Synthesis and characterization of hydroxyapatite nanoparticles from eggshell without thermal treatment

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The management of large amounts of food waste presents a significant challenge. Eggshell (ES) is a common and widespread waste. Each year, 65.5 million metric tons of eggs are produced globally, with production on the rise, projected to reach 90 million tons by 2030. The ES accounts for approximately 11% of the egg's weight, resulting in 7.2 million tons of ES waste produced annually. This waste is typically disposed of in landfills, where it generates unpleasant odors and promotes microbial growth.[1] The ES, composed of calcium carbonate (~ 94%), calcium phosphate (~1%), magnesium carbonate (~1%) and organic matter (~4%), can represent a biomass source that can be valorised by conversion into different Ca precursor(s) to obtain hydroxyapatite (Hap)[2] and various methods have been proposed so far to synthesize Hap nanoparticles from ES. Most of the studies in literature involve a preliminary thermal treatment step ($T \geq 800°C$) to obtain CaO from ES.[3,4] This step is highly energy-intensive and generates a significant amount of CO_2 due to the decomposition of calcium carbonate.

This study explores a sustainable approach to synthesize Hap nanoparticles using ES as a calcium source without employing thermal treatment. The synthesis was carried out through a wet chemical precipitation method. Hap nanoparticles, designed as solid fertilizer to promote the slow release of nutrients, was initially obtained via precipitation by adding KOH, selected for its potassium nutrient content, after dissolving the ES in a nitric acid solution. To reduce environmental impact and use a non-toxic, cost-effective reagent, ascorbic acid (HAsc) was employed. Its sufficient acidity (pKa = 4.17) promotes carbonate dissolution, while its reducing properties help trap the CO_2 produced as oxalate ions.[5]

Experimental results, obtained by means of different characterization techniques (including Powder X-Ray Diffraction (PXRD), Fourier Transform Infrared Spectroscopy Attenuated Total Reflection (FTIR-ATR) and Field Emission Scanning Electron Microscope - FESEM), confirmed the formation of crystalline Hap nanoparticles.

During the rapid dissolution of ES powder in an HNO_3 solution, a significant release of CO_2 was observed, with part of it being incorporated into the Hap lattice. The formation of carbonate-substituted Hap is supported by FTIR-ATR spectra, which display multiple bands attributable to carbonate ions (see Figure 1A). FESEM images reveal the synthesis of homogeneous acicular nanoparticles with dimensions below 200 nm (Figure 1B). The process, starting from 1 g of ES powder, demonstrates a high yield (>95%) and excellent reproducibility. The dissolution of eggshell powder in HAsc solution requires a longer reaction time (at least 4 hours) and produces a limited amount of CO_2, as it reacts with ascorbate ions to form oxalate species. The FTIR-ATR spectrum confirms the formation of Hap alongside signals attributed to oxalate ions (marked with * in the red-trace spectrum). FESEM images reveal the formation of rounded nanoparticles that not only aggregate but also show a tendency to coalesce (Figure 1C). PXRD analysis indicates the presence of crystalline calcium oxalate phases, specifically whewellite and weddellite.

To assess the potential use of the obtained materials as solid fertilizers, release tests were conducted to measure the availability of nutrients such as Ca, K, and P provided by the Hap particles. Specifically, 210 mg of Hap were suspended in 10.0 mL of pure water, and every 24 hours the solid was separated via centrifugation, re-adding the same volume of fresh water. The concentrations of Ca, K, and P in the solution were determined using inductively coupled plasma optical emission spectroscopy (ICP-OES). The dissolution behaviour of Hap derived from ES (Hap HNO_3 and Hap HAsc) was compared to that of Hap synthesized through wet precipitation using $Ca(OH)_2$ as the calcium source.[6]

Hap from ES shows a higher release of nutrients compared to Hap obtained from standard synthesis.

	Ca_{TOT} (mg)	Ca%	P_{TOT} (mg)	P%	K_{TOT} (mg)	K%
Hap std	0.30	0.39	0.04	0.12	0.02	0.10
Hap HNO_3	0.30	0.70	0.44	2.1	6.9	35
Hap HAsc	1.4	3.8	1.20	8.2	5.3	54

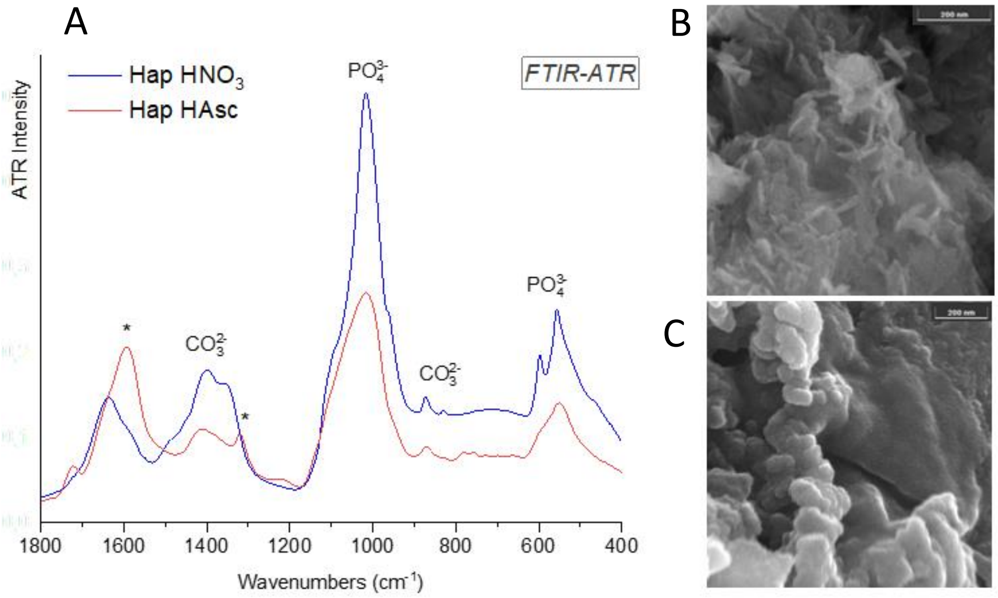

Figura 1 FTIR-ATR spectra (A); FESEM Hap HNO_3 (B) and Hap HAsc (C)

The release profiles of Ca and P ions follow similar trends, with their concentrations gradually increasing over the course of a week. In contrast, K ions reach a peak concentration within the first 24 hours, after which the release stabilizes (Figure 2). These results identify Hap HAsc as the most promising candidate to be used as a solid fertilizer, capable of delivering a significant amount of nutrients. Additionally, the presence of calcium oxalate may offer added benefits by helping to regulate soil pH.

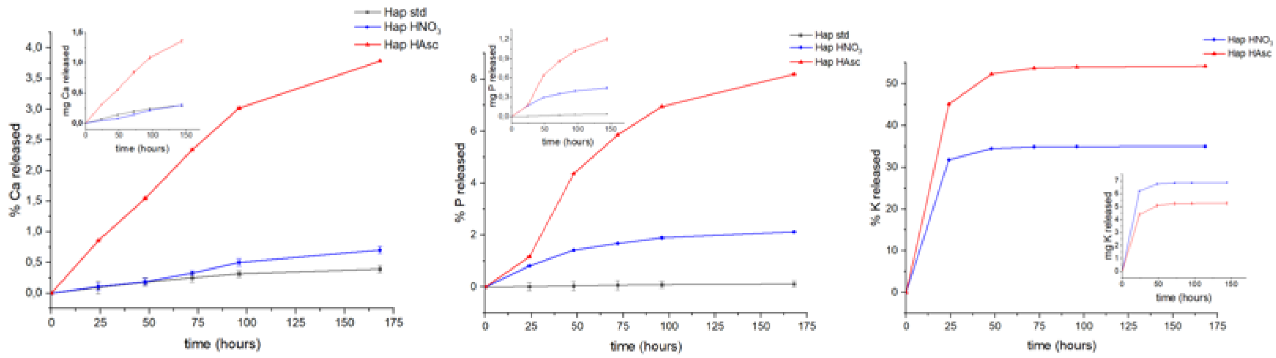

Figura 2 % of ion Ca, P, K and mg (in the insept) released by Hap std, Hap HNO_3 and Hap Hasc

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