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# Modeling of sorption isotherms of spring barley kernels : Microwave density-independent permittivity function correlated to water activity

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## ABSTRACT

The present study aims at correlating water activity ($a_w$) to density independent microwave permittivity function ($\Psi$) for spring barley (*Hordeum Vulgares L.)* kernels in the sorption isotherm corresponding to $24^0$C. The data for $\Psi$ were derived from the experimental results of relative permittivity and loss factor measured at 2.45 GHz and nine moisture levels from 8.2 % to 25.1 %,(wet basis) all taken from the literature. These values of relative permittivity for bulk materials were then converted to those for solids with the help of eight equations for effective permittivity of random media, such as the logarithmic law of mixing. With these data, quadratic model for variation of two dielectric properties, relative permittivity and loss factor, as functions of decimal moisture contents, have been proposed. Four[Equilibrium Relative Humidity (ERH)/Equilibrium moisture content (EMC)] sorption isotherms were converted to $a_w/\Psi$ type of sorption isotherms. The comparative goodness-of-fit for the four different isotherms was quantified through sigmoidal curve -fitting technique. The evaluated parameters showed that Modified Henderson Equation (MHE) provided the best fit with experimental results having minimal [chi-square/degrees of freedom (DOF)]$\approx 7.65\times10^{-12}$ and maximum coefficient of determination ($r^2$) $\approx$0.9999. Consequently, it was supposed to be the most appropriate model in predicting sorption processes of spring barley kernels for the chosen range of temperature and water activity.

## KEYWORDS

Water activity;
Density-independent microwave permittivity function;
Spring barley;
Sorption sotherms;
Modified henderson equation;
Modified chung-Pfost equation;
Modified halsey equation;
Modified oswin equation.

## INTRODUCTION

Data relating equilibrium moisture content (EMC) to equilibrium relative humidity (ERH) for hygroscopic particulate materials, like grains and cereals, are needed for designing post harvest processing, aeration, storage, drying as well as for mathematical modeling of such systems. The adsorption plays a significant role in chemical reaction of foodstuffs[1-2]. A number of theoretical and empirical sorption isotherm equations have been developed for the ERH/EMC relations for grains, at different temperatures. On the bases of reviews of a series of papers on a number of cereals sorption isotherms[3], opined that a standard method for the determination of sorption isotherms should be established. A survey of literature shows that available sorption isotherm moisture data for grains are inconsistent due to the effects of variety, harvest year, maturity, methods of treatment of crops in drying or in methodology of measurement. A series of works on different types of grains endorsed the view that no single model could adequately fit the experimental ERH/EMC data for all foods tested. The concept of water activity ($a_w$) has been used as a tool for reliable assessment of microbial growth, lipid-oxidation, non-enzymatic and enzymatic activation and the texture mouth feel of foods following manufacture. Water activity and corresponding moisture content at a given temperature are characterized by the water-sorption isotherms. Water-sorption isotherms are used to evaluate the storage stability and are employed in process design and control, such as in predicting the end-point of drying and optimizing ingredient selection in food formulations[4]. Further, the knowledge of sorption models of a given product is useful in modeling drying process. Thus, it may be assumed that these studies may be able to provide data to draw a generalized food stability map with regard to water activity in food materials. This may prove valuable in maintaining stability in food packaging requirement. Although water activity ($a_w$) is the thermodynamic measure linked with water bonding in the food matrix, from an engineering standpoint, it is equal to decimal ERH of air. It is also related to surface interaction energy of the material at a given temperature Labuza et al.[5] and then Labuza alone[6] conducted a number of studies based on water activity measurements. Further, a separate study on model food material, animal gelatin gel, has explored the possibility of accessing information on water activity via dielectric measurements[7]. The present study was proposed to be confined to a single grain i.e. for spring barley kernels. It encountered the difficulty in that sorption isotherms and the different established ERH/EMC models like Modified Henderson equation (MHENDE), Modified Chung Pfost equation (MCPE), Modified Halsey equation (MHALE), and Modified Oswin equation (MOSE), etc. for spring barley kernels were available for study[8], while most of the available dielectric properties' data were those for bulk materials. The corresponding estimated values for solid materials (kernels) were proposed through extrapolations or model-fittings or through the use of dielectric mixture equations for random media. Density-variation is another major disturbing factor in dielectric measurements. Since the dielectric properties of grains are dependent both on density and moisture content, sensing moisture content in flowing grain is usually difficult, because the dielectric sensors cause errors in moisture and density measurements in flowing grains[9]. As regards the frequency of operation/measurement, microwaves were always preferred to lower frequencies in that the effects of ionic conductivity and bound-water relaxation were supposed to disappear almost completely at microwave frequencies, especially above 5-10 GHz[10]. A considerable study has been devoted to the development of density- independent permittivity functions by several workers[11-15]. Generally, the functions are in the form of ratio of relative permittivity to dielectric loss factor of granular materials or its inverse, with additional constants and powers. Alternatively, the ratio of microwave phase shift to attenuation coefficients (or its inverse) are used. Successful application of these tools is supposed to materially improve the accuracy of on-line moisture sensing for practical uses. The objectives of this study were:

- to convert the data of measured relative permittivity of bulk spring barley samples at different moisture contents (wet basis) corresponding to 2.45 GHz to those of kernels with the help of eight dielectric mixture equations for random media[16]
- to use authors' quadratic models connecting relative permittivity and loss factor of kernels to the moisture content (wet basis)[16], for applying least-squares-fit method for nonlinear regression with experimental data points in order to get the values of $\varepsilon_2'$ and $\varepsilon_2''$ for different computed values of m.
- to convert the moisture content, wet basis, into that on dry basis with the help of equation (2) to fit them suitably into four ERH/EMC equations, all of which contained % moisture content, dry basis, terms.
- to modify the four ERH/EMC equations namely MHENDE, MCPE, MHALE, and MOSE, to represent $a_w$ as a function of a suitable density-independent permittivity function for spring barley kernels.
- to study the curve of spring barley kernel samples

in the light of proposed four $a_w/M_w$ models and consequent $a_w/\Psi$ plots, to evaluate their comparative performances through the criteria of goodness-of-fit like the values of coefficient of determination ($r^2$), standard deviation (SD), mean relative deviation (p), Chi-square/ DOF etc.

## MATERIALS AND METHODS

The four ERH/EMC models namely MHENDE, MCPE, MHALE, and MOSE, chosen for their modifications in the present study, were taken from the work of Basunia and Abe[8]. Test materials specifications and experimental methods for measurements are described in those works[1,8,17-21]. To restrict the study in the microwave region of frequencies, data of measured values of relative permittivity at 2.45 GHz were taken from Nelson's works[18] and those of dielectric loss factor were derived from the plot of loss factor vs. moisture content at the same frequency[20] (Figures 1 and 2). Keeping in view that at microwave frequencies, especially above 3 GHz, the temperature dependence of relative permittivity and loss factor are minimal[22-23], it was intended to reckon these data of ε' and ε" corresponding to $24^0$C almost identical to those for $25^0$C. These data were used to create data points for density-independent dielectric function (Ψ) for replacing M by Ψ in ERH/EMC models and plots to obtain $a_w/\Psi$ models and plots for the present study. The second point of anomaly was that all the ERH/EMC models contained terms relating to % moisture content, dry basis, whereas the authors' models were concerned with the variation of ε' and ε" as functions of decimal moisture content, wet basis. In order to remove the anomaly, use of the conversion equation was made[24]. The relation reads as follows:

$$\mathbf{m_d = m_w/(1 - m_w)} \tag{1}$$

$$\mathbf{\Rightarrow M_d = 100\, m_d = M_w/(1 - 0.01\, M_w)} \tag{2}$$

The density-independent permittivity function used in this study is the ratio of attenuation coefficient (A/t) to phase coefficient (Q/t), as is given below :

$$\mathbf{\Psi = C\, \varepsilon'' / (\varepsilon' - \varepsilon'')} \tag{3}$$

where, C(=0.0758) is the constant numerical coefficient, and 't' is the thickness of the sample in the direction of the propagation of microwaves used.

### Mathematical models

The proposed models are:

$$\mathbf{\varepsilon_2' = am^2 + bm + K_1} \tag{4}$$

$$\mathbf{\varepsilon_2'' = cm^2 + dm + K_2} \tag{5}$$

The four ERH/EMC models namely, MHENDE, CPE, MHALE, and MOSE, in modified form, renamed as $a_w$ / EMC models, read as follows:

$$\text{(i) MHENDE: } \mathbf{a_w = 1 - [Exp(-A(T+C)\,(M_w/(1-0.01M_w))^B]} \tag{6}$$

$$\text{(ii) MCPE: } \mathbf{a_w = Exp[(-A/(T+C)\,Exp(-B(M_w/(1-0.01M_w))]} \tag{7}$$

$$\text{(iii) MHALE: } \mathbf{a_w = Exp[-exp(A+B)\,(M_w/(1-0.01M_w))^{-C}]} \tag{8}$$

$$\text{(iv) MOSE: } \mathbf{a_w = [((A+BT) \div (M_w/(1-0.01M_w))^{+C} + 1)]^{-1}} \tag{9}$$

### Procedures for data acquisition

The values of constants $K_1$(1.72) and $K_2$ (0.037) were estimated through the interpolation of plots of experimental results of relative permittivity and loss factor as function of moisture content, taken from the literature[18,20]. The $K_1$ and $K_2$ are the values of relative permittivity and loss factor, respectively, corresponding to M = 0. The method for evaluation of $\varepsilon_2'$ and $\varepsilon_2''$ as functions of m may briefly be described as follows:

Using any measured value of $\varepsilon_r(=\varepsilon')$ and corresponding values of $\rho_b$ and $\rho_k$, and hence the value of volume fraction of the inclusion material (f), $\varepsilon_2'$ was calculated using any of the eight equations. The two sets of constants viz (a, b) and (c, d) of the equations (4) and (5) of the present study, were evaluated by using the least-squares-fit method for second order polynomial regression, with the data of measured relative permittivity and loss factor as functions of decimal moisture content. Using the computed constants for equation (4) i.e. (a, b), and computed value of $\varepsilon_2'$, the value of m was computed. The constants 'c' and 'd' being known, the same values were put in the equation (5) to get the value of $\varepsilon_2''$. The same process was repeated for different f's and also for different eight dielectric mixture equations, one by one, to get data points for $\varepsilon_2'$ and $\varepsilon_2''$ as functions of computed values of m. The values of $\varepsilon_2'$ and $\varepsilon_2''$ corresponding to a given value of m were then converted to the values of Ψ for this set, using equation (3). The process was repeated for all the values of m as derived through the eight dielectric mixture equations. Only the data corresponding to unacceptable computed values of m, like m>1, were omitted from further computations for Ψ. Thus, four sets of data for $a_w$ corresponding to each computed value of m(=$M_w$/100) were obtained through four $a_w/M_w$ equations i.e., equations(6)-(9), and thus four $a_w/\Psi$ plots (sorption isotherms) were drawn. Parameters were evaluated for all the four models, using second and third order polynomial regression as well as sigmoid fit method for curve fitting with data points. This method of analysis eventually paved the way for finding a correlation between dielectric properties and water activity in spring barley kernels.

## RESULTS AND DISCUSSION

Data of measured values of moisture content (%, wet basis), volume fraction of material in the mixture, relative permittivity, and loss factor of bulk samples of spring barley as derived from Nelson's works[18,20] at nine moisture levels of 8.2% to 25.1%, measured at 2.45 GHz and 24°C are presented in TABLES 1 and 2 contains the evaluated constants and parameters for the two models proposed through equations (4) and (5), using the method of least-squares-fit for non-linear regression analysis. The data were combined together to have a single set of 45 data points for $\Psi$ as functions of $a_w$. Using constants, such as A, B, and C, for adsorption, all at 24°C, data points for $a_w$, for each of the four ERH/EMC models, were obtained in the present study. In an attempt at adsorption isotherms of spring barley kernels, the data points for adsorption, were used in a single $a_w/\Psi$ plot. The curve fitting was done adsorption data points. A software called "ORIGIN-6.1" was used to estimate the parameters and quantitative statistical standards or comparison criteria for different models namely, (Chi-square/degrees of freedom), coefficient of determination ($r^2$), standard deviation (SD), and mean relative error (p). Since the sorption isotherms obtained in this investigation presented sigmoid shapes as expected from previous studies, "sigmoidal fit" analysis was used along with second and third order polynomial regression for curve-fitting with data points, to evaluate the comparative goodness-of-fit of the different models. In spite of the conclusive remarks like "Modified Henderson and Chung-Pfost equation are suitable for most starchy grains like barley, corn, rice, wheat and high fiber materials like crn cobs and peanut hull as found in literature[1], all the four models were proposed to be retained in the present study in order to see their quantitative comparative goodness-of-fit in sorption isotherms of spring barley kernels. The different plots were

**TABLE 1: Measured values of relative permittivity of spring barley at 24°C and 2.45GHz at the indicated % moisture contents (wet basis) and volume fractions of the inclusion material in the mixture**

| Moisture content % | Volume fraction (f) | Measured values of relative permittivity and loss factor of the bulk material | |
|---|---|---|---|
| | | Relative permittivity ($\varepsilon'$) | Loss factor ($\varepsilon''$) |
| 8.2 | 0.473 | 2.05 | 0.284 |
| 11.3 | 0.485 | 2.28 | 0.328 |
| 12.8 | 0.488 | 2.36 | 0.375 |
| 14.9 | 0.484 | 2.54 | 0.409 |
| 17.4 | 0.48 | 2.68 | 0.437 |
| 19.7 | 0.484 | 2.92 | 0.484 |
| 21.1 | 0.481 | 3.05 | 0.512 |
| 23.4 | 0.463 | 3.26 | 0.575 |
| 25.1 | 0.459 | 3.17 | 0.597 |

**TABLE 2: Coefficients for quadratic regression equation relating relative permittivity $\varepsilon'$, and loss factor $\varepsilon''$, to decimal moisture content, m, (wet basis), of spring barley kernels (*Hordeum Vulgares L.)* at 2.45 GHz and 24°C in the light of authors' proposed model**

| Quadratic model for | Moisture range (%) | Constants |
|---|---|---|
| (A) Relative permittivity | 8.2-25.1 | |
| ($\varepsilon'$) | | a = –0.3256<br>b = 7.3844<br>$k_1$= 1.45<br>$r^2$= 0.999<br>Average % error of prediction = 1.408 |
| (B) Loss factor | 8.2-25.1 | |
| ($\varepsilon''$) | | c = –0.4760<br>d = 2.0891<br>$k_2$= 0.01<br>$r^2$= 0.999<br>Average % error of prediction = 0.406 |

**TABLE 3 : The comparison criteria[a] for sigmoid fittings in different models of $a_w$ vs. $\Psi$**

| Equation | Chi-square/D.O.F | $r^2$ |
|---|---|---|
| MHE :<br>Adsorption | 7.6511E-12 | 0.99985 |
| MCPE:<br>Adsorption | 1.34304E-10 | 0.99992 |
| MHALE:<br>Adsorption | 1.11264E-8 | 0.99976 |
| MOSE :<br>Adsorption | 3.30782E-9 | 0.99985 |

[a] Smaller values of (chi-squared / D.O.F.) and greater values of $r^2$ indicate better model performance

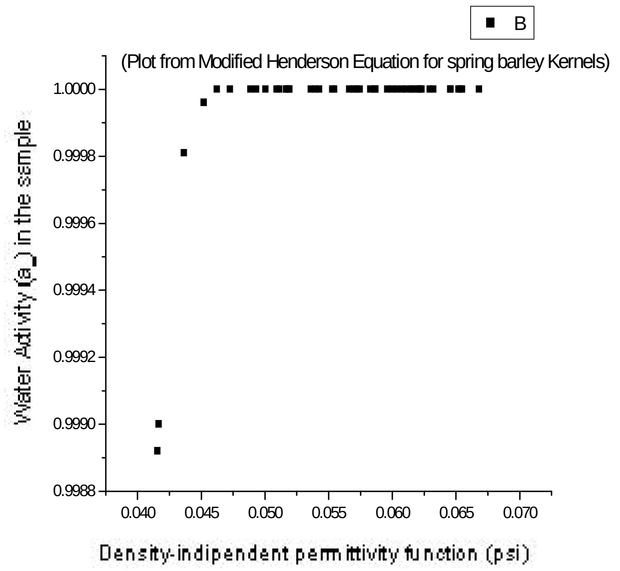

**Figure 1 : Variation of water activity(aw) as a function of density-independent permittivity function (psi) in a adsorption isotherms at $24^0$C and 2.45 GHz, for spring barley kemels, in the light of modified Henderson equation**

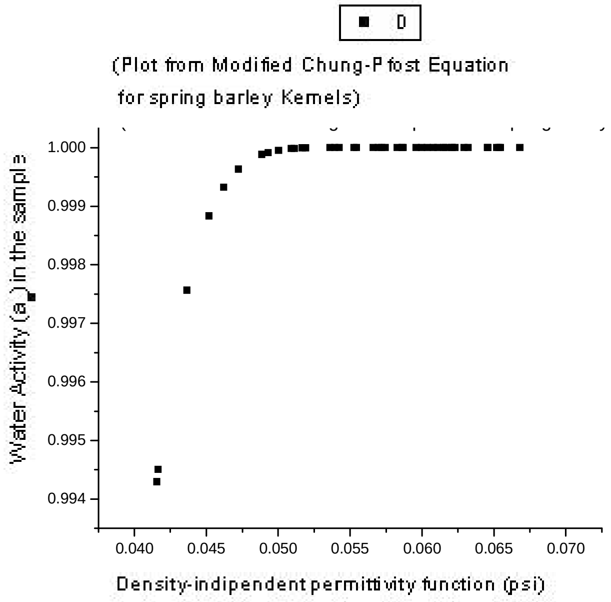

**Figure 2 : Variation of water activity(aw) as a function of density-independent permittivity function (psi) in a adsorption isotherms at $24^0$C and 2.45 GHz, for spring barley kemels, in the light of modified Chung-Pfost equation**

also drawn with the help of the same software "ORIGIN-6.1". The comparison criteria for the different models aquired through sigmoid fits are listed in TABLE 3. The plots for $a_w/\Psi$ for the four models namely, MHENDE, MCPE, MHALE, and MOSE are illustrated in figures 1,2,3 and 4 respectively. Data for spring

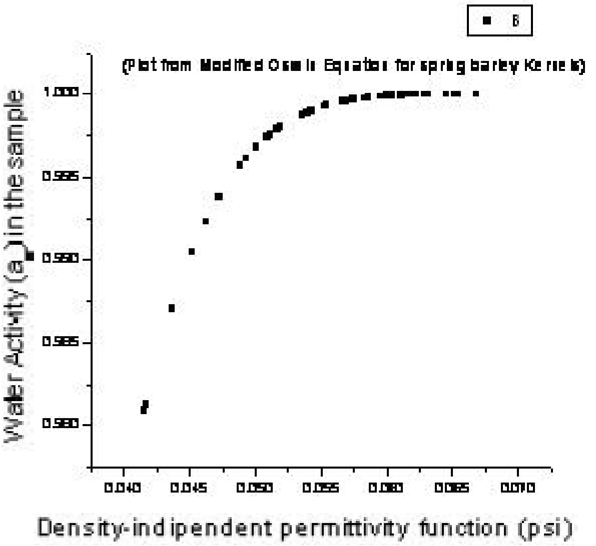

**Figure 3 : Variation of water activity(aw) as a function of density-independent permittivity function (psi) in a adsorption isotherms at $24^0$C and 2.45 GHz, for spring barley kemels, in the light of modified Oswin equation**

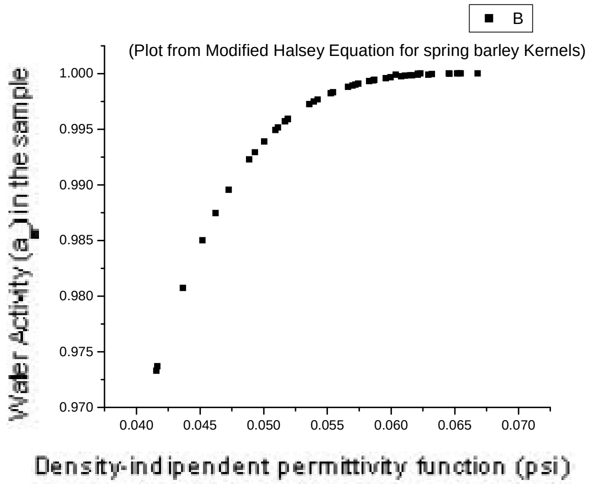

**Figure 4 : Variation of water activity(aw) as a function of density-independent permittivity function (psi) in a adsorption isotherms at $24^0$C and 2.45 GHz, for spring barley kemels, in the light of modified Halsey equation**

barley fitted to different regression equations and their analysis revealed that with second as well as third-order polynomial regression equations in all the tested models (MHE, MCPE, MOSE and MHALE) provided poor fittings (having $r^2 \approx 0.7$-0.8). Sigmoidal-fit in MOSE, and MHALE and their analysis showed poorear fittings as compaired to MHE and MCPE. MHE provided the fitting in having maximum $r^2(\approx 0.9999)$ and minimum value of [((chi-square)/(dof)) $\approx 7.65\times10^{-12}$].

MCPE also provided an acceptable fit in having ((chi-square)/(dof))$\approx 1.34\times 10^{-10}$ and $r^2 \approx 0.9999$. Further, the values obtained from statistical analysis are considered at 99.99% confidence level ($p<0.0001$), in all test cases. Although, graphical data were available in the literature[8] but for want of sufficient accurate tabular experimental data points for ERH/EMC, the analysis through residual plots as function of different predicted values, which otherwise, would have been a valuable tool for diagnosis, could not be made in the present study. Analysis through the well-accepted modified Guggenheim-Anderson-de Boer (GAB) equation could not be made for want of parameters and constants required for the study.

### Nomenclature

| | |
|---|---|
| $Q_s$ | Surface interaction energy, kJ/mole |
| R | Universal gas constant, in Equation (1) only [=8.314 J $mol^{-1}K^{-1}$] |
| $m_d$ | Decimal moisture content, dry basis |
| $m_w$ | Decimal moisture content, wet basis |
| $M_d$ | Moisture content, % dry basis |
| $M_w$ | Moisture content, % wet basis |
| w | Moisture content (kg water/kg dry mass) at water activity $a_w$ |
| $\varepsilon'$ | Relative permittivity of bulk material |
| $\varepsilon_2'$ | Relative permittivity of particles (kernels) |
| $\varepsilon''$ | Dielectric loss factor of bulk material |
| $\varepsilon_2''$ | Dielectric loss factor of particles (kernels) |
| $a_w$ | Water activity (decimal), dimensionless |
| T | Temperature ($^0$C), except in Equation 1, where it is in Kelvin (K) |
| A, B and C | Model parameters having their different values for different models |
| $\Psi$ | Density-independent microwave permittivity function, as defined by equation (3) of the present study |
| F | Volume fraction of the material in the mixture, also equal to the ratio of bulk density ($\rho_b$) to kernel density ($\rho_k$) of the material |
| h | hour |

## CONCLUSIONS

Results concern of dielectric parameter namely density independent permittivity function ($\Psi$) of spring barley correlated to water activity ($a_w$) of the material samples in the light of four $a_w/M_w$ models, modified from the corresponding four ERH/EMC models viz. Modified Henderson equation (MHENDE), Modified Chung Pfost equation (MCPE),Modified Halsey equation (MHALE), and Modified Oswin equation (MOSE), for adsorption isotherms, corresponding to 24$^0$C. The sorption isotherms may prove their candidatures for being used in evaluating the storage stability, in modeling of drying processes' design and control for grains in general, and spring barley kernels in particular. The modified Henderson and Chung-Pfost equations proven themselves to give better fits.

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