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Critical Analysis of the Use of Semiempirical Models on the Dehydration of Thin-Layer Foods Based on Two Study Cases

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Abstract
Moisture transport during food drying can be phenomenologically described by Fick's second law and by the so-called anomalous diffusion model. However, in the literature, many studies have shown the extensive use of empirical/semiempirical models (EMs/SEMs) to adjust experimental data for the drying of thin-layer foods. This research aims to perform a critical analysis of the most commonly used EMs/SEMs and compare them with Fick's second law and an anomalous diffusion model using two different sets of hot-air drying data. Two waste byproducts from the food industry, spent coffee grounds and passion fruit peels, were selected for analysis. The selected EMs/SEMs were found to be mathematically interrelated (i.e., some are a subset of others), and their appropriateness was incorrectly justified mainly by their statistical goodness-of-fit. As shown, it is highly recommended that researchers start analyzing drying data with phenomenological models. The extensive use of EMs and SEMs can be replaced by the anomalous diffusion model, which has a high capacity to adjust empirical data and a sound phenomenological description of the process.

Keywords Food drying · Moisture transport · Modeling · Convective drying · Diffusion

1 Introduction

Convective drying is one of the most commonly used drying methods for the dehydration of solid foods, including fruit, vegetables, meat, and a wide variety of food waste byproducts. Convective drying consists of passing a stream of hot air through the food material, where heat is transferred to the surface of the food by convection [1]. Typical mathematical models used to describe the drying process can be classified into three main groups: theoretical models (TMs), semiempirical models (SEMs), and empirical models (EMs).

From a theoretical point of view, the moisture transport mechanism that occurs in the dehydration process in fruits and vegetables is often described by Fick's second law, in which diffusion is considered the main mechanism by which water is removed from food [2–4]. Models based on Fick's second law are favored because they are the best-known phenomenological models for representing diffusional mechanisms [5]. However, several assumptions inherent in Fick's second law are not fulfilled in food materials, i.e., the water diffusion process described by Fick's second law assumes that the amount of water in a material is initially uniform [2]; the model also assumes that the mass transfer is unidirectional, constant and governed only by diffusion and does not take into account the structural variations that occur in foods during the dehydration process, such as shrinkage, changes in density and porosity, changes in the thermal properties of the food and the movement of soluble molecules such as salts and sugars [1, 4, 5]. Although classical diffusion theory is normally utilized, it is widely acknowledged that the applicability of this theory to food materials is questionable. There is abundant evidence in biological systems that

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diffusion theory is not adequate for explaining most molecular movements, mainly in the crowded, heterogeneous, and highly organized interior of cells [6, 7].

The fractional calculus approach is a recent and powerful mathematical tool to represent a theoretical anomalous diffusion phenomenon and considers many of the changes that occur in food materials during drying processes [5–8]. This tool is used to mathematically represent the anomalous diffusion of solutes whose movements can be faster or slower than those postulated by Fick's second law due to the microstructure of the food matrices [5–7].

On the other hand, EMs and SEMs frequently originate from Fick's second law, with a similar functional form and a simplified mathematical expression developed for drying time. Namely, these EMs and SEMs are adapted from the solution of Fick's second law for a long processing time, and the infinite summation is explained only for the first term. As described by Simpson et al. [7], the mathematical solution of the anomalous diffusion model explains the successful implementation of one of the most popular EMs and SEMs, such as Page's model and related empirical equations. In addition, similar to Page's model, some models include an exponential constant over time [9, 10]. Additionally, a typical way—not necessarily a correct way—to estimate or select the most adequate EMs and SEMs to better represent data has been through the use of the model goodness-of-fit summarized in the correlation coefficient (R^2), even when restricted to the R^2 value and not complemented with an error analysis to further test the appropriateness of the model. It is worth noting that the improvement in the goodness-of-fit in EMs and SEMs is due to the increase in the polynomial order or to a greater number of parameters than to the fact that they are better at describing the phenomenology of the thin-layer drying process [11]. As a result, when using EMs and SEMs, it is not possible to extrapolate data to different operating conditions. There are several reports in which different EMs and SEMs have been used to successfully fit data characterizing water migration processes during food drying [3, 12, 13]. However, the main disadvantage of EMs and SEMs is their limited extrapolation and prediction capacities under different drying conditions (e.g., different process temperatures or sample thicknesses), as discussed by Simpson et al. [7] for Page's model case.

We hypothesize that simple but phenomenological models such as Fick's second law and anomalous diffusion are sufficient not only to adequately fit the thin layer drying process but also to extrapolate data to different operating conditions. Therefore, the extensive use of several EMs and SEMs should be avoided for this purpose. However, food structure and composition play an important role in the control of drying rates and mechanisms involved in the models proposed.

This research aims to perform a critical and in-depth analysis of the most commonly used EMs and SEMs and to compare them to phenomenological models such as Fick's second law and anomalous diffusion through the fitting of two different sets of dehydration data for two waste byproducts from the food industry (spent coffee grounds and passion fruit peels) and testing their appropriateness for different processing conditions.

2 Methodology

2.1 Experimental Data

To perform a critical analysis of EMs and SEMs and then compare these models to phenomenological models (Fick's second law and anomalous diffusion), two drying datasets derived from spent coffee grounds and passion fruit peels were used. For spent coffee grounds (SCGs), the drying process was performed according to Osorio-Arias et al. [14]. The data used for this analysis corresponded to hot-air dehydration of spent coffee considering two thicknesses, 0.01 and 0.02 m, performed at 50 °C and at an airflow rate of 2 m/s. For the passion fruit peels, the drying conditions were established according to Duarte et al. [4]. In this case, the data used corresponded to those obtained throughout hot-air dehydration of passion fruit peels at three temperatures, 50, 55, and 60 °C, with a 5-mm thickness. The diffusion coefficients (D_{eff}) using Fick's second law and the anomalous model were determined according to Simpson et al. 2017. A dimensionless moisture ratio MR_t was calculated from the moisture content, as shown in Eq. (1):

$$\mathrm{MR}_t = \frac{X_t - X_e}{X_0 - X_e} \tag{1}$$

where X_t is the moisture content at any time t (g water/g dry basis), X_e is the moisture content at equilibrium (g water/g dry basis) and X_0 is the initial moisture content (g water/g dry basis). Values of X_e are considered relatively small compared to X_t or X_0 [4]. The determination of the effective diffusion coefficients (D_{eff}) was performed using the solution for an infinite slab of Fick's second law (Eq. 2) [2]. The solution of Fick's law was used for one-dimensional transport, with the assumptions that moisture migrates only by diffusion, that negligible shrinkage occurs and that the diffusion coefficients and temperature are constant [15], Eq. (2).

$$\mathrm{MR}_t = \frac{8}{\pi^2}\sum_{i=0}^{\infty}\frac{1}{(2i-1)^2}e^{\left(\frac{-(2i-1)^2\pi^2 D_{\mathrm{eff}}t}{4L^2}\right)} \tag{2}$$

However, for long drying times ($MR_t < 0.6$), Eq. (2) can be simplified as follows:

$$MR_t = \frac{8}{\pi^2} e^{\left(\frac{-D_{eff} \times \pi^2 \times t}{4L^2}\right)} \tag{3}$$

where D_{eff} is the effective diffusion coefficient (m^2/s), t is the drying time (s), and L is the half-thickness of the slice (m).

Additionally, an anomalous diffusion model based on the fractional calculus approach was applied.

$$MR_t = \frac{8}{\pi^2} \sum_{i=0}^{\infty} \frac{1}{(2i-1)^2} E_{\alpha}^{\left(\frac{-(2i-1)^2 \pi^2 D_{eff} t^{\alpha}}{4L^2}\right)} \tag{4}$$

where D_{eff} is the effective diffusion coefficient (m^2/s^{α}), t is the drying time (s), L is the half-thickness of the slice (m) and E_{α} corresponds to a Mittag–Leffler function. For long drying times, Eq. (4) can be simplified to Eq. (5), where E_{α} converges to the exponential function

$$MR_t = \frac{8}{\pi^2} e^{\left(-D_{eff} \left(\frac{\pi}{2L}\right)^2 t^{\alpha}\right)} \tag{5}$$

The α value indicates the transport mechanism that dominates the mass transfer process: if $0 < \alpha < 1$ corresponds to subdiffusion, and if $\alpha > 1$, the mechanism can be considered to be superdiffusivity, in the case of a converging to unity, the anomalous diffusion model converges to Fick's second law [14].

The data for both samples were adjusted to Fick's second law, an anomalous diffusion model, and nine EMs and SEMs, as depicted in Table 1. Mathematical modeling, mean squared error-x^2 (MSE-x^2), and root mean square (RMS) for both samples were analyzed and performed using DATA FIT software (Oakdale Engineering, Version 9.0, Pennsylvania, USA) and MATLAB (MATLAB version 2019a, The Mathwork, Inc., Natik, MA, USA).

2.2 Empirical and Semiempirical Drying Models (EMs and SEMs) on the Dehydration of Thin-Layer Foods

As mentioned in Sect. 2.1, nine EMs and SEMs on the dehydration of thin-layer foods (Table 1) were selected to statistically analyze their goodness of fit. EMs and SEMs were selected after critically reviewing a long list of proposed thin-layer drying models [16, 17, 21, 22]. The EMs and SEMs depicted in Table 1 were selected, as mentioned, due to their common use in many different research articles and for their reported proven goodness-of-fit [11–13, 18, 19, 23].

2.3 Phenomenological Drying Models for the Dehydration of Thin-Layer Foods

As shown by Einstein in 1905, diffusion phenomena are macroscopic observations of microscopic stochastic processes, that is, the random walk of diffusing particles [24]. The result of the random walk is a Brownian process that is represented by the traditional Fickian equation (Fick's second law). However, this requires that the diffusing particles be described by a random walk with parameters distributed from a finite variance distribution. Nevertheless, in cases where these parameters are distributed from a heavy tail distribution (i.e., infinite variance), the macroscopic process is no longer represented by Fickian diffusion but is instead represented by the so-called anomalous diffusion model [25]. These cases are expected to occur in heterogeneous media and/or amorphous media, as is the case for food matrices. For these cases, fractional calculus represents the diffusive process in these systems [16, 26]. Fractional calculus takes into account the anomaly in the random process of the diffusant and represents it macroscopically and, more relevantly, their appropriateness regarding their capabilities to provide a phenomenological meaning to the drying process. Furthermore, Fick's second law and anomalous phenomenological models are also included in Table 1 as theoretical (phenomenological) models (TMs).

Therefore, phenomenological models such as Fick's second law and the anomalous diffusion approach were selected for their commonality and ease of use to model the thin layer drying process [6, 7]. Since foods are hierarchically structured at a molecular scale, it seems relevant to develop a multiscale model. In this research, it is assumed that Fick's second law and the anomalous diffusion model are sufficient to obtain a clear understanding of the drying phenomena involved in the dehydration of thin-layer foods.

3 Results and Discussion

3.1 Critical Analysis of EMs and SEMs Applied to the Dehydration of Thin-Layer Foods

TMs and EMs/SEMs have been useful in approaching many complex phenomena that arise in the food science and technology field [3, 7, 27]. EMs and SEMs are particularly helpful in fitting drying data; for different reasons, TMs cannot be implemented and applied adequately, mainly due to the high complexity of the transport phenomena in food matrices [23, 28]. Most food processes, such as drying, freezing, and thermal processing, have been approximated using TMs and EMs/SEMs, and in specific cases, the approximation output by TMs has been successful, even reaching the point where they represent a reliable alternative to EMs/SEMs [3].

Table 1 Phenomenological and empirical/semiempirical thin-layer models used in the food drying process

Model's name	Mathematical model	References
1. Newton	$MR = \exp(-kt)$	El-Beltagy et al. [16]
2. Page	$MR = \exp(-kt^n)$	Onwude et al. [3]
3. Modified Page (II)	$MR = \exp[-(K\,t)^n]$	Vega et al. [12]
4. Henderson and Pabis	$MR = a\exp(-kt)$	Hashim et al. [17]
5. Midilli	$MR = a\exp(-kt) + bt$	Onwude et al. [3]
6. Logarithmic	$MR = a\exp(-kt) + c$	Demir et al. [19]
7. Two-term exponential	$MR = a\exp(-k_0 t) + (1-a)\exp(-k_1 at)$	Midilli and Kucuk [13]
8. Demir et al	$MR = a\exp(-K\,t)^n + b$	Demir et al. [19]
9. Modified Midilli	$MR = a\exp(-kt^n) + bt$	Gan and Poh [18]
10. Fick's second law	$MR\frac{8}{\pi^2}\left[\sum_{n=1}^{50}\frac{1}{2n-1}\exp\left(-D_{\text{eff}}\left(\frac{(2n-1)\pi}{2L}\right)^2 t\right)\right]$	Crank [20]
11. Anomalous	$MR\frac{8}{\pi^2}\left[\sum_{n=1}^{50}\frac{1}{2n-1}E_{\alpha,1}\left(-D_{\text{eff}}\left(\frac{(2n-1)\pi}{2L}\right)^2 t^\alpha\right)\right]$	Simpson et al. [6]

Although EMs/SEMs can help in the forecasting process of a particular situation, they cannot predict the process under different operating conditions [27]. On the other hand, TMs have the advantage of being able to extrapolate information not only beyond the range of experimental data but also to different operating conditions [7]. Generally, in the dehydration of thin-layer foods, TMs such as Fick's second law or the anomalous diffusion model require only a few parameters. In addition, the parameters of these TMs have a physical interpretation, which is not the case with EMs/SEMs [9, 20, 27, 29].

One of the characteristics that emerges with the indiscriminate use of EMs/SEMs is that when more parameters are added to improve the goodness-of-fit, this capacity invariably increases, but in the same way, the models lose their predictive capacity and physical interpretation. Sometimes it appears that the goal is to search for better data fitting regardless of which model best interprets the phenomenological aspect of the food process [6, 7]. As an example, the mathematical analysis of the nine EMs/SEMs presented in Table 1 shows that only one or two of the EMs/SEMs would be sufficient to fit the data expanded in the paper [30]. This scenario occurs because, as discussed below, some EMs/SEMs are a subset of others; therefore, they do not strictly represent a new mathematical model. As analyzed by Simpson et al. [7], "*Alibas [21] discusses twenty-one empirical and semiempirical thin-layer drying models (including Page's equation) and concluded that the modified Henderson & Pabis and Alis models were the best in terms of R^2*". However, as discussed in Simpson et al. [7], the criterion to select such models is biased in favor of their statistical appropriateness, disregarding their phenomenological understanding.

To be precise, here, we describe the application of SEMs to the thin-layer drying process as involving the direct mimicking of the solution of Fick's second law in the model and the anomalous diffusion model for long drying times [15]; for an infinite slab, the solution of Fick's second law is as follows, Eq. (6):

$$MR_t = \frac{8}{\pi^2}e^{-kt} \tag{6}$$

where MR_t is the moisture ratio, k is the kinetic drying constant ($D_{\text{eff}}*\pi^2/(4L^2)$) and t is the drying time (s).

In addition, for regular geometries (spheres, infinite cylinders, cubes, etc.), the solution can be written as follows, Eq. (7):

$$MR_t = ae^{-kt} \tag{7}$$

where MR_t: Moisture ratio, a: geometric constant; k: kinetic drying constant ($D_{\text{eff}}*\pi^2/(4L^2)$) and t: drying time (s).

On the other hand, as presented in Simpson et al. [6, 7], the anomalous diffusion model for an infinite slab can be written as fractional Eq. (8) as follows:

$$\frac{\partial^\alpha C}{\partial t^\alpha} = D_{\text{eff}}\left[\frac{\partial^2 C}{\partial x^2}\right] \tag{8}$$

where D_{eff} is the effective diffusion coefficient.

Considering a long drying time and a fractional order α close to 1 (Simpson et al., 2017) [7], the solution of Eq. (8) can be expressed as follows:

$$MR = \frac{8}{\pi^2}e^{-kt^\alpha} \tag{9}$$

Table 2 Summary of parameters obtained to fit the dehydration data for yellow passion fruit (Duarte et al. [4]) to empirical/semiempirical and phenomenological models

Semiempirical models	Model	Parameters	Passion fruit peel dehydration temperatures									Arrhenius model fitting
			50 °C			55 °C			60 °C			
			Value	R^2	R^2 adj	Value	R^2	R^2 adj	Value	R^2	R^2 adj	R^2
1. Newton model	$MR = \exp(-kt)$	k	0.000136	0.99351	0.99351	0.000171	0.99906	0.99906	0.000216	0.99940	0.99940	0.9923
2. Page model	$MR = \exp(-kt^n)$	k	0.000046	0.99687	0.99676	0.000140	0.99915	0.99912	0.000191	0.99945	0.99943	0.9726
		n	1.13			1.02			1.02			
3. Modified Page (II)	$MR = \exp[-(k\,t)^n]$	k	0.000140	0.99687	0.99676	0.000172	0.99915	0.99912	0.000217	0.99945	0.99943	0.9876
		n	1.13			1.02			1.02			
4. Henderson and Pabis model	$MR = a\exp(-kt)$	a	1.04	0.99647	0.99634	1.01	0.99932	0.9993	1.00	0.99940	0.99938	0.9887
		k	0.000145			0.000174			0.000216			
5. Midilli	$MR = a\exp(-kt) + bt$	a	1.03	0.99667	0.99642	1.01	0.99933	0.99928	1.00	0.99942	0.99937	0.9938
		b	− 6.42E−07			− 5.89E−08			- 1.42E−07			
		k	0.000142			0.000174			0.000215			
6. Logarithmic model	$MR = b\exp(-kt) + a$	a	− 0.01784	0.99667	0.99642	0.00039	0.99932	0.99927	− 0.00411	0.99942	0.99938	0.9984
		b	1.05			1.01			1.00			
		k	0.000139			0.000175			0.000214			
7. Two-term exponential model	$MR = a\exp(-kt) + (1-a)\exp(-akt)$	a	1.66	0.99635	0.99621	1.27	0.99907	0.99904	1.32	0.99944	0.99942	0.6822
		k	0.000186			0.000182			0.000236			
8. Demir et al	$MR = a\exp(-k\,t)^n + b$	a	1.05	0.99667	0.99629	1.01	0.99932	0.99925	1.00	0.99942	0.99936	0.9995
		b	− 0.01785			0.00040			− 0.00411			
		k	0.000104			0.000117			0.000131			

Table 2 (continued)

Semiempirical models	Model	Parameters	Passion fruit peel dehydration temperatures									Arrhenius model fitting
			50 °C			55 °C			60 °C			
			Value	R^2	R^2 adj	Value	R^2	R^2 adj	Value	R^2	R^2 adj	R^2
		n	1.34			1.49			1.63			
9. Modified Midilli	$MR = a\exp(-kt^n) + bt$	a	1.01	0.99723	0.99691	1.01	0.99935	0.99927	0.99	0.99958	0.99953	0.3852
		b	2.86E−07			− 1.46E−07			1.11E−07			
		k	0.000057			0.000192			0.000141			
		n	1.11			0.99			1.05			
Phenomenological models												
10. Fick's second law model	$MR\frac{8}{\pi^2}\left[\sum_{n=1}^{50}\frac{1}{2n-1}\exp\left(-D_{eff}\left(\frac{(2n-1)\pi}{2L}\right)^2 t\right)\right]$	D_{eff}	8.61E−10	0.941	0.941	1.09E−09	0.967	0.967	1.34E−09	0.9660	0.9660	0.9979
11. Anomalous model	$MR\frac{8}{\pi^2}\left[\sum_{n=1}^{50}\frac{1}{2n-1}E_{\alpha,1}\left(-D_{eff}\left(\frac{(2n-1)\pi}{2L}\right)^2 t^{\alpha}\right)\right]$	D_{eff}	1.43E−10	0.974	0.974	1.86E−10	0.985	0.985	2.39E−10	0.9840	0.9840	0.9940
		α	1.19			1.19			1.19			

Table 3 Summary of parameters obtained to fit the dehydration data for spent coffee grounds (Osorio-Arias et al., 2020) to empirical/semiempirical and phenomenological models

Semiempirical models	Model	Parameters	Spent coffee ground thickness							
			0.01 m				0.02 m			
			Value	R^2	R^2 adj	RMSE	Value	R^2	R^2 adj	RMSE
1. Newton model	$MR = \exp(-kt)$	k	0.000153	0.98063	0.98002	4.699	0.000105	0.98076	0.98039	4.814
2. Page model	$MR = \exp(-kt^n)$	k	0.000020	0.99311	0.99288	2.803	0.000017	0.98728	0.98703	3.914
		n	1.23				1.20			
3. Modified page (II)	$MR = \exp[-(k\,t)^n]$	k	0.000153	0.99311	0.99288	2.803	0.000105	0.98728	0.98703	3.914
		n	1.23				1.20			
4. Henderson and Pabis model	$MR = a\exp(-kt)$	a	1.03	0.98254	0.98198	4.461	1.02	0.98178	0.98143	4.684
		k	0.000159				0.000108			
5. Midilli	$MR = a\exp(-kt) + bt$	a	0.99	0.99835	0.99824	1.370	0.99	0.99729	0.99718	1.808
		b	− 1.00E−05				− 1.33E−05			
		k	0.000117				0.000066			
6. Logarithmic model	$MR = b\exp(-kt) + a$	a	1.26	0.99858	0.99849	1.271	1.60	0.99706	0.99694	1.833
		b	− 0.26996				− 0.61405			
		k	0.000098				0.000048			
7. Two-term exponential model	$MR = a\exp(-kt) + (1-a)\exp(-akt)$	a	1.00	0.68422	0.67404	18.972	0.00	0.98075	0.98037	4.815
		k	0.000080				2.072248			
8. Demir et al	$MR = a\exp(-k\,t)^n + b$	a	1.17	0.99875	0.99862	1.196	5.94	0.99831	0.99821	1.425
		b	− 0.19293				− 4.91965			
		k	0.000109				0.000006			
		n	1.07				0.76			
9. Modified Midilli	$MR = a\exp(-kt^n) + bt$	a	1.17	0.99875	0.99862	1.196	8.33	0.99832	0.99822	1.422
		b	− 0.19				− 7.31			
		k	0.000057				0.000084			

Table 3 (continued)

Semiempirical models	Model	Parameters	Spent coffee ground thickness							
			0.01 m				0.02 m			
			Value	R^2	R^2 adj	RMSE	Value	R^2	R^2 adj	RMSE
		n	1.07				0.74			
Phenomenological models										
10. Fick's second law model	$\mathrm{MR}\frac{8}{\pi^2}\left[\sum_{n=1}^{50}\frac{1}{2n-1}\exp\left(-D_{\mathrm{eff}}\left(\frac{(2n-1)\pi}{2L}\right)^2 t\right)\right]$	D_{eff}	4.57E−09	0.925	0.925		1.26E−08	0.932	0.932	
11. Anomalous model	$\mathrm{MR}\frac{8}{\pi^2}\left[\sum_{n=1}^{50}\frac{1}{2n-1}E_{\alpha,1}\left(-D_{\mathrm{eff}}\left(\frac{(2n-1)\pi}{2L}\right)^2 t^{\alpha}\right)\right]$	D_{eff}	7.07E−11	0.995	0.995		1.74E−10	0.997	0.997	
		α	1.47				1.47			

According to Eqs. (6) and (9) (solutions for long drying time, Fick's second law, and the anomalous diffusion model), it can be argued that Models 1–4 depicted in Table 1 fall within the category of SEMs mimicking Eqs. (6) and (9). On the other hand, Models 5–9 can be categorized as EMs because of the extra parameters in the models. Furthermore, Models 10 and 11 in Table 1 can be categorized as TMs. As observed in Table 1, the Henderson and Pabis model (Model 4 in Table 1) mimics Fick's second law for long drying times for regular geometries (Eq. 6). It is worth noting that as stated before, the more parameters there are in EMs or SEMs, the more RMSE is achieved, which brings the risk of overfitting. In this way, the modified model of Midilli and Kucuk [13] (Model 9 in Table 1) is the one model among the nine models presented in Table 1 that has the best fit with the experimental data (highest R^2 value), as depicted in Tables 2 and 3. However, it is not necessarily the best model; it only has the highest R^2 value, but all the other models also present a high R^2 value. Even in mathematical terms, Models 1, 2, 3, 4, 5, and 8 are subsets of the modified Midilli model (Model 9 in Table 1). More specifically, as an example, for the case of $n = 1$ in Model 9 (Table 1), the modified Midilli model is transformed into Model 5 (Midilli). Even if $a = 1$ and $b = 0$, then the modified Midilli model is transformed into the Page model. The same type of analysis can be conducted for Models 2 and 3, when $n = 1$, converged to model because both models are strictly the same in mathematical terms. The original and modified Page models (2 and 3) are identical in algebraic terms. However, there are differences in the correlation between the parameters in these equations [30]. As depicted in Table 1, the Page and modified Page models are $\mathrm{MR} = \exp(-\,kt^n)$ and $\mathrm{MR} = \exp[-\,(K\,t)^n]$, where the latter can be rewritten as $\mathrm{MR} = \exp(-\,K^n t^n)$. According to the results presented in Table 2, the values of n are the same for both models ($n = 1.13$). In addition, k from the Page model is 0.000046, and to test if both models are the same, then K^n should be 0.000046, where $K = 0.000140$; therefore, $K^{1.13} = 0.000046$, confirming that both models generate the same simulated data and are strictly the same model. Furthermore, the same analysis from Table 3 confirms that the modified Page model is the same as the Page model (in both cases, $n = 1.23$, $k = 0.000020$, and $K^n = 0.000020$).

As was derived and explained in Simpson et al. [7], the goodness-of-fit presented by the Page model (and other EMs/SEMs) occurs because the Page model is similar too and a subset of the anomalous diffusion model applied for long drying times. Thus, this mathematical similarity, and not a phenomenological character, explains the extraordinary capacity of Page models and similar EMs/SEMs thin-layer drying models to successfully adjust experimental data. Even Fick's second law model is a subset of the anomalous model [7].

Another aspect that should be considered when comparing models is the number of parameters input into the models. Thus, a fair way to compare R^2 values is to adjust them for the number of considered parameters. As depicted in Tables 2 and 3, the correction through the adjusted R^2 value slightly modified the value of R^2, mainly due to a large amount of experimental data and the reduced number of extra parameters in each of the analyzed EMs/SEMs. Additionally, as depicted in Fig. 3, error analysis is a necessary complement for R^2 values, where for an appropriate model, the residuals should be approximately zero and present a random distribution. In Fig. 3, all nine EMs/SEMs models and Fick's second law model show a clear trend in the residuals, whereas for the anomalous diffusion model, the residuals not only are lower (approximately zero) but also show certain randomness in their distribution.

As a corollary, instead of using a large number of EMs/SEMs to fit drying data for thin-layer foods, it is highly recommended that a phenomenological model be used. In this respect, Fick's second law and the anomalous diffusion model have a theoretical basis, normally require only a few parameters and can be used to extrapolate and predict the drying process under different operating conditions. Although multiscale modeling could be desirable for a better understanding of the drying phenomena, Fick's second law and anomalous models seem plausible and sufficient to phenomenologically interpret the drying process data for the dehydration of thin-layer foods.

3.2 Critical Analyses of EMs/SEMs and TMs for the Drying of Thin-Layer Foods

Fick's second law model for thin-layer drying (only 1 parameter) and the anomalous diffusion model with two parameters have the same capability to fit all drying experimental data through a nonlinear regression, as occurs with EMs/SEMs (Table 1) [8]. For example, in Table 2, the goodness-of-fit of Fick's second law model developed for an infinite slab can be observed for yellow passion fruit peels dried at 50, 55, and 60 °C, considering an adequate number of terms for the summation (> 50) [4]. The goodness-of-fit values, according to the R^2 values, are in the range of 0.941 to 0.967; these values are slightly lower than but close in value to the EMs/SEMs values depicted in Table 2 (over 0.99) and displayed in Fig. 1. However, the D_{eff} values obtained for the three temperatures for Fick's second law are 8.61 × 10^{-10} m^2/s at 50 °C, 10.862 × 10^{-10} m^2/s at 55 °C, and 13.419 × 10^{-10} m^2/s at 60 °C; these results adequately follow Arrhenius behavior ($R^2 = 0.9979$), which is highly expected for a diffusion-based model.

As stated in Sect. 3.1, as more parameters are added, as is the case in the modified Midilli model (4 parameters), the

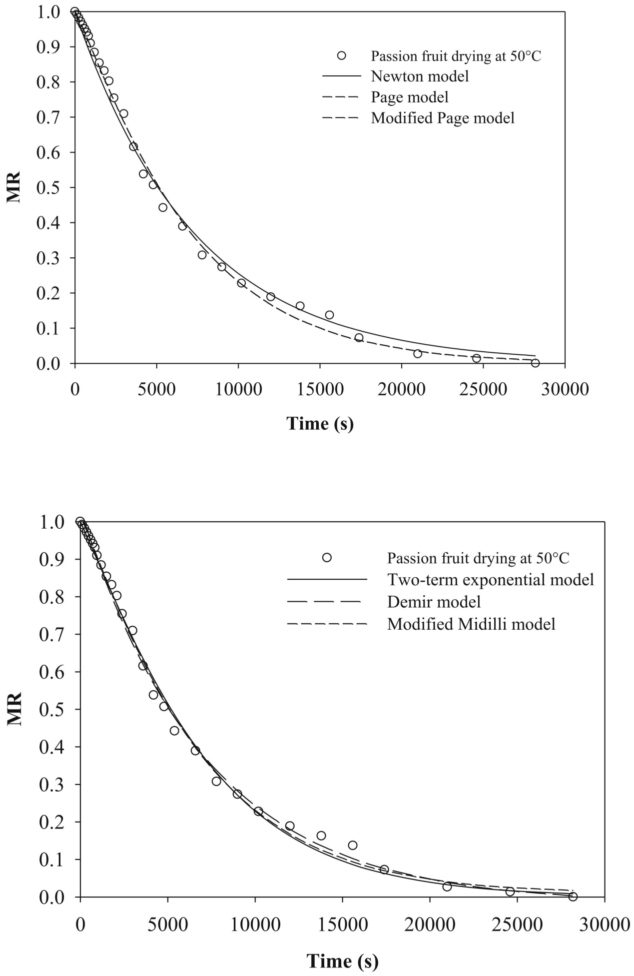

Fig. 1 Empirical/semiempirical (**a–c**) and phenomenological models (**d**) fitted to passion fruit peels hot-air dried at 50 °C with a thickness of 0.005 m

model gains goodness-of-fit but significantly loses its predictive capacity to assess the process under other conditions, and even worse, it lacks physical interpretation. Following the analysis presented in Sect. 3.1, the targets of the EMs/SEMs are more focused on maximizing the goodness-of-fit of the experimental data but not on understanding the drying phenomena (Fig. 1). On the other hand, Fick's second law and anomalous diffusion models can represent this drying process. Note that for anomalous diffusion, the fractional order is the same for different temperatures because α is related to the food microstructure [7]. This result supports that anomalous diffusion gives a phenomenological representation for the temperatures analyzed.

The dehydration experiments of spent coffee grounds were also analyzed by Fick's second law and anomalous diffusion models considering an infinite slab geometry and fitting all experimental data (using at least 50 terms to quantify the summation) (Fig. 2). In this case, two drying curves for samples with 0.01-m and 0.02-m thicknesses were performed at 50 °C with an air rate of 2 m/s [14]. For this example, the results are summarized in Table 3. Fick's model can adequately fit both cases, with a D_{eff} of 4.574 × 10^{-9} m^2/s for a thickness of 0.01 m (R^2 = 0.925) and 12.622 × 10^{-9} m^2/s for a thickness of 0.02 m (R^2 = 0.932) (Fig. 2d). This effect of thickness over D_{eff} was reported by Tütüncü and Labuza [31]. Since D_{eff} is an intrinsic property of the material, it is not expected to change with thickness. However, the empirical evidence shows that D_{eff} changed with thickness. According to Tütüncü and Labuza [31], a possible explanation for this is related to the air between the particles, which facilitates moisture diffusion by increasing its value.

When the anomalous diffusion model based on the fractional calculus tool was implemented to fit the entire curve (also using at least 50 terms of the summation), the R^2 values were higher than those of Fick's second law model (Table 2). In the case of yellow passion fruit dehydration, the goodness-of-fit of Fick's second law model is improved, with R^2 values between 0.974 and 0.985 (Fig. 1d). The effective diffusion

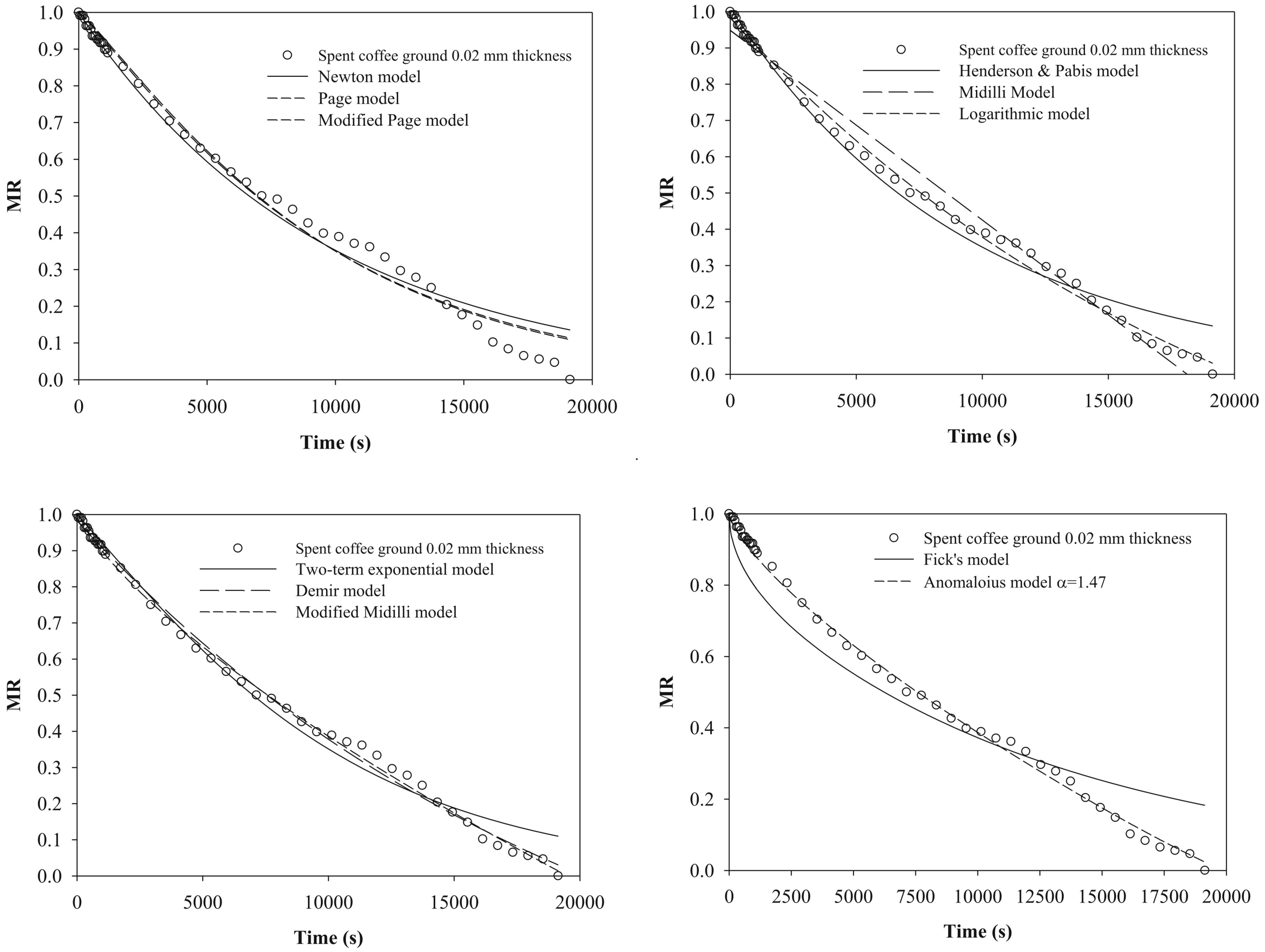

Fig. 2 Empirical/semiempirical (**a–c**) and phenomenological models (**d**) fitted to spent coffee grounds hot-air dried at 50 °C, with an air rate of 2 m/s and a thickness of 0.02 m

values, D_{eff}, were 1.43 × 10^{-10} $m^2/s^{1.19}$ at 50 °C, 1.86 × 10^{-10} $m^2/s^{1.19}$ at 55 °C and 2.39 × 10^{-10} $m^2/s^{1.19}$ at 60 °C, and the time exponent α for this case was higher than 1 (1.19); thus, the diffusion process was considered superdiffusive (α > 1). According to Simpson et al. [6], the time exponent can be related to the microstructure of food material, and this microstructure must remain constant independent of the temperature used for dehydration. The D_{eff} values follow an Arrhenius behavior ($R^2 = 0.994$), which is the expected temperature dependence for D_{eff}. The analysis of Page's model in Simpson et al. [7] concluded that the success of that model was because its parameters could be explained through an anomalous diffusion model based on fractional calculus (Fig. 3).

For the drying data for spent coffee grounds, the anomalous model was also applied, obtaining R^2 values over 0.99. Then, the fitting showed that for samples with a 0.01 m thickness, the D_{eff} was 7.07 × 10^{-11} $m/s^{1.47}$, while for samples with a 0.02 m thickness, the D_{eff} was 1.74 × 10^{-10} $m/s^{1.47}$, and the α value was 1.47. Thus, the process could be considered superdiffusive. As expected, the values of D_{eff} presented the same behavior as those of the second Fick's model; however, the data fitting, as can be observed in Fig. 2d, was significantly higher.

4 Conclusions

In general, it can be concluded that for the analysis of dehydration data characterizing thin-layer foods, it seems appropriate and sufficient to use theoretical models such as Fick's second law and anomalous diffusion models, and there is no need to appeal to more intricate models such as multiscale modeling. The appropriateness of EMs/SEMs is commonly incorrectly justified by their statistical ability to fit data, disregarding their capability to extrapolate data and

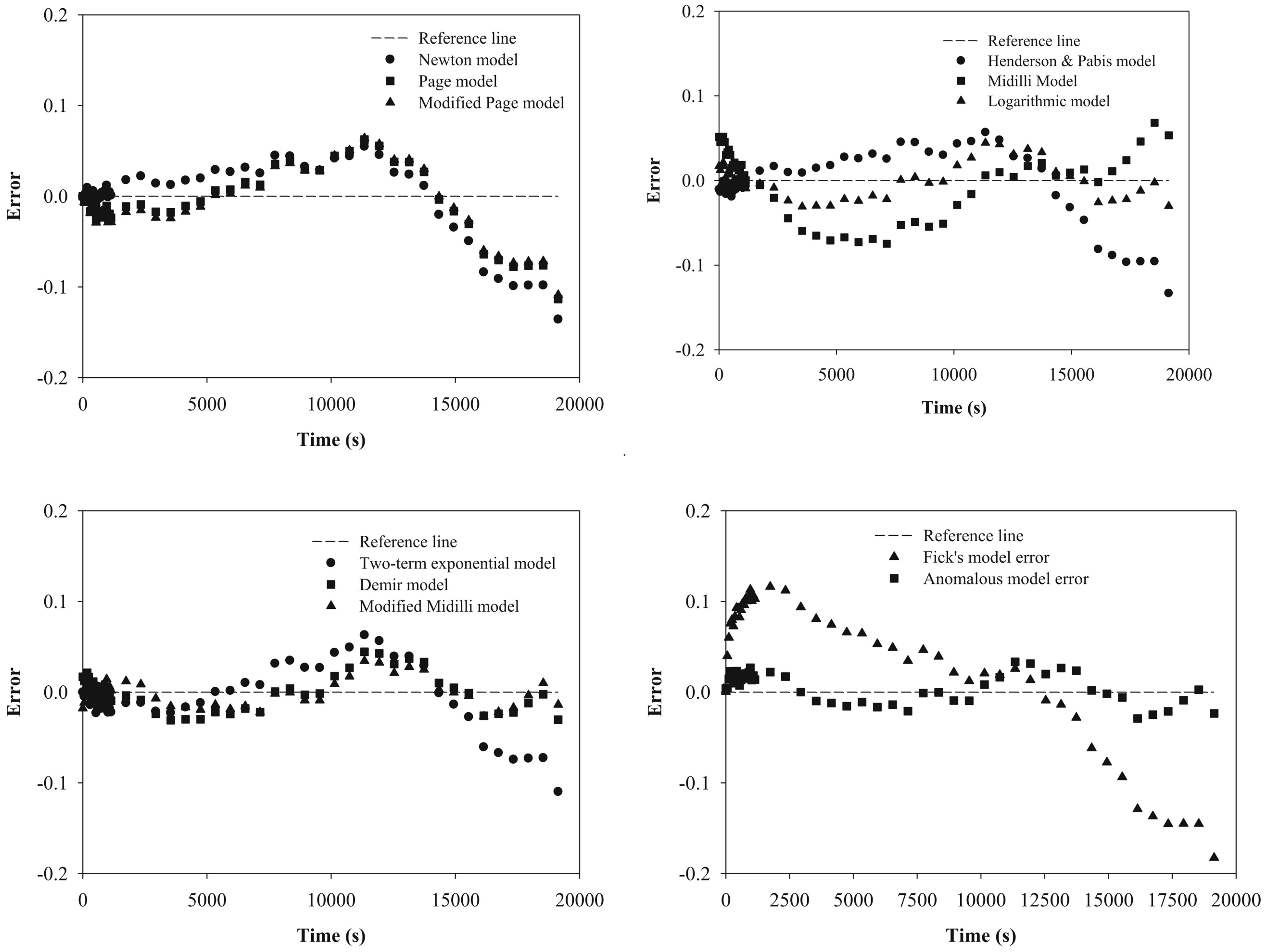

Fig. 3 Errors determined from semiempirical (**a–c**) and phenomenological models (**d**) fitted to spent coffee grounds hot-air dried at 50 °C, with an air rate of 2 m/s and a thickness of 0.02 m

interpret physical phenomena. As a final remark, there is no need to use EMs or SEMs for the dehydration of thin-layer foods.

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Declarations

Conflict of interest The authors declare that they have no conflicts of interest.

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