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## Effect of calcium precursors and pH on the precipitation of carbonated hydroxyapatite

Radzali Othman<sup>a,\*</sup>, Zaleha Mustafa<sup>a</sup>, Chong Wee Loon<sup>b</sup>, Ahmad Fauzi Mohd Noor<sup>b</sup>

<sup>a</sup>Faculty of Manufacturing Engineering, Universiti Teknikal Malaysia Melaka, Hang Tuah Jaya, 76100 Durian Tunggal, Malacca, Malaysia

<sup>b</sup>School of Materials & Mineral Resources Engineering, Universiti Sains Malaysia, Engineering Campus, 14300 Nibong Tebal, Penang, Malaysia

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### Abstract

Three types of calcium precursors (nitrate, hydroxide and carbonate) were used in the synthesis of carbonated hydroxyapatite (cHA) using a precipitation method via a chemical reaction with di-ammonium hydrogen phosphate as the phosphate precursor. The precipitation method was chosen over many other methods due to its flexibility to changes in processing parameters to control the phases formed, the particle size, as well as, the morphology of the as-synthesized powders. The focus of the study was on cHA as it is deemed to mimic the composition of the human bone much closer as compared to the stoichiometric hydroxyapatite. When the chemical reaction was completed, the precipitate was dried, ground and characterized by x-ray diffraction (XRD), electron microscopy (both FESEM and TEM) and particle size analysis. Only the nitrate precursor produced a single-phase carbonated hydroxyapatite (cHA), whilst the other two precursors produced a secondary calcite phase or did not react fully. This is due to the low solubility of the calcium hydroxide and the incomplete reaction of the calcium carbonate. An increase in pH has been observed to lead to higher carbonate content in the synthesized cHA and a smaller crystallite size.

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\* Corresponding author *E-mail address:* radzali@utem.edu.my

### 1. Introduction

In recent decades, orthopaedic medication, such as bone repair and regeneration were rapidly studied to improve the health level in the society. Various artificial materials, such metallic, ceramic, polymeric and composite

materials were used for orthopaedic repair and reconstruction<sup>1</sup>. The materials used in orthopaedic application have to be biocompatible, biodegradable and able to provide the function of tissue regeneration<sup>2,3</sup>. Of all the choices of materials, calcium phosphates, especially hydroxyapatite (HA), is currently regarded as the best biomaterial to be used in bone repair and regeneration. This is due to the fact that natural bone is made up of an organic compound (collagen) as well as an inorganic compound (HA). The inorganic apatite compound offers osteoconductivity, osteoinductivity and a bone-bonding ability in the process of bone growth or bone healing<sup>4,6</sup>.

As HA is the main constituent of the bone, synthetic HA, with the chemical formula  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ , was introduced and widely applied in orthopaedic surgeries<sup>7</sup>. Similarity in chemical composition to natural bone allows HA to form at the interface of the surrounding bone tissue, by mimicking the natural bone apatite phase<sup>8</sup>. However, carbonated hydroxyapatite (cHA) was found to have a much closer compositional similarity to the mineral in natural bone. Carbonated hydroxyapatite (cHA) shows a higher bioactivity than HA, and the smaller particle size of cHA would inevitably bring about better tissue-implant interactions<sup>9,10</sup>. It has also been proven that nano-sized apatite particles, which have larger surface, lead to an enhancement in biological properties<sup>11</sup>.

The properties and reactivity of the apatite cement were found to have been influenced by both the calcium precursors and firing temperature<sup>12</sup>. They have found that identical synthesis history, morphology and crystallinity does not culminate in producing similar reactivity. Besides, the presence of impurities could hamper reactivity of the cement.

Various synthesis methods had been introduced to produce HA or cHA, which included hydrothermal, sol-gel, precipitation, mechano-chemical, mechanical activation and other methods. Amongst these synthesis methods, the precipitation route is one of the most promising techniques to produce nano-sized apatite particles<sup>13,14</sup>. Moreover, the precipitated particle sizes can be controlled by the synthesis temperature and pH conditions<sup>15</sup>.

It is the objective of this work to establish the processing parameters for cHA which have not been as intensively studied as HA. These would include the effects of using different calcium precursors as well as the effect of pH on the phase(s) formed, the changes in particle sizes and the particle morphologies as the pH is varied.

## 2. Experimental methods

### 2.1 Precursor materials

Three different chemical grade calcium precursor materials were used, viz. calcium nitrate tetrahydrate,  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (Merck,  $\geq 99.0\%$  purity), calcium hydroxide,  $\text{Ca}(\text{OH})_2$  (Fluka,  $\geq 96\%$  purity), and calcium carbonate,  $\text{CaCO}_3$  (Sigma Aldrich,  $\geq 99.0$  purity). The calcium precursor was reacted dropwise with a phosphate precursor, viz. di-ammonium hydrogen phosphate,  $(\text{NH}_4)_2\text{HPO}_4$ , (Fluka,  $\geq 98.0$  purity). In the reaction to produce cHA, sodium hydrogen carbonate ( $\text{NaHCO}_3$ ) was used as the source to supply  $\text{CO}_3^{2-}$  whilst ammonium hydroxide ( $\text{NH}_4\text{OH}$ ) was used as a pH control for alkaline solutions. All solutions were prepared to an initial 1M concentration.

### 2.2 Flowchart for the synthesis of cHA

Firstly, the solution containing the carbonate ions was added dropwise into the solution containing the phosphate ions at a rate of 40 drops per minute and continuous stirring.  $\text{NH}_4\text{OH}$  was also added dropwise to adjust the pH of the mixed solution. In this work, the pH used were 8.5, 9, 10 and 11. When all the carbonate-containing solution had been added, stirring was continued for another 30 minutes. The carbonate-phosphate mixture was then added dropwise (at a rate of 40 drops per minute) into the calcium ions solution whilst being continuously stirred. The colour of the mixed solution started to change slowly from transparent to milky white in colour. This change indicated that precipitation had taken place immediately when the dropwise process started. An additional 30 minutes of stirring was performed after the solutions were fully mixed to ensure complete reaction. The solution was then filtered using a Whatman 90mm filtration set with a 542 grade filter paper of average pore size 2.7  $\mu\text{m}$ . A vacuum pump was used to enhance the filtration rate. The white precipitate produced was washed three times with deionized water to remove any possible residue in the precipitate. The precipitate was finally dried in an oven at

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