

Strategy for Boosting Rock Phosphate Efficiency and Conversion into Nano Zeolite

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Abstract Present investigation aimed to convert rock phosphate ore into nano zeolite using calcination (from 200 to 700°C) for 48 hrs. and zeolitization (replacement by a zeolite mineral) processes in order to boost rock phosphate ore efficiency as a source of P₂O₅ even under high soil pHs. Crystallization, phases, physico-chemical characteristics and surface morphology were studied by visual techniques. Using scanning electron microscopy (SEM) coupled with energy dispersive spectroscopy (EDS) which cleared that, the converted rock phosphate gave different shapes and sizes of crystals and distribution of its components (elements and oxides mass percentage). While TEM appears the crystals size of converted rock phosphate was found in nano size (19.7 -39.1 nm). Moreover Sterio microscopy illustrated that, after calcination and zeolitization processes, the nano zeolite converted from rock phosphate ore took different shapes with three dimension crystals growth as end of crystallization process. Whilst XRD manifested that, the dominant mineral was zeolite associated with different minerals represented by mica muscovite, montmorillonite, calcite, pyrite, alkali feldspar, plagioclase feldspar and quartz. At the same time, XRF was used to verify nano rock phosphate converted in to zeolite (heulandites type). Also the XRF analysis recorded Si/Al ratio (3.42%) of nano zeolite its properties tended to both hydrophilic and organophilic. Furthermore, DTA (differential thermal analysis) and TGA (thermo-gravimetric analysis) were used for measure percentages of water molecules attached with nano rock phosphate and its thermal stability. Therewithal, Surface area (BET) was (14.93m²/g), pore sizes distribution from 3.98 to 56.87 nm, pore volume 19.96 nm and pore width 4.846 cm³ / g. It was observed that there is little change in particles density in both real and bulk densities. Finally, the highest CEC (cation exchange capacity) and lowest AEC (anion exchange capacity) values of the conversion rock phosphate were acquired. In a nutshell, our results designated for more liberate of P₂O₅ in available and safety form to uptake easily by cultivated crops, and construct an appropriate media for loading by beneficial microorganisms.

Keywords: rock phosphate, nano zeolite, calcinations, zeolitization

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1. Introduction

The utilize of rock phosphate as a fertilizer in phosphorus deficient soils received a remarkable interest as being a cheap and rich source of phosphorus element. Naturally a concentrated phosphate mineral deposit has limited economic recovery. Hence, for economic utilization the ore must be concentrated and boosting by thermal treatment (calcinations) where, calcination process of heating solid material lead to drive off volatile chemically combined components, e. g., carbon dioxide and calcium oxide [1]. Countries which produce phosphate rock recorded more than 40 million ton (Mt). In 2005, the world phosphate production up to 148 Mt., 143 Mt were produced by sixteen major phosphate producing countries. Only the remaining 5Mt produced by other countries (countries whose production exceeds 1 million tons per year) [2,3].

In spite of the soil rich in phosphorus level, it is repeatedly present in engaged forms or in available outside of the rhizosphere. Poor soils release phosphorus prompts adequate to hold up the high growth rates of crop plant species. The submission of phosphorus to the soil is essential to guarantee plant productivity; the revival of applied phosphorus by crop plants in a growing season is very low, for the reason that in the soil more than 80% of the phosphorus becomes unavailable and immobile for plant uptake because of alteration to the organic form, adsorption and precipitation [4].

Soil phosphorus is originated in different pools, such as mineral and organic phosphorus. It is imperative to accentuate that 20 to 80% of phosphorus in soils is found in the organic form, of which phytic acid is usually a main constituent [5]. The rest is found in the inorganic portion containing 170 mineral types of phosphorus [4]. Soil microbes liberate immobile forms of phosphorus to the soil solution, meanwhile are also in charge for the immobilization of phosphorus. The diminishing availability of phosphorus in the soil bounds plant uptake.

It worth mentioning that, phosphorus is moved mostly by diffusion, its rate of diffusion is slow (10^{-12} to 10^{-15} m^2s^{-1}), high plant uptake rates create a zone in the region of the root that is depleted of phosphorus. [6]

The sedimentary phosphate ores having similarity in the physic-chemical properties of surfaces ore constituents represented in carbonate-apatite ($Ca_5(PO_4, CO_3)_3F$) as the main phosphate minerals and carbonates (calcite $CaCO_3$ and/ or dolomite $CaMg(CO_3)_2$). These three formulas usually exist in the soil in inactive form of phosphorus for plant uptake [7]. Also, if considerable amount of organic matter added or mixed to the main gangue material, the upgrading of the phosphate ore remains difficult.

From Pervious investigations for upgrading of phosphates according to ore type were generally fall into one of the following categories, based on the major associated gangue materials:

(1) Siliceous ores: could be upgraded economically by some techniques such as flotation or gravity separation methods [8].

(2) Clayey ores: This associated with gangue materials as clays and hydrous iron and aluminum silicates or oxides. These impurities could be removed by simple beneficiation techniques such as scrubbing and washing.

(3) Calcareous ores of sedimentary origin: contain the major impurities (calcite and/or dolomite) with small amounts of silica. It is usually difficult to remove the carbonate minerals efficiently from such ores by physical separation methods or conventional techniques as flotation. [9,10,11].

(4) Phosphate ores associated with organic matter (one gangue minerals), which sometimes called "black phosphates" generally upgraded by heating up to about $800^\circ C$ [12].

(5) Phosphate ores containing more than one type of the gangue minerals: These ores require series of upgrading operations in their flow sheets depending on the type of gangue minerals existing in each ore, including: size reduction, combination of attrition scrubbing, des-liming, flotation, gravity separation, and/or calcination [14].

(6) Igneous and metamorphic phosphate ores: The main gangue materials in these ores type are sulfides, magnetite, carbonates (calcite, dolomite, siderite, and ankerite), nephelinesyenite, pyroxenite, foskorite. Upgrading processing of these ores include; crushing, grinding, washing, desliming, magnetic separation, and flotation depending on the types of gangue minerals present [13].

(7) In mine soil rehabilitation, rock phosphates such as apatites ($Ca_{10}(PO_4)_6(OH)_2$) are used as sources of phosphorous. But they have no effect on enhance plant

growth in reclaimed mine soil, due to high values of soil pH [7].

(8) Zeolites have also been used to solve this problem: researchers have used a mixture of zeolite and ground apatite to increase the dissolution of the apatite to produce more available Phosphorous especially at high soil pHs [8].

2. Objective of the Research

Our aims of this research were as following:

1- To convert rock phosphate ores into nano zeolite particles using calcinations and zeolitization processes to provide more available phosphorus even at high soil pHs.

2- To boosting the efficiency of rock phosphate as a source of some other nutrients beside P_2O_5 .

3- To examine the characteristics (morphology, physico-chemical and phases identification) of the converted nano zeolite for applied in free access uses.

3. Material and Methods

The present research was started in January 2015 and finished in August 2015 where, the ore of rock phosphate has been brought from Aswan province in the Upper Egypt then converted into (A.M.1) nano zeolite by zeolitization and calcination processes. Chemical composition of rock phosphate ore was carried out at Agriculture Research Center (A.R.C), Soil & Water and environment Institute presented in Table 1. The reaction mixture was performed according to the following composition of 100 g of rock phosphate and 10 ml of (TEOS) solution as tetrahedral molecule prepared by alcoholysis of silicon tetrachloride, and used as the silica source and pre-cursor for conversion rock phosphate into nanoparticles of zeolite, 50ml of NaOH and 300 H_2O . The sodium hydroxide (NaOH) solution is used as caustic environment for the synthesis process and alkali source. The mixture of rock phosphate was treated gradually hydrothermally up to crystallization temperatures, then the reaction mixture was transferred to a Teflon lined stainless steel pressure vessel and placed in preheated oven at autogeneous pressure 2PSi and static conditions for 72hrs where the hydrothermal crystallization was starting from $200^\circ C$ for 24h, subsequently at 300, 400, and $500^\circ C$ for 48 h, and $600,700^\circ C$ for 48 hrs. respectively. After completion of crystallization, the solid products were washed several times with distilled water until PH=7.5, then dried at $100^\circ C$ overnight.

Table 1. Chemical composition of rock phosphate ore

Constituents %											
P_2O_5	CaO	MgO	Al_2O_3	Fe_2O_3	SiO_2	F	Na_2O	SO_4	LiO_2	CO_2	CO_3
30.20	49.00	0.62	0.40	1.48	6.02	3.10	0.50	1.00	7.68	12.72	2.00

After that, the samples were thoroughly characterized by instrumental techniques viz. EDX, scanning electron microscopy (SEM) model JSM.6390LA (JEOL) analytical scanning electron microscope at Holding Company For Drinking Water and Waste Water, Greater Cairo Company For Drinking Water, Central Laboratory.

TEM transmission electronic microscope the work was done in TEM lab (FA-CURP) Faculty of Agriculture Cairo University Research Park.

3.1. Specimen Preparation

Acceptable specimens:

1. Sonicate the delution 5 min.
2. Place two 2-5 μl drops of specimen onto sheet of Parafilm
3. Make EM grids carbon-coated (400-mesh copper grids) directly off on specimen

- Use filter paper to wick away specimen drop and place grids, specimen-side up in specimen petri dish.
- Examined by transmission electron microscope JEOL (JEM-1400 TEM) at the candidate magnification. Images were captured by CCD camera model AMT, optronics camera with 1632 x 1632 pixel format as side mount configuration. This camera uses a 1394 fire wire board for acquisition.

Stereo microscopy LEICA M216 was used to appear the growth of crystals of nano rock phosphate in three dimensions at Cairo univ. Faculty of Agric. Microbiology Research Lab.

BET determination using Nova 2000 series (America) Quantachrome at Central Metallurgical research and development institute and ion exchange properties.

X-ray diffraction Analysis of nano rock phosphate was determined using X-ray diffraction of powder samples. EMPYREAN diffractometer model, with Anode material Cu, generator setting at 45 kV, 30 mA was used. A step size of $0.0260^\circ 2\theta$ and a counting time of 4 second per step were applied over a 2θ range of 5.01313° to 79.9711° .

X-ray fluorescence analysis of Nano rock phosphate was determined by using Axios, sequential, Wdxf Spectrometer analytical model 2005. at National research Center, Giza. Egypt.

3.2. Porosimetry of the Nanorock Phosphate

The nano rock phosphate pore size and distribution was determined using Nova 2000 series surface area analyzer America -Quantachrome. For the adsorption-desorption curves the adsorbate was N₂ and pore size distribution was calculated from the desorption branch using the BET model. Prior to the pore measurement, the samples were pretreated by degassing at -196°C .

Particle density in both real and bulk density were determined according to [15]

3.3. Ion Exchange Capacity Analysis

The pH titration method was used to determine the cation and anion exchange capacity of the natural and synthetic zeolites [16]. The method included measurement of the moisture content, total cations and total anions exchange capacities. For moisture content determination a pill vial was weighed with a lid closed, then an amount of Nano of rock phosphate (1-2 g) was placed inside and weighed again. The pill vial with the sample was placed open into the oven for 24 hours at 600°C . Upon the removal of the pill vial from the oven, the pill vial was weighed with a closed lid and a dried sample. The moisture content of each sample was calculated using Eq. (1).

$$\text{Moisture } W(\%) = (m_2 - m_3) / (m_2 - m_1) * 100 \quad (1)$$

Where; m_1 - weight of pill vial with lid

m_2 - weight of closed pill vial with (1 - 2 g) Nano rock phosphate

m_3 - weight closed pill vial with dried Nano rock phosphate sample.

The method of capacity determination is called pH titration. For the total cations exchange capacity (CEC) test, 5 g of pulverized sample of conversion rock

phosphate into Nano zeolite was mixed with 500 ml of 0.1 M HCl for 24 hours in a rolling bottle. Solids were separated from solution by filtration. A 10 ml filtrate was titrated with 0.1 M NaOH solution to determine the HCl concentration after adsorption. Three drops of a mixed indicator were added to the 10 ml filtrate solution and the solution turned from colorless to purple. Upon titrating with NaOH the solution turned green. Eqs (2) and (3) were used to calculate the CEC.

$$C_2 \text{ HCL} = C \text{ NaOH} \times V \text{ NaOH} / V_s \quad (2)$$

$$Q(\text{totalcat., meg/g}) = C_1 \text{ HCl} - C_2 \text{ HCl}(V)(100 - W) / 100 / m \quad (3)$$

Where: C_1 HCl- initial concentration of HCl (0.1 M); HCl C_2 - concentration of HCl after cation exchange (M); NaOH C - concentration of NaOH (0.1 M); NaOH V - volume of NaOH required for titration of the sample of filtrate (ml); s V - volume of filtrate for titration (10 ml); V - volume of HCl solution (500ml); m - mass of zeolite (5g) and W defined by Eq. (1).

The determination of the anion exchange capacity (AEC) involved thoroughly mixing 5 g of a pulverized sample of zeolite with 500 ml of 0.1 M NaOH for 24 hours in rolling bottle. 10 ml of filtrate was titrated with 0.1 M HCl solution to determine the HCl concentration after adsorption. Phenolphthalein was used as an indicator. About 3 drops were added to the 10 ml solution, which remained colorless until the addition of HCl. The end point was reached when the solution turned pink. Equations (4) and (5) were used to determine the AEC.

$$C_2 \text{ NaOH} = C \text{ HCl} \times V_{\text{HCl}} / V_s \quad (4)$$

$$mQ(\text{totalan., meg/g}) = C_1 \text{ NaOH} - C_2 \text{ NaOH}(V)(100 - W) / 100 / m \quad (5)$$

Where: C_1 NaOH - initial concentration of NaOH (0.1 M); NaOH C_2 - concentration of NaOH after anion exchange (M); HCl C - concentration of HCl (0.1M); HCl V - volume of HCl required for titration of the sample of filtrate (ml) s V - volume of the sample titrated (10 ml); V - volume of NaOH solution (500ml); m - mass of zeolite (5g) and W defined by Eq. (1).

4. Results and Discussion

4.1. SEM and EDS Analyses

Images from (1 to 6) explained the morphology of the conversion rock phosphate using a scanning electron-microscope (SEM) coupled with energy dispersive spectroscopy. It was remarkable that the conversion rock phosphate into nano particles conglomerates as compact crystals. These crystals had monoclinic symmetrical blades with different shapes such as a ball, eggs, and pyramids. Generally the crystals composed mainly as flaky material with little crystals on sight.

The largest width of the nano particles formed was 562.11 nm while the tallest recorded 701.95 nm. The images of SEM scan revealed that formation of clustered crystals of nano-rock phosphate, which are a resemblance of clinoptilolite crystal plates.

SEM images (1, 2, 3, 4, 5, and 6) of conversion rock phosphate into A.M.1 nano zeolite after calcinations and zeolitization processes.

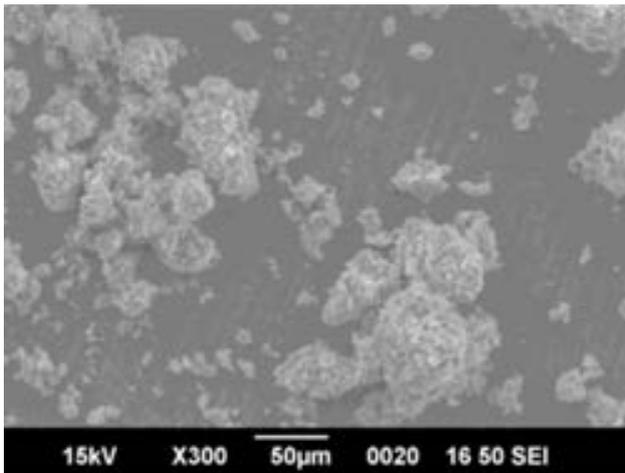


Image.1

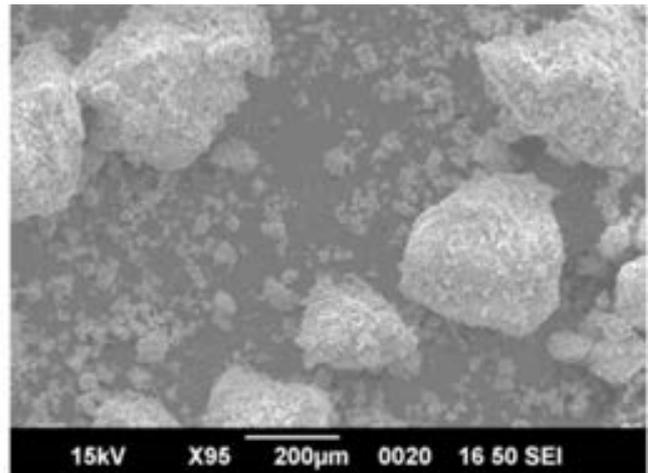


Image.2

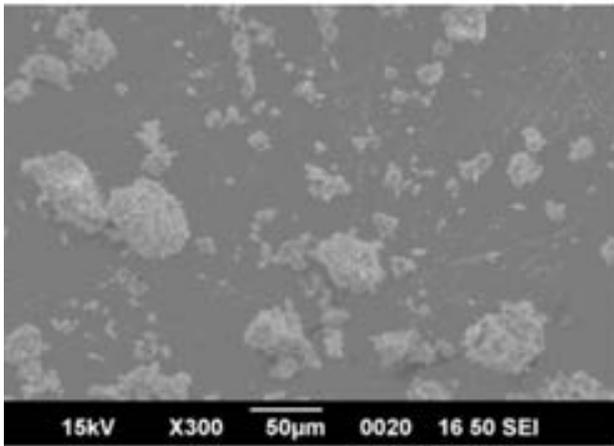


Image.3

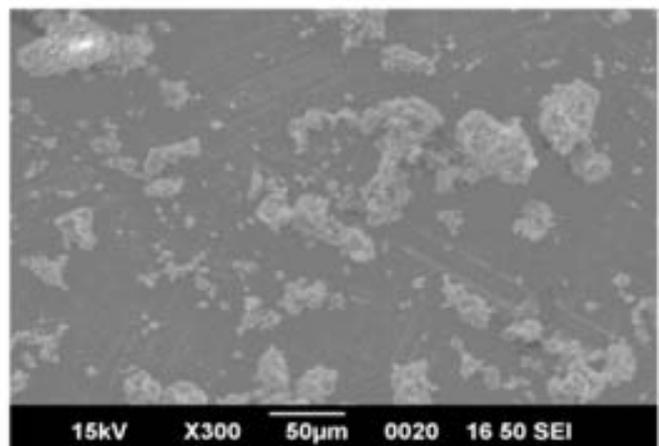


Image.4

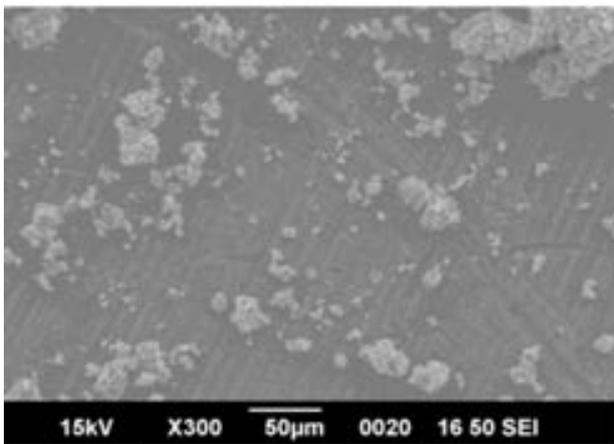


Image.5

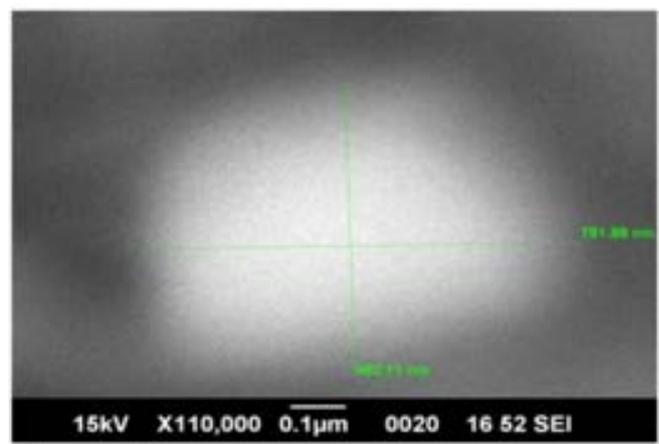


Image.6

SEM images (1,2,3,4,5, and 6) of conversion rock phosphate into A.M.1 nano zeolite after calcinations and zeolitization processes

Image. (7) Specimen atoms mapping of A.M.1 nano rock phosphate after calcination and zeolitization processes.

Meanwhile, the images of specimen atoms mapping Image. (7) of nano rock phosphate after calcinations and zeolitization processes appeared that, silica was the majority component of nano rock phosphate while Alumina takes second grade. The atom ratio between

Si/Al was 3.43 %, this ratio indicated that converted rock phosphate is hydrophilic and organophilic material. The most abundant single extra-framework cations in converted rock phosphate was found to be potassium (K), which elaborate its percentage within converted rock phosphate.

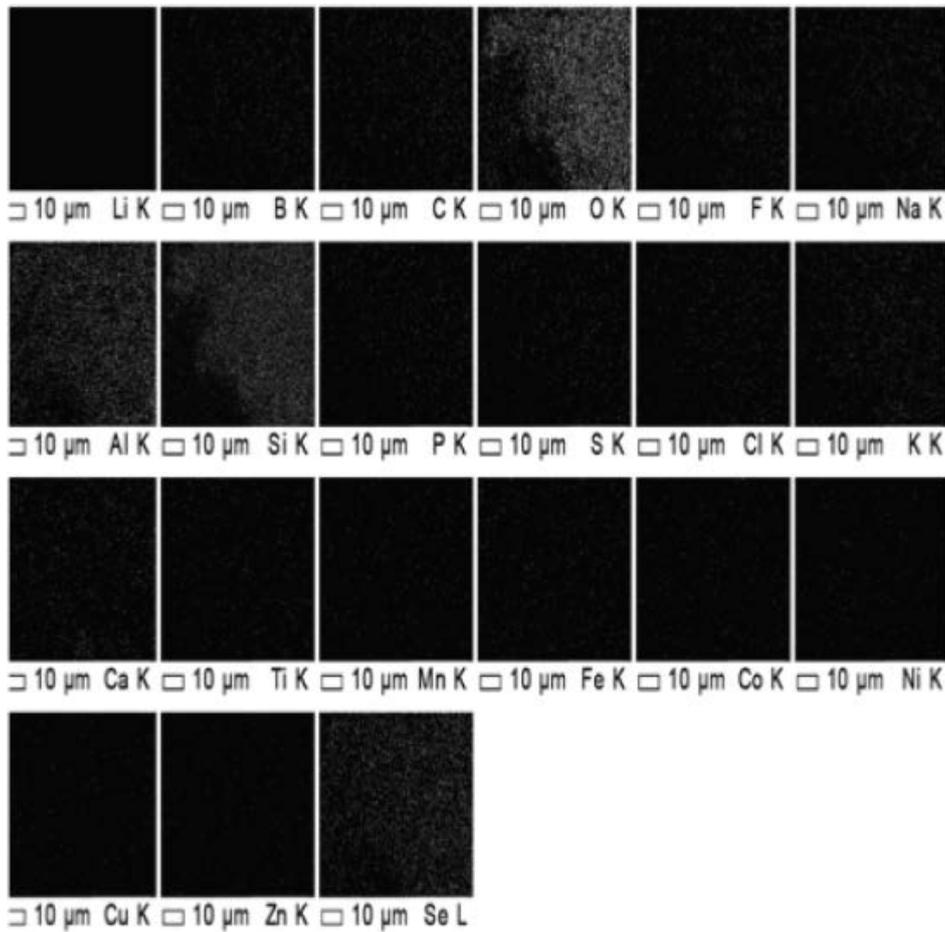


Image 7. Specimen atoms mapping of nano rock phosphate after calcintion and zeolitization processes

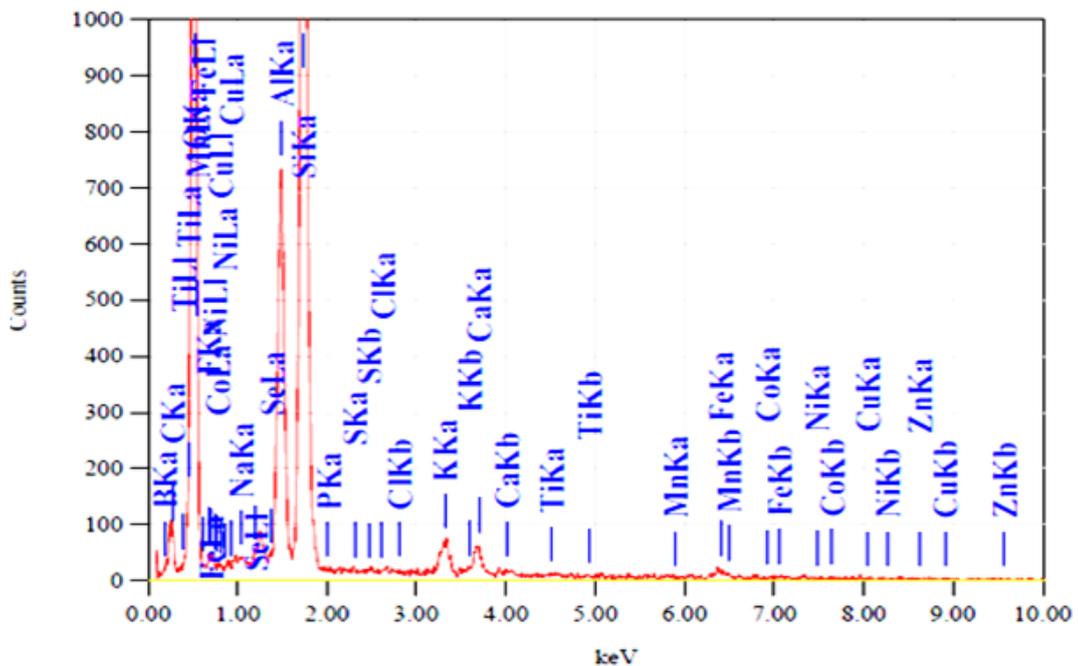


Figure 1. Energy dispersive elements of A.M.1 nano rock phosphate

4.2. EDX Analysis

Figure 1 and Table 2 donated that, specimen atoms mapping of Nano zeolite resulted from conversion rock phosphate after calcinations and zeolitization processes. It was clear that silica was the dominant component of nano

zeolite as elements mass percentage followed by Allumina, copper, manganese, potassium, iron, calcium, selenium, phosphorous, zinc, chloride, titanium, and sulfur. Focusing on oxides mass percentage are descending as follow: silica, alumina, manganese, potassium, phosphorous, titanium, chloride, zinc, copper, iron,

calcium, selenium, and sulfur. Moreover the atoms mass percentages revealed that, the absence of sulfur, copper, manganese, iron, and zinc, and come down as follow: silica, alumina, potassium, selenium, titanium, phosphorous, copper, chloride. Also it was remarkable that magnesium phases (element, oxide, and atom mass

percentages) were absent. On the other side the most abundant single extra-framework cations in Nano zeolite formed after conversion rock phosphate was found to be potassium (K), phosphorous(P), manganese, (Mn), zinc (Z), iron (Fe), calcium(Ca) selenium(Se), copper(Cu), Titanium (Ti) and sulfur (S).

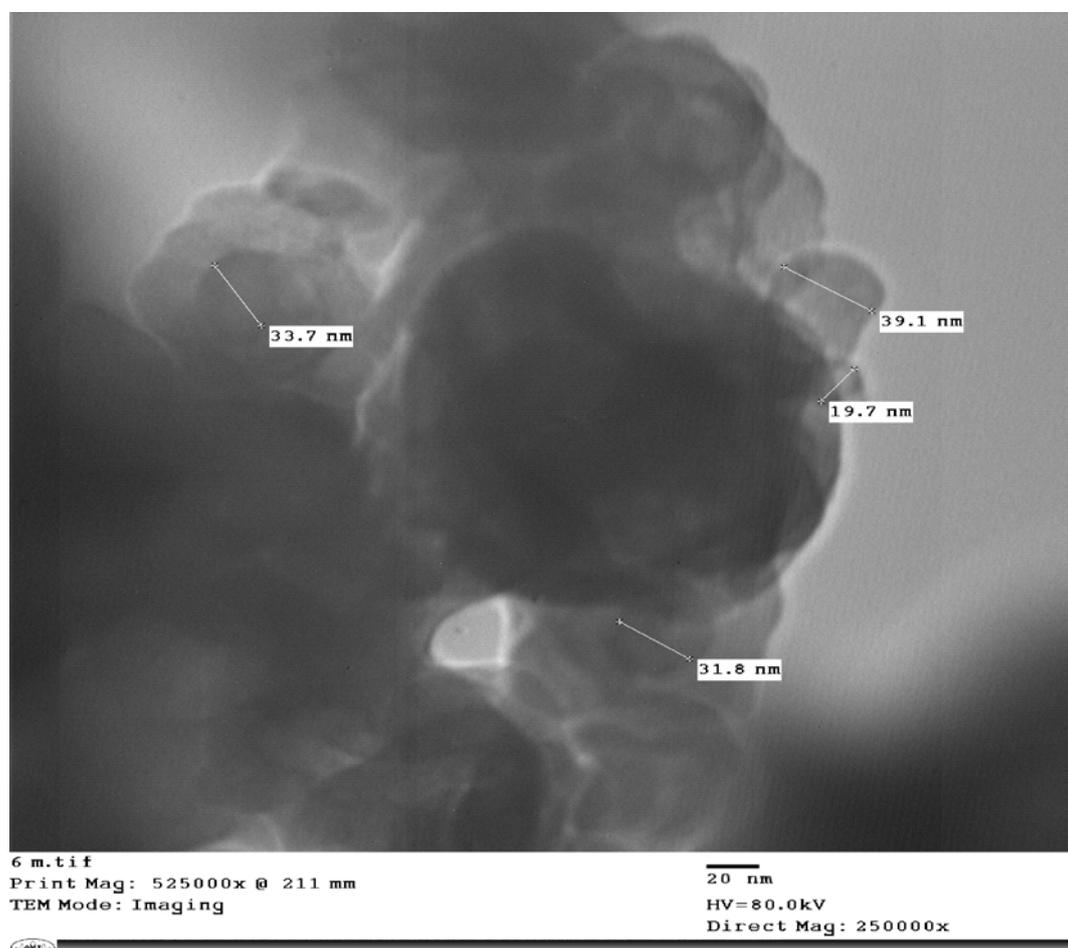


Image 8. TEM of converted rock phosphate into A.M.1 nano zeolite formed after calcinations and zeolitization processes at 700 °C

Table 2. Energy dispersive elements of A.M.1 nano rock phosphate as elements, oxides and atoms

Elements	Mass%	Compound	Mass%	Atoms	Mass%
O	45.24	O	-	O	41.35
C	3.92	C	3.92	C	10.98
F	0.60	F	0.60	F	-
Na	0.09	Na ₂ O	0.12	Na	-
Al	8.67	AL ₂ O ₃	16.37	Al	10.16
Si	29.65	SiO ₂	62.43	Si	33.22
P	0.62	P ₂ O ₅	1.41	P	0.40
S	0.08	SO ₂	0.08	S	-
Cl	0.38	-	0.38	Cl	0.02
K	1.87	K ₂ O	2.25	K	2.10
Ca	1.14	CaO	0.24	Ca	-
Mg	-	MgO	-	Mg	-
Ti	0.29	TiO ₂	0.48	Ti	0.54
Mn	2.04	MnO	2.60	Mn	-
Fe	1.84	FeO	0.28	Fe	-
Cu	2.33	CuO	0.31	Cu	0.03
Zn	0.45	ZnO	0.36	Zn	-
Se	0.78	SeO	0.11	Se	0.66
Li	-	Li	-	Li	-
B	-	B	-	B	-
Ni	-	Ni	-	Ni	-

4.3. TEM Image

Image 8 illustrates the size of conversion rock phosphate into nano zeolite (A.M.1) ranged between 19.7 -39.1 nm after zeolitization and calcinations processes.

4.4. Stereo Microscopy Study

Stereo microscopy Image 9 A, B, C and D demonstrated that, the growth of nano crystalline was formed after calcination and zeolitization processes, it was remarkable that the agglomeration of nano particles appears like fog (A&B), moreover, The nano particles take three dimentials in its formation and different shapes, such as eggs, teeth, hurt, ball and nails (C&D).

4.5. XRD Study of the Nano Rock Phosphate

The calcinations process lead to a phosphate establishment in the form of P₂O₅ and CaO content relatively higher than phosphate ore and a low level of CO₂ concentration [17].

Our XRD patterns of the nano zeolite (A.M.1) shown in Figure 2 where, two major peaks were found in

conversion rock phosphate into nano zeolite. The first peak was located in the region of 8-10 2θ while the second one located in the region of 10 -20 2θ . These two major peaks in the patterns of conversion rock phosphate corresponded to zeolite. The presence of mica muscovite and montmorillonite clay indicated that the ore type of

rock phosphate was clayey ore which associated with gangue materials as clays and aluminium silicates or oxides. The others remaining peaks represented minority minerals in the patterns which attributed to the presence of calcite, parite, alkali feldspare, plajuclase fildespare and quartz.

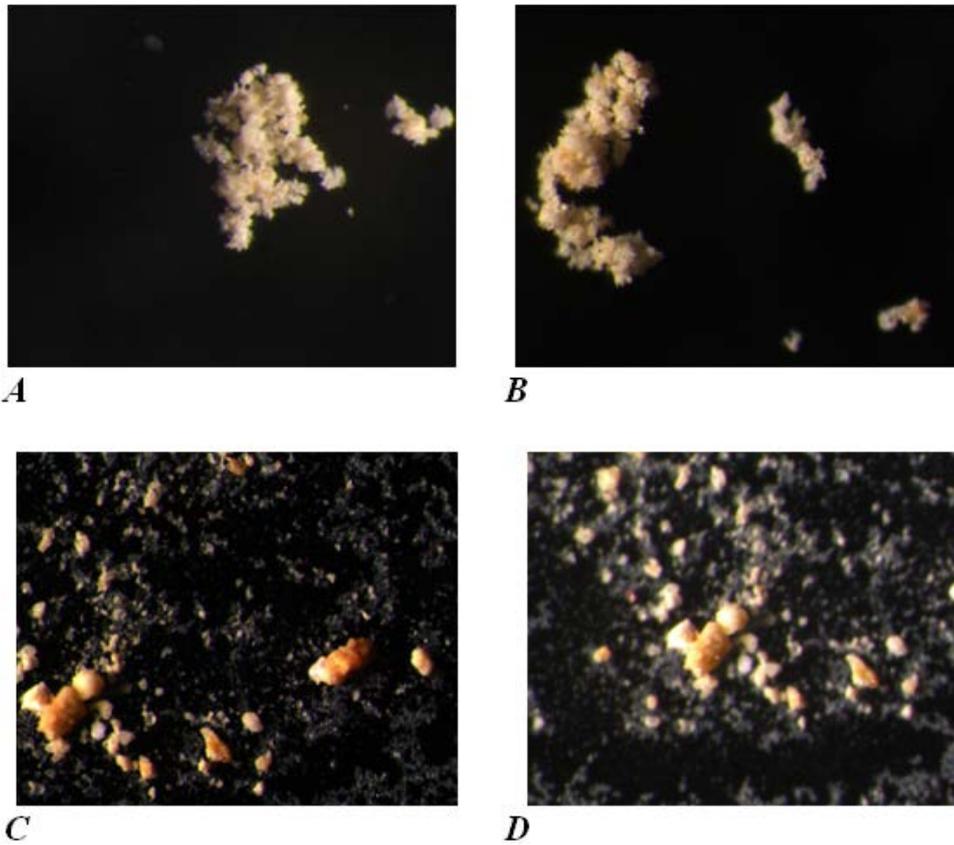


Image 9. A, B, C and D Stereo microscopy of A.M.1 nano rock phosphate conversion after calcinations and zeolitization processes at 700 °C

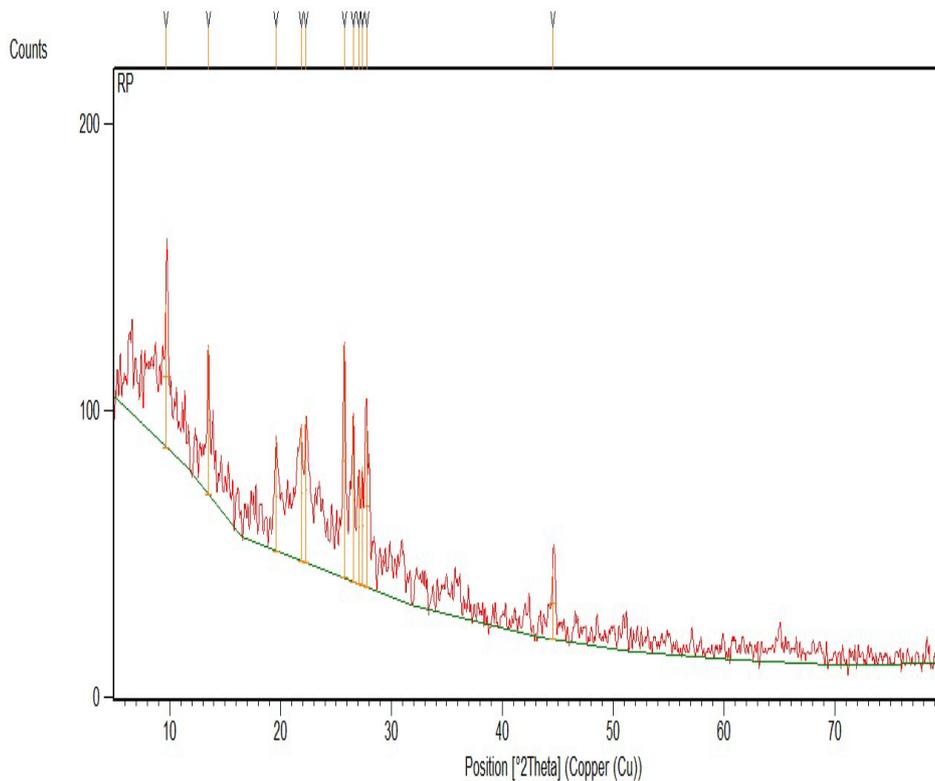


Figure 2. XRD of A.M.1 nano rock phosphate after calcinations and zeolitization processes

4.6. XRF Study of the Nano Rock Phosphate

The XRF analysis presented in Table 3 used to distinguish the rock phosphate converted into nano zeolite type and determined either hydrophilic or hydrophobic. Regarding to the International Mineralogical Association, Commission on New Minerals and Mineral Names's (IMACONMMN) third rule, [18] illustrated that, only heulandite and clinoptilolite zeolites can solely be distinguished on the basis of the silica and aluminium framework. Heulandite has a Si/Al ratio of less than 4, whilst clinoptilolite has a Si/Al of equal or more than 4.

Our results showed a high composition of Calcium, phosphorous, silicon, and alumina in nano zeolite converted from rock phosphate ore after calcinations and zeolitization processes. Calcium (Ca) and Potassium (K) were the major single extra-framework cations in the nano zeolite converted. [19] Reported that, the synthesized nano zeolite contains potassium (K) and calcium (Ca) were the major single extra-framework cations in synthesized nano zeolite.

Table 3. XRF analysis of the A.M.1 nano zeolite converted from rock phosphate after zeolitization and calcinations process at 700 °C

CONSTITUENTS %							
Si	Al	Ca	P	Fe	K	Ti	Se.
16.54	4.82	45.65	29.34	0.64	1.87	0.69	0.45

The most abundant single extra-framework cations in A.M.1 nano rock phosphate was found to be calcium (Ca), potassium (K), Nano rock phosphate of low Si/Al ratio

(less than 4 % about 3.42 %), meaning with high aluminium atoms content, lead to be hydrophilic and organophilic, vice versa a high silica content will become hydrophobic.

Finally the XRF results of nano zeolite converted revealed that the Si/Al ratio was (3.42 %) less than 4 %, therefore tend Nano zeolite to be hydrophilic and organophilic.

4.7. DTA/TGA Study of Synthesized (A.M.1) Nano Zeolites

The number of water molecules attached with the calcinations of Nano rock phosphate and its thermal stability was investigated using TGA (thermo-gravimetric analysis) and DTA (differential thermal analysis) as represented in Figure 3. Upon heating the sample from room temperature to 700°C a continuous loss of weight from 9.15% to 21.08% is clearly observed in rock phosphate ore, while in conversion nano rock phosphate a continuous loss of weight from 5.14% to 10.35% less than rock phosphate ore (about two fold). This loss of weight conversion rock phosphate is may be due to dehydration of physically adsorbed water. When the sample was further heated in the temperature range of (200 to 700°C) the weight loss observed is attributed to desorption of remaining water enclosed in the material matrix. Reduced weight loss in this region was monitored with an increase in crystallization temperature (when calcined appeared at 700°C) as well as Si/Al ratio of the sample. which becomes more hydrophilic since the Al content decreases.

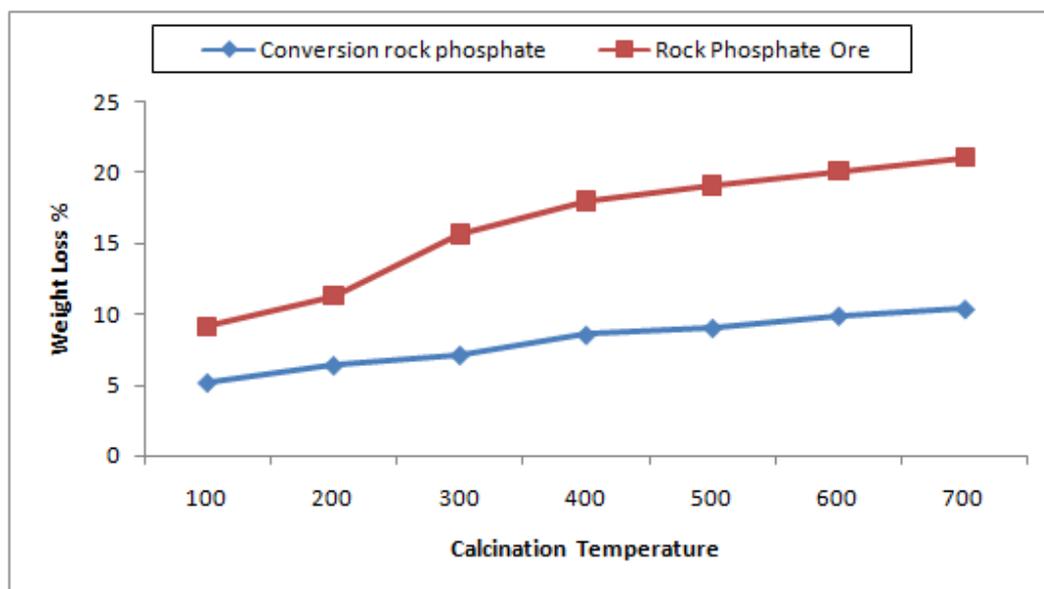


Figure 3. Weight loss as a function of calcinations temperature for original and a conversion nano rock phosphate samples

Concerning this, [21] described the synthesis of alumina nanoparticles using a chemical wet method in at changeable pH. and calcined at different temperatures. The results exposed that the nanoparticles calcined at 500°C comprise an Al₂O₃ tetragonal arrangement and tetragonal deformation decreases with increasing calcination temperature up to 750 °C then increased with increasing temperature. Another segment similar to γ -Al₂O₃ was created in preference to δ -Al₂O₃ in the transition sequence from the γ to θ phase. FT-IR analysis; suggests that there are a little different types of functional

groups on the surface of the alumina nanoparticles such as hydroxy groups and oxy groups. The transmittance spectra showed that, the absorption bands in the UV region strongly rely on the calcination temperature.

4.8. Porosimetric Study of the Nano Rock Phosphate

Adsorption/desorption isotherm curves were used to determine Nano rock phosphate pore morphology. The different nano rock phosphate material's specific surface

area was measured using Brunauer-Emmett-Teller (BET) equation isotherm.

4.9. Surface Area

Figure 4 improved that, surface area of conversion rock phosphate was low value and recorded ($14.93\text{m}^2/\text{g}$), this results were agreement with previous investigation [19] which concluded that, that AM1 zeolite had a high value of surface area ($68.71\text{ m}^2/\text{g}$) at 1000°C . Another research [20] showed that the increasing calcination temperature led to decreasing of specific surface area of the calcined product of phosphate rock. Also found that, sharp decrease in specific surface area with increasing temperature in two different phosphate samples (Morocco and Utah) between

500°C and 800°C , with the Morocco sample more remarkable in the density decrease. This change in surface area due to the aggregation (agglomeration) of elementary fine grains (nano particles) at this temperature range suggesting that consolidation of these nano particles occurs. The drastic decrease in specific surface area of the Nano rock phosphate may be render to the contribution of the destruction of the pore structure of the conversion rock phosphate. The low surface area of synthesized nano zeolite was thought to be underestimates of actual and accurate surface area measurements. This we can attributed to pores constrictions smaller than 0.5 nm which opposite N_2 adsorption and lead to underestimates for surface area of nano zeolite synthesized. [21,22].

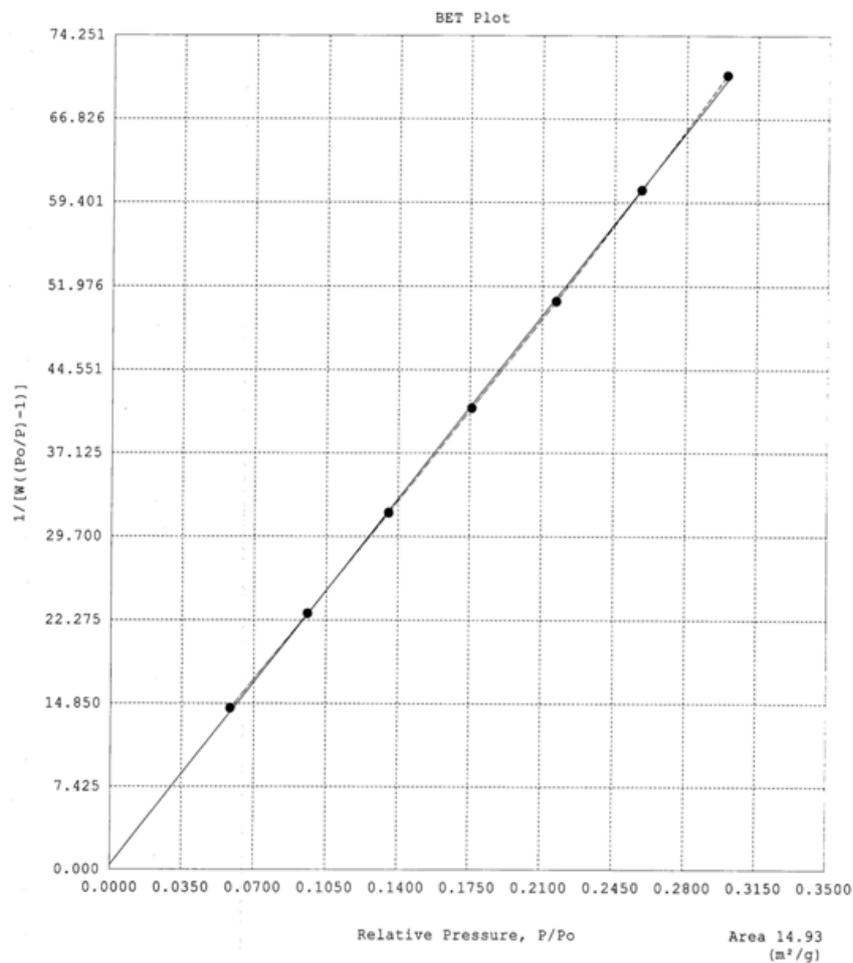


Figure 4. Surface area of conversion A.M.1 nano-rock phosphate by using calcinations and zeolitization processes

4.10. Porosity

Figure 5 demonstrated that, conversion rock phosphate into Nano zeolite has total Pore volume ($4.846\text{ cm}^3/\text{g}$) for pores with diameter less than (25.8 nm) at $P/P_0 = 0.29987$ and pore diameter generally fall within a range 3.98 to 56.87 nm with average 19.96 nm . Supported evidence [17] depicted that, the porosity of the phosphate rock sometimes increases with increasing temperature up to about 700°C then decreases from this level as in the case of Utah phosphate rock. Vis versa, some other rock phosphates, such as the Morocco rock phosphate, its porosity gradually decreased with increasing temperature and then suddenly fell to minimum at 700°C . The

porosity trends suggest destruction of the pore systems in both previous samples macro and Micro pores, but particularly the fine pores. On the base of this [23] Depicted that, two techniques have been applied to characterizations of porosities and microporous structures for the zeolites of NaA, KA, CaA, NaX and ZSM-5. Small-angle X-ray scattering (SAXS) using synchrotron radiation and nitrogen adsorption. Analyses of the data suggest that the determined sizes of the micropores imply the pore spaces engaged by the probe molecules of water in the SAXS and nitrogen in adsorption techniques, respectively. The microporous information of NaA and KA are fiddly to acquire from nitrogen adsorption, due to the clogging of nitrogen by their narrow channels, but have been properly measured by SAXS.

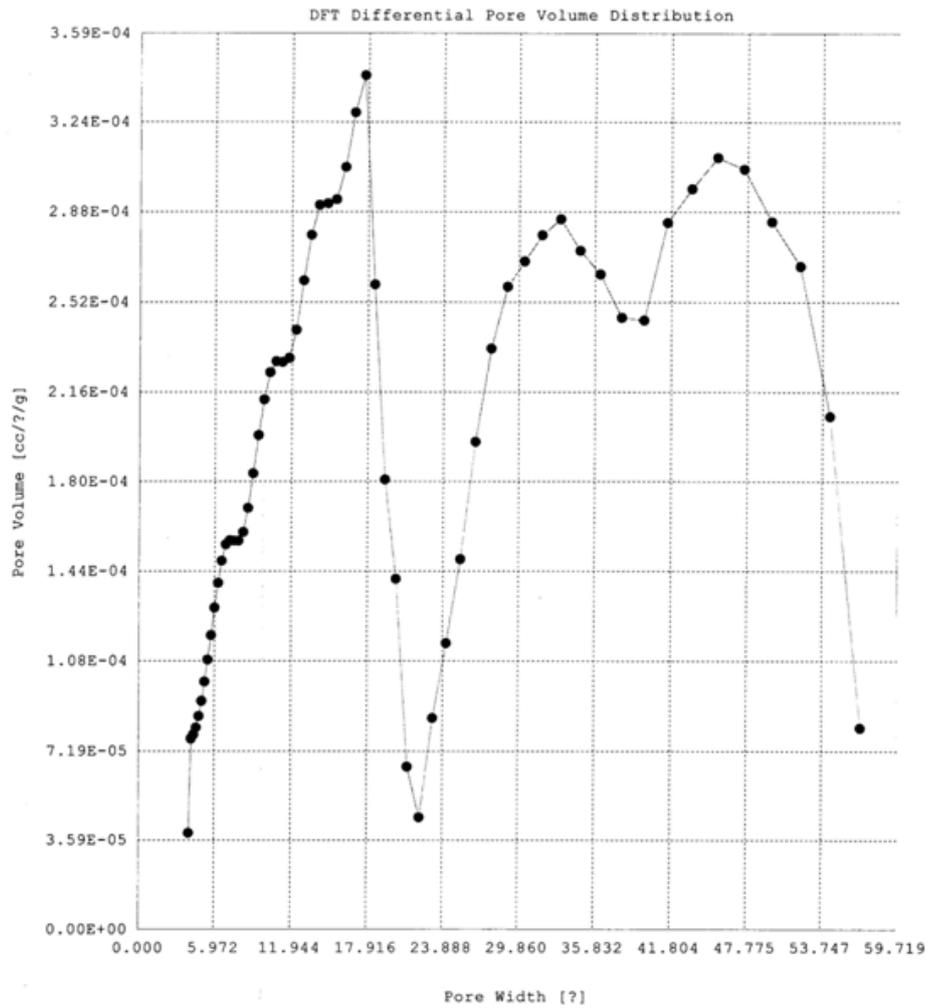


Figure 5. Pore volume and pore diameter of conversion rock phosphate after calcintion and zeolitization processes

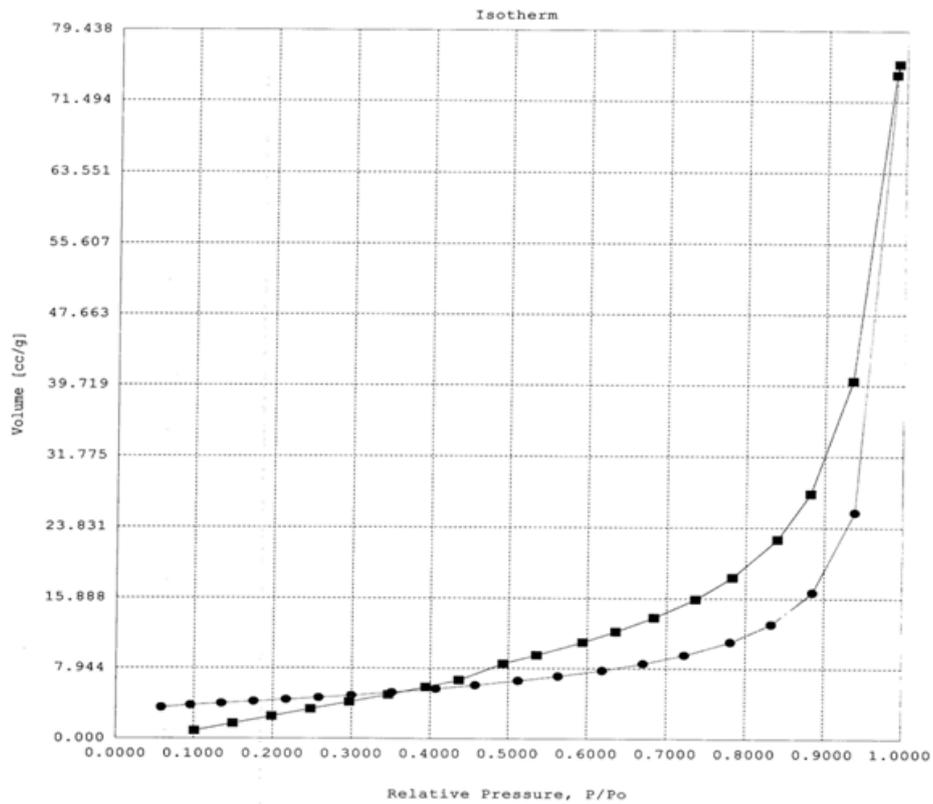


Figure 6. Pore volume of conversion nano rock phosphate after calcinations and zeolitization processes

4.11. Pore Size and Surface Area Relationship for the Conversion Nano Rock Phosphate

There are implications to be resulted from the data of pore size and surface area measurement. For the natural zeolites analysis the surface areas were found to be in the range of 14.46 - 55.03 m²/g. These surface areas are generally lower in comparison with adsorbents which used in the catalysis industry. According to literature, Almost industrial adsorbents have surface areas in the range of 500 – 2000 m²/g, with polymeric adsorbents having 150 – 1000 m²/g, this could enhance that the use of conversion rock phosphate (A.M.1 nano zeolite) in such applications. Since the pore sizes of conversion rock phosphate is in the range of 3.98 to 56.87 nm with average pore diameter 19.96 nm (Figure 6), this nano zeolite can be use in many purposes such biomedicine, foliar fertilizers, source of

phosphorus. To reach that target it needs further investigations, particularly the effect of various impurities on the hygienic of the nano zeolite.

4.12. Density

From Table 4 it was observed that, there was little change in particle density (real and bulk density) below 700 °C. Some changes in density occur above this temperature, where the density slightly increases with increasing calcination temperature. The particles densities reflect the internal collapse of the particles porosity between temperatures, of 600 °C to 700 °C. The real density is almost did not affect by the calcination temperature except at relatively high temperatures where, crystal transition may take place and cause the values real density to be lower [17].

Table 4. The effect of calcinations temperature on bulk and real density g/cm³ of nano zeolite created from rock phosphate ore

Calcination temperature	200°C	300°C	400°C	500°C	600°C	700°C
Bulk density g/cm ³	1.57	1.58	1.57	1.59	1.57	1.57
Real density g/cm ³	2.65	2.63	2.60	2.56	2.48	2.44

4.13. Study on the Ion Exchange Capacity

The results of the determined total cation and anion exchange capacities are summarized in Table 5. The natural zeolites analysis has a low but acceptable cations exchange capacity compared to the theoretical capacity of clinoptilolite (according to literature CEC is 216 meq./100g). The conversion rock phosphate (A.M.1 nano zeolite) had the highest cation exchange capacity which gave 32 meq. / 100g.

Table 5. Ion exchange capacity analysis of conversion rock phosphate to A.M.1 nano zeolite

Types of rock phosphate	CEC meq./g.	AEC meq./g.
Rock phosphate ore	0.08	.02
Conversion rock phosphate(A.M.1 nano zeolite)	0.32	.04

The anion exchange capacity of the conversion rock phosphate (A.M.1 nano zeolite) has extremely low anion exchange capacity (4meq./100g), this required that conversion rock phosphate into A.M.1 nano zeolite must be pre-treated or modified to be ideal for anions exchanging. According to these results the A.M.1 nano zeolite obtained from conversion rock phosphate could be used as cations exchangers, but not anions exchangers. Our results were convenience with (24) who, Stated that a proficient synthesis slant to acquire homogeneous nanosized high-silica Beta zeolites (10–20 nm) with high solid yields (above 95%) using simple alkyl-substituted flexible dicationic OSDAs is described. These dicationic OSDAs permit the synthesis of nanosized Beta zeolites with different Si/Al ratios (15–30) in fluoride and alkaline media, resulting in nanocrystalline materials with special physicochemical properties. These nanosized Beta zeolites show enhanced catalytic performance on the way to the industrially-relevant alkylation of benzene with propylene to obtain cumene compared with other commercially available nanosized Beta zeolites.

5. Conclusion

In our research we boost rock phosphate ores by conversion into Nano zeolite via calcinations and zeolitization processes. The idea is to create exchange sites or a “sink” for Ca²⁺ in zeolites and P₂O₅ liberate from minerals ore.via calcinations process which lead to remove or volatile Co₂ and to decompose the CaCO₃ and MgCO₃ to CaO and MgO formed from rock phosphate ore. Then suggested dissociation reaction goes as follows:

CaCO₃ + Heat (700°C) → CaO +CO₂↑ +42.9 Kcal/mol. Followed by zeolitization process which lead to formation of nano zeolite by using pre-cursor for conversion rock phosphate ore into nano particles of zeolite enrich by P₂O₅. Different techniques and measurements were used to identify conversion rock phosphate minerals into nano zeolite represented in X-ray diffraction, X-ray flourescence, Stereo microscopy, SEM, TEM, DTA, TGA, The BET surface area of the converted rock phosphate into Nano zeolite was 14.93 m²/g. On the other side, real and bulk densities were not affected by calcinations temperatures. While the pore size distribution was 3.98 to 56.87 nm with average19.96 nm. the total CEC of nano zeolite was approximately 0.32meq/g; while total AEC of nano zeolite was approximately 0.04 meq./g. Finally A.M.1 nano zeolite resulted was hydrophilic and organophilic enriched by Macro & micro elements and available source of phosphorous in form P₂O₅ that could be used as friendly fertilizer in agriculture and environment.

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