

Biomimetic Synthesis and characterization of precipitated CaCO₃ nanoparticles using different natural carbonate sources: A novel approach

V. Ramasamy^{a*}, P. Anand^a and G. Suresh^b

^aDepartment of Physics, Annamalai University, Annamalai nagar, Tamilnadu, India.

^bDepartment of Physics, Theivanai Ammal College (Autonomous), Villupuram, Tamilnadu, India.

Abstract

In the recent years, Calcium carbonate (CaCO₃) is manifest filler in the wide range of industrial applications. In this work, nanoCaCO₃ have been successfully synthesized by the biomimetic method using different natural carbonate sources. The synthesized products were characterized by FTIR, XRD, SEM-EDS techniques to recognize the mineralogy, morphology and crystallites size. The synthesized products are in rhombohedral structure within the crystalline of 20-30 nm range. It has crystalline and flower-like structure. Achieved characteristics show that the biomimetic products may be used for various industrial applications. This method is Eco-friendly and hot chemical free.

Keywords; Nano CaCO₃; Natural sources; Dolomite; Mineralogy

1. INTRODUCTION

Calcium carbonate is the world's most versatile mineral. The calcite is the principal mineral of lime stones and marbles. Dolomite occurs as a replacement for calcite in limestone. Aragonite occurs in some recent sediment and in the shells of organisms that have calcareous skeletons

*Corresponding Author. E-mail address: srsaranram@rediffmail.com (Ramasamy.V).

This material can easily to get at lower prices with low toxicity and stumpy pollution, high brightness, fill volume and mixing characteristics of good performance and processing. However, due to its hydrophilic nature and the limitations of traditional production processes, usually, calcium carbonate particles are relatively coarse, smaller than the surface area. According to Kosuke Sato et al., (2015) [1], nanomaterials can have high specific area and nanomaterials play a vital role to glue the peculiar characterization which is highly essential for specific applications. Nanometer superfine calcium carbonate developed a new type of ultra-fine solid material.

In recent years, Calcite is widely used as filler in many industrial applications such as rubber, plastic, paper making, printing ink, cosmetics, toothpaste, food industries, pharmaceutical industries, nutritional supplements, adhesives, sealants and cement [2,3] it is also used to produce high-level art paper, high-grade ink, auto paint (polyester paint the chassis, car paint, etc.) which increases market demand. However, there is nanometer superfine calcium carbonate production is still low, and less product variety, cannot meet market demand, most of the products are imported.

Therefore, the nano-level research and development of ultra-fine calcium carbonate are needed for the application in domestic and international attention. The present work is mainly focused on to synthesis of nano Calcium carbonate from different natural sources of carbonate varieties.

2. MATERIALS AND METHODS

2.1 Chemicals

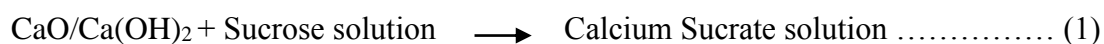
Sucrose and Sodium carbonate, analytical grade with 99% purity were used without further purification. All the glassware's used in this work were acid washed. Ultrapure water was used for all dilution and sample preparation. The high-grade crystalline natural limestone, dolomite and calcitic rock samples collected from Padaivedu, Salem district and sea shells collected from Parangipettai, Cuddalore district, Tamilnadu, India were used in this work as raw materials.

2.2 Preparation of calcium sucrose solution

All samples were crushed, ground using ball mill and filtered through ASTM 230 (62.5 micrometers) mesh sieve. The powdered sample was calcined at 900 °C for 2 h in a muffle furnace to get CaO. 10.00 g of CaO powder was dissolved in 100 ml of 1.00 M sucrose solution and vigorously stirred for an hour at room temperature. The solution was filtered under suction to obtain soluble calcium sucrose solution.

2.3 Synthesis of CaCO₃

The prepared calcium sucrose solution was placed in a 500 ml three-necked rounded bottom flask and 80 ml of 1M sodium carbonate solution were added dropwise to get nano PCC without polymer, while the solution vigorously stirred, maintained at 80°C for two hrs. The possible mechanism to synthesize nano PCC as follows [4]. CaCO₃ calcined at 900 °C yielded CaO/Ca(OH)₂.



2.4 Characterization Techniques

The FT-IR spectra were recorded using SHIMADZU-8400 with a resolution of $\pm 4 \text{ cm}^{-1}$ in transmittance mode. The fine powder samples were mixed with pure KBr in the ratio of 1:30 and then the mixture was pressed under vacuum at about 10 tons by placing the mixture in 13 mm diameter to get a disc of about 1 mm thickness. All the spectra were recorded in the region 4000-400 cm^{-1} .

The X-ray diffraction (XRD) patterns of the powdered samples were recorded using Inel equinox-1000 diffractometer. Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$) source was used to record the samples at room temperature. During the recording of the diffractogram, a narrow slit of 0.1mm was used with a scanning speed of 0.02 /s. The sample was scanned from 10° to 70°.

The morphological studies of the products were analyzed using scanning electron microscopy. These measurements were performed on a JEOL- 6610 scanning electron microscope. Energy-dispersive X-ray analysis (EDX) measurement was carried out using Bruker 129 eV, to get elemental composition (%). Before the measurement, the samples were mounted on copper stubs by double sided carbon tapes and the gold is coated using the sputtering technique.

3. RESULTS AND DISCUSSION

3.1 Functional group analysis

FTIR spectroscopy is an important instrument used to identify different phases of organic and inorganic compounds and, specifically, calcium carbonate phases due to the differences in their carbonate ions, CO₃²⁻. Carbonate ions and similar molecules have four normal modes of vibration peaks: ν_1 , symmetric stretching; ν_2 , out-of-plane bending; ν_3 , doubly degenerate planar asymmetric stretching; and ν_4 , doubly degenerate planar bending [5].

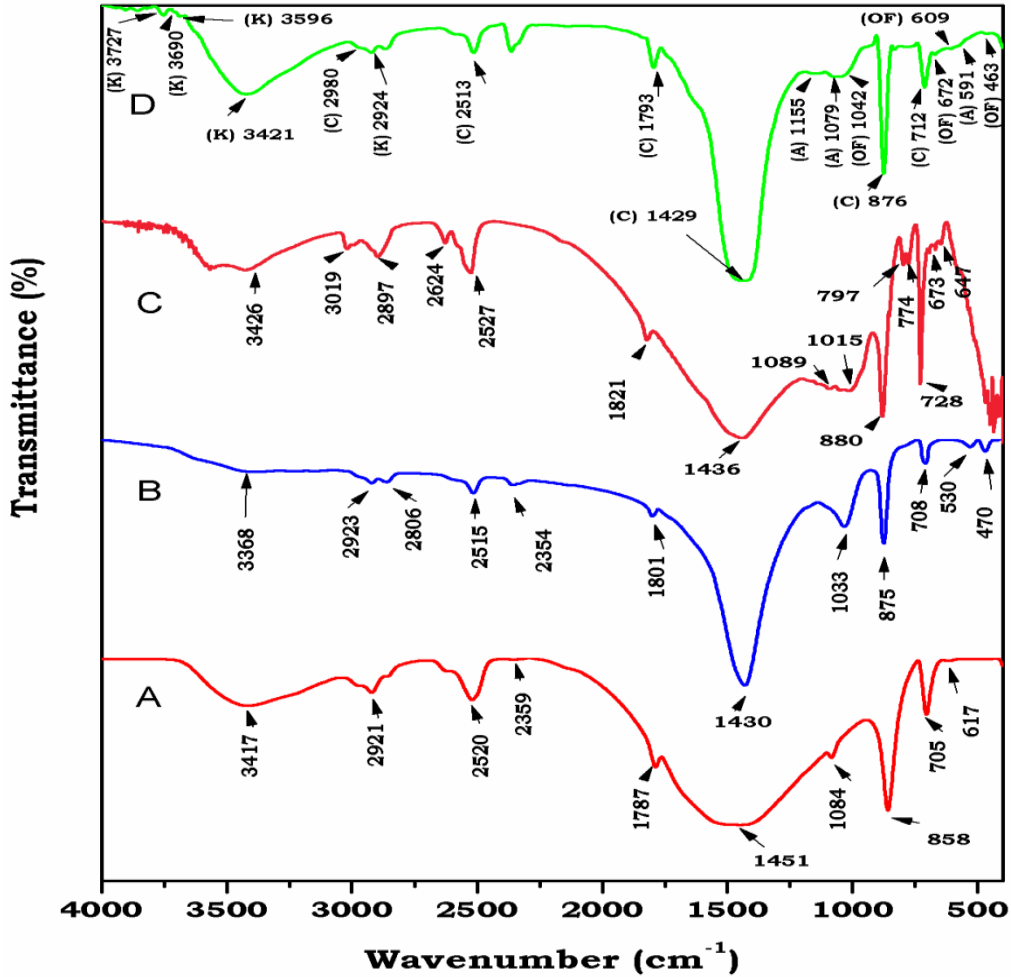


Figure 1: FTIR spectra of different raw natural sources shell(A), limestone (B), dolomite (C) and calcite rock (D)

Figure. 1(A-D) depicts the representative spectrum of shell, limestone, dolomite and calcitic rock at RT. From Fig.1A spectral data obtained for the samples reveal a broad absorption peak of CO_3^{2-} at $1451(\nu_3)$, $1084(\nu_1)$, 1787 , $858(\nu_2)$ and $705(\nu_4)\text{ cm}^{-1}$, which have been reported to be the common characteristic features of the carbonate ions in calcium carbonate and are the fundamental modes of vibration of this molecule [6]. The peak at 1084 cm^{-1} was only observed in the spectrum of aragonite phase calcium carbonate, whose CO_3^{2-} ions are inactive in the infrared region. This observation was verified by other reports in the literature on characteristic infrared bands, which are experimentally not observed in the spectrum of calcite. This degeneracy can only be removed by splitting the band into two; thus, the band is attributed to the aragonite phase only, which has been confirmed through the literature [7]. A similar result was also reported by Abdullahi Shafiu Kamba 2013 [8].

From Fig 1B and D, absorption peaks indicate the presence of calcite (C) (major), kaolinite (K), orthoclase feldspar (OF) and anorthite (A). The molecular symmetry and structural relations in carbonate molecules were discussed in a detailed manner in the earlier publication [5]. The frequency assignments reported by Herzberg (1945) [9], for various calcite group minerals in the region of absorption are at approximately $1430\text{ cm}^{-1}(\nu_3)$, $909\text{-}833\text{ cm}^{-1}(\nu_2)$ and $769\text{-}666\text{ cm}^{-1}(\nu_4)$. In the present investigation, the calcite rock and limestone mineral occupy major proportion having the absorption band at approximately $712, 876$ and 1429 cm^{-1} and $708, 875$ and 1430 cm^{-1} respectively, and minor bands calcitic rock and limestone at $1793, 2513$ and 2980 cm^{-1} and $1801, 2515$ and 2983 cm^{-1} . The absence of ν_1 mode confirms the presence of calcium carbonate in calcite form (D_{3h}).

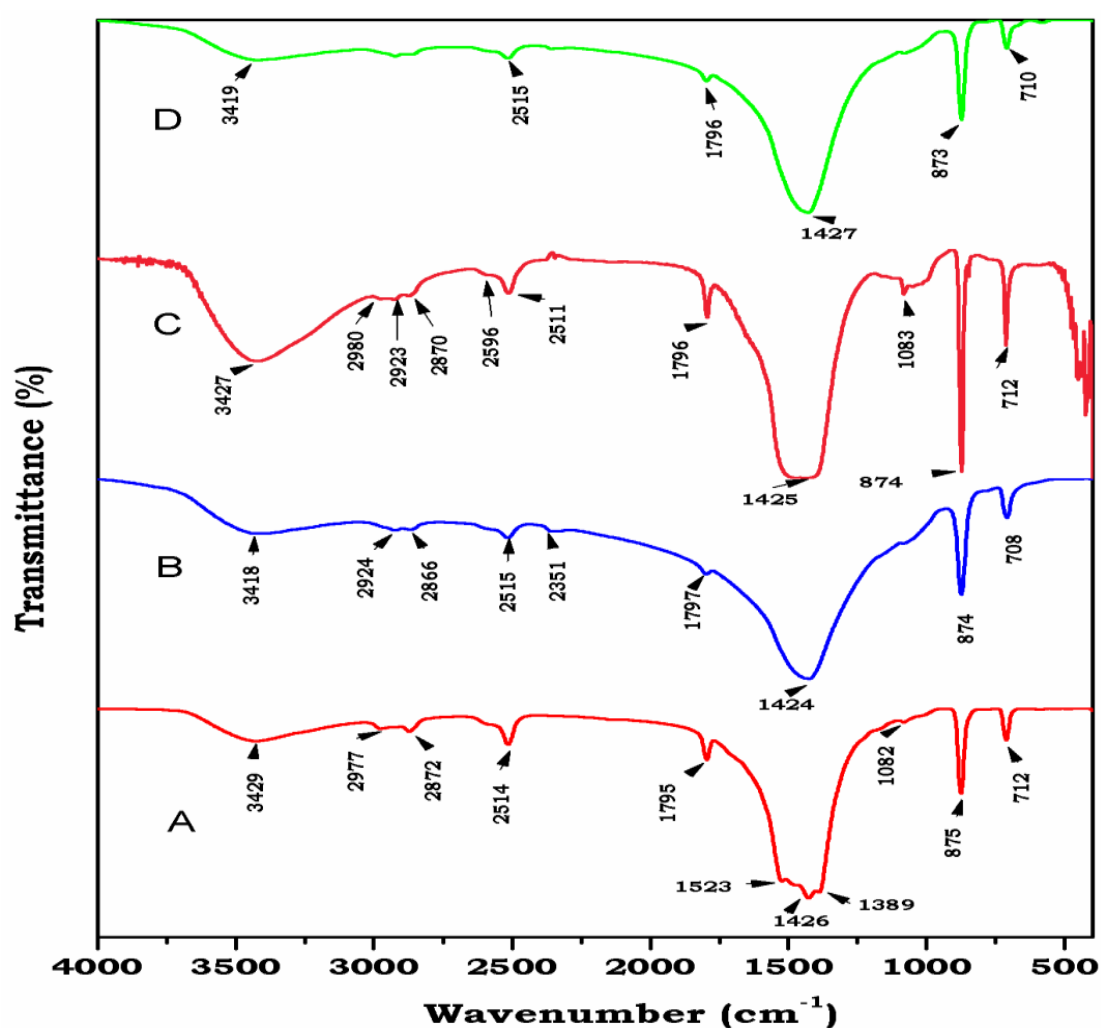


Figure 2: FTIR spectra of synthesized PCC from different raw natural sources shell (A), limestone (B), dolomite C) and calcite rock (D)

The IR spectra of calcite and dolomite are characterized by bands at 711 cm^{-1} and 727 cm^{-1} respectively. These bands appear unperturbed and sharp with varying intensity depending on the concentration of these minerals. But in the present study, the 727 cm^{-1} peak is completely absent in all the samples. It may mean that dolomite is either absent or undetected. If dolomite is not present, then naturally, a phase change will not occur at lower temperature itself. The peaks observed at 3727 , 3690 , 3656 , 3421 and 2924 cm^{-1} are the characteristic peaks of kaolinite. In the present study, the spectrum shows two bands at 3690 and 3656 cm^{-1} with weak absorption. This is due to the weak hydrogen bonding to the Si-O surface. According to Keyser et al., (1969) [10], the appearance of absorption frequency 3421 cm^{-1} is partly due to disordered kaolinite lattice. According to Mackenzie and Rahman (1987) [11], Kaolinite and calcite frequently co-exist in the clay fraction of soil and sediments. Hence, the presence of kaolinite in calcite is unavoidable.

According to Ghosh (1978) [12] and Russell (1987) [13], the absorption peaks observed at 463 cm^{-1} (Si-O-Si bending vibration), 591 and 609 cm^{-1} (O-Si(Al)-O symmetrical bending vibration), 672 cm^{-1} (O-Si(Al)-O symmetrical bending vibration), 1042 and 1079 cm^{-1} (Si(Al)-O stretching vibrations) and 1155 cm^{-1} (Si-O stretching vibrations) for the samples are due to the presence of feldspar (potassium and plagioclase feldspar) minerals. In the present case, comparing above studies, the peaks at 463 , 609 , 672 and 1042 cm^{-1} indicate orthoclase feldspar and 591 , 1079 and 1155 cm^{-1} indicate anorthite feldspar.

According to Ben Xu and Kristin M. Poduska (2014) [14], absorption frequencies such as 728 , 880 and 1436 cm^{-1} of raw dolomite observed from IR spectrum (Fig.1C) confirmed the presence of dolomite.

Figure. 2 A-D show the FTIR spectrum of precipitated CaCO_3 particles (PCC). It reveals that all the major and minor bands of CaCO_3 appear, almost at the same position as observed and other mineral peaks are completely absent. Since all the characteristic fundamental peaks with intensities are very well matched with the peaks of CaCO_3 , it is confirmed that the synthesized product is pure CaCO_3 . The observed wavenumbers are tabulated in Table 2.

Table.2 Observed wavenumbers (cm⁻¹) from FTIR analysis of synthesized PCC from different natural sources

Synthesized CaCO ₃ (wavenumber (cm ⁻¹))			
(from Shell)	(from limestone)	(from dolomite)	(from calcite)
712	708	712	710
875	874	874	873
1082		1083	
1389			
1426	1424	1425	1427
1523			
1795	1797	1796	1796
2514	2515	2511	2515
	2531	2596	
2872	2866	2870	
2977	2924	2923	
		2980	
3429	3418	3427	3419

3.2 XRD analysis

The crystal structure and phase identification of the samples are analyzed using the X-ray diffraction pattern. The **XRD** spectra were recorded for all the samples of the shell, limestone, dolomite and calcitic rocks and observed 2θ and hkl values shown in table 1.

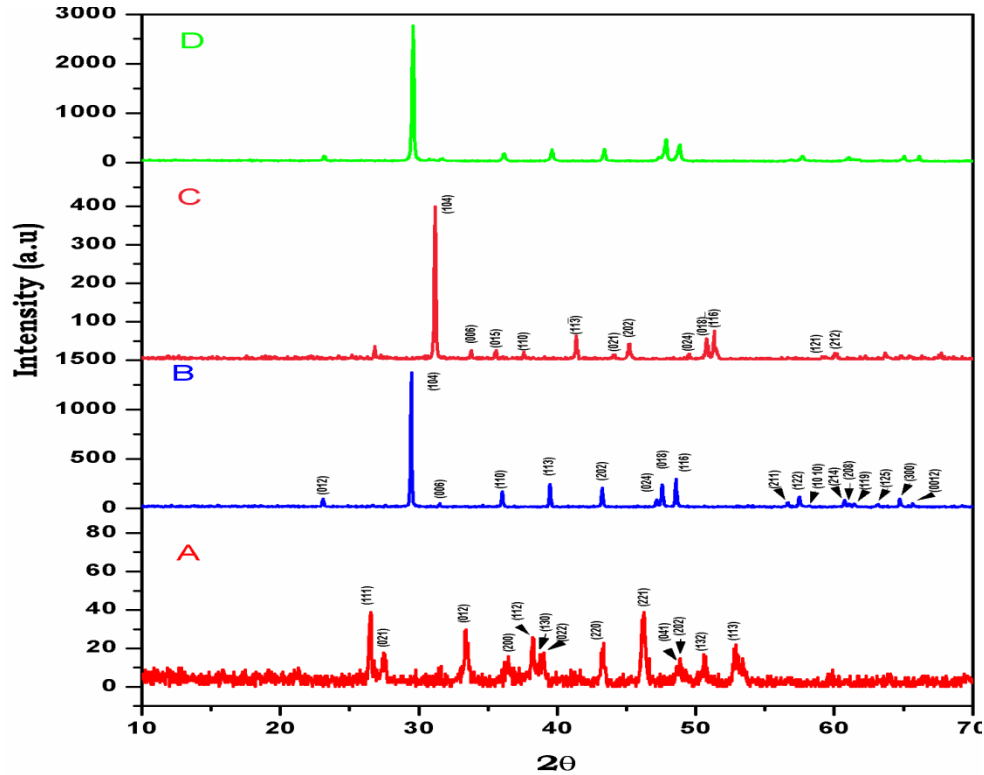


Figure 3. XRD pattern of different raw natural sources shell (A), limestone (B), dolomite (C) and calcite rock (D)

Fig 3(A-D) depicts that the composition of the crystals was in pure of aragonite (orthorhombic), limestone (hexagonal), dolomite (rhombohedral) and calcite (rhombohedral) with reference to (JCPDS: 01-071-4891), (JCPDS: 96-901-6707), (JCPDS: 01-083-1766) and (JCPDS: 01-086-2335). Figure. 4A-D shows X-ray diffraction patterns of synthesized nano PCC. All the samples reveal the 13 major and minor planes. The position of these planes dictated that the product is having, only pure CaCO_3 , rhombohedral (JCPDS: 83-1762) structure and calcite phase. No other additional peaks are observed.

The average crystallite size of nano PCC particles are calculated using Scherer' formula [15, 16]

$$D = \frac{k\lambda}{\beta \cos\theta} \text{ (\AA)} \dots \dots \dots (4)$$

Table 3. XRD data of different natural sources

Raw shell	hkl	Raw lime	hkl	Raw dolomite	hkl	Raw calcite	hkl
26.27	111	23.07	012	30.94	104	23.13	012
27.27	021	29.46	104	33.53	006	29.61	104
33.20	012	31.52	006	35.30	015	31.65	006
36.26	200	36.03	110	37.34	110	36.18	110
37.97	112	39.47	113	41.11	11-3	39.62	113
38.48	130	43.23	202	43.77	021	43.41	202
38.70	022	47.57	018	44.91	202	47.85	018
43.00	220	48.58	116	49.25	024	48.86	116
45.96	221	56.67	211	50.52	018	56.85	211
48.40	041	57.48	122	51.05	11-6	57.69	122
48.56	202	60.78	214	58.86	12-1	61.05	214
50.33	132	64.73	300	59.78	21-2	65.06	300
52.58	113						

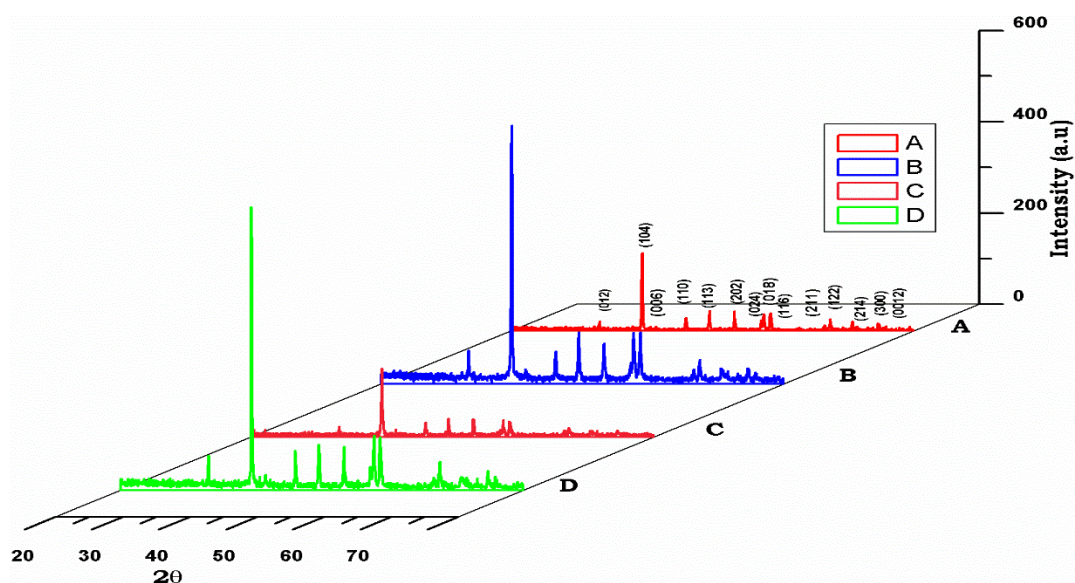


Figure 4. XRD pattern of different synthesized PCC from different raw natural sources shell (A), limestone (B), dolomite (C) and calcite rock (D)

Where D denotes crystallite size (nm) λ - wavelength of the $\text{CuK}\alpha$ (1.5406 \AA), K – constant (0.94), β - FWHM (full-width half maximum) and θ is the diffracted angle.

Table.4 XRD data of synthesized PCC from different natural sources

Synthesized nano calcite from				
(shell)	(lime)	(dolomite)	(calcite)	hkl
23.16	23.10	23.16	23.13	012
29.55	29.49	29.52	29.52	104
31.55	31.58	31.64	31.61	006
36.06	36.06	36.06	36.06	110
39.56	39.50	39.50	39.56	113
43.29	43.26	43.20	43.32	202
47.60	47.63	47.72	47.81	018
48.65	48.65	48.55	48.77	116
56.73	56.67	56.73	56.70	211
57.51	57.51	57.42	57.60	122
60.84	60.75	60.87	60.81	214
64.67	64.73	64.73	64.82	300
Particle size (nm)				
27.81	17.51	25.05	32.64	

The crystallite size is calculated for all the 13 planes of nano PCC from shell, limestone, dolomite and calcitic rock. The observed 2θ values and mean values of crystallite size are reported in Table 4. From the table values, all the synthesized samples have particle size in the range of 20-30 nanometer scale. Among them, synthesized nano CaCO_3 from calcitic rock has higher intensity with lower particle size. From the XRD analysis, it may be concluded that the calcitic rock sample has more purity than others.

3.3 SEM- EDS analysis

The morphology and elemental compositions of the calcitic raw sample and the synthesized nano products were analyzed using SEM (low and high magnifications) with EDX techniques. The surface morphology of the calcitic rock and synthesized has been observed by SEM analysis [Fig. 5A and B]. From the Fig. 5(A-B), raw calcitic rock has monodispersed and well crystal morphology and higher magnification were recorded. The synthesized CaCO₃ nanomaterials (Fig. 5(C-D)), shows aggregation and irregular shapes with small crystal-like structure. When compared with raw calcitic rock, synthesized CaCO₃ nanomaterial has different morphology.

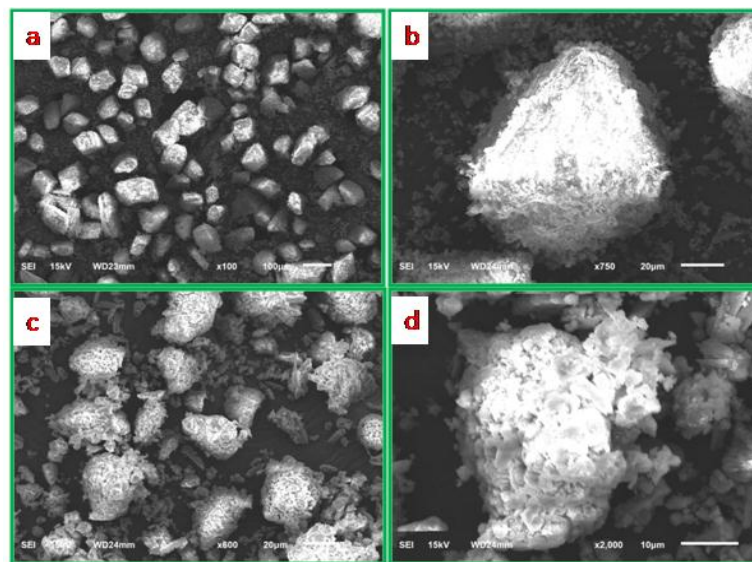


Figure 5. SEM image of raw calcitic rock (A, B) and synthesized nano PCC (C, D) with different magnification

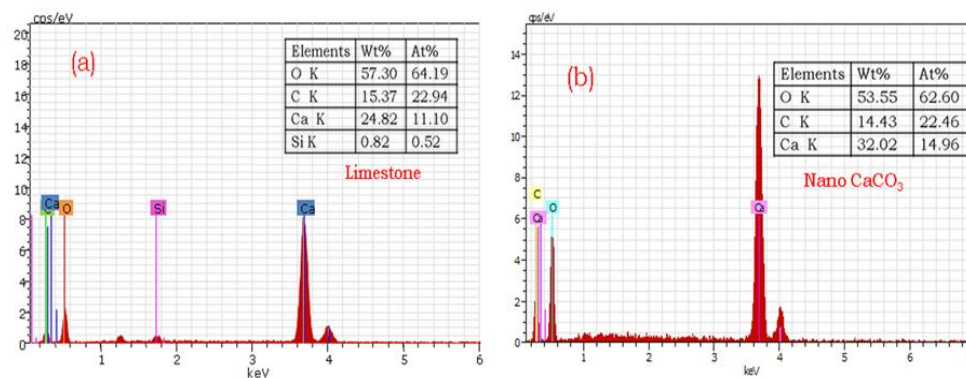


Figure 6. EDX spectra of raw calcitic rock (A) and synthesized nano PCC (B)

Figure. 6 (A-B) shows the EDX spectrum of raw calcitic rock and synthesized CaCO_3 nanomaterials. The synthesized product (Fig. 6(A and B)) confirmed the presence of Ca, C and O elements in the sample. However, 0.82 wt% of Si is present in the raw calcitic rock. The synthesized products (nano CaCO_3) do not have the Si content, which means that the process filters the impurities other than CaCO_3 . The raw calcitic rock sample has low wt% of Ca. However, synthesized products have the high percentage of Ca content.

4. CONCLUSION

The precipitated calcium carbonate (PCC) nanoparticles were successfully synthesized by biomimetic method using different natural carbonate sources. The obtained products are well characterized through XRD, FTIR and SEM-EDX analysis. Eventhough the raw natural different carbonates are having different structure; the synthesized products are in rhombohedral structure within the 20-30 nm range. The mineralogical composition of obtained products is in the pure form of calcite, compared with raw natural sources. The other minerals (impurity) are filtered through this biomimetic method. The precipitated nano calcium carbonate has different morphology like crystal and flower. It is concluded that this method is best suited method for the precipitation of nano calcium carbonate from different natural carbonate sources without any impurities. Thus it is recommended that instead of huge chemicals which are used as a source, natural sources may be used for getting nano CaCO_3 composite for extensive industrial rations with lesser cost.

REFERENCE

- [1]. Sato, K., Oaki, Y., Takahashi, D., Toshima, K., & Imai, H., 2015, "Hierarchical CaCO_3 Chromatography: A Stationary Phase Based on Biominerals," *Chemistry - A European Journal*, 21(13), pp. 5034–5040.
- [2]. Shimpi, N., Mali, A., Hansora, D.P., Mishra, S., 2015, "Synthesis and Surface Modification of Calcium Carbonate Nanoparticles Using Ultrasound Cavitation Technique," *Nanosci. Nanoeng.* 3(1), pp. 8–12.
- [3]. Kemperl, J., and Macek, J., 2009, "Precipitation of calcium carbonate from hydrated lime of variable reactivity, granulation and optical properties," *Int. J. Miner. Process.* 93(1), pp. 84–88.
- [4]. Zhao, T., Guo, B., Zhang, F., Sha, F., Li, Q., and Zhang, J., 2015, "Morphology Control in the Synthesis of CaCO_3 Microspheres with a Novel CO_2 -Storage Material," *ACS Applied Materials & Interfaces*, 7(29), pp. 15918–15927.

- [5]. Ramasamy, V., Ponnusamy, V., and Hemalatha, J., 2005, "Study on effect of baking of natural calcitic crystalline limestone at various temperatures through FTIR, XRD and TG- DTA analysis," *Indian J.Phys.* **79**, pp. 847-855.
- [6]. Linga Raju, C., Narasimhulu, K. ., Gopal, N. ., Rao, J. ., and Reddy, B. C., 2002, "Electron paramagnetic resonance, optical and infrared spectral studies on the marine mussel *Arca burnesi* shells," *Journal of Molecular Structure*, 608(2-3), pp. 201–211.
- [7]. Nan, Z., Chen, X., Yang, Q., Wang, X., Shi, Z., & Hou, W., 2008, "Structure transition from aragonite to vaterite and calcite by the assistance of SDBS," *Journal of Colloid and Interface Science*, 325(2), PP. 331–336.
- [8]. Shafiu Kamba, A., Ismail, M., Tengku Ibrahim, T. A., and Zakaria, Z. A. B., 2013, "Synthesis and Characterisation of Calcium Carbonate Aragonite Nanocrystals from Cockle Shell Powder (*Anadara granosa*)," *Journal of Nanomaterials*, 2013, pp. 1–9.
- [9]. Herzberg, G., 1945, "Molecular Spectra and Molecular Structure. II. Infrared and Raman Spectra of Polyatomic Molecules," New York: D Van Northstrand, p178.
- [10]. Keyser, W. L., Wollast R., and Laet, Z., 1969, "International clay conference," London: Pergaman, **2**, pp. 75.
- [11]. Mackenzie, R. C., and Rahman, A. A., 1987, "Interaction of kaolinite with calcite on heating," *Thermochimica Acta*, 121, pp. 51–69.
- [12]. Adler, H. H., and Kerr, P. F., 1962, "Infrared study of aragonite and calcite," *Am. Mineral.* 47, pp. 700–717.
- [13]. Russell, J. D., 1987, "Infrared methods: A Handbook of determinative methods in clay mineralogy (ed) Wilson, M. J., London: Blackie and sons, pp. 133-173.
- [14]. Xu, B., and Poduska, K. M., 2014, "Linking crystal structure with temperature-sensitive vibrational modes in calcium carbonate minerals," *Physical Chemistry Chemical Physics*, 16(33), pp. 17634.
- [15]. Scherrer, P., and Gottinger Nachrichten, *Math. Phys*, 2, pp. 98-100.
- [16]. Mishra, S., Sonawane, S. H., Badgujar, N., Gurav, K., and Patil, D., 2005, "Comparative study of the mechanical and flame-retarding properties of polybutadiene rubber filled with nanoparticles and fly ash," *Journal of Applied Polymer Science*, 96(1), pp. 6–9.

