Chapter III

Dielectric Study of Medicinal Seeds Fenugreek and Black Cumin

*(Trigonella Foenum Graecum, Nigella Sativa Linn)*

3.1 Introduction

3.1.1 Fenugreek Seeds

Fenugreek (Trigonella foenum graecum), a leguminous medicinal plant, is cultivated in North Africa, China, India, Pakistan, Egypt and the Mediterranean countries (1). Its leaves are consumed as green vegetable throughout India and are also used as a supplement to wheat and maize flours for bread.

Fenugreek seeds contain many nutrients such as carbohydrates, protein, fiber, fats, saponins, choline and trigonellin, vitamins, minerals and enzymes, among which Fiber and saponin show bioactivity. Moreover, the presence of steroidal sapogenins, especially diosgenin (25 R-spirostan-5-en-3β-ol), has also been reported in fenugreek seeds (2, 3), which is a basic component in the hemi synthesis of steroid drugs. This makes fenugreek seeds a significant base material in pharmaceutical industry. These seeds contain almost 26.8% fenugreek galactomann gum, a chemical with blood glucose reducing property (4), and this gum, in fact, has a greater hypoglycemic effect compared to that of the seed itself. The fenugreek galactomann has extensive application in many industries, like food, pharmaceuticals, cosmetics, paper products, paint, plasters, etc (4, 5).

The chemical constituents of fenugreek seeds contain 6.2% moisture, 23.2% protein, 8% fat, 9.8% fiber, 26.3% mucilaginous materials and 4.3% ash. According to Duke, whole grain contains (per 100g of edible portion), 369 calories, 7.8% moisture, 28.2g protein, 5g fat, 54.5g total carbohydrate, 8g fiber, 3.6g ash. Its flour contains 375 calories, 9.9% moisture, 25.5g protein, 8.4g fat, 53.1g total carbohydrate, 7.1g fiber, 3.1g ash. Raw leaves contain 35 calories, 87.6% moisture 4.6g protein, 0.2g fat, 6.2g total carbohydrate, 14g fiber, 1.4g ash (1, 6).

The medicinal properties of fenugreek seeds have been extensively explored. The following are some the well known studies of fenugreek seeds’ medicinal properties:
G.M.S El-Bahy reported FTIR and Raman Spectroscopic study of fenugreek (7), while J. X. Jiang et al. reported characterization of galactomann gum of seeds and rheological properties (8), Ebubekir Altuntas et al. reported some physical properties of fenugreek seeds (9). Preethi B Gopalpura et al. reported its effect on the glycemic index of food (10). Amira Kassem et al., reported its effect on antifertility in male and female rabbits (11). R. D. Sharma et al. reported hypoglycemic effect of it in non-insulin dependent diabetic subjects (12), while Valette et al. have shown the hypocholesterolaemic effect of the same seeds (13). M. Prasanna, Moosa et al. and Vijaya Kumar et al. reported the hypolipidemic effect of fenugreek seeds (14-16).

Even though a lot of literature is available describing the medicinal behavior of the fenugreek seed and the dielectric and conductive studies on variety of seeds have also been done by many researchers (17 - 28), the dielectric properties of the fenugreek seed remain inadequately explored. The study of moisture-dependent dielectric properties of these seeds will yield valuable information on the storage and germination of fenugreek seeds and will also describe the behavior of these seeds under high frequency electric fields or dielectric heating (29).

3.1.2 Black Cumin

Black cumin (Nigella sativa L), which is also known as black cumin. Black cumin belongs to the ranunculaceae family, it is cultivated in various places in the world and is especially grown in East Mediterranean countries. Black cumin is a harvest plant with green- to blue-colored flowers in shape of star and small black seeds that grows in temperature and cold climates. It is commonly known as Fitch (Siah-Daneh in Persian). The cultivation of this plant is in abundance in India, Bangladesh, Turkey and Eastern countries. Black cumin (Nigella sativa L) seeds are used in food and medicines which have a special smell. The (Nigella sativa L) seeds contain thymoquinone, monoterpenes such as p-cymene and α-pinene, nigellidine, nigellimine and a saponin (30-33). Black cumin (Nigella sativa L) has long been known for its antispasmodic properties, especially in gastrointestinal and respiratory diseases. Ancient Iranian medical books state that
Black Cumin was used in digestive and gynecologic disorders as well as in asthma and dyspnea (34). The Bible describes black seed as the “curative black cumin” (Isaiah 28:25, 27 NKJV) (35). Kalonji (Nigella sativa L) seeds are the common drug used in Islamic Prophet’s medicine, since prophet Muhammad (PBUH) stated that it is the remedy for all disease except death (36). It is stated that he himself [PBUH] used to take these seeds with honey syrup for therapeutic purpose (37). Ibni Sina, known in the West as Avicenna, also referred black cumin as the seed “that stimulates the body’s energy and helps recovery from fatigue” in his great book “The Canon of Medicine” (38). Nigella sativa L has been found beneficial against rheumatoid arthritis in both animal and human studies (39, 40). In another study the Nigella sativa L is found beneficial in cardiovascular disease (41).

Fig. 3.0: Whole Plant, Flower and Seeds, of Black Cumin (41).

3.2 Material and Methods

3.2.1 Fenugreek Seeds

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<td>3</td>
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3.2.2 Black Cumin

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<td>3</td>
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<td>4</td>
<td>Family name</td>
<td>Renunculcea</td>
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3.2.3 Experimental Details

The dust and other foreign materials were removed from the fenugreek and black cumin used in the present study. The seeds were kept in an air-tight container to avoid any moisture gain or loss. The seeds were then kept in a hot-air oven for 24 hours at 60\(^\circ\)C to make the moisture content of all seeds the same. Then, the different moisture contents viz.2, 4, 6, 8, 10, 12, and 14% were made on weight basis. The samples were subjected to frequent agitation to aid uniform distribution of moisture. These samples were further kept in an air-tight container to avoid moisture loss.

The temperature of the seeds was varied by placing the sample holder in a specially-designed glass jacket through which heated oil was circulated using refrigerated circulator of Julabo (model number F-25, Germany). The accuracy of temperature measurement was up to ±0.01\(^\circ\)C.

Moisture contents in the seeds were determined on the wet-basis method. The moisture contents were adjusted by adding distilled water and conditioning of the sample at 20\(^\circ\)C. These were stored in sealed jars at 20\(^\circ\)C and permitted to reach room temperature (30\(^\circ\)C) in sealed jars before the jars were opened and the dielectric constant and the dielectric loss for the seeds were measured. The samples were kept in this condition for about 24 hours before the measurements were taken. The moisture content of the samples was determined by approved oven method (42). Thus, the prepared samples were measured for the dielectric constant and the dielectric loss.
3.3 Results and Discussion

3.3.1 Dielectric Properties of Fenugreek Seeds (Trigonella Foenum Graecum)

3.3.1.1 Frequency Dependence

As figure-(3.1a) and figure-(3.1b) indicate, the dielectric constant and dielectric loss decrease with increase in frequency for all moisture content at a given temperature. Because of dispersion mechanism, in the lower frequency region the rate of decrease of dielectric constant is higher than that of it in the higher frequency region. The high values of dielectric constant in the lower frequency region for higher moisture content may be because of the high mobility of water dipole due to free water state and electrode polarization, whereas for dielectric loss, it may be due to high mobility of water dipole, electrode polarization and increase in ionic and surface conductivity. The higher values of dielectric loss due to ionic conductivity have already been reported by Magario and Yamaura (43)

\[ \varepsilon'' = \varepsilon_d'' + \frac{\sigma_i}{2\pi\varepsilon_o f} \]

Thus, the ionic loss is higher in lower frequency region than in the higher frequency region. In the higher frequency region, dipolar energy loss is the predominant loss, and ionic loss is negligible. The combined effects of these losses make the expression of dielectric properties of seeds (heterogeneous system) more complex. The nature of decrease is almost the same for all the seeds of all moisture content. This type of behaviour has been reported by many groups including our own group (16 to 27).
Fig. 3.1: Frequency dependence of dielectric constant and dielectric loss of fenugreek seeds at indicated moisture content and 30°C.

3.3.1.2 Moisture Dependence

In figure-(3.2a) and figure-(3.2b) the variation of dielectric constant and dielectric loss with moisture at a fixed temperature is shown. It is well established that the water content of a seed affects its physiological activities (44, 45). In seeds, water binds with varying strengths at different water concentrations and therefore has different thermodynamic properties (44). The main components of seeds are carbohydrates, lipids and proteins. Carbohydrates (mainly starch) and proteins are the most important for water retention, and proteins contain more polar sites for attraction of water molecule than carbohydrates. Hence they can adsorb a large amount of water. In fenugreek seed, protein is about 23%, and hence its dielectric properties are highly affected by moisture content. For low moisture content, dielectric constant is low while for high moisture content it is high. It may be because at high moisture content more water dipoles contribute to polarisation, as water molecules easily follow up the applied field variation (free water). It can also be seen that both $\varepsilon'$ and $\varepsilon''$ are low below 6% moisture content. This is because of strong bound water state (monolayer) where distance between the water molecule and the cell wall is very small, and attraction force is very large. This strong force prevents water molecules from aligning in the varying electric field. Therefore, the dielectric constant and loss are small. Beyond 6% moisture content the values of dielectric constant and loss
increase which may be because of the change in bound water state from the first (monolayer) to the second (multilayer) type (free water). At high moisture content and low frequency, the ionic conductivity is high, therefore at high moisture content and low frequency the dielectric loss is quite high.

Fig. 3.2: Moisture dependence of dielectric constant and dielectric loss of fenugreek seeds at indicated frequencies and constant temperature 30°C.

3.3.1.3 Temperature Dependence

Figure-(3.3a) and figure-(3.3b) demonstrate variation in the dielectric constant and dielectric loss of the seeds with respect to temperature at a fixed frequency (50 kHz). It is clear from the figures that the dielectric constant and dielectric loss increase with increase in temperature. For lower moisture content the variation of $\varepsilon'$ and $\varepsilon''$ with temperature is almost linear, however, a slight nonlinearity is observed at high moisture content. As temperature changes, the energetic status of the molecule and their aptitude to rotate with electric field also change, thus, a change in contribution of water molecule for polarisation ultimately changes into effective complex permittivity. As temperature increases, the molecular mobility increases and relaxation frequency which is strongly related to the molecular mobility decreases (46). Hence the peaks of $\varepsilon'$ and $\varepsilon''$ shift to higher frequency. Increase in temperature also increases the ionic conduction, leading to an increase in dielectric loss factor. Thus, both $\varepsilon'$ and $\varepsilon''$ increase as temperature
increases. At lower frequency and high moisture content, ionic conduction as well as molecular mobility are more affected by the increase of temperature because of decrease of viscosity in osmotic or free water state. Therefore, under these conditions, the rate of increase in $\varepsilon'$ and $\varepsilon''$ with temperature is high and might be nonlinear. The dielectric constant is less affected by temperature than that of the dielectric loss factor because the increase of ionic conduction gives additional effect on dielectric loss factor, whereas dielectric constant is least or not at all affected by the ionic conduction.

The regression of moisture (M) on permittivity ($\varepsilon'$, $\varepsilon''$), yielded the following equations:

- $\varepsilon'(10\text{kHz}) = 0.000M^4 - 0.009M^3 + 0.038M^2 + 0.605M + 5.353$
- $\varepsilon'(50\text{kHz}) = 0.000M^4 - 0.001M^3 + 0.061M^2 + 0.907M + 4.108$
- $\varepsilon'(10\text{MHz}) = -0.000M^4 + 0.012M^3 - 0.111M^2 + 0.450M + 2.989$
- $\varepsilon'(2\text{MHz}) = -0.000M^4 + 0.012M^3 - 0.113M^2 + 0.526M + 3.089$
- $\varepsilon''(10\text{kHz}) = -0.000M^4 + 0.017M^3 - 0.035M^2 + 0.101M + 1.167$
- $\varepsilon''(50\text{kHz}) = 0.000M^4 + 3\times10^{-6}M^3 + 0.015M^2 + 0.013M + 0.900$
- $\varepsilon''(10\text{MHz}) = -0.000M^4 + 0.005M^3 - 0.059M^2 + 0.257M + 0.191$
- $\varepsilon''(2\text{MHz}) = 0.000M^4 - 0.002M^3 + 0.005M^2 + 0.119M + 0.259$

With coefficients of determination $R^2$ is 0.987, 0.985, 0.981, 0.993, 0.976, 0.978, 0.951, 0.992 respectively and all very close to unity.
3.3.1.4 Behaviour of Electrical Conductivity

Figures (3.4), (3.5) and (3.6) show that, the electrical conductivity for the fenugreek seeds increases with increase in the frequency, moisture content and temperature. As temperature increases, the contribution to dielectric loss from dielectric polarisation decreases whereas contribution from ionic conduction increases with temperature. At given moisture content, it has been found that conductivity shows increasing trend with increase in frequency. The conductivity of fenugreek seeds also increases with increase in moisture content at a given temperature.

Fig.3.4: Frequency dependence of electrical conductivity of fenugreek seeds at indicated moisture content and constant temperature at 30°C.
Fig. 3.5: Moisture dependence of electrical conductivity of fenugreek seeds at indicated frequency and constant temperature 30°C.

Fig. 3.6: Temperature dependence of electrical conductivity of fenugreek seeds at indicated moisture and constant frequency 50 kHz

3.3.2 Dielectric Properties of Black Cumin (Nigella sativa Linn.)

3.3.2.1 Frequency Dependence

As shown in figure-(3.7a) and figure-(3.7b) it is observed that both the dielectric constant and dielectric loss of the complex permittivity decrease with increase in the frequencies. This exhibits dielectric dispersion in the material with frequency. The dispersion phenomena have already been discussed in chapter –II.

The high values of dielectric constant at lower frequencies and high moisture content could be attributed to high mobility of dipole for free water state and electrode polarization. The high values of the dielectric loss can be attributed to high mobility of water dipole, electrode polarization and increase in ionic and surface conductivity (47).
As we go towards the lower frequency side the ionic loss \( \left( \frac{\sigma_t}{2 \pi f \varepsilon_0} \right) \) is inversely proportional to frequency and it becomes almost absent at higher frequencies due to the dipolar energy dissipation, which is the predominant and the ionic loss become almost absent. The dielectric properties of the seeds and other food materials can be represented as combination of ionic and dipolar polarization losses.

From figure-(3.7a) and figure-(3.7b) it can be observed that the curves diverse and the separations increase between the curves for different moisture levels as we move to the lower end of the frequency range but no change in the curve have been observed for the kalonji seed and it shows nearly a straight line.

![Fig.3.7: Frequency dependence of dielectric constant and dielectric loss of black cumin at indicated moisture content and 30°C.](image)

### 3.3.2.2 Moisture Dependence

From figure-(3.8a) and figure-(3.8b) it is clear that the complex dielectric permittivity increases with increase in the moisture content at a given frequency and temperature. It has been observed that the dielectric constant \( (\varepsilon') \) and dielectric loss \( (\varepsilon'') \) are high at low frequency because the water dipoles easily follow the applied field variations. As moisture content increases, the free water in the system increases which ultimately increases the contribution to dielectric constant, similarly for dielectric loss as moisture
increases beyond the critical level i.e. as the free water content increases, dielectric loss increases, in present case critical moisture level being approximately 6%.

Low values of dielectric constant may be because of strong interaction between protein and carbohydrate with water. This interaction further reduces amount of free water present in the system. Also the seed contains 35.5% fat and the fat content reduces the free water content in the system i.e. the reduction in dielectric constant of seed. It can also be seen that below critical moisture content (6%) variation in dielectric constant and dielectric loss are small while the same above critical moisture content are pronounced.

![Figure 3.8](image)

Fig.3.8: Moisture dependence of dielectric constant and dielectric loss of black cumin at indicated frequencies and constant temperature 30°C.

### 3.3.2.3 Temperature Dependence

Figure figure-(3.9a) and figure-(3.9b) show temperature dependence of dielectric constant ($\varepsilon'$) and dielectric loss ($\varepsilon''$) in the temperature range of 30°C - 50°C. At different frequencies and moisture levels, dielectric constant and dielectric loss increase with increase in the temperature. The slope of the curve increases with the increase in moisture. As temperature increases the protein denaturation occur, which further increases the structural deterioration of protein, hence charge asymmetry results in higher values of dielectric constant. The similar variations are also seen for other seeds also (48, 49).
3.3.2.4 Behavior of Electrical Conductivity

Figure-(3.10) shows that the behaviour of electrical conductivity of black cumin at different frequencies. As frequency increases the electrical conductivity also increases. Figure-(3.11) and figure-(3.12) shows the behaviour of electrical conductivity for black cumin at different moisture content and temperature. The higher conductivity values in the given frequency and moisture range are observed for the black cumin.

Variation of the electrical conductivity with temperature of black cumin at a given moisture content and frequency is shown in the figure-(3.12). From figure it is observed that the variations with temperature are almost linear in general for all moisture levels at higher frequencies, however non-linearity is present at lower frequencies.

Fig.3.10: Frequency dependence of electrical conductivity of black cumin at indicated moisture content and constant temperature at 30°C.
Fig. 3.11: Moisture dependence of electrical conductivity of black cumin at indicated frequency and constant temperature 30°C.

Fig. 3.12: Temperature dependence of electrical conductivity of black cumin at indicated moisture and constant frequency 50 kHz.

3.4 Conclusions

In the present study, it is found that the complex permittivity of fenugreek seeds shows dependence on the moisture, temperature and frequency. Moisture content of the seeds largely affects the permittivity of fenugreek seeds. Both the dielectric constant and dielectric loss increase with the increase in the moisture content. On the other hand dielectric constant and dielectric loss decrease with frequency and increase or decrease with increase in temperature.

The similar behaviours have also been monitored for black cumin.

The electrical properties can also be used to measure moisture level.
3.5 References


