Synthesis and Characterization of Hydroxyapatite Produced From Egg Shells; A Micellar Templated Approach

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ABSTRACT: In the present study hydroxyapatite (HA) powder has been synthesized using egg shells as source of calcium. The synthesis has been carried out using CTAB, surfactant micelles as templates through hydrothermal approach. The phase purity and crystallinity of synthesized powder synthesized was conducted using FTIR and XRD analysis respectively. Whereas, FESEM and TEM analysis was conducted to observe morphology of synthesized sample. Results indicated synthesis of low crystalline HA nanopowders with rodlike morphology.

Key words: Biomaterials, egg shells, hydroxyapatite, CTAB micelles.

INTRODUCTION

Over the past few years, there has been observed a tremendous interest in the synthesis of biomaterials with increased mechanical strength and advanced interfacial properties. In other words, it should be capable of creating an efficient and stable interface when implanted into the living system. With this key concept, a good biomaterial is believed to possess these properties; it should be bioresorbable, bioactive, inert and porous when implanted for tissue ingrowths (Roveri and Iafisco 2010), Roveri and Iafisco (2011).

It has been found that in the living system, almost 70 – 90 wt% of animals and humans hard tissues are composed of biological apatites (Saini, Bajpai et al. (2017), Reddi 1994). Among various apatites, hydroxyapatite (HA) has a significant importance in biomedical applications particularly in bone replacements ((LeGeros 2008). This increased demand of synthetic
hydroxyapatite is due its similar chemical and crystal structure with that of natural bone (Neuman and Neuman 1953, LeGeros 1981). Owing to its similar mineral ratio, synthetic HA shows excellent biocompatibility in clinical applications. Studies indicate a large number of methods related to HA synthesis (Nancollas 1977, Isobe, Nakamura et al. 2002, Bose and Saha 2003, Beniash, Simmer et al. 2005, Rautaray, Mandal et al. 2005, Wu and Bose 2005, Hui, Meena et al. 2010). All these methods are characterized due to their inherent simplicity, easily optimization capabilities and good results.

In our everyday life routine, a huge number of egg shells are produced on everyday basis. Despite being used for a productive purpose, these shells are considered as waste. Studies indicate that the shell of an egg constitute about 11% of its total weight. The composition of shell can be described as; it consists of 94% calcium carbonate, 1% calcium phosphate, 4% organic matter and 1% magnesium carbonate (Rivera, Araiza et al. 1999). Due to this composition, egg shells are considered as one of the richest source of calcium ions.

In the present study an attempt has been made to use egg shells as a source of calcium for HA synthesis. The idea of extracting calcium from the living system and its usage for synthesizing HA biomaterial can be greatly helpful in reducing the cost production. Also, this method can be also useful in reducing the contamination percentage in synthetic HA e.g silica which is usually found as an impurity in synthetic HA (Dasgupta, Singh et al. 2004).

MATERIALS AND METHODS

Experimental Procedure

Hen’s egg shells were collected in bulk. These were then mechanically cleaned and thoroughly washed with de-ionized water. After washing the shells were dried and grinded into very fine powder. This powder was then calcined at a temperature range of 400 – 1000 °C. As a result of heat treatment the egg shells were converted into CaO (Dasgupta, Singh et al. 2004). The obtained CaO was then converted into CaCl₂ solution by treating with conc. HCl. This CaCl₂ solution was further used as a calcium ions precursor for HA synthesis using CTAB micelles as templates (Mujahid, Sarfraz et al. 2015).

The assynthesized HA powder was then characterized using Fourier Transform Infrared (FTIR) spectroscopy for phase purity, and X-ray diffraction analysis (XRD) for crystallinity and phase composition. Morphological analysis was conducted using field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM).

RESULTS AND DISCUSSION

FTIR Analysis:

FTIR analysis was conducted using Perkin and Elmer FTIR spectrophotometer. FTIR spectrum of as-synthesized sample was recorded in the wavelength range of 500 cm⁻¹ to 4500 cm⁻¹ and is given in Fig. 1. All peaks and bands observed in this spectrum are found in agreement with the earlier reported studies related to HA characterization (Fowler 1974). The peaks observed in Fig. 1 can be divided into three main categories i.e. peaks corresponding to hydroxyl group, phosphate group and carbonate group. A relatively stronger peak at 1036 cm⁻¹ and two sharp peaks at 566 cm⁻¹ and 606 cm⁻¹ indicate stretching vibrations of phosphate group (Tanaka, Hirata et al. 2003, Bahrolololoom,
Javidi et al. 2009). A broad band observed in the range of 3151 cm\(^{-1}\) to 3500 cm\(^{-1}\) is due to the presence of hydroxyl ions. The presence of small peaks at 1399 cm\(^{-1}\) and 722 cm\(^{-1}\) has also been attributed to hydroxyl group. The hydroxyl groups may be either due to adsorbed water or due to lattice water in the crystal structure (Haberko, Bučko et al. 2006). Very small peaks at 1636 cm\(^{-1}\) and 2357 cm\(^{-1}\) indicate presence of carbonate ions (Markovic, Fowler et al. 2004). These carbonate ions may be considered as a common impurity in both synthetic and natural HA.

**FIGURES.**

![FTIR spectra of as-synthesized HA sample](image)

**Fig. 1:** FTIR spectra of as-synthesized HA sample

**X-ray Diffraction:**

X-ray diffractometry analysis was conducted using CuK\(\alpha\), Bruker D8 x-ray diffractometer and x-ray diffraction pattern of the as-synthesized sample is given in Fig. 2. From this pattern, it is seen that most of the peaks found in this pattern matches with those reported for pure HA (JPCD card no. 01-082-1944). Thus, confirming presence of HA in synthesized powder. However, wider and broader peaks indicate poor crystalline nature of the sample. Some other phases are also found in this pattern, these include CaO and \(\beta\)-TCP. The presence of CaO can be assumed due to the result of CaCO\(_3\) decomposition due to heat treatment as per given equation (Dasgupta, Singh et al. 2004).

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\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2
\]

Whereas, presence of \(\beta\)-TCP has been attributed to the autocatalytic conversion of calcium phosphate, followed by secondary nucleation processes during HA formation (Lin, Liu et al. 2011).
Morphological Analysis:

To confirm the morphology of synthesized HA sample, field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) were used. The micrographs obtained are given in Fig. 3 and Fig. 4 respectively. These micrographs provide an insight into the HA structure with respect to particle shape and size. From Fig. 3, it is observed that the synthesized HA sample possesses somewhat irregular shape. Some particles appear spherical in shape and are agglomerated together and some appear to be small thin rods. Also from these micrographs, it is found that the particle/agglomerates lie in the range of few submicro meters to few nano meters. This size is confirmed further from TEM micrograph given in Fig. 4, confirming a single HA particle to be of few nanometer and rod shaped.
CONCLUSIONS

The study at hand concludes that HA can be successfully synthesized using waste egg shells. The percentage of carbonate ion contamination is also found lesser by this method. The crystallinity can be achieved by optimization of other operational parameters. Thus, this methodology can be of great value in terms of low cost production of a high valued biomaterial.

REFERENCES


12. Markovic, M., B. O. Fowler and M. S. Tung (2004). "Preparation and
Hydroxyapatite Produced From Egg Shells


