



Transformations of neat and heated struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$)

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ABSTRACT

Struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) is the mineral phase of one of the urinary tract stones of humans and animals, besides being an important phase seen in waste water treatment and purification plants. Single-phase and highly crystalline struvite powders were synthesized in this study at room temperature in aqueous solutions containing dissolved salts of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{HPO}_4$ at the Mg/P molar ratio of 1.00. As-synthesized, crystalline struvite powders (neat powders) completely transformed into cryptocrystalline apatitic calcium phosphate (Ap-CaP), in less than 72 h, when soaked in Ca-containing saline solutions at 37 °C. Moreover, crystalline struvite powders heated at temperatures from 90° to 200 °C became x-ray amorphous. Amorphous powders stirred for 4 h at room temperature in water containing dissolved diammonium hydrogen phosphate recrystallized back into struvite.

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1. Introduction

Struvite (MAP, magnesium ammonium orthophosphate hexahydrate; $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) is a common component of urinary tract calculi (around 10% of human, 85% of feline and 70% of canine stones) [1–3]. If the stone formation is the result of an infection by microorganisms producing urease, then struvite is the usually observed crystalline phase of urinary tract calculi [4].

Struvite is a phase deposited along the pipelines of the waste water treatment and sewage sludge purification plants, causing the undesired clogging of pipes [5]. On the other hand, intentional and controlled precipitation of struvite is practiced in the landfills and waste water treatment plants to reduce the environmentally harmful free ammonium and phosphorus presence [6,7]. Struvite may have the potential of being used as a fertilizer, as well [8].

Magnesium phosphate cements (MPC), which form crystalline struvite upon setting, were developed as bone substitute biomaterial or bioceramic [9–11]. Ibasco *et al.* [12] reported that struvite-coated titanium samples exhibited better biocompatibility with the osteoblastic cells, *in vitro*, than pure titanium.

One may get the impression from the previous literature that struvite would be mostly stable in neutral or basic aqueous solutions [5,7,13–20]. The previous work usually did not use the starting materials of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{HPO}_4$ in the synthesis of struvite. In the most comprehensive struvite synthesis and characterization study of the previous literature, Sarkar [21] used hygroscopic Mg (NO_3)₂ and $\text{NH}_4\text{H}_2\text{PO}_4$ as the starting chemicals.

The current study [22] was performed to find answers to the following questions.

- (1) Is it possible to synthesize single-phase, neat struvite powders by mixing solutions of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{HPO}_4$, without using any pH control, at room temperature (RT)?
- (2) Is it possible to transform struvite powders into cryptocrystalline apatitic CaP just by soaking those in Ca-enriched saline or synthetic body fluid (SBF) solutions at 37 °C?
- (3) Is it possible to transform the heated, amorphous powders back into crystalline struvite by soaking those in ammonia-containing aqueous solutions at RT?

2. Experimental

A solution of 20.331 g $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (Carlo Erba, Italy) in 200 mL of distilled water was rapidly added to a solution of 13.206 g $(\text{NH}_4)_2\text{HPO}_4$ (Merck, Germany) in 750 mL of distilled water, followed by stirring at room temperature (RT, 22 ± 1 °C) for 2 h. Precipitates were filtered, washed with water, and dried at 37 °C to obtain the “neat” powders. One gram aliquots of neat powders were heated either in glass watch glasses in an oven at 90 °C for 72 h or heated in an automatic moisture analyzer (MX-50, A&D Corp., Japan) to 200 °C for 1 h to obtain the “heated” samples.

Ca^{2+} -containing saline and synthetic body fluid (SBF) solutions were used to test the apatite-inducing ability of the neat struvite powders. Ca^{2+} -containing saline solutions of pH 5.8 were prepared by dissolving 0.373 g KCl (Merck), 8.299 g NaCl (Merck), and 7.351 g $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (Merck) in 1 L water, as described previously [23]. 525 mg portions of neat struvite powders were soaked in 150 mL of Ca^{2+} -containing saline solutions (with 5 mM K^+ , 142 mM Na^+ and 50 mM

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Ca²⁺) at 37 °C for 3 days in glass bottles. Samples were filtered, washed with water, and dried at 37 °C.

27 mM HCO₃⁻-containing, Tris-HCl-buffered (pH 7.4 at 37 °C) SBF solutions were prepared by dissolving 6.547 g NaCl, 2.268 g NaHCO₃ (Merck), 0.373 g KCl, 0.178 g Na₂HPO₄·2H₂O (Merck), 0.305 g MgCl₂·6H₂O, 0.368 g CaCl₂·2H₂O, 0.071 g Na₂SO₄ (Merck) and 6.057 g Tris (Merck), respectively, in 1 L water [24]. 525 mg portions of neat struvite powders were soaked in 150 mL of SBF solutions (with 5 mM K⁺, 142 mM Na⁺, 2.5 mM Ca²⁺, 1 mM HPO₄²⁻, 27 mM HCO₃⁻, 1.5 mM Mg²⁺, 0.5 mM SO₄²⁻ and 125 mM Cl⁻) at 37 °C for 3 and 6 days in glass bottles. Samples were filtered, washed with water and dried at 37 °C.

750 mg portions of struvite powders previously heated at 200 °C in air for 3 h were stirred at RT for 4 h in sealed glass bottles having 80 mL of aqueous solutions (initial pH of 8.1) only containing 179 mg (NH₄)₂HPO₄ (Merck). Samples were then filtered, washed with water and dried at 37 °C.

Samples were characterized by using XRD (Advance-D8, Bruker), FTIR (Spectrum One, Perkin-Elmer) and SEM (Evo-40, Carl Zeiss). Samples for XRD were first ground into a fine powder by using an agate mortar and then radiated with Cu-K_α at 40 kV and 40 mA in 2θ steps of 0.02° and 3 s preset time. 1 mg portions of sample powders were mixed with 300 mg KBr, followed by pelletizing, to collect the FTIR data by using 128 scans. SEM samples were sputter-coated with ca. 25 nm-thick gold prior to imaging.

3. Results and discussion

The neat struvite powders were easily synthesized according to the recipe given in Section 2. In that procedure the solution pH was initially measured as 5.5 at RT and remained the same after 2 h of mixing. The reversal of the mixing order (i.e., addition of (NH₄)₂HPO₄ solution into MgCl₂·6H₂O solution) did not change the solution pH values or the product characteristics. NH₄OH additions were not necessary. If large-scale production of struvite is desired, using an economical process, such as the one described here, free of any pH measurements or pH adjustments with base and/or acid additions would be advantageous.

Fig. 1 depicted depicts the combined XRD, SEM and FTIR data of the neat powders. XRD data indicated single-phase struvite (orthorhombic;

space group *Pmn*2₁) with the experimental lattice parameters of *a* = 11.215, *b* = 6.954, *c* = 6.141 Å (Fig. 1a). Lattice parameters were calculated by using the TREOR90 software. The experimental lattice parameters were in very good agreement with those reported by Ferraris *et al.* [25]. Neat struvite powders comprised of dendritic particles [4,26] approximately 75 μm in length and 20 μm in width (Fig. 1b). The first four bands observed at about 3600, 3500, 3260 and 3115 cm⁻¹, in the FTIR spectrum of Fig. 1c of neat struvite, belonged to the OH stretching vibrations. The band at 2970 cm⁻¹ was the antisymmetric stretching vibration of NH₄ groups. The broad band between 2500 and 2200 cm⁻¹ was assigned to water-phosphate H bonding. HOH deformation of water was at 1680 cm⁻¹, and the bands seen over the range of 1600 to 1400 cm⁻¹ were those of the HNH deformation modes of NH₄. The bands of PO₄ units were observed at 1006, 571, 463 and 438 cm⁻¹. Water-water H bonding was at 760 and 695 cm⁻¹, whereas ammonium-water H bonding was observed at 890 cm⁻¹. These were in agreement with the previous studies [27,28].

Neat struvite powders soaked in Ca-containing saline solutions at 37 °C for 3 days did completely transform into cryptocrystalline apatitic CaP (Ap-CaP). Fig. 2a and b proved that the resultant phase is Ap-CaP. Struvite is a high solubility phase with a *pK_{SP}* value of 9 to 13 [5,29], and when it finds enough Ca²⁺ in a solution it dissolves, it would induce the re-precipitation of lower solubility (*pK_{SP}* of 85 [23]) Ap-CaP. Bobbierite (Mg₃(PO₄)₂·8H₂O) has an FTIR pattern similar to Ap-CaP [30]. Fig. 2c, on the other hand, showed the XRD traces of neat struvite powders soaked in SBF solutions at 37 °C for 3 and 6 days, respectively. Since SBF solution had a low Ca²⁺ concentration (2.5 mM), in comparison to 50 mM Ca²⁺ of the Ca-containing saline, it was not able to transform struvite into Ap-CaP even in 6 days, however a noticeable decrease in the XRD peak intensities (from 3 to 6 days) should be noted.

One gram of neat struvite powders heated at 90 °C for 72 h on a watch-glass exhibited a 30.7% weight loss, and 0.693 g of x-ray amorphous powder was obtained [22]. On the other hand, 1 g of neat struvite powders heated from RT to 200 °C in a moisture analyzer displayed a total weight loss of 51.5%, and 0.485 g of x-ray amorphous powder was obtained, as shown in Fig. 3a[22]. The FTIR trace of the 200 °C-heated powders was given in Fig. 3c. Theoretical water in struvite (i.e., 6H₂O) is 44.046% by weight. While heating struvite at 90 °C

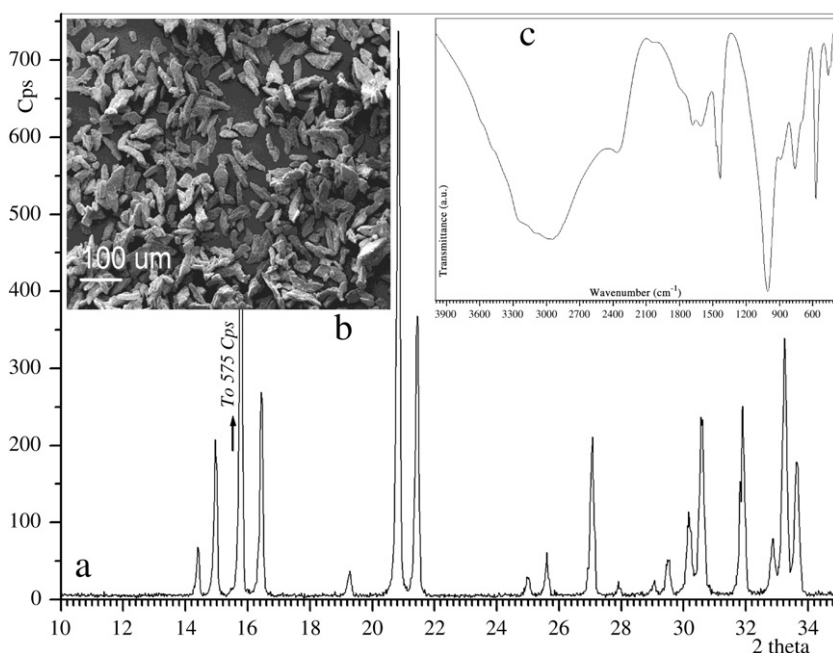


Fig. 1. Characterization of neat struvite powders; (a) XRD, (b) SEM, (c) FTIR data.

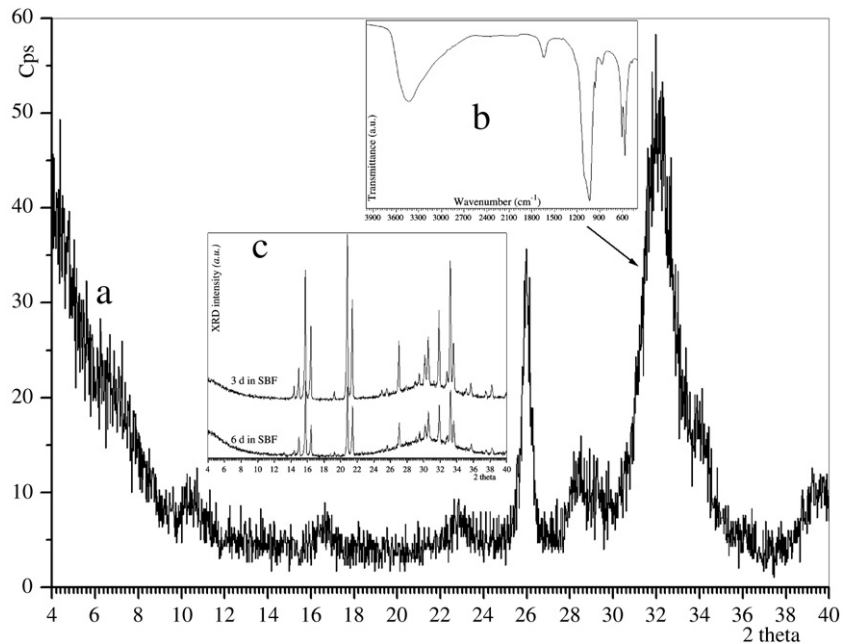


Fig. 2. Transformation of neat struvite powders into apatitic CaP powders; (a) XRD, (b) FTIR data, (c) XRD traces of neat struvite powders soaked in SBF for 3 and 6 days.

did not cause the evaporation of all crystal water, heating struvite at 200 °C also caused the loss of some of the ammonium ions in the form of NH_3 (g). The ammonium-containing solution (179 mg $(\text{NH}_4)_2\text{HPO}_4$ in 80 mL H_2O) described in Section 2 was able to regenerate crystalline struvite from the 200 °C-heated amorphous powders (Fig. 3b and d) upon few hours of stirring the substance at RT in that solution. In contrast, amorphous powders kept in pure water at 37 °C for 48 h mostly transformed into newberyite ($\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$). The ability of the 90°-to-200 °C-heated powders to recrystallize/regenerate crystalline struvite is remarkable. The *in situ* transformation of amorphous powders (previously heated at 200 °C) back to the crystalline struvite, upon

soaking in ammonium-containing aqueous solutions at RT, presented a technological venue for the simple ammonium removal from contaminated water reservoirs.

4. Conclusions

Neat struvite powders were synthesized in large quantities in aqueous solutions at RT by using Mg-chloride and diammonium hydrogen phosphate. No pH control was necessary. Neat struvite powders were shown, for the first time, to fully transform into apatitic calcium phosphate when soaked at 37 °C in Ca^{2+} -containing saline

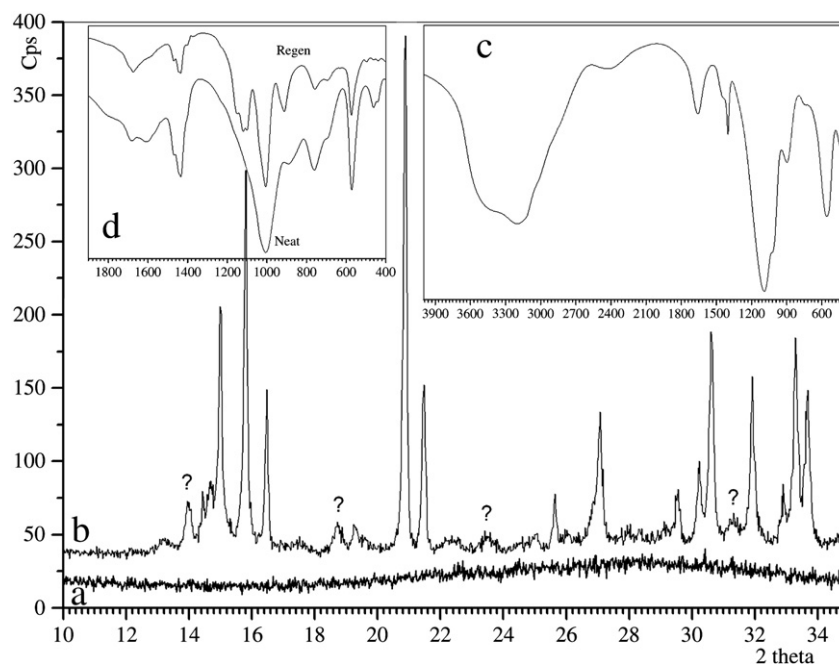


Fig. 3. Transformation of heated struvite powders; (a) XRD trace of neat struvite powders after heating at 200 °C for 1 h, (b) XRD trace of regenerated/recrystallized struvite upon stirring the amorphous powders in ammonium-containing aqueous solution for 4 h at RT (? : unknown phase), (c) FTIR trace of 200 °C-heated struvite powders, (d) comparative FTIR data of neat and regenerated struvite.

solutions. Crystalline struvite powders decomposed into an amorphous residue upon heating at 90°-to-200 °C from 1 to 3 h. Amorphous powders readily crystallized back into struvite when stirred at RT in simple aqueous solutions containing dissolved $(\text{NH}_4)_2\text{HPO}_4$.

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