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RESEARCH ARTICLE

GREEN TEMPLATES ASSISTED SYNTHESIS OF NANO HYDROXYAPATITE AND ITS APPLICATIONS- A COMPREHENSIVE REVIEW

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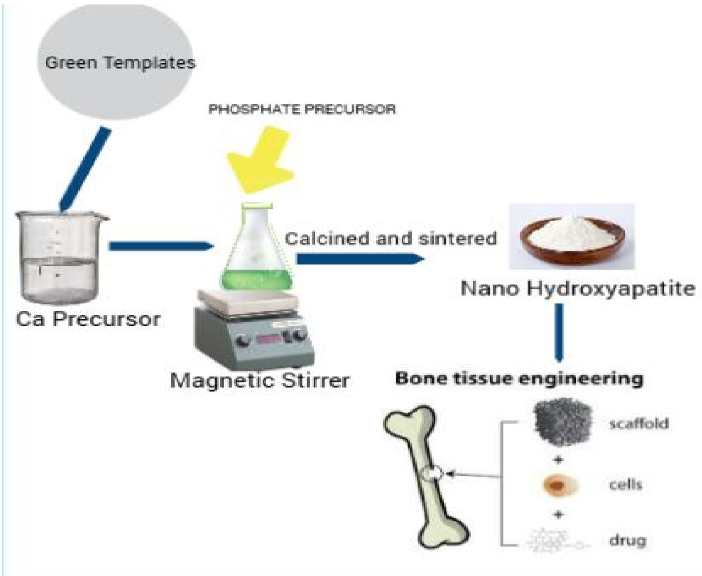
Abstract

Hydroxyapatite (HAP) is a calcium phosphate mineral that has the composition very similar to that of bone and teeth and it is used in a variety of biomedical applications such as implants in orthopaedic field, dental filling material and tissue engineering. Hydroxyapatite can be synthesised using precursors of calcium and phosphate with the addition of various chemical or natural occurring templates. Templates play a significant role in controlling the size and morphology of nanoparticles. In this article we have discussed the various templates which were occurred naturally such as banana peel, licorice root extract, tamarind, pear fruit, grapes, neem leaf extract, tea saponin, Moringa Oleifera flower extract, Manoon Longifolium leaf extract and Wrightia tinctoria for the synthesis of nano hydroxyapatite. Also how the properties such as size and morphology of hydroxyapatite are significantly influenced by the addition of these templates have been highlighted.

KEYWORDS

Biomaterial, Hydroxyapatite, Nanoparticle, Synthesis, Green Templates

Graphical Abstract :



Introduction

Hydroxyapatite is a biocompatible inorganic material which has the chemical formula $Ca_{10}(PO_4)_6(OH)_2$ and it has been used widely in bone and teeth replacement applications such as scaffold filler for bones, coating for bones and tooth implant and also in the delivery of various drugs[1,2]. The properties such as antimicrobial activity, biocompatibility, particle size and morphology of HAP plays a major role in the manufacturing of bone implants and scaffolds [3,4,5]. Researchers find a great deal of interest in synthesizing nano hydroxyapatite with various morphology and size. Synthesis of HAP can be performed by wet method and dry method. The wet method consists of chemical precipitation and hydrothermal whereas the dry method consists of solid state synthesis and mechanochemical method [6,7]. In recent years nanoparticles synthesised by means of green route have gained much importance because of its sustainability and environmental friendliness.

This review demonstrated the synthesis of hydroxyapatite using green templates which were available in natural sources such as banana peel, licorice root extract, tamarind, pear fruit, grapes, neem leaf extract, tea saponin, Moringa Oleifera flower extract, Manoon Longifolium leaf extract and Wrightia tinctoria leaf extract.

The various Green Templates employed for the synthesis of HAP is presented in table 1:

Table 1: Green templates employed for the synthesis of HAP

S.No	Sources of Template	Applications	Reference
1	Banana Peel Extract	Antibacterial	[8]
2	Licorice Root Extract	-	[10]
3	Tamarind fruit Extract	Antibacterial	[12]
4	Pear Fruit Extract	Antibacterial	[14]
5	Grape Fruit Extract	-	[16]
6	Neem Leaf Extract	-	[19]
7	Tea Saponin Extract	-	[21]
8	Moringa Oleifera flower Extract	Antibacterial, Antifungal	[23]
9	Manoon Longifolium leaf Extract	Fluoride ion removal from water	[25]
10	Wrightia tinctoria leaf Extract	Antibacterial	[26]

BANANA PEEL EXTRACT

Gopi et. al., [8,9] reported the synthesis of Hydroxyapatite nanoparticles using pectin as the template which was derived from banana peel extract and the resultant product were investigated with various analytical techniques. The synthesised HAP was evaluated for its antibacterial activity using gram positive and gram negative bacteria such as Staphylococcus aureus (S. aureus) and Escherichia coli (E. coli), respectively.

They varied the concentration of pectin ranging from 0.01-0.15 wt.% and from the SEM result they concluded that the optimum concentration of pectin for controlling the particle size of HAP nanoparticles was 0.15 wt. %. The research group also found that the antibacterial activity of synthesised HAP nanoparticles increases with increase in the concentration of HAP from 25 µl to 100 µl.

LICORICE ROOT EXTRACT

Ashraf and his co workers [10,11] reported the synthesis of HAP nanorods by means of microwave hydrothermal method using Licorice root (Glycyrrhiza glabra) extract as the green template and it contains Glycyrrhizic acid (GA), a water soluble biosurfactant.

They analysed the purity of the samples using FTIR and Raman Spectroscopy and demonstrated that HAP is free of carbon. The Particle Size Distribution analysis (PSA) was done for the synthesised HAP and they found that the nanorods of HAP with average dimensions of 105 nm length and 25 nm width.

TAMARIND FRUIT EXTRACT

Synthesis of Hydroxyapatite nanorods using fruit extracts as templates was reported by Gopi and his colleagues [12,13]. They employed the extracts of banana, tamarind and grape fruit as green templates. The research team identified that tamarind extract plays a vital role in lowering the particle size and crystallinity when compared to other fruit extracts such as banana and grapes. Further they revealed from the investigation that the particle size distribution depends on the concentration and nature of tartaric acid from natural sources.

They found that the biocompatibility of as synthesised HAP samples using antibacterial studies with the pathogenic gram negative bacterial strains such as E. Coli, and *Klebsiella*. The antibacterial activity of HAP using tamarind as a green template showed more inhibition zone even at lower concentration when compared to other natural sources of tartaric acid such as banana, grape and commercially available tartaric acid.

PEAR FRUIT EXTRACT

Gopi et. al.,[14,15] reported the synthesis of Hydroxyapatite nanoparticles using pectin as template and it was derived from peel of pear (*Opuntia ficus indica*) fruits. The various concentrations of pectin like 0.01, 0.04, 0.07, 0.1, 0.15, 0.2 and 0.25 wt.% were used for the synthesis of HAP. The research team found from the XRD data that the crystallinity of the HAP nanoparticles increases with increase in the concentration of pectin from 0.15 wt%.

They revealed from the SEM results that the particle size of the synthesised HAP reduced significantly when the concentration of pectin increased from 0.01 to 0.15 wt.%. Finally they concluded that the concentration of pectin plays a major role in controlling the morphology of HAP nanoparticles.

The research group also investigated the antibacterial activity of synthesised HAP in the absence and presence of pectin using the S. aureus, E. coli, and C. albicans bacterial strains. The inhibition zone of HAP with 0.15 wt.% pectin was shown to be higher ie., 11.4 mm for 100 μl than the HAP synthesised with absence of pectin (2.3 mm for 100 μl).

GRAPE FRUIT EXTRACT

Maritza and coworkers [16,17] synthesised Hydroxyapatite Nanorods using fruit extracts such as mango, grapes and ripe tamarind as green templates by hydrothermal method. The hydroxyapatite nanorods were characterised for the study of their morphology and formation using Scanning Electron Microscopy (SEM), X-ray Diffraction, Infrared spectroscopy analysis. They concluded that grape fruit extract used for the synthesis of HAP showed that the particle size reduced significantly by about 41.7% when compared to mango and tamarind fruit extracts.

Vijayalakshmi and her research team [18] investigated about the synthesis of hydroxyapatite nanoparticles using different green templates such as banana peel extract, grape fruit extract, tamarind leaves extract and pear fruit extract and compared the properties of synthesised HAP.

They concluded from the DLS data that the particle size of the HAP was found to be lower by using grapes (292 nm) and pear (291.3 nm) as the green template when compared to banana (422.1 nm) and tamarind fruit (319.8 nm) extract. They declared from the XRD data that the crystallinity of the HAP nanoparticles reduced by using grape as a green template (129 nm) when compared to banana peel (188 nm), tamarind leaves (192 nm), and pear fruit (187 nm). They found that uniform particle size was observed by using grape fruit as the template when compared to other templates.

NEEM LEAF EXTRACT

Punita and her research team [19,20] reported the synthesis of hydroxyapatite nanoparticles using the egg shell waste and the addition of neem leaf (*Azadirachta indica*) extract as the green template by microwave assisted and also conventional wet precipitation method. They reported from the SEM and TEM analysis data that the synthesised HAP using neem extract by microwave method possesses less agglomeration when compared to conventional method and without the addition of neem leaf extract.

They demonstrated that the average size of HAP in the absence of neem leaf extract for both the methods was found to be 30-31 nm and 53-55 nm whereas in the presence of neem leaf extract it was 27-28 nm and 44-46 nm in width and length respectively. They found that the crystalline size was reduced for the synthesised HAP by means of microwave method in the presence of neem leaf extract.

TEA SAPONIN

Tao Zhang et. al., [21,22] reported the synthesis of hollow porous hydroxyapatite microspheres by the addition of tea saponin as green template. They varied the concentration of tea saponin from 0 to 0.15% and found from the XRD data that the crystallinity of HAP reduced with increase in the concentration of tea saponin.

The research team concluded from the SEM analysis data that the size and the morphology of HAP varies significantly with the concentration of tea saponin. With zero concentration of tea saponin HAP exhibits rod or ellipse like granules. The spherical nanorods of HAP were obtained with the average diameter of 2.0 μm at 0.002% concentration of tea saponin whereas with 0.008% of tea saponin the HAP formed as a sheet like structure with the average diameter of 2.3 μm.

The research team revealed from the surface and pore analysis data that the average pore size was reduced from 57.6 nm to 29.7 nm with an increase in the concentration of tea saponin from 0 to 0.11% respectively. Further they concluded that HAP synthesised using tea saponin was mesoporous in nature.

MORINGA OLEIFERA FLOWER EXTRACT

Kalaiselvi and her research team [23,24] reported the green synthesis of Hydroxyapatite nanorods using Moringa Oleifera flower extracts by microwave assisted method. The green synthesised HAP nanorods and chemically synthesised HAP nanorods were compared for its antimicrobial properties. They carried out the antibacterial activity using both gram positive and gram negative bacterial strains.

The zone of inhibition for the chemically synthesised HAP using gram positive bacteria species such as Monococcus Luteus, Staphylococcus aureus and Bacillus subtilis were found to be 10 mm, 11 mm and 9 mm respectively whereas the high antibacterial activity were observed for the green synthesized HAP nanorods and found to be 15 mm, 13 mm and 14 mm respectively.

Likewise for gram negative bacterial species such as Salmonella paratyphi, Pseudomonas aeruginosa and Klebsiella pneumoniae, the Zone of inhibition for chemically synthesized HAP were found to be 10 mm, 9 mm and 9 mm respectively, whereas for green synthesized HAP it was observed as 12 mm, 10 mm and 10 mm respectively.

The research team also carried out the antifungal studies using Aspergillus fumigatus, Aspergillus niger and Candida albicans for HAP deived frrom chemical method and green method. They concluded that more antifungal property was seen for green synthesized HAP when compared to chemically derived HAP.

MANOON LONGIFOLIUM LEAF EXTRACT

The removal of Fluoride ions using green synthesised hydroxyapatite nanoparticles was reported by Dawit Darcha Ganta et. al., [25]. Manoon Longifolium Leaf Extract was used as template for the synthesis of HAP. They found that the percentage of removal of Fluoride ions and adsorption capacity increases from 73% to 93% with increase in pH of the solution from 1 to 7. Further increase in the pH of the solution results in the decrease of the percentage removal of Fluoride ions to 81%. They emphasised that the optimal pH for the removal of Fluoride ions from the aqueous solution is at pH 7.

They also studied the adsorption capacity by varying the adsorbent dose from 0.1 g/L to 1.0g/L. They reported that the percentage of removal of Fluoride ions significantly increases upto 0.75 g/L of adsorbent dosage and beyond that no significant change in the adsorption capacity.

WRIGHTIA TINCTORIA LEAF EXTRACT

Ragunath et. al., [26] reported the green synthesis of Hydroxyapatite nanoparticles and its antibacterial activity using Wrightia tinctoria. They carried out the XRD and SEM analysis and found that the crystals of HAP were hexagonal in shape and polycrysatalline in nature. They also reported that the high antibacterial activity of HAP was observed against various bacterial strains such as Psuedomonas aeruginosa, Klebsiella pneumonia, Escherichia coli and Staphylococcus aureus.

CONCLUSIONS

In this review article we have discussed the synthesis of Hydroxyapatite nanoparticles using different green templates such as Banana peel extract, Licorice root extract, Tamarind fruit extract, Pear fruit extract, Grape fruit extract, Neem leaf extract, Tea saponin, Moringa Oleifera flower extract, Manoon Longifolium leaf extract and Wrightia tinctoria leaf extract. We conclude that addition of green templates played a significant role in controlling the morphology, crystallinity, shape and size of synthesised nano hydroxyapatite. Even though many chemically derived templates are employed for the synthesis of HAP, nowadays scientists are of keen interest in employing naturally available green templates due to its environmental sustainability. The Green templates are readily available, low cost, non toxic and biocompatible in nature. In this era green synthesis of nanoparticles gained much importance due to its benefits to the environment and human health.

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