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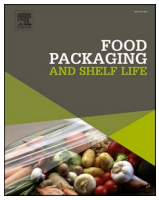

Effect of biopolymer active coating on alteration kinetics of minimally processed fennel stored at different temperatures

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ABSTRACT

The effect of an active coating based on sodium caseinate and propyl gallate on the physical and nutritional quality indices changes of minimally processed fennel stored at different temperatures was investigated. Pseudo-zero and pseudo-first-order models well described the quality changes of the product over time, whereas the Arrhenius-type model was used to estimate the activation energy of the alteration processes in the range of temperatures tested. The kinetic constants of the total antioxidant capacity (TAC) and vitamin C loss were reduced by 30% and 20% thanks to the presence of the coating. Whereas for the physical properties, the kinetic constants were not affected. Additionally, the TAC loss of coated samples was less sensitive to temperature change (Ea $_{TAC}$ 113) than the control sample (Ea $_{TAC}$ 130). In conclusion, sodium caseinate coating enriched with propyl gallate can be a technological solution to preserve the nutritional quality of minimally processed fennels.

1. Introduction

A kinetic modelling approach, based on the knowledge of the rate of alteration process and the relationships between kinetic parameters and factors activating or slowing down these processes, is advantageous to study the quality change of a product during storage or the effect of an innovative process on food shelf life (Labuza, 1982; Zanoni et al., 2005, Giannakourou & Taoukis, 2003). Knowledge of process alterations is crucial for mathematical modelling in order to control food quality (Datta & Sablani, 2007). Alteration reactions in food can be of two types: (bio)chemical and physical. In particular, any food undergoes chemical, physical and nutritional deterioration during storage. One approach that allows these changes and their rates to be quantified is kinetic modelling (Nisha et al., 2005).

In the literature, reaction models, based on chemical kinetics (zero-, first-, or second pseudo-order) have been used to describe antioxidant changes in fresh-cut melon (Oms-Oliu et al., 2009), polyphenol oxidase activity of fresh-cut potatoes (Zhao et al., 2022), physical and nutritional quality indices of shiitake mushrooms (Li et al., 2022), of tomatoes (Esua et al., 2019) and of fresh-cut melons (Amodio et al., 2013). Among the environmental factors that mainly influence the rate of reaction of alteration of a food product, temperature plays a crucial role. In order to study how this parameter influences the degradation of food products, the Arrhenius type-equation was successfully used (Du et al., 2022, Corradini & Peleg, 2007), which showed how the variation of the product changes as a function of storage temperature. Few studies have been conducted on the decay kinetics of fresh and/or minimally processed produce treated with new preservation technologies (e.g. coatings). Although the benefits of biopolymer coating on the quality conservation of minimally processed fruits and vegetables are well known, the results are not always easily transferable or used to implement a shelf life prediction model to manage the food supply chain.

The main alteration process limiting the minimally processed fennel shelf life are senescence, microbial growth, and oxidation (Capotorto et al., 2018; Escalona et al., 2005). Biopolymer coating is a promising preservation technology to preserve the freshness and extend the shelf life of minimally processed fruit and vegetables (Baldwin et al., 1995; Yousuf et al., 2018). Furthermore, they can be used as carriers of active compounds, helping to create a gas barrier to preserve the senescence (Volpe et al., 2019; Khan et al., 2021), and also to improve the nutritional properties of MPV by extending shelf life (Baldwin et al., 1995; Valentino et al., 2020).

No previous work has been done on the application of biopolymer active coating on minimally processed fennel. In a previous work. Casein-based coatings have shown promising results in extending the shelf-life of fresh-cut fruits and vegetables related to their excellent gas

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barrier characteristics and good mechanical properties (Khan et al., 2021). Moreover, sodium caseinate coating showed to be a good carrier for the gallic acid (Valentino et al., 2020). However, gallic acid is not included in the list of allowed food additives, thus propyl gallate ($C_{10}H_{12}O_5$), a generally recognized safe antioxidant (GRAS), has been used as an alternative. Thus, the objective of this work was to study the effect of an active coating based on sodium caseinate and propyl gallate on the physical and nutritional quality indices of minimally processed fennel stored at different temperatures. Preliminary investigation has been done to select the critical quality attributes able to describe the quality changes during storage.

Thus, the changes in colour, firmness, antioxidant capacity, total phenolic, and vitamin C content have been monitored and the effect of storage temperatures and active coating on alteration kinetics have been quantified.

2. Materials and methods

2.1. Materials

Sodium caseinate from bovine milk, glycerol, propyl gallate, sodium bicarbonate, sodium hydroxide, riboflavin, methanol, Folin-Ciucalteu, and DPPH reagent was purchased from Sigma-Aldrich (Milan, Italy). Fennels were supplied by Commerciale Export Company (Pagani, Italy).

2.2. Methods

2.2.1. Coating solution preparation

The coating solution based on caseinate has been properly characterized in a previous work (Valentino et al., 2020). Sodium caseinate (SC) from bovine milk at 8% (g mL^{-1}) and glycerol (10% weight ratio of SC) were dispersed in deionized water and shaken for 4 h at room temperature, following the method reported by Valentino et al. (2020). Finally, propyl gallate (PG) (3,4,5-trihydroxybenzoic acid propyl ester) as antioxidant compound, was also added to the solution at 0.13 mg mL^{-1}, at room temperature.

2.2.2. Minimally processed fennel preparation

Fennels (*Foeniculum vulgare* Mill. subsp. *vulgare* var. *azoricum* cv *Augusto* and *Tiziano*) were cultivated in two different Italian regions (Puglia and Calabria). Samples (about 400–500 g each) were preliminary processed by Commerciale Export cutting the external part of the product with a sharp knife. Then, the fennels were transported to the laboratory of the Agricultural Science Department of the University of Napoli Federico II and were stored for 24 h at 4 °C before processing. Fennel bulbs were cut by using a sharp knife to eliminate the bottom and top parts, washed, and dried with paper. The fennel samples were divided into two batches: one batch was packed as reported in the next paragraph and used as control samples. The second batch was processed by dipping to apply the coating solution. The fennel bulbs were immersed in the active solutions (500 mL) for 2 min and dried for one hour at 30 °C and 50% humidity, as reported by Valentino et al., (2020) before packaging. The coated samples were coded as active samples.

2.2.3. Packaging and storage conditions

Control and active fennel (about 1 kg, two for each package) were packed in polypropylene trays (26 ×16.5 ×10 cm) and covered with LDPE film. Samples were stored for 21 days at 4 °C, 18 days at 10 °C, and 15 days at 15 °C. The storage time has been chosen to observe the maximum quality changes of the product in order to properly describe it by using kinetic model. Physical (colour and firmness) and nutrition (total antioxidant capacity, total phenolic content, and vitamin C content) properties were evaluated at different storage times.

2.2.4. Physical properties

The colour of the fennels was determined with an electronic eye (visual analyser VA400 IRIS, Alpha MOS, France) equipped with a CCD (charge-coupled device) camera (resolution 2592 ×1944 pixels and 24 bit). The camera, with a 25 mm f1:2.2 Basler lens by Fujion, was in a light box equipped with top and bottom lightning (each position using 4 ×4 White LED) which was stabilized for 15 min before use (Tretola et al., 2017). Raw images were processed in RGB scale and subsequently converted in Cie L* a* b* scale using Alphasoft software (version 16.0). For each image, the white background was automatically removed and the L* , a* , and b* measured in the different parts of the fennel sample (bottom, top, and side) were averaged (Cevoli et al., 2023). Total colour change (ΔE) was also calculated as reported by Volpe et al. (2019).

Firmness (N) was measured at four opposite points per bulb in the equatorial zone by doing a compression test with a TMS-Pro texture analyzer (Food Technology Corporation) using a 6.3 mm diameter plate and with load-bearing cells (500 N). The firmness parameter identifies the maximum force required by the sample to be compressed to a depth of 8 mm. To calculate this parameter, the samples were compressed with a transverse speed of 25 mm/min (Artés et al., 2002a). Data were acquired through Texture Lab Pro Software.

2.2.5. Nutritional quality indices

The total antioxidant capacity (TAC) was calculated as reported by Volpe et al. (2019), with slight modifications. 0.5 g of freeze-dried fennel was added in 10 mL of methanol/water (80:20) solution, mixed with constant shaking at room temperature for 60 min, and put on an ultrasound bath for 30 min. Subsequently, the sample was centrifuged, using a centrifuge (Hermle Z 326 K, Germany, European Union) for 15 min at 10,000 rpm (Pérez-Jiménez et al., 2008). 100 μl of supernatant was added in 4.9 mL of DPPH solution (methanol+DPPH 0.1 Mm). Then, the sample was placed in the dark at room temperature for 30 min and the absorbance at 515 nm was measured using a spectrophotometer UV–VIS (UV-550 Jasco, Japan). TAC was expressed as mg of Trolox equivalents g^{-1} of dry matter (mg TE g^{-1}_{dm}) using a Trolox standard curve (0–625 mg mL^{-1}). The TAC value was normalized to the TAC value of the sample at time 0.

The total phenolic content (TPC) was measured as reported by Di Giuseppe et al. (2019). Specifically, 0.5 g of freeze-dried sample was crushed with mortar and pestle with 10 mL of sodium bicarbonate (6%); the solution was filtered through a paper filter and 0.5 mL of the filtrate was added with 2.5mL of Folin-Ciocalteau reagent and 2 mL of sodium bicarbonate. The samples were incubated for 1h at 35 °C and then for 1h at 6 °C. After 2 h of incubation in the dark, the absorbance was read at 760 nm against a blank (2.5 mL of Folin-Ciocalteau reagent and 2.5 mL of sodium bicarbonate), using a spectrophotometer UV-VIS (UV-550 Jasco, Japan). To express TPC in fennel, mg gallic acid equivalent g^{-1} of dry matter (mg GAE g dm^{-1}) was used and the calibration curve was prepared using 0–8 mg mL^{-1} gallic acid. The TPC values were normalised respect with the TPC value of the sample at time 0.

Vitamin C of fennels was extracted by homogenizing 1 g of product tissue with 10 mL of glacial acetic acid solution in water (8%) for 1 min by using an Ultraturrax (IKA, T18 Basic; Wilmington, NC, USA). The homogenate was centrifugated for 7 min at 7000 rpm. The sample was filtered using a paper filter, and the supernatant was recovered. Then, 5 mL of glacial acetic acid solution was added to the pellet and centrifugated at 7000 rpm for 7 min. This procedure was replicated four times for vitamin C extraction. Then, the method reported by Jung et al. (1995), with minor modifications, was used to determine vitamin C content in MP fennels. 1 mL of sample filtered was added in 4 mL of riboflavin stock solution, and 0.06 g riboflavin in 100 mL of 0.01 M potassium buffer (pH=7.5). Absorbances of samples before and after light storage (5500 Lux) were measured at 265 nm using a spectrophotometer UV–VIS (UV-550 Jasco, Japan). Differences in absorbance of samples before and after 15 min-illumination were used for the calculation of ascorbic acid. The vitamin C content was calculated based on the calibration curves of ascorbic acid in the buffer of riboflavin (0–10.5 μg mL^{-1}) and expressed as mg of vitamin C g^{-1} of dry matter (mg

of Vit C g_{dm}^{-1}). Vit C value was normalized to the Vit C value of the sample at time 0.

2.3. Mathematical modelling: zero and first-order kinetic models

Generally, first- and zero-order kinetics are used to model degradation reactions in food. The equation used is (Giannakourou & Taoukis, 2003; Polydera et al., 2005):

$$\frac{dQ(t)}{dt} = -kQ^n \quad (1)$$

Decay functions can be obtained by easily integrating the equations. Specifically, for the pseudo-zero-order kinetic model, the following equation can be used to predict the quality of a product as a function of storage time:

$$Q = Q_i - kt \quad (2)$$

whereas for pseudo-first kinetic order (n = 1), the equation will be:

$$Q = Q_i e^{-kt} \quad (3)$$

Or

$$Q = Qeq + (Q0 - Qeq)e^{-kt} \quad (4)$$

where.

Q(eq) is the concentration of the quality index at equilibrium, *Q(t)* is the concentration of the quality index at the time *t*, and *k* is the rate constant. The negative sign is generally referred to as a quality decrease. However, if the quality index related to the alteration process increases during storage, the function will have a positive sign.

To describe the effect of storage temperature on kinetic constants, an Arrhenius-type equation was used:

$$k = k0 \quad exp^{-\frac{Ea}{R}\left(\frac{1}{T}-\frac{1}{T0}\right)} \quad (5)$$

Where:

k is kinetic constant at temperature, k_0 is kinetic constant at the reference temperature (T); E_a is activation energy (J mol^{-1}), independent of temperature; R is gas constant (8.31 J mol^{-1} K^{-1}); T_0 is the reference temperature, T is absolute temperature (°Kelvin).

2.4. Statistical analysis

Linear and non-linear regression were used to estimate the kinetic constants by using XLSTAT 16.0 (Addinsoft, France, 2023). To test the reliability of the fit used different coefficients were calculated: the regression coefficients (R^2), mean squared error (MSE) and root mean square error (RMSE). The highest the values of R^2, the lowest the values of RMSE and MSE, the better the fitting of the models to experimental data. Paired t-test analysis was carried out to find the source of the significant differences within the samples examined; the significance of differences was defined at $p \leq 0.05$. The results of kinetic constants are expressed as mean values ± standard deviation.

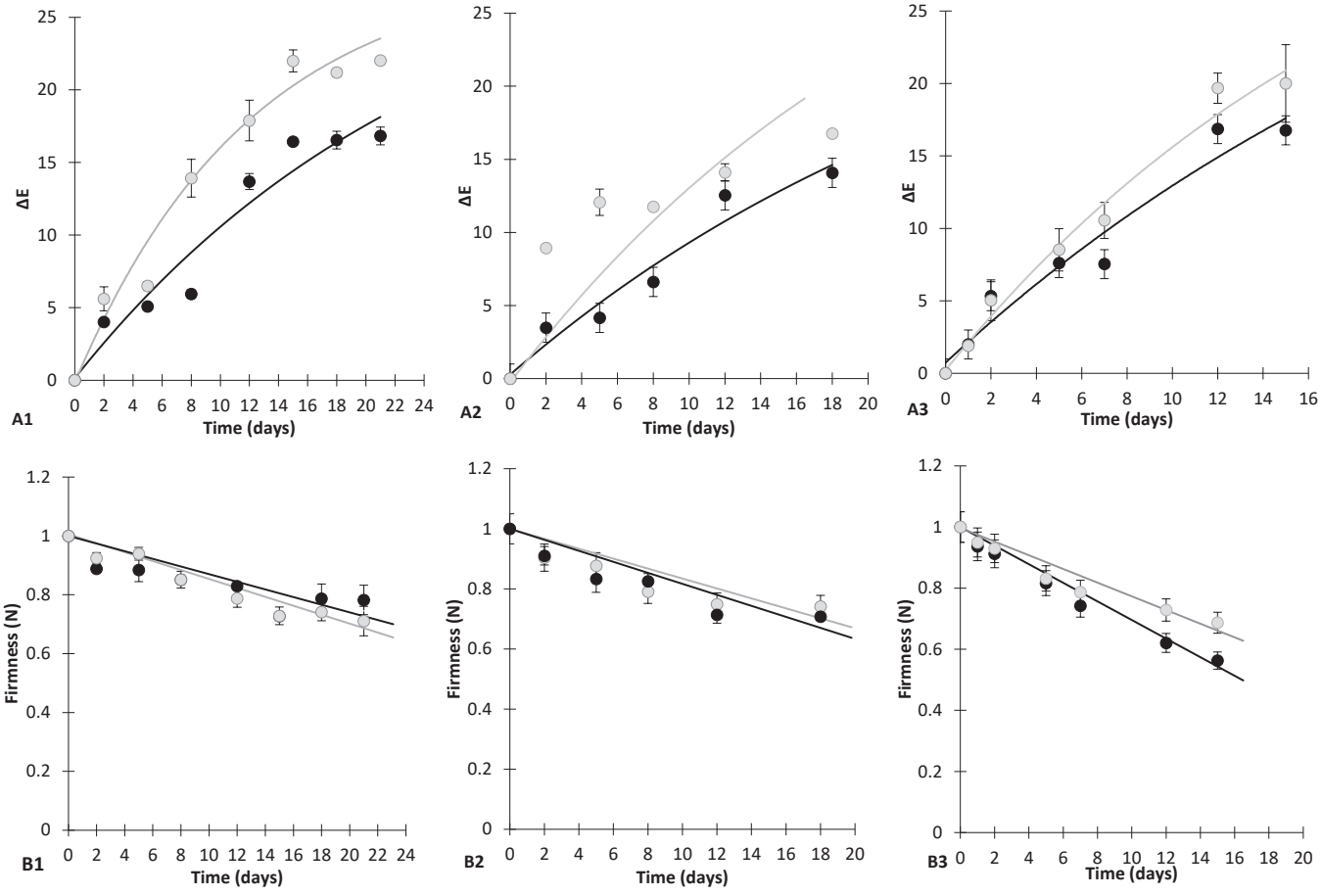

Fig. 1. Values of ΔE (A1, A2 and A3) and firmness (B1, B2 and B3) of control (●) and active (●) samples stored at 4, 10 and 15 °C for 21, 18 and 15 days respectively. —and ● are the dates predicted by the model for control and active samples, respectively.

3. Results and discussions

3.1. Physical quality indices

During vegetable storage tests, colour is one of the most studied quality parameters, as it influences the final choice, and thus purchase, of the consumer (Toivonen and De Ell (2002)). Indeed, minimally processed fennels undergo a cutting process, affecting the browning of the surfaces and limiting the preservation of fennels (Artés et al., 2002a,b; Escalona et al., 2005) as well as whole fennels that browning in the bottom part (Capotorto et al., 2018).

Fig. 1 shows the variations in the physical parameters of samples stored at 4, 10 and 15 °C. The colour of the samples expressed as ΔE exponentially increased for all samples during the storage time. A pseudo-first-order model with the quality index value reaching an equilibrium at the infinitive time well describes the colour changes of the product (Fig. 1 A1, A2, A3). The values of R^2 ranged from 0.79 to 0.92, the values of RMSE ranged from 1.9 to 4.2 and the values of MSE ranged from 3.7 to 12.9 for control and coated samples (Table 1). In Table 2 the values of kinetic constants and ΔE values at equilibrium for the samples stored at 4, 10, and 15 °C are reported. The kinetic constants range between 0.05 day^{-1} to 0.17 day^{-1} as function of temperature and process parameters (coating). Equilibrium value of ΔE was estimated equal to 31. The time to reach the equilibrium changes between 20 days at 15 °C to more than 50 days at 4 °C and 10 °C.

The presence of the active coating caused a significant increment of the kinetic constant of the browning process than the control sample of about 37% at 4 °C and 23% at 15 °C ($p \leq 0.05$). The kinetic constant also increased as temperatures increased from 4 °C to 15 °C, for both samples ($p \leq 0.05$). Arrhenius-type equation has been used to predict the effect of the temperature on the kinetics constant ($R^2 = 0.98$) as reported in Fig. 3 A. The activation energy assumed a value of 42 kJ mol^{-1} for control samples and a value of 53 kJ mol^{-1} for active samples. Thus, results showed that the presence of the active coating had a negative impact on the browning of the minimally processed fennel. Moreover, the Ea increased due to coating presence, meaning that the active samples were more sensible to temperature variation than control samples. These differences can be justified by the presence of the active compound propyl gallate which is sensible to oxidation and can have contributed to the changes in colour (Medina et al., 2013). However, by considering that consumers will recognize the colour difference when ΔE reached a value of 5 (Mokrzycki and Tatol (2012)), it is clear that the browning process is a critical alteration phenomena for MP fennel; in fact, the time to reach that value is very short for both control (3 days at 4 °C) and active coated samples (2 days at 4 °C). Previous work has reported that the coating, depending on its composition and the nature of the antioxidant compound, can delay the browning of fresh produce. It should, however, be emphasised that browning is a parameter mainly intrinsic to the food, so the coating applied can not always demonstrate good effects (Sanchís et al., 2016). Therefore, browning is a limiting alteration mechanism for fennel, due to the enzymatic action of polyphenol oxidase (PPO). Confirming this, Garcia and Barrett (2002) demonstrated that this enzyme utilises phenolic products, causing browning of the vegetable or fruit product. The activity of enzymes can be monitored by studying enzyme kinetics, which can be classified in two ways: transient (yielding detailed mechanistic information) and steady-state kinetics (yielding less detailed mechanistic information than transient kinetics). Steady-state kinetics is divided into two types: initial velocity analysis and progression curve analysis. The first step of the enzymatic reaction can be studied using rate analysis, but it provides limited information because it does not consider subsequent steps as well. On the other hand, the progression curve is difficult to analyse because a nonlinear regression is needed to estimate the relevant kinetic parameters (van Boekel, 2008), as obtained in the present work.

Among the various physical-chemical parameters, firmness is a key quality attribute because, in addition to being palatable, its level conditions the behaviour of other compounds (such as sugars or volatile substances) perceived during chewing (Maringgal et al., 2020). In addition, firmness can decrease due to changes in cell structure caused by cell rupture or changes in pectins present in the product (Du et al., 2022). In this study firmness decreased about 20% for the control and active samples from a value of 65 to a value of 50, 45 and 40 N after 21, 18 and 15 days stored at 4, 10 and 15 °C. A pseudo-zero-order model

Table 1
Goodness of fitting of model used to estimate physical and nutritional quality properties of control and active MP fennels at different temperatures over time.

Variables	Samples	T (°C)	Kinetic	MSE	RMSE	R^2
ΔE	Control	4	First-order	12.9	3.6	0.79
		10		3.7	1.9	0.78
		15		17.8	4.2	0.80
	Active	4		6.0	2.4	0.92
		10		4.6	2.1	0.75
		15		4.4	2.1	0.92
Firmness	Control	4	Zero-order	0.002	0.04	0.72
		10		0.002	0.04	0.84
		15		0.001	0.03	0.97
	Active	4		0.001	0.03	0.93
		10		0.002	0.04	0.84
		15		0.001	0.04	0.92
Total antioxidant capacity	Control	4	First-order	0.02	0.12	0.79
		10		0.01	0.09	0.85
		15		0.01	0.12	0.86
	Active	4		0.01	0.10	0.76
		10		0.006	0.08	0.90
		15		0.005	0.07	0.97
Total polyphenols content	Control	4	Zero-order	0.01	0.14	0.82
		10		0.008	0.08	0.85
		15		0.03	0.16	0.93
	Active	4		0.01	0.11	0.85
		10		0.005	0.07	0.65
		15		0.07	0.27	0.83
Vitamin C content	Control	4	First-order	0.01	0.11	0.84
		10		0.003	0.05	0.90
		15		0.002	0.05	0.91
	Active	4		0.01	0.11	0.85
		10		0.006	0.08	0.91
		15		0.005	0.07	0.92

Table 2
Constant kinetics of physical and nutritional quality indices of control and active samples stored at different temperatures.

Variables	Samples	4 °C		10 °C		15 °C	
		k (day^{-1})	Q_{eq}	k (day^{-1})	Q_{eq}	k (day^{-1})	Q_{eq}
ΔE	Control	$0.05^a \pm 0.02$	31 ± 2	$0.07^a \pm 0.02$	31 ± 2	$0.13^a \pm 0.03$	31 ± 2
	Active	$0.08^b \pm 0.02$	31 ± 3	$0.14^b \pm 0.04$	31 ± 1	$0.17^b \pm 0.02$	31 ± 2
Firmness	Control	$0.01^a \pm 0.01$	/	$0.02^a \pm 0.02$	/	$0.03^a \pm 0.02$	/
	Active	$0.01^a \pm 0.01$	/	$0.02^a \pm 0.03$	/	$0.03^a \pm 0.03$	/
Total Antioxidant capacity	Control	$0.05^b \pm 0.01$	/	$0.09^b \pm 0.02$	/	$0.30^b \pm 0.03$	/
	Active	$0.02^a \pm 0.02$	/	$0.06^a \pm 0.02$	/	$0.20^a \pm 0.05$	/
Total polyphenol content	Control	$0.05^b \pm 0.01$	/	$0.03^b \pm 0.01$	/	$0.10^b \pm 0.01$	/
	Active	$0.04^a \pm 0.01$	/	$0.01^a \pm 0.01$	/	$0.09^a \pm 0.01$	/
Vitamin C content	Control	$0.07^b \pm 0.02$	/	$0.06^b \pm 0.01$	/	$0.08^b \pm 0.01$	/
	Active	$0.05^a \pm 0.01$	/	$0.05^a \pm 0.01$	/	$0.07^a \pm 0.00$	/

Letters indicate significant differences between the treatments at each temperature ($p \leq 0.05$)

well describes the firmness decrement of fennels (Fig. 1 B1, B2, B3), showing a correlation coefficient of the R^2 ranging from 0.72 to 0.97, RMSE of 0.03 and 0.04 and MSE of 0.001 and 0.002 (Table 1). Values of kinetic constants for the samples stored at 4, 10 and 15 °C are reported in Table 2. Also, other authors found that the zero-order-kinetic model was the best to estimate experimental data for firmness loss of fresh-cut melon (Amodio et al., 2013), cabbage (Jaiswal & Abu-Ghannam, 2013), Sichuan Sauerkraut (Du et., 2022), and avocado (Maftoonazad & Ramaswamy, 2005). The kinetic constants of firmness reached a maximum value of 0.03 day^{-1} (Table 2), but statistical analysis showed that the coating technology and the temperature of storage had no significant effect on the kinetic constant of MP fennel ($p > 0.05$). The values of kinetic constants obtained for MP fennels were lower than fresh-cut melons (0.12 day^{-1}) stored at 4 °C (Amodio et al., 2013), Sichuan Sauerkraut stored at 25 °C (1.7 day^{-1}) (Du et a., 2022) and cabbage (2.8 day^{-1}) stored after microwave processing (Jaiswal & Abu-Ghannam, 2013), but were the same order of magnitude of the avocado (0.03 day^{-1}) stored 20 °C (Maftoonazad & Ramaswamy, 2005). Thus, process (time, temperature and treatment) and storage variables (time and temperature) can affect the mathematical model used and, therefore, the kinetic constant obtained (Datta, 2008).

3.2. Nutritional quality indices

The critical stage for minimally processed vegetables is post-harvest, as damage caused by prolonged storage at high or low temperatures

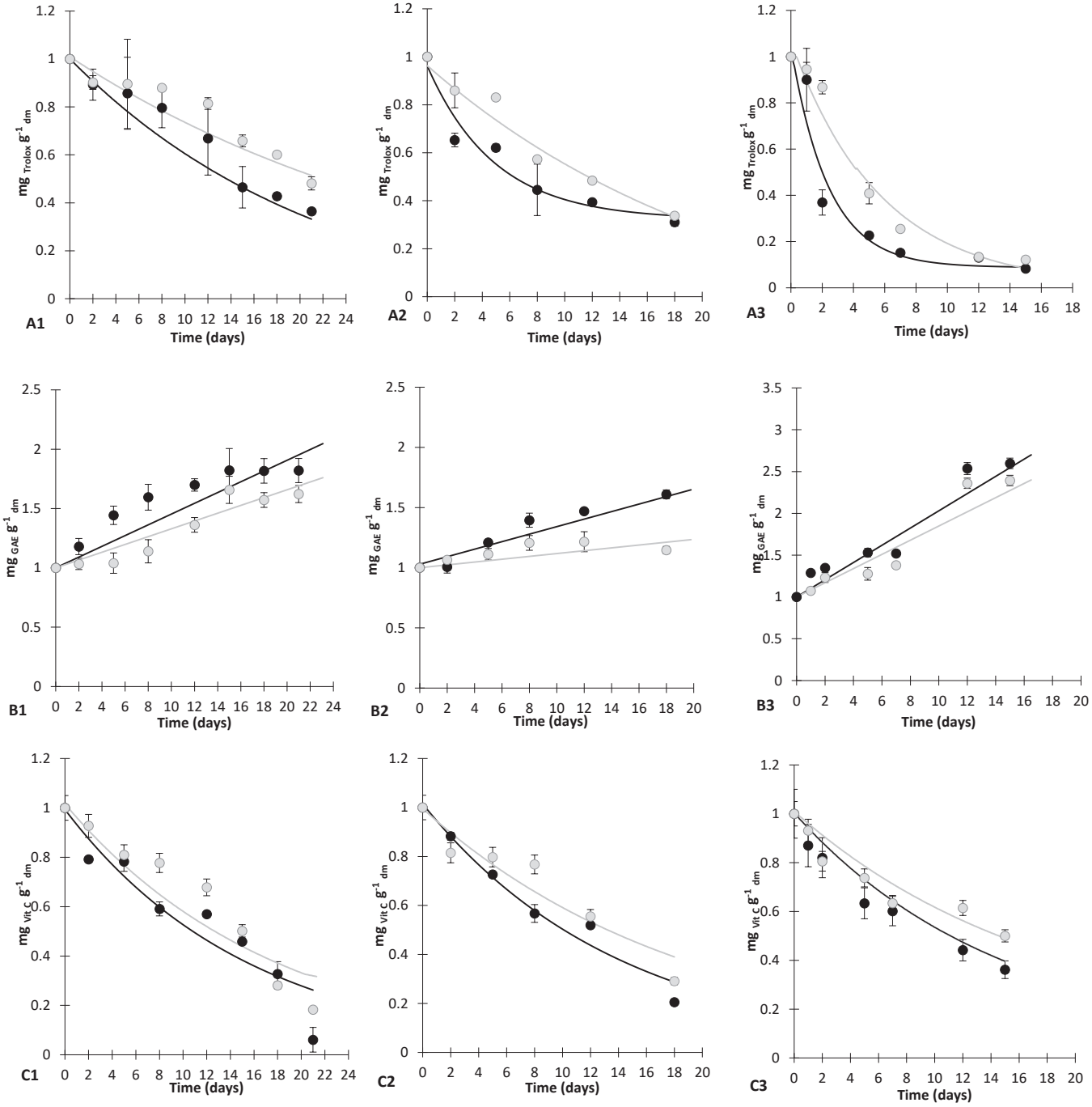

Fig. 2. Values of TAC (A1, A2 and A3), TPC (B1, B2 and B3) and vit C (C1, C2 and C3) of control (•) and active (●) samples stored at 4, 10 and 15 °C for 21, 18 and 15 days respectively. —and ● are the dates predicted by the model for control and active samples, respectively.

and/or low humidity affects the nutritional quality indices. In fact, during this process, vitamin C, total polyphenol content and antioxidant capacity deteriorate faster than in fresh fennel (Navarro et al., 2006; Lee and Kader (2000)). These nutritional properties of fennels vary according to numerous genetic, environmental, and technological factors, some of which may be controlled to slow down their decrement during storage time (Manach et al., 2004), using edible coating.

Fig. 2 shows the changes in nutritional parameters of MP fennels stored at 4, 10 and 15 °C.

TAC decreased during storage time for all samples following a pseudo-first-order kinetic model (Fig. 2 A). Statistical data for evaluating the goodness of the fitting are reported in Table 1, indeed R^2 ranged from 0.79 to 0.97, MSE ranged from 0.005 to 0.02 and RMSE ranged from 0.07 to 0.12. The TAC of control samples decreased from an initial value of 1.2 mg $_{Trolox}$ g^{-1} $_{dm}$ reaching values of 0.4, 0.36, and 0.14 mg $_{Trolox}$ g^{-1} $_{dm}$ after 21, 18 and 15 days at 4, 10, and 15 °C, respectively; while for active samples TAC decreased until a value of 0.62, 0.40, and 0.19 mg $_{Trolox}$ g^{-1} $_{dm}$ after 21, 18, and 15 days at 4, 10, and 15 °C, respectively. The k- values of TAC were included between 0.02 day^{-1} to 0.30 day^{-1} (Table 2). The presence of the active coating showed values of kinetic constants lower than control samples with statistically significant differences at all temperatures ($p \leq 0.05$), as reported in Table 2. Indeed, the active coating was able to preserve the loss of TAC of about 30% for samples stored at different temperatures than the control sample ($p \leq 0.05$). This effect can be due to the antioxidant compound propyl gallate, which allows a protective effect against oxygen. Capotorto and colleagues (2018), in order to preserve the antioxidant capacity of fresh fennel, treated the fennels with ascorbic acid solutions, as an antioxidant compound. The authors found that the ascorbic acid solution was able to preserve the total antioxidant capacity of fennels stored at 5 °C after 6 days, about 40% compared to untreated samples.

The dependence of the k-value by temperature was adequately described by the Arrhenius relationship, with a high R^2 (0.98). The reduction in TAC appears to be more sensitive to increasing temperature than the other parameters studied on MP fennel, as reported in Fig. 3 B.

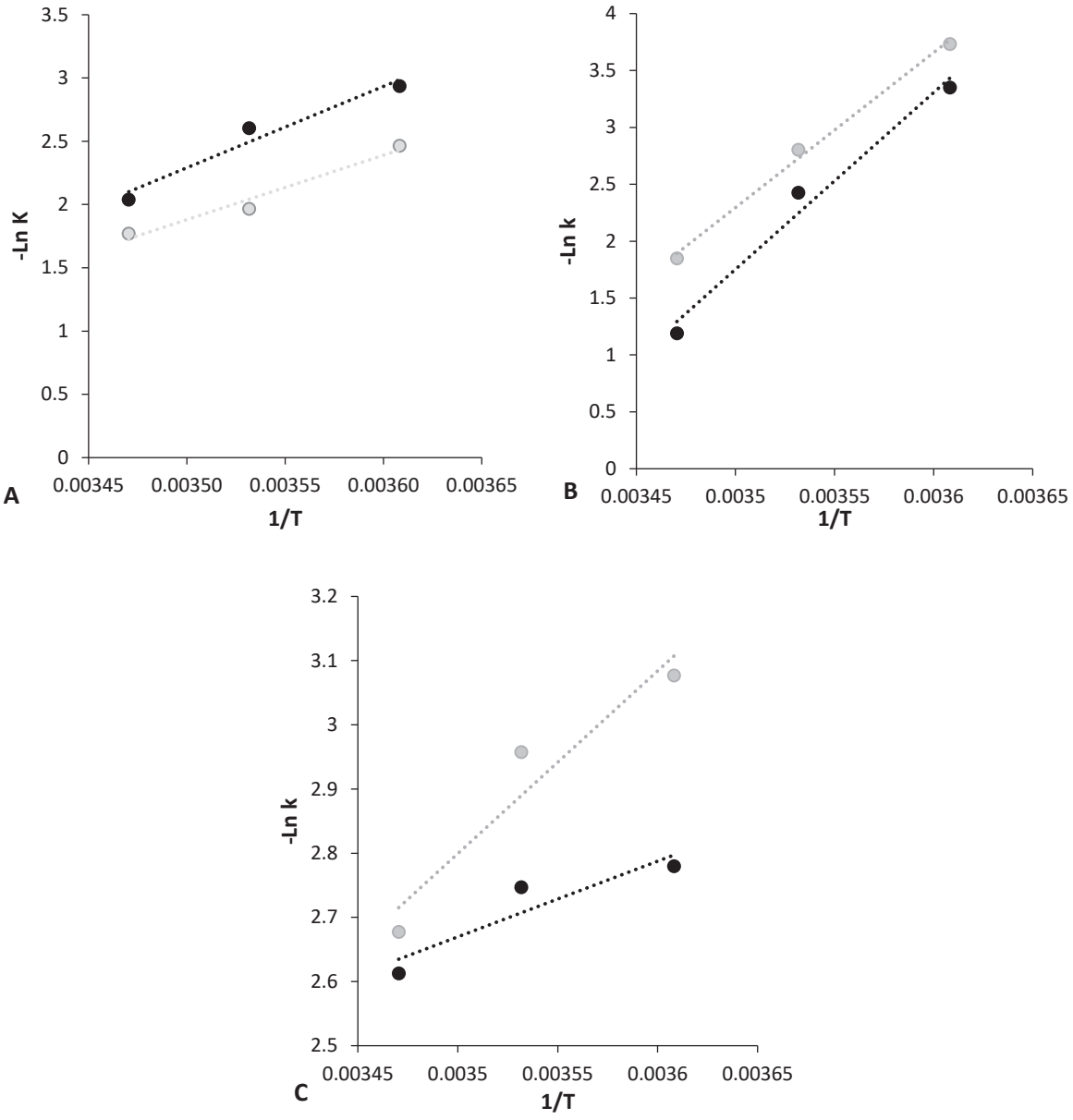

Fig. 3. Reaction rate constant of ΔE, (A), total antioxidant capacity (B) and vitamin C (C) of MP fennels control (•) and active (●) samples as affected by storage temperature on a log-lin scale.

Moreover, the samples with the active coating are less sensitive to temperature with regard to antioxidant capacity (Ea_{TAC} 113 kJ mol^{-1}) than the control sample (Ea_{TAC} 130 kJ mol^{-1}).

Oms-Oliu and colleagues (2009) predicted the TAC of fresh-cut watermelon using a Weibull model and showed that fresh-cut watermelon samples stored at a maximum temperature of 15 °C had a higher antioxidant capacity than those stored at 20 °C. Indeed, samples stored at 20 °C showed a significant decrease in TAC after 2 days of storage, and then stabilised at 30% of the initial TAC after 14 days of storage. Furthermore, the TAC of fresh cut watermelon stored at temperatures lower than 20 °C varied from 55% to 65% after 2 weeks.

Different results were obtained for TPC, indeed this nutritional parameter increased during storage time for all samples, due to sample cutting and, thus, by the activation of polyphenol oxidase. Several authors documented that the increase in phenolic content was associated with the up-regulation of browning levels (Campos-Vargas and Saltveit, 2002; Garcia and Barrett (2002); Capotorto et al., 2018). For MP fennels, as reported in the previous paragraph, ΔE increased during storage time, confirming that the cutting process influenced the browning, correlated with the increase in polyphenol oxidase enzyme activity. TPC of control samples increased from an initial value of 32 mg $_{GAE}$ g^{-1} $_{dm}$ until 57, 50, and 75 mg $_{GAE}$ g^{-1} $_{dm}$ after 21, 18 and 15 days stored at 4, 10, and 15 °C respectively; while active samples increased until a value of 50, 37, and 70 mg $_{GAE}$ g^{-1} $_{dm}$ after 21, 18, and 15 days at 4, 10, and 15 °C, respectively. A pseudo-zero-order kinetic model was used to describe the increment of TPC during storage time. Fig. 2 reports the experimental and predicted data of TPC of control and active samples stored at 4 °C (B1), 10 °C (B2), and 15 °C (B3). A good correlation between the experimental and model predicted was demonstrated using R^2, MSE and RMSE, as reported in Table 1. The kinetic constants of the TPC of fennels were between 0.01 day^{-1} and 0.10 day^{-1} as function of coating ($p \leq 0.05$) but not for temperature, as demonstrated in Table 2. The presence of active coating well-preserved the increment of TPC of MP fennels by about 10% for samples stored at 4 and 15 °C than control samples, whereas for samples stored at 10 °C, the active coating was able to preserve the increment of TPC of about 20% ($p \leq 0.05$).

In contrast to other attributes (ΔE and TCA), the k-values of TPC were lower at 10 °C (control and active) compared to samples stored at 4 and 15 °C, showing a non-temperature dependence. These results can be justified because 10 °C is the optimal temperature to reduce enzyme activity and metabolic rates (Garcia and Barrett (2002)). Several studies have shown that cutting operations stimulate phenolic metabolism in fresh-cut tissue (Saltveit, 2000; Klaiber et al., 2005). Indeed, the cutting process acts on PAL (phenylalanine ammonia lyase), allowing the accumulation of phenolic compounds; on the other hand, these compounds can be oxidised by oxidative enzymes, resulting in a browned appearance (Degl'Innocenti et al., (2005), Capotorto et al., 2018). Nevertheless, in our study, the mechanisms of action of the active coating, using propyl gallate as an antioxidant compound, slowed down the action of PPO, preserving TPC compared to control samples (Medina et al., 2013).

Another nutritional parameter studied of fennels was the vitamin C content. Vitamin C is very sensitive to external factors, in fact, exposure of the plant product to high oxygen concentrations, high temperatures or relative humidity negatively affects the concentration of this vitamin (Uddin et al., 2001). In our study, vitamin C content decreased during storage time from a value of 0.12 mg $_{vitC}$ g^{-1}_{dm} to a value of 0.01, 0.009, and 0.007 mg $_{vitC}$ g^{-1}_{dm} for control samples stored after 21, 18 and 15 days at 4, 10, and 15 °C, respectively; while for the active sample vitamin C content reached values of 0.05, 0.04 and 0.02 mg $_{vitC}$ g^{-1}_{dm} after 21, 18 and 15 days at 4, 10, and 15 °C, respectively. A pseudo-first-order model well describes the vitamin C loss of fennels (Fig. 2 C1, C2, C3), showing a correlation coefficient of the R^2 ranging from 0.84 to 0.92 (Table 1). Values of kinetic constants for the active and control samples, stored at 4, 10 and 15 °C are reported in Table 2. The maximum value of the kinetic constant of vitamin C was 0.08 day^{-1} (Table 2), as function of temperature and process parameter (coating). The active coating was able to preserve vitamin C loss of about 20% for samples stored at 4 °C and 15 °C and of about 10% for samples stored at 10 °C than the control sample ($p \leq 0.05$). The barrier effect of the coating reduces the amount of oxygen available to fennel plant tissue, thus delaying vitamin C degradation reactions (Mditshwa et al., 2017, Ayranci & Tunc, 2003). Other studies have found the same effect of the biopolymer coating on fresh plant products stored for 3 months at refrigeration temperature (Mahajan et al., 2013). Nevertheless, the addition of an antioxidant compound in the coating helps to preserve the loss of vitamin C (Ayranci & Tunc, 2004).

The kinetic constant also increased as temperatures increased from 4 °C to 15 °C, for both samples ($p \leq 0.05$). Arrhenius-type equation has been used to predict the effect of the temperature on the kinetics constant ($R^2 = 0.90$) as reported in Fig. 3 C. The activation energy assumed a value of 10 kJ mol^{-1} for control samples and a value of 24 kJ mol^{-1} for active samples, showing that the presence of active coating has a positive impact on vitamin C loss. Furthermore, the Ea increased due to coating presence, showing that the active samples were more sensible to temperature variation than control samples. Thus, high temperatures significantly influenced the degradation of vitamin C compared to low-temperature storage. This effect is also shown by other authors on different fruit products (Satsuma mandarins) in similar temperature ranges (Qiu & Wang, 2015). Other studies demonstrated that 10 °C can be the best temperature to store fruits, for example, sweet oranges or lime fruit (Rab et al., 2012; Maftoonazad & Ramaswamy, 2019). However, as demonstrated by Gil et al. (2006), Oms- Oliu et al. (2009) and Amodio et al. (2013), vitamin C can also degrade by following the Weibull model.

4. Conclusions

The study investigated the variation of physical (ΔE and firmness) and nutritional quality indices (TCA, TPC, Vitamin C) of minimally processed fennels during storage time at the temperature of 4, 10 and 15 °C with and without an active coating. The quality indices analysed were well explained by a pseudo-zero or pseudo-first order reaction kinetic model, and the dependence of k by storage temperature was well described by an Arrhenius-type equation. The active coating was able to preserve the change in nutritional quality, but not the physical properties for all temperatures. Future studied are required to improve the coating composition to allow a better preservation of the product. The quality indices analysed were well explained by a pseudo-zero or pseudo-first order reaction kinetic model, and the dependence of k by storage temperature was well described by an Arrhenius-type equation.

According to the values of Ea obtained from Arrhenius equations, TAC was more sensitive to temperature change with respect to the other parameters, and firmness and TPC were not temperature-dependent. Overall, the storage temperature played a pivotal role in vegetable metabolism during long-term storage, causing changes in the physical and nutritional attributes of MP fennels. As expected, low temperatures helped to better preserve the quality of MP fennels. However, the kinetic model can be a useful tool to predict the quality changes of the product during distribution in order to optimize the food chain management and quality assurance management. Further studies can apply the models and active coating in this study to other minimally processed fruits and/or vegetables.

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Declaration of Competing Interest

The authors declare no conflicts of interest.

Data Availability

No data was used for the research described in the article.

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