Growth and Spectral studies on Gel technique struvite crystals

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Abstract

Magnesium ammonium phosphate hexahydrate, also known as struvite (MAP) is a major component of urinary calculi. In the present study growth of struvite crystals using sodium meta silicate gel techniques by single diffusion method. The crystals were characterized by FT-IR, powder XRD, SEM with EDS and thermal analyses such that TG-DTA respectively. FT-IR revealed that the all the functional groups present in the samples. Further, XRD revealed the phase, purity and crystalline nature with orthorhombic in nature of struvite crystals. The morphology, topography and the elemental compositions of samples were determined by SEM and with EDS. In addition, the endothermic, exothermic and phase transition of were found from TG-DTA analyses. The results of the present study are so useful to the scientific community because it provides the adequate information to the people and society those are affected from the struvite crystals. These struvite crystals mostly affected the women as compare to the men.

Keywords: Crystal morphology, struvite crystals, single diffusion, Gel growth.

1. Introduction

The majority of the urinary calculi are composed of oxalates and phosphates. Among the phosphates, magnesium phosphates namely ammonium magnesium phosphate hexahydrate-[$NH_4MgPO_4.6H_2O$], miner logically known as struvite and magnesium hydrogen phosphate trihydrate,i.e., new beryite were reported to occur as constituents in urinary calculi not only in adults but also in children. Struvite is also known as ‘urine sand’, ‘triple phosphate stone’, ’phosphate stone’, ‘Infection stone’ or ‘urease stone’. Struvite is the main component of the infectious urinary stones and is associated with the chronic urinary tract infections (UTI) with ureolithic micro organisms, which split urea into ammonium and cause persistently alkaline urine, which further combines with

phosphate and magnesium. Struvite stones are among the most difficult and dangerous problems in stone disease because of the potential of life threatening complications from infection. Worldwide, struvite compose 30% of all kidney stones in humans. In contrast to humans, struvite stones account for 75% of urinary calculi found in the animals like dogs and cats. Epidemiological studies from various countries reported a frequency of struvite stones between 25% and 38%.

Struvite stones are associated with the development of chronic kidney disease (CKD), and these patients require special attention. Further, they confirmed significantly greater risk of CKD in patients with a diagnosis of struvite stone disease. Modern crystallographic analysis has shown that in some cases struvite stones were found as a mixture of struvite and carbonate- apatite. Struvite stones are found more frequently in women and also in persons older than 50 years. These stones can grow rapidly forming 'Staghorn-calculi', which is a more painful urological disorder. It also has a high degree of recurrence. Patients with struvite stones could lose renal function because of obstructive or pyelonephritic episodes and surgical interventions on the kidney. Patients with infected Staghorn calculi who do not receive any treatment have about 50% chance of losing the kidneys.

2. Materials and methods

2.1. Crystal growth

Sodium metasilicate ($Na_2SiO_3.9H_2O$) and ammonium dihydrogen phosphate (Na_2HPO4) was used for preparing the gel and glacial acetic acid was used for adjusting the pH value. All the reagents used in this experiment are of analar grade. Crystallizations were conducted in the gel densities between 1.03 and 1.06 g/cc and pH values from 4 to 6.5. Optimum values of gel density and pH values for the crystallization were found to be 1.03 g/cc and 6 respectively. Magnesium acetate was placed over the set gel. Tiny crystallites appeared in the gel solution after about 24 hours.

The growth was completed within a period of 21 days of pouring solutions to avoid microbial contaminations. The experiment was conducted at room temperature. Fig.1 illustrates the schematic diagram of gel growth technique and the actual photograph depicting struvite crystals in the gel medium in the test tube. The grown struvite crystals were carefully removed from the gel medium. The struvite crystals were sparingly soluble in water

were quickly rinsed in distilled water and then air dried. The grown crystals were kept in air tight bottles and used for further investigation.

Fig.1 Struvite crystals grown in the gel medium

3. Results and discussion

3.1 Crystal growth and its morphology

The growth of crystals of morphologies is commonly found in bio-mineralization. In the gel growth technique by changing the growth conditions, crystal morphology and sizes can be obtained. The gel growth technique was described in detail by Henisch et al. The study of the growth of struvite crystals using the solution growth technique by mixing equal volumes of equi-molar solutions of $NH_4H_2PO_4$ and $MgSO_4.7H_2O$,whereas struvite crystals were grown by using the gel growth technique and studied the effect of impurities on the morphology of crystals. Moreover, struvite crystals were grown by gel growth technique and the effect of sunlight on growth was studied by Sundaramoorthi and Kalainathan.

The growth and characterization of the gel grown struvite crystals was reported by Chauhan et al. From the study it was found that the struvite crystal morphology as well as growth process were strongly dependent on growth parameters. Struvite crystals of morphology is x shaped dendritic type crystal were grown by single diffusion gel growth technique. The morphology of gel grown x-shaped dendritic type struvite crystal is as shown in fig.2.

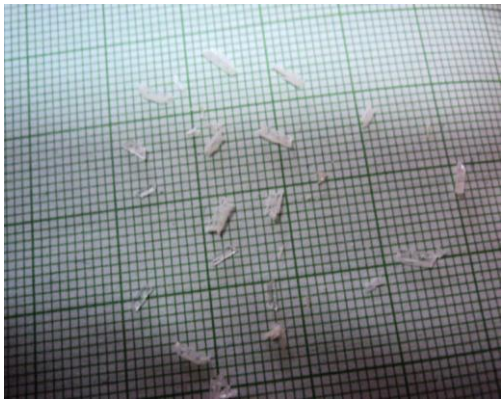

Fig.2. X-shaped dendritic type struvite crystal

3.2 FTIR analysis

FT-IR spectrum was recorded on Shimazdu range 400-4000cm^{-1} and KBr beam splitter. The FT-IR spectrum of the struvite crystals is presented in Fig.3 and the vibrational band assignments to literature and experimental data are summarized in Table-1 which are closely matched to the previously reported peaks in several inorganic hydrated compounds. NH_4^+cation is a tetrahedron having four vibrational modes and all the four appeared in FTIR spectra due to its general position in the crystal, which correspond to the previously reported peaks in several inorganic NH_4^+ containing compounds vibrational modes of tetrahedral PO^{3-} anions are also in accordance with reported values . FTIR spectrum proved the presence of water of hydration, N-H bond, P-O bond, $NH4^+$ ion and metal-oxygen bond

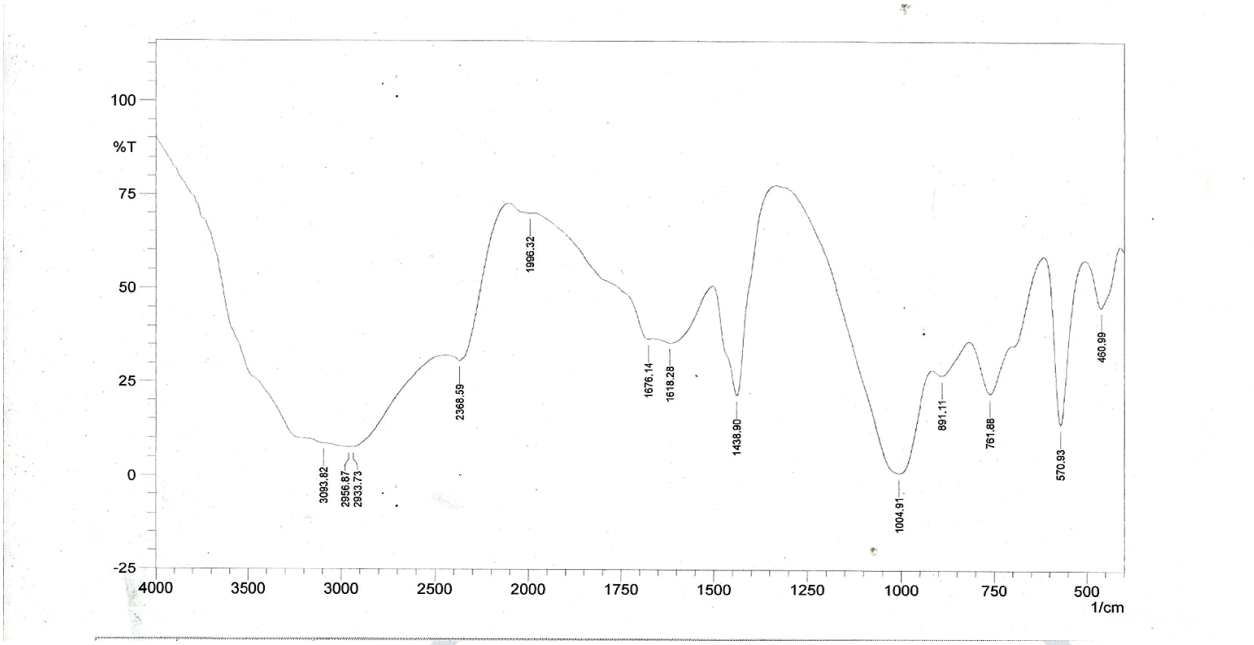

Fig.3 FT-IR Spectrum of Struvite crystal

Table 1

Assignments of absorption bands in the FT-IR spectrum of struvite

Assignments	Vibration modes	Reported IR Frequencies Wave number (cm^{-1})	Observed Frequencies Wavenumber (cm^{-1})
Absorption peaks due to vibration of water of crystallization	H-O-H stretching vibrations of water of crystallization	3280-3550	2933,2956,3093
	H-O-H stretching vibrations of cluster of water molecules of crystallization	2060-2460	1996,2368
	H-O-H bending modes of vibrations	1590-1650	1618,1676
	wagging modes of vibration of coordinated water	808	891
Absorption peaks due to NH_4^+ units	υ_1 symmetric stretching vibration of N-H in NH_4^+ units	2800-3000	2933, 2956
	υ_2 symmetric bending vibration of N-H in NH_4^+ units	1630-1750	1618,1676,1996
	υ_3 asymmetric stretching vibration of N-H in NH_4^+ units	3130- 3693	3093
	υ_4 asymmetric bending vibration of N-H in NH_4^+ units	1390-1640	1438
Absorption peaks due to PO_4^{3-} units	υ_1 symmetric stretching vibration of PO_4^{3-} units	930-995	891

	υ_2 symmetric bending vibration of PO_4^{3-} units	404-470	460
	υ_3 asymmetric stretching vibration of PO_4^{3-} units	1017-1163	1004
	υ_4 asymmetric bending modes	509-554	570
Metal-Oxygen bonds	Metal-Oxygen bonds	400-650	761
	Deformation of OH Linked to Mg^{2+}	847	891

3.3 SINGLE CRYSTAL XRD

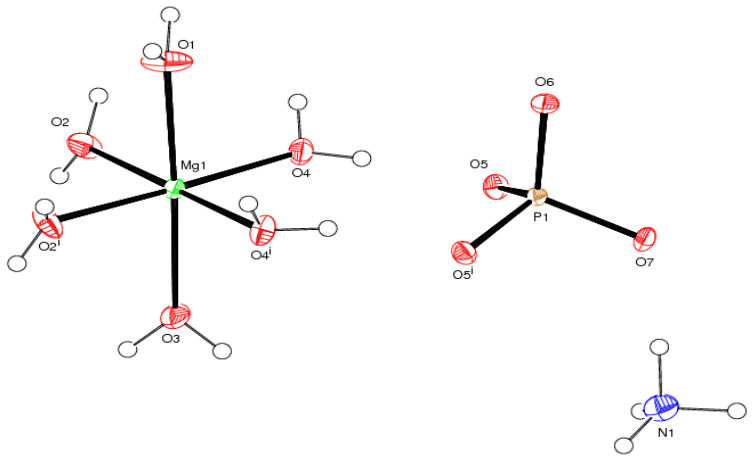

Fig.4 Crystal structure of magnesium ammonium phosphate hexahydrate

The crystal structure and packing diagrams of Magnesium Ammonium Phosphate Hexahydrate crystal is shown in the Fig.4.

The H_2O molecules are co-ordinated to the divalent cation, building a distorted octahedron around it and act as donars in hydrogen bonds which are among shortest ones ever found in crystalline hydrates (Chiari and Ferraris, 1982).In the crystal structure of all mentioned compounds (Ferraris et al.,1986),namely the H_2O molecules are donors in six hydrogen bonds with O_i .....O distances ranging from 263.0 to 269.5 pm in $MgNH_4PO_4$, and the acceptors in both cases, are phosphate oxygen.

3.4 Powder XRD

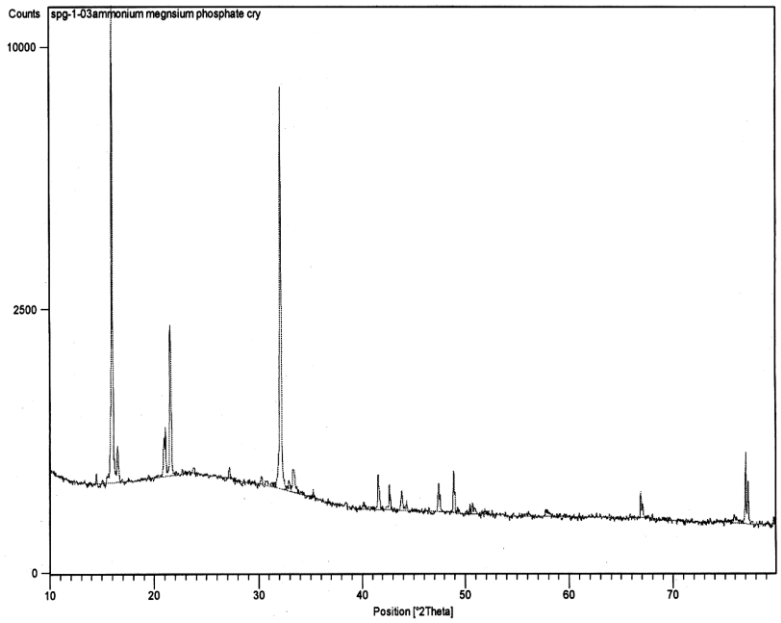

Fig.5 Powder XRD analysis of struvite crystal

XRD was recorded on XPERT-PRO diffractometer system. In general, all the XRD patterns agree well the JCPDS (71-2089) value for struvite as shown in Table 2. The results confirm the phase purity and crystalline nature of the samples is as shown in Fig.5. Struvite crystallizes in the orthorhombic $Pmn2_1$ space group with unit cell parameters; a=6.954Å, b=6.140Å, c=11.216Å and α=β=γ=90˚. These values are closely matching with those reported previously. There are two molecules in a unit cell of a struvite. The struvite crystal structure consists of the three structural units (functional groups),namely (i)PO_4tetrahedron,(ii)$Mg.6H_2O$ octahedron and (iii)NH_4 groups held together of hydrogen bonding

Table 2

XRD analysis of struvite crystal

Pos. [°2Th.]	Height [cts]	FWHM [°2Th.]	d-spacing [Å]	Rel. Int. [%]
15.9924	11495.34	0.0984	5.54198	100.00
16.4979	223.86	0.2362	5.37331	1.95
21.0623	426.29	0.0787	4.21803	3.71
21.5474	1895.51	0.1378	4.12416	16.49
32.1027	8274.28	0.1181	2.78819	71.98
41.5904	176.52	0.1574	2.17146	1.54
47.4240	146.42	0.1574	1.91707	1.27
48.9164	171.60	0.2362	1.86202	1.49
77.0430	434.51	0.0960	1.23682	3.78

3.*5 SEM analysis with EDS*

The SEM photographs are taken in the version S-300-I instrument. The investigation of surface morphology of crystal by using SEM is as shown in fig6. SEM pictures of struvite crystal. The SEM was taken at magnification values 100X. The magnification of SEM was about 250 times.SEM acceleration voltage is 20,000 volts and kept the sample in highly vacuumed. Surface of the grown struvite crystal appeared clean and free major defect. The elemental position of the sample is identified using energy dispersive X-ray analysis. The EDS spectrum of struvite is shown in Fig 7. The higher peak of Mg and P shows that the more concentrated the element present in the spectrum. Mg present in the value 1.25 kev. The phosphorus energy value appeared at 2.0 kev. The atomic percentage of Mg/P is 34:66.

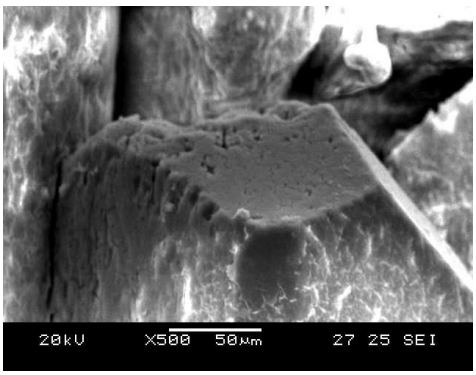

Fig.6 SEM image of Struvite Crystal

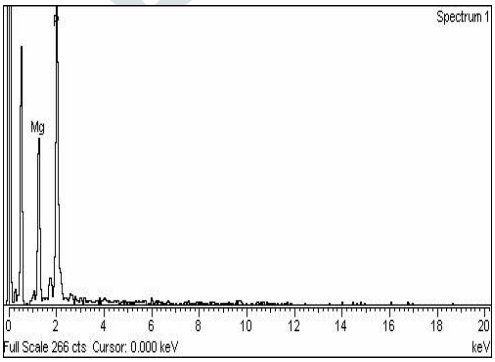

Fig.7 EDS analysis of Struvite crystal

Conclusion

Struvite crystals can be grown by single diffusion gel growth technique. Growth conditions played important role in the growth of crystals. The crystal morphology of struvite was strongly dependent on growth parameters. The absorption peaks obtained in FT-IR spectrum confirmed the water of crystallization, symmetric as well as asymmetric stretching and bending vibration of PO_4 units and metal oxygen bonds in struvite. Single crystal XRD confirms the crystal structure. The powder XRD confirmed that struvite crystallized in the orthorhombic $pmn2_1$ space group with unit cell parameters as a=6.954Å, b=6.140Å, c=11.216Å and α=β=γ=90°. The SEM-EDS micro analysis gives precise information about the surface morphology of the samples and their compositions. The presence of phosphorous, and magnesium were detected.

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