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Mass Transfer Mechanisms during Dehydration of Vegetable Food: Traditional and Innovative Approach

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1. Introduction

All along people well know that through the reduction of water content it is possible to preserve food for a long time. Among foods, fresh fruits and vegetables show an average water content ranged between 90\% and 98\% which greatly affect their perishability. So, back in the past sun dehydration was the first drying method used to assure fruits and vegetables during long period of drought, winters, etc. In terms of stability, drying processes not only inhibit microbial growth but also several biological and chemical degradation reactions; nevertheless, they also affect sensorial and nutritional characteristics promoting the collapse of vegetable tissues and the degradation of vitamins and antioxidants (Ibarz and Barbosa-Canovas, 2003). Nowadays, it is well known that the “state” of water rather than its mass fraction is responsible of microbial growth and degradation reactions. Moreover, in the last 30 years the need of new technologies allowed to develop several dehydration methods such as hot air dehydration, osmotic dehydration, microwave dehydration, infrared (IR) dehydration, ultrasonic dewatering, hybrid technologies, etc. The introduction of these technologies in food industries has increased the quality of dried vegetables leading to an exponential increase of the market of these products. For instance, a report published from Research and Markets showed that the total West European dehydrated food market was worth euros 11.5 bilion in 2009.

Strictly speaking, during drying processes, the key factor of all traditional and innovative techniques is the mass transfer from vegetable tissues to its surrounding and vice versa. In general, water is the component that moves from vegetable tissues toward the surrounding air but this transfer may occurs through several mechanisms such as capillary flow, diffusion of water due to concentration differences, surface diffusion, vapor diffusion in the pores due to pressure gradient, water vaporization-condensation (Ibarz and Barbosa-Canovas, 2003), etc.; moreover, some of these mechanisms may affect each other, making the drying a very complex phenomenon. Furthermore, in the case of osmotic dehydration a countercurrent mass transfer occurs: a. water flows from vegetables to hypertonic solution; b. osmotic agents move toward vegetable tissues. On these bases, the possibility to obtain safe dried vegetables with high nutritional and sensorial quality, also maintaining a high production output and low energy costs, is strictly related to the ability in controlling mass
transfer. To reach these purposes several questions need to be satisfied: which are the mass transfers mechanisms involved during each dehydration technologies? how is possible to increase the dehydration rate? which mathematical models may be used to predict mass transfer? how the mass transfer may affect the quality of dehydrated vegetable food? Even though much has been done to give correct responses, much more remains to be explained. For instance, Fickean diffusion is widely recognized from food scientists as the predominant internal mass transfer mechanism during drying processes. Under this approach, water moves randomly from a region with high concentration toward a region at low concentration assuming that the moisture gradient inside vegetables is the only driving force of the motion. On this basis several empirical equations have been proposed to predict mass transfer. Although these models significantly increased the knowledge of dehydration, much more must be explained. For instance, Fick’s laws which are widely used to model water diffusion during drying require several assumptions and simplifications that are often unrealistic. Some of these are: food are homogeneous and isotropic media; diffusion coefficients are independent of moisture concentration; samples are approximately considered as spheres, cylinders or slabs; heat transfer during drying is ignored; collapse of vegetable tissues during dehydration (easily detected by a visual aspect) is neglected (Saguy et al., 2005). The effects of microscopic structure on mass transfer has been completely dropped and only in the last years few pioneering papers were published on this topics. It should be considered that most food structures generally exhibit a disordered geometry, often due to percolation phenomena, which in many cases can be described in terms of fractal geometry. This feature dramatically affects diffusion phenomena, giving rise to anomalous laws (subdiffusion), involving universal geometrical parameters such as fractal dimension and spectral dimension.

This chapter serves to provide at the readers the conventional and emerging theories on mass transfer during traditional and innovative drying technologies of fruits and vegetables. After a first evaluation of the basic principles concerning the relation between water and food quality, the most important mechanisms of molecular motion, the variables affecting the rate of the most important drying technologies and their effects on kinetics are reviewed and discussed. Also, the most used mathematical models will be reported analyzing their advantages and the related assumption and limitation with the aim to give the basis for the modeling of mass transfer during vegetable dehydration. Moreover, the application of statistical-physic approach to study the random movement of water and solutes inside food three-dimensional microstructure will be reported.

2. The importance of dehydration treatments for safety and quality of vegetable food

2.1 Basic principles on the relation between water and food quality

Water is the most abundant component in foods. Among these, fruits and vegetables show a mass fraction of water in the range of 90% and 98%. Its amount and its peculiar chemical and physical characteristics make it the key factor for biological and chemical degradation reactions. In particular, water is the most important medium in which chemical and biological reagents may move, collide and react. Moreover, water may act as reagent and co-reagent of several degradation reactions (i.e. hydrolysis of lipids which degrades vegetable oils or the fat content of vegetables) and it stabilizes the most important biological structures such as enzymes, proteins, DNA, cellular membranes, etc. by its ability to produce a large number of hydrogen bounds. On these basis, taking into account the safety and quality of
vegetable food, it is possible to state that water controls the growth of pathogen and/or alternative microorganisms, chemical and enzymatic reactions such as enzymatic browning (EB), lipid oxidation, Maillard reaction (NEB), vitamin degradation, texture degradation, etc. which are able to make food not safe and/or organoleptically or nutritionally unacceptable for the consumers. Furthermore, water significantly modify physical and chemical properties of vegetables such as thermal conductivity, heat capacity, dielectric properties, electrical conductivity, boiling and freezing point, firmness, etc., which are key factors for all dehydration technologies as well as for others important industrial processes. So, the knowledge regarding the correlation between both the above reactions, food properties and water is crucial for the correct production of dried vegetables. However, these correlations not always are linear but often very complex. For these reasons the fundamental aspects concerning the water in food are summarized hereafter.

In general, all people well know that reducing the amount of water in food it is possible to significantly increase its shelf life. So, for many years the water concentration in food was considered the only factor affecting their perishability. Nevertheless, Scott (1957) highlighted the importance of the “state” of water in food rather than its mass fraction stating that it is a key factor for degradation reactions. Scientific literature reports many terms to define the “state” of water in food some of which cannot be as synonymous: “free” and “bound” water, “unfreezable water”, “structured water”, “rotationally water”, “water mobility”. These are often related to the analytical techniques used to detect them as in the case of “unfreezable water” estimated by differential scanning calorimeter (DSC) or “rotationally water” that is measured by nuclear magnetic resonance (NMR) which allows to measure the rate of rotational mobility of water molecules. However, all above terms may be considered similar if the follows general meaning it is taken into account: the state of water means the availability of water molecules to be freely used for all biological and chemical reactions. Significant different levels of water availability may be detected in vegetable food with the same water concentration. On the other hand foods with different water content may show the same water availability. So, vegetable foods with the same water content may show significantly different shelf life. These behaviours are caused by different interactions between water molecules and chemical compounds of vegetables such as sugars, proteins, salts, fats, vitamins, etc. Under this consideration “free” water may be considered as an unperturbed systems (also called bulk water) in which water molecules may interact with each other keeping constant their chemical and physical characteristics such as bound angle, internuclear distance, etc. Instead, “bound water” may be considered as a perturbed system in which water preferentially interacts with other molecules. Fennema (1999) defined bound water as: “water that exists in the vicinity of solutes and other non aqueous constituents and that exhibits properties that are significantly altered from those of bulk water in the same system”. “Free” water may be freely used from microorganisms for their intracellular reactions or as reagent for chemical degradation reactions; instead, “bound” water is chemically bounded to solid matrix (solute) and it is unavailable for microbial growth and chemical reactions. In 1957 Scott defined a mathematical parameter to measure the water availability in food: water activity ($a_w$). This index has thermodynamic basis:

$$\mu = \mu_0 + RT \ln \left( \frac{f}{f_0} \right)$$  \hspace{1cm} (1)

where $\mu$ and $\mu_0$ are respectively the chemical potential of water and those of pure water (the reference state); $f$ is the fugacity of the system at given conditions and $f_0$ is the fugacity at the

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reference state (Van der Berg & Bruin, 1981); \( T \) and \( R \) are the temperature (K) and gas constant \( (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \) respectively. Since in practical condition fugacity may be considered equal to partial vapour pressure \( (p) \) it is possible to obtain the following equation:

\[
\mu = \mu + \mu_0 RT \ln \left( \frac{P}{P_0} \right)
\]  

(2)

if thermodynamic equilibrium is reached it is possible to use the following:

\[
\mu = \mu + \mu_0 RT \ln \left( a_w \right)
\]  

(3)

So, water activity may be defined as the ratio between vapor pressure surrounding food \( (P) \) and the vapor pressure of pure water (reference state, \( P_0 \)) both measured at the same temperature and pressure values:

\[
a_w = \frac{P}{P_0}
\]  

(4)

It is worth nothing that this parameter is valid only if thermodynamic equilibrium is reached (no water molecules move inside food due to different chemical potential) although in practical application this condition is often not satisfied. Since 1975, water activity is the most important parameter used to relate the water availability with the rate of degradation reactions and several books have been published on this topics (Ruand & Chen, 1998; Rockland & Beuchat, Roos et al., 1999).

2.2 Water activity and degradation reaction of vegetable food

In 1970, Labuza reported a food stability map in terms of water activity values (figure 1). In particular, the figure shows the rate of some degradation reactions as a function of \( a_w \) values. Moreover, a general moisture sorption isotherm of food is reported. According to Frank & Wen (1957), the map is subdivided in three regions. In the first one \( (0 - 0.2) \) water is strictly bounded with solid matrix of food and it cannot be used as reagent or co-reagent. Moreover, in this region viscosity is so high that mobility of chemical reagents is restricted and the rate of degradation reactions is reduced. In the second region, characterized from water activity values ranged between \( 0.2 \) and \( 0.7 \), water molecules progressively becomes available for some biological and chemical reactions such as Maillard reaction (non enzymatic browning) and enzyme activities but they are still unavailable for microbial growth with the exception of some molds. In the third region \( (0.7 - 1.0) \) water molecules are weakly bounded to the solutes or restrained by capillary forces; here, water molecules are freely usable for both microbial growth and chemical reactions which may quickly occur. In terms of microbial growth it is possible to observe a direct relation: as lower the water activity, as slower the growth rate of molds, yeasts or bacteria.

When microbial cells are exposed to a system with a high osmotic pressure (low water activity) they lose water because cellular membranes are semi-permeable. This phenomenon, called plasmolysis, proceeds until the osmotic equilibrium is reached but, in this condition microorganisms are unable to reproduce and they will die or remain dormant (Sperber, 1983; Troller, 1985; Amezaga-Johnston et al., 1999). In general, the reduction of \( a_w \) values has two inhibitory effects on the growth rate of microorganisms: 1. the increase of lag phase; 2. the reduction of generation time (Troller, 1985). Moreover, from figure 1 it is possible to observe that the resistances among the microorganisms are very different and may be graded as follows: molds > yeasts > bacteria. Furthermore, among these, different microorganisms may show significant variation in term of water activity resistance. For
instance, the out-growth of Clostridium botulinum spores, one of the most dangerous pathogen microorganisms, is inhibited at $a_w$ values < 0.935 (Clavero et al., 2000). The generation times of Listeria monocytogenes at $a_w$ values of 0.98 and 0.92 were reported respectively as 6.1 h and 12.7 h in systems at pH 6.2. Colatoni & Magri (1997) reported that the minimum value for the Clostridium perfringens spore germination is 0.935. Beuchat (1985) reported that Staphylococcus aureus, which is very tolerant to $a_w$ values, shows a minimum for toxin production of 0.90 and a minimum of 0.86 for growth. In table 1 are reported the minimum $a_w$ values for some of the most important microorganisms for food degradation.

It should be taken into account that the threshold reported in table 1 are often measured in model system with specific environmental conditions. In vegetable foods, the minimum $a_w$ values for growth or toxin production of each microorganism must be considered as range of ranges of $a_w$ values inside which the “true” limiting value may change when other inhibitory factors are applied. In fact, it should be considered that the resistance of microorganisms on $a_w$ values is affected by several parameters such as pH, temperature, oxygen concentration, preservatives, solutes, etc. For instance, the type and the amount of solutes in food (their chemical composition) greatly affect the tolerance of microorganisms on water activity. This is because microorganisms have different levels of ability to adapt at an hypertonic environment regaining turgor pressure and excluding certain incompatible solutes (Kang et al., 1969; Gould & Measures, 1977; Christian, 1981; Buchanan & Bagi, 1997; Lenovich, 1985 Gould, 1985). For instance, it was reported that the limiting $a_w$ values for several microorganisms is lower when sodium chloride rather than glycerol is used (Gould and Measures, 1977). Since a comprehensive analysis of the effects of water availability on microbial degradation is out of the principal aim of this chapter we report the most important papers and books where the effect of water activity on safety and quality of food was studied in details. (Dukworth, 1975; Labuza 1980; Rockland & Nishi, 1980; Rockland & Stewart, 1981; Troller, 1985; Simato & Multon, 1985; Troller, 1985; Drapon, 1985; Gould, 1985).
Table 1. Limiting $a_w$ values for the growth of some microorganisms of interest for vegetable food (adapted from Leistern and Radel, 1978)

<table>
<thead>
<tr>
<th>Water activity ($a_w$)</th>
<th>Bacterial</th>
<th>Yeast</th>
<th>Mold</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.98</td>
<td>Some <em>Clostridium pseudomonas</em></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.97</td>
<td>Some <em>Cl. perfringens</em> and <em>Cl. botulinum E</em></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.95</td>
<td><em>Bacillus</em>, <em>Cl. botulinum A and B</em>, <em>Escherichia</em>, <em>Pseudomonas</em>, <em>Salmonella</em>, <em>Serratia</em></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.94-0.92</td>
<td><em>Lactobacillus</em>, <em>Streptococcus</em>, <em>Pediococcus</em>, <em>Microbacterium</em>, <em>Vibrio</em></td>
<td><em>Rhodotorula</em>, <em>Pichia</em>, <em>Rizhopus</em>, <em>Mucor</em></td>
<td></td>
</tr>
<tr>
<td>0.91-0.88</td>
<td><em>Staphylococcus</em>, <em>Streptococcus</em>, <em>Lactobacillus</em></td>
<td><em>Hansenula</em>, <em>Saccharomyces</em>, <em>Candida</em>, <em>Torulopsis</em></td>
<td><em>Paecilomyces</em>, <em>Aspergillus</em>, <em>Penicillium</em>, <em>Emericella</em></td>
</tr>
<tr>
<td>0.87-0.80</td>
<td><em>Staphylococcus</em></td>
<td><em>Saccharomyces</em></td>
<td></td>
</tr>
<tr>
<td>0.80-0.62</td>
<td><em>Saccharomyces</em></td>
<td><em>Eurotium</em>, <em>Monascus</em>,</td>
<td></td>
</tr>
</tbody>
</table>

As in the case of microbial growth, enzymatic activity increases with increasing of $a_w$ values. Nevertheless, figure 1 shows that enzymes may catalyze biological reactions also at $a_w$ values very low (close to 0.2). This is the case of lipase and lipoxygenase enzymes which are responsible of the vegetable oils degradation even if the $a_w$ value is around of 0.025 and 0.05 respectively (Drapon, 1985; Brokmann & Acker, 1977). This behavior was explained by the action of lipid as plasticizing medium which may increase the mobility of reagents.

Non enzymatic browning (NEB) is a complex chemical reaction between reducing sugars, like glucose, and amino groups such as amino acids. NEB is responsible to modify the appearance, the taste and the nutritional value of food (Maillard, 1912; Martins et al., 2001). As reported from Martins et al. (2001) Maillard reaction consists in consecutive and parallel reaction steps affected by several parameters. For the production of dried vegetables, NEB is among the most important degradation reactions because the high temperature promotes the production of brown melanoidin pigments making the vegetables brown. Moreover, other changes such as degradation of the nutritive value of the involved proteins, production of volatile (Fors, 1983) and antioxidant compounds (Griffith & Johnson, 1957; Brands et al., 2000; Martins et al., 2001) are involved during NEB reaction. In terms of water availability the Maillard reaction has been reviewed from several authors (Mauron, 1981; Baltes, 1982; Yaylayan, 1997; Martins et al., 2001) which showed no direct relation between its rate and the $a_w$ values. Figure 1 shows a bell-shaped trend in which the rate of NEB increases until a maximum value almost at 0.7 and then significantly decreases. The trend of NEB is a consequence of two different effects: 1. the changes of the mobility of chemical reagents; 2. the dilution of the system (Eichner, 1975; Labuza & Saltmarch, 1981). By increasing $a_w$ values, water molecules progressively become free and may act as plasticizing media imparting mobility to the chemical reagents which produce the melanoidin pigments. This effect progressively increases until the maximum $a_w$ values of ∼ 0.7, after which the high water concentration dilutes the chemical species reducing their probability to interact each other (Labuza & Saltmarch, 1981; Maltini et al., 2003).
Moisture plays an important effect on lipid degradation in particular at medium-high temperature as in the case of drying processes. Perhaps the trend of lipid oxidation as a function of water activity is the most complex among the others degradation reactions. Lipid oxidation is a chemical auto-catalytic reaction during which unsaturated fatty acids and oxygen react producing off-flavors and increasing rancidity. Several factors may influence oxidation rate: moisture content, type of fatty acids, the amount on metal ions, light, temperature, oxygen concentration, antioxidants, etc. From the figure 1 it is possible to observe an inverse correlation as \(a_w\) increase until values of 0.2, then a direct correlation till 0.75 and again a decrease of reaction rate as \(a_w\) value increases. This behavior was well studied from Labuza (1975) and Karel (1980) which hypothesized a combined effect of pro- and antioxidant factors. In comparison with other degradation reactions when water activity value is very low (\(\sim 0.1\)) lipid oxidation rate is very high. This is because when solid matrix is dry a maximum contact between oxygen and lipid exists. Instead, as water activity increases until \(a_w\) value of 0.25, water molecules obstacle the collision between fatty acids (on solid matrix) and oxygen leading to a reduction of oxidation rate. Instead, between \(a_w\) values of \(\sim 0.2\) and \(\sim 0.75\) the pro-oxidant factors such as the increased mobility of chemical reagents, the solubilization of chemical species inside water, makes reaction rate and water activity directly correlated. Others quality indexes are affected by water activity such as carotenoid content and texture properties of dehydrated food. Carotenoids are lipid soluble pigments responsible of the color of many fruits and vegetables such as tomato, carrot, grape, orange, cherry, etc. During drying they may undergo the same degradation reactions of lipids (Stephanovic & Karel, 1982). Chlorophylls were shown to be more resistant to degradation at lower \(a_w\) value, probably because the mobility of reagents is restricted and the probability to react is low due to the high viscosity of the system (Lajollo and Marquez, 1982). Betalaines, the major pigments of red beet showed a high stability in model system at low \(a_w\) values (Saguy et al., 1980; Saguy et al., 1984). As reported from Cohen and Saguy (1983) a reduction of \(a_w\) values from 0.75 to 0.32 produced an increase of half life of betanine in beet from 8.3 to 133 days.

3. Dehydration technologies for vegetable food: mass transfer mechanisms and process variables

3.1 The behavior of vegetables during drying processes

With the aim to correctly deal mass transfer mechanisms during dehydration processes it is important to briefly remind the importance of chemical composition of vegetables on drying. As previously reported, vegetables with the same water content may show significant different \(a_w\) values because of their chemical composition lead to different affinity for water. Solutes such as sugars, salts, proteins, lipids and their relative concentration in fresh fruits or vegetables, interact with water molecules through different chemical bounds, making the water molecules more or less easily removable from biological tissues. In this way, each vegetable shows a unique behavior in terms of equilibrium between its water content and water activity values. This equilibrium may be described by sorption or desorption isotherms which respectively refer to the case in which vegetable food is under the process of increasing or decreasing its water content (Wolfe et al., 1972; Slade & Levine, 1981; van den Berg, 1985; Slade & Levin, 1985; Kinsella and Fox, 1986; van der Berg, 1986; Slade & Levine, 1988a; Slade & Levine, 1988b; Karel & Lund, 2003).
should be always considered that knowledge of the isotherms are a basic requirement to plan a correct drying process with the aim to maximize its advantage and minimize degradation reactions. In figure 2 are reported typical sorption and desorption isotherms of food. Usually they show a general S-shaped trend in which three regions may be clearly observed. These exactly reflect the regions of food stability map previously discussed (figure 1). For instance, the first section of desorption isotherms, in a range of $a_w$ values between 0 and 0.2 - 0.3, is called “monolayer” and it is characterized from water molecules strictly absorbed on hydrophilic, charged and polar molecules such as sugars and proteins (Kinsella & Fox, 1986; Lahsasni et al., 2002; Hallostrom et al., 2007; Okos et al., 2007). Usually, the water in this region is considered as “unfrozen” and it is not available for chemical reactions and it cannot act as plasticizer. Also, as known, sorption and desorption isotherms are not overlapped, stating a completely different behavior in the cases in which water is removed from or added to vegetables. Moreover, during drying foods show higher water activity values in comparison with rehydration process.

Fig. 2. Typical sorption and desorption isotherm of food (adapted from Okos et al., 2007)

This different behavior is called hysteresis and it may have different intensity and/or different shape as a consequence of several factors among which the chemical composition of food is one of the most important (Okos et al., 2007). So, vegetables with high content of sugars/pectins show an hysteresis in the range of monolayer while in starchy food the hysteresis occurs close to $a_w$ of 0.7 (Wolf et al., 1972; Okos et al., 2007). Nevertheless, Slade & Levine (1991) stated that other factors such as temperature, physical structure (i.e. amorphous or crystalline phases), experimental history (i.e. previous desorption/sorption cycles) and sample history (i.e. pretreatments, thermal history during storage before drying, etc) may greatly affect the shape of hysteresis. For instance, it is commonly accepted that as temperature increases, the moisture content decreases leading to a reduction of isotherms; this effect is greater in desorption that on adsorption, producing a reduction of hysteresis.

3.2 Dehydration techniques and mass transfer mechanisms
Dehydration is one of the most important unit operation in Food Science. The terms dehydration and drying are generally used as synonymous but they not are exactly the same. Dehydrated vegetables are considered to have a mass fraction of water lower than
2.5%; instead dried vegetables may contain more than the 2.5% (Ibarz & Barbosa-Canovas, 2003). A complete and correct analysis of dehydration or drying technologies is an hard work. Traditionally, conventional and innovative dehydration techniques are the two most important classes considered in scientific literature. In the first group sun dehydration, hot air dehydration, spray drying, osmotic dehydration, freeze drying, fluidized bed drying, are the most important; instead, microwave drying, infrared drying, ultrasonic dehydration, electric and magnetic field dewatering, solar drying, are among the most studied innovative techniques. Another usual classification is based on the analysis of dryer plant. Craspite & Rotstein (2007) analyzing the design and the performance of several dryers stated that it is possible to classify them on the basis of supplying heat, type of drying, equipment, method of the product transporting, nature and state of feed, operating conditions and residence time. In the same way, Okos et al. (2007) analyzed several different drying techniques on the basis of a classification of dryer design. However, since many dehydration techniques may be combined and/or several methods to increase the dehydration rate may be used, the number of drying technologies available or in development stage is very high. For instance, Chua and Chou (2005) well reviewed new hybrid drying technologies classifying them in three groups: 1. Combined drying technology; 2. Multiple-stage drying; 3. Multiple-process drying. Moreover, the use of new methods to increase the mass transfer of the above technologies, may promote new dehydration techniques. This is the case in which the use of vacuum pressure was combined with osmotic dehydration giving two innovative techniques: vacuum osmotic dehydration (VOD) and pulsed osmotic dehydration (PVOD).

However, with the aim to study and classify the drying techniques on the basis of mass transfer mechanisms it is necessary to take into account the following factors: the physical state in which water molecules leave vegetable tissues; the physical state in which water molecules move inside vegetable pieces; the location from which water molecules leave the vegetables. Water may leave vegetables or move inside it as liquid and/or vapor; also, water molecules may leave the vegetables from their surface and/or internal regions. Moreover, some of these possibilities may occur simultaneously or also they could change during drying. In addition, if water evaporates from the surface or inside vegetables, the heating method should be taken into account because it has a great influence on the mass transfer mechanisms inside vegetables. Considering some of these key factors, Okos et al (2007) classified the most important internal water transfer mechanisms reported in scientific literature (table 2).

<table>
<thead>
<tr>
<th>Vapor</th>
<th>Liquid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mutual diffusion</td>
<td>Diffusion</td>
</tr>
<tr>
<td>Knudsen diffusion</td>
<td>Capillary flow</td>
</tr>
<tr>
<td>Effusion</td>
<td>Surface diffusion</td>
</tr>
<tr>
<td>Slip flow</td>
<td>Hydrodynamic mechanisms</td>
</tr>
<tr>
<td>Hydrodynamic flow</td>
<td></td>
</tr>
<tr>
<td>Stepan diffusion</td>
<td></td>
</tr>
<tr>
<td>Poiseuille flow</td>
<td></td>
</tr>
<tr>
<td>Evaporation/condensation</td>
<td></td>
</tr>
</tbody>
</table>

Table 2. Proposed internal mass transfer mechanisms during drying process (from Okos et al., 2007)

Although classical literature recognized that these internal transport mechanisms have a great importance during drying processes (Craspite & Rotstein, 1997; Genkoplis, 2003; Okos
et al., 2007), their knowledge and their use in the planning of dehydration processes is very limited. The difficulty to theoretically study these mechanisms, to measures the microstructure properties of food and to obtain easy mathematical model, lead to assume, in practical application, liquid diffusion as the only molecular motion during drying of fruits and vegetables. Nevertheless, in the last years some pioneering researches focused their aims on the study of mass transfer in food, taking into account their nature of porous media. So, below the most important internal mass transfer mechanisms are discussed with particular attention on diffusion and capillary flow.

3.2.1 Water diffusion

Water diffusion is probably the most studied transport mechanism during drying of vegetables. Diffusion is the process by which molecules are transferred from a region to another on the basis of random motions in which no molecules have a preferred direction. Moreover, during diffusion the molecules move from the region of high concentration to that lower. Fick (1855) was the first scientist that translate diffusion in mathematical language stating that the diffusion in a isotropic substance is based on the hypothesis that the rate transfer of diffusing substance through unit area of a section is proportional to the concentration gradient measured normal to the section (Crank, 1975). So, often it is generally assumed that during drying water diffuses from internal regions (with a high moisture content) toward its surface (with low moisture content) where it evaporates if sufficient heat is supplied. This mechanism is described by the second Fick’s law which may be expressed as:

$$\frac{\partial m}{\partial t} = D_{\text{eff}} \frac{\partial^2 m}{\partial x^2}$$

(5)

where \(m\) is the moisture content, \(t\) is time, \(x\) is the spatial coordination and \(D_{\text{eff}}\) is the effective diffusion coefficient. If the diffusion occurs in three dimension, eq. 5 becomes:

$$\frac{\partial m}{\partial t} = D_{\text{eff}} \left( \frac{\partial^2 m}{\partial x^2} + \frac{\partial^2 m}{\partial y^2} + \frac{\partial^2 m}{\partial z^2} \right)$$

(6)

The solutions of equation 6 are different depending on the geometry of samples. Solutions for simple geometries such as finite and infinite slabs, infinite cylinders, finite cylinders, spheres, rectangular parallelepipeds, were developed from Crank (1975). For instance, equations 8 and 9 are the solution of Fick’s law for infinite slabs and spheres.

$$MR = \frac{M - M_e}{M_0 - M_e} = \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp \left[ \frac{(2n+1)^2 \pi^2 D_{\text{eff}} t}{4 L^2} \right]$$

(7)

$$MR = \frac{M - M_e}{M_0 - M_e} = \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp \left[ \frac{n^2 D_{\text{eff}} t}{r^2} \right]$$

(8)

Where \(MR\) is the moisture ratio, \(M\) is the moisture content at time \(t\), \(M_e\) and \(M_0\) are the moisture content respectively at time zero and at equilibrium; \(D_{\text{eff}}\) is the effective diffusion coefficient (m²/s), \(L\) is the half thickness of slab, \(r\) is the radius (m) of sphere and \(t\) is time (s). Diffusion is strictly related to the random motion of molecules, hence, with their kinetic
energy, the effective diffusion coefficient may be increased by increasing temperature. Arrhenius type equation is the most used model to represent the dependence from temperature and $D_{eff}$ (Craspite et al., 1997; Okos et al., 2007; Orikasa et al., 2008):

$$D_{eff} = D_0 \exp\left(-\frac{Ea}{RT}\right)$$

(9)

where $D_0$ is a constant (m$^2$/s), $Ea$ is activation energy (KJ/mol), $R$ is the gas constant (8.134 J/mol/K) and $T$ is temperature (K). A wide list of diffusion coefficient for several foods and at different temperature may be look up in Okos et al. (2007). An enormous number of scientific papers used the Fick’s law to study the kinetic of drying processes of fruits and vegetables and on its capacity to model the moisture content as a function of time no doubts exist (Ponciano et al., 1996; Sarvacos & Maroulis, 2001; Rastogi et al., 2002; Orikasa et al., 2008; Margaris & Ghiaus, 2007; Giner, 2009). Nevertheless, as reported from Saguy et al. (2005) Fick’s laws contain several assumptions that are often unrealistic for food: fruits and vegetables are considered to have simple geometries; they are considered homogeneous and isotropic media; the heat transfer during the motion of water is completely neglected; the collapse, which refers to dramatic changes in shape and dimension during drying, is completely dropped. Moreover, as it is possible to observe from the Eq. (7) and (8) only the shape and the dimension of samples are taken into account as internal variables. For these reasons, the use of Fick’s law on the basis of the idea that water transfer inside vegetable is driven only by concentration gradient shows to have several limits from the theoretical point of view. However, it allows us to estimate with good approximation the effective average of water diffusion coefficients during drying.

3.2.2 Capillary flow

On the basis of above consideration and taking into account the mass transfer mechanisms reported in table 2, some researchers begun to consider food as porous media rather than homogeneous materials and studying mass transfer on the basis of a different approach. Porous media were defined those having a clearly recognizable pores space (Vanbrakel, 1975). Moreover, by using a definition of Khaled & Vafai (2003), food may be defined as biological material volume consisting of solid matrix with interconnected void. These definitions recognizes the importance of the three dimensional microstructure of food, stating that the mass transport of water is a more complex phenomena than in a non-porous material (Datta, 2007a). Starting from this idea, capillary forces flow must be considered as one of the most important mass transfer mechanism during drying (Datta, 2007a), rehydration (Saguy et al., 2005) as well as during frying, and fat migration in chocolate (Aguilera et al., 2004).

As known, capillary forces are responsible to the attraction among liquid molecules and between them and the solid matrix. Moreover, capillary rise into a pore space is a consequence of an interfacial pressure difference (Hamraoui & Nylander, 2002). These force are very important in food science; for instance, food cannot be completely drained by gravity because capillary forces held water inside capillaries. Moreover, as a consequence of different intensity of capillary forces, water is hardly held in the regions in which solid matrix has low water content and it is less held in the regions highly moist. So, capillary force are among the reasons of: a. the water transport from a region with more water to a region with less one due to the differences in capillary force; b. the difficulty to remove
water from vegetable structure. Historically, Lucas-Washburn equation is recognized as the best equation to model capillary rise into a small pore (Aguilera et al., 2004). The equation shows that the pressure inside a cylindrical capillary is balanced by viscous drag and gravity (Lucas, 1912; Washburn, 1921; Krotov and Rusanov, 1999). From this it is possible to observe that the equilibrium height within a capillary (when the hydrostatic pressure balances the interfacial pressure differences) may be expressed as:

\[ h_e = \frac{2\gamma \cos(\theta_0)}{r \rho g} \]  

where \( h_e \) is the height of capillary, \( \gamma \) is the surface tension of liquid, \( r \) is the radius of capillary, \( \theta_0 \) is the equilibrium contact angle, \( \rho \) is the density of liquid and \( g \) is the gravitational acceleration. So, as the radius of pores reduces as the height of capillary increases. For instance, Hamraoui & Nylander (2002) showed that for glass capillaries with different radius the equilibrium height may change such as those reported in figure 3.

Fig. 3. Equilibrium height of water inside glass capillaries with different radius as a function of time (From Hamraoui & Nylander, 2002)

However, on the basis of a porous media approach, capillary flow in food may be expressed by Darcy’s law (Khaled and Vafai, 2003; Saguy et al., 2005; Datta, 2007a):

\[ u = -\frac{k_l \partial P}{\mu \partial x} \]  

where \( u \), \( P \), \( \mu \) and \( k_l \) are the Darcy velocity (the average of the fluid velocity over a cross section), fluid pressure, dynamic viscosity of the fluid and the permeability of the porous medium, respectively. In the case of liquid transport and taking into account that \( u = n^{\text{press}}/p_l \), where \( n^{\text{press}} \) is the mass flux of liquid and \( p_l \) is the density of liquid, it is possible to define the hydraulic conductivity (Saguy et al., 2005; Datta, 2007a):
where $k_l$ is the permeability of the medium (m$^2$) given by $k_l = k^r k_k$, where $k$ is the intrinsic permeability and $k_k$ is the relative permeability, in the liquid phase, $\rho$ is fluid density (kg/m$^3$), (Datta, 2007a; Weerts et al. 2003). By substituting Eq (12) in Eq. (11) it is possible to observe that hydraulic conductivity, that is the coefficient determining the velocity of flow in the Eq (11), is affected from both liquid and solid matrix properties. The formers are expressed by density and viscosity of liquid (water in the case of vegetable dehydration); instead the latter are characterized by the three dimensional structure of vegetable tissues such as size distribution and shape of pores, porosity and tortuosity. For instance, particles with small size show a high surface area that increases the drag of water molecules that through the porous medium. The result is a reduced intrinsic permeability, hence a reduced hydraulic conductivity and capillary flow (Saguy et al., 2005). Moreover, with the aim to better express in mathematical language the importance of solid matrix on capillary flow, Datta (2007a) reported the hydraulic conductivity in the following form:

$$K = \frac{\rho_l k_l}{\mu_l} = \frac{\rho_l}{\mu_l} \frac{1}{8\pi} \sum \beta_i r_i^2$$

(13)

where $\rho_l$ and $\mu_l$ are respectively the density and viscosity of gas, $k_l$ is the permeability in the liquid phase and $\Delta\phi_i$ is the volume fraction of pores the $i$-th class having radius $r_i$. Again, in the Eq. (13) hydraulic conductivity is affected by two factors: 1. fluid properties by density, $\rho_l$, and viscosity, $\mu_l$; 2. matrix properties. In particular, matrix properties were included into a parameter called intrinsic permeability (Datta, 2007a):

$$k = \frac{1}{8\pi} \sum \beta_i r_i^2$$

(14)

Starting from these basic equations and with the aim to study the capillary flow inside vegetable tissues during drying, it is necessary to consider some aspects. The negative pressure of Eq. (11) (opposite with gravity) due to capillary forces is a function of water content and temperature. The effect of water content is specific for each food (see below) but in general two main cases are reported: porous medium close to saturation (food in which the pores are filled with water); porous medium unsaturated (food in which air is trapped within the structure). Datta (2007a) with the purpose to highlight the effect of water content and temperature on capillary flow, reported Darcy’s law in the following form:

$$n_{i,\text{press, cap}} = -p_1 \frac{k_1}{\mu_1} \frac{\partial P}{\partial s} + p_1 \frac{k_1}{\mu_1} \frac{\partial c}{\partial s} + p_1 \frac{k_1}{\mu_1} \frac{\partial T}{\partial s}$$

(15)

where the first, second and third terms on the right hand are the mass flux due to gas pressure, the capillary flux due to concentration gradient (i.e. the gradient of water content) and the capillary flux due to temperature gradient, respectively. Also Datta (2007a) reported that in the case of food close to saturation, only the first term may be considered because the capillary pressure of water ($P_c$) is very small. Instead, for an unsaturated food (as in the case of drying process) into the Eq. (15) may be included only the second and third terms because the pressure of gas phase ($P$) is negligible. Nevertheless, as above reported, the
effect of water content on capillary force is hardly to obtain and little (almost none) data are available in food science. In particular, the relation between moisture content and capillary pressure head and/or hydraulic conductivity are commonly available for soil science (retention curves) but very hard to find in literature concerning food. In general, capillary pressure head (h) is inversely related to moisture content; instead hydraulic conductivity (k) shows a direct correlation (figure 4). Retention curves are difficult to obtain in food but, as reported from Saguy et al. (2005), a possible approach is to convert moisture content into a volumetric water content (θ, m³/m³) and the aw values in a capillary pressure head (m); briefly, the approach is to convert isotherm into a water retention curve. Again this is experimentally possible measuring h by common techniques used in soil science (Klute, 1986) or by using the Kelvin equation:

\[ h = \frac{RT}{\rho_w g V_m} \ln(a_w) \]  

(16)

where h is the capillary pressure head (m), R is the gas constant (m³ Pa/mol K), T the temperature (K), \( \rho_w \) is the density of water (kg/m³), g is the acceleration due to gravity and \( V_m \) is the molar volume of water (0.018 m³/mol). In figure 5 the adsorption isotherms and the water retention curves obtained from Eq. (16) for tea (type I), wheat (type II) and apricot (type III) are reported. Another example of water retention curve was reported from Weerts et al. (2003) which studied the rehydration of tea leaf. Now, the concept of hysteresis of isotherms shown in figure 3 may be explained on the basis of different phenomena: the ink bottle effect due to the non uniformity of shape and size of interconnected pores; different liquid-solid contact angle during dehydration or rehydration process; the entrapped air in newly wetted porous media; swelling and shrinking during dehydration or rehydration (Saguy et al., 2005). At last, since water hardly interacts with biological tissues of food it is important to consider that the parameters such as porosity, size and shape of pores and tortuosity may significantly change during dehydration due to collapse, leading to a change of intrinsic permeability, hence, the capillary flow.

Fig. 4. Relation between volumetric moisture content and capillary head (h), hydraulic conductivity (k) and capillary diffusivity (Dc) for porous soil structure (from Datta, 2007b)
3.2.3 Gas flow due to pressure gradient

Gas flows such as water vapor and air flow due to differences in pressure gradient inside pores may be expressed by Darcy's law with the same equation previously discussed. We reported only the analogue of Eq (11) for gases:

$$n_g^{\text{press}} = - \rho_g \frac{k_g}{\mu_g} \frac{\partial P}{\partial s}$$  \hspace{1cm} (17)

where $n_g^{\text{press}}$ is the mass flux of gas, $\rho_g$ is the density, $\mu_g$ is the viscosity, $P$ is the total pressure in the gas phase.

3.2.4 Other mechanisms

Others mass transport mechanisms have been hypothesized in literature although the difficult to modeling vapor, gases, and liquid motion, which are also greatly affected by heat transfer, makes the literature very poor. Stephan diffusion refers to motion of vapor across a layer of stagnant air that is the case of convective drying. Knudsen diffusion occurs when the mean-free path of the molecules is long in comparison with the pore diameter. A combined condensation and evaporation phenomena may promote water flow. In fact, in a closed pore, water may be vaporized by heating at its end and it may condense at the opposite end. So, liquid is transport in the opposite direction of vapor flow along the wall of the pore. Furthermore, the importance of the cross influence of mass and heat transfer should be considered in food science but, in general, it is completely drop. Irreversible thermodynamic theory studies these cross influence. In particular, when heat and mass transfers occur simultaneously, the temperature gradient may influence mass transfer (Soret effect) and the concentration gradient may influence heat transfer (Dufour effect) (Hallstrom et al., 2007).

3.3 Air drying

During air dehydration heat is transferred from surrounding air to the surface of vegetables by convection and inside it by conduction as predominant mechanisms (due to internal thermal gradient) and by convection (due to moisture migration) with less extent. At the
same time, water evaporates from the surface of vegetable toward the surrounding hot air (which has a low humidity) and it moves inside vegetables toward its surface by liquid diffusion, vapor diffusion, capillary flow and viscous flow. A schematic representation of air drying is shown in figure 6. Even though it is recognized that all the above water transfer mechanisms may occurs simultaneously, the trend of drying processes are usually represented by a drying curve obtained plotting moisture content as a function of time (figures 7a) and the kinetics by plotting rate constant as a function of moisture content (Figure 7b). Traditional literature divides the drying curve into three regions. When the drying is at time zero the moisture concentration may be at the points A or A’ respectively in the case in which food is at cold or hot temperature. As time as process proceeds, a region called “constant rate period” is met. Here, during heating water evaporates from the surface of food and the vapor moves away by convective air. At the same time, water molecules move from the core of vegetable to the surface replacing the water just evaporated. This phenomenon, usually considered as diffusive, maintains the water concentration at the surface and drying rate at constant levels. At point C, named “critical moisture content”, the time necessary at the water molecules to reach the surface becomes significantly high due to the increment of the path length. In this condition the rate of diffusing water is lower than the evaporation rate leading to a progressive reduction of the overall drying rate. This behavior is represented from the region C-D and it is called as “falling rate period”. Moreover due to this condition, the surface of food progressively dried until it becomes completely dehydrated (point D). Once this condition is reached the evaporation will continue from the internal regions of vegetable pieces.

Fig. 6. Schematic representation of air drying technology (from Craspite et al., 2007)
Mass Transfer Mechanisms during Dehydration of Vegetable Food: Traditional and Innovative Approach

Datta (2007) reported the temperature, moisture content and total pressure profiles across general biological food systems with high moisture content as in the case of several fresh vegetables during air drying (figure 8a, 8b and 8c). It is possible to observe that temperature increases slowly reaching a value of 55°C after 60 minutes; moreover, it remains almost constant across the sample. Moisture content profile shows a maximum value (close to saturation) at zero time which begins to reduce after 20 minutes of heating. The trend across the sample did not show difference in the first 40 minutes of heating. Nevertheless, as heating proceeds a slight decrease of the moisture content at the surface occurs. This is because the rate of internal diffusion of water is less and it becomes unable to replace the evaporated water. Pressure profile shows values close to atmospheric pressure leading to the absence of intense vapor formation.

From an engineering point of view the constant rate period is recognized as externally controlled and the falling rate period as internally controlled. External control means that the process is controlled by variables which are independent from the properties of fresh vegetables (external variables) such as air temperature, relative humidity, air flow. Instead, internal control means that the process is controlled from vegetable characteristics (internal variables) among which the size and shape, the collapse phenomenon during drying, chemical composition of vegetables and its three dimensional microstructure are the most important. So, it is worth noting that the falling rate period is specific for each systems and it

Fig. 7a, 7b. Typical trend of convective drying. A) moisture content as a function of time. B) drying rate as a function of moisture content. (Adapted from Okos et al., 2007)
Fig. 8a, 8b, 8c. General temperature, water content and total pressure profiles of high moisture material submitted to convective drying (From Datta, 2007) could significantly change among different vegetables. As reported from Okos et al. (2007) the importance of the external and internal mass transfer may be highlighted by using the concept of overall mass transfer coefficient:

\[
\frac{1}{K} = \frac{1}{K_c} + \frac{L}{D_{\text{eff}}}
\]

(18)

where \( K \) is the overall mass transfer coefficient (m\(^2\)/s), \( K_c \) is the external controlled mass transfer (m\(^2\)/s), \( L \) is the characteristic dimension of the sample and \( D_{\text{eff}} \) is the effective diffusion coefficient (m\(^2\)/s).
The effects of external variables have been extensively studied (Lee et al., 1983; Mulet et al., 1989; Karathanos & Belessiotis, 1997; Krokida et al., 2003). For instance, Krokida et al. (2003) studied the effect of air temperature, air humidity and air velocity on the drying kinetics of several vegetables such as green, yellow and red peppers, pumpkin, green peas, carrots, tomatoes, corn, garlic, mushrooms, spinach, onions, celery and leek. As expected, the authors reported that air temperature is directly correlated with drying rate and that is the most important external variables. This result is in accordance with several researchers (Senadeera et al., 2003; Leiva Diaz et al., 2007; Orikasa et al., 2008). For example, Senadeera et al. (2003) showed an increase of rate constant as temperature increased from 30°C to 40°C and 50°C during air dehydration of green beans, potatoes and peas. Orikasa et al (2008) studying the air drying of kiwifruit slices showed a significantly increase of rate constants as temperature increased from 40°C to 70°C. Krokida et al. (2003) studied the effects of both the flow and the humidity of air on drying rate of several vegetables showing that these variables were less important in comparison with temperature. In fact, air velocity (in a range of 1.5 and 2.6 m/s), which is considered important to limit the external resistance to the drying, was shown to be almost negligible. Thus the authors stated that the water diffusion toward surface was high and that the external resistance was not very important. Furthermore, they showed that the effect of air humidity was significant only when its value increased from 20% to 40%. Senadeera et al. (2003) studied the effect of shape of samples on drying rate of some vegetables. In particular, green beans with a length to diameter ratio (L:D) of 1:1, 2:1 and 3:1 and potatoes with an aspect ratio (A:R) of 1:1, 2:1 and 3:1 were used during drying in fluidized bed. Results showed that in both cases the rate constants decreased increasing L:D and A:R values as a consequence of an improvement of surface area per unit of volume. The importance of the externally and internally controlled period during air drying is historically recognized but in the last years some new finding need to be considered. In general assuming that constant rate period is only externally controlled none water diffusion due to moisture gradient inside food should be detected. Analyzing the drying curve of onions, carrots, mushrooms and garlic Pabis (1999) found that the initial linear segment could be significantly extended; the author ascribed this behavior to an external control of the process. Fiorentini et al. (2008) studying the drying curve of a tomato pectic gels, showed that the falling rate period may be divided in two sub-regions among which the first (at high moisture content) appeared to be both internally and externally controlled and the second one was strictly controlled by internal diffusion. Giner (2009) studied the drying curves of a sucrose-added apple pectic gels in the first 90 minutes of the process, showing, in accordance with Pabis (1999), a linear trend. Nevertheless, the author showed that the experimental data were well fitted from a form of Fick’s law valid for both internal and external controlled drying process. An accurate fitting was obtained by using a Biot number of 2 which states that the external resistance is twice of internal one. Furthermore, the author estimated the local moisture content along the thickness of the samples showing that a moisture gradient exists hence, this constant rate period cannot be exclusively governed by external variables.

3.4 Microwave drying
Microwaves (MW) are electromagnetic waves with a frequency in the range of 300 MHz and 300 GHz. Among these only two are permitted for food application: 915 MHz for industrial application and 2450 MHz for microwave ovens. The use of microwaves is regulated by the
maximum exposure or absorption of human working in a microwave environment and by the maximum leakage of the microwave equipment (Reiger & Schubert, 2005). MW dehydration of fruits and vegetables is based on the absorption of the electromagnetic waves from biological tissues and their conversion in thermal energy. As known, these factors are included in the relative permittivity of food ($\varepsilon^*$):

$$\varepsilon^* = \varepsilon' - j\varepsilon''$$  \hspace{1cm} (19)

where $\varepsilon'$ is the dielectric constant which refers the ability of food to absorb microwave and $\varepsilon''$ is the dielectric loss factor which is a measure of the conversion of electromagnetic energy into a thermal one. These two constants are affected by frequency, temperature, and composition of food materials with particular reference to salt, fat and water content. The influence of these variables have been studied in details and several information may be find in the book of Schubert & Reiger (2005). Briefly, since microwave are absorbed from polar molecules of water, due to its high content and its homogeneous distribution, that is the most important internal variable affecting microwave processing of food. For these reasons, microwaves promote a volumetric heating that proceeds from the core of vegetables foods (with higher moisture content) to the surface (the region with less moisture content). In this way, when microwaves are used as drying method the mass transfer mechanism is extremely different from the convective dehydration. At first, it is during the falling rate period that microwave drying exhibit the most important advantage. As previously reported this phase of the process is usually considered as internally controlled by diffusion mechanism; so, the volumetric heating promotes a fast water diffusion inside the core of food (Erle, 2005). However, although the internal diffusion is very fast, a reduction of drying rate as a function of time, is observed. This is because $\varepsilon'$ and $\varepsilon''$ values decrease during the process due to the reduction of water content. However, the main peculiar characteristic associated with MW drying is the formation of a high vapor pressure into the internal region of sample that push water toward the surface significantly increasing water transport. Ni et al. (1999) and Datta (2007) by using a multiphase porous media model, showed the characteristic profiles of temperature, water content and total pressure across a generalized food system during microwave heating (figures 9a, 9b and 9c). In the case of fruits and vegetables (high moisture porous material), the increase of temperature across all layer of samples is very fast reaching the boiling temperature (with a maximum of 107°C) in only three minutes. In particular, an heating rate of 0.69°C/s was estimated. After, temperature begins to reduce due to the decreasing of moisture content that lead a drop of dielectric properties of vegetable tissues; nevertheless, temperature on the surface is always lower than the internal part. Pressure profile is extremely different in comparison with convective drying. After three minutes, the intensive heating in the internal regions leads to the formation of a high vapor pressure gradient across the sample with its maximum value of 32 kPa (0.32 atm). Again, this is the cause of a fast water transport from the core of samples toward its surface. Obviously, total pressure at the surface remains at its initial value (atmospheric pressure) because there is a open structure in contact with surrounding air. Moisture content at time zero is homogeneous across the sample but after three minutes the generated vapor pressure push water promoting its accumulation at the surface of sample which becomes fully saturated (Figure 9c). As time proceeds (after 6 minutes), moisture content inside the sample reduces but at the surface it remain approximately constant. Different behavior is observed in the case of microwave
heating of low moisture materials (Ni et al., 1999). In this case, the temperature across the sample increases slowly as a function of time due to the lower initial moisture content. Also, the heating rate was estimated to be 0.27°C/s. Pressure gradient shows the same trend of temperature and its maximum values (about 1.20 kPa) is less than those estimated for high moisture materials. Again, the moisture profile shows a fairly reduction at the surface in the first 6 minutes but after at 7 and 8 minutes the prolonged heating produce an internal vapor pressure sufficient to promote the water motion toward the surface that consequently becomes more moist. On the other hand, the core of sample dehydrated progressively (Ni et al., 1999).

Microwave drying has been used to remove water from several vegetable such as herbs (Giese, 1992), potato (Bouraout et al., 1994), carrot (Prabhanjan et al., 1995), banana (Maskan, 2000), kiwifruit (Maskan, 2001). Since microwave heating is volumetric the number of process variables are reduced and the predominant are the microwave power, the dielectric properties of food, size and shape of samples. For instance Maskan et al. (2000) studied the effect of microwave power and the thickness of banana slices on drying rate. As expected, the author reported a significantly increase of drying rate as a function of energy power in a range of 350 W and 790 W. Also, the rate constants were 10-fold greater that the estimated value during air convective drying. However, when banana slices with a thickness of 4.3 mm, 7.3 mm and 14 mm were respectively used, the rate of the process directly increased. This result seems to be in disagreement with the increase of path length.

Fig. 9a, 9b and 9c. General profile of temperature, moisture content and total pressure across sample submitted to microwave drying (from Ni et al., 1999)
of water; nevertheless it was explained by taking into account that the volumetric heating may produce a vapor pressure gradient as greater is the size of the sample (Maskan et al., 2000).

### 3.5 Osmotic dehydration

Osmotic dehydration (OD) is widely applied to partial removal of water from fruits and vegetables. OD occurs when vegetables are immersed into a hypertonic solution leading to the formation of an osmotic pressure gradient able to remove water from vegetable tissues. However, since cell membranes are not completely semi permeable a countercurrent flow occurs: 1. water moves from vegetable tissues toward hypertonc solution; 2. osmotic agent flows inside vegetable. Also, some chemical compounds of vegetables such as pigments, vitamins, salts, etc., may be leak into osmotic solution promoting changes of nutritional and sensorial properties of food products. The scientific and industrial interest for osmotic dehydration is related to the possibility to drying fruits and vegetables at room temperature or by a low heating minimizing the heat damages on food and significantly reducing energy cost of the treatment. Moreover, OD may improve texture, pigments stability and color of dried products (Rault-Wack, 1994; Krokida et al., 2000). In this way, OD has been used as pretreatment for air drying, vacuum drying, freeze-drying, freezing, microwave drying, etc., with the aim to increase nutritional, sensorial and functional properties by maximizing the integrity of vegetable tissues (Torreggiani, 1993). In terms of water and solutes transport, osmotic dehydration is usually considered as a diffusive phenomenon in which the driving force is the osmotic pressure gradient between vegetables and osmotic solution. The predominant resistance for water and solutes flow is characterized from cell membranes, their mechanical properties and their changes during the process. Unfortunately, these changes are not commonly considered in literature and several papers are still based on a macroscopic point of view which implies that the dehydration occurs under a uniform moisture gradient and that diffusion coefficient is constant through the food (Figure 10a). Instead, this is not realistic assumption because several changes on cell structure have been reported in literature (Marcotte et al., 1991; Alzamora et al., 1997; Ferrando and Spies, 2001; Lewicki et al., 2005). For instance, Ferrando and Spies (2001) observed a degradation of middle lamella for onion tissue and a reduction of cross section area of 40%-60%; moreover, in the case of strawberries the authors showed a typical plasmolysis with the detachment of plasmalemma from the cell wall. Lewicki et al., (2005) showed that osmotic dehydration causes changes in size and shape of apple cells. More generally, Barat et al., (2001) reported that cells surrounding intercellular spaces shrunk, the solid matrix is deformed and the porosity increases. On the basis of these results, it must be assumed that the resistance of cell membranes significantly change during drying, hence different constant diffusion coefficients across the vegetables should be expected. Rastogi et al. (2000) proposed a mechanism to describe the behavior of biological tissue submitted to osmotic dehydration taking into account the structure changes of cell membranes (figure 10b). The mechanism is based on the existence of a dehydration front (Δx) that during drying moves toward the centre of the sample. Dehydration front is considered a region in which the cell membranes is damaged and shrunk as a results of a critical value of osmotic pressure gradient. So, diffusion coefficient value at dehydration front (D2) is the greater across the sample. In the region close to the surface (in contact with osmotic solution) cell membranes are damaged and shrunk and water molecules flow toward hypertonic solution with a diffusion coefficient D3<D2. This is because the osmotic pressure gradient is less than in dehydration front. Moreover, the internal region shows cells at their natural turgor pressure hence, with a diffusion coefficient (D1) much lower than D2 and D3. Moreover,
Rastogi et al (2000) proposed to use of a cell disintegration index ($Z_p$) (also called permeabilization index) to measure the relative reduction of intact cells across the sample. Figure 10b shows the profiles of moisture content ($M/M_0$) and $Z_p$ as a function of the relative distance from the hypertonic solution. It is possible to observe that in the dehydration front cell disintegration index sharply increased and moisture content reduces significantly because of the cells are dehydrating.

However, some researchers showed that this model does not completely explain the water mass transfer mechanism. For instance, De rossi et al. (2008), studying the osmotic dehydration of apple cylinders by MRI techniques showed a reduction of spin-spin relaxation time ($T_2$) in all layers of samples leading to the idea that drying occurs in all layer of samples (figure 11).

![Fig. 10a, 10b. Schematical representation of osmotic dehydration in homogeneous (non biological) material (a) and for biological system (b). (from Rastogi et al., 2000)](image)

It should be noted that several factors may affect the rate of the osmosis among which external variables such as concentration of osmotic solution, type of osmotic agents, temperature, agitation rate, product solution mass ratio as well as the internal variables such as dimension and shape of vegetables, structure properties of vegetables (porosity, permeability of cell membrane, ripening index, etc) are the most important. A wide number of scientific papers described in considerable details the influence of these variables on the kinetics of OD (Lerici et al., 1985; Torreggiani, 1993; Raoult-Wack, 1994; Rastogi and Raghavarao, 1994; Rastogi and Raghavarao, 1995; Rastogi et al., 1997; Mavroudis et al., 1998; Spiazzi and Mascheroni, 1997; Chiralt and Talens, 2005; Sacchetti et al., 2001; Rastogi et al., 2000;...
Fig. 11. T2 profiles along the cross of apple cylinders submitted to osmotic dehydration in sucrose solution (from Derossi et al., 2008).

2002; Azoubel et al., 2004; Tsamo et al., 2005). Obviously, temperature and concentration of osmotic solution are directly correlated with osmotic dehydration rate. However, by using a solution with high concentration, water loss is favored in comparison with solid gain; instead, the use of osmotic solution at low concentration favors the impregnation at the expense of dehydration. Due to the dilution effect that proceed during the process, osmotic solution with a product:solution mass ratio of 1:20 is considered sufficient to maintain a uniform driving force during drying. Nevertheless, it should be considered that this condition is unrealistic in practical application due to the lower production output and high costs. With an industrial point of view a product:solution mass ration of 1:4 or 1:5 may be used. The type of osmotic agents is an important process variables. Traditionally, hypertonic solutions are prepared by dissolving different type of sugars in tap water. In these cases the use of compounds with high molecular weight promotes the dehydration rather than the impregnation; on the other hand, sugars with low molecular weights are used from candy industries (Rastogi et al., 2002). However, in the last years the use of complex solutions prepared with water, sugar, sodium chloride, etc., received much attention but it appeared to be more complex in terms of dehydration kinetics (Sacchetti et al., 2001; Tsamo et al., 2005; Derossi et al., 2010). For instance, in disagreement with the higher impregnation effect caused by solutes with low molecular weight, Tsamo et al. (2005) reported that water loss of tomato and onion samples submitted to OD in salt solution was higher than in sucrose solution. This behavior was explained taking into account that the small molecules of NaCl may through cell membranes producing a double source of pressure gradient: at cytoplasm and vacuole level. In this way, more water could be removed from cells. Moreover, the authors showed that the maximum dehydration was obtained when a mixed solution was used probably because the increase of concentration gradient. Nevertheless, when the rate of OD in sucrose, sodium chloride and mixed solution were studied, different behaviors were observed (Sacchetti et al., 2001). The authors showed that at low concentration of sucrose, the initial rate constant of OD reduced as NaCl concentration increased. This antagonist effect was explained by a reduction of the cell membrane permeability. Also, in accordance
with other researchers (Collignan and Raout-Wack, 1994) it was hypothesized that sodium chloride due to its small molecular dimension may penetrate into the cells leading to a reduction of the osmotic pressure gradient. The agitation rate of the solution is an important variable able to modify the mass exchanges at the surface of vegetable tissues. Mavroudis et al. (1998) studying the effect of agitation level on osmotic dehydration rate of apple cylinders showed that water loss increased rising, the Reynolds number; in fact a higher dehydration in the turbulent flow region rather than in the laminar flow region, was observed. So, an external obstacle to the water transfer was confirmed. Instead, solid gain was not influenced from the agitation rate.

As previously reported, diffusion coefficients of water and solutes are greatly hindered from the resistance of cell membranes which is related to the Zp value. Under these consideration, a technological approach to improve mass transfer is the imposed increase of cell’s permeability. This is possible by performing some treatments such as high hydrostatic pressure (Rastogi et al., 1999), pulsed electric field (Omowayne et al., 2003; Amami et al., 2007), ultrasound (Simal et al., 1998; Fernandes et al., 2008), centrifugal force before osmotic dehydration. As known, high hydrostatic pressure damage the cell walls increasing their permeability hence, the mass transfer. It was shown that water diffusion coefficients for pineapple samples submitted to osmotic dehydration increased of 4-fold by using a pressure range between 100 and 800 Mpa (Rastogi et al., 1999). Also, Rastogi et al. (2000) showed that hydrostatic pressure and osmotic dehydration had a synergistic effect on the enhancement of water removal from potato samples. Pulsed electric field has been shown to have a permeabilization effect on cells due to local structure damage and the breakdown of cell membranes. In general, it is widely accepted that if an electrical potential is applied between the both side on cell membrane the related motion of the charges along the electric field lines produces a deformation of cell membranes. If the electric potential (E) is greater than a critical value ($E_{cr}$), which depends from the properties of membranes, rupture and breakdown occurs (Lebovka et al., 2001; Amami et al., 2007). In general an electric potential of 1 V is sufficient to produce the permeabilization phenomenon. Amami et al. (2007) studying the effects of PEF and centrifugal force on osmotic dehydration, showed that the application of PEF improved water loss and solid gain. The same results were reported from Ade-Omowaye et al., (2003). Ultrasounds are characterized from a series of compression and rarefaction waves. The most important effect of these waves is the cavitation with a formation of bubbles of vapor or gases. Under certain conditions this bubbles becomes unstable and collapse, generating mechanical forces that damage the its increasing cell permeability. Simal et al (1998) applying ultrasound of 40 KHz showed an increase of water loss of 14%-17%. Other results on the use of these pretreatments to increase mass transfer of fruits and vegetables during OD are available on Bohuon et al. (1998), Carlcel et al., (2002); Taiwo et al., (2003) Fernandes et al., (2008), Stojanovic & Silva (2007).

In the first section of this paragraph, although the importance of internal factor such as permeability of cell membranes variables are reported, OD has been exclusively considered as diffusive phenomenon and none different mass transfer mechanisms was taken into account. Nevertheless studies at microscopic level detected an effectiv diffusion coefficient of 2-fold greater than the $D_e$ value obtained or estimated taking into account the only diffusion (by experiment at macroscopic level). These results stated the existence of an additional mass transport mechanism. This is the hydrodynamic mechanism (HDM) which is a result of a capillary flow caused by a pressure gradient (externally imposed or generated) as a consequence of the changes in intercellular spaces during OD (Fito, 1994;
In figure 12, HDM is schematically subdivided in five steps. Before the immersion of vegetables inside osmotic solution, the pressure inside pores is equal to atmospheric pressure (step 1, $t_0$). After the immersion, osmotic solution partially penetrates inside capillaries and it compresses internal gas with a result of an increase of internal pressure (step 2, $t_1$). Nevertheless, drying process begins due to osmotic pressure gradient, cells leak water and shrink (step 3, $t_2$). In this condition, the volume of capillary pores increases leading to a decrease of internal pressure that becomes less that external one. In this way a pressure gradient is created and the suction of osmotic solution is promoted (step 4, $t_3$). This phenomenon will continue until the complete impregnation occurs or the equilibrium between external and internal pressure is reached (step 5, $t_n$) (Chiralt & Fito, 2003). This mechanism based on the involving of the internal volume of vegetable structure was exploited to increase the rate of osmotic dehydration by externally imposing an high pressure gradient. Vacuum osmotic dehydration (VOD) is a treatment based on the filling of capillary pores of vegetables that increases the liquid-solid surface contact area improving mass transfer. VOD is performed by applying two steps: the application of a vacuum pressure for a short period called vacuum period ($t_1$); the restoration of atmospheric pressure and its maintaining for a relaxation period ($t_2$). In the first period, by the application of a pressure usually in a range of 50 mbar and 400 mbar, the removal of native liquids and gases from capillary pores as well as gas expansion, are promoted. In the second step the restoration of atmospheric pressure produces the suction of the osmotic solution inside the pores and the deformation-relaxation phenomenon which is able to modify the dimension of pores (Fito, 1994; Zhao & Xie, 2004; Atares et al., 2008). A wide bibliography concerning the main process variables of VOD, the mathematical modeling and the effect on quality of vegetables is available (Fito, 1994; Fito & Chiralt, 1995; Salvatori et al., 1998; Fito et al., 2001; Gras et al., 2002; Mujica-Paz et al, 2003; Zhao & Xie, 2004; Atares et al., 2008). Moreover, if the relaxation period is extended like those of a traditional osmotic dehydration, the process is defined pulsed vacuum osmotic dehydration (PVOD). In this case a short vacuum pulse is applied at the initial stage of osmotic treatment. It is worth nothing that the interest in the exploiting of capillary pores to impregnate food by different substances such as ingredients, antioxidants, pigments, organic acids, nutritional or functional compounds etc. has exponentially increased in the last 10 years (Zhao & Xie, 2004; Betoret et al., 2003; Derossi et al., 2010).

### 3.6 Infrared drying

In the last years, the interest on the use of infrared as method to dehydrate thin food is greatly increased. In general the supply of heat by infrared radiation has given good results for thin vegetables with a high surface area exposed at radiation. However, the transmissivity characteristics of food depends on their chemical composition: FAR-infrared radiation seems to be more effective for thin layer and NEAR-infrared (NIR) should give better results for thick material. The use of infrared has several advantages in comparison with traditional convective methods. Novak and Lewicki (2004) summarized them as follow: heat efficiency, high diffusion coefficient, low drying time, the process is performed at room temperature because of air is transparent to infrared; the equipment may be compact. In terms of mass transfer mechanism during infrared drying of food, few information are available. Infrared are absorbed on the surface of a moist food and the hot point is at a distance from the surface depending from the extinction coefficient. As small is
this coefficient as more is the distance between surface and the layer with the maximum temperature. From this region, heat moves simultaneously toward surface and the core of sample by conduction promoting the evaporation of water (at the surface) and increasing diffusion coefficient of water (in internal regions). So, water and heat move in the same direction above the absorbent layer and in countercurrent below it. Nowak and Lewicki (2004) studied the effect of some process variables such as air velocity and the distance of the emitters from the samples on the kinetics of infrared drying of apples slices. The results showed that emitter distance is directly related to drying rate. The flux of water was 1.25 (g/m²s), 1.10 (g/m²s) and 1.0 (g/m²s) when a distance of 10 cm, 20 cm and 30 cm were used with an air velocity of 0.5 m/s. Moreover, it is worth noting that drying rate resulted inversely correlated with air velocity. This behavior was explained taking into account that air is transparent at IR but, in turn, it may be heated from the surface of food. During drying the surrounding air is heated by the surface of food leading to its cooling. Obviously as greater is air velocity as faster is the cooling of food surface hence, water evaporation is reduced. Other examples on the use of infrared drying are available by Lampinen et al (1991); Sakai & Hanzawa (1994), Ratti & Mujumdar (1995), Nowak & Lewicki (1998).
3.7 Ultrasonic drying
As previously reported ultrasonic waves are characterized from a subsequent series of compression and expansion. This forces, crossing vegetable tissue, may increase their permeability creating microscopic channels in which water may easily flow. Moreover, the cavitation promotes the formation of unstable gas bubbles which may collapse reducing the mass transfer resistance of cell membranes (Mason et al., 2005). Even if wide evidence on the mechanism involved during ultrasonic wave not exists and although this is an emerging technology not still used at industrial scale, some researchers reported interesting results. Fluente-Blanco et al (2006) studied the ultrasonic dehydration applied to carrot cylinder by using a laboratory system equipped with a trasductor, a vacuum chamber and a forced air-generator. The vacuum chamber performs the suction of water from the samples and the fan was used to increase the removal of internal moisture. The authors showed a significantly reduction of moisture content in comparison with traditional convective drying. Also, it was shown a direct influence of ultrasonic power on the weight reduction of carrots.

3.8 Hybrid technologies for vegetable dehydration
The analysis of the above dehydration methods allows to highlight their extremely different characteristics such as mass transfer mechanism involved, heating rate, pressure gradient inside vegetable tissues, effect of cell membranes, etc. So, each of these shows to have some advantages and some disadvantages. For instance, the most important problem related to the use of hot air dehydration is the low water diffusivity during the falling rate period. Osmotic dehydration may be performed at room temperature drastically reducing heat damage but it is characterized from a low drying rate. So, when the use of a single drying techniques is not the best way to obtain vegetable food with high quality, the possibility to apply hybrid technologies is very interesting. Microwave-air assisted drying is probably the most studied hybrid dehydration techniques. Since air drying is low efficient during the falling rate period due to internal resistance, the use of microwave heating may significantly increase the rate of process. Microwave-vacuum dehydration is used to obtain a fast removal of water from the food structure. This is the result of an external negative pressure which is added at the internal pressure gradient promoted from the vapor generation. Osmotic dehydration may be used as pre-treatment to air drying, microwave drying, microwave-vacuum drying, etc. For instance, Erle & Schubert (2001) studied the application of a combined osmotic and microwave-vacuum dehydration of apples and strawberries. The use of osmosis during the first stage of dehydration allowed to remove water reducing the energy consumption of the treatment. In the last stage of drying curve (when osmosis is less effective) microwave-vacuum allowed to remove water minimizing heat damage. In fact the authors showed a vitamin C retention of 60% and the volume of fresh sample was preserved of 60% for apple and of 50% for strawberries. Other example of hybrid technologies are: ultrasonic-air drying, radio-frequency, infrared-microwave drying; microwave-vacuum drying, infrared-heat pump drying, infrared convective drying. A more deep description of these technologies was reported from Chua & Chou (2005).

4. Mathematical modeling of water and solute transfer during vegetable dehydration
Mathematical modeling is a fundamental research field in food science. The term model is difficult to precisely define. An intuitive definition may be expressed as follows: a model is a structure similar to the original (Pabis, 2007). A model is an abstract system that may be
obtained also from the results of experimental process performed on the existing original. If the model is an empirical equation, it may give only information on the existing original under the condition in which the experiments have been carried out. Empirical model is obtained using as starting point a phenomenon experimentally observed. From it, the model is extracted and proposed with the aim to obtain information on the principal characteristics of the existing original. In other word, empirical model states the existence of a new empirical regularity between independent and dependent variables but it cannot provides any scientific explanation. Instead, if the model is theoretical it may provide information on both the action of the original and its structure which promoted that action (Pabis, 2007). Theoretical model is obtained deductively from the true statements of the theory; it results logically from the theory. Often, empirical models are also called phenomenological and theoretical models as named mechanistic.

In terms of vegetable dehydration a wide number of equations have been proposed and used to model mass transfer during several dehydration techniques. Instead, less are the theoretical models available. Here, the most important are going to discuss taking into account both traditional and innovative equations.

4.1 Empirical models

As known, the most important empirical models for mass transfer during drying processes of food are the Fick’s laws. As previously reported, it must be emphasized that Fick’s laws are diffusion equations. So, when these models are used, the main assumption is that water and solutes diffuse inside vegetable tissues on the basis of the following equation:

$$ F = -D \frac{\partial C}{\partial x} $$  (20)

where $F$ is the rate of transfer per unit area of section, $C$ the concentration of diffusing substance, $x$ the space coordinate, $D$ is the diffusion coefficient. From the equation (20) it was obtained the fundamental differential equation for diffusion:

$$ \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} $$  (21)

The equations (20) and (21) are usually referred as the first and second Fick’s laws. Solutions of the second Fick’s law are reported for simple geometries such as infinite flat plate, rectangular parallelepiped, infinite cylinder, finite cylinder and sphere (Crank, 1975). The solutions for infinite flat plates and spheres were previously reported in Eq (7) and (8). Instead, Eq. (22), (23) and (24) report the solution of second Fick’s law for rectangular parallelepiped, infinite and finite cylinder, respectively (Crank, 1975; Rastogi et al., 2002; Azoubel et al., 2004)

$$ MR = \frac{M - M_e}{M_0 - M_e} = \sum_{a=1}^{\infty} C_a \exp \left[ -D_{\alpha \epsilon} q_{\alpha} \left( \frac{1}{a^2} + \frac{1}{b^2} + \frac{1}{c^2} \right) \right] $$  (22)

$$ MR = \frac{M_f}{M_e} = 1 - \sum_{a=1}^{\infty} \frac{4}{(ab)^3} \exp \left[ -F_0 \left( \frac{a \epsilon}{ab} \right)^3 \right] $$  (23)
where for Eq (22): $C_e$ is equal to $2a/(1+a)/(1+a+a^2q_n^2)$, where $q_n$ values are the non zero positive roots of the equations $\tan q_n = aq_n$, $a$, $b$ and $c$ are the sides of the parallelepiped.

For Eq (23): $a$, $b$, $c$ are the roots of the equations $J_0(au_n) = 0$; $F_3$ is the Fourier number that is given by $D_n t/a^2$, where $D_n$ is diffusion coefficient.

For Eq (24): $C_p=0$; $C_{cm}$ is equal to $4a(1+a)/(4+4a+a^2q_n^2)$, where $q_n$ are the roots of the equation $aq_n^2 + (q_n + 2)J_1(au_n) = 0 = 0$. The $J_0(au_n)$ and $J_1(au_n)$ are given by the roots of Bessel function of zero and first order respectively. Furthermore, $1/A^2 = 1/r^2 + 1/(t^n/2)(q_{pm}/q_{cm})^2$.

In general when the Fourier number is greater than 0.1 only the first term of the equation is significant and other terms may be neglected (Rastogi et al., 2002). Moreover, some author simplified the second Fick’s law by using the following (Torregiani et al., 1986; Giangiacomo et al., 1987; Muijaffar & Sankat, 2005):

$$\frac{X_L}{X_\infty} = K\sqrt{t}$$

(25)

Second Fick’s law has been widely used to study the kinetics of several drying technologies also applied to different fruits and vegetables Rastogi & Nirajan (1998), Rastogi et al. (1999), Senadeera et al., (2003) Azoubel & Murr (2004), Babalis & Belessiotis (2004); Margaris & Chiaus (2007); Oriakasa et al. (2008), Giner (2009). In all cases a good accuracy between experimental data and the fits was obtained. However, as previously reported it should be considered that several assumptions, often unrealistic for vegetable dehydration, are assumed into Fick’s laws. Some of these were previously discussed in this chapter (paragraph 3.2.1) but others may be find from Ertekin & Sutunagolu (2000) and Saguy et al (2005). Nevertheless, it is worth nothing that no doubt exist of the capacity of Fick’s laws to well fit experimental drying curves hence, they are very useful if our aim is to study dehydration kinetics in different operative conditions or to predict the time length of the process necessary to reach a desired moisture content into the product. Maybe the most simple empirical model was born on the observation that drying curves has, in general, an exponential trend. In this way, some researchers (Orikasa et al., 2008; Senadeera et al. 2003) modeled experimental data of moisture content as a function of time by a first order kinetics:

$$MR = \frac{M - M_e}{M_0 - M_e} = \exp(-Kt)$$

(26)

where $MR$ is the moisture ratio, $K$ is kinetic constant and $t$ is time. Nevertheless, as reported from Senadeera et al. (2003), Eq (26) tends to over-predict the first region and under-predict the last region of drying curve. To avoid this problem an exponent $n$ was introduce in the equation leading to the Page’s model which is commonly used for vegetable dehydration:

$$MR = \frac{M - M_e}{M_0 - M_e} = \exp\left(-Kt^n\right)$$

(27)

where $MR$ is the moisture ratio, $K$ is the drying constant (min$^{-1}$), $t$ (min) is time, $n$ is a dimensionless exponent and the subscript 0 and e represent the time zero and the equilibrium. Another empirical equation, widely used to model vegetable dehydration process, is the Peleg’s model:
where $MC$ is the moisture content, $t$ is time, $k_1$ and $k_2$ are kinetic constants. Moreover, $1/k_1$ and $1/k_2$ represent respectively the initial rate mass transfer (at $t=0$) and the value at equilibrium (at $t=\infty$).

Page’s model has been used to fit experimental results of several dehydration methods such as microwave drying (Ozkan et al., 2007), hot air dehydration (Sharma & Prasad, 2001; Soysal, 2004; Margaris & Ghiaus, 2007), microwave/air dehydration (Maskan, 2000), solar drying of apricots (Togrul & Pehlivan, 2002) etc., showing, in all cases, a high accuracy. In the same way, Peleg’s model well fitted dehydration data of several vegetables such as papaya (Palou et al., 1994), apples (Sacchetti et al., 2001), cherry tomato (Azoubdel & Murr, 2004), chesnut (Moreira et al., 2007), etc.

Again, Azuara et al. (1992) starting from second Fick’s law obtained the following equation to model water loss and solid gain during osmotic dehydration:

$$ML_\theta = \frac{S_1 \theta (ML_\infty)}{1 + S_1 \theta} = \frac{\theta (ML_\infty)}{S_1 + \theta}$$

(29)

where $ML_\theta$ is the moisture loss fraction at any time, $S_1$ is constant related to the rate of water diffusion, $\theta$ is the time and $ML_\infty$ is the moisture loss fraction at equilibrium. Similar equation may be written to model solid gain:

$$SG_\theta = \frac{S_2 \theta (SG_\infty)}{1 + S_2 \theta} = \frac{\theta (SG_\infty)}{S_2 + \theta}$$

(30)

where $SG_\theta$ is the solid gain fraction at any time, $S_2$ is constant related to the rate of solid diffusion, $\theta$ is the time and $SG_\infty$ is the solid gain fraction at equilibrium. This model was shown to be accurate in the modeling of osmotic dehydration of several vegetables such as apples (Erketein & Sultanoglu, 2000) and onion slices (Sutar & Gupta, 2007). Since the lack of space in this chapter a list of others empirical models commonly used to model vegetable drying curves is reported in table 3.

### 4.2 Theoretical models

Mechanistic models for drying process are difficult to find in literature. In general, some theoretical models have been developed using as starting point the biological theory related to the cell membrane changes as in the case of osmotic dehydration, the volume changes during drying or on the basis of porous media approach.

Pabis (2007) developed a non linear theoretical model of the kinetics of convective drying of cut vegetables that takes into account the shrinkage of vegetable tissue:

$$M_f = M_0 \left[ \frac{1}{1-b} \left( 1 - \frac{1-b}{NM_0} k_1 \right)^N - \frac{b}{1-b} \right]$$

(31)
where $M_t$ and $M_0$ are the moisture content at each time and at time zero, $N$ is equal to $3n/3n-2$, $b$ is the shrinkage coefficient. This model was used in different operative conditions showing a good capability to fit experimental moisture content values in the first region of drying curves (Pabis, 1999; Sojak, 1999; Pabis, 2007).

<table>
<thead>
<tr>
<th>Empirical equation</th>
<th>Name</th>
<th>Field of application</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>$MR = a \exp(-K_i)$</td>
<td>Handerson and Pabis</td>
<td>General application</td>
<td>Chhinman, 1984</td>
</tr>
<tr>
<td>$t = a\ln(MR) + (\ln(MR))^2$</td>
<td>Thomson</td>
<td>General application</td>
<td>Paulsen &amp; Thomson (1973)</td>
</tr>
<tr>
<td>$MR = \exp(-kt)^n$</td>
<td>Modified Page’s model</td>
<td>General application</td>
<td>White et al. (1981)</td>
</tr>
<tr>
<td>$MR = \left[ -k\left( \frac{t}{L^2} \right)^n \right]$</td>
<td>Modified page equation II</td>
<td>Air drying, general application</td>
<td>Diamante &amp; Murno (1991)</td>
</tr>
<tr>
<td>$W_{L_0} - W_L = C_{W_e} \exp^{-k_{e,t}} + C_{de} \exp^{-k_{s,t}}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$W_L = [WL_0]_e (1 - \exp(-K_i WL_t))$</td>
<td>Panagiotou</td>
<td>Osmotic dehydration</td>
<td>Panagiotou et al. (1999)</td>
</tr>
<tr>
<td>$M_t = M_0 + (M_0 - M_c)\exp(-kt)$</td>
<td>Mulet</td>
<td>General application</td>
<td>Pabis (2007)</td>
</tr>
</tbody>
</table>

Table 3. Empirical equation generally used to model vegetable drying processes

Based on the biology, Toupin et al. (1989) developed a mathematical model able to describe intercellular transport and the thermodynamic irreversible processes for transmembrane transport. Although the model is recognized as valid, it requires a wide number of physical and biological parameters that, often, are difficult to find in literature. Starting to this model, Spiazzi & Mascheroni (1997) developed a model composed by a system of ordinary differential equations that take into account the main mass transfer ways in cellular tissues, product shape, size and variation during drying as well as the chemical composition of the product, of the osmotic solution and their mass ratio.

In the last years, some theoretical models have been studied on the basis of the increasing interest of porous media approach. Maybe, the most deep work on mass transfer is by Whitaker (1997) who, starting from consideration at microscopic level as well as conservation equation for heat and mass for each phase (liquid, solid and gas plus phases), obtained representative information at macroscopic level. However, since the complexity of the theoretical modeling of fruits and vegetables submitted to different drying technologies and also the difficulty to experimentally validate these models, these equations are still far to be commonly used. Details of two mechanistic models such as distributed evaporation formulation and sharp interface formulation may be found from Ni et al. (1999), Farid (2002), Datta (2007).
5. Diffusion in inhomogeneous structures

The classical mathematical models of diffusion, usually applied to food systems, strongly depend on the hypotheses of homogeneity of the medium where the diffusion process occurs. However, food matter is far from being homogenous: at every scale at which it is observed, it presents relevant irregularities, making the description in terms of continuous space models essentially unrealistic.

The mathematical study of the most typical inhomogeneous structures occurring in nature is rather recent. Even if the deviation of the geometry of nature from analytical models was already pointed out by Perrin at the beginning of 20th century (Perrin, 1913), only in 1975 Mandelbrot introduced the concept of fractal to define a general class of geometrical patterns suitable to describe natural shapes (Mandelbrot, 1975).

"Clouds are not spheres, - Mandelbrot writes - mountains are not cones, coastlines are not circles, and bark is not smooth, nor does lightning travel in a straight line." (Mandelbrot, 1982). According to Mandelbrot, a fractal is "a rough or fragmented geometric shape that can be split into parts, each of which is (at least approximately) a reduced-size copy of the whole" (Mandelbrot, 1982). This defining property, called self-similarity, is often summarized saying that in a fractal the part is similar to the whole.

Some examples of fractal shapes in vegetables are shown in Figure 13, 14, 15 and 16.

Fig. 13. Romanesco Broccoli (Brassica Oleracea Botrytis)
An important consequence of self-similarity is the absence, in a fractal, of a characteristic length scale and the presence of details of any size. However, this is true only for ideal mathematical fractals. Real objects have a finite size and are usually constituted of elementary parts having a characteristic size. Therefore, they exhibit fractal behavior only in a limited range of length, called the fractal range and defined by a minimal and a maximal length, $l_{\text{min}}$ and $l_{\text{max}}$.

Obviously, every fractal structure has its specific features and we need to classify all possible fractals in order to study their properties. The first classification, introduced by Mandelbrot, is based on a parameter called the fractal dimension, which is a generalization of the usual concept of dimensionality of a system.

There exist several possible definitions of fractal dimension, differing only in some specific case of purely theoretical interest. The most useful definition for practical application is the following:
Take a point O on the fractal and a series of spheres with varying radius $r$ and with centre in O: on a fractal, number of elementary building blocks (or, equivalently in most cases, the mass) of the part of the fractal contained in each sphere depends on $r$ according to the law:

$$N(r) \propto r^{d_f}$$

(32)

where $d_f$ is a real number less or equal to the dimension of the space where the fractal is embedded. Such a number is defined to be the fractal dimension of the fractal, and it does not depend on the choice of O. Notice that, for regular (non fractal) shapes, it coincides with the usual space dimension (e.g. it is 1 for a straight line, 2 for a plane figure, 3 for a solid figure).

In Figures 17, 18, 19 and 20 we show some examples of mathematically generated fractals, together with their fractal dimension.
Fig. 18. DLA cluster \( (d_f=1.71, \mu=1.2) \)

Fig. 19. Percolation cluster \( (d_f=1.89, \mu=1.3) \)
A further step in the understanding of the geometry of natural objects is the extension of the concept of fractal dimension to structures which are not self similar. Indeed, while self-similarity implies Eq. (32), the inverse is not true. Therefore, whenever Eq. (32) holds, even in absence of self-similarity, we can define a fractal dimension and we can introduce the concept of fractal behavior of a particular structure, replacing and generalizing the concept of fractal geometry. Two mathematical examples of non self-similar structures for which fractal dimension can be defined are shown in Figure 21 and 22.
According to its definition given in Eq. (32), fractal dimension can be experimentally determined using several techniques. The simplest ones are imaging techniques combined with image analysis, but also elastic scattering of photons or neutrons can be very useful. In the years following the discovery of fractals, many studies proved the presence of fractal structures in several food systems (Peleg & Barbosa, 1993; Barrett & Peleg, 1995) and many authors began to apply the new ideas to describe physical and chemical processes occurring in inhomogeneous structures.

In particular, fractal dimension plays a fundamental role in the understanding of hydration and dehydration processes. Indeed, the water and vapor exchange rate between an object and its environment is proportional to the interface between them, i.e. to the object surface. In regular three dimensional objects, the surface area scales as the square of the object linear size, but in the case of fractal surfaces, the area scales with an exponent greater than 2, making the hydration-dehydration mechanism more rapid and effective (De Marchi and Cassi, 1993). A simplified dimensional analysis can shed more light on the role of fractality in this kind of processes. Assume that the total amount of water to be removed from a fractal object is proportional to its volume $V$, and that the dehydration rate is proportional to its surface $S$. Let us call $d_V$ the fractal dimension of this object and $d_S$ the fractal dimension of its surface. Now, the total time $t$ required to remove all the water is given by the ratio between the amount of water and the dehydration rate, i.e., calling $l$ the linear size of the object:

$$t \propto \frac{V}{S} = \frac{l^{d_V}}{l^{d_S}} = l^{d_V - d_S}$$  \hspace{1cm} (33)$$

For regular, homogeneous solid shapes, $d_V=3$ and $d_S=2$, therefore $t$ is proportional to $l$. For fractal objects, usually $d_V \leq 3$ and $d_S \geq 2$, therefore $t$ is proportional to $l^a$ with $a < 1$. This would imply that dehydration processes in fractals are more rapid and that their effectiveness increases with the fractals linear size. However, in this simplified analysis, we have completely neglected the water diffusion mechanism inside the fractal, which turns out to have a competing role with the surface dehydration enhancement due to fractal geometry.
In general, geometrical or topological inhomogeneities produce a dramatic slowing down of diffusion processes. This fact was first pointed out by De Gennes in a seminal paper where he proposed to study the random motion of “the ant in a labyrinth”, (De Gennes, 1976). The problem was studied in the following years in the framework of fractal geometry, but the first attempts to describe such anomalous diffusion in terms of the fractal dimension failed. Only in 1982 Alexander and Orbach (Alexander & Orbach, 1982) succeeded in finding a suitable diffusion law, by introducing a further generalized dimension, called the spectral dimension. In order to understand the meaning of such a new parameter, we first notice that, to mathematically investigate diffusion on fractals and inhomogeneous structures, we cannot apply the usual analytical formalism based on continuous space and differential operators (Perrin, 1913; Mandelbrot, 1975), but we have to introduce discrete models. Diffusion on inhomogeneous structures is usually described by random walks on graphs, i.e. by stochastic hopping of a particle (walker) over a set of sites joined pairwise by links (Burioni & Cassi, 2005). The sites represent the elementary building blocks of the structure, and the links the connections between them, making it possible the passage of the diffusing particle. According to Eq. (32), the fractal dimension describes the spatial distributions of the sites. However, diffusion is affected not only by the sites position, but also by the positions of the links between the sites. This is a crucial point, since the same sites can be connected in very different ways by links: for example, the set of sites of the comb lattice of Figure 21, and the set of sites of a square lattice are the same, but, due to the different link distribution, diffusion processes on these two structures are very different. Spectral dimension takes into account the effect of links distribution on diffusion. It is denoted by $\tilde{d}$ and it can be defined by the long time behavior of the random walk autocorrelation function $P_{ii}(t)$, giving the probability that a walker, starting from site $i$, returns to $i$ after time $t$:

$$P_{ii}(t) \sim t^{-\frac{\tilde{d}}{2}}$$

(34)

Notice that it can be shown that $\tilde{d}$ is independent of the choice of the starting site $i$ and that, for regular structures, it coincides with the usual spatial dimension $d$.

Spectral dimension is independent of fractal dimension. The only constraint relating them is the inequality

$$\tilde{d} \leq d$$

(35)

The spectral dimension is the relevant parameter to describe also a variety of physical phenomena different from diffusion, ranging from vibrational dynamics to phase transitions, and including electrical conductivity and anomalous specific heat at low temperature; therefore it can be measured in real systems using very different techniques: inelastic scattering, calorimetry, time resolved spectroscopy, and many others. It is rather interesting to notice that, in all experimental measure of spectral dimension of fractals, its value always turned out to be less than 2.

Now, the main result concerning diffusion on fractals and inhomogeneous structures involves both $d$ and $\tilde{d}$: the mean square displacement of a diffusing particle after time $t$, at long times is given by
\[ \langle r^2(t) \rangle \sim t^{\alpha_f} \]  
\[ \langle r^2(t) \rangle \sim t \] 

Notice that, for regular structures, \( \alpha_f \leq d_f \), and therefore Eq. (36) reduces to the classical diffusion law

On the other hand, on fractals, due to Eq. (35), the exponent of \( t \) is usually smaller than 1, therefore the diffusion is slower with respect to the classical case. Due to this property, such anomalous diffusion is often called subdiffusion.

However, anomalous diffusion can occur even in absence of fractal geometry as well as a non integer value of fractal dimension does not imply anomalous diffusion: in the case of the comb lattice (Figure 21) we have subdiffusion without fractality while for the Nice Tree (Figure 22) diffusion is not anomalous.

The effect of subdiffusion on dehydration processes is a significant slowing down, which is most relevant for large objects with smooth surfaces. The presence of rough, fractal surfaces, as we discussed before, tends to accelerate water removal. Therefore, the dehydration kinetics has to be considered as the results of two competing mechanism, both due to inhomogeneous and fractal geometry. From a theoretical point of view, Monte-Carlo simulations and analytical trapping-diffusion models are the most suitable tools to investigate them and we expect that in the next years new relevant results will shed more light on this class of processes.

### 6. Conclusion

The water removal from fruits and vegetables is the older method to increase their shelf life. In terms of mass transfer, drying processes could be summarized the motion of water molecules from the core of vegetables to their surface and from it to the external region (i.e. surrounding air). The control of these motion is essential to obtain vegetables with a high quality also maintaining a high output production as well as minimum energy costs. The deep knowledge of mass transfer mechanisms is the only way to reach the desired moisture content minimizing the microbial growth and the degradation reactions of vegetable products. In general, the internal mass transfer during vegetable drying is still considered as diffusive phenomena on the basis of which water molecules randomly move without a preferred direction under the control of a moisture gradient. On this basis, several empirical mathematical models have been proposed and are commonly used to fit the macroscopic features (i.e. moisture content) of food during drying. Among these Fick’s laws are the most used mathematical equation to model drying curves of all traditional and innovative dehydration techniques.

However, molecular motion during drying is a much more complex phenomenon. Water may flow inside vegetables and may leave their surface in liquid and/or vapor state. Moreover, each of the drying technologies promotes unique (usually combined) mass transfer mechanisms rather than the only diffusion. Also, it is well known that due to the high number of assumptions, some of which are unrealistic for food, diffusive phenomenon should be used with the utmost care. Nowadays, several mechanisms such as capillary flow,
surface diffusion, vapor diffusion in the pores due to pressure gradient, water vaporization-condensation, etc., have been recognized as participating to the overall mass transfer. For instance, capillary forces are responsible of a negative pressure inside capillary pores able to maintain water inside vegetable structure at atmospheric pressure and to hinder water removal during drying. Moreover, due to the dependence of capillary pressure from moisture content, water moves from the region at low moisture concentration toward the highly moist regions. So, the study of water retention curve of vegetable tissues under different operative conditions and/or different dehydration methods rather than the only isotherm should be recommended. Nowadays, it is clear the great importance of three dimensional structure properties of biological tissues such as pore size distribution, shape of pores, permeability, tortuosity, etc., on mass transfer of food. Food should be considered as inhomogeneous structures inside which water and solutes move inside unique motion pathways before to reach their surface and leave food. Moreover, these pathways are subject to significant changes during drying due to the collapse of vegetable tissues. Under this approach, geometrical or topological inhomogeneities produce a dramatic slowing down of diffusion processes. Unfortunately, apart few exceptions, these aspects are rarely considered in food science. The future challenge in the field of mass transfer mechanisms of drying food is to obtain microstructure information of biological tissue and their changes during dehydration process. Also, starting from these information, it will be necessary to develop new theoretical models that include the different concentration and pressure gradients involved during each dehydration process as well as the three dimensional pathway inside which the vapor, the liquid and/or the gas phase may move. This approach will be the only way to precisely control fruits and vegetable drying, to obtain high quality of the products.

7. References


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Mass Transfer Mechanisms during Dehydration of Vegetable Food: 
Traditional and Innovative Approach 


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This book introduces a number of selected advanced topics in mass transfer phenomenon and covers its theoretical, numerical, modeling and experimental aspects. The 26 chapters of this book are divided into five parts. The first is devoted to the study of some problems of mass transfer in microchannels, turbulence, waves and plasma, while chapters regarding mass transfer with hydro-, magnetohydro- and electro-dynamics are collected in the second part. The third part deals with mass transfer in food, such as rice, cheese, fruits and vegetables, and the fourth focuses on mass transfer in some large-scale applications such as geomorphologic studies. The last part introduces several issues of combined heat and mass transfer phenomena. The book can be considered as a rich reference for researchers and engineers working in the field of mass transfer and its related topics.

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