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COUPLING STATISTICAL DESIGN AND DIFFUSION-BASED MODELING TO INVESTIGATE DRYING KINETICS AND EFFECTIVE MOISTURE TRANSPORT

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Abstract

Drying is a key unit operation in the processing of industrial residues, ensuring microbiological stability and preserving attributes relevant for subsequent applications. This study proposes a two-step framework integrating statistical optimization and mechanistic modeling to investigate and improve the drying performance of eggshell waste. First, a 2^3 full factorial design evaluated the effects of temperature, particle size, and sample mass on total water loss, identifying temperature, sample mass, and their interaction as the main determinants. Second, drying kinetics under optimal conditions were analyzed using six empirical thin-layer models and a mechanistic model based on Fick's second law of diffusion. Multi-parameter empirical models, such as Page, Midilli–Kucuk, and Verma, provided excellent fits ($R^2 > 0.98$), while the Fickian model yielded a physically consistent effective moisture diffusivity ($D_{eff} = 4.77 \times 10^{-11}$ m².s⁻¹). However, diffusivities estimated from empirical model constants differed by several orders of magnitude from the mechanistic value, highlighting equifinality: distinct models may fit experimental data but lack physical interpretability. This integrated approach supports process optimization and provides insights for design, scale-up, and industrial application.

Keywords: Factorial design, Drying kinetics, Effective moisture diffusivity

Resumo

A secagem é uma operação unitária fundamental no processamento de resíduos industriais, garantindo estabilidade microbiológica e preservando atributos relevantes para aplicações subsequentes. Este estudo propõe uma abordagem em duas etapas, integrando otimização estatística e modelagem mecanística, para investigar e aprimorar o desempenho da secagem de resíduos de casca de ovo. Na primeira etapa, um planejamento fatorial completo 2^3 avaliou os efeitos da temperatura, do tamanho de partícula e da massa da amostra sobre a perda total de água, identificando a temperatura, a massa da amostra e sua interação como os principais determinantes. Na segunda etapa, a cinética de secagem, sob condições ótimas, foi analisada por meio de seis modelos empíricos de camada fina e de um modelo mecanístico baseado na segunda lei de difusão de Fick. Modelos empíricos multiparamétricos, como Page, Midilli–Kucuk e Verma, apresentaram excelente ajuste ($R^2 > 0{,}98$), enquanto o modelo fickiano forneceu uma difusividade efetiva de umidade fisicamente consistente ($D_{eff} = 4{,}77 \times 10^{-11}$ m².s⁻¹). No entanto, difusividades estimadas a partir de constantes empíricas divergiram por várias ordens de magnitude, evidenciando a equifinalidade. Essa abordagem integrada contribui para a otimização de processos e fornece subsídios para projeto, escala e aplicação industrial.

Palavras-chave: Planejamento fatorial; Cinética de secagem; Difusividade efetiva de umidade.

1 Introduction

Drying is one of the most important unit operations in the processing of biomaterials and agro-industrial residues. It ensures microbiological stability, reduces storage and transportation costs and determines physicochemical attributes such as porosity, surface area and reactivity that directly affect subsequent applications, including adsorbents, catalysts, functional foods and biomaterials (Mujumdar, 2015). Optimizing drying conditions and accurately modeling drying kinetics are therefore essential to guarantee product quality, ensure process reproducibility and facilitate industrial scale-up.

Several mathematical models have been proposed to describe drying behavior. Empirical thin-layer models such as Henderson & Pabis, Page, Logarithmic, Two-term, Midilli–Kucuk and Wang & Singh are widely applied due to their simplicity and predictive capacity (Vega et al., 2007; Rosa et al., 2015). The Henderson & Pabis model has shown excellent performance for various biomaterials including orange seeds and red bell peppers (Vega et al., 2007; Rosa et al., 2015), while the Page model has been applied to agricultural products such as bay leaves and turnip (Gharehbeglou et al., 2014). However, these models often lack a direct physical basis and are best suited for describing the falling rate period of drying (Koukias and Karapantsios, 2009). In contrast, diffusion-based models derived from Fick's second law provide a mechanistic interpretation of internal mass transfer, which is often the rate-limiting step (Ratti, 2001; Park et al., 2014). Selecting appropriate models is crucial to balance statistical accuracy and physical meaning.

In parallel, design of experiments (DOE) has emerged as statistical tool to optimize drying processes. DOE allows for the efficient planning of experiments, simultaneous evaluation of multiple factors and identification of significant main effects and interactions, thereby reducing experimental effort while increasing process robustness (Box et al., 2005; Weissman and Anderson, 2015; Dar et al., 2024; Anderson and Bezener, 2024). Factorial design approaches have been successfully applied to optimize drying conditions for various agricultural products, including dandelion root and onion slices (Moussaoui et al., 2019; Kholikov et al., 2021).The integration of ANOVA with factorial experiments provides robust statistical validation for process optimization (Taguchi and Yokota, 1993). Despite its advantages, only a few studies have combined DOE with detailed kinetic modeling of drying, especially for agro-industrial residues. Recent studies have demonstrated the growing importance of integrated approaches that combine statistical design and mechanistic modeling for process optimization, particularly in the context of sustainable biomaterial processing (Dar et al., 2024; Anderson and Bezener, 2024).

In this work, eggshells were selected as a representative material because they are generated in large amounts worldwide, with global estimates exceeding several million tons annually. They are mainly composed of $CaCO_3$ and have been investigated for applications such as low-cost adsorbents, catalysts and bioceramics (Mubarak et al., 2021). Recent advances in green processing technologies have highlighted the potential of eggshell waste valorization for sustainable construction materials and environmental remediation (Mignardi et al., 2020; Ngayakamo and Onwualu, 2022; Shah and Bhat, 2024; Kechkar et al., 2024; Nawawi, 2025). The development of eggshell-based biocomposite adsorbents has gained attention in the circular economy context (Babalola and Wilson, 2024). The quality and functionality of eggshell-derived products depend strongly on drying conditions, making them a suitable model system for this methodological study. The high temperature range (200-400°C) employed in this study is specifically justified for eggshell processing, as this predominantly inorganic material ($CaCO_3$) requires elevated temperatures to ensure complete removal of not only moisture but also residual organic matter, which is crucial for applications such as catalysts and bioceramics where material purity is necessary (Tangboriboon et al., 2012; Kolekar et al., 2020; Kathalingam et al., 2024).

Therefore, this study was designed in two sequential stages. First, a full 23 factorial design was applied to evaluate the effects of temperature, particle size, and sample mass on eggshell drying performance after 2 h, aiming to identify statistically optimal conditions. Second, the drying kinetics at the optimal condition were investigated by applying experimental data to six empirical thin-layer models and to the analytical solution of Fick’s second law (three-term series) to estimate the effective moisture diffusivity. This two-step approach establishes a methodological framework that combines statistical optimization and mechanistic validation, which can be adapted for other agro-industrial residues to support their valorization into high-value products.

In this study, eggshell waste was selected as a model agro-industrial residue. Experimental drying data were obtained through controlled gravimetric experiments, in which ground eggshell samples were subjected to high-temperature drying and their mass loss was monitored over time. These experimental data formed the basis for both the factorial design analysis and the subsequent kinetic and diffusion-based modeling.

2 Material and Methods

2.1 Raw material

Eggshells were collected from local food services in Cuité, Paraíba, Brazil, manually washed with distilled water and air-dried at 25 °C. The initial moisture content (X_0) of the material after air-drying was determined to be 0.085 ± 0.012 g water/g dry matter. The inner membranes were removed and the shells were ground with a mortar and pestle. The material was sieved to obtain two particle size ranges: < 1.68 mm and > 1.68 mm, which were later used as experimental factors in the design.

2.2 Experimental design (DOE)

Drying experiments were planned according to a full factorial 2^3 design performed in duplicate, totaling 16 runs. The three independent variables investigated were: Temperature (A): 200 °C (−1) and 400 °C (+1); Sample mass (B): 2.0 g (−1) and 4.0 g (+1); Particle size (C): < 1.68 mm (−1) and > 1.68 mm (+1).

The choice of these levels was based on preliminary trials and literature reports. The temperature range was selected to ensure effective removal of moisture and organic matter without causing significant thermal decomposition of calcium carbonate, which typically occurs above 600 °C (Luo et al., 2020). While this temperature range (200-400°C) is higher than typical industrial drying processes for thermosensitive biomaterials (usually <150°C), it is appropriate for the inorganic nature of eggshells and their intended applications. However, it is important to note that the integrated DOE-kinetic modeling methodology presented here is equally applicable and even more critical for lower temperature processes, where optimization of time and energy becomes a significant industrial challenge. The mass interval reflects common practice in laboratory scale drying studies, balancing sample representativeness and heat transfer control. The particle size fractions were defined to represent fine and coarse powders that could influence drying rates and effective diffusivity (Mubarak et al., 2021). A full factorial design was chosen to allow for the estimation of all main effects and interaction effects. The complete experimental matrix is shown in Table 1.

Table 1. Full factorial 2^3 design in duplicate with coded and natural values.

Assay	Variables					
	T (ºC)	Size	Mass (g)	TºC	Size (mm)	Mass (g)
1	-	-	-	200	<1.68	2.0
2	+	-	-	400	<1.68	2.0
3	-	+	-	200	>1.68	2.0
4	+	+	-	400	>1.68	2.0
5	-	-	+	200	<1.68	4.0
6	+	-	+	400	<1.68	4.0
7	-	+	+	200	>1.68	4.0
8	+	+	+	400	>1.68	4.0
9	-	-	-	200	<1.68	2.0
10	+	-	-	400	<1.68	2.0
11	-	+	-	200	>1.68	2.0
12	+	+	-	400	>1.68	2.0
13	-	-	+	200	<1.68	4.0
14	+	-	+	400	<1.68	4.0
15	-	+	+	200	>1.68	4.0
16	+	+	+	400	>1.68	4.0

Source: Research data

2.3 Drying procedure

Drying experiments were carried out in a laboratory muffle furnace, installed at the Food Quality Control Laboratory at Federal University of Campina Grande (UFCG), Cuite, Paraiba, Brazil. The furnace temperature was controlled in 105 °C. Drying experiments were conducted according to the DOE matrix (Table 1) to determine the mass loss after 2 h, which was used as the response variable for factorial analysis. In addition, an independent kinetic experiment was performed at the optimal condition identified by the DOE to record complete drying curves for model fitting. For each test, the corresponding sample (2.0 or 4.0 g) was spread in a thin layer in a pre-weighed ceramic crucible from the furnace, placing it in a desiccator to cool for 60 seconds and weighing it on an analytical balance (precision ± 10^{-4} g). This process was repeated until the sample mass remained constant for three consecutive readings, which was considered the equilibrium point. The total drying time varied depending on the experimental condition. The moisture content on a dry basis (X, g water.g^{-1}dry matter) was calculated as:

$$X = \frac{m_t - m_d}{m_d} \tag{1}$$

where m_t is the sample mass at time t and m_d is the dry mass.

The moisture ratio (MR) was obtained as:

$$MR = \frac{X - X_e}{X_0 - X_e} \tag{2}$$

where X is the moisture content at time t, X_0 is the initial moisture content and X_e is the equilibrium moisture content. Since drying was conducted until constant mass, the equilibrium moisture content (X_e) was considered to be zero for all conditions.

2.4 Kinetic models

Kinetic modeling was applied only to the drying curve obtained at the optimal condition identified by the DOE analysis. The factorial design itself was based solely on the final mass loss after 2 h as the response variable, without collecting full drying curves for each experimental run. Once the optimal condition was established, a complete drying experiment was conducted under this condition, and the resulting moisture ratio (MR) versus time data were fitted to six empirical thin-layer models (Table 2) and to the analytical solution of Fick's law (Eqs. 3–4).

2.4.1 Empirical thin-layer models

Six empirical thin-layer drying models (Table 2) were fitted to the experimental moisture ratio (MR) data. In addition, the analytical solution of Fick’s second law was fitted to the same MR data in order to estimate the effective moisture diffusivity.

2.4.2 Diffusion model (Fick’s second law)

To describe internal moisture transport, the analytical solution of Fick’s second law for a spherical geometry was used, assuming uniform initial moisture distribution and negligible external resistance. It is important to acknowledge that the assumption of spherical geometry represents a simplification, as eggshell particles are typically irregular and lamellar in nature. This geometric approximation may impact the calculated effective diffusivity values, as the equivalent radius used does not fully capture the complex morphology and tortuosity of the actual particles (Ewing et al., 2010; Starkov et al., 2020; Rodrigues et al., 2022). The model is given by:

$$MR(t) = \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}exp\left(-\frac{n^2\pi^2 D_{eff}}{r^2}t\right) \tag{3}$$

Table 2. Empirical drying models applied

Model	Equation	Parameters
Newton	MR = *exp(-kt)*	*k*: drying constant (min^{-1})
Henderson–Pabis	MR = *a exp(-kt)*	*a*: dimensionless constant; *k*: drying constant (min^{-1})
Logarithmic	MR = *a exp(-kt) + c*	*a, c*: constants; *k*: drying constant (min^{-1})
Page	MR = *exp(-k t^n)*	*k*: drying constant (min^{-1}); *n*: empirical exponent
Midilli–Kucuk	MR = *a exp(-k t^n) + bt*	*a, b*: constants; *k*: drying constant (min^{-1}); *n*: exponent
Verma (from k)	MR = *a exp(-kt) + (1-a) exp(-gt)*	*a*: constant; *k, g*: drying constants (min^{-1}); $D_{eff,app}$ from *k*
Verma (from g)	MR = *a exp(-kt) + (1-a) exp(-gt)*	Same as above; $D_{eff,app}^{*}$ from *g*

*Deff,app: apparent effective moisture diffusivity."

Source: Research data

For practical purposes, the first three terms of the series provide an excellent approximation:

$$MR = \frac{6}{\pi^2}\left[exp\left(-\frac{\pi^2 D_{eff}t}{r^2}\right) + \frac{1}{4}exp\left(-\frac{4\pi^2 D_{eff}t}{r^2}\right) + \frac{1}{9}exp\left(-\frac{9\pi^2 D_{eff}t}{r^2}\right)\right] \tag{4}$$

where D_{eff} is the effective moisture diffusivity ($m^2.s^{-1}$), *r* is the equivalent particle radius (m) and *t* is the drying time (s). The equivalent particle radius (*r*) was estimated from the characteristic particle diameter of the selected granulometric fraction, assuming spherical particles of equal volume. For the particle size fraction < 1.68 mm used in the kinetic experiments, the equivalent radius was calculated as $r = d/2$. Although eggshell particles present irregular and lamellar morphologies, this geometric simplification provides a representative diffusion length scale and is widely adopted in diffusion-based drying models. The use of an equivalent radius for non-spherical particles introduces uncertainty in the diffusivity calculations, as the actual diffusion path is more tortuous than assumed in the spherical model.

2.5 Statistical analysis and Model Fitting

The factorial design was analyzed by Analysis of Variance (ANOVA) and Pareto charts at a 95% confidence level ($p < 0.05$) using Statistica® 8 software and regression coefficients were estimated (Box et al., 2005). The significance of factors and their interactions was confirmed by the F-test, comparing the calculated F-value with the tabulated F at the same degrees of freedom (Montgomery, 2017). Nonlinear regression was used to fit the kinetic models (Table 2) and the three-term analytical solution of Fick's second law (Eq. 4) to the experimental MR data using the Levenberg-Marquardt algorithm (Marquardt, 1963). The goodness of fit was evaluated based on three statistical criteria: the coefficient of determination (R^2), the reduced chi-square χ^2, and the root mean square error (RMSE) (Kashaninejad et al., 2007).

2.6 Estimation of effective moisture diffusivity (*D_{eff}*)

The estimation of D_{eff} was performed exclusively for the optimal condition, using the experimental MR–t data obtained under this condition. Two complementary approaches were adopted:

– **Mechanistic (Fickian) fit:** D_{eff} was directly estimated by fitting the three-term spherical solution of Fick's law (Eq. 4) to the experimental data;
– **Apparent *D_{eff}* from empirical models:** for descriptive comparison, an apparent diffusivity ($D_{eff,app}$) was calculated from the parameters of each empirical model by mapping their asymptotic rate constant to the first term of the Fickian solution. This calculation is only illustrative and does not imply physical equivalence, since models such as Page and Midilli–Kucuk deviate from monoexponential behavior. The relationship is:

$$D_{eff,app} = \frac{k_{eq} r^2}{\pi^2} \quad (5)$$

where k_{eq} is an equivalent rate constant derived from the parameters of each empirical model as follows:

Lewis Newton**:** $k_{eq} = k$

Henderson–Pabis: $k_{eq} = k$

Logarithmic: $k_{eq} = k$

Page: $k_{eq} = k^{(1/n)}$, obtained from the characteristic time $\tau = (1/k)^{1/n}$ where MR = $1/e$.

Midilli–Kucuk: same mapping as Page, using $k^{(1/n)}$.

Verma (from k): $k_{eq} = k$.

Verma (from g): k_{eq} = g, where the slower exponential mode governs long-time behavior (mode $n = 2$, divisor $4\pi^2$).

This dual approach allows for a more robust interpretation of moisture transport during drying.

3 Results and Discussion

3.1 Optimization of Drying Conditions by Factorial Design (DOE)

The 2^3 full factorial design provided a comprehensive evaluation of Temperature (A), Sample Mass (B) and Particle Size (C) effects on the drying process. The response variable was total water loss in grams after 2 hours, revealing both the magnitude and statistical significance of each factor for process optimization.

3.2 Model Significance and Analysis of Variance (ANOVA)

The regression model demonstrated statistical significance (F = 22.27, p = 0.000121), confirming that the experimental factors explain the response variability better than experimental error alone. This result aligns with previous factorial design applications in biomaterial drying (Liu et al., 2012; Garza Villegas, 2017).

Table 3. Overall F-test (Model Significance)

Source	DF	SS	MS	*F*	*p*-value
Model	7	0.091861	0.013123	22.27	0.000121
Residual (Error)	8	0.004714	0.000589		
Total	15	0.096575			

DF: degrees of freedom; SS: sum of squares; MS: mean square.
Null hypothesis H_0: all regression coefficients (except the intercept) are zero. The high F-value and the small p-value indicate that the model is statistically significant at the 95% confidence level.

The individual factor significance is summarized in Table 4 and visualized in the Pareto chart (Figure 1).

Table 4. Estimated effects, regression coefficients and significance tests for each factor.

Factor/Interaction	Effect	Regression Coefficient	*F*-value	*p*-value	Significant (95%)
Temperature (A)	0.132	0.066	115.22	0.000005	**Yes**
Mass (B)	0.060	0.030	24.88	0.001068	**Yes**
Interaction (A x B)	0.040	0.020	9.57	0.014805	**Yes**
Particle Size (C)	-0.012	-0.006	0.97	0.354216	No
Interaction (A x C)	-0.024	-0.012	3.56	0.095750	No
Interaction (B x C)	-0.009	-0.004	0.49	0.502442	No

Source: Research data

3.3 Interpretation of Effects

Three effects exceeded the significance threshold (p = 0.05): Temperature (A), Mass (B) and their interaction (A×B) as shown in Figure 1.

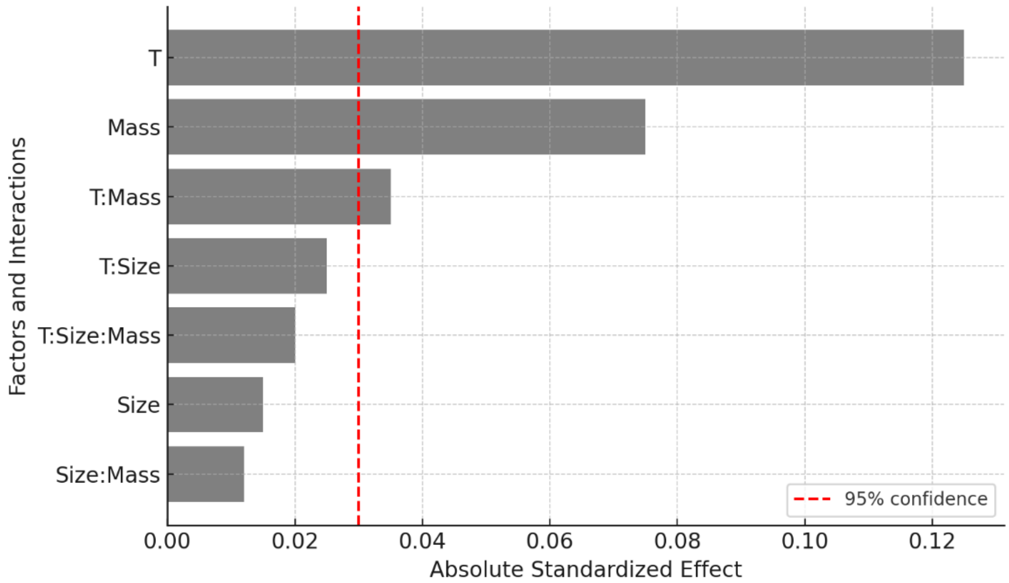

Figure 1. Pareto chart of standardized effects for water loss. The vertical dashed line indicates the threshold for statistical significance at the 95% confidence level (*p* = 0.05). Effects extending beyond this line are considered significant.

Temperature emerged as the dominant factor, with higher temperatures (400°C vs 200°C) significantly enhancing water removal through increased vapor pressure and heat transfer rates. Mass also showed significant positive effects, reflecting greater absolute water content in larger samples despite potentially slower relative drying rates. The significant Temperature-Mass interaction indicates synergistic effects, where temperature impact becomes more pronounced for larger masses due to increased thermal load requirements.

Particle size showed no statistical significance within the studied range, suggesting external heat and mass transfer limitations dominate over internal diffusion resistance under these high-temperature conditions.

However, for the subsequent kinetic assays, the smaller particle size (< 1.68 mm) was selected. This apparent contradiction between the DOE results and the kinetic study selection requires clarification. The non-significance of particle size in the DOE can be attributed to the experimental design being optimized for a fixed time response (2 hours) under high temperatures (200-400 °C). Under these conditions, the extremely high driving force for drying means that the process is predominantly controlled by external heat and mass transfer at the particle interface, with external convective resistance dominating over internal diffusion resistance. This masks the effect of particle size on the macroscopic response (total water loss).

For detailed kinetic modeling, however, the internal diffusion resistance cannot be ignored, even if it is not the global rate-limiting step (Qi, 1996; Chen et al., 2013; Kaczmarski and Bellor, 2003). By selecting the smaller granulometry (< 1.68 mm), we maximize the specific surface area, which theoretically minimizes external resistance and allows for a more precise investigation of the internal diffusional phenomenon. This choice is important for the correct application and interpretation of Fick's model, which describes moisture diffusion within the solid. Therefore, while the effect of particle size is negligible for process optimization under the studied batch-scale conditions, it remains a critical variable for mechanistic modeling and determination of effective diffusivity (D_{eff}).

3.4 Reduced Regression Model

Based on the significance analysis, a reduced regression model was developed including only the statistically significant terms (A, B and AB). The resulting empirical equation, in terms of coded variables, is:

$$Loss\ Water = 0.1061 + 0.066T + 0.0303M + 0.020TM \quad (6)$$

In Eq. (6), T and M represent the coded variables corresponding to the statistically significant factors identified in the factorial design (DOE). Specifically, T refers to temperature (factor A) and M refers to sample mass (factor B). As the regression model is expressed in terms of coded variables, the values of T and M do not correspond to the actual temperature and mass values, but to the normalized levels used in the factorial design (−1 and +1).

This model achieved a high coefficient of determination ($R^2 = 0.951$). This indicates that the model explains over 95% of the variability in water loss, confirming its excellent predictive capability. The small standard deviation observed across duplicates (S_x = 0.006, as shown in Table 5) further reinforces the precision of the experiments and the reliability of the model.

Table 5. Significance analysis of the 2^3 factorial design in duplicate.

X **(Mean);** R^2 **(coefficient of determination);** S_x **(standard deviation).**	
Number of experiments: 16	
	Statistical analysis; 95% confidence level
X	0.110
S_x	0.006
R^2	0.951

3.5 Drying Kinetics and Mass Transfer Modeling

To elucidate the mass transfer mechanisms and to describe the drying behavior and understand moisture transport mechanisms for the drying process kinetic data obtained exclusively under the optimized condition (400 °C, 4.0 g, <1.68 mm) were fitted to six empirical thin-layer models and one mechanistic diffusion model based on Fick's second law. This comparative analysis allows for the evaluation of both predictive capability and physical significance of different modeling approaches, while addressing the critical issue of equifinality in mathematical modeling of drying processes.

3.6 Performance of Empirical Models

The kinetic parameters and statistical indicators of fit quality for the six empirical models are presented in Table 6. The empirical thin-layer models were fitted to the experimental moisture ratio (MR) data obtained under the optimized drying condition. These models were evaluated solely for their ability to accurately describe the drying curve under the optimized condition, without implying any physical meaning for their parameters. The results reveal a clear hierarchy of descriptive performance among the models, which is useful for interpolation and process control within the studied range.

Table 6. Kinetic parameters and statistical indicators for empirical and mechanistic drying models fitted to eggshell drying data.

Model	Parameter	Value	Unit	R^2	χ^2	RMSE
Newton	K	0.0577	min^{-1}	0.9457	0.0054	0.0735
Henderson–Pabis	A	0.9845		0.9460	0.0054	0.0733
	K	0.0568	min^{-1}			
Logarithmic	A	0.9050		0.9797	0.0020	0.0451
	K	0.0872	min^{-1}			
	C	0.0937				
Page	K	0.4232	min^{-n}	0.9869	0.0013	0.0361
	N	0.4017				
Midilli–Kucuk	A	0.9999		0.9903	0.0010	0.0311
	K	0.9726	min^{-n}			
	N	0.1000				
	B	-0.0017	min^{-1}			
Verma	A	0.6725		0.9882	0.0012	0.0343
	K	0.2514	min^{-1}			
	G	0.0170	min^{-1}			
Fick’s Law	D_{eff}	4.77×10^{-11}	$m^2.s^{-1}$	0.9211	0.0079	0.0887

R^2: coefficient of determination; χ^2: reduced chi-square; RMSE: root mean square error

The Page, Midilli-Kucuk and Verma models distinguished themselves by providing the best fits to experimental data, with coefficients of determination (R^2) exceeding 0.98 and the lowest values of chi-square (χ^2) and root mean square error (RMSE).

Specifically, the Midilli-Kucuk model exhibited the best statistical performance, followed by the Verma and the Page models. The superiority of these multi-parameter models is consistent with the literature, which highlights their flexibility in describing the complex curvature of moisture ratio decay, particularly during the falling rate period when internal diffusion resistance becomes predominant (Akpinar, 2006, Akpinar and Demirci, 2018, Taşova et al., 2020).

The good results of the Page model can be attributed to its empirical exponent n = 0.4017, that allows the model to capture the non-exponential behavior characteristic of materials with complex internal structure. Similarly, the Midilli-Kucuk model superior fit (R^2 = 0.9903) results from its additional parameters, that provide mathematical flexibility to describe both the initial lag period and the long-term asymptotic behavior.

In contrast, the simpler Newton and Henderson-Pabis models, although achieving acceptable fits, exhibited systematic deviations during the initial stages of drying. Their mono exponential form was unable to adequately capture the complexity of the eggshell drying process, a limitation frequently observed in the drying of heterogeneous biomaterials where multiple transport mechanisms operate simultaneously (Mujumdar, 2015). The Logarithmic model offered intermediate performance, significantly improving the description of the initial period compared to first-order models by introducing an additive offset (c = 0.0937) that partially compensates for the limitations of the simple exponential form.

Although some empirical models provided excellent statistical fits ($R^2 > 0.98$), their parameters are purely phenomenological and should not be interpreted as physical quantities or used to estimate mass transfer coefficients.

3.7 Mechanistic Analysis Using Fick's Diffusion Model

The analytical solution of Fick's second law (three-term series, Eq. 3) was fitted to the drying curve obtained under the optimized condition. The model yielded an effective moisture diffusivity of 4.77×10^{-11} $m^2.s^{-1}$ (Table 6), which lies within the 10^{-11} - 10^{-9} $m^2.s^{-1}$ range reported for other agricultural materials (Park et al., 2014), supporting the plausibility of the result. The agreement between the mechanistic prediction and the experimental data can also be observed in Figure 2, which illustrates the moisture ratio decay and the corresponding model fits.

Although the Fickian model showed a lower R^2 (0.9211) than the best empirical models, this is expected because it uses only one physical parameter (D_{eff}) and does not account for factors such as particle heterogeneity, external resistances or structural changes during drying. Nevertheless, the Fickian analysis remains essential because it provides a physically meaningful parameter for comparing materials and designing equipment. The obtained D_{eff} value represents the overall internal resistance to moisture transport within the porous eggshell matrix, consolidating the mechanistic interpretation of the drying process

3.8 Comparison Between Fickian Diffusivity and Apparent Diffusivities Derived from Empirical Models

To illustrate the discrepancies that can arise when attempting to extract mechanistic parameters from empirical models, apparent diffusivities ($D_{eff,app}$) were calculated from the parameters of each empirical model as described in Section Estimation of effective moisture diffusivity (D_{eff}). The results are shown in Table 7.

Table 7. Comparison between mechanistic diffusivity (Fick's law) and apparent diffusivities derived from empirical models.

Model	$D_{eff,app}$ ($m^2.s^{-1}$)	Relative Error vs. Fick (%)	Physical Interpretation
Newton	6.87×10^{-11}	+43.88	Moderate overestimation
Henderson–Pabis	6.76×10^{-11}	+41.63	Moderate overestimation
Logarithmic	1.04×10^{-10}	+117.65	Significant overestimation
Verma (from *k*)	3.00×10^{-10}	+527.42	Severe overestimation
Verma (from *g*)	5.06×10^{-12}	-89.40	Severe underestimation
Page	3.15×10^{-13}	-99.34	Unrealistically low value
Midilli–Kucuk	8.96×10^{-26}	-100.00	Physically impossible
Fick's Law	$\mathbf{4.77\times10^{-11}}$	**Reference**	**Mechanistically meaningful**

$D_{eff,app}$: apparent effective diffusivity calculated from empirical model parameters using the methodology described in Section: Estimation of effective moisture diffusivity (D_{eff}). Source: Research data

The Newton and Henderson–Pabis models moderately overestimated D_{eff} by 43.88% and 41.63%, respectively, while the Verma model produced highly inconsistent values depending on the parameter used: the '*k*'-based approach overestimated by 527.42%, whereas the '*g*'-based approach underestimated by 89.40%. Even more strikingly, the models that achieved the best statistical fits (Page and Midilli–Kucuk) yielded completely unrealistic apparent diffusivities, several orders of magnitude below the mechanistic value from Fick's law.

This divergence exemplifies the concept of equifinality, whereby models with very different mathematical structures can fit the same data well but yield parameters with no physical meaning. Such behavior is especially evident when the empirical exponent n deviates strongly from unity, as observed in the Page (n = 0.4017) and Midilli–Kucuk (n = 0.1000) models.

These results reinforce that empirical models should be applied solely for descriptive curve fitting and process control within their experimental range. In contrast, the estimation of mechanistically valid parameters must rely on first-principles models such as Fick's law, even if they provide lower statistical fits.

3.9 Visual Analysis of Model Fits

To complement the statistical indicators, the experimental drying curve under the optimized condition was visually compared with the curves predicted by the tested models. Figure 2 shows the moisture ratio (MR) as a function of time together with the fitted curves for each model. This qualitative inspection confirms that the Page, Midilli–Kucuk and Verma models followed the experimental trend more closely throughout the entire drying period, while the Newton and Henderson–Pabis models deviated in the initial stages. The Logarithmic model provided an intermediate description. These visual observations are consistent with the statistical results in Table 6 and reinforce the descriptive nature of the empirical models.

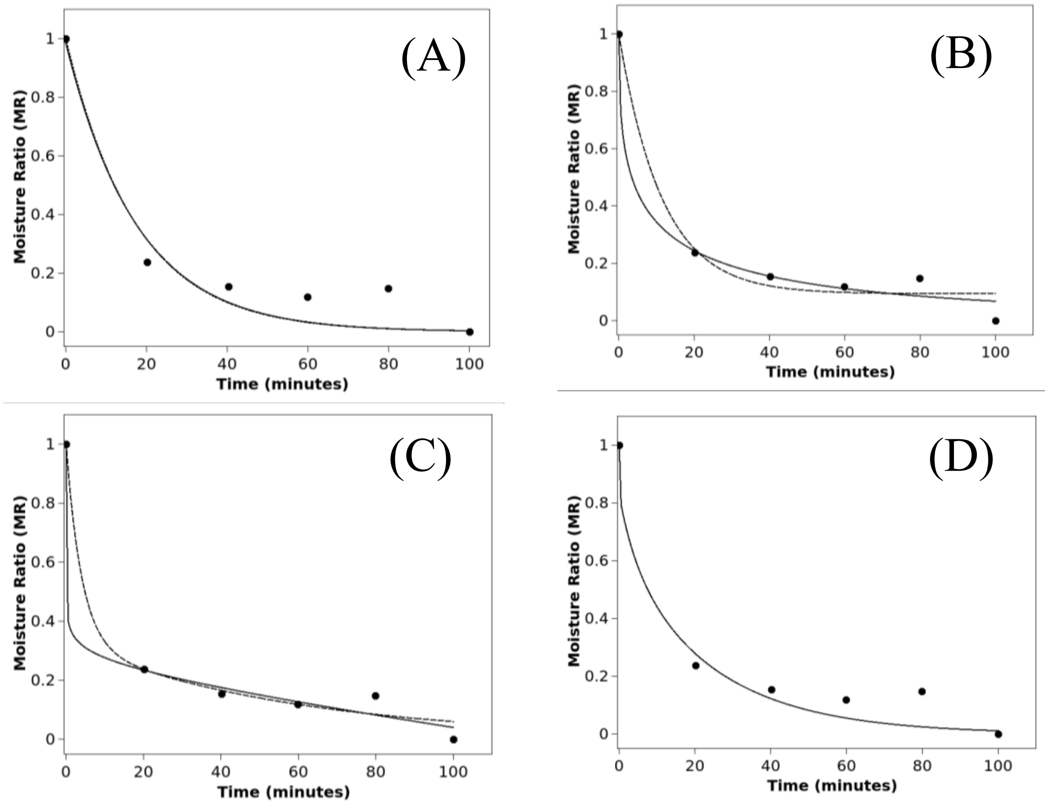

Figure 2. Comparison between experimental drying data (●) and kinetic model predictions for eggshell dried at 400°C. (A) Newton model (---) and Henderson-Pabis model (–); (B) Logarithmic model (---) and Page model (–); (C) Verma model (---) and Midilli-Kucuk model (–); (D) Fick's diffusion model (–).

These visual observations corroborate the statistical analysis and confirm that the empirical models can accurately reproduce the experimental drying curve within the studied range, while the Fickian model, despite its lower statistical fit, provides a physically meaningful parameter (D_{eff}) for interpreting internal moisture transport. The Fickian model slightly underpredicted the initial moisture ratio but converged toward equilibrium at long times, reflecting its simplified representation of the dominant long-term diffusion process. This comparison reinforces that empirical models are valuable descriptive tools for curve fitting, whereas only the Fickian approach yields mechanistic insight suitable for design and scale-up purposes.

3.10 Implications for Process Design and Scale-up

The effective moisture diffusivity (D_{eff}) obtained from the Fickian model provides a physically meaningful parameter that can support process design, material comparison and drying equipment scale-up. In contrast, empirical models, although offering excellent statistical fits, should be used only for curve fitting and process monitoring within the experimental domain.

They do not capture underlying transport mechanisms and therefore cannot be reliably extrapolated to other conditions. The combined use of factorial design for condition screening and Fickian modeling for mechanistic parameter estimation offers a practical framework for developing drying protocols for agro-industrial residues, supporting the transition from laboratory experiments to pilot and industrial scales.

3.11 Study Limitations

This study presents some limitations that must be considered when interpreting the results. First, the factorial design used the total water loss after 2 h as the response variable, without collecting full drying curves for each condition. Consequently, the kinetic analysis was performed only at the optimal condition identified by the DOE, which limits the generalization of the kinetic parameters to other process conditions. Second, the application of Fick's diffusion model assumed spherical geometry, while the real eggshell particles are irregular and lamellar, which may affect the accuracy of the estimated effective diffusivity (D_{eff}).

Third, empirical models were applied solely as descriptive curve-fitting tools and their parameters are not physically interpretable or suitable for extrapolation. Finally, the drying experiments were conducted under uncontrolled ambient humidity and without kinetic replicates, which may introduce variability not captured in the statistical analysis. Despite these constraints, the combined use of factorial design and kinetic modeling provides a valuable framework for guiding future studies on drying optimization and scale-up of agro-industrial residues.

4 Conclusion

This study demonstrated a two-step strategy for the optimization and modeling of eggshell drying, combining factorial design and kinetic analysis. The 23 factorial design identified temperature and sample mass as the main factors affecting water removal after 2 h, while particle size had no significant effect within the studied range. Kinetic experiments conducted under the statistically optimal condition (400 ∘C, 4.0 g, < 1.68 mm) showed that multi-parameter empirical models (Page, Midilli–Kucuk, Verma) provided the best statistical fits, whereas the Fickian model yielded a physically meaningful effective diffusivity (Deff = 4.77×10−11 m2.s−1).

The comparison between Deff and apparent diffusivities derived from empirical models revealed large discrepancies, illustrating the concept of equifinality: distinct mathematical structures can fit the same data well but produce parameters with no physical meaning. This confirms that empirical models are valuable descriptive tools for curve fitting and process control, while mechanistic models based on Fick's law are essential for obtaining transferable parameters for design and scale-up. Overall, this integrated approach provides a robust framework for optimizing drying conditions and understanding moisture transport in agro-industrial residues, supporting future developments in sustainable materials processing.

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