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Chapter 5

Moisture Evaporation from Granular Biopesticides Containing Quiescent Entomopathogenic Nematodes

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Additional information is available at the end of the chapter

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Abstract

The moisture evaporation process from granular biopesticides (GBs) containing entomopathogenic nematodes (EPNs) has influence in the shelf-life of these biological products, but the approach to design GBs with desired transport properties lacks of theoretical support to get closer in a better way to formulations design of long-term storage. In this chapter we review the state of art in theoretical studies about the physics of the moisture evaporation to elucidate what are the mechanisms of drying of GBs. We found that several external and internal factors influence the transport process of moisture exchange among others phenomenon that happened in a porous media such as GBs; consequently, complex and highly dynamic interactions between medium properties, transport processes, and boundary conditions result in a wide range of evaporation behaviors. The theory of drying process in two stages for porous materials with high moisture content seems to be a good starting point to explore further the drying of GBs at different scales and mechanistic and correlative models of evaporation are available to analyze the desiccation in different stages of the elaboration process, which is also of interest in the subject area of science and technology of the formulation of EPNs.

Keywords: evaporation, entomopathogenic nematodes, storage stability, reservoir
1. Introduction

Moisture evaporation from porous media is studied by its importance in the drying of foods, building materials and biological products such as biopesticides. The formulation of biopesticides is a process to transform biocontrol agents in a product to exploit their pathogenicity against insect pests. The functions of the formulation oriented towards the biocontrol agents are to improve their storage stability (increased survival time and maintained infectivity), protect them of adverse conditions and potentiate their pathogenicity against insect pests in different developmental stages, which facilitate their transport and use as functions oriented towards the final users [1]. Entomopathogenic nematodes (EPNs) are natural regulators of insect populations and are also applied as biocontrol agents of insect pests in agricultural crops. The infective juvenile (IJ) is the unique free-living stage of EPN; typically, they dwell in the soil, their natural reservoir, until they are able to infect an insect to resume their development and reproduction [2]. The IJs have many strategies to survive when they are subjected to adverse abiotic factors. Particularly, under low moisture conditions in soil, as in drought, they experiment a desiccation process that, when happens as a gradual moisture reduction, allows them to diminish their metabolism gradually until they reach an anhydrobiosis state (life without water) in which they are capable to survive for many years waiting for better moisture conditions to continue their life cycle [2]. Regarding this survival strategy, the granular biopesticides (GBs) as granules or pellets were designed to replicate the desiccation regime of IJs, to gradually arrest their metabolism and to extend their storage stability at room temperature [1].

Each GB can contain up to $3 \times 10^5$ IJs and compared with the conventional aqueous suspension it is a better media for long-term storage of IJs at moderate temperature. The main phenomenon that governs the functional performance of the GBs is that if the rate of water reduction from their structure is optimal, the IJs are properly desiccated at a suitable rate and their storage stability is increased [1]. In laboratory, it has been found that the removal of moisture content from pellets by evaporation is well related to the survival of the IJs (Pearson $r = 0.725$) and infectivity on Galleria mellonella larvae (Pearson $r = 0.904$), suggesting that the relationship between the pellet drying rate and the storage stability may be an important factor to improve the shelf life of GBs containing Steinernema glaseri IJs [3].

On the one hand, the rate of water reduction of IJs to survive to desiccation is influenced by their size, energy reserves, metabolism, genetic, historical adaptations, origin and other characteristics that are unique to each EPN species and even strains. Also, as a living entity, they receive stimulus from the ambient biotic and abiotic factors. Knowledge of EPNs biological fitness is needed for their optimal formulation, particularly their desiccation tolerance (survival under water evaporation at low relative humidity or hypertonic osmotic conditions) and also to evaluate the possibility of improvement through pre-adaptation, selective breeding, genetic engineering or others methods [4]. On the other hand, the drying process of the formulated must be optimal to induce the IJs into an anhydrobiotic state. To produce an EPN product with best performance, a proper selection of carrier’s materials, adjuvants, elaboration process to produce them and a certain combination of ambient storage conditions that allow
the evaporation of enough moisture from the GB at a rate reduction particularly suitable to gradually remove the water from the IJs body is required [1, 5]. However, it is worth mentioning that the materials selection and its combination to achieve the desired drying characteristics of the GBs are carried out by the formulator in an iterative way until the proper solution is found.

Actually, both research lines (EPN biological fitness and optimal drying of GBs) are ongoing, but the second is less common, although the major factor to enhance EPN longevity and, perhaps, increase the range of applications, given the inherent limitations of EPNs survival ability, it is likely to be the improvement of the formulation [4] and theoretical literature concerning energy and mass transfer is extensive. In this regard, if the mechanisms of transport of moisture, temperature and oxygen in these GB were understood and focused on the transport properties of the materials formulation based on the materials science approach, the extensive empirical knowledge in formulation of EPNs would be complemented with theoretical support. It is suitable for the design of these biological products because it can help to build mathematical models that describe the migration patterns of moisture, the thermodynamic equilibrium and exchange of oxygen [6], and would serve for analytical solving of design problems. Afterwards, several methods could be tested to optimize the moisture removal in the formulated product. Also, modelling could help to avoid too long, unnecessary or expensive experiments on the EPN-GB system.

Recently, it has been found that the drying kinetics of pellets is reproduced by a surface evaporation model [7] with a percent relative average deviation value of 21.95%; consequently, there is room for improvement through the proposed simplifying assumptions, but they need to be determined experimentally and expressed in mathematical form to feedback the model [3]. But, to improve this theoretical approach, it is necessary as first step to understand the water migration by evaporation from GBs towards the surrounding atmosphere and its variation factors. Hence, the objective of the present work is to make a review and discuss the state of the art in theoretical studies about the physics of moisture evaporation process from porous media to elucidate what are the basic mechanisms of moisture migration from GB, which is of paramount interest in the subject area of science and technology for the formulation of EPNs.

2. Problem statement of moisture evaporation from granular biopesticides

The pellets are solid particles in the form of spherical granules of 10–20 mm in diameter (Figure 1). Drops of a suspension of nematodes are dropped on a powdery material to entrap the IJs into a solid matrix, which results in the formation of the granules or pellets. The powder material may be one, or a combination of, several different carrier materials and adjuvants to produce GBs with the desired characteristics [1, 5]. Experimental wettable powder formulations have been reported to include inert powders such as talc, sand, diatomaceous earth and various clays. Natural ingredients are often used in formulations in order to maintain the
environmentally “green” concept associated with biopesticides. Polymers are a usual material for pelletisation of EPNs and often include natural carbohydrate and/or protein polymers such as starch, sodium alginate, acacia gum, lignin and gelling agents amongst others [6, 8, 9].

The nematodes can be divided into two groups, slow-dehydration strategists and fast-dehydration strategists, depending upon the rates of water loss in the environment that they will survive. *S. carpocapsae* IJs survive well at high rate of water removal and *S. glaseri* IJs survive better at low rate of water removal [10, 11]. Therefore, the major cause of nematode survival to desiccation in anhydrobiosis is the controlled rate of water removal from the IJs [12]. Therefore, the quiescent state of IJs and their shelf life in GB are strongly influenced by moisture content [12–14].

In laboratory, the GBs are stored in closed room where evaporation occurs in calm air, and they are subject to artificial variations to replicate the shelf storage conditions and to test their storage stability over time (temperature from 20 to 30°C, relative humidity of 0–100% and no wind-flow present). It has been observed that the initial moisture content of GBs containing EPNs is usually between 40 and 100%, from which a part can be removed faster in few days or slowly in various months. In the most successful case, *S. carpocapsae* IJs survived up to 7 months (Figure 2) and maintained their infectivity on *G. mellonella* above 70% in water dispersible granules (WDG) stored at 25°C, whose moisture is reduced at a rate of 8.26 × 10^{-7}% s^{-1} [13, 15]. In the less successful case *S. glaseri* IJs survived 8 days and maintained its infectivity on *G. mellonella* above 80% in diatomaceous earth pellets (Figure 3) stored at 23 ± 3°C, whose rate of pellet moisture reduction is 6.134 × 10^{-5}% s^{-1} [3]. This reduced shelf life at room temperature limits their commercial exploitation, especially if GBs contain *S. glaseri* IJs and if these are compared with the long shelf life of commercial chemical pesticides.

Figure 1. Various diatomaceous earth pellets containing *S. glaseri* IJs.
Figure 2. Mean survival of *S. carpocapsae* IJs and moisture content of the WDG formulation stored at 25°C, reported in [13].

Figure 3. Mean survival of *S. glaseri* IJs and moisture content of the diatomaceous earth pellet formulation stored at 23 ± 3°C and high RH (96%), reported in [3].
It is thought that the desiccation process of IJs happened by slow absorption of the aqueous suspension containing them for the carrier material, starting a reduction process of moisture, which developed at an appropriate rate, and diminished the metabolism of the IJs [5]. In fact, 52% of the variation in its survival rate is explained by the behaviour of the moisture content of the DE pellet, whereas 84% of the variation in infectivity on *G. mellonella* is explained by the survival of *S. glaseri* IJs in diatomaceous earth pellets [3]. The hypothesis is that the sudden death of the IJs formulated under these conditions is due to the diffusional migration of water molecules surrounding the IJs to the DE pellet surface followed by the contact of the DE particles with the nematode cuticle which absorbs moisture faster from the IJ's cells [3]. Also as it can be observed in Figure 4, the behaviours of drying kinetics of diatomaceous earth pellets are different with or without *S. glaseri* IJs.

Recent inspection of cross-sectional area of diatomaceous earth pellets using scanning electron microscopy showed particles as plate-form and non-uniform pore distribution that form a complex and disordered microstructure [6], probably dominated by a double porosity due to two distinct distributions, one for the region of macroscopic porosity between particles, and another for the region of microscopic porosity within particles [16]. Due to the above-mentioned facts, in next sections, we will be dealing with theories applied to understand the moisture evaporation from porous media to understand how the evaporation from pellets happened, which can be useful to set design criteria to elaborate GB reservoirs for the optimum storage of EPNs.

![Figure 4](image-url)

*Figure 4.* Drying kinetics of diatomaceous earth pellets without EPNs with several initial moisture contents, stored in quiescent surrounding at room temperature (23 ± 3°C).
3. Theoretical background

3.1. The evaporation process in porous media

In the evaporation process, liquid water is transformed to water vapour and transferred from the surface of evaporation to the surrounding atmosphere, while a porous medium is a material with a skeletal solid structure with interconnected void spaces that allow fluid to pass through the medium and is mainly characterized by its porosity, i.e. the ratio of the void space to the total volume of the medium [17–19]. The permeability is a measure of the flow conductivity in the porous body and the tortuosity represents the hindrance to flow diffusion imposed by local boundaries or local viscosity; both these are important characteristics for the combination of the fluid and structure of the porous medium, respectively [17].

In porous media, evaporation involves mass and energy transport including phase change, vapour diffusion and liquid flow, resulting in complex displacement patterns affecting drying rates [20] and is the only one mechanism by which moisture can leave the GBs. Moreover, at the pore scale several mechanisms influence the macroscopic behaviour of the drying process. Among others, the phase change at the liquid-gas interface, diffusion and convection of mass and heat, type of flow and the effect of the combined viscous, capillary and buoyancy forces on the receding of the liquid-gas interfaces are also the influencing factors in drying process [21]. Most evaporation processes are assumed to be viewed as transport at the pore space where water is displaced by air; this moving zone between wet and partially dry zones is named the drying front in [22].

According to the theory of drying in two stages, drying rates from an initially saturated porous medium often exhibit distinct transitions whereby initially high drying rate (denoted as stage I or constant rate period) abruptly drops to a lower rate (stage II or falling rate period) governed by vapour diffusion through the porous medium [20, 23]. The drying stage 1 occurs by convection on the material surface at an evaporation rate relatively high and nearly constant. The factors involved in its development are the external conditions of mass and heat exchange in the system related to the properties of the surrounding air (temperature, pressure, humidity, convective airflow velocity and area of the exposed surface) and supplied by capillary liquid flow connecting a receding drying front with an evaporating surface [24].

The drying stage 2 starts when the moisture content of the porous media is less than its critical moisture content. At a certain drying front depth, continuous liquid pathways are interrupted when gravity and viscous effects overcome capillary forces in porous media and simultaneously the moisture content is less than its critical moisture concentration. These events marks the onset of a new evaporation regime with lower evaporation rate limited by transport properties of porous media, known as the drying stage 2 [22]. In this period the process is influenced by internal factors related to the properties of the material such as water activity, internal structure (porosity and tortuosity), chemical composition and transport properties (thermal and hydraulic conductivities, moisture diffusivity and vapour diffusion) [22–24]. The rate of drying in the two different periods has mainly been modelled numerically from...
a set of equations taking into account vapour and liquid transfers along with boundary conditions.

In [25], the convective drying is considered as a process of three successive steps. The first step is liquid movement in porous media from the wet interior to the gas-solid interface across internal pore, particle surface, etc. This step is slower for larger solids and/or low moisture concentration in the porous material. The second is evaporation due to heat by energy supplied to change liquid into vapour. The third step is vapour movement to the surrounding gas by diffusion and convection. In general, different stages are often used for diagnostics and classification of evaporative drying of porous media, which depend on the focus of the studies and the interpretation of the rate limiting processes. Consequently, complex and highly dynamic interactions between medium properties, transport processes and boundary conditions result in a wide range of evaporation behaviours [20] and internal and external factors are common influences on most of the evaporation behaviours.

3.2. External mass transfer

3.2.1. Classic evaporation theory

A brief history of the theories of evaporation is presented in reference [26]. The Dalton’s assay was one of the major events in the development of the evaporation theory and states that the rate of water evaporation is proportional on the saturation deficit of the air, which is given by the difference between the saturation vapour pressure at the water temperature, \( e_w \) and the actual vapour pressure of the air \( e_a \) [27, 28]:

\[
E_L = C \left( e_w - e_a \right) \tag{1}
\]

where \( E_L \) = rate of evaporation (mm/day) and \( C \) = constant; \( e_w \) and \( e_a \) are in mm of mercury. Eq. (1) is known as Dalton’s law of evaporation. Also, this proportionality is affected by the wind velocity, the RH and the moisture concentration in the solid surface; therefore, the moisture will evaporate from the surface until the surrounding air saturates [28]. The similarity theory is a standard basis for predicting evaporation rate from a free water surface and states that convective heat and mass transfer are completely analogous phenomena if the mass flow from the surface is caused by diffusion, which requires that the content of the diffusing species be low and the diffusional mass flux is low enough that it does not affect the imposed velocity field. However, these two analogies are not valid if applied to a capillary porous media containing a liquid [28].

3.2.2. The constant rate period

According to the theory of two stages of drying of porous media, during the 1-stage, the rate of water loss per unit surface area remains nearly constant and close to evaporation rate from free water surface and is attributed to the persistence of continuous hydraulic pathways between the receding drying front and surface of porous media where liquid flow is sustained by hydraulic gradient towards the evaporation surface [29]. Numerous experimental and
theoretical studies have established the existence of such a constant phase during drying of porous media, typically under mild atmospheric demand [20, 30].

The intrinsic characteristic length $L_C$, a measure of the extent of hydraulic continuity and the strength of capillary driving force deduced from pore size distribution of a medium that control the transition from liquid-flow–supported stage 1 to diffusion-controlled stage 2 during evaporation from porous media is proposed in [20]. The $L_C$ is used for predicting the end of stage 1 evaporation and considering balance between gravitational, capillary and viscous forces. The theory assumes that in the stage-1, air first enters the largest pores in a complex porous medium while menisci in smaller pores at the evaporating surface may remain in place (albeit with decreasing radii) of curvature. Thereby, liquid moves into the pore space (large size pores with lower air-entry value to smaller size water-filled pores) and then towards the surface of the body where the moisture evaporation happens; according to [20], such mass flow may be sustained as long as capillary driving forces are higher than gravitation and viscous forces. In [20], characteristic lengths for evaporation from porous media are theoretically developed for the following three conditions:

1. pore size distribution and gravity characteristic length $L_G$,

$$L_G = \frac{1}{\alpha(n-1)} \left( \frac{2n-1}{n} \right)^{(2n-1)/n} \left( \frac{n-1}{n} \right)^{(1-n)/n}$$

2. pore size distribution effects on the viscous characteristic length $L_V$,

$$L_V = \frac{K(\theta)}{e_0} \Delta h_{\text{cap}}$$

3. combined gravity and viscous length $L_C$,

$$L_C = \frac{L_G}{1 - \frac{\alpha}{K(\theta)}}$$

where $K(\theta)$ is the unsaturated hydraulic conductivity, $\alpha$ is the inverse of a characteristic pressure head, $n$ is the pore size distribution, $e_0$ is the water flow supporting evaporation rate and $\Delta h_{\text{cap}}$ is the maximum capillary driving force. This theoretical approach is based on experimental data of evaporative drying of two quartz sand media with particle sizes ranging from 0.1 to 0.5 mm (denoted as “fine sand”) and from 0.3 to 0.9 mm (“coarse sand”) to quantify the evaporation rates from sand-filled cylindrical Plexiglas columns of 54 mm in diameter and 50–350 mm in length and rectangular Hele-Shaw cells 260 mm in length, 10 mm in thickness and 75 mm in width with a top boundary open to the atmosphere. As expected, the highest initial evaporation rate corresponds to high temperature and low humidity (28°C and 31% RH), whereas the lowest evaporation occurred for cool and humid conditions (21°C and 58% RH).
3.2.3. Natural convection theory

Natural convection is defined as air movements brought about by density differences in hot and cool air, whereas forced convection is the movement of air brought about by an external force. In natural convection, fluid motion is due to gravity that creates a buoyant force within the fluid, which lifts the heated fluid upward. Since the fluid velocity associated with natural convection is relatively lower than those associated with forced convection, the corresponding convection transfer rates are also smaller [31]. The Rayleigh number that measures the intensity of natural convection, based on the macroscopic length scale \( L \), is defined in reference [19] as

\[
Ra_L = \frac{g \beta \Delta T L^3}{\nu \alpha_f} \tag{5}
\]

where \( g \) is the gravity constant, \( \alpha_f \) is the thermal diffusivity of fluid, \( \beta \) is the volumetric temperature expansion coefficient, \( L \) is the macroscopic scale length scale, \( \Delta T \) is the temperature scale and \( \nu \) is the kinematic viscosity of fluid. Based on natural convection theory, heat and mass transfer from porous media in quiescent fluid environments have been extensively studied by its importance in the design or performance of the systems when it is desirable to minimize heat transfer rates or to minimize operating costs [32].

3.3. Internal mass flow in porous media

The internal process of mass transfer during drying is usually described using a convective model (known as a capillary-porous model) based on fluid pressure gradients (Darcy’s law) and techniques of scale change as a representative elementary volume (REV) in order to express the transition from a microscopic level to a macroscopic one in the conservation equations and a diffusive model based on the gradients of moisture concentration, a phenomenon described by Fick’s law. This model is a simplification of the capillary porous model if the drying is supposed isothermal with no gravity effects in the solid-liquid water system [33–35].

3.3.1. Fickean diffusion

The diffusion is known as the preponderant internal mass transfer mechanism during drying of porous media. According to Fick’s first law, the matter flows erratically from moist regions towards dry regions inside bodies, assuming that the moisture gradient is the unique driving force of the flow [37]. However, although several empirical equations have been proposed to predict mass transfer on this basis, much more must be explained [37]. For instance, this laws make several assumptions and simplifications that are often unrealistic to model water diffusion during drying as materials are non-heterogeneous and isotropic media and diffusion coefficients are not correlated to moisture content; samples are in most cases considered as having regular shapes; heat transfer during drying is disregarded and collapse of vegetable tissues by water loss is also neglected [36, 37].

The effect of microscopic structure on mass transfer has been completely discarded, but a disordered internal geometry caused by the percolation phenomena is very common in the structure of most porous media, sometimes described by the fractal geometry. The complex
microstructure affects the water diffusion phenomena, resulting in anomalous diffusion and involving complex parameters such as fractal dimension and spectral dimension [37]. The inclusion of a porous medium affects the forms of Fick’s first and second laws for diffusion of chemical species in aqueous solution in two general ways: first, the existence of the solid particles comprising the porous medium results in diffusion pathways that are more tortuous. This increased tortuosity reduces the macroscopic concentration gradient and, therefore, reduces the diffusive mass flux relative to that which would exist in the absence of the porous medium as in single droplets. Second, there may be interactions between the diffusing species and the solid porous media that either directly affect the mass of the diffusing species in aqueous solution (e.g. sorption) and/or result in physicochemical interactions that affect the tortuosity [18]. All forms of Fick’s first and second laws for governing macroscopic diffusion through porous media include an effective porosity, $\varepsilon_f$ and a mass diffusion coefficient $D$ [18].

3.3.2. Capillarity

The migration of the liquid phase in a deformable porous matrix, by convective transport, is managed by the generalized Darcy’s law [33-35]. Darcy’s law in its simplest form expresses the proportionality between the average velocity $v$ of a fluid flow and the flow potential, comprised by the pressure gradient $\Delta p$ existent through porous media and the gravitational contribution and is applicable to multiphase mixtures as opposed to Fick’s law, which requires the assumption of a homogeneous mixture [19]. The proposed relationship is as follows:

$$v = \frac{k}{\Delta x} \frac{\Delta p}{\Delta x}$$

in this expression, $k$ is the hydraulic conductivity and describes the ease with which a fluid can flow through the pore spaces. Darcy’s equation is valid for incompressible and isothermal creeping flows. In a complex form of Darcy’s law, the rate of flow is related to the pressure gradient in the liquid, $\nabla \langle V_l \rangle_l$ [33]. Eq. (7) expresses the relationship between the liquid-phase velocity $\langle V_l \rangle_l$ and solid one $\langle V_s \rangle_s$ as follows:

$$\langle V_l \rangle_l = \frac{\langle V_s \rangle_s}{C_0} \frac{K}{\varepsilon_l \mu_l} \langle \nabla \langle P_l \rangle_l \rangle$$

where $K$ is the permeability of the porous medium, $\varepsilon_l$ is the liquid fraction, $\mu_l$ is the liquid dynamic viscosity and $\Delta \langle P_l \rangle_l$ is the gradient of fluid pressure.

3.3.3. The falling rate period

The stage 2 is governed by vapour diffusion through the porous medium. This period is divided in a first decreasing-rate period (FDR) characterized by breaks in the uniformity of water content close to the surface and slight augmentation of the heat surface; and a second decreasing-rate period (SDR), correlated with a discontinuous liquid network into the porous
medium and with the development of a dry receding front from the free surface of the porous sample [38].

The falling rate period is expected to be short for two reasons: (1) the liquid mass corresponding to the films is small compared to the mass of liquid initially present in the medium and (2) the external mass transfer length scale (the mass external boundary layer typically) is typically greater than the thickness of the medium, which implies that the mass transfer resistance due to the receding of film tips within the medium is weak compared to the external mass transfer resistance [39].

3.4. Mathematical models of moisture evaporation from porous media

The drying behaviour of porous material can be described with a model and the porous media is described in multiple length scales [40, 41]. The macroscopic length scale is defined by the overall physical domain indicated by the length scale \( L \). The microscopic length scale captures the detailed morphology and is indicated by \( d \). A REV is defined as a volume whose size \( L_{REV} \) lies between length scale \( d \) and \( L \), i.e. \( d \ll L_{REV} \ll L \) [19]. Thus, the modelling of drying process of porous media can be developed at different scales in a process that should be initiated typically to the pore-scale and then model it at larger and larger scales up to dryer scale or product scale in the case of designs of dryers.

The macroscopic variables of the drying process are commonly defined by the volume average of the microscopic variables over the REV and the nature of the product is the result of a diversity of multiple factors and their relationships among themselves that increases the complexity of the evaporation process [19, 41]. In the formulation of EPNs, the interesting scale is the product scale, being one single granular biopesticide. The continuum approach and pore network models are approaches for the modelling of the drying process of the porous media [41].

3.4.1. The continuum approach

In the continuum approach, variables (e.g. temperature) are averaged over the volume, the REV. Equations for the conservation of liquid, air and energy are supplemented with boundary and initial conditions. The continuum approach can be solved by efficient numerical techniques at a large scale in comparison to the pore scale, which is a great advantage. The effective parameters, such as vapour diffusivity, permeability, thermal conductivity and capillary pressure have to be determined by dedicated experiments. The continuum approach fails when the pores are large compared with the system and is not able to easily take structural features of the medium into account. Moreover, the computation of the effective properties at the scale of a REV is necessary in the continuum approach [41]. The parameters of the continuum model can be assessed for a certain pore structure using a pore network model.

3.4.2. The pore network approach

Porosity is a primary property of the granules, which dominates a wide range of secondary properties as water flow or air entrapment, both strongly linked to the microstructure [42, 43]. Pore network models are based on a porous structure represented as a network of pores and
throats and these models can be used to simulate the drying process at the pore level because they can take into account important features of the microstructure as the role of large pores and their distribution on motion of the gas-liquid menisci in the pores, diffusion, viscous flow, capillarity and liquid flow [40, 41, 44]. The developing of models that permit to analyse the influence of the porous microstructure has at least two motivations. One is the computation of the effective parameters at the scale of a representative elementary volume REV of the microstructure. A second one is to analyse drying at the scale of the product without assuming a priori existence of the REV that is associated with the continuum approach. Pore network models have been used in both cases and have been described in two and three dimensions [44].

3.4.3. Pore network models

A pore network model for the evaporative drying of macroporous media was presented in [30]. The model takes into account the heterogeneity of the pore size distribution and the pore wall microstructure, expressed through the degree of pore wall roundness for viscous flow through liquid films, gravity, and for mass transfer, both within the dry medium and also through a mass boundary layer over the external surface of the medium. The model is used to study capillary, gravity and external mass transfer effects through the variation of the three dimensionless numbers: a film-based capillary number $Ca_f$, that expresses the ratio of viscous forces to capillary forces in the films;

$$Ca_f = \frac{4\mu_1 D_M C_e}{\rho_1 \gamma r_t}$$

the Bond number, $Bo$, that expresses the ratio of viscous forces to capillary forces in the films;

$$Bo = \frac{g_x \rho_1 r_t^2}{\gamma}$$

and the Sherwood number, $Sh$, that describes mass transfer conditions within the mass boundary layer over the product surface.

$$Sh = \frac{\lambda}{\delta} = \frac{\Lambda r_t}{\Delta}$$

where $\lambda = \frac{D_{eff, ext}}{D_{eff, int}} > 1$ is the ratio of external to internal effective (volume-averaged) diffusivities, $\delta = \Delta / r_t$ is the dimensionless value of the mass boundary layer and $\Lambda$ is its corresponding thickness. $g_x$ is the gravity acceleration component in the flow direction, $\mu_1$ and $\rho_1$ are the liquid-phase viscosity and density, $\gamma$ is the interfacial tension, $r_t$ is the average throat radius within the porous medium, $D_M$ is the molecular diffusivity and $C_e$ is the equilibrium (at vapor pressure) concentration of the volatile species. The film and dry pore regions are coupled through mass conservation at the front evaporation in a single scalar variable, $\Phi$, mass transport through both the film and dry regions:
where the variable $\Phi$ is subject to the following boundary conditions; at the percolation front $P$, where the films emanate as $\zeta = 1$ and $\rho = 1$, at the evaporation front $I$ as $\zeta = 1$ and $\rho = \rho$ and at the top of the mass boundary layer as $\zeta = 0$ and $\rho = 0$. The effect of gravity is analysed for two cases, when it is opposing and when it is improving drying. For the second case, a two-constant rate period evaporation curve was found when viscous forces are strong and mass transfer in the dry region is fast enough compared to gravity forces. Especially in this regime, water flow is driven primarily by gravity to compensate for evaporation occurring at the film tips [30].

The incorporation of gravity can be done by considering a well-chosen invasion throat potential dependent on variables such as its width of the throat, the relative position in the gravity field and the Bond number [30]. If thermal effects are not included, the pore network model requires to be coupled with mass transfer at the open surfaces and under isothermal conditions. But certainly, temperature has an effect on viscosity and surface tension of the liquid and vapour diffusion coefficient, among others. Moreover, the temperature gradient affects the drying process and distribution of moisture during its development. The effect of heat and mass flow on the drying process in simulation has been reviewed recently in [45].

3.4.4. The diffusion model

Until now, the unique effort to study the moisture migration from GB was the application of a classical temporal surface evaporation model (Eq. (12)) of Crank [7] based in the Fick’s second law to calculate the moisture content of a diatomaceous earth pellet at any given time in the drying process [3]. In this model, differences at initial and final concentration are the driving force of change of moisture in time of a sphere and to take into account all relevant physical transport mechanism in the drying process all effects are lumped on the diffusion coefficient, implying that the detailed effects of the pore microstructure are ignored.

$$\frac{\text{MC}(t) - \text{MC}_1}{\text{MC}_1 - \text{MC}_0} = \sum_{n=1}^{N} \left[ \frac{6 \cdot L^2 \cdot \exp\left(-\frac{\beta L}{\sqrt{\lambda}}\right)}{\beta_i (\rho_n + L \cdot (L-1))} \right]$$

The use of a large number of series term in Eq. (12) makes their practical use difficult. Also, this approach model is limited to the two phases’ system (solid and liquid) and the experimental determination of the effective diffusion coefficient is difficult because of its variation in space [3]. The evaluation of moisture diffusivity using numerical techniques has become a usual methodology in recent years [46] and these numerical methods seem to be a powerful tool for the researchers in formulation of EPNs in GBs.

3.4.5. Drying-strain relation

Studies for optimal control of drying of porous media focused on the assessment of drying effectiveness were found in the literature review. Although for now the use of dryer
technology where GBs could be properly dried is non-existent, these approaches are of interest for the formulation process of EPNs. The work of Kowalski and co-workers [47] is dedicated to numerical simulations of optimal control applied to saturated capillary-porous materials subjected to convective drying based in a thermo-hydro-mechanical model. The differential equation expressed in terms of strains, temperature and moisture content is as follows:

\[
2Me_{ij} + (Ae + \gamma_T \frac{\partial}{\partial \theta} - \gamma_X \theta)\delta_{ij} + \rho g_i = 0
\]

where \(K\) and \(M\) are the elastic shear and bulk modulus, \(\varepsilon\) is the volumetric strain, \(g\) is the gravity acceleration (neglected in further considerations), \(T\) is the temperature, \(X\) is the moisture content and the index \((j)\) denotes differentiation with respect to coordinate \(j = \{x, y, z\}\). \(A = (K - 2M)/3\), \(\gamma_T = 3Kk^T\), \(\gamma_X = 3Kk^X\). Here, \(k^T\) and \(k^X\) are the respective coefficients of linear thermal and humid expansion. Eq. (13), after differentiating with respect to the coordinate \(j\) and using the tensor of small strains expressed by the derivative of displacement \(u_i\), becomes

\[
\varepsilon_{ij} = \frac{1}{2}(u_{i,j} - u_{j,i})
\]

which is the displacement differential equation, jointly with the differential equations expressing liquid concentration and temperature supplemented with appropriated initial and boundary conditions that allow to realize numerical estimations of the drying kinetics and deformations of the drying media, and by implication, of the drying-induced stresses. The whole set of differential equations were initially elaborated for the 2-D geometry of a cylindrical shape [47]. The optimization procedure is illustrated on the kaolin-clay material in the form of cylindrical samples (40 mm in radius and 40 mm in height) and the genetic algorithm method was used to simulate the optimal work of the dryer. The authors conclude that drying rates are accelerated if the drying induced stresses are small, and slowed down if the stresses tend to overcome the strength of the material. The formulation of mathematical optimization procedure based in such rigorous principles of rational control of drying and their experimental validation are useful to find optimal drying processes of porous media [47].

3.4.6. Drying of droplets

Drops are subject to theoretical and experimental analysis to determine how the moisture is lost under different conditions [41, 48–56]. Theoretical models for the drying of single droplets are of interest for applications of formulation of EPNs since GBs can be made by liquid penetration in powders or can contain soluble and insoluble adjuvants subject to evaporation. The theoretical study of evaporation of liquid droplets on solid substrate is based on the assumptions of diffusion-controlled mass transfer in the gas phase, constant temperature over the whole system (isothermal conditions) and neglects the effect of convection in the vapour phase [41]. However, when the thermal effects due to evaporative cooling in the classic model are introduced, the results show that the evaporation slows down by increase of the latent heat of evaporation and the substrate thickness as well as by a decrease of the substrate thermo-conductivity. The theoretical predictions using this model do not have good agreement if the substrate
temperature deviates from the room temperature and the possible reason of this deviation is the increasing importance on thermal-buoyancy convection at higher temperatures [54].

The regular regime method is useful to determine the content-dependent diffusion coefficient for systems in which the relation among moisture diffusivity and moisture content are lineal and the last one decreasing below the critical moisture concentration or also for situations where the drying rate is dominated by mass transfer inside the drying specimen [57]. Under this theory, the drying curves show an induction period in which the drying rate is conditioned by the moisture distribution at the beginning of the drying process and a regular regime period in which the drying rate is not correlated and thereby of the moisture distribution at the beginning of the process. The establishment of the moisture range at which the regular regime occurs during the isothermal drying is the condition to apply this method, particularly for a given material and conditions, the drying curves will converge in a regular regime curve, even for different moisture contents in a single curve named the regular regime curve [49].

The objective of the work of [49] was to develop a method for quantitatively calculating the effective moisture diffusivity of isothermally dried biopolymer drops and to acquire activation energy to be used as a discriminating parameter for selecting effective wall materials against lipid oxidation. The biopolymer’s effective moisture diffusivity was dependent on moisture content and temperature. Therefore, air temperatures must be lower than 80°C for an appropriate analysis of the water diffusion mechanism using the regular regime methodology. Also, the activation energy provides a quantitative measurement for selecting potential good wall materials against lipid oxidation [49].

In other approach, the interactions of droplets during its deposition on porous material for the agglomeration of particles by spray-fluidized process were studied by [55]. In this work, the penetration of liquid into the porous layer was assumed to be governed by Darcy’s law. In reference [48] the molecular kinetic theory was used to model the droplet spreading, and Darcy’s law to describe the one-dimensional liquid penetration into the substrate. Particularly, this approach is of interest for applications of formulation of EPNs because the elemental principle of the methods of formation of GBs is to deposit droplets of aqueous suspension containing EPNs over a layer of a mixture of material (carrier and adjuvants) and then the penetration of the liquid carrier happened [5, 9]. After that, the materials are mixed and compacted in different ways (i.e. agitation, eccentric rotational motion and compaction by rolling, among others). These are reasons to optimize the capillary penetration of aqueous suspension into the porous layer; the initial moisture content and moisture evaporation are critical factors in the design of granules for storage and transport of EPNs for biological applications [3, 50]. Following this approach, in [56] was developed a method to quantitatively describe the evaporation effect on radial capillary penetration of liquids in thin porous layers.

3.4.7. Natural convection in cavities

The case study of Prakash et al. [32] is moisture migration in a rectangular cavity (2 m in height and 1 m in diameter) with half the cavity filled with silica gel and their paper presents a
general method of solving heat and moisture transfer by analysing a two layer system with a fluid overlying a hygroscopic porous medium where turbulence in the fluid layer affect the natural convection flow. Also, these approaches are of interest for applications of formulation of EPNs if the phenomenon is scaled adequately to small containers in which GBs are deposited for storage, transportation and commercialization, because they permit air in the container to contact the exposed surfaces of the packages for oxygen exchange with EPNs [58, 59]. The model is based in equations for fluid flow and heat transfer and equations for moisture migration in porous media. The model equations were discretized using the control volume formulation and solved using the SIMPLE algorithm. The model is capable of simulating flow only when turbulence in the porous medium can be considered to be negligible. However, this would not be the case for porous media of high permeability. In order to overcome this limitation, the authors suggest that a turbulence model for the porous medium needs to be incorporated into the existing model.

4. Concluding remarks

According to this review focus, it has been found that the evaporation theory from porous media is well developed, and is affected by temperature, atmospheric pressure, humidity, water quality, topology, size and organization of particles and pores, fissures, type of elaboration process and shape of surface among others in an interdependent form. Therefore, as a design object, GBs are the porous granular structure whose key evaporative processes are subject to multiple extra- and intra-structure factors that affect the way of water removal and even other physical, chemical and mechanical processes in a complex way. For the above, considering all the phenomena in the design process of GBs without theoretical support and mathematical tools for the analysis of the transport processes limits the design of optimized solutions. Nevertheless, it is reasonable to think that some improvements can be achieved on this topic because the optimization methods (as the topology optimization procedure used to design heterogeneous materials and stochastic optimization methods employed to reconstruct or construct such microstructures gave limited but targeted structural information) provide a systematic means of designing of microstructures with tailored properties for a specific application. Also, mechanistic and correlative models of evaporation are available to analyse the desiccation of GBs, i.e. describe most of the moisture evaporation process from GBs that could be useful to estimate the time required to reach optimum moisture or conditions to achieve the adequate drying rate of different EPNs. The theory of drying processes in two stages for porous materials with high moisture content seems to be a starting point to explore further the moisture evaporation from GBs at different scales. We suggest that considering the complex physical, chemical and mechanical processes carried out in soil to supply the necessary conditions (i.e. oxygen, humidity, temperature, mechanical strength) for the nematodes to achieve their survival and persistence in soil, and the actual development of the research area, new characteristics should be accomplished in the formulates to mimic the anhydrobiosis induction processes and maintain the stationary state of quiescence for the successful long-term storage of viable EPNs, as if the formulates were a microstructured porous reservoir. This also implies previous work to improve the EPNs biology fitness, e.g. on the pre-acclimatization
of IJs before and after formulation. For which, the use of desiccators’ technology to gradual drying of large amounts of IJs is a potential topic not commonly explored in the formulation process of EPNs.

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