



**CATÓLICA**  
**ESCOLA SUPERIOR DE BIOTECNOLOGIA**

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PORTO

**MODELLING AND OPTIMIZATION OF OSMOTIC DEHYDRATION  
COMBINED WITH OTHER METHODS FOR DRYING FRUITS**

Thesis submitted to the Universidade Católica Portuguesa to attain the degree of PhD in  
Biotechnology – with specialization in Food Science and Engineering

Fernanda Rosa Assis

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Co-supervisor: Prof. Dr. Rui Manuel Santos Costa de Morais

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## Resumo

O objetivo geral deste programa de doutoramento foi estudar e otimizar o desenvolvimento, a nível da eficiência do processo e da qualidade, de produtos à base de frutos desidratados, de teor intermédio de água por desidratação osmótica, ou de teor reduzido de água por combinação desta técnica com outros métodos subsequentes de secagem.

A primeira parte do trabalho incidiu na desidratação osmótica (DO) de cubos de maçã e fisális. A capacidade de ajuste de alguns modelos matemáticos em descrever as cinéticas de transferência de massa nos produtos também foi estudada. Os objetivos consistiram em realizar a DO de cubos de maçã e estudar os efeitos do soluto (sacarose ou sorbitol) e da concentração (40 e 60 °Bx) na solução osmótica, da razão mássica amostra: solução (1:4 e 1:10), da temperatura (25, 40 e 60 °C), e da pressão (1 bar e 150 mbar) na perda de água (PA) e no ganho sólidos (GS). Relativamente à fisális, a DO foi efetuada com uma razão mássica amostra: solução de 1:4, a 60 °C e a pressão foi de 1 bar ou 150 mbar. Outro dos objetivos foi avaliar as alterações da microestrutura do tecido da maçã após o tratamento osmótico com sacarose e sorbitol. Assim, nos cubos de maçã, o sorbitol, o aumento da temperatura e o aumento da concentração do soluto na solução osmótica resultaram num aumento da velocidade da DO, mas a razão mássica amostra: solução e a pressão não afetaram o processo. Na fisális, a velocidade inicial de PA aumentou quando o vácuo foi aplicado durante a DO com sacarose e apresentou tendência a aumentar com o uso de sorbitol. No final da DO de cubos de maçã, observou-se, por análise da microestrutura, que este processo afetou os parâmetros de tamanho e forma das células vegetais e as alterações foram mais pronunciadas em amostras osmoticamente desidratadas com sorbitol. O processo de DO provocou o encolhimento das células e conseqüentemente uma redução de volume, a plasmólise e o dobramento das paredes celulares.

Na segunda parte do trabalho, foram estudados métodos de secagem para obter maçã cortada com teor de água reduzido, nomeadamente a secagem a ar quente, a secagem por micro-ondas e a liofilização. Estudou-se também o efeito do pré-tratamento osmótico com soluções de sacarose e sorbitol. Para as melhores condições de cada método, foi efetuada a comparação das cinéticas de secagem entre os diferentes métodos e foi avaliada a qualidade — atividade da água ( $a_w$ ), cor, teor fenólico total (TFT), atividade antioxidante (AA) e capacidade de reidratação — dos cubos de maçã secos. A capacidade de ajuste de alguns modelos matemáticos para descrever o teor de água durante a secagem também foi avaliada.

Assim, foi avaliado o efeito da temperatura (25, 55, 70 e 80 °C) na secagem a ar quente de cubos de maçã osmoticamente desidratados (60 °C, solução de sacarose ou sorbitol a 60 °Bx, razão mássica amostra: solução 1:4). Na secagem por micro-ondas, foi também avaliado o efeito do pré-tratamento osmótico e da potência (160, 350, 500, 650, 750 e 850 W) na cinética de PA de cubos de maçã. Finalmente, estudou-se a cinética de PA de cubos de maçã na liofilização. No que diz respeito à maçã cortada seca com teor reduzido de água, a desidratação osmótica como pré-tratamento antes da secagem a ar quente aumentou a velocidade e reduziu o tempo de secagem. O agente osmótico não afetou a velocidade de secagem, mas a utilização de sorbitol reduziu mais o tempo de secagem e a  $a_w$  do produto final. Na secagem por micro-ondas, o aumento do nível de potência reduziu o tempo de secagem e esta redução foi maior para as amostras osmoticamente desidratadas com sorbitol. A DO antes da liofilização não apresentou uma vantagem relevante e a  $a_w$  foi menor em amostras sem tratamento osmótico. O tipo de secagem e o pré-tratamento não afetaram a velocidade de reidratação dos cubos de maçã secos, mas as amostras controle apresentaram um teor de água de equilíbrio superior às amostras osmoticamente desidratadas.

A DO e a secagem subsequente, por ar quente, micro-ondas e liofilização, diminuíram significativamente o TFT e a AA. Nas amostras osmoticamente desidratadas, estes parâmetros de qualidade não foram afetados pela secagem subsequente, mas apenas pela DO.

Com o objetivo de comparar o efeito do agente osmótico utilizado na DO na aceitação pelo consumidor, foi efetuada a análise sensorial de cubos de maçã secos a ar quente pré-tratados osmoticamente com sacarose ou sorbitol. Não houve diferença nos resultados e o produto final foi bem aceite pelos consumidores.

De entre os métodos de secagem estudados, a secagem por micro-ondas sem pré-tratamento produziu cubos de maçã secos de boa qualidade e num tempo reduzido. O sorbitol é uma boa alternativa à sacarose como agente no pré-tratamento osmótico de cubos de maçã e fisális. Para além disso, o sorbitol é um prebiótico com benefícios para a saúde.

## Abstract

The general objective of this Ph.D. programme was to study and to optimize the development, in terms of process efficiency and the product quality, of fruit-based dry products with intermediate water content through osmotic dehydration, or reduced water content by subsequent combination of this technique with other drying methods.

The first part of the work focused on the osmotic dehydration (OD) of apple cubes and physalis. The adequacy of the fit of some mathematical models to describe the mass transfer kinetics in the products was also studied. The objectives were to perform the OD of apple cubes and to study the effects of the solute (sucrose or sorbitol) and the concentration (40 and 60 °Bx) in the osmotic solution, the mass ratio of sample to solution (1:4 or 1:10), the temperature (25, 40 and 60 °C), and the pressure (1 bar and 150 mbar) on the water loss (*WL*) and the solid gain (*SG*). Regarding physalis, the OD was performed with a mass ratio of sample to solution of 1:4 at 60 °C and the pressure was 1 bar or 150 mbar. Another objective was to evaluate the changes in the microstructure of the apple tissue after the osmotic treatment with sucrose or sorbitol. Thus, in the apple cubes, the sorbitol, the increase of the temperature and of the solute concentration in the osmotic solution resulted in an increase of the OD rate, but the mass ratio of the sample to the solution and the pressure did not affect the process. In the physalis, the initial *WL* rate increased when the vacuum was applied during the OD with sucrose and tended to increase with the use of sorbitol. At the end of the DO of apple cubes, it was observed, by microstructure analysis, that this process affected the size and shape parameters of plant cells and the changes were more pronounced in samples osmotically dehydrated with sorbitol. The OD process caused the shrinkage of the cells and, consequently, a reduction of volume, the plasmolysis and the folding of the cell walls.

In the second part of the work, some drying methods were studied to obtain cut apple with reduced water content, namely hot air drying, microwave drying and freeze-drying. The effect of the osmotic pre-treatment with sucrose or sorbitol solutions was also studied. For the best conditions of each method, the drying kinetics were compared among the different methods and the quality — water activity ( $a_w$ ), the colour, the total phenolic content (TPC), the antioxidant activity (AA) and the rehydration ability — of the dried apple cubes were evaluated. The adequacy of the fit of some mathematical models to describe the water content during drying was also evaluated. Thus, the effect of the temperature (25, 55, 70 and 80 °C) was studied on the hot air drying of osmotically dehydrated apple cubes (60 °C, 60 °Bx sucrose or sorbitol solutions, mass ratio of sample to solution 1:4). In the microwave

drying, the effect of the osmotic pre-treatment and the power (160, 350, 500, 650, 750 and 850 W) on the WL kinetics of apple cubes was also evaluated. Finally, the WL kinetics of the freeze-drying of apple cubes were studied. Concerning the dried cut apple with reduced water content, the osmotic dehydration as pre-treatment before the hot air drying increased the drying rate and reduced the drying time. The osmotic agent did not affect the drying rate, but the use of sorbitol reduced more the drying time and the  $a_w$  of the final product. In the microwave drying, the increase of the power level reduced the drying time and this reduction was higher for samples osmotically dehydrated with sorbitol. OD prior to freeze-drying did not present a relevant advantage and the  $a_w$  was lower in non-treated samples. The type of drying and the pre-treatment did not affect the rehydration rate of the dried apple cubes, but the control samples presented higher equilibrium water content than the osmotically dehydrated ones.

The OD and subsequent drying by hot air, microwave and freeze-drying, significantly decreased the TPC and the AA. These quality parameters of the osmotically dehydrated samples were not affected by the subsequent drying, but only by the OD.

In order to compare the effect of the osmotic agent used in the OD on the consumer's acceptance, the sensory analysis of hot air dried apple cubes pre-treated osmotically with sucrose or sorbitol was carried out. There was no difference in the results and the final product was well accepted by consumers.

Among the drying methods studied, microwave drying without osmotic pre-treatment produced dried apple cubes with good quality and in a short time. Sorbitol is a good alternative to sucrose as the agent in the osmotic pre-treatment of apple cubes and physalis. Furthermore, sorbitol is a prebiotic with health benefits.

## **Keywords**

Apple

Physalis

Osmotic dehydration

Mathematical modelling

Microstructure

Hot air drying

Microwave drying

Freeze-drying

Colour

Total phenolic content

Antioxidant activity

Rehydration

Sensory analysis



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## Table of Contents

Resumo.....	iii
Abstract .....	v
Keywords .....	vii
Aknowledgements.....	ix
Table of Contents .....	xi
List of Figures .....	xvii
List of Abbreviations.....	xxiii
Part I – General Introduction.....	1
Scope and outline .....	3
Chapter 1 – Critical literature review .....	7
1.1 Introduction.....	7
1.2 Osmotic dehydration .....	8
1.2.1 Sorbitol.....	9
1.3 Hot air drying.....	10
1.4 Microwave drying .....	12
1.5 Freeze-drying .....	13
1.6 Combined drying technologies.....	14
1.7 Mathematical models .....	14
1.7.1 Osmotic dehydration .....	14
1.7.2 Hot air, microwave and freeze-drying .....	28
1.8 Quality of the dried products.....	30
1.8.1 Water activity .....	30
1.8.2 Colour .....	31
1.8.3 Total phenolic content and antioxidant activity .....	32
1.8.4 Rehydration ability.....	32
Part II – Study of the osmotic dehydration process.....	35
Chapter 2 – Osmotic dehydration of apple cubes at 60 °Bx.....	37
2.1 Abstract .....	37
2.2 Introduction.....	37
2.3 Material and methods.....	39
2.3.1 Samples .....	39
2.3.2 Osmotic dehydration .....	40

2.3.3	<i>Moisture content and Water activity determination</i> .....	40
2.3.4	<i>Viscosity determination</i> .....	40
2.3.5	<i>Osmotic dehydration parameters</i> .....	41
2.3.6	<i>Mathematical models</i> .....	41
2.3.7	<i>The Arrhenius behaviour</i> .....	42
2.3.8	<i>Statistical analysis</i> .....	42
2.4	Results and discussion.....	43
2.4.1	<i>OD at atmospheric pressure</i> .....	46
2.4.2	<i>OD under vacuum</i> .....	54
2.4.3	<i>Water activity</i> .....	57
2.5	Conclusion.....	59
Chapter 3 – Osmotic dehydration of apple cubes at 40 °Bx.....		61
3.1	Abstract.....	61
3.2	Introduction.....	61
3.3	Material and methods.....	62
3.3.1	<i>Samples and osmotic dehydration process</i> .....	62
3.3.2	<i>Moisture content and water activity determination</i> .....	62
3.3.3	<i>Osmotic dehydration parameters and mathematical models</i> .....	62
3.4	Results and discussion.....	63
3.4.1	<i>Mass transfer kinetics</i> .....	63
3.4.2	<i>Comparison between 40 °Bx and 60 °Bx</i> .....	65
3.5	Conclusion.....	66
Chapter 4 – Osmotic dehydration of physalis.....		67
4.1	Abstract.....	67
4.2	Introduction.....	67
4.3	Material and methods.....	68
4.3.1	<i>Samples</i> .....	68
4.3.2	<i>Osmotic dehydration</i> .....	68
4.3.3	<i>Osmotic dehydration parameters and mathematical models</i> .....	68
4.3.4	<i>Moisture content and water activity determination</i> .....	69
4.4	Results and discussion.....	69
4.5	Conclusion.....	71
Chapter 5 – Microstructural changes after osmotic dehydration of cut apple.....		73
5.1	Abstract.....	73

5.2	Introduction.....	73
5.3	Materials and methods .....	74
5.3.1	<i>Preparation of samples</i> .....	74
5.3.2	<i>Osmotic dehydration experiments</i> .....	75
5.3.3	<i>Moisture content determination</i> .....	75
5.3.4	<i>Light microscopy</i> .....	75
5.3.5	<i>Image analysis</i> .....	75
5.3.6	<i>Statistical analysis</i> .....	75
5.4	Results and discussion.....	76
5.4.1	<i>Osmotic dehydration</i> .....	76
5.4.2	<i>Microstructure</i> .....	76
5.5	Conclusion.....	79
Part III – Study of the drying processes subsequent to osmotic dehydration.....		81
Chapter 6 – Optimization of air drying after osmotic treatment .....		83
6.1	Abstract .....	83
6.2	Introduction.....	83
6.3	Materials and methods .....	85
6.3.1	<i>Samples</i> .....	85
6.3.2	<i>Osmotic dehydration</i> .....	85
6.3.3	<i>Hot air drying</i> .....	86
6.3.4	<i>Moisture content and water activity determination</i> .....	86
6.3.5	<i>Mathematical models</i> .....	86
6.3.6	<i>The Arrhenius behaviour</i> .....	87
6.3.7	<i>Quality evaluation</i> .....	87
6.3.8	<i>Statistical analysis</i> .....	88
6.4	<i>Results and discussion</i> .....	88
6.4.1	<i>Mathematical modelling</i> .....	90
6.4.2	<i>Water activity</i> .....	94
6.4.3	<i>Quality of the final product</i> .....	96
6.5	Conclusions.....	98
Chapter 7 – Optimization of microwave-drying after osmotic treatment .....		99
7.1	Abstract .....	99
7.2	Introduction.....	99
7.3	Materials and methods .....	100

7.3.1	<i>Samples and osmotic dehydration</i> .....	100
7.3.2	<i>Microwave drying</i> .....	101
7.3.3	<i>Moisture content determination and water activity</i> .....	101
7.3.4	<i>Quality evaluation</i> .....	101
7.3.5	<i>Mathematical models</i> .....	101
7.3.6	<i>The Arrhenius behaviour</i> .....	101
7.4	<i>Results and discussion</i> .....	102
7.4.1	<i>Mathematical modelling</i> .....	102
7.4.2	<i>Mass transfer kinetics</i> .....	104
7.4.3	<i>Water activity (<math>a_w</math>)</i> .....	106
7.4.4	<i>Quality of the final product</i> .....	107
7.5	<i>Conclusions</i> .....	110
Chapter 8 – Optimization of freeze-drying after osmotic treatment .....		111
8.1	<i>Abstract</i> .....	111
8.2	<i>Introduction</i> .....	111
8.3	<i>Materials and methods</i> .....	113
8.3.1	<i>Samples and osmotic dehydration</i> .....	113
8.3.2	<i>Freeze-drying</i> .....	113
8.3.3	<i>Moisture content and water activity determination</i> .....	113
8.3.4	<i>Mathematical models</i> .....	113
8.3.5	<i>Quality evaluation</i> .....	114
8.4	<i>Results and discussion</i> .....	114
8.4.1	<i>Mass transfer kinetics and mathematical modelling</i> .....	114
8.4.2	<i>Water activity</i> .....	118
8.5	<i>Quality of the final product</i> .....	119
8.6	<i>Conclusions</i> .....	120
Chapter 9 – Sensory analysis of osmotically treated apple cubes after air drying .....		123
9.1	<i>Abstract</i> .....	123
9.2	<i>Introduction</i> .....	123
9.3	<i>Materials and methods</i> .....	124
9.3.1	<i>Samples and osmotic dehydration</i> .....	124
9.3.2	<i>Drying</i> .....	124
9.3.3	<i>Sensory analysis</i> .....	124
9.4	<i>Results and discussion</i> .....	125

9.5	Conclusions .....	125
Chapter 10 – Rehydration of dried apple cubes osmotically dehydrated .....		127
10.1	<i>Abstract</i> .....	127
10.2	Introduction .....	127
10.3	Materials and methods .....	128
10.3.1	<i>Samples preparation and osmotic dehydration</i> .....	128
10.3.2	<i>Drying</i> .....	128
10.3.3	<i>Rehydration experiments</i> .....	129
10.3.4	<i>Mathematical modelling of rehydration process</i> .....	129
10.4	Results and discussion .....	130
10.5	Conclusions .....	132
Part IV – Conclusions and futures perspectives .....		135
Chapter 11 – Conclusions .....		137
Chapter 12 – Future perspectives .....		141
References .....		143
Appendice .....		169
<i>Sensory analysis sheet</i> .....		169



## List of Figures

Figure 2.1 Experimental data and the fit of Page's model of <i>WL</i> and <i>SG</i> of apple cubes osmotically dehydrated in a sucrose solution at atmospheric pressure and at 25, 40 and 60 °C, using the mass ratio of sample to solution of 1:4 .....	44
Figure 2.2 Experimental data and the fit of Page's model of <i>WL</i> and <i>SG</i> of apple cubes osmotically dehydrated in a sorbitol solution at atmospheric pressure and at 25, 40 and 60 °C, using the mass ratio of sample to solution of 1:4 .....	44
Figure 2.3 Experimental data and the fit of Page's model of <i>WL</i> and <i>SG</i> of apple cubes osmotically dehydrated in a sucrose solution at atmospheric pressure and at 25, 40 and 60 °C, using the mass ratio of sample to solution of 1:10 .....	44
Figure 2.4 Experimental data and the fit of Page's model of <i>WL</i> and <i>SG</i> of apple cubes osmotically dehydrated in a sorbitol solution at atmospheric pressure and at 25, 40 and 60 °C, using the mass ratio of sample to solution of 1:10 .....	45
Figure 2.5 Experimental data and the fit of Page's model of <i>WL</i> and <i>SG</i> of apple cubes osmotically dehydrated in a sucrose solution under vacuum (150 mbar) and at 25, 40 and 60 °C, using the mass ratio of sample to solution of 1:10 .....	45
Figure 2.6 Experimental data and the fit of Page's model of <i>WL</i> and <i>SG</i> of apple cubes osmotically dehydrated in a sorbitol solution under vacuum (150 mbar) and at 25, 40 and 60 °C, using the mass ratio of sample to solution of 1:10 .....	45
Figure 2.7 Residuals vs. predicted values for <i>WL</i> of apple cubes during the OD process in sucrose solution at 25 °C using the mass ratio of sample to solution of 1:10, fitted by the Page's model .....	46
Figure 2.8 Viscosity of the solutions before and after the OD process using the mass ratio of sample to solution of 1:4 .....	53
Figure 2.9 Water activity of the solutions before and after the OD process using the mass ratio of sample to solution of 1:4.....	57
Figure 3.1 Experimental data and the fit of Peleg's model of <i>WL</i> and <i>SG</i> of apple cubes osmotically dehydrated in a 40 °Bx sucrose solution at atmospheric pressure and at 25, 40 and 60 °C, using the mass ratio of sample to solution of 1:4 or 1:10 .....	63

Figure 3.2 Experimental data and the fit of Peleg’s model of <i>WL</i> and <i>SG</i> of apple cubes osmotically dehydrated in a 40 °Bx sorbitol solution at atmospheric pressure and at 25, 40 and 60 °C, using the mass ratio of sample to solution of 1:4 or 1:10 .....	63
Figure 4.1 The experimental data and the fit of Peleg’s model of <i>WL</i> and <i>SG</i> of physalis osmotically dehydrated in a sucrose or sorbitol solution at atmospheric pressure and under vacuum (150 mbar) and at 60 °C .....	70
Figure 5. 1 Location of sampling of apple tissue .....	74
Figure 5.2 Microstructure of apple parenchyma analysed before (a) and after the osmotic dehydration with sucrose (b) and sorbitol (c).....	77
Figure 5.3 Microstructure of apple parenchyma with vascular site (arrow) .....	78
Figure 6.1 Experimental data and the fit of Page’s model of the normalized moisture content ( $M/M_0$ ) during the air drying of control apple cubes .....	89
Figure 6.2 Experimental data and the fit of Page’s model of the normalized moisture content ( $M/M_0$ ) during the air drying of apple cubes osmotically dehydrated in sucrose solutions .....	89
Figure 6.3 Experimental data and the fit of Page’s model of the normalized moisture content ( $M/M_0$ ) during the air drying of apple cubes osmotically dehydrated in sorbitol solutions .....	89
Figure 7.1 Experimental data and fit of modified Page’s model of the normalized moisture content ( $M/M_0$ ) during the microwave drying of fresh apple cubes .....	103
Figure 7.2 Experimental data and fit of modified Page’s model of the normalized moisture content ( $M/M_0$ ) during the microwave drying of apple cubes osmotically pre-treated with sucrose solutions.....	103
Figure 7.3 Experimental data and fit of modified Page’s model of the normalized moisture content ( $M/M_0$ ) during the microwave drying of apple cubes osmotically pre-treated with sorbitol solutions .....	103
Figure 8.1 Experimental data and the fit of modified Page’s model of the normalized moisture content ( $M/M_0$ ) during the freeze-drying of apple cubes.....	117
Figure 8.2 Experimental data and the fit of GAB’s model during the freeze-drying of apple cubes .....	119
Figure 10.1 Experimental data and the fit of the first order kinetic model during the rehydration of apple cubes.....	131

Figure 10.2 Experimental data and the fit of the first order kinetic model during the rehydration of apple cubes osmotically dehydrated with sucrose solution ..... 132

Figure 10.3 Experimental data and the fit of the first order kinetic model during the rehydration of apple cubes osmotically dehydrated with sorbitol solution..... 132



## List of Tables

Table 1.1 Classification of the different models to predict the mass transfer in OD processes .....	16
Table 2.1 Effective diffusivity of the fit of Crank's model for the mass transfer during OD .....	47
Table 2.2 Parameters of the fit of Peleg's and Page's models of <i>WL</i> and <i>SG</i> during OD of apple cubes at atmospheric pressure.....	49
Table 2.3 Parameters of the fit of Peleg's and Page's models of <i>WL</i> and <i>SG</i> during DO of apple cubes under vacuum with a mass ratio of sample to solution 1:10.....	55
Table 2.4 Water activity of the osmotically dehydrated apple cubes .....	58
Table 2.5 Determination coefficient ( $R^2$ ) of the linear regression between the water activity and the final water content of dehydrated apple cubes.....	58
Table 3.1 Parameters of the fit of Peleg's model for <i>WL</i> and <i>SG</i> during OD of apple cubes at 40 °Bx .....	64
Table 4.1 The fit of Crank's and Peleg's model for the mass transfer during OD of physalis at 60 °C, at atmospheric pressure and under vacuum .....	70
Table 5.1 Average cellular size and shape parameters of fresh and osmotically dehydrated apple samples.....	78
<b>Table 6.1</b> Parameters of the fit of Newton's, Page's, modified Page's and Henderson and Pabis' models of <i>MR</i> during air drying of apple cubes .....	91
Table 6.2 Parameters of the fit of Two-term exponential and Midilli et al.'s models of <i>MR</i> during air drying of apple cubes .....	92
Table 6.3 GAB parameters and regression coefficients for isothermal desorption of osmotically .....	96
Table 6.4 Quality parameters of osmotically pre-treated apples cubes dehydrated by hot air drying.....	97
Table 7.1 Parameters of the fit of modified Page's model of experimental data from microwave drying of apple cubes.....	104

Table 7.2 Water activity of osmotically treated apple cubes dehydrated by microwave ..	106
Table 7.3 Quality parameters of osmotically treated apples cubes dehydrated by microwave at 500 W .....	109
Table 8.1 Parameters of the fit of Newton's, Page's, modified Page's and Henderson and Pabis' models of $M/M_0$ of freeze-dried dapple cubes .....	116
Table 8.2. Quality parameters of osmotically pre-treated apples cubes dehydrated by freeze-drying.....	120
Table 9.1 Sensory attributes of dried apple cubes pre-treated with sucrose or sorbitol ....	125
Table 10.1 Parameters of the first order kinetic model for the rehydration of the dried apple cubes .....	130

## List of Abbreviations

$a$	half of the side of the cube (m)	$nj_{cs}$	symplastic transmembranary transfer (kg s <sup>-1</sup> m <sup>-2</sup> )
AA	antioxidant activity	$nj_0$	extracellular mass flux (kg s <sup>-1</sup> m <sup>-2</sup> )
$A_i$	area (m <sup>2</sup> )	$N_{il}$	molar flux (kgmol m <sup>-2</sup> s <sup>-1</sup> )
$A_w, B_w$	Page's parameters (OD)	OD	osmotic dehydration
$A, B$	Page's parameters	$P$	pressure (N m <sup>-2</sup> )
$A, x, y$	Magee's parameters	$P_c^0$	cellular hydrostatic pressure (reference state at the temperature considered and at atmospheric pressure (N m <sup>-2</sup> ))
$a, k$	Henderson and Pabis' and Two-term exponential models parameters	$p_0$	Arrhenius's parameter at the reference temperature
$a, k_1, k_2$	Two-term model parameters	$P$	microwave power (W)
$a, k, c$	Logarithmic model parameters	$p$	Arrhenius's parameter
$a, b$	Wang and Singh's model parameters	$p_{ref}$	Arrhenius's parameter at the reference temperature
$a, k, n, b$	Midilli et al.'s model parameters	$P_c$	cellular hydrostatic pressure (N m <sup>-2</sup> )
$a, k, b, B$	Weibull's model parameters	$r$	sphere radius (m)
$A_m$	membrane surface area (m <sup>2</sup> )	$R$	universal gas constant (J kgmol <sup>-1</sup> K <sup>-1</sup> )
$a_t$	thermodynamic activity	$R_i$	radius of the extracellular space (m)
$a_w$	water activity	$R_{wm}$	transmembrane transport of water (kg m <sup>-2</sup> s <sup>-1</sup> )
$\hat{a}_{wv}$	water activity of vacuole	$s$	Azuara's parameters (h <sup>-1</sup> )
$\hat{a}_{wi}$	water activity of the extracellular space	$SG$	solid gain (kg DM kg initial total weight <sup>-1</sup> )
$c, k$	GAB's model constants	$SG_\infty$	solid gain at equilibrium (kg DM kg initial total weight <sup>-1</sup> )
$C_0$	initial solute concentration (kg m <sup>-3</sup> )	$s_1, s_2$	Azuara's parameters (s <sup>-1</sup> )
$C$	mass fraction	SHW	standard half width
$C_n$	$2\alpha(1 + \alpha)/(1 + \alpha + \alpha^2 q_n^2)$	$T$	temperature (°C, K)
$d$	diameter (m)	$t$	time (s)
$D_{apj}$	apparent diffusion coefficient (m <sup>2</sup> s <sup>-1</sup> )	TPC	total phenolic content
$D_e$	effective diffusivity (m <sup>2</sup> s <sup>-1</sup> )	$t_v$	thickness of the transfer pathway (m)
DM	dry matter	$q_n$	non-zero positive roots of $\tan q_n = -\alpha q_n$
$d_{PM}$	thickness of plasma membrane (m)	$u$	average velocity (m s <sup>-1</sup> )
$\bar{D}_s$	apparent diffusivity of sucrose (m <sup>2</sup> s <sup>-1</sup> )	$u_b$	barycentric velocity (m s <sup>-1</sup> )
$E_a$	activation energy (J mol <sup>-1</sup> )	$V$	volume (m <sup>3</sup> )
$FO$	Fourier number, $D_e t/l^2$	$V_c$	cellular volume (m <sup>3</sup> )
FD	freeze-drying	$V_l$	intercellular volume (m <sup>3</sup> )
$H$	parameter of exponential association equation	$\bar{V}_w$	partial molar volume of water (m <sup>3</sup> kgmol water <sup>-1</sup> )
HAD	hot air drying	$X$	volumetric fraction of the total volume occupied by the liquid
$J_w^P$	transmembrane molar water flux of the protoplast (kgmol m <sup>-2</sup> s <sup>-1</sup> )	$X_v$	volumetric fraction of the pore occupied by the liquid
$J_{jm}$	transmembrane molar flux of species j, water or solute (kgmol m <sup>-2</sup> s <sup>-1</sup> )	$x_w$	water molar fraction
$J_{jp}$	symplastic molar flux of species j, water or solute (kgmol m <sup>-2</sup> s <sup>-1</sup> )	$z_L$	length (m)
$k$	rate parameter for $WL$ or $SG$ (mol kg <sup>-1</sup> s <sup>-1/2</sup> )	$w_0$	initial weight of the sample (kg)
$k$	Newton's model parameter	$WL$	water loss (kg water kg initial total weight <sup>-1</sup> )
$k$	mass transfer coefficient for $WL$ or $SG$ (kg water or DM kg initial total weight s <sup>-1/2</sup> )	$WL_\infty$	water loss at equilibrium (kg water kg initial total weight <sup>-1</sup> )
$k$	First order kinetic's parameter	$w_{s\infty}$	dry solids content of the sample at equilibrium (kg DM kg total weight <sup>-1</sup> )
$k_1$	Peleg's parameter (s kg DM kg water <sup>-1</sup> )	$w_s$	dry solids content of the sample after treatment (kg DM kg total weight <sup>-1</sup> )
$k_2$	Peleg's parameter (kg DM kg water <sup>-1</sup> )	$w_{s0}$	initial dry solids content of the sample (kg DM kg total weight <sup>-1</sup> )
$k_1^w, k_1^s$	Peleg's parameter (s kg total weight kg water or DM <sup>-1</sup> ) (OD)	$w_{s0}$	initial dry solids content of the sample (kg DM kg total weight <sup>-1</sup> )
$k_2^w, k_2^s$	Peleg's parameter (kg total weight kg water or DM <sup>-1</sup> ) (OD)	$w_{w\infty}$	water content of the sample at equilibrium (kg
$k_w, k_s$	mass transfer coefficient for $WL$ or $SG$ (kg water or DM kg total weight s <sup>-1/2</sup> )		
$k_1$	Peleg's parameter (h kg total weight kg water or DM <sup>-1</sup> )		

$k_2$	Peleg's parameter (kg total weight kg water or DM <sup>-1</sup> )	$w_{w0}$	initial water content of the sample (kg water kg total weight <sup>-1</sup> )
$kj_p$	plasmalemmatic transmembranary mass transfer coefficients (m s <sup>-1</sup> )	$w_w$	water content of the sample after treatment (kg DM kg total weight <sup>-1</sup> )
$kj_s$	symplastic transmembrane mass transfer coefficients (m s <sup>-1</sup> )		
$l$	semi-thickness of sample (m)		
$L_{kjm}$	macroscopic phenomenological coefficient of plasmalemma (kgmol <sup>2</sup> J <sup>-1</sup> m <sup>-2</sup> s <sup>-1</sup> )	$\alpha$	volume ratio of solution to the parallelepiped
$L_{kjp}$	macroscopic phenomenological coefficient of plasmodesmata (kgmol <sup>2</sup> J <sup>-1</sup> m <sup>-2</sup> s <sup>-1</sup> )	$\alpha_w, \alpha_s$	Weibull's scale parameter (s)
$L_{wm}$	phenomenological coefficient of water (kgmol <sup>2</sup> Pa <sup>-1</sup> s <sup>-1</sup> m <sup>-5</sup> )	$\alpha_n$	positive roots of the equation
$m$	mass of sample (g)	$\beta$	Weibull's shape parameter
$M$	moisture content (kg water kg DM <sup>-1</sup> )	$\tau$	Weibull's scale parameter
$M_0$	initial moisture content (kg water kg dry solids <sup>-1</sup> )	$\beta_w, \beta_s$	Weibull's shape parameter
$M_{dm}$	mass of dry matter in the cellular volume (kg)	$\gamma_i$	number from the comparison between Page's and Crank's models
$Mm$	monolayer moisture content (kg water kg dry matter <sup>-1</sup> )	$\varepsilon_e$	effective porosity
$MR$	moisture ratio	$\mu$	liquid viscosity (Pa s)
$MW$	molecular weight (g mol <sup>-1</sup> )	$\mu_{km}$	plasmalemma chemical potential (J kg mol <sup>-1</sup> )
$MWD$	microwave drying	$\mu_{kp}$	plasmodesmata chemical potential (J kgmol <sup>-1</sup> )
$M_e$	moisture content at equilibrium (kg water kg dry matter <sup>-1</sup> )	$\nu$	partial molar volume (m <sup>3</sup> kgmol <sup>-1</sup> )
$nj_{cp}$	plasmalemmatic transmembranary mass flux (kg s <sup>-1</sup> m <sup>-2</sup> )	$\pi$	osmotic pressure
		$\pi^*$	osmotic pressure at equilibrium
		$\pi_0$	initial osmotic pressure
		$\rho$	mass concentration (kg m <sup>-3</sup> )
		$\rho_s$	volume mass of sucrose (kg m <sup>-3</sup> )
		$\rho j_0$	cellular mass concentrations (kg m <sup>-3</sup> )
		$\rho j_c$	extracellular mass concentrations (kg m <sup>-3</sup> )

### Greek letters

## **Part I – General Introduction**



## **Scope and outline**

This thesis is organized in four parts, which include 12 chapters, which describe how the research/project progressed along time.

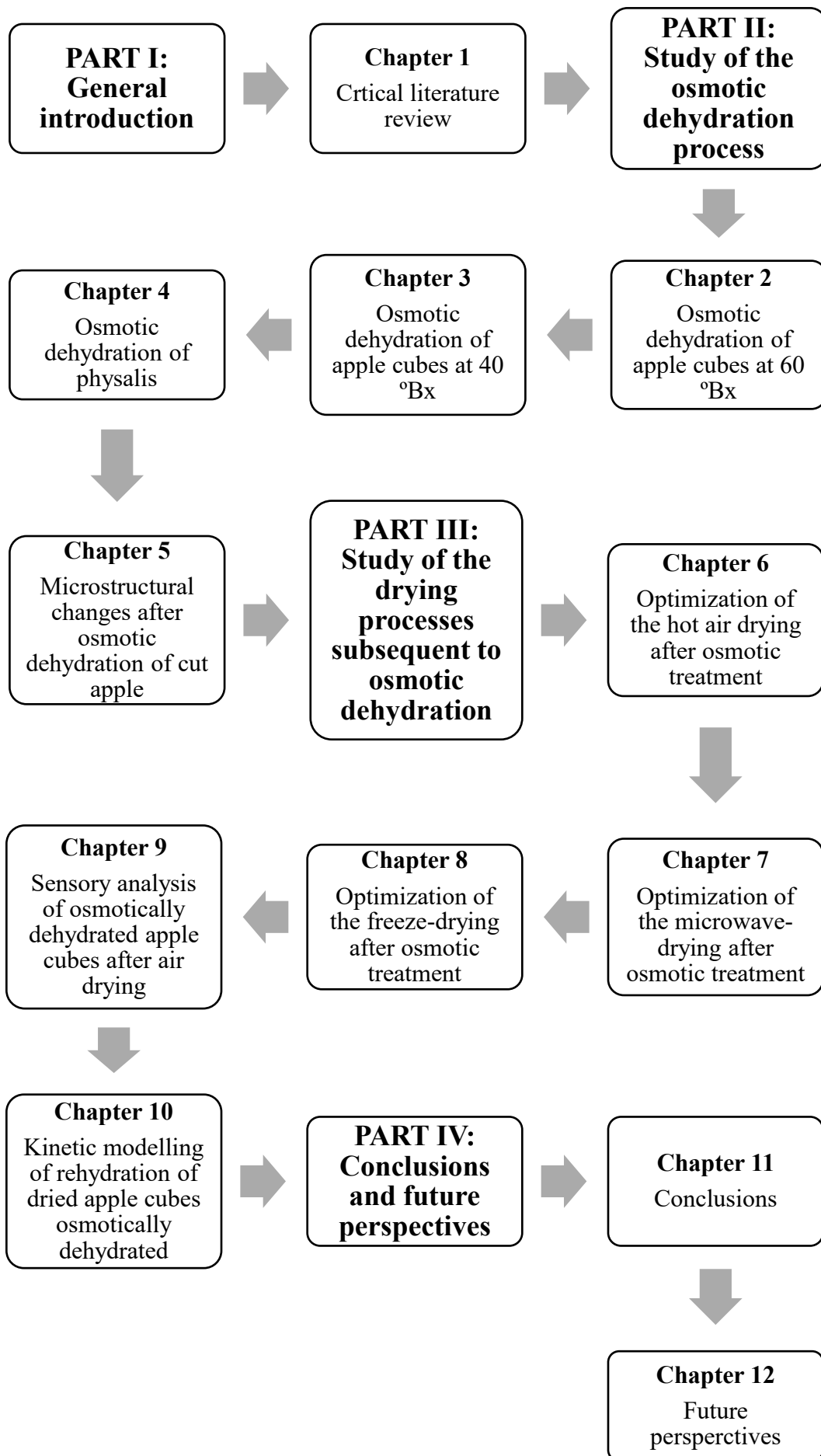
The general objective was to study and to optimize the development of fruit-based dried products, in terms of the process engineering and the product quality, with intermediate water content through osmotic dehydration; or reduced water content, by the combination of this technique with other subsequent drying methods.

Part I includes Chapter 1 that is a general literature review about the methods used for drying fruits, the mathematical models that are usually tested to fit the drying kinetics and the quality parameter of dried fruits.

Part II encompasses Chapters 2, 3, 4, and 5 and describes the effect of some process variables during the osmotic dehydration of apples and physalis. Chapters 2 and 3 describe the optimization of the osmotic dehydration of apple cubes, based on the temperature and the concentration of the solution, the type of osmotic agent, the mass ratio of sample to solution and the pressure. Chapter 4, based on the previous chapters, describes the optimization of the osmotic dehydration in physalis. Chapter 5 describes the microstructure after the osmotic dehydration of apple tissue using two different solutes as the osmotic agent.

Part III is divided in five chapters, three of which are about the subsequent drying process (6, 7 and 8) and two are related to the quality (9 and 10). Chapter 6 describes the optimization of the air drying of osmotically dehydrated apple cubes, Chapter 7 focus the optimization of the microwave drying of osmotically dehydrated apple cubes and Chapter 8 concerns the freeze-drying of osmotically dehydrated apple cubes. Chapters 9 and 10 report the sensory attributes and the rehydration capacity of dried apple cubes by different methods of drying.

In Part IV, the general conclusions are presented in Chapter 11 and the future perspectives in Chapter 12.



Part of the work presented in the 12 chapters has been already published, accepted or submitted to international journals, according to the following list:

**Part of Chapter 1:**

Assis, F.R., Morais, R.M.S.C., Morais, A.M.M.B., 2016. Mass transfer in osmotic dehydration of food products: comparison between mathematical models. *Food Engineering Reviews*. **8**, 116–133. doi:10.1007/s12393-015-9123-1.

**Chapter 2:**

Assis, F.R., Morais, R.M.S.C., Morais, A.M.M.B., 2017a. Mathematical modelling of osmotic dehydration kinetics of apple cubes. *Journal of Food Processing and Preservation*. **41** (3), 1–16. doi:10.1111/jfpp.12895.

**Part of Chapter 6:**

Assis, F.R., Morais, R.M.S.C., Morais, A.M.M.B., 2017b. Osmotic dehydration with sorbitol combined with hot air convective drying of apple cubes. *Journal of Food Science and Technology*. doi: 10.1007/s13197-017-2751-0

**Chapter 7:**

Assis, F.R., Morais, R.M.S.C., Morais, A.M.M.B., 2017c. Microwave drying of apple cubes — effect of the osmotic pre-treatment and comparison with hot air drying. *Advances in Food Science and Engineering*. In press.

**Chapter 8:**

Assis, F.R., Morais, R.M.S.C., Morais, A.M.M.B., 2017d. Osmotic dehydration combined with freeze-drying of apple cubes and comparison with microwave drying and hot air drying. *Advances in Food Science and Engineering*. In press.

**Chapters 3 and 5:** Osmotic dehydration of cut apple: mass transfer kinetics and microstructural changes. Submitted for publication in the *Journal of Food Process Engineering*.

**Chapter 4:** Mathematical modelling of osmotic dehydration of physalis. Submitted for publication in the *Brazilian Journal of Food Technology*.

**Chapter 10:** Rehydration of osmotically pre-treated apple cubes dried by hot air, microwave and freeze-drying. Submitted for publication in the *International Journal of Food Engineering*.

## Chapter 1 – Critical literature review

### 1.1 Introduction

The world fruit production is around 400 million ton per year. The losses of fruits and vegetables in most countries are considerably high. The development of new manufacturing processes has become necessary for the maintenance of the nutritional properties and quality, as well as the sensory characteristics, due to the high perishability of fruits.

The apple is a popular fruit and it is consumed as fresh or as raw material for many products (Sacilik and Elicin, 2006). The world production of apples in 2014 was 84,630,275 ton (FAO, 2017). Apples are rich in bioactive compounds, such as phenolic, vitamin C, sugars, several organic acids, and minerals, which can protect against chronic diseases (Koutsos and Lovegrove, 2014; Reyes et al. 2011). The chemical composition is dependent of the variety and can be modified by postharvest factors, such as storage and processing (Robards et al. 1999). Some processes are commercially available and can preserve the product.

The dehydration is the most common method to preserve fruits and vegetables, increasing the shelf life by reducing the water content of the food and decreasing the water activity ( $a_w$ ), thereby inhibiting the growth of microorganisms and delaying the physico-chemical deterioration (Alibas and Köksal, 2014; Cano-Chauca et al., 2004; Prabhanjan et al., 1995). The dehydration has other benefits, such as the weight and volume reduction, and, consequently, the reduction of packaging and transportation costs (Kowalski and Mierzwa, 2013; Sagar and Suresh Kumar, 2010).

In this Chapter, some topics that support the experimental work are discussed below. The first topic is about the main process, osmotic dehydration, used to produce dehydrated food with intermediate water content. The next four topics focus on some processes used in the production of dehydrated food with reduced water content — hot air drying, microwave drying and freeze-drying — and the respective theoretical fundamentals and some applications. Finally, some quality parameters are approached, such as the water activity, the colour, the total phenolic content, the antioxidant activity and the rehydration ability of the dried products.

## 1.2 Osmotic dehydration

Osmotic dehydration (OD) is a food preservation technique, which is used to produce final products with intermediate moisture (up to 50 % of the initial content in fruits and vegetables), or as a pre-treatment in the production of dehydrated foods (Aguilera et al., 2000; Rastogi and Raghavarao, 1997; Torres et al., 2006). This mild process allows to retain vitamins and minerals, colour, flavour and taste of the raw material (Chavan and Amarowicz, 2012; Khan, 2012; Yadav and Singh, 2014).

The OD process consists in the immersion of foods (fruits, vegetables, meat or fish) in an aqueous solution of high osmotic pressure for the partial removal of water (El-Aquar and Murr, 2003; Khan, 2012; Torreggiani, 1993). The difference in osmotic pressure between the food and the solution results in the diffusion of water from the food into the solution and diffusion of the solute from the solution into the food (An et al., 2013; Rastogi et al., 2014; Tortoe, 2010). The osmotic agent used in OD can be a salt, an alcohol, a starch solution, a sugar or even a combination of different agents, depending on the final product. The solutes more frequently used are fructose, corn syrup, glucose, sodium chloride and sucrose (Yadav and Singh, 2014). Low molar mass saccharides have been used to facilitate the sugar uptake due to the high diffusion of these molecules (Khan, 2012).

The OD process may be evaluated by the parameters water loss (*WL*) and solid gain (*SG*). The *WL* and *SG* during OD depend on the temperature and concentration of the osmotic solution, the type of solute (nature and molecular weight), the level of agitation of the solution, the mass ratio of food to solution, the immersion time, the material structure (porosity), the sample geometry (size, shape, and surface area), the pressure and the pre-treatments of the food (Conway et al., 1983; Khan, 2012; Mišljenović et al., 2011; Mújica-Paz et al., 2003; Uddin et al., 2004; van Nieuwenhuijzen et al., 2001). The selection of the values of the process variables is performed considering the final application and characteristics of the final product.

The increase in the concentration, temperature and level of agitation of the osmotic solution normally results in an increase in the rate of dehydration (*WL* and *SG*) (Khan, 2012). The increase in concentration of the osmotic solution results in an increase in the osmotic driving force between the sample and the surrounding solution. The increase in temperature decreases the viscosity of the osmotic solution, decreases the resistance to mass transfer between the surface and the osmotic solution, and, thus, facilitates the outflow of water from the sample and the diffusion rate of solute into the sample (Matuska et al., 2006). However,

high temperatures may cause flavour deterioration and enzymatic browning (Khan, 2012). The agitation during the OD process reduces the external resistance to the mass transfer, increasing the water loss and solute uptake in the product.

At the beginning of the process, the rate of OD is high due to the difference in osmotic pressure between the osmotic solution and the food. Subsequently, the water loss and solute uptake decrease because the concentration gradient between the solution and the food decreases over time (Mundada et al., 2011).

An extensive water loss with low solute uptake is desired in most cases, because of the negative impact on the nutritional and natural product profile induced by the modification of the composition of the final osmotic dehydrated product (Azulara et al., 2002; Matuska et al., 2006).

Many researchers have investigated the effect of osmotic pre-treatment on the subsequent drying processes. Alvarez et al. (1995) studied the effect of the blanching and the glucose concentration in the osmotic solution on the air drying of strawberries at 55°C. They observed that the pre-treatment affected the effective diffusion coefficient of water, but the OD after blanching caused no additional effect. Aminzadeh et al. (2012) found that the OD reduced the total processing time of air drying of melon. Ciurzynska et al. (2014) did not find any difference in the water content when they compared freeze-dried pumpkin with or without a previous osmotic treatment. Kaur et al. (2014) observed a lower air drying rate in mushrooms pre-treated with salt due to the deposition of salt molecules on the surface of mushroom tissues. Heredia et al. (2012) found that the osmotic pre-treatment with sucrose solution followed by hot air drying is the best combination to preserve the typical aroma of fresh cherry tomato.

### **1.2.1 Sorbitol**

The osmotic agent used in OD can be a salt, an alcohol, a starch, a sugar, or even a combination of different agents (Yadav and Singh 2014). The nutritional values, organoleptic properties and the cost of the final product are determining factors in the choice of the osmotic agent (Ferrari et al., 2005).

The osmotic agent more used in the OD of fruits is sucrose because of its effectiveness, convenience and desirable flavour (Lenart, 1996). Others solutes have been used in the osmotic process, such as sorbitol (Brochier et al., 2014, Chauhan et al., 2011)

Sorbitol is a polyol and it is naturally found in appreciable quantities in several fruits (e.g., berries, cherries, and apples), and it was one of the first polyols to become commercially available (Deis and Kearsley, 2012). The use of the polyols presents some advantages because they are non-cariogenic (sugar-free tooth-friendly), low-glycaemic (potentially helpful in diabetes and cardiovascular disease), low-energy and low-insulinaemic (potentially helpful in obesity), low-digestible (potentially helpful in the colon), osmotic (colon-hydrating, laxative and purifying) carbohydrates (Livesey, 2003).

Sorbitol is becoming popular and it is a prebiotic with proven health properties (Chandra and Kumari 2015; Chauhan et al. 2011; Patel and Goyal 2012). The beneficial health effects of prebiotics are associated with the gut health maintenance, colitis prevention, cancer inhibition, immunopotentiality, reduction of cardiovascular disease, prevention of obesity and constipation, bacteriocin production (Patel and Goyal, 2012). Sorbitol, as well as others nutritive sweeteners, has been considered as a possible alternative for glucose and sucrose (Brunzell, 1978).

Therefore, the use of sorbitol as osmotic agent in OD is a promising alternative to replace the sucrose because of its low calorie value and a relative sweetness of around 60 % compared with sucrose (Silveira and Jonas, 2002). Besides, the reductions in caries scored 89 % with the use of sorbitol in relation to sucrose (Grenby, 1988). In food products, the sorbitol is widely used in confectionery, chewing gum, candy, desserts, ice cream, and foods for diabetics, not only as a sweetener, but also as a humectant, a texturizer, and a texture softener (Ladero et al., 2007; Silveira and Jonas, 2002).

### **1.3 Hot air drying**

The hot air drying is the most common and oldest method of water removal used not only by the food industry, but also for domestic purposes, due to the low investment and easiness to be carried out (Kowalski and Mierzwa, 2013). During this process, the food is exposed to a continuously flowing of hot air causing the water evaporation. So the hot air is used as a drying medium, convection being the mode of the heat transfer (Bruijn and Bórquez, 2014; Ratti, 2001).

The convective drying may be described by a constant rate period followed by a falling rate period. The constant rate drying is governed by the rates of external heat and mass transfers, where free water is always available at the evaporating surface. This period finishes when the surface becomes unsaturated or when the critical moisture content is

achieved. In general, this period is determined by the external conditions and is independent of the material. After this period, the drying becomes governed by the internal flow of liquid or vapour and the falling rate period starts. This period depends of the material and drying conditions (Barbosa-Cánovas and Vega-Mercado, 1996; Japngam and Mujumdar, 2010).

In most fruits, the constant drying rate period is not observed, meaning that the diffusion is the dominant physical mechanism governing the movement of moisture during the air drying (Garcia et al., 2014; Ispir and Tòrul, 2009; Mandala et al., 2005). The diffusion of the liquid occurs due to the difference between the concentration in the surface and in the interior of the material (Barbosa-Cánovas and Vega-Mercado, 1996).

The hot air drying results in a final product of high stability, but it may change the taste, the colour and the nutrient content due to the high temperature and long drying time (Alibas and Köksal, 2014; Kowalski and Mierzwa, 2013). The low energy efficiency and the long drying time result in the reduction of the surface moisture and, consequently, in the shrinkage and shape deformation of the sample (Maskan, 2001; Ramos et al., 2003). Moreover, the rehydration capability decreases due to the shrinkage (Mayor and Sereno, 2004). McMinn and Magee (1997) found that the volumetric shrinkage during the air drying of potatoes was related to the process temperature.

Some process variables can affect the convective drying. The air temperature, the air-flow velocity and the dimensions of the sample can affect the drying. Amami et al. (2017) dried strawberries at different temperatures (40 – 60 °C) and concluded that an increase in the temperature increased the drying rate and, consequently, decreased the drying time. Unal and Sacilik (2011) studied the air drying of hawthorn fruits and found that the air temperature (50 – 70 °C) and the blanching in hot water prior to the drying resulted in a decrease of the drying time. Doymaz (2004) evaluated the effect of the air temperature (50 – 70 °C), the air-flow velocity (0.5 and 1.0 m s<sup>-1</sup>) and the dimensions (1 × 1 × 1 and 2 × 2 × 2 cm) of the cut carrot during the convective drying. This author observed that the diffusion was facilitated by a lower dimension of the sample and the drying rate increased with the temperature and the air-flow rate. Sacilik and Elicin (2006) also observed that the decrease of the slice thickness of the sample from 9 to 5 mm resulted in an increased drying rate and a decrease in the drying time of organic apple. Velić et al. (2004) found that the increase of the air-flow velocity (0.64 – 2.75 m s<sup>-1</sup>) during the convective drying of apple resulted in an increase of both the heat transfer coefficient and the effective diffusion coefficient. Besides temperature and the air-flow velocity, Hui et al. (2011) also investigated the influence of the size (small, medium or large) and the maturity (70 % – complete mature) on the hot air drying of litchi

pulp. They found that the smaller and complete mature fruits presented higher drying rate than in others conditions.

#### **1.4 Microwave drying**

The microwave drying (MWD) is a relatively new technology by which the heat is absorbed within the product, leading to faster heating rates than hot air drying and making the drying more effective by reducing the drying time and, consequently, preventing the reduction of the quality of the final product. Besides, it destroys the microorganisms (Alibas and Köksal, 2014; Balbay and Şahin, 2012; Bondaruk et al., 2007; Hatibaruah et al., 1985).

Microwaves are a form of electromagnetic energy and the heat generation is caused by the interactions between the microwaves and the material (Al-Harashseh et al., 2009; Feng et al., 2012). The heating of the interior of the product, during this type of drying, leads to the build-up of an internal vapour pressure that makes the moisture come out of the product (Feng et al., 2012).

The advantages of the microwave drying are the improvement of the heat and mass transfer processes, the development of internal moisture gradients, which enhance the drying rates, and the increase of the drying rates without increasing the surface temperatures (Chua and Chou, 2005). The disadvantage is the relatively high cost and low life span of the magnetron (Feng et al., 2012).

The influence of the process variables on the microwave drying has been studied by many researchers. Walde et al. (2002) found that, during the microwave drying of wheat, the water loss decreased with the decrease of the microwave power. Ding et al. (2012) dried daylily flower buds in a microwave oven (60 – 240 W) and observed that the drying rate increased initially and then decreased at the end of the process. Demirhan and Özbek (2010) also found that the increase of the microwave power (180 – 900 W) decreased the drying time of basil leaves. Krishna Murthy and Manohar (2012) investigated the microwave drying of mango ginger and observed that the drying rate and effective diffusivity increased as the microwave power output increased (315 to 800 W). Evin (2011) studied the microwave drying of white mulberry and found that the drying rate constant and the effective diffusivity increased with the increase of the microwave power level. Çelen and Kahveci (2013) studied the effects of the microwave power level on the microwave drying of tomato slices. The drying time, the energy consumption and the colour quality decreased considerably with the increase in the microwave power.

## 1.5 Freeze-drying

The freeze-drying is a process by which the water is removed from the material by sublimation under reduced pressure (Argyropoulos et al., 2011; Ratti, 2001). This process consists mainly of two steps: the product is frozen, and the product is dried by direct sublimation of the ice under reduced pressure (Barbosa-Cánovas and Vega-Mercado, 1996). The process performed at low temperatures results in a product with low damage (normally caused by thermal and chemical degradation), high porosity and reduced shrinkage (Barbosa-Cánovas and Vega-Mercado, 1996; Marques and Freire, 2005). The excellent quality of the final product is a result of the reduced deterioration and microbiological reactions due to the absence of liquid water and the low temperatures of the process. Besides that, the solid state of the water protects the primary structure resulting in a minimal reduction of the product volume and shape (Ratti, 2001).

The freeze-drying guarantees high-quality products with superior sensory and nutritional properties with enhanced stability, and high rehydration capacity (Jiang et al., 2010; Serna-Cock et al., 2015). Besides, it is considered the best drying method for foods because it results in final products with high quality (Claussen et al., 2007; Jiang et al., 2014). The flavour, aroma, colour, shape, dimension and appearance are claimed to be retained in the freeze-dried product (Kopjar et al., 2008). The disadvantages of this process are the high cost, due to the low drying rates and the use of vacuum, and time-consuming (Barbosa et al., 2015; Jiang et al., 2014).

Most of studies carried out using the freeze-drying process are related with the quality of the final product. Marques et al. (2007) freeze-dried acerola fruits and observed that the important nutritional parameters were preserved after the process. Serna-Cock et al. (2015) investigated the structural, physical, functional and nutraceutical changes after the freeze-drying of some fruits. They noted that properties such as shape, dimension, appearance, flavour, colour, texture and nutraceutical ingredients were retained in most fruits.

Ayala-Aponte et al. (2010) found that the freeze-drying was suitable to preserve the pitahaya slices. This because, after the process, the volume was maintained, increased the porosity and, after the rehydration, the water content was recovered reaching a value close to the initial one.

## 1.6 Combined drying technologies

Some works on the combination of different drying methods have been carried out. Due to the high cost of some methods, such as microwave and freeze-drying, an advantage would be a combination of these methods with other dehydration technologies.

Andrés et al. (2007) studied different combinations of osmotic dehydration followed by microwave-assisted hot air drying and observed that the microwave level power and the osmotic dehydration time were the variables that most affected the drying time of mango cylinders. Paengkanya et al. (2015) investigated the drying of sliced durian pulp using different drying methods: microwave vacuum, combined microwave-hot air and hot air drying. The combination of the microwave and hot air drying resulted in higher drying rates and the rates increased with the microwave power level, leading to shorter drying times. Maskan (2000) dried banana using convection, microwave and convection followed by microwave, and found that the combination of the two drying methods increased the drying rate and reduced the drying time by 64 %. Yang and Atallah (1985) used four methods of drying to dry blueberries: air, vacuum, microwave/convection and freeze-drying. The combination of microwave and convection drying methods reduced the drying time, however, resulted in berries with the worst quality in comparison with the berries dried by any of the other methods.

Jiang et al. (2010) studied the influence of the microwave power intensity on the microwave freeze-drying of banana slices. They found that the increase in the microwave power reduces the drying time and increase the rehydration rate. Pei et al. (2014) dried mushroom slices using freeze-drying and freeze-drying combined with microwave vacuum and concluded that the combination of different drying processes lead to higher drying efficiency due to shorter drying times.

## 1.7 Mathematical models

### 1.7.1 Osmotic dehydration

Different models have been proposed with the objective to predict the mass transfer kinetics of the OD process and they may be classified as empirical and semi-empirical, mechanistic, and phenomenological. The parameters  $WL$  and  $SG$  can be calculated by the following equations, respectively:

$$WL = \frac{w_{w0} - w_w}{w_0} \quad (1.1)$$

$$SG = \frac{w_s - w_{s0}}{w_0} \quad (1.2)$$

The advantages and disadvantages of the different types of models are presented in Table 1.1. Empirical and semi-empirical models correlate the process variables with  $WL$  and  $SG$ , without taking into account the underlying simultaneous transport phenomena of water and solutes, and include multivariable regressions, response surface analysis, and mass balances (Azuara et al., 1992; Herman-Lara et al., 2013; Mercali et al., 2011; Sereno et al., 2001). Knowledge on microscopic histological and cellular features, such as the types of tissue, the geometric properties of the cell, the cellular water potential, the mechanical properties of the cell wall, the presence of intercellular spaces, etc. is important to understand structure-property relationships and then to estimate the rate of mass transfer of water and solutes in food (Aguilera et al., 2000; Mebatsion et al., 2006; Mebatsion et al., 2008). Thus, mechanistic models have been developed taking into account structure and/or macroscopic and microscopic approaches. The phenomenological models take into account the phenomenological mechanisms in the process and it is used for classical geometries. Among these, the most used model comprises a group of analytical solutions proposed by Crank (1975), based on the Fick's second law to represent the diffusional mechanism in OD performed at atmospheric pressure.

Several studies have been carried out to evaluate the fitting adequacy of the models. The experimental data have been interpreted based on models that allow to relate the characteristics of the dehydrated product with the raw material and the process variables, but they only reproduce conditions similar to those under which they were obtained (Ochoa-Martinez et al., 2007).

**Table 1.1** Classification of the different models to predict the mass transfer in OD processes

<b>Classification</b>	<b>Models</b>	<b>Advantage</b>	<b>Disadvantage</b>
Empirical and semi-empirical	<ul style="list-style-type: none"> <li>• Azuara's</li> <li>• Peleg's</li> <li>• Page's</li> <li>• Penetration</li> <li>• Magee's</li> <li>• Weibull's</li> <li>• Raoult et al.'s</li> <li>• Biswal and Bozorgmehr's</li> <li>• Panagiotou et al.'s</li> <li>• Rastogi and Raghavarao's</li> </ul>	<ul style="list-style-type: none"> <li>• Applied to non-classical geometries</li> <li>• Some models can predict the equilibrium values</li> </ul>	<ul style="list-style-type: none"> <li>• Limited to validity only within the experimental range for which the parameters of the model were obtained some model can predict the equilibrium values (Ochoa-Martinez, Ramaswamy, and Ayala-Aponte, 2007)</li> <li>• Do not take into account the phenomenological mechanisms in the process</li> </ul>
Mechanistic	<ul style="list-style-type: none"> <li>• Toupin et al.'s</li> <li>• Marcotte et al.'s</li> <li>• HDM</li> <li>• Spiazzi and Masheroni's</li> <li>• Seguí et al.'s</li> <li>• Mebatsion et al.</li> </ul>	<ul style="list-style-type: none"> <li>• Involve the cell structure of the food sample</li> </ul>	<ul style="list-style-type: none"> <li>• Require a large quantity of nonreadily available properties, such as cell membrane permeability, elastic module, porosity and tortuosity of the cell wall (Kaymak-Ertekin and Sultanoglu, 2000)</li> </ul>
Phenomenological	<ul style="list-style-type: none"> <li>• Crank's</li> <li>• Hough et al.'s</li> <li>• Mauro and Menegalli's</li> <li>• Mayor et al.'s</li> <li>• Peleg's modified model</li> </ul>	<ul style="list-style-type: none"> <li>• Can determine the diffusion coefficient</li> <li>• Take into account the phenomenological mechanisms in the process</li> </ul>	<ul style="list-style-type: none"> <li>• Require the equilibrium values</li> <li>• Classical geometries</li> <li>• If there is external resistance, shrinkage of the sample, or if effective diffusivity changes with temperature the model requires numerical methods</li> </ul>

### 1.7.1.1 Empirical and semi-empirical

#### 1.7.1.1.1 Azuara's model

Azuara's model was developed in 1992 and it is used to predict the  $WL$  and  $SG$  in OD based in mass balances. The equation of the model requires two adjustable parameters,  $s_1$  or  $s_2$  and  $WL_\infty$  or  $SG_\infty$ , and it is able to predict the mass transfer coefficients and the final equilibrium point, which is considered the main advantage. The  $WL$  and  $SG$  are given by the following equations:

$$WL = \frac{s_1 \cdot t \cdot WL_\infty}{1 + s_1 \cdot t} \quad (1.3)$$

$$SG = \frac{s_2 \cdot t \cdot SG_\infty}{1 + s_2 \cdot t} \quad (1.4)$$

Eq. (3) and Eq. (4) can be linearized:

$$\frac{t}{WL} = \frac{1}{s_1 \cdot WL_\infty} + \frac{t}{WL_\infty} \quad (1.5)$$

$$\frac{t}{SG} = \frac{1}{s_2 \cdot SG_\infty} + \frac{t}{SG_\infty} \quad (1.6)$$

The equilibrium water loss ( $WL_\infty$ ) and solid gain ( $SG_\infty$ ) are estimated from the slope and intercept of the plot of ( $t/WL$ ) and ( $t/SG$ ) versus  $t$ , using  $WL$  and  $SG$  values determined from the experimental data at different times.

#### 1.7.1.1.2 Peleg's model

Peleg (1988) proposed an equation to describe the moisture sorption curves that approach the equilibrium asymptotically. This equation is described using two parameters,  $k_1$  and  $k_2$ :

$$M = M_0 \pm \frac{t}{k_1 + k_2 \cdot t} \quad (1.7)$$

Some papers consider the  $WL$  instead of the moisture,  $M$  (Mišljenović et al., 2011; Sangeeta and Hathan, 2013; Schmidt, Carciofi, and Laurindo, 2009):

$$WL = \frac{t}{k_1^w + k_2^w \cdot t} \quad (1.8)$$

$$SG = \frac{t}{k_1^s + k_2^s \cdot t} \quad (1.9)$$

The Peleg constant  $k_1$  relates to the initial rate of mass transfer,  $t = t_0$ .

$$\left(\frac{d(WL \text{ or } SG)}{dt}\right)_{t \rightarrow 0} = \lim_{t \rightarrow 0} \left[ \frac{d\left(\frac{t}{k_1^{(w \text{ or } s)} + k_2^{(w \text{ or } s)} t}\right)}{dt} \right] = \frac{1}{k_1^{(w \text{ or } s)}} \quad (1.10)$$

The Peleg constant  $k_2$  relates to the minimum attainable moisture content. Values of  $1/k_2$  are the mass transfer at equilibrium, when  $t \rightarrow \infty$ .

$$\lim_{t \rightarrow \infty} (WL \text{ or } SG) = (WL \text{ or } SG)_{\infty} = \lim_{t \rightarrow \infty} \frac{t}{k_1^{(w \text{ or } s)} + k_2^{(w \text{ or } s)} t} = \frac{1}{k_2^{(w \text{ or } s)}} \quad (1.11)$$

$k_1$  and  $k_2$  may be calculated through the linearization of equation (1.8) and (1.9):

$$\frac{t}{WL} = k_1^w + k_2^w \cdot t \quad (1.12)$$

$$\frac{t}{SG} = k_1^s + k_2^s \cdot t \quad (1.13)$$

### 1.7.1.1.3 Page's model

In a study to determine the effects of the temperature and relative humidity of the drying air and of the initial moisture content of the product on the rate of drying, Page (1949) found that the drying of a thin layer of shelled corn followed a simple exponential equation:

$$\frac{WL}{WL_{\infty}} = 1 - \exp(-A_w \cdot t^{B_w}) \quad (1.14)$$

where  $A_w$  is the dehydration constant and  $B_w$  is the Page's parameter. Experiments were performed using air at a temperature of 75 °F (23.9 °C) with relative humidity of 35, 50 and 70 %, and at temperatures of 60 and 90 °F with 50 % of relative humidity (Page, 1949).

When this model was applied to the drying of a thin layer of material, only  $A_w$  parameter depends on the temperature, while  $B_w$  parameter remained constant (Holowaty et al., 2012).

In studies on osmotic dehydration, this model can also describe the solid gain in the process and this may be expressed by the following equation:

$$\frac{SG}{SG_{\infty}} = 1 - \exp(-A_s \cdot t^{B_s}) \quad (1.15)$$

#### 1.7.1.1.4 *The Penetration model*

Experimental data can be analysed assuming unsteady state Fickian diffusion to obtain the diffusion coefficients. By means of simplifying assumptions relative to the indefinite series expressions,  $WL$  and  $SG$  are considered proportional to the square root of contact time (Hawkes and Flink, 1978):

$$WL = k_w \cdot t^{1/2} \quad (1.16)$$

$$SG = k_s \cdot t^{1/2} \quad (1.17)$$

This model is valid for short periods of times and for application it is necessary that the external solution concentration remain constant and the resistance at the surface is negligible.

Equations (1.16) and (1.17) can be combined to give the relationship between  $WL$  and  $SG$ :

$$SG = \left( \frac{k_s}{k_w} \right) WL \quad (1.18)$$

#### 1.7.1.1.5 *Magee's model*

Magee et al. (1983), during the osmotic dehydration of apple slices with sucrose solution (30-70 %) at different temperatures (25-60 °C), found different relationships between the rate parameter ( $k$ ) and the initial solute concentration ( $C_0$ ), but the best correlation is the power law relationship:

$$k = A' \cdot C_0^x, \text{ at constant temperature} \quad (1.19)$$

Relating the rate parameter with temperature ( $T$ ), the equation becomes:

$$k = A \cdot C_0^x \cdot T^y \quad (1.20)$$

where  $A$ ,  $x$  and  $y$  are constants of the model.

It was observed that the rate of OD increase with increasing concentration of the solute in the solution, and the  $y$  does not vary significantly with temperature.

#### 1.7.1.1.6 Weibull's distribution model

The Weibull's model is about the probability distribution functions used to describe the behaviour of complex processes with some degree of variability (Cunha et al., 1998), such as OD process (Cunha et al., 2001).

The fractional amount of moisture content and solids gain during OD can be expressed as:

$$\frac{WL}{WL_{\infty}} = 1 - \exp \left[ - \left[ \frac{t}{\alpha_w} \right]^{\beta_w} \right] \quad (1.21)$$

$$\frac{SG}{SG_{\infty}} = 1 - \exp \left[ - \left[ \frac{t}{\alpha_s} \right]^{\beta_s} \right] \quad (1.22)$$

$\alpha$  is the parameter of the Weibull's model associated to the process rate: the time required for  $\frac{WL}{WL_{\infty}}$  or  $\frac{SG}{SG_{\infty}}$  to reach the value  $(1 - e^{-1})$ .

#### 1.7.1.1.7 Other empirical/semi-empirical models

According to Raoult-Wack et al. (1991), a bi-exponential model showed the best fit of the experimental data. The equation of this model has four empirical parameters with no physical meaning, and it makes possible to calculate the mass transfer rate and the equilibrium values of  $WL$  and  $SG$ . The model described by Biswal and Bozorgmehr (1992) takes into account the osmotic solution composition, temperature and time. But this model is valid just for solutions with sucrose-NaCl-water, with 50 % water content and temperature between 20 and 50 °C. The model suggested by Panagiotou et al. (1998) assumed that  $WL$  and  $SG$  are dependent of the solution concentration, temperature, time, level of agitation and size of fruit sample. The mathematical model proposed by Rastogi and Raghavarao (1996) is based on a fundamental parameter, the osmotic pressure,  $\pi$ , defining the osmotic pressure ratio,  $(\pi - \pi^*)/(\pi_0 - \pi^*)$ , for dehydration under atmospheric conditions and under vacuum.

#### 1.7.1.2 Mechanistic

##### 1.7.1.2.1 Toupin et al.'s model

Toupin et al. (1989) developed a mathematical model that takes in consideration the cell membrane characteristics to describe the water and solute fluxes in complex cellular

structures. This model uses an extended form of the second Fick's law to describe the intercellular transport of water and solute, and the thermodynamics of irreversible processes for transmembrane transport. An arrangement of cylinders was used to simulate the system because of the complexity of biological tissue structures. The validation of the model was made with experimental data of osmotically dehydrated beetroot and potatoes with sucrose and mannitol solutions, respectively.

There are two ways for water and solutes to pass into plant storage tissues: through the apoplast, which is external to the cell membrane (plasmalemma), or through the symplast, which is internal to the plasmalemma of neighbouring cells. Plasmalemma transport is the movement of material into the cell wall and the intercellular free space, while symplastic transport involves transport of material from one cell directly into another by means of small channels (plasmodesmata) (Moorby, 1981; Nobel, 1983). The transport flux across the plasmalemma and symplastic flux transport of species  $j$  (water or solute) is calculated, respectively, by:

$$J_{jm} = \left| \sum_k L_{kjm} \cdot \Delta\mu_{km} \right| \quad (1.23)$$

$$J_{jp} = \left| \sum_k L_{kjp} \Delta\mu_{kp} \right| \quad (1.24)$$

where  $L_{kjm}$  and  $L_{kjp}$  are macroscopic phenomenological coefficients describing the permeability characteristics of the membranes considered and  $\Delta\mu_{km}$  and  $\Delta\mu_{kp}$  are the differences in the chemical potential of species  $k$  between cellular and extracellular solutions, or between the solution inside a cell and that of a neighbouring cell, respectively. As the cell wall is normally permeable to most solutes used in osmotic dehydration, the space between the cell wall and cell membrane is considered to be part of the extracellular volume. The chemical potential may be given by the following equation:

$$\Delta\mu = R \cdot T \cdot \Delta \ln a_t + v \cdot \Delta P \quad (1.25)$$

where  $R$  is the universal gas constant,  $T$  is the absolute temperature of the system,  $a_t$  is the activity of species  $j$ ,  $v$  is the partial molar volume and  $\Delta P$  is the pressure resulting from the static, osmotic and matrix potentials.

The intercellular transport of species  $j$  is calculated by:

$$\frac{\partial \rho_j}{\partial t} = \frac{\partial}{\partial z} \left( D_{ej} \cdot \frac{\partial \rho_j}{\partial z} \right) - \frac{\partial}{\partial z} (\rho_j \cdot u) - \rho_j \cdot \frac{\partial V_1}{\partial t} - \frac{A_m}{V_1} \cdot (J_{jm} + J_{jp}) \quad (1.26)$$

where  $\rho_j$  is the mass concentration of species  $j$ ,  $V_1$  is the intercellular volume,  $A_m$  is the membrane surface area.  $u$  is the average velocity, defined as:

$$u = \sum_j v_j \cdot N_{j1} \quad (1.27)$$

where  $N_{j1}$  is the molar flux of species  $j$  with respect to a fixed frame of reference chosen as the centre of the infinite slab.

### 1.7.1.2.2 *Marcotte et al.'s model*

Marcotte et al. (1991) improved the model of the mass transport phenomena in plant material developed by Toupin et al. (1989), in order to give a closer thermodynamic description of the forces acting in the osmotic process. The symplastic transport was not considered, the surface area of the plasmalemma was fixed, and the sucrose was used as the solute of the osmotic solution. The movement of sucrose was restricted to the extracellular space between protoplasts due to the impermeability of the cell membrane. The model was used to simulate the movement of water and sucrose in potato tubers.

The flux of water across the membrane is expressed by:

$$R_{wm} = L_{wm} \cdot M_w \cdot \left[ R_g \cdot T \cdot \ln \left( \frac{\hat{a}_{wv}}{\hat{a}_{wi}} \right) + \bar{V}_w \cdot (P_c - P_c^0) \right] \quad (1.28)$$

where  $L_{wm}$  is phenomenological coefficient, the term  $R_g \cdot T \cdot \ln \left( \frac{\hat{a}_{wv}}{\hat{a}_{wi}} \right)$  is the osmotic potential with the vacuole phase contribution and the  $\bar{V}_w \cdot (P_c - P_c^0)$  is the cellular pressure potential.

The convective diffusion in the extracellular space for sucrose is given by:

$$\frac{\partial \rho_s}{\partial t} = \frac{\partial}{\partial z} \left[ \bar{D}_s \frac{\partial \rho_s}{\partial z} \right] - \rho_s \cdot \frac{\partial u_b}{\partial z} - u_b \cdot \frac{\partial \rho_s}{\partial z} - \frac{\rho_s}{A_i} \cdot \frac{\partial A_i}{\partial t} \quad (1.29)$$

where  $\rho_s$  is the volume mass of sucrose,  $\bar{D}_s$  is defined as apparent diffusivity of sucrose,  $A_i$  is the cross-sectional area and  $u_b$  is the barycentric velocity.

Since a dehydration process happens in the cellular volume, the changes in the mass concentration,  $M$ , of the species present in the cellular volume and the cellular volume,  $V_c$ , variation is given, respectively, by:

$$\frac{\partial M}{\partial t} = -\frac{2\pi R_i}{M_{dm}} \int R_{wm} dz \quad (1.30)$$

$$\frac{\partial V_c}{\partial t} = -\frac{2\pi R_i}{M_w} \int \bar{V}_w R_{wm} dz \quad (1.31)$$

where  $M_{dm}$  is the mass of dry matter (DM) in the cellular volume,  $M_w$  is the molecular weight of water and  $R_i$  is the radius of the extracellular space.

### 1.7.1.2.3 The Hydrodynamic mechanism model

The Hydrodynamic mechanism model (HDM) may be used in the OD under vacuum and it is a combination of the diffusional and hydrodynamic mechanisms. The HDM is related with the product structure and it is important to know the porosity and the deformation behaviour when vacuum is applied to determine the amount of external liquid that can go into the product (Barat, 1998; Fito, 1994).

The mass transfer produced by driving forces due to pressure gradients (capillary and/or imposed) can be calculated according to HDM. This model was studied considering an ideal situation in which a pore is represented by a cylinder of constant diameter  $d$  and length  $z_L$ . Thus, the penetration of the liquid into the pore, as an effect of the pressure gradient, can be calculated by:

$$-\Delta P + \frac{32\mu z_L^2}{d^2} X_v \frac{dX_v}{dt} = 0 \quad (1.32)$$

where  $\mu$  is the liquid viscosity, and  $X_v$  is the penetration of the volume fraction of the pore occupied by the liquid. After calculating the mean value of  $X_v$  it is possible to extend to the total food volume, which is defined as the fraction of the food total volume occupied by gas and is given by the following equation:

$$X = \varepsilon_e X_v \quad (1.33)$$

where  $\varepsilon_e$  is the effective porosity.

This model was studied in the OD of apple.

### 1.7.1.2.4 Spiazzi and Mascheroni's model

Spiazzi and Mascheroni (1997) developed a mathematical model based on mass transfer in plant tissues with the application scope in the osmotic dehydration of foods. The

model takes into account the main mass transfer ways in cellular tissues, the product shape and size variation over the process, the chemical composition of the product and osmotic solution, and their mass ratio.

The transmembrane mass fluxes, the plasmalemmatic transmembranary flux and the symplastic transmembranary flux for the species  $j$  in the volume  $V^i$  is given, respectively, as follows:

$$n_{j_{cp}}^i = k_{j_p} \cdot (\rho_{j_c}^i - \rho_{j_0}^i) \quad (1.34)$$

$$n_{j_{cs}}^y = k_{j_s} \cdot (\rho_{j_c}^{i+1} - \rho_{j_c}^i) \quad (1.35)$$

where  $k_{j_p}$  and  $k_{j_s}$  are the plasmalemmatic and symplastic transmembrane mass transfer coefficients, respectively;  $\rho_{j_c}^i$  and  $\rho_{j_0}^i$  are the mass concentrations of the species  $j$  in the cell volume and in the extracellular volume, respectively and  $i$  is the division volume number.

The extracellular mass flux of species  $j$  is:

$$n_{j_0}^i = \frac{D_{apj} \cdot (\rho_{j_0}^{i+1} - \rho_{j_0}^i)}{t_v^i} + \rho_{j_0}^i \cdot u^i \quad (1.36)$$

where  $D_{apj}$  is the apparent diffusion coefficient of the species  $j$ ,  $t_v^i$  is the thickness of the transfer pathway and  $u^i$  is the velocity associated with the backward movement of the transfer area.

#### 1.7.1.2.5 *Seguí et al.'s model*

The driving force that promotes water transfer during an OD process was analysed by Seguí et al. (2006) considering the difference in concentration between phases or the difference in chemical potential.

The transmembrane molar water flux ( $J_{wm}$ ) was calculated as the average molar water flux across the plasmalemma of the protoplasts ( $J_w^P$ ) analysed and is given by the following equation:

$$J_{wm} = \frac{\sum_N J_w^P}{N} \quad (1.37)$$

The kinetic equation based on the diffusion mechanism (first Fick's law) was used to determine the permeability ( $D_{ew}/d_{PM}$ ):

$$J_w^P = -\frac{D_{ew}}{d_{PM}} \cdot \frac{P}{R_g T} \cdot (x_w^{EP} - x_w^{IP}) \quad (1.38)$$

where  $x_w^{EP}$  and  $x_w^{IP}$  are the water molar fraction of the external and internal phases, respectively.

A phenomenological equation based on irreversible thermodynamics was used to obtain the phenomenological coefficient for water transport across plasmalemma ( $L_{wm}$ ):

$$J_w^P = -L_{wm} \cdot R_g \cdot T \cdot \ln\left(\frac{a_w^{EP}}{a_w^{IP}}\right) \quad (1.39)$$

where  $a_w^{EP}$  and  $a_w^{IP}$  are the water activity of the external and internal phases, respectively. The water chemical potentials inside and outside the protoplast were considered to depend exclusively on the water activity of the solution ( $a_w^{EP}$ ,  $a_w^{IP}$ ).

The model developed by Seguí et al. (2006) was validated in osmotic experiments of apple isolated protoplasts at different temperatures (30, 40 and 50 °C) and different concentrations of sucrose solution (25, 35 and 45 %).

#### **1.7.1.2.6 Other mechanistic model**

In order to enable a multiscale modelling approach to investigate water and gas transport in fruits, Mebatsion et al. (2006) established geometrical models based on virtual cell tissues with the same statistical properties as the real tissues. These virtual models were produced by a Poisson Voronoi tessellation algorithm in conjunction with quantitative descriptors, namely the statistical distributions of the cell area, cell aspect ratio and cell orientation, these cell orientation and cell aspect ratio being calculated based on the moments of inertia (area moments) and least-square ellipse fitting, respectively. These models were validated with microscopic images of tissues of four different apple cultivars.

The Poisson Voronoi algorithm allowed the generation of a two-dimensional diagram (Okabe et al., 1992), which geometry could be transferred into a finite element code via mathematical tools. The cell wall was defined by shrinking the cell geometry until the desired cell wall thickness was obtained, and the cells, pores and cell walls were exported as separated bodies. The meshed representative virtual tissues could be used for the simulation of moisture transport in pome fruit tissues (Mebatsion et al., 2006).

### 1.7.1.3 Phenomenological

#### 1.7.1.3.1 Crank's model

Based on the Fick's second law, Crank (1975) proposed a group of analytical solutions for diffusion in different geometries with several initial and boundary conditions. This model is used to evaluate the mass diffusivities of  $WL$  and  $SG$ , and the analytical solutions were used to obtain the diffusion coefficient for classical geometries (Azarpazhooch and Ramaswamy, 2010; Zogzas and Maroulis, 1996). The diffusion model for the products subjected to OD was developed considering: that the moisture transfer is predominantly one-dimensional; that the initial moisture content is distributed uniformly in the product; a constant solution concentration; a negligible shrinkage (in most cases); a constant diffusion coefficient ( $D_e$ ) during drying and a negligible resistance to mass transfer at product surface. The mathematical solutions to problems of unidirectional diffusion in unsteady state were considered for the geometries of infinite plane sheet, infinite cylinder and sphere.

#### Infinite plane sheet

In practice, the following equation applies to the diffusion into a plane sheet of material so thin that the diffusing substance enters through the plane faces and a negligible amount through the edges.

$$\frac{WL}{WL_\infty} \text{ or } \frac{SG}{SG_\infty} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left(- (2n+1)^2 \cdot \frac{\pi^2}{4} \cdot Fo\right) \quad (1.40)$$

#### Infinite cylinder

A long cylinder in which diffusion through the flat ends can be neglected in comparison to the moisture removed through its curved surface may be defined as an infinite cylinder. The concentration distribution is then a function of radius  $r_c$  and time  $t$  only:

$$\frac{WL}{WL_\infty} \text{ or } \frac{SG}{SG_\infty} = 1 - 4 \sum_{n=1}^{\infty} \frac{1}{\alpha_n^2} \exp\left(-\alpha_n^2 \cdot \frac{D_e t}{r_c^2}\right) \quad (1.41)$$

#### Sphere

In this case the diffusion is radial and  $WL$  and  $SG$  is calculated through:

$$\frac{WL}{WL_\infty} \text{ or } \frac{SG}{SG_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-n^2 \cdot \pi^2 \cdot D_e \cdot \frac{t}{r^2}\right) \quad (1.42)$$

### 1.7.1.3.2 Hough et al.'s model

Hough et al. (1993) developed a model, which takes into account the outgoing water, incoming solute and shrinkage of fruit during the OD process. The diffusional equations of mass balance for transport of water and solute used were, respectively:

$$\frac{\partial WL}{\partial t} = D_{ew} \frac{\partial^2 WL}{\partial z^2} \quad (1.43)$$

$$\frac{\partial SG}{\partial t} = D_{es} \frac{\partial^2 SG}{\partial z^2} \quad (1.44)$$

where  $D_{ew}$  and  $D_{es}$  are the effective diffusivity of water and solute, respectively.

Equations 43 and 44 were solved numerically by the Crank-Nicolson method (Crank and Nicolson, 1947).

For diffusional purposes it was assumed that fruit pieces were infinite slices, although in reality the slices were approximately cylindrical in shape. In order to consider the shrinkage in the numerical solution of the model, the half side of the slice was adjusted at each time step according to:

$$r_c = r_{c0} \cdot \sqrt{V/V_0} \quad (1.45)$$

where the subscripts zero is relative to the fresh fruit.

From the assumption that the only diffusional species are water and solute,  $V/V_0$  can be calculated as follows:

$$\frac{V}{V_0} = \frac{(w_w + w_s)}{(w_{w0} + w_{s0})} \cdot \frac{\rho_s}{\rho_{s0}} \quad (1.46)$$

where  $\rho_s$  is density of sucrose solution within the apple after OD and  $\rho_{s0}$  is the density of sugar solution in fresh fruit.

The model was validated in the osmotic dehydration of apple slices at 45 °C using 55 % glucose syrup.

### 1.7.1.3.3 Other phenomenological models

Mauro and Menegalli (2003) suggested a mathematical model using an osmotic solution composed of a ternary system of species that considers the bulk flow in a shrinkage solid matrix, and the dependence of the diffusion coefficients on the concentration. Mayor

et al. (2006) modelled the mass transfer using Fick's second law of diffusion taking into consideration the shrinkage of samples. The Peleg's modified model proposes a new parameter, the half-life rate, which is the time required for a half reduction of the dehydration initial rate. This model is based on the equation of diffusion in one dimension in a flat sheet (proposed by Crank), and gives a physical meaning to Peleg's model (Barbosa Júnior et al., 2013).

### 1.7.2 Hot air, microwave and freeze-drying

The theoretical model most used to describe different processes of drying that produce food with low moisture content is also Crank's model, which, as already mentioned (section 1.7.1.3), is a phenomenological model. Semi-theoretical models are based on the simplification of the general series solution of the Fick's second law (Akpinar, 2006). However, these models are valid only for the specific conditions which they were developed for and do not need the restriction of geometric considerations or diffusivity. Some empirical and semi-empirical models are Newton's, Page's, the modified Page's, Henderson and Pabis', the logarithmic, the two-term, the two-term exponential, the diffusion approach, Verma et al.'s, Midilli et al.'s, Weibull's and Wang and Singh's models, which are used widely. These models do not take into account the phenomenological mechanisms and their parameters do not represent a physical meaning. The advantages and disadvantages of the use of the phenomenological and empirical and semi-empirical models were presented in the section 1.7.1.

The moisture ratio ( $MR$ ) is used to describe the experimental data during the drying process:

$$MR = \frac{M - M_{\infty}}{M_0 - M_{\infty}} \quad (1.47)$$

$M_0$  is the initial moisture content,  $M$  is the moisture content at time  $t$ , and  $M_{\infty}$  is the moisture content at equilibrium, all in dry basis (kg water kg DM<sup>-1</sup>).

Crank

$$MR = \left[ \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} \exp\left(-\frac{(2n+1)^2 \pi^2 D_e t}{4a^2}\right) \right]^3 \quad (1.48)$$

Newton

$$MR = \exp(-k.t) \quad (1.49)$$

Page

$$MR = \exp(-A.t^B) \quad (1.50)$$

Modified Page

$$MR = \exp(-(A.t)^B) \quad (1.51)$$

Henderson and Pabis

$$MR = a.\exp(-k.t) \quad (1.52)$$

Logarithmic

$$MR = a.\exp(-k.t) + c \quad (1.53)$$

Two-term

$$MR = a.\exp(-k_1.t) + b.\exp(-k_2.t) \quad (1.54)$$

Two-term exponential

$$MR = a.\exp(-k.t) + (1 - a).\exp(-k.a.t) \quad (1.55)$$

Verma et al.'s

$$MR = a.\exp(-k.t) + (1 - a).\exp(-b.t) \quad (1.56)$$

Midilli et al.

$$MR = a.\exp(-k.t^n) + b.t \quad (1.57)$$

Weibull

$$MR = a - b.\exp(-(k.t^B)) \quad (1.58)$$

Diffusion approach

$$MR = a.\exp(-k.t) + (1 - a).\exp(-k.b.t) \quad (1.59)$$

$$MR = 1 + a.t + b.t^2 \quad (1.60)$$

## 1.8 Quality of the dried products

Nowadays, consumers are increasingly demanding about the quality of products. A good food product should have good texture, appearance and nutritive value. Therefore, the priority is not only the efficiency of the process, but also the quality of the final product, which is important for the commercialization of dried products (Wang et al., 2010).

### 1.8.1 Water activity

During the storage, the food deterioration by microorganisms can occur quickly, whereas the enzymatic and chemical reactions occur slowly (Fellows, 2000). However, the food stability is not given by the moisture content of food, but by the availability of free water (water activity) (Barbosa-Cánovas and Vega-Mercado, 1996).

The water activity ( $a_w$ ) is defined as ‘the ratio of the vapour pressure of water in a food to the saturated vapour pressure of water at the same temperature’ and it is a reference parameter in most applications of food processing and storage due to various factors (Fellows, 2000; Maltini, Torreggiani, Venir, and Bertolo, 2003):

- $a_w$  is determinant for the growth of microorganisms;
- $a_w$  is related with most degradation reactions of chemical, enzymatic, and physical natures;
- moisture migration in foods follow the  $a_w$ , not the moisture content;
- the “monolayer” derived from water vapour sorption isotherm gives an indication of the optimum moisture content in dried foods;
- $a_w$  is easier to measure than moisture content, and the measure is non-destructive.

Almost all microbial activity is inhibited below  $a_w$  of 0.6, most fungi, yeasts and bacteria being inhibited below  $a_w$  of 0.7, 0.8 and 0.9, respectively (Erkmen and Bozoglu, 2016). The interaction of  $a_w$  with other factors, such as temperature, pH, oxygen and carbon dioxide, or chemical preservatives, has an important effect on the inhibition of microbial growth (Fellows, 2000).

### 1.8.2 Colour

The colour of dehydrated fruit is very important for the consumer acceptability (Chong et al., 2013; Krokida et al., 2001). According to the Chong et al. (2013), the colour change of dried fruits is typically due to Maillard reaction, pigment degradation, enzymatic browning or ascorbic acid (vitamin C) oxidation.

The most common method to evaluate the colour uses the CIE  $L^*a^*b^*$  mode CIELAB colour space (Commission Internationale de L'Eclairage, CIE, 1978). The parameters are  $L^*$  (lightness),  $a^*$  (green– red coordinate),  $b^*$  (blue–yellow coordinate), and the saturation index or chroma (C), the total colour difference ( $\Delta E$ ) and the browning index can be calculated by the following equations:

$$\text{Chroma} = \sqrt{a^{*2} + b^{*2}} \quad (1.61)$$

$$\Delta E = \sqrt{(L_0^* - L^*)^2 + (a_0^* - a^*)^2 + (b_0^* - b^*)^2} \quad (1.62)$$

the index “0” indicates the sample before the process.

$$\text{Browning index} = \frac{100(x-0.31)}{0.17} \quad (1.63)$$

$$\text{with } x = \frac{a^* + 1.75L^*}{5.645L^* + a^* - 3.012b^*}$$

Changes in the colour of products have been studied by some researchers. Stojanovic and Silva (2006) studied the effect of osmo-concentration, ultrasound and air drying on the colour of the rabbiteye blueberries. They found that the largest total colour difference ( $\Delta E$ ), compared to the control samples, were found in samples dried by osmo- concentration and then by air drying, but these colour changes were subtle to the human eye. Moreira et al. (2011) evaluated the effect of the osmotic dehydration with sodium chloride on the air drying of chestnuts and observed that the pre-treatment did not improve the colour of the samples. On the contrary, the  $\Delta E$ -values of osmosed peeled chestnuts were significantly higher than those without pre-treatment. One of the objective of the study of Chauhan et al. (2011) was to evaluate the effect of the osmotic agent (glucose, fructose, sucrose, maltose, sorbitol, honey) on the colour of the apple slices and observed that, among these solutes, sucrose produced the best colour.

### ***1.8.3 Total phenolic content and antioxidant activity***

The phenolic compounds constitute a large group of antioxidants that are present in almost all plant-based foods (Serna-Cock et al., 2015). Studies have demonstrated that apple has a high antioxidant activity and a potential role in reducing the risk of chronic disease, inhibiting cancer cell proliferation, decreasing lipid oxidation, and lowering cholesterol (Aprikian et al., 2001; Feskanich, 2000; Hertog et al., 1993). The content of the phenolic compounds depends on the type of fruit and varies with the variety, ripeness, agricultural and climatic factors, post-harvest storage conditions and method of anti-oxidant extraction (Shofian et al., 2011). These compounds have been gaining attention due to their antioxidant activities and health benefits (Carbone et al., 2011).

In general, the apple phytochemicals do not seem to be greatly affected by the storage, but the processing can result in a very significant decrease in the phenolic content (Boyer and Liu, 2004). The effects of the type of process and the process variables, among others, on total phenolic content (TPC) and antioxidant activity (AA) of fruits have been studied by many authors. López et al. (2010) studied the effect of the air temperature (50 – 90 °C) on the AA and TPC of blueberries and found that TPC decreased with the increase of the air temperature. The AA was higher at higher temperatures (80 and 90°C) than at low temperatures (50, 60 and 70°C). ÍzĪ (2016) compared three different methods of drying (convective, microwave and freeze-drying) in date fruit and observed that the microwave-dried samples presented the highest TPC and AA. Rahman et al. (2015) determined the TPC and AA of mango before and after freeze-drying and they did not observe significant differences in AA. The TPC presented a tendency to decrease after the drying process.

### ***1.8.4 Rehydration ability***

Dehydrated products are usually rehydrated prior to their consumption. The rehydration is evaluated by the ability to restore fresh product properties when the dried material is in contact with water or a solution, and is also an important factor in determining the quality of the dried product (Maldonado et al., 2010).

The rehydration capacity can be influenced by the product characteristics (size, geometry, composition, water content), the internal structure of the food and the rehydration temperature. It can be considered as a measure of the damage caused by the drying process (Krokida and Maroulis, 2001; Sanjuán et al., 2001; Vega-Gálvez et al., 2009).

There are many research reports measuring the ability of rehydration of dried materials, but there is no consistency in the procedures used and the way of the expressing this parameter. Mothibe et al. (2014) used the rehydration rate defined as the ratio of the weight of the rehydrated sample to that of dried sample. Vega-Gálvez et al. (2009) calculated the rehydration rate taking into account the weight and moisture content of the rehydrated and dried samples. Noshad et al. (2012) used some mathematical models to describe the rehydration kinetics.

Agnieszka and Andrzej (2010) studied the influence of the osmotic dehydration and the osmotic agent (sucrose and glucose solutions and starch syrup) on freeze-dried strawberries and found a decrease of the rehydration capacity in samples pre-treated with sucrose and glucose. Prothon et al. (2001) evaluated the effect of the osmotic pre-treatment on the rehydration capacity of apple cubes dried by microwave-assisted air-drying and the results showed that the rehydration was higher of non-treated samples than osmotically dehydrated samples. Giri and Prasad (2007) dried mushrooms using different methods (microwave-vacuum and hot-air) and observed that microwave-vacuum dried samples rehydrated more quickly than the air dried product.

The general objective was to study and to optimize the development of fruit-based dry products, in terms of the product quality and process efficiency: with intermediate water content through osmotic dehydration; or reduced water content, by subsequent combination of this dehydration technique with other drying methods. The main fruit studied was apple due to the high production volume, storage stability and high consumption. Besides this, apple is a porous matrix that facilitates the exchanges within the vegetable tissues.

The first part of the work focused on the osmotic dehydration (OD) of apple cubes and physalis. The adequacy of the fit of some mathematical models to describe the mass transfer kinetics in the products was also studied. The objectives were to perform the OD of apple cubes and to study the effects of the solute (sucrose and sorbitol) and the concentration (40 and 60 °Brix) in the osmotic solution, the mass ratio of sample to solution (1: 4 and 1:10), the temperature (25, 40 and 60 °C), and the pressure (1 bar and 150 mbar) on the water loss (*WL*) and the solid gain (*SG*). Regarding physalis, the OD was performed with a mass ratio of sample to solution of 1:4 at 60 °C and the pressure was 1 bar or 150 mbar. Another objective was to evaluate the changes in the microstructure of the apple tissue after the osmotic treatment with sucrose or sorbitol.

In the second part of the work, some drying methods were studied to obtain cut apple with reduced water content, namely hot air drying, microwave drying and freeze-drying. The

effect of the osmotic pre-treatment with sucrose or sorbitol solutions was also studied. For the best conditions of each method, the drying kinetics were compared among the different methods and the quality — water activity ( $a_w$ ), the colour, the total phenolic content (TPC), the antioxidant activity (AA) and the rehydration ability — of the dried apple cubes were evaluated. The adequacy of the fit of some mathematical models to describe the water content during drying was also evaluated. Thus, the effect of the temperature (25, 55, 70 and 80 °C) was studied on the hot air drying of osmotically dehydrated apple cubes (60 °C, 60 °Bx sucrose or sorbitol solutions, mass ratio of sample to solution 1:4). The effect of the osmotic pre-treatment and the microwave power (160, 350, 500, 650, 750 and 850 W) on the *WL* kinetics of microwave drying of apple cubes was also evaluated. Finally, the *WL* kinetics of the freeze-drying of apple cubes were studied.

## **Part II – Study of the osmotic dehydration process**



## Chapter 2 – Osmotic dehydration of apple cubes at 60 °Bx

### 2.1 Abstract

Apple cubes were osmotically dehydrated at 25, 40 and 60 °C, using sucrose or sorbitol and the mass ratio of sample to solution of 1:4 or 1:10, in atmospheric pressure or vacuum pressure of 150 mbar. Six mathematical models were tested to describe the mass transfer kinetics of water loss (*WL*) and solid gain (*SG*). Crank's, Azuara's, Peleg's, Page's and Weibull's models could fit well the experimental data, but the Penetration model resulted in a poor fit. The mass ratio of sample to solution did not have an influence on the mass transfer kinetics at atmospheric pressure. The increase of temperature and the use of sorbitol as osmotic agent resulted in an increase of the osmotic process rate at both pressures used. Therefore, sorbitol is a good alternative to sucrose. The vacuum presented a tendency to increase the initial rate of *WL*.

**Keywords:** apple cubes, osmotic dehydration, mass transfer, mathematical models

### 2.2 Introduction

The osmotic dehydration (OD) is the process that consists of the immersion of foods in aqueous solutions of high osmotic pressure for the partial removal of water, which is used to produce food with intermediate water content (in fruits and vegetables up to 50 % of the initial content) or as a pre-treatment (An *et al.* 2013; Khan 2012). The difference of the osmotic pressure between the food and the solution results in the diffusion of water from the food into the solution and diffusion of the solute from the solution into the food (An *et al.* 2013). The solute may modify the colour, texture and sensory properties of the material (Chauhan *et al.* 2011). Chauhan *et al.* (2011) evaluated the effects of different osmotic agents (glucose, fructose, sucrose, maltose, sorbitol, and honey) on the *WL* and *SG* of osmotically dehydrated apple slices at 40 °C for 2 hours, and they concluded that the use of sorbitol in the osmotic solution increases the *WL*. Ispir and Toğrul (2009) studied the effect of the solution concentration, temperature, ratio of sample to solution, time and sample geometry also on the *WL* and *SG* of apricot during OD using different agents (sucrose, glucose, fructose, maltodextrin and sorbitol), and found that the highest *WL* was achieved when a

sucrose solution was used. Rodriguez *et al.* (2014) determined the *WL* and *SG* for stone fruit dehydrated in glucose and sorbitol solutions for 8 hours at 35 °C. Different results were obtained by these authors in relation to the effect of sorbitol on the kinetics of *WL* and *SG*.

The OD process may be evaluated through the *WL* and *SG*. At the beginning of the process, the rates of these parameters are high due the difference of the osmotic pressure between the solution and the food, but, then, they decrease over time with the decrease of the concentration gradient between the medium and the food (Mundada *et al.* 2011). The *WL* and *SG* are influenced by the process variables such as temperature and concentration of the osmotic solution, the type of solute (nature and molecular weight), the mass ratio of the food to solution, the immersion time, the pressure, the material structure (porosity), and the sample geometry (size, shape, and surface area), among others (Khan 2012; Mišljenović *et al.* 2011). The increase of the concentration of the agent in the solution results in an increase of the osmotic driving force between the sample and the surrounding solution. The increase in temperature decreases the viscosity of the osmotic solution, decreases the resistance to the mass transfer between the surface and the solution, and, thus, facilitates the outflow of water from the sample and the diffusion rate of solute into the sample (Mundada *et al.* 2011). However, high temperatures may cause flavour deterioration and non-enzymatic browning. The agitation during the OD process reduces the external resistance to the mass transfer, increasing the *WL* and *SG* of the product (Khan 2012).

The use of vacuum in the OD process may increase the *WL* in comparison to the atmospheric pressure. This increase of mass transfer rate, when vacuum pressure is used, was explained by the hydrodynamic mechanism (HDM). The OD under vacuum consists in the application of a vacuum pressure to a solid–liquid system, followed by restoration of the atmospheric pressure. During the application of vacuum in the osmotic process the gas and/or liquid contained in the product pores is removed from the porous space of the food. When the atmospheric pressure is restored, the external solution penetrates into the porous space of the food (Fito 1994).

Most studies on OD of fruits, vegetables, meat and fish have been performed during short periods. Nonetheless, it is difficult to predict the behaviour of the *WL* and *SG* at the equilibrium point when different osmotic agents and solution temperatures, among others, are compared.

Mathematical modelling has been used to describe the OD mass transfer kinetics, consequently, to study the effects of process variables on the process. The models may be classified as empirical and semi-empirical, phenomenological and mechanistic. The

empirical and semi-empirical models have the advantage of to be applied to non-classical geometries, not taking into account the phenomenological mechanisms in the process, and some of them can predict the equilibrium values. Azuara's, Peleg's, Page's, the Penetration and Weibull's model are examples of this type of models. The phenomenological model can determine the diffusion coefficient, but require the equilibrium values and must be used for classical geometries. The mechanistic models describe the OD process considering the cell structure of the food sample. Crank's (1975) is a phenomenological model often used, that comprises a group of analytical solutions based on the Fick's second law. Assis *et al.* (2016) established equivalences between the parameters of some different models based on the affinity of the respective equations.

The objectives of this study were: i) to carry out the osmotic dehydration of apple cubes (variety Royal Gala) until reaching the equilibrium values of *WL* and *SG*, using two solutes (sucrose or sorbitol), and to study the effect of the temperature (25, 40 and 60 °C), the mass ratio of sample to solution (1:4 or 1:10), and the pressure (1 bar and 150 mbar) on the *WL* and *SG*; ii) to test the adequacy of the fitness of some mathematical models (Crank's, Azuara's, Peleg's, Page's, the Penetration, Weibull's) for describing the *WL* and the *SG* of the product; iii) to confirm the equivalences between the parameters of some different models established in a previous work (Assis et al. 2016).

## **2.3 Material and methods**

### **2.3.1 Samples**

Apples (*Malus* spp., variety Royal Gala) were graciously supplied by Campotec, Portugal, and stored at 4 °C. The fruits were washed and sanitized with aqueous solution with 7500 ppm active chlorine for 5 min. Then, the samples were cut in cubes (12 mm) with a vegetable cutter (Secret de Gourmet, France) and immersed in a solution with 0.9 % sodium chloride for 3 minutes to prevent enzymatic browning. The samples were blotted gently with tissue paper in order to remove the excess of sodium chloride solution from the surface. The soluble solids content of the apple was  $15.3 \pm 1.3$  °Bx (Hand Refractometer, Atago, China).

### **2.3.2 Osmotic dehydration**

The osmotic solutions were prepared with ultra-pure water, commercial sucrose or sorbitol (Fagron Iberica, Spain). The apple samples were immersed in the osmotic solution of 60 °Bx and submitted to temperatures of 25, 40 and 60 °C at atmospheric pressure. The mass ratio of sample to solution used was 1:4 or 1:10. The OD was carried out in beakers placed in a shaking incubator (Wiggenhauser, Germany) at constant temperature and agitation (50 rpm). The apple cubes (approximately 7 g) were removed from the solution at different time intervals (every 30 minutes during the first 2 hours, and then every 2 hours until reaching the equilibrium). Then, the samples were rinsed with ultra-pure water to remove the solution adhered to the surface and blotted with tissue paper to remove the excess of water from the surface.

The  $a_w$  of the apple cubes was determined before and after the OD. The  $a_w$  and the viscosity of the solution were determined before and after the osmotic dehydration process in atmospheric pressure, with the mass ratio of sample to solution of 1:4, for each process temperature.

The OD in vacuum was carried out by applying 150 mbar pressure to hermetic containers with the apple samples. The mass ratio of sample to solution used in the experiments was 1:10. The experiments were performed in duplicate.

### **2.3.3 Moisture content and Water activity determination**

The moisture content was determined by placing the fresh and osmotic dehydrated samples in an oven (FP115, Binder, Tuttlingen, Germany) at 105°C until constant weight (A.O.A.C. 2002).

The water activity ( $a_w$ ) of the apple samples and the osmotic solutions was determined with a hygrometer (Aqualab Series 3, Decagon Devices Inc., Pullman, Washington, USA) at 25 °C, by placing approximately 3.5 g of apple sample, or 5.5 mL of solution in the measuring container. The determinations were performed in triplicate.

### **2.3.4 Viscosity determination**

The viscosity analyses were performed in a Gemini Advanced Rheometer (Bohlin Instruments, UK), coupled with a peltier unit, with a 4°/40 mm stainless steel cone-and-plate geometry probe. One mL of solution was placed in the measuring plate and viscosity was measured at shear rates of 10 - 100 s<sup>-1</sup>. In order to determine the viscosity of the solutions

previous to the osmotic dehydration process, temperature ramps were performed, with 5 min equilibrium time and viscosity measurements, at 25, 40 and 60 °C. Five measurements were performed, in duplicate.

### 2.3.5 Osmotic dehydration parameters

The fresh and osmotic dehydrated apples were placed in an oven (Binder, Germany) at 105 °C until constant weight to determine the dry matter and moisture content (A.O.A.C., 2002). The parameters  $WL$  and  $SG$  were determined through the equations 1.1 and 1.2.

### 2.3.6 Mathematical models

The Crank's, Azuara's, Peleg's, Page's, the Penetration and Weibull's were the mathematical models used to fit the experimental data. The model's equation of Azuara's, Peleg's, Page's, the Penetration and Weibull's were presented in 1.7.1. The Crank's model equation will be presented below. For all models that consider  $WL_{\infty}$  and  $SG_{\infty}$ , these variables were predicted by the model.

#### 2.3.6.1 Crank's model

The solution of Fick's second law for diffusion in a rectangular parallelepiped (dimensions  $2a$ ,  $2b$ ,  $2c$ ) results in the following equation for  $WL$  or  $SG$  (Crank 1975; Rastogi and Niranjana 1998):

$$\frac{WL}{WL_{\infty}} \text{ or } \frac{SG}{SG_{\infty}} = 1 - \sum_{n=1}^{\infty} C_n^3 \cdot \exp \left[ -D_e \cdot q_n^2 \cdot \left( \frac{1}{a^2} + \frac{1}{b^2} + \frac{1}{c^2} \right) \cdot t \right] \quad (2.1)$$

where  $WL_{\infty}$  and  $SG_{\infty}$  are the water loss and solid gain at equilibrium, respectively;  $D_e$  is effective diffusivity of water or solute, respectively, and  $C_n = \frac{2\alpha(1+\alpha)}{1+\alpha+\alpha^2 \cdot q_n^2}$ , where  $q_n$ 's are the non-zero positive roots of the equation  $\tan q_n = -\alpha q_n$ , and  $\alpha$  is the ratio of volume of solution to volume of the parallelepiped.

For cubes, all the sides are equal ( $2a = 2b = 2c$ ). Then, for cubical configuration eq. 2.1 is reduced to:

$$\frac{WL}{WL_{\infty}} \text{ or } \frac{SG}{SG_{\infty}} = 1 - \sum_{n=1}^{\infty} C_n^3 \cdot \exp \left[ -D_e \cdot q_n^2 \cdot \frac{3}{a^2} \cdot t \right] \quad (2.2)$$

For diffusion in a cube, Fourier number is defined as  $D_e \cdot \frac{3}{a^2} \cdot t$ . When this value is greater than 0.1 only the first term in eq. 2.2 is significant, and the other terms can be neglected. Eq. 2.2, therefore, may be reduced to:

$$-\ln \left( 1 - \left( \frac{WL}{WL_\infty} \text{ or } \frac{SG}{SG_\infty} \right) / C_1^3 \right) = q_1^2 \cdot \frac{3}{a^2} \cdot D_e \cdot t \quad (2.3)$$

The values of  $D_e$  for the water and solute can be determined from the slope of the linear regression plotting  $-\ln \left( 1 - \frac{WL}{WL_\infty} / C_1^3 \right)$  and  $-\ln \left( 1 - \frac{SG}{SG_\infty} / C_1^3 \right)$  versus  $t$ , but it requires the experimental values of  $WL_\infty$  and  $SG_\infty$ .

### 2.3.7 The Arrhenius behaviour

The linearized Arrhenius equation gives the dependence of the parameter  $p$  of the models on the temperature:

$$\ln p = \ln p_{ref} + \frac{E_a}{R \cdot T_{ref}} - \frac{E_a}{R} \cdot \frac{1}{T} \quad (2.4)$$

where  $p$  is the parameter;  $p_{ref}$  is the parameter at the reference temperature;  $E_a$  is the activation energy ( $\text{kJ mol}^{-1}$ );  $R$  the universal gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ); and  $T$  and  $T_{ref}$  are the temperature used and the reference temperature (K), respectively.  $T_{ref} = 298.15 \text{ K}$  was used in this work.

A linear regression was performed with 95 % confidence level to determine the Arrhenius parameters relative to the OD using sucrose or sorbitol solution independently of the mass ratio of sample to solution.

### 2.3.8 Statistical analysis

The statistical analysis was performed using Microsoft Excel 2000 (Microsoft Corporation, USA) (mean and standard deviation calculations) and IBM SPSS<sup>®</sup> Statistics 20.0 for Windows<sup>®</sup> (2012, SPSS Inc., Chicago, USA). The normality of the data of water activity at the different conditions used was tested using the Kolmogorov-Smirnov test. When the normality was verified, ANOVA was used to detect significant differences between the conditions. Post-hoc tests were posteriorly performed for multiple comparisons (Tukey test). For data that did not follow normality, an alternative non-parametric test,

Kruskal–Wallis, was used. In this situation the Mann-Whitney test was subsequently performed to detect which values were significantly different.

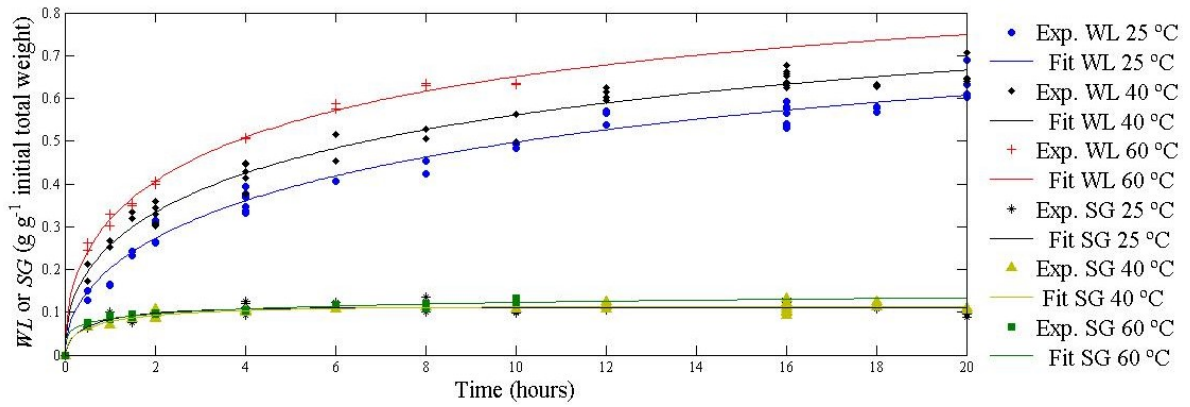
The models presented in section 2.3.6 were fitted to the experimental data obtained at the different conditions tested. The model parameters were estimated by non-linear regression procedures and the margin of error of the estimates was calculated at 95 % (margin of error = is the half width of the confidence interval at 95 %). The regressions were also assessed by ANOVA approaches.

The adequacy of the model fit was evaluated by the determination coefficient ( $R^2$ ) and by the residual analysis. The residual analysis was performed in order to check the assumptions of independence, randomness and normality (mean equal to zero and constant variance). Randomness and homoscedasticity was assessed by visual inspection of the dispersion of residuals vs. predicted value by the model. Normality of the residuals was evaluated by Kolmogorov-Smirnov test.

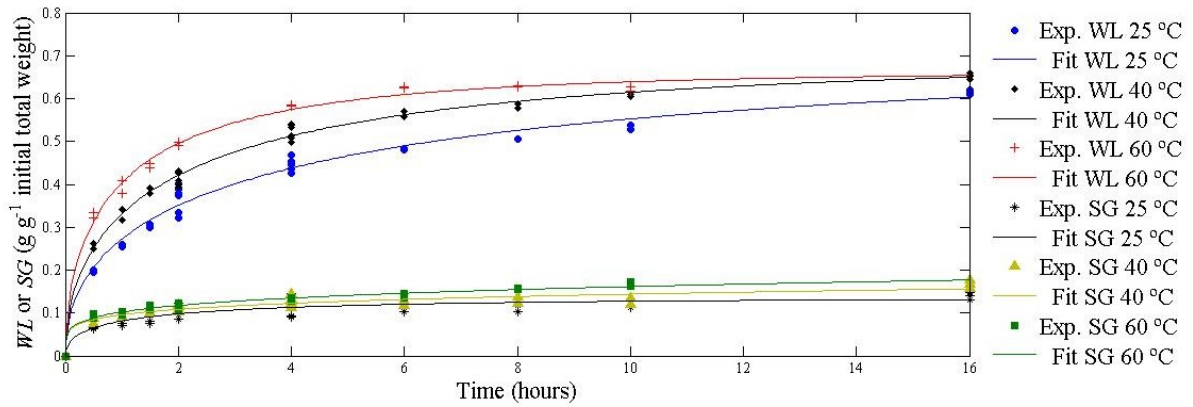
In all tests and analysis performed the significance level assumed was 5 %.

## 2.4 Results and discussion

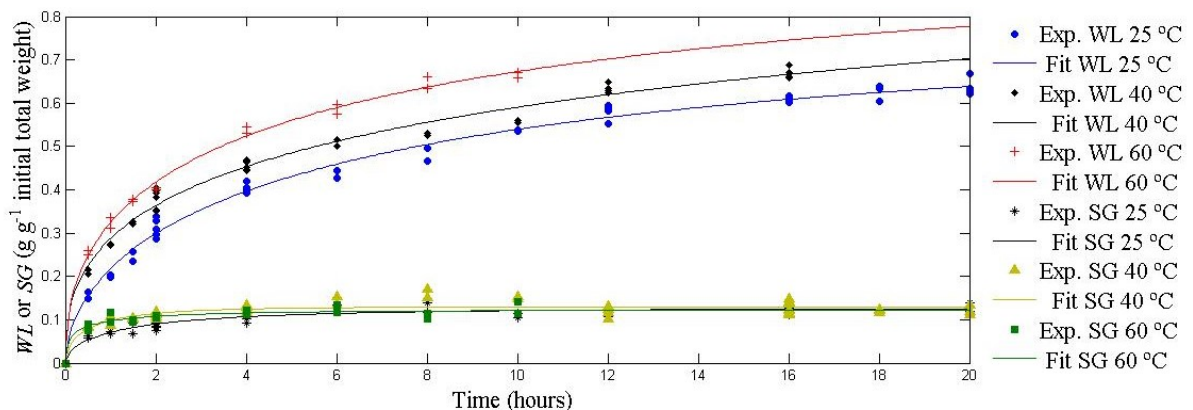
For all curves analysed, the rates of  $WL$  and  $SG$  ( $\Delta WL/\Delta t$  and  $\Delta SG/\Delta t$ ) were higher in the early hours of the process (Figures 2.1 to 2.6) due to a large osmotic driving force between the apple cubes and the hypertonic surrounding medium (sucrose or sorbitol). Mišljenović et al. (2011) studied the OD of apple cubes in sugar beet molasses solution and reported a rapid increase in  $WL$  and  $SG$  at the beginning of the process. Silva et al. (2012) observed that the  $WL$  increased with the processing time for the first two hours during the osmotic dehydration process of West Indian cherry using different mass ratios of fruit to solution.



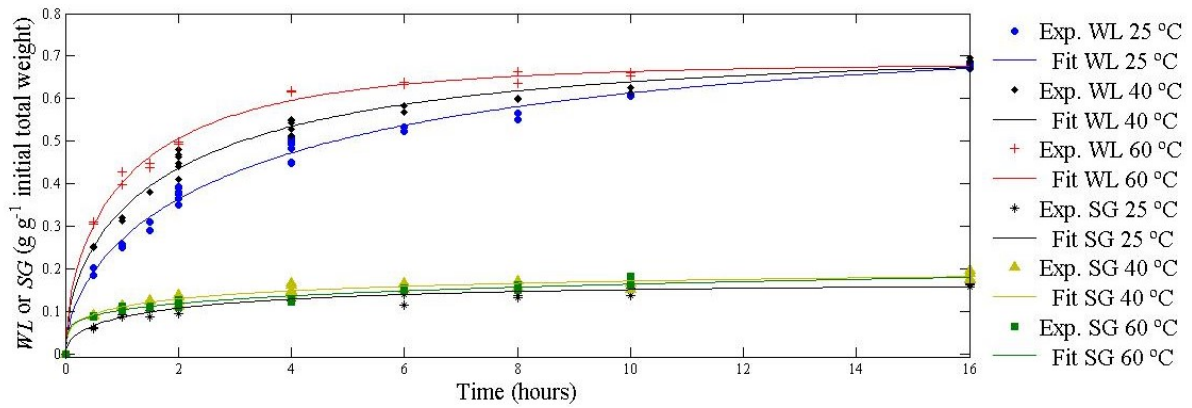
**Figure 2.1** Experimental data and the fit of Page’s model of *WL* and *SG* of apple cubes osmotically dehydrated in a sucrose solution at atmospheric pressure and at 25, 40 and 60 °C, using the mass ratio of sample to solution of 1:4



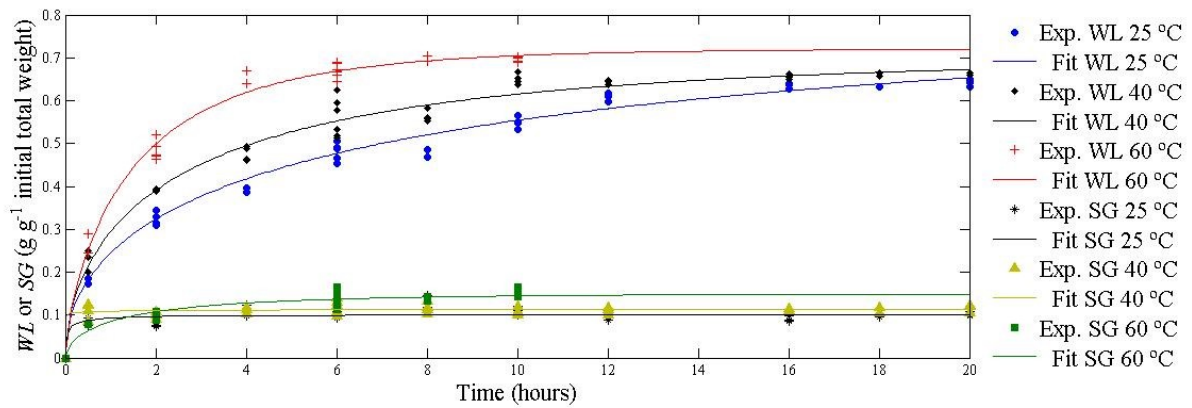
**Figure 2.2** Experimental data and the fit of Page’s model of *WL* and *SG* of apple cubes osmotically dehydrated in a sorbitol solution at atmospheric pressure and at 25, 40 and 60 °C, using the mass ratio of sample to solution of 1:4



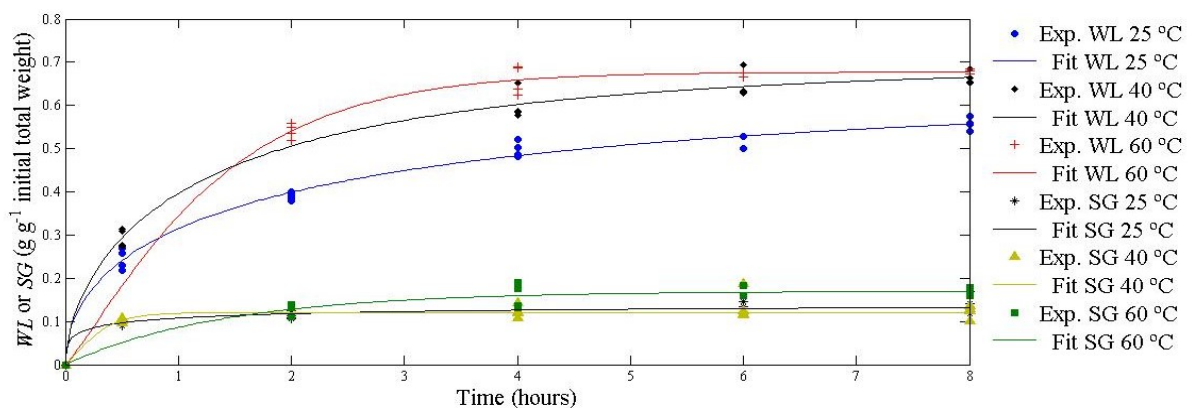
**Figure 2.3** Experimental data and the fit of Page’s model of *WL* and *SG* of apple cubes osmotically dehydrated in a sucrose solution at atmospheric pressure and at 25, 40 and 60 °C, using the mass ratio of sample to solution of 1:10



**Figure 2.4** Experimental data and the fit of Page's model of *WL* and *SG* of apple cubes osmotically dehydrated in a sorbitol solution at atmospheric pressure and at 25, 40 and 60 °C, using the mass ratio of sample to solution of 1:10



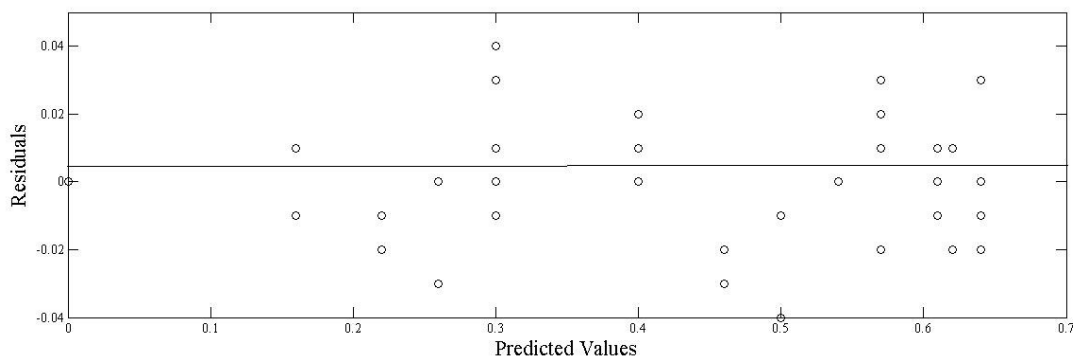
**Figure 2.5** Experimental data and the fit of Page's model of *WL* and *SG* of apple cubes osmotically dehydrated in a sucrose solution under vacuum (150 mbar) and at 25, 40 and 60 °C, using the mass ratio of sample to solution of 1:10



**Figure 2.6** Experimental data and the fit of Page's model of *WL* and *SG* of apple cubes osmotically dehydrated in a sorbitol solution under vacuum (150 mbar) and at 25, 40 and 60 °C, using the mass ratio of sample to solution of 1:10

### 2.4.1 OD at atmospheric pressure

The results of the non-linear regression of *WL* and *SG* data of the OD process of apple cubes are shown in Tables 2.1 and 2.2. In general, Crank's, Azuara's, Peleg's, Page's and Weibull's models presented high values of determination coefficients ( $R^2$ ) for both *WL* and *SG*, but the values are greater for *WL*, because of the higher variability of the experimental data of *SG*. This fact was also reflected in a higher margin of error of the predicted parameters. The residual analysis showed that the residuals are normally distributed at the significance level of 5 % and the visual analysis of the scatterplot of residuals vs. predicted values allowed to observe that the residuals were distributed randomly around zero with no systematic patterns. Therefore, homoscedasticity and zero mean of errors were satisfied. As an example, the residuals vs the predicted values by the Page's model for the *WL* of apple cubes during the OD process in sucrose solution at 25 °C using the mass ratio of sample to solution of 1:10 are presented in Figure 2.7. Thus, these models could fit the experimental data well. Some other authors also compared models among the ones presented in this work. They found similar results during the OD of pomegranate arils, apple, mango, papaya, banana, kiwi and eggplant (Bahmani et al. 2015; Mundada et al. 2011; Ochoa-Martinez et al. 2007).



**Figure 2.7** Residuals vs. predicted values for *WL* of apple cubes during the OD process in sucrose solution at 25 °C using the mass ratio of sample to solution of 1:10, fitted by the Page's model

The Penetration model did not describe successfully the experimental data of *WL* and *SG*, as  $R^2 < 0.9$ , and the residuals were not random and they were not normally distributed. The low adequacy of this model to fit the experimental data was also found by Mundada et al. (2011) and Sangeeta and Hathan (2013), when they studied the OD of pomegranate arils and yam, respectively.

**Table 2.1** Effective diffusivity of the fit of Crank's model for the mass transfer during OD of apple cubes at atmospheric pressure

Temperature (°C)	Mass ratio of sample to solution	Solute	Water Loss		Solid Gain	
			$D_e \times 10^9 \pm$ margin of error ( $\text{m}^2 \text{s}^{-1}$ )	$R^2$	$D_e \times 10^9 \pm$ margin of error ( $\text{m}^2 \text{s}^{-1}$ )	$R^2$
25	01:04	sucrose	0.198±0.042	0.951	1.271±0.369	0.829
25	01:04	sorbitol	1.099±0.245	0.941	2.413±0.912	0.817
25	01:10	sucrose	0.266±0.041	0.971	0.856±0.284	0.781
25	01:10	sorbitol	0.577±0.106	0.963	1.120±0.268	0.920
40	01:04	sucrose	0.225±0.044	0.957	0.874±0.240	0.841
40	01:04	sorbitol	1.389±0.252	0.952	2.340±0.840	0.832
40	01:10	sucrose	0.355±0.077	0.941	1.542±0.519	0.789
40	01:10	sorbitol	0.927±0.164	0.957	1.395±0.400	0.886
60	01:04	sucrose	0.525±0.138	0.965	1.432±0.463	0.935
60	01:04	sorbitol	2.483±0.519	0.970	2.802±1.130	0.897
60	01:10	sucrose	0.629±0.163	0.966	2.653±1.122	0.915
60	01:10	sorbitol	1.463±0.273	0.977	1.228±0.519	0.888

Margin of error is the half width of the confidence interval at 95 %

The effective diffusivity ( $D_e$ ) was calculated considering the first term of eq. 4 (the Fourier number was higher than 0.1), and the values of this parameter at the different operations conditions are presented in Table 2.1. The determination coefficients ( $R^2$ ) were between 0.941 and 0.977 for *WL* and for *SG* were 0.781 – 0.935 (Table 2.1). The values of  $D_e$  for *WL* are between  $1.98 \times 10^{-10}$  and  $2.48 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$  and are in agreement with some works that carried out the OD of fruits using different temperatures, solutes and solute concentration (Da Silva et al. 2014; Rodríguez et al. 2013). The  $D_e$ , for *WL* and *SG*, are higher at 60 °C. This means that the higher process temperature promoted an enhanced diffusion of water and solute in the food system. This behaviour was also observed by Souraki et al. (2012) in green bean at 30 – 50 °C. The agent osmotic used also had an influence on the diffusion of water and solute during the OD of apple cubes in the conditions applied, higher diffusivities being obtained when the OD was carried out with sorbitol solution. The maximum value of  $D_e$  was found for experiments with sorbitol solution at 60 °C. This may be explained by the fact that at the sorbitol solution used in the OD process presented lower

viscosity than the sucrose solution, and, at 60 °C, it presented the lowest viscosity (Figure 2.8). This is in agreement with Barbosa Júnior et al. (2013), who defended that the a solution with lower viscosity facilitates the water and solute transport from the product to solution. The results of  $De$  of the present study could also be explained by the fact that sorbitol has lower molar mass than sucrose and, therefore, it has higher mobility though the tissue. Brochier et al. (2015) also found a higher mass diffusivity of water during the OD of yacon with glycerol in relation to sorbitol (sorbitol has higher molecular weight than glycerol). The high temperatures are also known to increase the mass transfer. This can be due to a direct effect on the moisture diffusion within the product, increasing it, but also to lowering the viscosity of the osmotic solution (Li and Ramaswamy 2006), which reduces the external resistance to mass transfer.

The effect of the mass ratio of sample to solution did not follow a clear pattern.

Table 2.2 presents the values of parameters of Peleg's and Page's models for the  $WL$  and  $SG$  of apple cubes osmotically dehydrated in atmospheric pressure. In the present work, the equivalences between the parameters of Peleg's and Azuara's models, and between Weibull's and Page's models, taking into consideration the affinity of the functions used in the equations of those models (Assis et al. 2016) were confirmed. From the comparison between the fits of Azuara's and Peleg's models, it was verified that the values of the parameter  $s$  were equal to the ones of  $k_2/k_1$ . Also, the parameters  $B$ , of Page's model, and  $\beta$ , of Weibull's model, presented the same values, and the values of parameter  $A$  were equal to  $1/\tau^\beta$ . The values of  $R^2$  obtained for the fit of Azuara's model were equal to the ones obtained for Peleg's, as well as the values of this coefficient were equal for Weibull's and Page's models.

**Table 2.2** Parameters of the fit of Peleg's and Page's models of *WL* and *SG* during OD of apple cubes at atmospheric pressure

Temperature (°C)	Mass ratio of sample to solution	Solute	<i>WL</i>						<i>SG</i>					
			Peleg			Page			Peleg			Page		
			$k_1 \pm$ margin of error (h kg kg <sup>-1</sup> )	$k_2 \pm$ margin of error (kg kg <sup>-1</sup> )	R <sup>2</sup>	$A \pm$ margin of error	$B \pm$ margin of error	R <sup>2</sup>	$k_1 \pm$ margin of error (h kg kg <sup>-1</sup> )	$k_2 \pm$ margin of error (kg kg <sup>-1</sup> )	R <sup>2</sup>	$A \pm$ margin of error	$B \pm$ margin of error	R <sup>2</sup>
25	01:04	sucrose	4.560±0.580	1.478±0.066	0.962	0.273±0.110	0.513±0.130	0.974	3.050±1.174	8.738±0.372	0.840	1.371±0.299	0.647±0.313	0.846
25	01:04	sorbitol	2.412±0.305	1.580±0.072	0.972	0.484±0.097	0.493±0.100	0.985	4.982±1.992	7.454±0.660	0.836	0.917±0.332	0.486±0.334	0.837
25	01:10	sucrose	3.968±0.340	1.410±0.042	0.983	0.336±0.038	0.562±0.068	0.992	5.577±2.024	8.171±0.490	0.795	0.943±0.238	0.641±0.317	0.796
25	01:10	sorbitol	2.698±0.261	1.366±0.055	0.983	0.438±0.050	0.579±0.080	0.990	5.902±1.088	6.114±0.311	0.952	0.725±0.139	0.516±0.164	0.954
40	01:04	sucrose	3.293±0.403	1.391±0.052	0.962	0.335±0.107	0.465±0.101	0.982	3.816±2.022	8.764±0.500	0.716	1.136±0.217	0.533±0.245	0.877
40	01:04	sorbitol	1.689±0.162	1.475±0.043	0.985	0.651±0.044	0.530±0.056	0.994	4.255±1.329	6.645±0.447	0.893	0.102±2.776	0.189±0.360	0.935
40	01:10	sucrose	2.675±0.291	1.384±0.043	0.971	0.305±0.165	0.406±0.093	0.989	2.450±1.105	7.531±0.360	0.806	1.406±0.348	0.605±0.345	0.815
40	01:10	sorbitol	1.663±0.161	1.413±0.042	0.985	0.651±0.056	0.559±0.079	0.989	3.694±0.847	5.575±0.281	0.938	0.746±0.347	0.351±0.176	0.957
60	01:04	sucrose	1.847±0.292	1.415±0.083	0.982	0.430±0.174	0.471±0.103	0.996	3.363±0.912	8.196±0.437	0.970	0.702±1.166	0.274±0.285	0.984
60	01:04	sorbitol	0.970±0.125	1.486±0.049	0.991	0.940±0.099	0.551±0.096	0.996	3.388±1.109	6.251±0.474	0.946	0.093±2.513	0.211±0.344	0.984
60	01:10	sucrose	1.805±0.276	1.367±0.078	0.983	0.419±0.164	0.470±0.096	0.997	1.950±1.053	8.158±0.609	0.932	1.569±0.843	0.419±0.492	0.933
60	01:10	sorbitol	1.056±0.118	1.409±0.043	0.992	0.890±0.084	0.607±0.097	0.995	3.578±1.233	6.086±0.508	0.938	0.081±2.848	0.223±0.417	0.976

Margin of error is the half width of the confidence interval at 95 %.

The adequacy of Peleg's, Page's, Azuara's and Weibull's models in data fitting was assessed through the observance of the independence, randomness and normality of the residuals. The  $R^2$  of Azuara's model, and Peleg's model, varied from 0.962 to 0.992 for water loss and from 0.716 to 0.970 for solid gain. The values of  $s$  parameter of Azuara's model were between 0.324 and 1.532 for  $WL$ , and between 1.036 and 4.184 for  $SG$ . These values are below those found by Ganjloo et al. (2011) in guava cubes osmotically dehydrated in a sucrose solution (30, 40 and 50 %) at 30, 40 and 50 °C, and by Mundada et al. (2011) in the OD of pomegranate arils in a sucrose solution (40, 50 and 60 °Bx) at 35, 45 and 55 °C. The predicted values of  $WL_\infty$  and  $SG_\infty$  are similar to the results found by Mundada et al. (2011). With respect to the parameter  $s$ , for  $WL$ , it tends to increase with the temperature of the osmotic solution, but this was not observed for  $SG$ . The  $s$ -value for the  $WL$  is higher when the sorbitol was used. Therefore, the sorbitol increased the water diffusion in comparison with sucrose, because  $s$  is a measure of the rate of the water diffusion out of the food. This is in agreement with the  $D_e$ -values of the fit of Crank's model (Table 2.1), as stated above. The equilibrium values did not show a specific trend for the different experiments. Some authors used Azuara's model to determine the  $WL_\infty$  and  $SG_\infty$  (Mokhtarian et al. 2014; Souraki et al. 2013).

The parameter  $k_1$  of Peleg's model for  $WL$  decreased with the use of sorbitol as osmotic agent and with the increase of the temperature (Table 2.2). Considering that the parameter  $1/k_1$  describes the initial mass transfer rate, the water loss rate using sorbitol solution at 60 °C was higher at the beginning of the process. The behaviour of  $k_1$  in relation to the temperature was in agreement with Ganjloo et al. (2012); Mišljenović et al. (2011); Vesna et al. (2015). For  $SG$ , the parameter  $1/k_2$ , that is related the equilibrium value, was lower for apples cubes dehydrated with the sucrose solution, but with respect to the temperature,  $k_1$  and  $k_2$  did not follow a particular trend. The ranges of the  $k_1$ -values are 0.970 – 4.560 for  $WL$  and 1.950 – 5.902 for  $SG$ . These results are in accordance with Ganjloo et al. (2012) that performed the OD of guavas in sucrose solution (30, 40, 50 %) at 30, 40 and 50 °C, but Mundada et al. (2011) obtained higher values than in the present work. The values of  $k_2$  are between 1.366 and 1.580 for  $WL$ , and between 5.575 and 8.764 for  $SG$  (Tables 2.2 and 2.3). Koprivica et al. (2014) found similar results for  $WL$  when sugar beet molasses solutions (40 – 80 %) were used during the OD of apple at 45, 55 and 65 °C.

The ranges of the  $R^2$  values of the Page's models are 0.974 – 0.997 for  $WL$  and 0.796 – 0.984 for  $SG$  (Table 2.2). The values of  $A$  and  $B$  are 0.273 – 0.940 and 0.406 – 0.607 for  $WL$ , and 0.081 – 1.569 and 0.189– 0.647 for  $SG$ , respectively. The  $A$  and  $B$ -values are below

that obtained by Ochoa-Martinez et al. (2007). The parameter  $A$  increased with temperature for  $WL$  and when sorbitol was used as the osmotic agent. For  $SG$ , the parameter  $A$  tends to be higher when sucrose is used, but at the temperature of 60 °C the  $A$ -values for the two solutes are not significantly different. No significant differences in the  $B$ -values for water loss and solid gain were observed among temperatures, solutes and ratios mass of sample: mass of solution used in this study.

The  $\tau$ -values are between 1.121 – 12.520 for  $WL$ , and 0.341 – 3.638 for  $SG$ . These results are in agreement with Cunha et al. (2001) and Khan et al. (2008) when they studied the OD of apple and mango, respectively, using different temperatures and sucrose concentrations. The  $\beta$ -values are between 0.406 – 0.607 for  $WL$ , and between 0.189 – 0.647 for  $SG$ . These values are in agreement with the results obtained by Khan et al. (2008). The parameter  $\tau$  of Weibull's model for  $WL$  presented higher values in experiments with sucrose solution and decreased with the increase of the temperature. This was in agreement with Corzo and Bracho (2008) who studied the OD of sardine sheets with temperatures of 30 – 38 °C. Comparing the different conditions, no defined relation exists between the parameters  $\tau$  or  $\beta$  and the process variables studied (solute, ratios of mass of sample to mass of solution and temperatures) for  $SG$ . Khan et al. (2008) also observed that the parameter  $\beta$  for  $SG$  did not show statistical differences at 30 – 50 °C in osmotic dehydration of mango.

The  $WL_{\infty}$ -values predicted by the Crank's, Azuara's, Page's and Weibull's models were not significantly different from the experimental values. Figures 2.1 – 2.4 show the experimental data and the fit of Page's model for  $WL$  and  $SG$  of apple cubes osmotically dehydrated in sucrose or sorbitol solutions at 25, 40 and 60 °C using the mass ratios of sample to solution of 1:4 or 1:10. The analysis of the effects of the process variables on the water loss and solid gain during the OD was carried out at the 5 % significance level based on the results from the models and are discussed below. The initial rate of  $WL$  was higher when sorbitol was used as osmotic agent for all temperatures and mass ratios of sample to solution used in this work. This may be explained by the by the lower viscosity of sorbitol solution at the beginning of the process, for all the temperatures tested (Figure 8). The fact that the lower viscosity of osmotic solution facilitates the mass transfer in OD process was also observed by Cháfer et al. (2001), El-Aouar et al. (2006) and Guillemín et al. (2008). According to El-Aouar et al. (2006), viscous sucrose solutions causes the fluctuation of food pieces, hindering the contact between the food material and the osmotic solution, thus, reducing the mass transfer rates. In addition, the molar concentration of the sorbitol solution (3.294 M) was higher than the one of sucrose solution (1.753 M), for the same mass

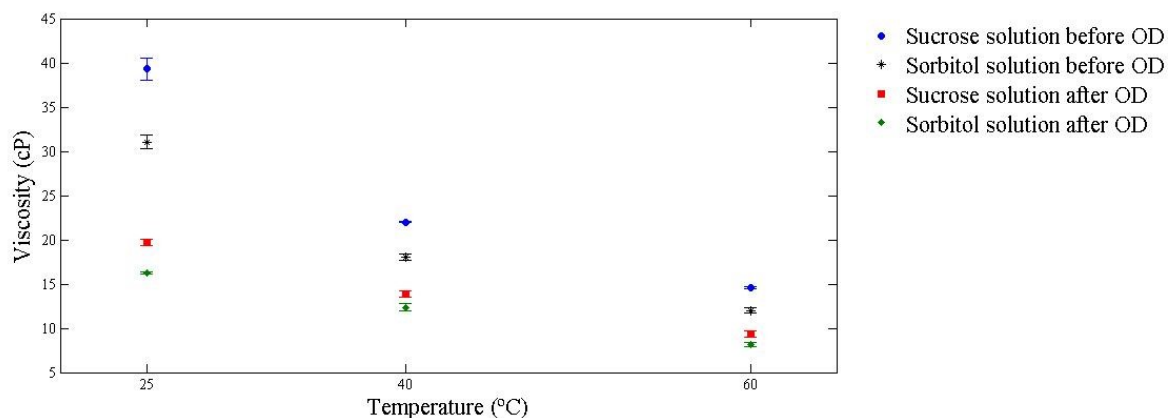
concentration (60° Brix initially), which increases the capacity of the solution to attract water molecules. This might justify the higher initial *WL* in OD with sorbitol. At the end of the OD process, the content of soluble solids of the solution was similar for both

Overall, the use of sorbitol as osmotic agent in the OD process reduced the time required to reach an approximately constant (equilibrium) *WL* by 15 to 20 %, in relation to sucrose. This may also be explained by the lower viscosity of the sorbitol solutions, facilitating and, therefore, accelerating the water transport from the product to the solution. This is reflected on the parameters  $k_1$  (Peleg),  $s$  (Azua) and  $\tau$  (Weibull), which are related with the process rate. After the end of the process, the samples osmotically dehydrated with sucrose or sorbitol solutions reached the same amount of water loss (no significant differences were observed in the values of  $k_2$  of Peleg's model). This may be related with the fact that the reduction of the viscosity during the OD process was similar for both solutions: 50 %, 37 %, 36 % for sucrose solution and 48 %, 31 %, 32 % for sorbitol solution at 25, 40 and 60 °C, respectively. Chauhan et al. (2011) and Rizzolo et al. (2007), when they compared sucrose with sorbitol, found the same results in the relation to the initial rate, but they did not carry out their experiments until reaching the equilibrium. In relation to the *SG*, the initial rates of *SG* did not show differences between sucrose and sorbitol. However, sorbitol showed higher equilibrium solids content than sucrose ( $1/k_2$  sorbitol >  $1/k_2$  sucrose). This could be explained by the fact that smaller molecules diffuse more easily than larger ones (the MW of sorbitol is almost half of the MW of sucrose). Ispir and Toğrul (2009) found that sucrose and fructose are the best osmotic agents in the OD of apricots, when compared with glucose, maltodextrin and sorbitol, considering the high *WL* and low *SG* obtained.

The temperature influenced the *WL* using sucrose or sorbitol in the osmotic solution. This behaviour was noted for both ratios of sample to solution. This temperature influence was shown by other authors Mišljenović et al. (2011); Mundada et al. (2011); Souraki et al. (2012) when different products (apple, pomegranate arils and green bean) and solutes (sugar beet molasses, sucrose and sodium chloride) were used. As expected, the water loss was higher at 60 °C due to the effect of temperature on decreasing the viscosity of the osmotic solution, swelling, plasticization and even destruction of the cell membrane structure, facilitating the mass transfer (Souraki et al. 2012, Brochier et al. 2015). The decrease of viscosity with temperature is more pronounced for the initial solutions, before the OD process (Figure 2.8). In what concerns the *SG*, the initial rate of mass transfer using sucrose

solution at 60 °C was higher than in 25 °C, but at the end of process the same amount solid gain was reached at both temperatures ( $k_2$  at 25 °C =  $k_2$  at 60 °C).

The increase of the mass ratio of sample to solution from 1:4 to 1:10 did not result in a higher  $WL$  for both osmotic agents, sucrose and sorbitol, and for all temperatures used. This increase did not affect the values of the models parameters, as well. Ispir and Toğrul (2009) studied various ratios of 1/4 to 1/20 in apricots osmotically dehydrated with 70 % of glucose and maltodextrin solutions and they also found that the  $WL$  considerably increases when the ratio decreases. In the present work, the mass ratio of sample to solution did not induce significant differences of the initial rate of  $SG$  at all temperatures, and with the two solutes used. The equilibrium solids content was higher in ratio of sample to solution of 1:10 at 25 °C for sorbitol and at 40 °C for both solutes studied. This is reflected on the value of  $1/k_2$  of Peleg's model since this parameter is related to the equilibrium values. Rodríguez et al. (2013) found similar results for the OD of nectarines pieces. Under the conditions used it may be considered that the mass ratio of sample to solution of 1:4 is a better alternative to the ratio 1:10 because it allows, reaching the same water loss with the use of lower quantity of solution.



**Figure 2.8** Viscosity of the solutions before and after the OD process using the mass ratio of sample to solution of 1:4

The Arrhenius's behaviour was observed for the parameters  $s$  and  $A$  of Azuara's and Page's models, respectively. Higher  $E_a$  indicates a greater sensitivity of the parameters to temperature. However, no significant differences were found between the two osmotic agents used in relation to the activation energy. But the parameter  $s_{ref}$  increased from 0.333 to 0.573, and parameter  $A_{ref}$  increased from 0.292 to 0.466. The values obtained for activation energy were between 19.2 and 21.5  $\text{kJ mol}^{-1}$  for parameter  $s$  (Azuara's model), and between

8.1 and 16.2 for parameter  $A$  (Page's model), for  $WL$ . The effective diffusivity ( $D_e$ ), the Peleg's rate constant ( $k_I$ ) and the scale parameter ( $\tau$ ) could not find a correlation with the temperature (low  $R^2$  values) in the experimental conditions used.

#### 2.4.2 OD under vacuum

For the OD experiments under vacuum, Peleg's and Page's models were used to fit the experimental data. The Peleg's model estimates the equilibrium values  $WL_\infty$  and  $SG_\infty$ . To perform the fit with Page's model, the experimental  $SG_\infty$ -values were taken because, in this case, it was clear that the equilibrium was reached (Figures 2.5 and 2.6). The parameters of Peleg's model are related to the initial mass transfer rate and to the minimum attainable moisture content. The Azuara's and Weibull's models were not used to fit these data, because their parameters can be obtained from Peleg's and Page's models, respectively, as confirmed by the previous fit of data obtained in atmospheric pressure.

The experimental data and the fit of Page's model are presented in Figures 2.5 and 2.6 for sucrose and sorbitol solutions, respectively. The parameters of Peleg's and Page's model are presented in Table 2.3. Both models predicted well the experimental data of  $WL$  and  $SG$ . The  $R^2$  obtained were higher than 0.8, again being higher for  $WL$ , and the independence, randomness and normality of the residuals was observed.

Thus, these models as noted in OD experiments at atmospheric pressure, the  $WL$  was higher with the use of the sorbitol solution. After 8 h the  $WL$  of apple cubes osmotically dehydrated with sorbitol solutions increased by 1.5 to 10 % (according to the temperature used), in relation to sucrose solutions. After the same time of dehydration in sorbitol solution, the vacuum increased the  $WL$  of apple cubes by 5 to 25 %, in relation to the atmospheric pressure. The  $k_I$ -values for experiments did not show differences between the atmospheric and vacuum pressures, but the initial rate of  $WL$  presents a tendency to be higher under vacuum in OD with sucrose and sorbitol (Figures 2.5 and 2.6). This could be explained by the fact that the relatively strong vacuum level (150 mbar) during rather long time (8 hours) could cause an irreversible deformation of the plant tissue, decreasing the free volume available for impregnation (Fito et al. 1996; Ito et al. 2007b; Mújica-Paz et al. 2003).

**Table 2.3** Parameters of the fit of Peleg's and Page's models of *WL* and *SG* during DO of apple cubes under vacuum with a mass ratio of sample to solution 1:10

Temperature (°C)	Solute	<i>WL</i>						<i>SG</i>					
		Peleg			Page			Peleg			Page		
		$k_1 \pm$ margin of error (h kg kg <sup>-1</sup> )	$k_2 \pm$ margin of error (kg kg <sup>-1</sup> )	R <sup>2</sup>	$A \pm$ margin of error (h)	$B \pm$ margin of error	R <sup>2</sup>	$k_1 \pm$ margin of error (h kg kg <sup>-1</sup> )	$k_2 \pm$ margin of error (kg kg <sup>-1</sup> )	R <sup>2</sup>	$A \pm$ margin of error (h)	$B \pm$ margin of error	R <sup>2</sup>
25	sucrose	3.605±0.481	1.405±0.058	0.963	0.354±0.068	0.501±0.089	0.984	0.952±0.967	9.673±0.479	0.809	2.646±1.191	0.358±0.571	0.805
25	sorbitol	1.420±0.248	1.671±0.082	0.981	0.667±0.183	0.521±0.122	0.991	1.476±0.907	7.472±0.587	0.895	1.471±0.271	0.326±0.168	0.910
40	sucrose	2.207±0.311	1.405±0.046	0.962	0.540±0.052	0.582±0.078	0.975	0.169±0.502	8.864±0.307	0.902	2.389±0.598	0.074±0.130	0.904
40	sorbitol	1.022±0.159	1.386±0.047	0.990	0.840±0.206	0.622±0.158	0.991	1.086±1.080	7.641±0.770	0.842	4.586±0.000	1.277±0.000	0.821
60	sucrose	1.434±0.188	1.267±0.045	0.983	0.710±0.068	0.731±0.118	0.987	6.166±2.699	6.192±0.620	0.919	1.424±0.989	0.731±0.968	0.761
60	sorbitol	0.986±0.256	1.324±0.067	0.990	1.030±0.000	5.574±0.000	0.930	4.991±3.066	5.184±0.765	0.926	0.705±0.539	0.992±0.849	0.928

Margin of error is the half width of the confidence interval at 95 %.

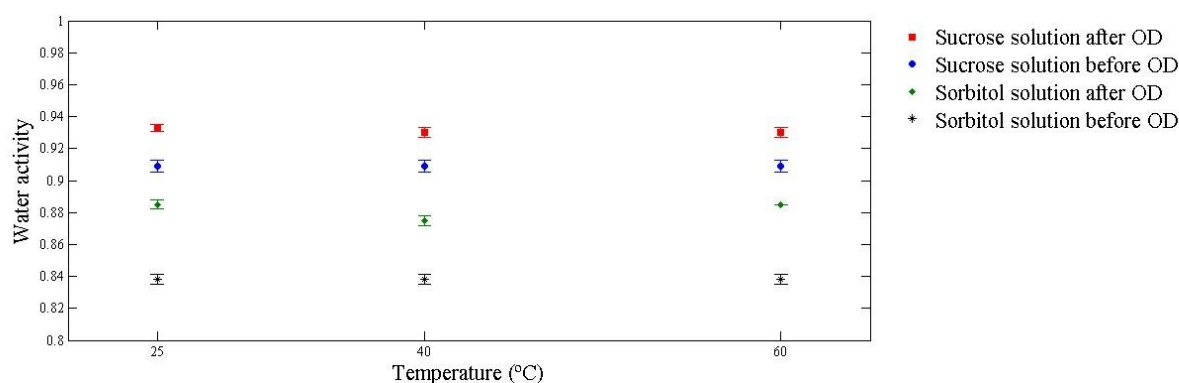
These authors used vacuum levels from 200 to 50 mbar during shorter times. When Corrêa et al. (2010) studied the OD of guavas at atmospheric pressure and under vacuum (100 mbar) in different concentrations of osmotic solutions at 40 °C, they concluded that the  $WL$  was higher under vacuum. Rastogi and Raghavarao (1996) studied the OD of coconuts circular pieces (diameter = 35 mm and thickness = 8 mm) at atmospheric pressure and under vacuum (235.3 mbar) in different concentrations of osmotic solutions at 50 °C, they concluded that the rate of mass transfer increased under vacuum. Shi et al. (1995) also found that  $WL$  was higher under vacuum than under atmospheric pressure during the OD of different fruits in a 65 °Bx sucrose solution at 30 – 50 °C. Ferrari *et al.* (2011) studied the mass transfer during the OD of melon in atmospheric and vacuum pressures with sucrose solutions (40, 50 and 60 °Bx) and they observed that the  $WL$  of samples treated with 60 °Bx was not affected by the application of vacuum. Ito et al. (2007b) found no significant effect of the vacuum (50 to 200 mbar) during the pulsed vacuum OD of mango slices in sucrose solutions (45 – 60 °Bx) at different temperatures (20 – 40 °C). In relation to  $k_2$ , no significant differences were found between the two pressure conditions used for both solutions.

Comparing the results of  $SG$ , it was observed that the initial rate, given by  $1/k_1$ , was higher in vacuum than at atmospheric pressure at 25 and 40 °C for sucrose and sorbitol solutions. However, the conditions of pressure used did not produce significant differences in the parameter  $B$  of Page's model. According to Chafer et al. (2003) and Corrêa et al. (2010), the use of vacuum caused an increase in the  $SG$  of pear and guava, respectively. The values of  $k_2$  was higher in vacuum at 25 and 40 °C, meaning that the experiments at atmospheric pressure reached higher values of  $SG$ . The experiments under vacuum pressure presented the same trend of experiments at atmospheric pressure for both solutes used. On the other hand, Shi et al. (1995) found no influence of the vacuum on the  $SG$  of fruits in the OD process.

The Arrhenius's behaviour was observed for the parameters  $A$  and  $k_1$  Page's and Peleg's model, respectively, in the OD under vacuum. The values of  $R^2$  were higher than 0.9, except for  $k_1$  of experiments with sorbitol solution that presented value of 0.783. The values of activation energy were between 10.21 and 16.28 kJ mol<sup>-1</sup> for  $A$ , and between 24.30 and 56.14 kJ mol<sup>-1</sup> for  $k_1$ , for experiments carried out with sucrose and sorbitol solutions, respectively, for  $WL$ . However, no significant differences were found between the two osmotic agents used in relation to the activation energy and to  $A_{ref}$  and  $k_{1ref}$ .

### 2.4.3 Water activity

The water activity ( $a_w$ ) of the initial apple cubes was  $0.993 \pm 0.003$ . The  $a_w$  of the osmotically dehydrated apple cubes ranged from 0.851 – 0.949 (Table 2.4). The  $a_w$  of the dehydrated samples decreased when their final water content decreased and the determination coefficients of the linear correlations were between 0.656 and 0.982 (Table 2.5). The  $a_w$  of the samples osmotically dehydrated with sorbitol solutions were significantly lower than with sucrose solutions, which is a positive aspect. According to Moraga et al. (2011), a slight reduction of  $a_w$  of foods with high water activity produces an considerable decrease of the microbial growth and of the relative rate of deteriorative reactions. The results obtained by Chauhan et al. (2011) are in agreement with those obtained in this work. Brochier et al. (2014) found that the  $a_w$  of samples of yacon osmotically dehydrated with glycerol solution showed greater reduction in comparison with the samples submitted in OD with sorbitol solution. As the water loss was influenced by the osmotic agent and the temperature of process, the  $a_w$  was also affected by these parameters. The increase of temperature promoted the reduction of  $a_w$ . Ito et al. (2007a) and Vieira et al. (2012) concluded the same about this parameter. As noted, the  $a_w$  of the apples decreased with the osmotic dehydration process, and, consequently, the  $a_w$  of solution increased with the process (Table 2.4). As it was observed in relation to the apple cubes, the sorbitol solutions also presented lower  $a_w$  values (0.875 – 0.885) than the sucrose solutions (0.930 – 0.933) (Figure 2.9), which may be an advantage under the safety point of view, accordingly to what was refereed above.



**Figure 2.9** Water activity of the solutions before and after the OD process using the mass ratio of sample to solution of 1:4

**Table 2.4** Water activity of the osmotically dehydrated apple cubes

Pressão (mbar)	Temperature (°C)	Mass ratio of sample to solution	Solute	$a_w$ final
1013	25	01:04	sucrose	0.949±0.001 <sup>a</sup>
	25	01:04	sorbitol	0.912±0.004 <sup>c</sup>
	25	01:10	sucrose	0.936±0.003 <sup>b</sup>
	25	01:10	sorbitol	0.862±0.003 <sup>i</sup>
	40	01:04	sucrose	0.946±0.003 <sup>a</sup>
	40	01:04	sorbitol	0.876±0.003 <sup>h</sup>
	40	01:10	sucrose	0.915±0.003 <sup>c,d,e</sup>
	40	01:10	sorbitol	0.851±0.002 <sup>j</sup>
	60	01:04	sucrose	0.894±0.002 <sup>f,g</sup>
	60	01:04	sorbitol	0.896±0.007 <sup>f</sup>
	60	01:10	sucrose	0.884±0.002 <sup>g,h</sup>
	60	01:10	sorbitol	0.876±0.001 <sup>h</sup>
150	25	01:10	sucrose	0.920±0.004 <sup>c,d</sup>
	25	01:10	sorbitol	0.891±0.006 <sup>f,g</sup>
	40	01:10	sucrose	0.921±0.002 <sup>c</sup>
	40	01:10	sorbitol	0.874±0.004 <sup>h</sup>
	60	01:10	sucrose	0.914±0.005 <sup>d,e</sup>
	60	01:10	sorbitol	0.861±0.005 <sup>i</sup>

Different letters mean significantly different values at  $p < 0.05$

**Table 2.5** Determination coefficient ( $R^2$ ) of the linear regression between the water activity and the final water content of dehydrated apple cubes

Solute	Pressure (mbar)	
	1013	100
sorbitol	0.773	0.982
sucrose	0.724	0.656

## 2.5 Conclusion

Some process variables can affect the parameters of evaluation of the OD process, such as  $WL$  and  $SG$ . The increase of the temperature and the use of sorbitol in the osmotic solution resulted in an increase of the process rate at atmospheric pressure and under vacuum. The sorbitol is, therefore, a good alternative to replace the sucrose as osmotic agent in OD. Since the mass ratio of sample to solution did not affect the mass transfer kinetics, thus the ratio of 1:4 is a better alternative to the ratio 1:10 at atmospheric pressure, allowing to achieve the same water loss with the use of lower quantity of solution and, therefore, solute.

Azuara's, Peleg's, Page's and Weibull's models could fit well the experimental data and the Penetration model presented low ability. Crank's model had good correlations only for  $WL$ , and the values of effective diffusivity were between  $1.98 \times 10^{-10}$  and  $2.48 \times 10^{-9} \text{m}^2 \text{s}^{-1}$  in OD under normal atmosphere. The values of the parameters determined confirmed the equivalences previously established between Azuara's and Peleg's models, and between Page's and Weibull's models. The parameter  $A$  of Page's model followed an Arrhenius relationship, but the activation energy did not show significant differences between the two osmotic agents used. The use of vacuum did not produce significant differences, but presented a tendency to increase the initial rate of  $WL$ , and this was reflected on the parameters  $k_1$  of Peleg's model, which followed an Arrhenius relationship.

The water activity of the apple cubes osmotically dehydrated with sorbitol solutions were significantly lower than with sucrose solutions.



## Chapter 3 – Osmotic dehydration of apple cubes at 40 °Bx

### 3.1 Abstract

The apple cubes were osmotically dehydrated at 25, 40 and 60 °C with sucrose or sorbitol solution at 40 °Bx and the mass ratio of sample to solution of 1:4 or 1:10. Crank's and Peleg's models were tested to describe the mass transfer kinetics of water loss (*WL*) and solid gain (*SG*). The Peleg's model could fit the experimental data at 40 °Bx. The mass ratio of sample to solution did not affect the *WL*. The use the sorbitol as osmotic agent, the increase of the temperature increased the *WL* during the osmotic dehydration. In addition, the increase in the solute concentration from 40 to 60 °Brix also increases the *WL* during the OD.

**Keywords:** apple cubes, osmotic dehydration, mass transfer, mathematical models

### 3.2 Introduction

The osmotic dehydration (OD) has been used for partial removal of water from fruit tissues by immersion in a hypertonic solution (Checamarev et al., 2014). The higher the difference between the concentration of the solute in the osmotic solution and the food, the greater the mass transfer (Khan, 2012). The mass transfer involves water loss (*WL*) and solid gain (*SG*), but in some cases a high increase in the solid gain is not desired.

Souraki et al. (2012) observed an increase of the equilibrium solid gain with the increase of the salt concentration during the osmotic dehydration of green bean. Mayor et al. (2006) osmotically dehydrated pumpkin at different temperatures and concentration of osmotic solution and found that the concentration had more influence on the equilibrium values than the temperature. During the osmotic dehydration of red cabbage with sugar beet molasses, Misljenovic et al. (2009) noted that the increase of the solution concentration in these molasses and the immersion time tended to increase the dry matter, consequently, the solid gain.

The objectives of this study were: i) to carry out the osmotic dehydration of apple cubes (variety Royal Gala), using two solutes (sucrose and sorbitol) at 40 °Bx, and to study the effect of the temperature (25, 40 and 60 °C), the mass ratio of sample to solution (1:4 or

1:10) on the *WL* and *SG*; ii) to test the adequacy of the fitness of some mathematical models to describe the *WL* and the *SG* of the product during the OD process; iii) to make a comparison between the effects at 40 and 60 °Bx (Chapter 2).

### **3.3 Material and methods**

#### ***3.3.1 Samples and osmotic dehydration process***

The samples were prepared as described in section 2.3.1. The soluble solids content of the apple was  $17.0 \pm 0.7$  °Bx.

The osmotic solutions with sucrose or sorbitol were prepared at 40 °Bx. The experiments were carried out at 25, 40 and 60 °C with the mass ratio of sample to solution 1:4 or 1:10.

#### ***3.3.2 Moisture content determination***

The moisture content of the apple samples were determined as described in section 2.3.3.

#### ***3.3.3 Osmotic dehydration parameters and mathematical models***

The parameters *WL* and *SG* were determined through the equations 1.1 and 1.2. according section 2.3.5. Crank's (section 2.3.6) and Peleg's (section 1.7.1.1.2) models were used to fit the water content during the OD. This latter model was able to describe well the mass transfer kinetics at 60 °Bx (Chapter 2).

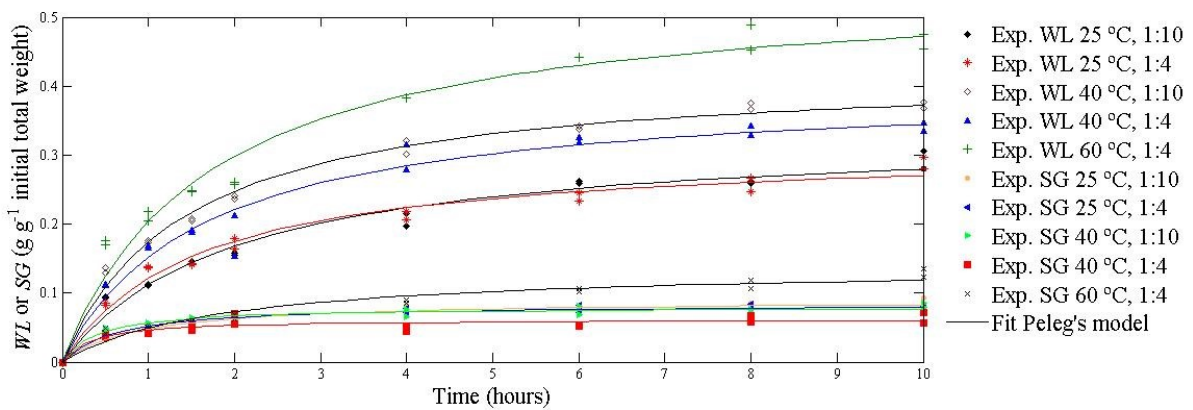
#### ***3.3.4 Statistical analysis***

The statistical analysis was performed as presented in section 2.3.8.

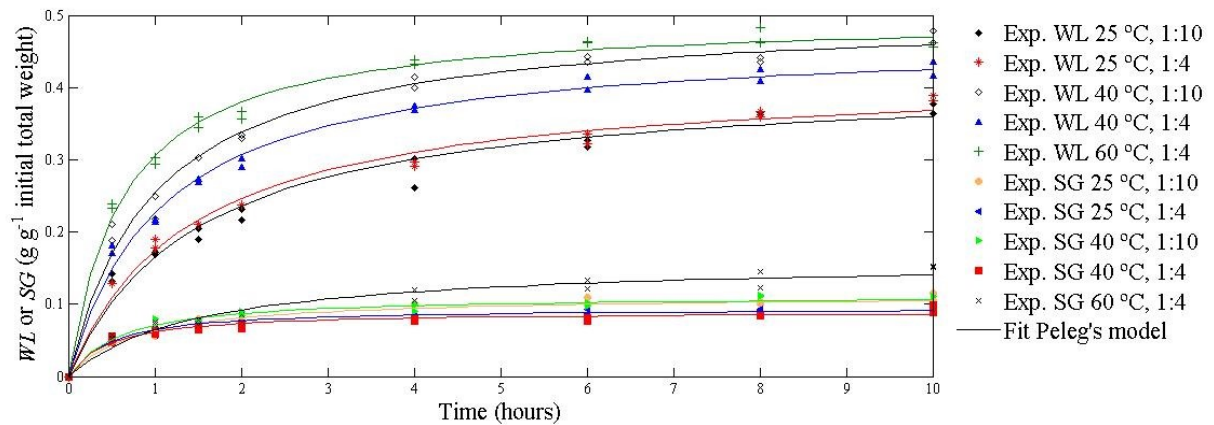
### 3.4 Results and discussion

#### 3.4.1 Mass transfer kinetics

The experimental data and the fits of Peleg's model of  $WL$  and  $SG$  of apples cubes osmotically dehydrated in sucrose and sorbitol solutions at 40 °Bx at 25, 40 and 60 °C, using the mass ratio of sample to solution of 1:4 or 1:10 are shown in Figures 3.1 and 3.2.



**Figure 3.1** Experimental data and the fit of Peleg's model of  $WL$  and  $SG$  of apple cubes osmotically dehydrated in a 40 °Bx sucrose solution at atmospheric pressure and at 25, 40 and 60 °C, using the mass ratio of sample to solution of 1:4 or 1:10



**Figure 3.2** Experimental data and the fit of Peleg's model of  $WL$  and  $SG$  of apple cubes osmotically dehydrated in a 40 °Bx sorbitol solution at atmospheric pressure and at 25, 40 and 60 °C, using the mass ratio of sample to solution of 1:4 or 1:10

Higher  $WL$  and  $SG$  rates were noted in the first two hours of the process, and these rates were higher in the OD with sorbitol solutions. This was probably because at the beginning, the large difference of the osmotic pressure between the solution and the samples

resulted in a higher diffusion of water from the food into the solution and diffusion of the solute from the solution into the food.

Crank's model could not describe this experimental data because it did not follow one or more of the assumptions described in section 2.3.8. Peleg's model satisfies all those assumptions and it is able to describe the mass transfer kinetics of apple cubes in the conditions used. The results of the non-linear regression of the experimental data of OD of the apple cubes at 40 °Bx are shown in Table 3.1.

**Table 3.1** Parameters of the fit of Peleg's model for *WL* and *SG* during OD of apple cubes at 40 °Bx

Temperature (°C)	Mass ratio of sample to solution	Solute	Peleg					
			<i>WL</i>			<i>SG</i>		
			$k_1 \pm$ margin of error (h kg kg <sup>-1</sup> )	$k_2 \pm$ margin of error (kg kg <sup>-1</sup> )	R <sup>2</sup>	$k_1 \pm$ margin of error (h kg kg <sup>-1</sup> )	$k_2 \pm$ margin of error (kg kg <sup>-1</sup> )	R <sup>2</sup>
25	01:04	sucrose	5.027±0.862	3.206±0.224	0.974	7.277±1.757	11.896±0.711	0.957
25	01:04	sorbitol	3.342±0.440	2.385±0.121	0.985	4.837±1.181	10.546±0.541	0.961
25	01:10	sucrose	5.925±1.104	2.987±0.257	0.970	9.972±2.533	11.000±0.855	0.947
25	01:10	sorbitol	3.623±0.686	2.417±0.182	0.968	7.071±2.025	8.824±0.725	0.934
40	01:04	sucrose	4.060±0.890	2.498±0.227	0.959	5.486±3.643	16.184±1.875	0.804
40	01:04	sorbitol	2.271±0.260	2.125±0.085	0.989	5.023±1.411	11.140±0.651	0.949
u40	01:10	sucrose	3.387±0.378	2.347±0.102	0.989	5.010±1.466	12.527±0.709	0.949
40	01:10	sorbitol	1.941±0.267	1.984±0.087	0.984	5.208±1.181	8.914±0.488	0.962
60	01:04	sucrose	3.085±0.580	1.812±0.145	0.969	13.129±3.499	7.154±0.845	0.937
60	01:04	sorbitol	1.260±0.139	2.003±0.056	0.991	9.256±2.521	6.207±0.671	0.934

Margin of error is the half width of the confidence interval at 95 %

The R<sup>2</sup> values of the fit of *WL* were higher than 0.9. The parameters of Peleg's model do not present a physical meaning, but they can be related to the parameters of the OD, *WL* and *SG*. The  $k_1$ -values varied from 1.260 to 5.925. The initial rate of *WL*, reflected on  $1/k_1$ , was higher using sorbitol in all tested conditions.  $1/k_1$  was also higher in experiments with sorbitol solution at 60 °C. The increase in temperature increased the rate of the *WL* and no significant differences were observed in *WL* between the two mass ratios of sample to

solution used. The equilibrium values of  $WL$  ( $1/k_2$ ) varied from 0.312 to 0.552 h kg DM kg water<sup>-1</sup>. At 25 and 40 °C, the  $WL$  at the equilibrium was higher in experiments with sorbitol.

The mass ratio of sample to solution did not affect the parameters ( $k_1$  and  $k_2$ ) of the  $WL$ .

The  $R^2$  values of the fit of  $SG$  was higher than 0.8. The solute did not have influence on the initial rate of  $SG$ . The experiments carried out at 60 °C resulted in a lower solute gain, while no significant differences were observed between 25 and 40 °C. In relation to the parameter  $k_2$ , it was observed that the use of sorbitol as osmotic agent promoted higher solid gain at the end of the process at 25 and 40 °C. The comparison between the temperatures did not show a clear pattern. The increase of the mass ratio of sample to solution slightly affected the  $SG_\infty$  in the experiments at 60 °C.

### ***3.4.2 Comparison of the mass transfer kinetics between 40 °Bx and 60 °Bx osmotic solutions***

In experiments at 60 °Bx, a similar behaviour had been noted, except for the equilibrium values: the samples treated with sucrose and sorbitol solutions achieved the same water loss at all temperatures (section 2.4.1). This could be explained by the fact that the experiments at 60 °Bx were carried out during longer times than the 40 °Bx, *i.e.*, in the first case, the equilibrium was reached, while in the second case no.

The comparison between the two concentrations of the osmotic solution was performed through the parameters of Peleg's model, since this model was able to describe both experimental data well.

In relation to the  $WL$ , experiments with sucrose and sorbitol did not follow the same trend for the parameter  $k_1$ , but  $WL$  tended to be higher in experiments at 60 °Bx. At the equilibrium (expressed by  $k_2$ -values), the samples treated with 60 °Bx had suffered higher  $WL$  than the samples treated with 40 °Bx solutions. The increase in the solute concentration produces a  $a_w$  decrease, which results an increase of water removal capacity by the syrup (Waliszewski et al. 2002). The results of Lazarides et al. (1995) were in agreement with this work. They found that the higher concentration of the solute resulted in an increase of the  $WL$  of apple slices.

In relation to the  $SG$ , the initial rate of  $SG$  at 25 and 40 °C was not significantly different between the two different solution concentrations, but, at the end of the process, the  $SG$  was higher in samples treated with 60 °Bx.

Roopa et al. (2012) observed that the increase of the solute concentration, the solution temperature and the dehydration time increased the *WL* and the *SG* of carambola slices. Palou et al. (1994) also used Peleg's equation to describe the mass transfer kinetics during the OD of papaya. They found the same  $k_1$  for *SG* in 60 and 70 °Brix sucrose syrup and a lower  $k_2$  at 70 °Brix. Waliszewski et al. (2002) dehydrated pineapple slabs with sucrose solutions and found that *WL* and *SG* at equilibrium increased significantly for a higher solute concentration.

### **3.5 Conclusion**

Peleg's model is able to describe the mass transfer kinetics of the osmotic dehydration of apples cubes at 40 °Bx. The use of sorbitol as osmotic agent, the increase of the temperature and solute concentration increased the water loss during the osmotic dehydration.

## Chapter 4 – Osmotic dehydration of physalis

### 4.1 Abstract

Physalis were osmotically dehydrated with sucrose and with sorbitol solutions at 60 °C and at a mass ratio of sample to solution of 1:4, at atmospheric pressure, or a vacuum pressure of 150 mbar. Crank's, Peleg's and Page's models were tested to describe the mass transfer kinetics of water loss (*WL*) and solid gain (*SG*). The effective diffusivity of both water and solute were around  $10^{-11} \text{ m}^2 \text{ s}^{-1}$  in all conditions. Peleg's model presented the best fit. The use of sorbitol as osmotic agent resulted in an increase of rate of the water loss. In experiments with sucrose solution, the higher *WL* was obtained under vacuum. The *SG* was particularly small during the OD.

**Keywords:** physalis, osmotic dehydration, vacuum, mass transfer, mathematical models

### 4.2 Introduction

Physalis, or cape gooseberry or goldenberry (*Physalis peruviana* L.) is an exotic fruit originated in South America, but nowadays it is commercialised in several tropical and subtropical countries (Izli et al., 2014; Yıldız et al., 2014). The berries are annual or short-lived perennial and the plant can grow up to 1.8 m. The fruit is protected by an accrescent calyx and covered by a brilliant yellow peel (Puenta et al., 2011).

The interest in the physalis has increased due to its nutritional composition and the presence of biologically active compounds that provide health benefits (Muniz et al., 2015; Puenta et al., 2011; Salazar et al., 2008). The fruit contains 15 % of soluble solids, mainly sugars, and it is an excellent source of bioactive compounds, such as provitamin A, vitamin C, iron, and some of the vitamin B-complex (Ramadan, 2011; Salazar et al., 2008). The production of physalis has increased in recent years, but it is a fruit of high perishability with recommended commercialization of 12 hours after the harvest, otherwise it require special conditions of storage (Luchese et al., 2015).

The osmotic dehydration allows to preserve fruits reducing in up to 50 % the initial water content, but there are few studies on the application of this technology to physalis

(Assis et al., 2017a; Luchese et al., 2015). Thus, the objectives of this study were: i) to carry out the osmotic dehydration of physalis, using sucrose or sorbitol as solute, and using a mass ratio of sample to solution of 1:4, at 60 °C, and to study the effect of the pressure (1 bar and 150 mbar) on the *WL* and *SG*; ii) to test the adequacy of the fitness of some mathematical models (Crank's, Peleg's, Page's) to describe the *WL* and the *SG* of the product.

### **4.3 Material and methods**

#### **4.3.1 Samples**

Physalis (*Physalis peruviana* L.) with  $15.7 \pm 2.7$  mm diameter were purchased from a local market and stored at 4 °C. The fruits were washed and sanitized with aqueous solution with 7500 ppm active chlorine for 5 minutes. The soluble solids content of the physalis was  $15 \pm 2$  °Bx (Hand Refractometer, Atago, China). The water activity ( $a_w$ ) of the fresh samples was  $0.988 \pm 0.003$  determined as described in section 2.3.3. The determinations were performed in triplicate.

#### **4.3.2 Osmotic dehydration**

The osmotic solutions with sucrose or sorbitol were prepared at 60 °Bx. The experiments were carried out at atmospheric pressure and under vacuum, at 60 °C, using the mass ratio of sample to solution of 1:4 and constant agitation of 50 rpm.

The samples (approximately 3 g) were removed from the solution at different time intervals (every 2 hours during the first 10 hours, and, then, every 5 hours until 30 h). Then, the samples were rinsed with ultra-pure water to remove the solution adhered to the surface, and blotted with tissue paper in order to remove the excess of water from the surface.

#### **4.3.3 Osmotic dehydration parameters and mathematical models**

The parameters were determined as in 2.3.5. Crank's (section 1.7.1.3.1), Peleg's (section 1.7.1.1.2) and Page's (section 1.7.1.1.3) models were used to fit the experimental data. The adequacy of the models was evaluated as described in section 2.3.8.

#### 4.3.4 *Moisture content determination*

The moisture content of the physalis samples was determined as described in section 2.3.3.

#### 4.3.5 *Statistical analysis*

The statistical analysis was performed as presented in section 2.3.8.

### 4.4 **Results and discussion**

The moisture content of the fresh samples was  $4.645 \pm 0.220$  kg water kg DM<sup>-1</sup>. During the osmotic dehydration of most fruits a rapid water loss can be noted in the first two hours of the process (Assis et al., 2017a; Silva et al., 2012). However, physalis did not present this behaviour. In Fig. 4.1 a low rate of water loss may be observed in the early phase of the process. This can be explained by the low permeability to fluid exchange of the surface of physalis (Puente et al., 2011; Ramadan, 2011).

In the experimental conditions used for OD of physalis, a low solute gain was observed during the whole process, besides presenting a great variability of the data. Luchese et al. (2015) observed the same in OD of physalis at 40 °C and 40 and 70 % sucrose concentration. This can be explained by the low permeability of the periderm of the fruit. Crank's model was used to determine the effective diffusivity ( $De$ ) of water and and solute during the OD, considering the geometry of a sphere. The  $De$  was calculated using four terms of the Eq. 1.42. The values of this parameter and the  $R^2$  are presented in Table 4.1. The values of  $De$  for  $WL$  are between  $3.34 \times 10^{-11}$  and  $8.69 \times 10^{-11}$  m<sup>2</sup> s<sup>-1</sup>. These values are near to the ones ( $1.4$  and  $2.9 \times 10^{-10}$  m<sup>2</sup> s<sup>-1</sup>) obtained by Luchese et al. (2015) in the OD of physalis. No difference in  $De$  was observed for the different osmotic agents and pressures used. In relation to the  $SG$ , the  $R^2$ -values of the fit were rather low, but the others assumptions of the adequacy of the models (residual normally distributed and distributed randomly around zero) were satisfied. The  $De$ -values of  $SG$  varied from  $2.56 \times 10^{-11}$  to  $5.40 \times 10^{-11}$  m<sup>2</sup> s<sup>-1</sup>. No significant differences were observed between the fitted parameters of samples submitted to different process variables.

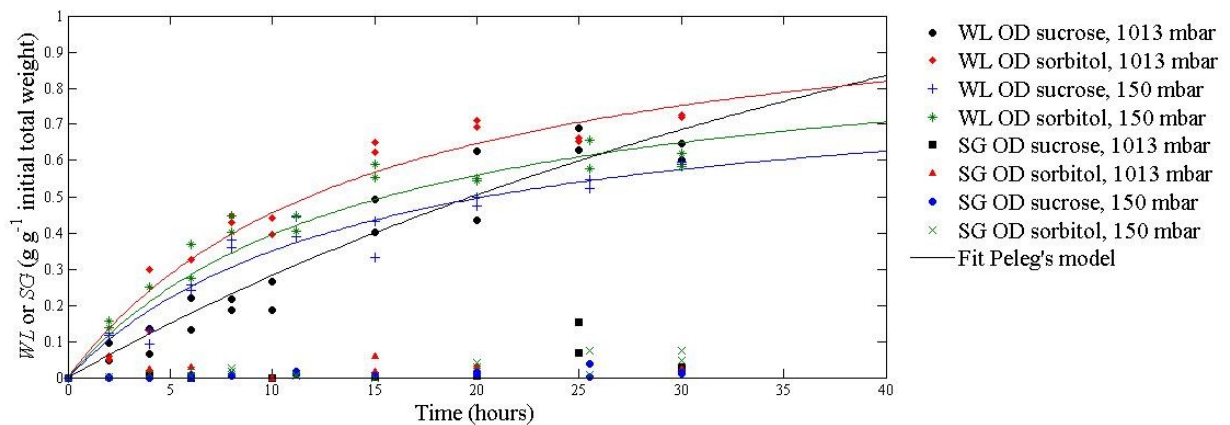
Peleg's and Page's model are able to describe well the mass transfer kinetics of osmotic dehydration of physalis at the conditions used. Therefore, the best fit was selected based on the precision of the parameter estimation, calculated though the Standard Half

Width (SHW = margin of error/ parameter value) at 95 % of confidence. Peleg's model described better the kinetics of OD of the physalis, with the highest precision of parameter estimates (i.e., lowest SHW) for all conditions used (Table 4.1). The  $WL$ , as well as the fit of Peleg's model for  $WL$  of physalis osmotically dehydrated in 60 °Bx sucrose or sorbitol solution, at atmospheric pressure or under vacuum (150 mbar), at 60 °C, and using a mass ratio of sample to solution of 1:4, are presented in Fig. 4.1.

**Table 4.1** The fit of Crank's and Peleg's model for the mass transfer during OD of physalis at 60 °C, at atmospheric pressure and under vacuum

Solute	Pressure (mbar)	Crank's model				Peleg's model		
		$WL$		$SG$		$WL$		
		$D_e \times 10^{10} \pm$ margin of error ( $m^2 s^{-1}$ )	$R^2$	$D_e \times 10^{10} \pm$ margin of error ( $m^2 s^{-1}$ )	$R^2$	$k_1 \pm$ margin of error ( $h kg kg^{-1}$ )	$k_2 \pm$ margin of error ( $kg kg^{-1}$ )	$R^2$
sucrose	1013	0.334±1.152	0.746	0.256±2.545	0.420	31.266±8.734	0.417±0.386	0.939
sucrose	150	0.509±0.949	0.873	0.308±4.668	0.161	16.792±1.179	1.179±0.246	0.954
sorbitol	1013	0.544±1.069	0.860	0.540±10.328	0.089	12.983±3.115	0.897±0.179	0.946
sorbitol	150	0.869±1.747	0.922	0.283±2.046	0.452	14.863±1.044	1.044±0.510	0.773

Margin of error is the half width of the confidence interval at 95 %



**Figure 4.1** The experimental data and the fit of Peleg's model of  $WL$  and  $SG$  of physalis osmotically dehydrated in a sucrose or sorbitol solution at atmospheric pressure and under vacuum (150 mbar) and at 60 °C

As the parameter  $k_1$  is related with the initial mass transfer rate during the OD, it can be observed that the initial rate of  $WL$  was higher in experiments with sorbitol. The

equilibrium values were not significantly different between the solutes. When different pressures were used, significant differences were noted only in experiments using the sucrose solution. With this, it was observed that the rate of  $WL$  in the OD under vacuum was higher than at atmospheric pressure and the equilibrium value ( $WL_{\infty}$ ) was lower.

Since Page's and Peleg's models could not describe the  $SG$  at both atmospheric pressure and vacuum pressure, the fit is not shown.

#### **4.5 Conclusion**

Crank's, Peleg's and Page's model could fit well the water content of physalis along OD. The effective diffusivities of water and solute during osmotic dehydration of this fruit were around  $10^{-11} \text{ m}^2 \text{ s}^{-1}$ . The osmotic agent and the pressure used did not affect this parameter. The use of the sorbitol can accelerate the initial rate of water loss. The vacuum only increased the rate of  $WL$  in physalis osmotically dehydrated with sucrose solution.



# Chapter 5 – Microstructural changes after osmotic dehydration of cut apple

## 5.1 Abstract

The microstructural changes of the apple tissue after the osmotic treatment with different solutes, sucrose and sorbitol, were studied. Light microscopy was used to observe the microstructure of fresh and osmotically dehydrated samples. The average cellular parameters, area and perimeter (size), and circularity, elongation, roundness and compactness (shape) of fresh samples was 14276.1  $\mu\text{m}^2$  and 0.485 mm, and 0.73, 1.56, 0.70, 0.83, respectively. After the osmotic dehydration (OD), folding of the cell walls, plasmolysis and cellular shrinkage were observed. The osmotically dehydrated samples presented a decrease in area, circularity, roundness and compactness and an increase in the elongation of the cells, and these changes were higher in samples treated with sorbitol.

**Keywords:** apple tissue, microstructure, osmotic dehydration, sucrose, sorbitol

## 5.2 Introduction

The osmotic dehydration is a process that partially removes the water content of foods and can be used as a pre-treatment of other processes with the aim to improve these or increase the shelf life of the final product. The water removal occurs when the food is immersed in a hypertonic solution and the high osmotic pressure of the solution promotes the diffusion of the water from the food into the solution and, simultaneously, the diffusion of solute from the solution into the food tissue. However, the leaching of cellular solutes into the osmotic solution may also occur during this process (Mayor, Pissarra, and Sereno, 2008; Nowacka, Tylewicz, Laghi, Dalla Rosa, and Witrowa-Rajchert, 2014).

Most food processes that involve heat and mass transfer cause many macroscopic and microscopic modifications of the plant tissue, including of volume, porosity, mechanical properties and colour (Lewicki and Porzecka-Pawlak, 2005; Nieto et al., 2004). These structural modifications, consequently, alter the mass transfer mechanisms during these processes (Seguí et al., 2012). During the osmotic dehydration, the shrinkage and stretching

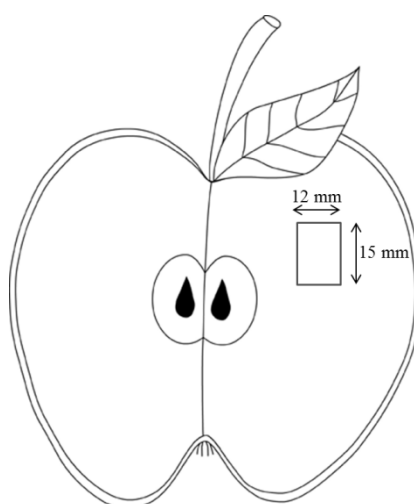
forces that act on the cell walls cause deformation, wrinkling and creasing of the cell surface, affecting the size and shape parameters (Lewicki and Porzecka-Pawlak, 2005).

The aim of this study was to evaluate the microstructural changes of the apple tissue after the osmotic treatment with different solutes, sucrose and sorbitol, and evaluate if these could help to understand the observations regarding the water loss and sugar gain during the OD.

### 5.3 Materials and methods

#### 5.3.1 Preparation of samples

Apples (*Malus* spp., variety Royal Gala) were graciously supplied by Campotec, Portugal, and stored at 4 °C. The fruits were washed and sanitized with aqueous solution with 7500 ppm active chlorine for 5 minutes. Then, the samples were cut in parallelepipeds (12 × 12 × 15 mm) with a vegetable cutter (Secret de Gourmet, France) and immersed in a solution with 0.9 % sodium chloride for 3 minutes to prevent enzymatic browning. With the aim to obtain a good structural and compositional homogeneity of the samples, the parallelepipeds were taken from the same location in the fruit as shown in Figure 5.1. The samples were blotted gently with tissue paper in order to remove the excess of sodium chloride solution from the surface.



**Figure 5. 1** Location of sampling of apple tissue

### **5.3.2 Osmotic dehydration experiments**

The apple samples were immersed in a 60 °Bx osmotic solution of sucrose or sorbitol (Fagron, Iberica, Spain) for 14 hours at 60 °C and atmospheric pressure. The mass ratio of sample to solution used was 1:4. The OD was carried out in a shaking incubator (Wiggenhauser, Germany) at constant temperature (60 °C) and agitation (50 rpm).

### **5.3.3 Moisture content determination**

The moisture content determination was carried out as described in section 2.3.3.

### **5.3.4 Light microscopy**

The samples were fixed in 2.5 % glutaraldehyde in 1.25 % PIPES buffer at pH 7–7.2 during 24 hours at room temperature (ca. 20 °C). For the osmotically dehydrated samples, the fixing solution was added to the osmotic solution with the same °Bx of the solution at the end of OD, which were 53.6 and 52.4 °Bx for sucrose and sorbitol, respectively. After that they were dehydrated in a water/ethanol series and embedded in LR White resin (London Resin Co., Basingstoke, UK). Sections (6 µm) of the resin blocks were obtained with a microtome (Jung RM 2035, Leica, Germany). The sections were stained with an aqueous solution Azure II 0.5 %, Methylene Blue 0.5 %, Borax 0.5 % during 30 seconds. After that, they were washed with distilled water and mounted in a glass slide.

The microimages were obtained under a light microscope equipped with a digital camera (BA310, Motic, China) and connected to a personal computer. The image acquisition was performed with an interface (Motic Images Plus 2.0 ML).

### **5.3.5 Image analysis**

The image analysis of the cells was performed using the free software “ImageJ” (version 1.51g), which allows to obtain some geometric cellular parameters, such as area, perimeter, length of the major axis, length of the minor axis, circularity, elongation, roundness, aspect ratio and compactness.

### **5.3.6 Statistical analysis**

The statistical analysis was performed using IBM SPSS® Statistics 20.0 for Windows® (2012, SPSS Inc., Chicago, USA). The normality of the data was tested using the Kolmogorov-Smirnov test. When the normality of data was not verified, an alternative non-

parametric test, Kruskal–Wallis, was used. In this case, the Mann-Whitney test was subsequently performed to detect which values were significantly different.

## 5.4 Results and discussion

### 5.4.1 Osmotic dehydration

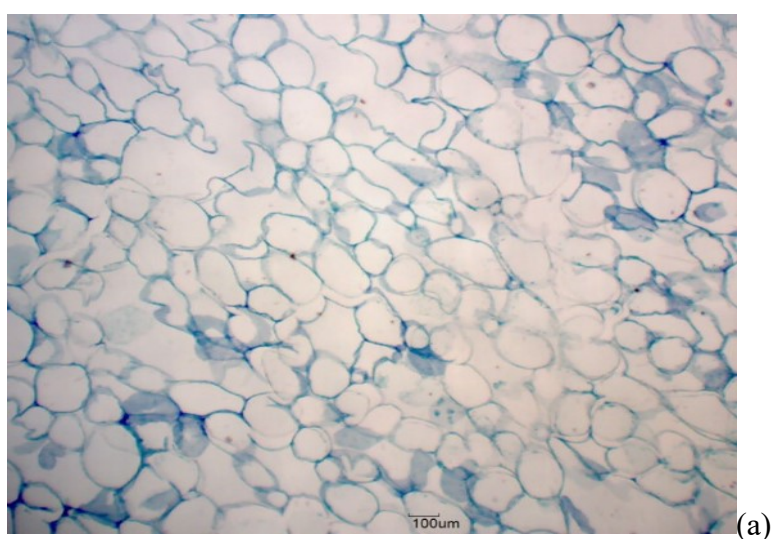
The osmotic dehydration process of decreasing the water content resulted in an increase of the dry matter. After 14 hours of the OD at 60 °Brix, it was considered that the equilibrium was achieved, *i.e.*, the maxima of the water loss and solid gain occurred.

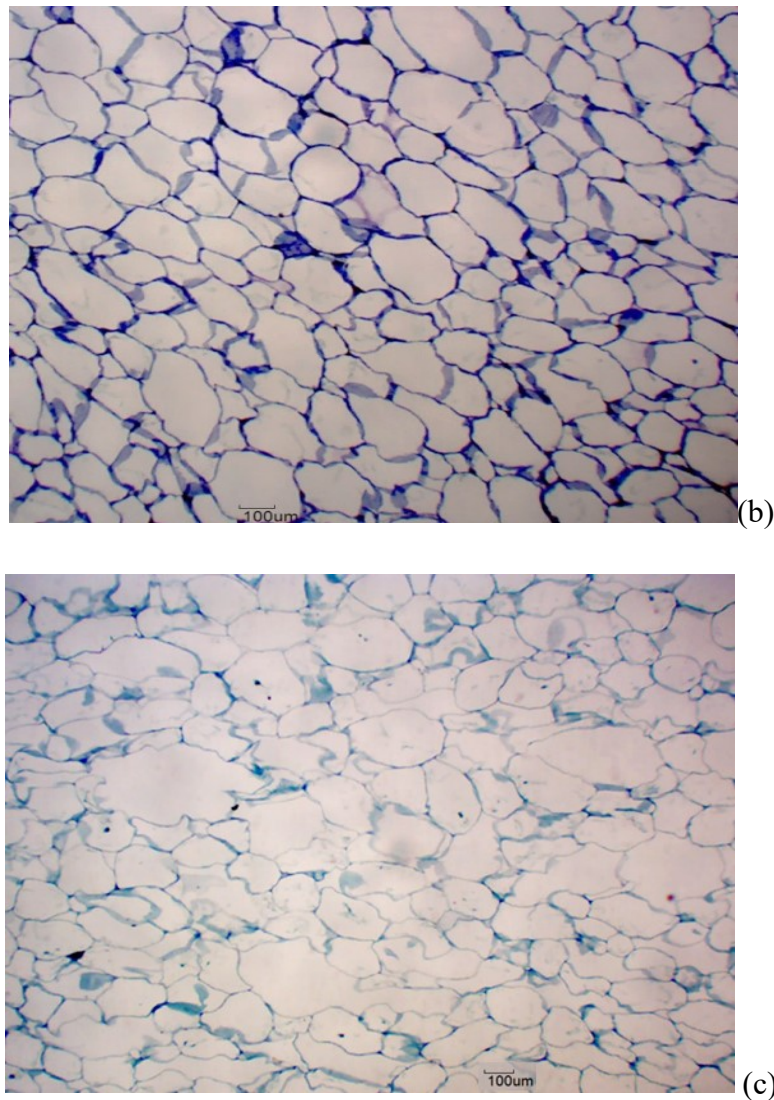
The initial moisture content of the fresh apples was  $5.431 \pm 0.205$  kg water kg DM<sup>-1</sup>. At the end of the osmotic dehydration process the moisture content was reduced to  $0.966 \pm 0.028$  and  $1.034 \pm 0.040$  kg water kg DM<sup>-1</sup> using sucrose and sorbitol solutions, respectively. Both solutes resulted in a moisture loss of around 80 %.

In a previous work (Assis et al., 2017b) it was observed that the solute used in the osmotic solution had an influence on the initial rate of the water loss. At the end of the OD process, both solutes resulted in the same water loss.

### 5.4.2 Microstructural changes

The microstructure of the apple parenchyma was analysed before (control) and after the osmotic dehydration with sucrose or sorbitol, as shown in Figure 5.2.

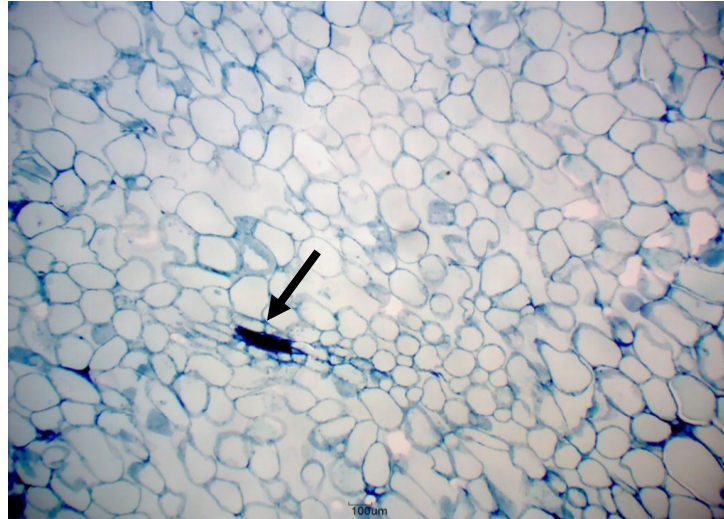




**Figure 5.2** Microstructure of apple parenchyma analysed before (a) and after the osmotic dehydration with sucrose (b) and sorbitol (c)

As can be observed in Figure 5.2 b and c, the cells submitted to osmotic treatment have different forms: the cells of the fresh samples are round and the treated samples are more wrinkled. The presence of intercellular spaces can also be noted.

In Figure 5.3 it is possible to observe a region with vascular site. The cells near this site present different orientation and irregular shape. With the aim to avoid the heterogeneity of the data, the parallelepipeds and the cuts of the tissue for the image analysis were performed in the same location (Figure 5.1) with the same orientation, and the cells near to vascular sites were not considered in the measurements.



**Figure 5.3** Microstructure of apple parenchyma with vascular site (arrow)

The average values of the size and shape cellular parameters for the fresh and the osmotically dehydrated samples are presented in Table 5.1.

**Table 5.1** Average cellular size and shape parameters of fresh and osmotically dehydrated apple samples

Pre-treatment	Area $\times 10^{-3}$ ( $\mu\text{m}^2$ )	Perimeter ( $\mu\text{m}$ )	Circularity	Elongation	Roundness	Compactness
Fresh	14.28 $\pm$ 6.65 <sup>a</sup>	485.6 $\pm$ 128.4 <sup>a</sup>	0.73 $\pm$ 0.11 <sup>a</sup>	1.56 $\pm$ 0.33 <sup>c</sup>	0.70 $\pm$ 0.12 <sup>a</sup>	0.83 $\pm$ 0.07 <sup>a</sup>
OD with sucrose solution	13.60 $\pm$ 8.07 <sup>b</sup>	487.8 $\pm$ 137.9 <sup>a</sup>	0.71 $\pm$ 0.09 <sup>b</sup>	1.60 $\pm$ 0.34 <sup>b</sup>	0.65 $\pm$ 0.14 <sup>b</sup>	0.80 $\pm$ 0.09 <sup>b</sup>
OD with sorbitol solution	12.91 $\pm$ 7.30 <sup>b</sup>	497.5 $\pm$ 159.2 <sup>a</sup>	0.64 $\pm$ 0.11 <sup>c</sup>	1.90 $\pm$ 0.51 <sup>a</sup>	0.56 $\pm$ 0.16 <sup>c</sup>	0.74 $\pm$ 0.11 <sup>c</sup>

Different letters in each column mean significantly different values at  $p < 0.05$

The area values of the fresh samples are  $14.28 \pm 6.65 \times 10^3 \mu\text{m}^2$ . These values are in the range with those obtained by Lewicki and Pawlak (2003), Lewicki and Porzecka-Pawlak (2005) and Mayor et al. (2005) in different varieties of apple. The correspondent values of the osmotically dehydrated samples are  $13.6 \pm 8.07 \times 10^3 \mu\text{m}^2$  using the sucrose solution and  $12.9 \pm 7.30 \times 10^3 \mu\text{m}^2$  using the sorbitol solution. It was noted that the area decreased significantly with the osmotic treatment. However, the perimeter of the cell was not affected by the osmotic dehydration, as the values are not significantly different and varied between 0.485 and 0.497. Mayor et al. (2008) also observed in pumpkin tissue that the perimeter was maintained and the area decreased with the OD process.

At the end of the osmotic process it is possible to observe folding of the cell wall, plasmolysis and cellular shrinkage (Figure 5.2 b, c). No differences were observed in the intercellular spaces, but there was shrinkage of the samples and, consequently, a reduction of the volume.

The osmotic dehydration affected all the shape parameters. The average of the shape parameters, roundness, compactness and elongation of the fresh samples are 0.70, 0.83 and 1.56, respectively. These values are near the values found by Karunasena et al. (2014) in the same variety of apple. The roundness and compactness decreased after the OD process and the cells were more elongated. The maximum decrease in roundness and the highest elongation was obtained in samples treated with sorbitol solution. The circularity was also affected by the OD process. The values of circularity decreased from 0.73 to 0.71, osmotically dehydrating with the sucrose solution, and to 0.64, with the sorbitol solution. The highest reduction was observed when the sorbitol was used as the osmotic agent. The decrease of this shape parameter could be explained by the fact that the initial *WL* was higher when the sorbitol is used, thus, causing more changes in the structure of the tissue in comparison with the tissue of the samples treated with sucrose.

## **5.5 Conclusion**

Besides reducing the moisture content, the osmotic dehydration process causes significant changes in the size and the shape parameters of the apple cells. The cellular area, roundness, compactness and circularity decrease, while the elongation increases and the perimeter of cells is maintained after the process. The osmotic process of the apple tissues results in shrinkage of the cells and, consequently, volume reduction, plasmolysis and folding of the cell walls. However, it does not cause any change in the intercellular spaces, since the intercellular spaces within the tissues are normally occupied with air.



**Part III – Study of the drying processes subsequent to  
osmotic dehydration**



## Chapter 6 – Optimization of air drying after osmotic treatment

### 6.1 Abstract

The aim of the present work was to study the effect of the osmotic dehydration (OD) pre-treatment on the mass transfer kinetics and water activity ( $a_w$ ) of apple cubes during hot air drying. The adequacy of different mathematical models to describe the moisture content of the product during this process was also evaluated. Apple cubes were osmotically dehydrated with sucrose or sorbitol solutions at 60 °C, and then dried by air at 25 to 80 °C. Overall, the OD and rise of the air temperature resulted in an increased water loss rate and a reduction of the  $a_w$ . The osmotic agent used in the OD was not relevant to the air drying kinetics, but the pre-treatment with sorbitol solutions produced dried samples with lower  $a_w$ . Newton's, Page's, modified Page's, Henderson and Pabis', Two-term, Two-term exponential, Logarithmic, Midilli et al.'s models could describe the moisture content well during the process.

**Keywords:** apple cubes, osmotic dehydration, hot air drying, mass transfer, mathematical models

### 6.2 Introduction

The dehydration confers properties, such as stability at room temperature, convenience in transportation and product versatility. This process consists of reducing the water content of the food, decreasing the water activity ( $a_w$ ), thereby, inhibiting the growth of microorganisms and delaying the deterioration of physico-chemical origin (Cano-Chauca et al. 2004). The osmotic dehydration (OD) consists of the immersion of foods in aqueous solutions of high osmotic pressure for the partial removal of water. This process can produce intermediate moisture food, but the moisture content and water activity levels reached are not enough to obtain shelf stable products. Thus, this is often used as pre-treatment before other drying process, also reducing the time of the subsequent process (Khan 2012).

The OD combined with other type of dehydration, such as convective, vacuum, microwave and freeze-drying, applied to fruits, vegetables, fish and meat, has been proposed

by many researchers. The use of OD previously to convective drying may be used in order to improve the rehydration characteristics, texture and colour of the final products (Kaur et al. 2014). The hot air dehydration is very common in food industry due to being considered an economical method to produce dehydrated products from higher initial moisture content, and also to involve easy operated drying equipment (Kaur et al. 2014; Kowalski and Szadzińska 2014). Velickova et al. (2014) evaluated the physical and sensory properties of apples chips produced by OD followed by convective drying. This product presented acceptable colour, mechanical properties and good acceptability by the consumers. Kowalski and Mierzwa (2013) examined the influence of OD on the convective drying of apples and they found that the OD improved the quality of dried product, but did not affect the drying rate. Araya-Farias et al. (2014) studied the vacuum and hot-air drying kinetics of seabuckthorn berries osmotically dehydrated and noted that the moisture content of air-dried samples decreased more than the vacuum dried ones. Kaur et al. (2014) found that the OD pre-treatment of oyster mushroom with sodium chloride (NaCl) 20 % at 45 °C produced lower hot air drying rate due to the deposition of salt on the outer surface of mushroom tissues. Moreira et al. (2011) studied the air drying kinetics of chestnuts pre-submitted to OD with NaCl and concluded that the drying time was not reduced by the OD pre-treatment due to the higher resistance of the salt (deposited on the product surfaces) to water removal during the air drying. Fernandes et al. (2006) optimized the OD process followed by air drying of banana and they concluded that the osmotic pre-treatment with higher solute concentrations reduced the total processing time.

Bruijn and Bórquez (2014) compared different drying methods including vacuum microwave drying subsequently or not to OD of strawberries. They observed that the moisture content decreased from 90 % to 75 % (wet basis) after OD and the drying rate decreased significantly when compared to the process without the osmotic pre-treatment. Ciurzynska et al. (2014) did not detect significant differences in the water content of freeze-dried pumpkin after OD in comparison to pumpkin without the osmotic pre-treatment.

To describe the mass transfer kinetics of the drying process, mathematical models (empirical, semi-empirical and phenomenological) may be used to fit the experimental data. The phenomenological model more used is based on the Fick's second law, but it is applied only for classical geometries. This model was able to determine the diffusion coefficient of several types of drying process of papaya, green peas and lemon waste (Garcia et al. 2014; Puente-Díaz et al. 2013; Zielinska et al. 2013). The empirical and semi-empirical models can be applied to non-classical geometries, but they do not take into account the

phenomenological mechanisms in the drying process. Some of these models are Newton's, Page's, modified Page's, Henderson and Pabis', Two-term, Two-term exponential, Verma et al.'s, Logarithmic, Wang and Singh's, Midilli et al.'s and Weibull's distribution. Yu et al. (2015) compared some of them and they found that the Weibull's distribution model was the most suitable to describe the drying of hawthorn slices by microwave associated with hot air drying. According to Menezes et al. (2013), the Page's model was the best to describe the experimental data of convective drying of pomace of yellow passion fruit. The logarithmic and Midilli et al.'s models could predict the moisture content during air drying of coroba slices in a study performed by Corzo et al. (2010). Hui et al. (2011) found that the two-term model presented a good fit to the experimental data of hot air drying of litchi pulp. For pepper dried in an air impingement dryer, Qian et al. (2011) found that the modified Page's model was more suitable to fit the experimental data.

The objectives of this work were: i) to carry out the osmotic dehydration of apple cubes (variety Royal Gala) at 60 °C for 8 hours, using two solutes — sucrose or sorbitol — at a mass ratio sample/ solution of 1:4 (based on a previous study, Assis et al. 2016), followed by hot air drying, and to study the effect of the air temperature — 25, 55, 70 and 80 °C — on the mass transfer kinetics and on the water activity of the product; ii) to test the adequacy of the fitness of some mathematical models — Crank's, Newton's, Page's, modified Page's, Henderson and Pabis's, Two-term, Two-term exponential, Logarithmic, Wang and Singh's, Midilli et al.'s and Weibull's distribution — to describe the moisture content of the product during the hot air drying.

## **6.3 Materials and methods**

### **6.3.1 Samples**

The samples were prepared as presented in 2.3.1. The soluble solids content of the apple was  $14.8 \pm 0.6$  °Bx.

### **6.3.2 Osmotic dehydration**

The apple samples were immersed in the osmotic solution at 60 °Bx for 8 hours at 60 °C in atmospheric pressure. The osmotic solutions were prepared with ultra-pure water and commercial sucrose or sorbitol (Fagron, Iberica, Spain). The mass ratio of sample to solution used was 1:4. The OD was carried out in beakers placed in a bench-top shaking incubator

(SI-100C, Wiggerhauser, Germany) at constant temperature and agitation (50 rpm). Then, the samples were rinsed with ultra-pure water to remove the solution adhered to the surface and blotted with tissue paper to remove the excess of water from the surface.

### **6.3.3 Hot air drying**

The hot air drying experiments were performed in an oven (UFP800DW, Memmert, Germany) with recirculation of air. The air velocity was measured with an anemometer (Airflow LCA 6000, England) and it was fixed at approximately  $1 \text{ m s}^{-1}$ . The relative humidity was measured with a hygroLog (HL-NT2, Rotronic, Switzerland) during the process.

Around 150 g of control (fresh) samples or 50 g of osmotically dehydrated samples were used in each drying experiment. The drying experiments were carried out at 25, 55, 70 and 80 °C. The longest drying time was 600 min at the lowest temperature. Each drying experiment was carried out twice and the experimental data were duplicated.

### **6.3.4 Moisture content and water activity determination**

The moisture content of the apple samples was determined as described in section 2.3.3.

The water activity of the samples was determined during the process at specific times between 0 and 600 min. The  $a_w$  of the samples was determined with a hygrometer (Aqualab Series 3, Decagon Devices Inc., Pullman, Washington, USA) at 22 °C. The determinations were performed in duplicate.

### **6.3.5 Mathematical models**

With the aim to describe the moisture loss of the osmotically dehydrated apple cubes during the hot air drying, some mathematical models, phenomenological and empirical or semi-empirical – Newton's, Page's, modified Page's, Henderson and Pabis', two-term, two-term exponential, logarithmic, Wang and Singh's, Midilli et al., Weibull's and Crank's model – were used to fit the experimental data. The model's equations were presented in 1.7.2.

The relation between the equilibrium moisture content and the water activity of the apple cubes dried was predicted using Guggenheim-Anderson-de Boer (GAB) model. This model is reported to be the best for fitting sorption isothermal data for the majority of food products (Barbosa-Cánovas and Vega-Mercado 1996). The GAB model is expressed as:

$$\frac{M_{\infty}}{M_m} = \frac{c.k.a_w}{(1-k.a_w).(1-k.a_w+c.k.a_w)} \quad (6.1)$$

$C$  and  $k$  are constants and  $M_m$  is described as the monolayer moisture content on dry basis (kg water kg DM<sup>-1</sup>).

### **6.3.6 The Arrhenius behaviour**

The linearized Arrhenius equation were presented in 2.3.7.

### **6.3.7 Quality evaluation**

The colour, the total phenolic content and the antioxidant activity of the product dried at the condition that produced the best hot air drying rate were evaluated.

#### **Colour**

The colour of the samples was measured using Minolta CR-300 colorimeter (Konica-Minolta, Osaka, Japan) in the CIE  $L^*a^*b^*$  mode CIELAB colour space (Commission Internationale de L'Eclairage, CIE, 1978). The colour was determined by five measures on three replicates for each sample. The saturation index or chroma ( $C$ ) (Eq. 1.61) and the browning index (Eq. 1.63) were calculated as described in section 1.8.2. The total colour difference ( $\Delta E$ ) was calculated according to equation 1.62, the index "0" indicating the sample before air drying.

#### **Total phenolic content**

The extracts were prepared for the determination of the total phenolic content and the antioxidant activity. The dried apple cubes were ground in liquid nitrogen with a pestle in a mortar. Subsequently, 1 g of sample was weighted, 10 mL of methanol (Sigma Aldrich) were added and the mixture was homogenised using an ultra-turrax (T25, IKA, Germany). After that, the homogenized solutions were centrifuged at 5000 rpm and 4 °C for 15 minutes, and filtered with a filter paper.

The total phenolic content was determined in the methanolic extracts by the Folin-Ciocalteu method (Singleton and Rossi, 1965). The reaction was performed by adding 0.5 mL apple extract, 0.5 mL Folin–Ciocalteu reagent, 1 mL sodium carbonate 75 (g L<sup>-1</sup>) (Sigma-Aldrich) and 1.4 mL of deionized water. The total phenolic content was determined after 1 hour at 750 nm in a UV-visible spectrophotometer (1240, Shimadzu, Japan). The quantification was performed with respect to the standard curve of the gallic acid.

The determinations were carried out in triplicate.

### **Antioxidant activity**

The ABTS method was used to determine the antioxidant activity (Gião et al., 2007). After addition of 1 mL of ABTS<sup>+</sup> solution (absorbance = 0.700 ± 0.02) to 0.2 mL of extract, the analysis was performed after 6 minutes at 734 nm and the antioxidant activity was expressed as mg ascorbic acid g DM<sup>-1</sup>.

The determinations were performed in triplicate.

#### **6.3.8 Statistical analysis**

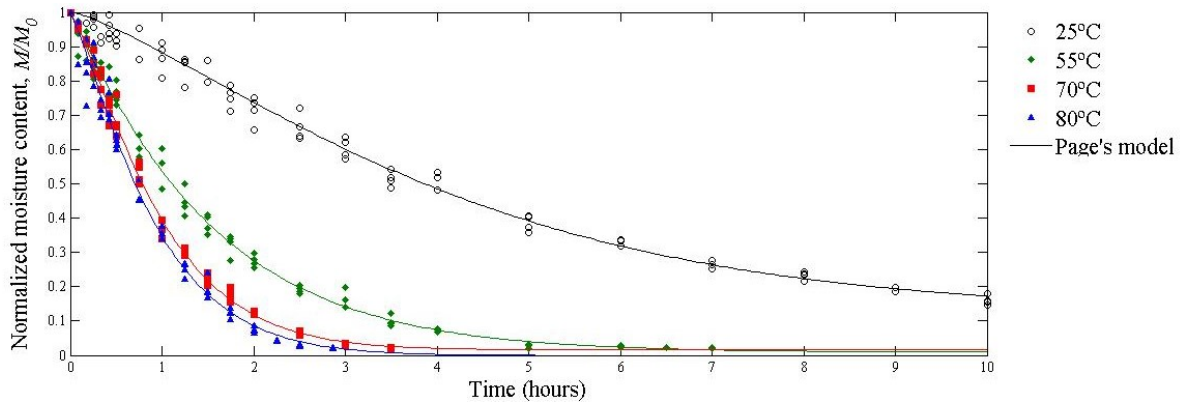
The statistical analysis was performed as presented in section 2.3.8.

### **6.4 Results and discussion**

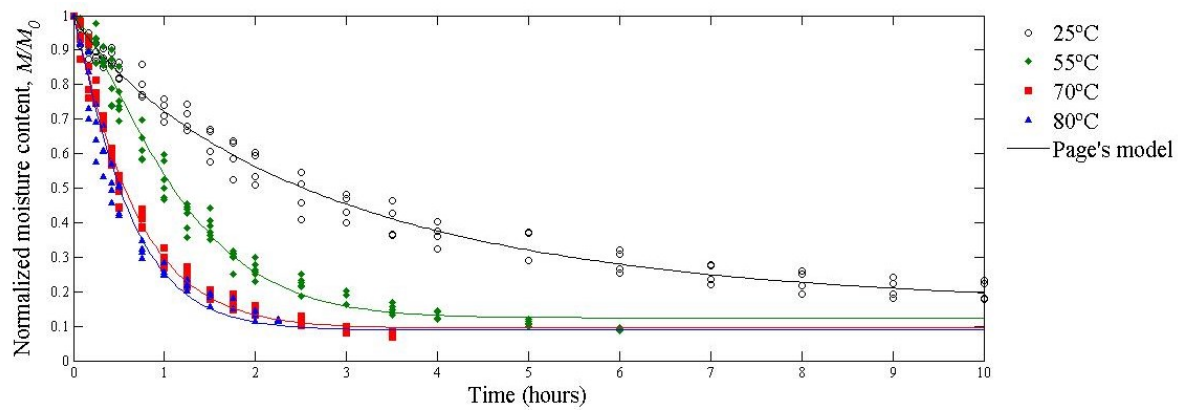
First, the air drying experiments were carried out with fresh samples (control) and samples osmotically dehydrated with the sucrose solution at temperatures from 25 to 80 °C. Then, air drying experiments were performed with the osmotically dehydrated samples with the sorbitol solution at 25 and 80 °C. As no significant differences were observed in the water loss rate between the two osmotic agents used in the OD, the experiments with the sorbitol solution at others temperatures (55 and 70 °C) were not carried out.

The moisture ratio of the apple cubes, fresh or osmotically dehydrated, dried at different air temperatures decreased with the drying time. Due the variability of the experimental data after the OD pre-treatment, the moisture content,  $M$ , was normalized to  $M/M_0$ . Only the falling rate period was noticed for all conditions (Figures 6.1 to 6.3). Araya-Farias et al. (2014), Garcia et al. (2014), Hemis and Raghavan (2014) and Yu et al. (2015) found the same in different types of drying of seabuckthorn fruit, papaya slices, soybean and

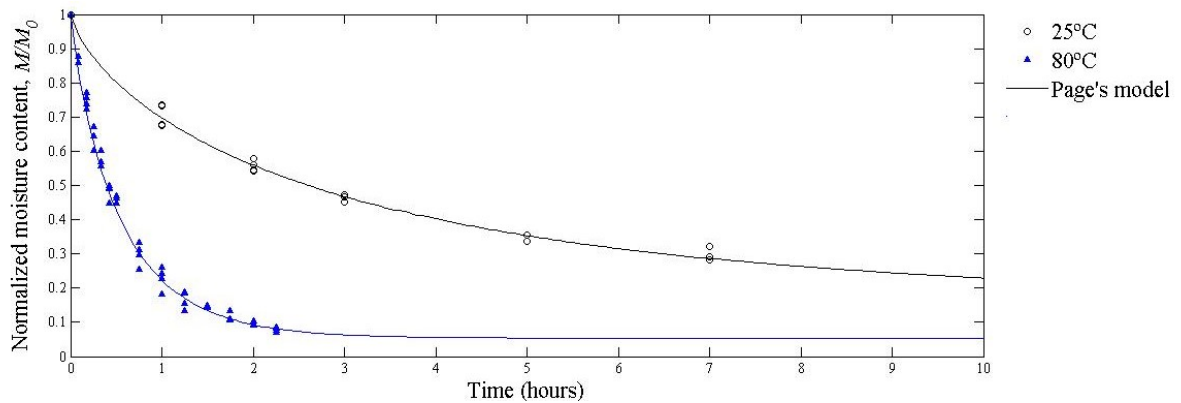
hawthorn slices. Nieto et al. (2001) also did not detect the constant rate period during the air drying of blanched and/or osmotically dehydrated mango.



**Figure 6.1** Experimental data and the fit of Page's model of the normalized moisture content ( $M/M_0$ ) during the air drying of control apple cubes



**Figure 6.2** Experimental data and the fit of Page's model of the normalized moisture content ( $M/M_0$ ) during the air drying of apple cubes osmotically dehydrated in sucrose solutions



**Figure 6.3** Experimental data and the fit of Page's model of the normalized moisture content ( $M/M_0$ ) during the air drying of apple cubes osmotically dehydrated in sorbitol solutions

### 6.4.1 *Mathematical modelling*

The results of the non-linear regression of the experimental data of the hot air drying of the apple cubes are shown in Tables 6.1 and 6.2. The Newton's, Page's, Modified Page's, Midilli et al.'s, Henderson and Pabis', Two-term, Two-term exponential and Logarithmic models presented high values of determination coefficients ( $R^2$ ) and the residual analysis showed that the residuals are normally distributed at the significance level of 5 %; the visual analysis of the scatterplot of residuals vs. predicted values allowed to observe that the residuals were distributed randomly around zero with no systematic patterns, satisfying the assumption of homoscedasticity and zero mean errors.

The  $k$  (Newton's, Henderson and Pabis', Midilli et al.'s and Logarithmic models) and  $A$  (Page's and Modified Page's models) parameters presented the same trend, in general, increasing with the air drying temperature (Tables 6.1 and 6.2). This tendency is in agreement with Puente-Díaz et al. (2013) and Qian et al. (2011), who used Newton's and Henderson and Pabis' models and the modified Page's model, respectively. Both these parameters can be related with the water diffusion rate (Kaur et al. 2014; Ruiz-López et al. 2010). Thus, the drying rate increased with the increase of temperature up to 70 °C, but at 80 °C no significant difference was observed in comparison with 70 °C. According to Simal et al. (1997), the air drying rates of apple cubes were similar at temperatures between 60 and 90 °C.

In general, the OD pre-treatment also influenced the air drying. The values of  $k$  parameter of Henderson and Pabis' model are higher for the osmotically dehydrated samples than the control samples. The solute used in the OD did not produce significant differences in this parameter. The  $A$ -values of the Page's model relative to the air drying of osmotically dehydrated samples are also higher than for the control samples, except for the osmotically dehydrated samples with sucrose solution at 80 °C (Table 6.1). According to Fernandes et al. (2006b), the convective drying rate of osmotically pre-treated papaya was higher than without the pre-treatment. Ruiz-López et al. (2010) also found an increase in  $A$  parameter of Page's model for osmotically pre-treated chayote slabs in comparison with the fresh samples. Lenart and Cerkowniak (1996) studied the effect of different solutes (sucrose and starch) in the osmotic dehydration of apples and found that the osmotic solute did not affect the kinetics of the subsequent convective drying at 30 °C.

**Table 6.1** Parameters of the fit of Newton's, Page's, modified Page's and Henderson and Pabis' models of *MR* during air drying of apple cubes

Osmotic agent of previous OD	T (°C)	Models										
		Newton's		Page's			Modified Page's			Henderson and Pabis'		
		$k \pm$ margin of error	R <sup>2</sup>	$A \pm$ margin of error	$B \pm$ margin of error	R <sup>2</sup>	$A \pm$ margin of error	$B \pm$ margin of error	R <sup>2</sup>	$k \pm$ margin of error	$a \pm$ margin of error	R <sup>2</sup>
sucrose	25	0.396±0.035	0.985	0.398±0.034	0.875±0.076	0.987	0.349±0.048	0.875±0.076	0.987	0.362±0.039	0.965±0.025	0.987
sorbitol	25	0.383±0.052	0.986	0.441±0.034	0.735±0.071	0.997	0.328±0.035	0.735±0.071	0.997	0.363±0.059	0.969±0.057	0.987
sucrose	55	0.673±0.093	0.977	0.748±0.071	1.343±0.138	0.988	0.805±0.062	1.343±0.138	0.988	0.814±0.091	1.095±0.036	0.988
sucrose	70	1.379±0.091	0.994	1.503±0.138	1.088±0.078	0.995	1.454±0.097	1.088±0.078	0.995	1.454±0.114	1.027±0.027	0.995
sucrose	80	1.469±0.343	0.951	1.710±0.713	1.123±0.318	0.952	1.612±0.429	1.123±0.318	0.952	1.804±0.417	1.106±0.090	0.961
sorbitol	80	1.989±0.134	0.993	1.718±0.246	0.892±0.087	0.994	1.834±0.205	0.892±0.087	0.994	1.838±0.150	0.959±0.027	0.995
-	25	0.173±0.034	0.980	0.144±0.018	1.317±0.138	0.989	0.230±0.030	1.317±0.138	0.989	0.181±0.028	1.049±0.020	0.990
-	55	0.630±0.026	0.997	0.629±0.023	1.059±0.043	0.998	0.645±0.027	1.059±0.043	0.998	0.636±0.032	1.010±0.014	0.997
-	70	0.916±0.116	0.986	0.954±0.063	1.250±0.069	0.997	0.963±0.052	1.250±0.069	0.997	0.901±0.086	1.053±0.024	0.995
-	80	1.036±0.155	0.982	1.044±0.130	1.179±0.109	0.993	1.045±0.106	1.213±0.112	0.993	0.902±0.128	1.028±0.030	0.991

Margin of error is the half width of the confidence interval at 95 %

**Table 6.2** Parameters of the fit of Two-term exponential and Midilli et al.'s models of *MR* during air drying of apple cubes

Osmotic agent of previous OD	T (°C)	Models							
		Two-term exponential			Midilli et al.'s				
		a ± margin of error	k ± margin of error	R <sup>2</sup>	a ± margin of error	k ± margin of error	n ± margin of error	b ± margin of error	R <sup>2</sup>
sucrose	25	0.306±0.179	0.819±0.487	0.987	0.973±0.043	0.397±0.063	0.977±0.163	-0.004±0.008	0.988
sorbitol	25	0.231±0.283	1.168±1.711	0.995	1.000±0.033	0.487±0.075	0.812±0.149	-0.005±0.007	0.997
sucrose	55	1.952±0.099	1.282±0.133	0.989	1.053±0.047	0.985±0.180	0.353±0.225	-0.040±0.034	0.992
sucrose	70	1.573±0.168	1.831±0.272	0.994	1.004±0.036	2.073±0.422	1.227±0.157	-0.064±0.038	0.996
sucrose	80	1.645±0.505	2.128±1.063	0.952	1.116±0.209	1.527±3.165	0.886±0.505	-0.020±0.572	0.962
sorbitol	80	0.353±0.187	3.626±1.854	0.994	0.967±0.038	1.818±1.001	0.955±0.180	-0.013±0.148	0.995
-	25	1.881±0.095	0.346±0.050	0.989	1.041±0.051	0.192±0.122	1.206±0.388	-0.019±0.134	0.991
-	55	1.515±0.114	0.786±0.076	0.998	0.994±0.021	0.626±0.090	1.078±0.100	-0.001±0.021	0.998
-	70	1.816±0.068	1.399±0.112	0.997	1.015±0.027	1.112±0.278	1.272±0.167	-0.042±0.076	0.997
-	80	1.721±0.130	1.377±0.220	0.993	1.001±0.030	0.780±0.819	1.115±0.281	-0.069±0.234	0.993

Margin of error is the half width of the confidence interval at 95 %

There was no clear tendency for some parameters of some models in relation to the different samples (osmotically dehydrated with different solutes and the control), such as  $k$  parameter of Newton's and  $a$  parameter of Henderson and Pabis' models (Table 6.1). In addition, the solute used in the OD did not have an influence on some other parameters:  $A$  and  $B$  of modified Page's model and  $A$  and  $B$  of Page's model at 25 and 80 °C.

The adequacy of Page's model was also observed by Yan and Jianwei (2012) during the hot air drying of schisandra. Assis et al. (2016) also found that this model was suitable as well to describe the experimental data of OD of apples cubes. As for the hot air drying,  $A$  parameter also increased with the temperature of the OD process.

Both parameters of the two-term exponential model did not present a clear pattern. The parameters  $a$ ,  $b$  and  $n$  of Midilli et al.'s model did not show differences either among the operation conditions or the samples (Table 6.2). The  $a$ -values are close to 1. This is in agreement with Corzo et al. (2010) and Kaur et al. (2014). The  $k$  parameter is higher for osmotically treated samples and higher temperatures, except at 80 °C. Corzo et al. (2010) also found that  $k$  increased with the temperature in hot air drying of coroba slices. Unal and Sacilik (2011) tested five models and concluded that Midilli et al.'s model presented an excellent fit of the experimental data of hawthorn fruits during the hot air drying.

The parameters of the two-term and the logarithmic models (data not shown) presented high values of margin of error, making them not significantly different among the different conditions used. However, this fact is not related with the quality of the fit model, since the  $R^2$  values are between 0.961 and 0.998 and the residuals are random and normally distributed. The  $k$  parameter of the logarithmic model increases with the air temperature, which is in agreement with Corzo et al. (2010).

However, all the models discussed above are empirical or semi-empirical and, therefore, they do not present any physical meaning. Crank's, Wang and Singh's and Weibull's models did not describe well the experimental data, as  $R^2 < 0.9$  and the residuals are neither random nor normally distributed. Among the models tested, Crank's is the only phenomenological model, which would allow for a physical meaning.

The inadequacy of Crank's model was not expected, as this model uses theoretical basis adequate to the geometry of the product. The dimensions of the samples in the present work were not very different from the ones used in other works. Velić et al. (2004) studied the convective drying of rectangle-shaped (20 × 20 × 5 mm) apple samples; Sacilik and Elicin (2006) studied the drying of apple slices (5 and 9 mm). In both works the effective diffusivity was calculated using the solution of Fick's second law for slab. In fact, Crank's

is the most used model, because it is a phenomenological one and is able to determine the effective diffusivity of the water, but in some studies the fit adequacy was not presented (An et al. 2013; Singh and Gupta 2007).

The Arrhenius's behaviour was observed for the  $k$  parameters of Newton's, Henderson and Pabis's, Midilli et al.'s and two-term exponential models and the  $A$  parameters of Page's and modified Page's. The linearity of the data ( $R^2 > 0.90$ ) shows that these parameters were influenced by temperature. The activation energy ( $E_a$ )-values of these parameters are between  $15.27 \pm 6.22$  and  $25.88 \pm 8.19$  kJ mol<sup>-1</sup> for samples osmotically dehydrated with sucrose, and between  $23.49 \pm 11.9$  and  $32.80 \pm 17.03$  kJ mol<sup>-1</sup> for the control samples during the air drying (data not shown). Higher  $E_a$  indicates a greater sensitivity of the parameter to temperature. However, no significant differences were found among the samples (osmotically dehydrated and control). The parameter  $p_{ref}$  did not present differences, except for  $k$  of the two-term exponential model:  $0.794 \pm 0.222$  (OD) vs.  $0.347 \pm 0.186$  (control). No correlation could be found between the other parameters and the temperature in the experimental conditions used.

#### 6.4.2 Water activity

The  $a_w$  of the fresh apple cubes was  $0.993 \pm 0.003$  and, after osmotic dehydration, it ranged from 0.851 to 0.949. The  $a_w$  of these samples subsequently dried by hot air decreased with the process time and, consequently, with the final water content. At the end of the process, the final  $a_w$  was between 0.245 and 0.493. The  $a_w$  of the hot air dried samples previously osmotically dehydrated with the sorbitol solution presented lower values than with the sucrose solution, for the same drying time. This is an advantage because food with low water activity is less susceptible to oxidation and non-enzymatic browning.

The fact that the use of sorbitol as osmotic agent did not affect the water loss rate, in comparison with sucrose, but resulted in a lower water activity of the product, which may be explained by the results found before the air drying, *i.e.* the osmotically dehydrated samples with sorbitol solutions presented already lower values of  $a_w$  than the samples osmotically dehydrated with sucrose solutions. These results followed the same pattern of the initial rate of water loss and it was attributed to the lower viscosity of sorbitol solutions, as well as to their higher molar concentration, in comparison to sucrose solutions at the same mass concentration (60 °Bx) (Assis et al., 2016). This difference in the  $a_w$  of the samples osmotically dehydrated by the two solutes was reflected in the  $a_w$  values of the final air-dried

product. Thus, after the same total air drying time at 80 °C, the reduction of the  $a_w$  was 68 % and 74 % for the osmotic pre-treatment with sucrose and the osmotic pre-treatment with sorbitol, respectively.

The drying time of the control samples was 10 h and 2.9 h at 25 and 80 °C, respectively (Figure 6.1). As expected, the OD pre-treatment reduced the air drying time, by 20 %, using sucrose, and 30 %, using sorbitol, for hot air drying at 25 °C. At 80 °C, the reduction was 22 % and 39 %, using sucrose or sorbitol as the osmotic agent, respectively. Therefore, the OD pre-treatment with sorbitol was more effective than sucrose in reducing the air drying time.

The GAB model fitted well the experimental data of moisture content versus  $a_w$ . The behaviour of the isotherms was different for the control and the pre-treated samples. For the control samples, the isotherms are close at the beginning of the drying process and they become separated in the end of the process. This behaviour is inverted for the osmotically dehydrated samples.

The GAB parameters (Table 6.3) did not follow the Arrhenius behaviour and no relation was observed between the process variables. The values of  $M_m$  ranged from 0.133 to 1.012 and were in agreement with Farahnaky et al. (2009) and Kaymak-Ertekin and Gedik (2004). The parameter  $M_m$  was higher for the control samples when compared with the osmotically dehydrated ones, except at 55 °C. However, no difference was observed in this parameter for the samples pre-treated with the two different solutes. This could be explained given that  $M_m$  is the amount of water that is strongly adsorbed to specific sites of the food surface, that cannot be removed by drying, and could be similar for the samples osmotically dried with both solutes (De Bruijn and Bórquez 2014; Vega-Gálvez et al. 2014).

**Table 6.3** GAB parameters and regression coefficients for isothermal desorption of osmotically dehydrated apple cubes

Osmotic agent of OD	Temperature of air drying (°C)	GAB model			R <sup>2</sup>
		$cI \pm$ margin of error	$k \pm$ margin of error	$Mm$ (kg water kg DM <sup>-1</sup> ) $\pm$ margin of error	
sucrose	25	3.085±4.922	0.934±0.029	0.140±0.040	0.975
sorbitol	25	2.607±2.161	0.863±0.059	0.246±0.081	0.988
sucrose	55	1.678±1.799	0.904±0.031	0.209±0.068	0.989
sucrose	70	7.192±13.356	0.950±0.014	0.133±0.024	0.993
sucrose	80	2.995±2.127	0.875±0.035	0.183±0.045	0.996
sorbitol	80	2.573±1.188	0.893±0.027	0.222±0.041	0.998
-	25	180.915±14098.6	0.943±0.012	0.451±0.081	0.983
-	55	0.210±0.727	0.913±0.104	1.012±2.639	0.988
-	70	2.032±5.629	0.957±0.020	0.360±0.149	0.987
-	80	1.911±1.972	0.956±0.007	0.376±0.053	0.998

Margin of error is the half width of the confidence interval at 95 %

### 6.4.3 Quality of the final product

The values of the quality parameters are presented in Table 6.4. The colour coordinates for fresh apples were 69.39±1.79, -4.78±0.54, and 28.96 ± 0.62 for L\*, a\* and b\*, respectively. In the osmotically dehydrated samples, the luminosity (L\*) and redness (a\*) increased after the HAD process. Izli et al. (2014) found lower values of L\*, a\* and b\* after the air drying process of goldenberries. Di Scala et al. (2011) also observed a decrease in the luminosity after the air drying of pepino fruit at different temperatures. The total colour difference and the browning index were not affected by the HAD process.

**Table 6.4** Quality parameters of osmotically pre-treated apples cubes dehydrated by hot air drying

Sample	L*	a*	$\Delta E$	Browning index	TPC (mg of gallic acid g DM <sup>-1</sup> )	AA (mg ascorbic acid g DM <sup>-1</sup> )
fresh	69.39±1.79 <sup>a,b</sup>	-4.78±0.54 <sup>c</sup>	0	46.77±1.25 <sup>c</sup>	6.02±0.07 <sup>a</sup>	6.79±0.25 <sup>a</sup>
control	71.82±5.07 <sup>a</sup>	-3.65±0.97 <sup>c</sup>	5.86±3.10 <sup>b</sup>	52.41±6.25 <sup>c</sup>	4.04±0.81 <sup>a</sup>	5.55±0.34 <sup>a</sup>
OD sucrose	61.83±2.96 <sup>c</sup>	-1.90±1.30 <sup>b</sup>	7.61±2.45 <sup>a,b</sup>	53.18±5.43 <sup>b,c</sup>	0.96±0.11 <sup>b</sup>	1.02±0.12 <sup>b</sup>
OD sucrose + HAD	66.47±5.34 <sup>b</sup>	1.85±1.41 <sup>a</sup>	8.27±2.90 <sup>a,b</sup>	59.68±10.26 <sup>a,b</sup>	0.94±0.14 <sup>b</sup>	1.12±0.14 <sup>b</sup>
OD sorbitol	62.35±3.75 <sup>c</sup>	-1.50±1.43 <sup>b</sup>	8.23±3.52 <sup>a,b</sup>	59.09±5.80 <sup>a,b</sup>	1.10±0.13 <sup>b</sup>	1.24±0.16 <sup>b</sup>
OD sorbitol + HAD	69.74±4.01 <sup>a,b</sup>	2.42±1.59 <sup>a</sup>	10.02±2.95 <sup>a</sup>	61.06±5.77 <sup>a</sup>	1.09±0.15 <sup>b</sup>	1.25±0.23 <sup>b</sup>

Different letters in each column mean significantly different values at  $p < 0.05$

The total phenolic content (TPC) of the fresh apple was 6.02±0.07 mg gallic acid g DM<sup>-1</sup>. After HAD, this content 33 % was lower. Patel et al. (2016) found a reduction in TPC of 29 % after air drying sliced guavas at 54 °C for 48 hours. Izli et al. (2014) also observed a reduction in TPC in air dried goldenberries. They explained this reduction by the fact that the drying does not immediately inactivate the oxidative enzymes, thus, the degradation of some polyphenols being likely to occur. Other reason could be that the extraction with solvent from dry material is more difficult than from fresh one, resulting in overall recoveries lower than expected (Garau et al., 2007). In osmotically dehydrated samples, the TPC was not affected by the HAD, the reduction in this parameter being observed just after the osmotic dehydration. The TPC was not significantly different between the samples dehydrated with sucrose and sorbitol solutions.

The antioxidant activity (AA) of the fresh apple was 6.79±0.25 mg ascorbic acid g DM<sup>-1</sup> and it decreased by 18 % after the HAD. A reduction of 11 % was observed in the air drying of tomatoes at 80 °C for 2 hours and, then, 60 °C for 6 hours (Chang et al., 2006). The same trend observed in the TPC for the osmotically dehydrated samples was also noticed in the AA.

The correlation coefficient ( $R^2$ ) between the TPC and the AA was 0.974, probably meaning that the phenolic compounds are the main responsible for the antioxidant activity.

## 6.5 Conclusions

The osmotic dehydration pre-treatment had a significant influence on both the mass transfer kinetics of the air drying and the water activity of apple cubes at the conditions tested. The increase of the air temperature resulted in an increase of the drying rate and, consequently, the drying time was reduced. The hot air drying process decreased the water activity of the apple cubes significantly. The use of sorbitol as osmotic agent did not affect the rate of water loss, in comparison with sucrose, but resulted in a lower water activity of the product. The hot air drying decreased significantly the total phenolic content and antioxidant activity in relation to the fresh apple, but the highest reduction was due to the osmotic dehydration.

Newton's, Page's, Modified Page's, Henderson and Pabis', Two-term, Two-term exponential, logarithmic, Midilli et al.'s models could describe the moisture ratio well during the hot air drying process.

## Chapter 7 – Optimization of microwave-drying after osmotic treatment

### 7.1 Abstract

The aim of the present work was to study the effects of the osmotic dehydration (OD) on the mass transfer kinetics of the microwave drying (MWD) and some quality parameters of apple cubes. The fit of several mathematical models was tested to describe the drying. A comparison between MWD and hot air drying (HAD) was performed. Apple cubes were osmotically treated with 60 °Bx sucrose or sorbitol solutions at 60 °C and dried at a microwave power between 160 and 850 W. Overall, the increase of the microwave power from 160 to 500 W resulted in an increase of the water loss rate, shown by the *A* parameter of modified Page's model, of 123 and 155 % for samples osmotically dehydrated with sucrose and sorbitol solutions, respectively. The OD tends to increase the drying rate, but the osmotic agent used did not have any effect. The modified Page's model described well the drying kinetics and MWD was faster than HAD. The water activity of the osmotically dehydrated products was reduced to below 0.4 after MWD at 500 W. The MWD of control samples resulted in a loss of 39 % and 28 % of the total phenolic content and the antioxidant activity, respectively. For osmotically dehydrated samples, a loss of around 75 % was observed for both these quality parameters after the osmotic treatment.

**Keywords:** apple cubes, osmotic treatment, microwave drying, hot air drying, mass transfer, mathematical models

### 7.2 Introduction

Dehydration aims to increase the shelf life of the food when compared with the fresh product due to the reduction of the water content, and, consequently, to the decrease of the water activity ( $a_w$ ) (Zhang et al., 2006). The OD is often used as pre-treatment with the aim to reduce the time and also the losses in volatile compounds and the risk of chemical and physical changes of the subsequent drying process (Arballo et al., 2012).

In the most conventional types of drying, such as HAD, the product is normally processed during long time. This can lead to undesirable flavour, colour, and nutrient content, besides presenting a high energy consumption. With the aim to reduce the

nutritional losses, as well as to achieve a fast and effective process, the MWD may be used (Bondaruk et al., 2007). The microwaves interact directly with the polar water molecules to generate heat, which, consequently, causes a rapid evaporation of water (Çelen and Kahveci, 2013; Doymaz et al., 2015).

The mass transfer kinetics of the MWD have been studied by many researchers, as well as the mathematical models to describe the kinetics of this process. Çelen and Kahveci (2013) studied the MWD of tomato slices and concluded that the drying time and the energy consumption decreased with the increase of the microwave power (90 – 600 W). Doymaz et al. (2015) also found that the increase of the microwave power decreased the drying time of green bean slices. They used several models —Lewis', Henderson and Pabis', Logarithmic, Verma *et al.*'s, Page's, Midilli *et al.*'s, Parabolic, Wang and Singh's, Weibull's — to fit the drying data and they concluded that the Midilli *et al.*'s model presented the best fit. This model was also able to describe well the MWD kinetics of white mulberry (Evin, 2011), mango ginger (Krishna Murthy and Manohar, 2012), with microwave powers between 90 and 900 W.

Fang et al. (2010) concluded that the MWD of Chinese jujube was better than HAD, resulting in a product with higher vitamin C content and less shrinkage. Horuz and Maskan (2013) also compared the same methods of drying pomegranate arils and found that the drying rate was higher in MWD.

The objectives of this work were: i) to evaluate the effect of the osmotic pre-treatment and the microwave power on the water loss kinetics of the MWD and some quality parameters, such as the water activity, the colour, the total phenolic content and the antioxidant activity of apple cubes (variety Royal Gala); ii) to test the adequacy of the fitness of several mathematical models to describe the moisture content of the product during the drying; iii) to carry out the comparison between the MWD and the HAD of osmotically pre-treated apple cubes.

## **7.3 Materials and methods**

### ***7.3.1 Samples and osmotic dehydration***

The samples were prepared as presented in 2.3.1. The soluble solids content of the apples was  $17.8 \pm 1.0$  °Bx (hand refractometer, Atago, U.S.A., Inc., WA, USA).

The osmotic dehydration process was carried out as presented in 6.3.2.

### **7.3.2 Microwave drying**

The MWD experiments were performed in a domestic microwave oven (MT-243, Whirlpool, USA).

The drying experiments were carried out at six different power levels — 160, 350, 500, 650, 750 and 850 W. Fifteen cubes were used in each drying experiment. The cubes were placed in a plastic container and this was put at the edge of the rotating glass plate. The samples were taken every 5 minutes until 20 to 40 min, depending on the power output and the sample appearance. Each drying experiment was carried out twice.

### **7.3.3 Moisture content and water activity determination**

The moisture content and water activity was determined as described in 2.3.3.

### **7.3.4 Quality evaluation**

The colour, the total phenolic content and the antioxidant activity of the product dried at the condition that produced the best MWD rate, were evaluated. These analyses were carried out as described in 6.3.8.

### **7.3.5 Mathematical models**

Eleven mathematical models – Newton’s, Page’s, modified Page’s, Henderson and Pabis’, two-term, two-term exponential, logarithmic, Wang and Singh’s, Midilli et al., Weibull’s and Crank’s model – were used to carry out the fit of the experimental data during the MWD of the osmotically dehydrated apple cubes. The equations of the models were presented in 1.7.2.

The GAB’s model (equation 6.1 in 6.3.6) was used to predict the relation between the equilibrium moisture content and the  $a_w$  of the dried apple cubes.

### **7.3.6 The Arrhenius behaviour**

The linearized Arrhenius equation was used to study the dependence of the parameters  $A$  and  $B$  of the modified Page’s model on the microwave power (Dadalı et al., 2007):

$$\ln p = \ln p_0 - \frac{m.Ea}{P} \quad (7.1)$$

$p$  is the parameter ( $A$  or  $B$ );  $p_0$  is the Arrhenius factor;  $m$  is the mass of sample;  $E_a$  is the activation energy ( $\text{W g}^{-1}$ );  $P$  is the microwave power (W).

### 7.3.7 *Statistical analysis*

The statistical analysis was performed as presented in section 2.3.8.

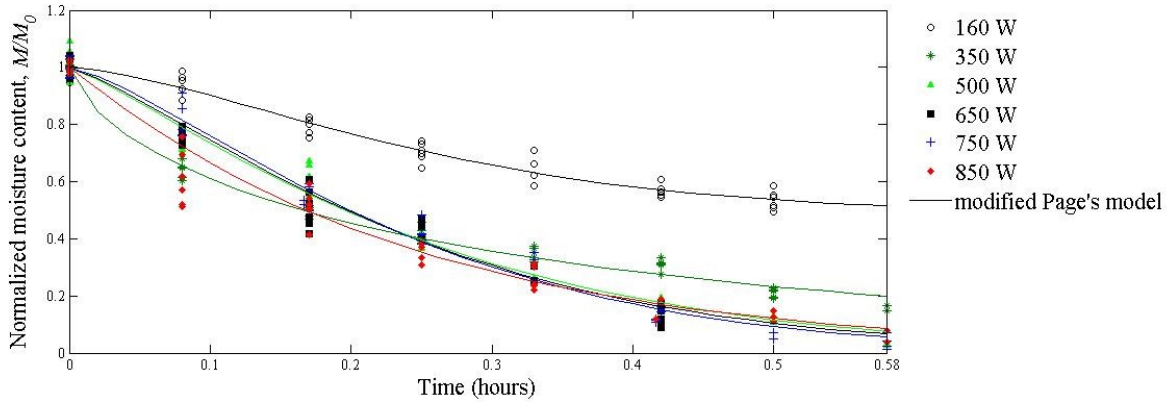
## 7.4 **Results and discussion**

The MWD experiments were first carried out with fresh samples for all power levels. Then, the MWD experiments were performed with the samples osmotically treated with the sucrose solution at 160, 350, 500, 750 and 850 W. In these experiments, no significant difference was observed between 500 and 750 W. Thus, the MWD experiments with the samples osmotically treated with sorbitol were first carried out at extreme power levels, 160 and 850 W, and, then, 500 W.

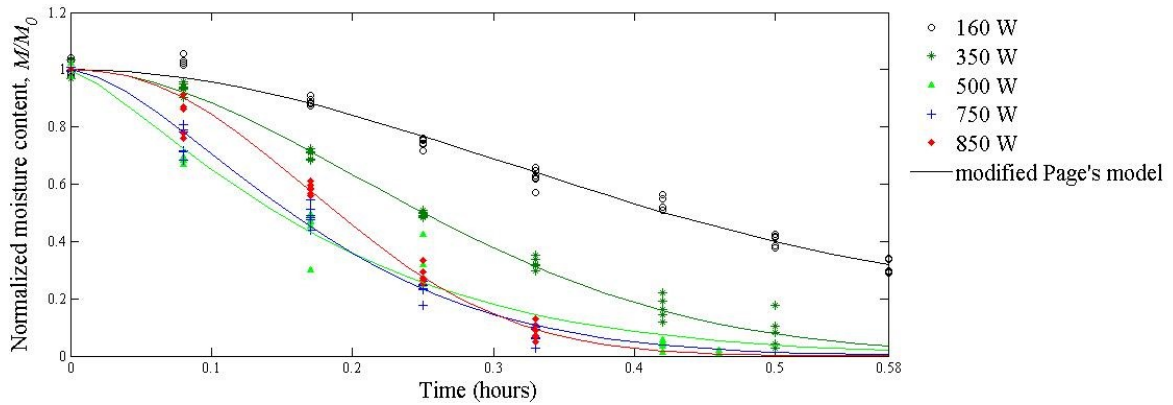
### 7.4.1 *Mathematical modelling*

The Page's, modified Page's, Midilli et al.'s, logarithmic, two-term exponential and Weibull's models presented high values of the determination coefficient ( $R^2 > 0.9$ ) of the non-linear regression of the experimental data of the MWD of apple cubes for all conditions. The residual analysis showed that the residuals were normally distributed at the significance level of 5 %; the visual analysis of the scatterplot of the residuals vs. the predicted values allowed to observe that the residuals were distributed randomly around zero with no systematic patterns, satisfying the assumption of homoscedasticity and zero mean errors. The others models did not describe well the experimental data because they did not follow one or more of the assumptions described above.

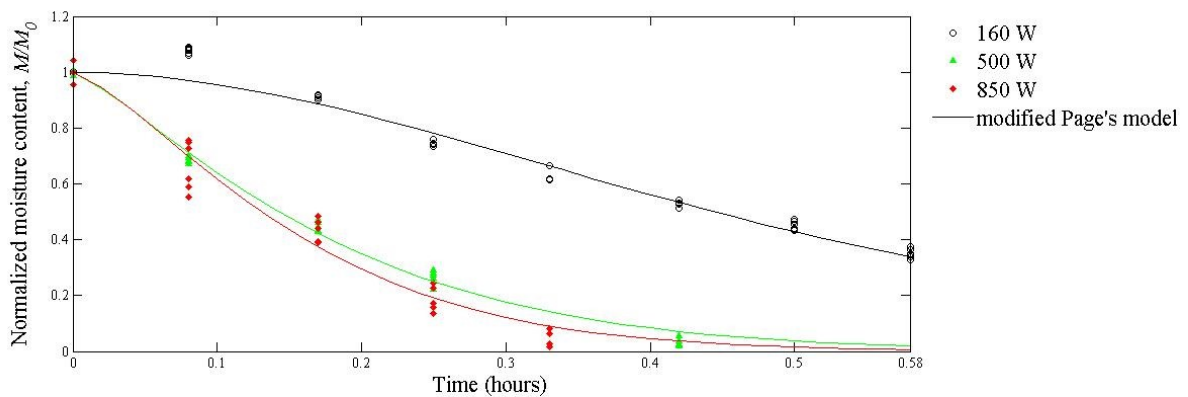
Weibull's, Two-term exponential and logarithmic models presented high values of margin of error, making the parameters not significantly different among the different conditions used. Therefore, the best fit was selected based on the precision in parameter estimation, calculated through the Standard Half Width (SHW = margin of error/ parameter value) at 95 % of confidence. The average of the SHW was 40 %, 18 % and 574 % for the Page's, modified Page's and Midilli et al.'s models, respectively. Thus, the modified Page's model described better the kinetics of MWD of apples cubes, with the highest precision of parameter estimates (i.e., lowest SHW) for all conditions used (Figures 7.1 – 7.3, Table 7.1).



**Figure 7.1** Experimental data and fit of modified Page's model of the normalized moisture content ( $M/M_0$ ) during the microwave drying of fresh apple cubes



**Figure 7.2** Experimental data and fit of modified Page's model of the normalized moisture content ( $M/M_0$ ) during the microwave drying of apple cubes osmotically pre-treated with sucrose solutions



**Figure 7.3** Experimental data and fit of modified Page's model of the normalized moisture content ( $M/M_0$ ) during the microwave drying of apple cubes osmotically pre-treated with sorbitol solutions

**Table 7.1** Parameters of the fit of modified Page's model of experimental data from microwave drying of apple cubes

Osmotic agent of OD	Power level	modified Page' s model		
		A (kg water kg DM <sup>-1</sup> h <sup>-1</sup> ) ± margin of error	B ± margin of error	R <sup>2</sup>
-	160	3.587±0.657	1.496±0.321	0.968
sucrose	160	2.287±0.159	1.979±0.192	0.988
sorbitol	160	2.037±0.312	1.872±0.295	0.975
-	350	3.497±2.274	0.672±0.151	0.990
sucrose	350	3.290±0.234	1.882±0.170	0.994
-	500	3.769±0.711	1.208±0.209	0.984
sucrose	500	5.101±0.759	1.262±0.213	0.958
sorbitol	500	5.200±0.718	1.240±0.179	0.991
-	650	3.806±0.698	1.265±0.199	0.984
-	750	3.814±0.641	1.343±0.232	0.983
sucrose	750	5.076±0.226	1.564±0.176	0.979
-	850	4.158±1.173	1.021±0.225	0.983
sucrose	850	4.477±0.376	2.209±0.299	0.993
sorbitol	850	5.806±1.818	1.339±0.396	0.962

Margin of error is the half width of the confidence interval at 95 %

#### 7.4.2 Mass transfer kinetics

From previous experiments (Assis et al., 2017a), the osmotically treated samples presented a water loss of 63 % for both solutions used and a solid gain of 11 % and 16 % for sucrose and sorbitol, respectively, after 8 hours of the OD process.

With the aim to minimize the variability of the experimental data at the beginning of the MWD, the moisture content,  $M$ , was normalized ( $M/M_0$ ).

The moisture ratio of the apple cubes, fresh or osmotically pre-treated, dried by MWD decreased with time and the process lasted less time when the microwave power was increased. These findings are in agreement with Çelen and Kahveci (2013); Doymaz et al. (2015) and Horuz and Maskan (2013).

The comparison of the process conditions was made based on the fit of the modified Page's model. The parameter  $A$  was used to compare the variables used, the pre-treatment and the power levels. The  $A$ -values varied between 2.037 and 5.806. In relation to the power of MWD used it was possible to observe that this variable did not affect the drying rate of the fresh apples. For samples osmotically pre-treated with the sucrose or sorbitol solution, the drying rate increased with the increase of power level until 500 W, but power levels higher than 500 W did not produce significant differences. The increase of the power level from 160 W to 500 W resulted in an increase in the  $A$ -value of 123 %, for the pre-treatment with sucrose solution. For the pre-treatment with the sorbitol solution, the drying rate increased 155 % when the power level increased from 160 W to 500 W, Doymaz et al. (2015) found that the drying rate of green bean slices increased 275 % when the microwave power output increased from 180 to 800 W.

$A$ -value did not follow a clear pattern for all the initial matrices used (fresh, osmotically dehydrated with sucrose or sorbitol solutions), but tends to be higher for pre-treated samples. Therdthai and Visalrakkij (2012) used the Page's model to describe the moisture ratio during the microwave vacuum drying of mangosteen and the parameter  $A$  presented the same tendency for all fruit matrices. Zhao et al. (2013) found lower MWD rates in osmotically treated chili, compared with the fresh samples. In relation to the osmotic agent used, it did not seem to affect the water loss rate during the MWD.

The Arrhenius's behaviour was not observed for the  $A$  and  $B$  parameters of modified Page's model, meaning that these parameters were not correlated (low  $R^2$ ) with the microwave power used in the experiments of the present work. Doymaz et al. (2015) and Krishna Murthy and Manohar (2012) found that the effective diffusivity correlated well with the microwave power and presented values for  $Ea$  of around 20 kW kg<sup>-1</sup> during the MWD of green bean and mango ginger, respectively. These findings may be explained by the fact that Crank's is a phenomenological model (Assis et al., 2017a) and would allow to obtain a correlation with physical meaning, while modified Page's is just an empirical one (as stated above, Crank's model could not produce a good fit of the experimental data).

Compared with the HAD previously studied (Assis et al., 2017b), the drying rate was significantly higher in MWD. This comparison is based on the results of the fit if modified Page's model, which was able to describe the mass transfer kinetics of both drying processes in the conditions used. Considering the best condition of each — MWD-500 W and HAD-80 °C —, the  $A$  parameter increased from 1.612 (HAD) to 5.101 (MWD), *i.e.* a 3.2-fold increase, and from 1.834 (HAD) to 5.200 (MWD), *i.e.* a 2.8-fold increase, for osmotically

treated samples with sucrose and sorbitol, respectively, and from 1.405 to 3.769 for control samples, *i.e.* around a 2.7-fold increase for control samples. Horuz and Maskan (2013) found a 16.8-fold increase of the *A*-value (Page's model) for MWD at MWD-490W in relation to HAD-70 °C of drying pomegranate arils.

### 7.4.3 Water activity ( $a_w$ )

The  $a_w$  of the fresh samples was  $0.986\pm 0.003$  and of the osmotically treated samples with sucrose and sorbitol was  $0.942\pm 0.006$  and  $0.899\pm 0.006$ , respectively. The  $a_w$  of all samples decreased with the decrease of the water content. The lowest  $a_w$ -value was achieved in the dried samples osmotically treated with sorbitol (Table 7.2).

**Table 7.2** Water activity of osmotically treated apple cubes dehydrated by microwave

Osmotic agent of OD	Power level	t (minutes)	$a_w$
-	160	35	$0.926\pm 0.004^a$
sucrose	160	45	$0.580\pm 0.033^c$
sorbitol	160	45	$0.463\pm 0.020^d$
-	350	35	$0.805\pm 0.004^b$
sucrose	350	30	$0.363\pm 0.029^{d,e,f,g}$
-	500	35	$0.451\pm 0.034^{d,e}$
sucrose	500	27.5	$0.340\pm 0.001^{f,g,h}$
sorbitol	500	25	$0.247\pm 0.020^h$
-	650	35	$0.414\pm 0.009^{d,e,f}$
-	750	35	$0.292\pm 0.102^{g,h}$
sucrose	750	20	$0.342\pm 0.003^{e,f,g,h}$
-	850	35	$0.411\pm 0.005^{d,e,f}$
sucrose	850	20	$0.472\pm 0.020^{c,d}$
sorbitol	850	20	$0.264\pm 0.011^{g,h}$

Different letters in each column mean significantly different values at  $p < 0.05$

The final  $a_w$  of fresh samples dehydrated at 500 W was around 0.4. The osmotic pre-treatment reduced the final  $a_w$  by 25 and 45 %, using sucrose and sorbitol, respectively, as osmotic agent.

The GAB's model expressed well the desorption isotherms of osmotically treated apple cubes dehydrated by MWD, but no significant differences were observed among the microwave powers and the pre-treatments did not show a clear pattern (data not shown). The values of  $Mm$  ranged from 0.031 to 0.290 and tend to be higher in osmotically treated samples. This may be due in part to the osmotic treatment, which may have caused a greater number of water molecules to be retained in the monolayer (Ferreira and Pena, 2003).

At the end of the drying process, the HAD produced samples with  $a_w$  around 0.3, near to the values found for MWD, but at different times. The MWD at 500 W reduced the drying time by 80 % in relation to the HAD at 80 °C (Assis et al., 2017b).

#### **7.4.4 Quality of the final product**

$L^*$  and  $a^*$  values (Table 7.3) were significantly ( $p < 0.05$ ) affected by the process. The  $L^*$  values decreased with the osmotic treatment and the MWD at 500 W and the highest  $L^*$  was found for the control. This can be explained by Maillard and non-enzymatic browning reactions that can occur during the drying process (Kammoun Bejar et al., 2011). This reduction was also observed by Doymaz et al. (2015) after the MWD of green bean slices. The redness/greenness component  $a^*$  increased after the processing. Chauhan et al. (2011) observed the same after the OD of apple slices using different types of osmotic agent. The parameter  $b^*$  (values not shown) was not affected by neither the OD nor the MWD. The  $C$ -values were not significantly different among the samples. Izli et al. (2014) observed that the goldenberry after the MWD presented lower  $C$  and  $a^*$  values compared with the fresh samples. The colour difference ( $\Delta E$ ) for all treatments did not show significant differences. So, it can be concluded that the MWD resulted in the same colour change independently if the pre-treatment was used. However and as expected, the lower browning index was found for the fresh samples. The dried samples previously osmotically treated presented the highest values of this parameter (Table 7.3).

The total phenolic content (TPC) of the fresh apple was  $4.21 \pm 0.09$  mg gallic acid g  $DM^{-1}$ , *i.e.*  $62.5 \pm 1.6$  mg gallic acid 100 g fresh weight<sup>-1</sup> (Table 7.3). This value was lower than those obtained by Imeh and Khokhar (2002) and Valavanidis et al. (2009) for the same fruit, which were 300 – 500 and 80 – 196 mg gallic acid 100 g fresh weight<sup>-1</sup>, respectively.

This difference can be explained by the fact that they used the whole fruit, while in this work the peel was removed, and TPC is higher in the peel (Valavanidis et al., 2009).

The MWD had an effect on total phenolic content of the control samples. This process significantly decreased this content from 4.21 to 2.58 mg gallic acid g DM<sup>-1</sup>, meaning a 39 % loss. Chong et al. (2013) found a reduction of these compounds of about 9 to 63 % when fruits were dried by different methods, in relation to the fresh sample. The same was not observed for the osmotically dehydrated samples, which did not present significant differences before and after the MWD. Therefore, the decrease in total phenolic content was mainly due the OD and was 75 % to 77 %. This decrease was also observed by Novaković et al. (2011) in a study OD of raspberries. According to them, the phenolic can migrate into the osmotic solution during the OD, inducing a loss of these compounds.

The results on the antioxidant activity (Table 7.3) showed a similar trend as the total phenolic content. The antioxidant activity of the fresh samples was 4.69±0.23 mg ascorbic acid g DM<sup>-1</sup> and the MWD reduced this value by 30 % in the control samples. In the osmotically dehydrated samples, the reduction of this parameter occurred during the OD, *i.e.*, the values being maintained after the MWD.

The type of solute used in the osmotic solution did not affect the total phenolic content or the antioxidant activity. The TPC of the apple cubes was related to the antioxidant activity. The correlation coefficient (R<sup>2</sup>) between these parameters was 0.984, suggesting that the phenolic are the main responsible for the antioxidant activity (Chong et al., 2013).

**Table 7.3** Quality parameters of osmotically treated apples cubes dehydrated by microwave at 500 W

Sample	L*	a*	C	$\Delta E$	Browning index	TPC (mg of gallic acid g DM <sup>-1</sup> )	AA (mg ascorbic acid g DM <sup>-1</sup> )
fresh	69.39±1.79 <sup>a</sup>	-4.78±0.54 <sup>c</sup>	29.30±0.69 <sup>a</sup>	0	46.77±1.25 <sup>d</sup>	4.21±0.09 <sup>a</sup>	4.69±0.23 <sup>a</sup>
control	61.96±11.07 <sup>b</sup>	4.34±3.82 <sup>a</sup>	30.30±0.98 <sup>a</sup>	7.31±0.83 <sup>a</sup>	55.01±4.02 <sup>b,c</sup>	2.58±0.09 <sup>b</sup>	3.39±0.09 <sup>b</sup>
OD sucrose	61.83±2.96 <sup>b</sup>	-1.90±1.30 <sup>b</sup>	27.92±1.46 <sup>a</sup>	7.61±2.45 <sup>a</sup>	53.18±5.43 <sup>c</sup>	1.06±0.01 <sup>c</sup>	1.21±0.08 <sup>c</sup>
OD sucrose + MWD	55.28±2.24 <sup>c</sup>	2.79±0.79 <sup>a</sup>	29.30±2.32 <sup>a</sup>	8.41±1.87 <sup>a</sup>	74.63±5.85 <sup>a</sup>	1.05±0.04 <sup>c</sup>	1.18±0.06 <sup>c</sup>
OD sorbitol	62.35±3.75 <sup>b</sup>	-1.50±1.43 <sup>b</sup>	29.27±1.99 <sup>a</sup>	8.23±3.52 <sup>a</sup>	59.09±5.80 <sup>b</sup>	0.96±0.06 <sup>c</sup>	1.01±0.02 <sup>c</sup>
OD sorbitol + MWD	58.99±4.97 <sup>b,c</sup>	3.05±0.51 <sup>a</sup>	30.13±3.79 <sup>a</sup>	9.44±1.96 <sup>a</sup>	68.99±4.49 <sup>a</sup>	0.91±0.09 <sup>c</sup>	1.07±0.12 <sup>c</sup>

Different letters in each column mean significantly different values at  $p < 0.05$

## 7.5 Conclusions

The OD pre-treatment had a significant influence on both mass transfer kinetics and  $a_w$  of the apple cubes during the MWD at tested powers. The increase of the microwave power in the MWD of osmotically pre-treated cubes resulted in an increase of the drying rate and, consequently, in a reduction of the drying time. The osmotic treatment reduced the final  $a_w$  of the apple cubes dried by microwave. The use of sorbitol as osmotic agent did not affect the water loss rate, but it produced a significantly lower  $a_w$  of the final product, in comparison with sucrose. Besides this, sorbitol presents benefits because it is a prebiotic with proven health properties. However, this pre-treatment causes the reduction of some important quality parameters, such as the phenolic content and the antioxidant activity.

The modified Page's model was selected to describe the kinetics of MWD of apples cubes, for presenting the highest precision of parameter estimates among some other models that could fit the moisture ratio well during the MWD process.

The MWD resulted in higher drying rates of osmotically pre-treated apple cubes when compared with HAD, which is an advantage for energy savings.

## Chapter 8 – Optimization of freeze-drying after osmotic treatment

### 8.1 Abstract

The effects of the pre-osmotic treatment on the mass transfer kinetics of the freeze-drying (FD) and on the water activity ( $a_w$ ) and the quality – colour, total phenolic content and antioxidant activity – of the processed apple cubes were studied. The fit of the moisture content was carried out using different mathematical models. The comparison among freeze-drying, microwave drying (MWD) and hot air drying (HAD) of osmotically treated apple cubes was also performed according to the drying rate and the  $a_w$ . The apple cubes were osmotically treated with 60°Bx sucrose or sorbitol solutions at 60 °C, then frozen and freeze-dried. The FD reduced significantly the moisture content from 6.259, 1.086 and 1.031 to 0.138, 0.099 and 0.074 kg water kg DM<sup>-1</sup> for the control, the samples osmotically pre-treated with sucrose and the samples osmotically pre-treated with sorbitol, respectively. The modified Page's model presented the highest precision of parameter estimates. The FD of samples osmotically pre-treated with the sucrose solution resulted in a higher drying rate than the others samples. The highest reduction in  $a_w$  was observed in the fresh samples. After FD, the total phenolic content and the antioxidant activity of the osmotically pre-treated samples decreased around 80 %, in comparison with the fresh apple, this reduction being due to the osmotic pre-treatment. The freeze-dried control samples achieved a lower  $a_w$  in comparison with HAD and MWD. However, FD presented a lower drying rate.

**Keywords:** osmotic treatment, freeze-drying, mathematical models, water activity, colour, total phenolic content, antioxidant activity

### 8.2 Introduction

Freeze-drying (FD) is considered the best type of drying for the preservation of the product quality, but it is a process that requires expensive equipment and takes a long time (Argyropoulos et al., 2011). The product is frozen in low temperatures and submitted to reduced pressure, thus causing the removal of the water by sublimation (Jiang et al., 2010). Compared with others type of drying, which normally are at high temperatures to evaporate the water, FD can maintain the original structure and colour of the product. This process also

provide a good rehydration ability and negligible loss of nutritional properties and flavour (Barbosa et al., 2015; Jiang et al., 2010).

The osmotic dehydration (OD) is a simple process that results in foods with intermediate moisture and can be used prior to freeze-drying with the aim to reduce the sublimation kinetics reducing the consumption of energy during the drying process and also the drying time (Khan, 2012; Pardo and Leiva, 2010). Agnieszka and Andrzej (2010) studied the effects of the OD prior to freeze-drying of strawberries and found that the pre-treatment, with sucrose and glucose solutions, increased the cell wall thickness. According to Ayala et al. (2010), the OD, with sucrose solution, followed by freeze-drying was not adequate to dry yellow pitahaya due to the shrinkage and low rehydration capacity of the final product. The OD did not cause significantly changes in the water content of freeze-dried pumpkin when compared with no pre-treated samples (Ciurzynska et al., 2014).

Different mathematical models have been proposed to describe the mass transfer kinetics in food drying, thus facilitating the optimization of the processes (Menges and Ertekin, 2006). The models may be empirical and semi-empirical, mechanistic and phenomenological. The empirical and semi-empirical models have been more used and they are based on polynomial and linear regressions. Newton's, Page's, modified Page's, Henderson and Pabis', Two term's, Midilli et al.'s, Wang and Singh's and logarithmic are examples of these types of models. Rudy et al. (2015) studied the freeze-drying of cranberries and found that the best model to describe the drying kinetics for the whole fruit was the logarithmic model, while for pulped fruits, Page's and Wang and Singh's models were. Page's model was also able to fit the experimental data of freeze-drying of apple slices (Rahimi et al., 2013), strawberries (Kırmacı et al., 2008), pineapple, guava, and mango pulps (Marques and Freire, 2005).

Argyropoulos et al. (2011) compared three types of drying (hot air drying, hot air plus microwave vacuum drying and freeze-drying) of mushrooms and found that the freeze-dried samples showed the best colour, the softest structure and the maximum rehydration capacity. In a sensory evaluation of dried carrots slices, the freeze-dried samples had better appearance according to the sensory panellists comparing with those dried by vacuum microwave drying and air drying (Lin et al., 1998).

The objectives of this work were: i) to study the mass transfer kinetics of freeze-drying of apples cubes (variety Royal Gala) previously osmotically dehydrated at 60 °C for 8 hours, using two solutes — sucrose or sorbitol — at 60° Brix and a mass ratio sample/solution of 1:4; ii) to test the adequacy of the fitness of several mathematical to describe the

moisture content of the product during the freeze-drying; iii) to carry out the comparison among freeze-drying, microwave drying and hot air drying of osmotically treated apple cubes.

### **8.3 Materials and methods**

#### ***8.3.1 Samples and osmotic dehydration***

The samples were prepared as presented in 2.3.1. The soluble solids content of the apples was  $16.6 \pm 0.8$  °Bx (hand refractometer, Atago, U.S.A., Inc., WA, USA).

The osmotic dehydration process was carried out as presented in 6.3.2.

#### ***8.3.2 Freeze-drying***

After the OD treatment, the samples were frozen at  $-18$  °C. Then the osmotically dehydrated and the control frozen samples were dried in a freeze-dryer (FT33A, Armfield, England), under a vacuum pressure of  $1.316 \times 10^{-4}$  atm (100 millitorr); the temperature in the freezing chamber was between  $-40$  and  $-45$  °C. The FD was carried out during 3, 6, 15, 17 and 24 hours.

#### ***8.3.3 Moisture content and water activity determination***

The moisture content was determined by placing the fresh and osmotic dehydrated samples in an oven (FP115, Binder, Tuttlingen, Germany) at  $105$  °C until constant weight (A.O.A.C., 2002). The determinations were performed in triplicate.

The water activity ( $a_w$ ) of the samples was determined during the process. It was determined with a hygrometer (Aqualab Series 3, Decagon Devices Inc., Pullman, Washington, USA) at  $22$  °C. Each determination was performed in duplicate.

#### ***8.3.4 Mathematical models***

The mathematical models used are Newton, Page, modified Page, Henderson and Pabis, two-term, two-term exponential, logarithmic, Wang and Singh, Midilli et al., Weibull and Verma et al. The model's equations were described in section 1.7.2.

The GAB's model (Equation 6.1 in 6.3.6) was used to predict the relation between the equilibrium moisture content and the  $a_w$  of the dried apple cubes.

### **8.3.5 Quality evaluation**

In order to evaluate the quality of the final product, the colour, the total phenolic content and the antioxidant activity of the product were determined. These analyses were carried out as described in 6.3.8

### **8.3.6 Statistical analysis**

The statistical analysis was performed as presented in section 2.3.8.

## **8.4 Results and discussion**

The freeze-drying experiments were carried out with control samples (without pre-treatment) and with previously osmotically dehydrated samples with sucrose or sorbitol solutions. The moisture content of the apple cubes after the osmotic treatment with sucrose and sorbitol solutions was reduced from 6.259 to 1.086 and 1.031 kg water kg DM<sup>-1</sup>, respectively, which represents a decrease of more than 80 %. These results are confirmed by previous studies (Assis et al., 2017a). At the end of the FD process the moisture content was reduced to 0.138 kg water kg DM<sup>-1</sup> for the control and further reduced to 0.099 kg water kg DM<sup>-1</sup> for the samples osmotically pre-treated with sucrose and 0.074 kg water kg DM<sup>-1</sup> for the samples osmotically pre-treated with sorbitol. These values represent a total water removal of around 98 %, being slightly higher for the samples osmotically pre-treated with sorbitol.

### **8.4.1 Mass transfer kinetics and mathematical modelling**

The experimental data of the freeze-drying of apple cubes were fitted using twelve mathematical models — Newton's, Page's, modified Page's, Henderson and Pabis', Two-term, Two-term exponential, logarithmic, Wang and Singh's, Midilli *et al.*'s, Weibull's and Verma *et al.*'s. The high values of R<sup>2</sup> and the satisfied assumptions of independence, randomness and normality of residual analysis showed that the Newton's, Page's, modified Page's, Henderson and Pabis', logarithmic and Weibull's models can describe the moisture ratio well during this drying process. The results of the non-linear regression of the experimental data of freeze-drying of apple cubes are presented in Table 8.1. The other

models could not describe the experimental data because they did not follow one or more of those assumptions.

The Newton's model is the most simple model with one parameter,  $k$ . The  $k$ -values are between 0.331 and 0.426 and no significant differences were observed between the control and the freeze-dried samples osmotically pre-treated with the sucrose solution. OD with the sorbitol solution resulted in the lowest  $k$ -value, meaning that the freeze-drying rate of the samples pre-treated with sorbitol was lower. Rahimi et al. (2013) also obtained lower  $k$ -values in apple slices submitted to different pre-treatments prior to the freeze-drying in comparison with the control (no pre-treatment).

The  $A$  parameter of the Page's model presented values of 0.112, 0.460 and 0.201 for the control and the freeze-dried samples osmotically pre-treated with sucrose and sorbitol solutions, respectively. The OD process resulted in an increase of this parameter, meaning that the drying rate increased. These  $A$ -values are closer to those obtained by Kırmacı et al. (2008) for freeze-dried strawberries. For the  $B$  parameter, the trend was the opposite, i.e.,  $B_{\text{control}} > B_{\text{OD}}$ , and the values varied between 0.924 and 1.968. The values of  $A$  were higher and the  $B$  closer than those obtained by Rudy et al. (2015) for freeze-dried cranberries and by Marques and Freire (2005) for freeze-dried pulp of tropical fruits, both studies being carried out without pre-treatment.

The modified Page's is very similar to the Page's model and the  $B$ -values are equal in both models. As with the Page's model, the drying rate, given by the  $A$ -parameter, was higher for samples osmotically pre-treated with the sucrose solution. This parameter was not significantly different between the control and the osmotically dehydrated sorbitol samples.

No significant differences were found in  $a$  parameter of Henderson and Pabis' model among all conditions used. The values of  $a$  are closer to 1, as it was also observed by Kırmacı et al. (2008). In relation to the pre-treatment, the  $k$  parameter was not significantly different between the control and the osmotically pre-treated samples, but this parameter was higher for the freeze-dried samples osmotically pre-treated with the sucrose solution than for those osmotically pre-treated with the sorbitol solution.

The  $a$  and  $c$  parameters of the logarithmic model presented high values of margin of error, making these parameters not significantly different among the different conditions used (data not shown). The  $k$  parameter presented low values of margin of error and varied between 0.333 and 0.416, but the conditions used did not produce significant differences in this parameter. These values are in agreement with Kırmacı et al.'s (2008) and Rudy et al.'s (2015).

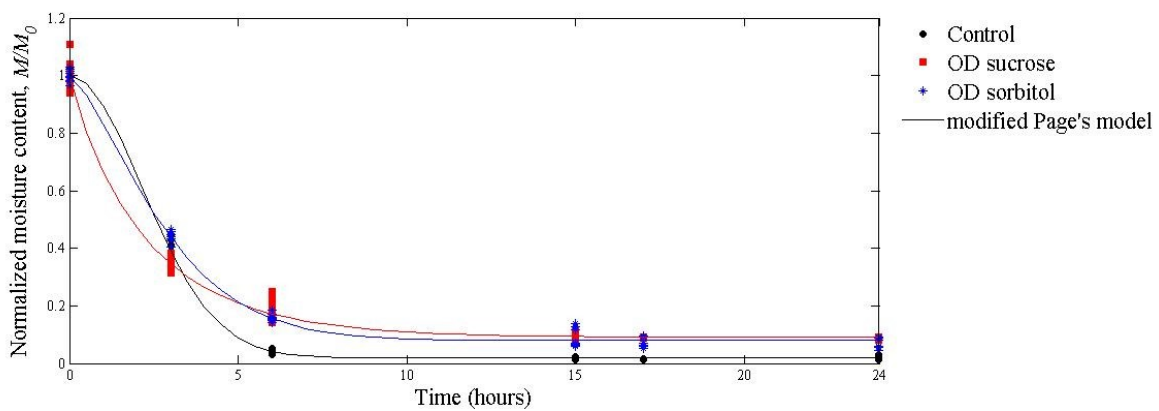
**Table 8.1** Parameters of the fit of Newton's, Page's, modified Page's and Henderson and Pabis' models of  $M/M_0$  of freeze-dried dapple cubes

Osmotic agent of OD	Newton		Page			modified Page			Henderson and Pabis		
	k ± margin of error	R <sup>2</sup>	A ± margin of error	B ± margin of error	R <sup>2</sup>	A ± margin of error	B ± margin of error	R <sup>2</sup>	a ± margin of error	k ± margin of error	R <sup>2</sup>
-	0.428±0.040	0.995	0.112±0.041	1.968±0.329	0.997	0.328±0.009	1.968±0.329	0.997	1.004±0.024	0.366±0.035	0.990
sucrose	0.420±0.019	0.996	0.460±0.071	0.924±0.125	0.996	0.431±0.029	0.924±0.125	0.996	0.988±0.014	0.416±0.019	0.997
sorbitol	0.331±0.019	0.993	0.201±0.032	1.402±0.127	0.997	0.319±0.009	1.402±0.127	0.997	1.005±0.020	0.333±0.020	0.993

Margin of error of the estimates was calculated at 95 %.

Although the Weibull's model presented high  $R^2$  and random and normally distributed residuals, all four parameters ( $a$ ,  $b$ ,  $k$  and  $n$ ) presented high values of margin of error (data not shown). Thus, according to this model, no significant difference was observed between the two OD pre-treatments used.

$k$  (Newton's, Henderson and Pabis', and Logarithmic models) and  $A$  (Page's and modified Page's models) parameters can be related with the water diffusion rate, but did not present the same trend using these different models. Considering the precision in the parameter estimation, calculated using the Standard Half Width (SHW = margin of error/parameter value) at 95 % of confidence, it is possible to conclude that the modified Page's model presented the highest precision of the parameter estimates, i.e., lowest SHW. Based on this model fit, the highest drying rate was observed for freeze-dried samples pre-treated with the sucrose solution (Figure 8.1). According to Wang et al. (2010), the high uptake of solute can reduce the tissue porosity due to solute infiltration or possible formation of a peripheral layer of solute, hindering the water transfer. This may explain the fact that the samples pre-treated with sorbitol solution presented lower freeze-drying rate since these samples obtained higher solute gain after the osmotic treatment (Assis et al., 2016).



**Figure 8.1** Experimental data and the fit of modified Page's model of the normalized moisture content ( $M/M_0$ ) during the freeze-drying of apple cubes

Based on the results of the fit by modified Page's model of previous works (Assis et al., 2017b,c), it is possible to make a comparison between different drying processes, because this model could also describe well the mass transfer kinetics of hot air drying (HAD) and microwave drying (MWD) of the osmotically pre-treated apple cubes. Comparing the parameter  $A$ , related with the drying rate, of the best condition of each drying — HAD-80 °C, MWD-500W and freeze-drying (FD) — the FD resulted in the lowest  $A$ -values. The MWD increased the drying rate 12 to 16-fold when compared with FD, and 3 to

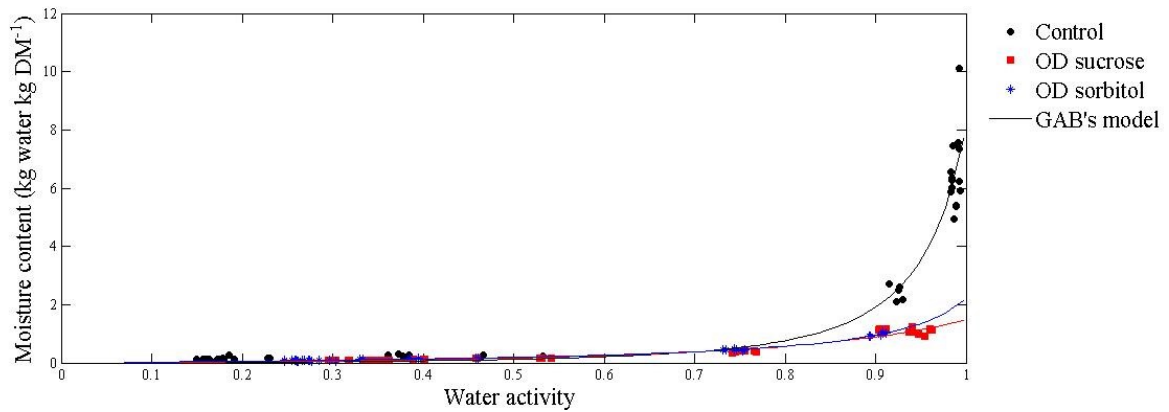
6-fold in comparison with the hot air drying. These results mean that FD is more time consuming than the other two processes, HAD and MWD. Lin et al. (1998) also reported the long-time of freeze-drying of carrot slices when compared with vacuum microwave and air drying.

#### **8.4.2 Water activity**

In spite of the high water content reduction (around 80 % in dry basis, referred above), the OD only reduced the initial water activity ( $a_w$ ) from 0.990 to 0.935 (with the sucrose solution) and 0.900 (with the sorbitol solution), which is in agreement with previous studies (Assis et al., 2016). During the freeze-drying process, the  $a_w$  decreased significantly with the decrease of the water content, but the difference in the initial reduction observed with the OD did not quite reflect in the lower final  $a_w$ . The subsequent  $a_w$  reduction of samples was 5-fold, 3-fold and 3.5-fold for the control and the samples osmotically pre-treated with sucrose and sorbitol solutions, respectively.

Although GAB's model fitted well the experimental data (high  $R^2$  and random and normally distributed residuals) (Figure 8.2), the values of its parameters presented high values of margin of error (data not shown), resulting in no significant differences among different conditions. Thus, the monolayer moisture content ( $Mm$ ) that indicates the theoretical moisture at which a product presents maximum stability, did not present significant difference between the control and the freeze-dried osmotically pre-treated samples. Sette et al. (2016) studied the effect of different pre-treatments, including OD, before freeze-drying of raspberries and found that the control samples presented higher  $Mm$  values than pre-treated samples.

Comparing the  $a_w$  of the freeze-dried, the hot air dried and the microwave dried samples, all processes produced samples with final  $a_w$  values around 0.3. In the control samples, the lowest  $a_w$  was achieved after the freeze-drying, while in samples osmotically pre-treated with sucrose solution, no significant difference was observed between the final  $a_w$  of the hot air dried and the freeze-dried samples, both achieved an  $a_w$  of around 0.3. Samples pre-treated with sorbitol presented the same  $a_w$  after all drying processes.



**Figure 8.2** Experimental data and the fit of GAB's model during the freeze-drying of apple cubes

## 8.5 Quality of the final product

All the colour parameters were affected by the osmotic pre-treatment (Table 8.2). The luminosity, given by  $L^*$ , was significantly affected by the freeze-drying process. After drying, all samples presented higher values of  $L^*$ . The increase of the luminosity after the FD was also found by Sosa et al. (2012) in apple disks with or without pre-treatment. The redness, reflected in the component  $a^*$ , also increased during the drying process. Rudy et al. (2015) also observed these increases in  $L^*$  and  $a^*$  in the FD of cranberries. The other parameters did not show a clear pattern in relation to the pre-treatment and/or subsequent FD. A decrease in the browning index of FD control samples was noted and  $b^*$  (values not shown) was not affected. The total colour difference ( $\Delta E$ ) between the freeze-dried osmotically pre-treated samples did not present significant differences and the highest difference,  $\Delta E = 16.67$ , was noted for control freeze-dried samples. This high value of  $\Delta E$  for the control sample is mainly due to a high increase in  $L^*$  value. The FD did not have an effect on  $\Delta E$  of the osmotically pre-treated samples.

The TPC of the fresh apple was  $6.02 \pm 0.07$  mg gallic acid g  $DM^{-1}$ . The FD process resulted in a loss of 48 % of the total phenolic content (TPC) in the control samples (Table 8.2). Rahman et al. (2015) observed a slight reduction of this compound in relation to the fresh samples of mango. Shofian et al. (2011) also found TPC in fresh starfruit, mango, papaya and watermelon higher than in the freeze-dried samples.

There was no reduction of this compound in the pre-treated samples after the FD. As observed in a previous work, using a different drying method, microwave drying (Assis,

Morais, and Morais, 2017), the reduction of TPC occurred during the osmotic dehydration and it was around 80 %.

The TPC of the dried control samples was higher than the osmotically pre-treated samples. These presented 73 and 62 % less TPC than the control samples after the FD, when sucrose and sorbitol were used as osmotic agent, respectively. However, the difference between the samples treated with the different solutes was not significant.

The antioxidant activity (AA) of the fresh apple was  $6.79 \pm 0.25$  mg ascorbic acid g DM<sup>-1</sup> and it decreased 23 % after FD. The AA was higher in the control samples than in the osmotically pre-treated samples (Table 8.2). The same trend as for the TPC was observed. The correlation coefficient ( $R^2$ ) between the TPC and the antioxidant activity was 0.990, meaning the phenolic is the main responsible for the antioxidant activity (Chong et al., 2013).

**Table 8.2.** Quality parameters of osmotically pre-treated apples cubes dehydrated by freeze-drying

Sample	L*	a*	$\Delta E$	Browning index	TPC (mg of gallic acid g DM <sup>-1</sup> )	AA (mg ascorbic acid g DM <sup>-1</sup> )
Fresh	69.39 $\pm$ 1.79 <sup>b,c</sup>	-4.78 $\pm$ 0.54 <sup>d</sup>	0	46.77 $\pm$ 1.25 <sup>c</sup>	6.02 $\pm$ 0.07 <sup>a</sup>	6.79 $\pm$ 0.25 <sup>a</sup>
control FD	85.03 $\pm$ 3.23 <sup>a</sup>	3.57 $\pm$ 0.69 <sup>c</sup>	16.67 $\pm$ 3.12 <sup>a</sup>	31.89 $\pm$ 5.51 <sup>d</sup>	3.14 $\pm$ 0.69 <sup>b</sup>	5.20 $\pm$ 0.75 <sup>b</sup>
OD sucrose	61.83 $\pm$ 2.96 <sup>d</sup>	-1.90 $\pm$ 1.30 <sup>b</sup>	7.61 $\pm$ 2.45 <sup>b</sup>	53.18 $\pm$ 5.43 <sup>b</sup>	0.96 $\pm$ 0.11 <sup>c</sup>	1.02 $\pm$ 0.12 <sup>c</sup>
OD sucrose + FD	69.71 $\pm$ 2.35 <sup>b</sup>	1.71 $\pm$ 0.52 <sup>a</sup>	9.04 $\pm$ 2.03 <sup>b</sup>	52.52 $\pm$ 5.46 <sup>b,c</sup>	0.84 $\pm$ 0.19 <sup>c</sup>	1.10 $\pm$ 0.17 <sup>c</sup>
OD sorbitol	62.35 $\pm$ 3.75 <sup>d</sup>	-1.50 $\pm$ 1.43 <sup>b</sup>	8.23 $\pm$ 3.52 <sup>b</sup>	59.09 $\pm$ 5.80 <sup>a</sup>	1.10 $\pm$ 0.13 <sup>c</sup>	1.24 $\pm$ 0.16 <sup>c</sup>
OD sorbitol + FD	65.95 $\pm$ 5.92 <sup>c</sup>	2.19 $\pm$ 1.39 <sup>a</sup>	8.01 $\pm$ 2.39 <sup>b</sup>	59.43 $\pm$ 9.43 <sup>a</sup>	1.20 $\pm$ 0.15 <sup>c</sup>	1.31 $\pm$ 0.13 <sup>c</sup>

Different letters in each column represent significant differences ( $p < 0.05$ )

## 8.6 Conclusions

The osmotic dehydration with a sorbitol solution, in alternative to sucrose, and combined with freeze-drying was studied. The osmotic dehydration pre-treatment had an influence on the mass transfer kinetics of the freeze-dried apple cubes, but it did not present a relevant advantage. The pre-treatment with the sucrose solution increased the drying rate, but it resulted in a lower quality, decreasing the total phenolic content and the antioxidant

activity. Therefore, with respect to quality sorbitol is more recommended than sucrose as the osmotic agent. The freeze-drying process decreased significantly the water activity of the osmotically dehydrated apple cubes. After FD, the control samples presented lower final  $a_w$  and lighter colour than the pre-treated samples.

Newton's, Page's, modified Page's, Henderson and Pabis', logarithmic and Weibull's models could describe well the moisture content during the freeze-drying process.

The freeze-drying resulted in a lower water activity when compared with hot air and microwave drying. However, it presented lower drying rate, which is a disadvantage in relation to the energy consumption.



# Chapter 9 – Sensory analysis of osmotically treated apple cubes after air drying

## 9.1 Abstract

The consumer acceptance of the air dried apple cubes pre-treated with sucrose or sorbitol was studied. The apple cubes were osmotically dehydrated with sucrose or sorbitol solution and then dried using hot air. The results showed that both products were accepted by the consumers, with sensory attributes around 6 ("like slightly"). Therefore, sorbitol can be a substitute for sucrose.

**Keywords:** sensory analysis, apple cubes, osmotic dehydration, hot air drying

## 9.2 Introduction

The sensory analysis is the definition and scientific measurement of the attributes of a product perceived by the senses: sight, sound, smell, taste and touch. The sensory quality of the food is an interaction between the food and the human (Dutcosky, 2007).

The consumer acceptance is crucial in the process of developing or improving food products. The sensory acceptance tests evaluate how much a consumer “likes” or “dislikes” a product. This is an important tool of sensorial analysis, which evaluates actual and potential consumers’ opinion (Nogueira et al., 2010).

Udomkun et al. (2014) evaluated the effect of calcium chloride and calcium lactate pre-treatments prior to osmotic dehydration in the consumer acceptance of dried papaya. They found that dried papaya pre-treated with 2.5 % calcium lactate was best in terms of consumers’ acceptance. Canizares and Mauro (2015) tested the acceptability of edible coatings applied before the drying of papaya and the best results were obtained when the pectin+vitamin C-coating was used. González-Herrera et al. (2016) performed the sensory acceptability of dehydrated apple matrix supplemented with different prebiotics, and they observed that the matrices supplemented with agave fructans and oligofructose were more qualified than the control. Thippanna and Tiwari (2015) evaluated the sensory quality

parameters of the osmotically dehydrated bananas in concentrations of 50-70 % and at different times, and found that the samples treated with 60 °Brix sugar syrup for 24 hours presented the higher sensory score.

The aim of this work was to analyse the consumer acceptance of the air dried apple cubes pre-treated with sucrose or sorbitol.

### **9.3 Materials and methods**

#### ***9.3.1 Samples and osmotic dehydration***

The samples were prepared as described in section 2.3.1 and the osmotic dehydration process was carried out as presented in section 4.3.2.

#### ***9.3.2 Drying***

The osmotically dehydrated samples were dried in an oven (UFP800DW, Memmert, Germany) with recirculation of air at approximately  $1 \text{ m s}^{-1}$ . The drying experiments were carried out at 70 °C until the  $a_w$  was around 0.3.

#### ***9.3.3 Sensory analysis***

The dried apples cubes, pre-treated with sucrose or sorbitol solution, were evaluated by 55 non-trained panellists, including students and staff of the university (14 male and 41 female, from 18 to 62 years old), for global acceptance, appearance, sweetness and texture. The samples were codified with three digits and presented randomly. A hedonic categorized 9-point scale was used, with each point associated to a qualitative appreciation, where 1 means “dislike extremely” and 9 means “like extremely” (Peryam, 1998).

To detect significant differences between the samples, the results were evaluated statistically using a two-way analysis of variance (ANOVA) and post-hoc tests were posteriorly performed for multiple comparisons (Tukey test).

## 9.4 Results and discussion

The sensory analysis was carried out on dried apple cubes previously pre-treated with sucrose or sorbitol solutions to obtain information on consumers' product preference and acceptance.

The results (Table 9.1) showed that in relation to overall acceptability, all samples were well accepted. Eighty five per cent of the scores for pre-treated samples with sucrose and 76 % for pre-treated samples with sorbitol varied between 6 and 9. The mean of dried samples pre-treated with sucrose was 6.48 (close to "like moderately") and of those pre-treated with sorbitol was 6.29 (close to "like slightly"), however, these differences were not significant.

**Table 9.1** Sensory attributes of dried apple cubes pre-treated with sucrose or sorbitol

Sample	Overall Acceptability	Appearance	Sweetness	Texture
Pre-treated with sucrose	6.78±1.27 <sup>a</sup>	6.48±1.34 <sup>a</sup>	6.52±1.38 <sup>a</sup>	6.43±1.66 <sup>a</sup>
Pre-treated with sorbitol	6.29±1.56 <sup>a</sup>	6.00±1.44 <sup>a</sup>	6.57±1.47 <sup>a</sup>	6.11±1.89 <sup>a</sup>

Different letters in each column mean significantly different values at  $p < 0.05$

In relation to the sensorial attributes, the samples treated with sucrose exhibited similar results to those treated with sorbitol. No significant differences were found in the appearance, the sweetness and the texture. The average was around 6 ("like slightly"). Chauhan et al. (2011) evaluated the sensory properties of osmotically dehydrated apple slices and found that the osmotic agents used affected the sensory parameters. The samples treated with maltose, sorbitol, or honey showed lower values for all the sensory parameters (colour, appearance, aroma, taste, texture and overall acceptability) than the ones treated with glucose, fructose and sucrose.

## 9.5 Conclusions

The dried apple cubes previously dehydrated with either sucrose or sorbitol solutions were both well accepted by the consumers. Thus, the sorbitol is an interesting alternative to

sucrose, as it is a prebiotic with proven health properties, presenting more benefits than traditional sugar.

# Chapter 10 – Rehydration of osmotically treated, dried apple cubes

## 10.1 Abstract

The effect of the osmotic pre-treatment and the different drying methods on the rehydration kinetics of apple cubes was studied. The adequacy of some models (Peleg's, Weibull's, the first order kinetic and the exponential association equation) to fit the rehydration data was also tested. The apple cubes were dried by hot air (HAD) at 70 °C, by microwave (MWD) at 500 W and by freeze-drying for 17 hours. The rehydration experiments of the dried samples were carried out in water at 80 °C and mass ratio of sample to water of 1:100, during 12 minutes. The first order kinetic model was found to produce the best fit. The type of drying and the pre-treatment did not affect the rehydration kinetics, but the equilibrium moisture content was higher in the control samples than in the osmotically dehydrated samples for all conditions.

**Keywords:** rehydration, apple cubes, osmotic dehydration, hot air drying, microwave drying, freeze-drying

## 10.2 Introduction

Dried fruits have long shelf lives unlike the fresh fruits that are seasonal. Dried fruits are produced to be consumed as final products with low moisture content, as powder or snacks, or also can be rehydrated to be used as ingredients (intermediate moisture) in prepared products or might also be rehydrated for other purposes (Contreras et al., 2012). The rehydration process aims to restore the properties of the fresh fruit by making the dried product contact with the rehydration solution (Lewicki, 1998). During this process, the transfer of water from the solution to the fruit and the soluble solids from the fruit to the solution occur (Sette et al., 2016). The quality of the rehydrated product depends on the structural and compositional changes occurred during the dehydration (pre-treatment and/or subsequent drying) (Contreras et al., 2012; Lewicki, 1998).

The capacity of rehydration can be affected by the tissue integrity and their hydrophilic properties (Sette et al., 2016). The rehydration ability and the influence of some factors (pre-

treatment, drying method, rehydration condition, etc.) on rehydration have been studied by many researchers. Pei et al. (2014) rehydrated mushroom slices at two temperatures and found that the rehydration rate was higher at 70 °C than at 20 °C, but the opposite occurred with the equilibrium moisture content (lower values at 70 °C). Moreira et al. (2011) dried osmotically treated chestnuts with hot air at 65 °C and, afterwards, rehydrated them with water at 25 °C. They observed that the cells swelled beyond the sizes of fresh samples during a short time of rehydration. Doymaz (2016) observed that the pre-treatments (citric acid and blanching) and the air temperature (50 – 80 °C) affected the rehydration characteristics of dried red kidney bean seeds. The rehydration ratio of the pre-treated samples was higher than the control samples. Maskan (2001) compared three different types of drying (hot air, microwave, and hot air-microwave drying) of kiwifruit slices and found that the hot air-microwave dried fruit presented higher rehydration capacity and the microwave dried fruit presented the lowest rehydration capacity.

The dried apple cubes can be consumed as a snack or as an ingredient in a yoghurt, for example. Thus, the aim of this study was to evaluate the effect of the osmotic pre-treatment and the different drying methods (hot air, microwave and freeze-drying) on the rehydration kinetics of apple cubes.

### **10.3 Materials and methods**

#### ***10.3.1 Samples preparation and osmotic dehydration***

The samples were prepared as described in section 2.3.1. The osmotic dehydration process was carried out as presented in section 6.3.2.

#### ***10.3.2 Drying***

The hot air drying (HAD) experiments were performed in an oven (UFP800DW, Memmert, Germany) with recirculation of air at approximately 1 m s<sup>-1</sup>. The HAD experiments were carried out at 70 °C for 3.5 hours.

The microwave drying (MWD) experiments were performed in a domestic microwave oven (MT-243, Whirlpool, USA) at 500 W during 40, 27.5 and 25 minutes, for the control, the samples osmotically dehydrated with sucrose solution, and the samples osmotically dehydrated with sorbitol solution, respectively.

In the freeze-drying, the samples after the OD treatment were frozen at -18 °C and then dried in a freeze-dryer at temperatures between -40 and -45 °C (FT33A, Armfield, England) for 17 hours.

For all drying methods a control was done. The control consisted of dried samples without osmotic pre-treatment.

### **10.3.3 Rehydration experiments**

The rehydration experiments were carried out in beakers placed in a water bath at 80 °C. The dried samples were immersed in the beakers with ultra-pure water during 1, 3, 5, 9 and 12 minutes. The mass ratio of sample to water used was 1:100. The moisture content of the rehydrated samples was determined in an oven (FP115, Binder, Tuttlingen, Germany) at 105 °C until constant weight (A.O.A.C. 2002).

The experiments were conducted with three replicates.

### **10.3.4 Mathematical modelling of rehydration process**

To describe the rehydration kinetics of the dried apple cubes, some mathematical models were used.

The models' equations are described below:

Peleg

$$M = M_0 + \frac{t}{k_1 + k_2 \cdot t} \quad (10.1)$$

Weibull

$$M = M_\infty + (M_0 - M_\infty) \cdot \exp(-(t/B)^A) \quad (10.2)$$

First order kinetic

$$M = M_\infty + (M_0 - M_\infty) \cdot \exp(-k \cdot t) \quad (10.3)$$

Exponential association equation

$$M = M_\infty \cdot [1 - \exp(-H \cdot t)] \quad (10.4)$$

where  $M$ ,  $M_0$  and  $M_\infty$  is the moisture content at time  $t$ , the initial and at the equilibrium moisture content and the moisture at the equilibrium, respectively.

### 10.3.5 Statistical analysis

The statistical analysis was performed as presented in section 2.3.8.

## 10.4 Results and discussion

Peleg's, Weibull's, the first order kinetic and the exponential association equation models presented high values of the determination coefficient ( $R^2$ ) of the non-linear regression of the experimental data under all conditions, except for freeze-dried control samples (Table 10.1). This was probably due to the variability of the experimental data. The residual analysis showed that the residuals of Peleg's and the first order kinetic models were normally distributed at the significance level of 5 %. The visual analysis of the scatterplot of the residuals vs. the predicted values indicates that the residuals are distributed randomly around zero with no systematic patterns, satisfying the assumption of homoscedasticity and zero mean errors. The other models did not describe well the experimental data because they did not follow one or more of the assumptions described above.

**Table 10.1** Parameters of the first order kinetic model for the rehydration of the dried apple cubes

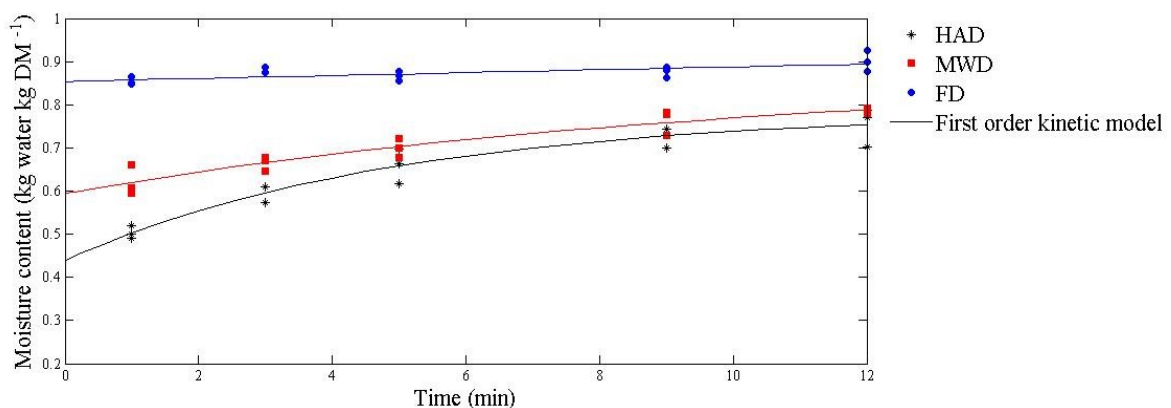
Drying	Pre-treatment/ Solute	First order kinetic		
		$k$	$M_{\infty}$	$R^2$
	Control	0.200±0.143	0.785±0.082	0.926
HAD	OD/sucrose	0.182±0.035	0.689±0.032	0.995
	OD/sorbitol	0.176±0.039	0.709±0.042	0.993
	Control	0.098±0.141	0.875±0.223	0.902
MWD	OD/sucrose	0.121±0.172	0.710±0.301	0.864
	OD/sorbitol	0.196±0.102	0.671±0.072	0.954
	Control	0.014±0.474	1.106±7.641	0.464
FD	OD/sucrose	0.161±0.073	0.664±0.070	0.974
	OD/ sorbitol	0.138±0.075	0.741±0.112	0.972

Margin of error is the half width of the confidence interval at 95 %.

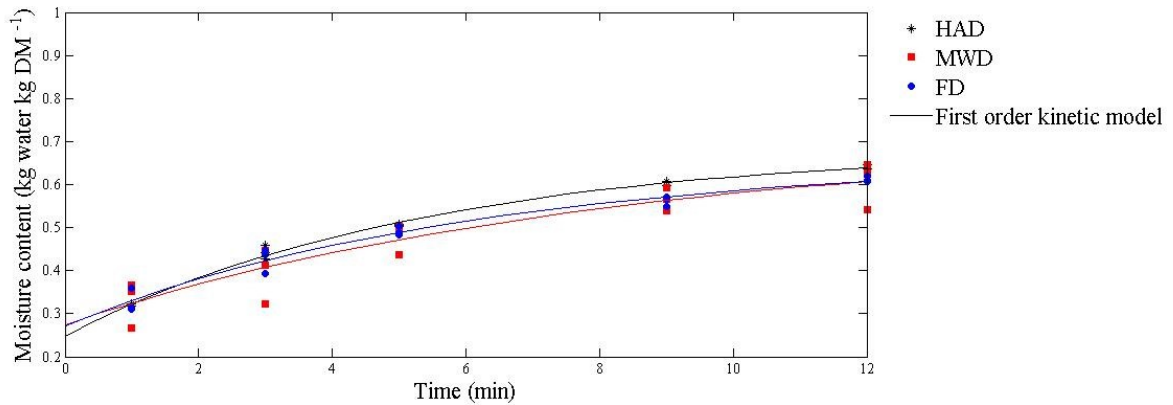
In order to select the best fit of the rehydration data of dried apple cubes, the Standard Half Width (SHW = margin of error/ parameter value) was calculated at 95 % confidence.

The first order kinetic model presented the highest precision of parameter estimates (*i.e.*, lowest SHW) for all conditions used, so it was used to compare the effect of these conditions. Figures 10.1 to 10.3 show the experimental data and the fit of the first order kinetic model during the rehydration. The parameters of the fit of the first order kinetic model are presented in Table 10.1. The parameter  $k$  of this model is related to the rate of the rehydration. Thus, no significant differences were found between the rehydration rate ( $k$ -values) of the different types of drying. Lin et al. (1998) dried blanched carrot slices by three different methods (vacuum microwave, hot air and freeze-drying) and found that vacuum microwave drying resulted in the highest rehydration ratio. As observed by Sette et al. (2016) in raspberries, the control freeze-dried samples (no pre-treatment) showed a rapid increase in the rehydration level, and then remained constant over time. A similar behaviour was observed in the present work for the freeze-dried apples cubes without pre-treatment (freeze-dried control samples). After the first minute, the rehydration was practically completed (Figure 10.1).

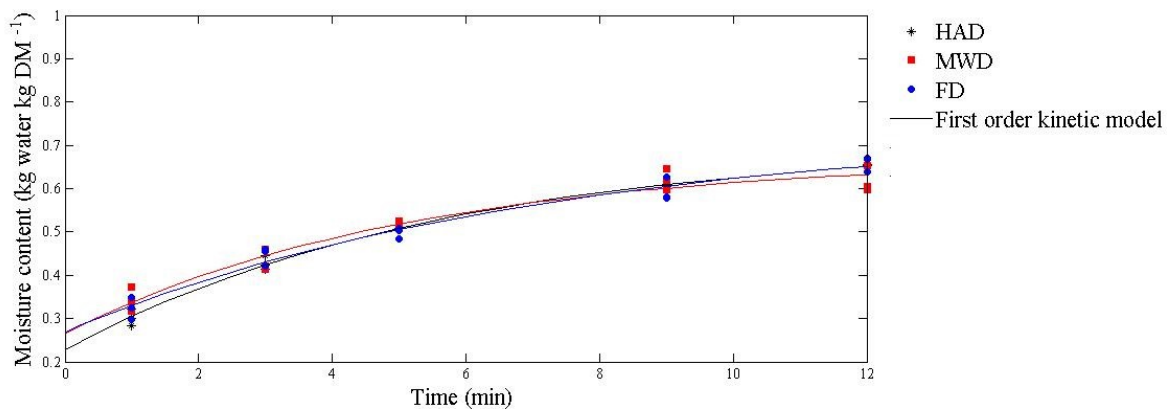
Based on the  $k$ -values of the first order kinetic model (Table 10.1), the osmotic dehydration carried out before each subsequent drying did not affect the rehydration rate of the dried samples. Maldonado et al. (2010) observed that mangoes osmotically pre-treated with sucrose or glucose and air dried did not show any difference in the weight gain during rehydration compared to untreated samples. Agnieszka and Andrzej (2010) and Sette et al. (2016) observed a higher rehydration rate of the control samples than freeze-dried strawberries and raspberries pre-treated with sucrose and glucose, and sucrose, respectively.



**Figure 10.1** Experimental data and the fit of the first order kinetic model during the rehydration of apple cubes



**Figure 10.2** Experimental data and the fit of the first order kinetic model during the rehydration of apple cubes osmotically dehydrated with sucrose solution



**Figure 10.3** Experimental data and the fit of the first order kinetic model during the rehydration of apple cubes osmotically dehydrated with sorbitol solution

The equilibrium moisture contents,  $M_{\infty}$ , given by the first order kinetic model of the microwave dried and freeze-dried control samples were significantly higher than the osmotically dehydrated samples (Table 10.1), meaning that the solute uptake that occurs during the pre-treatment reduces the rehydration ability. In HAD, the  $M_{\infty}$  is not significantly different but tends to be higher in control samples, which means that these can get more rehydrated.

## 10.5 Conclusions

The first order kinetic model was selected as the most adequate to fit the rehydration kinetics of dried apple cubes. The drying method and the osmotic pre-treatment did not affect the rehydration rate. However, the equilibrium moisture content at the end of the rehydration

was higher in the control samples than in the osmotically dehydrated samples, for all drying methods.



## **Part IV – Conclusions and futures perspectives**



## Chapter 11 – Conclusions

Some processes to produce dried fruits were studied. From the whole work it was possible to conclude that, among hot air drying, microwave drying and freeze-drying, the microwave drying with no pre-treatment can produce dried cut apple with good quality in reduced time. Sorbitol is a good alternative to sucrose as the osmotic agent in the pre-treatment of both apple cubes and physalis. Furthermore, sorbitol is a prebiotic with more benefits.

The optimization of the osmotic dehydration is an important issue to produce fruits with intermediate water content. In apple cubes, some process variables, such as the solute, the concentration in the osmotic solution and the temperature, affected the osmotic dehydration process. Some models - Azuara's, Peleg's, Page's and Weibull's models – were adequate to describe the mass transfer kinetics (water loss and solute gain) of apple cubes during the osmotic dehydration. The effective diffusivity of water in apple cubes during OD at 60 °Bx was between  $1.98 \times 10^{-10}$  and  $2.48 \times 10^{-9}$  m<sup>2</sup> s<sup>-1</sup>. The rate of the water loss varied from 0.273 to 0.940 kg water kg initial total weight<sup>-1</sup> h<sup>-1</sup> in Page's model (A), and from 0.219 to 1.031 kg water kg initial total weight<sup>-1</sup> h<sup>-1</sup> in Peleg's model (1/k<sub>1</sub>). In relation to sucrose, sorbitol as the osmotic agent reduced the time required to reach the equilibrium of the water loss by 15 to 20 %. At the end of the process, the samples achieved the same water loss and the reduction of the viscosity was similar for both solutes. The increase in the temperature (from 25 to 60 °C) resulted in a decrease of the viscosity of the osmotic solution and in a higher water loss. The mass ratio of sample to solution and the pressure did not affect the water loss. In experiments under vacuum, the rate of water loss tended to be higher. With regard to the solute gain, the type of solute did not affect the initial rate of solute gain, but sorbitol solutions induced a higher equilibrium solids content. Samples osmotically dehydrated at 60 °C had higher initial rate of solute gain than at 25 °C, but at the equilibrium, the amount of the gain was the same for both temperatures. The mass ratio of sample to solution did not influence the initial rate of the solute gain. At the end of process, the water activity of the osmotically dehydrated samples with sorbitol solution was lower than with sucrose solution.

In experiments at 40 °Bx the same behaviour as at 60 °Bx was observed regarding the solute and temperature of the solution. The increase of 40 to 60 °Bx in both solutions (sucrose and sorbitol) resulted in an increase of the water loss and the solute gain during the osmotic

dehydration. In physalis, the effective diffusivities of water and solute were around  $10^{-11} \text{ m}^2 \text{ s}^{-1}$ . The Peleg's model described better the kinetics of water loss, thus, the use of sorbitol could accelerate the initial rate of water loss of physalis. The vacuum applied, in experiments with sucrose solution, increased the rate of water loss. A low solute gain was observed during whole osmotic process.

The osmotic dehydration process resulted in shrinkage of the cells and, consequently, in plasmolysis and folding of the cell walls. However, it did not cause changes in the intercellular spaces. After the osmotic dehydration, decreases in the cellular area, roundness, compactness and circularity, and an increase of the elongation were observed.

The osmotic pre-treatment succeeded in improving the subsequent hot air drying kinetics. A temperature of 70 °C resulted in the highest hot air drying rate for a final  $a_w$  around 0.3. The pre-treatment increased the drying rate of the hot air drying, reducing the time required. The use of sorbitol as osmotic agent did not affect the rate of water loss, in comparison with sucrose, but it is more effective in reducing the drying time to reach the same  $a_w$ . The Newton's, Page's, modified Page's, Henderson and Pabis', two-term, two-term exponential, logarithmic, and Midilli et al.'s models were adequate to describe the moisture ratio during the HAD process.

In microwave drying, the drying rate of pre-treated samples tended to be higher than those non-treated. The drying rate of osmotically dehydrated samples increased with the increase of the power level until 500 W, but power levels above this value did not produce significant differences. The drying time reduced with the increase of the power level and this reduction was more pronounced in osmotically dehydrated samples with sorbitol. The modified Page's model presents the best fit of the MWD of apples cubes, due to its highest precision in the parameter estimates.

The osmotic pre-treatment did not present a relevant advantage for the freeze-drying process. The OD with sucrose increased the drying rate of the freeze-drying, but a lower  $a_w$  was achieved in non-treated samples. Newton's, Page's, modified Page's, Henderson and Pabis', logarithmic and Weibull's models could describe well the moisture content during the FD process.

With respect to the quality of the product, dried by different methods, it was possible to conclude that the osmotic pre-treatment reduced the total phenolic content and the antioxidant activity, but the subsequent drying processes did not affect these parameters. In control samples, the hot air drying decreased the total phenolic content (33 %) and the antioxidant activity (18 %), the microwave drying resulted in a loss of total phenolic content

(39 %) and antioxidant activity (30 %). The freeze-drying also reduced the total phenolic content (48 %) and antioxidant activity (23 %) (control samples). Comparing the methods of drying, the lowest water activity was achieved by the freeze-drying process. However, this drying presented the lowest drying rate, presenting a disadvantage in relation to the energy consumption. The hot air drying and the freeze-drying increased the luminosity of the samples, and the microwave drying decreased the value of this parameter. The osmotic pre-treatment did not affect the rehydration rate, but it decreased the equilibrium moisture content at the end of the rehydration process. The first order kinetic model resulted in the best fit of the rehydration kinetics.

In sensory analyses tests, the consumers evaluated positively the air dried apple cubes pre-treated with sucrose or sorbitol solutions. The acceptance of the samples treated with sorbitol makes this osmotic agent a good sugar replacer. Besides, sorbitol increases the rate of water loss during the osmotic dehydration, decreasing the time of the process, and a product with lower water activity is also obtained. The use of sorbitol presents several health benefits because it is non-cariogenic, low-glycaemic and insulinaemic, low-digestible and with a low energy content.



## Chapter 12 – Future perspectives

With no intention to exhaustively suggest the possible directions for further work, some points that might be interesting to be further exploited and completed are here highlighted.

Based on the quality of the samples at the end of the osmotic dehydration process, a quality study during this process would be interesting aiming to reduce the losses. It would be interesting to evaluate the quality parameters over time, such as total phenolic content, antioxidant activity and colour, aiming to find the best condition to the osmotic process with lower losses. Other quality parameters could also be studied, such as vitamin C and carotenoids.

Concerning the subsequent drying processes and with the objective to improve the quality of the final product and the mass transfer kinetics, studies with a combination of different methods of drying, such as MWD followed by HAD and MWD followed by FD could be performed. Different methods of drying could also be tested, such as the combination of the infrared heating with the hot air drying, or other method. The fruit used in this study was mainly apple (cubes), an also physalis (berry). It would interesting to investigate these drying methods with other fruits (different geometries and structures) to evaluate whether follow the same trend;

To perform packaging studies of the final dried product. Studies regarding the shelf life and the quality during storage of the final product pre-treated with sucrose or sorbitol, and dried by the different subsequent methods also could be done.

Based on the composition of the final product (dried apple cubes previously osmotically pre-treated with sorbitol), it could be insert in the formulation of new functional foods. This type of food is becoming a popular item perceived as healthy by consumers.

These types of studies are important for the food industry because there is an increasing demand for products with high quality and at affordable prices. Thus, it is important that studies on the process scale-up are performed.



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## Appendix

### Sensory analysis sheet

#### Avaliação Sensorial de maçã desidratada

Provedor					Data
Idade					
Sexo	Feminino	<input type="checkbox"/>	Masculino	<input type="checkbox"/>	
Nacionalidade:	Portuguesa	<input type="checkbox"/>	Outra	<input type="checkbox"/>	Especifique _____
Pais de residência:	Portugal	<input type="checkbox"/>	Outro	<input type="checkbox"/>	Especifique _____
Escolaridade:	<input type="checkbox"/> 1º Ciclo do Ensino Básico (4º ano)				
	<input type="checkbox"/> 2º Ciclo do Ensino Básico (6º ano)				
	<input type="checkbox"/> 3º Ciclo do Ensino Básico (9º ano)				
	<input type="checkbox"/> 11º ou 12º ano				
	<input type="checkbox"/> Bacharelato				
	<input type="checkbox"/> Licenciatura ou Mestrado				
	<input type="checkbox"/> Doutoramento				
<hr/>					
É apreciador/consumidor de maçã?	Sim	<input type="checkbox"/>	Não	<input type="checkbox"/>	
Costuma consumir frutas desidratadas?	Sim	<input type="checkbox"/>	Não	<input type="checkbox"/>	
Com que frequência consome frutas desidratadas?					
	Todos os dias	<input type="checkbox"/>	1 ou mais vezes por semana	<input type="checkbox"/>	1 ou mais vezes por mês <input type="checkbox"/>
<hr/>					
Por favor prove a amostra 108:					

#### Qual a APRECIÇÃO GLOBAL da amostra 108?

(Por favor assinale com X a caixa que melhor representa a sua opinião)

- |                              |                          |
|------------------------------|--------------------------|
| 9 - Gostei extremamente      | <input type="checkbox"/> |
| 8 - Gostei muito             | <input type="checkbox"/> |
| 7 - Gostei moderadamente     | <input type="checkbox"/> |
| 6 - Gostei ligeiramente      | <input type="checkbox"/> |
| 5 - Não gostei nem desgostei | <input type="checkbox"/> |
| 4 - Desgostei ligeiramente   | <input type="checkbox"/> |
| 3 - Desgostei moderadamente  | <input type="checkbox"/> |
| 2 - Desgostei muito          | <input type="checkbox"/> |
| 1 - Desgostei extremamente   | <input type="checkbox"/> |

Avalie por favor a amostra 108 assinalando para cada um dos seguintes atributos sensoriais a caixa que melhor representa a sua opinião:

**ASPECTO**

(Por favor assinale com X a caixa que melhor representa a sua opinião)

- |                              |                          |
|------------------------------|--------------------------|
| 9 - Gostei extremamente      | <input type="checkbox"/> |
| 8 - Gostei muito             | <input type="checkbox"/> |
| 7 - Gostei moderadamente     | <input type="checkbox"/> |
| 6 - Gostei ligeiramente      | <input type="checkbox"/> |
| 5 - Não gostei nem desgostei | <input type="checkbox"/> |
| 4 - Desgostei ligeiramente   | <input type="checkbox"/> |
| 3 - Desgostei moderadamente  | <input type="checkbox"/> |
| 2 - Desgostei muito          | <input type="checkbox"/> |
| 1 - Desgostei extremamente   | <input type="checkbox"/> |

**DOÇURA**

(Por favor assinale com X a caixa que melhor representa a sua opinião)

- |                              |                          |
|------------------------------|--------------------------|
| 9 - Gostei extremamente      | <input type="checkbox"/> |
| 8 - Gostei muito             | <input type="checkbox"/> |
| 7 - Gostei moderadamente     | <input type="checkbox"/> |
| 6 - Gostei ligeiramente      | <input type="checkbox"/> |
| 5 - Não gostei nem desgostei | <input type="checkbox"/> |
| 4 - Desgostei ligeiramente   | <input type="checkbox"/> |
| 3 - Desgostei moderadamente  | <input type="checkbox"/> |
| 2 - Desgostei muito          | <input type="checkbox"/> |
| 1 - Desgostei extremamente   | <input type="checkbox"/> |

**TEXTURA**

(Por favor assinale com X a caixa que melhor representa a sua opinião)

- |                              |                          |
|------------------------------|--------------------------|
| 9 - Gostei extremamente      | <input type="checkbox"/> |
| 8 - Gostei muito             | <input type="checkbox"/> |
| 7 - Gostei moderadamente     | <input type="checkbox"/> |
| 6 - Gostei ligeiramente      | <input type="checkbox"/> |
| 5 - Não gostei nem desgostei | <input type="checkbox"/> |
| 4 - Desgostei ligeiramente   | <input type="checkbox"/> |
| 3 - Desgostei moderadamente  | <input type="checkbox"/> |
| 2 - Desgostei muito          | <input type="checkbox"/> |
| 1 - Desgostei extremamente   | <input type="checkbox"/> |

COMENTÁRIOS \_\_\_\_\_

\_\_\_\_\_

Por favor prove a amostra 706:

**Qual a APRECIÇÃO GLOBAL da amostra 706?**

(Por favor assinale com X a caixa que melhor representa a sua opinião)

- |                              |                          |
|------------------------------|--------------------------|
| 9 - Gostei extremamente      | <input type="checkbox"/> |
| 8 - Gostei muito             | <input type="checkbox"/> |
| 7 - Gostei moderadamente     | <input type="checkbox"/> |
| 6 - Gostei ligeiramente      | <input type="checkbox"/> |
| 5 - Não gostei nem desgostei | <input type="checkbox"/> |
| 4 - Desgostei ligeiramente   | <input type="checkbox"/> |
| 3 - Desgostei moderadamente  | <input type="checkbox"/> |
| 2 - Desgostei muito          | <input type="checkbox"/> |
| 1 - Desgostei extremamente   | <input type="checkbox"/> |

Avalie por favor a amostra 706 assinalando para cada um dos seguintes atributos sensoriais a caixa que melhor representa a sua opinião:

**ASPECTO**

(Por favor assinale com X a caixa que melhor representa a sua opinião)

- |                              |                          |
|------------------------------|--------------------------|
| 9 - Gostei extremamente      | <input type="checkbox"/> |
| 8 - Gostei muito             | <input type="checkbox"/> |
| 7 - Gostei moderadamente     | <input type="checkbox"/> |
| 6 - Gostei ligeiramente      | <input type="checkbox"/> |
| 5 - Não gostei nem desgostei | <input type="checkbox"/> |
| 4 - Desgostei ligeiramente   | <input type="checkbox"/> |
| 3 - Desgostei moderadamente  | <input type="checkbox"/> |
| 2 - Desgostei muito          | <input type="checkbox"/> |
| 1 - Desgostei extremamente   | <input type="checkbox"/> |

**DOÇURA**

(Por favor assinale com X a caixa que melhor representa a sua opinião)

- |                              |                          |
|------------------------------|--------------------------|
| 9 - Gostei extremamente      | <input type="checkbox"/> |
| 8 - Gostei muito             | <input type="checkbox"/> |
| 7 - Gostei moderadamente     | <input type="checkbox"/> |
| 6 - Gostei ligeiramente      | <input type="checkbox"/> |
| 5 - Não gostei nem desgostei | <input type="checkbox"/> |
| 4 - Desgostei ligeiramente   | <input type="checkbox"/> |
| 3 - Desgostei moderadamente  | <input type="checkbox"/> |
| 2 - Desgostei muito          | <input type="checkbox"/> |
| 1 - Desgostei extremamente   | <input type="checkbox"/> |

**TEXTURA**

(Por favor assinale com X a caixa que melhor representa a sua opinião)

- |                              |                          |
|------------------------------|--------------------------|
| 9 - Gostei extremamente      | <input type="checkbox"/> |
| 8 - Gostei muito             | <input type="checkbox"/> |
| 7 - Gostei moderadamente     | <input type="checkbox"/> |
| 6 - Gostei ligeiramente      | <input type="checkbox"/> |
| 5 - Não gostei nem desgostei | <input type="checkbox"/> |
| 4 - Desgostei ligeiramente   | <input type="checkbox"/> |
| 3 - Desgostei moderadamente  | <input type="checkbox"/> |
| 2 - Desgostei muito          | <input type="checkbox"/> |
| 1 - Desgostei extremamente   | <input type="checkbox"/> |

COMENTÁRIOS \_\_\_\_\_

\_\_\_\_\_

Avaliação Sensorial de maçã desidratada

Provador					Data
Idade					
Sexo	Feminino	<input type="checkbox"/>	Masculino	<input type="checkbox"/>	
Nacionalidade:	Portuguesa	<input type="checkbox"/>	Outra	<input type="checkbox"/>	Especifique _____
Pais de residência:	Portugal	<input type="checkbox"/>	Outro	<input type="checkbox"/>	Especifique _____
Escolaridade:	<input type="checkbox"/> 1º Ciclo do Ensino Básico (4º ano) <input type="checkbox"/> 2º Ciclo do Ensino Básico (6º ano) <input type="checkbox"/> 3º Ciclo do Ensino Básico (9º ano) <input type="checkbox"/> 11º ou 12º ano <input type="checkbox"/> Bacharelato <input type="checkbox"/> Licenciatura ou Mestrado <input type="checkbox"/> Doutoramento				
É apreciador/consumidor de maçã?	Sim	<input type="checkbox"/>	Não	<input type="checkbox"/>	
Costuma consumir frutas desidratadas?	Sim	<input type="checkbox"/>	Não	<input type="checkbox"/>	
Com que frequência consome frutas desidratadas?	<input type="checkbox"/> Todos os dias <input type="checkbox"/> 1 ou mais vezes por semana <input type="checkbox"/> 1 ou mais vezes por mês <input type="checkbox"/>				
Por favor prove a amostra 706:					

Qual a APRECIÇÃO GLOBAL da amostra 706?

(Por favor assinale com X a caixa que melhor representa a sua opinião)

- |                              |                          |
|------------------------------|--------------------------|
| 9 - Gostei extremamente      | <input type="checkbox"/> |
| 8 - Gostei muito             | <input type="checkbox"/> |
| 7 - Gostei moderadamente     | <input type="checkbox"/> |
| 6 - Gostei ligeiramente      | <input type="checkbox"/> |
| 5 - Não gostei nem desgostei | <input type="checkbox"/> |
| 4 - Desgostei ligeiramente   | <input type="checkbox"/> |
| 3 - Desgostei moderadamente  | <input type="checkbox"/> |
| 2 - Desgostei muito          | <input type="checkbox"/> |
| 1 - Desgostei extremamente   | <input type="checkbox"/> |

Avalie por favor a amostra 706 assinalando para cada um dos seguintes atributos sensoriais a caixa que melhor representa a sua opinião:

**ASPECTO**

(Por favor assinale com X a caixa que melhor representa a sua opinião)

- |                              |                          |
|------------------------------|--------------------------|
| 9 - Gostei extremamente      | <input type="checkbox"/> |
| 8 - Gostei muito             | <input type="checkbox"/> |
| 7 - Gostei moderadamente     | <input type="checkbox"/> |
| 6 - Gostei ligeiramente      | <input type="checkbox"/> |
| 5 - Não gostei nem desgostei | <input type="checkbox"/> |
| 4 - Desgostei ligeiramente   | <input type="checkbox"/> |
| 3 - Desgostei moderadamente  | <input type="checkbox"/> |
| 2 - Desgostei muito          | <input type="checkbox"/> |
| 1 - Desgostei extremamente   | <input type="checkbox"/> |

**DOÇURA**

(Por favor assinale com X a caixa que melhor representa a sua opinião)

- |                              |                          |
|------------------------------|--------------------------|
| 9 - Gostei extremamente      | <input type="checkbox"/> |
| 8 - Gostei muito             | <input type="checkbox"/> |
| 7 - Gostei moderadamente     | <input type="checkbox"/> |
| 6 - Gostei ligeiramente      | <input type="checkbox"/> |
| 5 - Não gostei nem desgostei | <input type="checkbox"/> |
| 4 - Desgostei ligeiramente   | <input type="checkbox"/> |
| 3 - Desgostei moderadamente  | <input type="checkbox"/> |
| 2 - Desgostei muito          | <input type="checkbox"/> |
| 1 - Desgostei extremamente   | <input type="checkbox"/> |

**TEXTURA**

(Por favor assinale com X a caixa que melhor representa a sua opinião)

- |                              |                          |
|------------------------------|--------------------------|
| 9 - Gostei extremamente      | <input type="checkbox"/> |
| 8 - Gostei muito             | <input type="checkbox"/> |
| 7 - Gostei moderadamente     | <input type="checkbox"/> |
| 6 - Gostei ligeiramente      | <input type="checkbox"/> |
| 5 - Não gostei nem desgostei | <input type="checkbox"/> |
| 4 - Desgostei ligeiramente   | <input type="checkbox"/> |
| 3 - Desgostei moderadamente  | <input type="checkbox"/> |
| 2 - Desgostei muito          | <input type="checkbox"/> |
| 1 - Desgostei extremamente   | <input type="checkbox"/> |

COMENTÁRIOS \_\_\_\_\_

\_\_\_\_\_

Por favor prove a amostra 108:

Qual a APRECIÇÃO GLOBAL da amostra 108?

(Por favor assinale com X a caixa que melhor representa a sua opinião)

- |                              |                          |
|------------------------------|--------------------------|
| 9 - Gostei extremamente      | <input type="checkbox"/> |
| 8 - Gostei muito             | <input type="checkbox"/> |
| 7 - Gostei moderadamente     | <input type="checkbox"/> |
| 6 - Gostei ligeiramente      | <input type="checkbox"/> |
| 5 - Não gostei nem desgostei | <input type="checkbox"/> |
| 4 - Desgostei ligeiramente   | <input type="checkbox"/> |
| 3 - Desgostei moderadamente  | <input type="checkbox"/> |
| 2 - Desgostei muito          | <input type="checkbox"/> |
| 1 - Desgostei extremamente   | <input type="checkbox"/> |

Avalie por favor a amostra 108 assinalando para cada um dos seguintes atributos sensoriais a caixa que melhor representa a sua opinião:

ASPECTO

(Por favor assinale com X a caixa que melhor representa a sua opinião)

- |                              |                          |
|------------------------------|--------------------------|
| 9 - Gostei extremamente      | <input type="checkbox"/> |
| 8 - Gostei muito             | <input type="checkbox"/> |
| 7 - Gostei moderadamente     | <input type="checkbox"/> |
| 6 - Gostei ligeiramente      | <input type="checkbox"/> |
| 5 - Não gostei nem desgostei | <input type="checkbox"/> |
| 4 - Desgostei ligeiramente   | <input type="checkbox"/> |
| 3 - Desgostei moderadamente  | <input type="checkbox"/> |
| 2 - Desgostei muito          | <input type="checkbox"/> |
| 1 - Desgostei extremamente   | <input type="checkbox"/> |

DOÇURA

(Por favor assinale com X a caixa que melhor representa a sua opinião)

- |                              |                          |
|------------------------------|--------------------------|
| 9 - Gostei extremamente      | <input type="checkbox"/> |
| 8 - Gostei muito             | <input type="checkbox"/> |
| 7 - Gostei moderadamente     | <input type="checkbox"/> |
| 6 - Gostei ligeiramente      | <input type="checkbox"/> |
| 5 - Não gostei nem desgostei | <input type="checkbox"/> |
| 4 - Desgostei ligeiramente   | <input type="checkbox"/> |
| 3 - Desgostei moderadamente  | <input type="checkbox"/> |
| 2 - Desgostei muito          | <input type="checkbox"/> |
| 1 - Desgostei extremamente   | <input type="checkbox"/> |

TEXTURA

(Por favor assinale com X a caixa que melhor representa a sua opinião)

- |                              |                          |
|------------------------------|--------------------------|
| 9 - Gostei extremamente      | <input type="checkbox"/> |
| 8 - Gostei muito             | <input type="checkbox"/> |
| 7 - Gostei moderadamente     | <input type="checkbox"/> |
| 6 - Gostei ligeiramente      | <input type="checkbox"/> |
| 5 - Não gostei nem desgostei | <input type="checkbox"/> |
| 4 - Desgostei ligeiramente   | <input type="checkbox"/> |
| 3 - Desgostei moderadamente  | <input type="checkbox"/> |
| 2 - Desgostei muito          | <input type="checkbox"/> |
| 1 - Desgostei extremamente   | <input type="checkbox"/> |

COMENTÁRIOS

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