

Direct Mathematical Models for Estimating the Shelf Life of Second- and Zero-Order Degradation Relationships of Food and Drugs

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Abstract

Recently, a direct model for evaluating the shelf life of lemon juice, depending on the loss of ascorbic acid concentration with time was derived by Al-Zubaidy and Khalil (Food Chem. 101 (2007) 254–259). By using this model, one could directly estimate the expiration date at any residual ratio and any specific temperature of the first-order degradation rate. But, in general, the kinetic model for degradation process is not limited to first-order reactions, as it could be second-, or zero-order according to the experimental data. Therefore, two direct models have been developed to evaluate shelf life based on these orders. These models have been verified using previously published results for vitamins C (zero-order) and D3 (2nd-order) in coconut powder. The results indicate that the prediction of shelf life for food, drugs and so on can also be evaluated directly for second-, and zero-order degradation processes using the developed models in the same way to that of pre-published for first order. A characteristic feature of the presented degradation orders is that the input data for determining the rate constant must be in percentage (%) rather than the real concentration in contrast to that of first order. It was concluded that the use of the derived equations avoids the complications resulting from changing the unit of the rate constant with the change in the reaction order. In addition to the gained simplicity when dealing with the developed models.

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1 Introduction

In general, the shelf life of goods can be considered as a very essential task, particularly for those of food and drugs industries. However, the prediction of the shelf life or expiration date

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is not that straightforward which needs specific models who depend on the permissible ratio of loss in product concentration nor on that of the common half-life of the residual. For example, in the case of estimating the shelf life of drugs, the loss in the amount of active material should not exceed 5%. In other words, for each ratio of loss one need to derive a special model for the specific sample when determining the kinetic of the loss in product at different temperatures [1]. Actually, such a percentage of loss is parallel to that of the minimum requirements for the standard or specification of products. In order to make the task of shelf life determination much easier, a direct model (1) was derived by Al-Zubaidy and Khalil throughout the kinetic investigation of vitamin C in lemon juice at different Brix and temperatures [1],

$$Ex = e^{-\left[\frac{S}{T} + I - \ln\left(-\ln\left(\frac{p\%}{100}\right)\right)\right]}, \quad (1)$$

where Ex is the shelf life of the product in any unit of time (depending on the unit of rate constant), I and S are the intercept ($\ln A$) and slope ($-\frac{E^\ddagger}{R}$) obtained from the application of the Arrhenius equation throughout the plot between natural logarithm of 1st-order rate constant against $1/T$; T is the Kelvin or absolute temperature and $p\%$ is the percent of residual that represents the minimum acceptable specifications for the materials to be examined. For example, if the maximum permissible percentage of loss in concentration or any other property is 10%, therefore $p\%$ will be equal to 90 [1]. Indeed, the last developed work is receiving wide attention from dozens of researchers in the field of food science [2–9]. Recently, Kim et al. [10] applied the developed model (1) to estimate the shelf life of rice during storage at different temperatures. On the other side, the developed Equation (1) is only applicable to the first-order degradation process, not to that of zero- or second-order [1]. Therefore, it seems very interesting to derive alternative models for determining the shelf life for those of zero- and second-order degradation processes. Thus, the present work introduces two direct models for evaluating the shelf life for second- and zero-order rates of degradation in a similar manner to that for first-order (1). The suggested models were proved using published data by Aguirre et al. [11] for the degradation kinetics of vitamins C (zero-order) and D_3 (2nd-order) in coconut powder.

2 Main results

The kinetic data for the degradation process of vitamins C and D_3 in coconut powder in terms of percentage at different temperatures were taken from Aguirre et al. [11] as listed in Table 1. Application of kinetic models of zero, first, and second-order to these data was carried out to find the best-fitted models as listed in Table 2. According to values of the square correlation coefficient (r^2), the results show that the suitable kinetic models for the degradation of vitamins C and D_3 are zero- and second-order, respectively. In other words, the value of r^2 is considered as an essential function of linearity that can be employed for testing the linear relationships of chemical kinetics equations. Thus, for D_3 , it is apparent from the values of r^2 that the degradation of this vitamin is consistent with 2nd order kinetic model. On the other side, the relatively high value of r^2 for the degradation of vitamin C at 25°C reflects the fitness with the zero-order model. In other words, the r^2 at 25°C is equal to 0.964 which is weightier than that of the first order (0.937), while at other temperatures (15 and 35°C) the values of r^2 for zero- and 1st-order are somewhat close to each other (Table 2). Such achievement is quite parallel to that of already published Aguirre et al. [11].

Table 1: Retention percentages of vitamins C and D₃ in coconut powder packaged with atmospheric air during storage at three temperatures (15, 25 and 35 °C) and different times as taken from Aguirre et al. (2020).

Vitamin	C			D ₃			
	Temp.	15 °C	25 °C	35 °C	15 °C	25 °C	35 °C
Time/ day							
0	100	100	100	100	100	100	
30	77.18	84.21	67.06	64.63	51.03	49.23	
60	76.07	77.06	61.70	62.36	50.75	42.70	
90	72.82	76.29	51.04	61.64	48.20	42.12	
120	61.58	54.06	18.25	53.06	48.11	41.95	
150	58.50	49.37	17.93	50.77	46.57	38.90	
180	44.94	35.53	11.90	48.68	38.73	32.86	

Table 2: Rate constants (k) obtained by application of zero-, first- and second-order reaction kinetics models at different temperatures with the related statistical data for vitamins C and D₃ in coconut powder.

Vitamin	C			D ₃			
	Temp.	15 °C	25 °C	35 °C	15 °C	25 °C	35 °C
Zero-order rate constant (mg.g ⁻¹ .day ⁻¹) ^a		0.2584	0.3406	0.4834	0.2274	0.2326	0.2653
<i>r</i> ²		0.9210	0.9640	0.9280	0.7130	0.5480	0.5730
<i>SE</i>		0.0339	0.0296	0.0604	0.06453	0.0945	0.1025
First-order rate constant (day ⁻¹) ^b		3.77 × 10 ⁻³	5.39 × 10 ⁻³	12.2 × 10 ⁻³	3.34 × 10 ⁻³	3.67 × 10 ⁻³	4.56 × 10 ⁻³
<i>r</i> ²		0.9270	0.9370	0.9330	0.7970	0.6290	0.6800
<i>SE</i>		4.73 × 10 ⁻⁴	6.27 × 10 ⁻⁴	1.46 × 10 ⁻³	7.52 × 10 ⁻⁴	1.26 × 10 ⁻³	1.40 × 10 ⁻³
Second-order rate constant (mg ⁻¹ .mg.day ⁻¹) ^c		5.73 × 10 ⁻⁵	9.13 × 10 ⁻⁵	40.8 × 10 ⁻⁵	5.11 × 10 ⁻⁵	6.23 × 10 ⁻⁵	8.63 × 10 ⁻⁵
<i>r</i> ²		0.8920	0.8710	0.8670	0.8710	0.7130	0.7870
<i>SE</i>		8.91 × 10 ⁻⁶	1.57 × 10 ⁻⁵	7.15 × 10 ⁻⁵	8.79 × 10 ⁻⁶	1.77 × 10 ⁻⁵	2.01 × 10 ⁻⁵

^aFrom slope of the plot of $[A]_0 - [A]_t$ versus t (day) according to zero-order model $kt = [A]_0 - [A]_t$.

^bFrom slope of the plot of $\ln \frac{[A]_0}{[A]_t}$ versus t (day) according to first-order model $kt = \ln \frac{[A]_0}{[A]_t}$.

^cFrom slope of the plot of $\frac{1}{[A]_t}$ versus t (day) according to second-order model $kt = \frac{1}{[A]_t} - \frac{1}{[A]_0}$, where $[A]_0$ and $[A]_t$ are the concentrations at 0 and t time respectively.

2.1 Second order model

The integral equation of second-order reaction can be represented as follows [12],

$$k_2 t = \frac{1}{[A]_t} - \frac{1}{[A]_o}, \quad (2)$$

where k_2 is the second-order rate constant, t is the time, $[A]_o$ is the initial concentration and $[A]_t$ is its concentration at time t . Let the initial concentration is equal to 100 ($[A]_o = 100$), therefore,

$$k_2 t = \frac{1}{[A]_t} - \frac{1}{100}. \quad (3)$$

Let $P\%$ be the residual percent at time t ($[A]_t = P\%$), then Equation (3) can be written as:

$$k_2 t = \frac{1}{P\%} - \frac{1}{100}. \quad (4)$$

Dividing both sides of Equation (4) by t gives

$$k_2 = \left(\frac{1}{P\%} - \frac{1}{100} \right) \frac{1}{t}. \quad (5)$$

The natural logarithm of Equation (5) is

$$\ln k_2 = \ln \left(\frac{1}{P\%} - \frac{1}{100} \right) + \ln \frac{1}{t}. \quad (6)$$

Then,

$$\ln k_2 = \ln \left(\frac{1}{P\%} - \frac{1}{100} \right) + \ln 1 - \ln t, \quad (7)$$

or

$$\ln k_2 = \ln \left(\frac{1}{P\%} - \frac{1}{100} \right) - \ln t. \quad (8)$$

On the other hand, the Arrhenius equation can be expressed in a similar manner to that of first order as [1],

$$\ln k_2 = \ln A - \frac{E^\ddagger}{RT}, \quad (9)$$

where E^\ddagger , A and R are activation energy, frequency factor and gas constant respectively. Also, let S be $(-\frac{E^\ddagger}{R})$ and let I be $(\ln A)$ which both represent the slope and intercept of the plot between $\ln k$ against $1/T$ (Equation (9)). Thus, Equation 9 can be written as,

$$\ln k_2 = \frac{S}{T} + I. \quad (10)$$

The left side of Equations. (8) and (10) are equal; so, the combination of those equations gives

$$\ln \left(\frac{1}{P\%} - \frac{1}{100} \right) - \ln t = \left(\frac{S}{T} + I \right), \quad (11)$$

and then,

$$\ln t = \ln \left(\frac{1}{P\%} - \frac{1}{100} \right) - \left(\frac{S}{T} + I \right). \quad (12)$$

Taking the exponential of Equation (12) one could get,

$$t = \left(\frac{1}{P\%} - \frac{1}{100} \right) e^{-\left(\frac{S}{T} + I\right)}. \quad (13)$$

Let Ex_2 be the shelf life of the second-order reaction (t); then, Equation (13) can be presented in its final form as follows:

$$Ex_2 = \left(\frac{1}{P\%} - \frac{1}{100} \right) e^{-\left(\frac{S}{T} + I\right)}. \quad (14)$$

Hence, Equation (14) is the direct model derived for estimating the shelf life of the second-order reaction at any degradation ratio and specific temperature. In order to prove this model, it was applied to the degradation data of vitamin D₃ in coconut powder Table 1 underwent a second-order process [11]. The data of Table 1 are already expressed in percentage (%) which are suitable as input data in the developed models of 2nd- and zero-order in contrast to that of 1st- order reaction kinetics. The latter issue can be attributed to that the fractional life of 2nd- and zero-order depends on the initial concentration in comparison to that of the first order as the half-life ($\tau_{1/2}$) of these models can be expressed as $\ln 2/k$, $1/[A]_0 k$, and $[A]_0/2k$ for first-, second-, and zero-order, respectively [12, 13]. The determined rate constants of the degradation of vitamin D₃ at different temperatures are listed in Table 2. The required slope (S) and intercept (I) were estimated from those rate constants using the Arrhenius Equation (9) as illustrated in Table 3. An example of the application of the derived model (14) can be carried out by taking the values of I and S from Table 3 with a residual of 90 percent (p%=90) and at 25 °C as demonstrated by the following model:

$$Ex_2 = \left(\frac{1}{90} - \frac{1}{100} \right) e^{-\left(\frac{-2320.0}{298.15} + (-1.854)\right)} = 16.995 \approx 17 \text{ days}. \quad (15)$$

Remarkably, the time consumed for losing 10% of vitamin D₃ at 25°C according to the above equation (17 days) is quite parallel to the input data of Table 1. Thus, one could also use the developed relationship (14) for calculating the shelf life at any degradation ratio and temperature as clearly shown in Figure 1.

Table 3: The obtained parameters (slope and intercept) by application of Arrhenius Equation (9) with the related statistical data from the plot of $\ln k$ versus $1/T$ for vitamins C and D₃ in coconut powder.

Vitamin/ n	C/zero-order	D ₃ /second-order
Slope	-2776.3	-2320
Intercept	8.2658	-1.854
r^2	0.992	0.975
SE	0.0387	0.0593

2.2 Zero-order model

The following relationship represents the integral equation for the zero-order reaction [12],

$$k_0 t = [A]_0 - [A]_t, \quad (16)$$

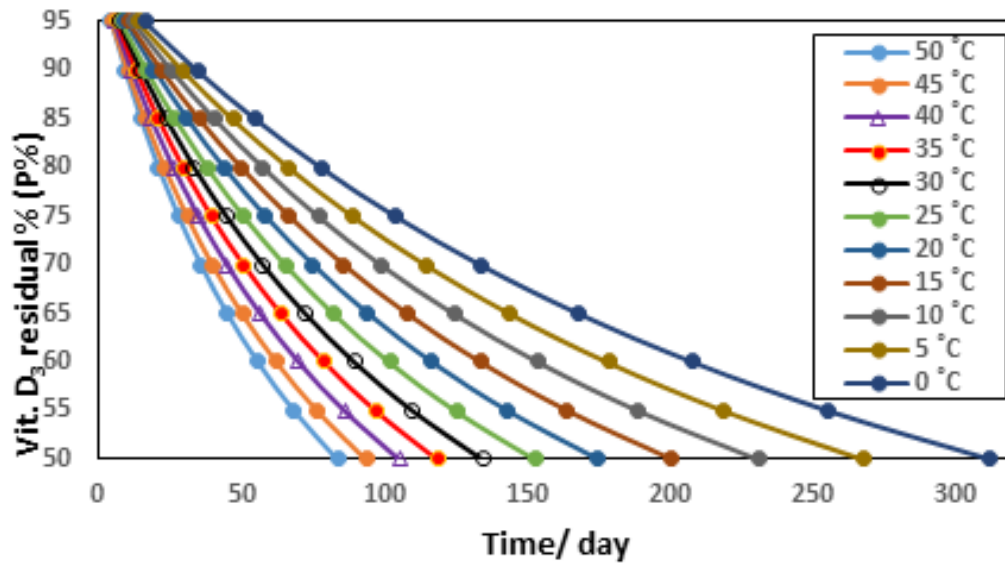


Figure 1: Plot of vitamin D₃ residual% (P%) versus time in day units at different temperatures resulting by application of the derived Equation (14).

where k_o is the zero-order rate constant. In a similar manner to that of the previous derivation of second-order one could get the following ($[A]_o = 100$ and $[A]_t = P\%$):

$$k_o t = 100 - P\%. \quad (17)$$

The natural logarithm of Equation (17) can be represented as:

$$\ln k_o + \ln t = \ln (100 - P\%). \quad (18)$$

Then,

$$\ln k_o = \ln (100 - P\%) - \ln t. \quad (19)$$

Again, as Equation (10) the Arrhenius equation can be expressed as

$$\ln k_o = \frac{S}{T} + I. \quad (20)$$

Equations (19) and (20) have the same left side; therefore,

$$\ln (100 - P\%) - \ln t = \left(\frac{S}{T} + I \right), \quad (21)$$

or,

$$\ln t = \ln (100 - P\%) - \left(\frac{S}{T} + I \right). \quad (22)$$

The exponential of Equation (22) is

$$t = (100 - P\%) e^{-\left(\frac{S}{T} + I\right)}. \quad (23)$$

Let Ex_o be the shelf life of zero-order reaction (t); then, Equation (22) can be written as

$$Ex_o = (100 - P\%) e^{-\left(\frac{S}{r} + I\right)}. \quad (24)$$

From now, Equation (24) is the direct model for calculating the shelf life of the zero-order reaction at any specific temperature and degradation ratio. In the same way as that of Equation (14), the values of slope and intercept of vitamin C were evaluated from the kinetic data of Table 1 as listed in Table 3 and then used to evaluate the shelf life of 90% residual at 25 °C according to the following equation:

$$Ex_o = (100 - 90) e^{-\left(\frac{-2776.3}{298.15} + 8.2658\right)} = 28.46 \text{ days}, \quad (25)$$

Again, according to Equation (25), the required period for losing 10% of vitamin C in coconut powder at 25°C (28.46 days) is quite close to that of the listed input data in Table 1. Figure 2 shows the estimated degradation period of vitamin C at different ratios and temperatures using the developed model for zero-order (24). It should be noted that Equations (14) and (24) can be applied in a more convenient way using computer programming or software as detailed in the mother article [1].

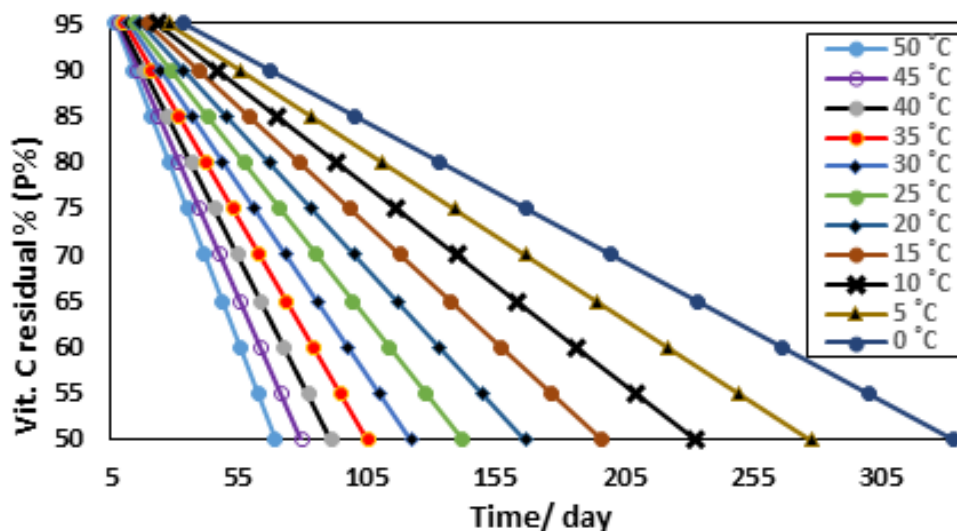


Figure 2: Plot of vitamin C residual% (P%) versus time in day units at different temperatures resulting by application of the derived Equation (24).

3 Concluding remarks

Interestingly, one could conclude that the shelf life of the second- and zero-order degradation processes can be determined directly using Equations (14) and (24) in a similar manner to that of the first-order [1]. It was found that the newly derived models of zero- and second-order reactions are mathematically simpler than that of first-order due to the absence of natural logarithm in their kinetic models. On the other side, as far as the fractional life of both 2nd- and zero-order reactions are depend on the initial concentration in contrast to that of 1st-order, the

input kinetic data must be expressed in percentage rather than the real concentration. In other words, for 1st-order topic, there is no problem in presenting the input kinetic data whether in percentage or real concentration unit as its fractional life not depending on initial concentration. Hence, the present work can be considered as complementary to all possible degradation processes in measuring the expiration date of products. Finally, the use of derived equations spares researchers from the complications resulting from changing the unit of the rate constant with the change in the order of the reaction.

Conflicts of Interest. The author declares that he has no conflicts of interest regarding the publication of this article.

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