SYNTHESIS OF SURFACANT ASSISTED HYDROXYAPATITE POWDER USING ULTRASONIC METHOD

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ABSTRACT

Hydroxyapatite [HAP], is chemically represented as Ca₁₀(PO₄)₆(OH)₂ and its excellent bioceramic material for the regeneration of hard tissue because of its high bioactivity, biocompatibility, non-toxicity and also osteoconductive properties. Hydroxyapatite is chemically and crystallographically similar to the natural bone. Especially this material is currently used in dental and orthopaedic applications. In this research work, the influence of non-ionic surfactant assisted hydroxyapatite powder was prepared by ultrasonic method. The particle size, morphology, and phase purity of the powder samples were characterised using analytical methods such as FTIR, XRD and SEM. This work report, the synthesis of hydroxyapatite powder using ultrasonic method offered an effective and economical route to succeed smaller particle size with high quality nano-sized hydroxyapatite and also high level of crystallinity after calcination. The as synthesised powder is to be tested further for its biocompatibility.

Keywords: Hydroxyapatite, Biomaterials, Tween, PVA, Ultrasonic method.

GRAPHICAL ABSTRACT FOR HYDROXYAPATITE
Introduction

Hydroxyapatite (HAP) is one of the main inorganic component and is mostly used in several biomedical applications due to its excellent biocompatibility, osteoconductivity, bioactivity and also non-toxicity and its economical and naturally friendly. Besides this, hydroxyapatite is also used in other applications such as catalysts and in column chromatography, gas sensors, etc. HAP prepared from natural sources can produce bone tissue with strong chemical bonds. This type of HAP has been known as a great bone substitute material. HAP are involved in the calcium phosphate material having the chemical formula Ca$_{10}$(PO$_4$)$_6$(OH)$_2$, is a prominent biomaterial for dental and orthopaedic applications and its similar in chemical composition to the mineral phase of bone and teeth tissues.

Many technique approaches have been developed for preparation of ceramic hydroxyapatite nanoparticles, including sol-gel, precipitation, microwave irradiation, hydrothermal, ultrasonic irradiation and so on. Till now, these chemical techniques suffer from inherent problems such as the uniform size distribution, morphology, agglomeration readily and aggregation due to stringent processes, rigid experimental condition and uncontrolled long term aging. Among these, ultrasonic method presented special features in controlling the particle properties such as particle agglomeration and reducing the particle size, morphology and homogeneity.

Recently, ultrasonic system has become a novel technique to achieve nano-particle. Ultrasonic method provides many advantages such as, nano-sized particles, shape control, simple and inexpensive, effectively decrease the particle aggregation to achieve in the formation of nano sized structures. Therefore it can be well expected that, ultrasonication route is promising and effective technique for formation of nano-hydroxyapatite particles. Since ultra-sonication mainly depends on parameters such as power, time, frequency, and temperature etc.

Poly vinyl alcohol (PVA) and Tween are a non-ionic surfactant, to prevent agglomeration and controlling the morphology. PVA gel used in various applications because of its excellent physical and chemical properties, biocompatibility as well as elastic modules, high mechanical properties and high water contents. In addition to this, the formations of hydroxyapatite powder have been attempted in the presence of surfactant and...
organic molecules in aqueous solution, since the product of hydroxyapatite in organs such as teeth and bone is controlled using surfactant and organic molecules. [24, 25]

In the present study, the preparation of nano-hydroxyapatite by ultrasonic method using two type of non-ionic surfactant (tween & PVA). PVA assisted-hydroxyapatite powder was well crystallinity with control the particle size and uniform flower morphology was achieved through this ultrasonic method and these powders could be successfully employed for biomedical applications.

2. EXPERIMENTAL METHOD

2.1. Chemicals and Reagents

Ca\(\text{2}(\text{NO}_3)\text{2}\cdot 4\text{H}_2\text{O}\), Na\(\text{2}\text{HPO}_4\), poly vinyl alcohol (PVA), tween-20 Ammonia, and ethanol which were purchased from merk. All the chemicals were of analytical grade and DI water was used throughout the experimental process.

2.2 Synthesis of Hydroxyapatite powder

Hydroxyapatite (HAP) nanoparticles were prepared according to the following procedure: 0.5M of calcium nitrate and 0.5g of poly vinyl alcohol (PVA) dissolving in 50 ml of (DI) water. 0.3M of Na\(\text{2}\text{HPO}_4\) dissolving in 50ml (DI) water. In order to obtain hydroxyapatite slurry, phosphate solution was added drop wise into calcium solution, conditions of continuously stirring for 1 hour. During the addition the pH was kept at 10 by using ammonia solution. The resulting suspension was stirred until a clear suspension was achieved without any visible solids. After the complete addition, the suspension was irradiated with an ultrasound for about 40 minutes at 60°C, a transparent dispersion was obtained. In order to eliminate any impurities the resulting suspension was kept 24 hours aging. The resulting precipitate was collected using centrifugation and washed several time for water with ethanol, followed by drying at 100 °C for 4 h in an oven to obtain a fine HAP powder. The resulting powder was calcinated and sintering, finally to achieve pure hydroxyapatite. The synthesis was repeated with 0.5g of tween-20 and without the addition of tween and PVA.
3. RESULTS AND DISCUSSION

3.1 FT–IR spectra

The FTIR spectra for hydroxyapatite and surfactant assisted hydroxyapatite sample are presented in Fig.1. The sharp peak at 3589 cm\(^{-1}\) is assigned to symmetric stretching vibration of the lattice OH\(^-\) ions, while the broad band at 3431 cm\(^{-1}\) attributed to adsorbed water, and a medium peak at 632 cm\(^{-1}\), is due to OH\(^-\) group of HAP. The PO\(_4^{3-}\) group appeared at 966 cm\(^{-1}\) which can be assigned to symmetric stretching mode of phosphate group, \(\nu_1\), and the band at 469 cm\(^{-1}\) is due to symmetric bending mode of phosphate group \(\nu_2\). The absorption band at 1087 cm\(^{-1}\), 1032 cm\(^{-1}\) corresponds to \(\nu_3\) mode [(P-O) asymmetric stretching] of phosphate group. The peak at 567 cm\(^{-1}\) and 606 cm\(^{-1}\) is attributed to asymmetric bending mode of phosphate group \(\nu_4\). Additionally, the peak at 1400 cm\(^{-1}\) is attributed to the presence of the CO\(_3^{2-}\) group in Fig (a, b),\(^{[26]}\). All characteristic peaks for hydroxyapatite are present in FTIR spectrum and no impurities appeared in Fig 1 (c)\(^{[27,28]}\). Hence the FT–IR result designates that the quality of our sample is good.

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![Fig. 1 – FTIR spectra of the HAP powder prepared by the ultrasonic technique at different surfactants: (a) HAP, (b) Tween and (c) PVA](image-url)
Table 1 FTIR spectral assignment of the functional groups

<table>
<thead>
<tr>
<th>Sample</th>
<th>OH</th>
<th>Phosphate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(Sharp) &amp; Broad</td>
<td>(Medium)</td>
</tr>
<tr>
<td>HAP</td>
<td>3580, 3450</td>
<td>643</td>
</tr>
<tr>
<td>HAP-Tween</td>
<td>3580, 3440</td>
<td>624</td>
</tr>
<tr>
<td>HAP-PVA</td>
<td>3589, 3431</td>
<td>632</td>
</tr>
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3.2. X-Ray Diffractions (XRD)

The XRD diffraction patterns of the synthesized hydroxyapatite powder with and without the surfactant are presented in Fig.2. In these XRD patterns, the major peaks were observed at 2θ values at 25.90, 29.10, 31.66, 32.72, 34.18, 39.59, 45.39, 49.32 and 53.48 corresponding to the (002), (210), (211), (300), (202), (310), (222), (213), and (004) confirming the formation of hydroxyapatite. Similar peaks were also detected in the XRD patterns of tween–HAP. The XRD spectra of surfactant assisted hydroxyapatite showed higher crystallinity when compared to without surfactant. It is clear that all demonstrable peaks in all samples were identified to pure hydroxyapatite with hexagonal phase and no impurities peaks according to standard JCPDS card no -09-0432. The particle size of surfactant assisted hydroxyapatite powder is found to be lower when compared to hydroxyapatite, which is calculated by Scherrer’s equation\(^{[29]}\). As a typical result from the XRD, the addition of non-ionic surfactant as a plays a major role in the crystallization and growth of HAP nano-particles and it is effective formation of biological hard tissue with strong chemical bond.

\[ D = \frac{K\lambda}{\beta\cos\theta} \]
Fig. 2 – XRD pattern of HAP powder prepared by the ultrasonic technique at different surfactants: (a) HAP, (b) Tween and (c) PVA

3.3 Scanning electron microscopic studies

The morphology of hydroxyapatite powder synthesize by ultrasonic method with different surfactants (PVA and tween-20). In Fig. 3(a), the hydroxyapatite powder formed were non-uniform particle in size, the particles are joined to each other and produced aggregated particles and irregular morphology present in micro metre range. Fig. 3(b, c) show the presence of surfacetant assisted hydroxyapatite powder, having a uniform size, well-controlled and regular array of nano-particles. Furthermore, converted from plate shape (b) to flower like morphology were clearly observable in the case of Fig.3 (c). It was observed that the morphology of a flower and plate like HAP powder was affected remarkably by the concentration of PVA and tween in the ultrasonic method. It has been well-known that, organic materials may have interacted with inorganic substances of calcium and phosphate in the ultrasonic method to obtained a uniformly arrangement structure. The flower structures were then retained after the removal of PVA and tween by calcination at a high temperature. Finally, the SEM images showed that the PVA (0.5g) was optimal for the preparation of flower morphology of hydroxyapatite powder and prevent agglomeration.
Fig. 3 – The surface morphology of the HAP powder prepared by the ultrasonic technique at different surfactants: (a) HAP, (b) Tween and (c) PVA
Conclusions

In this study, hydroxyapatite nanoparticles have been successfully prepared by ultrasonic irradiation method using poly vinyl alcohol (PVA) and tween-20 as a non-ionic surfactant. The result indicated that, in FT-IR spectrum showed that no impurities peaks was observed and in XRD, the synthesis of surfactant assisted hydroxyapatite powder has a hexagonal structure with higher crystallinity and smaller particle size. The SEM image revealed that uniform morphology, control the size and regular array of nanoparticles was achieved using PVA. It can be concluded that, ultrasonic method with PVA as a growth regulator can result in fine nanometre sized HAP. The obtained HAP powder could serve as a favourable candidate in biomedical applications and hence this technique could be a novel approach to synthesis of HAP nanoparticles.

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