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Modeling the quality decay kinetic of encapsulated ground coffee

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ABSTRACT

A fully predictive model for quality decay kinetic of ground coffee packaged in bioplastics is not available today. Therefore, a new model is proposed to predict the kinetics of quality decay of encapsulated ground coffee (indicated as EGC), stored under constant temperature and relative humidity conditions. The proposed model assumed that a first-order type equation, with a kinetic constant dependent on water activity, can be used to describe the quality decay of EGC. To predict the variation of water activity inside the capsule over time, the mass balance of the water inside the capsule was carried out. Specific tests were conducted at 23 °C to estimate the model's parameters. Tests on ground coffee were run to estimate the parameters used to relate the kinetic constant to the water activity; the capsule filled with silica gel was used to determine the dependence of water permeability coefficient on the water activity inside and outside the capsule. The ground coffee water sorption isotherm at 23 °C was also determined. The quality decay kinetic of EGC was measured by monitoring the pH as reliable quality descriptor and it was used to assess the goodness of the model prediction. Results indicated that notwithstanding the numerous assumptions made to derive the new model, its ability to predict the quality decay kinetic of EGC is quite acceptable.

Symbol	Definition
$t[day]$	The time
$pH(t)$	The pH at time t
pH^{∞}	The equilibrium value of $pH(t)$
$k\left[\frac{1}{day}\right]$	The kinetic constant
$a_w^i(t)$	The water activity inside the capsule at the time t
a_w^{av}	The average water activity
a_w^{in}	The initial water activity inside the capsule
a_w^e	The external water activity
$p_w^0\ [kPa]$	The water vapor pressure
V_{hs}	The volume of the capsule headspace
$m_d\ [g]$	The mass of dry EGC
R	The universal gas constant
T	The storage temperature
P_w^{CB}	The water permeability of the capsule body
P_w^{TF}	The water permeability of the top film
P_w^{BF}	The water permeability of the bottom film
ℓ_{CB}	The thickness of the capsule body
ℓ_{TF}	The thickness of the top film

(*continued on next column*)

(*continued*)

Symbol	Definition
ℓ_{BF}	The thickness of the bottom film
A_{CB}	The mass exchange area of the capsule body
A_{TF}	The mass exchange area of the top film
A_{BF}	The mass exchange area of the bottom film
$K\left[\frac{moles\ of\ water}{g\ db}\right]$	The slope of the straight line used to describe the water sorption isotherm of ground coffee powder
$\beta_0\left[\frac{moles\ of\ water}{day \cdot kPa}\right]$	One of the parameters of Equation (4)
$\beta_1\left[\frac{moles\ of\ water}{day \cdot kPa}\right]$	One of the parameters of Equation (4)
β_2	One of the parameters of Equation (4)
$k_0\left[\frac{1}{day}\right]$	One of the parameters of Equation (6)
$k_1\left[\frac{1}{day}\right]$	One of the parameters of Equation (6)
k_2	One of the parameters of Equation (6)

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1. Introduction

The key role of packaging for dry foods consists in providing a barrier against environmental moisture income, to keep their moisture content low and preserve the quality during storage. In this regard, the extensive use of petrol-based plastics in the production of dry food packaging is primarily attributable to their constant and high barrier properties against water vapor (Lindh et al., 2016; Nilsen-Nygaard et al., 2021; Piergiovanni and Limbo, 2012; Wu et al., 2021). Therefore, such unique barrier performance (P_i) of petrol-based materials guarantees to packaged dry foods to virtually maintain their intrinsic characteristics (C_i) even under abuse environmental relative humidity (RH) conditions. Consequently, developed shelf life (SL) assessment protocols and relevant associated predictive models were based only on temperature as environmental accelerating factor (Alongi et al., 2023; Calligaris et al., 2008; Manzocco et al., 2006; Nicoli, 2012).

The urgency of moving toward the use of sustainable biopolymeric alternatives mandated by global initiatives like the European Single-Use Plastics Directive (European Union, 2019) exposes the food sector to a critical gap. In contrast to their petrol-based counterparts, bioplastic packaging often shows humidity-dependent permeability, $P_i = d(RH)$, which consequently induces an undesired moisture uptake during storage and change in product characteristics, i.e., $C_i = g(P_i)$. Such cascading interactions have already been shown to have a significant impact on degradation kinetics (Lopriore et al., 2024, 2025). Within this framework, direct application of existing predictive models developed for petrol-based packaging, to bioplastic systems represents a methodological limitation. In fact, the impossibility to account for humidity-dependent barrier properties, $P_i = f(RH)$, can compromise the SL estimation, causing misalignment between labelled expiration dates and real product stability.

Therefore, the need to engineer current mathematical models to predict the quality loss of a dry food undergoing dynamic moisture changes during storage represents the only viable way to correctly compute the SL of dry foods packaged in biobased materials.

Current predictive approaches for SL of dry foods in bioplastic packaging remain constrained by paradigms developed for petrol-based ones. In fact, research studies typically modelled the decay of quality indicator and neglected dynamic changes in barrier properties and/or moisture uptake during storage (Adiletta et al., 2024; Peelman et al., 2016; Phothapaeree et al., 2017; Romani et al., 2014; Strocchi et al., 2023a). Conversely, Lee and Robertson (2021) first proposed an integrated approach using degradation models and water vapor transmission rates for biobased films reported in literature. However, regarding the data related to barrier properties it should be remarked that the adopted methodology was still based on a conventional approach, in which progressive changes in RH occurred only at the upstream side film (Macedo et al., 2013). This simplification disregards how water vapor barrier properties evolve when the internal vapor pressure varies with the increase of moisture content. Furthermore, unaccounted variables such as headspace volume posed some limitations to prediction estimates under realistic storage conditions. Limitations whose magnitude remain underexplored due to lack of validation by Authors against the underlying assumptions.

To solve this issue, the present work attempts to introduce a novel mechanistic framework. It formalize the SL function as $SL = f(g(P_i); d(RH); RH)$, explicitly embedding the dynamic interdependence of environmental variables, packaging properties, and product evolution. Therefore, an integrated approach was used where the rate of quality change (dQ/dt) was expressed as a function of three key drivers: the moisture sensitivity of packaging permeability ($P_i = d(RH)$), the moisture-food interactions (i.e., $C_i = g(P_i)$), and the relative humidity as environmental acceleration factor. The idea consists of developing a tool that can help food manufacturers to reduce waste-related losses during green transitions and costly recalls from premature spoilage. This approach not only improves sustainability and economics but also enhances consumer trust in biobased packaging, strengthening brand loyalty for products using these materials.

To this aim, in this work was considered, as a case-study, the development of a quality decay kinetic predictive model for ground and roasted coffee when packaged in biobased compostable capsules. To accomplish this goal, packaging water vapor barrier performances, quality decay of bulk coffee and coffee packaged in capsules have been assessed at 23 °C considering a wide range of environmental water activity (a_w^e). The effect of the moisture uptake on coffee staling was indirectly assessed by monitoring the pH of the beverage during storage, since this analytical indicator has been proven to be the most reliable quality descriptor among various quality parameters (Manzocco and Nicoli, 2007; Mardjan and Hakim, 2019; Ruthenberg and Chang, 2017; Santanatoglia et al., 2024).

2. Materials and methods

2.1. Chemicals

Lithium chloride (LiCl, purity ≥99 %) and magnesium nitrate hexahydrate ($Mg(NO_3)_2 \bullet 6\ H_2O$, purity ≥99 %) were purchased from Merck KGaA (Darmstadt, Germany). Potassium acetate ($C_2H_3O_2K$, purity = 98 %), magnesium chloride hexahydrate ($MgCl_2 \bullet 6\ H_2O$, purity ≥97 %), potassium carbonate (K_2CO_3, purity ≥99 %), and sodium nitrite ($NaNO_2$, purity ≥97 %) were purchased from Avantor (Radnor, USA). Ammonium sulfate ($(NH_4)_2SO_4$, purity ≥99 %) and pure phosphorous pentoxide (P_2O_5) were purchased from Carlo Erba (Rodano, Italy). Water was purified with a Milli-Q system (Millipore, Bedford, MA, USA).

2.2. Samples and storage conditions

Freshly produced ground and roasted coffee (*i.e.*, 100 % *Coffea Arabica*) (340 μm as medium-fine grind size) was provided by Lavazza Torino S.p.A., in bioplastic capsules and in bulk. Capsules used in this study are 100 % compostable capsules, as blend of different bio-based polymers, primarily belonging to the PHA family. Each capsule contained 7 g of ground and roasted coffee packed under a nitrogen atmosphere. All samples were kept under 23 °C (±1) in a thermostatic incubator (Pol-Eko, Wodzislaw Slaski, Poland) at different environmental water activities (a_w^e). The coffee powder in bulk was stored at 4 different a_w^e, namely, 0.23, 0.43, 0.65, and 0.82, while the coffee capsules were stored at 0.43, 0.54, and 0.65 a_w^e. Following the experimental setup reported in Lopriore et al. (2024), the aforementioned a_w^e conditions were guaranteed within sample equilibration chambers by placing a thin layer of supersaturated solutions of $C_2H_3O_2K$ (0.23), K_2CO_3 (0.43), $Mg(NO_3)_2 \bullet 6\ H_2O$ (0.54), $NaNO_2$ (0.65), and $(NH_4)_2SO_4$ (0.82). At different storage times, the coffee powder and the coffee capsules were sampled to measure the pH of the extracted coffee brew. The sampling was defined on a case-by-case basis, depending on the results obtained.

2.3. Measure of coffee brew pH

Coffee brewing was performed by solid/liquid extraction, using two different kinds of domestic espresso machines, depending on the absence or presence of the primary packaging (*i.e.*, the capsule). For ground and roasted coffee, a Dedica Style (De'Longhi) domestic espresso machine was used and a quantity of 7 g of coffee powder was weighed for obtaining 40 mL of beverage. Similarly, for coffee capsules, a Nespresso Inissia (De'Longhi) machine was used to analogously obtain a final volume of the beverage of 40 mL. After extraction, the coffee brews were rapidly cooled down to 20 °C using a blast-chiller (Air-O-Chill, Electrolux Professional, Pordenone, Italy). The pH of the brew was measured by a pH-meter (Basic 20, Crison, Barcelona, Spain). The results are reported as the average of 3 measurements obtained on the

brew extracted from 3 coffee samples.

2.4. Ground and roasted coffee sorption isotherm

Sorption isotherm of ground and roasted coffee was determined according to static, gravimetric method. The reported data are the result of 3 replicas. Aliquots of 1.5 ± 0.5 g of fresh coffee powder were put in 3 glass jars, placed on suspended perforated trays in 3 desiccators hermetically closed, and stored at 23 °C (±1). The obtained samples were firstly dehydrated by using P_2O_5 ($a_w = 0.01$) as desiccant material. After reaching the equilibrium with P_2O_5, coffee powder samples were progressively equilibrated at different water activity (a_w^i) by means of supersaturated solutions of inorganic salts. The salts used are listed, with their respective a_w^i values reported in brackets, as follows: LiCl (0.11), $C_2H_3O_2K$ (0.23), $MgCl_2 \bullet 6\,H_2O$ (0.32), K_2CO_3 (0.43), $Mg(NO_3)_2 \bullet 6\,H_2O$ (0.53), and $NaNO_2$ (0.65). The weight of the samples was monitored for each sorption step until the equilibrium occurred. The equilibrium was defined as reached when the sample mass variation was equal to 2 mg/g dry weight.

2.5. Water vapor transport properties of coffee capsule

The transport properties of capsules to water vapor, expressed as $mol_{water} \cdot day^{-1}\ kPa^{-1}$, were investigated at 23 (±0.1) °C. Therefore, empty capsules were filled with 1 (±0.5) g of silica gel, which acted as a desiccant material keeping the internal $a_w \sim 0.1$. The so-obtained capsules were sealed with the top and bottom film and kept in a desiccator containing P_2O_5 under vacuum (10^{-9} mbar) at 23 (±1) °C for at least 48 h. The permeation tests were conducted by putting the afore-mentioned capsules in the climatic chamber of the "Vsorp Basic" (VSORP, dynamic moisture sorption analyzer, ProUmid, Ulm, Germany) and setting the a_w^e at 0.30, 0.45, 0.60, 0.75, and 0.90. Data from each test were fitted with a regression line.

2.6. Model validation

The model proposed in this study was validated according to the following methodology: first, each model parameter was determined; second, the model parameters were used to predict the EGC quality decay kinetics; third, the model prediction was compared with the experimentally determined EGC quality decay kinetics. It is worth noting that the experimental data set used to calculate the model parameters differs from data set used to validate the model.

3. Results and discussion

The aim of this study was to predict the quality decay kinetic of EGC during its storage in a controlled environment (*i.e.,* constant storage temperature and relative humidity). The quality of ground coffee is indirectly measured by using the *pH* of the brew obtained from it; therefore, the aim of the research became the prediction of the function $pH(t)$, given the initial and boundary conditions (*i.e.,* initial *pH* and water activity of EGC and external water activity). The following illustrates how the model was derived, the method used to estimate the model parameters, and the ability in predicting the kinetics of EGC quality decay.

3.1. Derivation of the mathematical model

The basic assumption is that the EGC quality decay kinetic follows a first-order kinetic type equation:

$$\frac{dpH(t)}{dt} = -k\left(a_w^i(t)\right)\cdot[pH(t) - pH^{\infty}] \tag{1}$$

where: pH^{∞} is the equilibrium value of $pH(t)$, k is the kinetic constant, $a_w^i(t)$ is the water activity inside the capsule at the time t. Equation (1) is an ordinary differential equation. To solve Equation (1) it is necessary to know the parameter pH^{∞}, and the function $k\left(a_w^i(t)\right)$ (*i.e.,* $k\left(a_w^i\right)$ and $a_w^i(t)$).

To predict the function $a_w^i(t)$ the water mass balance inside the capsule is necessary. In the present study the following hypotheses were used: a) the water vapor in the capsule headspace behaves as an ideal gas; b) the equilibrium between water vapor in the capsule headspace and water adsorbed in the EGC is reached instantaneously; c) the EGC water sorption isotherm can be described with a straight line passing through the origin; d) the pseudo-steady state condition was used to calculate the water mass flux entering the capsule (*i.e.,* the permeation transient state was neglected; therefore, the water molecules absorbed by the capsule body, top film and bottom film were neglected); e) the water permeability of the capsule body, top film and bottom film only depends on the average between the initial water activity inside the capsule and the external water activity (*i.e.,* $a_w^{av} = \frac{a_w^e + a_w^{in}}{2}$; where: a_w^{av} is the average water activity, a_w^{in} is the initial water activity inside the capsule, and a_w^e is the external water activity). Under these hypotheses, it can be demonstrated that the water mass balance inside the capsule can be written as follow:

$$\frac{da_w^i(t)}{dt} = \frac{\left[\frac{P_w^{CB}}{\ell_{CB}}\cdot A_{CB} + \frac{P_w^{TF}}{\ell_{TF}}\cdot A_{TF} + \frac{P_w^{BF}}{\ell_{BF}}\cdot A_{BF}\right]\cdot p_w^0\cdot\left(a_w^e - a_w^i(t)\right)}{\frac{p_w^0\cdot V_{hs}}{R\cdot T} + m_d\cdot K} \tag{2}$$

where: p_w^0 is the water vapor pressure, V_{hs} is the volume of the capsule headspace, m_d is the mass of dry EGC, R is the universal gas constant, T is the storage temperature, P_w^{CB} is the water permeability of the capsule body, P_w^{TF} is the water permeability of the top film, P_w^{BF} is the water permeability of the bottom film, ℓ_{CB} is the thickness of the capsule body, ℓ_{TF} is the thickness of the top film, ℓ_{BF} is the thickness of the bottom film, A_{CB} is the mass exchange area of the capsule body, A_{TF} is the mass exchange area of the top film, A_{BF} is the mass exchange area of the bottom film. K is the slope of the straight line used to describe the water sorption isotherm of ground coffee powder.

It is worth noting that the term $\frac{\left[\frac{P_w^{CB}}{\ell_{CB}}\cdot A_{CB} + \frac{P_w^{TF}}{\ell_{TF}}\cdot A_{TF} + \frac{P_w^{BF}}{\ell_{BF}}\cdot A_{BF}\right]}{\frac{p_w^0\cdot V_{hs}}{R\cdot T} + m_d\cdot K}$ is constant; therefore, the following equation is the solution of Equation (2):

$$a_w^i(t) = a_w^e - \left(a_w^e - a_w^{in}\right)\cdot exp\left[-\frac{\left[\frac{P_w^{CB}}{\ell_{CB}}\cdot A_{CB} + \frac{P_w^{TF}}{\ell_{TF}}\cdot A_{TF} + \frac{P_w^{BF}}{\ell_{BF}}\cdot A_{BF}\right]\cdot p_w^0}{\frac{p_w^0\cdot V_{hs}}{R\cdot T} + m_d\cdot K}\cdot t\right] \tag{3}$$

Regarding the dependence of $\left[\frac{P_w^{CB}}{\ell_{CB}}\cdot A_{CB} + \frac{P_w^{TF}}{\ell_{TF}}\cdot A_{TF} + \frac{P_w^{BF}}{\ell_{BF}}\cdot A_{BF}\right]$ on the a_w^{av}, the following empirical expression was used:

$$\left[\frac{P_w^{CB}}{\ell_{CB}}\cdot A_{CB} + \frac{P_w^{TF}}{\ell_{TF}}\cdot A_{TF} + \frac{P_w^{BF}}{\ell_{BF}}\cdot A_{BF}\right] = \beta_0 + \beta_1\cdot exp\left(-\frac{\beta_2}{a_w^{av}}\right) \tag{4}$$

where: β_0, β_1, and β_2 are the parameters of Equation (4). Substituting Equation (4) in Equation (3) one obtains the following expression:

$$a_w^i(t) = a_w^e - \left(a_w^e - a_w^{in}\right)\cdot exp\left[-\frac{\left[\beta_0 + \beta_1\cdot exp\left(-\frac{\beta_2}{a_w^{av}}\right)\right]\cdot p_w^0}{\frac{p_w^0\cdot V_{hs}}{R\cdot T} + m_d\cdot K}\cdot t\right] \tag{5}$$

It is worth noting that once the parameters appearing in Equation (5) are known, the above equation can predict the function $a_w^i(t)$ once the initial and boundary conditions (*i.e.,* a_w^{in} and a_w^e) are given.

Concerning the function $k\left(a_w^i\right)$, the following empirical expression was used:

$$k(a_w^i) = k_0 + k_1 \cdot exp\left(-\frac{k_2}{a_w^i}\right) \tag{6}$$

where: k_0, k_1, and k_2 are the parameters of Equation (6). Substituting Equations (5) and (6) in Equation (1), one obtains the following expression:

$$\frac{dpH(t)}{dt} = -\left\{k_0 + k_1 \cdot exp\left\{-\frac{k_2}{\left\{a_w^e - \left(a_w^e - a_w^{in}\right)\cdot exp\left[-\frac{\left[\beta_0+\beta_1\cdot exp\left(-\frac{\beta_2}{a_w^{av}}\right)\right]\cdot p_w^0}{\frac{p_w^0\cdot v_{hs}}{R\cdot T}+m_d\cdot K}\cdot t\right]\right\}}\right\}\right\}\cdot\left[pH(t) - pH^{\infty}\right] \tag{7}$$

Equation (7) was numerically solved using the 4th-order Runge-Kutta formula (Press et al., 1989) and it was used to predict the function $pH(t)$.

3.2. Model's parameters estimation

To estimate the parameters k_0, k_1, k_2, and pH^{∞}, the pH of fresh ground coffee not encapsulated was monitored as described in the Materials and Methods section. The tests were conducted at four different water activities; the results are shown in Fig. 1. It is worth noting that according to the setup used for this test, the external and internal water activity are the same and both will be referred to as a_w^i; moreover, a_w^i did not change over time. As one would expect, the pH of the brew obtained from the investigated freshly ground coffee powder decreased over time, its initial value was found to be 5.47 ± 0.04, a value that aligns well with previous findings reported in the literature (Lopriore et al., 2024; Manzocco and Nicoli, 2007; Strocchi et al., 2023a). As can be inferred from data shown in Fig. 1, a progressive reduction in the pH was found at all storage conditions. This behavior is in accordance with literature findings where a strong correlation was observed between the pH of the extract and the moisture content of the coffee powder (Strocchi et al., 2023a, 2023b). In this framework, the suggested mechanism for this correlation assumes that the gradual moisture uptake could lead to the overcoming of the monolayer level of the ground coffee powder. Once this physico-chemical threshold is reached, enhanced interaction between the reactants triggers the hydrolysis of the ester bond of the chlorogenic acids, thus forming both caffeic and quinic acids (Dawidowicz and Typek, 2017), that are both water-soluble acidic compounds. The release in the medium of these acidic moieties could result in a decrease of the pH of the coffee brew (Strocchi et al., 2023a, 2023b; Yeager et al., 2023; Dawidowicz and Typek, 2017). To the best of our knowledge, there are no other similar studies in the literature that investigated the staling of fresh ground coffee powder by means of monitoring the pH decay at different a_w. In fact, available works mainly focused on coffee brews and its concentrated derivatives (Manzocco and Nicoli, 2007; Nicoli et al., 2009). Moreover, from data shown in Fig. 1 can be also inferred that, as the water activity increased, the pH decreased more rapidly. These results are not unexpected since an increase in water activity presumably increased the mobility of the agents involved in reactions that determine the pH decay.

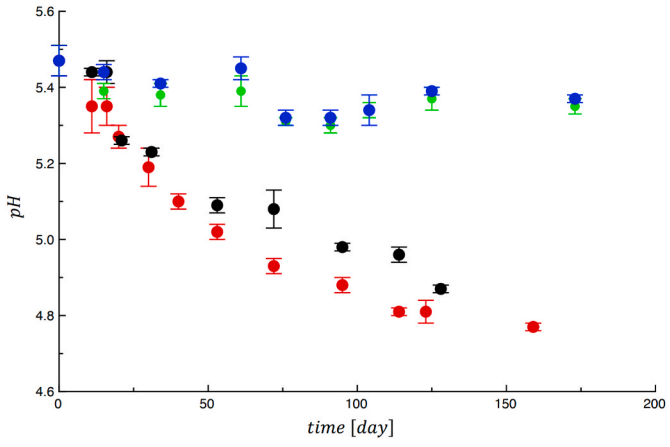

Fig. 1. pH obtained from bulk ground coffee stored at 23 °C plotted as a function of time. ● $a_w^i = 0.82$; ● $a_w^i = 0.65$; ● $a_w^i = 0.43$; ● $a_w^i = 0.23$.

Under constant water activity, the following equation is the solution of Equation (1):

$$pH(t, a_w^i) = pH^{\infty} + \left(pH^0 - pH^{\infty}\right)\cdot exp\left(-k(a_w^i)\cdot t\right) \tag{8}$$

where: pH^0 is the initial value of $pH(t)$. Substituting Equation (6) in Equation (8) one obtains the following expression:

$$pH(t, a_w^i) = pH^{\infty} + \left(pH^0 - pH^{\infty}\right)\cdot exp\left(-\left[k_0 + k_1\cdot exp\left(-\frac{k_2}{a_w^i}\right)\right]\cdot t\right) \tag{9}$$

To estimate the parameters pH^0, k_0, k_1, and k_2, Equation (9) was treated as a function with two independent variables (*i.e.,* t and a_w^i); it was simultaneously fitted to the four set of available data. Fig. 2 shows the pH (Z-axis) plotted as a function of a_w^i (X-axis) and time (Y-axis) and in the same picture the best-fitting surface is also shown. The goodness of fit was expressed by the mean of the relative deviation modulus ($\overline{E}\%$) (Buonocore et al., 2003):

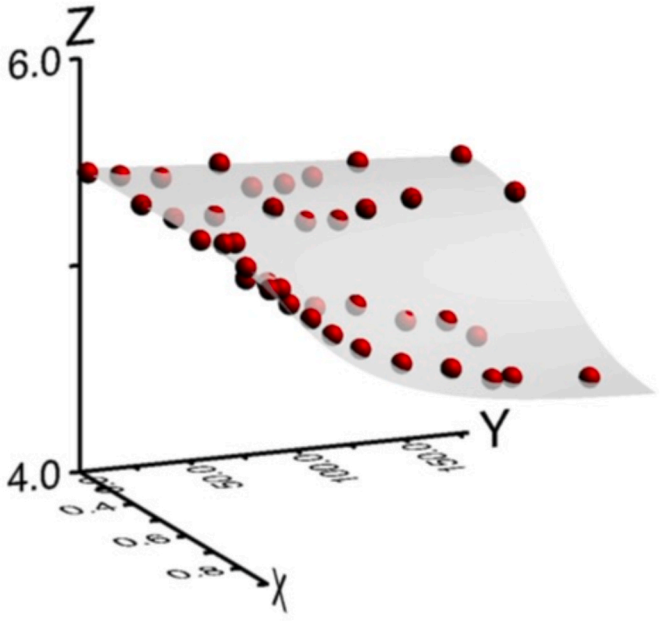

Fig. 2. pH (Z-axis) evolution of bulk coffee stored at 23 °C plotted as a function of a_w^i (X-axis) and time (Y-axis). The grey surface is the result of fitting the experimental observations (red dots) with Equation (9). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

$$\bar{E}\% = \frac{100}{N} \cdot \sum_{i=1}^{i=N} \frac{\left| M_i^{exp} - M_i^{pred} \right|}{M_i^{exp}} \tag{10}$$

where: N is the number of experimental data, M_i^{exp} is the experimental value, M_i^{pred} is the predicted value. The parameter values estimated according to the fitting procedure are reported in Table 1. A value of $\bar{E}\% = 0.7312$ was found, which can be considered more than acceptable.

To estimate the value of K, the fresh ground coffee water sorption isotherm was measured, the data are shown in Fig. 3. Considering that the water activity higher than 0.65 are unusual in real storage conditions, this value was set as the maximum tested water activity. In accordance with the extant literature about moisture affinity in ground roasted coffee, the results obtained in this study (Fig. 3) showed a clear sigmoidal-like shape (Anese et al., 2006; Lopriore et al., 2024).

This evidence would indicate that the Guggenheim-Anderson-De Boer (GAB) equation should be the most appropriate choice for fitting water sorption isotherm data. The reason lies in the fact that the GAB equation allows a better fit, associated with a better estimation of the monolayer content. The latter for ground and roasted coffee was commonly found to wave between $1.27 \cdot 10^{-3}$ and $2.11 \cdot 10^{-3}$ $\frac{moles\ of\ water}{g\ dry\ base}$ (Anese et al., 2006; Hayakawa et al., 1978; Lopriore et al., 2024; Mutlu et al., 2020). Although the ability of these non-linear mathematical models to fit the data, it must be noted that a simpler linear model is commonly preferred when it is possible to take a linearity between the humidity content and the water activity. Therefore, a straight line was chosen to describe the water sorption isotherm of ground coffee powder. The line shown in Fig. 3 was obtained by fitting a straight line passing through the origin to the sorption data. The value of K is reported in Table 1. A value of $\bar{E}\% = 11.2151$ was calculated, which can be considered acceptable.

To estimate the parameters β_0, β_1, and β_2, the capsule was filled with silica gel and its weight was monitored. Tests were conducted using several values of a_w^e, according to details reported in the Materials and Methods section. The results of this test are shown in Fig. 4. As expected, after the initial transient, the capsule reached the steady state, and the absorbed water increased linearly over time. It can be demonstrated that the water transport properties of the entire capsule depend on the slope of the linear part of the curve, through the following expression:

$$\left[\frac{P_w^{CB}}{\ell_{CB}} \cdot A_{CB} + \frac{P_w^{TF}}{\ell_{TF}} \cdot A_{TF} + \frac{P_w^{BF}}{\ell_{BF}} \cdot A_{BF} \right] = \frac{\frac{dAW(t)}{dt}}{p_w^e - p_w^i} \tag{11}$$

where: $AW(t)$ is the weight of water absorbed by the capsule at time t, p_w^e and p_w^i are the external and internal water vapor partial pressure, respectively.

Fig. 5 shows the water transport properties of the entire capsule plotted as a function of a_w^{av}. The capsule transport properties increased as a_w^{av} increased. This is because the polymers used to make the capsule are

Table 1
Parameter values estimated according to the fitting procedure.

Model parameter	Parameter value
pH^{∞}	4.7223 ± 0.051296
K	0.0055829 ± 0.00013349 $\frac{moles\ of\ water}{g\ db}$
β_0	$0.00079899 \pm 0.00074545$ $\frac{moles\ of\ water}{day \cdot kPa}$
β_1	0.081931 ± 0.036081 $\frac{moles\ of\ water}{day \cdot kPa}$
β_2	1.0698 ± 0.2362
k_0	0.0010403 ± 0.00029451 $\frac{1}{day}$
k_1	0.3074 ± 0.1352 $\frac{1}{day}$
k_2	2.3520 ± 0.2837

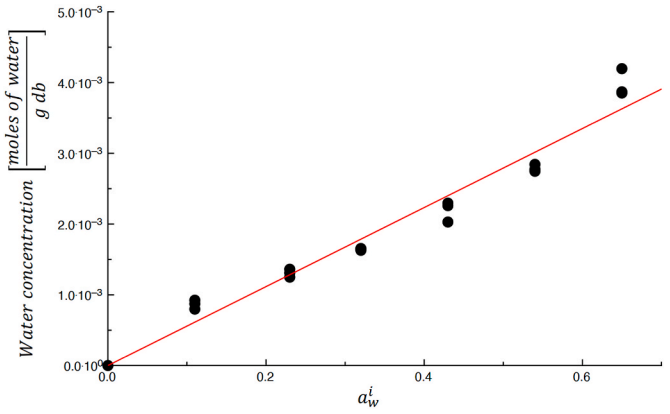

Fig. 3. Ground coffee water sorption isotherm at 23 °C. The red line ( ) represents the best fitting obtained by using a simple linear equation passing through the origin. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

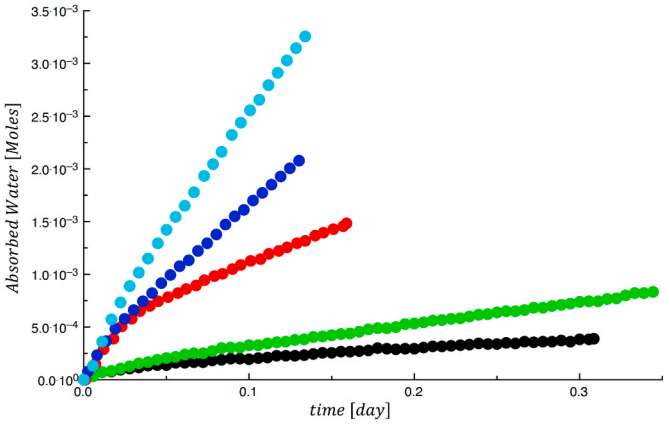

Fig. 4. Water absorbed by the capsule filled with silica gel plotted as function of time. ● $a_w^e = 0.30$; ● $a_w^e = 0.45$; ● $a_w^e = 0.60$; ● $a_w^e = 0.75$; ● $a_w^e = 0.90$.

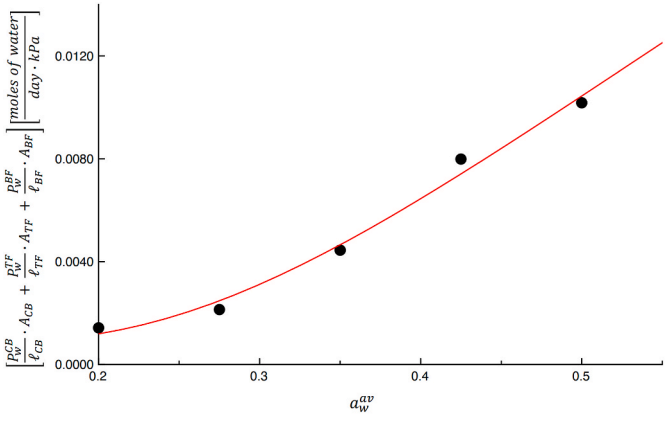

Fig. 5. Water transport properties at 23 °C of the entire capsule plotted as a function of a_w^{av}. The displayed red line ( ) represents the best fitting with Equation (4). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

hydrophilic, which means that water can increase the polymer macromolecular mobility (*i.e.*, water molecules can plasticize the polymers used to make the capsule). This in turn produces an increase of the polymer water diffusion coefficient. It must be also considered that the water solubility coefficient of hydrophilic polymers is also an increasing function of the water activity. Both the above-mentioned aspects cause the permeability coefficient of hydrophilic polymers to increase as the water activity increases. Data reported in Fig. 5 show slight deviations from values reported in the literature for biobased hydrophilic polymers, such as various commercial and biodegradable packaging films. For instance, water vapor transport properties at 20 °C and 0.38 a_w^{av} for commercial films NatureFlex 30 NK, 23 NM, and 55 N913 were found to be equal to 0.00059, 0.001409, and 0.000186 $\frac{moles\ of\ water}{day \cdot kPa}$, respectively (Macedo et al., 2013). Additionally, the PLA demonstrates a value of 0.00192 $\frac{moles\ of\ water}{day \cdot kPa}$ at 23 °C and 0.43 a_w^{av} (Karkhanis et al., 2021) and the PBS a value of 0.000793 $\frac{moles\ of\ water}{day \cdot kPa}$ at 38 °C and 0.49 a_w^{av} (Durmaz et al., 2024).

The values of β_0, β_1, and β_2 are also reported in Table 1. A value of $\overline{E}\% = 9.3805$ was obtained, which can be considered acceptable.

3.3. Model validation

It is necessary to highlight that the value of pH^0 of fresh ground coffee (*i.e.*, the one used to run the tests used to determine k_0, k_1, k_2, and pH^∞) and that of the encapsulated ground coffee (*i.e.*, the one used to run the tests used to validate the model) are different. Precisely, the difference between these two values is 0.11. Consequently, the pH^∞ values used to predict the quality decay kinetic of EGC were reduced to the same amount (*i.e.*, 0.11). Therefore, the value of pH^∞ used for prediction is 4.6123 (*i.e.*, 4.7223 − 0.11).

Regarding the term $\frac{p_w^0 \cdot V_{hs}}{R \cdot T}$ appearing in Equation (7), it was not possible to measure the volume of the capsule headspace (i.e., V_{hs}). Therefore, the term $\frac{p_w^0 \cdot V_{hs}}{R \cdot T}$ was calculated assuming that the volume of the capsule and the volume of the capsule headspace are the same. It is worth noting that this hypothesis brings to an overestimation of the term $\frac{p_w^0 \cdot V_{hs}}{R \cdot T}$. Under the above-mentioned hypothesis, it was found that $\frac{p_w^0 \cdot V_{hs}}{R \cdot T} = 1.98 \cdot 10^{-5}$ *moles of* H_2O. Considering that the term $m_{ss} \cdot K$ is equal to 0.0385 *moles of* H_2O, in Equation (7) the term $\frac{p_w^0 \cdot V_{hs}}{R \cdot T}$ was neglected.

Fig. 6 (a, b, and c) shows the evolution of ECG *pH* stored under controlled temperature and relative humidity. The curves shown in the figure were predicted by using Equation (7), the value of the model's parameter are those reported beforehand. In the following are reported the calculated $\overline{E}\%$ values: $a_w^e = 0.43 \rightarrow \overline{E}\% = 1.3907$, $a_w^e = 0.54 \rightarrow \overline{E}\% = 1.0044$, $a_w^e = 0.65 \rightarrow \overline{E}\% = 0.7052$. Considering the complexity of the phenomena involved, and the numerous simplifications made to derive the model, it can be stated that it satisfactorily predicts the quality decay of EGC stored under controlled conditions. To the best of our knowledge, despite the many references focus on the modelling of the chemical and physical properties of ground and roasted coffee, these studies predominantly address the secondary SL or stability of coffee derivatives (Anese et al., 2006; Manzocco and Nicoli, 2007; Mardjan and Hakim, 2019; Nicoli and Savonitti, 2005).

Models comparable to the one proposed in this study have been developed for other types of dry foods (Del Nobile, 2001; Jena and Das, 2012; Lee and Robertson, 2021; Yan et al., 2008). A particularly similar approach was proposed by Lee and Robertson (2021). The Authors simulated the dynamic moisture changes in dried onion flakes, cabbage, and green beans when packaged in biobased materials, to predict the associated quality decay. Notably, the water vapor transmission rate was predicted by using a model mimicking an Arrhenius-type dependency. However, unlike the model proposed in this study (Equation (7)), Lee and Robertson (2021) used the GAB model for predicting the moisture

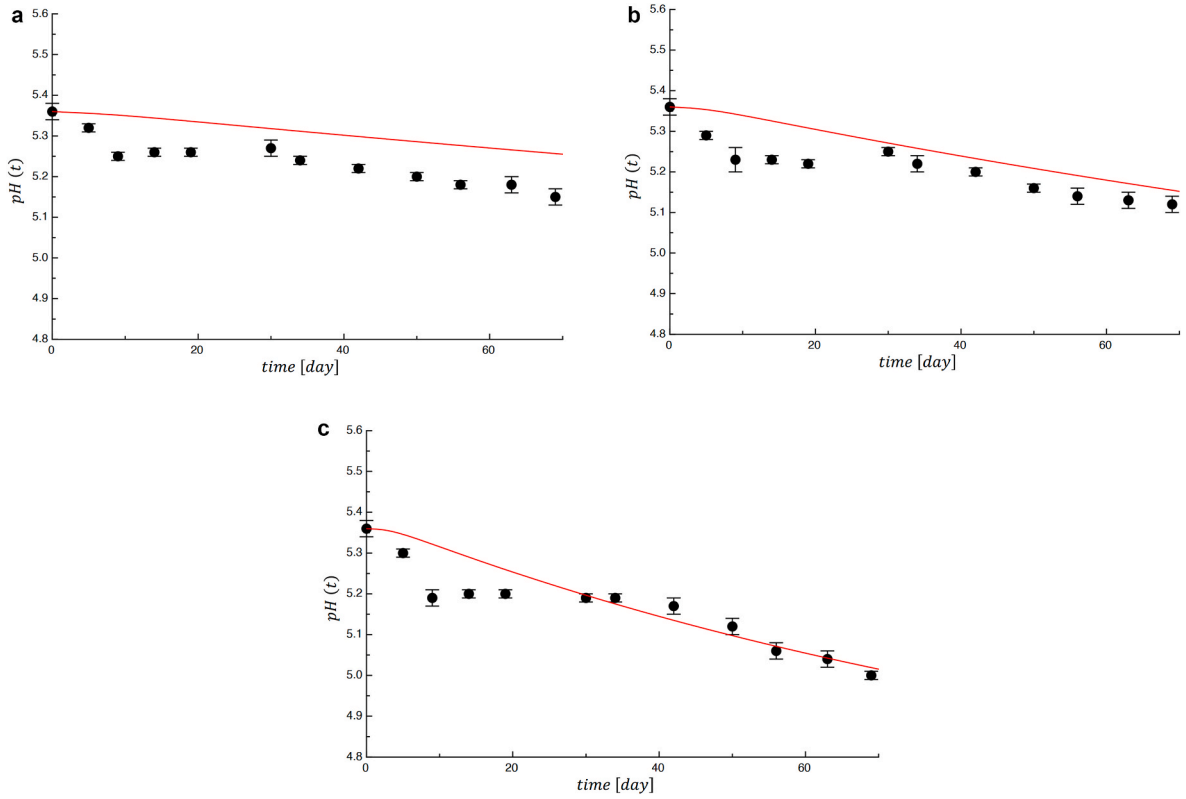

Fig. 6. EGC *pH* plotted as a function of storage time where the red line ( ) represents the prediction obtained by using Equation (7). Letters from *(a)* to *(c)* represent respectively the different studied environmental water activities (a_w^e), namely, 0 .43, 0.54, and 0.65. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

changes of the selected food items. Unfortunately, these Authors did not experimentally validate their model; therefore, it is not possible to compare the goodness of prediction of the model presented in this study with that presented by Lee and Robertson (2021). Other research addressed water transport properties, predominantly assuming constant water vapor barrier characteristics (An et al., 2018; Del Nobile, 2001; Macedo et al., 2013; Robertson and Lee, 2021; Taoukis et al., 1988). These studies also typically used either linear or simplified nonlinear sorption isotherms for food products, rather than using the GAB model.

4. Conclusions

A new model was proposed to predict the quality decay kinetic of EGC. The main hypothesis on which the proposed model is based is that the EGC quality decay kinetic can be described using a first-order kinetic type equation. The dependence of the kinetic constant on the water activity was described with an empirical equation. On the other hand, the function describing the change of water activity over time was obtained by carrying out the mass balance of water inside the capsule. In calculating the mass flow entering the capsule, it was assumed that the water permeability of the capsule depends on the average between the initial value of the internal water activity and the external water activity. This hypothesis is an attempt to keep as simple as possible the above-mentioned water mass balance equation, and to consider the fact the water plasticizes the polymers used to make the capsule. The model parameters were estimated by performing specific tests on both fresh ground coffee and capsule filled with silica gel. The quality decay kinetic of EGC was experimentally determined and data were compared with the model prediction. Despite the numerous assumptions made to derive the model, the results showed that the goodness of the prediction was quite acceptable. Among the hypotheses made to develop the model the most critical are probably those used to calculate the water mass flux entering the capsule. In fact, the dependence of capsule water permeability on the external and internal water activity was oversimplified. Moreover, it was assumed that the amount of water absorbed by the capsule body, top film and bottom film is negligible (pseudo-steady state hypothesis). In the future, the possibility of using the present model to describe the decay kinetics of other capsule-coffee systems will be evaluated. It is worth highlighting that the fully predictive nature of the proposed model makes it an excellent candidate to be advantageously used at industrial level to predict the shelf life of EGC.

CRediT authorship contribution statement

Marco Lopriore: Writing – original draft, Visualization, Formal analysis. **Marika Valentino:** Formal analysis. **Giulia Ravaioli:** Writing – review & editing. **Maria Cristina Nicoli:** Writing – review & editing, Validation, Conceptualization. **Amalia Conte:** Writing – review & editing, Validation, Data curation, Conceptualization. **Matteo Alessandro Del Nobile:** Writing – review & editing, Validation, Data curation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

References

Adiletta, G., Di Matteo, P., Russo, P., 2024. Stability of dried pumpkin snacks packed in bio-polymeric films through accelerated shelf-life testing. Food Bioprocess Technol. 17.

Alongi, M., Lopriore, M., Calligaris, S., Manzocco, L., Nicoli, M.C., 2023. Identifying the acceptability limit for shelf-life assessment of potato chips: mismatching between quality and safety issues. J. Food Eng. 357.

An, D.S., Lee, J.H., Lee, D.S., 2018. Shelf life model of powdered infant formula as function of temperature and oxygen concentration. Food Packag. Shelf Life 15, 130–133.

Anese, M., Manzocco, L., Nicoli, M.C., 2006. Modeling the secondary shelf life of ground roasted coffee. J. Agric. Food Chem. 54, 5571–5576.

Buonocore, G.G., Del Nobile, M.A., Di Martino, C., Gambacorta, G., La Notte, E., Nicolais, L., 2003. Modeling the water transport properties of casein-based edible coating. J. Food Eng. 60 (1), 99–106.

Calligaris, S., Da Pieve, S., Kravina, G., Manzocco, L., Nicoli, M.C., 2008. Shelf-life prediction of bread sticks by using oxidation indices: a validation study. J. Food Sci. 73, 51–56.

Dawidowicz, A.L., Typek, R., 2017. Transformation of chlorogenic acid during the coffee beans roasting process. European Food Research and Technology 243, 379–390.

Del Nobile, M.A., 2001. Packaging design of potato chips. J. Food Eng. 47, 211–215.

Durmaz, B.U., Nigiz, F.U., Aytac, A., 2024. Active packaging films based on poly (butylene succinate) films reinforced with alkaline halloysite nanotubes: production, properties, and fruit packaging applications. Appl. Clay Sci. 259, 107517.

European Union, 2019. Directive (EU) 2019/904 of the European parliament and of the council of 5 June 2019 on the reduction of the impact of certain plastic products on the environment. Off. J. Eur. Union 155, 1–19.

Hayakawa, K., Matas, J., Hwang, M.P., 1978. Moisture sorption isotherms of coffee products. J. Food Sci. 43, 1026–1027.

Jena, S., Das, H., 2012. Shelf life prediction of aluminum foil laminated polyethylene packed vacuum dried coconut milk powder. J. Food Eng. 108, 135–142.

Karkhanis, S.S., Stark, N.M., Sabo, R.C., Matuana, L.M., 2021. Potential of extrusion-blown poly(lactic acid)/cellulose nanocrystals nanocomposite films for improving the shelf-life of a dry food product. Food Packag. Shelf Life 29, 100689.

Lee, D.S., Robertson, G.L., 2021. Interactive influence of decision criteria, packaging film, storage temperature and humidity on shelf life of packaged dried vegetables. Food Packag. Shelf Life 28, 100674.

Lindh, H., Williams, H., Olsson, A., Wikstrom, F., 2016. Elucidating the indirect contributions of packaging to sustainable development: a terminology of packaging functions and features. Packag. Technol. Sci. 29, 225–246.

Lopriore, M., Alongi, M., Calligaris, S., Manzocco, L., Ravaioli, G., Nucci, A., Nicoli, M.C., 2024. Moisture uptake during storage of coffee packed into compostable capsules decreases the quality of coffee brew. Food Packag. Shelf Life 46, 101403.

Lopriore, M., Alongi, M., Valentino, M., Anese, M., Nicoli, M.C., 2025. Impact of environmental humidity on instant coffee stability: defining moisture thresholds for quality degradation and shelf life prediction. Foods 14 (10).

Macedo, I.S.M., Sousa-Gallagher, M.J., Oliveira, J.C., Byrne, E.P., 2013. Quality by design for packaging of granola breakfast product. Food Control 29, 438–443.

Manzocco, L., Calligaris, S., Nicoli, M.C., 2006. Modeling bleaching of tomato derivatives at subzero temperatures. J. Agric. Food Chem. 54, 1302–1308.

Manzocco, L., Nicoli, M.C., 2007. Modeling the effect of water activity and storage temperature on chemical stability of coffee brews. J. Agric. Food Chem. 55, 6521–6526.

Mardjan, S., Hakim, F.R., 2019. Prediction shelf life of arabica Java preanger coffee beans under hermetic packaging using Arrhenius method. IOP Conf. Ser. Mater. Sci. Eng. 557, 012077.

Mutlu, C., Candal-Uslu, C., Kılıç-Büyükkurt, Ö., Erbaş, M., 2020. Sorption isotherms of coffee in different stages for producing Turkish coffee. J. Food Process. Preserv. 44, 1–7.

Nicoli, M.C., Calligaris, S., Manzocco, L., 2009. Shelf-life testing of coffee and related products: uncertainties, pitfalls and perspectives. Food Eng. Rev. 1, 159–168.

Nicoli, M.C., Savonitti, O., 2005. Storage and packaging. In: Illy, A., Viani, R. (Eds.), Espresso Coffee. the Science of Quality. Elsevier Academic Press, San Diego, CA.

Nicoli, M.C., 2012. The shelf life assessment process. In: Nicoli, M.C. (Ed.), Shelf Life Assessment of Food. CRC Press, Boca Raton, FL, pp. 17–36.

Nilsen-Nygaard, J., Fernández, E.N., Radusin, T., Rotabakk, B.T., Sarfraz, J., Sharmin, N., Sivertsvik, M., Sone, I., Pettersen, M.K., 2021. Current status of biobased and biodegradable food packaging materials: impact on food quality and effect of innovative processing technologies. Compr. Rev. Food Sci. Food Saf. 20, 1333–1380.

Peelman, N., Ragaert, P., Verguldt, E., Devlieghere, F., De Meulenaer, B., 2016. Applicability of biobased packaging materials for long shelf-life food products. Packaging Research 1 (1), 7–20.

Phothapaeree, N., Jarusaksakul, N., Somwangthanaroj, A., Tananuwong, K., 2017. Influence of packaging and storage conditions on quality parameters and shelf life of solar-dried banana. Songklanakarin J. Sci. Technol. 39, 253–260.

Press, W.H., Flannery, B.P., Teukolsky, S.A., Vetterling, W.T., 1989. Numerical Recipes in Pascal. Univ. Press, Cambridge, p. 602.

Piergiovanni, L., Limbo, S., 2012. Packaging-food interactions in shelf life modeling. In: Nicoli, M.C. (Ed.), Shelf Life Assessment of Food. CRC Press, Boca Raton, FL, pp. 199–246.

Robertson, G.L., Lee, D.S., 2021. Comparison of linear and GAB isotherms for estimating the shelf life of low moisture foods packaged in plastic films. J. Food Eng. 291, 110317.

Romani, S., Tappi, S., Balestra, F., Rodriguez-Estrada, M., Siracusa, V., Rocculi, P., Dalla Rosa, Marco, 2014. Effect of different new packaging materials on biscuit quality during accelerated storage. J. Sci. Food Agric. 95.
Ruthenberg, K., Chang, H., 2017. Acidity: modes 518 of characterization and quantification. Stud. Hist. Philos. Sci. 65, 121–131.
Santanatoglia, A., Angeloni, S., Caprioli, G., Fioretti, L., Ricciutelli, M., Vittori, S., Alessandroni, L., 2024. Comprehensive investigation of coffee acidity on eight different brewing methods through chemical analyses, sensory evaluation and statistical elaboration. Food Chem. 454, 139717.
Strocchi, G., Bagnulo, E., Ravaioli, G., Pellegrino, G., Bicchi, C., Liberto, E., 2023a. Evaluation of the behaviour of phenols and alkaloids in samples of roasted and ground coffee stored in different types of packaging: implications for quality and shelf life. Food Res. Int. 174, 113548.
Strocchi, G., Müller, A.B., Kuhnert, N., Martina, K., Bicchi, C., 2023b. Diterpenes stability of commercial blends of roasted and ground coffees packed in copolymer coupled with aluminium and eco-friendly capsules. Food Res. Int. 174, 113577.
Taoukis, P.S., Meskine, A.E., Labuza, T.P., 1988. Moisture transfer and shelf life of packaged foods. In: Hotchkiss, J.H. (Ed.), Food Packaging Interactions. American Chemical Society, Washington, D.C., pp. 243–261
Wu, F., Misra, M., Mohanty, A.K., 2021. Challenges and new opportunities on barrier performance of biodegradable polymers for sustainable packaging. Prog. Polym. Sci. 117, 101395.
Yan, Z., Sousa-Gallagher, M.J., Oliveira, F.A.R., 2008. Mathematical modelling of the kinetic of quality deterioration of intermediate moisture content banana during storage. J. Food Eng. 84, 359–367.
Yeager, S.E., Batali, M.E., Guinard, J.X., Ristenpart, W.D., 2023. Acids in coffee: a review of sensory measurements and meta-analysis of chemical composition. Crit. Rev. Food Sci. Nutr. 63, 1010–1036.