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Sono-synthesis of nanohydroxyapatite: Effects of process parameters

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Abstract

Hydroxyapatite (HA) [$Ca_{10}(PO_4)_6(OH)_2$] is a bioactive ceramic with excellent osteoconductive properties. This characteristic helps HA to be integrated into the bone without provoking an immune reaction, thus making it a useful biocompatible material for load bearing bone implant. In this study, nanohydroxyapatite (NHA) was synthesised using a precipitation method assisted with ultrasonication. The process parameters such as ultrasonic time (t) (10–30 min), ultrasonic amplitude (A) (50–70%), solution temperature (T) (50–90 °C), and solution pH (7–9) were varied on the basis of single factor and their effects on NHA synthesis was investigated. Besides that, the effect of calcination on the NHA powder morphology was also studied by varying the calcination time (2, 4 and 6 h) and temperature (400, 800 and 1200 °C). The characterisations of the synthesised NHA powder were conducted using thermogravimetric analysis (TGA), field emission scanning electron microscope (FESEM), energy-dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD), Brunauer–Emmett–Teller (BET), transmission electron microscope (TEM), zeta-sizer and Fourier transform infrared spectroscopy (FTIR). It was found that nano-sized HA particles can be produced at optimum set of process parameters of $t=25$ min, $T=90$ °C, $A=65\%$, and pH=8. Results revealed that the thermal stability, morphology and crystallinity of the NHA powder was further improved by calcinating the powder at optimum temperature and time of 800 °C and 2 h, respectively.

Keywords: A. Calcination; Nanohydroxyapatite; Precipitation; Ultrasonication; Thermal stability

1. Introduction

The interaction of materials with biological tissues and their adaptation to them play a vital role in developing new tissues, including bone implants [1,2]. Bones are nanocomposites consisting of an organic collagenous fibre network embedded with inorganic calcium phosphate and calcium carbonate [3]. These calcium phosphates, categorised as either bioinert or bioactive in nature can be synthesised and used in different medical applications including bone implants [4–6]. The difference being that bioinert calcium phosphates have no control over the bone tissue unlike the bioactive calcium phosphates, which have the ability to interact with the bone tissue. One of the bioactive calcium phosphates is hydroxyapatite (HA), a biocompatible component that happens to be a major constituent of the inorganic segment of the bone [7]. This HA present in natural bone is nanosized with a needle like shape having low degree of crystallinity and high surface reactivity. The excellent osteoconductive property and biocompatibility of HA makes it the best material for bone implant applications [8].

Therefore, the synthesis of NHA has evolved with time where various techniques have been implemented in the past few decade [9], such as wet-chemical [10–12], solid-state [13], hydrothermal [14], precipitation [15–17] and mechanochemical [18]. However, the precipitation technique is the most reported method used to

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synthesis NHA. This is due to its simplicity, low cost and suitability compared to the rest. Yet, the quality of the NHA powder produced is low, with large and wide range of particle size, having higher tendency of agglomeration. To improve this quality, ultrasonication is used to break up the agglomerates, reduce the particle size and disperse the nanoparticles [19].

Although many techniques have been used to synthesis NHA, only little attention is given to investigate the influence of different parameters on the size, shape and crystallinity of the nanopowder [8]. For instance, the pH of the solution influences the solubility of the precipitates, whereby at a higher pH value the solubility of the precipitates is lowered; leading to the formation of agglomerates. Parameters such as temperature and mixing time can influence the shape of NHA powder formed, that is either rod-like [20] (needle, whisker, wires, etc.) or plate-like (spherical) shape [21]. Furthermore, calcination/sintering process has shown to improve the crystallinity of the NHA powder by heating at a very high temperature [22].

As of now, the quality of the NHA powder synthesised through the precipitation method has been studied by varying either one of the processing parameters such as solution pH, temperature, stirring time or CaP ratio [23,24]. However, till date no study on the combination of these parameters were found, particularly when ultrasonication is used. Therefore, this paper focusses on the effect of ultrasonication related parameters such as ultrasonic time and amplitude, solution temperature and pH on the properties of the NHA powder using single factor analysis. The effect of calcination time and temperature on the quality of NHA was also investigated.

2. Materials and method

2.1. Materials

The chemicals used for the synthesis of nanohydroxyapatite such as di-ammonium hydrogen phosphate (A.P.) (UK), calcium nitrate tetrahydrate (C.P.) (UK), ammonium solution (30%) (A.P.) (UK) and absolute alcohol 99.7% (Denatured) (A.P.) (UK) were purchased from LGC scientific, Malaysia. Hydroxyapatite nanopowder ($\geq 97\%$ and < 200 nm (BET)) used for comparison purpose was purchased from Sigma-Aldrich (USA). All chemicals were of analytical grades and were used as received without any further modification.

2.2. Sample preparation

The experimental flow of this work is summerised in Fig. 1. A solution of 50 mL of 1 M calcium nitrate tetrahydrate and 35 mL of 0.6 M diammonium hydrogen phosphate were mixed using Cole Palmer ultrasonic processor. The pH of the solution was adjusted with ammonium solution. The operating conditions for the ultrasonication process are presented in Table 1. Upon completion of the reactions, the solutions were vacuum filtered and washed with water and ethanol. The washed precipitate

Table 1
Parameters affecting NHA synthesis.

Studied parameters	Constant parameters
pH of solution 7, 8 and 9	• **solution temperature** at 60 °C • **ultrasonic amplitude** at 60% • **ultrasonic time** at 20 min
Ultrasonic time 10 min, 15 min, 20 min, 25 min and 30 min.	• **pH** of 8, • **solution temperature** at 60 °C • **ultrasonic amplitude** at 60%
Ultrasonic amplitude 50%, 55%, 60%, 65% and 70%	• **pH** of 8, • **solution temperature** at 60 °C • **ultrasonic time** at 20 min
Solution temperature 50 °C, 60 °C, 70 °C, 80 °C and 90 °C	• **pH** of 8, • **ultrasonic amplitude** at 60% • **ultrasonic time** at 20 min

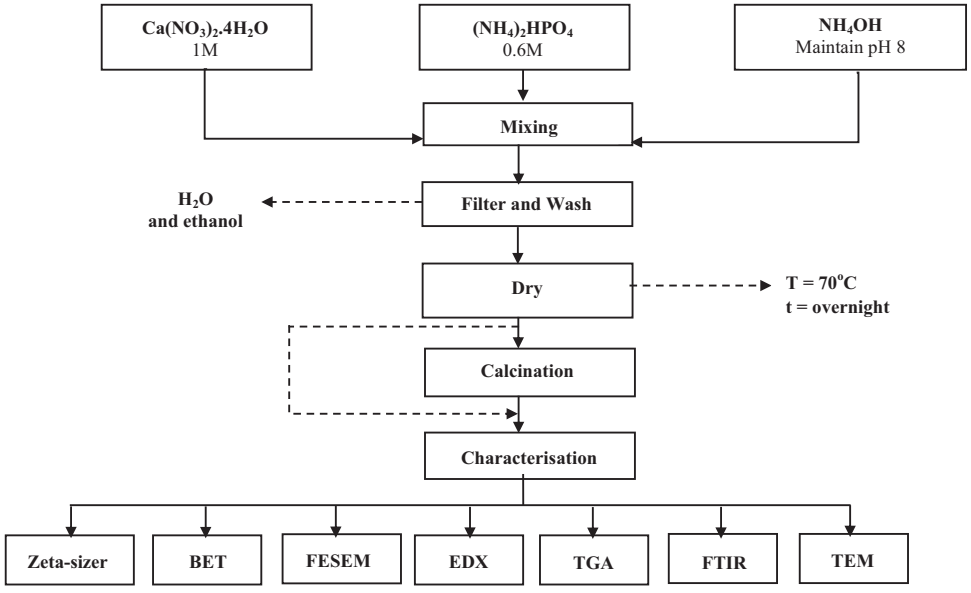

Fig. 1. Schematic presentation of synthesising of NHA.

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