WATER SORPTION BEHAVIORS OF COTTONSEED MEAL, WASHED COTTONSEED MEAL, AND COTTONSEED PROTEIN ISOLATE

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Because of their hygroscopic characteristics, equilibrium moisture contents of agricultural products and byproducts are very important for their quality. Defatted cottonseed meal (CSM), washed cottonseed meal (WCSM), and cottonseed protein isolate (CSPI) can be used as an energy and protein source for animal feedstuff or industrial raw materials. Information on their moisture adsorption behaviors is needed for their storage conditions and quality control. Thus, this work measured the equilibrium moisture sorption isotherms of CSM, WCSM and CSPI, at 15, 25, 35 and 45 ^{0}C. When the moisture contents of the samples were compared at a constant temperature, the general trend of decreasing moisture content was in the order of CSPI < WCSM < CSM at water activity < 0.6, but the trend reversed to the order of CSM < WCSM < CSPI at water activity > 0.6. Modelling results indicated that the G.A.B. model was a consistently good fit for the data among all sample types and all temperatures. This work provides useful insight on designing or selecting appropriate procedures for the handling, aeration, storing and processing of these cottonseed meal products.

Introduction

In view of their hygroscopic characteristics, agricultural products and byproducts are often studied for their equilibrium moisture contents (Alpizar-Reyes et al., 2018; Taitano et al., 2012; Verbeek and Koppel, 2012). Excessive critical moisture content would promote hydrolytic/enzymatic cleavage of macromolecules in these natural products. Defatted cottonseed meal (CSM) and its water washed product (washed cottonseed meal -WCSM) appear promising as renewable and green industrial raw materials, especially as wood adhesives (He and Chiozza, 2017; Li et al., 2019; Liu et al., 2018). While the pilot-scale production of relevant products has been reported (He et al., 2016), information on their moisture adsorption behaviors is needed to design or select appropriate equipment for their handling, aeration, storage and processing. Thus, the purposes of this work were to obtain equilibrium moisture sorption isotherms of CSM, WCSM and cottonseed protein isolate (CSPI, as a control) at 15, 25, 35 and 45 ^{0}C, and test 13 mathematical equations to fit the experimental sorption behaviors.

Materials and Methods

Mill-scale produced CSM was provided by Cotton, Inc. (Cary, NC, USA). WCSM and CSPI were obtained previously in a pilot-scale production with CSM as the starting material (He et al., 2016). These products were freeze-dried and ground to pass a 0.5-mm screen and stored in a freezer (-22 ºC) until use. Selective properties of the three products are listed in Table 1. All chemicals used were of reagents grade. Eight chemicals [LiCl, $MgCl_2$, K_2CO_3, $Mg(NO_3)_2$, KI, NaCl, $(NH4)_2SO_4$, KCl] were used to obtain constant water activity environments. Distilled water was used to make the saturated salt solutions.

Table 1. Selected organic and mineral components of defatted cottonseed meal (CSM), water washed defatted cottonseed meal (WCSM), and cottonseed protein isolate (CSPI). Adapted from (He et al., 2016).

	Protein	Oil	Cellulose	Ash	P	Ca	K	Mg	Na	S
	% of product weight									
CSM	34.1	2.5	13.6	7.2	1.5	0.3	1.8	0.7	0.2	0.5
WCSM	46.3	1.0	17.6	5.2	1.2	0.3	1.0	0.7	0.1	0.5
CSPI	94.8	0.2	0.6	2.2	0.5	<0.1	0.3	0.1	0.2	0.7

Sorption isotherms

Sorption isotherms of CSM, WCSM, and CSPI were determined at four working temperatures at 15, 25, 35 and 45 °C were determined through the static gravimetric method (Tunc and Duman, 2007). Before the moisture adsorption isotherm experiments, samples were dried in a vacuum oven at 60 °C for three days. Glass desiccating jars placed in a conditioning incubator were used to create a closed environment with desired temperature and relative humidity. A beaker with a saturated salt solution with known water activities (a_w) (Tunc and Duman, 2007) was placed in a jar to create the required relative humidity in that jar. Samples (about 0.8 g) were weighed into small plastic weighing boats and places into the jars. Thymol in small cups was placed in the jars with $a_w > 0.7$ to prevent microbial growth (Miranda et al., 2012; Taitano et al., 2012). Closed jars were maintained in the incubator at 15, 25, 35 or 45 ^{0}C for the equilibration of samples for about 20 days (Fig. 1). The experiments were conducted in duplicates. The equilibrium moisture content was considered to be reached when weight measurements taken on consecutive days (from 17-24 days) showed a difference of less than 0.001 g. The equilibrium moisture contents of samples were expressed as g/100 g dry solids. The average values were used in the determination of the moisture adsorption isotherms.

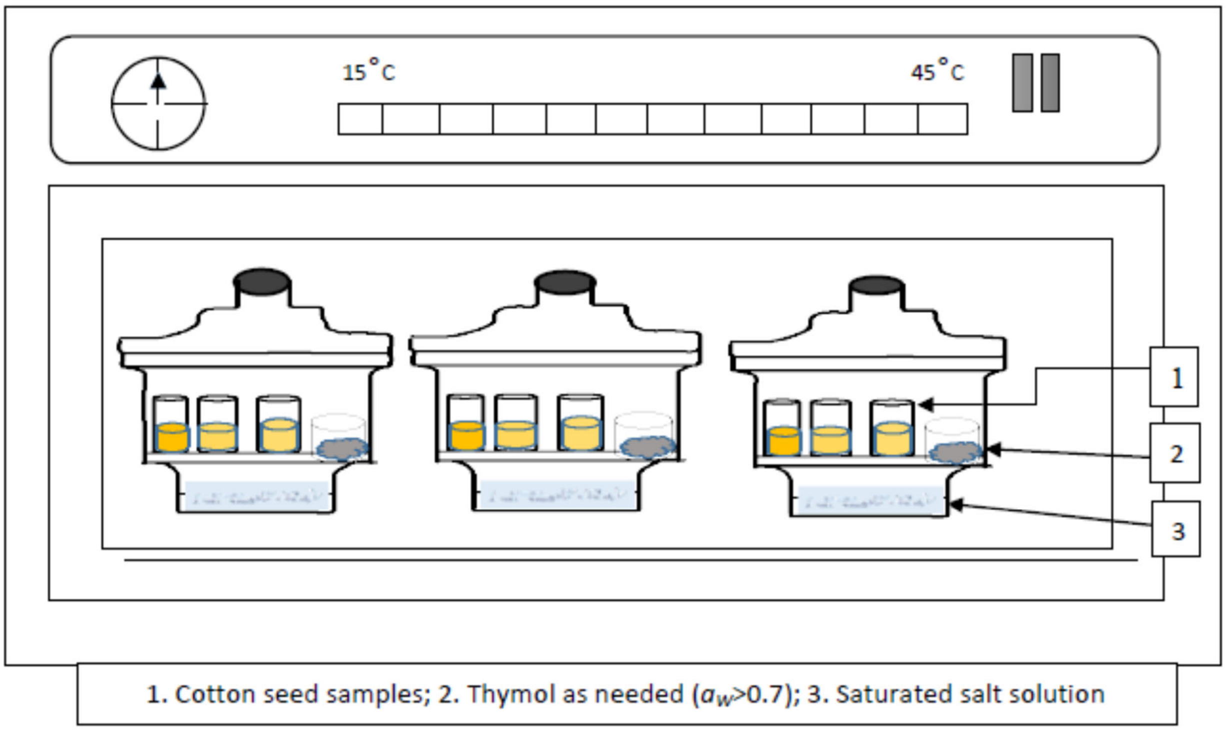

Fig. 1. Apparatus illustration for the sorption isotherm measurement

Results and Discussion

The moisture adsorption isotherms of the three cottonseed products at four working temperatures (15, 25, 35 and 45 ^{0}C) are shown in Fig. 2. This observation of the moisture content features of cottonseed products was consistent with those of agricultural products and byproducts in literature (Taitano et al., 2012; Tunc and Duman, 2007; Verbeek and Koppel, 2012).Visually, the adsorption isotherm of CSM increased slowly initially at low water activity values, and then followed by a steep rise at higher water activity values (Fig. 2a). This trend was more obvious with the low temperature (15 ^{0}C). These moisture adsorption isotherms were sigmoid in shape, a characteristic typical of amorphous, hydrophilic polymers (Kristo and Biliaderis, 2006; Verbeek and Koppel, 2012). The sigmoid feature generally described as a gradual increase in moisture content at low water activities and then a rapid increase at higher water activities. This is likely caused by exposure of more polar hydroxyl groups as molecular mobility and free volume increase with increasing moisture content (Verbeek and Koppel, 2012). Similar increasing feature with smaller slopes was observed with other two products WCSM and CSPI (Fig. 2b and 2c). The less typical sigmoid shapes of the adsorption isotherms of the two products were apparently due to their less amorphous and less hydrophilic properties as shown previously by surface imaging and fluorescence analysis (He et al., 2014; He et al., 2018).

The moisture content of all three products generally increased as the temperature decreased from 45 to 15 ºC. The biggest difference was from 35 ºC to 45ºC. (Tunc and Duman, 2007) explained this trend with the mechanism of excitation states of molecules. In other words, increased temperatures decreased the attractive forces between molecules due to an increase in kinetic energy of water molecules, leading to increase their distance apart from each other. Therefore, water molecules with slow motion at low temperatures bound more easily to suitable binding sides on surface. This explanation suggested that in our work, the defatted cottonseed products became less hygroscopic as the temperature increased. Because water molecules become more active at higher temperatures, they easily dissociate from the water-binding sites in the cottonseed meal (more carbohydrates) or protein surface.

When the moisture contents of the samples were compared at a constant temperature, the general trend of decreasing moisture content was in the order of CSPI < WCSM < CSM at the water activity < 0.6, but the trend reversed to the order of CSM < WCSM < CSPI at the water activity > 0.6. (Taitano et al., 2012) reported that raw almonds with brown skin reversed the order and had higher moisture content than blanched almonds when water activity was above 0.30. The order changes were also observed with water/sorbitol-plasticized composite biopolymer of caseinate-pullulan bilayers and blends (Kristo and Biliaderis, 2006). They found that the isotherms of the samples plasticized with 25 and 15% sorbitol swung upwards and crossed over those of the free-polyol samples at water activity higher than 0.53. They attributed the drastic increase in water sorption by the sorbitol itself in the region of water activity > 0.53. While we could not figure out the exact cause of our observation. (Tunc and Duman, 2007) did not report a similar observation with their cottonseed samples. In contrast, they observed a same trend of decreasing moisture content in all range of water activities in the order of fuzzy cottonseed > black cottonseed > cottonseed protein isolate > whole cottonseed kernel ≈ blended cottonseed kernel. However, there were significant amounts of lipid (17-40%) in their products. In contrast, lipid was a minor component in our products, accounting for only 0.2, 1.0, 2.5% of CSPI, WCSM, and CSM, respectively (Table 1). Hydrophobic character of lipids might lead a decrease in the water uptake of cottonseed kernel and provided the lower value in the moisture content. They proposed that linters which is composed of mainly cellulose with hydrophilic characters may cause an increase in the water adsorption of their fuzzy cottonseed samples. We thus could assume that in our samples, cellulose contents played a major role in the differences in the moisture content between CSM, WCSM and CSPI under same water activity conditions.

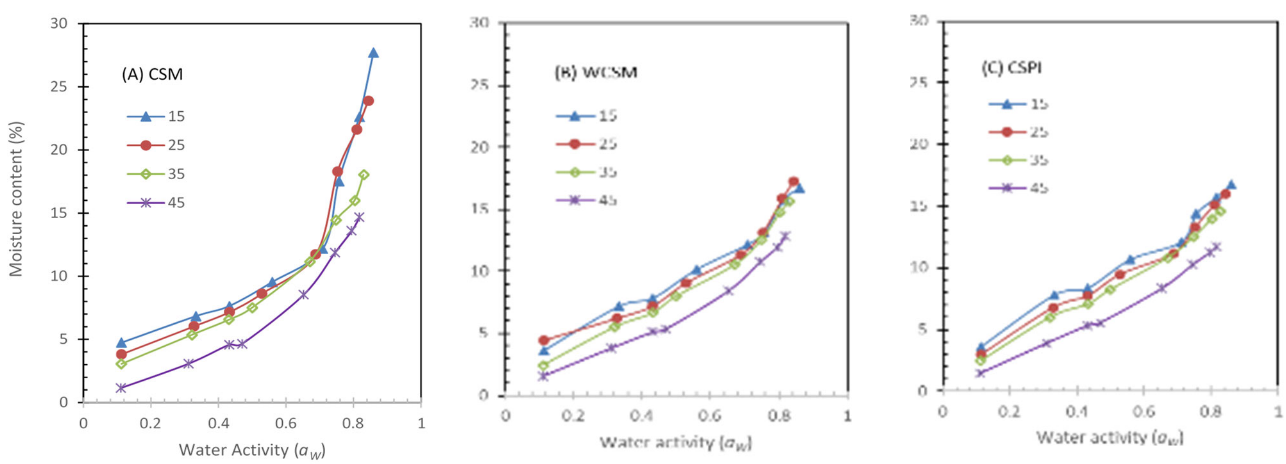

Fig. 2. Moisture adsorption isotherms for defatted cottonseed meal (CSM), water washed defatted cottonseed meal (WCSM), and cottonseed protein isolate (CSPI) at 15°C, 25°C, 35°C, and 45°C, respectively.

Many mathematical equations have been proposed in the literature to describe the sorption isotherms (Miranda et al., 2012; Tunc and Duman, 2007). In this current work, we tested 13 sorption isotherm equations out of the 14 equations tested by (Tunc and Duman, 2007)(i.e., without Chung & Pfost equation). Among them, six sorption isotherm models are more or less, fitting the experimental data better (Table 2).

Specifically, for CSM, the G.A.B. model was found to be the best fit with the lowest average *P* and *SE* values and relatively high R^2 value across all temperatures. For WCSM, the G.A.B. model fit the data the best with the lowest average *P* and *SE* values across all temperatures. The Henderson and Oswin models also had good statistical values, indicating a fairly good fit. For CSPI, the G.A.B model gave the best fit with the lowest average *P* value and second.

Table 2. Parameters of relevant models, R^2 (regression coefficient), mean relative deviation modulus (*P*), and standard error of estimate (*SE*) for isotherms of three cottonseed products at 15, 25, 35 and 45 °C

(a) Defatted cottonseed meal (CSM)

Temp (°C)	G.A.B.						B.E.T.					Halsey				
	M_0	C	K	R^2	P	SE	M_m	C	R^2	P	SE	a"	r	R^2	P	SE
15	4.302	-180.9	0.9779	0.9312	5.419	1.173	3.961	-30.46	0.9736	8.390	1.079	19.04	1.494	0.9733	8.224	1.637
25	4.227	36.03	0.9868	0.9422	4.380	1.233	4.008	143.3	0.9660	6.193	1.231	12.41	1.349	0.9874	5.532	1.138
35	4.443	13.65	0.9190	0.9863	1.590	0.3967	3.334	-31.78	0.9617	13.93	1.294	11.36	1.400	0.9953	3.712	0.5454
45	3.866	3.114	0.9399	0.9779	2.731	0.3870	3.037	4.989	0.9511	6.052	0.6915	3.180	0.9773	0.9760	11.52	1.107

(b) Washed cottonseed meal (WCSM)

Temp (°C)	G.A.B.						Henderson					Oswin				
	M_0	C	K	R^2	P	SE	k	n	R^2	P	SE	a	n	R^2	P	SE
15	6.591	11.92	0.7231	0.9589	3.010	0.4485	0.01137	1.848	0.9939	3.262	0.5126	19.04	1.494	0.9733	8.224	1.637
25	4.829	42.36	0.8564	0.9812	2.112	0.3119	0.008515	1.979	0.9427	9.508	1.266	12.41	1.349	0.9874	5.532	1.138
35	5.899	6.404	0.7812	0.9502	2.101	0.2642	0.03287	1.467	0.9973	2.636	0.3800	11.36	1.400	0.9953	3.712	0.5454
45	4.542	4.486	0.8334	0.9719	1.403	0.1518	0.06921	1.268	0.9978	2.689	0.2601	3.180	0.9773	0.9760	11.52	1.107

(c) Cottonseed protein isolate (CSPI)

Temp (°C)	G.A.B.						Bradley					Henderson				
	M_0	C	K	R^2	P	SE	K1	K2	R^2	P	SE	k	n	R^2	P	SE
15	7.755	9.812	0.6590	0.9254	3.584	0.5635	0.8151	4.832	0.9888	4.248	0.5108	0.01066	1.849	0.9906	3.551	0.5296
25	7.338	7.384	0.6816	0.9107	2.927	0.4585	0.8201	3.983	0.9938	2.706	0.3784	0.01883	1.659	0.9940	3.002	0.4242
35	7.451	5.595	0.6648	0.9370	1.745	0.2017	0.8165	3.647	0.9989	1.592	0.1547	0.02776	1.540	0.9960	2.491	0.2517
45	6.474	3.178	0.6834	0.9272	1.286	0.1161	0.7975	2.857	0.9975	3.986	0.2022	0.06995	1.281	0.9978	2.482	0.2027

lowest average *SE* value across all temperatures. The Bradley and Henderson models had the highest regression coefficients while also having very satisfactory *P* and *SE* values. Therefore, among all cottonseed types and all temperatures, It is only the G.A.B. model with a consistently good fit for the data which is not unexpected because the third parameter adds an additional degree of freedom to the model which gives it greater versatility (Timmermann et al., 2001). Practically, the G.A.B. model is a semi-theoretical, multi-molecular, localized homogenous adsorption model and is considered to the most versatile sorption model (Ariahu et al., 2005; Bajpai and Pradeep, 2013).

Summary

The adsorption isotherms of defatted cottonseed meal (CSM), water washed cottonseed meal (WCSM), and cottonseed protein isolate (CSPI) were determined and the data were analyzed using 13 models. The G.A.B. model was found to be most suitable for all three products in describing the adsorption isotherms in the temperature range of 15–45 ^{o}C. When the moisture contents of the samples were compared at a constant temperature, the general trend of decreasing moisture content was in the order of CSPI < WCSM < CSM at water activity < 0.6, but the trend reversed to the order of CSM < WCSM < CSPI at water activity > 0.6. The moisture adsorption of all three products was an enthalpy-controlled process, rather than entropy controlled, whereas the entropy of moisture adsorption was strongly dependent on the moisture content.

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