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Diffusion mechanisms during the osmotic dehydration of Granny Smith apples subjected to a moderate electric field

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ABSTRACT

Osmotic dehydration is a process wherein foods are partially dehydrated by immersion in an aqueous hypertonic solution. Osmotic dehydration reduces the water activity of the food, thereby minimizing the potential growth of microorganisms and extending the shelf life of food products. A major disadvantage of the osmotic dehydration process is the long time required to reduce the water activity, which makes its industrial implementation impractical.

The aim of this research is to determine the diffusion mechanisms in Granny Smith apples exposed to different electric fields varying from 0 to 17 V/cm.

Osmotic dehydration was performed at 40 °C for both the conventional treatment and for the MEF treatment. The fruit/solution ratio used was 1:11 w/w to prevent and minimize the change in concentration of the solution during the experiment. The osmotic solution was exposed to electric fields of 0, 9, 13 or 17 V/cm, respectively. To determine the diffusion mechanisms two phenomenological models were tested: Fick's second law and Anomalous diffusion model.

Sucrose diffusion in Granny Smith apples is highly influenced by the application of a MEF, meaning that as the application of the electric field increases, the higher the effective diffusion coefficient (D_{eff}) becomes. The exponential decay from the Fick law, in the tail of the diffusion profile, does not represent the shape of the data. However, as the application of the electric field increases the fit of Fick's model improves, and specifically for an electric field of 17 V/cm it is observed that the behavior of the experimental data resembles the behavior predicted by Fick's second law. The empirical parameter α for the anomalous diffusion model was always greater than one, but as the MEF increased, α was monotonically tending to one.

1. Introduction

Osmotic dehydration is a process wherein foods are partially dehydrated by immersion in an aqueous hypertonic solution. Osmotic dehydration reduces the water activity of the food, thereby minimizing the potential growth of microorganisms and extending the shelf life of food products. Osmotic dehydration is a technology with broad applications in food processing. Nevertheless, the osmotic dehydration process can achieve only partial dehydration of food. Another disadvantage of the osmotic dehydration process is the long time required to reduce the water activity, which makes its industrial implementation impractical (Simpson et al., 2007).

The application of a moderate electric field (MEF) means that an electric current passes through a food material. When applied, an electric field can cause changes in the permeability of cell membranes of plant tissue at lower temperatures at which these membranes are permeabilized by thermal effects, a phenomenon known as electroporation (An and King, 2007; Lima and Sastry, 1999). The resulting effect is that the diffusion process increases, the electrical conductivity changes and the moisture more easily migrates out of the plant tissue (Leizerson and Shimoni, 2005).

In general, structural changes of cells such as cell disruption, electroporation, and cell damage tend to improve the diffusion rate because water movement through the cell membrane and cell wall is easier. For example, Ramírez et al. (2011) evaluated some pre-treatments from a microstructural point of view and their effect on water diffusion rate, finding that those pre-treatments that induced more damage to the cellular structure produced an increase in diffusion rate during air drying. The case of electroporation is the same concept, with cell damage favoring the diffusion of water during the dehydration process. Moreno et al. (2013)

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showed the effects at the microstructural level in strawberries of applying an electric field of 130 V/cm, where the cells presented changes in shape and thickness of lamellae and an increase in cell breakage.

The phenomenon of osmotic dehydration can be modeled by the fundamentals of mass transfer that describe the origin of the diffusive forces that are involved in and control these processes (Spiazzi and Mascheroni, 1997). In recent years, numerous studies have been conducted to improve knowledge regarding the internal mass transfer occurring during osmotic dehydration of foods and to model the mechanism of the relevant process (Spiazzi and Mascheroni, 1997; Kaymak-Ertekin and Sultanoglu, 2000).

This process is usually represented by Fick's second law. The best known phenomenological model to represent the diffusional mechanism is the model of Crank (Crank, 1975), consisting of a set of solutions of Fick's law of diffusion for different geometries, boundary conditions and initial conditions. This model has been used by many authors because it is the best known phenomenological model for representing diffusional mechanisms (Ochoa and Ayala, 2005). To these ends, researchers have developed several mathematical models (Barat et al., 2001; Fito, 1994; Salvatori et al., 1999; Toupin et al., 1989; Agnelli et al., 2005) and determined effective diffusion coefficient values in different fruits and geometries using Fick's second law (Rastogi et al., 2002; Rastogi and Raghavarao, 2004; Azuara et al., 1992). However, the complexity of the mass transfer process due to the complex nature of plant tissues, their strongly heterogeneous cell structure, shrinkage and volume changes during dehydration process due to moisture removing makes accurate prediction challenging, so that the exact analytical solutions cannot normally be applied because several of the assumptions of Fick's second law do not fit heterogeneous tissues such as apple (Varea and Hernández, 2010; Zaritzky and Califano, 1999). These structural changes are also present in osmotic dehydration, however is less significant than in traditional dehydration which can reach values close to 60–70% (Sturm et al., 2014). For example, Souraki et al. (2014) and Nieto et al. (2004) have reported that the effect of osmotic dehydration on shrinkage of apple could be around 10% up to 30%. In the present study the effect of shrinkage will be neglected, because the fractional diffusion formulation for shrinking geometries has not been developed yet.

Anomalous or non-Fickian diffusion has been proven to be a useful tool for quantitatively describing diffusion during drying of foods because it considers many of the changes that occur in the food material and its microstructure during the process such as shrinkage and porosity. Fractional calculus modeling is a new and innovative approach in the food processing field that requires rethinking the diffusion process in food materials (Simpson et al., 2013). Fractional calculus is a mathematical tool for mathematically representing the phenomena of real anomalous diffusion of solutes whose movement can be faster or slower than postulated in Fick's second law due to the influence of the cellular structure of the food material (Simpson et al., 2013). Descriptions of mass transfer behavior can be modeled with differential equations of non-integer order as fractional numbers.

The aim of this research is to determine the diffusion mechanisms in Granny Smith apples exposed to different electric fields varying from 0 to 17 V/cm by application of fractional diffusional formulation using fractional calculus tool.

2. Materials and methods

2.1. Sample preparation

Granny Smith apples were acquired in a supermarket in the city of Valparaiso, Chile and kept under refrigeration at 2 °C. The apples were peeled and cut into sheets 40 mm in diameter and 7 mm thick and were subsequently immersed in 1% ascorbic acid solution and 2% citric acid solution to prevent enzymatic browning. Osmotic solutions of 45, 55 and 65 °Brix were prepared using sucrose (commercial sugar). The osmotic solutions contained 7 mg/L of potassium sorbate ($C_6H_7KO_2$) as a preservative, inhibiting any unwanted microbiological activity and 1.27, 1.33 or 1.13 g/L of calcium chloride ($CaCl_2$) to increase the conductivity of the solution.

2.2. Osmotic dehydration

Osmotic dehydration was performed at 40 °C for both the conventional treatment and for the MEF treatment. The fruit/solution ratio used was 1:11 w/w to prevent and minimize the change in concentration of the solution during the experiment. The samples were immersed in a cylindrical cell made of stainless steel with a plastic bottom. The cell was composed of two concentric cylinders (3.7 cm and 19 cm diameter) connected to a generator by means of two electrodes (Moreno et al., 2011). The osmotic solution was exposed to an alternating current with voltage of 70, 100 or 130 V, generating electric fields of 9, 13 or 17 V/cm, respectively. The cell was immersed in a thermo-regulated bath (BS-21 Jeio Tech, Korea) with the aim of maintaining the medium temperature at 40 °C during the experiment. In addition, constant and gentle stirring was provided to attain a homogeneous solution without damaging the fruit. To monitor the temperature of the solution and the applied electric field, two T type thermocouples (copper–constantan) were used. Data on temperature, voltage and current were recorded every three seconds with a data logger (Omega 220, USA) having a connection via modem and connection port to a computer. The data logger includes HiperWareTM software version 4.77 (1996–2005), which communicates with and gathers data from the program online. Each experimental run was performed for 12 h with sampling at different times (optimal sampling for diffusion experiments) to measure the concentration of sugar in the apple.

2.3. Analytical determinations

Moisture was determined by drying the samples for 24 h at 60 °C in a vacuum oven to constant weight according to the method defined by the Association of Official Analytical Chemists (AOAC) (Association of Official Analytical Chemists, 2000) for fruits rich in sugar. The determination of soluble solids was performed, after homogenization of the samples, using a digital refractometer (Hanna Instruments, model HI 96811, USA).

2.4. Mathematical models

2.4.1. Fick's second law of diffusion

To develop the model, the following assumptions were considered: (a) the apple slices are assumed to be infinite slabs, (b) the initial soluble solids are evenly distributed, (c) the process is isothermal (40 °C), (d) the diffusion coefficient is assumed to be constant, (e) simultaneous counter-current flows: diffusion of water from the fruit and diffusion of sugar to the fruit are considered only, and (f) other transfer mechanisms and shrinkage of the sample are neglected. Therefore, the analytical solution to Fick's second law for solid diffusion in one dimension is given by Eq. (1).

$$C^*(t) = \frac{C(t) - C_e}{C_0 - C_e} = \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left(-D_{eff} \left(\frac{(2n+1)\pi}{L} \right)^2 t \right) \tag{1}$$

where $C^*(t)$ is the dimensionless solid concentration of the sample at instant t, $C(t)$ the concentration of the product at instant t, C_0 is