

Conversion of calcium hydroxide fouled with gases evolved from smokestack of glass industry to calcium hydroxyapatite

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Research Article

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Abstract

Conversion of industrial wastes to valuable products has become a global requirement to reduce the pollution of environment. This study intended to utilize the solid waste of calcium hydroxide fouled with gases which produced from smokestacks of glass industry by using low-cost and simple procedure. In the current work, this waste was converted to calcium sulfate by treatment with sulfuric acid for preparation of calcium hydroxyapatite (HAp) nanoparticles. The produced HAp was characterized by X-ray diffraction (XRD) and fourier transform infrared spectroscopy (FTIR) to evaluate the crystalline structure and main functional groups. The thermal stability, the particle size and morphology were studied by thermal gravimetric analysis (TGA), transmission electron microscopy (TEM) and scanning electron microscopy (SEM). The obtained results confirmed that the produced HAp is well-crystalline, with main surface functional groups of hydroxyapatite which appeared as rods-like of particle size ranged from 11 to 15 nm. Also, the obtained HAp has Ca/P ratio of 1.60 and exhibited high total surface area of 146 m²/g with mesoporous structure leading to this material can be used in medical and water purification applications.

Statement Of Novelty

The novelty of this work concerns with the management of the industrial waste which produced sustainably from glass industries and has harmful impact on the environment causing land pollution if it buried underground.

The management process depended on the conversion of different components of waste to only one phase as calcium sulfate then the conversion of it to valuable material as calcium hydroxyl apatite which has several applications in many fields as medical, dental and water treatment the conversion processes were very simple and low cost without using complicated procedures or equipment.

Introduction

Hydroxyapatite (HAp) is an inorganic ceramic material rich in calcium and phosphorus contents and has a chemical formula $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$. The synthesized HAp powder has a similar chemical composition with the natural bone where it contains about 70% bone tissues, 20% collagen and 10% water [1]. Moreover, it has unique properties such as high chemical and thermal stability, good mechanical properties, excellent biocompatibility, affinity to biopolymer and high estrogenic potential. For these properties, it is the most common in the biomedical applications such as replacement and reconstruction of bones, dental materials, coating on metallic osseous, implant, middle and general tissue engineering system [1, 2]. On the other hand, it has porous structure and high surface area which offers high active sites for binding a variety of pharmaceutical substances such as antibiotics, hormones, enzymes, antibody fragments and steroids [2]. Moreover, the hydroxyl group (OH) of HAp can be substituted by other anions such as fluoride (F^-), chloride (Cl^-) and carbonate (CO_3^{-2}) or other cations such as sodium (Na^+), (Pb^{++}) and etc. So that it can be used to remove the pollutant materials from aqueous solutions [3–6]. Owing to the importance of this material, HAp can be synthesized in different forms of particle size, structure and etc [7–10] through different methods such as precipitation, hydrothermal, sol-gel, dry method, mechanical, multiple emulsion and electro-deposition methods. Each method required several processing parameters such as pH, temperature, the molar ratio and nature of the precursors. However, these methods exhibit some advantages and disadvantages for the end product [11–15]. Hence, it is necessary to select the appropriate method of preparation to become suitable for its applications. On the production scale, HAp can be prepared from different precursors rich in Ca^{+2} and PO_4^{-3} such as the calcium carbonate, phosphate ores, phosphoric acid, ammonium dihydrogen phosphate, and etc. Also, it was prepared successfully from biogenic wastes such as egg shells, sea shells, animal bone and corals [16–20]. From the point view of the environment, several attempts were carried out to utilize the chemical wastes which resulting from the chemical

industrial units to minimize the impact of pollution and to add economic benefits. Depending on this strategy, the authors previously have synthesized nanoparticles of HAp from phosphogypsum which is produced from manufacturing of phosphoric acid and the phosphates [21–25]. To continuation of this strategy, the present study aims to prepare HAp nanoparticles from another industrial waste. The used waste is produced from the smokestack of glass industry, where a lot of fumes and gases are evolved from the fuel and the constituents of the glass. These fumes and gases according to the environmental regulations are very harmful and absorbed over calcium hydroxide where it becomes loaded with the gases such as SO₃, CO, CO₂ and etc. Accordingly, the main target is the utilization of the calcium hydroxide waste after absorption of such gases to produce HAp. Therefore, in order to know the chemical composition of the industrial waste used in this study, the sample was analyzed using XRF. The characterization of produced HAp from prepared calcium sulfate was performed by X-ray diffraction (XRD) and fourier transform infrared spectroscopy (FTIR), thermal gravimetric analysis (TGA), transmission electron microscopy (TEM) and scanning electron microscopy (SEM) and porosity.

Materials And Methods

Materials are used as the follows:

Solid waste was supplied kindly from Guardian Glass industry located at 10th Ramadan City, Egypt. Caustic soda 99% (Merck), hydrochloric acid (33% HCl,- Adwic), sulfuric acid (98% H₂SO₄-Adwic), ammonium dihydrogen phosphate((NH)H PO 99% - Merck), ammonia solution (26%NH OH -Adwic) and distilled water were used.

Pretreatment Of Industrial Waste

The waste was analyzed by XRF (Table 1) and used without grinding due to its extreme fineness. The following steps were carried out and its effect on the chemical composition of sample using XRF analysis was listed also (Table 1).

Table 1

XRF analysis of industrial waste, treated waste with distilled water (sample 1), alkaline solution (sample 2), with HCl (sample 3) and H₂SO₄ (sample 4).

Main constituents (Wt%)	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	SO ₃	F	Cl	LOI
Waste	0.64	0.11	0.06	0.25	23.13	21.63	0.30	0.14	38.59	0.45	3.98	10.51
Sample (1)	0.71	0.16	0.11	0.89	41.52	2.07	0.09	0.20	36.58	1.13	0.89	15.50
Sample (2)	1.45	0.35	0.21	3.55	47.79	0.22	0.02	0.40	5.17	2.79	0.13	37.66
Sample (3)	0.22	0.03	0.01	0.03	32.97	0.34	0.00	0.03	60.17	0.00	0.04	6.84
Sample (4)	0.15	0.04	0.06	0.04	33.19	0.34	0.00	0.03	59.60	0.00	0.01	0.48

a) Water treatment

The waste was washed with distilled water for several times, then filtered and dried at 100°C.

b) Alkaline treatment

The industrial waste was mixed in a 10% caustic soda solution for an hour at room temperature, and the mixture was left for 24 hours. Then the excess of caustic soda solution was removed by washing with distilled water for several times until the pH of the filtrate become neutral. Then the pretreated sample was filtered and dried at 100°C.

c) Acidic treatment

The industrial waste was mixed separately in 50% of HCl and 10% of H₂SO₄ solutions for an hour at room temperature and the mixtures were left for 24 hour. Then the excess acid solution was removed and the treated waste was washed with distilled water for several times until the pH of the filtrate become neutral. Then the pretreated sample with acids was filtered, dried at 100°C and analyzed by XRF (Table 1).

d) Effect of sulfuric acid concentration

The washed waste sample was treated with different concentrations of sulfuric acid (i.e., 2, 4, 6, 8 and 10%) and calcined at 450°C for 2 hours to identify the best concentration that can be used without excess to save the water spent in the washing process. The produced phases were compared using XRD (Fig. 1).

Preparation Of Hap

The starting materials used in preparation of HAp were the pretreated industrial waste after acidic treatment with 6% H₂SO₄, ammonium dihydrogen phosphate and ammonia solution for pH adjustment. The tap water was used during all preparation steps. Simple method was applied for preparation where the industrial waste was mixed with tap water under vigorous stirring at room temperature for 30 min. The required amount of ammonium dihydrogen phosphate solution was slowly added. The pH of the reaction was adjusted to be 11 by using ammonia solution. The reaction was continued for 2 hours and the produced HAp was filtrated and dried at 100°C then calcined at 700°C for 2 h. The expected reaction is occurred according to the following equation:



Characterization Of The Products

The chemical compositions of industrial waste and all pretreated samples by water, alkaline and acidic solutions were analyzed by Axios advanced Sequential WD_XRF Spectrometer, PANalytical2005 to quantify their percentages. The produced phases and crystalline nature of the prepared materials were studied using X-ray diffraction (XRD), Bruker D8 advanced diffractometer (Germany) with copper (K α) radiation which works at (40 kV and 40 mA) with 0.02°/0.4 s. The characteristic groups were measured by using JASCO-FT/CR-3000E infrared spectrometer from 4000 to 400 cm⁻¹. The surface morphology of HAp was investigated by SEM (JEOL JXA-840A, Electron probe micro-analyser, Japan) at 20 kv. The shape and size of nanoparticles of HAp were performed using High resolution-transmission electron microscope (HR-TEM, JEM-1230, Japan) operated at 200 kV. Thermal stability of HAp (TG and DTG) was measured using (Shimadzu TGA-50 H) under N₂ flow over rate 30 ml/min at 10°/min). Brunauer-Emmett-Teller surface area (S_{BET}, m²/g) and pore size distributions were analyzed using nitrogen adsorption analysis at -196°C (BEL-Sorp-max, Microtrac Bel Crop, Japan).

Results And Discussions

Chemical components of the waste sample before and after physical and chemical treatments as recorded by XRF are listed in Table 1. The results showed that the studied solid waste contains high weight percent of CaO, Na₂O and SO₃. This means that Ca(OH)₂ is partially converted to calcium sulfate and CaCO₃ by action of both sulfur oxide and carbon oxide gases. Thus, many trials were carried out to treat the industrial waste for eliminating all other impurities and to obtain a pure calcium sulfate which used for production of HAp. Different factors were being studied to optimize the conditions of treatment as follows.

Effect Of Water Treatment

Comparing to chemical compositions of industrial waste, XRF analysis of treated waste by water washing (sample1) indicated that the washing with distilled water led to a drastic decrease in the percentage of sodium oxide. Otherwise, an increase in the percentage of calcium and water content is obtained. Thus, there is an enhancement in calcium content on expense the dissolution of sodium salts in the waste sample as a result of water washing (Table 1).

Effect Of Alkaline Treatment

XRF results affirmed that the treatment with 10% of caustic soda (sample 2) led to a considerable increase in the percentage of calcium and water content of the sample. Whereas it is negatively affected the percentage of sulfate, as the weight percentage is decreased from 36.58–5.17%. This observation is due to the chemical reaction which occurred between alkaline solution and sulfate ions (Table 1).

Effect Acidic Treatment

Treatment with H₂SO₄ acid obviously is converted all unwanted impurities into soluble materials in addition to raising the concentration of sulfate ions. But treatment with HCl acid has negative influence on the amount of carbonates that react with acid and turn into soluble chlorides. In case of H₂SO₄, the carbonates convert into insoluble sulfates (Table 1). Hence, the acidic treatment with H₂SO₄ is the preferable usage to produce calcium sulfate as starting materials for preparing HAp.

Effect Of Sulfuric Acid Concentration

Because sulfuric acid exhibited good results in above section, series of experiments were carried out to explore the best H₂SO₄ concentration. (Fig. 1). represents the XRD patterns of industrial waste after treatment with different concentrations of H₂SO₄ (2, 4, 6, 8 and 10%) and calcined at 450°C for 2 hours. It is obvious that the pattern of the sample which treated with 2% contains traces of CaCO₃ (JCPDS (88-1809)) beside the main phase of CaSO₄ (JCPDS (72-0916)) while all the patterns of the other treated samples contains only one pure phase of CaSO₄. Depending on the phase purity and good crystallinity, the best acid concentration for treatment was 6%.

Characterization Of Hap

The obtained calcium sulfate from chemical treatment of solid waste with 6% sulfuric acid was calcined at 700°C for 2h to prepare hydroxylapatite (HAp) which characterized by the following techniques.

Xrd Analysis

(Fig. 2) depicts the XRD patterns of the calcium hydroxyapatite which was obtained after drying at 100°C for 2 hours. XRD patterns confirmed that HAp was obtained in weakly crystalline form. After calcination at 700°C for 2 hours, the calcium hydroxyapatite was formed as a monophasic material belonging to reference (JCPDS (76-0694)) with high crystallinity.

Ftir Characterization

(Fig. 3) illustrates the FTIR spectrum of HAp calcined at 700°C where the characteristic functional groups of HAp are observed. For example, the appearance of O–H stretching bands at 3443–2851 cm^{-1} confirms the formation of HAp and the band at 1640 cm^{-1} corresponds to O–H bending vibrational mode [26]. The double bands at 606 and 561 cm^{-1} which attributed to the ν_4 vibrational modes of phosphorous groups are appeared [27]. The band at 1022–1100 cm^{-1} which existed as a doublet or a shoulder is related to ν_3 vibrational mode of P-O groups [28, 29]. While the weak band occurred at 1430 cm^{-1} is ascribed to the ν_3 asymmetric stretching vibrations of CO_3^{2-} . This finding indicates that partially carbonated hydroxyapatite can be formed during preparation process in agreement with results reported by Stanic et al. [30].

Morphological Properties

The TEM image of the synthesized sample (HAp) is presented in (Fig. 4a). It is clear from TEM that hydroxyapatite formed in a nanostructure of rods-like shape (11-15nm of thickness and 25-32nm of length) which would candidate for many important applications in the science of bone tissue engineering. It is also evident from the corresponding selected area electron diffraction (SAED) patterns of prepared hydroxyapatite that the brightness and intensity of the rings are strong, so the material is well crystalline (Fig. 4b). The SEM image of HAp sample is presented in (Fig. 4c). It could be observed that the surface morphology of the sample was appeared as an ellipsoidal shape. The SEM micrograph emphasized that the HAp nanoparticles formed with high agglomeration as result of nanometric dimensions of the particles [31].

Thermal Analysis

The thermal gravimetric analysis for prepared HAp at 700°C is illustrated in (Fig. 5). The TGA profile of HAp showed that three regions are occurred according to DTG also. The first one is appeared at 155°C with mass loss about 6% which corresponded to evaporation of humidity water and volatile matter. The second region at 290 °C with mass loss of 22% is due to the removal of residual ammonia. The last one at 790 °C with small mass loss of 4% is attributed to the partial conversion of HAp to tri-calcium sulfate (TCP) [32]. This finding confirmed the high thermal stability of the produced HAp sample.

Bet Surface Area Measurements

The measured BET surface area was found to be 146 m^2/g with pore diameter (16.3 nm) and total pore volume (0.593 nm). The pore size distribution analysis is illustrated according to NLDFT theory at (Fig. 6). It is noted that the

maximum pore size of the HAp sample is mainly centered at 9.6 nm, confirming that the prepared sample has mesoporous structure [33].

Determination Of Ca/p Molar Ratio

XRF data of HAp sample shows that the Ca /P molar ratio is 1.60 as presented in Table 2. The obtained value is closely to the Ca /P ratio (1.67) that found in human bone [34]. This result affirmed the validity of utilizing of glass waste in production of HAp.

Table 2
XRF analysis of HAp

Main Constituents	Wt%
CaO	32.2
P ₂ O ₅	32.91
LOI	3.43

Conclusion

This study aimed to utilize the solid waste of calcium hydroxide fouled with gases which produced from smokestacks of glass industry. From the analysis of data it may conclude that:

1. All the impurities were removed by treating with 6% H₂SO₄ while using HCl or NaOH was not affected.
2. Pretreated waste with 6% H₂SO₄ was converted completely to nanoparticles HAp (11-15nm of thickness and 25-32nm of length).
3. The characterization of HAp indicated that the prepared HAp is closely to the human bone structure.
4. The produced HAp exhibited high total surface area of 146 m²/g and a mesoporous structure which candidates this material for medical and water purification applications.
5. This work can be considered as a case study for achieving environmental and economic aspects through converting industrial wastes of glass industry to valuable materials.

Declarations

Acknowledgment

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Declarations

Conflict of interest: The authors have not disclosed any competing interests.

Ethical Approval: Not applicable.

Consent to Participate: Not applicable.

Consent for Publication: Not applicable.

Data Availability

The data that support the findings of this study are available on request from the corresponding author.

Code Availability

Not applicable.

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Figures

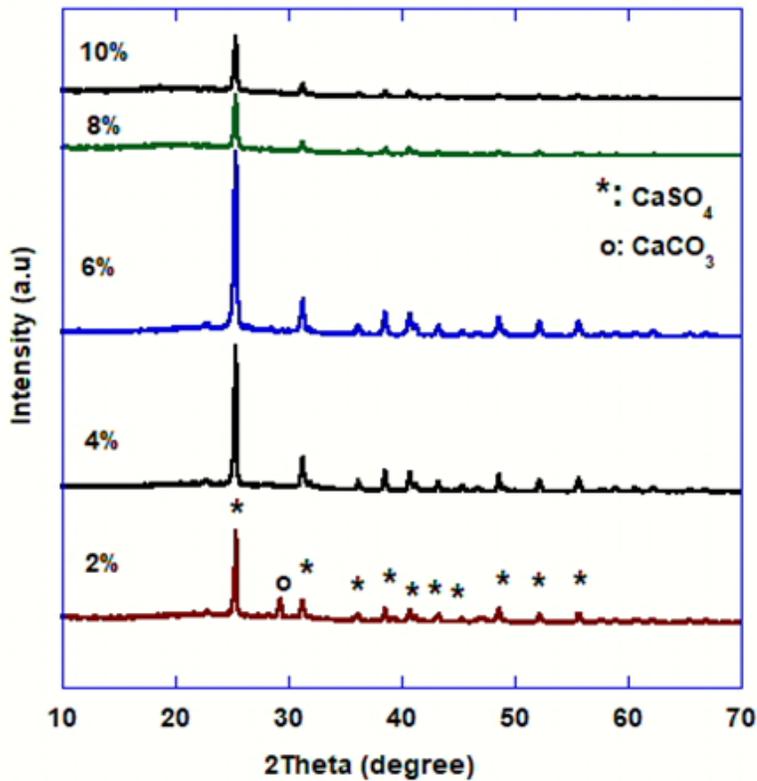


Figure 1

XRD patterns of treated industrial waste by different concentrations of H_2SO_4 (2, 4, 6, 8 and 10%).

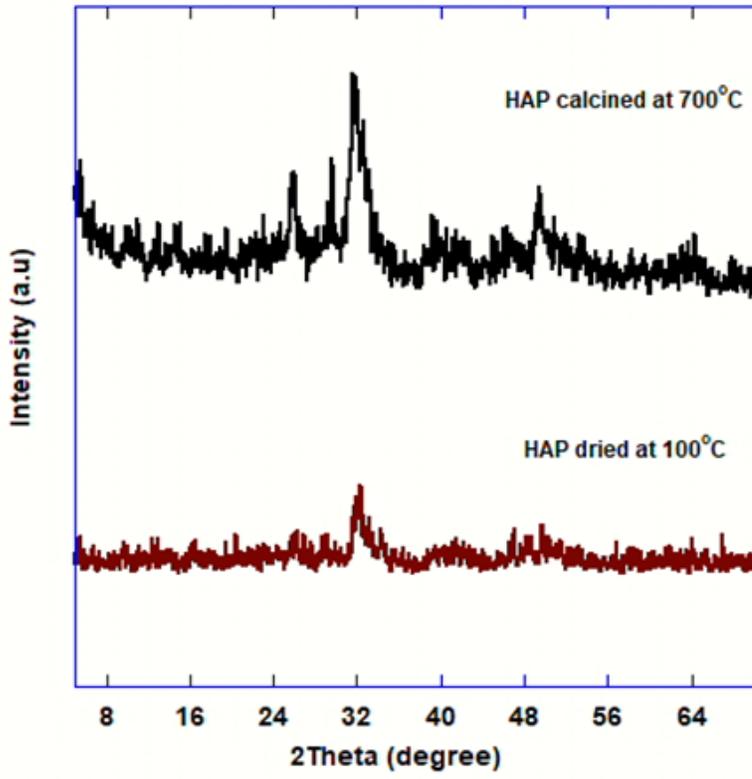


Figure 2

XRD patterns of HAp dried at 100°C and calcined at 700°C

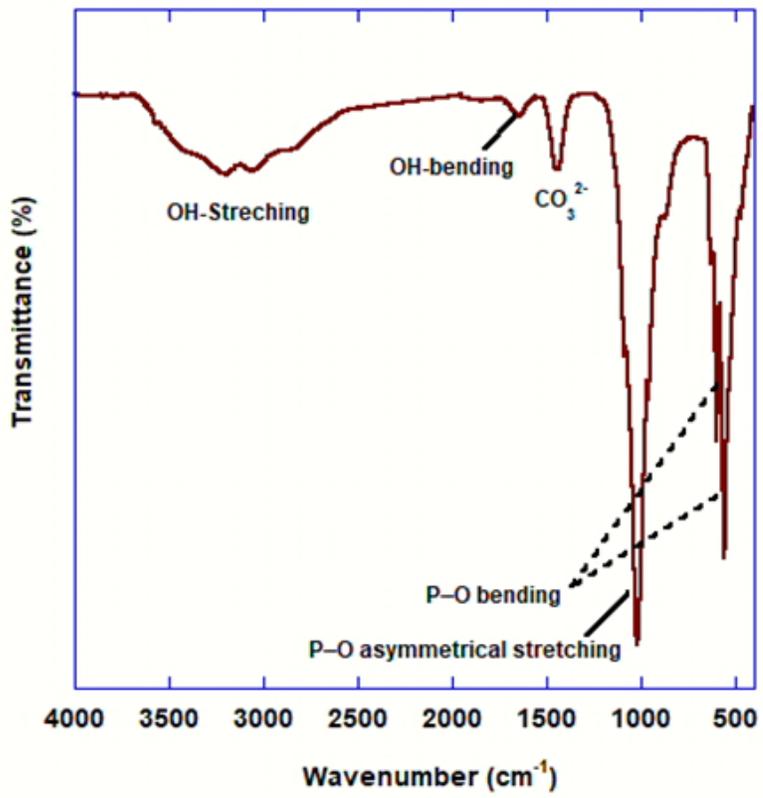


Figure 3

FTIR spectrum of HAp calcined at 700°C

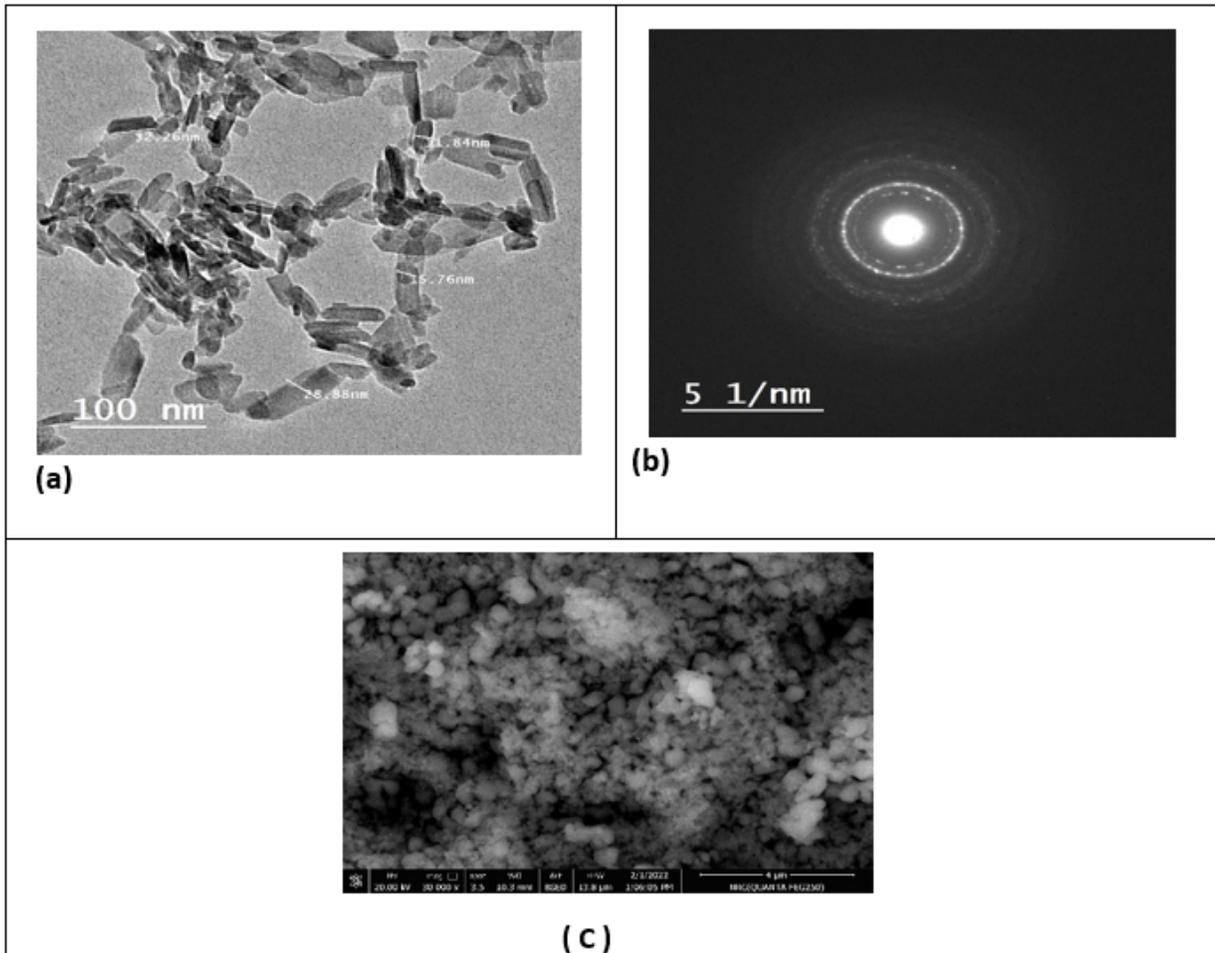


Figure 4

(a) TEM image, (b) SAED pattern and (c) SEM image of HAp calcined at 700°C

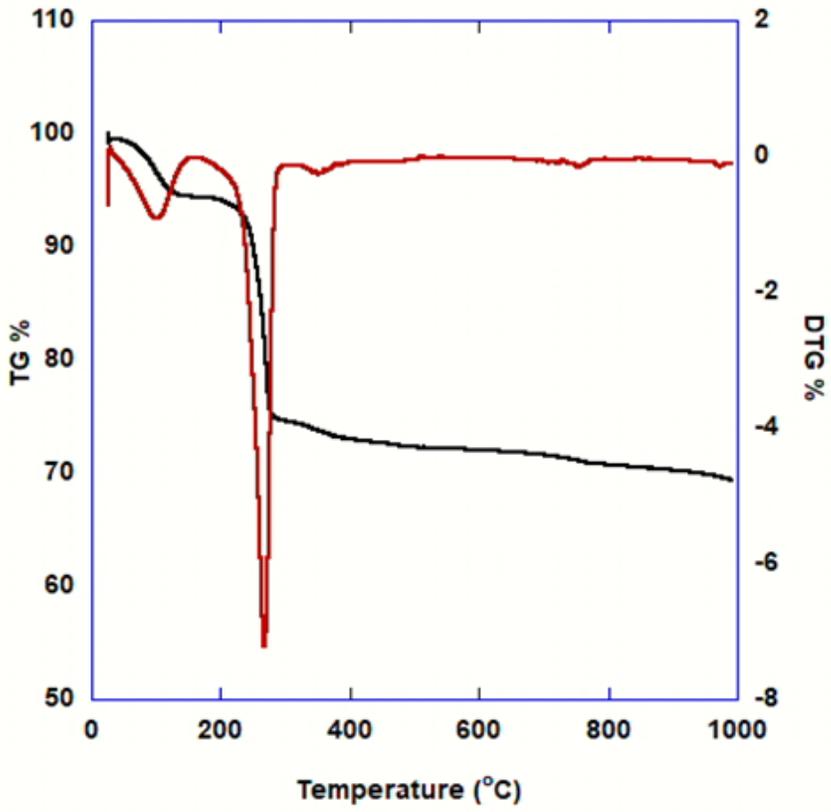


Figure 5

TG and DTG of prepared HAp

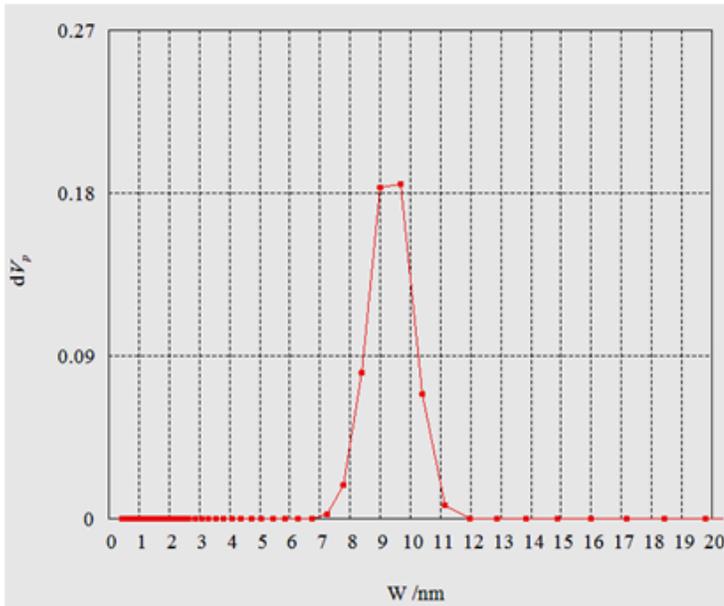


Figure 6

Pore size distribution analysis of HAp by NLDFT

