



SYNTHESIS, CHARACTERIZATION OF NANO-HYDROXY APATITE FROM WHITE SNAIL SHELLS AND REMOVAL OF METHYLENE BLUE

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ABSTRACT: In this study, NanoHAP synthesized from white snail shells, were acts as an adsorbent material to remove Methylene blue. The adsorption mechanisms of adsorption process were studied by FTIR and Raman spectroscopy, and then the percentage removal of MB and optical density data was measured. FTIR spectrum of snail shell derived NanoHAP before and after adsorption of Methylene blue showed the characteristics bands for PO_4^{3-} . The broad bands were attributed to adsorbed water. After MB adsorption the bands are remained the same as those of HAP. Some new bands appeared due to adsorption of MB on the HAP were mainly a physical adsorption. Further it is concluded that NanoHAP has high potential for the removal of Methylene Blue.

Keywords: Snail shells, NanoHAP, Methylene Blue, Adsorption, FTIR, Raman

I. INTRODUCTION

White snail shells are invertebrate exoskeletons made up of calcium carbonate 95-99% and other components. The use of naturally renewable shells as fillers helps us to replace commercial calcium carbonate. In this study shell waste can be converted into useful products, which is used to synthesis the NanoHAP materials²⁻⁵ by sintering method that can be used to treat effluents and biological applications⁸. The role of NanoHAP powders as adsorbent material in the removal of dyes from water was studied, therefore it is interesting to develop NanoHAP of the snail shell used as adsorbent and it has high adsorption capabilities due to its high surface area and porosity was used for removal of Methylene Blue. The synthesized and adsorption power of NanoHAP were characterized by Raman and FTIR spectroscopy⁵. It indicates that NanoHAP is the most efficient adsorbent, cost effective, easily available and used for Methylene Blue dye removal^{6,9,11,12}.

II. EXPERIMENTAL SAMPLING

Snail shells were collected by hand picking from rice field near to lakes and Palar river bank near Chengalpattu. They are separated based on size, shape, color etc. and placed in properly labeled plastic bags from that we separated six types of snail shell samples.

Experimentation and method

The collected shells are washed, dried and powdered followed by heat treatment at 1000° C for the period of 2hrs to convert calcium carbonate to calcium oxide and finally calcium oxide converted to calcium hydroxide. Calcium hydroxide was weighed in a beaker and 20ml of nitric acid was added and filtered, calcium nitrate is prepared.

Preparation of Nano Hydroxy apatite:

Nano-Hydroxy apatite was prepared by precipitation method²⁻⁵. 1M calcium nitrate and 0.6M Di-ammonium hydrogen phosphates was dissolved in distilled water and adjust the pH 10-11 by adding ammonia with cationic surfactant CTAB. The precipitate was obtained after washing with distilled water and ethanol. Finally Nano particles were rinsed with distilled water and dried in an oven at 80° C for 12hrs and then powder was crushed and kept at 800° C in a muffle furnace for 2hrs.

Results and discussion:

Raman spectra: The Raman spectrum provides complementary information for the identification of functional groups present in HAP synthesis from the snail shell sample. The samples are subjected to Raman spectral analysis in the range 50 to 2000 cm⁻¹.

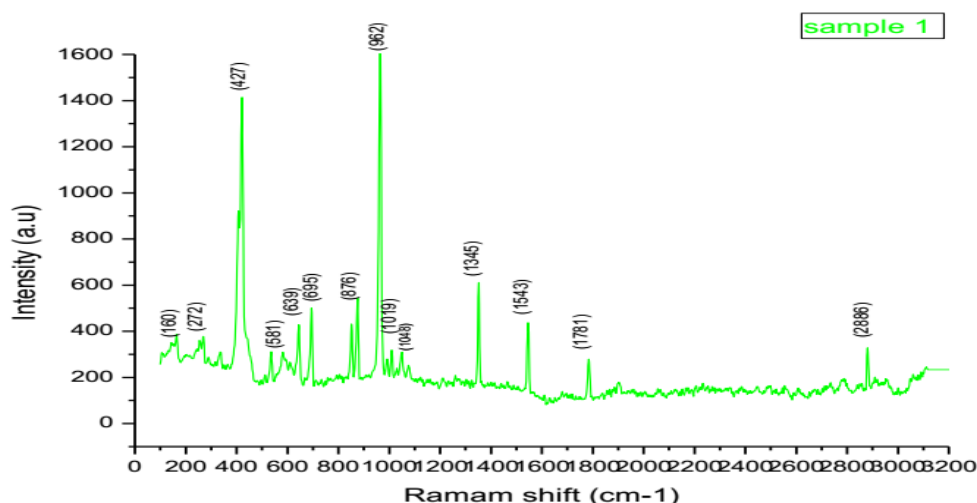


Fig1: Raman spectra of HAP from the snail shell sample

The peaks observed around 962, 427, 1048, 581, 638 cm⁻¹ is the characteristics ν_1 , ν_2 , ν_3 , ν_4 modes of PO₄ group. the peak observed at 272 cm⁻¹ are characteristics to that of calcite form of calcium carbonate, the peak observed at 1019 cm⁻¹ is the P-O stretching mode ν_1 of the HPO₄²⁻ group in tri calcium phosphate, the peak at 876 cm⁻¹ is the P-O stretching mode ν_1 of the PO₄ group of (DCDP) the peak observed around 1345, 1543 cm⁻¹ is the nitro group stretching, The weak bands at 160 cm⁻¹ were assigned to Ca-PO₄.

FTIR

Fourier transform infra-red spectroscopy is an efficient and adequate analytical technique that is being used to characterize inorganic materials. The characteristic group frequencies detected for a sample sheds light on the nature and purity of the compound. The FTIR peaks indicate the presence of carbonate, oxide and moisture peaks which could be as a result of decomposition of the shell matrix to calcium oxide. The less intense bands at 454-449 cm⁻¹ corresponds to the bending mode of ν_2 phosphate group in HAP, The bands at 1020 ν_3 , asymmetrical stretching mode of P-O bond in PO₄ ν_3 moiety, The vibration bands at 567-605 cm⁻¹ are assigned due to symmetric P-O bond in phosphate group and presence of PO₄³⁻ in HAP crystal lattice. The strong bands at 640 and 3702 cm⁻¹ indicate the presence of hydroxyl groups in hydroxy apatite. The band at 1976 cm⁻¹ is the presence CO₃²⁻ groups.

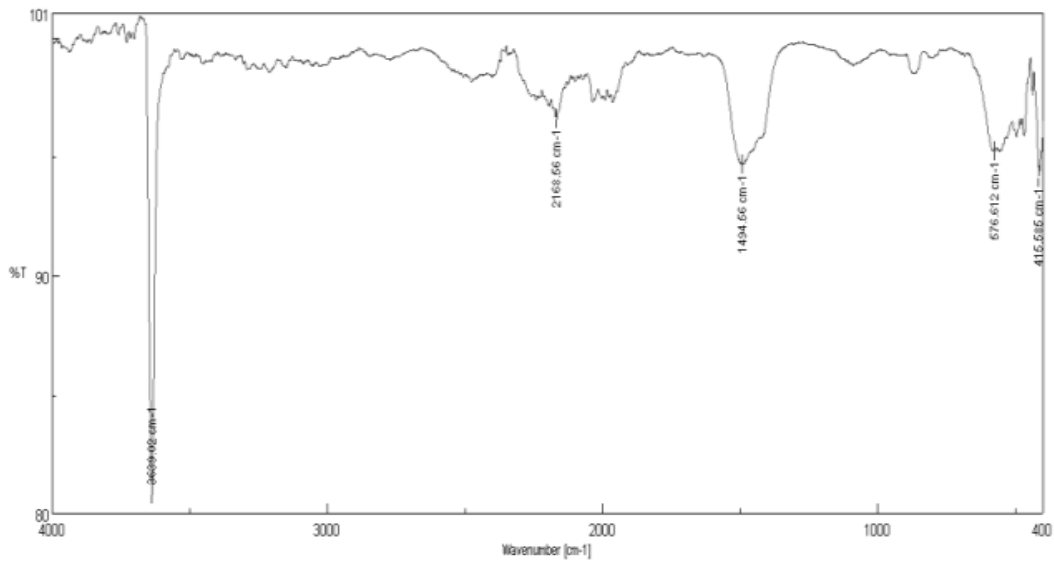


Fig2: FTIR spectrum of snail shell Powder obtained after sintering

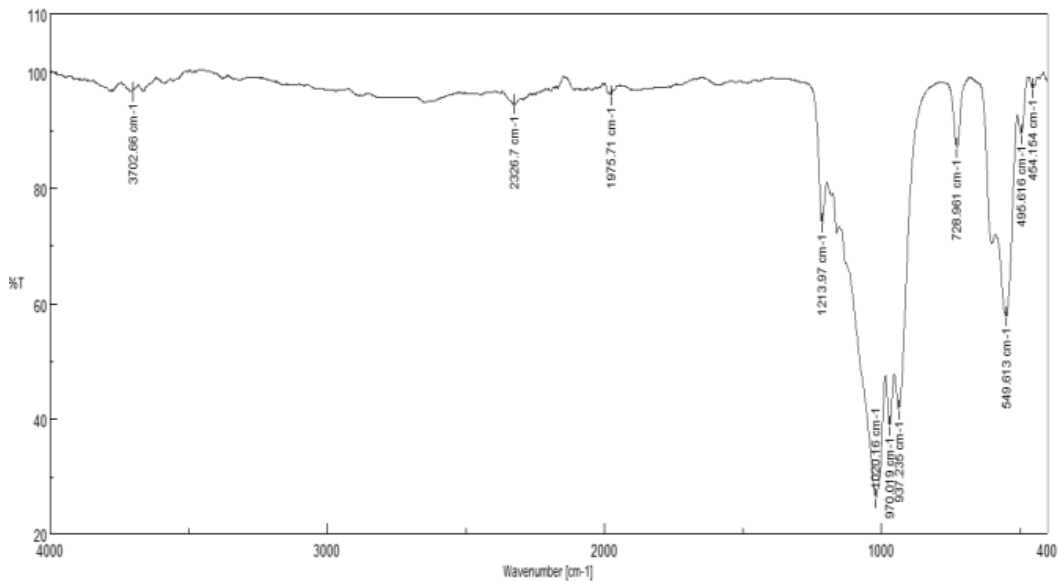


Fig3: FTIR Spectrum of Nano HAP prepared from snail shell powder after sintering.

Table1: Nano HAP used as a adsorbent for removal of Methylene Blue

| S.No | Nano HAP - adsorbent power | Optical density | | % of MB removal | |
|------|----------------------------|-----------------|--------|-----------------|-------|
| | | 3Hrs | 24Hrs | 2Hrs | 24Hrs |
| 1 | WS-HAP | 0.0622 | 0.0211 | 84.1 | 94.6 |
| 2 | WS-HAP | 0.0837 | 0.0235 | 78.6 | 94.0 |

FTIR spectra of HAP before and after adsorption were shown in Fig 3-4. The FTIR spectrum of HAP showed the characteristics of bands for PO₄³⁻ (549,728,930,970 and 1213cm⁻¹) and the phosphate bond stretching occurring at 970cm⁻¹ indicated the crystalline structure of the apatite phase formation.

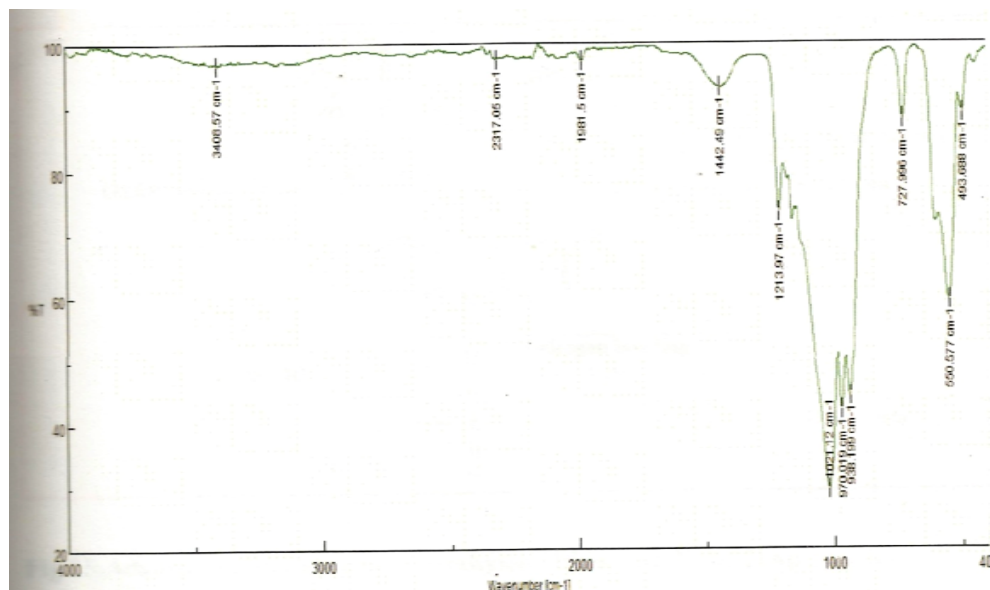


Fig4: FTIR Spectrum of snail shell derived Nano HAP after adsorption of Methylene Blue

The broad bands at 1775 and 3702 cm^{-1} were attributed to adsorbed water. After the MB adsorption, most of these characteristics peaks of MB-loaded HAP remained the same as those of HAP, some new band appeared 1442 cm^{-1} due to MB in suggesting that the process of MB adsorption on the HAP was mainly a physical adsorption similar results reported by Amuda.O et al (2014)¹⁰.

CONCLUSION

The present work was concluded by three objectives were carried out namely collection of shell samples from fresh water lakes and Palar river bed near Chengalpattu. The samples were further washed and isolated based on the size and weight. This was followed the synthesis of NanoHAP from the shell powders by sintering in a muffle furnace at 800° C for 1hr and characterized using FTIR and Raman to confirm the structure of NanoHAP. The synthesis NanoHAP used as an adsorbent which has high adsorption capabilities due to its high surface area and porosity was used for removal of Methylene Blue. Further study indicates that NanoHAP has a promising role in future to be used as an adsorbent for the treatment of MB dye.

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