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Modelling of sorption isotherms of corn 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 (Ψ) for corn(*zea mays, L.*) kernels in the sorption isotherm corresponding to 25^{0}C. The data for Ψ were derived from the experimental results of relative permittivity and loss factor measured at 2.45 GHz and six moisture levels from 10.3% to 33.4 %, 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/Ψ type of sorption isotherms. From the study, it transpired that small hysteresis was shown by almost all the models, except in Halsey's, which manifested a large amount of hysteresis. The comparative goodness of fit for the four different isotherms was quantified through sigmoidal curve -fitting technique. The evaluated parameters showed that Modified Chung-Pfost equation (MCPE) provided the best fit with minimal [chi-square/ degrees of freedom(DOF)]$\approx 9\times10^{-9}$-9×10^{-6} and maximum coefficient of determination (r^2) $\approx$0.94-0.99. Consequently, it was supposed to be the most appropriate model in predicting sorption processes of corn kernels for the chosen range of temperature and water activity.

KEYWORDS

Water activity;
Density-independent microwave permittivity function;
Corn;
Sorption isotherms;
Modified henderson equation;
Modified Chung-Pfost equation;
Modified Halsey equation;
Modified Oswin equation;
Monolayer values.

INTRODUCTION

Data relating equilibrium moisture content (EMC) to equilibrium relative humidity (ERH) for hygroscopic particulate materials, like grains and cereals, are needed for designing postharvest processing, aeration, storage, drying as well as for mathematical modeling of such systems. The difference in EMC's at desorption and adsorption is called hysteresis effect and it plays a significant role in chemical reaction of foodstuffs[1-3]. 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 corn sorption isotherms[4], 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[5]. Further, the knowledge of sorption models of a given product is useful in modeling drying process. 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, Acott, Tatini, Lee, Flink and McCall[6] and then Labuza alone[7] conducted a number of studies based on water activity measurements. Further, a separate study on model food material, animal gelatin, has explored the possibility of accessing information on water activity via dielectric measurements[8]. The present study was proposed to be confined to a single grain i.e. for corn 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 corn kernels were available for study[3], while most of the available dielectric properties' data were 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 5GHz[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 vice versa, with additional constants and/or 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 corn 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].
- 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 ε_2' and ε_2'' for different computed values of m.
- Convert the moisture content (wet basis) into that on dry basis with the help of equation (3) to fit them suitably into four ERH/EMC equations, all of which contained % moisture content, dry basis, terms.
- 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 corn kernels.
- Study the hysteresis effect in corn kernel samples in the light of proposed four a_w/M_w models and con-

sequent a_w/Ψ plots, to evaluate their comparative performances through the criteria of goodness-of fit like the values of coefficient of determination (r^2),standard dev.

MATERIALS AND METHODS

Materials

The four ERH/EMC models namely MHENDE, MCPE, MHALE, and MOSE, chosen for their modifications in the present study, were taken from the Chen's works[3].Test materials' specifications and experimental methods for measurements are determined in the same papers[3,17-19] 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[19] and those of dielectric loss factor were derived from the plot loss factor vs. moisture content at the same frequency[20]; Figure 1. At this juncture, two difficulties were encountered-one in that the data for ε´ and ε´´ were for 24^{0}C whereas there were no such ERH/EMC data available for corn kernels corresponding to 24^{0}C, for their constants and parameters to be used in the study. The data corresponding to 25^{0}C were available in the cited literature[3]. As is evident from equation (33) of the literature[20], the increment in relative permittivity corresponding to a change of 1^{0}C (25^{0}C-24^{0}C) of temperature is ≈0.013 only. On the other hand, the loss factor could increase or decrease for this small increase in temperature, depending on whether the operating frequency was higher or lower than the relaxation frequency[21]. Further, keeping in view that at microwave frequencies, especially above 5-10 GHz, the temperature dependence of loss factor is minimal [10,22], 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/Ψ 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[23]. The relation reads as follows:

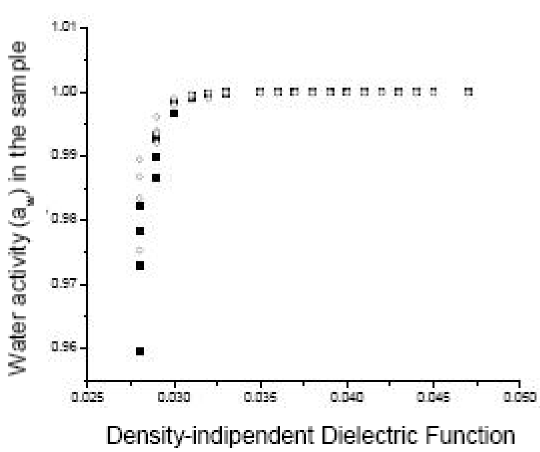

Figure 1: Variation of water activity (aw) as a function of density-independent permittivity function in desorption/ adsorption isotherms at 25^{0}C and 2.45 GHz, for corn kernels, in the light of Modified Henderson equation. ■ Data points for desorption; ◦ Data points for adsorption

$$m_d = m_w/(1 - m_w) \quad (1)$$

$$\Rightarrow M_d = 100 m_d = M_w/(1 - 0.01 M_w) \quad (2)$$

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

$$\psi = c\varepsilon''/(\varepsilon' - \sqrt{\varepsilon'}) \quad (3)$$

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

Mathematical models

$$\varepsilon_2' = am^2 + bm + K_1 \quad (4)$$

$$\varepsilon_2'' = cm^2 + dm + K_2 \quad (5)$$

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

(i) MHENDE:

$$\alpha_w = 1 - [\exp(-A(T + C)(M_w/(1 - 0.01M_w))^B \quad (6)$$

(ii) MCPE :

$$\alpha_w = \exp[(-A/(T + C)\exp(-B(M_w/(1 - 0.01M_w))] \quad (7)$$

(iii) MHALE :

$$\alpha_w = \exp[-\exp(A + B)(M_w/(1 - 0.01M_w))^{-C}] \quad (8)$$

(iv) MOSE :

$$\alpha_w = [1/\{(A + BT) \div (M_w/(1 - 0.01M_w))^{-C} + 1\}] \quad (9)$$

Procedures for data acquisition

The value of the constant K_1 in equation (5) was taken to be equal to the average of values derived from equations (36) and (37) of the Nelson's works[20] with the use of data contained in Table 6, for shelled yellow dent field corn, *zea mays*, *L.*, by putting M=0 in both the equations. The value of K_2 was equal to the value of loss factor derived from equation (41) of the same paper [20] and by taking the bulk density corresponding to M = 0 from equation (4) of Nelson's other paper [24]. The expression for K_2 may thus be given as:

$$K_2 = 0.146[(\rho_b)_0]^2 \qquad (10)$$

where $(\rho_b)_0 = 0.6829$ g/cm^3, for corn.

The method for evaluation of ε_2' and ε''as functions of m with the help of equations (14) and (6) may, briefly, be described as follows:

Using any measured value of $\varepsilon_r(=\varepsilon')$ and corresponding values of ρ_b and ρ_k, and hence the value of volume fraction of the inclusion material (f), ε_2' was calculated using any of the eight equations. The two sets of constants viz. (a, b) and (c, d) of the equations (5) and (6) 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 (5) i.e. (a, b), and computed value of ε_2', the value of m was computed. The same value was then put in equation (6) to get the value of ε_2'', on account of the constants c and d being known. 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 ε_2' and ε_2'' as functions of computed values of m. The values of ε_2' and ε_2'' corresponding to a given value of m, were then converted to the values of Ψ for this set, using equation (4). 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(7)-(10), and thus four a_w/Ψ plots (sorption isotherms) were drawn. Parameters were evaluated for all the four models, and also separately for desorption and adsorption, 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 corn 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 shelled yellow-dent field corn, *Zea mays, L.*, as derived from Nelsons works[19-20] at six moisture levels of 10.3% to 33.4%, measured at 2.45 GHz and 24^{o}C are presented in TABLE 1. TABLE 2 contains the evaluated constants and parameters for the two models pro-

TABLE 1 : Measured values of relative permittivity of shelled yellow-dent field corn at 24^{0}C and 2.45 GHz 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 (ε')	Loss factor (ε'')
10.3	0.582	2.47	0.30
12.2	0.581	2.59	0.37
17.7	0.568	3.20	0.63
19.5	0.563	3.59	0.69
22.9	0.550	3.98	0.80
33.4	0.517	5.25	0.85

TABLE 2: Coefficients for quadratic regression equation relating relative permittivity ε', and loss factor ε'', to decimal moisture content, m, (wet basis), of shelled yellow-dent field corn *Zea mays, L.* at 2.45 GHz and 24^{0}C in the light of authors' proposed model

Quadratic model for	Moisture range (%)	Constants
(A) Relative permittivity (ε')	10.3 - 33.3	a = 7.2307 b = 9.3904 k_1= 1.4456 r^2= 0.9994 Average % error of Prediction = 2.1684
(B) Loss factor (ε'')	10.3 - 33.4	c = 7.90057 d = 1.08605 k_2= 0.06808 r^2= 0.990 Average % error of Prediction = 3.3016

TABLE 3 : The comparison criteria[a] for sigmoid fittings in different models of a_w vs. Ψ

Equation	Model a_w/Ψ	Chi-square/D.O.F r^2
MHE :		
(a) esorption	1.09488E-5	0.88515
(b) Adsorption	4.18338E-6	0.88325
MCPE :		
(a) Desorption	9.00695E-6	0.94587
(b) Adsorption	5.72125E-6	0.94803
MHALE:		
(a) Desorption	1.06138E-5	0.98663
(b) Adsorption	2.75837E-7	0.98694
MOSE :		
(a) Desorption	1.72747E-10	0.97143
(b) Adsorption	4.33505E-9	0.98124

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

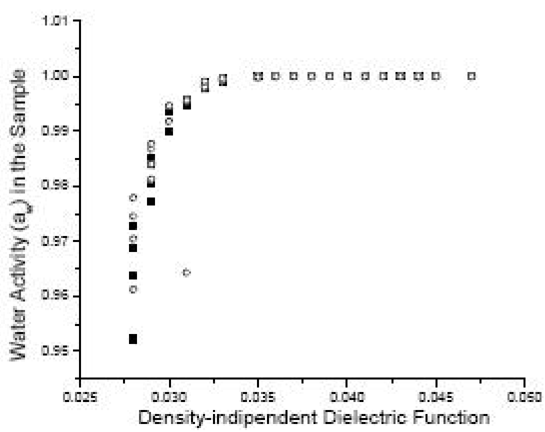

Figure 2: Variation of water activity (aw) as a function of density-independent permittivity function in desorption/ adsorption isotherms at 25°C and 2.45 GHz, for corn kernels, in the light of Chung-Pfost equation. ■ Data points for desorption; ◦ Data points for adsorption

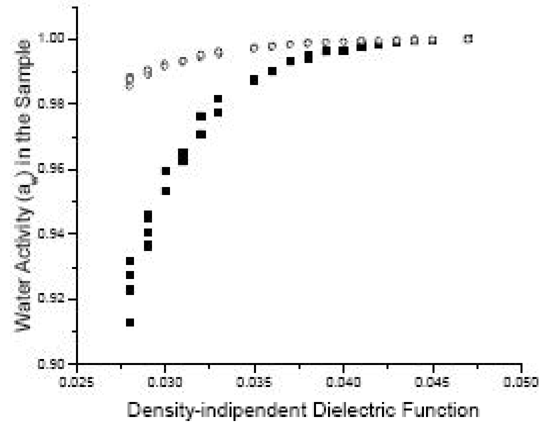

Figure 3: Variation of water activity (aw) as a function of density-independent permittivity function (R) in desorption/adsorption isotherms at 25°C and 2.45 GHz, for corn kernels, in the light of Modified Halsey equation. ■ Data points for desorption; ◦ Data points for adsorption

posed through equations (5) and (6), using the method of least-squares-fit for non-linear regression analysis. Using the two separate sets of constants, such as A, B, and C, for desorption and adsorption, all at 25°C, two sets of data points for a_w, for each of the four ERH/ EMC models, were obtained in the present study. In an attempt at finding hysteresis effect in sorption isotherms of corn kernels, the data points both for desorption and adsorption, were used in a single a_w/Ψ plot. The curve fitting was done separately for desorption and 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) etc. 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 Oswin equation can serve as an excellent model for popcorn, corncobs and some varieties of corn and wheat, found in literature[1], all the four models were proposed to be retained in the present study in order to see the comparative degree of hysteresis in sorption isotherms of corn kernels. The idea behind choosing Ψ, instead of relative permittivity and loss factor, separately, is that kernel densities as well as kernel volumes and weights exhibit a hysteresis in the desorption/adsorption cycles[25]. The different plots were also obtained with the help of the same software "ORIGIN-6.1". The comparison criteria for the different models acquired through sigmoid fits are listed in TABLE 3. The plots for a_w/Ψ for the four models namely, MHENDE, MCPE, MHALE, and MOSE are illustrated in figures 1,2,3 and 4 respectively. Examination of the fitting of data points with second and third order polynomials for a_w/Ψ plots, by taking four a_w/M_w models, both for desorption and adsorption isotherms, all at 25°C, revealed that with MHENDE, the second order polynomial regression gave poor fittings in having $r^2 \approx 0.60$ and

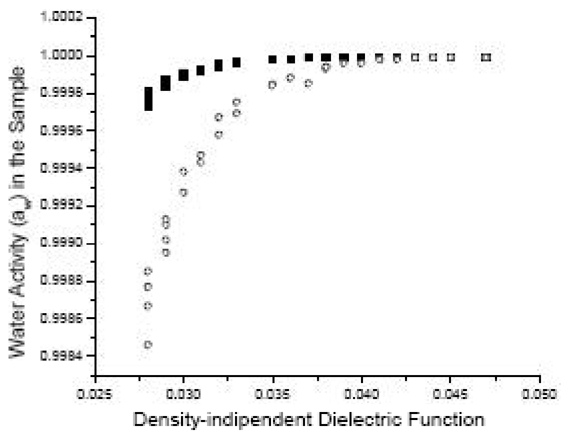

Figure 4: Variation of water activity (aw) as a function of density-independent permittivity function in desorption/ adsorption isotherms at 25^{0}C and 2.45 GHz, for corn kernels, in the light of Modified Oswin equation. ■ Data points for desorption; ◦ Data points for adsorption

SD˜0.004, but the third order polynomial regression for the same a_w/Ψ plot gave a better fitting, with $r^2 \approx$ 0.75-0.78 and S.D$\approx$0.003. Using second order polynomial regression with MCPE, the fitting was a bit improved in having $r^2 \approx 0.75$ and S.D.$\approx$0.005 - 0.006. The corresponding values for third order polynomial regression were: $r^2 \approx 0.88$ to 0.90 and SD$\approx$ 0.003, thus showing a further improvement in fit. With Modified Halsey Equation (MHALE), the comparison criteria for second order polynomial regression are: $r^2 \approx 0.95$-0.97 and SD$\approx 2.5\times10^{-5}$. The corresponding values for third order polynomial regression were: $r^2 \approx 0.97$-0.99 and SD$\approx 1.2\times10^{-5}$. Thus, fittings in both second and third order polynomial regression models, using MHALE, were a bit improved, and more so in third order. However, the quantitative hysteresis is also large with this model as compared with the other three models. With the Modified Oswin equation (MOSE), the r^2- and SD- values for the second and third order polynomial regression analysis were:

(i) Second order : $r^2 \approx 0.89$ - 0.93 and SD $\approx 2.5\times10^{-5}$ to 1.2×10^{-4}

(ii) Third order : $r^2 \approx 0.95$ - 0.98 and SD $\approx 1.2\times10^{-5}$ to 1.2×10^{-4}

Thus, from the brief data analysis given above, it is evident that the best fit was obtained with third order polynomial regression and also reasonably good sigmoid fit in MHALE. However, the hysteresis is maximum in this case. On the other hand, MOSE, yielded reasonably good fitting with third order polynomial as well as with sigmoid fits with minimal hysteresis. 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[1], 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.

CONCLUSIONS

Results concern two types of dielectric parameters namely, loss tangent (ratio of dielectric loss factor to relative permittivity, tanδ), and density independent permittivity function (Ψ) of shelled yellow-dent field corn 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 desorption and adsorption isotherms, separately, both corresponding to 25^{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 corn kernels in particular. The modified Chung-Pfost equation proven itself to give better fit with minimal hysteresis.

Although, the fitting was found to be much better with Modified Halsey model, but the hysteresis effect was found to be maximal with this model. Further, modified Oswin equation showed opposite trend of variation in that it gave slightly greater a_w for desorption than that for adsorption for the same value of Ψ, i.e., at a given moisture content, and that too almost over the entire range of variation. This conclusion posed a serious threat to its theoretical interpretation on physically sound grounds, when compared with the established modes (Basu et al., 2006). In other way it could be seen that for the same value of a_w, $\Psi_{ads} > \Psi_{des}$ i.e., $(EMC)_{ads} > (EMC)_{des}$ i.e., Hysteresis $[(EMC)_{des} - (EMC)_{ads}]$ was found to be negative.

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