The impact of alternate pretreatment methods and osmotic dehydration for the preservation of wild blueberries *(Vaccinium angustifolium)*

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Abstract

This study investigated the effects of selected pretreatments and rigorous optimization of osmotic dehydration (OD) of lowbush blueberries using Response Surface Methodology (RSM) to produce dehydrated blueberries with high antioxidants content and long shelf life. Fresh wild blueberries (WB) were initially pretreated and then subjected to osmotic dehydration before they were oven dried to the required level (18g/100g of fresh sample). Microwave pretreated WB had shown better moisture loss during osmotic dehydration as compared to other pretreatment methods investigated. The highest levels of phenolics, flavonoids, and anthocyanin content of the dehydrated WB were found to be 742.61 mg/100 g, 263.12 mg/100 g, and 428.11 mg/100 g dry mass respectively, at optimized temperature of 40 °C, for 5 h with 65% (w/w) Brix osmotic solution at 1:5 ratio of sample to Brix%. With rigorous optimization of the critical osmotic dehydration parameters high level of antioxidants could be retained in the dehydrated product. Wild blueberries pretreated in the microwave before osmotic dehydration and oven drying had shorter drying time of 5h compared to the control sample and significantly maintained a higher rehydration ratio ($p<0.05$) and lower shrinkage ratio compared to the oven dried control. Preliminary mathematical modeling of the process was also carried out to determine the mass transfer coefficients of the system. The results suggest that the drying process developed was a promising alternative method that decreases drying time, achieves high product quality, uses simple process steps for superior drying and retains higher level of antioxidant in the final product.

Keywords: Osmotic dehydration, Antioxidants, Pretreatment, Response Surface Methodology, Optimization, rehydration, shrinkage and mathematical modeling

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“To succeed in life, you need two things: Ignorance and confidence”

(Mark Twain)

Abbreviations

a	The model's rate constant (min^{-1})
a_0 - a_i - a_{ii} - a_{ij}	Constant regression coefficients
$AlCl_3$	Aluminium chloride
ANOVA	Analysis of variance
ΔA	Absorbance change
BB	Blueberries
Brix	The sugar content of aqueous solution (w/w)
BW	Boiling water
C3G eq	Cyanidin-3-glucoside equivalent (ε = 26,900).
CCD	Central composite design
D	Desirability
d.m.	Dry matter
D_{em}	Effective diffusivities of moisture
D_{es}	Effective diffusivities of solid
Df	Dilution factor of the sample
d_o	The diameter of fresh sample
d_t	The diameter of dried sample
ε	Molecular absorbance extinction coefficient of cyaniding-3-glucoside (26900 M^{-1} cm^{-1})
f	The number of independent variables
GAE	Gallic acid equivalent
HACD	Hot air convective drying

K	The number of center point runs
k_m	The moisture mass transfer coefficients
k_s	The solid mass transfer coefficients
kt	Kilotons
MC	Moisture content
M_e	The moisture content at equilibrium state
ML	Moisture loss
ML_e	Time of equilibrium
ML_t	Moisture loss at time
M_o	The initial moisture content
MR	Moisture ratio
Mt	The moisture content at ant time
MW	Microwave treatment
MW	Molecular weight of cyaniding-3-glucoside
MWODHACD	Microwave (30s)+ osmotic dehydration +hot air convective drying
N	The number of repartitions
OD	Osmotic dehydration
PEF	Pulsed electric field
PT	Pretreatments
R^2	Root mean square error
RME	Relative mean error
RMSE	Root mean square error
RR	Rehydration ratio

RSM	Response surface methodology
S_e	The solid concentration at equilibrium state
SG	Solid gain
S_i	Initial solid content
S_o	The initial solid concentration
SR	Shrinkage ratio
S_t	The solid concentration at any time
t	Time
TFC	Total flavonoids content
T_n	The total number of experiments
TPC	Total phenolic content
UB	Ultrasonic bath treatment
US	Ultrasonication probe treatment
WB	Wild blueberries
w.b	Wet basis
W_d	The weight of dried sample
W_i	Initial weight of fruit
WR	Weight reduction
W_r	The weight of rehydrated sample
x	The coded independent factor
X1	Temperature
X2	Treatment time
X3	Sucrose concentration

X4	Sample to sucrose ratio
x^{i}_{exp}	The experimental value
x^{i}_{pre}	The predicted value
S	Current solid content
W	Current weight of fruit

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Chapter 1

Introduction and objectives of study

1.1 Introduction

All cultivated and wild species of blueberries are native to North America, Australia, New Zealand and some South America natives. Lowbush blueberries is another name for wild blueberries, while highbush refers to farm grown cultivated blueberry plants developed from the wild varieties in the 20th century (AgriFood-Canada, 2011). Canada is the largest producer of lowbush blueberries and the second-largest global producer and exporter of highbush blueberries. In 2016, Canada produced 132.2 kt of lowbush blueberries with a value of C$90.7 million while highbush blueberries yielded 85.8 kt with a value of C$170.8 million (Statistics-Canada, 2017). The United States produced 347.7 kt of blueberries with a value of approximately US$748 million in 2016 (USDA-NASS, 2017). Over the last decade, there has been a considerable increase in demand for blueberries, especially for the lowbush ones due to their bioactivity, unique flavor and high nutritional value (Correia et al., 2017; Dróżdż et al., 2017; Khalid et al., 2017). Lowbush blueberries have been reported to show significantly high levels of phenolics, anthocyanins, and antioxidant capacity as compared to cultivated blueberries (Correia et al., 2017; Del Bo et al., 2016; Mallik &Hamilton, 2017). The health –relevant bioactivity of wild blueberries have been widely studied such as depression control, counteract lipid accumulation, anti-inflammatory, anti-hypertensive, cognitive, and cardiovascular risk factors (Chorfa, et al., 2016; Correia, et al., 2017; Dudonné, et al., 2015; Lee, et al., 2014). However, the fresh fruits are highly perishable. The bioactive components of the fruits can easily deteriorate when exposed to light, heat, and oxygen (Michalska et al., 2015). Hence, drying and processing techniques have been used to stabilize and extend the shelf life of lowbush blueberries and maintain their bioactive properties (Ekezie et al., 2017; Flores et al., 2014; Kamiloglu et al., 2016; Struck et al., 2016).

The selection of suitable and efficient drying system is very vital for food preservation due to the heat sensitivity of many products, constituent's degradation, products morphology, etc. Inadequate choice of drying techniques and conditions can lead to substandard physical and nutritional properties of the dried food products. The selection of a drying technique for a specific food product depends on the following factors: heat sensitivity, moisture content, type of feed, drying kinetics, physical structure and morphology of the food material, and predetermined product quality (Mannozzi, et al., 2018; Zhang, et al., 2017).

Different drying techniques for lowbush and highbush blueberries processing have been reported in the literature such as freeze drying (Nemzer, et al., 2018; Ngo, et al., 2017), microwave-assisted drying (Zielinska & Michalska, 2016), osmotic dehydration (Kucner, et al., 2013), combined hot air drying and microwave-assisted drying (Zielinska, Sadowski, et al., 2016), individual quick freezing (Beaudry, et al. 2004). Individual quick freezing has been reported to be most effective drying technique that retains high amounts of bioactive compounds of lowbush blueberries (Beaudry, et al. 2004). However, this process is time-consuming and requires high levels of energy making the technique costly (Yemmireddy et al., 2013). Although, different drying techniques have been employed to dehydrate wild blueberries many of these techniques are slow and energy intensive due to the structure of blueberries peel that is covered by a waxy layer which acts as a barrier to moisture removal (Alfaro, et al., 2018; Kucner, et al., 2013; Moreno, et al., 2016). The peel pretreatments by chemical and physical processes before drying to facilitate moisture removal have shown significant results as well as drying time reduction (Alfaro, et al., 2018; Rodriguez, et al., 2016; Yuanshan, et al., 2017).

Osmotic dehydration (OD) has been found to be an effective, simple and economical method compared to the traditional techniques for preservation of fruits and vegetables (Akharume, et al., 2018; Yadav, et al., 2014). It involves a non-heat process that reduces the moisture content and water activity in food, thus prolonging its shelf life. OD can offer numerous benefits when used for the preservation of products with high nutrient and antioxidant content such as wild blueberries. It causes moisture flow from the product into the osmotic solution while osmotic solute is transferred from the solution into the product (Dermesonlouoglou, et al., 2018; Zielinska, et al., 2018). It can be employed as a pre-treatment at mild temperatures in combination with other preservation techniques to improve the quality of final product, reduce energy and/or develop new products (Derossi, et al., 2015; Rahman, et al., 2018; Yadav, et al., 2014). The combination of air-drying with osmotic dehydration has been widely studied leading to improvements in the quality of the product and to energy savings (Dehghannya, et al., 2018; Katsoufi, et al., 2017; Prosapio, et al., 2017).

Recently, the effects of liquid nitrogen pretreatment on the osmotic dehydration and quality of cryogenically frozen blueberries (Vaccinium angustifolium Ait.) was investigated by Alfaro, et al. (2018). They reported that liquid nitrogen pretreated blueberries experienced greater moisture loss and solids gain after osmotic dehydration than non-pretreated samples, while similar anthocyanin and total phenolic contents were observed in both pretreated and non-pretreated samples. Also, Yu et al. (2018) studied biochemical degradation and physical migration of polyphenolic compounds in osmotic dehydrated blueberries using the pulsed electric field (PEF) and thermal pretreatments.

Biochemical degradation and physical migration of the nutritive compounds from blueberries to osmotic solutions were observed during the pretreatments and osmotic dehydration. It was further reported that PEF pretreated, and dehydrated fruits showed superior appearance to thermally pretreated and control samples. Yu, et al. (2017) also attempted pulsed electric fields (PEF) pretreatment on osmotic dehydration of blueberries, and its effects on dehydration kinetics, microbiological qualities, and nutritional qualities. It was reported that higher rates of water loss and solid gain during osmotic dehydration were obtained using PEF pretreatment, while the dehydration time was reduced from 130 to 48 h. The influence of microwave-assisted drying techniques on the rehydration behavior of blueberries (*Vaccinium corymbosum* L.) was also investigated by Zielinska and Markowski (2016). Degradation kinetics of anthocyanins in freeze-dried microencapsulates from lowbush blueberries (*Vaccinium angustifolium Aiton*) extract and prediction of shelf-life were studied by Celli et al. (2016). Combinations of hydro-thermodynamic processing and different drying methods for natural lowbush blueberries leather were investigated by Y. Chen et al. (2018). Likewise, Zielinska et al. (2015) investigated the freezing/thawing pretreatment and microwave-assisted drying of blueberries (*Vaccinium corymbosum L.*). They reported that freezing/thawing promotes high moisture transfer during drying and reduces drying time as compared to drying of blueberries without freezing/thawing pretreatment. Rodriguez et al. (2016) evaluated the final quality of highbush blueberries after microwave drying by comparing two pretreatment techniques (osmotic dehydration and hot air drying). They reported that combination of hot air–microwave-drying technique decreased the process time and improved drying rate as compared to the osmotic dehydration–microwave technique. The waxy skin of blueberries results in low drying rate, a gradual reduction of moisture and a long time of drying (Zielinska & Michalska, 2016).The application of different pretreatments before osmotic dehydration or second drying could reduce mechanical resistance and increase moisture permeation through the skin.

However, there is a need for a rigorous optimization of the osmotic dehydration parameters such as sucrose concentration (Brix), temperature, Brix to sample ratio and treatment time using a response surface methodology (RSM). This is a useful statistical technique which has been applied in research to optimize complex variable processes. Multiple regression and correlation analyzes are the mains tools of RSM that are employed to assess the effects of two or more independent variables on the dependent parameters (He et al., 2016; Jiang et al., 2017). The main advantage of using a response surface methodology RSM is that the number of experimental runs required to generate a statistically acceptable result can be reduced (Chen et al., 2018; Ganesan et al., 2018). It was also observed that application of the current pretreatment techniques such as radiant zone, far infrared radiation, ohmic heating, ultrasound-assisted, PEF, electrohydrodynamic, microwave-assisted, etc. have not been well explored on wild blueberries processing and limited information is available in the literature on the same. Inspite of this, a critical review of the current trends of pretreatment techniques before osmotic dehydration of fruits in the literature with special attention to wild blueberries is presented in this study.

The composition of osmotically dehydrated samples such as moisture loss and solid gain can be controlled based on information about a mass transfer during osmotic dehydration (OD) (Zielinska, M., & Markowski, M. 2018).Various approaches based on Ficks' second low have been proposed to model the mass transfer kinetics during osmotic dehydration (OD) and hot air convetional drying of food products (Horuz et al., 2018;

Kumar, et al., 2016; Sareban, M., & Souraki, B. A. 2016; Zielinska, M., & Markowski, M. 2017). A two parameter mathmatical modle developed by Azuara for describing the mass transfer during osmotic dehydration (OD) and hot air convective drying (HACD) of agrifood estimating the changing in moisture loss and solid gain in equilibrium state (Azuara, E et al.1992; Zielinska, M., & Markowski, M. 2017)

To the best of our knowledge, the application of rigorous optimization techniques for lowbush blueberries osmotic dehydration has not been reported in literature. The optimization of osmotic dehydration variables using RSM to understand the effect of these variables on dehydration performance and dried fruit quality in term of antioxidant content would provide important information in designing and optimizing a drying method for wild blueberries. In addition, there is a general scarcity of research into the effects of emerging technologies such as microwave (MW) combined with osmotic dehydration (OD) as pretreatment for hot air convective drying (HACD). Knowledge of mass transfer kinetics in terms of moisture loss, solids gain, effective moisture diffusivity and effective solids diffusivity during OD and HACD of whole wild blueberries, will also help in better understanding and scale up of the drying process.

1.2 Objectives of this study

1.2.1 Overall Objective

The overall objective of this study was to dry wild blueberries by osmotic dehydration in order to extend its shelf life and retain its antioxidant properties.

1.2.2 Specific objectives

The specific objective of the study were to:

I: Study the effect of different pretreatment methods on osmotic dehydration of wild blueberry and determine the most effective process to achieve low antioxidant loss and high moisture loss.

II: Rigorously optimize the osmotic dehydration process critical parameters using Response Surface Methodology (RSM) with the aim of reducing loss of antioxidants.

III: Compare the product obtained by osmotic dehydration method to the conventional method in terms of process time, shrinkage and rehydration properties.

IV: Determine the mass transfer coefficients of the osmotic dehydration and conventional drying of wild blueberries by preliminary mathematical modeling.

Chapter 2

Literature review

2.1 Origin and varieties of blueberries

Blueberries belong to the family of “Ericaceae,” subfamily of “Vacciniaceae,” genus “Vaccinium,” and subgenus “Cyanococcus” (Powell, et al., 2003; Lyrene, et al., 2003; Winny, et al., 2011). There are two main categories of blueberries namely lowbush blueberries and highbush blueberries. The wildly grown blueberries are called lowbush blueberries (wild blueberries) while the cultivated blueberries are called highbush blueberries (AgriFood-Canada, 2011; USDA-NASS, 2017). Wild blueberries (*Vaccinium angustifolium*) is a calcifuge shrub that is native to the northeastern North America (Ferrier, et al., 2016; Strik, et al., 2005). Cultivation of blueberries was dated back to the beginning of the 20th century, when Frederick V. Coville selectively bred northern highbush blueberry (Vaccinium corymbosum L.) cultivars (Mainland, 2012; Michalska, et al., 2015). Some of the cultivar of blueberries species in the United States and Canada are lowbush blueberry (Vaccinium angustifolium L.), northern highbush blueberry (Vaccinium corymbosum), southern highbush blueberry (Vaccinium darrowii Camp.), rabbiteye blueberries (Vaccinium virgatum Aiton.), Elliott’s blueberry (Vaccinium elliottii Chapm.), etc. (Kang, et al., 2015; Li, et al., 2016; Su, et al., 2017). Northern highbush blueberries are the most well known species out of the other cultivars due to high fruit quality and low temperatures resistance (Michalska, et al., 2015; Winny, et al., 2011). Wild blueberries have a lower moisture content, are smaller and are known to have more antioxidant content as compared to cultivated blueberries (Mallik, et al., 2017; Skrovankova, et al., 2015). Nowadays, blueberries are cultivated in other parts of the world such as Australia, Argentina, New Zealand, Chile, China, Uruguay, and South Africa (Bizabani, et al., 2016;

Strik, 2007; Su, et al., 2017). The United States is the largest producer of highbush blueberries, while Canada is the second-largest global producer and exporter of highbush blueberries. For the wild blueberries, Canada is the largest world producer (AgriFood-Canada, 2011).

Blueberries can be consumed fresh but are highly susceptible to deterioration within a few days of harvest due to its high-water content (Kucner, et al., 2013; Yu, et al., 2018). Immediate preservation of blueberries after harvest is necessary to maintain the bioactive content and reduce spoilage of the fruit. In the cold winter of North America, the preservation method of blueberries that was passed from the natives to colonists includes sun-drying, freezing, or smoke drying where sufficient sunlight was not available and to decrease the reliability over solar energy (Michalska, et al., 2015; Winny, et al., 2011). Over the last few decades, more than 50% of blueberries are processed into different products such as jams, juices, yoghurts, canned fruits, etc. (Skrovankova, et al., 2015). Regardless of the harvesting methods, blueberry fruits are immediately sorted and placed in cold storage to reduce fruit dehydration and respiration (Mallik, et al., 2017; Nemzer, et al., 2018). Due to the growing demand of blueberries and large production that exceed fresh fruit consumption, the processing of blueberries using different pretreatments and drying techniques has led to considerable research (Kucner, et al., 2013; Moreno, et al., 2016; Zielinska, et al., 2015). In this review, challenges wit the pretreatment methods and drying techniques as applicable to highbush and lowbush blueberries are examined.

2.2 Pretreatments and Drying Techniques

Pretreatment of waxy fruits before drying has been shown to improve moisture removal and reduce loss of bioactive content of the fruits (Luchese, et al., 2015; Peng, et al., 2018; Sunjka, et al., 2004; Tarhan, 2007). In the many combined drying techniques involving OD, fruit pretreatment is recommended. Limited information is available in the literature on the application of pretreatment methods for wild blueberries. Pretreatments before OD enhances cell membrane permeability which strongly affects the dehydration rate (Ramya, et al., 2017). Good membrane permeability ultimately leads to more rapid osmotic dehydration. The cellular membrane exerts high resistance to transfer and slows down the osmotic dehydration rate (Bialik, et al., 2018; Katsoufi, et al., 2017). This phenomenon limits the rate of mass transfer during osmotic dehydration of fruits, vegetables, and food (Zielinska, et al., 2018). Hence, it is essential to develop additional techniques to enhance mass transfer without adversely affecting the quality.

Different pretreatment methods have been investigated to improve mass transfer during drying of fruits, vegetables. These include blanching (Cesa, et al., 2017; Jaiswal, et al., 2012; Wu, et al., 2014; Yonny, et al., 2018), peeling (Pan, et al., 2018), coating (Jung, et al., 2015; Kerch, 2015; Sunjka, et al., 2004; Xiao, et al., 2010), freezing or thawing (Ando, et al., 2016; Peng, et al., 2018; Zielinska, et al., 2015), high hydrostatic pressure (Jung, et al., 2018; Verma, et al., 2014; Welti-Chanes, et al., 2016), pulsed electric field (Ade-Omowaye, et al., 2003; Jin, et al., 2017; Puértolas, et al., 2016; Yu, et al., 2018), ultrasound (Azoubel, et al., 2015; Horuz, Jaafar, et al., 2017; Luchese, et al., 2015; Rodríguez, et al., 2018; Zhao, et al., 2018), ohmic heating (Kaur, et al., 2016; Makroo, et al., 2017; Mannozzi, et al., 2018; Moreno, et al., 2016), microwave (García-Martínez, et al., 2018; Sharif, et al., 2018; Tan, et al., 2017), enzymatic treatment (Abdullah, et al., 2007; Kucner, et al., 2013), etc. Fig. 2.1 shows recent pretreatment methods for food, fruits, and vegetables processing. Most of the discussed pretreatment methods have not been well investigated on wild blueberries. Thus there is scope for research to identify the best pretreatment and drying techniques that befit wild blueberry processing.

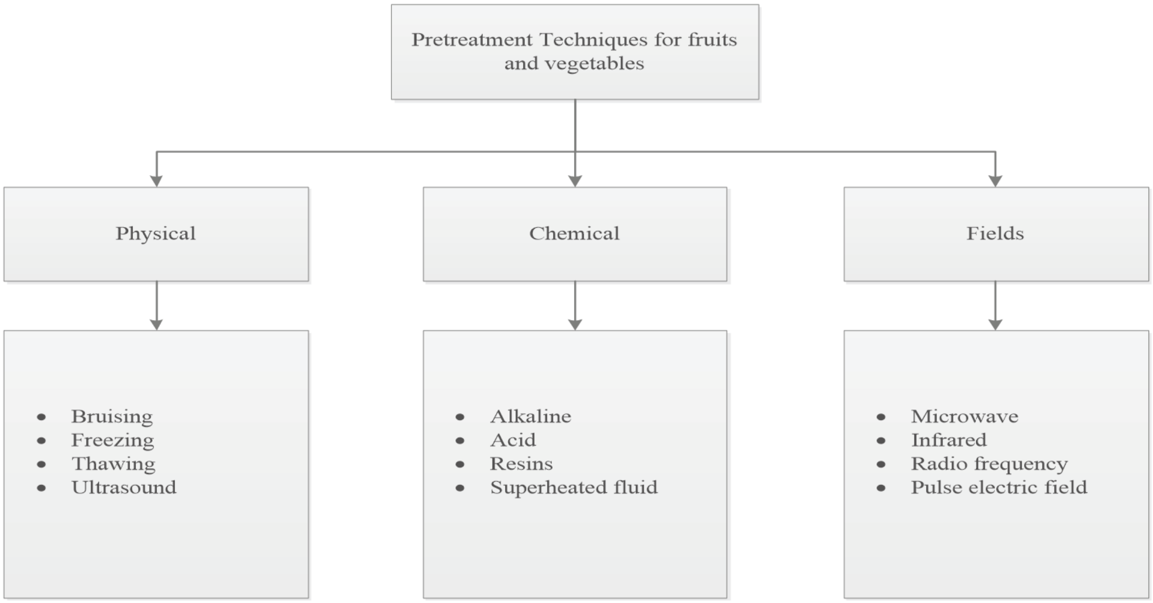


Fig. 2.1: Typical pretreatment techniques used for fruits and vegetables before subsequent processing.

Fruit pretreatment should minimize quality degradation. For example, a banana blanching in steam at 100˚C for 4 minutes prevents enzymatic activity and then sulfating with 0.5% potassium metabisulphite (KMS) solution for 20 minutes prevents non-enzymatic browning (Mahomud, et al., 2015). Another pretreatment method is the treatment of the blueberry with pectinolytic and lipolytic enzymes. In one reported experiment, 90 g of the blueberry was taken in a 600 mL beaker and added 0.6 mL of Pectinex Yield Mash preparation was added along with and 360 mL of water. This was allowed to stand for 30 minutes at 22˚C (Kucner, et al., 2013). The 90 g of blueberry may also be immersed in a 0.7 mL lipolytic preparation palate.

Before adding the lipase enzyme, the water and fruits are brought to pH 6.5 by adding 0.1 M NaOH (Kucner, et al., 2013). For papayas, mangoes, and bananas, pretreatment may involve dipping the fruit in 0.4 % ascorbic acid or 0.4 % ascorbic acid plus 0.1 per cent KMS solution for 30 minutes (Chavan and Amarowicz, 2012).

Fig. 2.2 shows some conventional drying techniques and some recently developed drying techniques for food, fruits, and vegetables processing. The study of suitable drying method for a specific food, fruit, and vegetable generally target the following quality parameters of the dehydrated product: a) retention of flavor of the dried products (Dulf, et al., 2016; Rodriguez, et al., 2016), b) retention of nutrients such as heat-sensitive and oxygen-sensitive components (Kamiloglu, et al., 2016; Nowicka, et al., 2015), c) products browning inhibition (Aral, et al., 2016; Nadian, et al., 2015; Wojdyło, et al., 2009), d) efficient dried product rehydration, which represents the ability of restoring fresh product properties (Horuz, Jaafar, et al., 2017; Seremet, et al., 2016), e) dried product morphology, appearance, and texture at macrostructural and microstructural levels (Chu, et al., 2017; Monteiro, et al., 2018; Vega-Gálvez, et al., 2015).

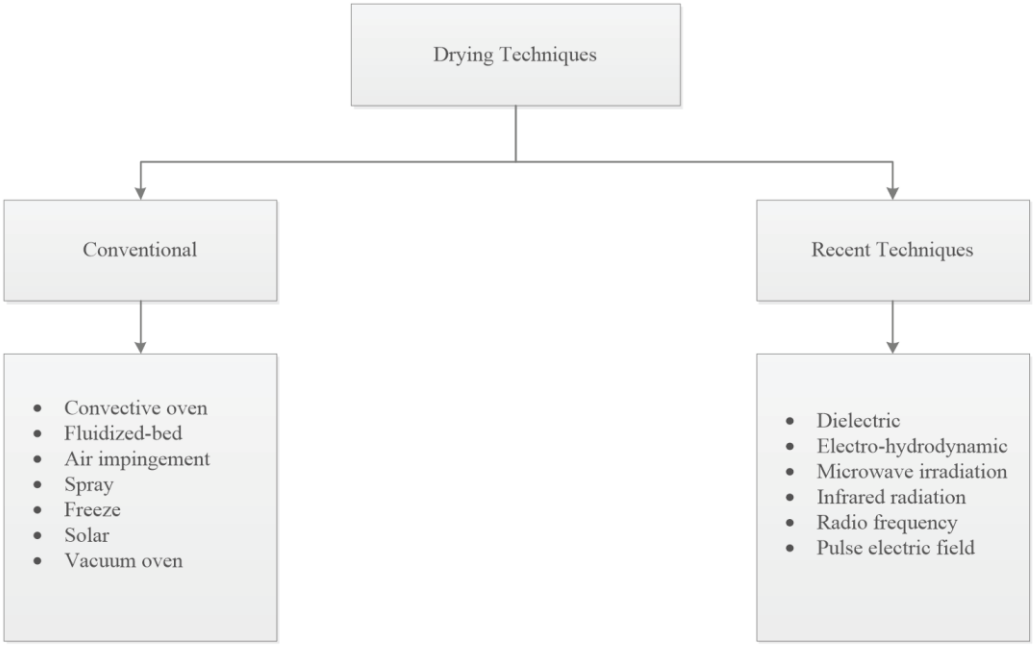


Fig. 2.2: Some of the recent and conventional drying techniques for food, fruits, and vegetables.

Many of the new drying techniques for fruits and vegetables have not been attempted on wild blueberries. Recently, Yu, et al. (2018) studied the effects of pulsed electric field and thermal pretreatments on the biochemical degradation and physical migration of polyphenolic compounds in osmotic dehydrated blueberries. They reported that the pulse electric field pretreated and dehydrated fruits showed better appearance to thermally pretreated and control samples. The authors also observed that pulse electric field pretreated samples had the least degradation loss but the most migration loss of these compounds compared to thermally pretreated and control samples (Yu, et al., 2018). The influence of microwave-assisted drying techniques on the rehydration behavior of blueberries (Vaccinium corymbosum L.) was investigated by Zielinska and Markowski (2016). The effects of microwave-vacuum, ultrasonication, and freezing on mass transfer kinetics and diffusivity during osmotic dehydration of cranberries were examined by Zielinska, et al. (2018). Freezing/thawing and microwave-assisted drying of blueberries

(Vaccinium corymbosum L.) were also studied by Zielinska, et al. (2015). Several of the current drying techniques such as electrohydrodynamic, infrared, and radio frequency drying of wild blueberries have not been reported in the literature. More studies are needed in the stated areas of drying techniques for wild blueberries processing.

In the recent years, combination of different drying techniques has been explored to dry many fruits, and vegetables by many researchers (Eltawil, et al., 2018; Łechtańska, et al., 2015; Musielak, et al., 2018). Fig. 2.3 shows two major categories of combined drying techniques. Tandem combination is also known as hybrid drying which refers to drying protocols that employ different drying techniques at different stage of the drying s cycle of a product (Deepika, et al., 2018; Zhang, et al., 2017). A multi –stage approach in a drying system for a product has been reported to improve the thermal performance and

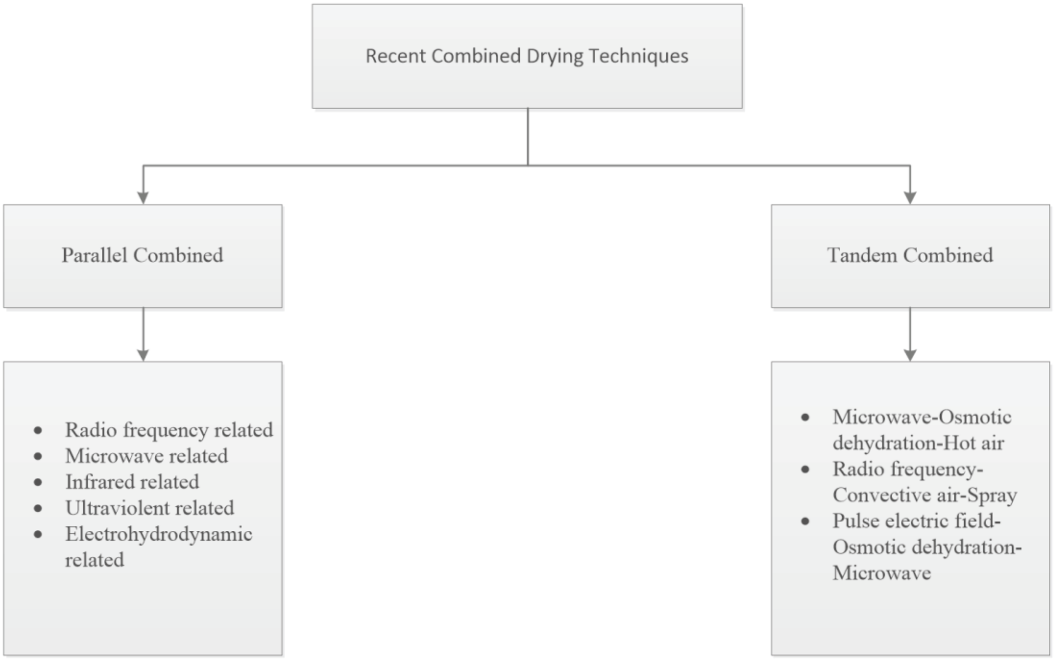


Fig. 2.3: Two major categories of combined drying techniques.

enhance the desirable product quality (Horuz, Bozkurt, et al., 2017; Horuz, Jaafar, et al., 2017; Vishwanathan, et al., 2013). Hybrid drying technologies include combinations as hot air drying followed by microwave or freeze drying, osmotic dehydration followed by hot air drying etc. (Fig. 2.3). Limited information is available in the literature on the application of current hybrid drying methods for wild blueberries processing. Recently, combined hot air convective drying and microwave-vacuum drying of blueberries (Vaccinium corymbosum L.) focusing on drying kinetics and quality characteristics was reported by (Zielinska, et al., 2016).

2.3 Conventional Drying

Food drying is one of the oldest methods of food preservation. The aim of drying is to remove moisture from a food product to prevent the growth of microbes and the enzymatic reactions, which cause food spoilage. Drying food is an important way of preserving seasonal foods to consume later. Dehydrated foods are also important for backpacking, hiking, and camping because they weigh much less than their non-dried equivalents and do not require refrigeration. However, traditional methods of dehydration such as solar drying, microwave, oven drying, or vacuum tend to reduce the product quality. Drying causes loss of color, change of texture, flavor, nutrients and freshness due to high temperature used as shown in Table 2.1. Results of experiments show that lowering the process temperature has great benefits for improving the quality of dried products (Sagar and Kumar, 2010).

Table 2.1: Effects of using conventional drying methods on blueberries and other fruits

Fruits	Initial Moisture Content %	Methods	Drying Conditions		Moisture	Final Product	References
			Temperature	Time	%	Comments	
Aonla	80.74	Oven drying	65C	72hrs.	7.07	A sharp drop in the ascorbic acid	P. S. Kumar, et al. (2014); Kumari, et al. (2018); Pragati, et al. (2000)
Bananas	74	Air drying	180-140C	8-11 hrs.	17-20	Slightly browned, the flavour differed distinctly from fresh banana	Brekke, et al. (1966)
Blueberry	85	Cabinet dryer	90 - 50C	5.5 hrs.	-	Reduction of the total anthocyanin by 49%	Lohachoompol, et al. (2004)
Golden berry	82	Drum drying	110C	A few minutes.	-	Reduce the phenolic content (11.12% - 42%), lightness	Tiwari, et al. (2013)
		Oven drying	60C	24hrs	-		
Peaches	88	Dehydrate	135C	8-12 hrs.	-	Lack sweetness	Hong, et al. (2004)
Pineapples	87	Oven	140F	2X than dehydrate	-	Pineapples will cook instead of dry.	Kendall, et al. (2007)

2.4 Osmotic Dehydration (OD)

OD is one of most significant complementary pretreatment method and food preservation technique in the processing of dehydrated foods (Akbarian, Ghasemkhani, & Moayedi, 2014). It is used for the partial removal of moisture from food by immersion in a hypertonic solution. The process may involve dehydration of food in two stages. The first stage is the removal of moisture from the food using an osmotic agent (osmotic concentration), while the second phase involves subsequent dehydration of the food in a dryer to reduce the moisture content further (Chavan and Amarowicz, 2012). The osmotic dehydration step can be done before, or even after the conventional drying process to enhance the mass transfer or to shorten the duration of drying time (Akbarian et al., 2014). The treatment involves the process of osmosis in which moisture migrates from a solution of lower concentration to a high concentration of solutes through a semi-permeable membrane. The objective of OD is to lower the water activity of the food materials. Yadav and Singh (2014) reported that OD could reduce from 30% to 70% of the food moisture content. The stable shelf life and distinctive characteristics of osmotically dehydrated fruits allow it to be widely used in cereals, confections, and baked goods (Yu et al., 2017). The solutes most commonly used in OD are sugar syrups for fruits such as blueberries. During the osmotic dehydration process, moisture flows from the fruits to the sugar syrup (Yadav, et al., 2014). Apart from reducing the water content of the fruits, the process also simultaneously increases the soluble solids content. The complex cellular structure of the fruit acts as the semipermeable membrane.

A list of on research on osmotic dehydration (OD) on various fruits is given in Table 2.2. Although OD results in partial dehydration, the food still retains some water activity, which should be removed through other processes such as conventional drying (De Mendonça, et al., 2016). The overall process however retains all the beneficial compounds like other non- heat processes. OD is a diffusive process, and as such, the diffusivities of the moisture and solids are affected by numerous factors discussed in the following sections.

Table 2.2: Osmotic dehydration of fruits.

Fruits	Osmotic agents and concentration	Temp (°C)	Sample to solution ratio	Agitation	Sample size (mm)	References
Apple and Golden delicous	Dry sugar and syrup	20 – 49	1 to 4	Yes	3	Ponting (1966)
	Invert sugar, 50% Sucrose, 55–75%	30 – 60	25	-	-	Farkas, et al. (1969)
	Sucrose, 70%	50	4	-	3	Contreras, et al. (1981); Dixon, et al. (1977)
	Sucrose, 59%	RT	5	-	6 to 10	Lerici, et al. (1985)
	Sucrose, 60–75%	40 – 80	26	-	15 to 20	Videv, et al. (1990)
	Sucrose, 70%	50	3	-	13	Sharma, et al. (1991)
	NaCl	-	-	-	-	Lerici, et al. (1985)
Apple	Sucrose 70%	37±2	1:02	-	Cubes, 10 mm^3	Allali, et al. (2009)
	Sucrose 25 - 65 %	30 – 50	1:05	-	Slices	Barat, et al. (2001)
	Sucrose 61. 5% (w/v)	30	1:02	Yes	10 mm	Khin, et al. (2007)
	Sucrose 34 - 63%	34–66	1:03	Yes	Cylindrical 20x20 mm	H. Li, et al. (2006)
Amla	Sucrose 40–50 °B	30 – 50	-	-	-	Singh, et al. (1999)
Aonla	Sugar syrup, 50–708Brix	30–60	1:4–1:8	-	-	Alam, et al. (2010)
	Sugar syrup, 30-50 Brix	30–50	1:5–1:15	-	Cubes, 10 mm^3	Tiroutchelvame, et al. (2015)
Apricot	Corn syrup, 81%	49	4	Yes	-	Ponting (1973)
Banana	Sucrose, 60%	NK	NK	-	-	Hope, et al. (1972)
	Sucrose, 60–80%	49	4	Yes	-	Ponting (1973)
	Sucrose, 65%	60	NK	-	-	Garcia-Noguera, et al. (2010)

Table 2.2: (Continued).

Fruits	Osmotic agents and concentration	Temp (°C)	Sample to solution ratio	Agitation	Sample size (mm)	References
Blueberries	Sucrose, 60Brix	23–25	5	-	-	Shi, et al. (2008)
	Sucrose, 60–80%	49	4	Yes	-	Ponting (1973)
	Sucrose	NK	-	-	-	Kim and Toledo (1987)
	Sucrose 65%	30	4	Yes	-	Kucner, et al. (2013)
	Commercial can syrup 70%	40	2	Yes	-	Yu, et al. (2017)
Cashew apple	Sucrose/corn syrup 40–60%	30 – 35	-	-	-	P. Azoubel, et al. (2003)
Cherry	Corn syrup/Sucrose, 70%	NK	-	-	-	Giangiacomo, et al. (1987)
Citrus fruit	Sucrose 60–80%	49	4	Yes	-	Ponting (1973)
	Sucrose	-	-	-	-	Mehta, et al. (1984)
Dashehari	Sucrose, 70%	RT	1	-	-	Teaotia, et al. (1976)
Dwarf cavendish	Sucrose, 70%	27 – 60	1 to 3	Yes	8 to 10	Bongirwar, et al. (1977)
	Sucrose 40–70 °B	25 – 35	-	-	-	N. Rastogi, et al. (1997)
	Sucrose 55–65 °B	-	-	-	-	Oliveira, et al. (2006)
	Sucrose + salt	25 – 55	-	-	-	Mercali, et al. (2011)
Fuji apple	Sucrose 50% + NaCl 10%	27	-	-	-	Monnerat, et al. (2010)
Giant kew	Sucrose 40–70%	20 – 65	10	-	6.5	M. Rahman, et al. (1990)
	Sucrose 50–70 °B+ 0.2% citric acid and 700 ppm KMS	60 – 65	-	-	-	Rashmi, et al. (2005)
Golden delicious and Jersey Mack	Sucrose, 70%	51	4	-	3	Dixon, et al. (1977)

Table 2.2: (Continued).

Fruits	Osmotic agents and concentration	Temp (°C)	Sample to solution ratio	Agitation	Sample size (mm)	References
Granny Smith cultivar	Glucose, 25–34.6%	30	-	-	-	Nieto, et al. (2004)
Grapes	Sucrose 60–80%	49	4	Yes	-	Ponting (1973)
Mango green	Salt, 25%	29	-	-	10	Jackson, et al. (1971)
Melntosh	Sucrose, 75%	25	-	-	-	Camirand, et al. (1968)
	Sucrose, 25–50%	23	20	-	3 to 4	HAWKES, et al. (1978)
	NaCl, 5–10%	RT	-	-	-	
	Sucrose, 50–70%	30 – 50	4	Yes	10	Conway, et al. (1983)
Peach	Sucrose 65–80%	49	4	Yes	-	Ponting (1973)
	Corn syrup/Sucrose, 70%	NK	-	-	-	Giangiacomo, et al. (1987)
Pineapple	Sucrose 65–80%	49	4	Yes	-	Ponting (1973)
	Sucrose,45–65 °B	30 -50	-	-	-	Lombard, et al. (2008)
	Sucrose	30 – 50	-	-	-	L. Ramallo, et al. (2004)
	Sucrose, 60%	30 – 50	-	-	0.6	L. A. Ramallo, et al. (2005)
Pomegranate	Sucrose 55 °B	40, 50,55, 60	-	-	-	Bchir, et al. (2012)
Pumpkin	Sucrose, 45%	25	-	-	15 to 25	Mayor, et al. (2008)
	Sucrose, 40–60%	27	-	-	-	Garcia, et al. (2007)
	Sucrose + salt	-	-	-	-	Mayor, et al. (2011)
Red delicious	Sucrose, 70%	70	4	-	15	BOLIN, et al. (1983)
	Sucrose, 30–45%	-	-	-	-	Mandala, et al. (2005)

2.4.1 Quality of raw material

For osmotic dehydration careful consideration must be made of the raw materials used. The maturity and variety of fruits and vegetables used have important roles in controlling water loss and solid gain during the osmotic process. Some raw material quality factors that influence the osmotic process includes intercellular spaces, the enzymatic activity of the fruit, initial insoluble and soluble solids content, tissue compactness etc. In many cases, ripe fruits are more suitable for osmotic dehydration than unripe products (Chavan, et al., 2012).

2.4.2 Type of Osmotic Agent

The type of osmotic agent used greatly affects the osmotic dehydration process (Charles Tortoe, 2010). For fruits and vegetables sucrose, glucose, starch syrup, fructose, sorbitol, glycerol, glucose syrup, corn syrup, honey and sodium chloride are the most commonly used osmotic agents (Akbarian et al., 2014). . Lactose, maltose, dextrose corn starch syrup, polysaccharides and maltodextrin are also used as osmotic agents. Desirable characteristics of osmotic agents are that they should be harmless, have good taste and have high diffusivity characteristics. Some osmotic agents show better performance than others due to their inherent characteristics. For instance, high fructose corn syrup has higher diffusivity compared to sucrose. However, sucrose is favored over fructose and is considered as the best osmotic agent because it can be recycled a minimum of five times without affecting fruit quality even though no new syrup is added (de Oliveira et al., 2017; Garcıa-Martınez et al., 2002; Germer et al., 2016). Also, it imparts acceptable sweet taste to the product. Sucrose can reduce browning by preventing the entry of oxygen. Lower molecular mass saccharides such as fructose, glucose, and sorbitol favor solid enrichment instead of water dehydration because they enhance sugar uptake due to the high velocity of molecule penetration. Sodium chloride can retard oxidation, stop browning and increase the driving force for the drying due to the lowering capacity of the salt. Yadav, et al. (2014) indicated that a combination of the different osmotic agent was more effective than only one due to a combination of properties of solutes. For instance, a combination of salt and sugar osmotic agents can be more effective in dehydration of fruits and vegetables (Nishadh, et al., 2014).

2.4.3 Concentration of osmotic agent

The concentration of the osmotic solution also has a major influence on the OD process. The osmotic solution concentration strongly affects the kinetics of water removal, equilibrium of moisture content, and the solid gain. For instance, moisture loss and dehydration are enhanced when the molar mass of the solute increases and the concentration of the solution is high. The increase of the osmotic solution concentration has also been shown to increase the equilibrium concentration and the drying rate (Chandra, et al., 2015). Evidence from past studies suggests that the rate of moisture loss and solute gain is proportional to the concentration of the osmotic solution. The higher the concentration of the osmotic solution, the faster the rate of osmosis. For instance, syrup strength in the range of 60 to 70 Brix has been found to be optimum for osmosis (Chavan, et al., 2012). Yadav, et al. (2014) reported that optimum osmosis found at approximately 40 Brix and salt concentration should be around 10% (w/w). According to Telis, et al. (2004), a high concentration of sucrose hinders the penetration of sodium chloride in tomato if they are used as a combination. Small quantities of salt to the sugar solution could increase the osmotic drying force due to its lower molecular weight and higher capability of reducing the water activity (Telis, et al., 2004). Shi, et al. (2008) found that osmotically dehydrated blueberries using 60% sugar solution had a low moisture content of 47g moisture /100g, while fresh blueberries had 85g moisture/100g. Lohachoompol, et al. (2004) demonstrated that osmotically treated blueberries with 60 Brix (w/w) and 1% (w/w) of sodium chloride had lower moisture content (33.6% wet basis) than untreated blueberries (36.9% wet basis). Partial dehydration of banana by osmosis in 70% sugar syrup reduces 50% of its initial weight (Yadav and Singh, 2014). Finally, if salt is used as an osmotic agent there is an increase in the loss of moisture content at the end of drying because salt uptake influences moisture sorption behavior of the product. However, using salt as a combination osmotic agent with sugar will affect and change the taste or the flavor of the final products of wild blueberries.

2.4.4 Osmotic solution ratio

In OD the sample to solution ratio has to be chosen wisely so that the driving force for the removal of the moisture exists till the end of the process. The product mass ratio and solution have different effects in the solution of dehydration process. The driving force decreased to remove of water when osmotic solutions become dilute. As the dehydration progresses, the osmotic solution become increasingly dilute and the driving force for further removal of water drops. However, higher ratio of material to osmotic solution (1:10 to 1:60) can be used to avoid significant dilution of the medium due to uptake of water from sample and loss of solute to the sample, and subsequent decrease in the osmotic driving force during the osmotic dehydration (Ahmed, et al., 2016; Chavan, et al., 2012; Dehghannya, et al., 2018). However, some investigators used a much lower ratio (1:1, 1:3, 1:4 or 1:5) to monitor the mass transfer by following changes in the concentration of the osmotic solution (Pacheco-Angulo, et al., 2016; Zahoor, et al., 2017).

2.4.5 Temperature and the immersion time of the osmotic solution

The temperature and time of the osmotic solution contact with the food to be dehydrated also influence the performance of the OD process. According to Chandra, et al. (2015), temperature is the most important parameter affecting the kinetics of mass transfer during the osmotic dehydration process. The optimum immersion time of OD for fruits is about 132 minutes (Yadav, et al., 2014). The initial time is crucial, since mass transfer phenomena are rapid and have a significant impact on further progression of the osmotic process (Tortoe, 2010). The rate of osmosis increases with increase in temperature. However, the osmosis process increases up to a certain optimum temperature beyond which the cell membranes are destroyed which results in a slowdown in osmosis rate (Chavan, et al., 2012). Above 50˚C, flavor deterioration and enzymatic browning take place. These are some of the changes OD tries to prevent, as compared to conventional drying. The moisture loss increases as the temperature increases, but a solid gain is less affected by temperature. Khan (2012) reported that undesirable changes appeared on the blueberries at temperature higher than 50ºC. Kucner, et al. (2013) also detected that the temperatures in the range 30 to 50ºC of OD in blueberry does not show any effect on the antioxidant content . Temperature at 70ºC led to 30% loss of the phenolic compound after 2h of dehydration. However, there is no significant influence on the color value of berry during OD at high temperature (Stojanovic, et al., 2007). Optimum conditions of time and temperature need to be determined for each food product on a case-by-case basis.

2.4.6 Agitation of the osmotic solution

Agitation is one of the key factors in OD, and an adequate level of agitation ensures minimization or elimination of liquid-side mass transfer resistance and provides a constant driving force (Rastogi, et al., 2015). The use of highly concentrated viscous sugar solutions creates significant problems such as floating of food pieces, hampering the contact between food material and the osmotic solution and leads to a reduction in the mass transfer rates. Thus, to enhance mass transfer and to prevent the formation of a dilute solution film around the samples, agitation by shaking or stirring process can be applied during osmotic dehydration (Akbarian, et al., 2014; Gupta, et al., 2012; Moreira, et al., 2007). However, agitation may be difficult and cause damage to the sample. Agitation has no effect on osmosis for short process periods. Tortoe, et al. (2009) investigated the effects of agitation on mass transfer during osmotic dehydration in plant materials. However, only minimal improvement in moisture loss and solids gain is observed following the agitation of the osmotic solution. For longer osmosis periods, the agitation of the osmotic solution reduces the rate of solid gain. That is due to the indirect effect of high moisture loss changing the solute concentration gradient in the food particle surface (Chandra, et al., 2015). Agitation has no direct impact on solid gain throughout the entire osmotic process since an external transfer of the osmotic solute is not limiting (Tortoe, 2010). Dynamic infusion (shaking) was found to be more effective than increasing temperature greater than 50 °C for increasing solid gain of blueberries in sugar infusion resulted in fast and high solid gain (Shi, et al., 2008).

2.4.7 Convective drying

After osmotic treatment, the next step in the process is drying where excess moisture is removed from the food. OD alone cannot provide longer shelf life and stability to the final product. A combination of drying such as osmotic and conventional drying is the best way to reduce the energy consumption, increase the throughput and improve quality. The combination has been evaluated successfully by many researches and the overview of the process is shown in Fig. 2.4. Air-drying is commonly used following OD to produce so called semi-candied dried fruits. Several methods of dehydration of osmotically treated foods are available. These include convective, freeze, microwave, vacuum or infrared drying steps (Ramya, et al., 2017). Beaudry, et al. (2004) compared four drying methods of drying (osmo-vacuum, osmo-microwave, osmo-freeze and osmo-convective) and found that the drying rate of osmo-vacuum treated cranberries is higher followed by osmo-microwave drying process. Moreover, the reduction in pressure causes the expansion and escape of gas enclosed in the pores. The pores can be occupied by osmotic solution, thus increasing mass transfer rate. Another option is using infrared drying steps, as an energy saving method (Wang, et al., 2006). The introduction of infrared heating increases the initial drying rate by 4 to 5 times for potato and pineapple drying. Shi, et al. (2008) evaluated drying and quality characteristics of fresh and sugar-infused blueberries dried with infrared (60, 70, 80 and 90 C) radiation heating. It was realized that infrared drying produced much firmer texture product with much-increased drying efficiency for fresh blueberries and sugar-infused blueberries compared to convective air-drying. Increasing the temperature (60–80 C) showed the enhancement of drying rate and reduction of drying time without causing significant negative on the quality of dried products.

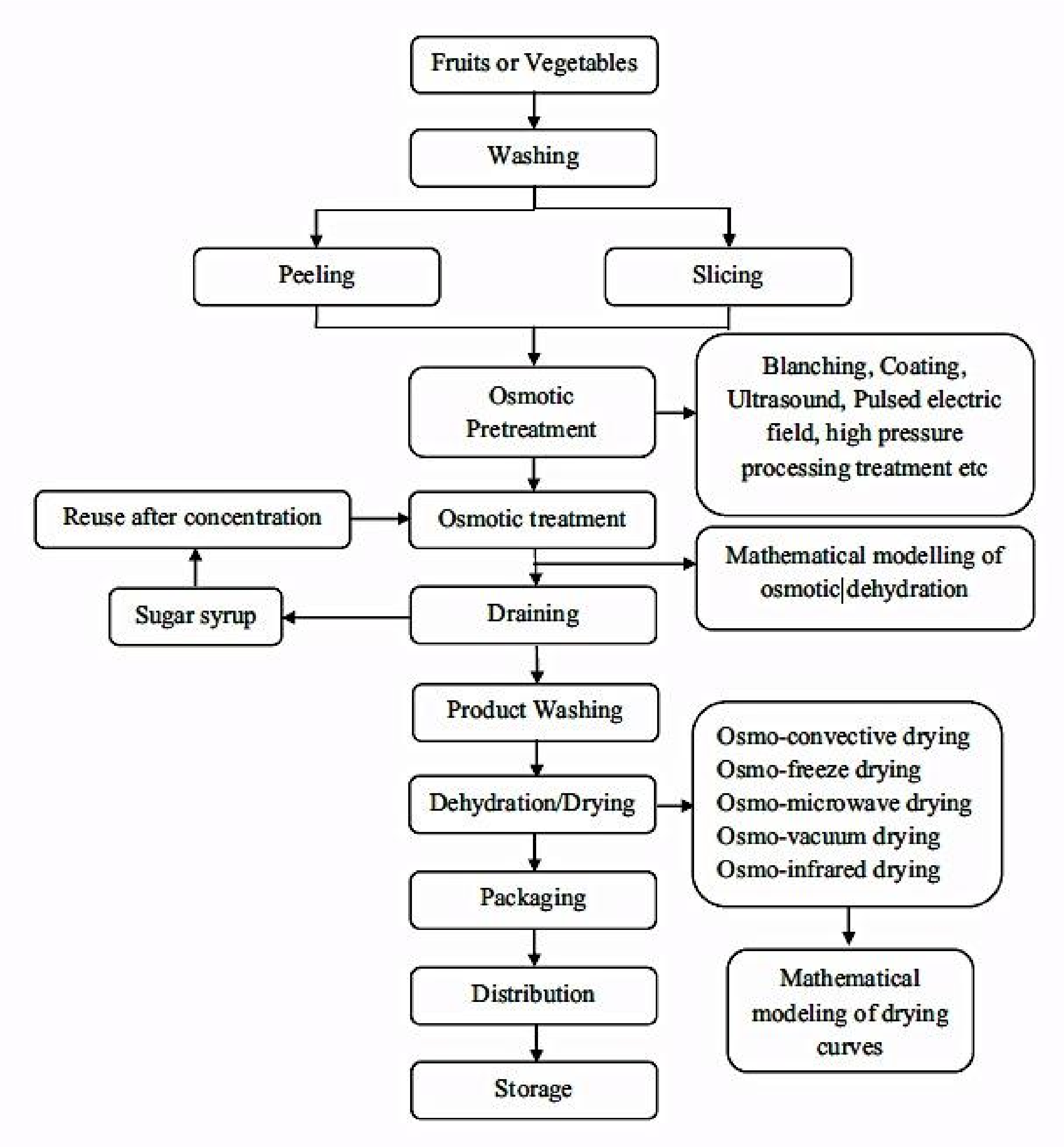


Fig. 2.4: Process flow chart for general method of OD (Ramya, et al., 2017).

2.5 Comparison between conventional drying and OD

Many researchers have reported that osmotically treated fruits have great advantages compared to conventional drying (Germer, et al., 2014; Prosapio, et al., 2017). Firstly, OD has the advantage of minimizing the effects of using temperature on food quality such as loss of color and flavor and that it preserves the wholeness of the product.

This is because no high temperature is required in the process compared to that used in conventional drying. It also increases the products resistance to heat treatment. Secondly, flavor and color retention are high when sugar or sugar syrup used as an osmotic agent and it also prevents the enzymatic and oxidative browning that occurs during conventional drying. Thirdly, the antioxidant activity retention of anthocyanins in berries is higher for osmotically treated samples than air-dried ones (Dermesonlouoglou, et al., 2016). Fourthly, removal of acid and absorbance of sugar during the OD by the fruit pieces enhance the taste of the product compared to conventionally dried products. OD can also improve the texture and rehydration properties of fruit and vegetable. For instance, it helps to protect the food from the structural collapse of food that can occur in conventional drying. Also, the process is simple and economical as energy requirement is 2-3 times less than the conventional drying. When OD is done in conjunction with conventional drying, it removes a majority of the water present and retains the quality of the fruit. It also improves the food stability during storage due to its low water activity.

2.6 Optimization of OD parameters using statistical design

The optimization of drying parameters is very important for heat sensitive food materials such as vegetables, fruits, and biological products (Abdullah, et al., 2007; Chen, et al., 2018). However, optimization of food, fruits, and vegetable dehydration process is a complex problem that demands evaluation of many nonlinear phenomena because of multifaceted drying process which involves simultaneous mass and heat transfer in the hygroscopic system (Corrêa, et al., 2014; De Mendonça, et al., 2016). The increasing desire and awareness for high-quality and shelf-stable dried food products necessitates adequate optimization of drying process conditions with the aim to obtain the desire quality of the final product and efficient drying process (Corrêa, et al., 2016; Sharif, et al., 2018). Different optimization methods have been employed for food, fruits, and vegetables such as: response surface methodology (RSM) (De Mendonça, et al., 2016; Derossi, et al., 2015), Taguchi orthogonal design (Rajat, et al., 2017), neutral network (Aghbashlo, et al., 2015), and full factorial design (Wong, et al., 2015).

2.7 Mathematical modeling and mass transfer

In osmotic dehydration processes, there is a simultaneous countercurrent mass transfer of water from the sample to the hypertonic or osmotic solution and of solute from solution into the sample. Mathematical model is a useful important tool for the optimization of operating parameters and to predict performance of a drying system (Assis, et al., 2016; Bialik, et al., 2018; Kumar, et al., 2016). Many mathematical models, empirical, and semi-empirical, have been demonstrated to estimate drying processes and properties of food products (Castro, et al., 2018; Horuz, et al., 2018). The most frequently used mathematical models of the drying of different fruits and vegetables are shown in Table 2.3. Most of these models are equally applied to simulate drying curves and predict mass transfer under different drying conditions (Assis, et al., 2016; Castro, et al., 2018). In the study of mass transfer in the osmotic dehydration of kiwiberry involving experimental and mathematical modeling, the authors reported that the Peleg’s equation exhibits better fitting for the experimental data from the statistical analysis of the mathematical modeling of the process.

Mass transfer kinetics and quality attributes of osmo-dehydrated candied pumpkins using nutritious sweeteners was investigated by Katsoufi, et al. (2017). An empirical model based on a first-order kinetic equation was developed to predict the products’ properties, in which the rate constant is a function of the process temperature. Zielinska, et al. (2018)

investigated the effect of microwave-vacuum, ultrasonication, and freezing on mass transfer kinetics and diffusivity during osmotic dehydration of cranberries. Microwave-vacuum and OD treatments produced cranberries with the highest values of moisture loss and solid gain while Azuara's and Peleg's models adequately fitted into the experimental data of the OD kinetics of whole cranberries in terms of moisture loss and solid gain. The advantage of most of these models is the ability to predict intricate parameter that might not easily accessible using conceptual experimental design. They are equally user friendly, but their applications are restricted and only valid within the range of drying parameters for product during the experiment. All these mass exchanges between the osmotic solution and food affect the quality of the dehydrated product such as nutritional value, texture, color, and taste.

Consequently, osmotic processes, diffusion, tissue shrinkage and flux interaction should all be considered for a precise explanation of the mass transfer phenomena during the osmotic dehydration process (Bera, et al., 2015). Understanding the mass transfer process during osmotic dehydration and modeling the kinetics of process has been the focus of several research activities. Mass transfer or exchange kinetics during osmotic dehydration usually depend on various solution to Fick's law of diffusion.

Table 2.3: Mathematical models used in OD.

Model name	**Model**	**Reference**
Page	MR = $\frac{MC(t)-MC_{eq}}{MC_0-MC_{eq}}$ = exp (-kt^n)	Antonio, et al. (2008); Calín-Sánchez, et al. (2015); Nabnean, et al. (2017); Olanipekun, et al. (2015); Rudy, et al. (2015); Simpson, et al. (2017); (Wilton, et al., 2018)
Herderson and Pabis	MR = a exp $(-kt)$	Doymaz (2008); Guzzo da Silva, et al. (2015); Hashim, et al. (2014)
Weibull	MR = exp (- $(\frac{t}{\beta})^{\alpha}$)	Fernanda R. Assis, et al. (2017); Lemus-Mondaca, et al. (2018); Quevedo, et al. (2016); Serment-Moreno, et al. (2017)
Newton	MR = exp (- kt)	Kadam, et al. (2004); Nabnean, et al. (2017); Rajat, et al. (2017)
Two-term	$MR = a\exp(-k_0t) + b\exp(-k_1t)$	Abbas, et al. (2017); Olanipekun, et al. (2015)
Peleg	$MR = 1 + {t}/{(a+bt)}$	Fernanda R. Assis, et al. (2017); Cheng, et al. (2014); S. Deepika, et al. (2017)
Wang and Singh	$MR = 1 + at + bt^2$	Kadam, et al. (2004); Omolola, et al. (2014); Rudy, et al. (2015); Şahin, et al. (2016)
Azuara		Fernanda R. Assis, et al. (2017); S. Deepika, et al. (2017); Jesus, et al. (2017)
Exponential	$MR = \exp(-kt)$	Fernanda R Assis, et al. (2016); Jorquera-Fontena, et al. (2017)
Logarithm	$MR = a\exp(-kt) + c$	Afolabi, et al. (2015); M. M. Rodríguez, et al. (2015); Rudy, et al. (2015)
Modified Page	MR = exp [- (k$t)^n$]	Calín-Sánchez, et al. (2015); Cano-Lamadrid, et al. (2017)
Modified Henderson and Pabis	$MR = a\exp(-kt) + b\exp(-gt) + c\exp(-ht)$	Aykın-Dinçer, et al. (2018); Thalerngnawachart, et al. (2016)
Parabolic	$MR = a + bt + ct^2$	Afolabi, et al. (2015); Bi, et al. (2015); Manzoor, et al. (2017); Olanipekun, et al. (2015)
Midilli et al.	$MR = aexp[-(kt)^n] + bt$	Doymaz (2017); Kadam, et al. (2004); Martins, et al. (2017); Pérez-Won, et al. (2016); Sonmete, et al. (2017)

Chapter 3

Materials and Methods

3.1 Materials

The study examined fresh wild blueberries *(V.angustifolium*) and cultivated blueberries *(V. corymbosum)* fruits obtained from different places that were stored in a refrigerator at -18°C until use. Wild blueberries harvested from a forest located in Nipigon, in summer 2017, ON, Canada. It had an initial moisture content (MC) of 82.38% of wet basis and 17.4% of dry matter. Cultivated blueberries were purchased from a local market in Thunder Bay, ON, Canada. Sucrose used to prepare the osmotic solutions was purchased from a local market in Thunder Bay, Ontario, Canada. Folin-Ciocalteu reagent, Hydrochloric acid (HCL), Sodium carbonate, methanol, Sodium nitrate, Aluminum chloride, potassium chloride buffer solution (pH 1.0), Sodium acetate buffer solution (pH 4.5), and Sodium hydroxide were purchased from Fisher Scientific (Ottawa, ON, Canada). Galic acid and catechin use for standard preparation were purchased from Sigma Aldrich (Oakville, ON, Canada).

3.2 Methods

The berries were thawed to the ambient temperature (room temp 22 °C) for 1 h before all experiments. Wild blueberries were subjected to the following processing steps:

- Pretreatments (PT), osmotic drying (OD) and hot air convective drying (HACD)
- Osmotic dehydration (OD) and hot air convective drying (HACD)
- Hot air convective drying by oven (HACD)

The pretreatments studied included Microwave exposure and Ultrasonication for which a Danby products microwave and a Brandson Ultrasonication were used respectively.

3.3 Pretreatment of wild blueberries prior to osmotic dehydration

The waxy skin of blueberries limits the osmotic dehydration by lowering drying rate resulting in extended time requirements. In order to speed up the drying process, the following four pretreatment techniques were investigated:

- Immersion in boiling water treatment
- Ultrasound water-bath treatment
- Ultrasound probe treatment
- Microwave treatment

3.3.1 Boiling water treatment (BW)

10g of thawed WB (approximately 18 pieces) were placed on sieves and immersed into boiling water for 15s. The wild blueberries were then cooled down by immersion in cold water.

3.3.2 Ultrasonic bath treatment (UB)

For the ultrasound water-bath pretreatment, specified amounts (10g) of thawed WB samples were placed in a 250 mL conical flask containing 65% Brix solution resulting in a sample to sucrose solution ratio of 1:4. The flask was placed in an ultrasonic water-bath (Fisher Scientific Ultrasonic Bath; 5.7 L, vibration frequency of 40 kHz, 110W) for 15 min.

3.3.3 Ultrasonication probe treatment (US)

For the ultrasound probe pretreatment, a specific amount (10g) of thawed WB samples was placed in a 250 mL conical flasks containing 65% Brix solution at a sample ratio of 1:4. The fruit samples in the flask were subjected to ultrasound treatment on Digital Sonifier (model 250, Brandson Ultrasonication Corporation, Connecticut, USA) equipped with a microtip-tapered probe having a diameter of 3.2 mm diameter. The probe amplitude, cycle, and pulse were set to be 30%, 0.5 per s and 0.5 per s, respectively. Ultrasound treatment time was varied to levels of 2, 5, and 10 min for different sets of samples.

3.3.4 Microwave treatment (MW)

During microwave pretreatment specified amounts (10g) of thawed WB samples were placed into 250 mL conical flasks containing 65% Brix solution at a sample ratio of 1:4. A kitchen microwave oven (Danby products DMW753BL – 800 W, Guelph, ON, Canada) was used to pretreat the samples before OD. The microwave treatment time was varied to levels of 30, 45, and 60 s using different sets of samples. All the experiments were carried out in triplicate.

3.4 Osmotic dehydration processes

Wild blueberries were dehydrated by immersing them in the aqueous osmotic solution 65 °Brix (%w/w sucrose sugar) in initial experiments. The osmotic solution was prepared by using commercial sugar and distilled water to give the desired concentration. The 65 °Brix solution was made by taking 65g of sucrose and diluted into 35g of distilled water (Magwaza & Opara, 2015; Yu et al., 2018). Similar approach was used for 60% and 70% Brix solution during the optimization experiments. All the solutions were prepared at room temperature. In each OD experiment, 10g of pretreated wild blueberries were placed into 40g of osmotic solution in Erlenmeyer flasks to target ratio of 1:4. A similar approach was used to obtain target ratios of 1:2 and 1:6 which were used for the optimization experiments. The flasks were transferring to an incubator (New Brunswick Innova 44, Mississauga, ON, Canada) for agitation (Shaking). The samples were kept in the shaker at 200 (cycles/min) (Kucner et al., 2013). A cover of poly- film metallic foil was used to prevent solution loss by evaporation during the OD process.

3.5 Hot air convective drying (HACD)

Treated and untreated WB were subjected to an oven temperature of 70°C (Stojanovic & Silva, 2006; Vega-Gálvez et al., 2012). The samples were placed on the middle of the Fisherbrand Isotemp 179L Model Forced-air convection oven (Fisher Scientific Co., ON, Canada). The hot air allowed circulating around all sides of the samples. The samples were kept in the oven until a final moisture content (MC) of 18 g/100g of wet samples (Prosapio & Norton, 2017; Shi et al., 2008). Drying time was defined as the period between the starting time of heating and time by that samples reach the desired moisture content (MC). The dehydrated samples were placed in a desiccator to cool down then were stored in Ziploc bags. In order to prevent oxidation, all the packaged samples were stored in a dry and cool place until further analyses.

3.6 Physical characterization measurements

3.6.1 Moisture content and dry matter content

The AOAC 934.06 standard method was employed to determine the moisture content and dry matter content of the samples (AOAC, 1999). A pre-weighted amount of the sample was placed in a drying oven at 70°C for 24 h until sample weight was stabilized. The measurement was done in triplicate.

3.6.2. Calculation of moisture loss and solid gain

The moisture loss (ML), weight reduction (WR) and solid gain (SG) during OD process was determined using following equations 3. 1, 2 and 3 expressed in g/100 g of fresh sample (Lech et al., 2018; Nowicka et al., 2015; Rahman M, 2015).

$$ML = WR + SG \qquad \text{Eq 3.1}$$

$$\mathrm{WR} = \frac{(W_I - W)}{W_I} \times 100 \qquad \text{Eq 3.2}$$

$$\mathrm{SG} = \frac{(S - S_i)}{W_I} \times 100 \qquad \text{Eq 3.3}$$

Where W, W_i and S, S_i are the current and initial weight of the fruit (g) and solid content in the fruit (g) respectively. The solid gain was determined by grinding 3g of the sample and 25 ml of distilled water (Moreno et al., 2016; Prosapio & Norton, 2017). A refractometer (VEE GEE BX-90) was used to measure the solid gain content (SG) of the homogenized solutions of fresh and treated samples at 20°C.

3.6.3 Shrinkage ratio (SR)

The diameter and thickness shrinkage ratio (SR) of dried WB was determined by using digital calipers. The measurements were conducted 3 times for sample. Based on the average diameter the WB sizes were calculated using Eq. 3.4 (Wang et al., 2014).

$$\text{Shrinkage ratio \%} = \frac{\boldsymbol{d_0 - d_t}}{\boldsymbol{d_0}} \times 100 \qquad \text{Eq 3.4}$$

Where d_0 (mm) and d_t (mm) are the diameter and thickness of fresh and dried WB, respectively.

3.6.4 Rehydration ratio (RR)

Rehydration ratio (RR) was determined by immersing the dried WB (1g) in 60 ml of distilled water in a 100 ml beaker. The rehydration ratio was determined using following equations number 3.5 (Dehghannya et al., 2018; Seremet et al., 2016; Stojanovic & Silva, 2006; Wang et al., 2018). The rehydration was done by two methods: Cold rehydration (CR) at room temperature and Hot rehydration (HR) at 50°C. In both methods beakers with dried WB were left for 2, 6, 10,14, 18, 22, 26, 30 minutes, the WB were taken out of the water dried thoroughly by paper towels to eliminate the surface water and the weight was recorded.

$$\text{Rehydration ratio } \% = \frac{W_r}{W_d} \times 100 \qquad \text{Eq 3.5}$$

Where W_r is the weight of the rehydrated WB (g) and W_d is the weight of the dried WB (g) used. Each rehydration experiment was performed in triplicate.

3.7 Chemical characterization measurements

The wild blueberries were characterized in term of their antioxidant content by the following methods:

3.7.1 Extraction Process

After osmotic dehydration, the samples were ground and prepared for further analyses. For extraction a 1.0 ± 0.001 g of the ground sample was weighed into centrifuge tubes (15 mL). Each tube was then filled to 10 mL with 2% HCL in methanol (w/v) and then put in the sonicator bath for 10 min. The mixtures were then centrifuged for 10 min at 2683xg (4000 rpm), after while the supernatant was transferred to another tube for further analysis (de Souza et al., 2014).

3.7.2 Determination of Phenolic Content

A standard calibration curve was developed for phenolics content using 99.98% pure gallic acid. A stock solution of gallic acid was prepared by weighing 25 mg in a 100 mL of methanol. Six different concentrations in the range of 10 - 200 µg/mL garlic acid were used to build the calibration curve. All calibration concentration points were run in duplicate.

A 100 µL of the extract obtained from the phenolic extraction was transferred into a 2 mL vial followed by 750 µL of Folin–Ciocalteu reagent and kept in the dark for 5 min. 750 µL of 6% (w/v) of Na_2CO_3 was then added and kept in the dark for 2 h. The absorbance of the solutions was then determined at a wavelength of 765 nm on a spectrophotometer (Thermo Scientific, Genesys 10S UV-VIS, Ottawa, ON, Canada) with water as the blank. The total phenolic content was expressed as mg of gallic acid equivalent (GAE/100g of sample) as determined from the standard curve generated with gallic acid (de Souza et al., 2014).

3.7.3 Determination of Flavonoid Content

From the extract, 100 µL was transferred into a 2 mL vial followed by 400 µL of distilled water and 30 µL of 5% Na_2NO_3. The mixture was allowed to stand 5 min before adding 30 µL of 10% $AlCl_3$. It was then left to stand for another 5 min before adding 200 µL of 1M NaOH and 240 µL of distilled water. The mixture was then agitated vigorously. The absorbance of the solutions was determined at a wavelength of 510 nm on a spectrophotometer (Thermo Scientific, Genesys 10S UV-VIS, Ottawa, ON, Canada) with distilled water as the blank. Total flavonoid content was expressed as mg of catechin/100g of sample using the standard curve generated with catechin (de Souza et al., 2014).

3.7.4 Determination of Anthocyanin Content

Two buffer solutions were prepared to enhance the absorbance of anthocyanins in the sample using a spectrophotometer. Buffer A was prepared by adjusting 25 m M KCl solution to pH 1.0 using HCl while Buffer B was prepared by adjusting 0.4 M sodium acetate solution to pH 4.5 using HCl. To determine the anthocyanins content, 100 µL of the extract was added to 900 µL of Buffer A in a 2 mL vial. Another 100 µL of the extract was added to 900 µL of Buffer B in a separate 2 mL vial. The mixtures were equilibrated for 2 h in the dark. The absorbance of the buffer A solution and sample followed by buffer B solution and sample were obtained at 512 nm and 700 nm on a spectrophotometer to determine the amount of anthocyanin in the samples (de Souza, et al., 2014; Lee et al., 2005). The anthocyanin content was expressed as mg cyanidin-3-glucoside/100g of sample using equations 3.6 and 3.7.

$$\Delta A = (A_{512nm} - A_{700nm})_{pH1.0} - (A_{512nm} - A_{700nm})_{pH4.5} \qquad \text{Eq 3.6}$$

$$Anthocyanin\ content = \frac{\Delta A \times MW \times DF \times 1000}{\varepsilon \times l} \qquad \text{Eq 3.7}$$

Where, ΔA = absorbance change, MW = molecular weight of cyaniding-3-glucoside (449.2 g/mol), Df = dilution factor of the sample, ε = molecular absorbance extinction coefficient of cyaniding-3-glucoside (26900 M^{-1} cm^{-1}) and 1000 = factor for conversion from g to mg.

3.8 Optimization of parameters using statistical design

3.8.1 Osmotic dehydration after microwave pretreatment

Previously weighed WB collected after the microwave pretreatment process for 30s was introduced into osmotic solutions for dehydration. The different parameters studied were sugar concentrations (60 %, 65 %, and 70% Brix w/w) under different temperatures (30, 40, and 50°C), processing times (2, 5, and 8 h) and sample to osmotic solution ratio (1:2, 1:4, and 1:6). Different combinations of the process parameters were maintained as per the experimental design (section 3.8.2). The sucrose solution and the WB were taken in 250 ml Erlenmeyer flasks and placed in a temperature, time and agitation-controlled incubator shaker (New Brunswick Innova 44, Mississauga, ON, Canada). The Erlenmeyer flasks were wrapped in parafilm during the experiments. An agitation speed of 200 rpm was maintained for all the experiments as this is considered sufficient for such system

(Kucner et al., 2013). At the end of each run, determined according to the experimental design explained in the result section, the flasks containing the sample were withdrawn from the incubator shaker. The WB samples were taken out from the osmotic medium, washed for 30 s with distilled water on a rubber mesh, and gently wiped with an absorbent paper and then weighed using an analytical balance (Sartorius-Secura, Goettingen, Germany) with an accuracy of ±0.0001 g. The water loss during OD process was determined according to the expression for weight reduction and SG (section 3.6.2). The phenolics, flavonoid, and anthocyanins content were measured to evaluate the antioxidants content of WB after osmotic dehydration (section 3.7). All the experiments were done in duplicate and the average value was taken for all the calculations.

3.8.2. Experimental Design and Statistical Analysis

Four parameters namely, temperature (X1), treatment time (X2), sucrose concentration (X3), and sample to sucrose solution ratio (X4) were selected as the most important (de Mendonça, et al., 2016; Yu, et al., 2017). RSM was used to determine the number of runs and levels at which experiments were to be carried out. The central composite design (CCD) with four variables at three levels (Table 3.1) was employed to study responses in terms of antioxidants content. The results of the experiments were used to determine the optimum combination of the variables for the best OD conditions. This is a face centered design whereby the star points are at the center of each face of the factorial space ($\alpha = \pm 1$). This type of CCD requires three levels of each factor. The dependent variables were phenolics content, flavonoid, and anthocyanins.

Table 3.1: Experimental design levels of actual and coded values for the OD process

Independent parameters		**Coded levels of parameters**		
		-1	0	1
Temperature (°C)	X1	30	40	50
Time (h)	X2	2	5	8
Brix (%)	X3	60	65	70
Sample: Brix (w/w)	X4	1:2	1:4	1:6

The complete design generated 30 experiments ($T_n = 2^f + 2f + K = 2^4 + 2*4 + 6 = 30$) as shown in Table 3.2. T_n represents the total number of experiments, f represents the number of independent variables, and K represents the number of center point runs. The center point runs provide a mean for estimating the experimental error and a measure of lack of fit. Coded values represent the natural values of each variable (Table 3.2). The second order polynomial model (Eq. 3.8) was fitted to the data. Three models of the following form were developed to relate three responses (Y): phenolics content, flavonoid, and anthocyanins to four process variables (x):

$$Y = a_0 + \sum_{i=1}^{4} a_i X_i + \sum_{i=1}^{4} a_{ii} {X_i}^2 + \sum_{i}^{3} \sum_{j=i+1}^{4} a_{ij} X_i X_j \qquad \text{Eq 3.8}$$

Where a_0, a_i, a_{ii}, and a_{ij} are constant regression coefficients; x is the coded independent factor. A mathematical model was developed for each of the responses using multiple linear regression analysis which involves linear, quadratic, and interaction terms of the independent factors. The significant levels of the factors in the model were determined using analysis of variance (ANOVA) for each response. The degree of confidence of the data was estimated using student's t-test to determine the probability level to be less than 5%. The model's accuracy was checked by coefficient of determination (R^2) and root mean square error (RMSE). A good model was expected to have a large predicted R^2 and a low RMSE.

Table 3.2: CCD in coded forms of process variables for osmotic dehydration WB.

Run	**Coded parameter values**			
	Temperature X1	Time X2	Brix X3	Sample ratio X4
1	1	-1	-1	-1
2	1	1	-1	1
3	0	0	0	0
4	-1	1	1	-1
5	-1	1	-1	-1
6	0	0	1	0
7	-1	-1	-1	1
8	0	0	0	1
9	1	0	0	0
10	1	-1	1	1
11	0	0	0	0
12	-1	1	1	1
13	0	-1	0	0
14	0	0	0	0
15	-1	-1	-1	-1
16	1	-1	-1	1
17	1	-1	1	-1
18	1	1	1	1
19	1	1	1	-1
20	0	0	0	0
21	-1	0	0	0
22	0	1	0	0
23	0	0	0	0
24	-1	-1	1	1
25	-1	1	-1	1
26	0	0	-1	0
27	-1	-1	1	-1
28	1	1	-1	-1
29	0	0	0	-1
30	0	0	0	0

3.8.3 Determination of optimum condition

The simultaneous optimization of the multiple responses was obtained using JMP® (Statistical Analysis Systems, Version 13.4, SAS Institute Inc., Cary, NC, USA) to determine an optimum condition of the variables for maximizing phenolics content, flavonoids content and anthocyanins content. The optimum value for each factor was depicted using the desirability function method (Amami et al., 2017). The desirability function transforms response variable into a 0 to 1 scale. The transformed response, represented as d_i, can have many different shapes. A zero response represents a completely undesirable response, and a response of one represents the most desirable response. The overall desirability (D) combines d_i of several responses using geometric mean for simultaneous optimization of the responses (Eq. 4.9)

$$D = \sqrt[n]{(d_1 * \ d_2 * d_3 * \ldots * d_n)} \qquad \text{Eq 3.9}$$

3.9 Mass transfer modeling in WB

The dehydration steps (OD and HACD) of the optimal process to obtained dried WB were repeated three times and their mass transfer kinetics were evaluated. For OD moisture loss (ML) and solid gain (SG) were determined every 30 minutes. For HACD (ML) was determined every five minutes in the first 30 min, every 15 minutes until 2h, and every 30 minutes until the end of process. As the experimental conditions did not reached the equilibrium in mass transfer, Azuara's model (Souraki et al., 2012; Zielinska, M., & Markowski, M. 2018) was used to estimate the moisture loss (ML) (for both dehydration steps) and solid gain (SG) (for OD) when equilibrium was reached with the following equations:

$$ML_t = \frac{at\ (ML_e)}{1+at} \qquad \text{Eq 3.10}$$

$$SG_t = \frac{at\ (SG_e)}{1+at} \qquad \text{Eq 3.11}$$

Where (ML_t), (ML_e) and (SG_t) and (SG_e) are the moisture loss or solid gain fractions (g/100g of fresh sample) at time (t) and time of equilibrium, (a) is the model's rate constant (min^{-1}) and (t) is time (min).

3.9.1 Diffusivity approach

The Fick's second law model of diffusion is used in order to predict and describe the moisture and solute diffusivity with the time during dehydration processes and it is used for OD and HACD (Horuz et al., 2018; Sareban, M., & Souraki, B. A. 2016; Zielinska, M., & Markowski, M. 2017). Crank's (1975) solution for Fick's second low of diffusion was used to determine the moisture (for both dehydration steps) and solid diffusivity (for OD) as showed bellow:

$$\text{MR} = \frac{M_t - M_e}{M_0 - M_e} = \frac{6}{\pi^2} \sum_{i=0}^{\infty} \exp\left(-i^2\, \pi^2 D_{em}\ \frac{t}{r^2}\right) \qquad \text{Eq 3.12}$$

$$\text{SR} = \frac{S_t - S_e}{S_0 - S_e} = \frac{6}{\pi^2} \sum_{i=0}^{\infty} \exp\left(-i^2\, \pi^2 D_{es}\ \frac{t}{r^2}\right) \qquad \text{Eq 3.13}$$

Where (MR) and (SR) are the average of moisture and solid content ratio of WB over dehydration time, respectively. $(\mathrm{M_0}, \mathrm{S_0})$, $(\mathrm{M_e}, \mathrm{S_e})$ and (M_t, S_t) represent the moisture and the solid concentrations initially, at equilibrium and at any time. (D_{em}) and (D_{es}) are effective diffusivities of moisture and solute, respectively $(m^2\ s^{-1})$.

The change in moisture and solute concentrations were calculated based on the following assumptions:

- The wild blueberries are considered as a sphere (mass transfer in three dimensions).
- Initial moisture and solute concentration in the WB are uniform.
- The moisture diffusion from WB and sugar diffusion into WB are the only transfers considered in OD, and the moisture diffusion from WB is the only transfer considered in HACD; other mass transfers are neglected.
- Solute concentration is equal at the center of a sphere.
- Moisture and sugar concentration are equal on the surface.
- The ratio of solution mass to WB mass in OD is sufficient to prevent alterations in the solution concentration.
- Shrinkage is neglected.
- Apparent diffusion is constant.

For ML (for OD and HACD) and SG (for OD) the equations were numerically solved using Crank's method with eleven terms eq.3 (12-13). By fitting the model to experimental values, the apparent diffusivity value for ML (for OD an HACD) and SG (for OD) were obtained

3.9.2 Equilibrium approach

The two main methods used to predict mass transfer during dehydration processes are the diffusion approach (Fick's second law solution) and the equilibrium approach. For equilibrium approach, the moisture and solid mass transfer coefficients in WB were calculated as described in the literature (Souraki et al., 2012) using the following equations:

$$-\frac{dM}{dt} = k_m(M - M_e) \qquad \text{Eq 3.14}$$

$$\frac{dS}{dt} = k_s(S - S_e) \qquad \text{Eq 3.15}$$

Where (k_m) and (k_s) are the moisture and the solid mass transfer coefficients, respectively.

The change in moisture and solute concentrations were calculated based on the following assumptions:

- All substances are well mixed in the product, except for near the interface.
- Changes in concentration are limited to the region near the interface.

3.9.3 Model's fitting

The math model's goodness of fit to the experimental data was determined based on the values of the root mean square error (RMSE), determination coefficient (R^2) and relative mean error (RME) were calculated for the equilibrium conditions. Apparent diffusivities and mass transfer coefficient estimations were calculated as the following equations (Horuz et al., 2018; Sareban & Souraki, 2016; Vallespir, F et al., 2018):

$$\text{RMSE} = \sqrt{\frac{\sum_{i=1}^{N}(x_{exp}^{i} - x_{pre}^{i})^{2}}{N}} \qquad \text{Eq 3.16}$$

$$\text{RME (\%)} = 100\,\frac{\sum_{i=1}^{N}.\frac{x_{exp}^{i} - x_{pre}^{i}}{x_{exp}^{i}}}{N} \qquad \text{Eq 3.17}$$

Where x_{exp}^{i} is experimental value, x_{pre}^{i} is predicted value and N is the number of repartitions. The model has to achieve the highest and closest possible linear regression coefficient (R^2) of the unit (1.0) and lower than 10% for the relative mean error (RME).

Chapter 4

Results and discussion

4.1 Initial characterization of blueberries

The wild blueberries used in this study were harvested from a forest located in Nipigon. The berries obtained from the food market were from cultivated sources. Initial chemical characterization of fresh blueberries was carried out. WB contain higher content of antioxidant compounds than BB (Table 4.1). The phenolic, flavonoid and anthocyanin content of WB were higher than the cultivated blueberries by 236%, 253% and 228% respectively. These results are showing the differences between WB and BB and emphasizes and confirms the importance of WB. Similar results were reported by Ketata et al. (2013), who found that the total antioxidant compounds of WB such as phenolics and anthocyanins were higher than BB by 39% and 64% respectively. The difference in the antioxidant compound between species could be due to variety, environmental conditions, stage of maturity, methods and time of harvest and duration and conditions of storage (Marjanovic-Balaban et al., 2012; Mallik & Hamilton, 2017; Michalska & Grzegorz, 2015; Skrovankova et al., 2015).There have been attempts to improve the antioxidant content of cultivated blueberries with some success. The rich sources of antioxidant in these products are important health food supplements (Mallik & Hamilton, 2017). The possibility of drying the products to extend self-life without loss of antioxidant is the major aim of this study.

Table 4.1: Initial characterization of fresh wild blueberries and blueberries.

Initial characterization	Blueberry	Wild blueberry
MC (g /100g)	85.2	82.4
Dry matter content (%w/w)	14.8	17.4
Sugar (Brix)	3.2	2.1
Phenolics (mg/100g of d.m) [a]	414.9	1394.7
Flavonoids (mg/100g of d.m) [b]	126.6	445.1
Anthocyanins (mg/100g of d.m) [c]	195.4	640.4

[a] Expressed as galic acid equivalent.
[b] Expressed as catechin equivalent.
[c] Expressed as cyanidin-3-glucoside equivalent (ε = 26,900).

4.2 Effect of pretreatments before OD on WB water loss, solid gain and antioxidants content

Drying is one of the most important processes used for preservation of food (Perussello et al., 2014). The reduction of moisture content and water activity prevent the deterioration of food. The use of wild blueberries as a component of breakfast cereals would require it to have low moisture content. The removal of moisture would have to be done without loss of antioxidants. OD has been proven to remove moisture content by utilization a higher gradient of sugar concentration as the dehydration agent. In most reports further dehydration to level that remove microbial contamination require heat treatment.

Initial experiments were done with the fresh wild blueberries by immersing them in high concentration sugar syrups. However, there was very little removal of water from the fruit. We decided to use four types of pretreatment before. These included; boiling water treatment, ultrasonic bath treatment, ultrasonication probe treatment and microwave treatment.

Fig. 4.1 shows the influence of pretreatments (immersion in boiling water, ultrasonic water-bath, ultrasonic probe, and microwave) and OD on the moisture loss, solid gain and antioxidants content of WB. It should be noted that the microwave and ultrasonic pretreatments were done in 65% Brix solution as our initial hot water pretreatment experiments showed considerable antioxidants loss as discussed later. This has also been reported in previous works (Moreno, et al., 2016; Nikkhah, et al., 2007), and hence it was decided to use Brix solutions of appropriate concentration that would limit the loss of antioxidants. Changes in the moisture content of WB samples due to pretreatments were shown in Fig. 4.1A. The moisture loss for WB samples pretreated with microwave for 60 s was observed to be the highest (37.71 g/100g fresh fruit) of all the pretreatment techniques. Ultrasonic probe treatment for 10 min led to a significant moisture loss (33.72 g/100g fresh fruit). All the three levels of microwave pretreatments (30 to 60 seconds) showed a similar effect on the moisture loss during the OD process (Fig. 4.1A). In comparison to the control (OD without pretreatment), improved water migration out of the samples was observed in all the pretreatment techniques employed in this study. The significant improvement in water loss due to pretreatment was investigated using the Student's t-test at a 95% level of confidence. The test was carried out to compare the results of the osmotic dehydration experiments with and without pretreatment. The moisture loss by osmotic dehydration alone without any pretreatment was significantly different ($p<0.05$) from all the samples resulted from pretreatment with subsequent osmotic dehydration. Although highest moisture loss was obtained at 60s of

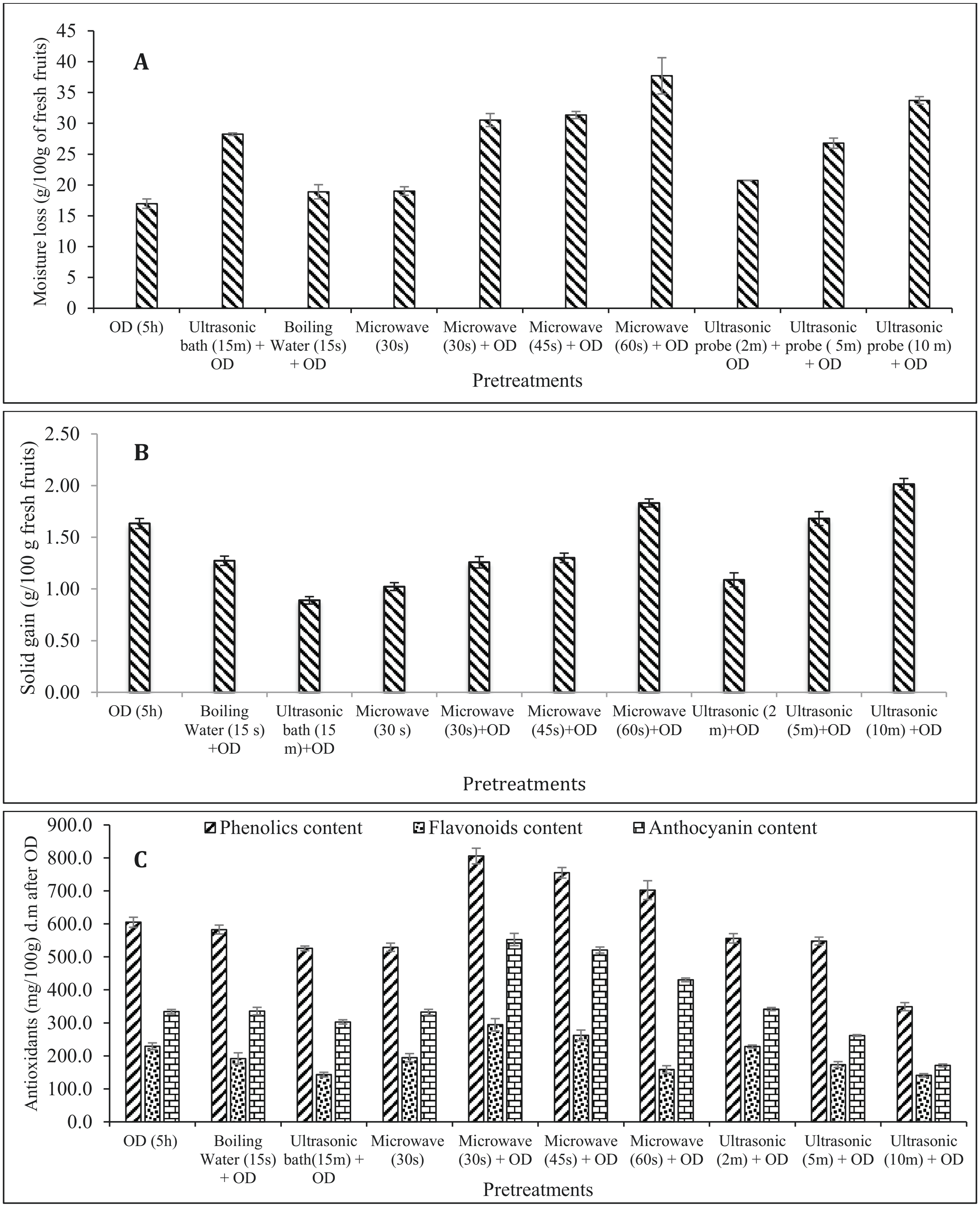


Fig. 4.1: Effects of pretreatments on (A) Changes in water loss (B) Changes in Solid gain (C) Changes in antioxidants during osmotic dehydration of WB at 40 °C.

microwave pretreatment, there was no significant difference (p>0.05) among the three different treatment durations of microwave pretreatment. Similar results were reported in the studies conducted by Kucner, et al. (2013) on the influence of selected osmotic dehydration and pretreatment parameters on dry matter and polyphenol content in highbush blueberry fruits.

With ultrasonic probe pretreatment, a significant difference (p<0.05) was observed among the three levels of the treatment time (2-10 min). The moisture loss is directly proportional to the ultrasonic probe treatment time. Beyond 10 min of treatment time, the complete absolute disintegration of the WB to form fruit juice was observed. Dry matter migration from the fruits to the osmotic solution increased with treatment time for the ultrasonic probe pretreatment. In conclusion, pretreatments had been proven to enhanced moisture loss during the OD process.

It is evident from Fig.4.1B that the increase in time and temperature enhanced solid gain (SG). Microwave pretreatment for 60 s at 90°C presented the highest after OD compare with microwave pretreatments for 30 s (72°C) and 45s (77°C). However, there was no significant difference (p>0.05) among the three levels of treatment time of microwave pretreatment. High temperature modifies the tissue characteristics favouring impregnation phenomena and thus increase SG (Chavan & Amarowicz, 2012). Similar results were obtained by using ultrasonic probe pretreatment for 2 m (54°C), 5 m (63°C), 10 m (90°C) and immersion in boiling water for 15 s at (100°C). For ultrasonic probe pretreatment SG, a significant difference of (p<0.05) was observed among the three levels of the treatment time The lowest uptake solid obtained using the ultrasonic bath for 15m at room temperature. Moreover, during the OD (without pretreatment) increased mass transfer of SG with high concentration is possible to membrane swelling effect, which might increase the cell membrane permeability and the low molecular weight of the osmotic agent (Akbarian et al., 2014; Prosapio & Norton, 2017). The results of SG obtained during OD with or without pretreatment are reasonable. However, a major challenge was to reduce the loss of the antioxidants content as much as possible.

In comparison to the control (OD without pretreatment), significant difference ($p<0.05$) in the antioxidants content (phenolics, flavonoids, and anthocyanin) of the pretreated WB measured on dry matter basis were observed (Fig. 4.1C). Microwave pretreatment for 30s showed the highest quantity of phenolics, flavonoids, and anthocyanin contents after OD process. Although more moisture loss was obtained with 60 s of microwave pretreatment (Fig. 4.1C), significant amount of the antioxidants accompanied the mass transfer of moisture from the fruit tissue into the osmotic agent. Effect of only microwave pretreatment without five hours of OD was investigated to confirm that the significant difference in antioxidants' content was due to microwave alone. The results show tha microwave pretreatment facilitated the water loss during the OD treatment of the sample, because greater moisture loss was achieved during the OD period and the antioxidants content of the samples were retained to in a large degree during the OD process. Higher moisture loss and higher dry matter content during OD process with a corresponding increase in the antioxidants in dry matter of the sample per equivalent weight of the fresh sample was obtained (Fig. 4.1C). However, further moisture removal by evaporation after OD is necessary to reach a final MC (18% wet basis) for achievement of shelf stability (microbiologically) (Grabowski, et al., 2007). Then study the effects of hot air convective drying (HACD) on the antioxidants content of the final products. Based on these results it was decided that the best pretreatment for the wild blueberry was 30s of microwave as it results in sufficient moisture loss and had limited loss of antioxidants.

4.3 Effect of hot air convective drying on the total antioxidant content of the final product of WB

As mentioned earlier, OD does not reduce moisture content to levels that prevent spoilage. Hence, the partially OD dried WB samples had to be dried by convective air-drying in an oven. The total phenolic content (TPC), total flavonoids content (TFC) and anthocyanin content of WB, the control only oven dried (without OD and pretreatments) and pretreatment samples processed at 40°C by osmotic treatment (65 °Brix, 5h, 1:4) followed by drying the samples in an oven at 70°C are shown in Fig. 4.2. TPC, TFC and anthocyanin content of fresh WB were 1394.661 mg/100g of d.m, 445.076 mg/100g of d.m and 640.440 mg/100g of d.m respectively. The samples subjected to oven drying at 70°C showed reduced antioxidant content of WB compared with the fresh sample. However, in general, OD improves the retention of the antioxidant content of WB compared with the oven dried. In the oven dried sample, TPC, TFC and anthocyanin content decreased to be 473.679 mg/100g of d.m, 125.000 mg/100g of d.m and 211.742 mg/100g of d.m respectively. The composition of the antioxidant content in all the samples including the control, changed with different pretreatment techniques used. TPC of microwave pretreatment for 30s followed by OD then hot air convective drying (HACD) was the highest (Fig. 4.2A). Similar results were obtained for TFC and anthocyanin (Fig. 4.2B and C). Using the ultrasonic probe showed a considerable loss of the antioxidants and the lowest amount of TPC, TFC and anthocyanin were obtained after

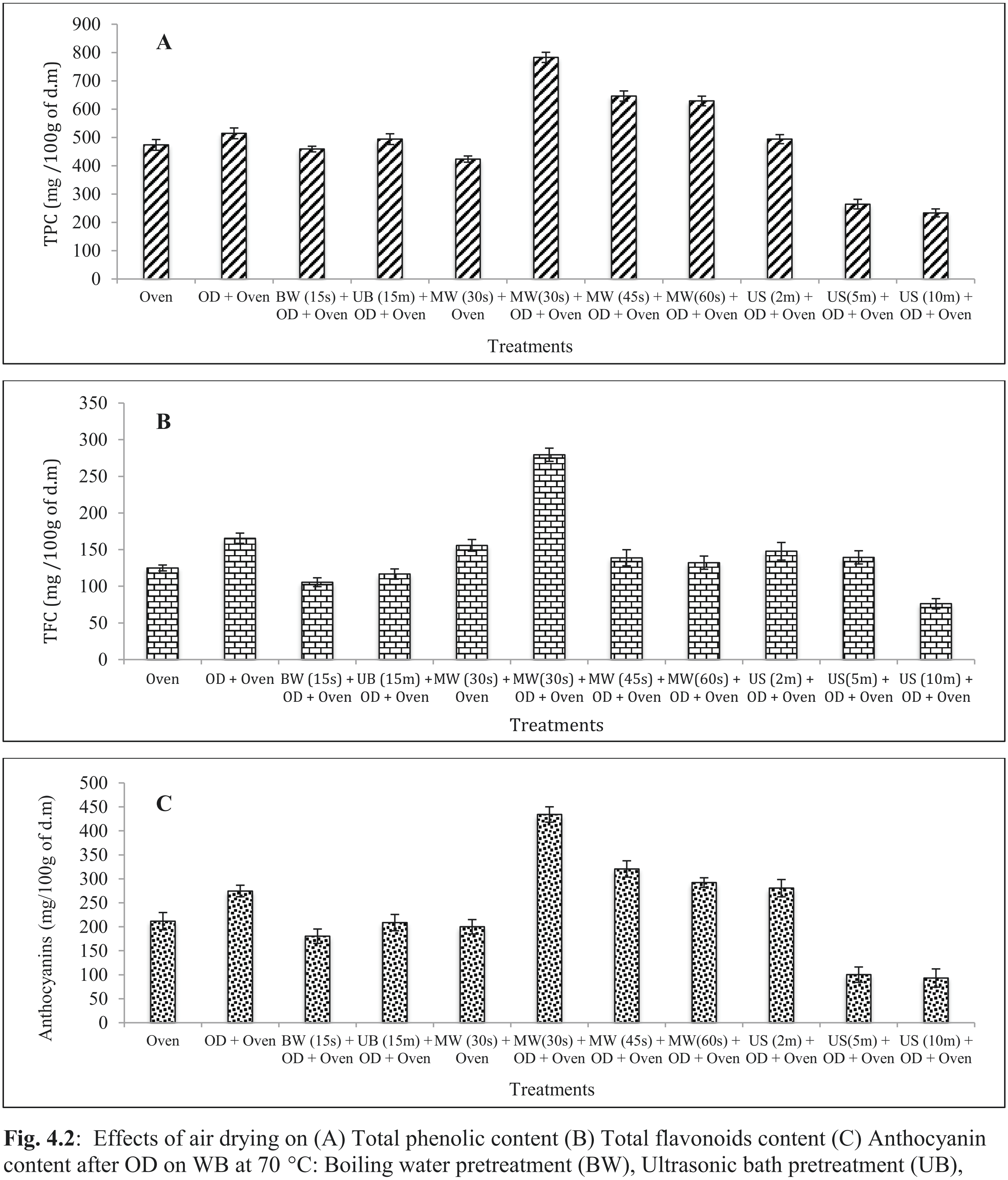


Fig. 4.2: Effects of air drying on (A) Total phenolic content (B) Total flavonoids content (C) Anthocyanin content after OD on WB at 70 °C: Boiling water pretreatment (BW), Ultrasonic bath pretreatment (UB), Microwave pretreatment (MW) and Ultrasonication probe pretreatment (US).

10min. For the ultrasonic bath treatment, the antioxidant content was little higher than the control because the ML during the pretreatment was low which take almost the same time to dry as the control without any pretreatments. The antioxidant content of boiling water, also showed decreases, likely due to the high temperature used during the pretreatment. The loss of the antioxidant content in the hot air convective drying (HACD) is possibly due to thermal instability which led to fruit cell damage or enzymatic oxidation especially during the pretreatments step (Tiwari, Hasan, & Islam, 2013). In a combined pretreatment using ohmic heating and pulsed vacuum, the treated samples retained more polyphenols after drying as compared to untreated samples (Moreno et al., 2016). Based on the results of our experiments summarized in Table 4.2, the optimum condition for pretreatment was found to be 30s microwave for all the samples before the OD process and subsequent oven drying.

Table 4.2: Impact of dehydration and drying process on total phenolic content (TPC), total flavonoids content (TFC) and anthocyanin content of WB.

Treatment	After Pretreatments			After OD			After Air-drying		
	TPC (mg /100g of d.m)	TFC (mg c/100g of d.m)	Anthocyanins (mg/100g of d.m)	TPC (mg/100g of d.m)	TFC (mg /100g of d.m)	Anthocyanins (mg/100g of d.m)	TPC (mg/100g of d.m)	TFC (mg 100g of d.m)	Anthocyanins (mg/100g of d.m)
Oven	–	–	–	–	–	–	473.7	125.0	211.7
OD (5)	–	–	–	605.1	229.2	333.0	514.6	165.6	274.7
Boling Water 15s	–	–	–	582.9	191.8	335.8	459.0	105.6	180.3
Ultrasonic bath 15m	–	–	–	525.8	143.1	302.0	494.0	116.7	208.7
Microwave 30s (without OD)	529.242	194.444	332.493	–	–	–	423.6	155.8	200.1
Microwave 30s	**–**	**–**	**–**	**805.7**	**274.2**	**552.7**	**782.9**	**279.4**	**434.2**
Microwave 45s	–	–	–	755.0	262.3	520.8	646.3	138.9	320.6
Microwave 60s	–	–	–	702.3	158.6	430.4	628.9	132.2	292.2
Ultrasonic 2m	–	–	–	556.3	228.5	341.9	494.0	147.8	280.5
Ultrasonic 5m	–	–	–	548.1	173.7	261.7	264.4	139.4	100.2
Ultrasonic 10m	–	–	–	349.2	140.9	170.9	233.5	76.1	93.2

4.4 Optimization experiments

Following optimization of the pretreatment conditions it was decided to optimum the parameters which control osmotic dehydration. These included; temperature (X1), time (X2), Brix (X3) and sample to Brix ratio (X4). The range of these parameters was chosen based on a review of initial experiments and results available in literature for osmotically dehydrated fruits and vegetables. In order to reduce the number of experiments required an RSM experimental design procedure was carried out. The results of the experiments under conditions suggested by the RSM are given in Table 4.3.

4.4.1 Experimental data analysis

Multiple regression tests were carried out on the experimental results of the dependent variables (phenolics content, flavonoids content, and anthocyanin content) are shown coded experiment points in Table 4.3. The regression coefficients for the three models generated and the ANOVA of the proposed model are shown in Table 4.4 The mathematical equation in terms of coded factors for OD of microwave pretreated WB on phenolics content, flavonoid content, and anthocyanin content model are shown in Eqs 4 (1–3), respectively.

$$Y = 726.29 - 30.06X2 + 24.61X3 + 36.38X4 + 28.24X1X2 + 32.09X1X3213.62X1X \quad \text{Eq 4.1}$$

$$Y = 262.02 - 31.33X2 + 18.98X3 + 24.79X1X2 - 141.54X1X1 \quad \text{Eq 4.2}$$

$$Y = 406 - 25.55X2 + 29.14X3 + 40.88X4 + 25.7X1X2 + 29.78X1X3 - 199.9X1X1 \quad \text{Eq 4.3}$$

Where X1, X2, X3 and X4 are temperature, time, Brix and sample to Brix ratio, respectively. The quadratic model in coded units showed the role of every variable and their interactions in independent variables at the level of confidence of 95% using student's t-test.

Table 4.3: CCD in coded forms of process variables and values of experimental data of response variables for osmotic dehydrated WB

Run	Coded parameter values				Antioxidant content		
	Temperature	Time	Brix	Sample ratio			
	X1	X2	X3	X4	Phenolics (Gallic acid eq.)	Flavonoids (Catechin eq.)	Anthocyanin (C3G eq.)
1	1	-1	-1	-1	493.460	76.389	173.000
2	1	1	-1	1	543.810	93.333	243.136
3	0	0	0	0	757.460	280.000	437.511
4	-1	1	1	-1	483.302	73.889	183.688
5	-1	1	-1	-1	499.365	85.278	199.719
6	0	0	1	0	782.857	226.111	442.520
7	-1	-1	-1	1	701.905	205.278	401.608
8	0	0	0	1	711.429	220.833	412.462
9	1	0	0	0	435.873	67.222	135.595
10	1	-1	1	1	673.333	202.500	373.387
11	0	0	0	0	811.429	282.778	471.743
12	-1	1	1	1	520.794	92.500	220.425
13	0	-1	0	0	690.794	279.444	391.589
14	0	0	0	0	752.698	278.333	452.540
15	-1	-1	-1	-1	588.254	108.611	228.441
16	1	-1	-1	1	528.730	91.667	228.441
17	1	-1	1	-1	534.286	90.556	234.452
18	1	1	1	1	630.476	120.000	331.306
19	1	1	1	-1	588.254	106.389	288.557
20	0	0	0	0	751.111	285.556	410.793
21	-1	0	0	0	514.444	92.778	214.414
22	0	1	0	0	681.270	132.778	381.403
23	0	0	0	0	759.048	286.667	418.307
24	-1	-1	1	1	657.460	128.056	358.024
25	-1	1	-1	1	488.381	83.056	188.363
26	0	0	-1	0	692.381	151.389	352.680
27	-1	-1	1	-1	535.873	164.167	235.120
28	1	1	-1	-1	427.429	68.056	127.579
29	0	0	0	-1	651.111	126.944	350.677
30	0	0	0	0	751.111	288.333	431.666

Table 4.4: Model parameter estimates: (A) Phenolics content (B) Flavonoids content (C) Anthocyanin content where the independent variables X1, X2, X3 and X4 are temperature, time, Brix and sample to Brix ratio respectively.

A

Parameter	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	726.29462	14.85319	48.90	<.0001*
X1	-7.4515	11.27041	-0.66	0.5185
X2	-30.05633	11.27041	-2.67	0.0176*
X3	24.606667	11.27041	2.18	0.0453*
X4	36.388	11.27041	3.23	0.0056*
X1*X2	28.238125	11.95407	2.36	0.0321*
X1*X3	32.08725	11.95407	2.68	0.0170*
X2*X3	10.952375	11.95407	0.92	0.3741
X1*X4	4.448375	11.95407	0.37	0.7150
X2*X4	-14.02775	11.95407	-1.17	0.2589
X3*X4	5.376875	11.95407	0.45	0.6593
X1*X1	-213.6212	29.70639	-7.19	<.0001*
X2*X2	-2.747746	29.70639	-0.09	0.9275
X3*X3	48.839254	29.70639	1.64	0.1210
X4*X4	-7.509746	29.70639	-0.25	0.8039

B

Parameter	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	262.02245	10.80974	24.24	<.0001*
X1	-13.02472	8.20229	-1.59	0.1332
X2	-31.32706	8.20229	-3.82	0.0017*
X3	18.981389	8.20229	2.31	0.0352*
X4	14.074056	8.20229	1.72	0.1068
X1*X2	24.791688	8.699842	2.85	0.0122*
X1*X3	9.2361875	8.699842	1.06	0.3052
X2*X3	-5.069438	8.699842	-0.58	0.5687
X1*X4	11.180563	8.699842	1.29	0.2182
X2*X4	0.9026875	8.699842	0.10	0.9187
X3*X4	-3.402813	8.699842	-0.39	0.7012
X1*X1	-141.5449	21.61948	-6.55	<.0001*
X2*X2	40.955105	21.61948	1.89	0.0776
X3*X3	5.9551053	21.61948	0.28	0.7867
X4*X4	-23.76689	21.61948	-1.10	0.2890

C

Parameter	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	405.99679	13.50834	30.06	<.0001*
X1	-5.241611	10.24995	-0.51	0.6165
X2	-25.54922	10.24995	-2.49	0.0249*
X3	29.139556	10.24995	2.84	0.0123*
X4	40.884389	10.24995	3.99	0.0012*
X1*X2	25.7685	10.87172	2.37	0.0316*
X1*X3	29.77625	10.87172	2.74	0.0152*
X2*X3	5.980375	10.87172	0.55	0.5904
X1*X4	1.951875	10.87172	0.18	0.8599
X2*X4	-19.1725	10.87172	-1.76	0.0982
X3*X4	0.53225	10.87172	0.05	0.9616
X1*X1	-199.8957	27.01668	-7.40	<.0001*
X2*X2	11.595754	27.01668	0.43	0.6739
X3*X3	22.699754	27.01668	0.84	0.4140
X4*X4	6.6692544	27.01668	0.25	0.8084

Table 4.4A represents the regression coefficient, and ANOVA of phenolics content experimental data analysis. The significant effect of each of the factors based on the phenolics content of WB are depicted in the Table 4.4A. All the linear terms significantly influenced ($p<0.05$) the amount of phenolics content of WB during OD except the process temperature. The linear effects related to OD treatment time and sucrose concentration for the decrease in water activity have been reported for the osmotic dehydrated pumpkin (Pinzi et al., 2010) and yacon slices (de Mendonça et al., 2016). Food stability and shelf life of food products usually increase with a decrease in water activity. Although osmotic processes promote the reduction, the effect of temperature on the OD process might not significantly influence the phenolics content for the range of temperature investigated in this study. Kucner, et al. (2013) had earlier reported that higher temperatures lead to substantial losses of phenolic compounds in the dehydrated material (30 % after 2 h of dehydration at 70 °C). The temperature range employed in this study was taken such that it limits significant loss of antioxidants. The quadratic effect of temperature was found to significantly influence ($p<0.05$) the phenolics content of WB during the OD process. Other factors quadratic effect had no significant influence on the samples phenolics content after OD process. In the investigattion of effect of ultrasound- assisted osmotic dehydration pretretment on the on the convective drying of strawberry, the authors reported that only the quadratic term of ultrasonic osmotic dehydration and temperature has significant effect on water loss and weight reduction (Amami et al., 2017). De Mendonça et al. (2016) studied the optimization of osmotic dehydration of yacon slices and reported a significant quadratic effect of treatment time of osmotic dehydrated assisted ultrasound on the solid gain.

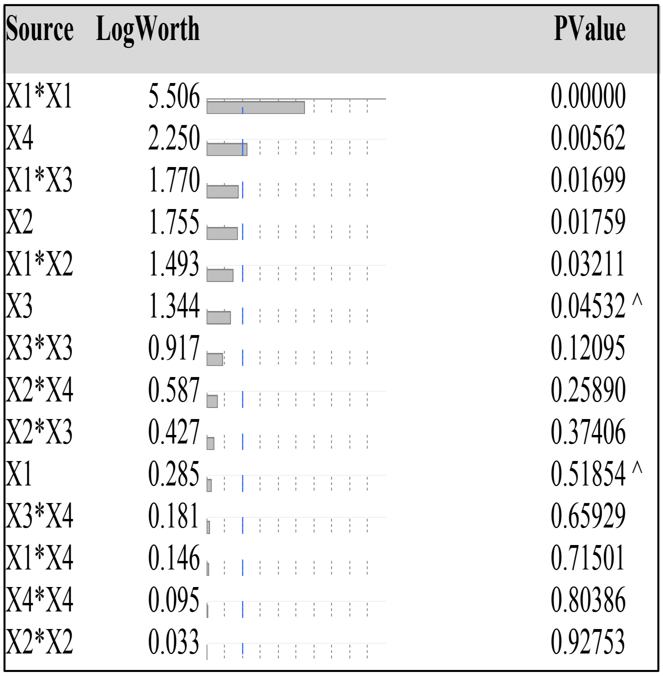
Table 4.4B shows the significant effect of each of the independent variables on the flavonoids content of WB during OD process. Treatment time and Brix% were found to significantly influence ($p<0.05$) the flavonoids content of WB, while the temperature and sample ratio to osmotic agent were not significant. Although the linear effect of temperature was observed to be insignificant on flavonoids content, the quadratic effect of temperature was found to significantly influence ($p<0.05$) the flavonoids content of WB during the OD process. Similar results as phenolic content were obtained for flavonoids content for temperature. For anthocyanin content, the significant effect of each of the independent variables on its variation in WB during the OD process was examined (Table 4.4C). All the linear terms were found to significantly influence ($p<0.05$) the anthocyanin content of WB except the process temperature. Although the linear effect of temperature was observed to be insignificant on anthocyanins content during, the quadratic term of temperature was found to significantly influence ($p<0.05$) the anthocyanin content of WB during the OD process. Other factors quadratic terms had no significant influence on the samples anthoocyanin content during the OD process.

4.4.2 Roles of process parameters on OD of WB

Further analysis to verify the order of significant effect of each independent variable and their interactions on the phenolic, flavonoid, and anthocyanin contents of WB are shown in Table 4.5. This technique using Log Worth and p-values helps to prioritize and focus resources visually. The output shows the significant influence of each variable on the response in decreasing hierarchy. As shown in Table 4.5A, the most significant parameter for phenolics content of the osmotic dehydrated WB was the quadratic effect of temperature.

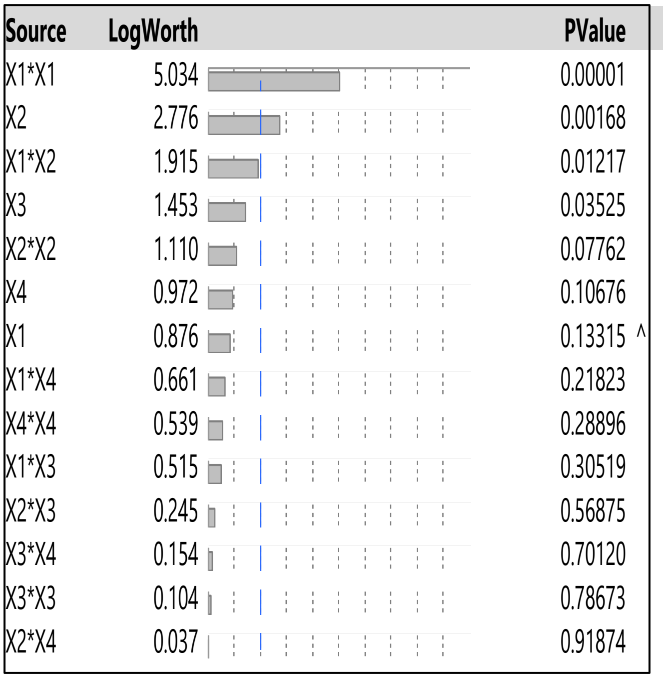
Table 4.5: Parametric effect summary estimates: (A) Phenolics content (B) Flavonoids content (C) Anthocyanin content where X1, X2, X3 and X4 are temperature, time, Brix and sample to Brix ratio respectively.

A



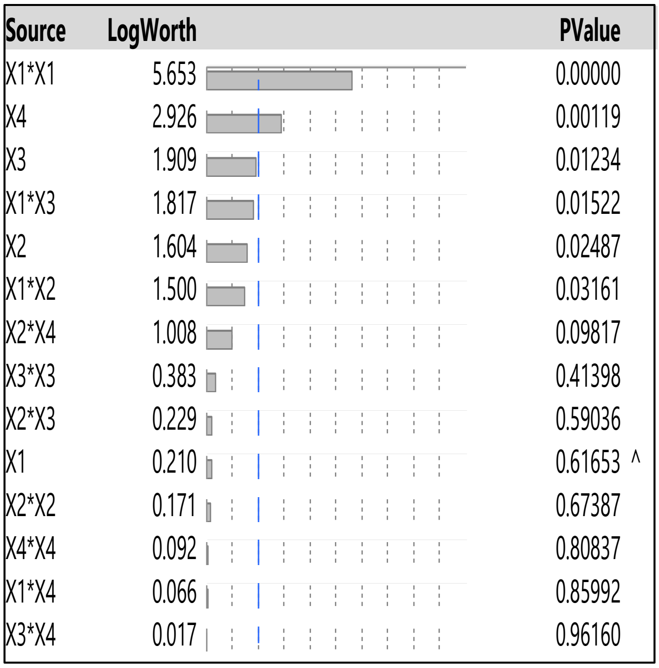
Source	LogWorth	PValue
X1*X1	5.506	0.00000
X4	2.250	0.00562
X1*X3	1.770	0.01699
X2	1.755	0.01759
X1*X2	1.493	0.03211
X3	1.344	0.04532 ^
X3*X3	0.917	0.12095
X2*X4	0.587	0.25890
X2*X3	0.427	0.37406
X1	0.285	0.51854 ^
X3*X4	0.181	0.65929
X1*X4	0.146	0.71501
X4*X4	0.095	0.80386
X2*X2	0.033	0.92753

B



Source	LogWorth	PValue
X1*X1	5.034	0.00001
X2	2.776	0.00168
X1*X2	1.915	0.01217
X3	1.453	0.03525
X2*X2	1.110	0.07762
X4	0.972	0.10676
X1	0.876	0.13315 ^
X1*X4	0.661	0.21823
X4*X4	0.539	0.28896
X1*X3	0.515	0.30519
X2*X3	0.245	0.56875
X3*X4	0.154	0.70120
X3*X3	0.104	0.78673
X2*X4	0.037	0.91874

C



Source	LogWorth	PValue
X1*X1	5.653	0.00000
X4	2.926	0.00119
X3	1.909	0.01234
X1*X3	1.817	0.01522
X2	1.604	0.02487
X1*X2	1.500	0.03161
X2*X4	1.008	0.09817
X3*X3	0.383	0.41398
X2*X3	0.229	0.59036
X1	0.210	0.61653 ^
X2*X2	0.171	0.67387
X4*X4	0.092	0.80837
X1*X4	0.066	0.85992
X3*X4	0.017	0.96160

The linear effect of sample ratio to osmotic agent was the second most important parameter followed by the interaction between process temperature and Brix% for the phenolics content of WB. Linear effect of OD time was the fourth most significant parameter and then the interaction between process temperature and OD time in that decreasing hierarchy for the remaining linear and quadratic terms (Table 4.5A). Different patterns of significant effects of the linear, interactions, and quadratic terms were observed for the other two dependent responses (flavonoids and anthocyanin contents) of the osmotic dehydrated WB (Tables 4.5B and C). The quadratic effect of temperature was also observed as most significant parameter for both flavonoids and anthocyanin contents of WB, but other parameters varied accordingly between both responses. As can be seen (Table 4.5B), the second most significant parameter for flavonoids content was the linear effect of the OD time followed by the interaction between temperature and OD time.

On the other hand, the second most significant parameter for anthocyanin content was the linear effect of sample ratio to osmotic agent concentration followed by the linear effect of Brix% (Table 4.5C). The flavonoids content of WB was also affected by the quadratic effect of OD time (5th position). This term was ranked as the least significant parameter for phenolics content (Table 4.5A) and 11th position for anthocyanin content of WB (Table 4.5C). The linear effects of OD time and Brix% on all independent variables were found to be highly significant. Similar findings were reported for the effect of ultrasound-assisted osmotic dehydration pretreatment on the convective drying of strawberry by Amami, et al. (2017). The authors reported that only the quadratic term of ultrasonic osmotic dehydration time and temperature has significant effect on water loss and weight reduction. They also reported that temperature had significant negative effect on water loss and weight reduction in quadratic term.

We demonstrated showed only the quadratic term of temperature had significant effect on phenolics, flavonoids, and anthocyanin content of WB at 5% level. The temperature also had significant negative effect on all the dependent variables in quadratic term. The result indicated that temperature could act as a limiting factor due to disruption of cell membranes which could lead to loss of selectivity of osmotic agent with an increase of the permeability of the cell wall for solute uptake (He, et al., 2016). The interaction between OD time and Brix% was the least significant parameter for flavonoid content, while the interaction between Brix% and sample ratio to Brix % was the least significant for anthocyanin content of WB. These results reveal that the OD processing parameters could be used to improve a specific antioxidant content of WB during processing. This approach could be employed industrially during OD of WB.

4.4.3 Optima model fitness

The accuracy of the linear fit of the experimental data for the phenolic, flavonoid, and anthocyanin contents was shown by their model estimation parameters (Fig. 4.3). The model parameters such as coefficient of determination (R^2), root mean square error (RMSE), and p-value were used to justify the model reliability. The predictability of the regression models was adequate, statistically significant ($p\text{-value}<0.0001$) with satisfactory coefficients of determination ($R^2 > 90\%$). These parameters are good indicators that the models can adequately predict response variable behavior. ANOVA for phenolics content, flavonoids content, and anthocyanin content showed that the second-order polynomial model (Eqs. 4(1-3)) was adequate to represent the actual relationship between the dependent and independent variables, with a high value of coefficient of determination (R^2

= 0.91 for phenolics content (Fig. 4.3A), R^2 = 0.90 for flavonoids content (Fig. 4.3B), and R^2 = 0.91 for anthocyanin content (Fig. 4.3C).

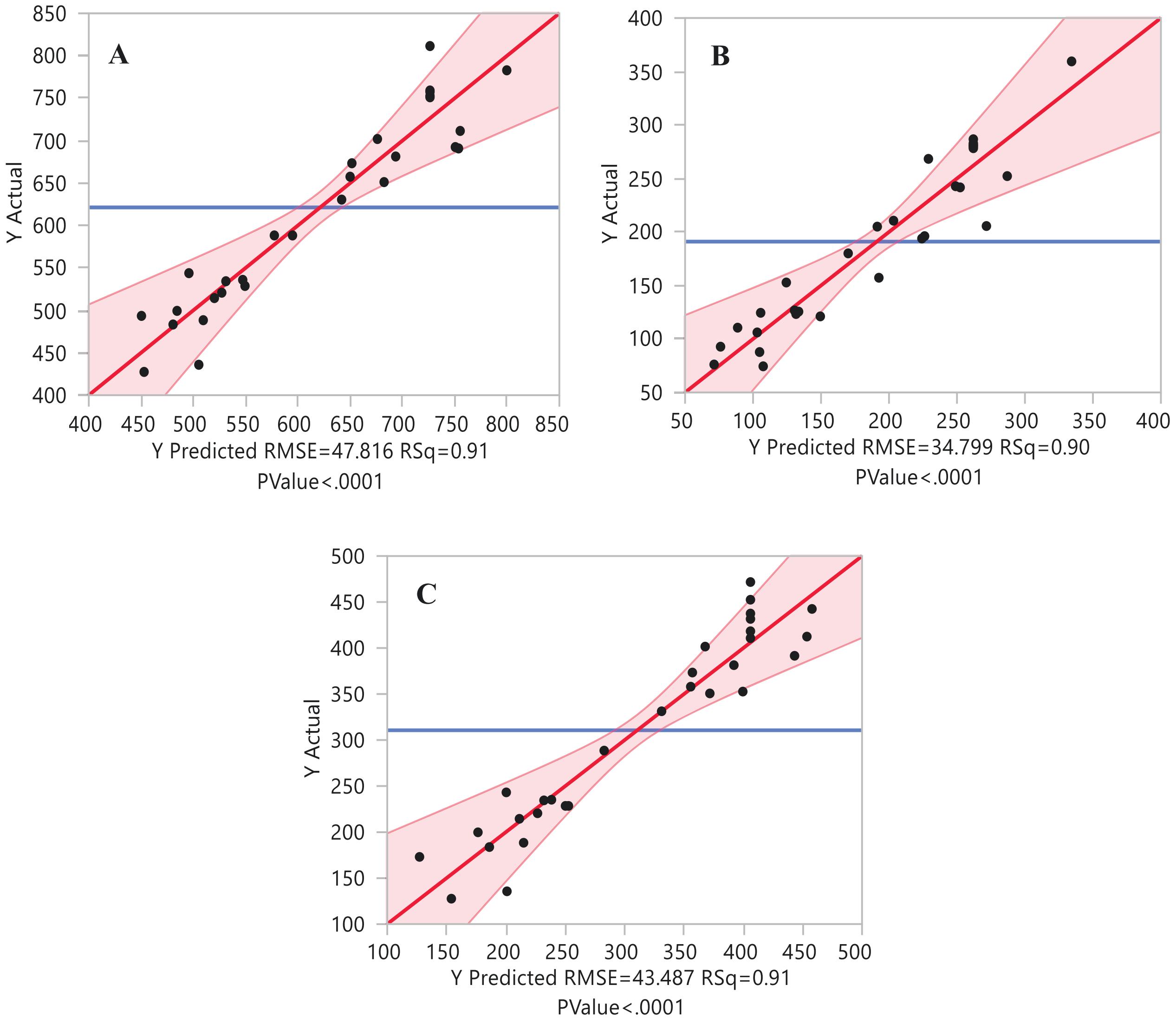


Fig. 4.3: Actual antioxidants concentration versus model predicted antioxidants in the dehydrated WB: (A) Phenolics content (B) Flavonoids (C) Anthocyanin content.

The response surface was generated as a function of two independent parameters against the dependent variable as the third dimension. For each of the dependent variables, six combinations of response surface curves were generated from the four independent factors (Figs. 4.4, 4.5 and 4.6). The 3D-surface curves were plotted to visualize both the main and the interactive effects of two factors at a time. These figures provide useful information about the behavior of the system within the experimental design. The response surface plots for phenolics content of osmotically dehydrated WB are shown in Fig 4.4(A-F), for significant factor interaction resulted from the ANOVA (Table 4.4A). The interaction between temperature and OD time showed a maximum effect on the phenolics content of dehydrated WB (Fig. 4.4(A). These two factors showed significant influence on the phenolics content of WB maximization which might due to the mass transfer of water enhanced by combine effect of temperature and OD time. A similar pattern was observed in interaction between temperature and Brix%, and temperature and sample ratio to Brix% on the phenolics content of WB as shown in Figs. 4.4(B and C). A possible decrease in the viscosity of the osmotic solution and reduction in the external resistance to mass transfer at WB surface might yield better water transfer responsible for this observation (Ahmed, et al., 2016; Amami, et al., 2017). The interaction between OD time and Brix% showed a minimum impact on the phenolics content of the dehydrated WB (Fig. 4.4D), while the interaction between OD time and sample ratio to Brix% showed increased phenolics content (Fig. 4.4E). A minimum impact on phenolics content of WB was also observed based on the interaction between Brix% and sample ratio to Brix%, while the highest peak of their interaction tends toward the sample ratio to Brix% variable (Fig. 4.4F). The response surface plots for flavonoids content of osmotic dehydration WB are shown in Fig 4.5 (A-B). The interaction between temperature and OD time, temperature and Brix% , and temperature and sample ratio to Brix% showed a maximum effect on the flavonoids content of dehydrated WB (Fig. 4.5(A, B, and C).

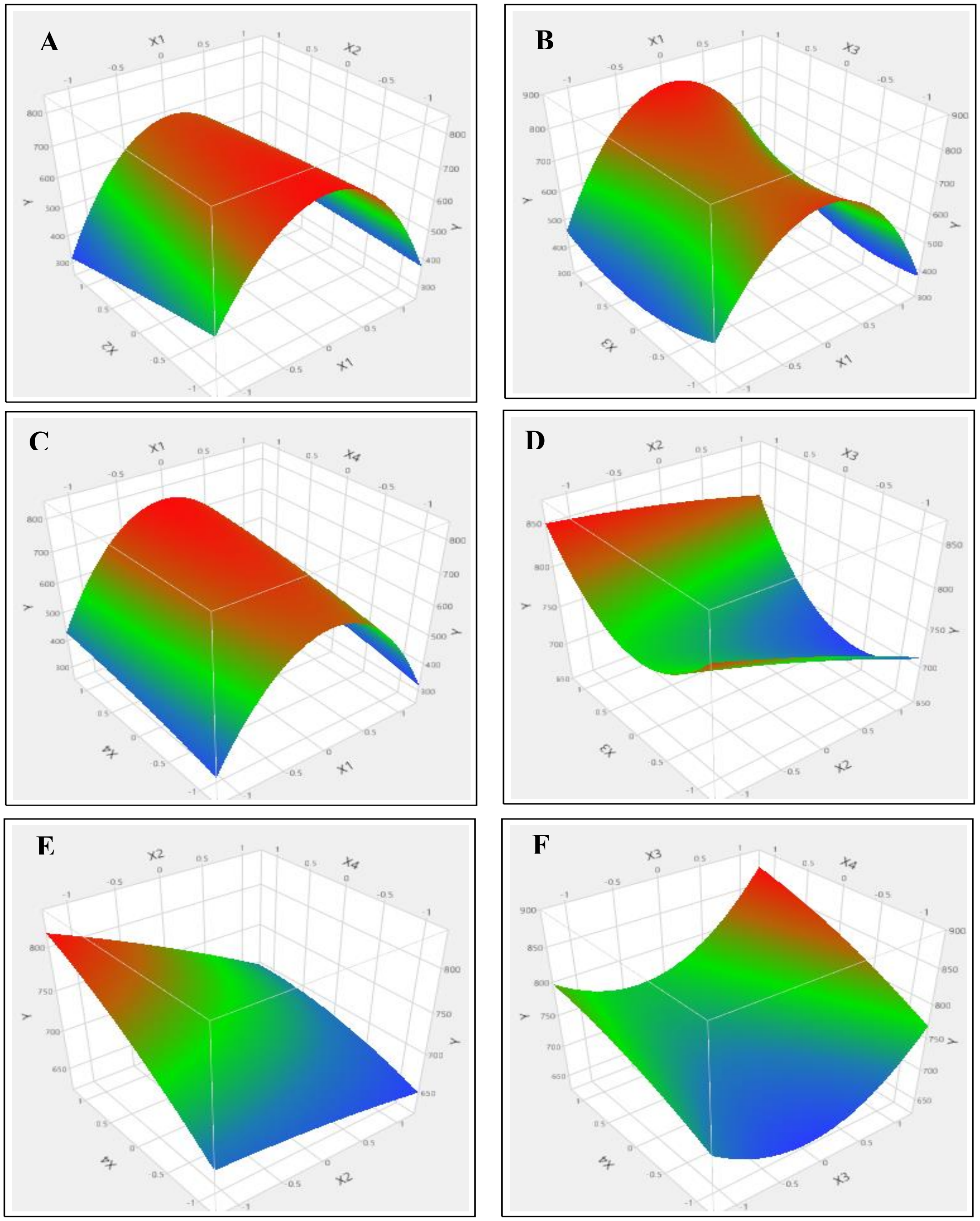


Fig. 4.4: Influence of process variables on phenolics content (A) Process temperature and OD time (B) Process temperature and Brix% (C) Process temperature and Sample ratio to Brix% (D) OD time and Brix% (E) OD time and Sample ratio to Brix% (F) Brix% and Sample ratio to Brix%.

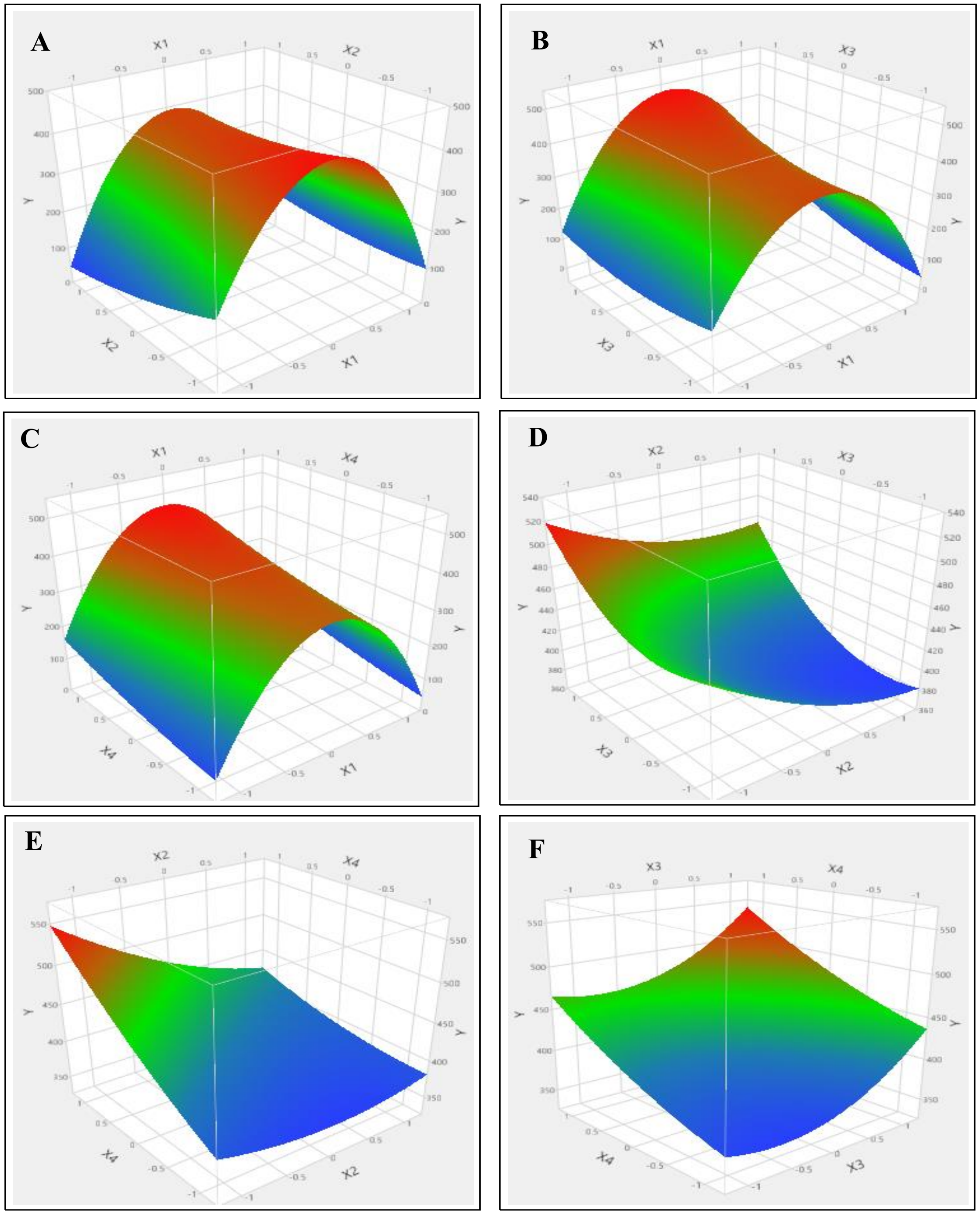


Fig. 4.5: Influence of process variables on flavonoid content (A) Process temperature and OD time (B) Process temperature and Brix% (C) Process temperature and Sample ratio Brix% (D) OD time and Brix% (E) OD time and Sample ratio to Brix% (F) Brix% and Sample ratio to Brix%.

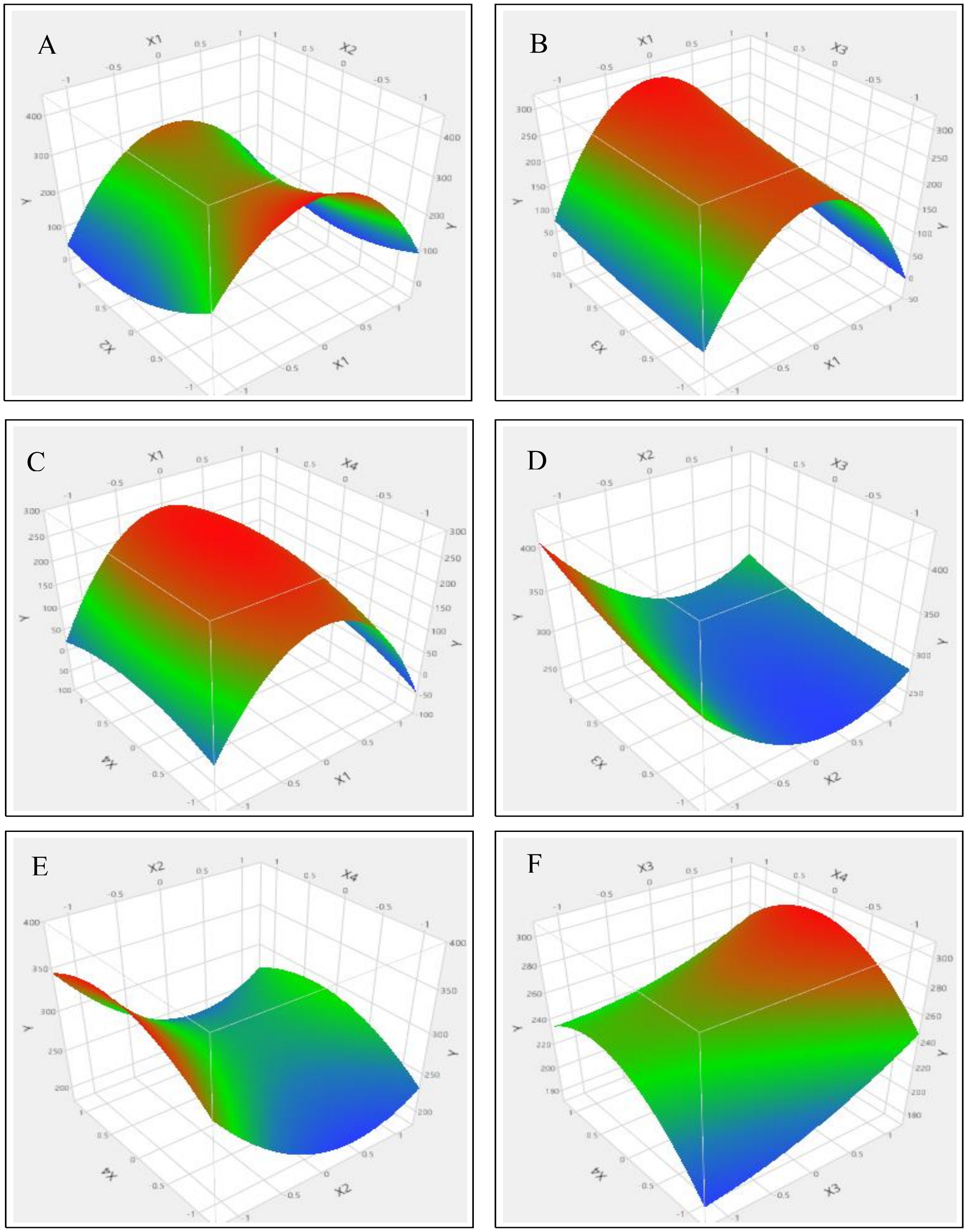


Fig.4.6: Influence of process variables on anthocyanin content (A) Process temperature and OD time (B) Process temperature and Brix% (C) Process temperature and Sample ratio to Brix% (D) OD time and Brix% (E) OD time and Sample ratio to Brix% (F) Brix% and Sample ratio to Brix%.

The synergy effect of the two factors showed significant influence on the flavonoids content of WB maximization which might due to the mass transfer of water enhanced by the combined effects of the factors. The interaction between OD time and Brix% showed a minimum impact on the flavonoids content of the dehydrated WB (Fig. 4.5D), while the interaction between OD time and sample ratio to Brix% showed increased flavonoids content (Fig. 4.5E). A minimum impact on flavonoids content of WB was also observed based on the interaction between Brix% and sample ratio to Brix% while the highest peak of their interaction tends toward the sample ratio to Brix% variable (Fig. 4.5F). Similar results were observed for anthocyanin content of WB (Fig 4.6 (A-F)). The only exception was the interaction between Brix% and sample ratio to Brix% which showed a maximum effect on the flavonoids content of WB.

4.4.4 Optimization and model validation

The desirability function method described in the materials and methods section was employed to analyze the process parameters concerning the dependent variables (phenolics content, flavonoids content, and anthocyanin content) optimization. The desired levels for each of the operational conditions (temperature, OD time, Brix% and sample ratio to Brix%) was selected within the range defined by (Kucner, et al., 2013), while the dependent variables were defined as maximum. Each of the dependent variables was analyzed separately. Fresh WB was the control sample with the initial phenolic, flavonoid, and anthocyanin content estimated as 1394.7, 445.1 and 640.4 (mg/100g of d.m), respectively. The optimum value of phenolics content of the dehydrated WB was 742.61 mg/100g d.m of WB at a process temperature of 40°C (Fig. 4.5A), OD time of 5 h, Brix of 65% (w/w), and sample ratio to Brix% of 1:5. The increase in temperature from 40 to 50°C showed a drastic decline in the phenolics content of WB. This is likely due to increasing of the permeability of the cell wall which might lead to migration of antioxidant to the osmotic solution and possibility of solute uptake (De Mendonça, et al., 2016). The prediction proved reliable as judged by the desirability of the predicted values of 0.75. Robustness of model is judge based on how close the desirability value is to 1.0, the closer the better the predictability of the model.

A gradual decrease in phenolics content of WB was observed with increase in OD time. For flavonoids content, the optimum value of the dehydrated WB was 263.12 mg/100g d.m of WB at a process temperature of 40°C (Fig. 4.7B), OD time of 5 h, Brix of 65% (w/w), and sample ratio to Brix% of 1:5. The independent variables showed similar effects as compared to phenolics content of WB with desirability value of 0.60. A similar trend of optimum processing parameters was observed for anthocyanin content of the dehydrated WB. The optimum value of the anthocyanin content of the dehydrated WB was 428.11 mg/100g d.m of WB at a process temperature of 40°C (Fig. 4.7C), OD time of 5 h, Brix of 65% (w/w), and sample ratio to Brix% of 1:5. The desirability of the predicted values was estimated as 0.81. Thus, the combination of coded values of X1, X2, X3, and X4 at 0, 0, 0, and 0.5, respectively produced the best antioxidants result and therefore presents the optimum condition except for the possible effect of interactions between the factors. The regression model was validated by performing the experiments at the optimum predicted conditions. The confirmatory experiments were performed in triplicate and the results were compared with the predicted dependent variables. The resulting phenolics content of trial 1 to trial 3 were 725.8, 751.5, and 745.35 mg /100g d.m, respectively.

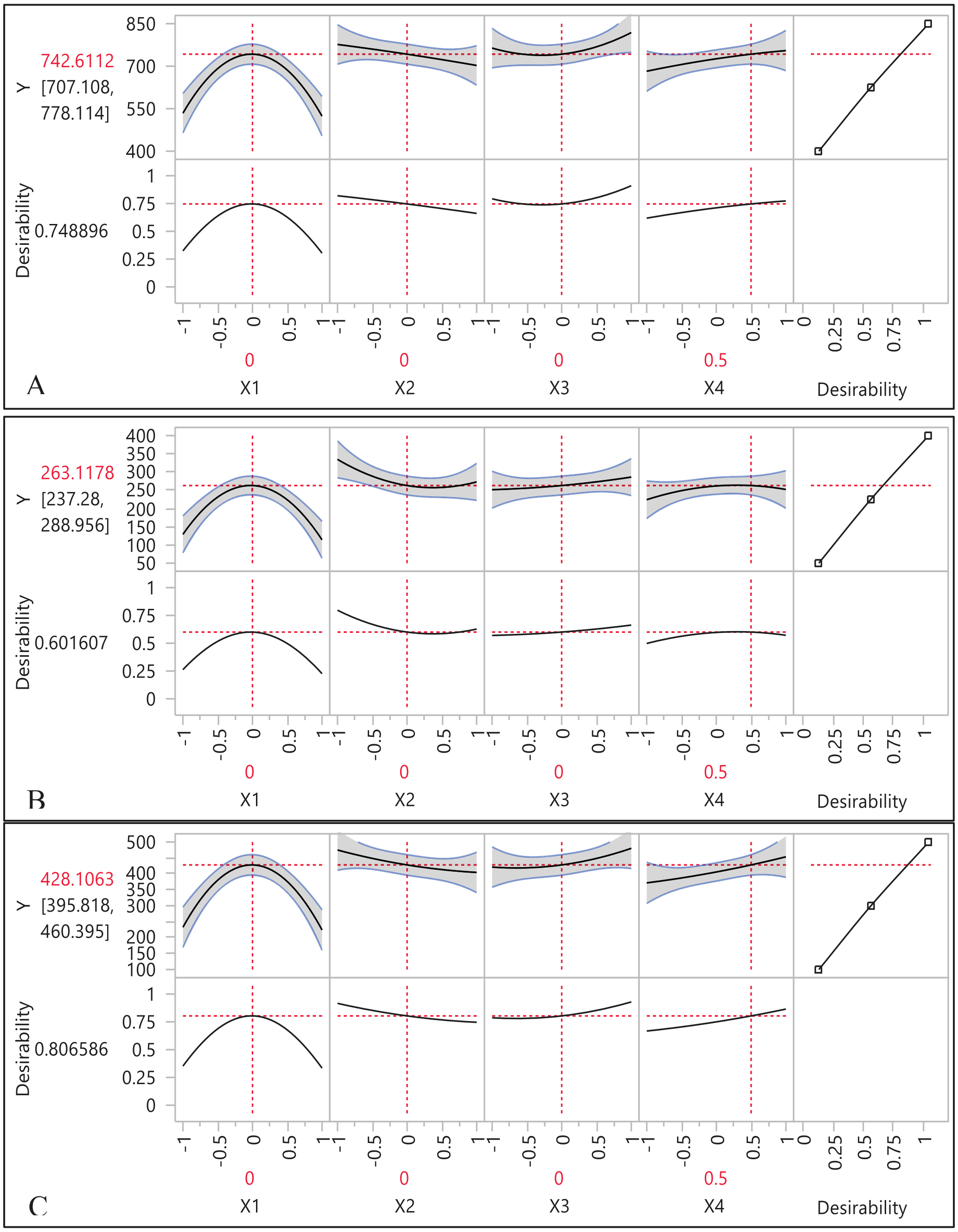


Fig. 4.7: Desirability plots of variables for maximum phenolics content, flavonoids content, and anthocyanin content for dehydrated WB.

The average of phenolics content of the confirmatory tests was in the range of the predicted value, 742.61 mg/100g d.m WB. Confirmatory tests were conducted for flavonoid content of the dehydrated WB. The resulting flavonoids content of trial1, trial2, and trial3 were

270.25, 267.55, and 258.54-mg/100g d.m, respectively. The same approach was used for anthocyanin content for trial1, trial2, and trial3 determined as 420.60, 431.23, and 425.80 mg/100g d.m, respectively. The results from the confirmatory experiments agreed with the predicted values of phenolic, flavonoid, and anthocyanin contents. Based in these results the optimum condition of OD were 40°C, 65 Brix, 1:5 sample to Brix ratio and 5h. Theses conditions were used before optimization of the oven drying procedure.

4.5 Drying time of optimum condition compared to hot air-drying

Drying is one of the most energy-intensive unit operations in the process industries. In a drying process, a significant amount of energy is needed to remove water. Any method for WB drying, that maintains its quality and decreases the drying time by reducing the moisture content (MC) faster is of considerable interest.

Fig. 4.8 shows MC versus drying time for the oven drying (control) and pretreatment sample by MW for the 30s and optimum OD condition (40°C, 65 Brix, 1:5 sample to Brix ratio and 5h followed by hot air convective drying (HACD). All the samples were dried to the final MC of 18g/100g of w.b). Using MW as a pretreatment followed by OD (at optimum condition) then HACD as a final step of drying process results in a significant reduction in drying time compared with the control (only oven) by 5h as that presented in Fig. 4.8. Similar results have been reported by Zielinska & Markowski, (2016) when they applied the MW to their process of drying BB. Our results indicate that the use of microwave and OD shorten the energy intensive oven drying process time of WB in comparison with deploying the hot air convective drying only.

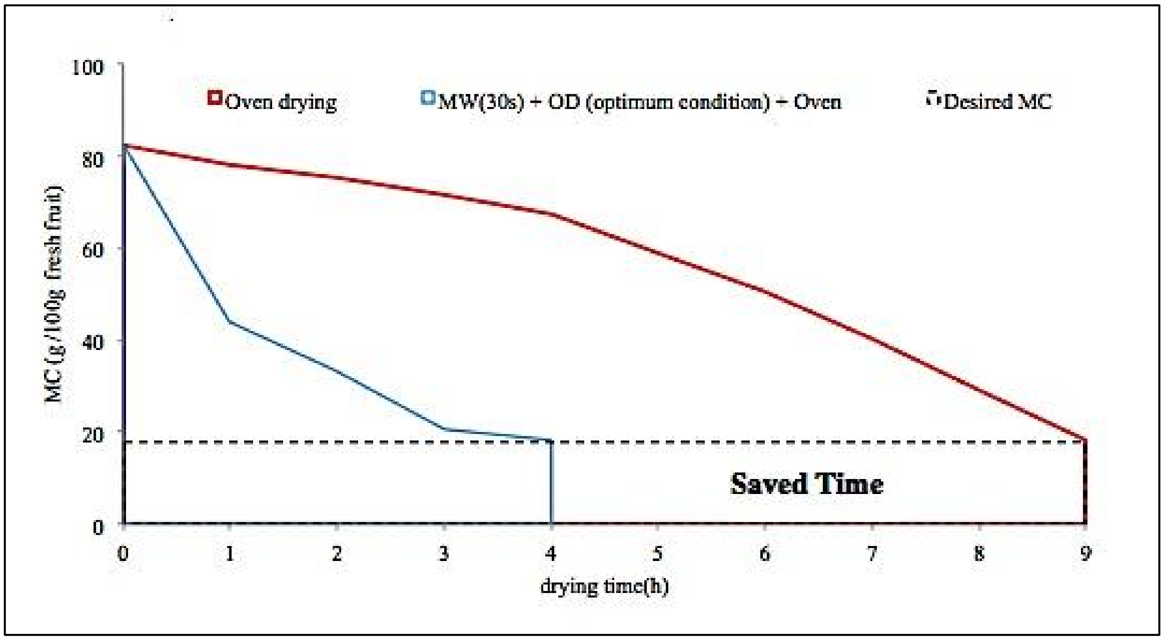


Fig. 4.8: Drying time of Microwave pretreatment (30s) and OD (40°C, 65 Brix, 1:5, 5h) followed by air-drying at 70°C of WB comparison with air-drying at 70°C without treatments.

This result is due to the advantage of the MW drying arising from the volumetric heating and internal generation. Heating from the interior of a fruit product leads to the buildup of an internal vapor pressure that drives the water out of the product (Feng et al., 2012). That is the evident that MW pretreatment (30s) period OD followed by HACD results in a significant reduction in drying time and maintaining a high antioxidants content of WB. WB final product dried by microwave foe 30s followed by OD (Optimum condition) then oven has been kept in a cold and dry place more than six months without getting spoiled.

4.6 Shrinkage ratio (SR) of dried WB

The high-quality products in the market require dehydrated fruits or vegetables that maintain a high level of nutritional and organoleptic properties of the initial fresh product. (Mayor, L., & Sereno, A. M. 2004). Shrinkage is the most important physical change to measure due to the negative consequence in the quality of the dehydrated product such as dehydration. Increasing product hardness causes a negative impression in the consumer.

The shrinkage of dried WB by hot air convective drying (HACD) and pretreatment microwave (30s) followed by OD optimum condition (40°C, 65 Brix, 1:5, 5h) then hot air convective drying (MWODHACD) is shown in Fig 4.9. There was a significant difference ($p<0.05$) in the shrinkage ratio between the two drying methods. MWODHACD of WB showed the lowest shrinkage ratio (31.84%) compared with HACD shrinkage ratio (44.62%). Similar result was reported by Wang et al., (2014), using HACD method only for drying mushrooms, caused significant shrinkage and reduced the water retention ability during the dehydration process due to collapsed capillaries. Drying WB with (MWODHACD) results in lower shrinkage indices than (HACD) by oven. In other word, drying by MWODHACD give less hardness to the final product compared with HACD of WB.

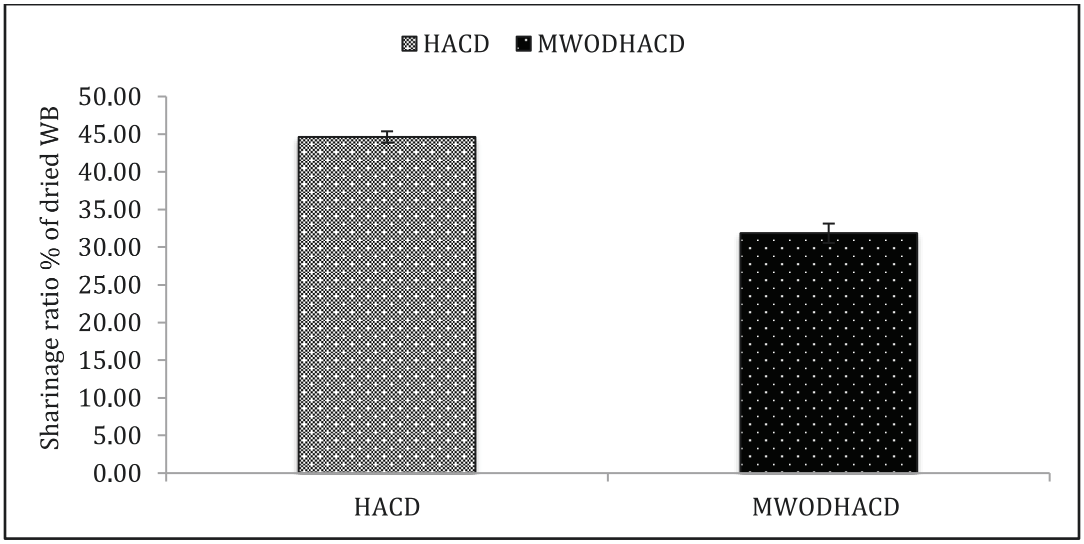


Fig. 4.9: Effects of different drying methods (MWODHACD) and (HACD) on shrinkage ratio of WB.

4.7 Rehydration ratio (RR) of dried WB

The rehydration capacity of dried products is an important parameter for many food product included breakfast cereals. This is a measure of the ability of dried product to take up moisture when required. This gives the food good texture when consumed. Dried WB by hot air convective drying HACD only and MW (30s) then OD (40°C, 65 Brix, 1:5, 5h) followed by hot air convective drying HACD were rehydrated at room temperature (CR) and at 50°C (HR) are shown in Fig. 4.8. The rehydration ratio in CR and HR conditions are necessary to predict the behavior of WB when rehydrated for a particular application where they will be soaked in water or milk. Dehydration at room temperature is especially important for the dried WB that will be used in cereals. The rehydration of dried WB was plotted based on laboratory measurements of changes in WB mass with soaking time. In comparison with HACD and MWOD followed by HACD at 70°C led to higher rehydration ratio of WB with increasing the soaking time. When the dried WB is placed in water to rehydrate, the cell walls absorb water due to the natural elasticity of the cellular structure. Then the cells returned to their original shape by drawing water into inner cavities. However, hot air convective drying (HACD) only usually destroys the cell structure (Sagar & Suresh Kumar, 2010).

The rehydration ratio of dried WB by MWODHACD at room temperature (22°C) and 50°C had the highest rehydration ratio compared with dried WB without any treatments as that shown in (Fig. 4.10). A similar result has been reported by Dehghannya Dehghannya et al.,(2018) using osmotic dehydration as pretreatment followed by microwave then hot

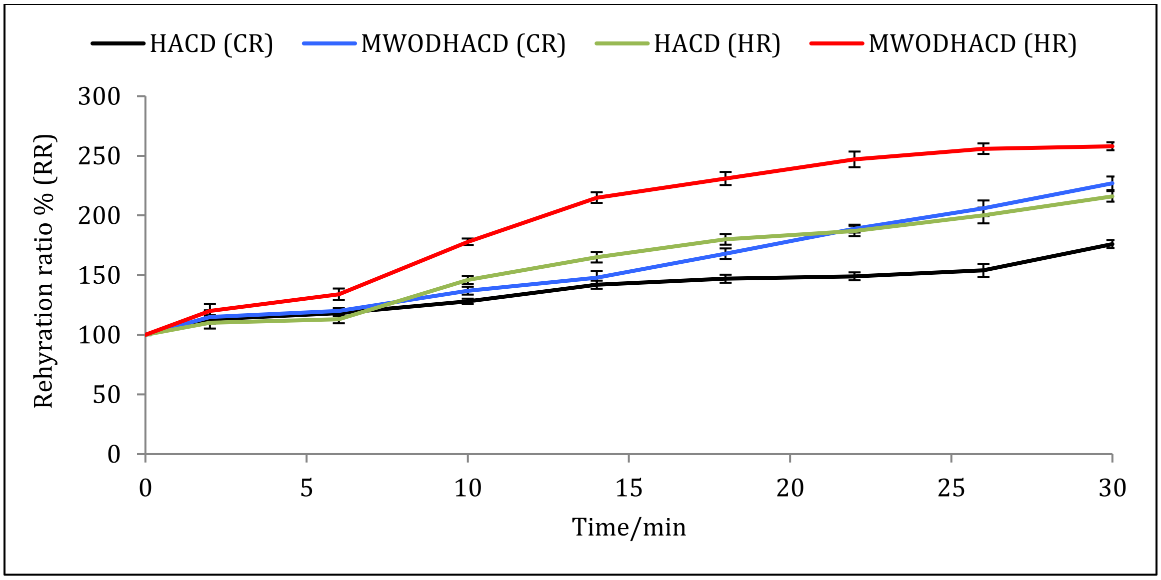


Fig. 4.10: Comparison of rehydration ratio in cold rehydration (CR), Hot rehydration (HR) at 50°C of WB dried by HACD and MWODHACD.

air convective drying to dry quince fruit characterized by the highest rehydration ratio compared with hot air convective drying (HACD) only. Statistically significant differences ($p<0.05$) in the rehydration-dried samples were started after 6 min of soaking in CR and HR. In the cause of MWODHACD the amount of solid uptake during the OD stage decreased the rehydration process, whereas, in the HACD could be to the cell damaged that caused the hardness. In general, the rehydration ratio of dried WB increased with increasing the rehydration time and shown better behaviour when it used to rehydrate with HR. A high rate of reconstitution could be beneficial for dried WB added to breakfast cereals that are consumed with milk. We show that dry WB intended for breakfast cereals should be dried by MWODHACD.

4.8 Mathematical modeling of dehydrated and drying WB

Mathematical modeling of the drying processes is considered an essential step in the scale up of drying technology (Horuz et al., 2018). Mathematical models are used for designing new or improving existing drying systems and control of the process. The WB osmotic dehydration optimum condition determined a process temperature of 40°C, concentration of 65% °Brix, samples to solution ratio of 1:5 and time of 5h. In samples treated with optimum condition of the moisture loss (ML) (for OD and HACD) and solid gain (SG) (for OD) were analyzed as a function of time (Fig 4.11). These data were used for mathematical modeling to obtain a better insight and understanding of the process.

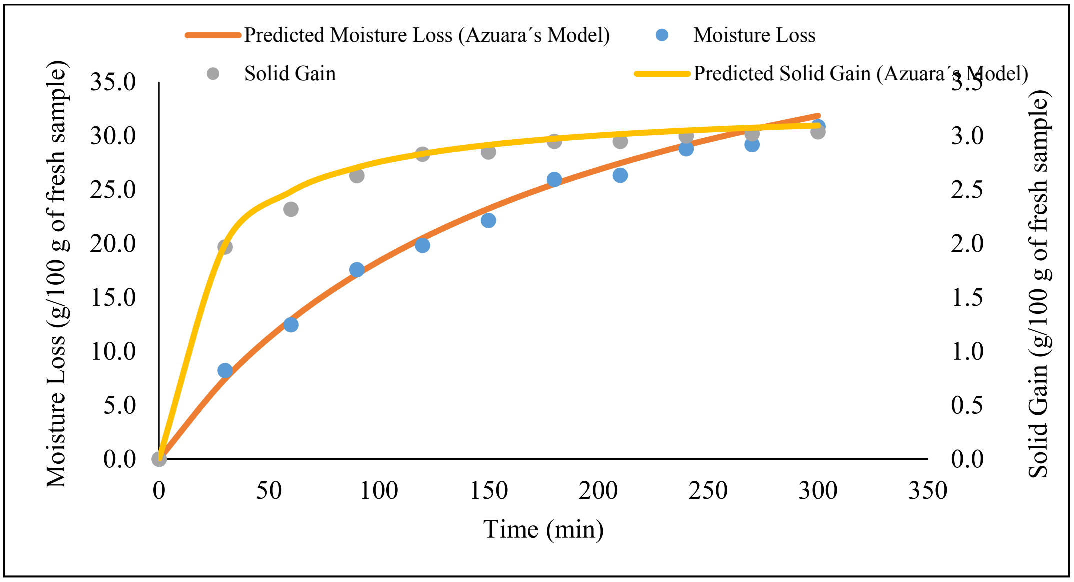


Fig. 4.11. Azuara's model prediction of moisture loss (ML) and solid gain (SG) of wild blueberry (WB) osmotic dehydration (OD).

4.8.1 Mathematical modeling of OD

The equilibrium state of moisture loss (ML) and solid gain (SG) prediction were made by fitting the date from Azuara's model (Equation 3.10 + 3.11) to the experimental data are given in Table 4.6. Nonlinear regression was applied in order to determine the parameter of the model. The low error (RME lower than 5%) and high determination coefficient (R^2 higher than 0.95) indicate that Azuara's model was appropriate to predict ML and SG at the equilibrium condition. The value of ML_e was 39.02g/100 g of fresh sample and the experimental value of ML after 5h of dehydration by using OD was

30.86g/100 g of fresh sample. In our study, equilibrium moisture loss $\mathrm{ML_e}$ was not reached in whole WB under the optimum condition. The experimental value of SG after 5h was 3.04g/100g of fresh sample, while the value of $\mathrm{SG_e}$ was 3.31g/100g of fresh sample. The Azuara's parameter a (min^{-1}) shows that the sugar impregnation happened faster than the moisture loss, as can be observed in Fig 4.11. This figure shows that the rate of water loss and solid gain (slope of the plots) increased with time. This could be due the effect of sucrose (osmotic agent) concentration, serving as the driving force of the solution. Similar result were reported by Zielinska, M., & Markowski, M. (2018), who found that, using MW as pretreatment before OD had the most significant and greatest effect on mass transfer (ML and SG) of cranberries.

Table 4.6: Moisture loss (ML) and Solid gain (SG) at equilibrium state of wild blueberries osmotic dehydration (OD) estimated by Azuara's model

	ML	**SG**
a (min^{-1})	0.009	0.051
Eq (g/100g of fresh sample)	39.02	3.31
MWOD (g/100g of fresh sample)	30.86	3.04
R^2	0.9572	0.9573
RMSE (g/100g)	0.81	0.067
RME (%)	3.547	1.946

*$ML_t = \frac{at\ (ML_e)}{1+at}$; $SG_t = \frac{at\ (SG_e)}{1+at}$; a (min^{-1}) = Azuara's model parameter; Eq = equilibrium condition; MW OD = Optimal condition of wild blueberry osmotic dehydration after 5 hours; RMSE $= \sqrt{\frac{\sum_{i=1}^{N}\left(x^i_{exp} - x^i_{pre}\right)^2}{N}}$; RME (%) = 100 $\frac{\sum_{i=1}^{N} \cdot \frac{x^i_{exp}-x^i_{pre}}{x^i_{exp}}}{N}$.

Diffusion coefficient (D_{eff}) is one of the significant factors in drying processing. This parameter describes all possible mechanisms of moisture and solid movements in fruits or vegetables. Diffusion coefficient (*D_{eff}*) is describing by Fick's second law. In this study, Fick's law was successfully used (low error and high determinations coefficient) to predict the apparent diffusivity of moisture (D_{em}) and solids (D_{es}) during WB OD (Table 4.7). The higher moisture diffusivity (D_{em}) 0.86 × 10^{10} for water than solids 0.69 × 10^{10} indicates a higher moisture loss than solid gain, as it was showed by the equilibrium conditions. In addition, the moisture and solid ratios for WB OD showed that the solid gain in the optimal treatment was closer to the equilibrium condition than moisture loss (Fig 4.12).

Table 4.7: Moisture loss (ML) and Solid gain (SG) diffusivity of osmotic dehydration (OD) of wild blueberries (WB) determined by Fick's second low.

	Moisture diffusivity	**Solid diffusivity**
D_{ff} × 10^{10} [m^2 s^{-1}]	0.86	0.69
R^2	0.95	0.93
RMSE (m^2 s^{-1})	0.02	0.02
RME (%)	5.48	6.52

*MR= $\frac{M_t - M_e}{M_0 - M_e} = \frac{6}{\pi^2} \sum_{i=0}^{\infty} \exp\left(-i^2 \pi^2 D_{em} \frac{t}{r^2}\right)$; SR= $\frac{S_t - S_e}{S_0 - S_e} = \frac{6}{\pi^2} \sum_{i=0}^{\infty} \exp\left(-i^2 \pi^2 D_{es} \frac{t}{r^2}\right)$ D_{ff} = apparent diffusivity; RMSE $= \sqrt{\frac{\sum_{i=1}^{N} (x_{exp}^{i} - x_{pre}^{i})^2}{N}}$; RME (%) = $100 \frac{\sum_{i=1}^{N} . \frac{x_{exp}^{i} - x_{pre}^{i}}{x_{exp}^{i}}}{N}$.

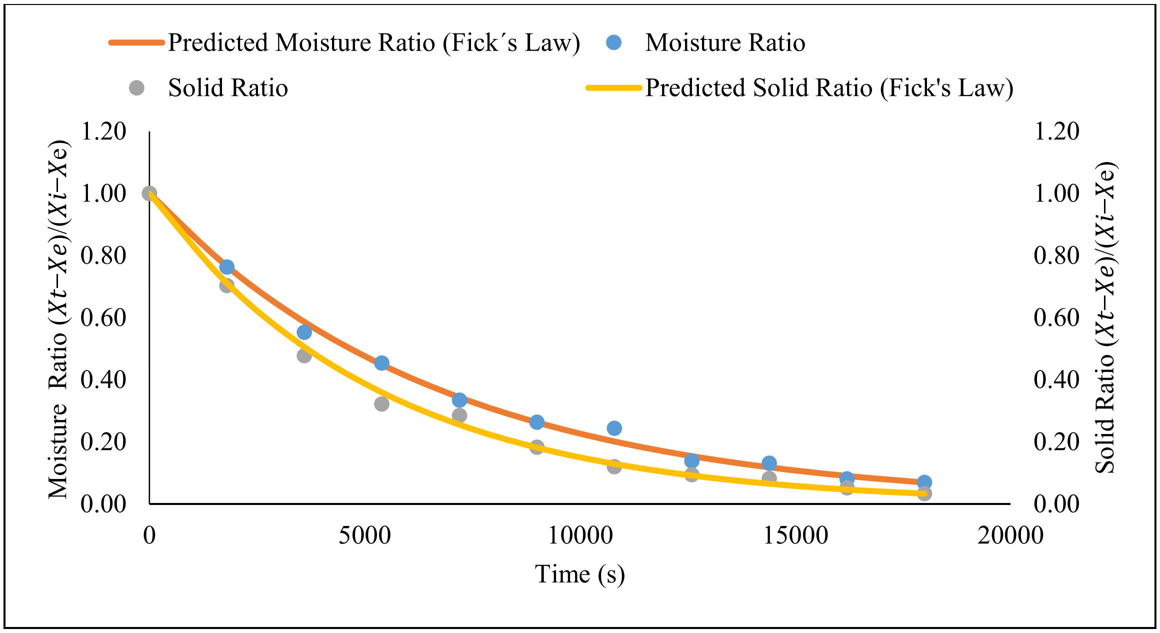


Fig. 4.12: Fick's law prediction of moisture ratio and solid mass transfer for osmotic dehydration (OD) of wild blueberry (WB).

The moisture and solid mass transfer during WB OD were evaluated using the equilibrium approach. The mass transfer coefficients (k) showed that the solid incorporation happened faster than the moisture loss (Table 4.8), in accord with the diffusion approach. The data also reflect that the moisture loss was higher than the solid gain (Fig. 4.13). Further studies have to be carried out in order to make use of these mass transfer data for scale up of the process.

Table 4.8: Moisture loss (ML) and Solid gain (SG) mass transfer coefficient (R^2) of OD wild blueberries (WB) osmotic dehydration (OD) by equilibrium approach.

	Moisture loss	**Solid gain**
k (s^{-1})	0.000167072	-0.000235583
R^2	0.97	0.96
RMSE (s^{-1})	0.00003757	0.00000332
RME (%)	3.63	6.902

* $-\frac{dM}{dt} = k_m(M - M_e)$; $\frac{dS}{dt} = k_s(S - S_e)$; k (s^{-1})= mass transfer coefficient; RMSE= $\sqrt{\frac{\sum_{i=1}^{N}\left(x_{exp}^{i} - x_{pred}^{i}\right)^{2}}{N}}$; RME (%) = 100 $\frac{\sum_{i=1}^{N}.\frac{x_{exp}^{i}-x_{pred}^{i}}{x_{exp}^{i}}}{N}$.

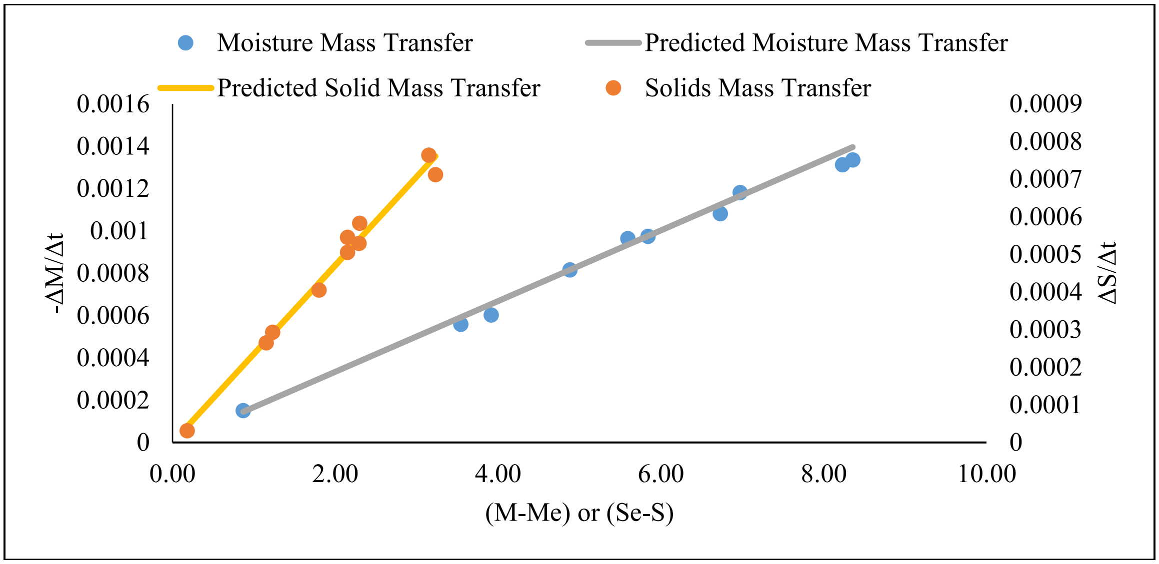


Fig. 4.13. Moisture and solid mass transfer in osmotic dehydration (OD) of wild blueberry (WB) by equilibrium approach.

4.8.2 Mathematical modeling of HACD

Wild blueberries (WB) that were osmotically dehydrated were subjected to hot air convective drying (HACD) at 70°C. Fick's second law solved by Crank's method and the engineering equilibrium approach were applied to the data. The modeling was performed considering the same conditions as for the OD, except that the moisture diffusion from WB was only mass transfer related. The experimental data of hot air convective drying (HACD) of WB after MWOD were measured until the desirable moisture content point (18g/100g of w.b) of the final product. The rate of dehydration as a function of time was determined.

The average behavior of the drying rate during drying by hot air convective drying (Oven) is presented in Fig 4.14. The drying of biological materials usually presents three distinct drying rate periods. The first phase, known as period zero or increasing drying rate, presents an increase in the drying rate. This happens because the drying material temperature is increasing from room temperature to the drying temperature. This is a very short period and difficult to detected in food. The second drying rate period, known as the constant rate period, presents a constant drying rate. This period is characterized by rapidly diffusion of water from the inside of the material to its surface, being able to maintain the moisture content at the surface almost constant. The third drying rate period, known as the decreasing rate period, presents decreasing drying rates. In this period the surface moisture content of the material decreases, because the moisture is remove from the surface faster than the moisture from inside diffuses to the surface. This change in moisture gradient between the material surface and the drying air causes the drying rate to decrease until reaching zero at the equilibrium condition, where there is no more significant mass transfer under the experimental conditions (Tadini et al., 2016). The absence of increasing and constant drying rate periods in this work can be attributed to the OD step performed before the HACD, that it was efficient to remove the moisture that can easily diffuse to the surface of the WB.

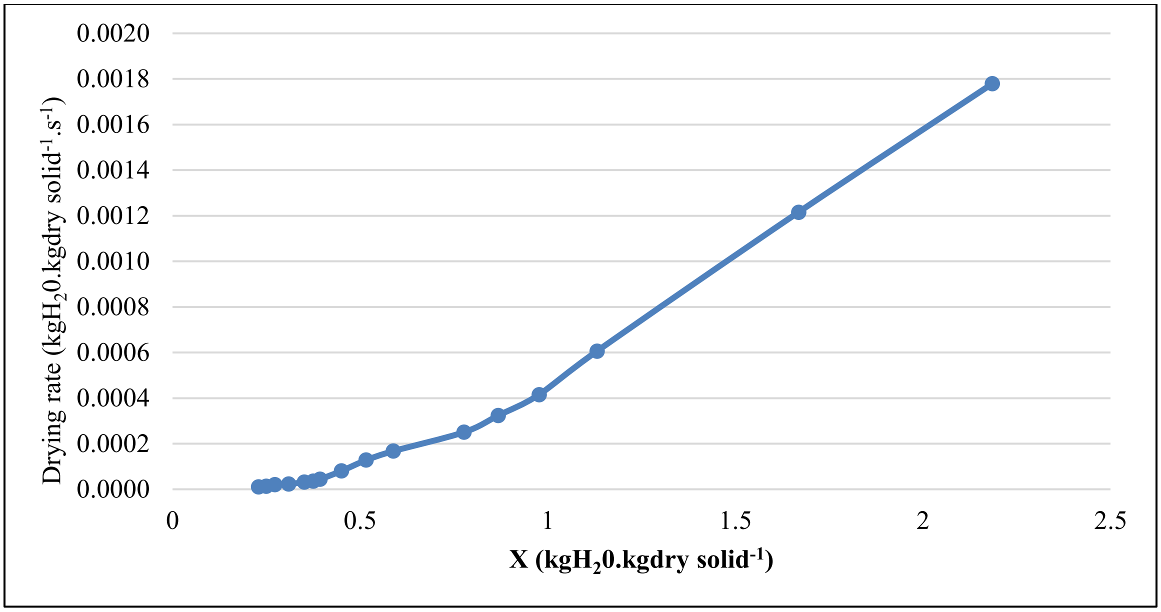


Fig. 4.14. Drying rate of Wild blueberries during hot air convective drying (HACD) after osmotic dehydration treatment.

The equilibrium state of moisture loss (ML) predicted and estimated by fitting the data from Azuara's model to the experimental data is given in Table 4.9. RME lower than 10% and high determination coefficient R^2 (higher than 0.99) indicate that Azuara's model was appropriate to predict ML at the equilibrium condition. The experimental value of ML was 67.04g/100g of fresh sample while the value of ML_e was 70.93g/100g of fresh sample. The Azuara's model has represented very well (99% of confidence) the data points as can be seen in the Fig 4.15.

Table 4.9: Moisture loss (ML) at equilibrium state of wild blueberries hot air convective drying (HACD) after osmotic dehydration OD estimated by Azuara's model**.**

	ML
a (min^{-1})	0.08242
Eq (g/100g of fresh sample)	70.93
WB HACD (g/100g of fresh sample)	67.04
R^2	0.99820
RMSE (g/100g)	2.99157
RME (%)	5.4944

*$ML_t = \frac{at\,(ML_e)}{1+at}$; a (min^{-1}) = Azuara's model parameter; Eq = equilibrium condition; WB = Hot air convective dried wild blueberries pretreated with microwave by 30s and osmotic dehydration optimal condition by 5h; RMSE = $\sqrt{\frac{\sum_{i=1}^{N}(x_{exp}^{i}-x_{pre}^{i})^{2}}{N}}$; RME (%) = 100 $\frac{\sum_{i=1}^{N}\cdot\frac{x_{exp}^{i}-x_{pre}^{i}}{x_{exp}^{i}}}{N}$.

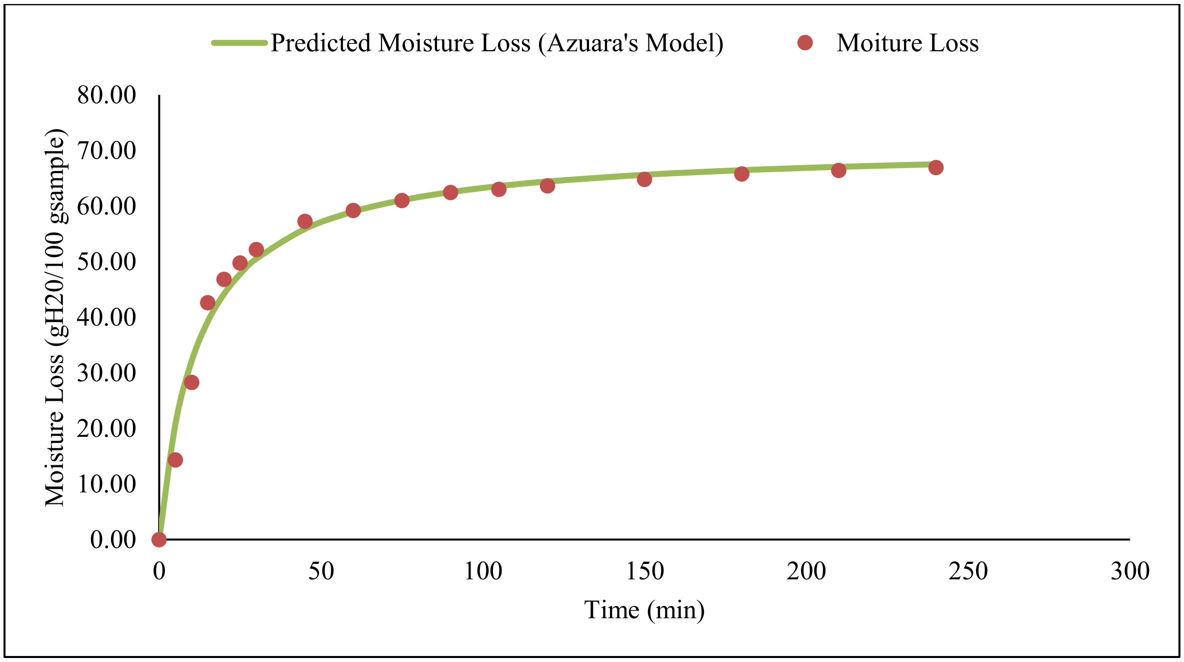


Fig. 4.15: Azuara's model prediction of moisture loss (ML) of wild blueberry (WB) hot air convective drying (HACD) after osmotic dehydration (OD).

Effective moisture diffusivity represents the overall transport property of moisture in WB during drying. In order to determine effective moisture diffusion (*D_{em}*) of WB, Eq. (3.12) was used. The experimental data was used to estimate the moisture effective diffusivity in WB during HACD after MWOD. Fick's law was successfully used (low error and high determinations coefficient) to predict the apparent diffusivity of moisture (D_{em}) during WB HACD (Table 4.10). Beigi. (2016) & Torki-Harchegani, et al. (2016) indicated that *D_{eff} values* of convective dried lemon and apple at 70°C were $8.11\times10^{-11,}$ and 1.08×10^{-9} m^2/s, respectively. The low moisture diffusivity in this study can be attributed to the presence of sucrose in the tissue and surface of WB that result in resistance against moisture removal. This result was in line with findings of (Dehghannya, et al., 2018). The moisture ratio shows that the HACD condition used was close to the equilibrium condition (Fig 4.16).

Table 4.10: Moisture loss (ML) diffusivity of hot air convective drying (HACD) after osmotic dehydration (OD) of wild blueberries (WB) determined by Fick's second law.

	Moisture D
$D_{ff} \times 10^{10}$ [m^2 s^{-1}]	0.13
R^2	0.9354
RMSE (m^2 s^{-1})	0.0475
RME (%)	7.8000

*MR= $\frac{M_t - M_e}{M_0 - M_e} = \frac{6}{\pi^2}\sum_{i=0}^{\infty} \exp\left(-i^2\,\pi^2 D_{em}\,\frac{t}{r^2}\right)$; D_{ff} = apparent diffusivity; RMSE = $\sqrt{\frac{\sum_{i=1}^{N}\left(x^i_{exp} - x^i_{pred}\right)^2}{N}}$; RME (%) = 100 $\frac{\sum_{i=1}^{N}\cdot\frac{x^i_{exp}-x^i_{pred}}{x^i_{exp}}}{N}$.

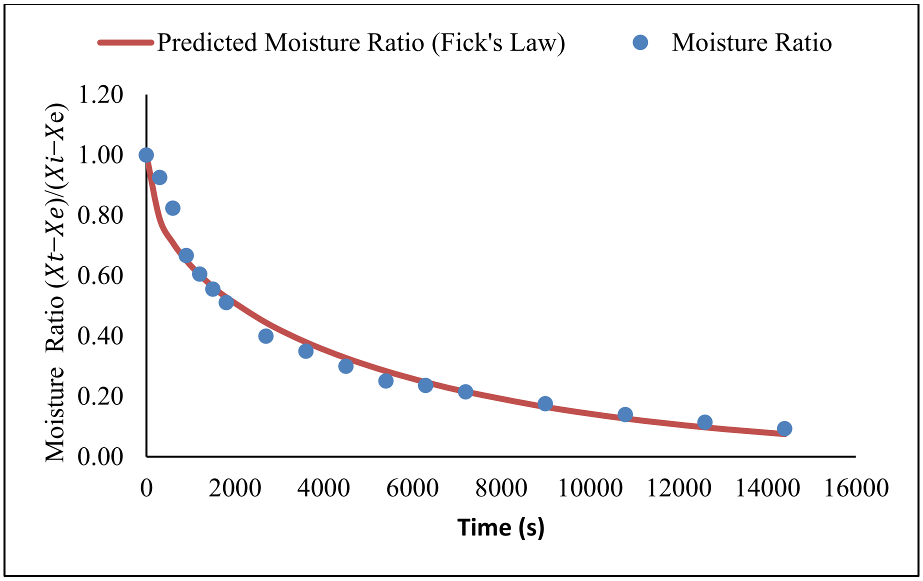


Fig. 4.16: Fick's law prediction of moisture and solid mass transfer for hot air convective drying after osmotic dehydration (OD) of wild blueberry (WB).

The diffusivity approach uses Fick's second law to model the data of mass transfer by detailed physical description and diffusion coefficient, while the equilibrium approach is an engineering approach based on the mass transfer coefficient (k). The mass transfer coefficient (k) presents in Table 4.11, while Fig 4.17 shows that the predicted mass transfer was close to the experimental mass transfer.

Table 4.11: Moisture loss (ML) mass transfer coefficient of hot air convective drying (HACD) of wild blueberries (WB) after osmotic dehydration (OD) by equilibrium approach

	Moisture
k (s^{-1})	0.00032
R2	0.92578
RMSE (s^{-1})	0.000446
RME (%)	0.039211

*$-\frac{dM}{dt} = k_m(M - M_e)$; k ($s^{-1}$)= mass transfer coefficient; RMSE= $\sqrt{\frac{\sum_{i=1}^{N}(x_{exp}^{i} - x_{pre}^{i})^2}{N}}$; RME (%) = $100\,\frac{\sum_{i=1}^{N}.\frac{x_{exp}^{i}-x_{pre}^{i}}{x_{exp}^{i}}}{N}$.

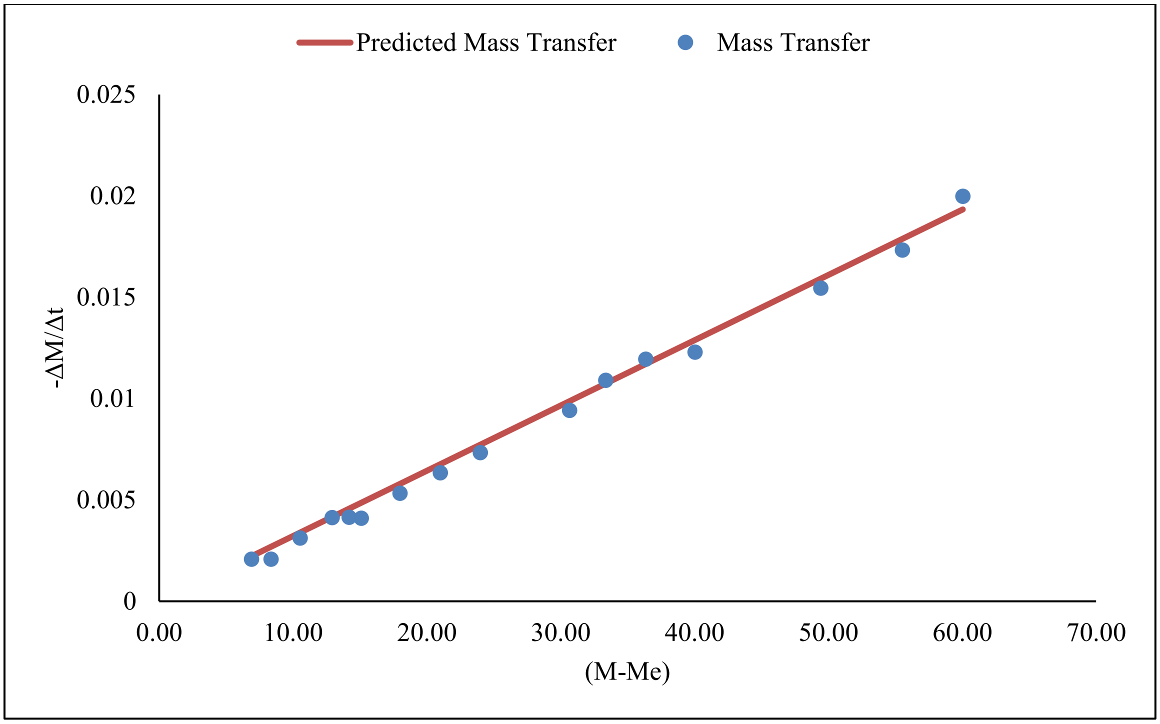


Fig. 4.17: Moisture mass transfer in hot air convective drying (HACD) of wild blueberry (WB) after osmotic dehydration (OD) by equilibrium approach.

Chapter 5

Conclusions and future work

5.1 Conclusions

The main conclusion that can be drawn from this study is that inclusion of the osmotic dehydration process in the drying of the wild blueberries results in much better retention of the antioxidants in the resultant product.

Initial studies without any pre-treatment resulted in very low moisture removal. Subsequently, a number of pre-treatment methods were attempted. This included immersion in boiling water, ultrasound water bath treatment, ultrasound probe treatment and microwave treatment. The amount of moisture removed and antioxidant retained were used as the basis for the selection of best pre-treatment method for all subsequent studies. Microwave pre-treatment for 30s followed by osmotic treatment at 40°C, with 65 Brix, 1:4 sample to osmotic solution over 5h was found to be the best method and resulted in moisture removal and antioxidant levels to 30% moisture loss and total phenolics levels of 805.8 mg/100 g, flavonoids 274.3 mg/100 g and 552.7 mg/100 g dry mass after osmotic dehydration and 782.9 mg/100 dry matter of phenolics, 279.5 mg/100dry matter flavonoids and 434.2 g/100g dry matter anthocyanin content after followed by oven drying to 18% water content.

There is a number of parameters which effects the extent of osmotic dehydration for fruits such as wild blueberries used in this study. These include temperature, exposure time, Brix % and sample to Brix ratio (w/w). In order to determine the optimum conditions, it was decided to use experimental design followed by rigorous optimization using Response Surface Methodology (RSM). A polynomial model which best fit the results of the 30 experiments carried out as per the statistical design was used to find the best conditions for moisture removal and antioxidant retention. Simultaneous optimizations of the multiple responses were carried out. Based on these methods the best conditions for osmotic dehydration of wild blueberries were found to be 30s, 40°C, 65 Brix, 1:5, 5h. Besides moisture removal and retention of the antioxidants, inclusion of osmotic dehydration also led to a five-hour reduction of oven drying time. Some additional characteristics of the dried wild blueberries were also determined. These include shrinkage and rehydration of the wild blueberries which showed a statistically significantly ($p<0.05$) lower shrinkage ratio (31.84%) compared with hot air convective drying method (the control) shrinkage ratio (44.62%). A high rate of rehydration within minutes of mixing after using optimum condition for treated and microwave pretreatment can be beneficial for dried WB added to breakfast cereals that consumed with milk.

Finally, based on time profiles of water dehydration and solid content time profile data, mathematical modeling of the system was carried out with the aim of determining of equilibrium conditions and the mass transfer coefficients. Mass transfer modeling using Azuara model predicts moisture loss and solid gain values at equilibrium state revealing a good correlation of experimental values with the model (due to the R2 values greater than 0.94 and less then10% for the relative mean error RME).

5.2 Future scope:

In order to test for the practical use of these dried fruits in products like breakfast cereals some additional work may have to be done. This will include testing the texture of the product after rehydration in milk; the softness and mouth feel of the product. Panel tests may also be done to determine the consumer acceptability of the same.

References

Abbas, M., Mohsen, M., Nasrin, F., Fatemeh, R., Shabnam, S., & Peiman, A. (2017). Modeling of drying kiwi slices and its sensory evaluation. *Food Science & Nutrition, 5*(3), 466-473.

Abdullah, A. L., Sulaiman, N., Aroua, M., & Noor, M. M. M. (2007). Response surface optimization of conditions for clarification of carambola fruit juice using a commercial enzyme. *Journal of Food Engineering,* 81(1), 65-71.

Ade-Omowaye, B. I. O., Taiwo, K. A., Eshtiaghi, N. M., Angersbach, A., & Knorr, D. (2003). Comparative evaluation of the effects of pulsed electric field and freezing on cell membrane permeabilisation and mass transfer during dehydration of red bell peppers. *Innovative Food Science & Emerging Technologies*, 4(2), 177-188.

Adiletta, G., Russo, P., Senadeera, W., & Di Matteo, M. (2016). Drying characteristics and quality of grape under physical pretreatment. *Journal of Food Engineering*, 172, 9-18.

Afolabi, T. J., Tunde-Akintunde, T. Y., & Adeyanju, J. A. (2015). Mathematical modeling of drying kinetics of untreated and pretreated cocoyam slices. *Journal of Food Science and Technology*, 52(5), 2731-2740.

Aghbashlo, M., Hosseinpour, S., & Mujumdar, A. S. (2015). Application of artificial neural networks (ANNs) in drying technology: a comprehensive review. *Drying Technology*, 33(12), 1397-1462.

AgriFood-Canada. (2011). Canadian blueberries. http://www.agr.gc.ca/eng/industry-markets-and-trade/buying-canadian-food-products/canadian-blueberries,1426167712421.

Ahmed, I., Qazi, I. M., & Jamal, S. (2016). Developments in osmotic dehydration technique for the preservation of fruits and vegetables. *Innovative Food Science & Emerging Technologies*, 34, 29-43.

Akbarian, M., Ghasemkhani, N., & Moayedi, F. (2014). Osmotic dehydration of fruits in *Food Industrial*: a review. Int. J. Biosci., 4(1), 42-57.

Akharume, F., Singh, K., Jaczynski, J., & Sivanandan, L. (2018). Microbial shelf stability assessment of osmotically dehydrated smoky apples. LWT, 90, 61-69.

Alam, M. S., Amarjit, S., & Sawhney, B. (2010). Response surface optimization of osmotic dehydration process for aonla slices. *Journal of Food Science and Technology, 47*(1), 47-54.

Alfaro, L., Siramard, S., Chouljenko, A., & Sathivel, S. (2018). Effects of liquid nitrogen pretreatment on the osmotic dehydration and quality of cryogenically frozen blueberries (Vaccinium angustifolium Ait.). *Food Bioscience*, 22, 165-169.

Allali, H., Marchal, L., & Vorobiev, E. (2009). Effect of blanching by ohmic heating on the osmotic dehydration behavior of apple cubes. *Drying Technology, 27*(6), 739-746.

Amami, E., Khezami, W., Mezrigui, S., Badwaik, L. S., Bejar, A. K., Perez, C. T., & Kechaou, N. (2017). Effect of ultrasound-assisted osmotic dehydration pretreatment on the convective drying of strawberry. *Ultrasonics Sonochemistry*, *36*, 286–300.

Ando, Y., Maeda, Y., Mizutani, K., Wakatsuki, N., Hagiwara, S., & Nabetani, H. (2016). Impact of blanching and freeze-thaw pretreatment on drying rate of carrot roots in relation to changes in cell membrane function and cell wall structure. *LWT-Food*

Science and Technology, 71, 40-46.

Antonio, G. C., Azoubel, P. M., Murr, F. E. X., & Park, K. J. (2008). Osmotic dehydration of sweet potato (Ipomoea batatas) in ternary solutions. *Food Science and Technology, 28*(3), 696-701.

AOAC (1999). Official methods of analysis (15th ed.). Washington, DC: *Association of Official Analytical Chemists.*

Aral, S., & Beşe, A. V. (2016). Convective drying of hawthorn fruit (Crataegus spp.): effect of experimental parameters on drying kinetics, color, shrinkage, and rehydration capacity. *Food Chemistry, 210, 577-584.*

Assis, F. R., M.S.C., M. R., & M.M.B., M. A. (2017). Mathematical Modelling of Osmotic Dehydration Kinetics of Apple Cubes. *Journal of Food Processing and Preservation, 41*(3), e12895.

Assis, F. R., Morais, R. M., & Morais, A. M. (2016). Mass transfer in osmotic dehydration of food products: comparison between mathematical models. *Food Engineering Reviews*, 8(2), 116-133.

Aykın-Dinçer, E., & Erbaş, M. (2018). Drying kinetics, adsorption isotherms and quality characteristics of vacuum-dried beef slices with different salt contents. *Meat Science*.

Azoubel, P., & Murr, F. (2003). Optimisation of osmotic dehydration of cashew apple (Anacardium occidentale L.) in sugar solutions. *Food Science and Technology International, 9*(6), 427-433.

Azoubel, P. M., da Rocha Amorim, M., Oliveira, S. S. B., Maciel, M. I. S., & Rodrigues, J. D. (2015). Improvement of water transport and carotenoid retention during drying of papaya by applying ultrasonic osmotic pretreatment. *Food Engineering Reviews,* 7(2), 185-192.

Azuara, E., Cortés, R., Garcia, H. S., & Beristain, C. I. (1992). Kinetic model for osmotic dehydration and its relationship with Fick's second law. *International journal of food science & technology*, *27*(4), 409-418.

Barat, J., Fito, P., & Chiralt, A. (2001). Modeling of simultaneous mass transfer and structural changes in fruit tissues. *Journal of Food Engineering, 49*(2-3), 77-85.

Bchir, B., Besbes, S., Karoui, R., Paquot, M., Attia, H., & Blecker, C. (2012). Osmotic Dehydration Kinetics of Pomegranate Seeds Using Date Juice as an Immersion Solution Base. *Food and Bioprocess Technology, 5*(3), 999-1009.

Beaudry, C., Raghavan, G., Ratti, C., & Rennie, T. (2004). Effect of four drying methods on the quality of osmotically dehydrated cranberries. *Drying Technology,* 22(3), 521-539.

Beaulieu, J. C., Stein-Chisholm, R. E., Lloyd, S. W., Bett-Garber, K. L., Grimm, C. C., Watson, M. A., & Lea, J. M. (2017). Volatile, anthocyanidin, quality and sensory changes in rabbiteye blueberry from whole fruit through pilot plant juice processing. *Journal of the Science of Food and Agriculture,* 97(2), 469-478.

Beigi, M. (2016). Hot air drying of apple slices: dehydration characteristics and quality assessment. Heat and Mass Transfer, 52(8), 1435-1442.

Bera, D., & Roy, L. (2015). Osmotic dehydration of litchi using sucrose solution: effect of mass transfer. *Journal of Food Processing & Technology*, 6(7), 1.

Bi, J., Yang, A., Liu, X., Wu, X., Chen, Q., Wang, Q., Lv, J., & Wang, X. (2015). Effects of pretreatments on explosion puffing drying kinetics of apple chips. *LWT - Food*

Science and Technology, 60(2, Part 2), 1136-1142

Bialik, M., Wiktor, A., Latocha, P., & Gondek, E. (2018). Mass Transfer in Osmotic Dehydration of Kiwiberry: *Experimental and Mathematical Modelling Studies. Molecules*, 23(5), 1236.

Bizabani, C., Fontenla, S., & Dames, J. F. (2016). Ericoid fungal inoculation of blueberry under commercial production in South Africa. *Scientia Horticulturae*, 209, 173-177.

Brasiello, A., Iannone, G., Adiletta, G., De Pasquale, S., Russo, P., & Di Matteo, M. (2017). Mathematical model for dehydration and shrinkage: Prediction of eggplant's MRI spatial profiles. *Journal of Food Engineering*, 203, 1-5.

BOLIN, H. R., HUXSOLL, C. C., JACKSON, R., & NG, K. C. (1983). Effect of Osmotic Agents and Concentration on Fruit Quality. *Journal of Food Science, 48*(1), 202-205.

Bongirwar, D., & Sreenivasan, A. (1977). Studies on osmotic dehydration of banana [India]. *Journal of Food Science and Technology*.

Brasiello, A., Iannone, G., Adiletta, G., De Pasquale, S., Russo, P., & Di Matteo, M. (2017). Mathematical model for dehydration and shrinkage: Prediction of eggplant's MRI spatial profiles. *Journal of Food Engineering, 203*, 1-5.

Brekke, J. E., & Allen, L. (1966). Banana dehydration. *Technical Progress Report*(153).

Calín-Sánchez, Á., Kharaghani, A., Lech, K., Figiel, A., Carbonell-Barrachina, Á. A., & Tsotsas, E. (2015). Drying kinetics and microstructural and SensoryProperties of black chokeberry (aronia melanocarpa) as affected by drying method. *Food and Bioprocess Technology, 8*(1), 63-74.

Camirand, W., Forrey, R., Popper, K., Boyle, F., & Stanley, W. (1968). Dehydration of membranecoated foods by osmosis. *Journal of the Science of Food and Agriculture, 19*(8), 472-474.

Cano-Lamadrid, M., Lech, K., Michalska, A., Wasilewska, M., Figiel, A., Wojdyło, A., & Carbonell-Barrachina, Á. A. (2017). Influence of osmotic dehydration pre-treatment and combined drying method on physico-chemical and sensory properties of pomegranate arils, cultivar Mollar de Elche. *Food Chemistry, 232*, 306-315.

Castro, A., Mayorga, E., & Moreno, F. (2018). Mathematical modelling of convective drying of fruits: *A review. Journal of Food Engineering*, 223, 152-167.

Cesa, S., Carradori, S., Bellagamba, G., Locatelli, M., Casadei, M. A., Masci, A., & Paolicelli, P. (2017). Evaluation of processing effects on anthocyanin content and colour modifications of blueberry (Vaccinium spp.) extracts: Comparison between HPLC-DAD and CIELAB analyses. *Food Chemistry*, 232, 114-123.

Chandra, S., & Kumari, D. (2015). Recent development in osmotic dehydration of fruit and vegetables: a review. *Critical Reviews in Food Science and Nutrition*, 55(4), 552-561.

Chavan, U. D., & Amarowicz, R. (2012). Osmotic Dehydration Process for Preservation of Fruits and Vegetables. *Journal of Food Research*, *1*(2), 202–209.

Chen, S., Zeng, Z., Hu, N., Bai, B., Wang, H., & Suo, Y. (2018). Simultaneous optimization of the ultrasound-assisted extraction for phenolic compounds content and antioxidant activity of Lycium ruthenicum Murr. fruit using response surface methodology. *Food Chemistry*, 242, 1-8.

Cheng, X.-f., Zhang, M., Adhikari, B., & Islam, M. N. (2014). Effect of Power Ultrasound and Pulsed Vacuum Treatments on the Dehydration Kinetics, Distribution, and Status of Water in Osmotically Dehydrated Strawberry: a Combined NMR and DSC Study. *Food and Bioprocess Technology, 7*(10), 2782-2792.

Chorfa, N., Savard, S., & Belkacemi, K. (2016). An efficient method for high-purity anthocyanin isomers isolation from wild blueberries and their radical scavenging activity. *Food Chemistry*, 197, 1226-1234.

Chu, W., Gao, H., Cao, S., Fang, X., Chen, H., & Xiao, S. (2017). Composition and morphology of cuticular wax in blueberry (Vaccinium spp.) fruits. *Food Chemistry*, 219(Supplement C), 436-442.

Contreras, J., & Smyrl, T. (1981). An evaluation of osmotic concentration of apple rings using corn syrup solids solutions. *Canadian Institute of Food Science and Technology Journal, 14*(4), 310-314.

Conway, J., Castaigne, F., Picard, G., & Vovan, X. (1983). Mass transfer considerations in the osmotic dehydration of apples. *Canadian Institute of Food Science and Technology Journal, 16*(1), 25-29.

Corrêa, J. L., Ernesto, D. B., Alves, J. G., & Andrade, R. S. (2014). Optimisation of vacuum pulse osmotic dehydration of blanched pumpkin. *International Journal of Food Science & Technology,* 49(9), 2008-2014.

Corrêa, J., Viana, A. D., de Mendonça, K. S., & Justus, A. (2016). Optimization of pulsed vacuum osmotic dehydration of sliced tomato. *In Drying and Energy Technologies* (pp. 207-228): Springer.

Correia, R., Grace, M. H., Esposito, D., & Lila, M. A. (2017). Wild blueberry polyphenol-protein food ingredients produced by three drying methods: Comparative physico-chemical properties, phytochemical content, and stability during storage. *Food Chemistry*, 235(Supplement C), 76-85.

Crank, J. (1975). *The mathematics of diffusion*. Oxford university press.

De Mendonça, K. S., Corrêa, J. L. G., de Jesus Junqueira, J. R., Pereira, M. C. d. A., & Vilela, M. B. (2016). Optimization of osmotic dehydration of yacon slices. *Drying Technology,* 34(4), 386-394.

Deepika, S., & Sutar, P. (2018). Combining osmotic–steam blanching with infrared–microwave–hot air drying: Production of dried lemon (Citrus limon L.) slices and enzyme inactivation. Drying Technology, 1-19.

Deepika, S., & Sutar, P. P. (2017). Osmotic dehydration of lemon (Citrus limon L.) slices: Modeling mass transfer kinetics correlated with dry matter holding capacity and juice sac losses. *Drying Technology, 35*(7), 877-892.

Dehghannya, J., Hosseinlar, S. H., & Heshmati, M. K. (2018). Multi-stage continuous and intermittent microwave drying of quince fruit coupled with osmotic dehydration and low temperature hot air drying. *Innovative Food Science and Emerging Technologies*,*45*(September 2017), 132–151.

Del Bo, C., Roursgaard, M., Porrini, M., Loft, S., Møller, P., & Riso, P. (2016). Different effects of anthocyanins and phenolic acids from wild blueberry (Vaccinium angustifolium) on monocytes adhesion to endothelial cells in a TNF-α stimulated proinflammatory environment. *Molecular Nutrition & Food Research*, 60(11), 2355-2366.

de Oliveira, L. F., Corrêa, J. L. G., Botrel, D. A., Vilela, M. B., Batista, L. R., & Freire,

L. (2017). Reuse of sorbitol solution in pulsed vacuum osmotic dehydration of yacon (Smallanthus sonchifolius). *Journal of Food Processing and Preservation*, *41*(6), e13306.

Dermesonlouoglou, E., Chalkia, A., & Taoukis, P. (2018). Application of osmotic dehydration to improve the quality of dried goji berry. *Journal of Food Engineering.* , 232, 36-43.

Dermesonlouoglou, E. K., Giannakourou, M., & Taoukis, P. S. (2016). Kinetic study of the effect of the osmotic dehydration pre-treatment with alternative osmotic solutes to the shelf life of frozen strawberry. Food and Bioproducts Processing, 99, 212-221.

Derossi, A., Severini, C., Del Mastro, A., & De Pilli, T. (2015). Study and optimization of osmotic dehydration of cherry tomatoes in complex solution by response surface methodology and desirability approach. *LWT - Food Science and Technology, 60(2), 641-648.*

de Souza, V. R., Pereira, P. A. P., Da Silva, T. L. T., De Oliveira Lima, L. C., Pio, R., & Queiroz, F. (2014). Determination of the bioactive compounds, antioxidant activity and chemical composition of Brazilian blackberry, red raspberry, strawberry, blueberry and sweet cherry fruits. *Food Chemistry*, *156*, 362–368.

Dixon, G., & Jen, J. (1977). Changes of sugars and acids of osmovac‐dried apple slices. *Journal of Food Science, 42*(4), 1126-1127

Doymaz, İ. (2008). Influence of blanching and slice thickness on drying characteristics of leek slices. *Chemical Engineering and Processing: Process Intensification, 47*(1), 41-47.

Doymaz, İ. (2017). Drying kinetics, rehydration and colour characteristics of convective hot-air drying of carrot slices. *Heat and Mass Transfer, 53*(1), 25-35.

Dróżdż, P., Šėžienė, V., & Pyrzynska, K. (2017). Mineral Composition of Wild and Cultivated Blueberries. *Biological Trace Element Research*.

Dudonné, S., Dubé, P., Anhê, F. F., Pilon, G., Marette, A., Lemire, M., Harris, C., Dewailly, E., & Desjardins, Y. (2015). Comprehensive analysis of phenolic compounds and abscisic acid profiles of twelve native Canadian berries. J*ournal of Food Composition and Analysis,* 44, 214-224.

Dulf, F. V., Vodnar, D. C., & Socaciu, C. (2016). Effects of solid-state fermentation with two filamentous fungi on the total phenolic contents, flavonoids, antioxidant activities and lipid fractions of plum fruit (Prunus domestica L.) by-products. Food Chemistry, 209, 27-36.

Ekezie, F.-G. C., Sun, D.-W., Han, Z., & Cheng, J.-H. (2017). Microwave-assisted food processing technologies for enhancing product quality and process efficiency: A review of recent developments. *Trends in Food Science & Technology*.

Eltawil, M. A., Azam, M. M., & Alghannam, A. O. (2018). Energy analysis of hybrid solar tunnel dryer with PV system and solar collector for drying mint (MenthaViridis). *Journal of Cleaner Production*, 181, 352-364.

Farkas, D., & Lazar, M. (1969). Osmotic dehydration of apple pieces: effect of temperature and syrup concentration on rates. *Food Technology*.

Feng, H., Yin, Y., & Tang, J. (2012). Microwave Drying of Food and Agricultural Materials: Basics and Heat and Mass Transfer Modeling. *Food Engineering Reviews*, *4*(2), 89–106. http://doi.org/10.1007/s12393-012-9048-x

Ferrier, J., Saleem, A., Djeffal, S., Schlarb, J., Haddad, P. S., Balick, M. J., Cuerrier, A., & Arnason, J. T. (2016). Comparison of the antiglycation activity of leaves of eight traditionally used wild blueberry species (Vaccinium L.) from northern Canada and Europe with their phytochemistry. Botany, 95(4), 387-394.

Flores, F. P., Singh, R. K., Kerr, W. L., Pegg, R. B., & Kong, F. (2014). Total phenolics content and antioxidant capacities of microencapsulated blueberry anthocyanins during in vitro digestion. Food Chemistry, 153, 272-278.

Garcia-Noguera, J., Oliveira, F. I., Gallão, M. I., Weller, C. L., Rodrigues, S., & Fernandes, F. A. (2010). Ultrasound-assisted osmotic dehydration of strawberries: effect of pretreatment time and ultrasonic frequency. *Drying Technology, 28*(2), 294-303.

García‐Martínez, E., Andújar, I., Yuste del Carmen, A., Prohens, J., & Martínez‐Navarrete, N. (2018). Antioxidant and anti‐inflammatory activities of freeze‐dried grapefruit phenolics as affected by gum arabic and bamboo fibre addition and microwave pretreatment. *Journal of the Science of Food and Agriculture,* 98(8), 3076-3083.

Garcıa-Martınez, E., Martínez-Monzó, J., Camacho, M. M., & Martınez-Navarrete, N. (2002). Characterisation of reused osmotic solution as ingredient in new product formulation. *Food research international*, *35*(2-3), 307-313.

Garcia, C. C., Mauro, M. A., & Kimura, M. (2007). Kinetics of osmotic dehydration and air-drying of pumpkins (Cucurbita moschata). *Journal of Food Engineering, 82*(3), 284-291.

Germer, S. P. M., Morgano, M. A., da Silva, M. G., Silveira, N. F. D. A., & Souza, E. D. C. G. (2016). Effect of reconditioning and reuse of sucrose syrup in quality properties and retention of nutrients in osmotic dehydration of guava. *Drying technology*, *34*(8), 997-1008.

Germer, S. P., Ferrari, C. C., Lancha, J. P., Berbari, S. A., Carmello-Guerreiro, S. M., & Ruffi, C. R. (2014). Influence of processing additives on the quality and stability of dried papaya obtained by osmotic dehydration and conventional air drying. *Drying Technology*, 32(16), 1956-1969.

Giangiacomo, R., TORREGGIANI, D., & ABBO, E. (1987). OSMOTIC DEHYDRATION OF FRUIT: PART 1. SUGARS EXCHANGE BETWEEN FRUIT AND EXTRACTING SYRUPS 1. *Journal of Food Processing and Preservation, 11*(3), 183-195.

Grabowski, S., Marcotte, M., Quan, D., Taherian, A. R., Zareifard, M. R., Poirier, M., & Kudra, T. (2007). Kinetics and quality aspects of Canadian blueberries and cranberries dried by osmo-connective method. *Drying Technology*, *25*(2), 367–374.

Gupta, R., Singh, B., & Shivhare, U. (2012). Optimization of osmo-convective dehydration process for the development of honey-ginger candy using response surface methodology. *Drying Technology,* 30(7), 750-759.

Guzzo da Silva, B., Frattini Fileti, A. M., & Pereira Taranto, O. (2015). Drying of Brazilian Pepper-Tree Fruits (Schinus terebinthifolius Raddi): Development of Classical Models and Artificial Neural Network Approach. *Chemical Engineering Communications, 202*(8), 1089-1097.

Hamedi, F., Mohebbi, M., Shahidi, F., & Azarpazhooh, E. (2018). Ultrasound-Assisted Osmotic Treatment of Model Food Impregnated with Pomegranate Peel Phenolic Compounds: Mass Transfer, Texture, and Phenolic Evaluations. *Food and*

Bioprocess Technology, *11*(5), 1061-1074.

He, B., Zhang, L.-L., Yue, X.-Y., Liang, J., Jiang, J., Gao, X.-L., & Yue, P.-X. (2016).

Hashim, N., Daniel, O., & Rahaman, E. (2014). A Preliminary Study: Kinetic Model of Drying Process of Pumpkins (Cucurbita Moschata) in a Convective Hot Air Dryer. *Agriculture and Agricultural Science Procedia, 2*, 345-352.

Hawkes, J., & Flink, J. M. (1978). Osmotic concentration of fruit slices prior to freeze dehydration 1. *Journal of Food Processing and Preservation, 2*(4), 265-284.

Hong, Y.-J., Barrett, D. M., & Mitchell, A. E. (2004). Liquid Chromatography/Mass Spectrometry Investigation of the Impact of Thermal Processing and Storage on Peach Procyanidins. *Journal of Agricultural and Food Chemistry, 52*(8), 2366-2371.

Hope, G., & Vitale, D. (1972). Osmotic dehydration: a cheap and simple method of preserving mangoes, bananas and plantains.

Horuz, E., Bozkurt, H., Karataş, H., & Maskan, M. (2017). Effects of hybrid (microwave-convectional) and convectional drying on drying kinetics, total phenolics, antioxidant capacity, vitamin C, color and rehydration capacity of sour cherries. *Food Chemistry*, 230, 295-305.

Horuz, E., Bozkurt, H., Karataş, H., & Maskan, M. (2018). Simultaneous application of microwave energy and hot air to whole drying process of apple slices: drying kinetics, modeling, temperature profile and energy aspect. *Heat and Mass Transfer*, 54(2), 425-436.

Horuz, E., Jaafar, H. J., & Maskan, M. (2017). Ultrasonication as pretreatment for drying of tomato slices in a hot air–microwave hybrid oven. *Drying Technology,* 35(7), 849-859.

Jackson, T., & Mohamed, B. (1971). The shambat process: new development arising from the osmotic dehydration of fruits and vegetables. *Sudan Journal of Food Science and Technology, 3*, 18-22.

Jaiswal, A. K., Gupta, S., & Abu-Ghannam, N. (2012). Kinetic evaluation of colour, texture, polyphenols and antioxidant capacity of Irish York cabbage after blanching treatment. *Food Chemistry,* 131(1), 63-72.

esus, J. J. R. d., G., C. J. L., & de, M. K. S. (2017). Evaluation of the Shrinkage Effect on the Modeling Kinetics of Osmotic Dehydration of Sweet Potato (Ipomoea batatas (L.)). *Journal of Food Processing and Preservation, 41*(3), e12881.

Jiang, N., Liu, C., Li, D., Zhang, J., Zhang, Z., Huang, J., & Yu, Z. (2018). Effect of Thermosonic Pretreatment and Microwave Vacuum Drying on the Water State and Glass Transition Temperature in Agaricus bisporus Slices. *Food and Bioprocess Technology*, 11(1), 172-184.

Jin, T. Z., Yu, Y., & Gurtler, J. B. (2017). Effects of pulsed electric field processing on microbial survival, quality change and nutritional characteristics of blueberries. LWT-*Food Science and Technology,* 77, 517-524.

Jorquera-Fontena, E., Génard, M., & Franck, N. (2017). Analysis of blueberry (Vaccinium corymbosum L.) fruit water dynamics during growth using an ecophysiological model. *The Journal of Horticultural Science and Biotechnology, 92*(6), 646-659.

Jung, J., Cavender, G., Simonsen, J., & Zhao, Y. (2015). Investigation of the mechanisms of using metal complexation and cellulose nanofiber/sodium alginate layer-by-layer coating for retaining anthocyanin pigments in thermally processed blueberries in aqueous media. *Journal of Agricultural and Food Chemistry,* 63(11), 3031-3038.

Jung, J., Simonsen, J., Wang, W., & Zhao, Y. (2018). Evaluation of Consumer Acceptance and Quality of Thermally and High Hydrostatic Pressure Processed Blueberries and Cherries Subjected to Cellulose Nanofiber (CNF) Incorporated Water-Resistant Coating Treatment. *Food and Bioprocess Technology*, 1-10.

Kadam, K. L., Rydholm, E. C., & McMillan, J. D. (2004). Development and validation of a kinetic model for enzymatic saccharification of lignocellulosic biomass. *Biotechnology Progress, 20*.

Kamiloglu, S., Toydemir, G., Boyacioglu, D., Beekwilder, J., Hall, R. D., & Capanoglu, E. (2016). A review on the effect of drying on antioxidant potential of fruits and vegetables. Critical Reviews in Food Science and Nutrition, 56(sup1), S110-S129.

Kang, J., Thakali, K. M., Jensen, G. S., & Wu, X. (2015). Phenolic Acids of the Two Major Blueberry Species in the US Market and Their Antioxidant and Anti-inflammatory Activities. *Plant Foods for Human Nutrition,* 70(1), 56-62.

Katsoufi, S., Lazou, A. E., Giannakourou, M. C., & Krokida, M. K. (2017). Mass transfer kinetics and quality attributes of osmo-dehydrated candied pumpkins using nutritious sweeteners. *Journal of Food Science and Technology,* 54(10), 3338-3348.

Kaur, R., Gul, K., & Singh, A. (2016). Nutritional impact of ohmic heating on fruits and vegetables—A review. Cogent Food & Agriculture, 2(1), 1159000.

Kendall, P., & Sofos, J. (2007). Drying fruits. *Food and nutrition series. Preparation; no. 9.309*.

Kerch, G. (2015). Chitosan films and coatings prevent losses of fresh fruit nutritional quality: A review. *Trends in Food Science & Technology*, 46(2), 159-166.

Ketata, M., Desjardins, Y., & Ratti, C. (2013). Effect of liquid nitrogen pretreatments on osmotic dehydration of blueberries. *Journal of food engineering*, *116*(1), 202-212.

Khalid, S., Barfoot, K., May, G., Lamport, D., Reynolds, S., & Williams, C. (2017). Effects of Acute Blueberry Flavonoids on Mood in Children and Young Adults. Nutrients, 9(2), 158.

Khan, M. R. (2012). Osmotic dehydration technique for fruits preservation-A review. Pakistan *Journal of Food Sciences*, 22(2), 71-85.

Khin, M. M., Zhou, W., & Yeo, S. Y. (2007). Mass transfer in the osmotic dehydration of coated apple cubes by using maltodextrin as the coating material and their textural properties. *Journal of Food Engineering, 81*(3), 514-522.

Kucner, A., Klewicki, R., & Sójka, M. (2013). The Influence of Selected Osmotic Dehydration and Pretreatment Parameters on Dry Matter and Polyphenol Content in Highbush Blueberry (Vaccinium corymbosum L.) Fruits. *Food and Bioprocess Technology*, 6(8), 2031-2047.

Kumar, C., Joardder, M., Farrell, T., Millar, G. J., & Karim, M. (2016). Mathematical model for intermittent microwave convective drying of food materials. *Drying Technology,* 34(8), 962-973.

Kumar, P. S., & Sagar, V. (2014). Drying kinetics and physico-chemical characteristics of Osmo-dehydrated Mango, Guava and Aonla under different drying conditions. *Journal of Food Science and Technology, 51*(8), 1540-1546.

Kumari, P., & Khatkar, B. (2018). Nutritional composition and drying kinetics of aonla fruits. *Journal of Food Science and Technology, 55*(8), 3135-3143.

Lech, K., Michalska, A., Wojdyło, A., Nowicka, P., & Figiel, A. (2018). The influence of physical properties of selected plant materials on the process of osmotic dehydration. *LWT - Food Science and Technology*, *91*(February), 588–594.

Łechtańska, J., Szadzińska, J., & Kowalski, S. (2015). Microwave-and infrared-assisted convective drying of green pepper: Quality and energy considerations. *Chemical Engineering and Processing: Process Intensification,* 98, 155-164.

Lee, J., Durst, R. W., & Wrolstad, R. E. (2005). Determination of total monomeric anthocyanin pigment content of fruit juices, beverages, natural colorants, and wines by the pH differential method: Collaborative study. *Journal of AOAC International,* 88(5), 1269–1278.

Lee, S., Jung, E. S., Do, S.-G., Jung, G.-y., Song, G., Song, J.-m., & Lee, C. H. (2014). Correlation between Species-Specific Metabolite Profiles and Bioactivities of Blueberries (Vaccinium spp.). *Journal of Agricultural and Food Chemistry*, 62(9), 2126-2133.

Lemus-Mondaca, R., Pizarro-Oteíza, S., Perez-Won, M., & Tabilo-Munizaga, G. (2018). Convective Drying of Osmo-Treated Abalone (Haliotis rufescens) Slices: Diffusion, Modeling, and Quality Features. *Journal of Food Quality, 2018*.

Lerici, C., Pinnavaia, G., ROSA, M. D., & Bartolucci, L. (1985). Osmotic dehydration of fruit: influence of osmotic agents on drying behavior and product quality. *Journal of Food Science, 50*(5), 1217-1219.

Li, D., Meng, X., & Li, B. (2016). Profiling of anthocyanins from blueberries produced in China using HPLC-DAD-MS and exploratory analysis by principal component analysis. *Journal of Food Composition and Analysis,* 47, 1-7.

Li, H., & Ramaswamy, H. S. (2006). Osmotic dehydration of apple cylinders: I. Conventional batch processing conditions. *Drying Technology, 24*(5), 619-630.

Lohachoompol, V., Srzednicki, G., & Craske, J. (2004). The change of total anthocyanins in blueberries and their antioxidant effect after drying and freezing. *BioMed Research International,* 2004(5), 248-252.

Lombard, G., Oliveira, J., Fito, P., & Andrés, A. (2008). Osmotic dehydration of pineapple as a pre-treatment for further drying. *Journal of Food Engineering, 85*(2), 277-284.

Luchese, C. L., Gurak, P. D., & Marczak, L. D. F. (2015). Osmotic Dehydration of Physalis—Influence of Ultrasound Pretreatment. *Food Engineering Reviews,* 7(2), 193-197.

Lyrene, P. M., Vorsa, N., & Ballington, J. R. (2003). Polyploidy and sexual polyploidization in the genus Vaccinium. Euphytica, 133(1), 27-36.

Magwaza, L. S., & Opara, U. L. (2015). Analytical methods for determination of sugars and sweetness of horticultural products-A review. *Scientia Horticulturae*, *184*, 179–192.

Mahomud, M. S., Ali, M. K., Rahman, M. M., Rahman, M. H., Sharmin, T., & Rahman, M. J. (2015). Effect of Honey and Sugar Solution on the Shelf Life and Quality of Dried Banana (Musa paradisiaca) Slices. *American Journal of Food Science and Technology,* 3(3), 60-66.

Mainland, C. M. M. (2012). Frederick V. Coville and the History of North American Highbush Blueberry Culture. International Journal of Fruit Science, 12(1-3), 4-13.

Makroo, H., Saxena, J., Rastogi, N., & Srivastava, B. (2017). Ohmic heating assisted polyphenol oxidase inactivation of watermelon juice: Effects of the treatment on pH, lycopene, total phenolic content, and color of the juice. *Journal of Food Processing and Preservation*, 41(6), e13271.

Mallik, A. U., & Hamilton, J. (2017). Harvest date and storage effect on fruit size , phenolic content and antioxidant capacity of wild blueberries of NW Ontario ,. *Journal of Food Science and Technology*, *54*(6), 1545–1554.

Mandala, I. G., Anagnostaras, E. F., & Oikonomou, C. K. (2005). Influence of osmotic dehydration conditions on apple air-drying kinetics and their quality characteristics. *Journal of Food Engineering, 69*(3), 307-316.

Mannozzi, C., Fauster, T., Haas, K., Tylewicz, U., Romani, S., Dalla Rosa, M., & Jaeger, H. (2018). Role of thermal and electric field effects during the pre-treatment of fruit and vegetable mash by pulsed electric fields (PEF) and ohmic heating (OH). I*nnovative Food Science & Emerging Technologies.*

Manzoor, M., Shukla, R., Mishra, A., Fatima, A., & Nayik, G. (2017). Osmotic Dehydration Characteristics of Pumpkin Slices using Ternary Osmotic Solution of Sucrose and Sodium Chloride. *J Food Process Technol, 8*(669), 2.

Martins, S. R., Monteles, N. J. P., Haber, P. V., K., M. S., A., B. M., & Rodrigues, S. L. (2017). Mathematical Modeling of Drying Kinetics of Persimmon Fruits (Diospyros kaki cv. Fuyu). *Journal of Food Processing and Preservation, 41*(1), e12789.

Marjanovic-Balaban, Z., Grujic, S., Jasic, M., & Vujadinovic, D. (2012). Testing of chemical composition of wild berries. In *Third International Scientific Symposium" Agrosym 2012", Jahorina, Bosnia and Herzegovina, 15-17 November, 2012. Book of Proceedings* (pp. 154-160). *Faculty of Agriculture, University of East Sarajevo*.

Mayor, L., Moreira, R., & Sereno, A. M. (2011). Shrinkage, density, porosity and shape changes during dehydration of pumpkin (Cucurbita pepo L.) fruits. *Journal of Food Engineering, 103*(1), 29-37.

Mayor, L., & Sereno, A. M. (2004). Modelling shrinkage during convective drying of food materials: a review. *Journal of Food Engineering*, *61*(3), 373-386.

Mehta, U., & BAJAJ, S. (1984). Changes in the chemical composition and organoleptic quality of citrus peel candy during preparation and storage. *Journal of Food Science and Technology, 21*(6), 422-424.

Mercali, G. D., Marczak, L. D. F., Tessaro, I. C., & Noreña, C. P. Z. (2011). Evaluation of water, sucrose and NaCl effective diffusivities during osmotic dehydration of banana (Musa sapientum, shum.). *LWT-Food Science and Technology, 44*(1), 82-91.

Michalska, A., & Łysiak, G. (2015). Bioactive Compounds of Blueberries: Post-Harvest Factors Influencing the Nutritional Value of Products. *International Journal of Molecular Sciences*, 16(8), 18642.

Monnerat, S., Pizzi, T., Mauro, M., & Menegalli, F. (2010). Osmotic dehydration of apples in sugar/salt solutions: Concentration profiles and effective diffusion coefficients. *Journal of Food Engineering, 100*(4), 604-612.

Monteiro, R. L., Link, J. V., Tribuzi, G., Carciofi, B. A., & Laurindo, J. B. (2018). Effect of multi-flash drying and microwave vacuum drying on the microstructure and texture of pumpkin slices. LWT, 96, 612-619.

Moreira, R., Chenlo, F., Torres, M., & Vázquez, G. (2007). Effect of stirring in the osmotic dehydration of chestnut using glycerol solutions. LWT-Food *Science and*

Technology, 40(9), 1507-1514.

Moreno, J., Gonzales, M., Zúniga, P., Petzold, G., Mella, K., & Munoz, O. (2016). Ohmic heating and pulsed vacuum effect on dehydration processes and polyphenol component retention of osmodehydrated blueberries (cv. Tifblue). *Innovative Food Science & Emerging Technologies*, 36, 112-119.

Musielak, G., Mierzwa, D., Pawłowski, A., Rajewska, K., & Szadzińska, J. (2018). Hybrid and Non-stationary Drying—Process Effectiveness and Products Quality. *In Practical Aspects of Chemical Engineering (pp. 319-337): Springer.*

Nabnean, S., S., T., S., J., & B.K., B. (2017). Drying Kinetics and Diffusivity of Osmotically Dehydrated Cherry Tomatoes. *Journal of Food Processing and Preservation, 41*(1), e12735.

Nadian, M. H., Rafiee, S., Aghbashlo, M., Hosseinpour, S., & Mohtasebi, S. S. (2015). Continuous real-time monitoring and neural network modeling of apple slices color changes during hot air drying. *Food and Bioproducts Processing*, 94, 263-274.

Nemzer, B., Vargas, L., Xia, X., Sintara, M., & Feng, H. (2018). Phytochemical and physical properties of blueberries, tart cherries, strawberries, and cranberries as affected by different drying methods. *Food Chemistry,* 262, 242-250.

Ngo, H. T., Tojo, S., Ban, T., & Chosa, T. (2017). Effects of Prior Freezing Conditions on the Quality of Blueberries in a Freeze-Drying Process. *Transactions of the ASABE*, 60(4), 1369.

Nieto, A., Salvatori, D., Castro, M., & Alzamora, S. (2004). Structural changes in apple tissue during glucose and sucrose osmotic dehydration: shrinkage, porosity, density and microscopic features. *Journal of Food Engineering, 61*(2), 269-278.

Nikkhah, E., Khayamy, M., Heidari, R., & Jamee, R. (2007). Effect of sugar treatment on stability of anthocyanin pigments in berries. *Journal of Biological Sciences, 7*(8), 1412-1417.

Nishadh, A., & Mathai, L. (2014). Osmotic dehydration of radish in salt and sucrose solutions. *Intl J Innov Res Sci Eng Technol*, 3(1), 1514-1521.

Nowicka, P., Wojdy, O, A., Lech, K., & Figiel, A. (2015). Influence of Osmodehydration Pretreatment and Combined Drying Method on the Bioactive Potential of Sour Cherry Fruits. *Food and Bioprocess Technology*, *8*(4), 824–836.

Nowicka, P., Wojdyło, A., Lech, K., & Figiel, A. (2015). Influence of Osmodehydration Pretreatment and Combined Drying Method on the Bioactive Potential of Sour Cherry Fruits. Food and Bioprocess Technology, 8(4), 824-836.

Optimization of Ultrasound-Assisted Extraction of phenolic compounds andanthocyanins from blueberry (Vaccinium ashei) wine pomace. *Food Chemistry*, 204, 70-76.

Olanipekun, B. F., T.Y., T.-A., O.J., O., M.G., A., & T.A., A. (2015). Mathematical Modeling of Thin-Layer Pineapple Drying. *Journal of Food Processing and Preservation, 39*(6), 1431-1441.

Oliveira, I. M., Fernandes, F. A., Rodrigues, S., Sousa, P. H., Maia, G. A., & Figueiredo, R. W. (2006). Modeling and optimization of osmotic dehydration of banana followed by air drying. *Journal of Food Process Engineering, 29*(4), 400-413.

Omolola, A. O., Jideani, A. I., & Kapila, P. F. (2014). Modeling microwave drying kinetics and moisture diffusivity of Mabonde banana variety. *International Journal of Agricultural and Biological Engineering, 7*(6), 107-113.

Pacheco-Angulo, H., Herman-Lara, E., García-Alvarado, M., & Ruiz-López, I. (2016).

Mass transfer modeling in osmotic dehydration: Equilibrium characteristics and process dynamics under variable solution concentration and convective boundary. *Food and Bioproducts Processing*, 97, 88-99.

Pan, Z., & El-Mashad, H. (2018). Infrared Peeling Technology for Fruits and VegetablesThe need for IR. Journal of Agricultural Safety and Health, 25(3), 4.

Peng, J., Yi, J., Bi, J., Chen, Q., Wu, X., & Zhou, M. (2018). Freezing as pretreatment in instant controlled pressure drop (DIC) texturing of dried carrot chips: Impact of freezing temperature. LWT-Food Science and Technology, 89, 365-373.

Pérez-Won, M., Lemus-Mondaca, R., Tabilo-Munizaga, G., Pizarro, S., Noma, S., Igura, N., & Shimoda, M. (2016). Modelling of red abalone (Haliotis rufescens) slices drying process: Effect of osmotic dehydration under high pressure as a pretreatment. *Innovative Food Science & Emerging Technologies, 34*, 127-134.

Perussello, C. A., Kumar, C., de Castilhos, F., & Karim, M. A. (2014). Heat and mass transfer modeling of the osmo-convective drying of yacon roots (Smallanthus sonchifolius). *Applied Thermal Engineering*, *63*(1), 23-32.

Pinzi, S., Lopez-Gimenez, F. J., Ruiz, J. J., & Dorado, M. P. (2010). Response surface modelingto predict biodiesel yield in a multi-feedstock biodiesel production plant. BioresourceTechnology, 101(24), 9587-9593.

Ponting, J. (1966). Osmotic dehydration of fruits. *Food Technology, 20*, 125-128.

Ponting, J. (1973). Osmotic dehydration of fruits: Recent modifications and applications. *Process Biochemistry*.

Powell, E. A., & Kron, K. A. (2003). Molecular systematics of the northern Andean blueberries (Vaccinieae, Vaccinioideae, Ericaceae). *International Journal of Plant*

Sciences, *164*(6), 987-995.

Pragati, S. D., & Dhawan, S. (2000). Effect of Different Drying Methods on the Nutritional Composition of Aonla Fruit (Emblica Officinalis Garten). *Journal of Agriculture in the Tropics and Subtropics, 101*(1), 85-89.

Prosapio, V., & Norton, I. (2017). Influence of osmotic dehydration pre-treatment on oven drying and freeze drying performance. LWT, 80, 401-408.

Puértolas, E., Saldaña, G., & Raso, J. (2016). Pulsed electric field treatment for fruit and vegetable processing. *In Handbook of Electroporation (pp. 1-21): Springer.*

Quevedo, R., Díaz, O., Valencia, E., Pedreschi, F., Bastias, J. M., & Siche, R. (2016). Differences between the order model and the Weibull model in the modeling of the enzymatic browning. *Food and Bioprocess Technology, 9*(11), 1961-1967.

Rahman, M., & Lamb, J. (1990). Osmotic dehydration of pineapple. *Journal of Food Science and Technology, 27*(3), 150-152.

Rahman M, S. M. A. (2015). Osmotic Dehydration of Pumpkin Using Response Surface Methodology -Influences of Operating Conditions on Water Loss and Solute Gain. *Journal of Bioprocessing & Biotechniques*, *5*(5). http://doi.org/10.4172/2155-9821.1000226

Rahman, N., Xin, T. B., Kamilah, H., & Ariffin, F. (2018). Effects of osmotic dehydration treatment on volatile compound (Myristicin) content and antioxidants property of nutmeg (Myristica fragrans) pericarp. *Journal of Food Science and Technology*, 55(1), 183-189.

Rajat, C., & Ritika, S. (2017). Concurrent Osmotic Dehydration and Vacuum Drying of Kiwi Fruit (Actinidia Deliciosa cv. Hayward) Under Far Infrared Radiation:

Process Optimization, Kinetics and Quality Assessment. *Journal of Food Process Engineering*, 40(2), e12391.

Ramallo, L., Schvezov, C., & Mascheroni, R. (2004). Mass transfer during osmotic dehydration of pineapple. *Food Science and Technology International, 10*(5), 323-332.

Ramya, V., & Jain, N. K. (2017). A Review on Osmotic Dehydration of Fruits and Vegetables: An Integrated Approach. *Journal of Food Process Engineering,* 40(3), e12440.

Rashmi, H., Doreyappa, G., & Mukanda, G. (2005). Studies on osmo-air dehydration of pineapple fruits. *Journal of Food Science and Technology, 42*(1), 64-67.

Rastogi, N., & Raghavarao, K. (1997). Water and solute diffusion coefficients of carrot as a function of temperature and concentration during osmotic dehydration. *Journal of Food Engineering, 34*(4), 429-440.

Rastogi, N. K., Raghavarao, K., & Niranjan, K. (2015). Recent developments in osmotic dehydration. *In Emerging Technologies for Food Processing (Second Edition) (pp. 181-212): Elsevier.*

Rodriguez, A., Zaro, M. J., Lemoine, M. L., & Mascheroni, R. H. (2016). Comparison of two alternatives of combined drying to process blueberries (O'Neal): *Evaluation of the final quality. Drying Technology,* 34(8), 974-985.

Rodríguez, M. M., Mascheroni Rodolfo, H., & Quintero-Ramos, A. (2015). Mathematical Modeling of Hot-Air Drying of Osmo-dehydrated Nectarines. In *International Journal of Food Engineering* (Vol. 11, pp. 533).

Rodríguez, Ó., Eim, V., Rosselló, C., Femenia, A., Cárcel, J. A., & Simal, S. (2018).

Application of power ultrasound on the convective drying of fruits and vegetables: effects on quality. *Journal of the Science of Food and Agriculture,* 98(5), 1660-1673.

Rudy, S., Dziki, D., Krzykowski, A., Gawlik-Dziki, U., Polak, R., Różyło, R., & Kulig, R. (2015). Influence of pre-treatments and freeze-drying temperature on the process kinetics and selected physico-chemical properties of cranberries (Vaccinium macrocarpon Ait.). *LWT - Food Science and Technology, 63*(1), 497-503.

Sagar, V. R., & Suresh Kumar, P. (2010). Recent advances in drying and dehydration of fruits and vegetables: A review. *Journal of Food Science and Technology*, *47*(1), 15–26.

Şahin, U., & Öztürk, H. K. (2016). Experimental investigation of drying kinetics of pretreated and non-pretreated figs (Ficus carica L.). *Mugla Journal of Science and Technology, 2*(1), 20-26.

Sareban, M., & Souraki, B. A. (2016). Anisotropic diffusion during osmotic dehydration of celery stalks in salt solution. *Food and Bioproducts Processing*, *98*, 161-172.

Seremet, L., Botez, E., Nistor, O. V., Andronoiu, D. G., & Mocanu, G. D. (2016). Effect of different drying methods on moisture ratio and rehydration of pumpkin slices. *Food Chemistry*, *195*, 104–109.

Serment‐Moreno, V., Franco‐Vega, A., Escobedo‐Avellaneda, Z., Fuentes, C., Torres, J. A., Dibildox‐Alvarado, E., & Welti‐Chanes, J. (2017). The Logistic‐Exponential Weibull Model as a Tool to Predict Natural Microflora Inactivation of Agave Mapsiaga Aguamiel (Agave Sap) by High Pressure Treatments. *Journal of Food Processing and Preservation, 41*(2), e12816.

Sharif, I., Adewale, P., Dalli, S. S., & Rakshit, S. (2018). Microwave pretreatment and optimization of osmotic dehydration of wild blueberries using response surface methodology. Food Chemistry.

Sharma, R., Joshi, V., Chauhan, S., Chopra, S., & Lal, B. (1991). Application of osmosis-osmo-canning of apple rings. *Journal of Food Science and Technology, 28*(2), 86-88.

Shi, J., Pan, Z., McHugh, T. H., Wood, D., Hirschberg, E., & Olson, D. (2008). Drying and quality characteristics of fresh and sugar-infused blueberries dried with infrared radiation heating. *LWT - Food Science and Technology*, *41*(10), 1962–1972.

Simpson, R., Ramírez, C., Nuñez, H., Jaques, A., & Almonacid, S. (2017). Understanding the success of Page's model and related empirical equations in fitting experimental data of diffusion phenomena in food matrices. *Trends in Food Science & Technology, 62*, 194-201.

Singh, M., Shivhare, U., Singh, H., & Bawa, A. (1999). Osmotic concentration kinetics of Amla preserve. *Indian Food Packer, 53*, 13-22.

Skrovankova, S., Sumczynski, D., Mlcek, J., Jurikova, T., & Sochor, J. (2015). Bioactive Compounds and Antioxidant Activity in Different Types of Berries. *International Journal of Molecular Sciences*, 16(10), 24673.

Sonmete, M. H., Mengeş, H. O., Ertekin, C., & Özcan, M. M. (2017). Mathematical modeling of thin layer drying of carrot slices by forced convection. *Journal of Food Measurement and Characterization, 11*(2), 629-638.

Sonmete, M. H., Mengeş, H. O., Ertekin, C., & Özcan, M. M. (2017). Mathematical modeling of thin layer drying of carrot slices by forced convection. *Journal of Food Measurement and Characterization, 11*(2), 629-638.

Souraki, B. A., Ghaffari, A., & Bayat, Y. (2012). Mathematical modeling of moisture and solute diffusion in the cylindrical green bean during osmotic dehydration in salt solution. *Food and bioproducts processing*, *90*(1), 64-71.

Statistics-Canada. (2017). Fruit and vegetable production, 2016. http://www.statcan.gc.ca/daily-quotidien/170201/dq170201c-eng.htm.

Stojanovic, J., & Silva, J. L. (2006). Influence of osmoconcentration, continuous high-frequency ultrasound and dehydration on properties and microstructure of rabbiteye blueberries. *Drying Technology*, *24*(2), 165–171.

Stojanovic, J., & Silva, J. L. (2007). Influence of osmotic concentration, continuous high frequency ultrasound and dehydration on antioxidants, colour and chemical properties of rabbiteye blueberries. Food Chemistry, 101(3), 898-906.

Strik, B. C. (2007). Horticultural practices of growing highbush blueberries in the ever-expanding US and global scene. *Journal-american pomological society*, 61(3), 148.

Strik, B. C. (2007). Horticultural practices of growing highbush blueberries in the ever-expanding US and global scene. *Journal-american pomological society, 61*(3), 148.

Strik, B. C., & Yarborough, D. (2005). Blueberry production trends in North America, 1992 to 2003, and predictions for growth. HortTechnology, 15(2), 391-398.

Struck, S., Plaza, M., Turner, C., & Rohm, H. (2016). Berry pomace–a review of processing and chemical analysis of its polyphenols. *International Journal of Food Science & Technology,* 51(6), 1305-1318.

Su, X., Zhang, J., Wang, H., Xu, J., He, J., Liu, L., Zhang, T., Chen, R., & Kang, J. (2017). Phenolic Acid Profiling, Antioxidant, and Anti-Inflammatory Activities, and miRNA Regulation in the Polyphenols of 16 Blueberry Samples from China. Molecules, 22(2), 312.

Sunjka, P., & Raghavan, G. (2004). Assessment of pretreatment methods and osmotic dehydration for cranberries. Canadian Biosystems Engineering, 46(1), 45-48.

Tan, J. C., Chuah, C. H., & Cheng, S. F. (2017). A combined microwave pretreatment/solvent extraction process for the production of oil from palm fruit: optimisation, oil quality and effect of prolonged exposure. Journal of the Science of Food and Agriculture, 97(6), 1784-1789.

Tarhan, S. (2007). Selection of chemical and thermal pretreatment combination for plum drying at low and moderate drying air temperatures. *Journal of Food Engineering,* 79(1), 255-260.

Teaotia, S., Mehta, G., Tomar, M., & Garg, R. (1976). Studies on dehydration of tropical fruits in Uttar Pradesh. I. mango (Mangifera indica L.). *Indian Food Packer*.

Telis, V., Murari, R., & Yamashita, F. (2004). Diffusion coefficients during osmotic dehydration of tomatoes in ternary solutions. Journal of Food Engineering, 61(2), 253-259.

Thalerngnawachart, S., & Duangmal, K. (2016). Influence of humectants on the drying kinetics, water mobility, and moisture sorption isotherm of osmosed air-dried papaya. *Drying Technology, 34*(5), 574-583.

Tiroutchelvame, D., Sivakumar, V., & Maran, P. J. (2015). Mass transfer kinetics during osmotic dehydration of amla (Emblica officinalis L.) cubes in sugar solution. *Chemical Industry and Chemical Engineering Quarterly, 21*(4), 547-559.

Tiwari, A. K., Hasan, M. M., & Islam, M. (2013). Effect of ambient temperature on the performance of a combined cycle power plant. *Transactions of the Canadian Society for Mechanical Engineering, 37*(4), 1177-1188.

Tortoe, C. (2010). A review of osmodehydration for the food industry. African Journal of Food Science, 4(6), 303-324.

Tortoe, C., Orchard, J., & Beezer, A. (2009). Effect of agitation and antagonism between sucrose and sodium chloride on mass transfer during osmo-dehydration in plant materials.

Torki-Harchegani, M., Ghasemi-Varnamkhasti, M., Ghanbarian, D., Sadeghi, M., & Tohidi, M. (2016). Dehydration characteristics and mathematical modelling of lemon slices drying undergoing oven treatment. *Heat and Mass Transfer*, *52*(2), 281-289.

USDA-NASS. (2017). Noncitrus fruits and nuts 2016 summary. *United States Department of Agriculture (USDA) and National Agricultural Statistics Service Handbook.*

Vega-Gálvez, A., Lara, E., Flores, V., Di Scala, K., & Lemus-Mondaca, R. (2012). Effect of Selected Pretreatments on Convective Drying Process of Blueberries (var. O'neil). *Food and Bioprocess Technology*, *5*(7), 2797–2804.

Vega-Gálvez, A., Zura-Bravo, L., Lemus-Mondaca, R., Martinez-Monzó, J., Quispe-Fuentes, I., Puente, L., & Di Scala, K. (2015). Influence of drying temperature on dietary fibre, rehydration properties, texture and microstructure of Cape gooseberry

(Physalis peruviana L.). Journal of Food Science and Technology, 52(4), 2304-2311.

Verma, D., Kaushik, N., & Rao, P. S. (2014). Application of high hydrostatic pressure as a pretreatment for osmotic dehydration of banana slices (Musa cavendishii) finish-dried by dehumidified air drying. Food and Bioprocess Technology, 7(5), 1281-1297.

Videv, K., Tanchev, S., Sharma, R., & Joshi, V. (1990). Effect of sugar syrup concentration and temperature on the rate of osmotic dehydration of apples. *Journal of Food Science and Technology (Mysore), 27*(5), 307-308.

Vishwanathan, K. H., Giwari, G. K., & Hebbar, H. U. (2013). Infrared assisted dry-blanching and hybrid drying of carrot. Food and Bioproducts Processing, 91(2), 89-94.

Wang, H., Fu, Q., Chen, S., Hu, Z., & Xie, H. (2018). Effect of Hot-Water Blanching Pretreatment on Drying Characteristics and Product Qualities for the Novel Integrated Freeze-Drying of Apple Slices, *2018*.

Wang, H., Zhang, M., & Mujumdar, A. S. (2014). Comparison of Three New Drying Methods for Drying Characteristics and Quality of Shiitake Mushroom (Lentinus edodes). *Drying Technology*, *32*(15), 1791–1802.

Wang, J., & Sheng, K. (2006). Far-infrared and microwave drying of peach. LWT-Food Science and Technology, 39(3), 247-255.

Welti-Chanes, J., & Velez-Ruiz, J. F. (2016). Combined Effect of High Hydrostatic Pressure Pretreatment and Osmotic Stress on Mass Transfer during Osmotic Dehydration. In Transport Phenomena in *Food Processing* (pp. 131-146): CRC

Press.

Wilton, P. d. S., Sousa, N. J., Palmeira, G. J., & Maria, D. P. d. S. e. S. C. (2018). Obtaining anthocyanin from jambolan fruit: Kinetics, extraction rate, and prediction of process time for different agitation frequencies. *Food Science & Nutrition, 0*(0).

Winny, R., & Valerie, O. (2011). Blueberries and Their Anthocyanins: Factors Affecting Biosynthesis and Properties. *Comprehensive Reviews in Food Science and Food Safety*, 10(6), 303-320.

Wojdyło, A., Figiel, A., & Oszmiański, J. (2009). Effect of drying methods with the application of vacuum microwaves on the bioactive compounds, color, and antioxidant activity of strawberry fruits. *Journal of Agricultural and Food Chemistry,* 57(4), 1337-1343.

Wong, W. H., Lee, W. X., Ramanan, R. N., Tee, L. H., Kong, K. W., Galanakis, C. M., Sun, J., & Prasad, K. N. (2015). Two level half factorial design for the extraction of phenolics, flavonoids and antioxidants recovery from palm kernel by-product. Industrial Crops and Products, 63, 238-248.

Wu, B., Pan, Z., Qu, W., Wang, B., Wang, J., & Ma, H. (2014). Effect of simultaneous infrared dry-blanching and dehydration on quality characteristics of carrot slices. LWT-*Food Science and Technology*, 57(1), 90-98.

Xiao, C., Zhu, L., Luo, W., Song, X., & Deng, Y. (2010). Combined action of pure oxygen pretreatment and chitosan coating incorporated with rosemary extracts on the quality of fresh-cut pears. *Food Chemistry*, 121(4), 1003-1009.

Yadav, A. K., & Singh, S. V. (2014). Osmotic dehydration of fruits and vegetables: a review. *Journal of Food Science and Technology*, 51(9), 1654-1673.

Yemmireddy, V. K., Chinnan, M. S., Kerr, W. L., & Hung, Y.-C. (2013). Effect of drying method on drying time and physico-chemical properties of dried rabbiteye blueberries. LWT - *Food Science and Technology*, 50, 739-745.

Yonny, M. E., Medina, A. V., Nazareno, M. A., & Chaillou, L. L. (2018). Enhancement in the oxidative stability of green peas by Ilex paraguariensis addition in a blanching process before their refrigerated and frozen storage. LWT, 91, 315-321.

Yu, Y., Jin, T. Z., Fan, X., & Wu, J. (2018). Biochemical degradation and physical migration of polyphenolic compounds in osmotic dehydrated blueberries with pulsed electric field and thermal pretreatments. *Food Chemistry*, *239*, 1219–1225.

Yu, Y., Jin, T. Z., Fan, X., & Xu, Y. (2017). Osmotic dehydration of blueberries pretreated with pulsed electric fields: Effects on dehydration kinetics, and microbiological and nutritional qualities. *Drying Technology*, 35(13), 1543-1551.

Yuanshan, Y., Tony, J., & Gengsheng, X. (2017). Effects of pulsed electric fields pretreatment and drying method on drying characteristics and nutritive quality of blueberries. Journal of Food Processing and Preservation.

Vallespir, F., Cárcel, J. A., Marra, F., Eim, V. S., & Simal, S. (2018). Improvement of Mass Transfer by Freezing Pre-treatment and Ultrasound Application on the Convective Drying of Beetroot (Beta vulgaris L.). *Food and Bioprocess Technology*, *11*(1), 72-83.

Zahoor, I., & Khan, M. (2017). Mass Transfer Kinetics of Osmotic Dehydration of Pineapple. J. Food Process. Technol, 8, 653.

Zhang, M., Chen, H., Mujumdar, A. S., Tang, J., Miao, S., & Wang, Y. (2017). Recent developments in high-quality drying of vegetables, fruits, and aquatic products.

Critical Reviews in Food Science and Nutrition, 57(6), 1239-1255.

Zhao, Y.-Y., Yi, J.-Y., Bi, J.-F., Chen, Q.-Q., Zhou, M., & Zhang, B. (2018). Improving of texture and rehydration properties by ultrasound pretreatment for infrared-dried shiitake mushroom slices. *Drying Technology*, 1-11.

Zielinska, M., & Markowski, M. (2016). The influence of microwave-assisted drying techniques on the rehydration behavior of blueberries (Vaccinium corymbosum L.). Food Chemistry, 196, 1188-1196.

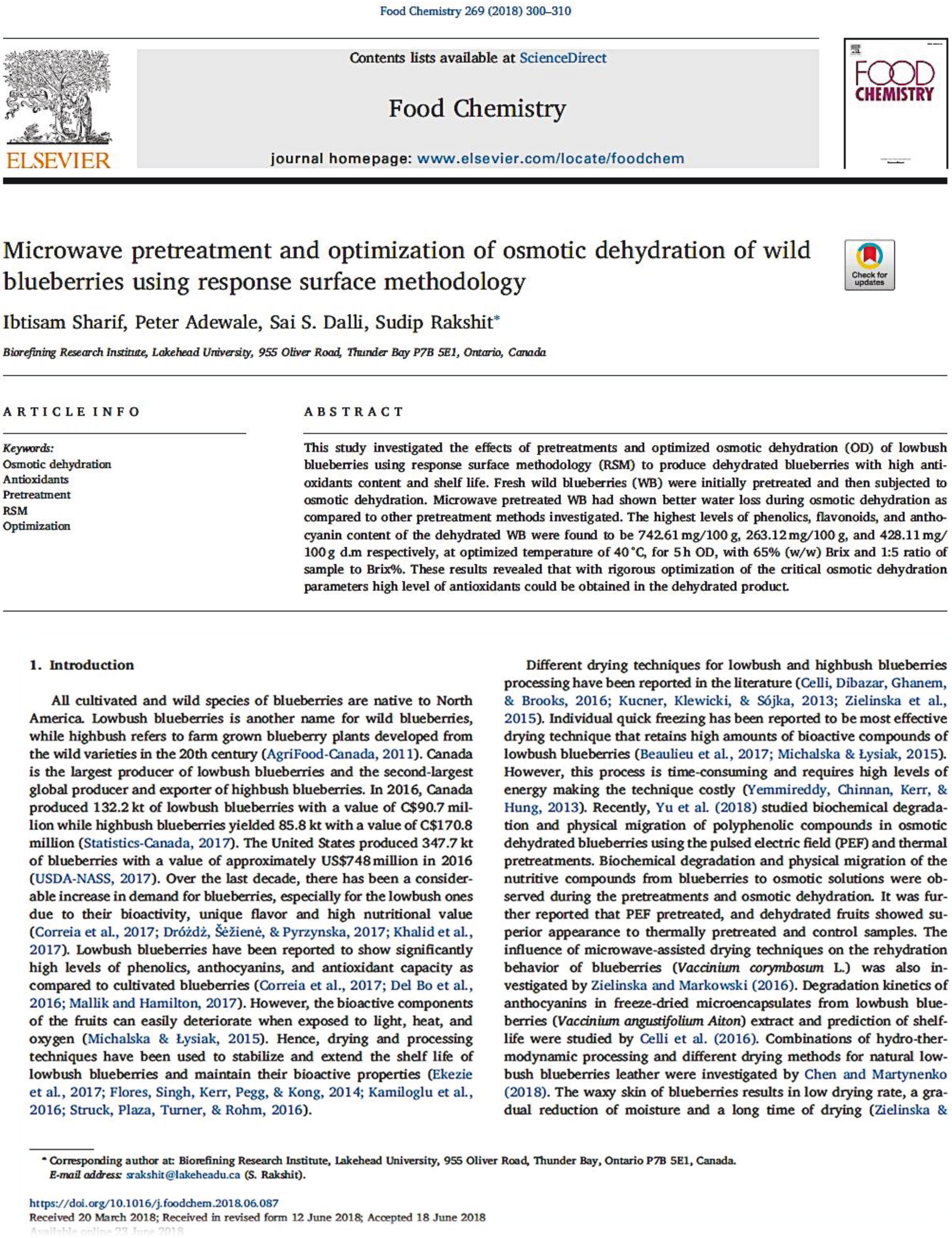
Zielinska, M., & Michalska, A. (2016). Microwave-assisted drying of blueberry (Vaccinium corymbosum L.) fruits: Drying kinetics, polyphenols, anthocyanins, antioxidant capacity, colour and texture. Food Chemistry, 212, 671-680.

Zielinska, M., & Markowski, M. (2018). Effect of microwave-vacuum, ultrasonication, and freezing on mass transfer kinetics and diffusivity during osmotic dehydration of cranberries. *Drying Technology,* 36(10), 1158-1169.

Zielinska, M., Sadowski, P., & Błaszczak, W. (2015). Freezing/thawing and microwave-assisted drying of blueberries (Vaccinium corymbosum L.). *LWT - Food Science and Technology*, 62(1, Part 2), 555-563.

Zielinska, M., Sadowski, P., & Błaszczak, W. (2016). Combined hot air convective drying and microwave-vacuum drying of blueberries (Vaccinium corymbosum L.): Drying kinetics and quality characteristics. *Drying Technology*, *34*(6), 665–684.

Appendix



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Microwave pretreatment and optimization of osmotic dehydration of wild blueberries using response surface methodology

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A B S T R A C T

This study investigated the effects of pretreatments and optimized osmotic dehydration (OD) of lowbush blueberries using response surface methodology (RSM) to produce dehydrated blueberries with high antioxidants content and shelf life. Fresh wild blueberries (WB) were initially pretreated and then subjected to osmotic dehydration. Microwave pretreated WB had shown better water loss during osmotic dehydration as compared to other pretreatment methods investigated. The highest levels of phenolics, flavonoids, and anthocyanin content of the dehydrated WB were found to be 742.61 mg/100 g, 263.12 mg/100 g, and 428.11 mg/100 g d.m respectively, at optimized temperature of 40 °C, for 5 h OD, with 65% (w/w) Brix and 1:5 ratio of sample to Brix%. These results revealed that with rigorous optimization of the critical osmotic dehydration parameters high level of antioxidants could be obtained in the dehydrated product.

1. Introduction

All cultivated and wild species of blueberries are native to North America. Lowbush blueberries is another name for wild blueberries, while highbush refers to farm grown blueberry plants developed from the wild varieties in the 20th century (AgriFood-Canada, 2011). Canada is the largest producer of lowbush blueberries and the second-largest global producer and exporter of highbush blueberries. In 2016, Canada produced 132.2 kt of lowbush blueberries with a value of C$90.7 million while highbush blueberries yielded 85.8 kt with a value of C$170.8 million (Statistics-Canada, 2017). The United States produced 347.7 kt of blueberries with a value of approximately US$748 million in 2016 (USDA-NASS, 2017). Over the last decade, there has been a considerable increase in demand for blueberries, especially for the lowbush ones due to their bioactivity, unique flavor and high nutritional value (Correia et al., 2017; Dróżdż, Šėžienė, & Pyrzynska, 2017; Khalid et al., 2017). Lowbush blueberries have been reported to show significantly high levels of phenolics, anthocyanins, and antioxidant capacity as compared to cultivated blueberries (Correia et al., 2017; Del Bo et al., 2016; Mallik and Hamilton, 2017). However, the bioactive components of the fruits can easily deteriorate when exposed to light, heat, and oxygen (Michalska & Łysiak, 2015). Hence, drying and processing techniques have been used to stabilize and extend the shelf life of lowbush blueberries and maintain their bioactive properties (Ekezie et al., 2017; Flores, Singh, Kerr, Pegg, & Kong, 2014; Kamiloglu et al., 2016; Struck, Plaza, Turner, & Rohm, 2016).

Different drying techniques for lowbush and highbush blueberries processing have been reported in the literature (Celli, Dibazar, Ghanem, & Brooks, 2016; Kucner, Klewicki, & Sójka, 2013; Zielinska et al., 2015). Individual quick freezing has been reported to be most effective drying technique that retains high amounts of bioactive compounds of lowbush blueberries (Beaulieu et al., 2017; Michalska & Łysiak, 2015). However, this process is time-consuming and requires high levels of energy making the technique costly (Yemmireddy, Chinnan, Kerr, & Hung, 2013). Recently, Yu et al. (2018) studied biochemical degradation and physical migration of polyphenolic compounds in osmotic dehydrated blueberries using the pulsed electric field (PEF) and thermal pretreatments. Biochemical degradation and physical migration of the nutritive compounds from blueberries to osmotic solutions were observed during the pretreatments and osmotic dehydration. It was further reported that PEF pretreated, and dehydrated fruits showed superior appearance to thermally pretreated and control samples. The influence of microwave-assisted drying techniques on the rehydration behavior of blueberries (*Vaccinium corymbosum* L.) was also investigated by Zielinska and Markowski (2016). Degradation kinetics of anthocyanins in freeze-dried microencapsulates from lowbush blueberries (*Vaccinium angustifolium Aiton*) extract and prediction of shelf-life were studied by Celli et al. (2016). Combinations of hydro-thermodynamic processing and different drying methods for natural lowbush blueberries leather were investigated by Chen and Martynenko (2018). The waxy skin of blueberries results in low drying rate, a gradual reduction of moisture and a long time of drying (Zielinska &

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Michalska, 2016). The application of different pretreatments before osmotic dehydration or second stage drying would reduce mechanical resistance and increase moisture permeation through the skin.

Zielinska et al. (2015) investigated the freezing/thawing pretreatment and microwave-assisted drying of blueberries (*Vaccinium corymbosum L.*). They reported that freezing/thawing promotes high moisture transfer during drying and reduces drying time as compared to drying of blueberries without freezing/thawing pretreatment. Rodriguez, Zaro, Lemoine, and Mascheroni (2016) evaluated the final quality of highbush blueberries after microwave drying by comparing two pretreatment techniques (osmotic dehydration and hot air drying). They reported that combination of hot air–microwave drying technique decreased the process time and improved drying rate as compared to the osmotic dehydration–microwave technique. Yu, Jin, Fan, and Xu (2017) attempted pulsed electric fields (PEF) pretreatment on osmotic dehydration of blueberries, and its effects on dehydration kinetics, microbiological qualities, and nutritional qualities. It was reported that higher rates of water loss and solid gain during osmotic dehydration were obtained using PEF pretreatment while the dehydration time was reduced from 130 to 48 h. However, there is a need for a rigorous optimization of the osmotic dehydration parameters such as sucrose concentration (Brix), temperature, Brix to sample ratio, and treatment time using an RSM. It is a useful statistical technique which has been applied in research to optimize complex variable processes. Multiple regression and correlation analyzes are the mains tools of RSM employ to assess the effects of two or more independent variables on the dependent parameters (He et al., 2016; Jiang, Yang, & Shi, 2017). The main advantage of using RSM is the number of experimental runs required to generate a statistically acceptable result, could be reduced (Chen et al., 2018; Ganesan et al., 2018).

The objective of this study was to investigate the effects of pretreatment and the optimization of crucial osmotic dehydration process parameters using RSM with the expectation (hypothesis) to maintain the antioxidant content and quality of the final product of dried lowbush blueberries. To the best of our knowledge, the application of rigorous optimization techniques for lowbush blueberries osmotic dehydration has not been reported in the literature. The optimization of osmotic dehydration variables using RSM to understand the effect of these variables on dehydration performance and dried fruit quality in term of antioxidant content would provide important information in designing and optimizing a drying method for wild blueberries.

2. Materials and methods

2.1. Materials

Fresh WB were harvested from the forest in Nipigon, Ontario, Canada and stored at −18 °C until used. The initial moisture content of the wild blueberries was estimated to be 82.38% on a wet basis. Sucrose used in the osmotic dehydration experiments was purchased from a local market in Thunder Bay, Ontario, Canada. Folin-Ciocalteu reagent, hydrochloric acid (HCl), sodium carbonate, methanol, sodium nitrate, aluminum chloride, potassium chloride buffer solution (pH 1.0), sodium acetate buffer solution (pH 4.5), and sodium hydroxide were purchased from Fisher Scientific (Ottawa, ON, Canada). Gallic acid and catechin standard were purchased from Sigma Aldrich (Oakville, ON, Canada). The blueberries samples were removed from the freezer and allowed to thaw for 1 h before the pretreatment and osmotic dehydration (OD) experiments.

2.2. Osmotic solution and sample preparation

WB are usually frozen immediately after harvest to prevent deterioration. Before further processing, the samples were thawed at room temperature for one hour. The thawed WB sample was gently wiped with soft wipe tissue paper to remove moisture on the surface of the fruit. Thawed WB was the control sample with the initial phenolic, flavonoid, and anthocyanin content estimated as 1394.7, 445.1, and 640.4 (mg/100 g of d.m), respectively. Sucrose solutions were prepared with distilled water with concentrations: 60%, 65%, and 70% Brix (Magwaza & Opara, 2015; Yu et al., 2018). The thawed blueberries samples (10 g) were weighed and placed in the sucrose solutions. All experiments were carried out in duplicates.

2.3. Pretreatments of WB

The waxy skin of blueberries limits the osmotic dehydration by lowering drying rate resulting in extended time requirements. In order to speed up the drying process, four pretreatment techniques (immersion in boiling water treatment, ultrasound water-bath treatment, ultrasound probe treatment, and microwave treatment) were investigated. For the boiling water pretreatment, thawed WB samples were placed in a sieve and immersed in boiling water for 15 s (Kucner et al., 2013). The fruits were then cooled down by immersion in cold water. In the ultrasound water-bath pretreatment specified amounts of thawed WB samples were placed in 250 mL conical flask containing 65% Brix solution resulting in a sample to sucrose solution ratio of 1:4. The flask was placed in an ultrasonic water-bath (Fisher Scientific Ultrasonic Bath; 5.7 L, vibration frequency of 40 kHz, 110 W) for 15 min. For the ultrasound probe pretreatment, a specific amount of thawed WB samples was placed in 250 mL conical flasks containing 65% Brix solution at a sample ratio of 1:4. The fruit samples in the flask were subjected to ultrasound treatment on Digital Sonifier (model 250, Brandson Ultrasonication Corporation, Connecticut, USA) equipped with a microtip-tapered probe having a diameter of 3.2 mm diameter. The probe amplitude, cycle, and pulse were set to be 30%, 0.5 per s, and 0.5 per s, respectively. Ultrasound treatment time was varied with duration of 2, 5, and 10 min for different sets of samples. During microwave pretreatment specified amounts of thawed WB samples was placed into 250 mL conical flask containing 65% Brix solution at a sample ratio of 1:4. A kitchen microwave oven (Danby products DMW753BL – 800 W, Guelph, ON, Canada) was used to pretreat the samples before OD. The microwave treatment time was varied to levels of 30, 45, and 60 s using different sets of samples. All the experiments were carried out in duplicate.

2.4. Osmotic dehydration after microwave pretreatment

Previously weighed WB collected after the microwave pretreatment process were introduced into osmotic solutions for dehydration. The different parameters studied were sugar concentrations (60%, 65%, and 70% Brix w/w) under different temperatures (30, 40, and 50 °C), processing times (2, 5, and 8 h) and sample to osmotic solution ratio (1:2, 1:4, and 1:6). Different combinations of the process parameters were maintained as per the experimental design (Section 2.8). The sucrose solution and the WB were taken in 250 mL Erlenmeyer flasks and placed in temperature, time and agitation-controlled incubator shaker (New Brunswick Innova 44, Mississauga, ON, Canada). The Erlenmeyer flasks were wrapped in parafilm during the experiments to prevent evaporation from the osmotic solution. Agitation is important to improve the mass transfer and prevent the formation of a dilute solution film around the samples during the experiment. It also results in uniform concentration and temperature profile inside the solution. An agitation speed of 200 rpm was maintained for all the experiments as this is considered sufficient for such system (Kucner et al., 2013).

At the end of each runtime, determined according to the experimental design, the flasks containing the sample were withdrawn from the incubator shaker. The WB samples were taken out from the osmotic medium, washed for 30 s with distilled water on a rubber mesh, and gently wiped with an absorbent paper and then weighed using an analytical balance (Sartorius-Secura, Goettingen, Germany) with an accuracy of ± 0.0001 g. A refractometer (VEE GEE BX-90) was used to

Table 1
CCD in coded forms of process variables and values of experimental data of response variables for osmotic dehydrated WB.

Run	Coded parameter values				Antioxidant content		
	Temperature	Time	Brix	Sample ratio	Phenolics (Garlic acid eq.)	Flavonoids (Catechin eq.)	Anthocyanin (C3G eq.)
	X1	X2	X3	X4			
1	1	−1	−1	−1	493.460	76.389	173.000
2	1	1	−1	1	543.810	93.333	243.136
3	0	0	0	0	757.460	280.000	437.511
4	−1	1	1	−1	483.302	73.889	183.688
5	−1	1	−1	−1	499.365	85.278	199.719
6	0	0	1	0	782.857	226.111	442.520
7	−1	−1	−1	1	701.905	205.278	401.608
8	0	0	0	1	711.429	220.833	412.462
9	1	0	0	0	435.873	67.222	135.595
10	1	−1	1	1	673.333	202.500	373.387
11	0	0	0	0	811.429	282.778	471.743
12	−1	1	1	1	520.794	92.500	220.425
13	0	−1	0	0	690.794	279.444	391.589
14	0	0	0	0	752.698	278.333	452.540
15	−1	−1	−1	−1	588.254	108.611	228.441
16	1	−1	−1	1	528.730	91.667	228.441
17	1	−1	1	−1	534.286	90.556	234.452
18	1	1	1	1	630.476	120.000	331.306
19	1	1	1	−1	588.254	106.389	288.557
20	0	0	0	0	751.111	285.556	410.793
21	−1	0	0	0	514.444	92.778	214.414
22	0	1	0	0	681.270	132.778	381.403
23	0	0	0	0	759.048	286.667	418.307
24	−1	−1	1	1	657.460	128.056	358.024
25	−1	1	−1	1	488.381	83.056	188.363
26	0	0	−1	0	692.381	151.389	352.680
27	−1	−1	1	−1	535.873	164.167	235.120
28	1	1	−1	−1	427.429	68.056	127.579
29	0	0	0	−1	651.111	126.944	350.677
30	0	0	0	0	751.111	288.333	431.666

measure the solids gain content (SG) of the osmotic solution at 20 °C. The AOAC 930.04 standard method was employed to determine the moisture content of the samples (AOAC, 1990). A pre-weighed amount of the sample was placed in a drying oven at 70 °C for 24 h until the sample weight was stabilized. The samples were then placed in the desiccator to cool down and then weighed again. The water loss during OD process was determined according to the expression of weight reduction and SG in previous studies (Lech, Michalska, Wojdyło, Nowicka, & Figiel, 2018; Nowicka, Wojdyło, Lech, & Figiel, 2015). The phenolics, flavonoid, and anthocyanins content were measured to evaluate the antioxidants content of WB after osmotic dehydration. All the experiments were done in duplicate, and the average value was taken for all the calculations.

2.5. Determination of phenolic content

According to de Souza et al. (2014), a 1.0 ± 0.001 g of the mashed sample was weighed into centrifuge tubes (15 mL) and filled to 10 mL with 2% HCl in methanol and then put in the Sonicator bath for 10 min. The mixtures were then centrifuged for 10 min at 2683× g, while the supernatant was transferred to another tube for further analysis. A standard calibration curve was developed for phenolics content using 99.98% gallic acid. A stock solution of gallic acid was prepared by weighing 25 mg in a 100 mL of methanol. Six different concentrations in the range of 10–200 μg/mL gallic acid were used to build the calibration curve. All calibration concentration points were run in duplicate. The absorbance of the solutions was then determined at a wavelength of 765 nm on a spectrophotometer (Thermo Scientific, Genesys 10S UV–VIS, Ottawa, ON, Canada) with water as the blank. The total phenolic content was expressed as mg of gallic acid equivalent (GAE/100 g of the sample) as determined from the standard curve generated with gallic acid (de Souza et al., 2014).

2.6. Determination of flavonoid content

From the extract, 100 μL was transferred into a 2 mL vial followed by 400 μL of distilled water and 30 μL of 5% Na_2NO_3. To the resultant mixture, 30 μL of 10% $AlCl_3$, 200 μL of 1 M NaOH and 240 μL were added with 5 min interval between each addition. The mixture was then agitated vigorously. The absorbance of the solution was recorded at a wavelength of 510 nm using a spectrophotometer (Thermo Scientific, Genesys 10S UV-VIS, Ottawa, ON, Canada). Distilled water was used as the blank. Total flavonoid content was expressed as mg of catechin/100 g of the sample using the standard curve generated with catechin (de Souza et al., 2014).

2.7. Determination of anthocyanin content

Two buffer solutions were prepared to enhance the absorbance of the sample on the spectrophotometer as previously reported by de Souza et al. (2014). A 100 μL of the extract was added to 900 μL of Buffer A in a 2 mL vial. Another 100 μL of the extract was added to 900 μL of buffer B in a separate 2 mL vial. The mixtures were equilibrated for 2 h in the dark. The absorbance of the buffer A solution and sample followed by buffer B solution and sample were obtained at 512 nm and 700 nm on a spectrophotometer to determine the amount of anthocyanin in the samples (de Souza et al., 2014; Lee, Durst, & Wrolstad, 2005). The anthocyanin content was expressed as mg cyanidin-3-glucoside/100 g of the sample using Eqs. (1) and (2).

$$\Delta A = (A_{512nm} - A_{700nm})_{pH1.0} - (A_{512nm} - A_{700nm})_{pH4.5} \quad (1)$$

$$Anthocyanin\ content = \frac{\Delta A \times MW \times DF \times 1000}{\varepsilon \times l} \quad (2)$$

where, ΔA = absorbance change, MW = molecular weight of cyanidin-

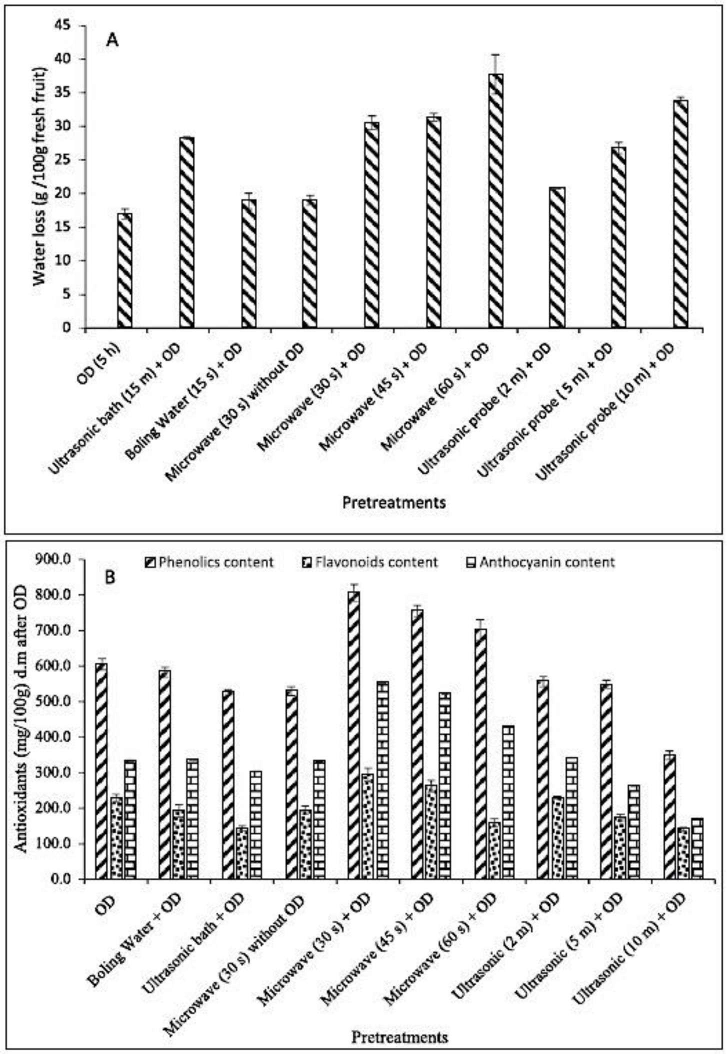

Fig. 1. Effects of pretreatments on (A) Changes in water loss (B) Changes in antioxidants during osmotic dehydration of WB.

3-glucoside (449.2 g/mol), Df = dilution factor of the sample, ε = molecular absorbance coefficient of cyanidin-3-glucoside (26,900 M^{-1} cm^{-1}), and 1000 = factor for conversion from g to mg.

2.8. Experimental design and statistical analysis

Four parameters, temperature (X1), treatment time (X2), sucrose concentration (X3), and sample to sucrose solution ratio (X4) were selected as the most important independent factors based on literature reports and preliminary experiments (De Mendonça, Corrêa, de Jesus Junqueira, Pereira, & d. A., & Vilela, M. B. , 2016; Yu et al., 2017). RSM was used to determine the number of runs and levels at which experiments were to be carried out. The central composite design (CCD) with four variables at three levels (Table 1) was employed to study responses regarding antioxidants content. The results of the experiments were used to determine the optimum combination of the variables for the best OD conditions. This is a face-centered design whereby the star points are at the center of each face of the factorial space (α = ± 1). This type of CCD requires three levels of each factor. The dependent variables were phenolics content, flavonoid, and anthocyanins. The complete design generated 30 experiments ($T_n = 2^f + 2f + K = 2^4 + 2*4 + 6 = 30$) as shown in Table 1. T_n represents the total number of experiments, f represents the number of independent variables, and K represents the number of center point runs. The center point runs provide a means for estimating the experimental error and a measure of lack of fit. The second order polynomial model (Eq. (3)) was fitted to the data. Three models of the following form were developed to relate three responses (Y): phenolics content, flavonoid, and anthocyanins to four process variables (x):

Table 2
Parametric effect summary estimates: (A) Phenolics content (B) Flavonoids content (C) Anthocyanin content.

A

Source	LogWorth	PValue
X1*X1	5.506	0.00000
X4	2.250	0.00562
X1*X3	1.770	0.01699
X2	1.755	0.01759
X1*X2	1.493	0.03211
X3	1.344	0.04532 ^
X3*X3	0.917	0.12095
X2*X4	0.587	0.25890
X2*X3	0.427	0.37406
X1	0.285	0.51854 ^
X3*X4	0.181	0.65929
X1*X4	0.146	0.71501
X4*X4	0.095	0.80386
X2*X2	0.033	0.92753

B

Source	LogWorth	PValue
X1*X1	5.034	0.00001
X2	2.776	0.00168
X1*X2	1.915	0.01217
X3	1.453	0.03525
X2*X2	1.110	0.07762
X4	0.972	0.10676
X1	0.876	0.13315 ^
X1*X4	0.661	0.21823
X4*X4	0.539	0.28896
X1*X3	0.515	0.30519
X2*X3	0.245	0.56875
X3*X4	0.154	0.70120
X3*X3	0.104	0.78673
X2*X4	0.037	0.91874

C

Source	LogWorth	PValue
X1*X1	5.653	0.00000
X4	2.926	0.00119
X3	1.909	0.01234
X1*X3	1.817	0.01522
X2	1.604	0.02487
X1*X2	1.500	0.03161
X2*X4	1.008	0.09817
X3*X3	0.383	0.41398
X2*X3	0.229	0.59036
X1	0.210	0.61653 ^
X2*X2	0.171	0.67387
X4*X4	0.092	0.80837
X1*X4	0.066	0.85992
X3*X4	0.017	0.96160

$$Y = a_0 + \sum_{i=1}^{4} a_i X_i + \sum_{i=1}^{4} a_{ii} X_i^2 + \sum_{i}^{3} \cdot \sum_{j=i+1}^{4} a_{ij} X_i X_j \quad (3)$$

where a_0 is a constant while a_i, a_{ii}, and a_{ij} are regression coefficients; x is the coded independent factor. A mathematical model was developed for each of the responses using multiple linear regression analysis which involves linear, quadratic, and interaction terms of the independent factors. The significant levels of the factors in the model were determined using analysis of variance (ANOVA) for each response. The degree of confidence in the data was estimated using student's *t*-test to determine the probability level to be less than 5%. The model's accuracy was checked by the coefficient of determination (R^2), and root means square error (RMSE). A good model will have a large predicted R^2 and a low RMSE.

2.9. *Determination of optimum condition*

The simultaneous optimization of the multiple responses was obtained using JMP® (Statistical Analysis Systems, Version 13.4, SAS Institute Inc., Cary, NC, USA) to determine an optimum condition of the variables for maximizing phenolics content, flavonoids content, and anthocyanins content. The optimum value for each factor was depicted using the desirability function method (Amami et al., 2017). The desirability function transforms response variable into a 0 to 1 scale. The transformed response, represented as d_i, can have many different shapes. A zero response represents a completely undesirable response, and a response of one represents the most desirable response. The overall desirability (D) combines d_i of several responses using geometric mean for simultaneous optimization of the responses (Eq. (4))

$$D = \sqrt[n]{(d_1 * d_2 * d_3 * \cdots * d_n)} \quad (4)$$

3. Results and discussion

3.1. *Effect of pretreatments before OD on WB water loss and antioxidants content*

Fig. 1 shows the influence of pretreatments (immersion in boiling water, ultrasonic water-bath, ultrasonic probe, and microwave) and OD on the water loss and antioxidants content of WB. It should be noted that the microwave and ultrasonic pretreatments were done in 65% Brix solution as our initial hot water pretreatment experiments showed considerable antioxidants loss as discussed later. This has also been reported in previous works (Moreno et al., 2016; Nikkhah, Khayamy, Heidari, & Jamee, 2007), and it was suggested that Brix solution would limit the loss of antioxidants. Changes in the water content of WB samples due to pretreatments were depicted in Fig. 1A. The water loss for WB samples treated with microwave for 60 s was observed to be the highest (37.71 g/100 g fresh fruit) of all the pretreatment techniques. Ultrasonic probe treatment for 10 min equally led to a significant water loss (33.72 g/100 g fresh fruit). All the three levels of microwave

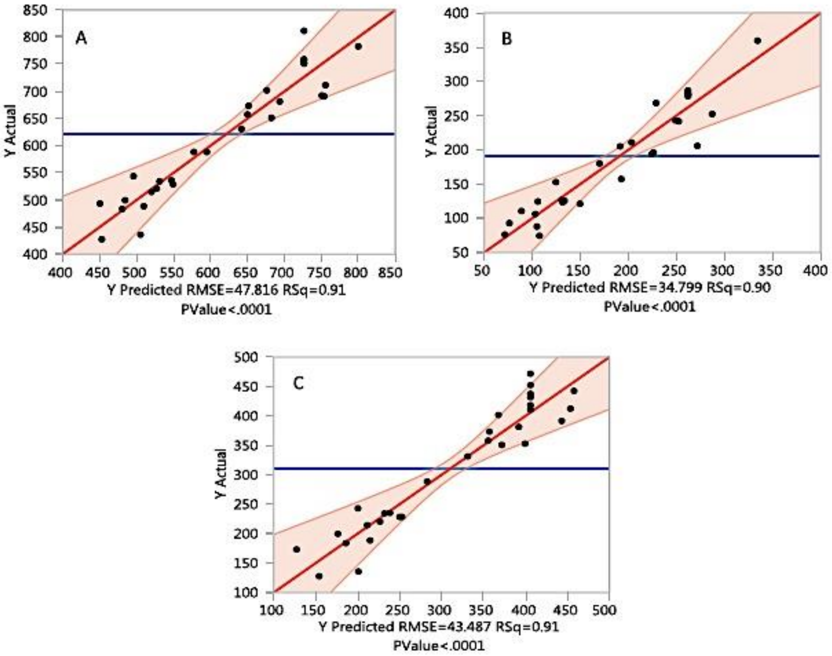

Fig. 2. Actual antioxidants concentration versus model predicted antioxidants in the dehydrated WB: (A) Phenolics content (B) Flavonoids (C) Anthocyanin content.

pretreatments showed a similar effect on the water loss during the OD process. In comparison to the control (OD without pretreatment), improved water migration out of the samples was observed in all the pretreatment techniques employed in this study. The significant improvement in water loss due to pretreatment was investigated using the Student's *t*-test at a 95% level of confidence. The test was carried out to compare the results of the osmotic dehydration experiments with and without pretreatment. The water loss by osmotic dehydration alone without any pretreatment was significantly different ($p < 0.05$) from all the samples resulted from pretreatment with subsequent osmotic dehydration. Although highest water loss was obtained at 60 s of microwave pretreatment, there was no significant difference ($p > 0.05$) among the three different treatment durations of microwave pretreatment. Similar results were reported in the studies conducted by Kucner et al. (2013) on the influence of selected osmotic dehydration and pretreatment parameters on dry matter and polyphenol content in highbush blueberry fruits.

For ultrasonic probe pretreatment, a significant difference ($p < 0.05$) was observed among the three levels of the treatment time. The water loss is directly proportional to the ultrasonic probe treatment time. Beyond 10 min of treatment time, the absolute disintegration of the WB to form fruit juice was obtained. It was also observed that dry matter migration from the fruits to the osmotic solution increased with treatment time for the ultrasonic probe pretreatment. Pretreatments had been proven to enhance water loss during the OD process. However, a major challenge was to reduce the loss of the antioxidants content as much as possible.

In comparison to the control (OD without pretreatment), a significant difference ($p < 0.05$) in the antioxidants content (phenolics, flavonoids, and anthocyanin) of the pretreated WB measured in dry matter basis was observed (Fig. 1B). Microwave pretreatment for 30 s showed the highest quantity of phenolic, flavonoid, and anthocyanin contents after OD process. Although more water loss was obtained with 60 s of microwave pretreatment (Fig. 1A), a significant amount of the antioxidants accompanied the mass transfer of water from the fruit tissue into the osmotic agent. Effect of only microwave pretreatment without five hours of OD was investigated to confirm that the significant difference in antioxidants' content was due to microwave alone. The results showed that microwave pretreatment facilitated the water loss during the OD treatment of the sample because more water loss was achieved during the OD period and the antioxidants content of the samples were retained in a large amount during the OD process. More water loss led to higher dry matter content during OD process with a corresponding increase in the antioxidant content in the dry matter of the sample per equivalent weight of the fresh sample (Fig. 1B). In a combined pretreatment using ohmic heating and pulsed vacuum, the treated samples retained more polyphenols after drying as compared to untreated samples (Moreno et al., 2016). Based on these results, the optimization experiments were carried out using 30 s microwave pretreatment for all the samples before the OD process.

3.2. Experimental data analysis

Multiple regression tests were carried out on the experimental data of the dependent variables (phenolics content, flavonoids content, and anthocyanin content) as shown in Table 1. The regression coefficients for the three models generated and the ANOVA of the proposed model are shown in Appendix 1. The mathematical equation in terms of coded factors for OD of microwave pretreated WB on phenolics content, flavonoid content, and anthocyanin content model are shown in Eqs. (5)–(7), respectively.

$$Y = 726.29 - 30.06X2 + 24.61X3 + 36.38X4 + 28.24X1X2 + 32.09X1X3 - 213.62X1X1 \quad (5)$$

$$Y = 262.02 - 31.33X2 + 18.98X3 + 24.79X1X2 - 141.54X1X1 \quad (6)$$

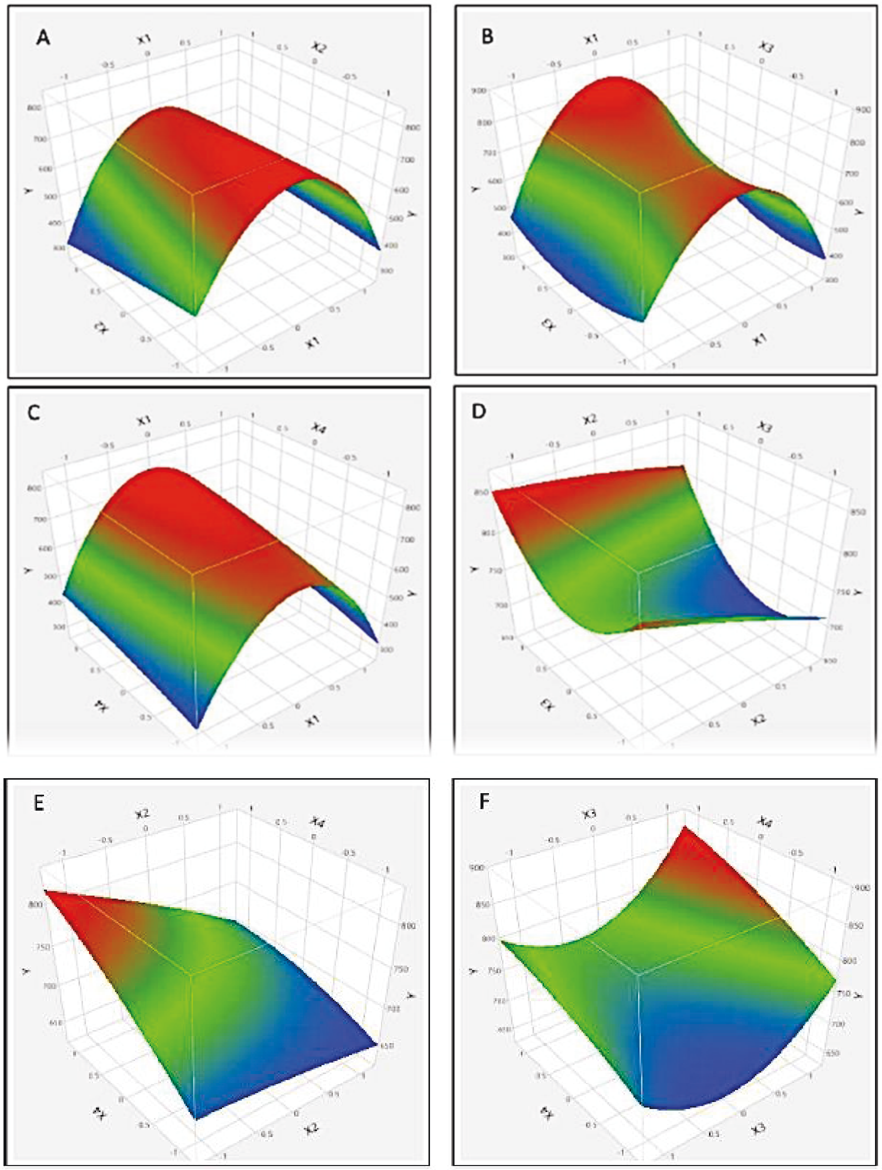

Fig. 3. Influence of process variables on phenolics content (A) Process temperature and OD time (B) Process temperature and Brix% (C) Process temperature and Sample ratio to Brix% (D) OD time and Brix% (E) OD time and Sample ratio to Brix% (F) Brix% and Sample ratio to Brix%.

$$Y = 406 - 25.55X2 + 29.14X3 + 40.88X4 + 25.7X1X2 + 29.78X1X3 - 199.9X1X1 \quad (7)$$

The quadratic model in coded unit showed the role of every variable and their interactions in independent variables at the level of confidence of 95% using student's *t*-test. Appendix 1A represents the regression coefficient, and ANOVA of phenolics content experimental data analysis. The significant effect of each of the factors based on the phenolics content of WB is depicted in the Appendix 1A. All the linear terms significantly influenced ($p < 0.05$) the amount of phenolics content of WB during OD except the process temperature. The linear effects related to OD treatment time and sucrose concentration for the decrease in water activity have been reported for the osmotic dehydrated pumpkin (Pinzi, Lopez-Gimenez, Ruiz, & Dorado, 2010) and yacon slices (De Mendonça et al., 2016). Food stability and shelf life of food products usually increase with a decrease in water activity. Although osmotic processes promote the reduction. The effect of temperature on the OD process might not significantly influence the phenolics content for the range of temperature investigated in this study. Kucner et al. (2013) had earlier reported that higher temperatures lead to substantial losses of phenolic compounds in the dehydrated material (30% after 2 h of dehydration at 70 °C). The temperature range employed in this study was taken such that it limits significant loss of

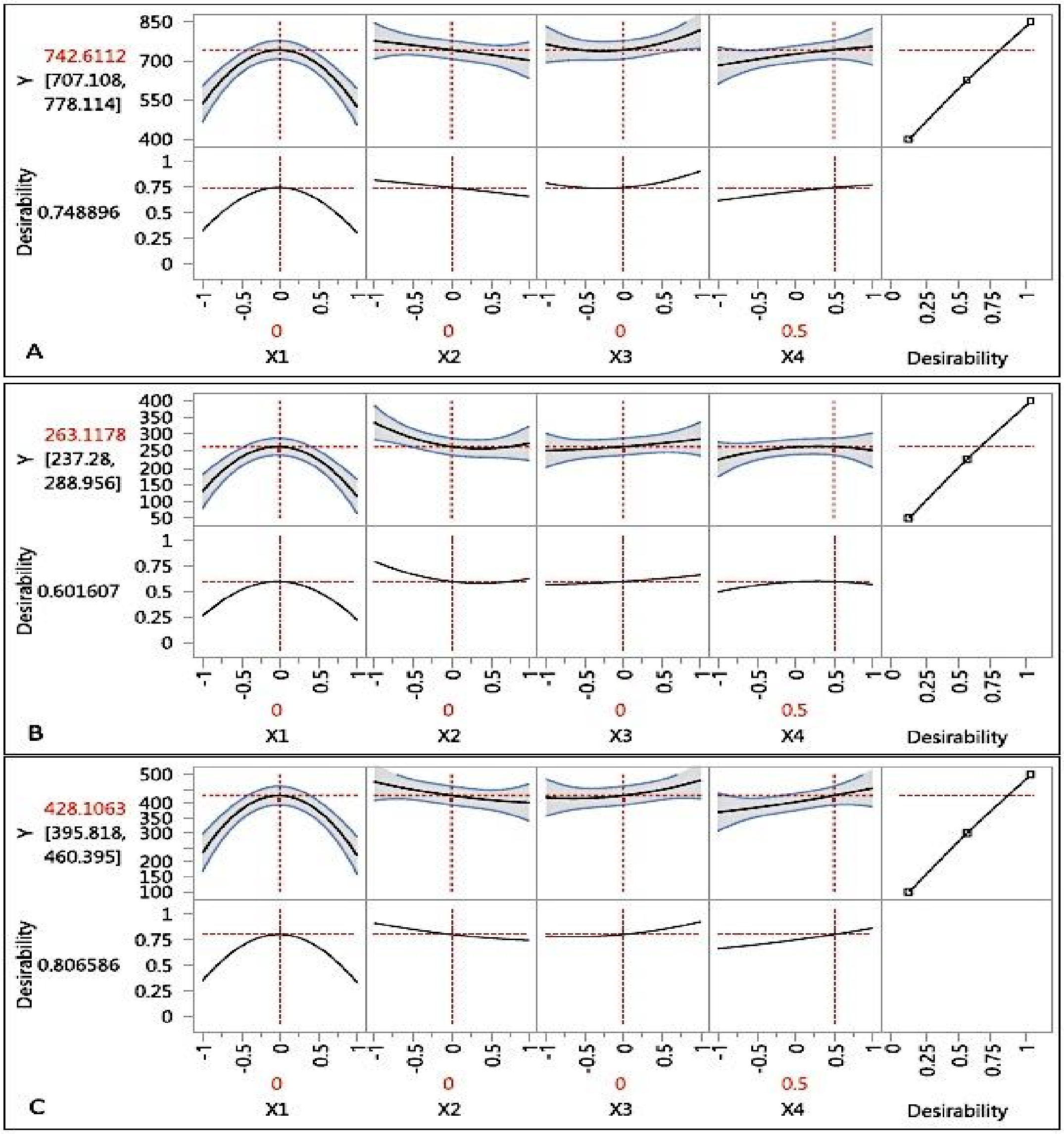

Fig. 4. Desirability plots of variables for maximum (A) Phenolic content (B) Flavonoid content (C) Anthocyanin content.

antioxidants. The quadratic effect of temperature was found to significantly influence ($p < 0.05$) the phenolics content of WB during the OD process. Other factors quadratic effect had no significant influence on the samples phenolics content after OD process. In the investigation of the effect of ultrasound-assisted osmotic dehydration pretreatment on the convective drying of strawberry, the authors reported that only the quadratic term of ultrasonic osmotic dehydration and temperature has a significant effect on water loss and weight reduction (Amami et al., 2017). De Mendonça et al. (2016) studied the optimization of osmotic dehydration of yacon slices and reported a significant quadratic effect of treatment time of osmotic dehydrated assisted ultrasound on the solid gain. Appendix 1B shows the significant effect of each of the independent variables on the flavonoids content of WB during OD process. Treatment time and Brix% were found to significantly influence ($p < 0.05$) the flavonoids content of WB, while the temperature and sample ratio to the osmotic agent were not significant. Although the linear effect of temperature was observed to be insignificant on flavonoids content, the quadratic effect of temperature was found to significantly influence ($p < 0.05$) the flavonoids content of WB during the OD process. Similar results as phenolic content were obtained for flavonoids content for temperature. For anthocyanin content, the significant effect of each of the independent variables on its variation in WB during the OD process was examined (Appendix 1C). All the linear terms were found to significantly influence ($p < 0.05$) the anthocyanin content of WB except the process temperature. Although the linear effect of temperature was observed to be insignificant on anthocyanins content, the quadratic term of temperature was found to significantly influence ($p < 0.05$) the anthocyanin content of WB during the OD process. Other factors quadratic terms had no significant influence on the samples anthocyanin content during the OD process.

3.3. Roles of process parameters on OD of WB

Further analysis to verify the order of significant effect of each independent variable and their interactions on the phenolic, flavonoid, and anthocyanin contents of WB are shown in Table 1. This technique uses Log Worth and p-values helps to prioritize and focus resources visually. The output shows the significant influence of each variable on the response in decreasing hierarchy. As shown in Table 2A, the most significant parameter for phenolics content of the osmotic dehydrated WB was the quadratic effect of temperature. The linear effect of sample ratio to the osmotic agent was the second most important parameter followed by the interaction between process temperature and Brix% for the phenolics content of WB. The linear effect of OD time was the fourth most significant parameter and then the interaction between process temperature and OD time in that decreasing hierarchy for the remaining linear and quadratic terms (Table 2A). Different patterns of significant effects of the linear, interactions, and quadratic terms were observed for the other two dependent responses (flavonoids and anthocyanin contents) of the osmotic dehydrated WB (Table 2B and C). The quadratic effect of temperature was also observed as the most significant parameter for both flavonoids and anthocyanin contents of WB, but other parameters varied accordingly between both responses. As it can be seen (Table 2B), the second most significant parameter for flavonoids content was the linear effect of the OD time followed by the interaction between temperature and OD time. On the other hand, the second most significant parameter for anthocyanin content was the linear effect of sample ratio to osmotic agent concentration followed by the linear effect of Brix% (Table 2C). The flavonoids content of WB was also affected by the quadratic effect of OD time (5th position). This term was ranked as the least significant parameter for phenolics content (Table 2A) and 11th position for anthocyanin content of WB (Table 2C). The linear effects of OD time and Brix% on all independent variables were found to be highly significant. Similar findings were reported in the study effect of ultrasound-assisted osmotic dehydration pretreatment on the convective drying of strawberry by Amami et al. (2017). The authors reported that only the quadratic term of ultrasonic osmotic dehydration time and temperature has a significant effect on water loss and weight reduction. They also reported that temperature had a significant negative effect on water loss and weight reduction in the quadratic term. The findings of our study showed only the quadratic term of temperature had a significant effect on phenolics, flavonoids, and anthocyanin content of WB at 5% level. The temperature equally had a significant negative effect on all the dependent variables in the quadratic term. The result indicated that temperature could act as a limiting factor due to disruption of cell membranes which could lead to loss of selectivity of the osmotic agent with an increase of the permeability of the cell wall for solute uptake (He et al., 2016). The interaction between OD time and Brix% was the least significant parameter for flavonoid content, while the interaction between Brix% and sample ratio to Brix % was the least significant for anthocyanin content of WB. These results reveal that the OD processing parameters could be used to improve a specific antioxidant content of WB during processing. This approach could be employed industrially during OD of WB.

3.4. Optima model fitness

The accuracy of the linear fit of the experimental data for the phenolic, flavonoid, and anthocyanin contents was shown by their model estimation parameters (Fig. 2). The model parameters such as coefficient of determination (R^2), root mean square error (RMSE), and p-value were used to justify the model reliability. The predictability of the regression models was adequate, statistically significant (p-value < 0.0001) with satisfactory coefficients of determination ($R^2 > 90\%$). These parameters are good indicators that the models can adequately predict response variable behavior. ANOVA for phenolics content, flavonoids content, and anthocyanin content showed that the second-order polynomial model (Eqs. (5)–(7)) was adequate to represent the actual relationship between the dependent and independent variables, with a high value of coefficient of determination ($R^2 = 0.91$ for phenolics content (Fig. 2A), $R^2 = 0.90$ for flavonoids content (Fig. 2B), and $R^2 = 0.91$ for anthocyanin content (Fig. 2C)).

The response surface was generated as a function of two independent parameters against the dependent variable as the third dimension. For each of the dependent variables, six combinations of response surface curves were generated from the four independent factors (Fig. 2, Appendices 2 and 3). The 3D-surface curves were plotted to visualize both the main and the interactive effects of two factors at a time. These figures provide useful information about the behavior of the system within the experimental design. The response surface plots for phenolics content of osmotic dehydrated WB are shown in Fig. 3(A–F), for significant factor interaction, resulted from the ANOVA (Appendix 1A). The interaction between temperature and OD time showed a maximum effect on the phenolics content of dehydrated WB (Fig. 3(A)). These two factors showed significant influence on the phenolics content of WB maximization which might due to the mass transfer of water enhanced by the combined effect of temperature and OD time. A similar pattern was observed in the interaction between temperature and Brix%, and temperature and sample ratio to Brix% on the phenolics content of WB as shown in Fig. 3(B and C). A possible decrease in the viscosity of the osmotic solution and reduction in the external resistance to mass transfer at WB surface might yield better water transfer responsible for this observation (Ahmed, Qazi, & Jamal, 2016; Amami et al., 2017). The interaction between OD time and Brix% showed a minimum impact on the phenolics content of the dehydrated WB (Fig. 3D), while the interaction between OD time and sample ratio to Brix% showed increased phenolics content (Fig. 3E). A minimum impact on phenolics content of WB was also observed based on the interaction between Brix% and sample ratio to Brix%, while the highest peak of their interaction tends toward the sample ratio to Brix% variable (Fig. 3F). The response surface plots for flavonoids content of osmotic dehydrated WB are shown in Appendix 2(A–F). The interaction between temperature and OD time, temperature and Brix%, and temperature and sample ratio to Brix% showed a maximum effect on the flavonoids content of dehydrated WB (Appendix 2(A–C)). The synergy effect of the two factors showed significant influence on the flavonoids content of WB maximization which might due to the mass transfer of water enhanced by the combined effects of the factors. The interaction between OD time and Brix% showed a minimum impact on the flavonoids content of the dehydrated WB (Appendix 2D), while the interaction between OD time and sample ratio to Brix% showed increased flavonoids content (Appendix 2E). A minimum impact on flavonoids content of WB was also observed based on the interaction between Brix % and sample ratio to Brix% while the highest peak of their interaction tends toward the sample ratio to Brix% variable (Appendix 3F). Similar results were observed for anthocyanin content of WB (Appendix 3(A–F)). The only exception was the interaction between Brix% and sample ratio to Brix% which showed a maximum effect on the flavonoids content of WB.

3.5. Optimization and model validation

The desirability function method described in the materials and methods section was employed to analyze the process parameters concerning the dependent variables (phenolics content, flavonoid content, and anthocyanin content) optimization. The desired levels for each of the operational conditions (temperature, OD time, Brix% and sample ratio to Brix%) was selected within the range defined by (Kucner et al., 2013), while the dependent variables were defined as maximum. Each of the dependent variables was analyzed separately. Fresh WB was the control sample with the initial phenolic, flavonoid, and anthocyanin content estimated as 1394.7, 445.1, and 640.4 (mg/100 g of d.m), respectively. The optimum value of phenolics content of the dehydrated WB was 742.61 mg/100 g d.m of WB at a process temperature of 40 °C (Fig. 4A), OD time of 5 h, Brix of 65% (w/w), and sample ratio to Brix% of 1:5. The increase in temperature from 40 to 50 °C showed a drastic decline in the phenolics content of WB. This is likely due to increasing the permeability of the cell wall which might lead to migration of antioxidant to the osmotic solution and possibility of solute uptake (De Mendonça et al., 2016). The prediction proved reliable as judged by the desirability of the predicted values of 0.75. Robustness of model is judge based on how close the desirability value is to 1.0, the closer the better the predictability of the model. A gradual decrease in phenolics content of WB was observed with increase in OD time. For flavonoids content, the optimum value of the dehydrated WB was 263.12 mg/100 g d.m of WB at a process temperature of 40 °C (Fig. 4B), OD time of 5 h, brix of 65% (w/w), and sample ratio to Brix% of 1:5. The independent variables showed similar effects as compared to phenolics content of WB with desirability value of 0.60. A similar trend of optimum processing parameters was observed for anthocyanin content of the dehydrated WB. The optimum value of the anthocyanin content of the dehydrated WB was 428.11 mg/100 g d.m of WB at a process temperature of 40 °C (Fig. 4C), OD time of 5 h, Brix of 65% (w/w), and sample ratio to Brix% of 1:5. The desirability of the predicted values was estimated as 0.81. Thus, the combination of coded values of X1, X2, X3, and X4 at 0, 0, 0, and 0.5, respectively produced the best antioxidants result and therefore presents the optimum condition except for the possible effect of interactions between the factors. The regression model was validated by performing the experiments at the optimum predicted conditions. The confirmatory experiments were performed in triplicate, and the results were compared with the predicted dependent variables. The resulting phenolics content of trial1, trial2, and trial3 were 725.8, 751.5, and 745.35 mg/100 g d.m, respectively. The average of phenolics content of the confirmatory tests was in the range of the predicted value, 742.61 mg/100 g d.m WB. Confirmatory tests were conducted for flavonoid content of the dehydrated WB. The resulting phenolics content of trial1, trial2, and trial3 were 270.25, 267.55, and 258.54 mg/100 g d.m, respectively. The same approach was used for anthocyanin content for trial1, trial2, and trial3 determined as 420.60, 431.23, and 425.80 mg/100 g d.m, respectively. The results from the confirmatory experiments agreed with the predicted values of phenolic, flavonoid, and anthocyanin contents.

4. Conclusions

Microwave pretreatment before osmotic dehydration significantly enhanced the dehydration of WB as compared to other pretreatment methods considered in this study. Retention of the antioxidants such as phenolics, flavonoids, and anthocyanins significantly improved in the dehydrated WB using microwave pretreatment. The factors influencing antioxidants of dehydrated WB using osmotic dehydration include OD time and Brix%. RSM results demonstrated to be an effective optimization technique for modeling the parametric effects of OD on the antioxidants content of dehydrated WB. The optimal conditions for maximum phenolics, flavonoids, and anthocyanin were 40 °C for temperature, 5 h for OD time, 65% (w/w) for Brix, and 1:5 for sample ratio to Brix% to obtain 742.61 mg/100 g d.m sample of phenolics, 263.12 mg/100 g d.m sample of flavonoids, and 428.11 mg/100 g d.m sample of anthocyanin. Microwave pretreatment of wild blueberries followed by dehydration under the optimized conditions produced a dehydrated WB product with low water activity and high antioxidant content.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.foodchem.2018.06.087.

References

AgriFood-Canada. (2011). Canadian blueberries. http://www.agr.gc.ca/eng/industry-markets-and-trade/buying-canadian-food-products/canadian-blueberries/?id = 1426167712421.

Ahmed, I., Qazi, I. M., & Jamal, S. (2016). Developments in osmotic dehydration technique for the preservation of fruits and vegetables. *Innovative Food Science & Emerging Technologies, 34*, 29–43.

Amami, E., Khezami, W., Mezrigui, S., Badwaik, L. S., Bejar, A. K., Perez, C. T., & Kechaou, N. (2017). Effect of ultrasound-assisted osmotic dehydration pretreatment on the convective drying of strawberry. *Ultrasonics Sonochemistry, 36*, 286–300.

AOAC (1990). *Moisture in dried fruits. Official methods of analysis* (16th ed.). Washington, USA: Association of Official Analytical Chemists.

Beaulieu, J. C., Stein-Chisholm, R. E., Lloyd, S. W., Bett-Garber, K. L., Grimm, C. C., Watson, M. A., & Lea, J. M. (2017). Volatile, anthocyanidin, quality and sensory changes in rabbiteye blueberry from whole fruit through pilot plant juice processing. *Journal of the Science of Food and Agriculture, 97*(2), 469–478.

Celli, G. B., Dibazar, R., Ghanem, A., & Brooks, M. S.-L. (2016). Degradation kinetics of anthocyanins in freeze-dried microencapsulates from lowbush blueberries (Vaccinium angustifolium Aiton) and prediction of shelf-life. *Drying Technology, 34*(10), 1175–1184.

Chen, S., Zeng, Z., Hu, N., Bai, B., Wang, H., & Suo, Y. (2018). Simultaneous optimization of the ultrasound-assisted extraction for phenolic compounds content and antioxidant activity of Lycium ruthenicum Murr. Fruit using response surface methodology. *Food Chemistry, 242*, 1–8.

Chen, Y., & Martynenko, A. (2018). Combination of hydrothermodynamic (HTD) processing and different drying methods for natural blueberry leather. *LWT-Food Science and Technology, 87*, 470–477.

Correia, R., Grace, M. H., Esposito, D., & Lila, M. A. (2017). Wild blueberry polyphenol-protein food ingredients produced by three drying methods: Comparative physicochemical properties, phytochemical content, and stability during storage. *Food Chemistry, 235*(Supplement C), 76–85.

De Mendonça, K. S., Corrêa, J. L. G., de Jesus Junqueira, J. R., Pereira, M. C.d. A., & Vilela, M. B. (2016). Optimization of osmotic dehydration of yacon slices. *Drying Technology, 34*(4), 386–394.

de Souza, V. R., Pereira, P. A. P., da Silva, T. L. T., de Oliveira Lima, L. C., Pio, R., & Queiroz, F. (2014). Determination of the bioactive compounds, antioxidant activity and chemical composition of Brazilian blackberry, red raspberry, strawberry, blueberry and sweet cherry fruits. *Food Chemistry, 156*, 362–368.

Del Bo, C., Roursgaard, M., Porrini, M., Loft, S., Møller, P., & Riso, P. (2016). Different effects of anthocyanins and phenolic acids from wild blueberry (Vaccinium angustifolium) on monocytes adhesion to endothelial cells in a TNF-α stimulated proinflammatory environment. *Molecular Nutrition & Food Research, 60*(11), 2355–2366.

Dróżdż, P., Šėžienė, V., & Pyrzynska, K. (2017). Mineral composition of wild and cultivated blueberries. *Biological Trace Element Research.*

Ekezie, F.-G. C., Sun, D.-W., Han, Z., & Cheng, J.-H. (2017). Microwave-assisted food processing technologies for enhancing product quality and process efficiency: A review of recent developments. *Trends in Food Science & Technology.*

Flores, F. P., Singh, R. K., Kerr, W. L., Pegg, R. B., & Kong, F. (2014). Total phenolics content and antioxidant capacities of microencapsulated blueberry anthocyanins during in vitro digestion. *Food Chemistry, 153*, 272–278.

Ganesan, V., Gurumani, V., Kunjiappan, S., Panneerselvam, T., Somasundaram, B., Kannan, S., Chowdhury, A., Saravanan, G., & Bhattacharjee, C. (2018). Optimization and analysis of microwave-assisted extraction of bioactive compounds from Mimosa pudica L. using RSM & ANFIS modeling. *Journal of Food Measurement and Characterization, 12*(1), 228–242.

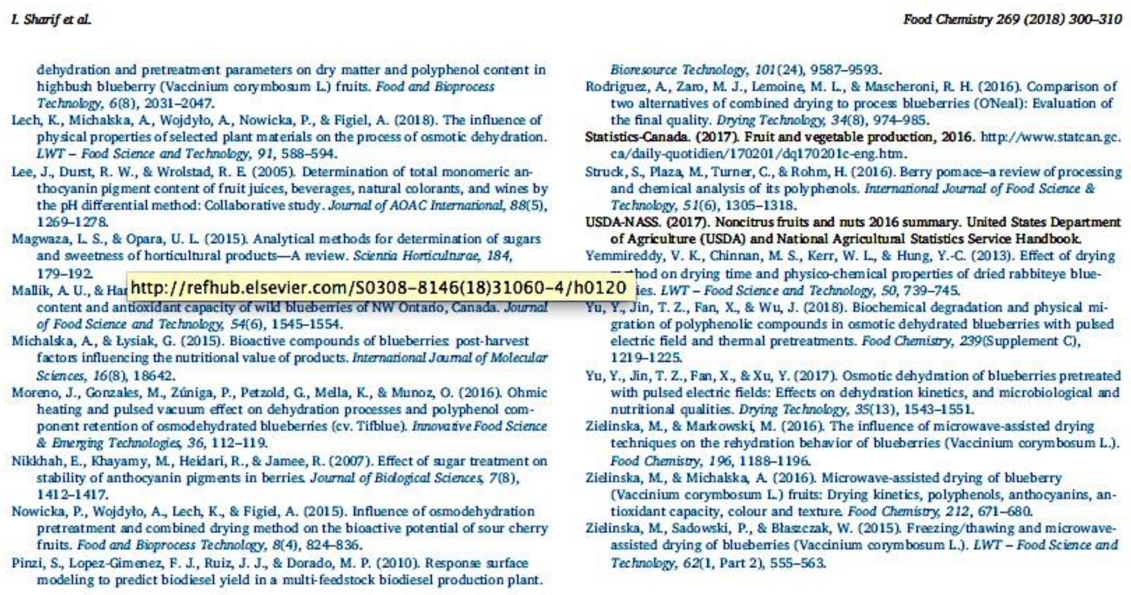
He, B., Zhang, L.-L., Yue, X.-Y., Liang, J., Jiang, J., Gao, X.-L., & Yue, P.-X. (2016). Optimization of Ultrasound-Assisted Extraction of phenolic compounds and anthocyanins from blueberry (Vaccinium ashei) wine pomace. *Food Chemistry, 204*, 70–76.

Jiang, H.-L., Yang, J.-L., & Shi, Y.-P. (2017). Optimization of ultrasonic cell grinder extraction of anthocyanins from blueberry using response surface methodology. *Ultrasonics Sonochemistry, 34*, 325–331.

Kamiloglu, S., Toydemir, G., Boyacioglu, D., Beekwilder, J., Hall, R. D., & Capanoglu, E. (2016). A review on the effect of drying on antioxidant potential of fruits and vegetables. *Critical Reviews in Food Science and Nutrition, 56*(sup1), S110–S129.

Khalid, S., Barfoot, K., May, G., Lamport, D., Reynolds, S., & Williams, C. (2017). Effects of Acute Blueberry Flavonoids on Mood in Children and Young Adults. *Nutrients, 9*(2), 158.

Kucner, A., Klewicki, R., & Sójka, M. (2013). The influence of selected osmotic



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Food Chemistry 269 (2018) 300–310

dehydration and pretreatment parameters on dry matter and polyphenol content in highbush blueberry (Vaccinium corymbosum L.) fruits. *Food and Bioprocess Technology, 6*(8), 2031–2047.

Lech, K., Michalska, A., Wojdyło, A., Nowicka, P., & Figiel, A. (2018). The influence of physical properties of selected plant materials on the process of osmotic dehydration. *LWT – Food Science and Technology, 91*, 588–594.

Lee, J., Durst, R. W., & Wrolstad, R. E. (2005). Determination of total monomeric anthocyanin pigment content of fruit juices, beverages, natural colorants, and wines by the pH differential method: Collaborative study. *Journal of AOAC International, 88*(5), 1269–1278.

Magwaza, L. S., & Opara, U. L. (2015). Analytical methods for determination of sugars and sweetness of horticultural products—A review. *Scientia Horticulturae, 184*, 179–192.

Mallik, A. U., & Har http://refhub.elsevier.com/S0308-8146(18)31060-4/h0120 content and antioxidant capacity of wild blueberries of NW Ontario, Canada. *Journal of Food Science and Technology, 54*(6), 1545–1554.

Michalska, A., & Łysiak, G. (2015). Bioactive compounds of blueberries: post-harvest factors influencing the nutritional value of products. *International Journal of Molecular Sciences, 16*(8), 18642.

Moreno, J., Gonzales, M., Zúniga, P., Petzold, G., Mella, K., & Munoz, O. (2016). Ohmic heating and pulsed vacuum effect on dehydration processes and polyphenol component retention of osmodehydrated blueberries (cv. Tifblue). *Innovative Food Science & Emerging Technologies, 36*, 112–119.

Nikkhah, E., Khayamy, M., Heidari, R., & Jamee, R. (2007). Effect of sugar treatment on stability of anthocyanin pigments in berries. *Journal of Biological Sciences, 7*(8), 1412–1417.

Nowicka, P., Wojdyło, A., Lech, K., & Figiel, A. (2015). Influence of osmodehydration pretreatment and combined drying method on the bioactive potential of sour cherry fruits. *Food and Bioprocess Technology, 8*(4), 824–836.

Pinzi, S., Lopez-Gimenez, F. J., Ruiz, J. J., & Dorado, M. P. (2010). Response surface modeling to predict biodiesel yield in a multi-feedstock biodiesel production plant. *Bioresource Technology, 101*(24), 9587–9593.

Rodriguez, A., Zaro, M. J., Lemoine, M. L., & Mascheroni, R. H. (2016). Comparison of two alternatives of combined drying to process blueberries (O'Neal): Evaluation of the final quality. *Drying Technology, 34*(8), 974–985.

Statistics-Canada. (2017). Fruit and vegetable production, 2016. http://www.statcan.gc.ca/daily-quotidien/170201/dq170201c-eng.htm.

Struck, S., Plaza, M., Turner, C., & Rohm, H. (2016). Berry pomace–a review of processing and chemical analysis of its polyphenols. *International Journal of Food Science & Technology, 51*(6), 1305–1318.

USDA-NASS. (2017). Noncitrus fruits and nuts 2016 summary. United States Department of Agriculture (USDA) and National Agricultural Statistics Service Handbook.

Yemmireddy, V. K., Chinnan, M. S., Kerr, W. L., & Hung, Y.-C. (2013). Effect of drying hod on drying time and physico-chemical properties of dried rabbiteye blue- ies. *LWT – Food Science and Technology, 50*, 739–745.

Yu, Y., Jin, T. Z., Fan, X., & Wu, J. (2018). Biochemical degradation and physical migration of polyphenolic compounds in osmotic dehydrated blueberries with pulsed electric field and thermal pretreatments. *Food Chemistry, 239*(Supplement C), 1219–1225.

Yu, Y., Jin, T. Z., Fan, X., & Xu, Y. (2017). Osmotic dehydration of blueberries pretreated with pulsed electric fields: Effects on dehydration kinetics, and microbiological and nutritional qualities. *Drying Technology, 35*(13), 1543–1551.

Zielinska, M., & Markowski, M. (2016). The influence of microwave-assisted drying techniques on the rehydration behavior of blueberries (Vaccinium corymbosum L.). *Food Chemistry, 196*, 1188–1196.

Zielinska, M., & Michalska, A. (2016). Microwave-assisted drying of blueberry (Vaccinium corymbosum L.) fruits: Drying kinetics, polyphenols, anthocyanins, antioxidant capacity, colour and texture. *Food Chemistry, 212*, 671–680.

Zielinska, M., Sadowski, P., & Błaszczak, W. (2015). Freezing/thawing and microwave-assisted drying of blueberries (Vaccinium corymbosum L.). *LWT – Food Science and Technology, 62*(1, Part 2), 555–563.