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Growth and Characterization of Struvite Crystals in Silica Gel Medium and Its Nucleation Reduction Process

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Urinary stone disease is one of the common diseases in the human history. The prevention of urinary stone formation lies in the exact identification of urinary stone constituents. Struvite is one of the frequently occurring constituents of urinary stone due to infection of urinary tract and urine. Struvite crystals were grown by SMS gel technique and effect of sunlight on growth was studied. Characterization studies like XRD, FTIR, TGA/DTA, AAS, SEM and etching were performed and the results analyzed.

Key Words: Urolithiasis, Biological crystal, Struvite, Gel growth.

INTRODUCTION

The process of mineralization or deposition of inorganic crystalline materials under normal or pathogenic condition occurs in all mammals. Bio-mineralization process gives many advantages and disadvantages. The beneficial role in mammals (human) includes formation of teeth, bone ear membranes etc. A pathological effect creates tissue damage, bone disease, caries formation, urinary stone formation and gall stone formation, pancreatic stone deposition, *etc*. From the above diseases the major one is the kidney stone formation.

In human body, many parameters are involved in the formation of stones in the urinary tract, such as less water intake, abnormal dietary habits, occupation, metabolic nature, hereditary, bacterial and viral infection in the urine tract and obstruction in the urinary path. Crystal deposition in the urinary tract is technically named as urinary stones, urinary lithiasis and urolithiasis. The terms kidney stones, renal stones, nephrolithiasis and urinary calculi are also used[1].

Kidney stone formation in the urinary tract is due to saturation, super saturation and ultra super saturation of body fluids such as urine, blood, glands, hormones, saliva etc. The stones are present in any part of the urinary system within the kidney, bladder, ureter and urethra. From the

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survey it has been understood that those countries that are industrialized would have upper urinary tract stones frequently.

Urinary stones were widely classified physically and chemically according to size, shape, colour composition of minerals and structures. Till now nearly thousand different types of stones have been reported. The weight of the stone varies from 100 mg to maximum 6.3 kg, which is removed from an 80 year-old woman, in the urinary tract (bladder diverticulum's)[2].

Urinary stones formed at a time may be one to several thousand of clusters, but single stones are frequent than poly one. The single stone come out through urine with out notice. Many single stones are combined to form poly crystals. The surface of the grown crystals was seen to be uneven and anisotropy nature. Each and every stone will have different hardness value. Stones having more hardness value will have more bond strength and have more density factor, which can' t be broken or ground at all[3].

From the 19th century gels have been used as a crystallization media. Gel growth is the only ideal medium to study the kidney stone components (biological crystal or bimolecular), as its viscous nature provides stimulation of biological fluids in which it grows. Therefore gel medium provides physiological nature[4]. The gel medium avoids convection current and turbulence and it reduces thermal vibrations. One can implement the experiment on ground under micro gravity or inside the capillary volumes[5]. Crystal growth in gel is very successful in obtaining large quality crystals of inorganic, organic compounds including kidney stones[6].

The major content of urinary stones are calcium oxalate, calcium phosphate OCP, HAP, tricalcium phosphate (whitlockite), dicalcium phosphate (brushite), ammonium magnesium hydrogen phosphate (struvite), *etc*. In the present study, struvite crystals were grown in silica gel media at various condition and characterization studies were done.

EXPERIMENTAL

Growth of struvite

Sodium meta silicate gel was prepared as stock solution with initial pH of 13.8 which has higher alkaline nature and has more density. Using distilled water the gel density was reduced[7] from 1.05 to 1.03 gm/cm^3.

The size of the test tube used in the experiment was 120 × 15 mm and 140 × 25 mm. Mixing of I N H_3PO_4 solution of orthophosphoric acid reduced the gel pH value. The pH of gel and H_3PO_4 varies from 6.0 to 7.8, which determines the gelling time or gel set[8]. The gelling time and pH value of gel solution confirms the reported values[9]. After gel set (10 min to 10 h)[8] supernatant solutions were added. Supernatant was the mixture of

NH_4Cl and Mg $(NO_3)_2.2H_2O$. The ratio of the chemical solution varies from 0.5 to 1 M *i.e.* (0.5 : 0.5), (0.5 : 1), *etc*. The growth parameters were tabulated in the Table-1.

TABLE-1
GROWTH PARAMETERS OF STRUVITE CRYSTALS

SMS gel density (g/cm^3)	Phosphoric acid (N)	pH (Gel + H_3PO_4)	Gel setting time	Supernatant concentration (M)	Nucleation observed (h)	Growth period (d)	Types of crystal observed / Harvested crystal size
1.03	1	6.0	24 h	0.5:0.5	30	40	Needle like crystals Rood like dendrite crystals Platelet crystals
		6.5	10 h	0.5:1, 1:1	20		
		6.7	2 min	0.5:1, 1:1	20		
		7.0	1 h	0.5:1, 1:1	30		
	2	6.0	20 h	0.5:1, 1:1	8	60	
		6.4	5 h	0.5:1, 1:1	46		
		6.7	2 h	0.5:1, 1:1	-		
		7.0	0.5 h	0.5:1, 1:1	-		
1.04	1	6.1	24 h	0.5:1, 1:1	10	30	Leaf like crystals Single, poly crystals 6.0 mmx 2.5 mmx 2.0 mmx
		6.5	10 h	0.5:1, 1:1	15		
		6.8	1 min	0.5:1, 1:1	24		
		7.1	5 h	0.5:1, 1:1	28		
	2	6.0	20 h	0.5:1, 1:1	48	90	
		6.4	5 h	0.5:1, 1:1	28		
		6.8	1 h	0.5:1, 1:1	20		
		7.3	36 h	0.5:1, 1:1	52		

The chemical reaction is:

$H_3PO_4 + H_3SiO_4 + NH_4Cl + Mg(NO_3)_2.2H_2O \rightarrow Mg\,NH_4PO_4.xH_2O$ + Waste

NH_4MgPO_4 (Struvite) is in the solid form.

The struvite crystals were grown in single diffusion method by two ways. (a) At room temperature (28ºC) (Fig. 1) and (b) at sunlight exposure medium at 42ºC (Fig. 2).

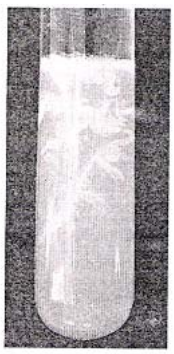

Fig. 1. Growth of struvite crystals at room temperature (28ºC)

Fig 2. Growth struvite crystals at sunlight medium (42ºC)

RESULTS AND DISCUSSION

The optimum condition for the growth of struvite crystals were identified (1.03, 1.04 g/cm^3, pH 6.7, 6.8, supernatant solution ratios are 0.5:0.5, 1:1), the nucleation rate was drastically reduced while exposed to sunlight medium. Liesegang rings were observed in the growth medium. The harvested crystals were shown in Fig. 3.

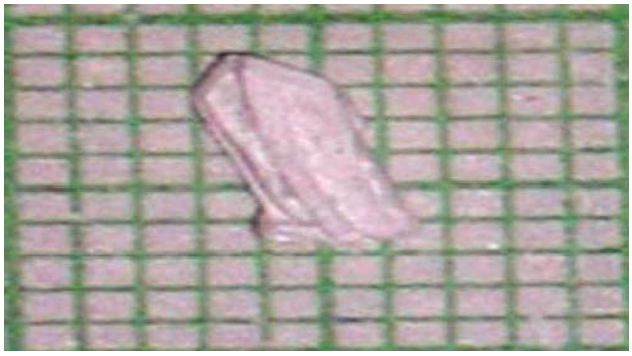

Fig. 3. Harvested crystal

X-rays results revealed that the grown crystal was single phase of struvite crystal. The XRD pattern and diffraction indices of the crystal are shown in Fig. 4. Treor programmer according to the values of 2θ in XRD calculates the orthorhombic unit cell parameters. The unit cell parameters are a = 7.0672 Å, b = 18.4739 Å, c = 23.7069 Å and $\alpha=\beta=\gamma=90^o$ the crystal system was orthorhombic.

FTIR spectrum was recorded to identify the chemical bonds, vibration bands of inorganic, organic and semi organic materials[10]. The struvite FTIR spectral results were matches with the reported value (Table-2).

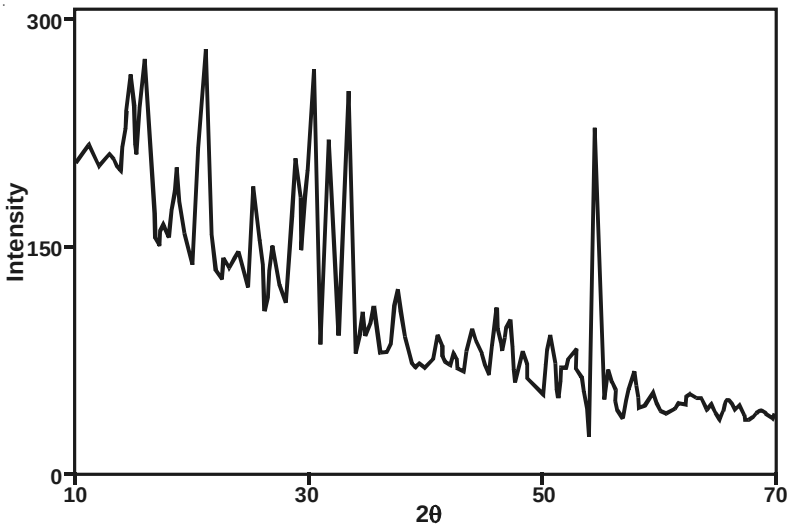

Fig. 4. Powder XRD pattern of struvite

TABLE-2
COMPARATIVE TABLE OF FTIR-SPECTRUM
OF STRUVITE CRYSTAL

Bands/Vibrations	Reported values[10-12] (cm^{-1})	Observed values (cm^{-1})	Absorption value (%)
NH-asymm. stretching mode & hydrogen bond	3284	3271	1.165
H–O–H symmetric	1651	1658	0.670
NH in plane stretching	1238	1237	0.680
P=O stretching	1217-1137	1166	0.861
PO_4	1100-1000	1117	1.361
PO_4-asymm. stretching mode	874	895	0.747
Acid phosphate	577	565	0.810

Etching study of strutive crystal

Etching study revels the various geometrical features of a crystal surface. Single crystal has an anisotropic nature. Dissolution of a particular single crystal depends upon the etching time and solvent concentration. Etching process is retreat or reverse process of crystal growth. Dissolution occurs in a single molecular step only[13-15]. In the present study, the chemical etching was carried out in a well-grown struvite crystal at room temperature (28ºC). The etching times were allowed was 1-5 min[16]. The etch pits are shown in the Fig. 5. The etch pits are observed in the grown struvite crystal are in spiral pits, step pits, line pits.

Fig. 5. Etch pattern of struvite crystal. (chemaical etching-HCl as etchant - 5 min, at room temperature)

Thermogravimetric analyses (TGA) experiment simply measures the weight change of a sample as a function of temperature. A plot of weight % as a function of temperature (T) can relate the weight changes to the stochiometry. In the present study, TGA was carried out for the sample NH_4MgPO_4 using STA 1500 instrument in air atmosphere A sample of weight 1.970 mg was analyzed under air atmosphere. The sample was heated to 800ºC. First decomposition of sample was observed at 77.2ºC. At this temperature the loss of sample weight was around 0.5% only. At 75.37ºC slightly decomposed at the major amount of decomposition takes place at 126.03ºC. But when the sample was brought to the temperature of about 364.79ºC the weight loss becomes 41 %. From TGA curve it was observed that the sample was decomposed largely at this stages. At 706ºC almost entire sample was decomposed. From the TGA/DTA trace it can be concluded that the sample was stable up to 126ºC (Fig. 6). The loss in weight percentage and temperature of the struvite crystals were tabulated in the Table-3.

TABLE-3
TGA/DTA ANALYSIS OF STRUVITE CRYSTALS

Points	TGA		DTA (ºC)
	Temperature (ºC)	% of CHP crystal present	
1	77.20	99.563	75.37
2	133.22	75.084	126.03
3	188.72	64.122	162.22
4	364.79	59.447	225.04
5	-	-	346.78
6	-	-	685.13
7	-	-	706.31

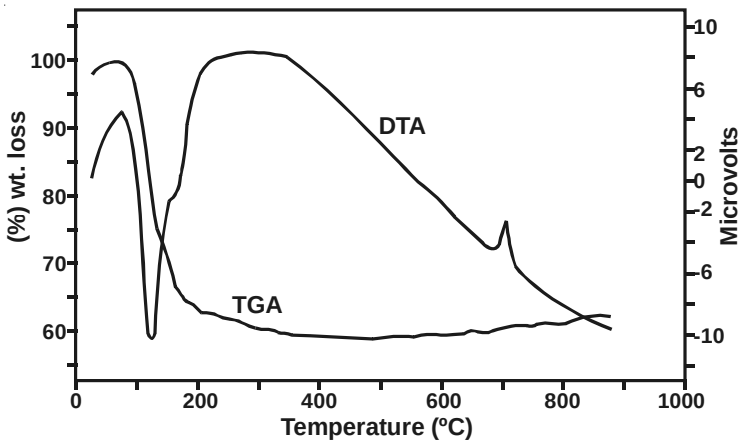

Fig.6 TGA and DTA of struvite crystal

The focusing of SEM may be varied from high step of 10-250 mm to low step 2.8-10 mm in a particular crystal[17]. The main features of surface analysis using SEM is (a) tiny particles of the same or another material absorbed or anchored on the surface, (b) shallow tiny inclusion[18], (c) optical effect of irradiation from outside the crystal or try a radioactive impurity, (d) crystal growth step, (e) identification of foreign substances inclusion on a surface corresponds to nucleation rate on the crystal lattice[19] and (f) grain boundary and dislocation edges of steps present on the surface[20]. In the present study SEM analysis was done and photographed for a well grown struvite crystals Fig. 7. The SEM picture of struvite crystals [100] having the surface morphology is in folder type grain; smooth boundaries and then many valley islands are observed in the plane.

Fig. 7. Scanning electron microscopy of struvite crystals

Atomic absorption spectroscopy spectrum of struvite crystals was recorded by magnesium flame technique. The spectrum was taken concentration *vs.* absorption. The following procedure was used to calculate the percentage of magnesium present in the struvite crystals. Phosphate, ammonium lamp not available in the AAS analysis.

58 mg of sample was dissolved in 25 mL of solvent.

This is equal to 4.6221 mg/L.

$= (4.6221 \times 25)/1000$

$= 0.1155$

$= (0.1155/58) \times 100$

= 0.199 % of magnesium present in the grown struvite crystals.

Conclusion

Struvite crystals were grown in SMS gel technique. Optimum growth parameters of the struvite crystals were found. The effects of the sunlight exposure in the growth column of struvite crystals were found out. From the observation, the nucleation rate was reduced in the sunlight exposure growth medium due to the under super saturation. Another part of the growth characterization studies were done in the grown crystal, the studies are XRD, FTIR, ETCHING, TGA/DTA and, AAS and the results analyzed and compared with the reported papers.

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