Synthesis and Characterisation of CaCO3 (Calcite) Nano Particles from Cockle Shells Using Chitosan as Precursor

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Abstract- Calcium carbonate nano particles were synthesized using precipitation method from cockle shells by employing chitosan as precursor. Synthesized Calcium carbonates were characterized using scanning electron microscopy (SEM), X-ray diffraction (XRD), UV-Visible and FTIR Spectroscopy. The results were compared with commercial calcium carbonate nano particles. Cockle shells are the potential source of calcium carbonate. The materials used were naturally occurring and also from the byproducts of sea food industry. The adopted methods were cost effective and ecofriendly.

Index Terms- calcium carbonate, synthesis, chitosan, nano particle.

I. Introduction

Calcium Carbonate is a naturally occurring inorganic biomaterial [1]. It is a white, insoluble solid occurring naturally as chalk, limestone, marble, and calcite, and is the main component of shells of marine organisms, snails, pearls, and eggshells**.** It is a white powder or a stone. Calcium carbonate exists in three polymorphs: calcite, aragonite, and vaterite [2]. Aragonite has got enormous research attention because of its biocompatible properties [3–6]. Among these three polymorphs, calcite is thermodynamically stable [4, 7]. Even though calcite is the most stable polymorphism of calcium carbonate, aragonite has higher density and hardness which make it very suitable material in plastic, paper, glass, fiber and other industry [8]. Among biological minerals, calcium carbonate has a special place since it is the main constituent of bones and shells. In both materials, the inorganic mineral is associated with biopolymers. $CaCO_3$ bio deposits exhibit variation in crystal size, shape, morphology, texture and aggregation. $CaCO_3$ nano particles (<100 nm) have shown many unique properties compared to regular particles.

Biological systems are capable of producing inorganic materials such as calcium carbonate with different structures, morphologies and polymorphs [9]. Cockle (a common name for a group of (mostly) small, edible, saltwater clams, marine bivalve mollusks in the family Cardiidae) shell, also known as '*Anadara granosa*' is one of the most common sources of calcium carbonate [10]. It is a type of edible bivalve shellfish that grows well in muddy coastal area. It is a cheap protein source which is quite common to be prepared as local dishes [11]. The distinctive rounded shells of cockles are bilaterally symmetrical, and are heart-shaped when viewed from the end. Cockle shells are composed of pure calcium carbonate, usually both in the form of calcite and aragonite. Sea shell contained of 95-99% by weight of $CaCO_3$ which has enable it to be applied for quite a number of purposes [12 – 13]. It was found that cockles shell is the potential biomass resource for bone repair material especially made for cancer patients [14]. Calcium carbonate is an extremely versatile filler and pigment that is utilized in a wide variety of products including paper, plastics, rubber and pharmaceuticals. Its final application is determined by different physical and chemical properties. The most important aspect with respect to the synthesis of nano particles is control of the particle size, polymorphism, and morphology of the desired material [15]. Control of this parameter has led to the development of new materials with unique properties that differ from those in the bulk material.

Tsuzuki et al. synthesized calcium carbonate nanoparticles using a mechano chemical reaction followed by heat treatment [16]. A solid-state displacement reaction would occur during mechanical milling of the reaction powder mixture. The heat treatment ensured completion of the reaction. This limited the morphology of the particle to calcite, and had high energy consumption. Mechanical milling causes irregularities in particle shape and distribution. Liu et al. prepared nanosized $CaCO_3/SiO_2$ composite particles by the sol-gel process of $CaCO_3$ and Na_2SiO_3 in an agitated tank reactor, with an average composite size of sol gel coated $CaCO_3$ of about 40 nm [17]. $CaCO_3$ nanoparticles have also been prepared using a microemulsion technique consisting of sodium dodecyl-sulphate (SDS)/isopentanol /cyclohexane/water, [18]. The synthesis of pure calcium carbonate nano crystals using a high pressure homogenizer (HPH) via a microemulsion system was reported by Abdullahi Shafiu Kamba et al. [9]

In the present study, nano calcium carbonate was synthesized by employing biopolymer chitosan as the size reducing agent. The synthesis of calcium carbonate (calcite) nano particles from cockle shells is greatly promising approach. Cockle shells are naturally purified source of aragonite polymorphs of calcium carbonate. However by applying high temperatures, the aragonite polymorph converts to calcite, which is thermodynamically most stable.

II. MATERIALS AND METHODS

2.1 Materials

Cockle shells obtained from local market, Analytical grade. Conc. HCl, Acetic Acid Glacial, Sodium carbonate supplied by

SD fine chem. Limited, Worli, Mumbai, Chitosan provided by CIFT Cochin were used for the synthesis of calcium carbonate nano particles.

2.2 Experimental methods

For the preparation of cockle shell $CaCO_3$ nano powder, approximately 100 grams of cockle shells were first washed by normal tap water to remove dirt from the outer surface and inside of the shells. The shells were then boiled for about 30 minutes using a steel container and stove followed by drying in an oven at 110 °C for 2 days. Washed and dried cockle shells were finely grounded using a grinder. The nano sized calcium carbonate was synthesized by an in situ deposition technique (Mishara et al 2005). This method was adopted here to synthesize calcium carbonate nano particles. The powder of calcium carbonate obtained from cockle shells was dissolved in about 150 gram of concentrated hydrochloric acid. Obtained calcium chloride solution was mixed with 1.5 gram of chitosan, which was dissolved in 3% acetic acid. This mixture was blended with 70 gram sodium carbonate solution and slightly heated the mixture to complete the reaction. The mixture was kept overnight. Obtained calcium carbonate precipitate was filtered off, washed several times with water to remove sodium chloride, hydroxide etc and dried. It was kept for two hours calcinations in a muffle furnace at 650 ^{0}C to burn out Chitosan and to obtain nano sized calcium carbonate nano particles. The obtained powder was stored in small air tight bottles to avoid absorption of any moisture.

XRD analysis: After thoroughly cleaning the sample holder, the $CaCO_3$ nano powder obtained from cockle shells was spread on the sample holder. The sample was then placed inside the XRD machine (Model-DY-1656) and the sample was investigated to understand the phase(s) and size of the $CaCO_3$ nano powder.

FT-IR analysis: The $CaCO_3$ powder was mixed with KBr at the ratio of 1:100. The mortar and pestle was thoroughly cleaned with acetone, the mixture of $CaCO_3$ powder and KBr was crushed. The $CaCO_3$ powder and KBr mixture was then put into the disc which was placed on a holder placed inside the FT-IR (Shimadzu IR Affinity-1 Spectrophotometer) machine to investigate the unknown materials present in the sample.

SEM Analyses: The sample of $CaCO_3$ nano powder was affixed to a metallic stub which is placed on the sample holder. The sample holder was then fixed on a rotatable disc inside the machine and the $CaCO_3$ nano powders were ready for SEM. The surface morphology of the powder sample was observed on SEM (JEOL-JSM 5800) operated under low vacuum at an accelerating voltage of 25 kV to get the sharp image of the sample.

UV-Spectrophotometer: Deionized water was taken in a quartz cuvette as the reference and was placed in UV spectrophotometer (Shimadzu UV 1800) to get the absorbance. The calcium carbonate nano powder obtained from cockle shells were partially dissolved in deionized water. These sample solution were taken in a quartz cuvette and placed in the spectrophotometer to obtain the absorbance.

III. RESULTS AND DISCUSSION

3.1 XRD

The size of the $CaCO_3$ nano powder obtained from cockle shell was demonstrated [XRD, PANalytical, (model: DY-1656)] machine (Position 2θ, range 20-60). The XRD pattern is shown in Figure 1. The analysis of crystal structure using XRD illustrates that the nano powder synthesized from cockle shell was made up of calcite, $CaCO_3$. It was one type of crystal form of calcium carbonate other than aragonite and vaterite. The strong and sharp peaks showed that the cockle shell $CaCO_3$ powder was well crystalline. The average crystallite size (D) of the calcium carbonate was calculated using Debye-Scherrer equation [19, 20].

$$D = \frac{0.9\lambda}{\beta \cos\theta}$$

D = shape factor, λ = x-ray wavelength, β = FWHM of diffraction peak, θ = Bragg angle.

The grain size was calculated to be 28.64 nm. However the calcium carbonate obtained from cockle shells was mainly in the form of aragonite, natural aragonite on heating converts to calcite, the conversion being very rapid at temperatures above 400 ^{0} C temperatures. It was concluded that all of the peaks obtained in the XRD pattern of cockle shell $CaCO_3$ nano powder matched perfectly with the standard calcite pattern [21] and JCPDS file (88-1807).

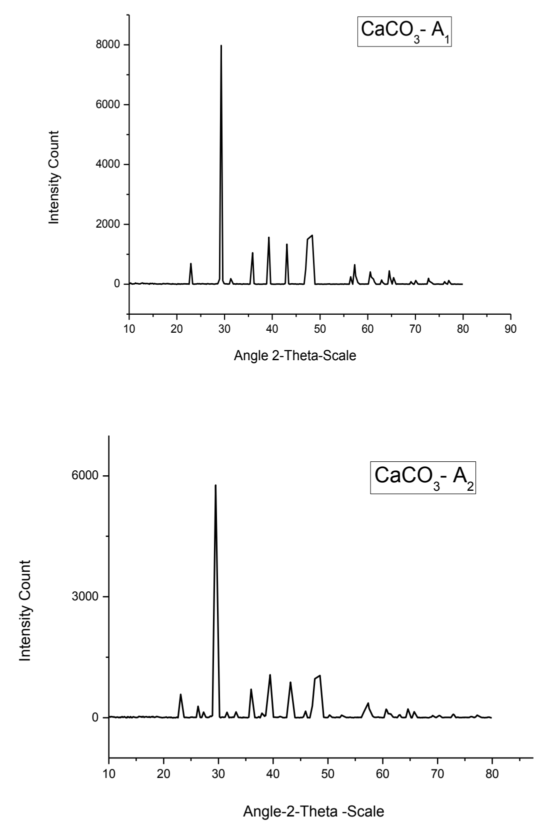

Figure 1.The XRD images for the commercial (A1) and synthesized calcium carbonate (A2)

3.2 Fourier transforms infrared analysis

The phase of the cockle shell $CaCO_3$ powder was further confirmed by (Shimadzu IR Affinity-1 Spectrophotometer)

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machine. An FTIR spectrum was generated by the absorption of electromagnetic radiation in the frequency range 400 – 4000 cm^{-1}**.** The obtained spectrum is shown in the figure 2.The spectrum showed vibrational bands at 1456.391 cm^{-1}, 876.72 cm^{-1}, 712.7281 cm^{-1} and 409.891 cm^{-1} indicates plane bending vibration of carbonate. FT-IR analysis confirmed that the $CaCO_3$ nano powder obtained from cockle shell had the characteristic peak of carbonate group. A sharp peak at 876.72 cm^{-1} confirmed that the $CaCO_3$ nano powder obtained from cockle shell was calcite. FT-IR analysis also evidenced that the powder consisted of $CaCO_3$ itself.

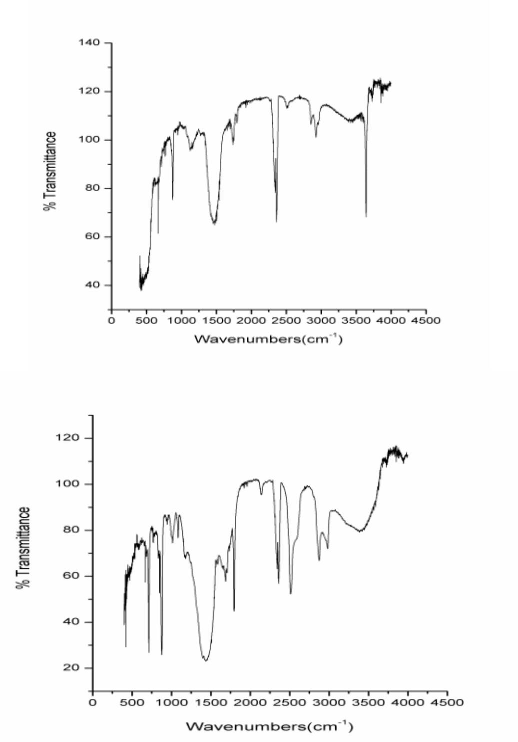

Figure2. FTIR images of commercial and synthesized of nano calcium carbonate.

3.3 UV-Visible

The calcium carbonate nano powder obtained from cockle shells were again confirmed by taking UV spectra using (Shimadzu UV 1800) spectrophotometer. Calcium carbonate nano powders were partially dissolved in distilled water to obtain the UV absorption bands for calcium carbonate nano powders. Obtained spectra are given in the figure 3. Particular absorbance will produce a band in UV spectrophotometer. The strong absorbance peak obtained for of calcium carbonate nano powders were in the range of 538, 685, 780,865, 963 nms.

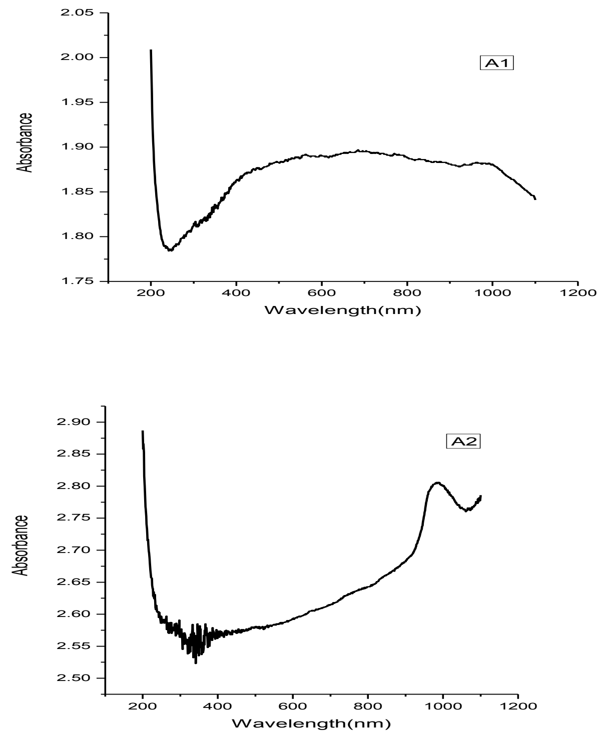

Figure3. UV Spectra of commercial and synthesized nano calcium carbonate.

3.4 Scanning Electron Microscopy

Scanning electron microscope is a very useful tool for studying morphology of nano powders. The surface morphology of the $CaCO_3$ nano powder synthesized was examined by SEM (JEOL-JSM 5800) scanning electron microscope operating at 25 kV accelerating voltage. The $CaCO_3$ nano powder is a non-conducting powder therefore the SEM images were taken at low vacuum mode to obtain sharp images. The images are shown in Figure 4. Calcite and aragonite possess different crystal growth patterns and crystal structure. Calcite is hexagonal and aragonite is orthorhombic. Cube-like crystals of calcite are stable as compared to Rod-like orthorhombic crystals of aragonite.

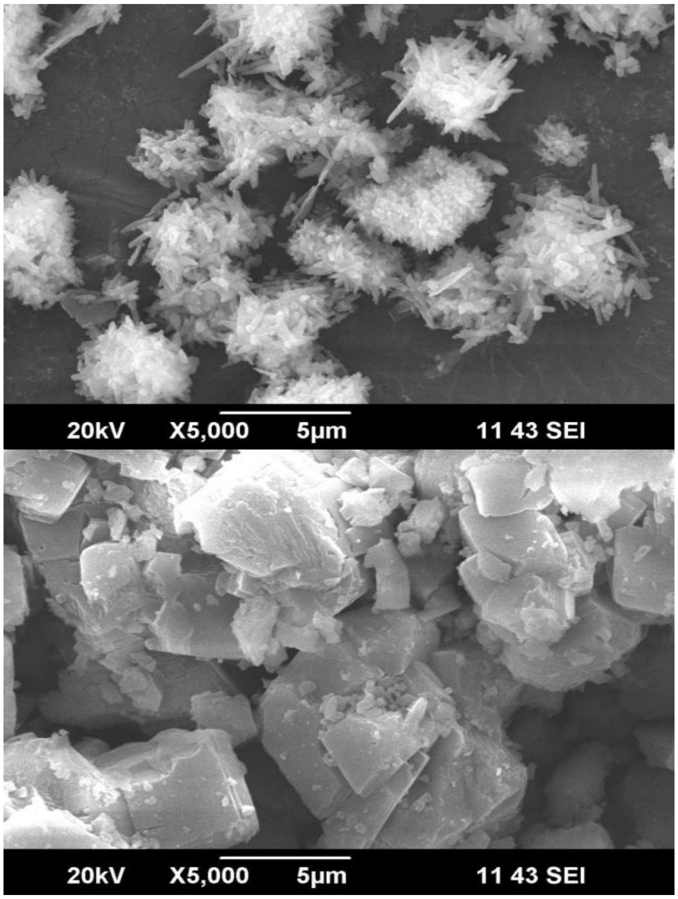

Figure 4. SEM morphology of commercial and synthesized calcium carbonate nanopowder.

IV. CONCLUSION

This work deals with the synthesis of nano particles of $CaCO_3$ using precipitation method from cockle shells by employing Chitosan. The obtained calcium carbonate is characterized by XRD, FTIR, UV-Visible and SEM. Using precipitation method and by applying Chitosan the obtained calcium carbonate powder is in nano metric scale. XRD analysis showed that the $CaCO_3$ nano powder synthesized from cockle shell had more stable calcite phase as compared to less stable aragonite phase. FT-IR analysis confirmed that the $CaCO_3$ nano powder obtained from cockle shell had the characteristic peak of carbonate group at 1456.391 cm^{-1}, 876.72 cm^{-1}, 712.7281 cm^{-1} and 409.891cm^{-1}. SEM images confirmed that the synthesized calcium carbonate nano powder from cockle shells have calcite phase. Calcium carbonate powders obtained at the nano metric scale, may have superior properties as compared to the powders obtained in larger particle sizes and can be used in various applications.

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