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Ethylene Glycol– assisted Synthesis of n-hap and Magnesium hap Nanocomposite

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ABSTRACT

Biomaterials were derived from nature and also it can be synthesized by chemical processes which can be utilized as metallic components, ceramics or composite materials. Nano Hydroxyapatite [n-HAp], a milky white coloured powder with calcium and phosphate ions stoichiometric ratio is 1.67. It was mainly used as bone and teeth fillers. The n-HAp [$Ca_{10}(PO_4)_6(OH)_2$] was prepared by sol-gel method, as it is known to be a simple economic technique which suits for industrial or large scale production. During precipitation, the grain growth may occur. In order to avoid this, Ethylene Glycol (EG) was used as a capping agent in synthesis of HAp nanoparticles and Magnesium HAp nanocomposites. The synthesized n-HAp and Magnesium HAp nanocomposites were characterized using SEM, XRD, EDAX, FTIR and Antibacterial activity in order to analyze its structure, elemental composition and functional group. XRD analysis shows the strongest 2θ peaks of n-HAp and Magnesium HAp nanocomposites at 32.1°, 25.9°,49.7°and 10.2°, 32°, 18.9° respectively.

Keywords: Biomaterial, Capping agent, n-HAp, grain growth, Sol-Gel Method

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1. Introduction

Nanotechnology manipulates matter at the atomic, molecular (or) macromolecular[1] to create and control objects on the nanometer scale.[2] The nanometer scale is commonly indicated as 1-100nm.[3] Nano Hydroxyapatite is a naturally occurring biomaterial which has prosthetic application due to its similar size.[4] It is a Hydroxyl end apatite biomaterial which may be occupied by Fluoride, chloride and carbonate ions. It belongs to Hexagonal crystal system and has specific gravity 3.08. It has properties of biocompatibility (it does not cause any toxic or immunological response when react with body), bioactivity (it gives response to living tissue), bioresorbable (it break and sucked by the body easily), osteo conductivity (it supports the growth of bone on surface), non-toxicity etc..,[5] It is used in bone replacement.[6] and remineralizing agent in tooth paste and desensitizing agent in teeth bleaching.[7]. It also gives protection against acid erosion. It also used as anti-aging for aged skin.[8] Though it forms strong chemical bond with host bone tissue, it was recognized as good bone graft material.

There is no need of special instruments for preparation of n-HAp so the preparation is simple. It also generated by treatment of waste streams containing calcium. The available methods for preparing n-HAp are Wet Chemical, Precipitation, Hydrothermal, Spray-dry, Micro emulsion, Mechanochemical, Electro deposition, Biometric deposition, Sol-Gel etc., Among these Sol-Gel method is chosen, Since it is a low cost and simple technique. In this work n-HAp and Magnesium HAp nanocomposite are prepared using Calcium nitrate and Diammonium Hydrogen Phosphate as precursors with Ethylene Glycol as capping agent.

2. ExperimenTAL PROCEDURE

2.1 Materials Used:

Calcium nitrate [$Ca(NO_3)_2$].$4H_2O$], Diammonium Hydrogen Phosphate [$(NH)_4HPO_4$], Ethylene Glycol, Ammonia solution, Magnesium tetrahydrate were procured from Merck, Mumbai.

2.2 Synthesis of n-HAP

To synthesize n-HAp, Calcium nitrate [$Ca(NO_3)_2$].$4H_2O$] and Diammonium Hydrogen Phosphate [$(NH)_4HPO_4$] were added in distilled water taken in such amount that Ca/P mole ratio maintained at 1.67.[9] 0.5M of Ethylene Glycol was added to

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the solution of Calcium nitrate. To that solution Diammonium Hydrogen phosphate solution was added drop by drop[10] and stirred for 30min using Magnetic stirrer.[11] During addition the pH of the solution maintained at 12 by adding Ammonia Solution and the solution is kept undisturbed. At the end of 24hrs, a gelatinous white precipitate is obtained.[12] It was centrifuged and washed thoroughly by distilled water and filtered. The filtrate was dried at 120°C for 17hrs.[13] The obtained precipitate was calcinated for one hour at 100°C. Thus, Ethylene Glycol capped HAp was synthesized.[14]

2.3 Synthesis of Magnesium Hap Nanocomposite

The same procedure was followed for the preparation of Magnesium-HAp nanocomposite but Magnesium Hexahydrate was added with calcium and thus maintaining the stoichiometric ratio as [(Ca+Mg)/ P] =1.67. Thus, Ethylene Glycol capped Magnesium substituted HAp nanocomposite was obtained.[15] The synthesized n-HAp and Magnesium HAp nanocomposite were characterized using Scanning Electron Microscope (SEM), X-ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), EDAX and Antibacterial activity.

3. RESULTS AND DISCUSSIONS

3.1 X-ray Diffraction analysis

The XRD pattern of n-HAp and Mg-HAp nanocomposite was shown in Fig. 1. The sharp peaks in the XRD pattern indicates that the prepared n-HAp and Mg-HAp are crystalline in nature. The crystalline size was calculated using Scherrer's formula,

$$D=K\lambda/\beta\cos\theta$$

Where,

D is the grain size in nm.

λ is the Wavelength of X-ray in nm.

β is the full width at half maxima(FWHM) of the diffraction peak.

θ is the Bragg's diffraction.

K is the proportionality constant.

The average crystallite size of n-HAp is 0.7849 nm and for Magnesium n-HAp composite is given by 19.2012 as shown in Table 1.1 and Table 1.2.

3.2 Scanning electron microscope (SEM) analysis

The surface morphology of synthesized n-HAp and Magnesium HAp nanocomposite were examined by Scanning Electron Microscope. The SEM images of n-HAp are shown in Fig. 2. It confirms that the particles are flakes with various shapes.[16] The SEM images of Magnesium HAp nanocomposite is shown in Fig. 3. It confirms that the particles are hexagonal in structure.[15]

Elemental analysis

The elemental composition of n-HAp and Magnesium HAp nanocomposite were analyzed using EDAX. The EDAX

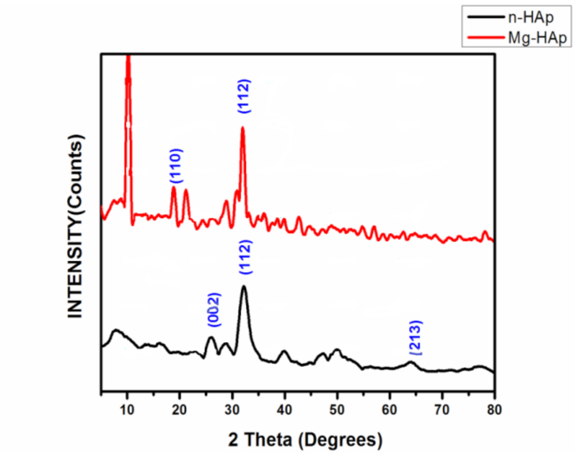

Fig. 1: XRD image of n-HAp and Mg-HAp nanocomposite

Table 1.1: Structural parameters of n-HAp

2θ (deg)	FWHM (deg)	$\beta \times 10^{-3}$	Crystallite size D (nm)	Dislocation density $\delta \times 10^{15}$ (lines/m)	Micro strain ($\varepsilon \times 10^{-3}$)
32.1651	1.4031	24.4763	0.6158	0.2674	5.8796
25.9618	0.8986	15.6756	0.9481	0.1113	3.8187
49.7214	1.1571	20.1849	0.7907	0.1599	4.5786

Table 1.2: Structural parameters of magnesium hap nanocomposite

2θ (deg)	FWHM (deg)	$\beta \times 10^{-3}$	Crystallite size D (nm)	Dislocation density $\delta \times 10^{15}$ (lines/m)	Micro strain ($\varepsilon \times 10^{-3}$)
10.2201	0.3903	6.8086	21.3550	2.1928	1.6953
32.0105	0.4678	8.1605	18.4624	2.9338	1.9609
18.9036	0.4661	8.1309	18.0562	3.0672	2.0051

image of n-HAp and Magnesium HAp nanocomposites are shown in Fig. 4 and Fig. 5. It confirms the presence of Ca, P and O elements and no other significant elements were detected in both n-HAp and Magnesium HAp nanocomposite.

3.3 Fourier Transforms Infrared Spectroscopy (FTIR) Analysis

The FTIR spectrum of synthesized n-HAp and Magnesium HAp nanocomposite were shown in Fig. 6. In n-HAp the peak at 2810.28, 2362.80 and 1363.67 assigned to hydroxyl (O-H) stretching.[16] The peak at 601.79 and 565.14 represents the vibration mode of PO_4^3. In Mg n-HAp composite, the peaks at 2802.57, 2360.87and 3400.50 corresponds to hydroxyl (O-H) Stretching. The peak at 1039.63 and 563.29 represent the vibration mode of PO_4^3.

3.4 Antibacterial Activity

The given samples were tested for antimicrobial activity by well diffusion method. Liquid Mueller Hinton agar media and the Petri plates were sterilized by autoclaving at 121°C for about 30 minutes at 15 lbs pressure. Under aseptic conditions in the laminar airflow chamber, about 20ml of the agar medium was dispensed into each Petri plate to yield a uniform depth of 4mm. After solidification of the media, 18hrs

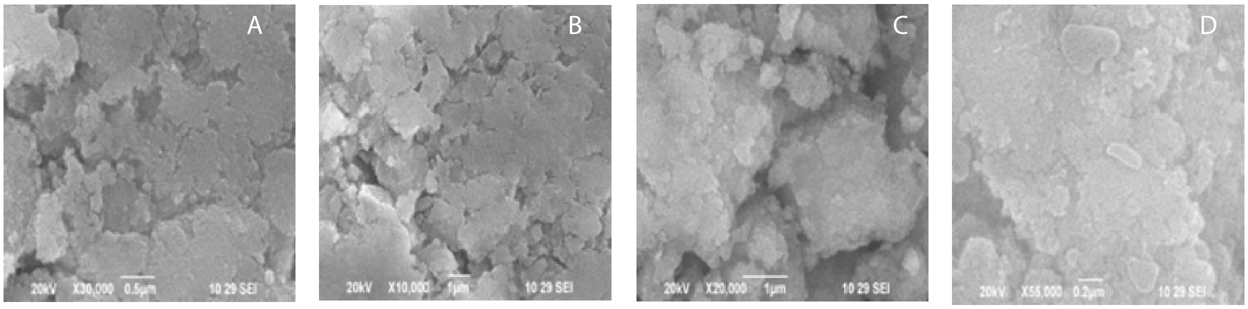

Fig. 2: SEM images OF n-HAp at different resolution

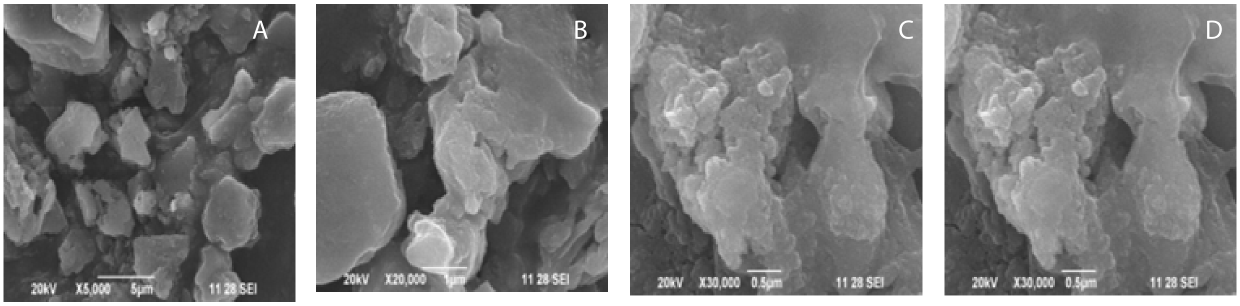

Fig. 3: SEM images OF Mg n-HAp at different resolution

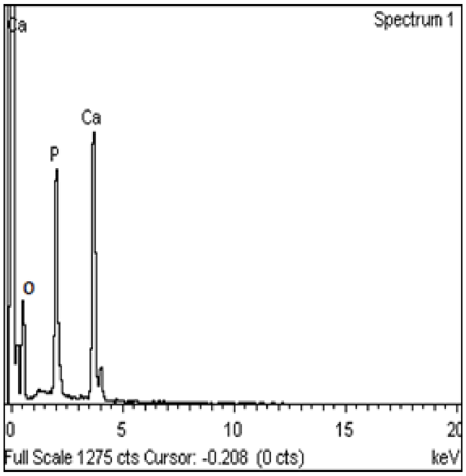

Fig. 4: n-HAp nanocomposite

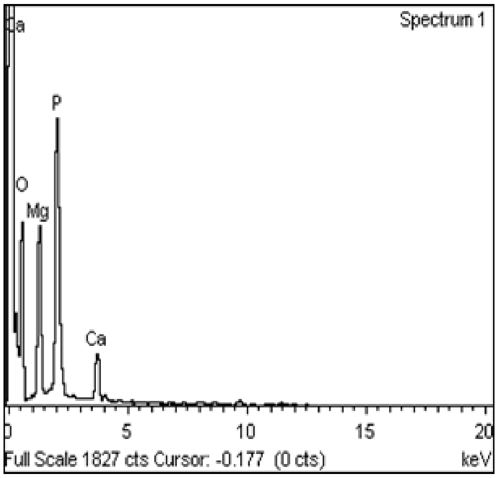

Fig. 5: Mg-HAp nanocomposite

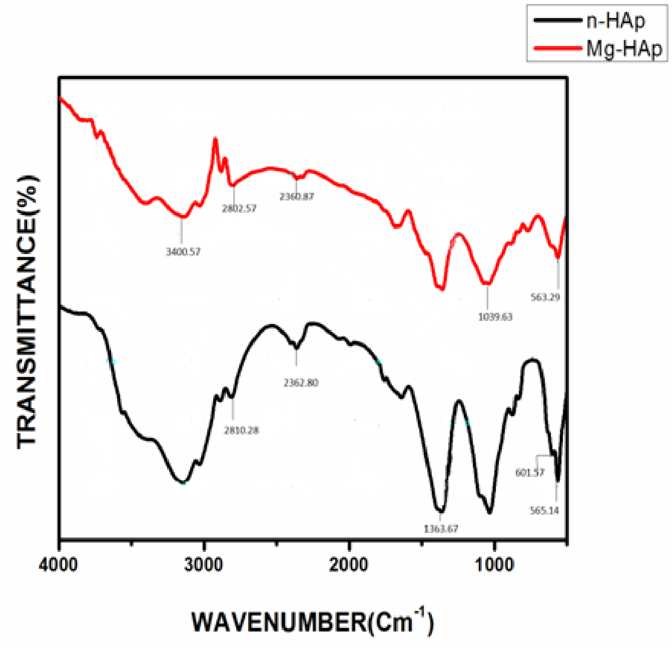

Fig. 6: FTIR image of n-HAp and Mg-HAp nanocomposites

culture of Gram positive microorganisms such as Bacillus cereus (MTCC 430), Staphylococcus aureus (MTCC 3160),Gram negative microorganisms such as E.coli (MTCC 1698) and Klebsiellapneumoniae (MTCC 10309) obtained from IMTECH, Chandigarh were swabbed on the surface of the agar plates. Well was prepared by using cork borer followed with loading of 50µl and 100 µl of each sample to the distinct well with sterile distilled water as negative control and streptomycin (30mcg/disc) as positive control. The sample loaded plates were then incubated at 37°C for 24 hours to observe the zone of inhibition.[14]

4. CONCLUSION

Nano HAp and Magnesium HAp nanocomposite has been synthesized by Sol-Gel Method using Ethylene Glycol as capping agent. The Ethylene glycol restricted the growth of agglomeration during precipitation and reduces the particle size when compared to their corresponding sample prepared without capping agent. It suits for large scale production with high specific area. The synthesized HAp and Magnesium HAp

S. No	Microorganisms	Zone of Inhibition in Diameter (mm)					
		Control (100 µl)	n-HAp		Mg-HAp Nanocom-posite		Std. Antibiotic (Streptomycin) 30mcg/disc
			50 µl	100 µl	50 µl	100 µl	
1	Bacillus cereus	Nil	Nil	Nil	Nil	Nil	20
2	Staphylococcus aureus	Nil	Nil	Nil	Nil	6	28
3	Escherichia coli	Nil	3	9	Nil	5	25
4	KlebsiellaPneumoniae	Nil	Nil	Nil	Nil	Nil	20

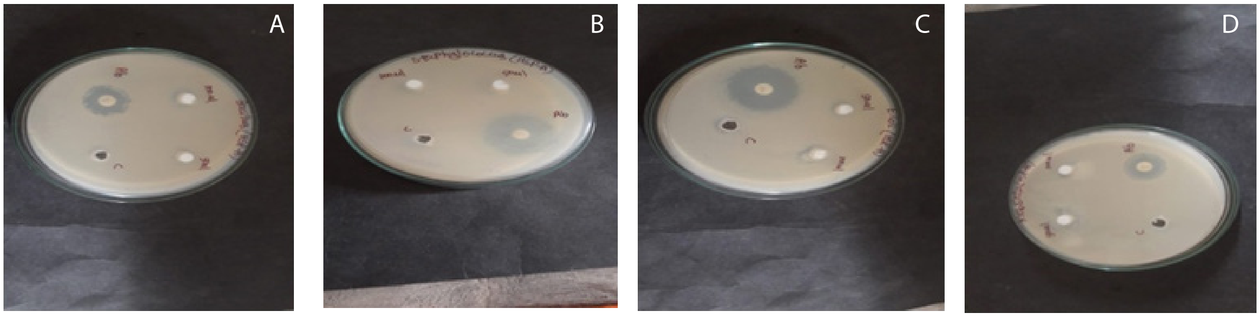

Fig. 7: Zone inhibition of n-HAP against (a) Bacillus cereus (b) Staphylococcus aureus (c) *E. coli* (d) Klebsiellapneumoniae

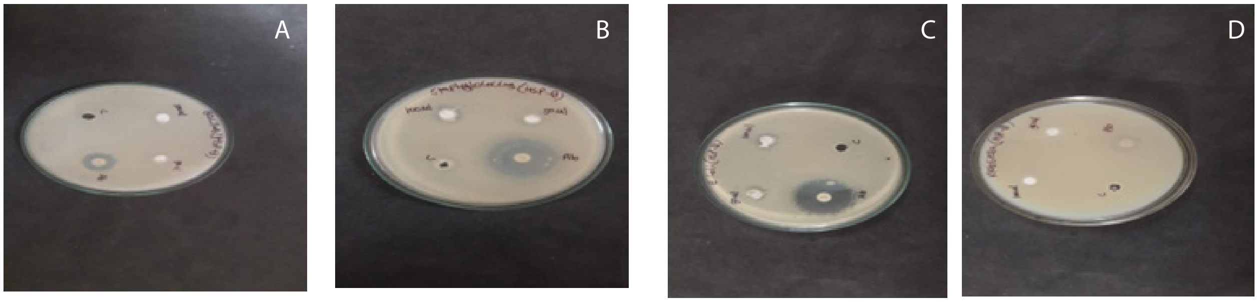

Fig. 8: Zone inhibition of Mg-HAp nanocomposite against (a) Bacillus cereus (b) Staphylococcus (c) *E.coli* (d) Klebsiellapneumoniae

nanocomposite were characterized using XRD, SEM, EDAX and FTIR. The crystallite structure of n-HAp was very much comparable to that of bone, enamel and dentine hence it will be attractive for biomedical application.

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