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Modelos geoestatísticos aplicados à hidratação de grãos
Geostatistical models used in grain hydration

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Resumo: Modelos empíricos que apresentam o comportamento de estabilização ou platô são largamente utilizados na Geoestatística (um ramo da estatística que lida com a variabilidade no espaço). Estes modelos podem ser aplicados a dados que possuem a variabilidade no tempo e que apresentem uma tendência de estabilização. Logo, o modelo exponencial e o modelo exponencial potência foram aplicados ao fenômeno da cinética de hidratação de grãos. Ambos os modelos foram ajustados a dados experimentais de umidade em função do tempo para cinco temperaturas de hidratação e seus parâmetros foram obtidos pelo método dos mínimos quadrados. Os tempos para que os grãos atingissem valores de umidade próximos aos de equilíbrio foram obtidos por um método que garante a obtenção destes valores quando o modelo atinge 99,99% do patamar da umidade de equilíbrio. Os resultados mostraram que o modelo exponencial potência é mais adequado para a descrição das principais tendências dos dados experimentais e que os tempos de equilíbrio obtidos neste trabalho são muito mais realistas, quando comparados aos dados experimentais, do que os obtidos pela abordagem tradicional, que considera a estabilização da curva a 95% do seu patamar final.

Palavras-chave: Hidratação; Modelagem matemática; Modelos empíricos; Soja.

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Abstract: Empirical models that present a behavior of stabilization (reaching a constant level) are widely used in Geostatistics (a branch of statistics that deals with spatial variability). These models can be applied to data which varies in time and tends to stabilize. Therefore, the exponential model and the powered exponential model were applied in the case of grain hydration kinetics. Both models were fitted to experimental data on moisture content as a function of time at five different hydration temperatures, using the least squares method to obtain their parameters. The times required for the grains to reach moisture content close to equilibrium were obtained using a method which corroborates the results when the model reaches 99.99% of the moisture content constant level. The results have shown that the powered exponential model is the most adequate one for describing the main trends of the experimental data. Equilibrium times obtained in the present work were much closer to experimental data than those obtained using the traditional approach, which considers the curve to be stable at 95% of its final constant level.

Keywords: Hydration; Mathematical modeling; Empirical models; Soybean.

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1. Introduction

Grain moisture content levels achieved during the hydration process are very important due to the moisture contained inside the grains defining textural properties of canned grains, as is the case with peas (Lima and Siqueira, 2008; Omoto et al., 2009), inactivating antinutritional factors and securing characteristics which ensure that the grain can be consumed, as is the case with beans (Lemos et al., 1996), making the grain palatable and digestible, as is the case with rice (Bello et al., 2004; Briffaz et al., 2014; Thakur and Gupta, 2006), favoring the diffusion of compounds into the grains to help in starch extraction, as is the case with corn wet-milling (Lopes Filho, 1999; Lopes Filho et al., 2006), among other examples. Hydration plays a crucial role in the extraction of soybean proteins as it causes the cell structure to soften, which reduces the energy requirements for grinding the grains. This increases protein extraction and emulsification of fats (Wang et al., 1979).

To avoid repeating tests for ascertaining moisture content as a function of time whenever the grain hydration kinetics is to be determined, mathematical models can be used for the description of the major trends of the experimental data, with adjustments being made according to experimental conditions. An immersion time of 12 h is traditionally used as pretreatment for the grains before protein extraction (Ciabotti et al., 2009), which is an empirical choice that may not be ideal. Several authors have devoted themselves to the mathematical description of the mass transfer that occurs in soybean hydration considering the elementary steps of the process. For this purpose, both phenomenological models of lumped parameters, which don't account for moisture content variation inside the grains (Coutinho et al., 2007, 2005; Nicolin et al., 2015b, 2013), and phenomenological models of distributed parameters, which account for said variation (Coutinho et al., 2010a, 2010b, 2009; Nicolin et al., 2015a, 2014, 2013, 2012), were proposed.

Phenomenological models provide physical information on the moisture diffusion process inside the grains, as they are based on mass transfer theoretical assumptions (Bequette, 1998; Pinto and Lage, 2001). However, when the modeling is focused on obtaining a good description of the trends of the hydration kinetics curve, empirical models may be used. These models are a direct representation of experimental data and generally require lower computational effort than phenomenological models. Although not suitable for extrapolating predictions outside the region in which they are validated, empirical models fit very well to experimental data (Pinto and Lage, 2001; Saguy et al., 2005). Some examples of empirical models widely used in the modeling of grain hydration are those of Pilosof et al. (1985), Singh and Kulshrestha (1987), and Peleg (1988).

For the studied phenomenon, models that reach a constant level are sought after. In Geostatistics, which is a branch of statistics that deals with spatial variability, this type of model

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is widely used (Carducci et al., 2015, 2014a, 2014b, 2014c; Silva et al., 2014; Yanagi Junior et al., 2012). These models can be applied to phenomena that vary in time instead of in space, since in the theory of stochastic processes time is nothing more than space in one dimension. In other words, if t is the time indexer and s the space indexer, then $t \in \mathbb{R} \Leftrightarrow s \in \mathbb{R}^d$ with d=1.

In this context, the objective of the present work was to mathematically model the hydration of soybean grains at different temperatures using two empirical models that describe the variation of grain moisture content as a function of time, the exponential model and the powered exponential model, both commonly used in Geostatistics. The use of these models for spatially correlated data is present in works that address the spatial variability of soil (Carducci et al., 2015, 2014a, 2014b, 2014c) and the spatial variability of sound dispersion (Silva et al., 2014; Yanagi Junior et al., 2012).

The models were validated using experimental data from soybean hydration and the model which better fitted the data was analyzed in detail, relative to both the behavior of its parameters as a function of temperature and its adequacy in describing the hydration kinetics. Equilibrium time, which is the required time for the grains to reach moisture content close to the equilibrium value, was obtained at all hydration temperatures for moisture contents equivalent to 99.99% of the equilibrium content. The results are consistent with the behavior of the soybean hydration kinetics and with the obtained experimental data, which leads to the conclusion that the method used for obtaining the equilibrium time is adequate for the soybean hydration process.

2. Materials and Methods

2.1 Obtaining experimental data

Initially, 300g of CD 202 cultivar soybean grains were weighed. A thermostatic bath was then prepared to control the hydration temperature. The tests were run at temperatures of 10, 20, 30, 40, and 50 C. While the bath reached the desired temperature, 1.5 liters of a diluted sodium benzoate solution (0.2 % m/m) were prepared for immersion of the grains. The sodium benzoate was used for inhibiting the proliferation of microorganisms during the immersion period. This solution was put in contact with the thermostatic bath to reach the desired temperature. Once the ideal temperature was reached, the grains were placed in the solution and a chronometer was started. At predetermined times, soybean samples of 10 grains were taken from the solution and excessive surface moisture was removed using paper towel. The samples were then weighed and put in a drying oven at 105°C for 24h (Lutz, 1985) for determination of the grain moisture content from the mass difference between moist and dry grains. The moisture

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content of the grains was calculated on dry basis $(\text{kg}_{\text{water}}/\text{kg}_{\text{ds}})$, where "ds" stands for dry solid).

2.2 Parameter fitting

The parameters of the models considered in the present work were fitted using linear regression with the "nls" command in the software "R" (R Development Core Team, 2014). The algorithm used in the regression was the Gauss-Newton Method, which is the default one for the "nls" command. In Eq.(1), which presents the objective function ϕ to be minimized (quadratic residual in $\text{kg}^2_{\text{water}}/\text{kg}^2_{\text{ds}}$), X^i_{calc} $(\text{kg}_{\text{water}}/\text{kg}_{\text{ds}})$ is the moisture content calculated using the model, and X^i_{exp} $(\text{kg}_{\text{water}}/\text{kg}_{\text{ds}})$ is the experimentally obtained moisture content, both as functions of time.

$$\phi = \sum_{i=1}^{N} \left(X^i_{\text{calc}} - X^i_{\text{exp}} \right)^2 \tag{1}$$

The fitting of the model to experimental data was assessed by the analysis of residuals between the values calculated using the model and those experimentally issued by the "nls" command (R Development Core Team, 2014). The main results used in the present work were the Q-Q plot of residuals, the fitting of residuals to a normal distribution, and the calculation of $\overline{p}$ -values for the Shapiro-Wilk test with 95% confidence.

2.3 Empirical models

The models used in the mathematical description of the soybean hydration kinetics were the exponential model represented by Eq.(2) and the powered exponential model represented by Eq.(3). In both equations, $X(t)$ is the moisture content as a function of time in dry basis $(\text{kg}_{\text{water}}/\text{kg}_{\text{ds}})$, C_0 $(\text{kg}_{\text{water}}/\text{kg}_{\text{ds}})$, C_1 $(\text{kg}_{\text{water}}/\text{kg}_{\text{ds}})$, a (s), and p (dimensionless) are parameters of the models, and t (s) is time.

$$X(t) = C_0 + C_1 \left\{ 1 - \exp\left[-\left| \frac{t}{a/9} \right| \right] \right\} \tag{2}$$

$$X(t) = C_0 + C_1 \left\{ 1 - \exp\left[-\left(\frac{t}{a/9} \right)^p \right] \right\} \tag{3}$$

Both models start at an initial value (represented, in this case, by C_0, which can also be interpreted as being the initial grain moisture content) and tend asymptotically and

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exponentially to a constant moisture content level that means an equilibrium moisture content value (X_{eq}) achieved for very long times ($t \to \infty$). In both models, the parameter a is divided by 9 according to the approach developed by Seidel and Oliveira (2013). The constant 9 is a result of obtaining the value of the parameter a when the model reaches 99.99% of its constant level. Ratios such as $a/3$ for the exponential model and $a/\sqrt{3}$ for the Gaussian model are also discussed in the work of Seidel and Oliveira (2013), however, they are results of obtaining the parameter a when the model reaches 95% of its constant level.

Models like this are widely used in Geostatistics. In the creation of semivariograms, which represent the spatial dependence between observations, models that allow the nature of the spatial dependence of the studied variables to be visualized are adjusted. In the context of Geostatistics, the parameter a indicates the distance within which the samples correlate spatially, C_0 corresponds to the unexplained variation in the experiment, and C_1 is the difference between the constant level of the model and the unexplained variation C_0 (Carvalho et al., 2002; Seidel and Oliveira, 2013). In the context of grain hydration, it is possible to infer that the parameter a is related to the time needed for hydration equilibrium to be achieved, with C_0 representing the initial moisture content of the grains and C_1 representing the amount of moisture the grains absorb until they achieve equilibrium. The parameter p represents, in both contexts, a parameter to be determined for the representation of the exponent present in Eq.(3).

3. Results and Discussion

Table 1 shows the fitted values of parameter for both considered models compared with the experimentally obtained initial moisture content along with the deviations relative to initial moisture content experimental data. For all considered temperatures, the parameter C_0 was closer to experimental values when the powered exponential model was used. As much as this parameter could have been fixed since it is easily obtained experimentally, the powered exponential model provided better estimates of this value in the considered experimental range, as shown by the deviations higher than 100% made by the exponential model relative to experimental data. Table 2 presents the values for the constant level of the model, defined as the equilibrium moisture content after very long hydration times and given by the sum $X_{eq} = C_0 + C_1$ together with the deviations relative to experimental equilibrium moisture content. Both models presented much smaller deviations when predicting equilibrium moisture content, with parameter contributing less in the exponential model, which balances the high values obtained for when calculating the constant level. Experimental values were obtained for

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as the average of values located in the constant level achieved by the experimental data after long hydration times.

Table 1: C_0 (kg_{water}/kg_{ds}) and deviation relative to experimental data for the exponential (Exp.) and the powered exponential (P. Exp.) models.

T(°C)	C_0 (Exp.)	C_0 (P. Exp.)	X_0	Deviation (%) Exp.	Deviation (%) P. Exp.
10	0.249	0.124	0.106	134.62	16.65
20	0.241	0.124	0.107	126.67	16.06
30	0.231	0.113	0.103	123.23	9.10
40	0.242	0.119	0.107	126.75	11.41
50	0.250	0.143	0.107	133.74	33.83

Table 2: $C_0 + C_1$ (kg_{water}/kg_{ds}) and deviation relative to experimental data for the exponential (Exp.) and the powered exponential (P. Exp.) models.

T(°C)	C_0+C_1 (Exp.)	C_0+C_1 (P. Exp.)	X_{eq}	Deviation (%) Exp.	Deviation (%) P.Exp.
10	1.718	1.779	1.741	1.29	2.19
20	1.668	1.694	1.708	2.31	0.83
30	1.680	1.702	1.758	4.41	3.20
40	1.653	1.673	1.675	1.27	0.10
50	1.705	1.722	1.747	2.43	1.44

The powered exponential model presented a better fitting to experimental data, as shown in Figure 1, which presents the comparison, at 10°C, between the exponential model, the powered exponential model, and the experimental data. This is evidenced by the Akaike test, which calculates a model selection criterion where the model presenting the lowest AIC (Akaike Information Criterion) value is the most likely to correctly represent a given set of data (Akaike, 1973). According to the Akaike test, as shown in Table 3, the powered exponential model proved to be the model with the highest probability of being correct in the description of soybean grain hydration data for all experimentally considered temperatures.

Table 3: Akaike Information Criterion (AIC) values for the fitting of the exponential (Exp.) and the powered exponential (P. Exp.) models.

T(°C)	AIC (Exp.)	AIC (P. Exp.)
10	-84.26	-264.98
20	-93.89	-253.44
30	-89.36	-212.21
40	-98.20	-259.62
50	-96.32	-223.66

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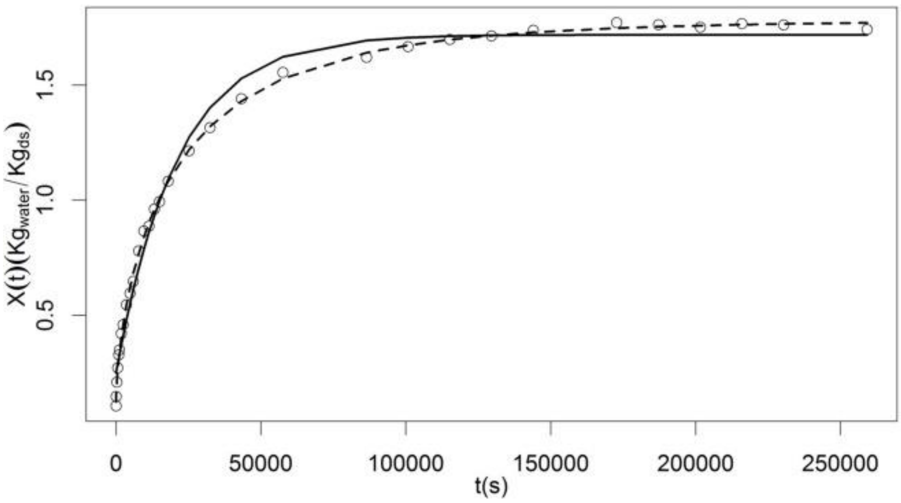

Figure 1: Moisture content as a function of time: powered exponential model (dotted line), exponential model (solid line), and experimental data (o).

Since the powered exponential model was proven to be the best model for the present work, analyses were made for results concerning this model only. To evaluate the adequacy of the powered exponential model relative to experimental data, an analysis of residuals was carried out between the moisture content calculated by the model and that from experimental data. The Shapiro-Wilk test with 95% confidence was used for verifying whether the residuals follow a normal distribution around zero, which is appropriate since that indicates a minimal distance between the values calculated by the model and those experimentally obtained.

Table 4: $\bar{p}$ -values for the Shapiro-Wilk test with 95% confidence.

T (°C)	$\bar{p}$ -Value
10	0.686
20	0.380
30	0.470
40	0.062
50	0.380

From Table 4 it can be observed that the null hypothesis of normality was not rejected for the temperature range used in the present work, since the $\bar{p}$ -value was higher than 0.05 ($\bar{p} > 0.05$) in all cases.

In the powered exponential model (Eq.(3)), the parameter C_0 corresponds to the unexplained variation in the experiment. Since the value was close to zero for the model, the experiment can be stated to have been well conducted and, therefore, it represents the studied

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phenomenon consistently. The parameter C_1 represents the required moisture content in the grains for the model to reach a constant level (equilibrium moisture content, reached after a very long time). When calculating the limit for $t \to \infty$ in Eq.(3), the result $X(t \to \infty) = C_0 + C_1$ is obtained. This makes it clear that the parameter C_1 represents the amount of moisture entering the grains throughout the hydration process. Thus, the equilibrium moisture content can be defined as $X_{eq} = C_0 + C_1$ since, for very long immersion times of the grains in water, moisture absorption tends to reach a state of equilibrium. In this state, there is very little or virtually no moisture absorption by the grains.

Figure 2 shows the behavior of parameter C_0 as a function of temperature for the powered exponential model. Although, in the temperature range considered, there was no clear trend for the behavior of C_0, the intersection of the confidence intervals indicate that, at all temperatures, there is no statistical difference between the obtained values.

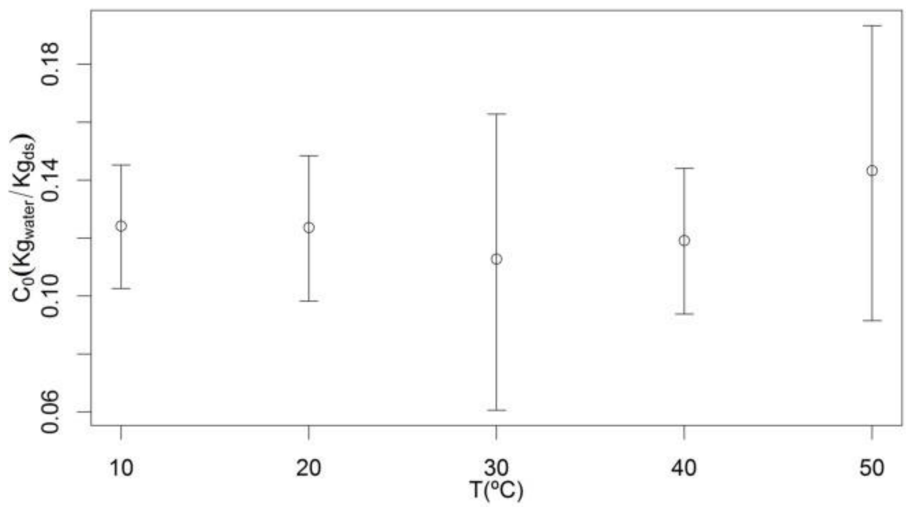

Figure 2: Parameter C_0 as a function of temperature – powered exponential model.

This was expected since the initial moisture content of the grains should be the same considering that the grain sample used in the present work was stored in order to prevent moisture absorption. Thus, the initial moisture content of the grains should be relatively constant in the tests carried out at all temperatures.

The sum $C_0 + C_1$, which represents the equilibrium moisture content (X_{eq}) achieved by the grains after long immersion times, had no significant variation relative to temperature (Figure 3). Even though the value at 10°C was slightly different from those at the other temperatures, the intersection of the confidence intervals suggests that there is no statistical difference between some of the values. The value of $C_0 + C_1$ at 10°C was statistically different

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from the values obtained at the remaining temperatures, since at 10°C the bars representing the confidence interval for $C_0 + C_1$ did not overlap those obtained at the other temperatures. Said differences are not significant enough to result in a completely different equilibrium moisture content (sum) at 10 C. As will be shown later, the curves for all temperatures tend to the same equilibrium moisture content, since the 95% prediction intervals overlap, which indicates that the model tends to a value which has the probability of being the same at all temperatures (Figure 7). As much as the grains are biologically complex, if they are from the same cultivar it is expected that the moisture absorption be constant for all grains and that the cultivar as a whole have characteristic moisture absorption curves for each temperature. The difference is in the rate of said water absorption by the grains, which increases as the temperature increases. Thus, although grains start with the same initial moisture content and virtually reach the same equilibrium moisture content, absorption rates vary depending on the temperature at which hydration takes place.

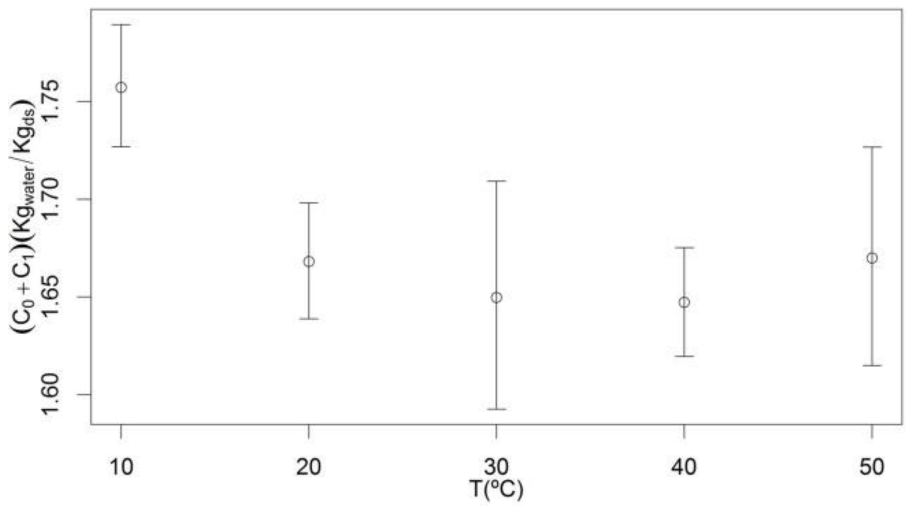

Figure 3: Sum of $C_0 + C_1$ as a function of time – powered exponential model.

The values for parameter a presented a clear behavior of decay as a function of temperature, as shown in Figure 4. Statistically, the values are different. This kind of behavior is consistent with what is experimentally observed. Since the parameter a is related to the time needed for the model to reach its constant level or to get very close to it, said values have to decrease as temperature increases. This is due to higher absorption rates being associated with higher immersion temperatures. Because the grains absorb moisture faster at higher temperatures, it is expected that the equilibrium moisture content also be achieved faster at higher hydration temperatures. Therefore, less time is required for the equilibrium moisture content to be achieved as the temperature increases.

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The parameter p increased as the temperature increased, although at some temperatures its values presented statistical equivalence. The exponential model (Eq.(2)) presents the term (t/a) squared, according to the very definition of the model. The powered exponential model, on the other hand, presents the term (t/a) raised to the power of p, which is obtained adjusting the model to experimental data. Figure 5 shows that the values obtained for p range from 0.65 to 0.80. This indicates that the constant power "2" as suggested in the definition of the exponential model is inadequate for describing the data set used for model validation in the present work.

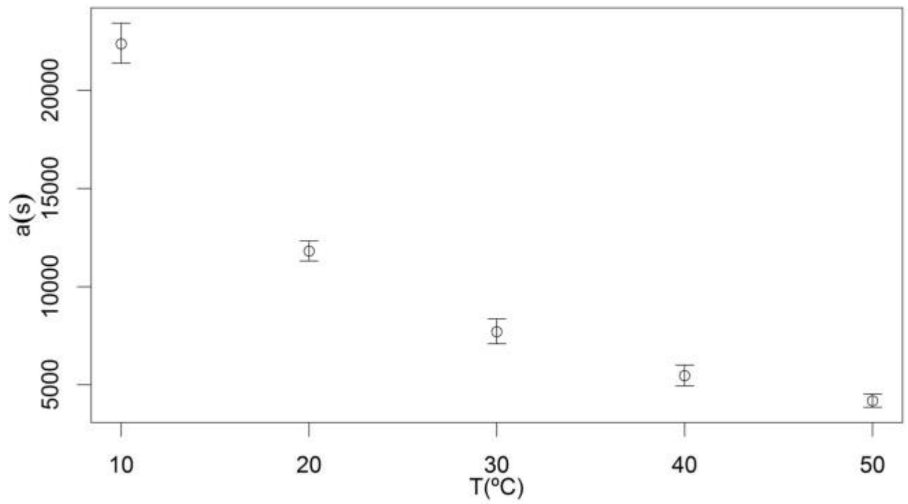

Figure 4: Parameter a as a function of temperature – powered exponential model.

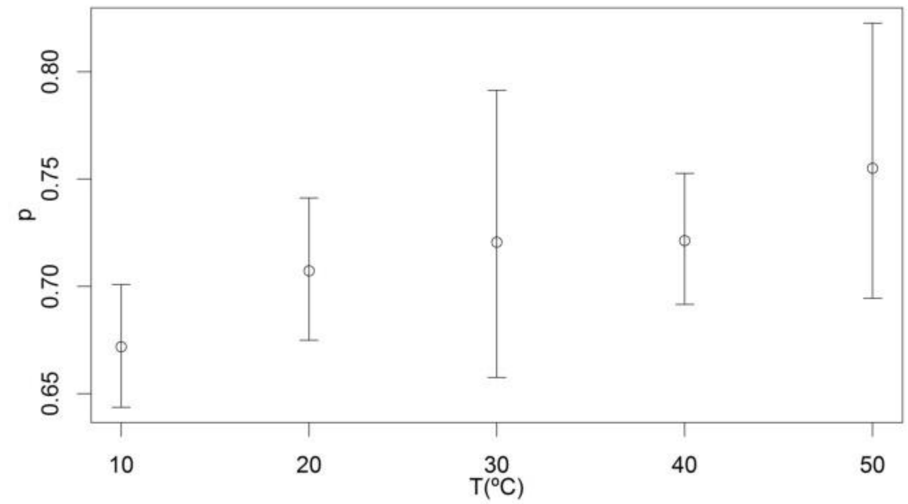

Figure 5: Parameter p as a function of temperature – powered exponential model.

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The chosen model, powered exponential, presented equilibrium moisture close to 1.78 kg_{water}/kg_{ds} at a temperature of 10 °C. The parameter a represents the theoretical range of the model, in other words, at what point (in time) the level $X_{eq} = C_0 + C_1$ becomes constant. This standard for the definition of a is commonly used in Geostatistical problem modeling (Seidel and Oliveira, 2013). In their work, Seidel and Oliveira (2013) have mathematically proven how to reach equilibrium within 99.99% of the constant level. Figure 6 presents the great difference between equilibrium points when faced with 95% and 99.99% of the constant level. At the temperature of 10°C, equilibrium was reached in 201330 s. From the analysis of Figure 6, it is evident that the moisture content achieved at 95% of the constant level (equilibrium moisture content) is still far from the region which characterizes a possible state of equilibrium. It can be observed, in fact, that the obtained value is in the region of transition between the highly transient and the steady states of the hydration process, in other words, far from a possible equilibrium. The moisture content obtained at 99.99% of the constant level, on the other hand, is in a region where it can be stated that hydration achieves equilibrium.

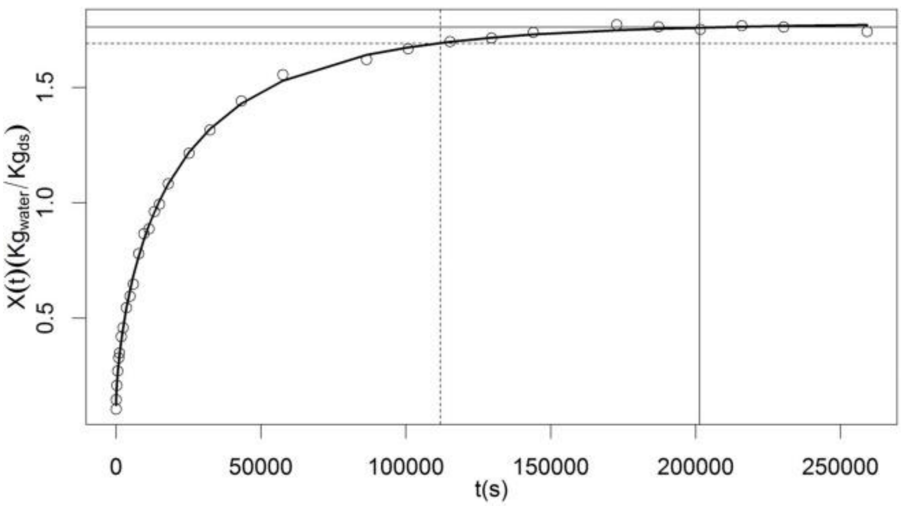

Figure 6: Moisture content as a function of time as calculated using the model (bold solid line) and experimentally (o), as well as equilibrium points at 95% (dashed lines) and 99.99% (solid lines) of the constant level.

Figure 7 presents the moisture content values calculated using the powered exponential model compared with experimental data at 10, 30, and 50°C.

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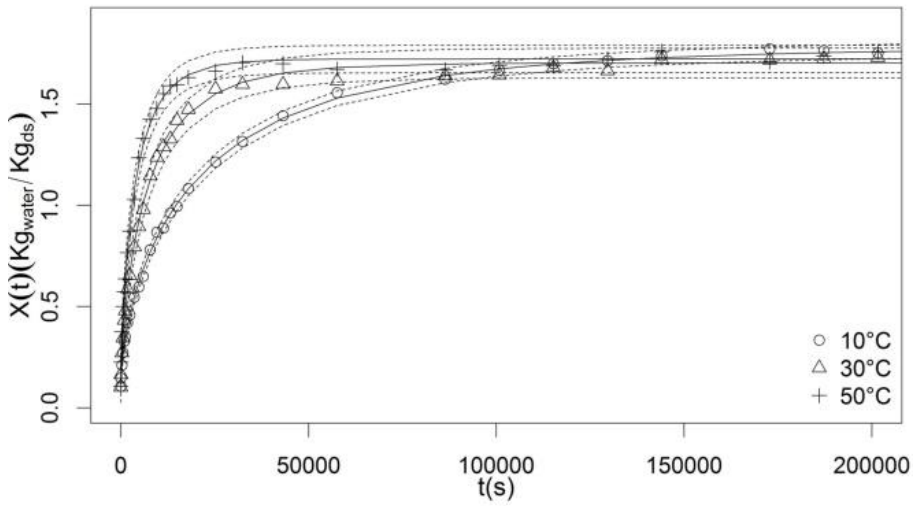

Figure 7: Moisture content for different temperatures as calculated by the model and experimentally, as well as 95% prediction intervals.

The graphic also presents, for each temperature, the 95% prediction intervals. Therefore, if the hydration experiment is carried out 100 times, 95 of them should present values within the prediction interval. In the figure, the difference in moisture absorption rates as a function of time can be observed. At 50°C, moisture is absorbed by the grains much faster than at 10°C.

As previously stated, although differences exist between absorption rates, the achieved equilibrium moisture content (model constant level) can be considered the same for all temperatures. This is corroborated by the overlapping prediction intervals, which indicate the absence of statistical differences between the intervals where they overlap. Thus, this result also helps conclude that there are no statistical differences between the equilibrium moisture contents obtained for each temperature.

In order to evaluate the quality of the powered exponential model relative to empirical models from the literature, the models of Peleg (1988), Pilosof et al. (1985), and Singh and Kulshrestha (1987) were fitted to the experimental data for moisture content as a function of time used in the present work. These three models are represented by Eq.(4), (5), and (6), respectively. They were written in a manner similar to the models analyzed in the present work with C_0 as the initial moisture content. A_1 ($kg_{ds}.s/kg_{water}$) and A_2 (kg_{ds}/kg_{water}) are the parameters of Peleg's model, A_3 (kg_{water}/kg_{ds}) and A_4 (s) are the parameters of Pilosof's model, and A_5 (1/s) is the parameter of Singh and Kulshrestha's model.

$$X(t) = C_0 + \frac{t}{A_1 + A_2 t} \tag{4}$$

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$$X(t) = C_0 + \frac{A_3 t}{A_4 + t} \tag{5}$$

$$\frac{X(t) - C_0}{X_{eq} - C_0} = \frac{A_5 t}{A_5 t + 1} \tag{6}$$

Evaluating the limit when $t \to \infty$,Peleg's model provides, for the equilibrium moisture content, the value $X_{eq} = C_0 + 1/A_2$ and Pilosof's model provides $X_{eq} = C_0 + A_3$, while Singh and Kulshrestha's model provides the exact result X_{eq}, which is a term that appears directly in the model (Eq.(6)). These limit values were used for comparison of the values obtained using the powered exponential model. In all three models, C_0 is also considered to be a parameter to be adjusted so the results can be directly compared with those obtained for the powered exponential model. Furthermore, the ability of these classic models to obtain the initial moisture content from the adjustment of a data set was also assessed. This approach was also used when obtaining the results of the powered exponential model, as the parameter C_0 has a particular meaning when this model is used in Geostatistics. Table 5 presents the values of the adjusted parameter for the powered exponential model compared with those obtained for Peleg's, Pilosof's, and Singh and Kulshrestha's models, as well as those obtained experimentally. This table also presents the values estimated for the equilibrium moisture content, considering the limit when $t \to \infty$ for all models. It can be observed that, in comparison with the experimental values, the powered exponential model was more successful than the other empirical models in predicting both the initial moisture content (C_0) and the equilibrium moisture content $(C_0 + C_1)$ when $t \to \infty$.

Table 5: Adjusted parameters compared with empirical models from the literature and experimental data.

T(°C)	Experimental		Powered Exponential		Peleg		Pilosof		Singh and Kulshrestha	
	X_0	X_{eq}	C_0	C_0+C_1	C_0	C_0+1/A_2	C_0	C_0+A_3	C_0	X_{eq}
10	0.106	1.741	0.124	1.779	0.191	1.872	0.191	1.872	0.158	1.741
20	0.107	1.708	0.124	1.694	0.168	1.771	0.168	1.771	0.150	1.708
30	0.103	1.758	0.113	1.702	0.147	1.768	0.147	1.768	0.143	1.758
40	0.107	1.675	0.119	1.673	0.142	1.726	0.142	1.726	0.124	1.675
50	0.107	1.747	0.143	1.722	0.147	1.775	0.147	1.775	0.137	1.747

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Unlike the other models, Singh and Kulshrestha's does not predict equilibrium values as a function of the parameter of the model due to the equilibrium moisture content (X_{eq}) being obtained exactly when $t \to \infty$.

Besides better predicting values such as initial and equilibrium moisture content relative to the other considered empirical models, the powered exponential model also fitted better to experimental data when comparing its mean squared errors with those from other models. Table 6 presents said values as well as values for the Akaike test, which corroborate the better results of the powered exponential model. It is important to consider that C_0 and C_1 were regarded as parameters to be adjusted in all the models since their meaning is not originally defined in the context of soybean hydration.

Table 1: Mean Squared Errors (MSE) and AIC for the powered exponential model and the other empirical models from the literature.

T(°C)	Powered Exponential		Peleg		Pilosof		Singh and Kulshrestha	
	MSE	AIC	MSE	AIC	MSE	AIC	MSE	AIC
10	2.908×10^{-4}	-264.98	1.038×10^{-3}	-223.86	1.038×10^{-3}	-223.86	4.736×10^{-3}	-174.70
20	3.235×10^{-4}	-253.44	1.049×10^{-3}	-216.67	1.049×10^{-3}	-216.67	2.149×10^{-3}	-194.63
30	1.173×10^{-3}	-212.21	1.194×10^{-3}	-212.53	1.194×10^{-3}	-212.53	1.188×10^{-3}	-213.61
40	2.666×10^{-4}	-259.62	1.046×10^{-3}	-216.75	1.046×10^{-3}	-216.75	2.040×10^{-3}	-196.30
50	1.017×10^{-3}	-223.66	2.066×10^{-3}	-201.16	2.066×10^{-3}	-201.16	2.371×10^{-3}	-197.53

Should the moisture content profiles predicted by these models be analyzed in a single figure (Fig. 8), the powered exponential model can be observed to have a behavior very similar to that of Peleg's and Pilosof's models. Even so, it can also be observed that, for certain time intervals, the powered exponential model gets even closer to the behavior of experimental data. Singh and Kulshrestha's model follows the other models and experimental data until times of $\approx$ 40000 s. After that, it tends to a lower constant level than that predicted by the others. This behavior of distancing itself from the other models and the experimental data can be attributed to the fact that, also for their model, the parameter corresponding to initial moisture content (C_0) was adjusted together with the single parameter of the model, A_5. The value reached for their model when $t \to \infty$ should be X_{eq}, which isn't, however, the case. This is because the maximum experimental time achieved (288000 s), which is virtually being considered as $t \to \infty$, does not guarantee that the term $A_5 t / (A_5 t + 1)$ from Singh and Kulshrestha's model equals 1 when initial moisture content and the parameter A_5 are fitted simultaneously instead of fitting A_5 independently. The term $A_5 t / (A_5 t + 1)$ is slightly below 1, which sets the limit

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slightly below X_{eq}. This is the reason why Singh and Kulshrestha's model does not reach the precise equilibrium moisture content. The work of Sopade et al. (2007) shows the mathematical equivalence between the models of Peleg, Pilosof, and Singh and Kulshrestha. This emphasizes the fact that the models should be equivalent in describing experimental data when their parameters are fitted considering initial and equilibrium moisture content to have been experimentally obtained. The equivalence between Peleg's and Pilosof's models is also noteworthy in Figure 8, as they overlap in virtually all moments of the hydration process.

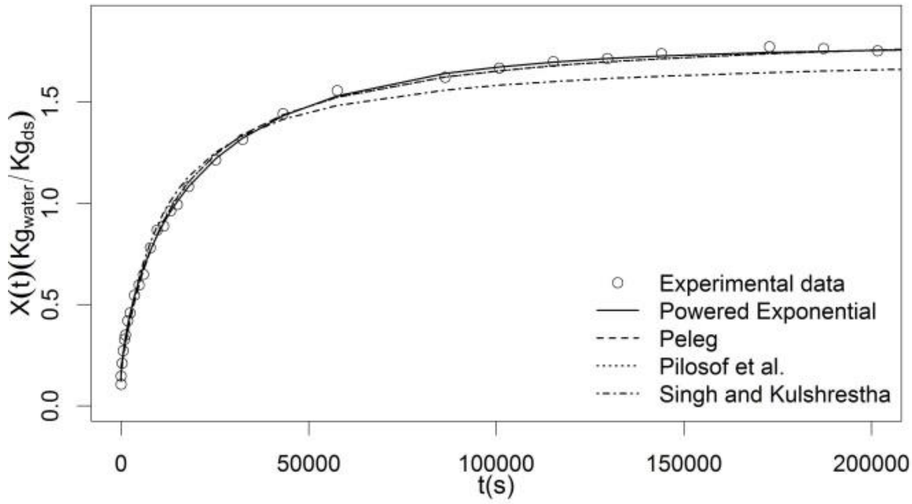

Figure 8: Comparison of the powered exponential model with experimental data and with the other empirical models from the literature.

4. Conclusion

The kinetics of soybean hydration was satisfactorily modeled using exponential models originally used in the field of Geostatistics, after making the proper considerations. The powered exponential model proved to be even more adequate than the exponential model in the description of the main trends of the experimental data, as concluded using the Akaike tests. Equilibrium times were obtained using the powered exponential model following a formal mathematical model which provided the time when the model reaches 99.99% of its constant level (equilibrium moisture). This method proved to be much more coherent, since the times obtained were consistent with the experimental curves of soybean moisture content as a function of time, making it an important tool for estimating equilibrium times in the models addressed in the present work. This has shown that the approach commonly used in Geostatistics, which provides values for the parameter a when the model reaches 95% of its constant level, is not adequate when implemented in the modeling of soybean hydration kinetics.

The powered exponential model was compared with three traditional models from the literature, namely Peleg's, Pilosof's, and Singh and Kulshrestha's models. When compared with

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these models, the powered exponential model presented a greater ability to predict values such as initial and equilibrium moisture content. When compared with the experimental values, the powered exponential model was closer to experimental data than the other empirical models considered in the present work. It also fitted better to experimental data since it provided lower MSE and Akaike test values.

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