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CALCINATIONS OF *CYPRAEA MONETA* (COWRY SHELL) LEADS TO PHASE TRANSFORMATION OF BIOGENIC ARAGONITE INTO CALCITE CRYSTALS

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ABSTRACT

Traditional Indian system of medicine like Siddha, Ayurveda uses various molluscan based medicines for treating various ailments like Jaundice, Gastro-intestinal disorders and other immunological clinical conditions. Molluscan shells are purified and subjected to various traditional calcinations processes. Almost all marine molluscan shells contain calcium carbonate as their major constituents. In the present study, Biogenic Calcium carbonate obtained from marine mollusk *Cypreae moneta* Linn. (Cowry shell) before and after calcinations were subjected to FTIR, FT-Raman and Powder X-ray diffraction studies. The before and after calcinations studies of cowry shells reveals a solid state phase transformation from thermodynamically less stable form of Aragonite Calcite, a thermodynamically more stable polymorphic form of Calcium carbonate.

KEYWORDS: Siddha, Ayurveda, Jaundice, Gastro-intestinal disorder, Immunological clinical conditions, Calcite, Aragonite, Biogenic, Cowry shell and Phase transformation.

INTRODUCTION

Calcium carbonate ($CaCO_3$) is an omnipresent inorganic component of the near-surface environment, occurring in aqueous systems, sediments and aerosols. It precipitates in both fresh and saline water and can form by biogenic or abiotic means (Tori Z. Forbes et al.,

2011). $CaCO_3$ exists in many forms namely, three anhydrous forms calcite, aragonite and vaterite and three hydrated forms, amorphous $CaCO_3$, monohydro calcite ($CaCO_3.H_2O$) and ikatite ($CaCO_3.6H_2O$) (Shanmukhaprasad Gopi et al., 2013). A study of the phase diagram of anhydrous $CaCO_3$ shows that calcite is thermodynamically most stable and most abundant phase under ambient conditions, aragonite is the high-pressure polymorph and vaterite is thermodynamically unstable (Burkhard C. Schmidt and Andrew Putnis,2011). Many sea shells and corals are composed either absolutely or in part of aragonite (Marko Ukrainczyk et al., 2013). Calcite has the ability to fix or structurally incorporate biologically active elements such as phosphorous, calcium, magnesium, zinc, iron (Manuel Aneul Prieto et., 2003). Due to its metastability under earth's surface condition, aragonite tends to transform into calcite by reaction with aqueous solutions (Shanmukhaprasad Gopi et al., 2013). Sequential polymorphic transformation of $CaCO_3$ in the presence of DTPA was reported (Jonas Baltrusaitis and Vicki H.Grassian, 2009). Structural transformation from aragonite to vaterite and calcite by the assistance of SDBS in the temperature range 90 to 150 ^oC was reported (Zhaodong Nan et., 2008). In traditional Indian medicine $CaCO_3$ obtained from various biogenic sources such as Pearl oyster, Conch shell, Snail shell and Cowry shell are mixed with other organic/inorganic compounds and calcined before final administration to patients. The *Palakarai parpam*, Calcium carbonate powder obtained from mollusk Cypraea moneta (cowry shell) after calcinations is widely used for the treatment diseases like bilious heat, burning micturition, renal calculus, gastric ulcers and Jaundice etc. Reports on the study of initial and final products of cowry shell are few. The aim of the paper is to find out in what polymorphic form $CaCO_3$ exists as obtained from biogenic sources and whether any phase transformations takes place after Calcination. In this regard Cowry shell obtained as such are Pulverized and calcined in a traditional manner. The as obtained and calcined samples are studied using Fourier Transform Infrared (FTIR), FT Raman spectroscopy and Powder X-ray diffraction techniques and the results are presented.

MATERIALS AND METHODS

Collection of Cowry shells

The Cowry shells are collected from in and around coastal areas of Chennai and also from country drug shop, Chennai and authenticated from Department of Advance zoology and Biotechnology, Govt. Arts College, Nandanam, Chennai -35.

Preparation of *Palakarai Parpam*

The cowry shells (*Cypraea moneta*) obtained were immersed in the lime water for 3 hours as a process of purification as per Siddha literature (R.Thiyagarajan, 2009) and rinsed with water. The purified shells were pulverized using mechanical grinding with mortar and titurated with lime juice and the resulting sample is made to form a coin shaped tablet and subjected to calcinations for about 3 to 5 hours (R.Thiyagarajan, 2009). The resultant product is further grinded with lime juice and calcined for two times for about 3 – 5 hours for each calcinations respectively (R.Thiyagarajan, 2009). The resultant coin shaped tablets is mechanically grinded in a mortar to form *Palakarai parpam.*

Characterization

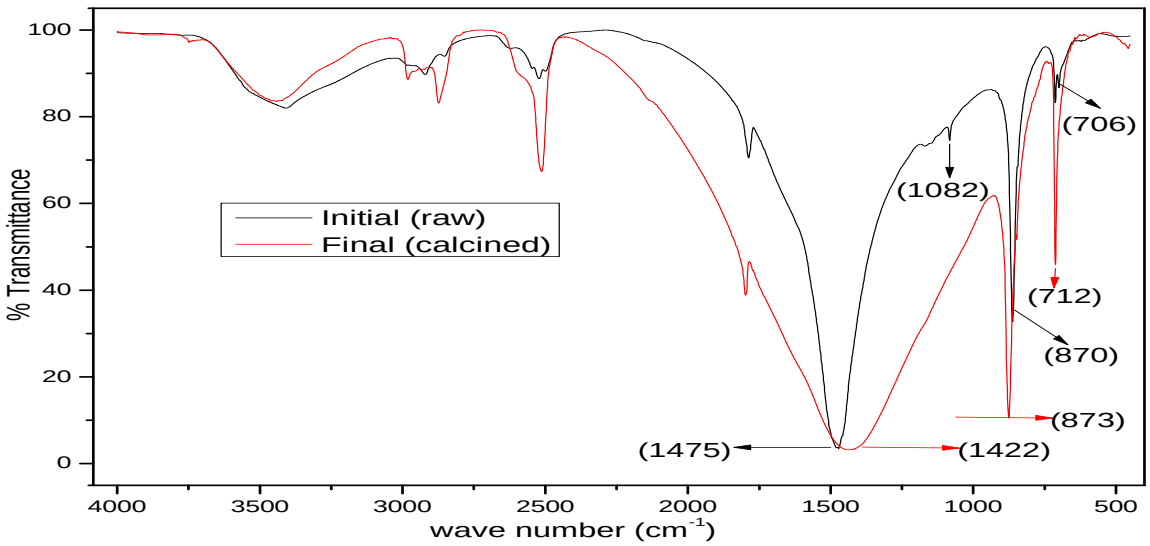
The initial compound (Cowry shell) and the finally obtained compound (*Palakarai parpam*) after calcinations are subjected to FTIR spectral analysis in the wavelength range 450 to 4000 cm^{-1}, FT Raman spectra analysis in the range 4000 to 100 cm^{-1}. and to powder X-ray diffraction in the 2theta range 10 to 80^0.

RESULTS

FTIR Spectrum

The initial raw compound (Cowry shell) and the finally obtained compound after various steps of calcinations are subjected to FTIR spectral analysis in the wavelength range 450 to 4000 cm^{-1}.

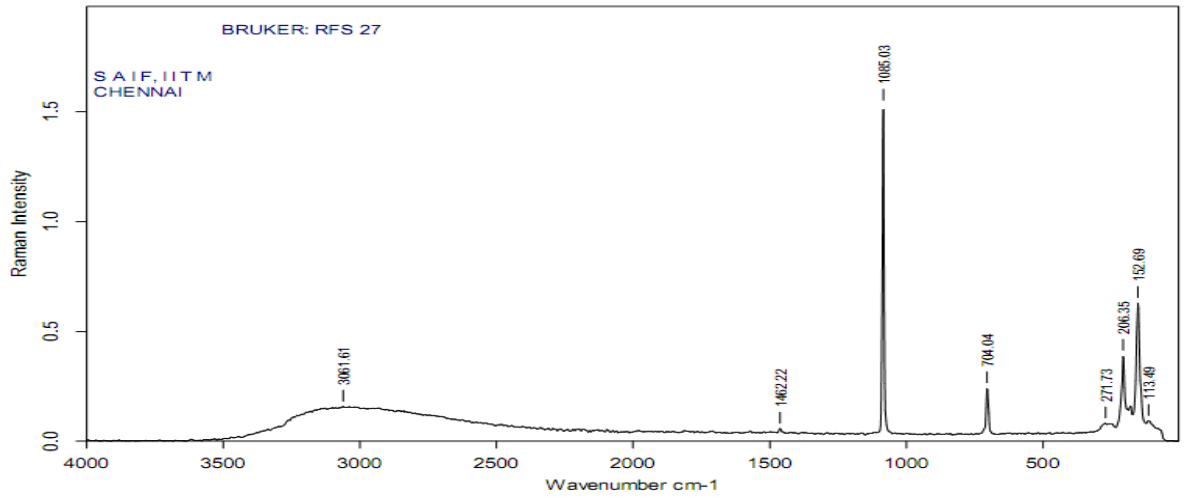
FTIR spectrum of as raw cowry shell and the calcined final product



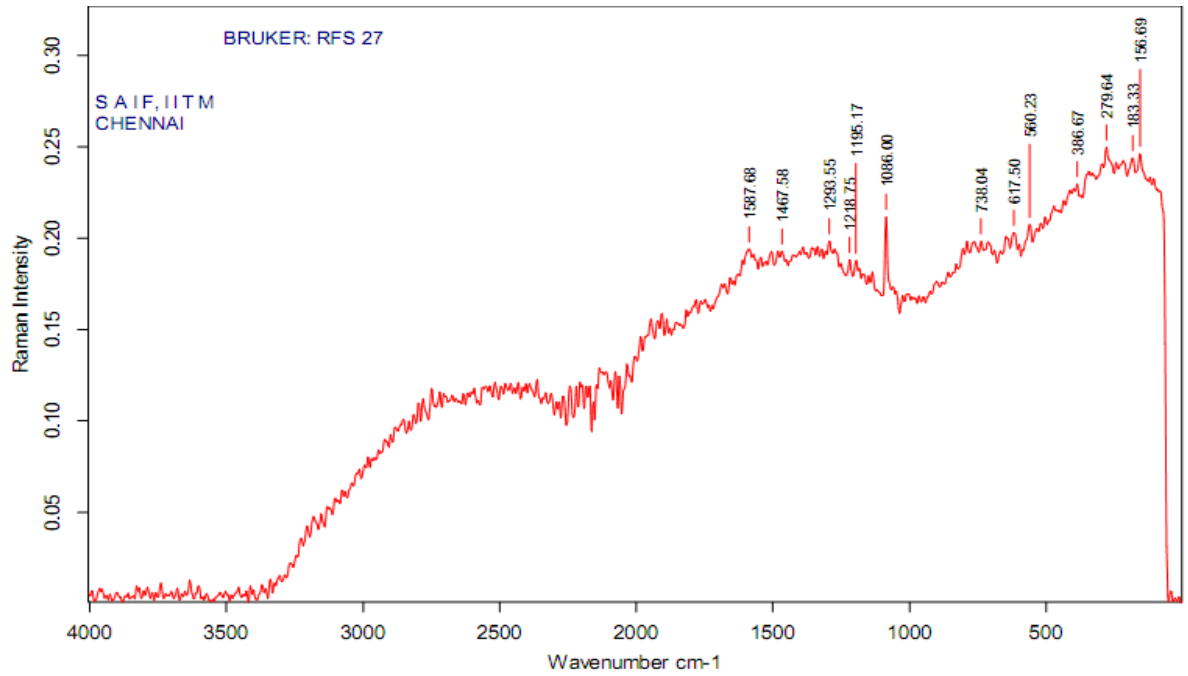
FT-Raman Spectrum

The initial compound cowry shell and the finally obtained compound are subjected to FT-Raman spectral analysis in the range 4000 to 100 cm^{-1}.

FT-Raman spectra of the initial compound



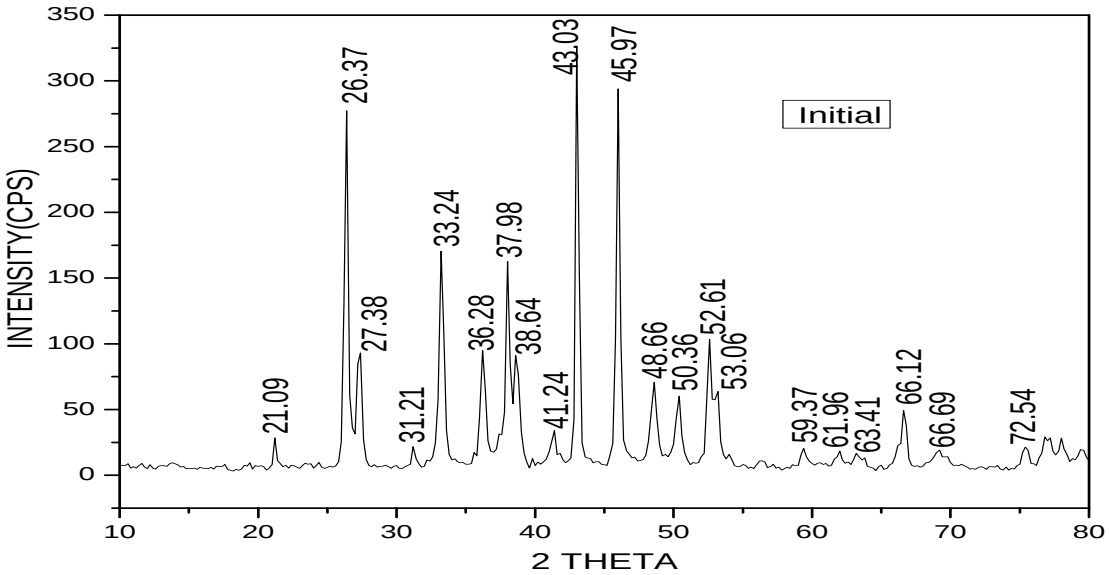
FT-Raman spectra of the final compound



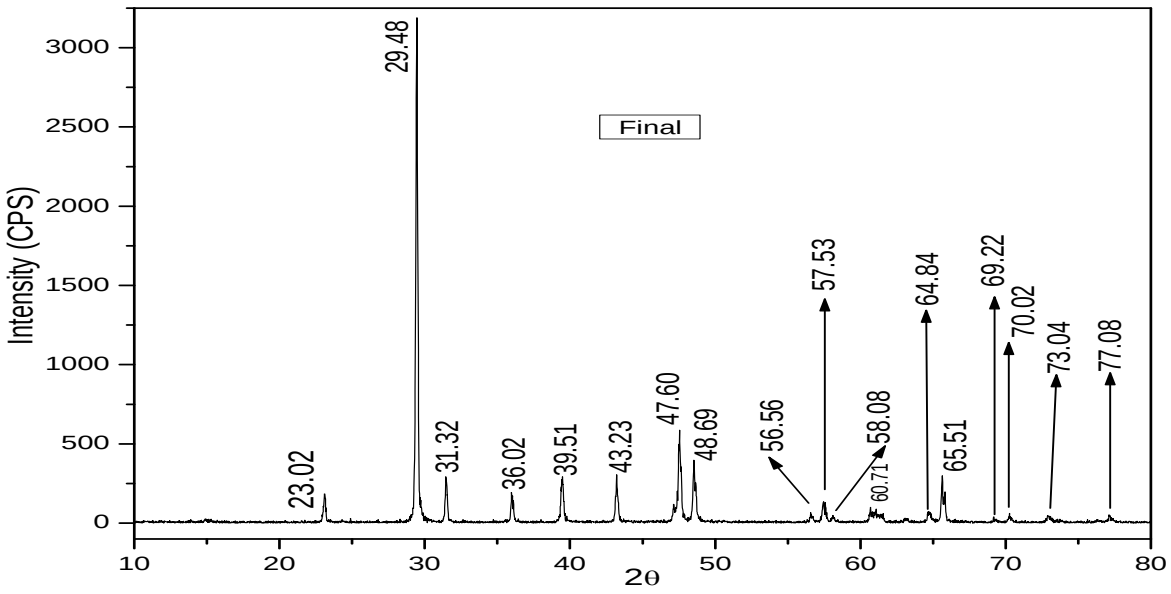
Powder X-ray diffraction analysis

Finely ground powder of the initial compound and final compound are subjected to powder X-ray diffraction analysis in the 2 theta range 10 to 80 degree. Sharp and well defined peaks at specific 2 theta values show the crystalline nature of the initial and final compounds.

Powder X-ray diffraction of the initial compound



Powder X-ray diffraction of the final compound



DISCUSSIONS

The absorption bands of FTIR were observed around 1475, 1082, 870 and 706 cm^{-1} for the initial compound are attributed to the vibrations of carbon-oxygen double bond in the carbonate ion present in aragonite. The absorption bands observed around 1422, 873 and 712 cm^{-1} in the final product are due to the vibrations of carbon-oxygen double bond in the carbonate ion present in calcite (Shanmukhaprasad Gopi et al, 2013). From the FTIR spectral analysis it can be concluded that the cowry shell contains calcium carbonate in the form of aragonite crystal and after calcinations it undergoes solid state phase transformation to

thermodynamically stable calcite crystalline phase. The other peaks present are attributed to the presence of organic compounds.

In the FT Raman Spectra of the initial compound, the peaks observed around 1085, 704, 206 and 152 cm^{-1} are characteristics to that of aragonite form of calcium carbonate and the peaks observed around 1086, 738 and 279 cm^{-1} in the FT Raman_spectra of the final compound are characteristics to that of calcite form of calcium carbonate (Shanmukhaprasad Gopi et al, 2013). There is slight shift in the peak positions observed around 738 and 279 cm^{-1} from that of the reference values. Raman Spectral analysis conforms once again that the Calcium carbonate present in the Cowry shell compound undergoes solid state phase transformation from aragonite to calcite phase due to calcinations.

The Powder XRD analysis, the peaks observed in initial compound are in accordance to the peaks observed to that of aragonite crystals and the peaks observed in final compound are characteristics to that of calcite crystals. The observations are in accordance with that of JCPDS values reported earlier (Sonali Dhamal, M.P. et al., 2013). The average particle size calculated from these XRD patterns using Scherer equation are 24.36 nm and 51.34 nm for the raw and calcined compounds respectively. The size of the particles obtained after calcinations is twice larger than that of initial particles. This is attributed to the effect of calcinations.

CONCLUSIONS

From the FTIR, FT-Raman and Powder X-ray diffraction studies it is concluded that the calcium carbonate is present in the form of aragonite crystals in the as obtained samples and upon calcinations it is undergoing irreversible solid state phase transformation in to stable calcite crystals. The study also gives insight into the role of phase transformation in delivering the respective pharmacological properties. This study also validates the traditional methodology of processing of medicine i.e. calcinations and provides newer technological support of optimizing temperature to scale up the process for bulk manufacturing of shell based pharmaceutical preparations of Traditional Indian medicines and to enhance their biological activity. Further work is in progress to study the synthesis of compound by microwave annealing.

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