



SPECTROSCOPIC STUDY OF Mn^{2+} DOPED URINARY STRUVITE-K CRYSTALS GROWN IN AGAR GEL

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Article Received on 20/02/2024

Article Revised on 10/03/2024

Article Accepted on 30/03/2024

ABSTRACT

The influence of manganese on the growth of urinary struvite-K crystals was studied using the Infrared spectroscopic techniques. It was found that, the four fundamental modes of vibrations band ν_1 , ν_3 , ν_2 , and ν_4 of undoped struvite-K crystals located at 1022.31 cm^{-1} , 1062.81 cm^{-1} , 1165.04 cm^{-1} , 1232.55 cm^{-1} , 425.00 cm^{-1} and 502.00 cm^{-1} were also observed in the spectrum of Mn^{2+} doped sample, but was slightly shifted to 930.68 cm^{-1} , 1139.97 cm^{-1} , 1224.84 cm^{-1} , 439.78 cm^{-1} , and 594.1 cm^{-1} respectively. The absorption at 684.75 cm^{-1} due to presence of Mg-O bond in undoped struvite-K was shifted to higher frequencies at 811.09 cm^{-1} in Mn^{2+} doped struvite-K crystals. The change in initial vibrations band of crystals was due to incorporation of impurities on the growth of struvite-k crystals.

KEYWORDS: Urinary Crystals, struvite-k, Agar Gel, Single diffusion, FTIR.

1. INTRODUCTION

Urolithiasis is a major medical problem hence researchers have been attracted a lot of attention in urinary crystallization.^[1] The occurrence of the urinary stones varies according to the environmental climate, diet, foreign substances etc. Struvite ($MgNH_4PO_4 \cdot 6H_2O$) is the renal and vesical calculi which is common constituents of magnesium phosphates. A series of orthorhombic Struvite analogues crystals were also reported in the literature. One of analogous compound of Struvite is potassium magnesium phosphate hexahydrate ($KMgPO_4 \cdot 6H_2O$), known as Struvite-K crystals is natural minerals as well as found in animal urinary calculi.^[2-4]

Agar gel method is used as the growth media. The preset paper is the continuation studies of struvite-K crystal,^[4-6] carried out to observe the effect of different additives on the nucleation, growth and influence on formed crystals. The numbers of investigations have been carried out on the effects of foreign ions on the crystal growth of struvite.^[7-9] However, the impact of manganese on the growth of struvite-K was not yet reported. So in the present study, we examine the impact of manganese ions on the molecular structure of struvite-K those are grown in agar gel by single diffusion techniques at ambient temperature.

2. Experimental

The preceding paper,^[4] reported the optimized condition for the growth of Struvite-K crystals in agar-agar gel by single diffusion technique. In the extension of such experiment, by adding the dopants like Mn^{2+} in the form of chloride solution in supernatant solution, the effect of crystallization on the growth of Struvite-K crystals was observed. For the experiment single glass tubes of 25 mm in diameter and 20 mm in height were used as the crystallization vessels. One gm of agar-agar powder (Himedia) was used in 100 ml double distilled water to prepare gel at concentration of 1.0 %. The prepared hot agar-agar solution was then mixed with an aqueous solution of 1.0M magnesium acetate (Qualigens) in appropriate amount and was allowed to set. Once the gel was set in different test tubes, 20 ml supernatant solution containing 1.0M potassium dihydrogen phosphate (KH_2PO_4 -Merck) and 0.25M, 0.5M and 1.0M manganese chloride (Qualigens) solution in 1 ml and 2 ml volumes was slowly poured over the set gel. Then the ends of the tubes were tightly closed by cotton plugs and kept undisturbed for crystallization. After crystallization of forty five days, the struvite-K crystals grown in Mn^{2+} were found to be in grown in agar gel. The growth parameters of manganese doped struvite-K crystals was shows in Table 1.

Table 1: Growth parameters of struvite-K crystals grown in manganese chloride.

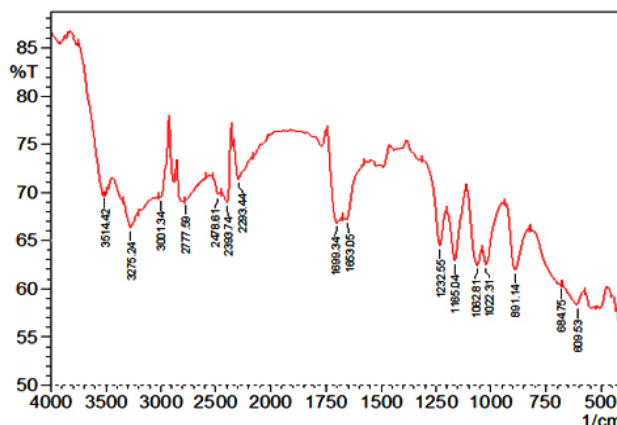
Set No.	Concentration of Mg (CH ₃ COO) ₂ ·4H ₂ O I Reactant (M)	Concentration of KH ₂ PO ₄ II Reactant (M)	Concentration of MnCl ₂ (Additives) (M)	Volume of Additives (ml)	Percentage of Agar-agar gel (%)
1	1.0	1.0	0.25	1.0	1.0
2	1.0	1.0	0.25	2.0	1.0
3	1.0	1.0	0.5	1.0	1.0
4	1.0	1.0	0.5	2.0	1.0
5	1.0	1.0	1.0	1.0	1.0
6	1.0	1.0	1.0	2.0	1.0

3. RESULT AND DISCUSSION

Struvite-K crystals were grown in manganese chloride additive solution by agar-agar gel method. There has been a significant change in the growth pattern as compared to the similar crystals those are grown with zinc doped and without doping manganese.^[4,6] In case of manganese added experiment, the manganese ions did not influence the selective nucleations, as that was found in zinc doped,^[6] but did have a pronounced effects on the growth habits of crystals. The colorless spherulite crystals those are found in calcium and zinc doped were not observed in this manganese doped process. In such experiment, the reddish irregular spherulites were noticed. The Liesegang ring phenomenon was observed in higher concentration of manganese ions. Because the formation of Liesegang rings is very sensitive to various

factors like concentration, pH and ageing of the gel medium, concentrations of the reactants, the presence of additives, temperature, light etc.^[10] It was also observed that the manganese doped struvite-K crystals are relatively in different morphology.

The samples were analyzed with the help of Fourier transform infrared spectroscopy (FTIR) which is one of the most versatile analytical techniques to provide fundamental information of the molecular structure of organic and inorganic components. In order to analyze the presence of functional groups in Mn²⁺ doped struvite-K crystals, the FTIR spectrum was recorded in the range of 400-4000 cm⁻¹. The FTIR spectra of undoped and Mn²⁺ doped struvite-K crystal was depicted in **Figure 1(a&b)**.

**Figure 1(a): FTIR spectrum of undoped struvite-K crystals.**

In the spectrum of pure sample as shown in **Figure 1(a)**, two bands located at 3514.42 cm⁻¹ and 3275.24 cm⁻¹^[11] are assigned to the H-O-H stretching vibrations of the water in crystals, and were found to be shifted at 3569.39 cm⁻¹, and 3426.66 cm⁻¹ attributed to H-O-H stretching vibrations. The modified peak due to stretching modes of the inner O-H group, as observed in calcium and zinc doped^[15,6] spectrum was not obtained in Mn²⁺ doping. The

two bands of cluster of water molecules assigned at 2478.61 cm⁻¹ and 2393.74 cm⁻¹^[12] in pure sample were found to be slightly disappearing and only one shifted peak was observed in doped spectrum at 2350.34 cm⁻¹ as shown in **Figure 1(b)**. These changes in the spectrum of manganese doped sample were attributed due to doping effect.

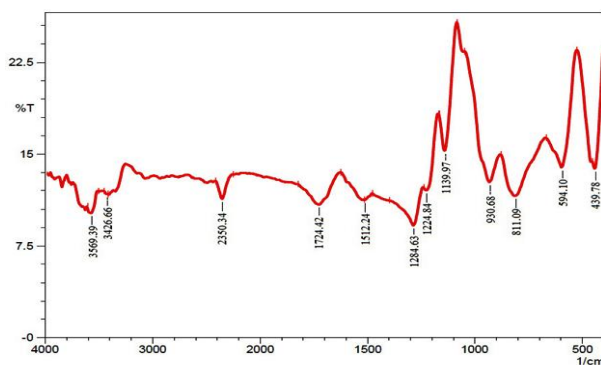


Figure 1(b): FTIR spectrum of manganese doped struvite-K crystals.

The slightly shifted medium intense bands appeared at 1724.42 cm^{-1} and 1512.24 cm^{-1} indicate the H-O-H bending modes of vibrations in manganese doped spectrum.^[13-14] The wagging modes of the coordinated water present in undoped struvite-K crystals was disappeared in the spectrum of Mn^{2+} doped struvite-K crystals.

The four fundamental modes of vibrations band ν_1 , ν_3 , ν_2 , and ν_4 of undoped sample located at 1022.31 cm^{-1} , 1062.81 cm^{-1} , 1165.04 cm^{-1} , 1232.55 cm^{-1} , 425.00 cm^{-1} and 502.00 cm^{-1} ^[15] were also observed in the spectrum of Mn^{2+} doped sample, but they are slightly shifted to 930.68 cm^{-1} , 1139.97 cm^{-1} , 1224.84 cm^{-1} , 439.78 cm^{-1} , and 594.1 cm^{-1} respectively. Moreover, the absorption at

684.75 cm^{-1} due to presence of Mg-O bond,^[12,13] in undoped sample was shifted to higher frequencies at 811.09 cm^{-1} in Mn^{2+} doped struvite-K crystals.

Apart from some obtained characteristic vibrational frequencies observed from undoped^[4] and manganese doped struvite-K crystals, the manganese doped frequencies were found to be slightly different from undoped struvite-K crystals. However the changes observed in the vibrations of the doped struvite-K crystals may be due to the mass of molecules of dopants. The FTIR wave numbers and vibrations assignment of struvite-K crystals grown in pure and manganese doped are shown in **Table 2**.

Table 2: FTIR wave numbers and vibrations assignment of struvite-K crystals grown in manganese chloride solution.

Sr. No.	Bonds/Vibrational assignments	Observed wave number in cm^{-1}	
		Without manganese chloride ^[4]	With Manganese Chloride Solution
1	H-O-H stretching vibrations of water	3514.42	3569.39
2	H-O-H stretching vibrations of water	3275.24	3426.66
3	H-O-H stretching vibrations of cluster of water molecules of crystallization	2478.61	--
4	H-O-H stretching vibrations of cluster of water molecules of crystallization	2393.74	2350.34
5	H-O-H bending modes of vibrations	1699.34	1724.42
6	H-O-H bending modes of vibrations	1653.05	1512.24
7	ν_3 asymmetric stretching vibrations of PO_4	1232.55	1224.84
8	ν_3 asymmetric stretching vibrations of PO_4	1165.04	1139.97
9	ν_3 asymmetric stretching vibrations of PO_4	1062.81	--
10	ν_1 symmetric stretching vibrations of PO_4	1022.31	930.68
11	wagging modes of vibration of the coordinated water	891.14	--
12	oxygen-metal bond	684.75	811.09
13	ν_4 asymmetric bending vibrations of PO_4	502.01	594.10
14	ν_2 symmetric bending vibrations PO_4	425.01	439.78

4. CONCLUSIONS

Struvite-K crystals was successfully grown by Mn^{2+} doped in agar- agar gel using single diffusion techniques. The presence of various functional groups obtained in Mn^{2+} doped sample was also confirmed by FTIR. Compared to undoped struvite-K crystals, additional small absorption band of stretching modes of inner O-H

groups was not observed in Mn^{2+} doped. The slightly shifting of wave numbers in H-O-H stretching and bending modes of vibrations, clusters of water molecules, symmetric and asymmetric vibrations (ν_1 , ν_2 , ν_3 , and ν_4) of PO_4 , wagging modes of coordinated water, metal- oxygen bonds was due to doping effect. The change in initial vibrations band of crystals was due to

incorporation of impurities of manganese on the growth of struvite-k crystals.

ACKNOWLEDGEMENT

The authors are thankful to The Principal Shri V S Naik Arts, Commerce & Science College Raver Dist.- Jalgaon for providing experimental facilities.

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