



A viable mathematical model for seed moisture prediction in multiple species

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ABSTRACT

Modeling of seed sorption kinetics have been routinely applied for predicting the equilibrium moisture content (EMC) of processed products and the information is used for determining their drying and storage parameters. Similar information is also valid for the seed industry because moisture content of the stored seed would determine its longevity and quality. But in seed industry, the storage facilities are used for multiple species having distinct physical and biochemical characteristics and there is a need to explore and identify a single mathematical model that can comprehensively predict moisture sorption behaviour of a wide range of species. In the present study, the Modified Henderson model could effectively describe the sorption kinetics of Pea, Okra and Chilli and gave the best fit for the data, when analyzed using mean relative error (MRE, %), standard error of estimate/moisture (SEM) and randomness of residual pattern as observed in the residual plots.

Key words: Modeling, Multiple species, Prediction, Seed, Sorption

Moisture sorption kinetics has been widely utilized as an effective tool for predicting storage characteristics of different hygroscopic products. It causes rapid equilibration with the atmospheric humidity of the contact environment till the equilibrium moisture content (EMC) is attained. In food processing industry, the isotherm data is utilized for customizing their product-specific drying and storage facility. For this purpose, modeling of isotherm data using empirical mathematical models is essential. Appropriate mathematical models that can describe these isotherms have been assessed and validated for a very large number of products (Chen and Morey 1989, Iglesias and Chirife 1995, Belghith *et al.* 2016, Shi and Avramidis 2017). In the case of agricultural products, the recommended mathematical models are, the modified Chung–Pfof (Chung and Pfof 1967), modified Henderson (1952), modified Halsey (1948), modified Oswin (1946) and Guggenheim–Anderson–de Bour (GAB) (Van den Berg 1984) models (ASAE 1995). These mathematical models account for both relative humidity and temperature and hence are practically significant. Another model used for products stored at low moisture is the Brunauer–Emmett–Teller (BET) (Brunauer *et al.* 1938), because BET equation (and GAB model) provides

the monolayer moisture content, which is the bound form of water that predominates in dried products.

But unlike food industry, the seed storage structures are customized to function under a common range of temperature and relative humidity conditions that are fixed and based on the duration of storage. Currently there is no information on isotherm modeling of diverse crops using the recommended mathematical models, and the previous reports also do not provide any conclusive evidence on the applicability of a single model for different seed species. In the present study, the sorption data of three seed species having distinct physical and biochemical characteristics have been determined and subjected to analysis using multi-parameter mathematical prediction models, so as to identify the most comprehensive approach for determining drying and storage parameters by the seed industry sector.

MATERIALS AND METHODS

Equilibrium moisture content: The study was conducted at ICAR- National Bureau of Plant Genetic Resources during 2016-17. Freshly harvested seeds of chilli (Var. CH-1), okra (Pusa A4) and pea (Pusa Pragati) were used for the experiment. The equilibrium moisture content of the seeds was calculated during adsorption and desorption, through static gravimetric method, at 5, 25 and 40°C. Desorption data was generated using seeds that were previously equilibrated over distilled water, within a closed desiccator. For adsorption experiment, seeds were initially dried over P₂O₅ at room temperature, till a moisture content of <1% was attained. The experiment was conducted with 4±0.2 g

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seeds, each in three replicates. The samples were placed in plastic wire mesh bags and placed in equilibration with 5 different saturated solutions (Conc. H₂SO₄, LiCl₂, K₂CO₃, NaCl, KNO₃), within closed desiccators, at 5, 25 and 40°C. The samples were weighed on every alternate day till the gain or loss in weight was less than 0.001 g. The equilibrium moisture content was determined using standard hot air oven method (ISTA 2015). Sorption isotherms were then plotted using EMC data.

Mathematical prediction models: The description of the Equilibrium Moisture Content (M) -Relative Humidity (RH) relationship was verified by applying the following six models:

1. Modified Henderson: $M = \left[\frac{\ln(1-RH)}{-A(t+B)} \right]^{1/C}$

2. Modified Halsey: $M = \left[\frac{\exp(A+Bt)}{-\ln(RH)} \right]^{1/C}$

3. Brunauer, Emmett & Teller Model (BET):

$$M = \left[\frac{A}{1 - (RH)B} \right]$$

4. Modified Chung-Pfost:

$$M = \left[\frac{1}{-C} \right] \ln \left[\frac{(t+B)\ln(RH)}{-A} \right]$$

5. Modified Oswin: $M = (A+Bt) \left(\frac{RH}{1-RH} \right)^C$

6. Modified Guggenheim-Anderson-de Burer (GAB):

$$M = \frac{AB'C'(RH)}{[1 - B'(RH)][1 - B'(RH) + B'C'(RH)]}$$

$$B' = B \exp\left(\frac{h_1}{RT}\right)$$

$$C' = C \exp\left(\frac{h_2}{RT}\right)$$

The suitability of the equation was evaluated and compared using the mean relative error (MRE, %), standard

error of estimate/moisture (SEM) and randomness of residual pattern as observed in the residual plots (Chen and Morey 1989).

In residual plots, the difference between experimental and predicted EMC values (by the models) are plotted to confirm the predictive ability of sorption models. Randomness in the pattern of the plot indicates acceptability of the model. The residuals obtained for each model with its respective coefficients were plotted against measured EMC and were assessed visually for the nature of distribution of pattern. The constants of the equations were determined by non-linear regression analysis.

RESULTS AND DISCUSSION

Sorption isotherms: Fig 1, 2 and 3 show the adsorption and desorption isotherms of chilli, okra and pea seeds at 5, 25 and 40°C wherein a standard sigmoidal pattern has been recorded, with desorption curve over-lying the adsorption curve, irrespective of species and temperature, thereby giving rise to the hysteresis loop. The lower region (region I) of the curve (0-7.5% relative humidity) accounts for around 7% of the total moisture sorbed; the middle region or region II (up to 40% relative humidity) accounts for around 12% of the sorption and the upper region or region III (above 40% relative humidity) accounts for more than 80% of sorption. The sorption at region I was known to be associated with the strong binding sites of the seed tissues where the bound water has an enthalpy of vaporization considerably higher than that of pure water. At this stage the water molecules are bound to highly hydrophilic macromolecules like proteins and polysaccharides and form the initial monolayer within the seed. The region II involves the weak water binding sites and the moisture was held within the macromolecular matrix by capillary condensation. Region III involves the multi molecular sorption sites and the excess water was present in macro capillaries, the extent of which varies according to the moisture content of the seed (Sun 2002).

The EMC attained by the seeds at a specific RH was lowest in case of chilli and highest in pea. This is primarily due to the higher seed fat content (SFC) of chilli seeds

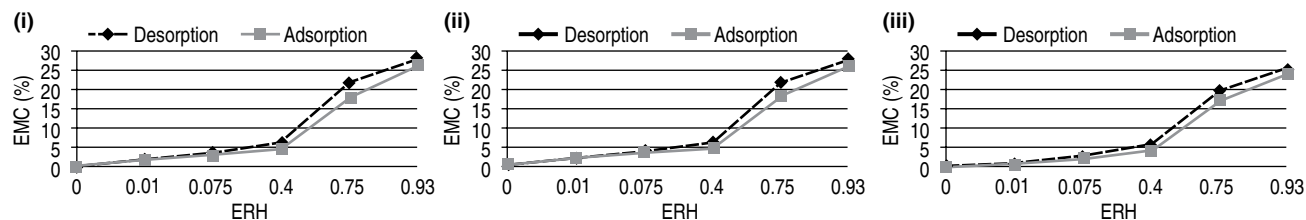


Fig 1 Desorption-adsorption isotherm of chilli seeds at (i) 5°C (ii) 25°C and (iii) 40°C.

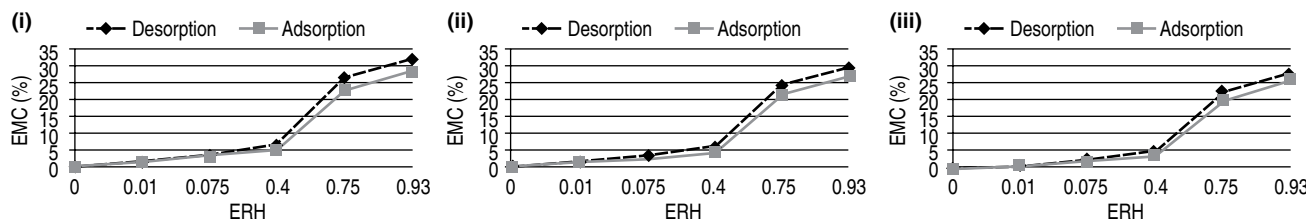


Fig 2 Desorption-adsorption isotherm of okra seeds at (i) 5°C (ii) 25°C and (iii) 40°C.

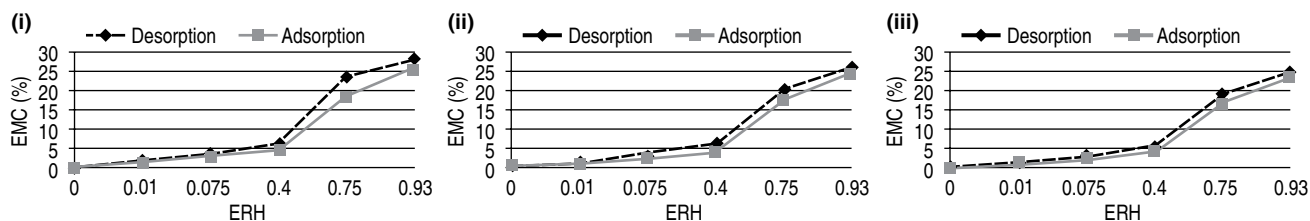


Fig 3 Desorption-adsorption isotherm of pea seeds at (i) 5°C (ii) 25°C and (iii) 40°C.

(upto 26%) as compared to both pea (around 2%) and okra seeds (around 18%). The SFC constitutes the hydrophobic component of seeds and thereby, proportionately regulates the equilibrium moisture content (Walters and Hill 1998). However, the chilli seeds recorded more rapid equilibration (minimum time to reach EMC) at a specific RH, owing to its larger surface area per unit weight. Pea seeds have a high proportion of hydrophilic carbohydrate and protein molecules that easily bond with water molecules and also have low SFC, due to which it recorded highest EMC

amongst the three species.

The area under the hysteresis loop is known to have direct negative correlation with the quality of seeds during storage (Nagarajan *et al.* 2005). All three species recorded a lowering of hysteresis effect, with increase in temperature. When dehydration is initiated during the desorption process, higher temperature leads to lowering of EMC values since the moisture equilibrium shifts towards the vapour phase due to gain in kinetic energy. This dynamic equilibrium between the adsorbed water and its vapour form is more apparent at

Table 1 Estimated values of different parameters of various prediction models for desorption isotherms

Species	Parameter	Models					
		Modified Henderson	Modified Halsey	BET	Modified Chung-Pfost	Modified Oswin	Modified GAB
Chilli	A	0.00009	4.419	-2.15	725.6	11.39	3321.9
	B	215.2	-0.00627	1.45	143.8	-0.03230	1.7
	C	0.696	0.487	-	0.151	-0.381	0.0002
	H1	-	-	-	-	-	-9.851
	H2	-	-	-	-	-	2017.0
	MRE	29.86	58.19	139.9	45.97	26.39	160.89
	SEM	2.027	3.307	11.51	2.54	2.62	11.47
	Residual plot pattern	Random	Random	Systematic	Random	Random	Random
	Rank	1			2	3	
Okra	A	0.00010	4.665	-2.60	630.0	12.98	5372.8
	B	182.0	-0.00718	1.450	129.8	-0.0422	0.498
	C	0.705	0.489	-	0.131	-0.384	0.0017
	H1	-	-	-	-	-	-1148.9
	H2	-	-	-	-	-	4481.9
	MRE	34.28	76.727	155.01	60.604	39.223	167.95
	SEM	3.125	4.652	12.58	3.643	3.90	13.79
	Residual plot pattern	Random	Random	Systematic	Random	Random	Random
	Rank	1			2	3	
Pea	A	0.0002	4.47	5.08	459.9	11.59	11843.5
	B	113.2	-0.0104	0.875	86.0	-0.053	1.73
	C	0.694	0.486	-	0.154	-0.380	0.000026
	H1	-	-	-	-	-	-66.44
	H2	-	-	-	-	-	3903.3
	MRE	30.36	65.64	89.59	53.68	31.46	177.68
	SEM	2.29	3.61	3.765	2.821	2.946	11.29
	Residual plot pattern	Random	Random	Systematic	Random	Random	Random
	Rank	1			2	3	

Table 2 Estimated values of different parameters of various prediction models for adsorption isotherms

Species	Parameter	Models					
		Modified Henderson	Modified Halsey	BET	Modified Chung-Pfost	Modified Oswin	Modified GAB
Chilli	A	0.00012	3.718	-2.052	822.9	9.34	578.3
	B	337.7	-0.004	1.461	179.3	-0.0204	1.188
	C	0.794	0.525	-	0.1654	-0.418	0.0002
	H1	-	-	-	-	-	-10.599
	H2	-	-	-	-	-	1413.7
	MRE	39.047	49.25	146.9	57.307	25.48	180.52
	SEM	1.781	2.683	10.35	2.521	2.202	10.205
	Residual plot pattern	Random	Random	Systematic	Random	Random	Random
	Rank	1			3	2	
Okra	A	0.00009	4.086	5.054	861.9	10.82	890.1
	B	328.9	-0.004	0.888	199.7	-0.023	1.177
	C	0.76	0.513	-	0.143	-0.406	0.00015
	H1	-	-	-	-	-	19.29
	H2	-	-	-	-	-	1644.5
	MRE	38.57	78.44	107.8	70.70	40.14	204.67
	SEM	2.71	4.08	4.12	3.29	3.43	12.19
	Residual plot pattern	Random	Random	Systematic	Random	Random	Random
	Rank	1			2	3	
Pea	A	0.00018	3.66	4.14	687.9	9.21	3.15
	B	227.4	-0.0060	0.898	153.8	-0.028	0.018
	C	0.794	0.53	-	0.168	-0.42	3.76E-10
	H1	-	-	-	-	-	10972.5
	H2	-	-	-	-	-	47361.1
	MRE	38.19	61.93	88.62	65.18	26.55	220.66
	SEM	1.798	2.861	2.995	2.506	2.328	10.007
	Residual plot pattern	Random	Random	Systematic	Random	Random	Random
	Rank	1			3	2	

higher water activity levels (Region III of sorption curve).

Best fit mathematical model: The estimated values of the parameters of all mathematical models used in the present study are listed in Tables 1 and 2. The main criteria to select models are the adjustment degree to experimental data and how simple the model is (Furmaniak *et al.* 2007). The reliability of the six models has been further validated by plotting the residuals of ERH.

Modified Henderson and Modified Oswin models had significantly lower values of MRE and SEM as compared to the other models, thereby indicating the probable application of both these models for a comprehensive assessment of multiple species. The MRE values were lowest in Modified Henderson model, for adsorption and desorption values of Bhindi and desorption value of Pea. But for both sorption isotherms of chilli and adsorption isotherm of pea, Modified Oswin had the MRE. In case of SEM, the values were consistently lower in Modified Henderson model for both desorption and adsorption isotherms of all the three crops.

But, it has been established that the standard error of estimate alone may not be sufficient evidence for the goodness-of-fit of a moisture sorption isotherm model (Aviara *et al.* 2006). The pattern of the residual plots is the crucial determining factor in such instances. A model should not be accepted if the residual plots indicate a clear pattern. In desorption residual plots, Modified Halsey, Modified Henderson and Modified Oswin qualified as suitable models based on the pattern of distribution. Modified BET and modified GAB were disqualified owing to the uniformity of their patterns. Similar trend was observed in the adsorption plots also, but there was a greater tendency for uniformity in the adsorption plots as compared to the desorption plots. From a comparison of the MRE and SEM values along with the residual patterns, it could be concluded that Modified Henderson model is best fit for describing the desorption and adsorption isotherms of all the three species. This model is adequate to be used for planning or evaluating the storage conditions of multiple seed species. The model has also been

reported to be the best model for predicting the EMC of cereal grains, lentils (Cenkowski *et al.* 1989), pearl millet (Goneli *et al.* 2010) and rapeseed (Raj kumar *et al.* 2011). This indicates the universal applicability of this model for a wide range of seed species. There can be exceptions in certain crops, where alternate models may give better fit of the data. But since this model can effectively predict the EMC of a wide range of species, it is the best practical tool for adding precision to seed processing and thereby ensuring safe storage.

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