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Dielectric studies on struvite urinary crystals, a gateway to the new treatment modality for urolithiasis

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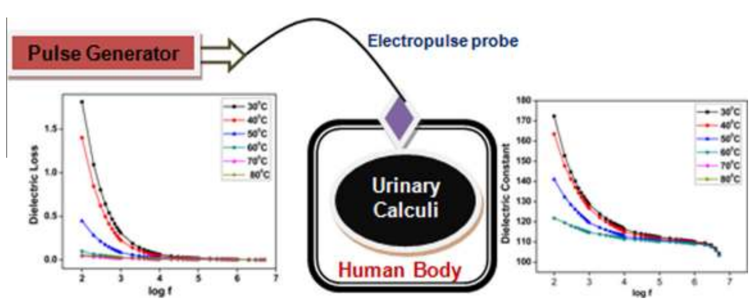
HIGHLIGHTS

- The work dealt with proposing a new treatment modality for urolithiasis.
- The urinary struvite crystals were developed using gel growth technique.
- The characterizations were done including the study on dielectric parameters.
- The new treatment modality known as dielectric therapy was proposed.
- The treatment *in vitro* set up model was designed.

GRAPHICAL ABSTRACT



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ABSTRACT

Struvite or magnesium ammonium phosphate hexahydrate (MAPH) are biological crystals, found in the kidney, which are formed due to the infection caused by urea splitting bacteria in the urinary tract. The struvite crystals observe different morphologies and were developed using single diffusion gel growth technique. The crystalline nature and its composition were studied from different characterization techniques like X-ray Diffraction (XRD) and FTIR. The dielectric behavior of the developed crystal was studied by varying temperature and at different frequencies. The parameters like dielectric constant, dielectric loss, *ac* conductivity, *ac* resistivity, impedance and admittance of the struvite crystals were calculated. The studies proved that the dielectric loss or dissipation heat is high in lower frequencies at normal body temperature, which develops a plasma state in the stones and in turn leads to the disintegration of urinary stones. The dielectric nature of the stones leads to the dielectric therapy, which will be a gateway for future treatment modality for urolithiasis.

Introduction

The struvite crystals are biological crystals which will be present in the kidney due to the improper renal filtration process. These crystals will aggregate inside the kidney to form a highly recurring painful disease known as urolithiasis [1]. The primary cause of the occurrence of struvite crystal is due to the infection produced by the urea splitting bacteria present in the urinary tract [2–4]. The chemical name of struvite crystal is magnesium ammonium phosphate hexahydrate (MAPH) [5]. The statistical analysis proves that females are more prone to this infectious disease [6]. The main treatment modalities existing now for urolithiasis are lithotripsy or surgical removal of stone [7]. The surgical removal of stones is highly painful and will be only done in the worst case of disease; hence lithotripsy is the most common and safe treatment modality for urolithiasis [8]. In order to design better lithotripsy treatment parameters, it is necessary to have a detailed in vitro study of the various characteristics of the stones. The biological crystals can be grown in vitro using gel growth technique

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[9]. This technique will initiate a slow growth of crystals in a gel medium, which act as a matrix. The main advantage of the gel growth technique is that the growth of the crystal can be monitored real time and the conditions of the crystal growth in the test tube imitate the environment inside the body [10]. The gel growth technique is basically of two different types, namely single diffusion technique and double diffusion technique [11]. The struvite crystals are developed here using single diffusion technique since this provides the simplest in vitro model. The dielectric behavior of a crystal gives relevant information about the polarizing nature of the crystal [12,13]. The dielectric parameters like dielectric constant, dielectric loss, *ac* conductivity, *ac* resistivity, impedance, admittance are calculated.

The treatments used for urolithiasis are lithotripsy, medication and surgical removal of stones. The laser lithotripsy parameters basically depend on the tensile and compression strength of the stones. The present study deals with the new property of the stone, namely dielectric breakdown which provides a gateway for new treatment.

Experimental procedure

Growth of struvite crystals

The struvite crystals were grown using single diffusion gel growth technique. Here, the gel was prepared by mixing sodium meta-silicate solution of density 1.03 g cm^{-1} with 0.5 M of ammonium dihydrogen phosphate solution and the pH was adjusted to 7.2 [2]. The solution was poured into the test tube and kept for gelling for around 48 h. After gelling, 1 M of magnesium acetate solution was added which act as a supernatant solution and it penetrates through the gel and to form struvite crystals as shown in Fig. 1 (a).

Characterization of crystals

The optical images of the grown crystals were captured which gives the details of the morphology of the grown crystals as well as the approximate size of the crystals too. The crystalline nature and crystal type of the developed crystal were confirmed by XRD characterization. The characterization was done with the instrument PANalytical Model X'pert PRO X-ray diffractometer with Cu-Kα radiation (of wave length 1.54060 Å). The FTIR characterization of the grown crystals was done to confirm the functional groups present in the crystal with the instrument Thermo Nicolet model AVATAR 330 Spectrometer.

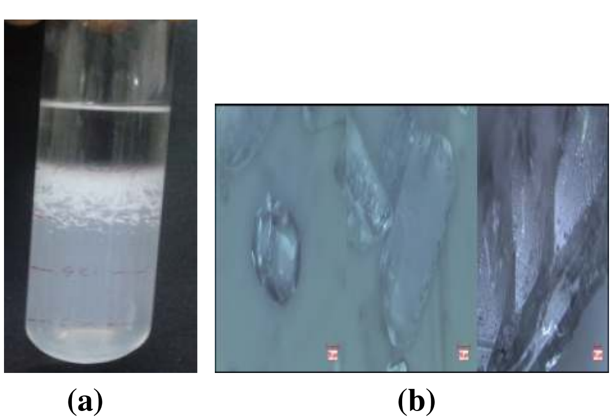

Fig. 1. (a) Struvite crystals grown in test tube (b) optical images of grown crystals.

Pellet preparation and dielectric analysis

The crystals developed in the test tube were carefully removed, dried and smashed into fine powder. The powdered crystal is made into pellets of thickness 2×10^{-3} m and area 1.326×10^{-4} m^2 by applying a pressure of 9–10 MPa at room temperature [14–22] for the dielectric study. The dielectric behavior of the prepared pellet was studied using N4L PSM-1735 Impedance Analyzer. The temperature was set to vary from 30 °C to 100 °C and frequency from 1 kHz to 1 MHz. The various dielectric parameters were also calculated.

Results and discussions

Optical image analysis and crystal size calculation

The optical image of the developed crystal is captured as shown in Fig. 1(b). The image confirms the morphology of the struvite crystal obtained. The crystals are mainly of dendrite, cubical and leaf structure. The surface of the crystals was not so smooth. The approximate size of the crystals can also be measured from the optical images which are about 1.5 μm approximately.

X-ray Diffraction (XRD) analysis and crystal size calculation

The XRD pattern of the developed crystal is shown in Fig. 2. The result obtained was verified with the Joint Committee for Powder Diffraction Standards (JCPDS) data [96-900-7675]. The crystal type and crystalline nature were confirmed to be of struvite. The highest intensity peaks were obtained at 35° and 15° as 2θ values which represent the 100% and 60% peak value for the struvite crystals. These highest peaks are due to the presence of phosphate and magnesium in the developed crystals.

The crystal size is calculated from the peaks obtained in the XRD pattern by using the Scherrer's formulae given below [23]:

$$\tau = \frac{K\lambda}{\beta \cos\theta} \quad (1)$$

where τ represents the size of the crystal, K is the shape factor, λ is the X-ray wavelength, β is the full wave half width maximum, θ is the Bragg angle. From the calculation the size of the crystal is obtained as 1.183 μm and the space between the crystal lattice, $d_{spacing}$ is 2.79 Å. The crystal size value which is obtained by calculation and optical imaging comes to be approximately same which

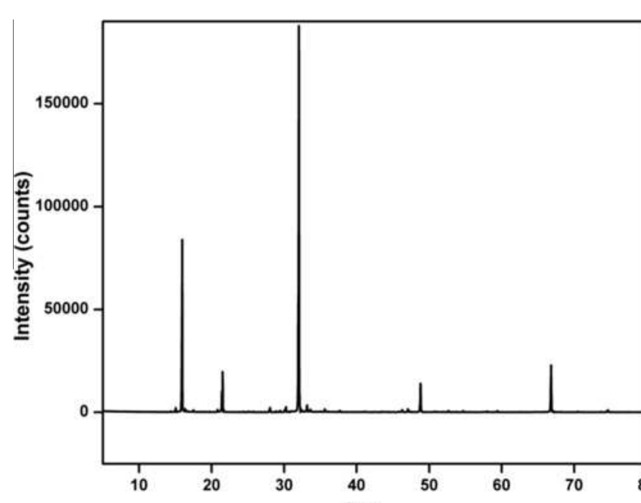

Fig. 2. The XRD pattern of the struvite crystal.

proves that the final size of the crystals comes to the range of 1–2 μm.

Fourier-Transform Infra Red (FT-IR) analysis

The FTIR characterization of the sample was done. Fig. 3 shows the FTIR spectrum of the sample and this spectrum shows the functional groups present in the sample. The struvite crystal contains magnesium, nitrogen, hydrogen, phosphate groups and oxygen. In the FTIR spectrum shown here, the absorptions at 3415.93 cm^{-1} and 698.23 cm^{-1} show the presence of N–H bond, whereas at 3124.68 cm^{-1} indicates the presence of an O–H bond in the sample. Due to the presence of the above said peaks, it can be confirmed that ammonia and hydrate groups are present in the sample. The absorptions at 1006.84 cm^{-1} is due to the presence of PO_4^- ions in sample struvite which confirms the presence of the phosphate group in the sample. The rest of the peaks are due to the carbon bonds present in the sample during its preparation for analysis.

Dielectric result analysis

Dielectric constant

The prepared pellet was given for dielectric studies. All the dielectric parameters are calculated for a varying temperature starting from 30 °C to 80 °C with a varying frequency from 1 kHz to 1 MHz. The dielectric constant was calculated by using the standard equation [11].

$$K = \frac{C_p t}{A\varepsilon_0} \quad (2)$$

where C_p is the parallel capacitance, t and A are the thickness and the area of the sample respectively, ε_0 is the absolute permittivity. The variation of dielectric constant with applied frequencies is plotted in Fig. 4(a). The dielectric constant value will be higher for lower frequencies, whereas it will drastically reduce as the frequency reaches its higher value. In low temperature and low frequency condition, the material will be highly polarized hence the dielectric constant will be high. As the temperature increases the polarizing ability of the material also will be decreased, which shows the drop down of dielectric constant value. The maximum dielectric constant value of the sample obtained here is 1.75 at 30 °C. The dielectric constant value obtained maximum at 80 °C is 120.

Dielectric loss

The dielectric loss (tan δ) variation of different frequencies at room temperature is plotted in Fig. 4(b). Dielectric loss is a unit less

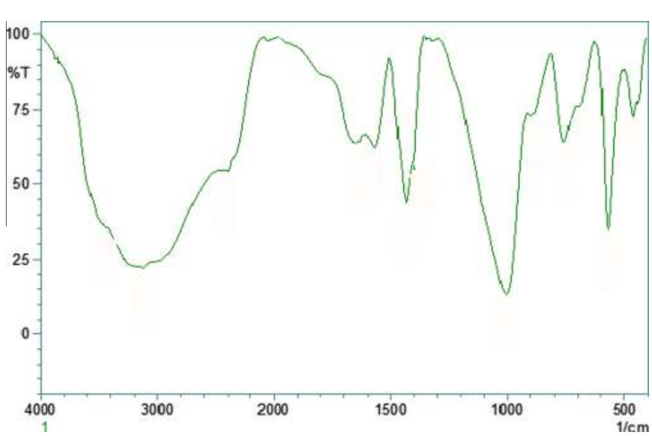

Fig. 3. The FTIR pattern of the grown struvite crystal.

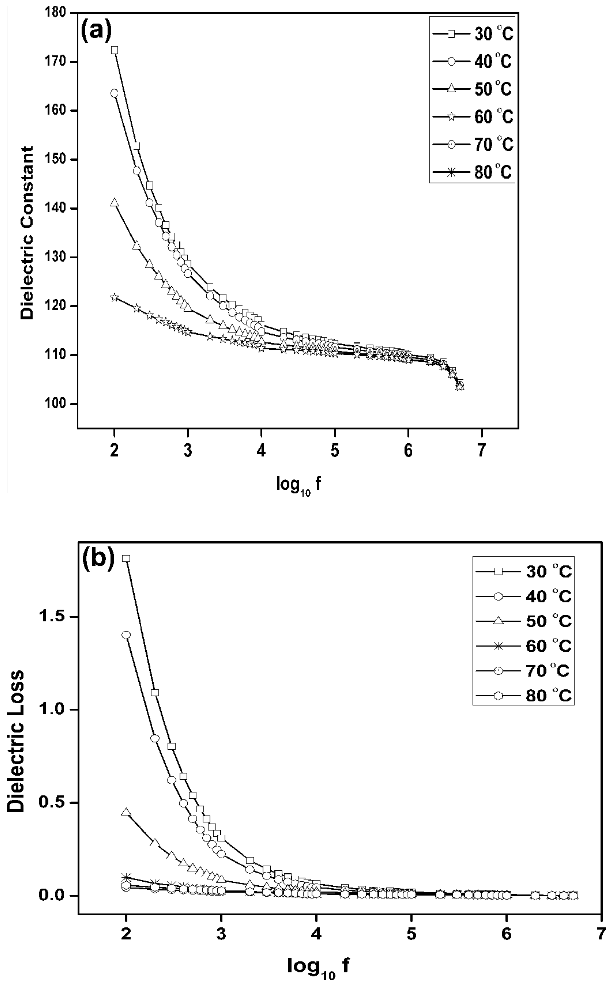

Fig. 4. Variation of (a) dielectric constant (b) dielectric loss with applied frequency.

quantity which shows the amount of energy dissipated by the material when it is applied by external fields. As the movement of ions or polarization is high in low temperature and low frequency, the dielectric loss will also be high. The dielectric loss will be gradually decreasing as the frequency increases. The dielectric loss is directly proportional to the dielectric constant value. The maximum dielectric loss obtained here 1.8 at 30 °C. For higher temperature the dielectric loss decreases hence the maximum loss at 80 °C is nearly 0.1.

ac resistivity and ac conductivity

The *ac* resistivity (ρ_{ac}) and *ac* conductivity (σ_{ac}) were calculated using the below given equations [24].

$$\rho_{ac} = \frac{2\pi f C t}{A} \quad (3)$$

$$\sigma_{ac} = \frac{1}{\rho_{ac}} \quad (4)$$

where f is the applied frequency, C is the parallel capacitance. The variation in the resistivity and conductivity of the sample for the applied frequencies for different temperature is plotted in Fig. 5. At the initial stage, for low frequency the ions will start separating will in turn produce an electric charge flow. Hence at lower frequencies the sample will show high conductivity compared to higher frequencies. Since the resistivity and conductivity are inversely proportional, at lower frequencies the resistance value is

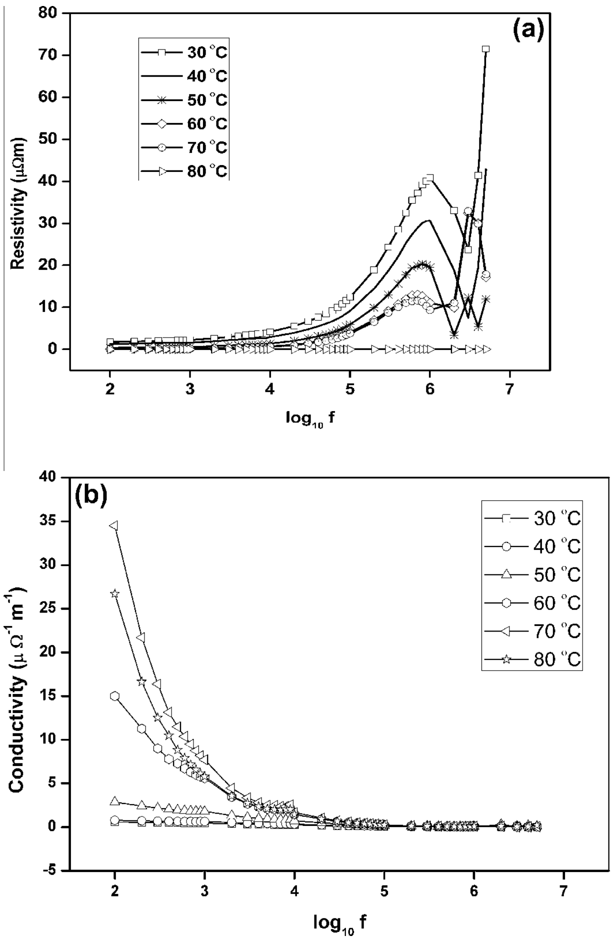

Fig. 5. Variation of (a) *ac* resistivity (b) *ac* conductivity with applied frequency.

almost nullified. As the frequencies increase the resistivity of the crystal will shoot up to 40 μΩ.

Impedance and admittance variation

The impedance and admittance variation for room temperature and higher temperature for different frequencies are plotted in Fig. 6. Impedance is the total resistance inside the impedance analyzer. The admittance value is inversely proportional to the impedance value [25] i.e.

$$|Y| = \frac{1}{|Z|} \tag{5}$$

where Y is the admittance and Z is the impedance of the entire set-up. It can be noted that the system impedance and admittance does not vary much for change in the temperature. The variation will depend only upon the change in the applied frequency in the system.

Dielectric therapy for urolithiasis

The urinary stones are removed from the body by either surgery or by lithotripsy treatment. The lithotripsy treatment is very common these days which use different external energy to disintegrate the stone inside the body itself without an external cut. The latest among these is laser lithotripsy in which different energy laser pulses will be used to smash the stones, which proves to have a disadvantage when it comes to its high treatment cost as well as the current technique proves not to be successful in disintegrating all kinds of stones [26].

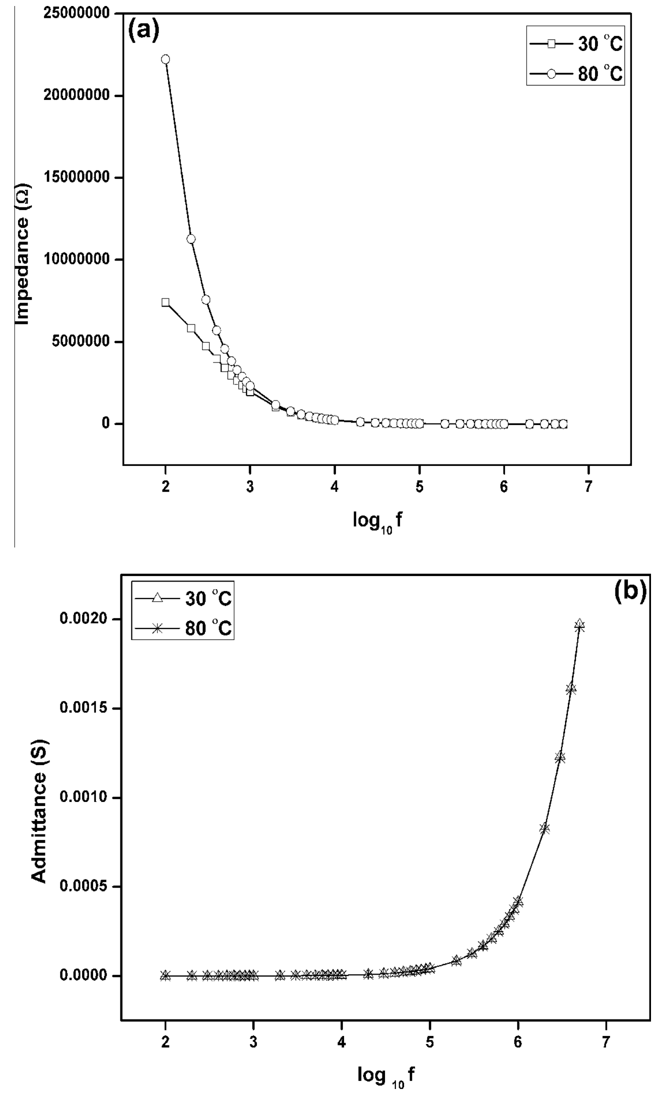

Fig. 6. Variation of (a) impedance (b) admittance with applied frequency.

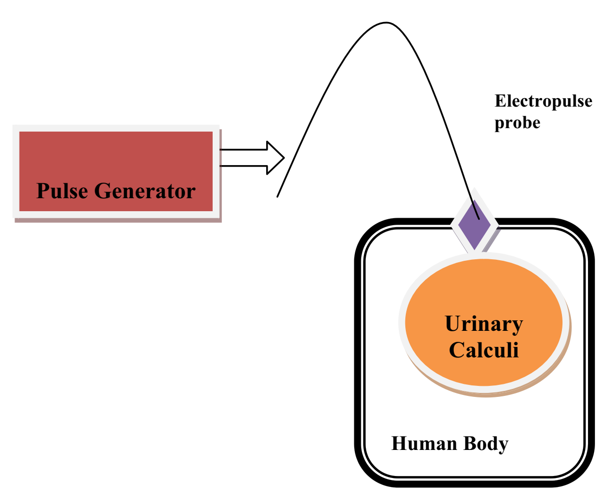

Fig. 7. Schematic diagram of dielectric therapy set-up.

The dielectric therapy enters into the new era of lithotripsy treatment. The study proves that there is maximum dielectric loss, in the form of heat, when low frequency signal is applied in the normal body temperature or room temperature i.e., 30 °C. The schematic diagram of the experimental setup is shown in Fig. 7.

The mode of giving the external source will be same like laser lithotripsy whereas instead of a laser source, a low frequency signal will be applied through a catheter or fibers which touch the stone [27]. The low frequency signal of range 100–500 Hz signal will be supplied using a pulse generator. The signals will be passed into the body using electropulse probe, which will avoid distortion as well as loss of energy. The probe enters the body and touches the calculi, which will be heated up due to the dielectric heating. As the heat dissipation increases, a plasma state will apply inside the stone which initiates the breakage of the stone [28]. The fiber used to transmit the signal can be made in such a way that the tip of the fiber can absorb the excess amount of heat without affecting the nearby tissues [26]. The movement of the probe as well as the position and fragmentation of the calculi can be monitored using ureteropyeloscope where it provides real time imaging in the monitor kept outside.

The treatment requires a very simple, low frequency signal generator as the source, which is of very less cost. This meets the disadvantage of the present treatment modality.

Conclusion

The dielectric study of struvite crystals will bring a great breakthrough in the treatment area for urolithiasis. It overcomes all the disadvantages of the existing laser lithotripsy treatment. The stone itself has a property of liberating heat in the form of dielectric loss when a proper external frequency signal is applied, which is proved by the above study. When a low frequency in the range of 500 Hz–1.5 kHz is applied to the stone it dissipates the heat, even at the normal body temperature which is around 30 °C. This property of the stone can lead to the disintegration of stones which leads to the gateway to a new design of treatment which can be a breakthrough for the lithotripsy treatment in future.

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