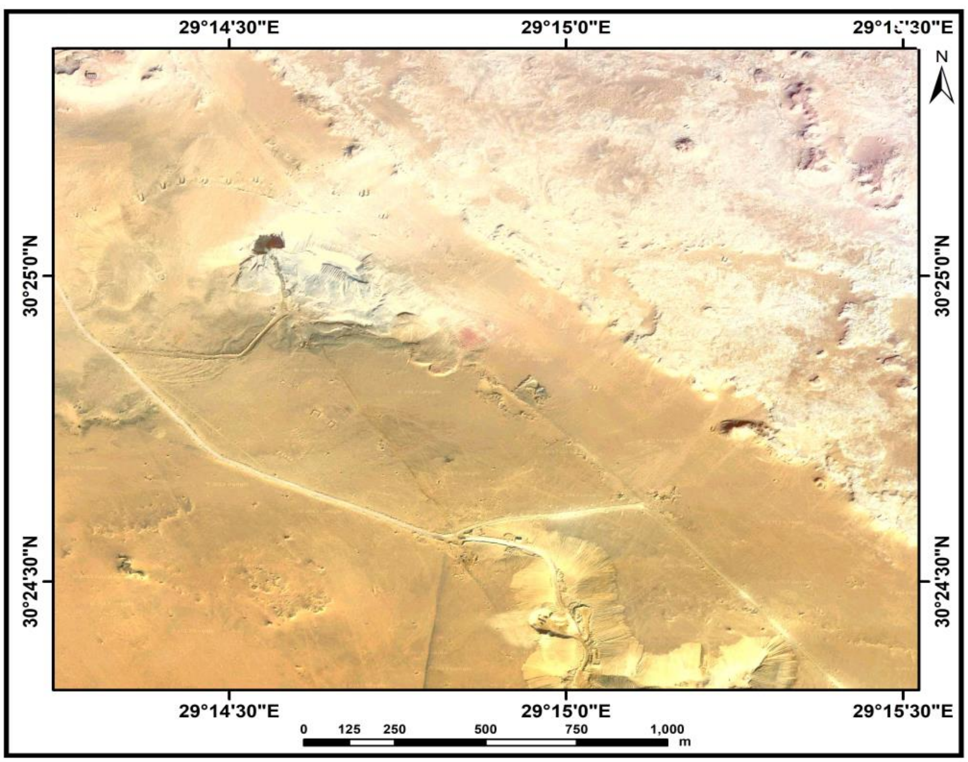


Fig. 1. Map of bentonite quarry in El Barqan area

Fig. 2. Non- clay mineral separated from bulk raw bentonite clay using sieves.

Fig. 3. Concentration of montmorillonite using centrifuge.

Methodology

Free swelling test based on a method by (Keen and Raczkowski, 1921) with a modified computation procedure by (Wickham and Tregenza, 1973). This test measures the free swelling of a disturbed soil on wetting from air-dry to saturation after pouring 5 g of dry soil into l00 cm3 graduated jar filled with distilled water, noting the swelled volume of the soil after it comes to rest. At the end of 24 h, the sediment volume or swollen volume was measured against the graduations of the jar as shown in Figure (4) and then the free swell is given by this equation:

$FS = ((V_f - V_I)/V_I) X 100)$

Where FS = the free swell (%), V_f = the final soil volume after swelling, ($cm^{3)}$, and V_I = the initial volume of soil.

Particle size distribution carried out by dry sieving test for larger sizes bigger than 75 µm by using the sieves assembly while by using hydrometer for sizes smaller than 75 µm. This test is carried out according to ASTM D 422. Both purified and raw Egyptian bentonite grain size was measured by sieve, hydrometer and XRD. Unit weight test is performed according to ASTM D 2937. The unit weight of the sample is the ratio between the mass of the sample to its volume. Specific gravity done to determine the specific gravity of fine-grained soil by density bottle method, as per IS: 2720 (Part III/Sec 1) – 1980. Specific gravity is the ratio of the weight in air of a given volume of a soil at a stated temperature to the weight in air of an equal volume of distilled water at the same stated temperature. Consistency limits is performed to determine the plastic and liquid limits of a fine-grained soil according to ASTM D 4318 - Standard Test Method for liquid limit, plastic limit, and plasticity index of soils. Casagrande liquid limit device is used for liquid limit determination as shown in figure (5). Cation exchange capacity (CEC) is an important parameter as it gives indication of the presence and content of clay minerals in the sample. CEC can be determined as a sum of exchangeable cations. Chemical composition determined by XRF and FT-IR for both purified and Egyptian bentonite clay. Describe the instruments of both. The mineralogical composition of both purified and Egyptian bentonite clay investigated using X-ray diffraction technique and thin section under polarizing light microscope. X-ray diffraction technique is the most widely used technique for determining mineral composition of clay minerals. Since all clay minerals have essentially the same general scheme structure and their diffraction patterns are somewhat similar, the most characteristic differences are provided by their basal spacing (001) which permits an unequivocal identification of the clay minerals even in mixtures (Brown and Brindley, 1980). Investigation under polarizing microscope for both purified and Egyptian bentonite clay using Nikon microscope model Eclipse LV100 Polarizing with digital camera of 10 MP. The particle shape of three-dimensional surface conformation of both purified and Egyptian bentonite clay was observed on SEM Model Quanta 250 FEG (Field Emission Gun) attached with EDX Unit (Energy Dispersive X-ray Analyses), with accelerating voltage 30 K.V., magnification14x up to 1000000 and resolution for Gun.1n). Thermal analysis (DTA & TGA) of both purified and Egyptian bentonite clay investigated using thermal analyzer model Shimadzu DTA-50 & TGA-50.

RESULTS AND DISSUCTION

A- Physical properties

Free swelling test

Free swelling results are shown Figure (4) and table 1. The results indicated that the swelling upgrade by every step of purification and the Egyptian bentonite clay swelling improve to about 13 times when become bentonite nanocomposite. This improve in swelling value due to the unique enhancement in Nanocomposite bentonite properties after synthesis to one dimension Nano-size where the surface area and breakup the bentonite layer make it to contain large number of water layers in interlayer zone than Egyptian bentonite.

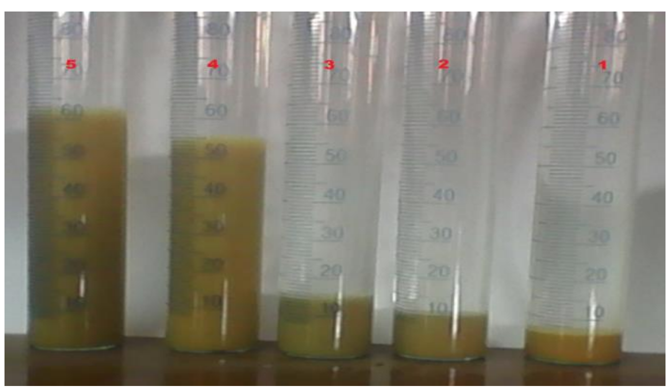


Fig. 4. Shown the following:

1- **swelling of bulk Egyptian bentonite clay**
2- **swelling of purification bentonite after remove non clay minerals**
3- **swelling of purification bentonite after remove ferromagnetic minerals**
4- **swelling of purification bentonite after remove impurity levels of AL and centrifugal time 5 min/ 2800pm**
5- **Swelling of purification bentonite after centrifugal time 30 min/ 2800pm (bentonite nanocomposite).**

Table 1. The swelling value of every step of Egyptian bentonite clay until bentonite Nanocomposite.

Sample	bulk	Removed non clay minerals	Removed Fe	Removed Al & centrifuged	Bentonite Nanocomposite
Free swelling Value	5 mm/5g	11 mm/5g	15 mm/5g	51 mm/5g	64 mm/5g

B- Physio-Chemical and Engineering properties

Particle size distribution

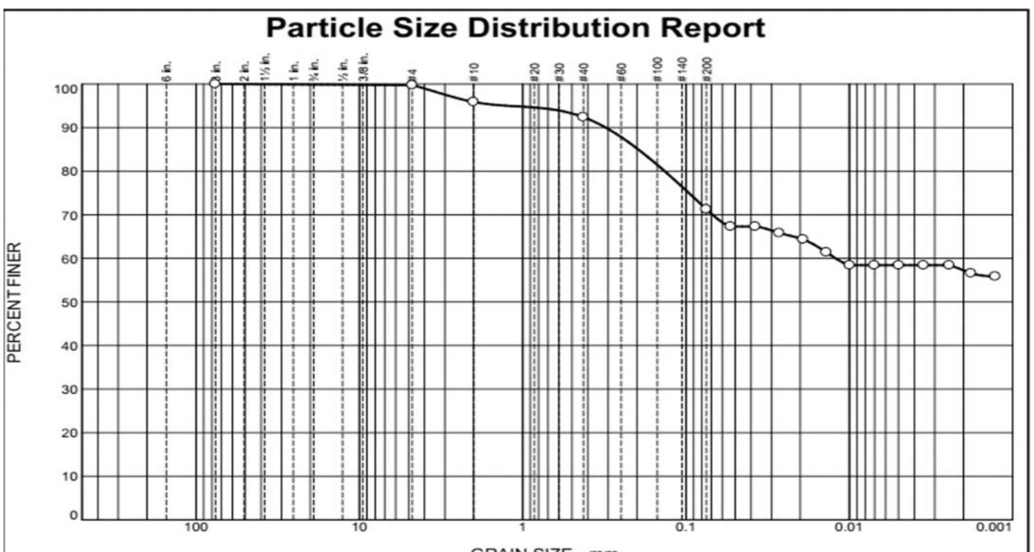
Particle size distribution are shown in Figures (5 and 6) using sieves and hydrometer. The results shown that the grain size distribution of Egyptian bent ontic clay have 0.3%gravel, 28.4% sand, 12.9% silt and 58.4% clay which indicated that the Egyptian bentonite clay have a lot of impurities of other minerals and materials. The results shown that the grain size distributions of purification bentonite have 0.2% fine sand, 1.4%silt and 98.4%clay which indicated that remove the most of impurities of Egyptian bentonite clay and the smallest size of bentonite grains are 800nm. However, using XRD chart to determine the crystal size of montmorillonite crystals can obtain according to The Scherer Equation published in 1918:

$$D = \frac{k\gamma}{B\cos\theta}$$

Whereas B, K, λ, and D, respectively half-peak width (FWHM) in radians, Scherer constant (0.9), x-ray wavelength (1.5406 Å), and the diameter of the crystallites (nm). Based on the calculation of average crystallite size of montmorillonite of Egyptian bentonite clay is 318.08 nm while the purified bentonite is 90.90nm, which indicated that reach to Nano-size.

Index properties

Both of Egyptian bentonite clay and purification bentonite index properties shown in table (2).



% +3"	% Gravel Coarse	% Gravel Fine	% Sand Coarse	% Sand Medium	% Sand Fine	% Fines Silt	% Fines Clay
0.0	0.1	0.2	3.8	3.5	21.1	12.9	58.4

Fig. 5. Particle size distribution of Egyptian bentonite clay

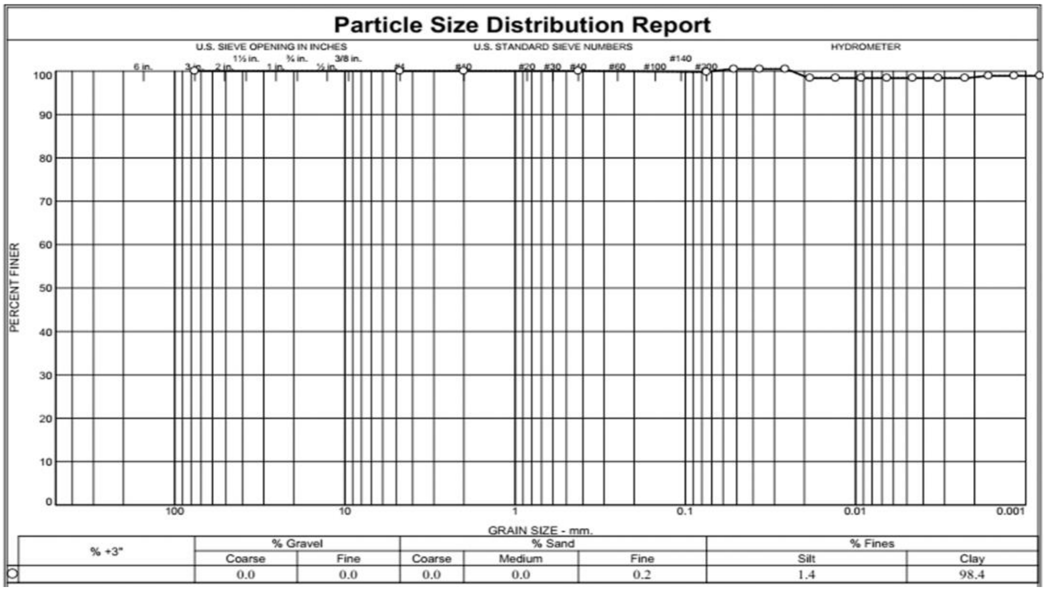


Fig. 6. Particle size distribution of purification bentonite.

Table 2. The index properties of both Egyptian bentonite clay and purified bentonite.

Index properties	Egyptian bentonite clay	Purified bentonite
Color	brown	creamy
Bulk density	1300 kg/m3	917 kg/m3
Dry density	903 kg/m3	860 kg/m3
Water content	3.9 %	3.2 %
Specific gravity	2.55	2.6

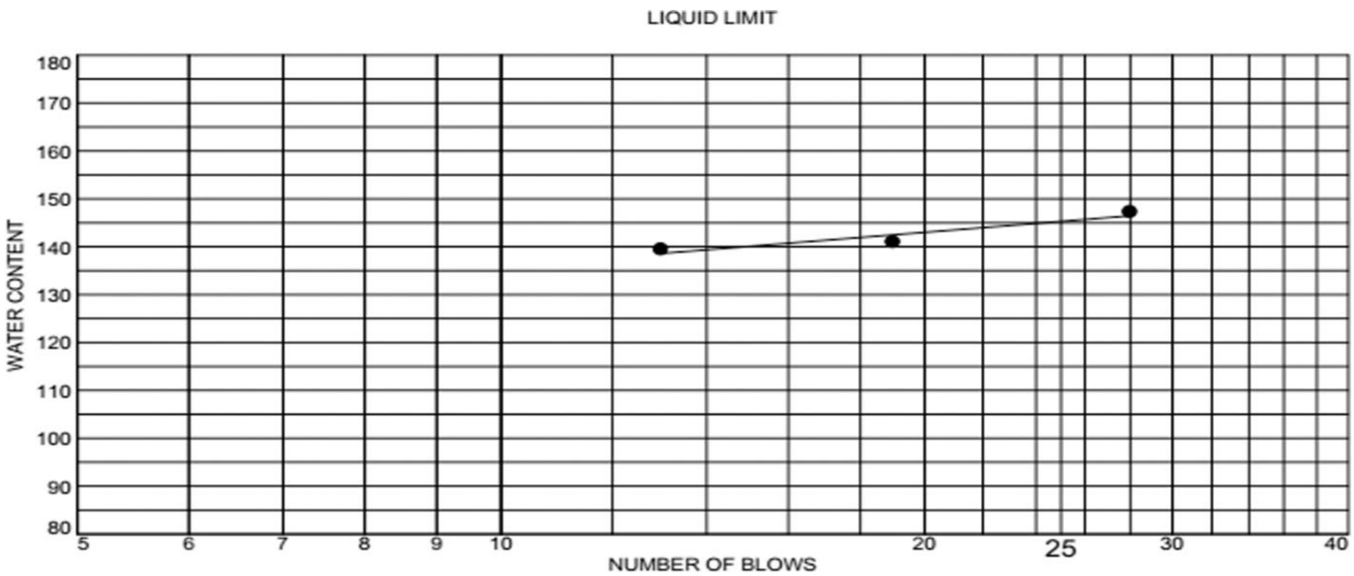
The results shown change in color and density of purified bentonite than Egyptian bentonite clay due to purification processes.

Consistency of the soils (Atterberg limits)

Atteberg limits have shown in Fig (7, 8). The result shown that the Atterberg limits of Egyptian bentonite clay are 145 liquid limit, 43 plastic limit and 102 plasticity index while the purification bentonite Atterberg limits are 465 liquid limit, 37 plastic limit and 428 plasticity index which interpretation the high swelling of it.

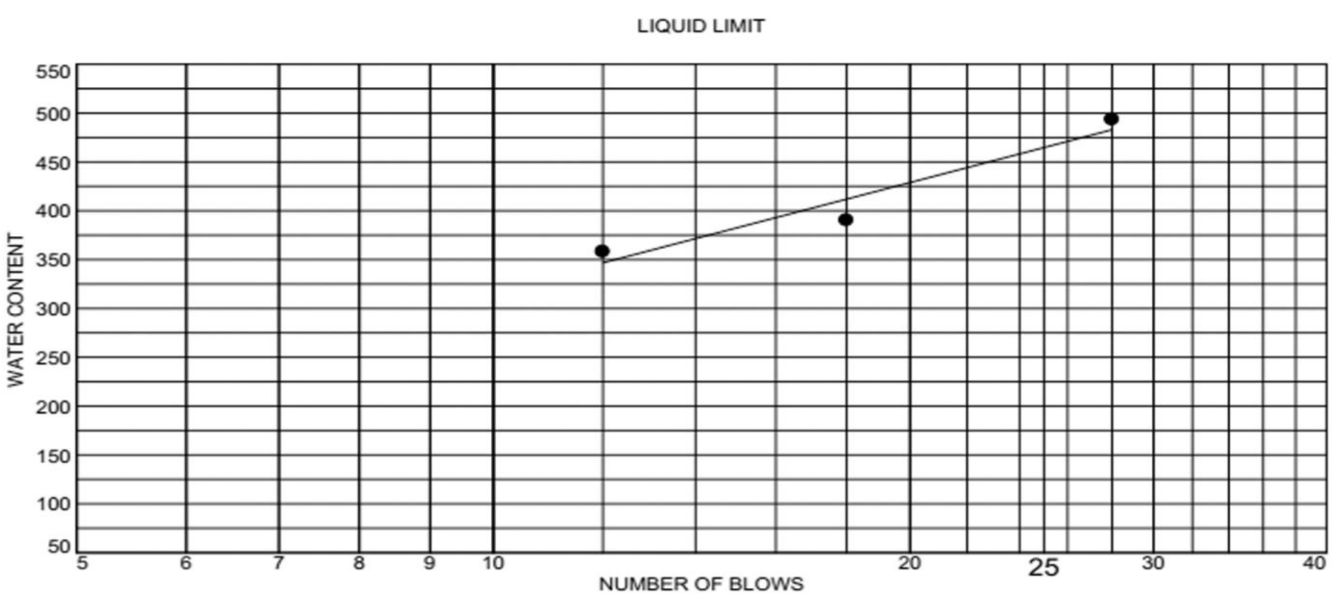
CEC and SSA results

The results of CEC and SSA for both Egyptian bentonite clay and purified bentonite shown in table (3) which indicated that the exchangeable cation is sodium Each of CEC and SSA are increase in purified bentonite than Egyptian bentonite clay, which interpreted its high swelling properties.



MATERIAL DESCRIPTION	LL	PL	PI	%<#40	%<#200	USCS
fat clay with sand	145	43	102	92.4	71.3	CH

Fig. 7. Atterberg limits of Egyptian bentonitic clay.



MATERIAL DESCRIPTION	LL	PL	PI	%<#40	%<#200	USCS
PURIFIED BENTONITE	465	37	428	100.0	99.8	CH

Fig. 8. Atterberg limits of purified bentonite

Table 3. The CEC & SSA of (1) purified bentonite and (2) Egyptian bentonetic clay.

sample	Ca^{2+} cmol/kg	K+ cmol/kg	Mg^{2+} cmol/kg	Na+ cmol/kg	CEC Meq/100g	MBI mmol/100g	SSA M^2/g
1	19.8	0.95	22.7	43.3	86.75	98	750.20
2	20.8	0.7	15.7	32.9	70.1	81	550.35

Chemical characterization

XRF

The XRF results of both Egyptian bentonite clay and purified bentonite have shown in table (4), the percentage of NaO and SiO2 increased while the percentage of Fe_2O_3, Al_2O_3 and CaO are decreased respect to the Egyptian bentonite clay, which indicated that the removal of non-clay minerals and impurities level of Fe and Al due to purification processes. The increase percentage of NaO was due to activation.

Table 4. The XRF results of both Egyptian bentonite clay and purified bentonite.

Sample	MgO %	Si O_2 %	Fe_2 O_3 %	Al_2 O_3 %	Ti O_2 %	Ca O %	Na_2O %	K2O %	LOI %
Egyptian bentonetic clay	0.62	56.3	10.02	22.12	1.32	4.39	1.13	1.40	10.75
Purified bentonite	0.71	59.33	7.72	18.02	1.02	1.24	4.02	1.41	5.62

FT-IR

The FT-IR results of both Egyptian bentonite clay and purified bentonite are shown in Figure (9) and table (5). The FT-IR spectra of the Egyptian bentonite clay and purified bentonite measured in transmittance between 400 and 4000 cm^{-1}. The band at 527.43 cm^{-1} and 3621.66 cm^{-1} are corresponding to montmorillonite. The band at 3699.91 cm^{-1} is corresponding to kaolinite. The band at 3699.91 cm^{-1} is corresponding to kaolinite. The band at 1031.73 cm^{-1} is corresponding to kaolinite, montmorillonite and quartz. The band at 879.38 cm^{-1} is corresponding to montmorillonite and illite. The band at 794 cm^{-1} is corresponding to quartz. The bands at 3441.35 cm^{-1} and 1635 cm^{-1} are corresponding to H_2O. The band at 1462.74 cm^{-1} is corresponding to CO_3 (carbonates). From FTIR spectra noted absent of peak Number 7 due to elimination of carbonates by purification, processes and small extend of peak number 14 result of increase the SiO_2 in purification bentonite. Some other studies have also reported the use of Transmission and reflection FTIR techniques were used to distinguish between different types of clay minerals (Djomgoue and Njopwouo, 2013).

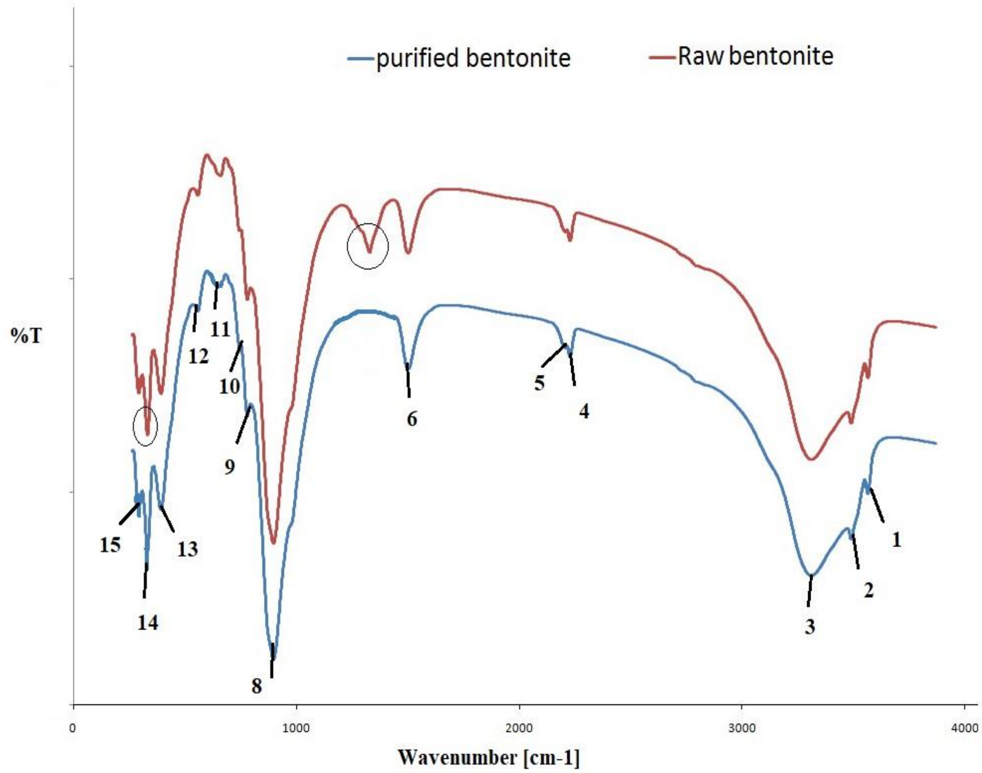


Fig. 9. FTIR chart of purified and Egyptian bentonite.

Table 5. FT-IR results for both Egptian bentonite clay and purified bentonite.

Sr. No.	Position	FTIR spectra indication
1	3695.91	Al-Al-OH(kaolinite)
2	3621.66	Al-Al-OH(Montmorillonite)
3	3441.35	H_2O
4	2360	Unsolved
5	2338.27	Unsolved
6	1635.022	H_2O
7	1462.74	CO_3
8	1031.73	M, kaolinite and quartz
9	914.093	Al-OH
10	879.38	Al-Mg-OH (montmorillonite and illite)
11	794.528	quartz
12	692.32	Al-O-Si-O
13	527.436	Al-O-Si (montmorillonite)
14	466.68	Si-O-Si
15	428.12	SiO2

Mineralogical characterization

XRD

The XRD results of both bentonite clay and purified bentonite are shown in Figure (10). The diffraction angle 2θ of purification bentonite was 6.99606 ° and inter planar distance was 1.0131 while the diffraction angle 2θ of Egyptian bentonite was 6.4133 ° and the inter planar distance was 1.3166, where the inter planar distance calculated according to Bragg equation: $2d\sin\theta = \lambda$. This indicated that the impurities were filling the Egyptian bentonite clay due to large inter planar distance. From XRD chart the Egyptian bentonite clay represented the clay mineral is kaolinite distinct at peak about 4.3 A. and montmorillonite distinct at peak 12.6 A while the non – clay mineral is mainly Quartz. The XRD chart of purification represented increase the montmorillonite percentage which distinct at peak about 13.77 A and kaolinite distinct at peak about 7.39 A. the increase d- spacing of montmorillonite of purification bentonite than Egyptian bentonite clay indicate that the decreased the crystal size of purification bentonite responding the high swelling of it.

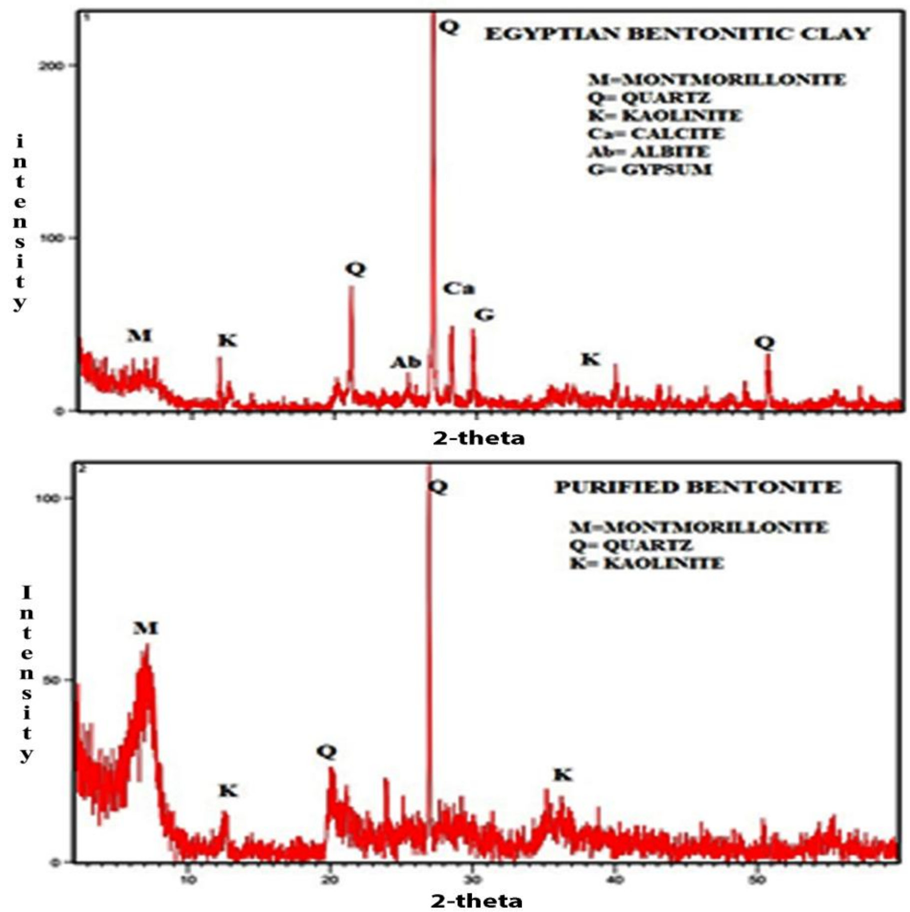


Fig. 10. XRD chart of Egyptian bentonite clay and the purification bentonite.

Petrography of non-clay mineralogy

Thin section studies of Egyptian bentonite clay under polarizing microscope shown in Figure (11) indicated that increase percentage of impurities mixed with bentonite where it composed of quartz and carbonates rock fragment with Quartz, plagioclase, calcite, opaque and organic matter. Quartz grains are numerous mainly sub rounded to sub angular in habit. Plagioclase grains represented by albite showing the characteristic lamellar twinning. Calcite is fine, medium and sometimes coarse grained they are found either as large isolated grains showing the characteristic twinkling and extreme birefringence. The thin section study of purified bentonite shown in figure (11) indicated that removal most of impurities such as quartz, carbonate, rock fragment and opaque.

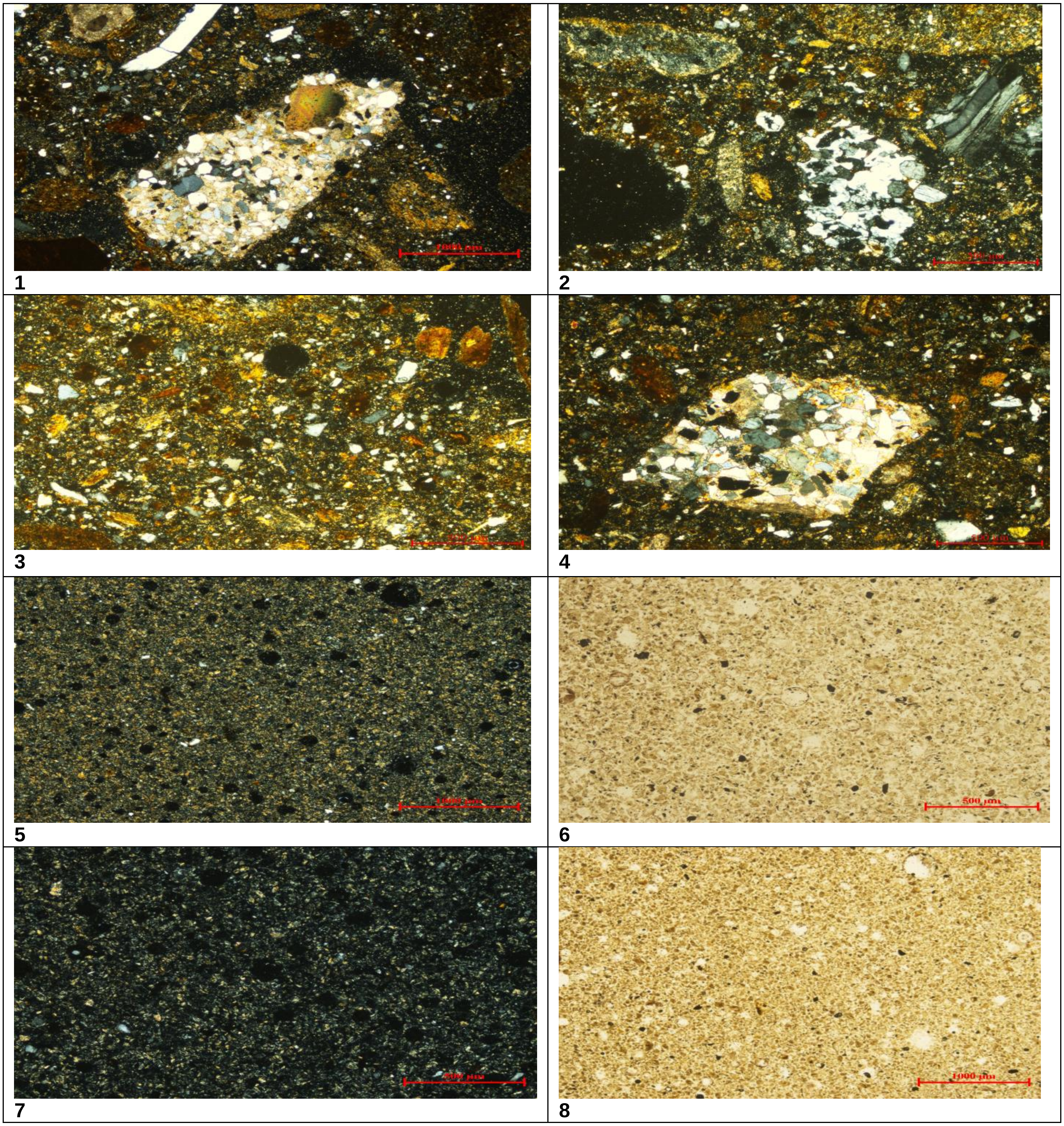


Fig. 11. The mineralogy of Egyptian bentonite clay (1, 2, 3, and 4) and purified (5, 6, 7, and 8) bentonite under polarizing microscope.

Thermal analysis

Thermal analyses used to confirm the mineralogical composition of both bentonite clay and purified bentonite. The study of DTA of Egyptian bentonite clay shown in figure (12) represented that presence of four endothermic peaks recorded at (63.26°C, 124.92. °C, 499.59 °C and 678.30) respectively, due to dehydration of adsorbed water, dihydroxylation and phase transformation of the clay fraction respectively while the study of DTA of purified bentonite shown un figure (12) represented that presence of three endothermic peaks recorded at (79.05°C, 482.71 °C and 942.61 C) respectively, due to dehydration of adsorbed water, dihydroxylation and phase transformation of the clay fraction respectively and one exothermic peaks recorded at 317.91 C due to sample decomposition. The TGA studies of Egyptian bentonite clay shown that loss of weight at start temperature (42,160, 304, 459, 590 and 755) while the loss of weight in purified bentonite at start temperature (48,159, 350, 483 and 703). The thermal analysis results indicate high heat resistance of purified bentonite than Egyptian bentonite clay. The results of TGA are shown in Figure (12).

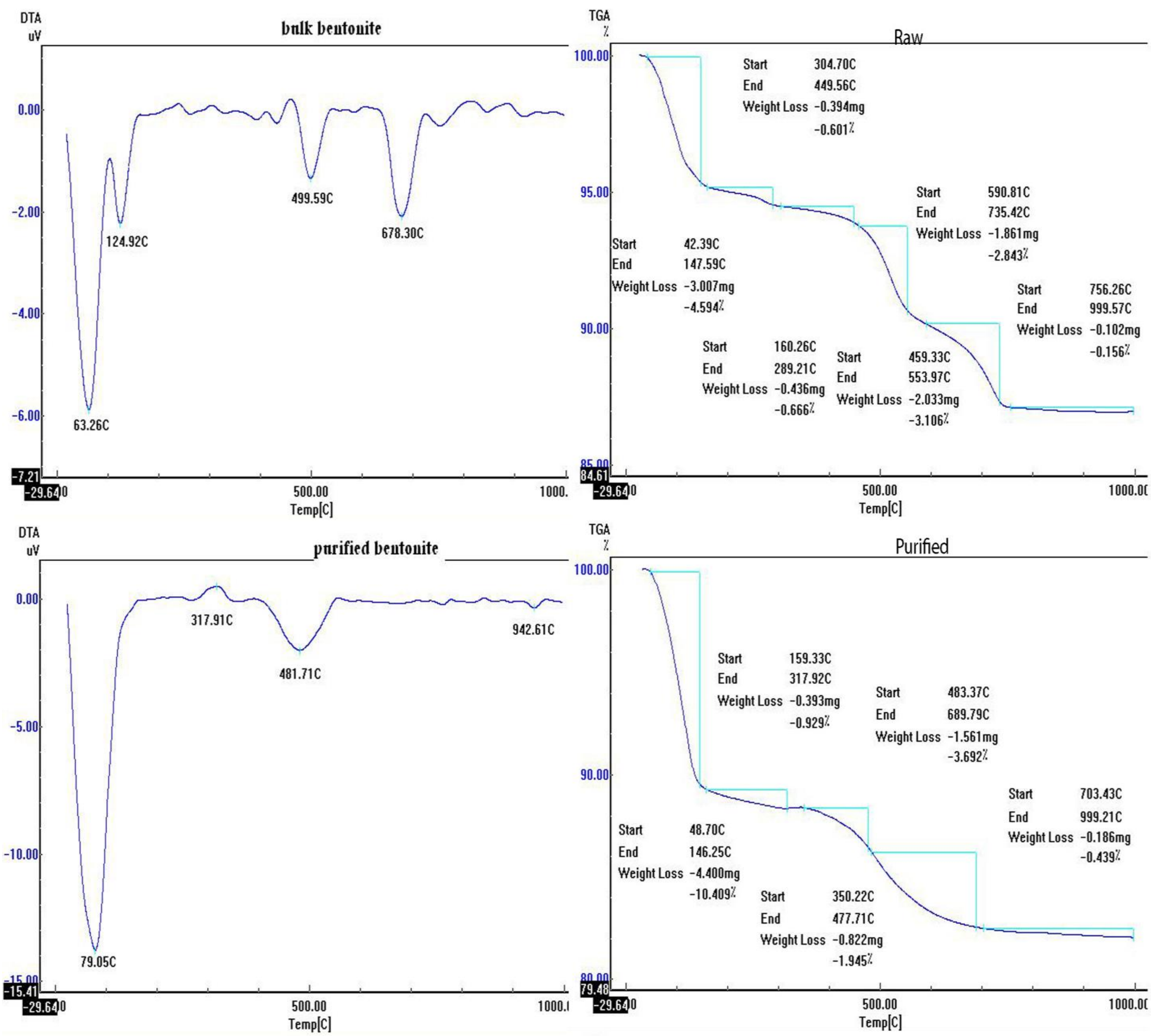


Fig. 12. TGA chart (right) and DTA chart (left) of both Egyptian bentonite clay and purified bentonite.

Scanning Electron Microscope

The result of scanning electronic microscope shown in Figure (13) which indicated that the Egyptian bentonite partials were close to each other formed aggregates while the purified bentonite were dispersed , flatter surface area, better continuity, clear outline, and obvious hole. With one dimension less than 100 nm.

A previous study reported the SEM microstructure images indicating that the bentonite samples are generally moderately dispersive to dispersive with some large flocs which were apparently separate and dispersed from one another rather than located on the totality of the image (Bilal *et al.,* 2016).

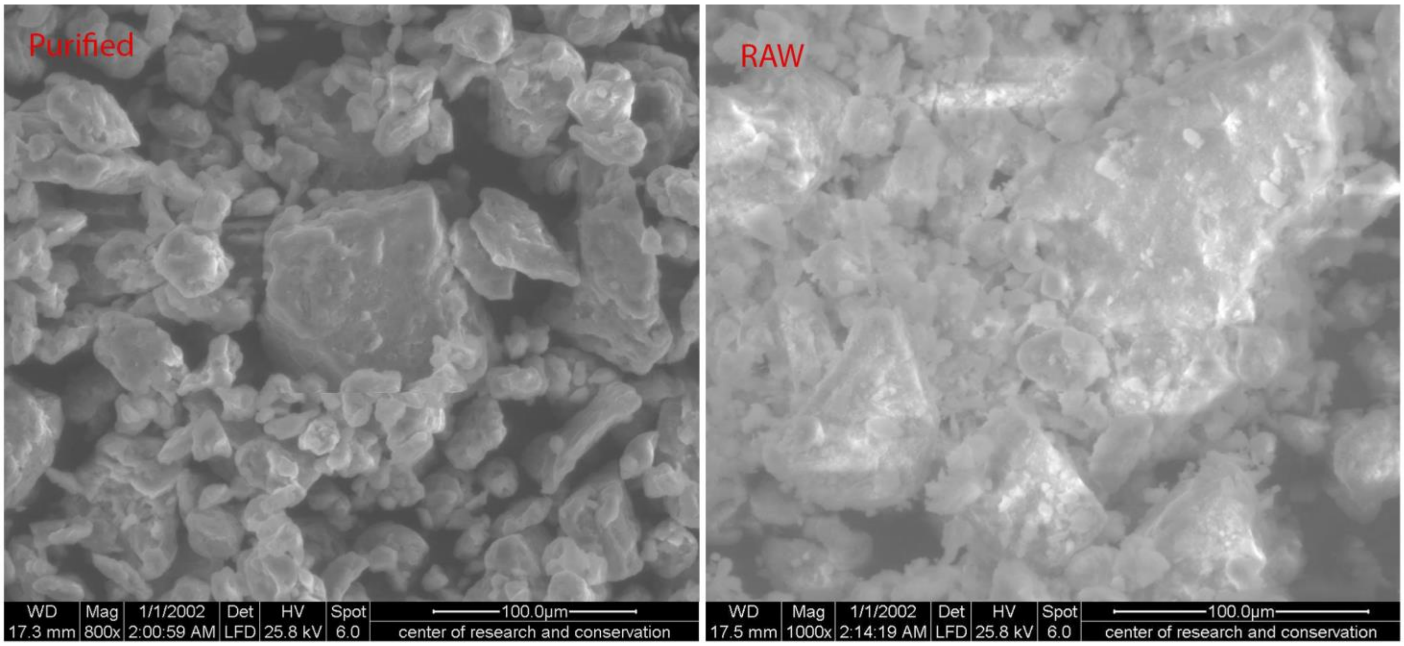


Fig. 13. SEM of purified bentonite [left] and Egyptian bentonite clay [right].

CONCLUSION

Synthesis of bentonite Nano composite was done by simple purification of Egyptian bentonite clay. Bentonite Nanocomposite has unique properties related to Egyptian bentonite clay where the swelling value of it about 13 times of Egyptian bentonite clay. Improving the swelling value of bentonite Nanocomposite is very useful in industry scale where we can use small quantity of bentonite Nanocomposite to replace large quantity of Egyptian bentonite clay.

RECOMMENDATIONS

Authors recommended that should be synthesis of Nano bentonite from Egyptian bentonite with two or three dimension in Nano-size (less than 100nm) using any method for synthesis Nanoparticles such as Ball Mill, Hydro-thermal, Sono-chemical and precipitation methods and characterization of its properties specially swelling.

ACKNOWLEDGEMENT

The authors wish to express their gratitude to MR Ahamed Ramadan in Nanotechnology and electronics lab – south valley university for his help.

Author Contributions

This work is part of the MSc studies of the first author mentioned in the author's list, Sameh Hamed Ismaeel, under the supervision of the second and third authors.

CONFLICT OF INTEREST

There is no conflict of interest.

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