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Shelf-life study of osmodehydrated white cabbage packaged in modified atmosphere: A mathematical approach

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Summary

Osmotic treatment (OT) is a process applied for drying of fruits and vegetables where the hypertonic solution is osmotic medium. White cabbage (cultivar „Futoški“) shelf-life analysis was conducted after OT in three different hypertonic solutions: a mixture of commercial sucrose and NaCl (S1), a mixture of S1 and molasses in the ratio 1:1 (S2) and. pure sugar beet molasses (85.4% dry matter) (S3). After the OT, cabbage samples were packed in high barrier bags in the modified atmosphere packaging (MAP). The composition of two mixtures of used gas (40:60/CO_2:N_2 and 80:20/CO_2:N_2) was imported into bags. The samples were analysed for L-ascorbic acid content, pH, acidity and a total number of microorganisms and sensorial attributes during 90 days of storage in a refrigerator at 4-8 °C in defined time intervals. During the 90-day storage in the MAP, microbiological analysis showed that the number of microorganisms decreased during the storage in the MAP. The highest retention of ascorbic acid (27.35%) was observed in OT cabbage dehydrated in pure molasses solution and 80:20/CO_2:N_2 gas mixture after 90 days of storage. Sensory analysis showed that osmodehydrated cabbage for 20 days in S1, and 45 days for OT cabbage in solutions S2 and S3 had acceptable consumable characteristics.

Key words: cabbage, osmotic treatment, molasses, shelf-life, storage

Introduction

Current globalization, growing industrialization and international food trade highlights food safety and product shelf-life extension perhaps as the most important issues of food and equipment manufacturers, stakeholders and consumers (Jermann et al., 2015). Interest in the development of novel food solutions capable of keeping food safe and fresh with minimal thermal processing is increased (Martynenko et al., 2015). From the ecological aspect, but also from the point of view of achieving the maximum profitability in the food industry, it is desirable to maximize the sustainability of processing with waste reduction.

White cabbage (*Brassica oleracea var.* Capitata) belong to the Brassica family, also has a positive impact on human health by reducing the risk of cardiovascular and cancer diseases (Ciska et al., 2016). It is a popular grocery in local markets due to availability, affordability, and consumer preference (Šamec et al., 2017). Consumption of cabbage in the Republic of Serbia is 20 kilograms per capita, which is significantly higher than the world average (Vlahovic, 2015). White cabbage has high nutritive value due to richness in active phytochemicals, such as vitamins C and E, minerals, dietary fibre, glucosinolates, phenolic acids, flavonoids and carotenoids (Liu et al., 2014; Podsędek, 2007; Williams et al., 2013). The post-harvest stability of cabbage is relatively short, so that minimal processing techniques can be applied to preserve the fresh-like characteristics.

One of these mild, non-thermal technologies is osmotic treatment (OT). Osmotically treated products are classified as intermediate moisture products, also having a reduced water activity and microbiological stability. The incorporation of the osmotic solutes (carbohydrates, salts, and other solutes of special characteristics) during the osmotic processing generates novel food characteristics of osmodehydrated food tissue including nutritional, sensory, and functionally modified characteristics (Dermesonlouoglou et al., 2019). Osmotic dehydration (OD) occurs due to immersion of the food in aqueous solutions of salt or sugar (hypertonic solutions), which results in the incorporation of solids (solute), and reduction of water activity (aw) in food (da Costa Ribeiro et al., 2016). There are many benefits of osmotic dehydration process in the food industry including improved food quality, energy efficiency, avoiding chemical treatments and stability of the product during storage, packaging, distribution and overall cost reduction (Ahmed et al., 2016). Usually used hypertonic solutions are concentrated sucrose solution, sodium chloride solutions or combination of these two. The suitability of sugar beet molasses as a hypertonic solution for OT has previously been demonstrated (Cvetković et al., 2013; Koprivica et al., 2014). Sugar beet molasses has a high content of dry matter (over 80%), high content of minerals, antioxidants, vitamins, and other specific bioactive compounds such as betaine and it provides the high osmotic pressure in the solution which makes it an excellent medium for OT (Šarić et al., 2016). Although the effect of osmotic treatment in molasses on the content of mineral and polyphenols in cabbage has already been reported (Cvetković et al., 2019), the shelf-life study of osmotically dehydrated cabbage is still missing.

Packaging in protective atmospheres, where packaging in modified atmosphere (MAP) has the widest application, is defined as the removal and/or replacement of the atmosphere surrounding the product prior to sealing in the packaging of highly barrier material (Workneh and Osthoff, 2010). Storing food in a modified gaseous atmosphere can maintain quality and extend shelf life, slowing chemical and biochemical spoilage reactions and slowing (or in some cases even preventing) the growth of microorganisms (Coles et al., 2003). The product is initially packaged in a mixture of gases (most commonly carbon dioxide, nitrogen and oxygen), which depends on the product, packaging material, expected shelf life and storage conditions (Jayas and Jeyamkondan, 2002; McMillin, 2008). In order to maximize the effect of the MAP, it is desirable to reduce the product storage temperature.

The main aim of this study was the evaluation of the shelf-life of osmodehydrated cabbage, packaged in various modified atmospheres in the MAP at refrigerator temperature.

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Material and methods

Plant material

Cabbage heads, cultivar "Futoški", late fall variety, were harvested in northern Serbia (Province of Vojvodina) in village Futog. Sugar beet molasses was obtained from the sugar factory Pećinci, Serbia. Overall dry matter content in sugar beet molasses was 85.04%.

Osmotic treatment (OT)

Cabbage leaves were cut into square shapes with dimensions of approximately 1×1cm. Solution S1 was a mixture of sucrose and NaCl in the relation of 1.200/350 g/l of distilled water. The second osmotic solution (S2) was a mixture of S1 and molasses in the same quantities with 70% dry matter. Sugar beet molasses was used as a third osmotic solution (S3). The cabbage leaves were put in a glass jar with osmotic solutions with a material/solution ratio of 1:5 (w/w). The experiments were conducted at the temperature of 20 °C, under atmospheric pressure, during 5 h. The cabbage samples were stirred for the purpose of solution homogenization on every 15 min. After the osmotic dehydration process, the cabbage samples were washed and gently blotted to remove excessive water. Sterilized water was used for washing samples.

From the obtained data, water loss (WL) was determined according to the following equation (Ganjloo et al., 2011):

$$WL = \frac{m_i z_i - m_f z_f}{m_i} \quad \left[\frac{g}{g\ fresh\ sample}\right] \tag{1}$$

where m_i and m_f are the initial and final weight (g) of the samples, respectively; z_i and z_f are the initial and final mass fraction of water (g water/g sample), respectively.

The initial moisture content of fresh cabbage samples was 90.4%, while the final WL for S1, S2 and S3 solutions, after OT, reached the values of 0.191; 0.282 and 0.228, after 5 h of the respectively (Cvetković et al., 2019).

Microbiological analysis

Microbiological profile of osmodehydrated cabbage was examined by determining a total number of microorganisms (TN) (ISO 4833, 1991), yeasts and moulds (ISO 21527, 2008), coagulase positive *Staphylococci* (ISO 6888-1, 1999), β-glucuronidase positive *Escherichia coli* (ISO 16654, 2001), sulphite-induced *Clostridium* (ISO 15213, 2003) and *Salmonella* spp. (ISO 6579, 2002).

Determination of acidity and pH

The pH of the cabbage was determined by a mobile pH meter (ExStickTM, Extech Instruments, USA), calibrated with buffers pH 4 and 7 before measuring. Acidity was determinate by the standard method (SRPS ISO 750, 2003).

Water activity

Water activity (a_w) of the osmotically treated samples was measured using a water activity measuring device (Testo 650, Germany) with an accuracy of ±0.001 at 25 ºC. Soluble solids content of the osmotic solutions was measured using an Abbe refractometer (CarlZeis, Jenna) at 20 °C. All analytical measurements were carried out in accordance to AOAC (2000) standard methods.

HPLC analysis of L-ascorbic acid (L-AA)

For L-ascorbic acid (AA) extraction 3% metaphosphoric acid in 8% acetic acid solution was used. Samples were directly injected (20 μl) in a HPLC system after filtration on 0,45 μm filter. HPLC system consisted of Liquid Chromatograph Agilent Technologies 1100 series, with diode array detector, in column GROM_SIL 120 ODS-5 ST (5 μm, 150×4 mm). As the mobile phase 100 mM ammonium acetate was used in isocratic flow at a rate of 0.4 ml/min. The temperature of the column was 37 °C, the wavelength was 254 nm. Calibration was performed with external standard method. Comparison of retention times and spectra of the ascorbic acid standard were used for L-ascorbic acid identification and quantification in samples.

The packaging of OT cabbage in the MAP

After OT in three different solutions, washing and draining, 50 g cabbage samples were packed using laboratory vacuum sealer (AudionElektro, Swissvac) with teflonized heating areas in polyamide/polyethylene (PA/PE) bags of 14×20 cm size (0.08 cm thickness, <20 g/m^2 (24 h, 1 ATM) water vapour permeability, and <20 cm^3/m^2 (24 h, 1 ATM) oxygen permeability). After vacuuming the content, the chosen gas mixture was inserted before bag heat sealing. The content of the gas mixture was 40:60/CO_2:N_2 (atmosphere 1) and 80:20/CO_2:N_2 (atmosphere 2). Storage of packed samples was conducted in a refrigerator at 4-8 °C for 90 days for all samples.

Sensory analysis

The methodology of the sensory analysis was carried out in accordance with the Guidelines for the Assessment of Food Products by Methods of Scale (ISO 4121, 2003). Samples were evaluated by 6 trained panelists. Samples presented to panelists under room temperature, in individual cabins under a light bulb and in a three-digit code. Before the main test, the panelists were defined and clarified particular attributes. Samples were assessed for the appearance-color, odor, taste, aftertaste and texture. The intensity of all sensory impressions was evaluated using a scale from 1 to 6 (1 = does not exist and 6 = extremely expressive).

Statistical analysis

The response surface method (RSM) was applied in order to investigate the primary impacts of the factors (solution type, CO_2 concentration and storage time), which affect the responses (AA, pH, acidity, TN). The concentration of CO_2 (X_1) (40 and 80%), storage time (X_2) (0, 20, 40, 70 and 90 days) and solution type (S1, S2 and S3) were used as the independent variables, while the dependent variables were the pH (Y_1), Acidity (Y_2), a total number of microorganisms TN (Y_3) and L-ascorbic acid AA (Y_4), (Tab. 1). The experimental design included 2 × 5 × 3 experiments. A model was fitted to the response surface created by the experimental results, and the models were developed in the form of the second order polynomial (SOP). The RSM was performed using StatSoft Statistical software v.10 (Stat soft Inc., Tulsa, OK, USA).

The principal component analysis (PCA) has been applied effectively to classify and segregate the different samples.

Results and discussion

Tab. 1 displays the studied quality attributes of OT cabbage dehydrated in three solutions packed in different MAP during 90 days of storage. A slight decrease in total acidity content in all measured samples was detected during the storage. The lowest acidity content after 90 days of storage was observed in cabbage dehydrated in solution S2. Some authors previously reported that the MAP slightly restrained the decrease intitratable acidity (TA) values compared to standard cold storage (Sabir et al., 2011). Decline in the acidity level can influence consumer's acceptability so it has been associated with quality loss during postharvest storage (Guillén et al., 2006; Zapata

et al., 2008). Other researchers also observed a decrease in the TA of the fruits during storage and they related this acidity reduction due to the hindrance of the ripening process (MARTÍNEZ-ROMERO et al., 2003; MORAGA et al., 2011). Raw Futoški cabbage L-ascorbic acid content is 10.76 mg/100 g.

Ascorbic acid is easily destroyed during processing and storage due its thermo-lability (WOLBANG et al., 2008) and the effect of a_w (COREY, et al., 2011). During osmotic dehydration process loss of L-ascorbic acid in the cabbage were about 16% for OT in solution S3 and 19% in solution S1. One of the possible reasons of L-ascorbic acid decrease is chemical degradation by oxidative reactions by enzyme activity such as cytochrome oxidase, ascorbic acid oxidase and peroxidase, aerobic and non-enzymatic anaerobic reactions (MARTÍNEZ-ROMERO et al., 2003; PATRAS et al., 2009; PHISUT et al., 2013). The results showed the significant decrease of L-ascorbic acid content during the storage (Tab. 1). The highest L-ascorbic acid retention during 90 days storage, was achieved in cabbage dehydrated in molasses (S3) and packaged in the MAP with 80% CO_2 (27.35% loss). Another cause for poor L-ascorbic acid retention is the fact that water soluble compounds leach out from the cell tissues during after osmotic dehydration process (RINCON and KERR, 2010). Although the amount of ascorbic acid reduces during conventional osmotic dehydration, it seems that higher sugar content may positively affect the retention of ascorbic acid during storage (SHARIF et al., 2013).

Microbiological profile of osmodehydrated cabbage samples is expressed by a total number of microorganisms as shown in Tab. 1. Source of microbiological contamination could be the manual preparation of the cabbage (cutting, washing) and present normal microflora. In the beginning, from 20th to 45th day in the MAP, a total number (TN) of microorganisms decreased probably due to the inaccessibility of oxygen (NOSEDA et al., 2012). At the later storage period re-growth of microorganisms was detected. At the 70th to 90th day of storage an increase in the TN of microorganisms was observed, probably anaerobic microorganisms. The development of yeasts and moulds in the samples during the storage was not observed. Pathogenic microorganisms as coagulase positive staphylococci, *E. coli,* sulphite-induced *Clostridium* and *Salmonella* spp. were not detected OT cabbage samples, which is in line with claims of some other authors (PEREIRA et al., 2004; RODRIGUES et al., 2006). The gained a_w values for samples at the end of the investigation reached the values between 0.84 and 0.85, which ensured that the growth of bacteria is inhibited (BARBOSA-CANOVAS et al., 2007; ŠOBOT et al., 2019).

Tab. 2 shows the ANOVA calculation of the developed SOP models. The analysis showed that the linear and quadratic terms of the solution type were the most dominant factors for ascorbic acid concentration, pH and acidity prediction using the SOP model. Interestingly, the CO_2 content in the modified atmosphere was not found as a significant factor to affect any of the studied parameters. The storage time exhibited significant effect only to microbial counts (TN), having linear and quadratic effects. These effects were statistically significant at $p<0.05$ level. None of these effects was significant at $p<0.01$, level except for the quadratic term of solution type on total microbial count (TN). The interaction of solution type and storage time was significant at $p<0.05$ level for the changes in pH and acidity of OT cabbage, whereas CO_2 content and storage time interaction was significant for acidity at $p<0.05$ level. The interaction between solution type and CO_2 content in the MAP were not significant for the output parameters.

Tab. 2: ANOVA analysis for ascorbic acid (AA), pH, acidity (AC) and microbial counts (TN) during the storage of OT cabbage

Term	df	AA	pH	AC	TN
Sol	1	0.023	1.603*	0.018*	$2.8 \cdot 10^5$
Sol^2	1	96.746*	0.707*	0.011*	$9.7 \cdot 10^6$**
CO_2	1	1.566	0.001	0.000	$4.4 \cdot 10^6$
t	1	0.668	0.064	0.001	$4.0 \cdot 10^7$*
t^2	1	0.034	0.056	0.000	$6.8 \cdot 10^7$*
Sol × CO_2	1	0.005	0.000	0.001	$3.5 \cdot 10^4$
Sol × t	1	0.158	0.315*	0.006*	$1.3 \cdot 10^6$
CO_2 × t	1	0.298	0.006	0.004*	$2.3 \cdot 10^5$
Error	15	6.579	0.397	0.012	$3.6 \cdot 10^7$
r^2		0.938	0.874	0.770	0.774

*Significant at $p<0.05$ level, 95% confidence limit

Sol – osmotic solution; CO_2-N_2 content in the MAP; T – storage time; AA – ascorbic acid (mg/100 g); AC – acidity (%); TN – a total number of microorganisms (cfu/g); df – degrees of freedom

In order to better explain the structure of the exploratory data that would contribute to the comprehension of likenesses and dissimilarities of the OT cabbage samples during storage, PCA was applied and the results are presented in Fig. 1 The first two PCs explained 69.10% of the total variance in the experimental data. The projection of the factors indicated that CO_2 concentration, pH and TM contributed mostly to the first principal component PC1 (31.2%, 22.3% and 48,9%, respectively), while the acidity and AA

Tab. 1: Experimental data for the shelf-life study of OT cabbage packaged in different MAP

No. sample	MAP CO_2 content (%)	Storage period (days)	Solution S1				Solution S2				Solution S3			
			AA	pH	AC	TN	AA	pH	AC	TN	AA	pH	AC	TN
1	/	0	8.79	5.36	0.590	1700	8.81	6.18	0.440	2400	8.98	6.15	0.48	2000
2	40	20	6.85	5.175	0.505	4650	6.91	6.2	0.440	7600	7.11	6.26	0.505	4750
3	40	40	5.45	5.515	0.435	1450	5.38	5.845	0.485	1400	5.53	6.33	0.490	500
4	40	70	3.59	5.33	0.450	610	3.93	5.9	0.415	1245	3.84	5.715	0.515	990
5	40	90	2.05	5.46	0.395	1250	n.d.	6.16	0.390	2150	2.3	5.715	0.495	1035
6	80	20	6.71	5.265	0.470	5000	6.78	6.25	0.415	7900	7.02	6.15	0.485	8000
7	80	40	5.55	5.425	0.410	3000	5.83	5.935	0.440	675	5.77	6.2	0.470	395
8	80	70	3.92	5.2	0.435	695	3.88	5.87	0.470	840	3.71	5.83	0.535	730
9	80	90	n.d.	5.575	0.430	2650	2.41	6.23	0.380	7250	2.11	5.81	0.565	785

*YM<100 for all samples

AA – ascorbic acid (mg/100 g); AC – acidity (%); TN – a total number of microorganisms (cfu/g); n.d. – not detected

concentration contributed more to the second principal component PC2 (72.4% and 21.8%, respectively).

The separation between samples could be observed from the PCA graph, where the highest TN content was noticed for the not-stored samples (sample 1) and the samples packed under lowest CO_2 concentration in the MAP (sample 5), regardless of the osmotic solution. The map of PCA analysis showed that the first principal component described the differentiation among the samples according to TN content, while the second principal component described the variations in acidity between samples.

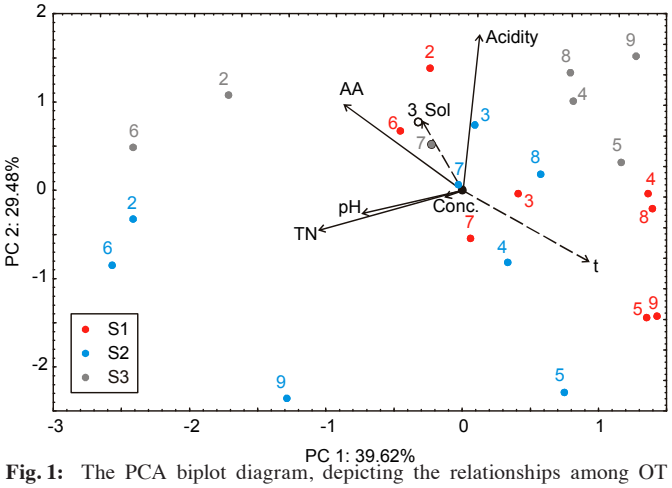

Fig. 1: The PCA biplot diagram, depicting the relationships among OT cabbage samples treated with different osmotic solutions and packaged in different MAP during storage.
Sol – osmotic solution; CO_2-N_2 content in the MAP; T – storage time; AA – ascorbic acid (mg/100 g); TN – a total number of microorganisms (cfu/g)

After the process of osmotic dehydration of the cabbage samples in solution S1, the sensory panel marked the lightest colour as the most intense property. Osmotically dehydrated samples in solutions S2 and S3 are described of yellow-brown colour. No significant change in colour or intensity was observed during the overall storage process in modified atmosphere packaging.

Cabbage dehydrated in S1 solution retained the odour of fresh cabbage, while the dominant odour of cabbage dehydrated in S2 and S3 solutions was that of molasses and caramel. During the 45-day storage period, a slightly distinctive off odour occurred with cabbage in solution S1 packed in both gas mixtures. In cabbage dehydrated in S2 solution, the taste was rated as sweet-salty and salty with equal intensity. During cabbage storage, after 20 days, bitter taste occurred in all samples dehydrated in S2 and S3 solutions. During storage, the gumminess decreased while the toughness and hardness increased in all observed samples.

In order to show the sensory analysis data which could be applied for better understanding of the properties of OT cabbage samples during storage, PCA results were shown in Fig. 2. The first three PCs clarified 58.13% of the total variance in the experimental data. The projection of the variables in the factor plane indicated that ACLY, ACLYG, OM, OCR, TSA, TM, TCR, TP, TB and ATS contributed mostly to the first principal component PC1 (5.6%; 6.5%; 6.7%; 5.6%; 8.0%; 8.5%; 7.3%; 5.0%; 5.1% and 6.5%, respectively), while TSW, ATSS, ATSB, ATS, ATB, ATSR, TXCW and TXTG contributed more to the second principal component PC2 (8.8%; 9.8%; 8.6%, 5.3%, 8.2%, 10.2%, 9.1% and 12.1%, respectively). The third principal component was mostly influenced by: ACB, OCB, OODRS, TCB, ATB and TXHD (8.6%; 5.6%; 20.0%; 5.3%; 6.7% and 21.5%, respectively).

The differentiation among samples could be realized from the PCA graphic, where the yellowish samples (ACLY, ACLYG), with the original cabbage (OCB, TCB) and salty taste (TSA, ATS) are grouped on the right side of the graphic, while the brown-colour samples (ACYB, ACLYBE, ACG) with a taste and smell like molasses (TM, TCR, OCR, OM) are grouped on the left side of the graphic. The bitter (ATSB, ATB) and pungent (ATP) after taste samples are grouped at the upper side of the graphic, while the acid samples (ATSR, ATSS, TSR) are grouped at the bottom of the graphic. Samples with the tough (TXTG) and hard (TXHD) texture are grouped on the top of the graphic, while chewy texture samples (TXCW) are grouped on the bottom of the graphic. PCA has led to the useful classification and segregation of the cabbage samples treated with different osmotic solutions (S1, S2, S3).

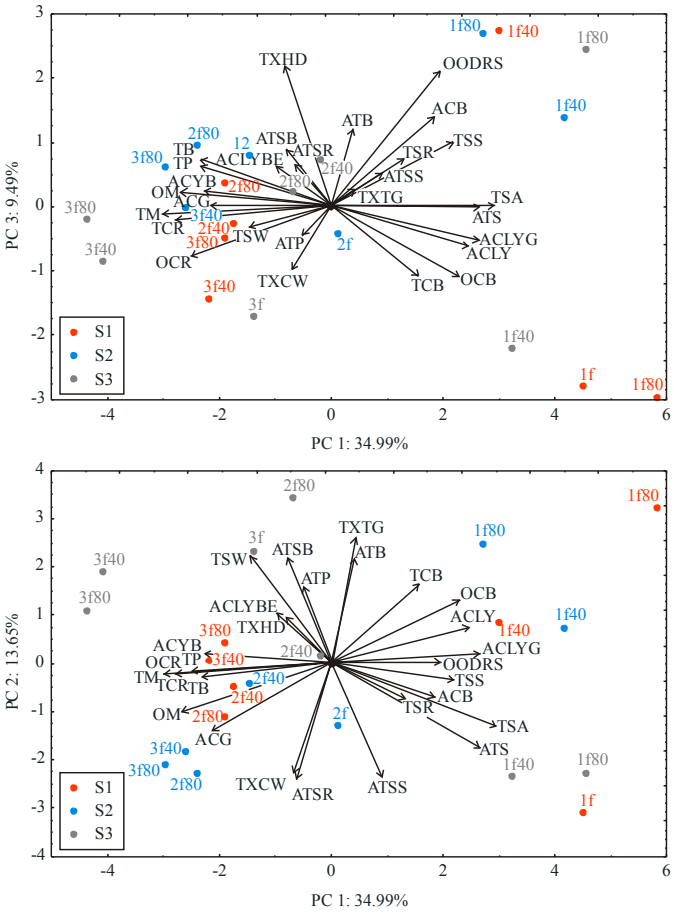

Fig. 2: The PCA biplot diagram, depicting the sensory analysis of OT cabbage samples treated with different osmotic solutions during storage.
ACLY-appearance-colour- light yellow, ACLYG -appearance-colour- light yellow green, ACLYBE-appearance colour light yellow brown edges, ACYB-appearance colour yellow brown, ACB-appearance colour brown, ACG-appearance colour grey, OM-odour molasses, OCR-odour caramel, OCB-odour cabbage, OODRS-off odour (rancid, sour), TSW-taste sweet, TSS-Taste sweet salty, TSA-taste salty,TCB-taste raw cabbage, TM-taste molasses, TCR- taste caramel, TP-taste pungent, TSR-taste sour, TB- taste bitter ATTS-aftertaste sweet salty, ATSB- aftertaste sweet bitter, ATS- aftertaste salty, ATB-aftertaste bitter, ATSR-aftertaste sour, ATP- aftertaste pungent, TXCW-texture chewiness, TXTG-texture toughness, TXHD- texture hardness

Conclusions

The obtained model was able to successfully predict experimental results. The model is easy to implement for osmotic treatment process with desired final quality and could be effectively used for predictive

purposes, modelling and optimization of the osmotic treatment. Solution type has a significant influence on pH and acidity, storage period on a total number of microoragisms and gas mixture content has no significant influence on analysed parameters. Considering that an impressive amount and wide assortment of information were utilized in the current study to develop the appropriate numerical model, and realizing that the model ended up yielding adequate results, its practical aplication could be expected.

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Conflict of interest
No potential conflict of interest was reported by the authors.

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