Determination of Equilibrium Moisture Content Characteristics of Manitoba Grown Soybeans as Affected by Post-harvest Conditions

by

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ABSTRACT

The relationship between Equilibrium Moisture Content (EMC) and Equilibrium Relative Humidity (ERH) was measured in three varieties of soybeans grown in Manitoba (Akras R2, Lono R2 and Podaga R2) with the objective of modelling mathematically the adsorption and desorption isotherms. The effect of three post-harvest conditions: (a) freshly harvested soybeans (b) soybeans subjected to three drying and wetting cycles, and (c) soybeans subjected to three freezing and thawing cycles was investigated on the sorption isotherms of the soybean varieties. The adsorption and desorption experiments were conducted at 5, 10, 15, 20, 25 and 30°C using a dynamic ERH apparatus.

Significant differences were found in all pairs of adsorption-desorption characteristics indicating the presence of hysteresis in the soybean samples at all the temperatures tested. The hysteresis magnitude ranged between 0.23 to 4.5% moisture content (MC) measured on dry basis. The modified Halsey equation and the modified Oswin equation were similar in predicting the sorption isotherms of the experimental data, with the former being superior in predicting the desorption data at low RH. The parameters calculated for the modified Halsey equation are applicable for temperatures above 10°C in the range of 10 to 80% RH for desorption and 30 to 80% RH for adsorption.

Freshly harvested samples of the three soybean varieties produced similar isotherms, without significant differences among them. However, soybeans varieties responded differently to the effect of pre-treatments (i.e. drying/wetting and freezing/thawing cycles). Significant differences at 10, 15, 20, 25 and 30°C were found in the adsorption isotherms of Akras and Lono soybeans subjected to drying and wetting cycles. Adsorption isotherms of Akras and Podaga soybeans subjected to freezing and thawing cycles were significantly different from the fresh samples of

these varieties. The effect of drying and wetting cycles on the desorption isotherms was only found in Akras soybeans at 10°C below 63% RH and at 15°C below 71% RH. The effect of drying and wetting cycles was found in Lono soybeans at 25 and 30°C above 69% RH at both temperatures. In general, the effect of both pre-treatments on the sorption isotherms of soybeans was reflected in a reduction in the EMC when compared to fresh samples.

ACKNOWLEDGMENTS

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1. INTRODUCTION

Soybean (*Glycine max* (L.) Merrill) is a crop of great economic and social importance at the global level given its high protein (approximately 40%) and oil (approximately 20%) content (Singh 2010). About 28 percent of the total oil production in the world comes from soybean sources, making this crop a major source of oil (USDA 2000). Soymeal is one of the most important sources of protein in the production of animal feed concentrates (FAO 2004). Traditionally, soy-based foods such as tofu, soy sauce, soymilk and others have been an essential part of the human diet in many eastern countries (i.e. China, Vietnam, Japan, Indonesia and Thailand) (FAO 2002, 2004).

In 2017, the total soybean production in the world was 353 million tonnes (FAO 2019). In2017, the leading producers of soybean were the USA, Brazil, Argentina, China and India (FAO 2019). Between 2006 and 2017 the production of soybeans in Canada increased 123% making it the third-largest crop in financial terms. In 2016, it generated a cash flow of CAD 2.8 million with a production of 6.46 million tonnes (Soy Canada 2019). Almost two-thirds of soybeans produced in Canada are exported either as a raw or processed product. Canada exports food grade soybeans with the primary export markets being China, USA, Southeast Asia, Europe and the Middle East (Soy Canada, 2019).

Soybean is an oil crop which has been traditionally known to grow best in temperate zones and is cultivated in late spring and harvested in early-to-mid fall. Thanks to breeding programs, new varieties have been developed to adapt the crop to different climate and geographic conditions. At present, more than 50 varieties are grown in Canada (Soy Canada 2019) and more are developed by private and public breeding programs.

In the 1950s, research conducted in Manitoba facilitated the development of new varieties of soybeans able to adapt to the climate conditions in the province (Manitoba Agriculture 2011). Current soybean varieties in Manitoba are classified by maturity zones (very early, early, mid and long season). These zones are based on long-term heat unit and frost-free period information (Manitoba Pulse and Soybean Growers 2017). The early maturating varieties have allowed growing soybeans in the northern and western areas of Manitoba, in addition to the southern areas (Manitoba Agriculture 2011).

The increasing interest among farmers in Manitoba in soybean crops has positioned the province in the second place after Ontario as the largest producer of soybeans in Canada. In order to grow and supply high quality of this important crop to the market, there is a need to establish optimal growing, post-harvest and storage conditions. Proper handling and safe storage are key areas to prevent economic losses related to quality (Yousif 2014).

The moisture content of agricultural commodities, including soybean, is an important factor in their preservation and storability. Soybeans need to be harvested, dried and stored at a safe moisture content to ensure maximum shelf life and high nutritional quality. During storage, agricultural products are susceptible to deterioration, mould spoilage, insect infestation and self-heating (Obaldo et al. 1991). Even when soybeans are stored at a safe moisture content, diurnal and seasonal variations in temperature and relative humidity within a bin can result in biochemical changes affecting their quality.

The interaction of factors such as temperature, relative humidity and moisture content plays a crucial role in the quality preservation of agricultural products. Sorption characteristics describe the heat and mass transport phenomena of a sample with its surrounding air. Hence, the knowledge

of when a sample attains equilibrium moisture content at corresponding relative humidity of air is extremely valuable for its safe storage. These two parameters are known as the equilibrium moisture content (EMC) and the equilibrium relative humidity (ERH).

During storage, agricultural products can undergo temperature increases caused by biological heating due to respiration of the seed and/or mould growth (Mills 1989). Unlike cereals, soybeans have a higher risk of self-ignition (Berglund 2002). Fines such as cracked beans, weed seeds and anything considered dockage have an adverse effect on the quality of soybeans during storage. These fines affect the in-bin air distribution, contributing to hot spots, thus facilitating fungal growth and heating the soybeans (Mills 1989).

Temperature gradients developed due to the differences in temperatures between the grain closer to the walls and the center of the grain bulk also cause constant moisture gains and losses in stored grains. These gradients can lead to moisture accumulation causing hotspots or high moisture pockets (Abramson et al. 2001).

Stored soybeans undergo many micro wetting and drying cycles, as well as micro freezing and thawing cycles as a result of diurnal and seasonal weather conditions. In-bin drying, and cooling processes also contribute to wetting and drying cycles. These cyclic changes might affect the EMC properties of stored soybeans (Bielewicz et al. 1993). Therefore, it is important to evaluate and determine the impact of those changes on the EMC properties of soybeans and to relate them to safe storage practices.

Although there is a considerable amount of information for other crops, the available information regarding the EMC characteristics of soybeans in Canada is limited, and most of the data is not up to date. Consequently, the study of the EMC properties of some soybean varieties grown in

Manitoba and how they might be affected by post-harvest conditions would be beneficial to establish safe storage guidelines.

1.1 Objectives

The objectives of this study were to:

1. determine the equilibrium moisture content characteristics between 5 and 30°C for soybeans grown in Manitoba;

2. test the suitability of mathematical models and determine the best model to predict the sorption isotherms for soybeans;

3. evaluate the effect of variety on the sorption isotherms of soybeans;

4. evaluate the effect of freezing and thawing cycles on the sorption isotherms of soybeans; and

5. evaluate the effect of drying and wetting cycles on the sorption isotherms of soybeans.

2. LITERATURE REVIEW

2.1 Equilibrium moisture content and equilibrium relative humidity relationship

Temperature and relative humidity play an important role in the preservation and safe storage of grains. The hygroscopic properties of agricultural products have been traditionally represented as curves that relate the moisture content of the product with their equilibrium relative humidity at a constant temperature. The knowledge of this relationship is needed for the designing of storage, aeration and drying systems as well as the prediction of shelf life (Osborn et al. 1989).

When a hygroscopic material at a specific initial moisture content is left in an environment at a given relative humidity for an extended period, the product exchanges moisture with the air until it reaches equilibrium (Cenkowski et al. 1989). Hence, the partial vapour pressure of the hygroscopic material at equilibrium is equal to the vapour pressure of water in the surrounding air (Labuza 1984). The moisture content at this point is defined as Equilibrium Moisture Content (EMC). In cases when the volume of air is relatively small compared to the volume of the material, there are significant changes between the partial vapour pressure of the material and the air as they reach equilibrium. The relative humidity of the air at that point is also referred to as the Equilibrium Relative Humidity (ERH).

During unaerated storage, the moisture content of grains at a constant temperature brings the intergranular air into equilibrium with the grains (Bern et al. 2008). At this point, there is an equilibrium relative humidity of the intergranular air corresponding to the moisture content of the grain. If the bin is aerated with ambient air, the grain bulk will reach the relative humidity of the air being passed through the bulk. In agricultural and engineering processes, it is practical to use

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the concepts of EMC and ERH. Sorption isotherms of agricultural products are typically represented as EMC-ERH curves.

2.2 Sorption Isotherms

The sorption isotherms of a product are a plot that represents the relationship between the moisture content of the product with the water activity at constant temperature and pressure (Andrade et al. 2011). The isotherms show at what moisture content certain water activity will be achieved, which might be beneficial or have adverse effects on the product (Troller and Christian 1978). The knowledge of the sorption isotherms of food products is used to model drying processes and equipment, to predict the shelf life of a product based on its water activity, and to predict possible moisture changes of the product during storage (Andrade et al. 2011; ASABE 2007).

Brunauer et al. (1940) classified sorption isotherms into five categories (Fig. 2.1). Type 2 and 4 are the most common isotherms found in food materials (Andrade et al. 2011). Type 1 isotherms are found in crystalline sugar, while type 3 represents the isotherms of anticaking agents (Rahman 1995). Type 5 is found on the adsorption isotherms of charcoal and are a variation of type 2 and 3 isotherms in porous materials (Andrade et al. 2011; Al-Muhtaseb et al. 2002).
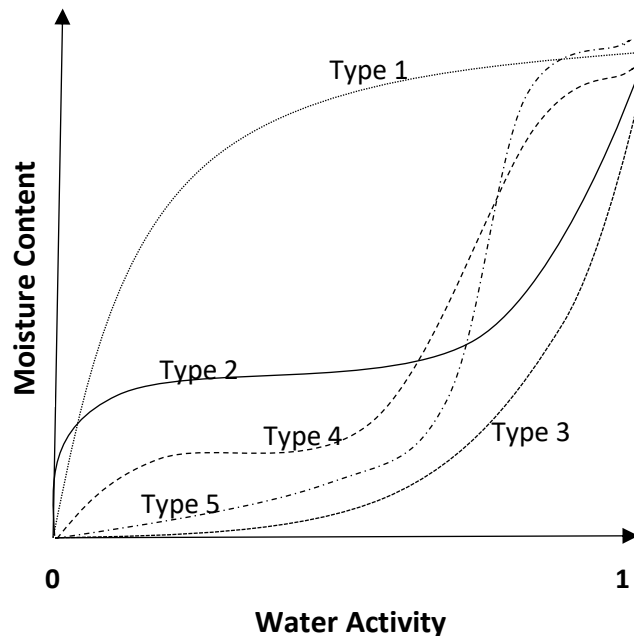
Fig 2.1 Brunaeur classification of sorption isotherms (Adapted from Andrade et al. 2011).

An example of a general sorption isotherm with a sigmoid shape is shown in figure 2.2, which is the type of curve typically encountered in food systems. The nature of interaction between water and food can be analyzed by making a distinction in three divisions of the curve (Van Den Berg and Bruin 1981). Region A represents strongly bound water that is not available for chemical reactions and is not freezable. This bound water is strongly absorbed by hydrophilic and polar components such as polysaccharides and proteins. Region B represents water that is less firmly bound than water in the previous region. This water enhances physical, chemical and physicochemical reactions. Water in region C acts as bulk water and is more easily available for physical processes and biochemical reactions.
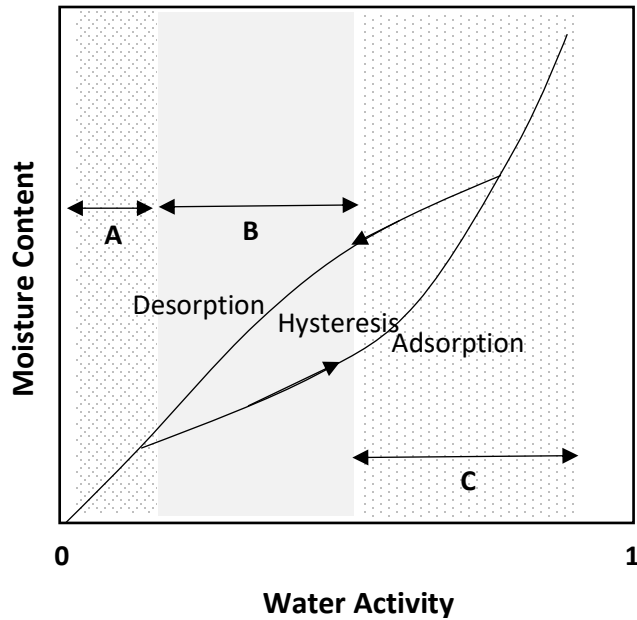
Fig 2.2 Sorption isotherm typically found in food products (modified from Rahman 1995).

2.3 Water activity and equilibrium relative humidity

Before the concept of water activity was defined, chemists and chemical engineers used the

relation between equilibrium vapour pressure and moisture content for drying processes, while

scientists knew the role of relative humidity as a microbial growth parameter (Van den Berg and

Bruin 1981). Water activity (a_w) is an intrinsic property of a substance and refers to the degree

of boundedness of water to the matrix of the food (Al-Muhtaseb et al. 2002). Water activity is a

thermodynamic concept derived from the chemical potential. It expresses the relationship

between equilibrium vapour pressure on the surface of a material and the vapour pressure of pure

water at a given temperature (Andrade et al. 2011):

$$a_w = \frac{p_w}{p_w^0} = \frac{RH}{100} \tag{2.1}$$

Where

p_w= vapour pressure of water in the material

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p_w^0 = vapour pressure of pure water

RH= relative humidity

Comparison of a_w with relative humidity is practical in systems at equilibrium, constant temperature and pressure. At ambient temperatures and pressures, the relationship $\frac{p_w}{p_w^0}$ is termed relative vapour pressure and in engineering, 100 times this ratio corresponds to the relative humidity (Eq. 2.1). Therefore, in an enclosed system, a_w can also be expressed as the relative humidity at equilibrium of the air surrounding the food system at a given temperature (Rahman 1995).

In food science, water activity (a_w) is an important property of food products (Rahman 1995). It has been shown that it is not the water content of a product that determines its stability, but rather its water activity (Van den Berg and Bruin 1981). Deterioration factors such as lipid oxidation, non-enzymic browning, enzyme activity, and bacteria and mould growth are related to the level of water activity in foods (Labuza et al. 1972). Hence, water activity is used to predict the shelf life of food products as it is related to biochemical changes and the available water that allows the growth of microorganisms.

The knowledge of the concept of water activity and its relationship to ERH is practical, given that throughout the literature, authors use these two terms interchangeably. However, as stated by Gal (1981), the relationship holds as long as specific conditions such as equilibrium of the system, constant temperature, and constant and low pressures are maintained (atmospheric pressures). This relationship showed by Gal (1981) has a difference of only 0.2% RH at ambient temperatures and pressures.

2.4   Hysteresis

Adsorption occurs when the water vapour pressure in the food is lower than that of its surroundings. When conditions are reversed, i.e. water vapour pressure of the surrounding is lower, desorption occurs (Labuza and Altunakar 2007). The phenomenon by which some materials exhibit different paths for their adsorption and desorption is called hysteresis (Kapsalis 1981)2002). Depending on whether the food is adsorbing or releasing water with the air, the EMC at a given temperature and RH is going to be different (Cenkowski et al. 2015). Usually, for materials that present hysteresis (Fig. 2.2) in their sorption behaviour, the amount of water being held in the desorption curve is higher at the same relative humidity compared to the adsorption curve (Labuza and Altunakar 2007).

A variety of factors affect the sorption hysteresis, among them, are composition of the product, storage conditions, temperature and successive drying and wetting cycles (Rahman 1995). Bielewicz et al. (1993) reported a widening in the hysteresis loop of canola seeds subjected to three consecutive drying and wetting cycles. They attributed this situation to some biophysical changes in the seed caused by heat, such as cracks and mould growth.

Several theories have been formulated to explain the hysteresis phenomenon, but to date, there is not a single general theory able to explain all the mechanisms involved in the process. The proposed interpretations can be classified for porous, non-porous, and non-rigid solids (Al-Muhtaseb et al. 2002; Andrade et al. 2011). The "ink-bottle theory" explains partially the hysteresis phenomenon in porous solids, which is based on capillarity condensation (McBain 1935; Rao and Das 1968). This theory is based on the structure of pores, which are said to have large diameter cavities and small diameter passages or "bottlenecks." On desorption, the controlling factor is the

small diameter passage, which limits the amount of water being removed from the pore (Labuza and Altunakar 2007).

2.5 Mathematical models

In practice, moisture content, temperature and relative humidity inside storage bins must be monitored periodically to assess grain quality and prevent spoilage or pest infestations. Using devices that measure relative humidity and temperature, the moisture content of a stored product can be calculated if a mathematical sorption model is available (Chen 2001).

Van den Berg and Bruin (1981) compiled 75 models and classified them into four groups: localized monolayer sorption models, localized multilayer sorption and condensed film models, sorption models from polymer science, and sorption models from food and agricultural engineering (which they further sub-divided into partially theoretical and empirical based models). There is not a single general model that can be used to describe all sorption isotherms. As sorption isotherms represent the hygroscopic behaviour of several components, the resulting water activity is produced by the combination of those components (Karel and Heidelbaugh 1973). Different proportions of components might respond differently based on the range of water activity. Therefore, the application of mathematical models varies depending on the composition of the product, and on the range of relative humidity.

Chirife and Iglesias (1978) compiled 23 mathematical equations used to describe the equilibrium moisture content of food systems. They discussed those models, their origin and range of applicability finding that several equations are equivalent despite having different origins. Many other studies have been published comparing several mathematical expressions to describe a given food system (Al-Muhtaseb et al. 2002; Andrade et al. 2011; Chen and Morey 1989a; Van den Berg

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and Bruin 1981). Those studies agreed that the applicability of the mathematical models to predict the EMC depends on the type of food (i.e. starch products, high oil or protein content products, etc.) and the RH range.

Chirife and Iglesias (1978) compared Henderson and Halsey equations on 220 foods and found that in 70.4% of the cases, Halsey equation described the sorption isotherm better, while in 21.9% the Henderson equation gave a better fit. For 7.7% of the cases, both equations gave a similar and good fit. They also emphasized that sorption isotherms cannot be extrapolated further than the range used experimentally. Halsey equation, for example, was a good fit for 69 food samples in the range between 10 and 80% RH.

Several researchers have investigated the dependency of equation parameters on temperature (Chen and Clayton 1971; Iglesias and Chirife 1976; Pfost et al. 1976; Thompson et al. 1968). Many equations, consequently, have been modified to include a temperature term and make it easier to explicitly solve for ERH as a function of temperature and EMC. The ASABE standards (ASABE 2007) list five mathematical models to describe the EMC of agricultural products, including soybeans. These models are the modified Henderson equation, modified Chung-Pfost equation, modified Halsey equation, modified Oswin equation and Guggenheim-Anderson-deBoer (GAB) equation (Appendix A).

Chen and Morey (1989a) compared four mathematical models (modified Henderson, Chung-Pfost, modified Halsey and modified Oswin equations) on selected grains and seeds. They concluded that there doesn't exist one general model that fits all agricultural products. For oily and high protein content products such as soybeans and edible beans, the modified Halsey equation describes the sorption isotherms well.

Cenkowski et al. (1989) found the modified Henderson equation to best predict the sorption isotherms of lentils. However, they found that the model only worked well for relative humidity up to 80%. Al-Muhtaseb et al. (2002) found the Henderson and Halsey equations to be useful to describe the sorption behaviour of high oil and protein grains at different temperatures in the range of 5 to 80% RH. Oswin equation gave a good fit in the range of 5 to 90% RH.

In order to evaluate the degree of fit, different statistical methods can be applied. Mean relative percentage deviation and standard error of the estimated value are used as quantitative evaluation methods (ASABE 2007; Aviara et al. 2004; Chen and Morey 1989a). Evaluation of the residual plots has been used as a qualitative method of comparison by other authors to complement quantitative comparisons (Chen and Morey 1989a).

Studies focused on the evaluation of several mathematical models to find the best prediction of the sorption characteristics of soybeans have found that the modified Halsey equation gives the best fit based on mean relative percentage deviation, standard error and residual plots (Osborn et al. 1985; Aviara et al. 2004; Chen and Morey 1989a). The modified Oswin equation has also shown potential for describing the EMC properties of soybeans based on the standard error and mean relative percentage deviation. Although when comparing the residual plots, after fitting the modified Halsey and the modified Oswin equations, the former has been found superior in fitting the experimental data (Aviara et al. 2004; Chen and Morey 1989a).

2.5.1 Modified Halsey Equation

The Halsey equation (Eq. 2.2) was initially proposed by Halsey (1948) on theoretical grounds as a refinement of the Brunauer, Emmett, and Teller (B.E.T.) equation (Brunauer 1943).

$$RH = \exp\left(-\frac{D}{RT\theta^C}\right) \tag{2.2}$$

Where,

 $RH=$ relative humidity in decimals,

 D and $C=$ constants,

T= temperature in °C,

R= constant of ideal gases,

$\theta=MC/M_m$,

MC= moisture content

M_m is the monolayer concept for estimating the amount of water bound to polar sites in the matrix of low moisture content foods (Chirife and Iglesias 1978). The intent of this equation was to develop an expression for moisture adsorption of multilayers. Halsey provided an interpretation for the parameter C by relating its magnitude to the type of interaction between the vapour and solid. For large values of C, the extent of attraction of the solid to the vapour is close to the surface. Small C values correspond to greater attraction forces that act farther from the surface and are typically related to van der Waals forces (Halsey 1948).

Iglesias and Chirife (1976) analyzed Halsey equation and found that the use of the temperature term in the equation did not eliminate the dependence of the parameters on temperature. The authors empirically modified Halsey equation with the goal of developing a modified equation that eliminated this dependence and explicitly related relative humidity, moisture content and temperature.

Modification of the Halsey equation involved the elimination of the monolayer value, leaving the equation as a function of the moisture content. Based on literature data of sorption isotherms of

different products, *C* was held constant while parameter *D* was varied. A dependence of parameter

D on temperature was found, and an empirical function was proposed for that parameter:

$$D = \exp{(A + BT)} \tag{2.3}$$

Where *A* and *B* are empirical parameters. By substituting these parameters and incorporating the

moisture content term, a Modified Halsey equation (eq. 2.4) was proposed. Iglesias and Chirife

(1976) applied this new equation to different food products finding a reasonably good fit and

highlighting the benefits of an equation that allows the characterization of temperature effects on

the isotherms while simplifying engineering calculations.

$$ERH = \exp{\left(-\frac{\exp(A + B(T))}{(MC)^C}\right)} \tag{2.4}$$

2.5.2 Modified Oswin Equation

Oswin (1946) initially developed an equation (eq. 2.5 with a mathematical series expansion for

sigmoid shaped curves.

$$MC = K\left(\frac{RH}{1 - RH}\right)^N \tag{2.5}$$

Where *K* and *N* are parameters that must be calculated at a constant temperature. This equation

was later modified, as parameter *K* was found to be a linear function of temperature (Chen and

Morey 1989a):

$$K = (A + BT) \tag{2.6}$$

The resulting modified Oswin equation placing E*RH* as the dependable variable as a function of

T and *MC* is as follows:

$$ERH = \left[\left(\frac{A + B \cdot T}{MC}\right)^C + 1\right]^{-1} \tag{2.7}$$

Where *C=1/N*. This equation, as the modified Halsey equation, allows calculating temperature-independent parameters *A, B* and *C*, while the equation is explicitly a function of temperature and moisture content.

2.6   Techniques to obtain sorption isotherms

Different methods have been applied by researchers to determine the water sorption isotherms. Gal (1981) classified those methods into two groups. In the first case, the system can be named dynamic or static depending on whether the air is being circulated or not. In the second classification, the method can be named (a) gravimetric, if a change in mass of the food sample is recorded, (b) manometric, if the vapour pressure of water around the food sample is recorded, or (c) hygroscopic, if the equilibrium relative humidity of the air is recorded.

The saturated salt solution (SSS) method consists of enclosing a small amount of food sample in a desiccator with a saturated salt solution (with a known RH) and recording the changes in food mass. This method is commonly used in academic laboratories and has been proved to be reliable, but the disadvantage is the long time it takes to achieve equilibrium. Those long equilibration times can create a problem in the high RH environment, as bacteria and mould growth could cause undesirable side effects.

The ERH method consists of enclosing a relatively large amount of sample in a container with a relatively small volume of air. In this system, the relative humidity of the air, which could be static or circulated within the system, is recorded until it reaches equilibrium with the sample. A convenient technique applied with the ERH method consists of using wet and dry samples of the same product in the same container (Gal 1981) and circulating air in a closed loop. By doing this, both adsorption and desorption data can be simultaneously obtained. The advantages of using this

dynamic ERH method, over a static method such as the SSS, is that it reduces significantly the time used to perform the experiments (Cenkowski et al. 1989).

The effectiveness of the dynamic ERH method was demonstrated by Cenkowski et al. (2015) who used it to obtain the sorption characteristics of red lentils. They circulated air through an enclosed system filled with a stack of lentils at predetermined moisture content while measuring the relative humidity until equilibrium was reached. By using this method, the authors were able to produce adsorption and desorption data sets for each variable tested (lentil variety, temperature and pre-treatment applied) and predicted the EMC properties of red lentils using the modified Halsey equation.

Rudy et al. (2017) compared two techniques to construct the sorption isotherm. They tested and compared a dynamic vapour sorption method (DVS) with the technique of SSS using barley as their hygroscopic food sample and found a difference of less than 0.1% in the sorption isotherms between the two methods. The authors also noted that although the DVS was more convenient and quicker, it was better suited for RH above 50% while the SSS technique performed well at humidity below 50%.

Research has been done to evaluate the performance of different static ERH methods. Chen et al. (2014) highlighted the advantages of a static ERH method that uses temperature and humidity sensors and compared it to the SSS method which is time-consuming. They found that the performance of the humidity sensors had a significant impact on the determination of the moisture characteristics of the sample studied after adjusting it to mathematical models. By calibrating the humidity sensors using saturated salt solutions, they reduced the error of the predicted moisture content and reached an accuracy of 0.5% MC on a wet basis.

2.6.1 Measurement with RH sensors

Electric hygrometers and RH sensors are widely used for data collection of relative humidity, water activity and vapour pressure for sorption properties of food materials. These sensors measure electrical properties such as resistance and capacitance of a sample (Fontana 2007). The material used in either of those sensors can have a salt film or hygrometer polymer film. They work on the principle of a change in electric properties of the material in response to the water vapour in the surrounding air. Regardless of the electrical property they measure, the sensors must be calibrated to relate the capacitance or resistance response to the relative humidity. For accurate measurements, the sensor must be in thermal and vapour equilibrium with its surrounding air.

Calibration and validation must be done based on known relative humidity standards. Salt standards (saturated or unsaturated salts) are typically used. Saturated salt solutions are attractive because they are easy to make and cover almost the entire range of relative humidity (Fontana 2007). A complete list of saturated salt solutions with their respective relative humidity at different temperatures is found in Greenspan (1977). Unsaturated NaCl solutions of different concentrations are sometimes preferred because their variation with respect to temperature is insignificant but only produce RH above 75% (Stekelenburg and Labots 1991).

The method of measuring relative humidity as a measurement of water activity is acceptable as long as the RH device is calibrated correctly and is sensitive enough for the entire RH range (Bell and Labuza 2000). Previous studies using humidity sensors to predict sorption isotherms of agricultural products have shown that the use of RH sensors should be for RH below 85% (Chen 2001). Other studies focused on the uncertainty evaluation of RH sensors for the prediction of sorption properties show that the performance of the RH sensor has a significant effect on the predicted moisture content value (Chen et al. 2014). Accurate and periodic calibration, as well as

proper handling of RH sensors, are critical to reducing sensor errors and compensate for drift (Stekelenburg and Labots 1991; Uddin et al. 2006).

Calibration times vary as shown by Labuza et al. (1976), who evaluated different methods and arrays to measure RH and found equilibration time between sensor and air to range from 20 minutes to 24 hours. They emphasized the importance of maintaining a constant temperature. At high relative humidity, small temperature changes as low as 0.1℃ might result in a 0.6% RH error (Fontana 2007). Although most sensor manufacturers claim that the relation between RH and voltage is linear, Lu and Chen (2007) found that polynomial calibrations were better at predicting the performance of some humidity sensors.

2.7 Previous sorption studies involving soybeans

Data on EMC versus ERH at different temperatures and their corresponding sorption isotherms are summarized in the ASABE standards (ASABE 2007). These standards include information based on data from 1944 to 2004, and from different growing regions such as Nigeria, Canada, Britain and U.S. Most of the data for soybeans are listed for the desorption curve. Data for adsorption are given only at 25 and 30℃.

Research carried out in 1944 aimed to determine the behaviour of the hygroscopic characteristics of flaxseed, sunflower seeds and soybeans (Larmour et al. 1944). In this study, changes in sample mass were measured periodically up to 35 days using the saturated salt solution method. Soybeans took longer to reach equilibrium as compared to flaxseed and sunflower seeds, and equilibration time depended on RH. The same authors highlighted the importance of oil distribution in the seeds and its influence in their moisture adsorption.

Osborn et al. (1989) predicted sorption isotherms of the variety Essex of soybeans from Kentucky and found the Modified Halsey equation to be more suitable to describe the sorption characteristics. They measured adsorption characteristics at 10, 25 and 40°C using a closed-loop dew-point method in a temperature-controlled chamber. Their experimental adsorption data were compared with previous desorption data (Sulaiman 1986) and based on statistical criteria, no hysteresis loop was found. They recommended that further research should be done regarding the hysteresis in soybeans and the effect of variety and experimental method.

Adsorption and desorption data for soybeans grown in Nigeria was collected by Denloye and Ade-john (1985) at 30°C). Constants for the BET equation were tabulated for 30, 40 and 50°C. The experiments were carried out with a dynamic system using sulfuric acid to change the relative humidity of the circulating air. As compared to non-oily grains, soybeans exhibited a lower hysteresis effect, which decreased with an increase in temperature.

The most recent data for EMC of soybeans added to the standard was reported by Aviara et al. (2004). They used the SSS method to obtain the desorption EMC characteristics of soybeans grown in Nigeria (variety TGX 1440-1E) at 40, 50, 60 and 70°C and found the modified Halsey equation to best predict the desorption behaviour as a function of EMC and temperature.

Information regarding the presence of hysteresis on soybean isotherms is contradictory. Presence of hysteresis loop has been reported by Alam and Shove (1973) and Atungulu et al. (2015). Both studies conclude that hysteresis decreases with the increase of temperature and relative humidity. However, other authors (Denloye and Ade-john 1985; Osborn et al. 1989) have reported low or zero hysteresis on the sorption isotherms.

2.8   Effects of post-harvest conditions on stored grains

During storage, grains are subjected to moisture and temperature changes due to diurnal and seasonal weather conditions, temperature gradients within the bin, and moisture migration. These conditions expose the stored beans in Canada to micro drying and rewetting cycles as well as micro freezing and thawing cycles. Moisture loss generates shrinkage, and higher temperature generates expansion of the grain, subjecting the grains to compressive and tensile stresses. Also, changes related to desorption and adsorption of moisture generate fissures in the grain affecting their physical properties as well as making the grain more susceptible to spoilage and mould growth (Bala 2017).

2.8.1   Harvest of Soybeans

In Manitoba, soybeans are generally harvested below 20% but stored below 14% moisture content. It is not advisable to harvest soybeans below 12% as they become susceptible to mechanical damage (Erkinbaev et al. 2019). Manitoba Agriculture estimates harvest losses in soybeans around 60 lb/acre (67 kg/Ha) (Anonymous 2011). Soybeans can be harvested at a higher moisture content and subsequently dried to a safe moisture content. The safe moisture content for soybeans is 13% for storage for up to one year, 10-11% for up to 4 years and 10% for up to five years (Mills 1989). These moisture contents and storage times are temperature-dependent and must be properly monitored and controlled.

Drying allows farmers to harvest soybeans early or at a higher moisture content and thus avoid field and mechanical losses. Drying also lowers the risk of spoilage during storage and permits farmers to have flexibility with market prices related to moisture content (Bala 2017). Drying could be done with heated or ambient air depending on the moisture content of beans, weather conditions, and time of the year (Sathya et al. 2008).

2.8.2 Storage

After harvesting, soybeans are stored until they are processed or shipped. During this time, storage must guarantee soybean availability while maintaining its quality (FAO 2002). In developed countries, such as Canada, soybeans are stored in cylindrical steel or concrete silos. Steel silos are usually equipped with aeration systems that can push air through perforated floor using fans (Ghosh and Jayas 2010).

The control of temperature and moisture content are fundamental for the safe storage of all agricultural produce, including soybeans. Qualitative and quantitative losses occur due to biological ageing, spoilage and insect infestation. The temperature of the heated air during drying affects the quality of soybeans and influences the storability of the beans. High temperatures produce cracks of the coats and cotyledons facilitating mould growth and reducing germinability and quality of the beans during storage (Erkinbaev et al. 2019). The maximum safe temperature for in-storage drying of soybeans is considered as 38°C (Mills 1989).

During unaerated storage, the moisture content of the soybeans at a constant temperature will bring the intergranular air into equilibrium. At this point, there is an equilibrium relative humidity of the intergranular air corresponding to the moisture content of the beans. If the bin is aerated with a fan using ambient air, the soybean bulk will reach the relative humidity of the air being passed through the bin (Bern et al. 2008).

Information obtained from historical weather data from Environment and Climate Change Canada (Anonymous 2019) shows climate conditions in Manitoba vary widely due to diurnal and seasonal changes as well as from region to region within the province. Winters in Manitoba are usually dry and cold with temperatures dropping below the average -20°C. Summers, on the other hand, are humid and warm with temperatures surpassing 20°C, on average. Temperatures in spring can move

from below to above the freezing point in a same day. As a result of these changes, stored soybeans can undergo many micro wetting and drying cycles, as well as micro freezing and thawing cycles.

Initial conditions before storage are very to important for shelf life and maintaining quality of grains. Moisture content and temperature of grains must be manipulated based on the projected storage period. Grains with slight or moderate spoilage or damage from the field, will have a shorter storage life than sound seeds under the same moisture content and temperature. Dockage and debris contribute negatively to heating problems, spoilage and hotspots given that they do not permit homogeneous ventilation through the bulk. Aeration in bins is done to maintain conditions and reduce the risk of spoilage and heating. It also reduces or eliminates moisture migration. In the prairies, airflow rates of 1-2 $(L/s)/m^3$ are commonly used for aeration (Mills 1989).

During storage, the ambient temperature outside of bin walls fluctuates much more than that of the grain bulk. Because of this, a temperature gradient develops within the grain bulk causing the air to move. This air picks up vapour from the air causing moisture accumulation in some points of the bulk (hotspots) (Bala 2017). Temperature gradients in the bin develop as a result of temperature differences between the center of the bulk grain and the walls of the bin, creating moisture migration. During winter, the cold air causes the wall and the top center of the bin to cool the grain around this area. The cool air moves down along the walls by convection and across the bottom, and then moves upward through the warmer center of the bin, picking up moisture. This moisture is released at the top center where it accumulates. In summer, the center of the bin is cooler than the edge, so warmer air around the wall moves upward along the walls and then downward through the center, releasing moisture in the center bottom. Most spoilage begins at these two points (top center and bottom center) depending on ambient temperature if measurements are not taken to address moisture migration. (Abramson et al. 2001; Bern et al. 2008).

Moisture migration in bulk grain storages is affected by initial moisture content and temperature of grain, size of the bin, and weather conditions. Chang et al. (1994) developed a mathematical model to predict moisture content changes of stored grains as a function of aeration, soil temperature, ambient air conditions and solar radiation. Predicted and measured moisture contents were in a close agreement with a standard error of the estimate between 0.11 and 0.54% M.C. for storage periods up to 15 months.

Fungi respond to the moisture content of individual grains and not to that of the bulk grain (Bern et al. 2008). Grains stored under cold and dry conditions, such as those in winter, have a lower risk of spoilage or insect infestation and therefore can be stored for long periods. But as temperatures start rising in spring and summer, conditions are no longer favourable and storage time becomes shorter.

2.8.3 Soybean harvest quality

The Canadian Grain Commission (2017) periodically reports statistics on the quality of soybeans. Export quality is reported overall for all samples in Canada whereas information by province is described for harvest quality.

Soybeans have mainly two types of end-use. The oilseed, also called "crushing" type by the industry, is used for oil production for different markets (i.e. cooking oil and salad dressings). The oil-free product resulting from crushing is utilized for livestock feed as a source of protein. The second type of end-use is food-grade soybean, which is used for human consumption to produce tofu, soy salsa, etc. For the crushing industry, oil and protein content are important characteristics that provide quantitative estimates for the oil and livestock feed products. Fatty acid composition is used to determine quality and nutritional composition of the extracted oil.

The compositional analysis of 104 samples from different varieties of soybeans grown in Manitoba reported by the Canadian Grain Commission (2017) indicates that the average protein content was 37.4% and the oil content was 21%, calculated on dry basis. As for the percentage of main fatty acids in oil, Manitoba soybeans in 2017 had in average 9.8% palmitic acid, 4.4% stearic acid, 21.6% oleic acid, 53.5% linoleic acid and 15.1% saturated fatty acids.

2.8.4 Previous studies on the evaluation of variety and pre-treatments as related to pos-harvest conditions on grains

Bielewicz et al. (1993) found that successive drying and wetting cycles affected the sorption characteristics of Canola, widening the hysteresis loop. Significant differences were found in the sorption characteristics for different harvest locations and growing years.

Among some parameters highlighted by Neuber (1981), variety and pre-treatment of the sample were critical considerations in developing sorption isotherms of cereal grains. The author compared 27 studies on sorption isotherms for corn and concluded that some pre-treatments such as drying temperature, time and rewetting method affected the resulting sorption isotherms.

Significant differences were found for sorption isotherms of yellow-dent corn as affected by different varieties, growing year and interaction of drying treatment and rewetting (Chen and Morey 1989b). The authors recommended that factors affecting the sorption isotherms of agricultural products should be considered when developing moisture content studies and drawing conclusions for safe storage. However, they found no significant differences among different rewetting methods or samples prepared from different initial moisture contents.

Cenkowski et al. (2015) determined the sorption characteristics of three varieties of lentils as affected by postharvest conditions. Two varieties showed a significant change effect on EMC when subjected to wetting and drying cycles, and all three varieties showed a significant difference

when subjected to freeze and thaw cycles. For samples subjected to freezing and thawing, the EMC was found to be lower than the samples not subjected to these changes.

Research on the effect of cultivar and growing location on the sorption characteristics of soybeans was conducted by Atungulu et al. (2015). The authors evaluated the EMC of soybeans at 15, 25 and 35°C finding no significant effect of cultivar and growing location.

Based on the literature review, it is evident that there have not been any studies on EMC and sorption isotherms of soybeans involving the effect of pre-treatments related to post-harvest conditions.

3. MATERIALS AND METHODS

3.1 Soybean samples

Freshly harvested Manitoba grown soybeans were brought to the University of Manitoba in November 2017. Three varieties viz. Podaga R2, Lono R2 and Akras R2 corresponding to long, early and mid season maturity zones, respectively (Manitoba Pulse Soybean Growers 2017) were used in this study. It was ensured via visual inspection that the samples were sound, clean and free of foreign material. Moisture and oil contents of these varieties were measured (Table 3.1) following the ASAE Standard S352.2 (ASABE 1988) for moisture content and the American Association of Cereal Chemists international method 30-25.01 (AACC 1999) for oil content. The soybeans were stored in a controlled-environment chamber at 5°C and 70% RH.

Table 3.1 Moisture and oil contents of the three soybean varieties as initially received.

Variety	Maturity zone[1]	Average maturity days[1]	Moisture content (%)[2]	Oil content (%)[3]	Protein content (%)[4]
Akras R2	Mid	116	15.9	20.8	37.3
Lono R2	Early	115	12.3	19.9	37
Podaga R2	Long	120	9.6	19.8	-

[1]Source: Manitoba pulse and soybean growers: 2017 soybean variety guide (2019)

[2]Moisture content on dry basis

[3]Oil content on dry basis

[4]Source: SEED Manitoba (2017). Protein content of Podaga R2 was not included in the 2017 report.

The selection of the three varieties used for this study was based on three representative maturity zones in Manitoba. Variety selection by farmers, as indicated by private and public sectors, is

based on the regional growing season length (Manitoba Pulse and Soybean Growers 2107; Anonymous 2011). Thus, varieties fit into specific zones depending on long-term heat data and number of days with temperatures above the freezing point (frost-free period). The majority of soybeans cultivated in Manitoba are Roundup resistant (glyphosate herbicide tolerant) as are the three varieties used in this study. Published information on average protein content by variety varies depending on different factors such as genetics, growth management and environmental factors (Manitoba Pulse and Soybean Growers 2017). Although a composition analysis of soybean samples was not included in this study, the average quality parameters of a representative sample of different varieties of soybeans grown in Manitoba in 2017 is described earlier in section 2.8.3.

3.2 ERH apparatus

Several considerations were evaluated for the selection of the method used to obtain the experimental data for the sorption isotherms. Based on descriptions of different techniques used for this purpose, a dynamic method with circulating air was deemed suitable given the number of experiments to be conducted. The apparatus used in this project was fabricated based on a previous ERH system used to evaluate the equilibrium moisture content characteristics of red lentils (Gervais 2007; Cenkowski et al. 2015). As described by the authors, this system enabled the acquisition of desorption and adsorption data from samples at two different moisture contents simultaneously, using a single set up.

As for the duration of experiments, the dynamic ERH apparatus considerably reduced the time required for a sample to reach equilibrium compared to the SSS method. Regarding materials, fewer resources were needed with the ERH apparatus. The SSS method requires a large number of desiccators with salt solutions in addition to different temperature-controlled chambers needed

to house the desiccators with samples inside. In contrast, the ERH method is much simpler to execute once the experimental chamber is fabricated and calibrated.

A single set up of the ERH apparatus (Fig. 3.1) consisted of a PVC container (1) within which an array of 8 plastic trays were stacked (2). The trays were made of a PVC ring with a 96 mm internal diameter. Each tray held a #30 stainless steel wire mesh to support the soybean sample. Each tray had a gasket (3) that assured complete sealing of the tray column. A threaded cap (4) on each container was installed to provide additional headspace to connect air tubing and a connector for a humidity sensor and thermocouple. A gasket was used on the internal edge of the cap to make the container airtight. The bottom of the container had an opening to allow air to enter. Using plastic tubing (5), the air was circulated through the stack within the container by an ELITE 802 aquarium air pump (6) (Rolf C. Hagen USA Corp, Mansfield, MA). In this manner, a completed sealed system was assured that prevented circulating air from coming in contact with the ambient air. The air within the column of trays was continuously re-circulated and only came in contact with the samples from the moment the container was closed.

Both, the RH sensors (HIH 4000 Honeywell Inc, El Paso, TX) and type-T thermocouples (7) were mounted together at the same point on top of the container cap. Therefore, they measured the properties of circulating air after it had passed through the column of trays.
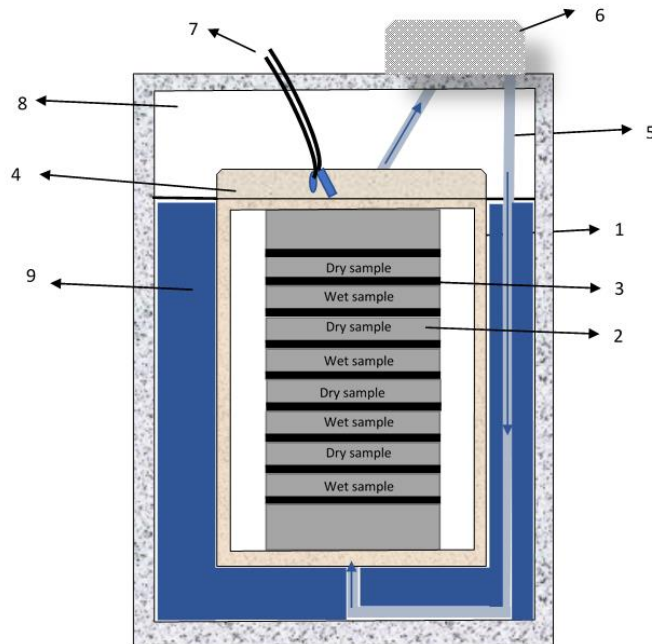
Fig 3.1 Diagram of a single experimental ERH experimental unit placed in a water-filled cooler. **(1)** container, **(2)** PVC tray, **(3)** gasket, **(4)** threated cap, **(5)** circulating air through plastic tubing, **(6)** air pump, **(7)** RH sensor and thermocouple, **(8)** headspace, **(9)** circulating water.

Figure 3.2 shows the complete ERH set up used for these experiments. Five experimental units (containers) were placed in a commercial cooler (1). A steel sheet (2) with openings for the containers (3) was placed at the middle top of the cooler. Additional openings were used to insert the tubing (4). An external water bath (5) was connected to maintain circulation of temperature-controlled water through the cooler. The steel sheet also prevented the water from coming in contact with the electrical connections (6) (i.e. RH sensors and thermocouples).

In order to maintain the temperature in the headspace between the steel sheet and the internal wall of the cooler lid, a small heat exchanger attached to a fan (computer fan) was placed on top of the steel sheet. The tubing was used to circulate water from a second external water bath (7) through the heat exchanger. An additional thermocouple was used to measure the temperature in the

headspace, with the purpose of monitoring and avoiding temperature gradients between the circulating water in the cooler and the headspace.

(a)   (b)
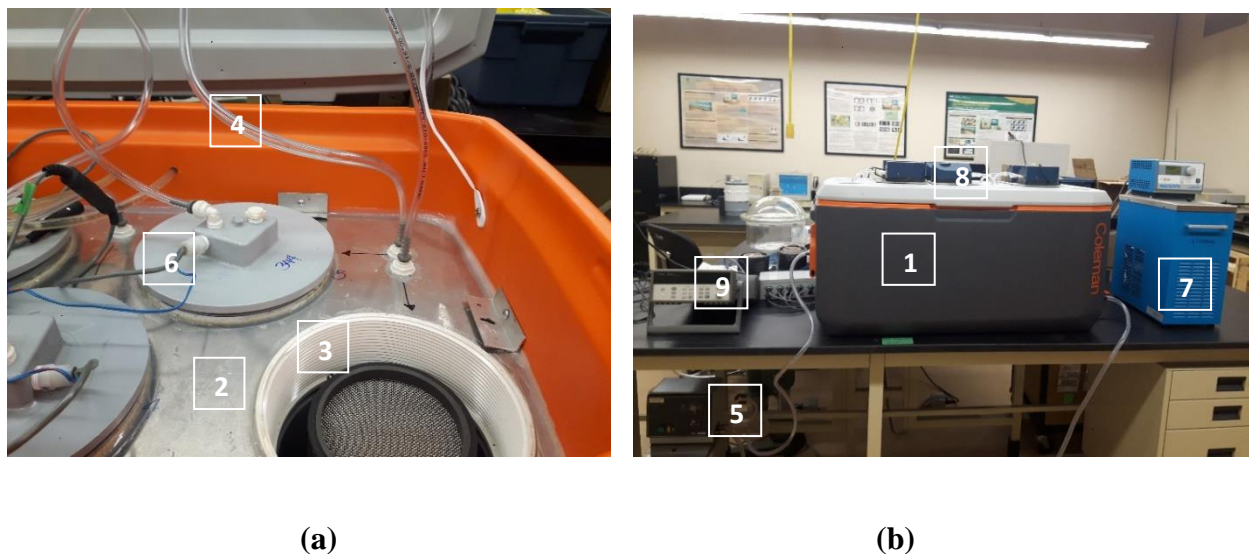
Fig 3.2 Internal **(a)** and external **(b)** view of the complete ERH set up. **(1)** cooler, **(2)** steel sheet, **(3)** container, **(4)** air tubing, **(5)** external water bath, **(6)** RH sensor and thermocouple, **(7)** external water bath connected to the heat exchanger, **(8)** air pumps, **(9)** data acquisition system.

Air pumps (8) were placed externally on top of the cooler lid and plugged into an external electrical connection. Undesirable heat generated by the pumps was transferred to the headspace and through the air in the tubing. To solve this problem, a heat exchanger was placed on the metal sheet inside the container, and by using a thermocouple, the temperature in the headspace was controlled. Before the air from the pump entered the container, the tubing was in contact with the water in the cooler, so the heat transferred by the pump was dissipated.

Humidity sensors were powered by a 5V regulated DC power supply. The thermocouples and the outcome from the power supply were attached to a data acquisition unit (9) (Model 34970A, Agilent Technologies Inc., Santa Clara, CA) to measure output voltages. The data acquisition

system was connected to a Windows desktop computer. Recording of voltages was done using a Benchlink data logger software (34825A BenchLink Data Logger 3 Software, Agilent Technologies, Inc.).

To attain temperatures of 10, 15, 20, 25 and 30°C, the water baths used pure water, whereas a mix of 10% v/v of Ethylene glycol and water was used to run experiments at 5°C. When using sub-ambient temperatures, the temperature indicated by the external device was approximately 2-3°C higher than the set temperature. So, in order to achieve 5°C inside the cooler, the temperature had to be set up around 2-3°C. The use of ethylene glycol lowered the freezing point of the mix, allowing to temperatures in the water baths between 2 and 4°C without ice built up on the walls and coils of the water baths.

3.3   Experimental Procedure

3.3.1   Calibration of Humidity Sensors

The manufacturer calibration of the RH sensors indicated a ratiometric response from 0 to 100% RH. However, published literature indicates that accuracy is lost for RH higher than 90% (Chen 2001; Lu and Chen 2007; Uddin et al. 2006). The manufacturing accuracy was 3.5% RH at 25°C. Based on literature and preliminary experiments, calibration using saturated salt solutions (SSS) was performed in order to assure greater precision. Initial calibration was performed at 25°C using five SSS as listed in Table 3.2. Selection of these five SSS was intended to cover the RH range that will likely be generated when carrying out the experiments.

Table 3.2 Relative humidity (%) of five saturated salt solutions used to calibrate RH sensors at different temperatures.

Temperature (°C)	Lithium Chloride	Potassium Acetate	Magnesium Nitrate	Sodium Chloride	Potassium Nitrate
5	11.26±0.47		58.86±0.43	75.65±0.27	96.27±2.1
10	11.29±0.41	23.28±0.53	57.36±0.33	75.67±0.22	95.96±1.4
15	11.30±0.35	23.4±0.32	55.87±0.27	75.61±0.18	95.41±0.96
20	11.31±0.31	23.11±0.25	54.38±0.23	75.47±0.14	94.62±0.66
25	11.30±0.27	22.51±0.32	52.89±0.22	75.29±0.12	93.58±0.55
30	11.28±0.24	21.61±0.53	51.40±0.24	75.09±0.11	92.31±0.60

Source: Adapted from Greenspan (1977).

Each of the five RH sensors used in the experiments was placed on top of a 200 mL flask containing SSS. The top of the flask was hermetically sealed to avoid external air to come in contact with the interior of the flask. The sensor measured RH in the headspace above the solution within the flask. The five flasks with sensors attached to them were placed in the ERH apparatus to control the temperature. The voltage response was recorded using the data acquisition system described in section 3.2. The sensors in this setup were left for enough time to equilibrate. Equilibration time varied depending on the temperature and SSS used. A calibration function was obtained by matching the voltage to the corresponding RH values from the SSS at each temperature. In addition to initial calibration, this procedure was repeated throughout the experimental phase of the study, as the sensors were affected by time, usage and condensation.

3.3.2 Pre-treatments to replicate post-harvest conditions

This study included the evaluation of the influence of post-harvest conditions on sorption characteristics of soybeans. As a result of seasonal and diurnal variations in Manitoba, there are changes in temperature and relative humidity that affect the stored product. The micro drying and wetting cycles, as well as the micro freezing and thawing cycles in stored beans, can be a result of such variations in storage. The intent of exposing soybeans to conditions related to condensation, drying, freezing and thawing was to artificially replicate the environmental variations that take place during storage.

Preparation of soybean samples to evaluate the effect of drying and rewetting post-harvest was done by subjecting the samples to three drying and wetting (DW) cycles. Fresh soybean samples (i.e. as they were initially received) were dried by placing a thin layer of seeds (approx. 2 cm) in a convection oven at 35°C for 24 hours. This temperature was chosen based on the maximum safe temperature used for drying soybeans in a bin (Abramson et al. 2001). After drying, samples were left to cool down for 10 minutes, divided into 1200 g subsamples and transferred into zip-lock plastic bags. Pre-calculated amount of water was added to each bag to increase the sample moisture content by 5%. The bag was gently shaken for an hour to allow water to disperse uniformly through the seeds. Each bag was kept at 5°C for 24 hours in a walk-in chamber. This procedure was repeated three times for each soybean variety.

To mimic post-harvest temperature variations, soybean samples were subjected to three continuous freezing and thawing (FT) cycles. Individual bags with 1200 g of soybeans were placed in a freezer with an average temperature of -10°C for 24 hours. After that, the bags were taken out of the freezer and left at room temperature for another 24 hours. This procedure was repeated three times for each variety of soybean.

3.3.3 Conditioning of samples

The initial moisture content of soybeans was determined using the oven convention method as per the ASABE standard (1988) for whole soybeans, which requires 15 g of sample to be dried at 103°C for 72 hours. Conditioning of samples was done to create samples with predetermined moisture contents, ranging from 5 to 14% MC (w.b.). As a starting point, the moisture content of all soybean samples was adjusted to the lowest moisture content achievable at indoor ambient conditions.

'Fresh' and FT samples were left to dry at room temperature in thin layers placed on plastic trays. After ten days, the overall moisture content of the samples was 5% (w.b.). Samples subjected to DW cycles were used as is after their third drying cycle, given that their moisture content was approximately 5% (w.b.). Based on the moisture content for each type of sample after drying, a calculated amount of water was added to each bag following equation 3.1.

$$\Delta G = \frac{G(M_f - M_i)}{100 - M_f} \tag{3.1}$$

Where

ΔG (g)= total amount of water to be added

$G(g)$ = total mass being conditioned

M_f = final moisture content

M_i = initial moisture content

Water was added to bags containing approximately 1200 g of sample. Next, each bag was manually shaken and tumbled to ensure uniform distribution of water on the soybeans. All samples were kept for at least one week at 5°C before starting experiments, to allow MC to equilibrate.

3.3.4 ERH Procedure

A total of 54 experiments were carried out for all combinations of variety, pre-treatment and temperature. For each variety, there were 'fresh', DW and FT subsamples with different moisture contents. For each of these subsamples, experiments were run at 5, 10, 15, 20, 25 and 30°C. A block design was used for experiments where blocking was done by temperature and treatments randomized on variety- pre-treatment combination. This led to nine experiments being conducted at each temperature.

For a single experiment, the following procedure was followed: in a set of 8 trays (one column), two different MC were used from a given type of sample (variety- pre-treatment). Each tray was loaded with 20 g of sample, alternating between the lower MC (dry sample) and the higher MC (wet sample). For the total of 5 of columns, five different combinations of MC were used, with a difference between them of 3% MC. Each column was placed inside a container. Thus, five different RH would be obtained as a result of the different combinations of MC used. Hence, by the end of each experiment, it was possible to obtain adsorption and desorption data for that specific temperature and condition.

Next, caps were tightly screwed to the containers, RH sensors and thermocouple connection were plugged into the data acquisition connections, and the cooler lid was shut. Air pumps and the fan attached to the heat exchanger were switched on. The temperature of the water bath connected to the heat exchanger was adjusted to attain the desired temperature in the headspace.

Voltage and temperature from each container were recorded using the data acquisition system at 10 s intervals and monitored periodically. The experiment was left to run until no changes or variation were observed in the voltage recordings for at least four consecutive hours. This steady condition was established to determine that the sample-air system within each container had

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reached equilibrium. Equilibration times varied depending on equilibration temperature and the MC of beans in each container. Equilibration time ranged from 8 to 24 hours. Experiments at 5°C were more sensitive to small temperature changes in the room, so longer times were necessary to determine if equilibrium had been reached.

The moisture content of samples in every single tray was measured in a convection oven. Weighing of samples was carried out rapidly to avoid moisture exchange with ambient air. Special care had to be taken with samples at sub-room temperatures to avoid surface condensation on the beans. Moisture content data from one container corresponded to the average adsorption data from four trays and average desorption data from the other four trays.

Given the large number of experiments and samples, and the long time needed to measure moisture contents, three different ovens were used. Moisture content variation was evaluated among the three ovens, by comparing moisture contents obtained from different MC samples and using three replicates. A total of 100 samples were used to evaluate the repeatability, finding no significant difference in the moisture content measured using the three ovens.

3.4   Data analysis

Voltages of each RH sensor were converted into relative humidity data using the calibration formulas previously obtained for each sensor. The average RH after reaching plateau data from each container was used as the ERH. The average values of the moisture content for each group of four trays from each container were used as the EMC values of adsorption and desorption.

Based on the literature review, and specifically on studies aimed to find the best mathematical model to predict sorption isotherm for soybeans (Osborn et al. 1985; Aviara et al. 2004; Chen and Morey 1989a), the modified Halsey equation and modified Oswin equation (eq. 2.4 and 2.7) were

used to fit the experimental data and predict the sorption isotherms. Nonlinear regression was performed to fit the experimental data and calculate the parameters for each equation. SigmaPlot 11.0 (SysStat Software Inc., San Jose, CA) statistical software was used to perform nonlinear regression, which uses the Marquardt-Levenberg algorithm to find the coefficients.

The quantitative standards used to evaluate the best fitting model were the mean relative percentage deviation (P) and the standard error of the estimated value (S.E.) as shown in eqs. 7 and 8, respectively.

$$P = \frac{100}{N} \times \sum \frac{|Y - Y'|}{Y} \tag{3.2}$$

$$S.E. = \sqrt{\frac{\sum (y - Y')}{df}} \tag{3.3}$$

where

Y = measured value

Y' = predicted value

N = number of measurements

df = degrees of freedom

4. RESULTS

4.1 Calibration of humidity sensors

Figure 4.1 shows a typical relationship between the standard relative humidity from the saturated salt solutions and predicted RH after calibration of RH sensors. Linear and quadratic models were tested. Four of the five sensors showed a better fit with linear models with coefficients of correlation (R^2) values greater than 0.994. Only one sensor had a better calibration with quadratic models with R^2 of 0.993, compared to its linear calibration (R^2 of 0.92) The calibrations for the five sensors provided similar responses (Fig. 4.1) with standard errors between 2.03 and 2.78% RH.
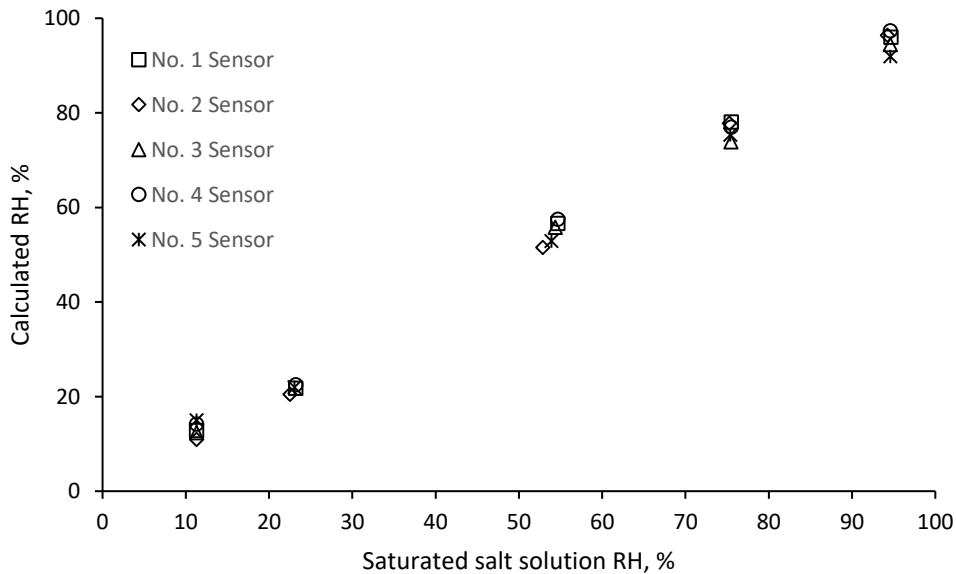
Fig 4.1 Relationship between reference relative humidity from saturated salt solutions and predicted relative humidity from the calibration of RH sensors.

Equilibration time varied depending on temperature and RH related to the saturated salt solution used. For sub-room temperatures, equilibration time was more than 12 hours before the sensors and solutions reached the desired temperature. Small fluctuations in room temperature also affected the equilibration time. Also, during the course of experiments, performance of the sensors

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varied slightly. To solve this problem, periodic calibration and inspection of sensors were performed.

4.2 Equilibration time on EMC experiments

The time needed to reach equilibrium varied substantially and was dependent on temperature and moisture content of the samples placed in the ERH apparatus. Overall, the samples with the lowest moisture content that produced lower relative humidity within the container would take longer to reach equilibrium. The equilibration time at lower temperatures was considerably longer than at higher temperatures. A typical graph of relative humidity as a function of time measured by the sensors in each container is shown in figure 4.2 at 10°C and figure 4.3 at 30°C.

Fig 4.2 Typical graph of relative humidity in each container of the ERH apparatus as a function of time at 10°C. Initial moisture content combinations of dryer and wetter samples were 5/8, 7/11, 9/12, 11/14 and 13/16% (w.b.) in each container measured by sensors No.1, 2, 3, 4 and 5 respectively.

The initial response at 10°C (Fig. 4.2) shows a high RH recorded by the sensors, especially in the case of sensors No. 3, 4 and 5 which were above 90% RH. The difference between the room and samples temperature (around 20-25°C) and the temperature within the ERH apparatus and sensors (10°C) might have produced an initial condensation on the surface of the sensors and the internal surfaces of the containers. A rapid decrease of RH is observed within the first 45 minutes after starting the experiments as the temperature of the soybean samples went down. Sensor No. 1 indicates that equilibrium at 38% RH was reached after 14 hours. Sensor No. 5 indicates that equilibrium at 74% RH was reached after 8 hours. Overall, for temperatures below 20°C, equilibration time ranged between 8 to 18 hours.
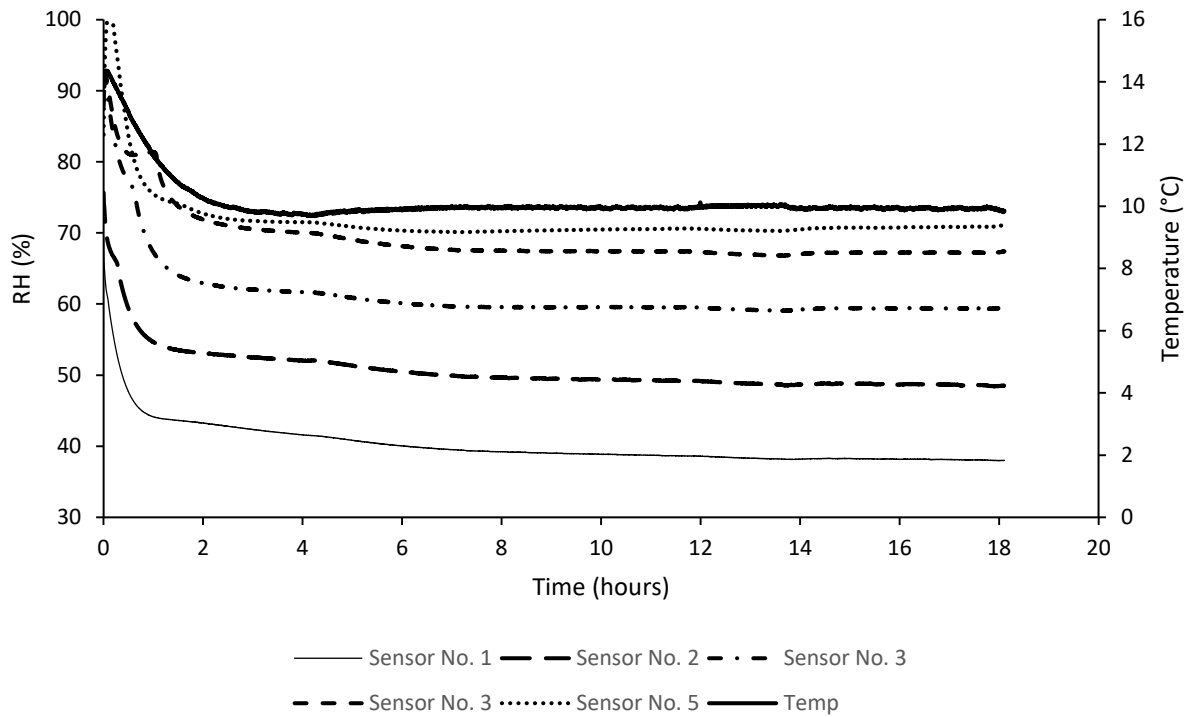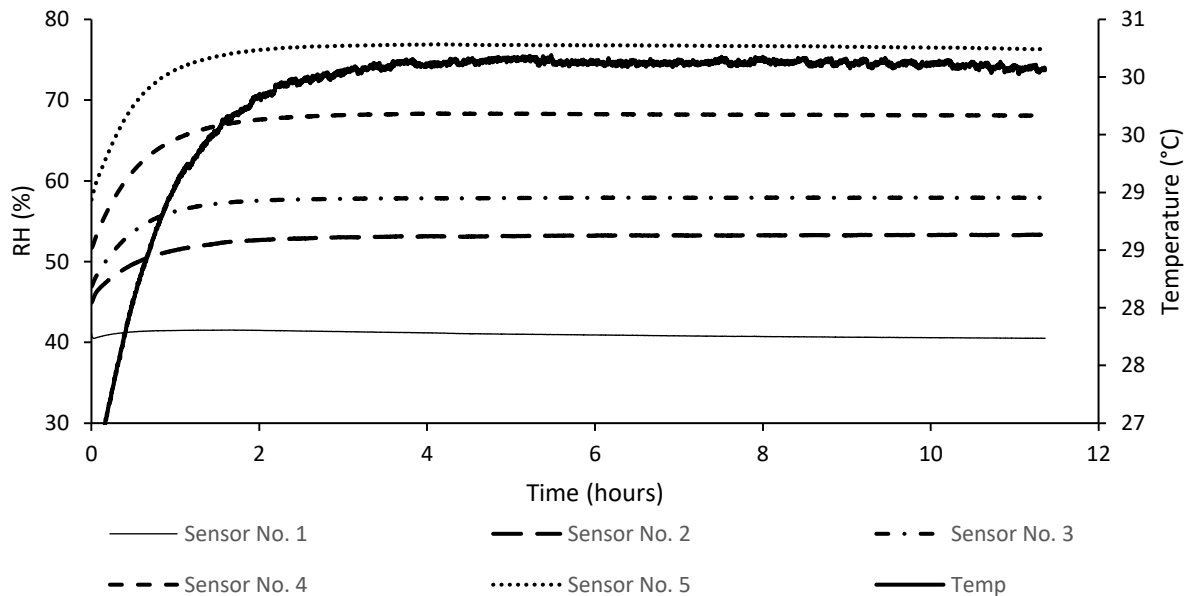

Fig 4.3 Typical graph of relative humidities in each container of the ERH apparatus as a function of time at 30°C. Initial moisture content combinations of dryer and wetter samples were 5/8, 7/11, 9/12, 11/14 and 13/16% (w.b.) in each container measured by sensors No.1, 2, 3, 4 and 5 respectively.

The equilibration time at 30°C (Fig 4.3) was considerably faster than the other temperatures studied. The RH values recorded by the sensors gradually increased after placing the samples in the ERH apparatus and starting the experiments. Overall, equilibrium at 30°C took between 7 and 9 hours. Similar equilibration times (between 8 to 12 hours) were reported by Yang (1992) using a dynamic ERH apparatus to measure the EMC of canola. In general, to assure that equilibrium was established, experiments were allowed to run for at least 12 hours.

4.3   EMC results

Experiments conducted in the ERH apparatus were described in section 3.2 for three varieties of soybeans grown in Manitoba (Akras, Lono and Podaga), each subjected to three different pre-treatments: freshly harvested ('fresh'), successive drying and wetting (DW) cycles and successive freezing and thawing (FT) cycles as described in section 3.3.2. Soybeans were equilibrated at 5, 10, 15, 20, 25 and 30°C.

The results of EMC for all treatments and varieties are presented in Appendix B in the range of RH obtained at each equilibrium temperature. Data points in these graphs show individual measurements, meaning that the four replicates of adsorption or desorption for a given temperature and RH are graphed. The ERH corresponding to each EMC data point is the average of the RH recorded for a one-hour period after three hours of equilibrium were achieved. Desorption EMC data were in all the cases higher than adsorption EMC data. Thus, desorption EMC data points are located above adsorption EMC in all the figures.

Standard errors of the average of four EMC replicates for a given sample were in the order of 0.01 to 0.25% MC (d.b.) indicating good repeatability of the measured moisture content. In general, the standard deviation was increased with higher moisture contents.

4.3.1 Desorption data at low RH

The lowest RH values (in the vicinity of 35%) were generated in the ERH apparatus by placing samples with the lowest combination of MC. Given that the measured EMC was produced by the moisture exchange between the "dry"/ "wet" samples and the air in the enclosed system, the RH generated within the container usually increased with respect to the initial RH of the ambient air (around 11% RH). However, it was desirable to have data points at a lower moisture content. If the ERH apparatus was to be used for this purpose, the "wet" sample would increase the RH in the container. Therefore, with the aim of producing data points corresponding to lower ERH, soybean samples at the initial moisture content of 5% (w.b.) were left to dry in a closed space with a low RH. In this case, the applicable principle was that the soybeans would reach equilibrium with the constant RH of the ambient air. One set of samples were placed in a convection oven at 30°C, and another set was placed in a room at 20°C. Three replicates were used for each sample. Changes in the samples' mass were measured periodically. Temperature and RH in the room and the oven were monitored to ensure they were constant.

These experiments were finished when there were no changes in the mass for three consecutive measurements (every two days between measurements). Given that the oven and the room were ventilated, the dynamic conditions of the air caused the samples to reach equilibrium more rapidly than if the conditions were stagnant. Afterwards, the moisture content was measured by the oven method. The measured moisture content and corresponding RH and temperature were used as the desorption points at 20°C and 30°C with ERH values of 14.5 and 10% respectively.

4.3.2 Comparison with previous studies on soybeans

After comparing published data with the experimental results from this study, it was noted that a number of different methods have been used to estimate EMC of soybeans (Osborn et a. 1989;

Alam and Shove 1973; Larmour et al. 1944; Pixton and Warburton 1975; Atungulu et al. 2015; Denloye and Ade-John 1985). These include static gravimetric method with saturated salt solutions, agitated air in an enclosed system with SSS, sorption vapour analyzer, dewpoint, dynamic methods using SSS and dynamic ERH with sulfuric solutions. Additionally, methods used to measure the moisture content also vary, as these include vacuum drying, two-step drying and convection oven using temperatures from 80 to 104°C for 48 to 72 hours.

The differences in these methods contribute to some degree of variability on the reported EMC-ERH relationship of soybeans. Nevertheless, adsorption and desorption EMC-ERH relationship from published data and experimental data from this study follow a similar trend and shape (Fig. 4.4). The EMC data from this study shown in figure 4.4 is the average of the four replicates for fresh Akras soybeans. 'Fresh' samples of the three varieties showed desorption EMC data similar to those of Osborn et al. (1989) who used a dynamic dew point method. Experimental adsorption data were in close agreement with data reported by Larmour et al. (1944) who used the SSS method.
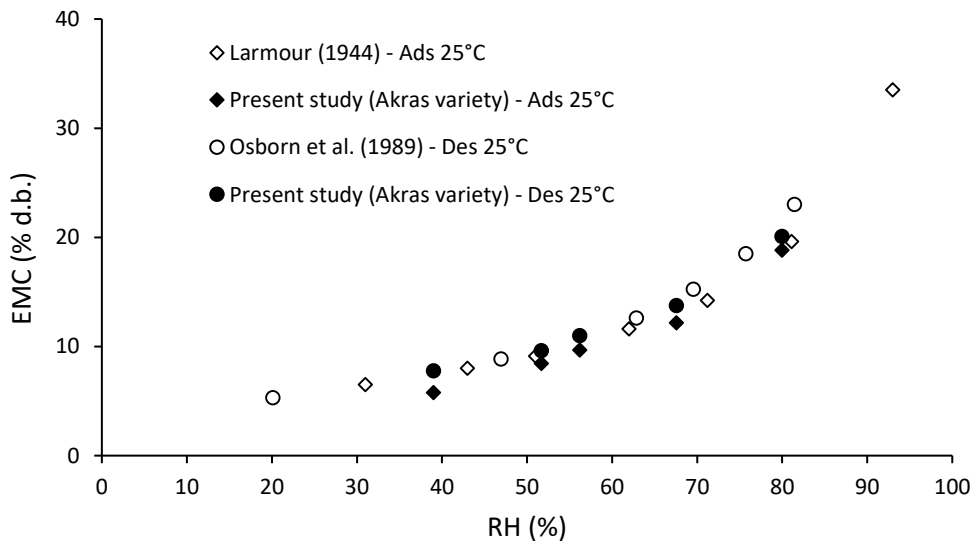
Fig 4.4 Comparison of EMC data obtained for Akras soybeans (fresh samples) at 25°C with those reported by Osborn et al. (1989) and Larmour et al. (1944).

4.3.3   Temperature effect on EMC

In general, the EMC data for a given sample decreased as the equilibrium temperature increased. Overall, the ERH at constant EMC was higher at higher temperatures. These results indicate that the amount of moisture held by the soybean samples changed with respect to temperature. A more pronounced effect of temperature was observed for the desorption process than for the adsorption process.

As observed in figures 4.5 and 4.6, the effect of temperature on EMC data is more pronounced in the case of desorption. For example, at 60% RH, the difference between EMC at 10 and 20°C of fresh samples of Lono soybeans is 0.8% MC (d.b.) for adsorption, whereas the difference for desorption is 1.4% MC (d.b.). A paired t-test indicates the EMC of those comparisons are statistically significant (P<0.001). The shift in the position of the EMC data was observed for all the samples as affected by different equilibrium temperatures.
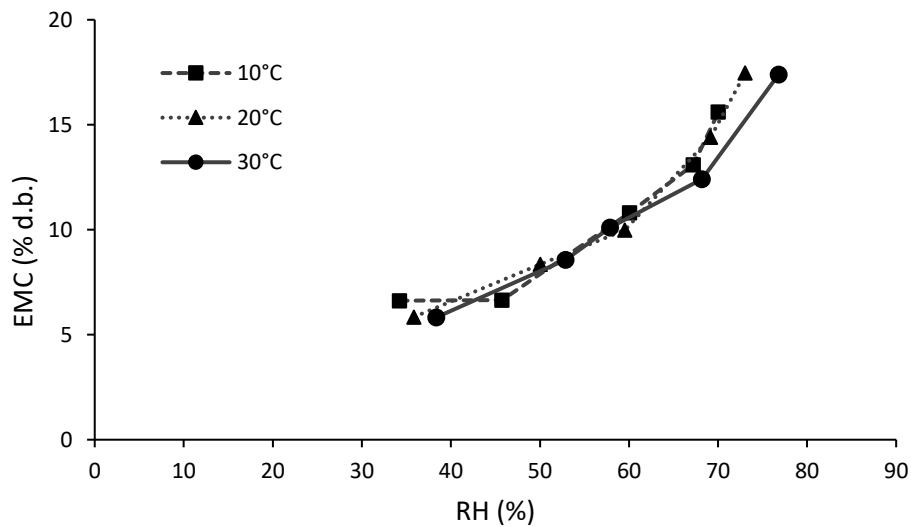
Fig 4.5 Adsorption data for fresh samples of Lono variety at 10, 20 and 30°C.
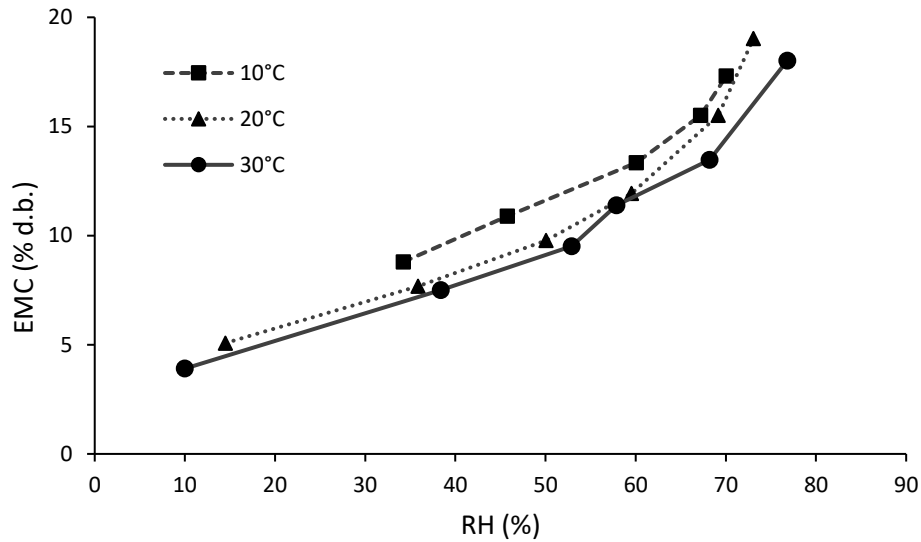
Fig 4.6 Desorption data for fresh samples of Lono variety at 10, 20 and 30°C.

When the EMC data at different temperatures is plotted (Fig. 4.7), it is noted that some points have a lower EMC at higher temperatures. Alam and Shove (1973) reported crossing of sorption isotherms as the change of trend in a curve at a given temperature, so the EMC at a low temperature was lower than at a higher temperature. The authors detected a change in the characteristics of the adsorption isotherms at 5 and 15°C compared to isotherms at higher temperatures, suggesting different adsorption mechanisms were associated at low and high relative humidities.
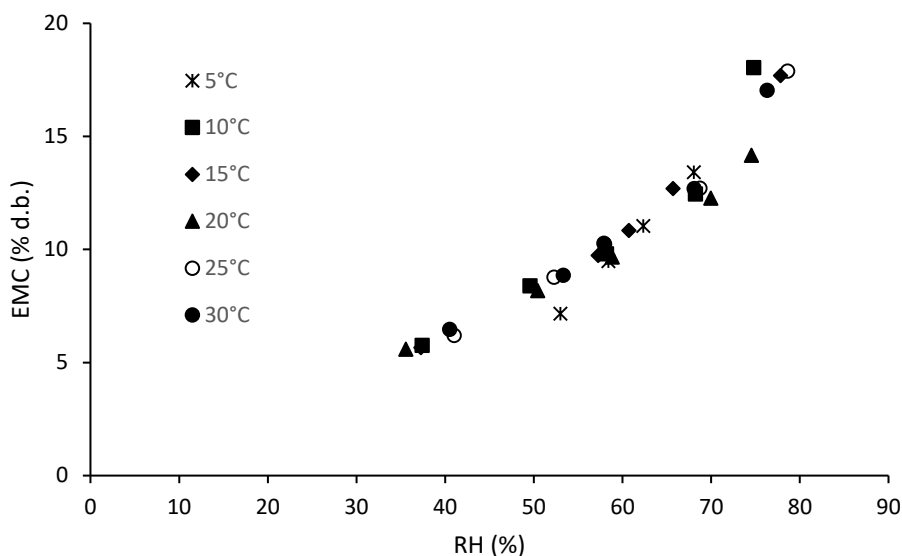
Fig 4.7 Adsorption EMC data of Fresh Podaga soybeans at various temperatures.

An unexpected trend was observed for the EMC of samples equilibrated at 5°C. It was expected that EMC at 5°C would be higher than other equilibration temperatures as it was the lowest temperature used in this study. However, EMC values at 5°C in many cases were lower than those at higher temperatures. After repeating the experiments and ensuring no possible technical problems existed, the trends and data continued to be similar, with almost no changes recorded.

The trend of EMC values at 5°C was attributed to some factors that were beyond our control. The temperature and RH difference between the ambient air in the lab and the ERH apparatus were greater when performing experiments at 5°C. The ERH produced within the container as a result of sub-room temperatures was considerably higher than RH in the room (around 11% RH). This situation is believed to have produced a rapid moisture exchange between the soybeans and the air in the room given the large difference between relative humidities. To reduce exposure time to room conditions, the tasks of unloading the samples from each container as well as weighing soybeans for moisture content determination were performed as quickly as possible. The combined

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task of unloading and weighing each sample set took approximately 5 minutes. As stated by Bielewicz (1991), who used a similar ERH device, moisture losses from high MC samples posed problems during sample handling.

4.3.4   Hysteresis

Hysteresis was observed for all pairs of adsorption and desorption data (Appendix B). Hysteresis loop evidently became narrower as the temperature increases. Overall, the hysteresis size ranged between 0.23 to 4.5% d.b. Multiple t-tests were performed for each pair of desorption-adsorption data at constant ERH and temperature. All comparisons were adjusted with Tukey method for multiple comparisons at 0.05 confidence level. Results show that all desorption-adsorption pairs of data are significantly different, indicating presence of hysteresis along the entire ERH range and temperatures tested in the experiments.

An example of the hysteresis magnitude trend at different temperatures found on all tested varieties and treatments is shown in figure 4.8. In general, the difference between adsorption and desorption characteristics at a given RH decreased at higher temperatures. In the case of fresh Podaga soybeans, for example, the hysteresis magnitude at 10°C was between 1.7 and 2.3% MC d.b., whereas at 30°C hysteresis magnitude was between 0.5 and 1.3% MC d.b.

A difference in the pattern of hysteresis magnitude as a function of RH was observed between the lower and higher temperatures. The gap between adsorption and desorption characteristics decreased as the RH increased at higher temperatures. At lower temperatures, the hysteresis size varied along the entire RH range. Similar trends were observed by Chen and Morey (1989b) with yellow-dent corn as the magnitude of hysteresis at 5 and 25°C increased in the range of 10 to 8% RH, while at 45°C the magnitude of hysteresis decreased for RH above 15%.
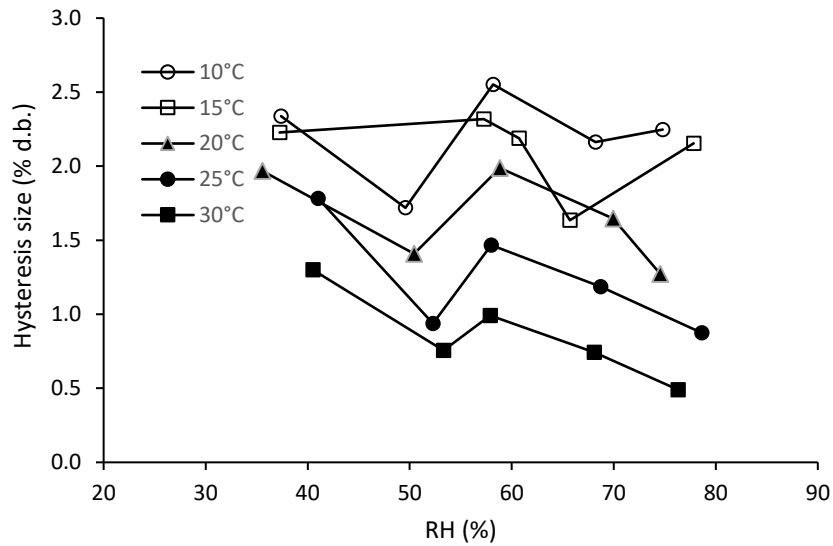
Fig 4.8 Hysteresis magnitude measured as the difference of moisture content in dry basis between adsorption and desorption data for fresh Podaga soybeans as a function of RH at different temperatures.

Majority of sorption studies with soybeans agree to the presence of hysteresis. Atulungu et al. (2015) used a vapour sorption analyzer and reported pronounced hysteresis in two soybean varieties studied at 15, 25 and 35°C. Denloye and Ade-Jhon (1985) found hysteresis at 30°C with a maximum value of 0.003% MC d.b. They reported that the presence of hysteresis was in the intermediate levels of RH. The sorption isotherms of soybeans presented in the compilation done by Iglesias and Chirife (1982) show a clear hysteresis loop for soybeans at 30°C, which narrows when moving towards high RH. Alam and Shove (1973) observed the presence of hysteresis and noted that it was greater at low temperatures and low relative humidities. Thus, the hysteresis loop narrowed as the sorption isotherm approached higher relative humidities.

4.4 Mathematical modelling of sorption isotherms

In order to determine an equation to predict the EMC-ERH relationship of the experimental data, a nonlinear regression procedure using the Marquart method was used to calculate the parameters A, B and C for the modified Halsey (Eq. 2.4) and modified Oswin equations (Eq. 2.7). The selection of these two models from all the available mathematical models was based on various studies dedicated exclusively to find the best equation to describe the sorption isotherms for soybeans (Chen and Morey 1989a; Osborn et al. 1989; Aviara et al. 2004). The chosen equations have the advantage of being a function of moisture content and temperature, so the parameters are calculated for the entire range of temperature used in this study.

A set of data corresponded to all individual EMC-ERH data obtained from each sample (variety-pre-treatment combination) at different temperatures. Given that a significant difference was found between adsorption and desorption data, the parameters of the equations were determined for adsorption and desorption separately. The goodness of fit of the regression was evaluated based on the coefficient of determination for nonlinear regression (R^2), the standard error of the mean (S.E.), the mean relative error (P) and the scattered plot of studentized residuals. These statistical tools were also used to compare the two equations and evaluate which one provided the best fit to the experimental data. Tables 4.1 and 4.2 show the results of the nonlinear regression fit to the modified Halsey and modified Oswin equations, respectively.

Table 4.1 Parameter estimates of modified Halsey equation for all soybean samples.

Post-harvest treatment	Sorption process	Modified Halsey - Model Parameters			Goodness-of-fit criteria		
		A	B	C	R^2 [d]	P [e] (%)	S.E.[f] (decimal)
Variety: Akras							
Fresh[a]	Ads	1.8766 ± 0.0588	-4.57×10^{-5} ± 0.0012	1.0988 ± 0.0237	0.9609	3.51	0.0264
	Des	3.1721 ± 0.0627	-0.0071 ± 0.0010	1.4923 ± 0.0234	0.9820	3.31	0.0227
DW[b]	Ads	1.5075 ± 0.0611	0.0068 ± 0.0012	1.0235 ± 0.0272	0.9377	4.31	0.0316
	Des	3.0423 ± 0.0983	-0.0014 ± 0.0014	1.4982 ± 0.0387	0.9495	6.27	0.0368
FT[c]	Ads	2.2461 ± 0.0776	0.0032 ± 0.0013	1.2830 ± 0.0320	0.9467	4.30	0.0314
	Des	3.4327 ± 0.1057	-0.0058 ± 0.0015	1.6071 ± 0.0394	0.9552	7.57	0.0366
Variety: Podaga							
Fresh	Ads	2.0151 ± 0.0525	0.0021 ± 0.0009	1.1761 ± 0.0221	0.9655	3.07	0.0241
	Des	3.0774 ± 0.0750	-0.0036 ± 0.001	1.4890 ± 0.0291	0.9671	4.33	0.0286
DW	Ads	2.1046 ± 0.1276	0.0032 ± 0.0021	1.2333 ± 0.0511	0.8734	6.96	0.0511
	Des	3.0247 ± 0.1438	0.0015 ± 0.0021	1.5149 ± 0.0544	0.917	7.92	0.0515
FT	Ads	1.647 ± 0.0516	0.0054 ± 0.001	1.0518 ± 0.0218	0.9593	3.68	0.0260
	Des	3.1212 ± 0.0833	-0.0034 ± 0.0012	1.5095 ± 0.0317	0.9655	5.02	0.0300
Variety: Lono							
Fresh	Ads	1.9968 ± 0.0534	0.0024 ± 0.0010	1.1722 ± 0.0235	0.9632	3.85	0.0273
	Des	3.2118 ± 0.0588	-0.00644 ± 0.0009	1.5144 ± 0.023	0.9817	3.75	0.0232
DW	Ads	2.5952 ± 0.0796	-0.0046 ± 0.0011	1.3804 ± 0.0314	0.9536	3.35	0.0272
	Des	3.6254 ± 0.1233	-0.0114 ± 0.0016	1.6486 ± 0.0452	0.9421	6.52	0.0401
FT	Ads	2.0135 ± 0.0440	0.0006 ± 0.0008	1.1795 ± 0.0179	0.9794	2.84	0.0206
	Des	3.4308 ± 0.0731	-0.0082 ± 0.0010	1.6052 ± 0.0273	0.9783	5.35	0.0256

a- Fresh: freshly harvested
b- DW: Drying and wetting cycles
c- FT: Freezing and thawing cycles
d- Coefficient of determination for nonlinear regression
e- Mean relative error (%)
f- Standard error of stated value (decimal)

Table 4.2 Parameter estimates of modified Oswin equation for all soybean samples.

Post-harvest treatment	Sorption process	Modified Oswin - Model Parameters[a]			Goodness-of-fit criteria		
		A	B	C	$R^{2\ d}$	P^e (%)	S.E.[f] (decimal)
				Variety: Akras			
Fresh[a]	Ads	7.9165 ± 0.1694	-0.0041 ± 0.0078	1.4697 ± 0.0298	0.9673	2.95	0.0241
	Des	10.8242 ± 0.1897	-0.0447 ± 0.0087	2.0271 ± 0.0424	0.9701	5.43	0.0293
DW[b]	Ads	6.3122 ± 0.1627	0.0457 ± 0.0080	1.3390 ± 0.0344	0.9435	4.04	0.0301
	Des	9.8548 ± 0.2105	-0.0075 ± 0.0100	2.0042 ± 0.0591	0.9375	8.06	0.0410
FT[c]	Ads	7.7461 ± 0.1709	0.0199 ± 0.0081	1.6714 ± 0.0418	0.9483	4.18	0.0310
	Des	10.7484 ± 0.2116	-0.0329 ± 0.0098	2.1836 ± 0.0597	0.9474	8.50	0.0396
				Variety: Podaga			
Fresh	Ads	7.7025 ± 0.1186	0.0123 ± 0.0058	1.5469 ± 0.0295	0.9663	2.62	0.0238
	Des	10.262 ± 0.1611	-0.0237 ± 0.0077	1.9975 ± 0.0466	0.9561	5.75	0.0330
DW	Ads	7.3657 ± 0.2846	0.0275 ± 0.0134	1.5965 ± 0.0658	0.8776	6.77	0.0503
	Des	9.4909 ± 0.2886	0.0139 ± 0.0136	2.0478 ± 0.0776	0.9117	8.85	0.0531
FT	Ads	6.9663 ± 0.1352	0.0350 ± 0.0065	1.4209 ± 0.0284	0.9643	3.43	0.0243
	Des	10.2823 ± 0.1479	-0.0208 ± 0.0069	2.1371 ± 0.0465	0.9659	5.64	0.0299
				Variety: Lono			
Fresh	Ads	7.6608 ± 0.1324	0.0148 ± 0.0066	1.5626 ± 0.031	0.9655	3.75	0.0264
	Des	10.7561 ± 0.1277	-0.0392 ± 0.0062	2.0909 ± 0.0364	0.9772	4.85	0.0259
DW	Ads	8.5206 ± 0.1473	-0.0230 ± 0.0065	1.7738 ± 0.0418	0.9529	3.39	0.0274
	Des	11.3152 ± 0.2197	-0.0658 ± 0.0100	2.2153 ± 0.0680	0.9327	6.78	0.0432
FT	Ads	7.6750 ± 0.1007	0.0042 ± 0.0047	1.5898 ± 0.0230	0.9827	2.60	0.0189
	Des	10.7554 ± 0.1442	-0.0465 ± 0.0067	2.2008 ± 0.0438	0.9721	5.65	0.0290

a- Fresh: freshly harvested
b- DW: Drying and wetting cycles
c- FT: Freezing and thawing cycles
d- Coefficient of determination for nonlinear regression
e- Mean relative error (%)
f- Standard error of stated value (decimal)

The coefficients of determination for nonlinear regression (R^2) for most samples ranged from 0.93 to 0.98 for both equations. Coefficients of determination for Podaga DW were 0.87 for adsorption and 0.91 for desorption with both equations. These lower R^2 values are related to greater dispersion of the experimental data. The standard error of the predicted values from the equations were between 0.02 and 0.03 (RH in decimals), the exception being Podaga DW samples with standard errors of around 0.05.

Evaluation of the scattered plot of the studentized residuals shows an acceptable random distribution of the residuals in all the samples with both equations. Example of the studentized residual plots of two samples with the modified Halsey and modified Oswin equations are shown in figures 4.9 and 4.10. Overall, very few data points had large studentized residual values indicating few outlying data points.

| (a) | (b) |

Fig 4.9 Studentized residuals of predicted values with **(a)** modified Halsey and **(b)** modified Oswin equations for the adsorption data of Lono soybeans subjected to freezing and thawing cycles.

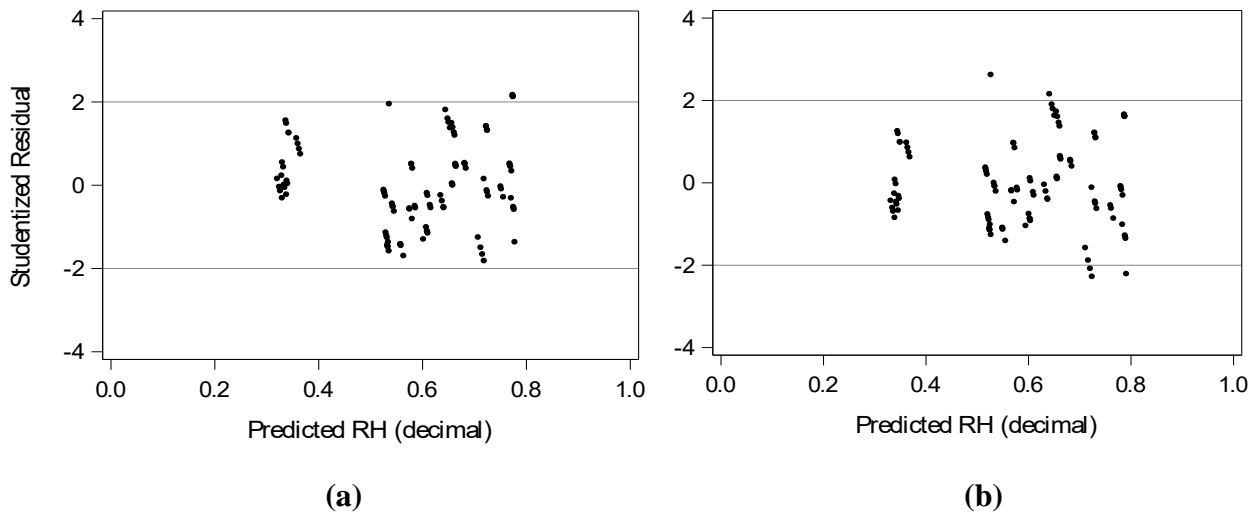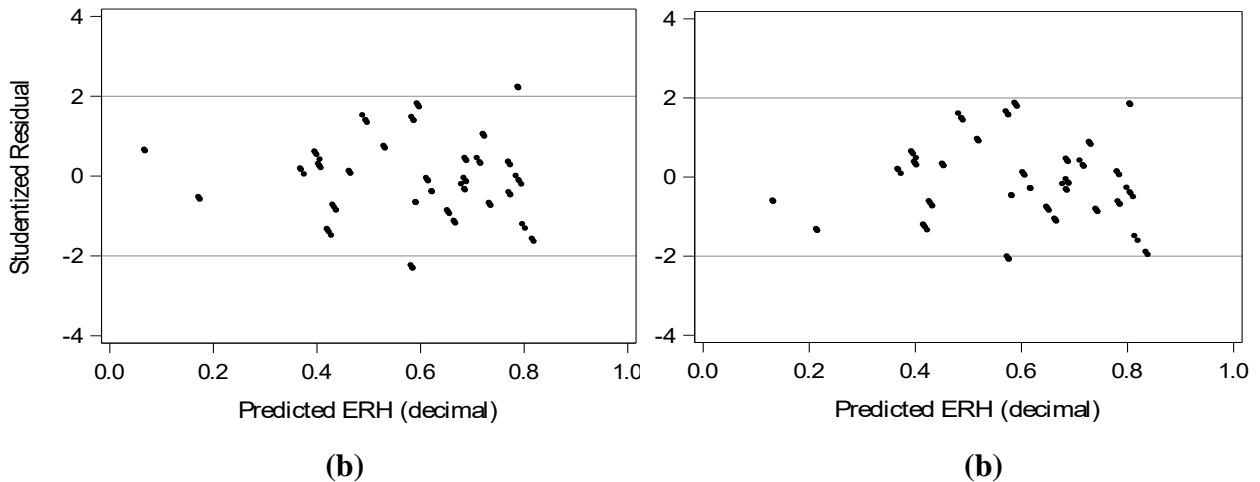| (b) | (b) |

Fig 4.10 Studentized residuals of predicted values with **(a)** modified Halsey and **(b)** modified Oswin equations for desorption data of Podaga soybeans subjected to drying and wetting cycles.

The regression statistical criteria show that the modified Halsey and modified Oswin equations are adequate to predict the experimental data of this study. In order to determine which equation provides the best prediction, the mean relative error (P) and the standard error are compared for each sample data. From the set of 9 adsorption sample data (variety-treatment combinations), 8 produced larger mean relative errors and larger standard errors with the modified Halsey equation (smaller relative error values indicate a better goodness-of-fit). However, the opposite occurs with the desorption data, where all mean relative errors and standard errors were smaller with the modified Halsey equation. The magnitude of the difference between the mean relative errors from the two equations for the adsorption data ranges from 0.19 to 0.56%. The difference of the mean relative errors for the desorption data ranges from 0.25 to 2.12%. This comparison indicates a greater difference in the prediction between the two equations for the desorption characteristic. In this case, the modified Halsey equation gives a superior prediction. As for the adsorption data, the modified Oswin equation provides a better fit although the prediction difference is minimal compared to the modified Halsey equation.

An explanation was sought for the difference between the adsorption and desorption datasets when comparing the predicted equation curves with the experimental data. In figure 4.8, it is observed that the predicted isotherms using the modified Halsey and the modified Oswin equations follow almost the same path along the experimental values. The adsorption isotherms follow the same path, as it is seen from the graph that the adsorption curves overlap with a slight difference only at the highest ERH data. The desorption isotherms have a more pronounced difference when approaching the lowest ERH, with the modified Oswin desorption isotherm underpredicting the EMC data.
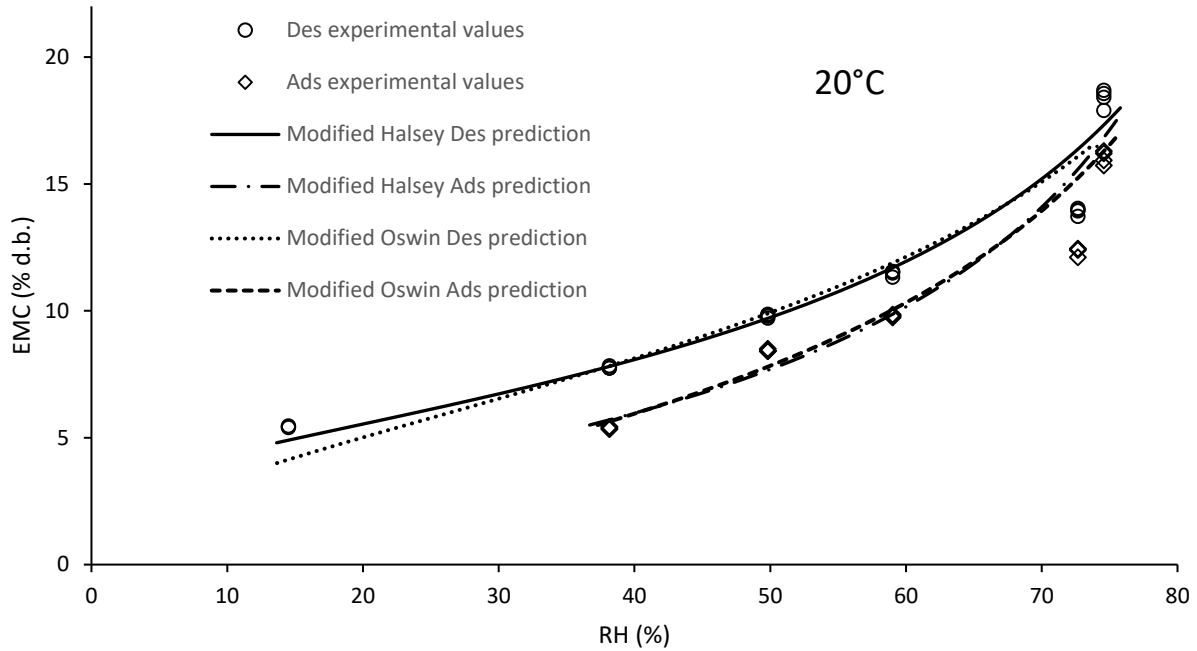
Fig 4.11 Experimental desorption and adsorption data and predicted isotherms with modified Halsey and modified Oswin equations for the Akras fresh samples at 20°C.

The isotherm curves predicted with the modified Halsey equation for each temperature and sample are shown in Appendix B along with the individual experimental data. The prediction was better and more accurate at low to intermediate RH and at higher temperatures (above 10°C). After comparing experimental data at 5°C with other temperatures and comparing the predicted isotherm versus the experimental data, there is an indication that the experimental data as well as the predicted isotherms are accurate for temperatures above 10°C.

The applicable range of the prediction of the modified Halsey equation based on experimental data, covers the RH range between 10 and 80% in the case of desorption and between 30 and 80% RH in the case of adsorption. The difficulty of EMC experiments at high RH restricts the accuracy and the applicability range above 80% RH. In experiments using saturated salt solutions, there is a risk of mould growth due to prolonged equilibration times and high RH. When using humidity sensors, the accuracy of the recorded values decreases at high RH, with some authors reporting

loss of confidence in the recorded values above 70% RH. At this high RH, problems such as drift and ageing are more pronounced in humidity sensors.

Uddin et al. (2006) found that the accuracy of the predicted EMC from three mathematical models (modified Henderson, modified Chung-Pfost and modified Oswin equations) is drastically affected by accuracy of the RH sensors. The predicted error calculated by these authors in a temperature range from 0 to 50°C was relatively low (0.25 to 0.65% MC d.b.) and stable for RH range from 10 to 70%. Beyond 70%, the predicted error increased substantially and varied depending on the equation. The authors suggested that considering practical aspects and the conditions normally encountered during safe storage, the predicted values using RH sensors were safe for RH below 80%. The authors also observed that accuracy decreased at the lower studied temperatures.

Chen et al. (2014) also concluded from their experiments that the accuracy of the predicted EMC after calibration of sensors and determination of modified Oswin parameters for Oolong tea, were within 0.5% MC (w.b.) for RH below 70%. Their measured predicted error increased in a similar fashion as shown by Uddin et al. (2006) for RH above 70% and drastically increased above 80%. In regards to the effect of temperature on the EMC prediction, Atungulu et al. (2015) found that the calculated parameters of the modified Henderson, modified Halsey, modified Oswin and modified Chung-Pfost equations provided a better prediction for temperatures above 35°C in contrast to their tested temperatures of 15 and 25°C.

The low prediction related to high RH and low temperatures might be related to the drift and aging problems on the RH sensors, which in turn might be related to condensation problems. When temperature of the RH sensor is lower than that of the samples, condensation occurs on the sensor surface (Stekelenburg and Labots 1991).

It is mentioned by several authors (Chen et al. 2001; Uddin et al. 2006; Chen et al. 2014) that at RH below 80%, the measurements using RH sensors are adequate considering the recommended moisture content and relative humidity for storage of soybeans falls in that range. Moreover, humidity sensors provide a rapid monitoring method. Based on the results of the present study and the experimental range of RH produced, the calculated parameters for the Halsey equation are valid for temperatures above 10°C in the range of 10 to 80% RH for desorption isotherms and 30 to 80% for adsorption isotherms.

4.5   Evaluation of effects of variables on sorption characteristics

The considerable amount of data generated by the dynamic ERH method and by the number of variables studied require special analysis to evaluate whether there are differences in the sorption isotherms due to soybean variety and pre-treatments. Additionally, it is to be noted that ERH was measured as a result of moisture exchange between the sample and the air at equilibrium, thus producing different points along the entire RH range for all 54 experiments. Therefore, direct comparison of the collected experimental data would be impractical.

Similar studies on sorption characteristics of agricultural products with the ERH method have used mathematical models to compare sorption isotherms and establish whether significant differences exist due to varieties and treatments. Chen and Morey (1989b) compared the ERH models of yellow-dent corn, and based on F-tests, found significant differences among varieties. Cenkowski et al. (2015) used a graphical method based on comparison of the confidence intervals of the predicted isotherms to find differences in the EMC properties of red lentils as affected by post-harvest conditions. The benefit of using the graphical method over the F-tests to compare isotherms is that the former allows determining in what RH range the differences (if they exist) appear at

constant temperature. The F-test, on the other hand, provides information on whether there are differences between the curves without being specific of RH or temperature.

4.5.1 Variety effect on sorption isotherm

The graphical method requires plotting the upper and lower 95% confidence intervals of the sorption isotherms for the variable that is to be compared. Overlapping confidence intervals of two isotherms would suggest that there is no significant difference between them (Cenkowski et al. 2015). The comparison of confidence intervals of the three varieties was done at 10, 15, 20, 25 and 30°C. From the graphical method shown in figures 4.12 and 4.13 at 20°C using individual data from the fresh samples of the three varieties used in this study, it is apparent that the upper confidence intervals as well as the lower intervals of the three varieties of soybeans overlap along the entire RH range, indicating no significant differences in the sorption isotherms were found among varieties. The relative humidity in the graphs is shown in decimal rather than percentage as the modified Halsey equation and most of the mathematical sorption models express RH in decimals.
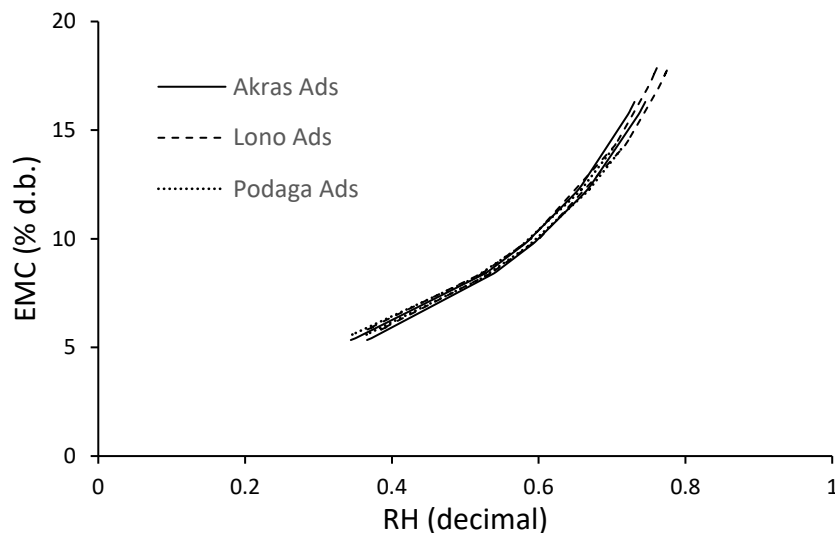

Fig 4.12 Plot of the 95% lower and upper confidence intervals of the adsorption isotherms modelled with the modified Halsey equation at 20°C for the Akras, Lono and Podaga soybean varieties.

Fig 4.13 Plot of the 95% lower and upper confidence intervals of the desorption isotherms modelled with the modified Halsey equation at 20°C for the Akras, Lono and Podaga soybean varieties.
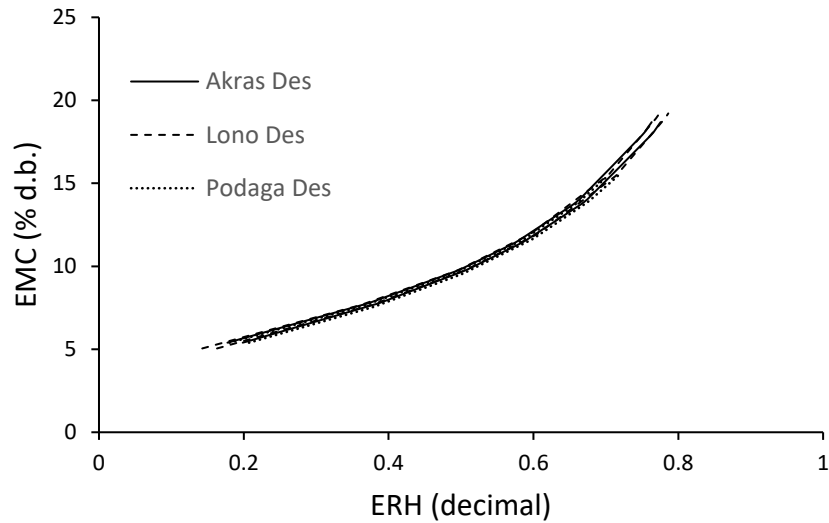
Given that no significant differences were found in the sorption models among varieties, the data could be combined to determine the parameters of a generalized sorption model for soybeans. Table 4.3 shows the estimated parameters of the modified Halsey equation for the combined varieties using the individual data of the three 'fresh' samples.

Table 4.3 Estimated parameters of modified Halsey and modified Oswin equations for combined varieties of soybeans.

Source of data	Sorption process	Model Parameters			Goodness-of-fit criteria		
		A	B	C	R^2 [a]	P^b (%)	S.E.[c] (decimal)
Combined data from present study	Ads	1.9589 ± 0.0316	0.0016 ± 0.0006	1.1486 ± 0.0134	0.9622	3.54	0.0261
	Des	3.149 ± 0.0384	-0.0054 ± 0.0006	1.4993 ± 0.0148	0.9763	3.74	0.0254
Osborn et al.	Des (U.S.)[d]	3.3109	-0.011635	1.5431		8.24	2.90
	Des (Britain)[e]	3.0446	-0.0054321	1.5245		0.87	0.59

a- Coefficient of determination for nonlinear regression
b- Mean relative error (%)
c- Standard error of estimated value (decimal)
d- Data set extracted from Alam and Shove (1973)
e- Data set extracted from Pixton and Warburton (1971)

The values for the coefficient of determination of the nonlinear regression (R^2), the mean percentage error and the standard error listed in table 4.3 indicate that the combined data fit the predicted adsorption and desorption isotherms well. The table also shows the estimated parameters of the modified Halsey equation calculated by Osborn et al. (1989) for two independent EMC data of soybeans through desorption. These parameters are also listed in the ASABE standard (ASABE 2007). The estimated parameters in this study are similar to the parameters calculated from the set of data from Britain (Pixton and Warburton 1971).

The standard error from the present study is lower than that of the two comparative studies presented by Osborn, while the mean relative error is lower than the one calculated from the set of data published by Alam and Shove (1973). These comparisons indicate that the modelled sorption isotherms using the Halsey equation based on the combined experimental data of this study adequately describe the EMC characteristics of soybeans.

4.5.2   Pre-treatment effect on sorption isotherm

The F-tests were performed at the 0.005 confidence level comparing differences on sorption isotherms on each variety due to the pre-treatments related to post-harvest conditions. Significant differences were found in most of the comparisons. Stronger differences (P<0.0001) were detected on the adsorption isotherms. No significant differences were detected among pre-treatments in the desorption isotherms of the variety Podaga.

In order to determine where the differences due to pre-treatments lie, the graphical method was used to compare the adsorption and desorption isotherms on each variety at specific temperatures. Given the greater differences between the experimental and predicted data at 5°C, comparisons were made at temperatures of 10, 15, 20, 25 and 30°C. In total, 30 graphs were evaluated in order

to find the differences at each temperature. Examples of these analyses are shown in figures 4.13 to 4.15 at 20°C.
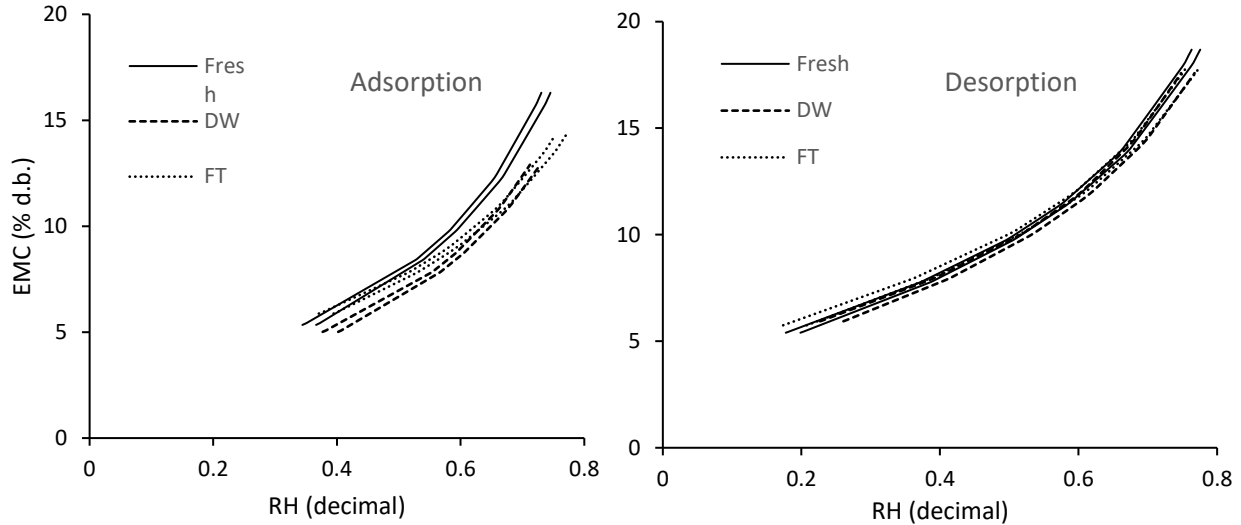

Fig 4.14 Plots of the 95% lower and upper confidence intervals of the adsorption and desorption isotherms modelled with the modified Halsey equation at 20°C of the fresh, dried and wetted (DW), and frozen and thawed (FT) Akras soybeans.

The Akras variety showed most pronounced effect of the pre-treatments on the adsorption isotherms (Fig. 4.14). The confidence intervals of the adsorption isotherms of the Akras samples subjected to the drying and wetting cycles (DW) do not overlap with the confidence intervals of the fresh samples along the entire RH range, indicating significant differences between the adsorption isotherms of these two samples. The position of the DW Akras isotherm shifted downwards with respect to the isotherm of the fresh sample. This means that Akras soybeans subjected to drying and wetting cycles adsorbed less moisture, and their corresponding EMC along the entire RH range is lower with respect to fresh samples. Adsorption confidence intervals of the FT pre-treatment overlap with the confidence intervals of the fresh sample below 53% RH, indicating that there is no significant difference in the EMC characteristics due to FT with respect to fresh Akras soybeans. Above 53%, the confidence limits between fresh and FT Akras adsorption

isotherms differ indicating significant differences. At 61% RH and above, the confidence intervals of FT and DW samples overlap, indicating that the EMC characteristics between these two pre-treatments are not significantly different.

Analysis of the confidence intervals of the desorption isotherms Akras soybeans at 20°C (Fig. 4.14) suggests that there are no significant differences in the sorption isotherms due to pre-treatments at that temperature. The confidence intervals of the three samples overlap along the entire RH range.

Fig 4.15 Plots of the 95% lower and upper confidence intervals of the adsorption and desorption isotherms modelled with the modified Halsey equation at 20°C for the fresh, dried and wetted (DW) and frozen and thawed (FT) Lono soybeans.

For the Lono soybeans (Fig 4.15), the confidence intervals of the adsorption isotherms of fresh and DW samples do not overlap above 64% RH, indicating significant differences in the EMC characteristics due to DW cycles at high RH. The EMC of the Lono DW samples at high RH is lower in comparison to the fresh samples. The adsorption confidence intervals of the FT sample overlap with the fresh sample through the entire RH range. The confidence intervals of the FT

samples do not overlap with the DW confidence intervals below 57% RH, indicating significant differences between these two pre-treatments at low RH. A comparison of the desorption confidence intervals of Lono soybeans shows that there are no significant differences due to pre-treatments at 20°C.
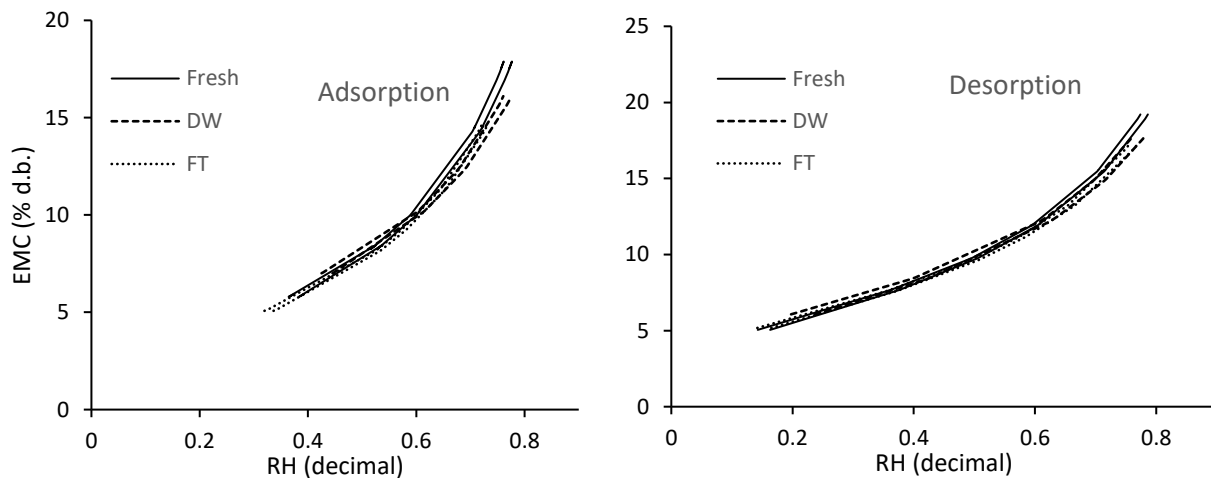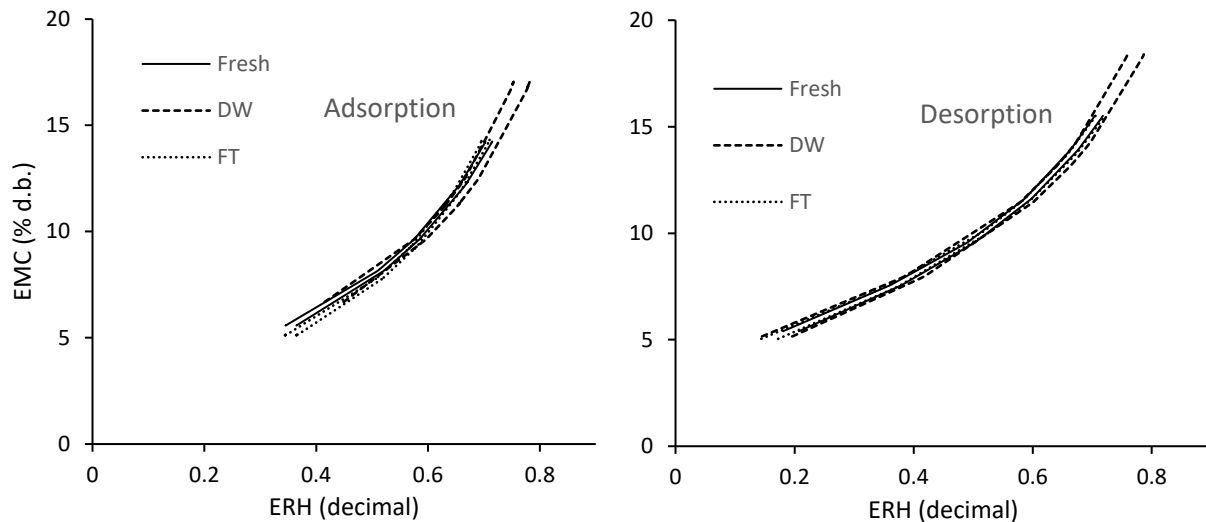

Fig 4.16 Plots of the 95% lower and upper confidence intervals of the adsorption and desorption isotherms modelled with the modified Halsey equation at 20°C for the fresh, dried and wetted (DW) and frozen and thawed (FT) Podaga soybeans.

In the case of Podaga soybeans, significant differences at 20°C are observed between the 'fresh' and FT samples below 56% RH (Fig 4.16) for the adsorption isotherms. The adsorption confidence intervals of the Podaga DW samples overlap with the other two samples in the entire RH range, indicating no significant differences. However, it is noteworthy to mention that the confidence intervals of the DW samples were wider compared to other samples and, therefore, overlapped with the confidence intervals of the other samples. These wider confidence intervals are related to a larger variation of EMC recorded data of the Podaga DW samples. When comparing the spread of the confidence intervals in the other varieties, the DW samples exhibited a wider range in comparison to the fresh samples. This could be attributed to a less uniform distribution of the

moisture on the beans due to the drying and wetting pre-treatments. No significant differences were found on the desorption curves for Podaga variety.

The analysis described above, was performed at 10, 15, 20, 25 and 30°C with all the samples. Tables 4.4 and 4.5 summarize the results of the graphical method, indicating the RH range where significant differences were found between two samples at each temperature. For example, a comparison of adsorption isotherms (table 4.4) for the Akras variety at 25°C, shows that there is a significant difference in the isotherms between the Fresh and the FT samples above 57% RH.

Table 4.4 Range of relative humidity where the 95% confidence intervals of two samples (graphical method) did not overlap indicating significant differences of the predicted adsorption isotherms.

Variety	Pre-treatments pair	10°C	15°C	20°C	25°C	30°C
Akras	Fresh – DW[1]	RH range[3]	RH range	RH range	RH range	Above 50%
	Fresh – FT[2]	Above 55%	Above 47%	Above 53%	Above 57%	Above 63%
	DW - FT	Below 64%	Below 64%	Below 61%	Below 57%	Below 48%
Lono	Fresh - DW	Below 59%	Below 55% & above 71%	Above 64%	Above 61%	Above 70%
	Fresh - FT	-[4]	-	-	-	-
	DW - FT	Below 60%	Below 57% & above 70%	Below 57%	Above 70%	-
Podaga	Fresh - DW	-	-	-	-	-
	Fresh - FT	Below 45%	Below 56%	Below 56%	-	-
	DW - FT	-	-	-	-	-

1- DW: samples subjected to multiple drying and wetting cycles
2- FT: samples subjected to multiple freezing and thawing cycles
3- Significant differences found in the entire RH range
4- No significant differences were found

Table 4.5 Range of relative humidity where the 95% confidence intervals of two samples (graphical method) did not overlap indicating significant differences of the predicted desorption isotherms.

Variety	Pre-treatments pair	10°C	15°C	20°C	25°C	30°C
Akras	Fresh – DW[1]	Below 63%	Below 71%	-	-	-
	Fresh – FT[2]	-[3]	-	-	-	-
	DW - FT	Below 54%	Below 55%	-	-	-
Lono	Fresh - DW	-	-	-	Above 69%	Above 69%
	Fresh - FT	-	-	-	Above 68%	Above 71%
	DW - FT	-	-	-	-	-
Podaga	Fresh - DW	-	-	-	-	-
	Fresh - FT	-	-	-	-	-
	DW - FT	-	-	-	-	-

1- DW: samples subjected to multiple drying and wetting cycles
2- FT: samples subjected to multiple freezing and thawing cycles
3- No significant differences were found

In general, for the cases where the differences were found, the effect of the pre-treatments caused a decrease in the EMC compared to the fresh samples. Overall, the most pronounced differences were found in the adsorption isotherms for the Akras variety between the fresh and the DW samples. Fewer differences were found in the desorption isotherms in general. Of the three varieties studied, Podaga soybeans showed fewer differences due to pre-treatments, especially in the desorption isotherms showing no significant differences along the entire RH range at all the studied temperatures.

When there was a difference between Fresh and DW samples, the effect of DW cycles resulted in lower EMC, particularly above 50% RH. These differences indicate a lower sorptive capacity of the beans as a result of micro drying and wetting cycles. Yang (1992) reported a decrease in hygroscopicity of canola after successive drying and rewetting cycles in the low to intermediate

RH. Bielewicz et al. (1993) reported lower adsorption and desorption EMC of canola below 8% MC d.b. after subjecting it to successive drying and rewetting cycles as compared to canola without any treatments. Similar to the results of this study, Cenkowski et al. (2015) found significant differences in the isotherms between red lentil samples subjected to drying and rewetting cycles and fresh lentil samples. The differences were found in two of three varieties studied for RH above 60%.

Stermer (1968) studied the effects of temperature and relative humidity on the stress cracks of milled rice, finding a difference between moisture adsorption damage and moisture desorption or drying damage. The damage caused by moisture adsorption was more severe, visible and irreversible. Bala (2007) explained that during drying, grains are subjected to tensile and compressive stresses as a result of the grain expansion due to increase in temperature and shrinkage due to loss of moisture. On the other hand, fissures perpendicular to the long axis of the grain develop as a result of water adsorption on the surface and the center of kernels. Cracks of the coat and cotyledons of grains facilitate mold growth reducing germinability and quality of beans (White et al. 1976). The effect of a reduction in moisture sorption of grains was explained by Chung and Pfost (1967) as a consequence of a decrease in the availability of sorptive sites due to a molecular shrinkage and crack formation after successive drying and rewetting.

In this study, fewer differences were found in the sorption isotherms due to FT cycles with respect to the fresh samples. Differences on the desorption isotherms were only found for the Lono variety at 25 and 30°C, while no differences were found for the adsorption isotherms of Lono soybeans. For Akras variety, the differences between FT and fresh samples laid on the intermediate to high RH, with the FT samples producing lower EMC. For Podaga soybeans, differences were found at 10, 15 and 20°C in the low to intermediate RH, with the FT samples producing lower EMC.

The applicability of the results derived from this study can be considered depending on the storage conditions. In the case of aerated storage, if soybeans previously subjected to FT cycles are exposed to high RH, air would likely increase their moisture content in a lower degree than fresh soybeans, which is beneficial since high moisture content is not desirable. In the case of unaerated storage, soybeans subjected to the studied pre-treatments will alter the relative humidity of the intergranular space, creating undesirable humid conditions. Nevertheless, in the case of Podaga soybeans, the difference between EMC of fresh samples and FT samples was observed at low temperatures and low RH, which corresponds to the recommended conditions for safe storage (White et al. 1976; Ghosh and Jayas 2010).

Conditions that subject soybeans to multiple micro drying and wetting cycles are not desirable as such conditions cause adverse changes in their structure. These include cracks, fissures and complex hydrothermal stresses impacting their quality and promoting mould growth. Even though DW samples showed less moisture content increase with respect to fresh samples due to a decrease in soybean's sorptive capacity, the damage related to the development of cracks and mould growth is undesirable.

The results from this study provide practical applications for the prediction of moisture content variations in Manitoba-grown soybeans during storage. The calculated sorption isotherms can be included as part of a safe storage guideline for farmers growing soybeans in Manitoba to set optimal storage conditions and preserve quality. The new data also provide the sorption characteristics specific for soybeans grown in Manitoba, allowing more accurate information for varieties and climate conditions in this Canadian province. As it was found that post-harvest conditions during storage affect the sorption properties of soybeans, the results can be used as a base for predictions of moisture content of soybeans when they are exposed to the studied changes.

5. CONCLUSIONS

Based on the results of this study, the following conclusions are drawn:

1. Hysteresis effect was present in all the samples of soybeans studied. The difference in moisture content between desorption and adsorption data of each sample was significantly different at all levels of relative humidity and temperature. Hysteresis loop decreased at high RH and at higher temperatures. For all the data, the hysteresis range was observed to be from 0.23 to 4.5% d.b. Samples equilibrated at 5°C showed an unusual EMC trend (lower moisture content) when compared to samples at higher temperatures. Differences in temperature and RH between the samples and the ambient air of the laboratory are attributed as the cause of these unusual trends.

2. The modified Halsey equation and the modified Oswin equation were similar in describing the sorption isotherms. The modified Halsey equation was a better fit in predicting the desorption isotherms of the experimental data, given that the modified Oswin equation under-predicts the desorption EMC at low RH. The parameters estimated from the nonlinear regression for the modified Halsey equation could adequately predict the experimental data in the range of 10 to 80% RH for desorption isotherms and 30 to 80% for adsorption isotherms. Differences between the predicted and the experimental data increased at higher RH and are related to the response of the RH sensors as these sensors are affected by condensation, drift or aging.

3. The effect of variety on the sorption isotherms of soybeans was not statistically significant. The parameters of the modified Halsey equation were re-calculated with the combined data of fresh samples of the three studied varieties (Akras, Podaga and Lono). The

statistical goodness-of-fit criteria indicated the adequacy of this model in predicting the adsorption and desorption isotherms of soybeans.

4. Soybean varieties responded differently to treatments related to post-harvest conditions. FT cycles decreased the EMC of the adsorption isotherms of Akras soybeans at low to intermediate RH. No effect of FT cycles was found on the adsorption isotherms of Lono soybeans while lower EMC at 25 and 30°C was observed on their desorption isotherms. Podaga soybeans subjected to FT cycles showed significantly lower EMC in the low to intermediate RH at 10, 15 and 20°C.

5. Differences in the desorption isotherms due to DW cycles were found on the Akras samples in the low to intermediate RH at 10 and 15°C, and in the Lono soybeans in the intermediate to high RH at 25 and 30°C. The adsorption EMC of Lono variety was lower in the DW samples compared to the fresh samples in the intermediate to high RH at temperatures of 20, 25 and 30°C and in the low to intermediate RH at 10°C. The effect of drying and wetting samples was not significant in the adsorption isotherms of the Podaga soybean.

6. RECOMMENDATIONS FOR FUTURE RESEARCH

1. The benefits of using the dynamic ERH system to obtain sorption data are a reduction of the equilibration time and the possibility of obtaining desorption/adsorption data in a single experiment. These benefits were proven as the equilibration time for a single experiment got reduced to 8 to 18 hours when compared to SSS method that can take several days. However, considerations such as the total number of experiments to be performed and the time required to measure moisture content should be given equal importance. If the number of experiments due to different variables to be tested is large, the total time required to complete the experiments might equal or exceed the time that would be necessary using the SSS method (assuming availability of resources such as controlled environment chambers and desiccators to allow equilibration of all the samples at different temperatures parallelly).

2. Sensor malfunction and drifting at low temperatures (under 10°C) were some technical limitations encountered during the course of this study using the ERH apparatus. Most of the errors due to sensors at low temperatures were caused by condensation. A possible way to avoid or reduce condensation could be achieved by reducing temperature differences between the sensor and the grain sample before starting the experiment.

3. The effect of multiple freezing and thawing cycles on structural and biochemical changes of individual soybeans should be studied in greater detail. A study dedicated to the topic of exploring the microstructural changes, germination and quality in single beans as a consequence of repeated freezing and thawing, would enhance our understanding of these freeze-thaw cycles. Such knowledgebase is well established for drying and wetting cycles but not for freezing and thawing.

4. Given the importance of soybeans for the oil and protein industries, a future scope could include the study of biochemical changes (i.e. fatty acid composition, protein composition, free fatty acids) under different storage conditions including the two micro-cycles (freezing/thawing and drying/wetting) covered in this study. The interaction and correlation of structural and biochemical changes with the sorption characteristics would provide a broader understanding of the constitutional changes under varying storage environments.

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Appendix A

Mathematical models to describe sorption isotherms as listed in the ASABE standard (Asabe 2007)

Modified Henderson equation:

$$ERH = 1 - \exp\left(-A \cdot (T + C) \cdot (MC)^B\right) \qquad \text{(Eq. A1)}$$

Modified Halsey equation:

$$ERH = \exp\left(-\frac{\exp(A + B(T))}{(MC)^C}\right) \qquad \text{(Eq. A2)}$$

Modified Oswin equation:

$$ERH = \left[\left(\frac{A + B \cdot T}{MC}\right)^C + 1\right]^{-1} \qquad \text{(Eq. A3)}$$

Modified Chung-Pfost equation:

$$ERH = \exp\left[-\frac{A}{T + C}\exp(-B \times MC)\right] \qquad \text{(Eq. A4)}$$

GAB equation:

$$EMC = \frac{A \cdot B \cdot C \cdot RH}{(1 - B \cdot RH)(1 - B \cdot RH + B \cdot C \cdot RH)} \qquad \text{(Eq. A5)}$$

where A, B and C are the equation parameters, ERH is in decimal, MC is the moisture content in dry basis and the temperature (T) is in Celsius.

Appendix B

**Experimental EMC data and predicted sorption isotherms
with the modified Halsey equation**
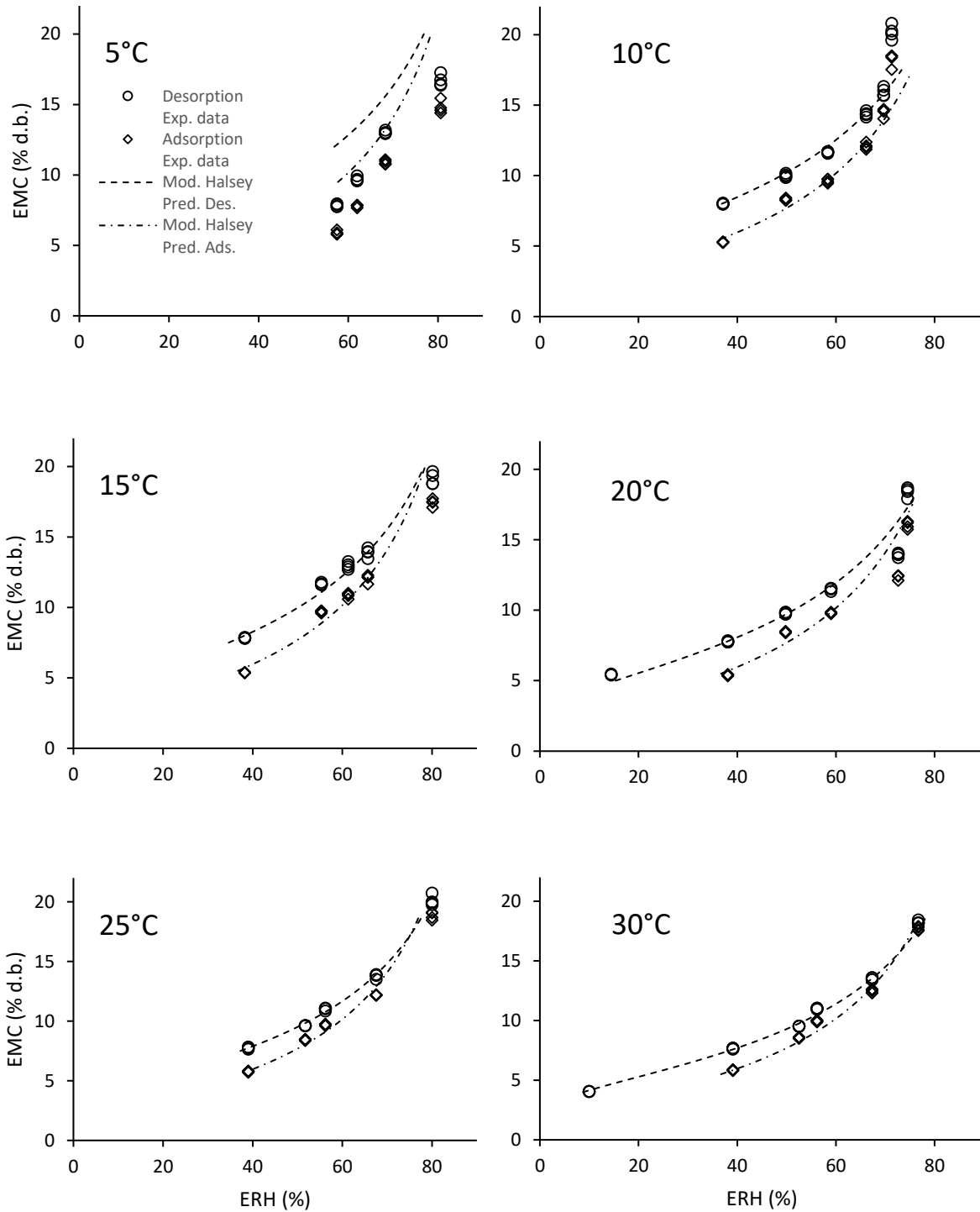
Fig B1. Individual adsorption and desorption data points of **freshly** harvested **Akras** soybeans at different temperatures and the predicted isotherms using the modified Halsey equation.
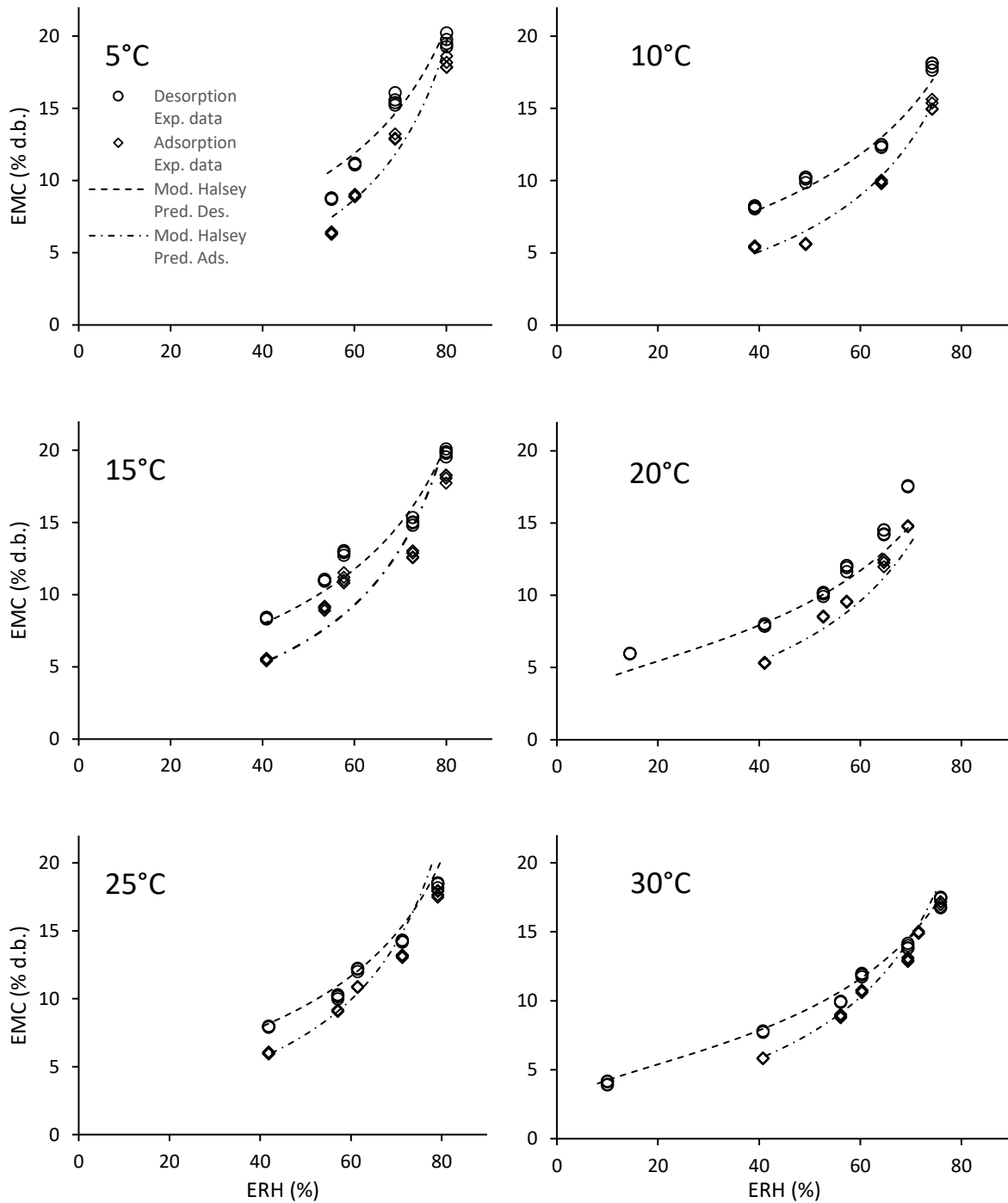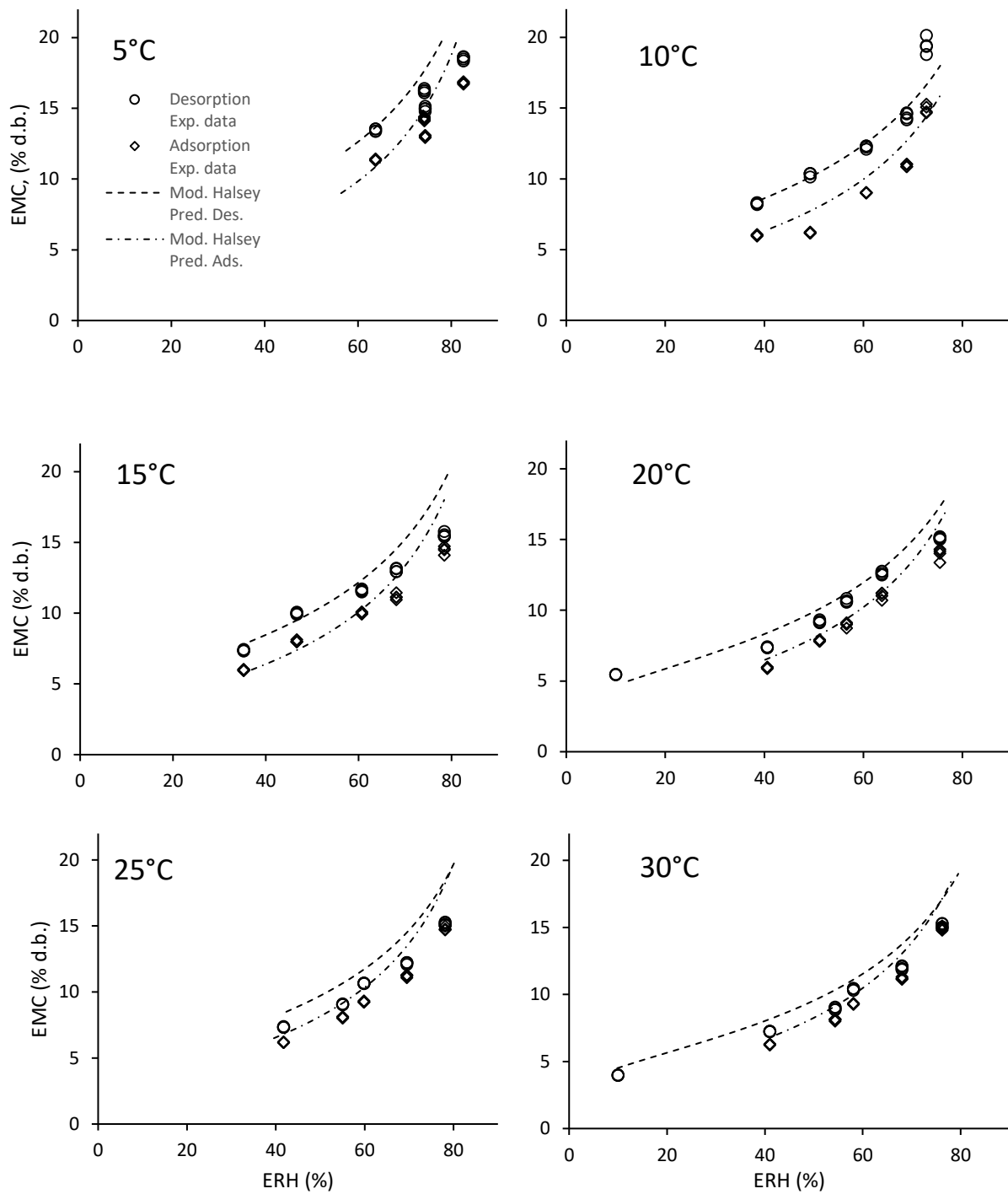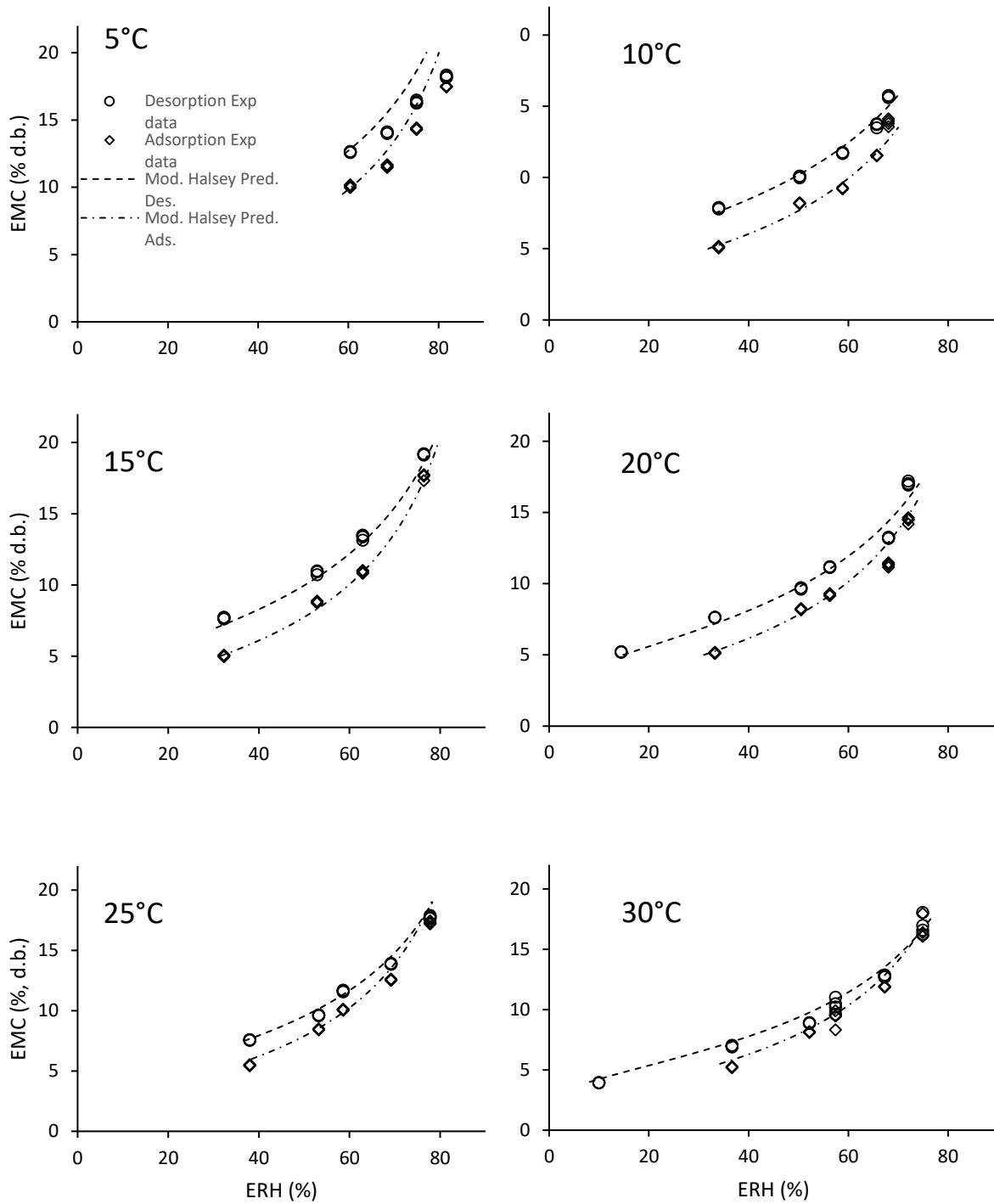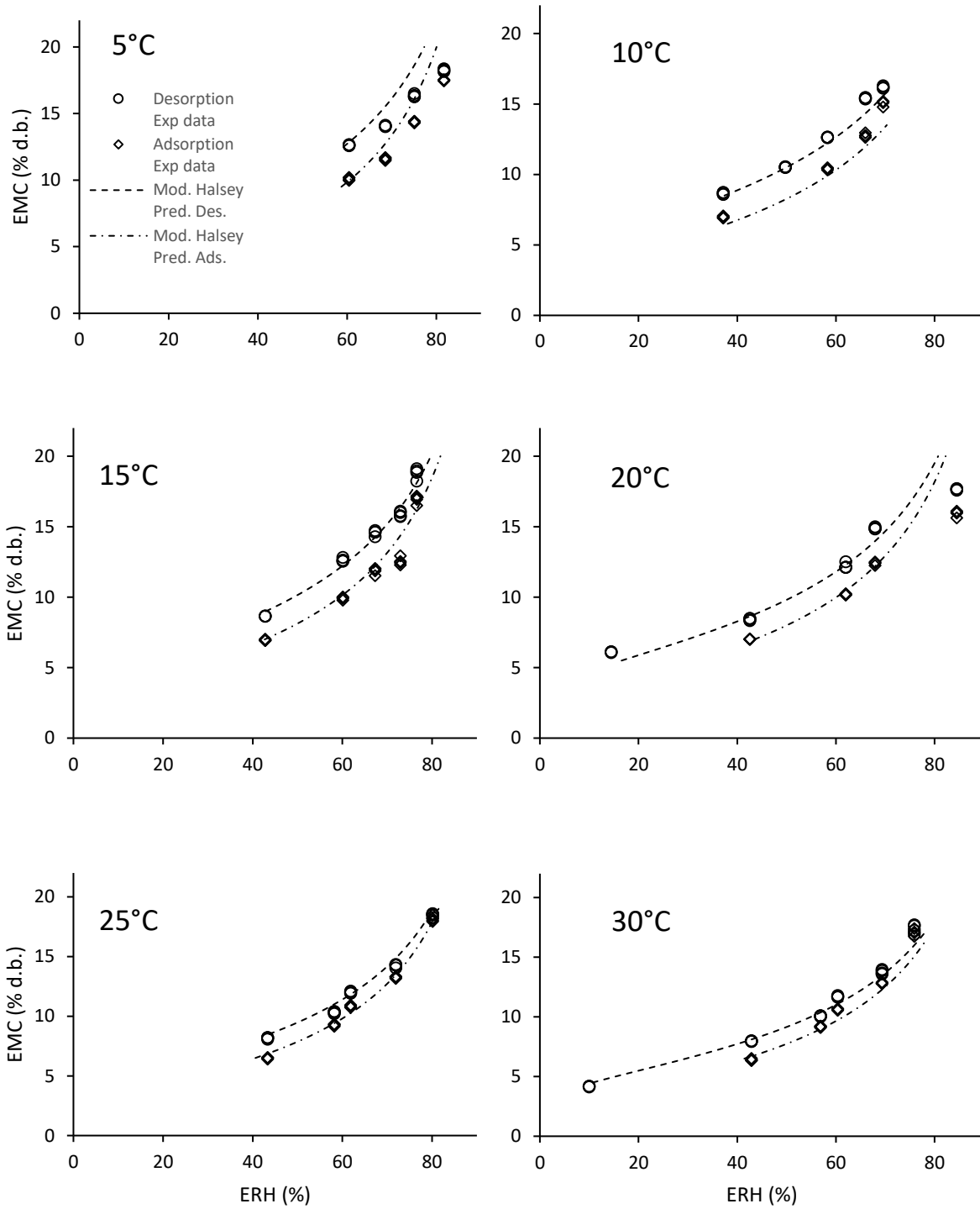
Fig B2. Individual adsorption and desorption data points of **Akras** soybeans subjected to the

drying and wetting cycles at different temperatures and the predicted isotherms using the
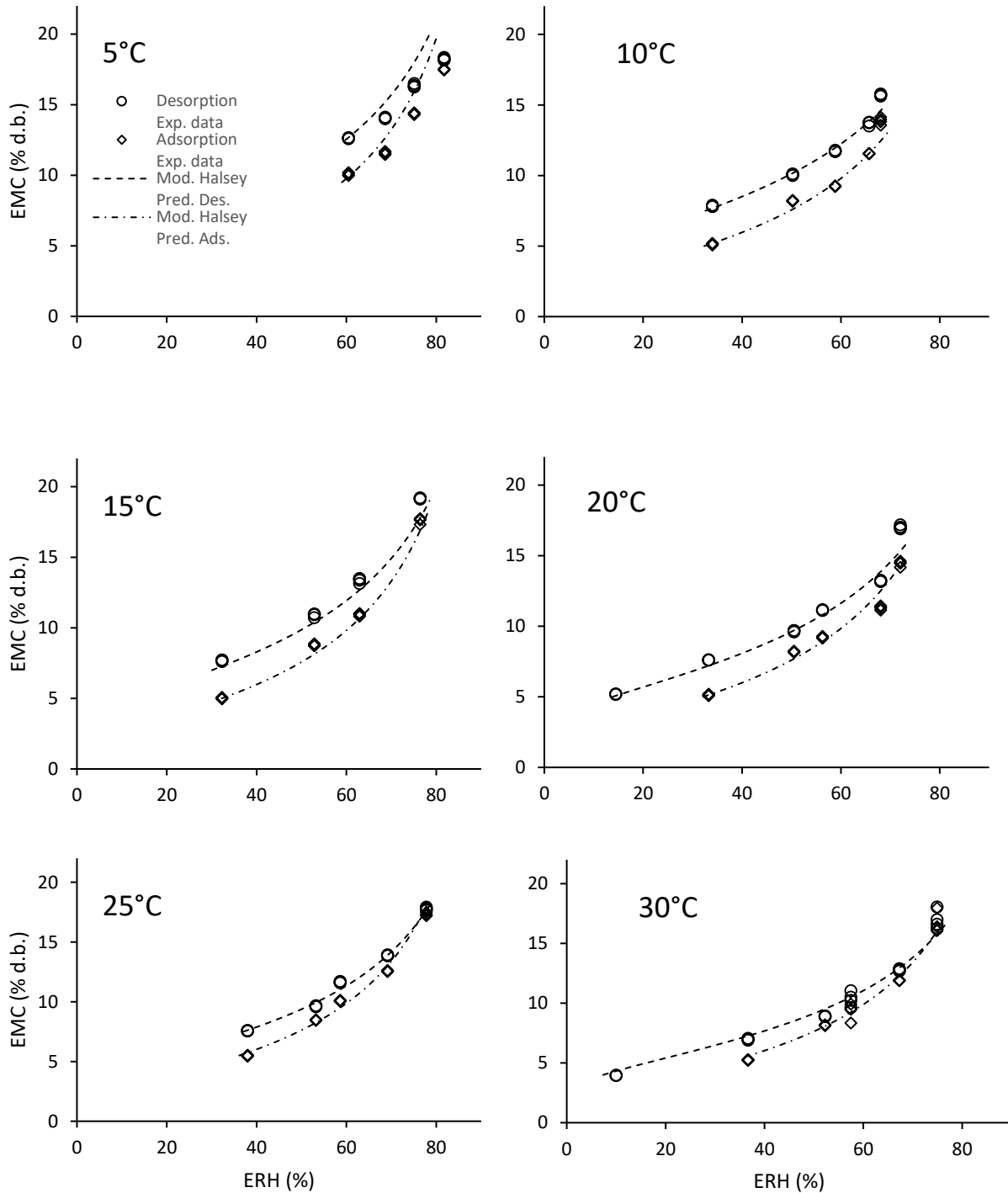
modified Halsey equation.

Fig B3. Individual adsorption and desorption data points of **Akras** soybeans subjected to the **freezing and thawing cycles** at different temperatures and the predicted isotherms using the modified Halsey equation.

Fig B4. Individual adsorption and desorption data points of **freshly** harvested **Lono** soybeans at different temperatures and the predicted isotherms using the modified Halsey equation.

Fig B5. Individual adsorption and desorption data points of **Lono** soybeans subjected to the **drying and wetting cycles** at different temperatures and the predicted isotherms using the modified Halsey equation.

Fig B6. Individual adsorption and desorption data points of **Lono** soybeans subjected to the **freezing and thawing cycles** at different temperatures and the predicted isotherms using the modified Halsey equation.
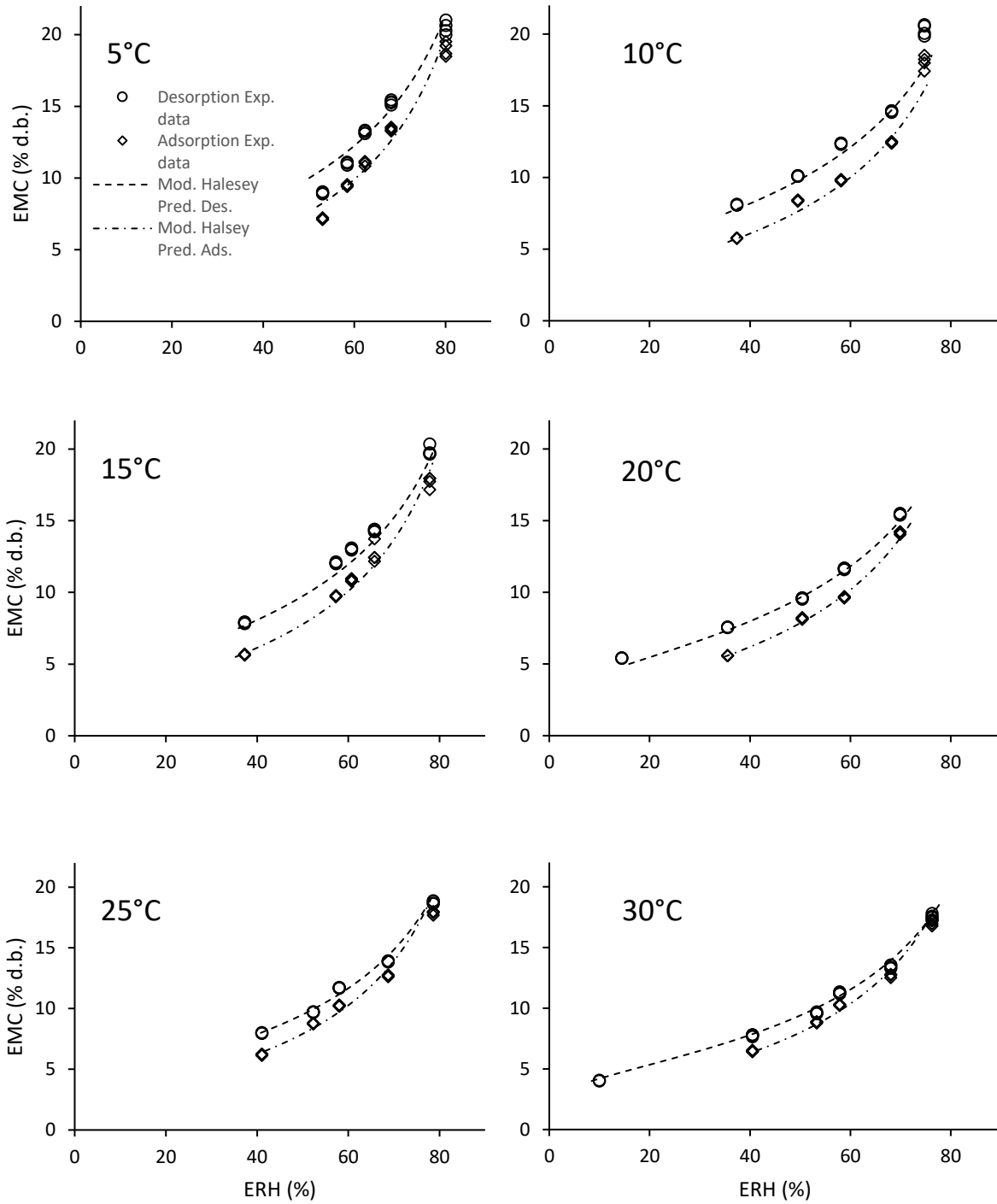
Fig AB. Individual adsorption and desorption data points of **freshly** harvested **Podaga** soybeans at different temperatures and the predicted isotherms using the modified Halsey equation.
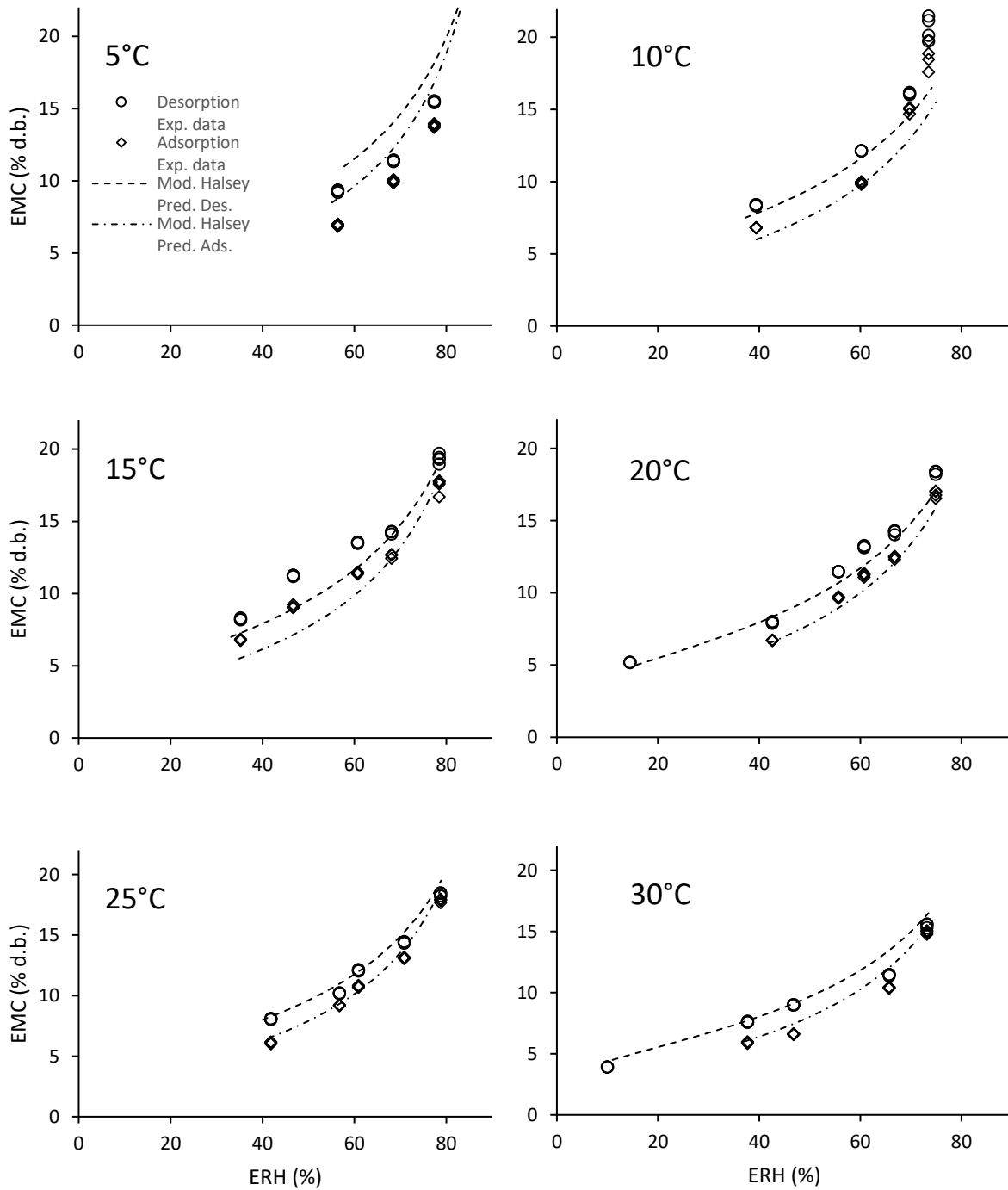
Fig B8. Individual adsorption and desorption data points of **Podaga** soybeans subjected to the

drying and wetting cycles at different temperatures and the predicted isotherms using the
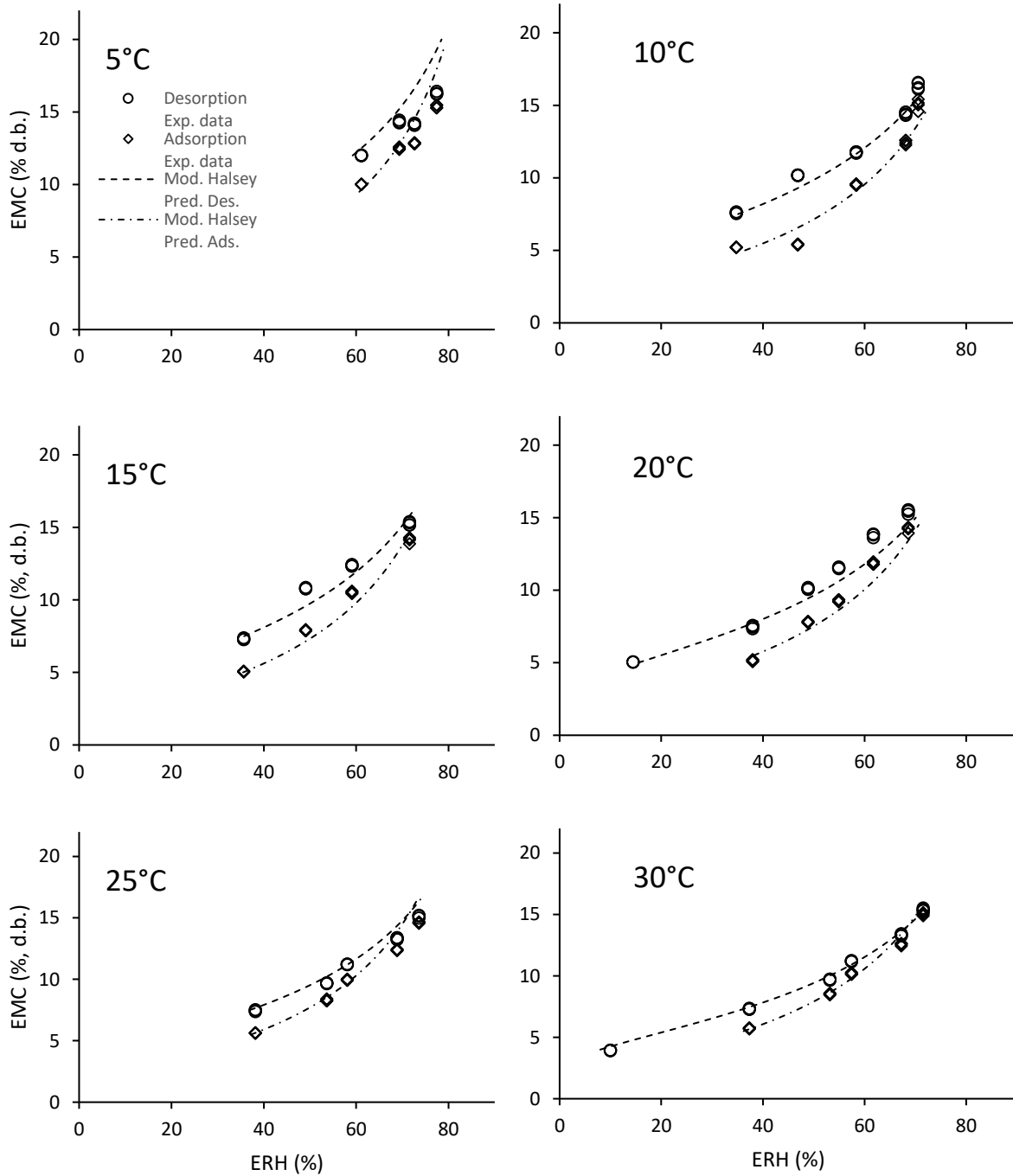
modified Halsey equation.

Fig B9. Individual adsorption and desorption data points of **Podaga** soybeans subjected to the **freezing and thawing cycles** at different temperatures and the predicted isotherms using the modified Halsey equation.