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MASS TRANSFER KINETICS AND EFFICIENCY OF OSMOTIC DEHYDRATION OF CELERY LEAVES
KINETIKA PRENOSA MASE I EFIKASNOST OSMOTSKE DEHIDRATACIJE LISTA CELERA

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ABSTRACT

This research was conducted in order to examine the mass transfer kinetics, during osmotic dehydration of celery leaves (Apium graveolens) in two different osmotic solutions (sugar beet molasses and the mixed solution of sodium chloride and sucrose), under atmospheric pressure, at room temperature. The significance of used hypertonic solutions and immersion time on the various kinetics parameters (water loss, solid gain and dehydration efficiency index) were tested during the process, using Analysis of variance. Principal component analysis and Cluster analysis were used for characterization of different samples, and standard score analysis was applied in optimal process parameters determination.

Key words: *osmotic treatment, celery, sugar beet molasses, mass transfer kinetics.*

REZIME

Ovo istraživanje je sprovedeno sa ciljem da se ispita kinetika prenosa mase za vreme osmotske dehidratacije lista celera (Apium graveolens), u dva različita osmotska rastvora (melasa šećerne repe i vodeni rastvor saharoze i natrijum-hlorida), na sobnoj temperaturi i atmosferskom pritisku. Primenom analize varijansi, praćen je uticaj korišćenih hipertoničnih rastvora i vremena imerzije na ispitivane kinetičke parametre (gubitak vode, prirast suve materije i koeficijent efikasnosti procesa). Analiza glavnih komponenata i klaster analiza su korišćene za karakterizaciju različitih uzoraka, a standardna "score" analiza je primenjena za određivanje optimalnih procesnih parametara.

Ključne reči: osmotski tretman, *celer, melasa šećerne repe, maseni transfer.*

INTRODUCTION

It has been proved that celery is a rich source of antioxidant nutrients and its cosumption has many health benefits, therefore is recognized as a healthy plant and spice (*Ježek et al., 2008*). But, its high water content (approximately 80%) is the main responsible for the growth of microorganisms, which causes the perishable or damaging changes of the sensory and nutritive characteristics of celery after short period (*Ježek et al., 2008; Vina and Chaves, 2006*). For this reason it is desirable to eliminate the water, which can be achieved by different methods of preservation (*Nistor et al., 2011*). Preservation methods like drying, canning and freezing have been applied to prolong the shelf life of foods, but these methods produce food products that are low in quality compared to their original fresh state (*Ratti, 2009*). In regard to the other preservation treatments osmotic treatment (OT) has a noticeable advantages providing shelf-stable and quality processed products, furthermore is environmentally acceptable and energy efficient process. (*El-Aouar et al., 2006*). OT process involves partial removal of water from food by immersion in a concentrated hypertonic solution. Due to low energy consumption and mild temperatures, which is considered minimal processing, OT is suitable as a pretreatment for many processes. OT improves nutritional, sensorial and functional properties of food without changing its integrity (*Sablani et al., 2002*; *Koprivica et al., 2010*). Mass transfer is caused by a difference in osmotic pressure: water outflow from product to solution, solute transfer from solution into the product, and leaching out of the products own solutes. Mass transfer mechanism and quality of final product are affected by many factors such as composition and concentration of osmotic agents, immersion time of the product in the solution, agitation /circulation of osmotic solution, operating temperature, solution to sample ratio, nature and thickness of food material and pre-treatment (*Ćurčić et al., 2013*). Great influence on the kinetics of water removal and solid gain has the type of osmotic agent. Concentrated sucrose solution, sodium chloride solutions and their combinations are usually used as hypertonic solution (*Mišljenović et al., 2010*). The use of a ternary system (water/sugar/salt) in the osmotic treatment of foodstuff has shown higher rates of water loss. When the salt is added, even with solutions with low concentrations of solutes, the process is more effective *(Rodrigues and Fernandes, 2007)*.

Recent research has shown that use of sugar beet molasses as a hypertonic solution improves OT processes *(Lević et al., 2007)* Molasses is a byproduct of sugar production from sugar beet which is no longer possible to get the crystal sugar by usual procedures of crystallization. However, due to a rich nutritive composition, over 200 nutritional valuable compounds, molasses as raw material has found its application in processing and fermentative industries and as a supplement in feed production *(Mišljenović et al., 2010)*. High content of solids (around 80%) provide high osmotic pressure in the molasses and maintains a high transfer potential favorable to water loss during OT and thus enhances the efficiency of this process. The application of sugar beet molasses as osmotic agent has many advantages: it is sensory acceptable, always accessible in large quantities and cheap raw material *(Filipović et al, 2012)*.The objective in this study was to investigate the influence of immersion time and the type of osmotic solution on the efficiency of OT process of celery leaves. For this purpose the quality of osmotically dried celery leaves produced at three different immersion time, using two different osmotic solutions was examined. To assess the quality of this products their water loss, solid gain and dehydration efficiency index have been determined. Experimental results have been subjected to analysis of variance (ANOVA) to show relations between applied assays. In order to enable more comprehensive comparison between investigated samples, standard score (SS) has been introduced. Principal Component Analysis (PCA) and Cluster Analysis (CA) have been applied to classify and discriminate analysed samples.

MATERIAL AND METHOD

Celery leaves (*Apium graveolens*) was purchased at local market, shortly before the treatment, to be used in the fresh state. Initial moisture content of celery leaves was 80.92 %. Before the OT, celery leaves were cut into pieces of dimension nearly 1x1 cm. As hypertonic mediums two different solutions were used. The first one, concentrated sugar beet molasses, with initial dry matter content of 80.00%, was obtained from the sugar factory Pećinci, Serbia (in further text indicated as sugar beet molasses). The second osmotic solution, mixed aqueous solution of NaCl and sucrose, was made from sucrose in the quantity of 1.200 g/kg water, NaCl in the quantity of 350 g/kg water and distilled water (in further text indicated as ternary solution). The material to solution ratio of 1:20 (w/w) was used during all experiments. The samples of celery leaves were submerged in laboratory jars at room temperature of 20°C, under atmospheric pressure. The OT process was performed in a period of 0-5 h under constant conditions. Samples were withdrawn from the osmotic solution at determined intervals of time (1, 3, and 5 h), then lightly washed with water and gently absorbed with paper towels to remove adhering solution. All experiments were repeated three times. Dry matter content of the fresh and treated samples was determined by drying at 105°C for 24h in a heat chamber (Instrumentaria Sutjeska, Croatia) until constant weight. All analytical measurements were carried out in accordance to AOAC (2000). In order to follow the mass transfer kinetics of the OT, three key process variables were measured: moisture content, change in weight and change in the soluble solids. Based on the experimental data, water loss (WL), and solid gain (SG), were calculated, as described by *Koprivica at al., 2010.*

Important process parameters as a function of different type of osmotic solution and dehydration time were analyzed using the ANOVA. During ANOVA calculation, the independent variables were: immersion time (X_1) - 1, 3 and 5h; the type of osmotic solution (X_2) - sugar beet molasses (1) and ternary solution (2), and the dependent variables were the responses: *WL* (Y_1) and *SG* (Y_2). Two mathematical models of the following form were developed to relate two responses (Y) to two process variables (X):

$$Y_k = \beta_{k0} + \sum_{i=1}^{2} \beta_{ki} X_i, \; k\text{=1-2}, \tag{1}$$

where: β_{k0}, β_{ki} are constant regression coefficients, k-index.

Min-max normalization is a technique which is commonly applied for comparison of various characteristics of complex samples determined using multiple assays, where samples are classified on the basis of the ratio of raw data and extreme values of the measurement used. Considering that the scale of the data from various parameters concerning mass transfer (WL and SG) are different, the data in each data set should be transformed into normalized scores, in accordance with the following equations:

$$\overline{x}_i = 1 - \frac{\max_i x_i - x_i}{\max_i x_i - \min_i x_i}, \quad \forall i, \tag{2}$$

In case of “the higher, the better” criteria, used for WL score calculation,or:

$$\overline{x}_i = \frac{\max_i x_i - x_i}{\max_i x_i - \min_i x_i}, \quad \forall i, \tag{3}$$

In case of “the lower, the better” criteria, used for SG score calculation.

Obtained data have been subjected to analysis of variance (ANOVA) for the comparison of means, and significant differences are calculated according to post-hoc Tukey’s HSD (“honestly significant differences”) test at p<0.05 significant level, 95% confidence limit. In addition, principal component analysis (PCA) and Cluster analysis (CA) have been applied successfully to classify and discriminate the different samples. All statistical analyses of the collected results have been performed using StatSoft Statistica 10.0® software.

RESULTS AND DISCUSSION

Table 1 provides an overview on the average values and standard deviations of *WL* and *SG* parameters, as a function of different type of osmotic solution and dehydration time. Dehydration efficiency index-DEI (WL/SG ratio) were calculated and shown in the table 1. This ratio is considered to best determine optimal condition for the OT. High DEI ratios point to intensive water removal from the samples accompanied with minimal solid uptake.

Table 1. Experimental results for celery leaves during osmotic treatment

Solution	Time	WL g/g initial sample weight	SG g/g initial sample weight	DEI	SS
Sugar beet molasses	1	0.28±0.00[b]	0.11±0.00[a]	2.49±0.06[b]	0.50
	3	0.34±0.01[d]	0.13±0.00[b]	2.65±0.05[b]	0.58
	5	0.49±0.02[a]	0.16±0.00[c]	3.10±0.13[d]	0.79
Ternary solution	1	0.32±0.01[c]	0.18±0.00[d]	1.75±0.03[c]	0.31
	3	0.40±0.01[e]	0.20±0.00[e]	2.03±0.07[a]	0.44
	5	0.50±0.01[a]	0.24±0.00[f]	2.11±0.03[a]	0.50
Polarity		+	-	/	/

The results are presented as mean±SD; Different letter within the same column indicate significant differences (p <0.05), according to Tukey’s test. Polarity: ‘+’ = the higher the better criteria, ‘–’ = the lower the better criteria

Because of the great difference in osmotic pressure between hypertonic solution and the celery leaves tissue, loss of the water was high at the beginning of the dehydration (0.32 g/g i.s.w. in the ternary solution and 0.28 g/g i.s.w. in the sugar beet molasses).

But, it was observed that increase of the OT process time resulted in greater removal of water from the samples, regardless of the type of solution. The highest value of WL was achieved in the ternary solution, after 5 hours. (0.50 g/g i.s.w.). Table 1 shows that *SG* also increases with immersion time in both solutions. Greater increase in values of SG was noticed in the samples which were treated in ternary solution, as compared to those treated with the molasses. Since, one of the objectives of OT is to achieve as low as possible solid uptake, the most acceptable value for SG was achieved by using molasses as solution (0.16 g/g i.s.w.), after 5 hours of osmotic process. The maximum value of DEI that indicates the most efficient dehydration process was 3.10, achieved by immersion of celery leaves for 5 hours in sugar beet molasses.

Optimum OT conditions which define maximum WL with lesser SG were determined using SS, Table 1.

Table 2. ANOVA table (sum of squares for each assay)

	df	WL	SG
Solution	1	0.002**	0.008*
Immersion time	1	0.038*	0.002**
Error	3	0.001	0.001
r^2		0.951	0.871

**Significant at p<0.05 level, **Significant at p<0.10 level, 95% confidence limit, error terms have been found statistically insignificant*

ANOVA analysis revealed that the linear terms contributed substantially in all of the cases to generate a significant second order polynomial (SOP) model. WL was significantly affected by all process variables, and the main influential variable seems to be the treatment time (statistically significant at p<0.05 level, 95% confidence level). The type of solution was also important for

WL calculation, statistically significant at $p<0.10$ level. *SG* was more influenced by the type of used solution, statistically significant at $p<0.05$ level (better results were obtained using sugar beet molasses solution). The impact of production time for evaluation of *SG* was also observed, statistically significant at $p<0.10$ level. Also shown in Table 2 is the residual variance where the lack of fit variation represents other contributions except for the first order terms. All SOP models had insignificant lack of fit tests, which means that all the models represented the data satisfactorily. A high r^2 is indicative that the variation was accounted and that the data fitted satisfactorily to the proposed model (SOP in this case). The r^2 values for *WL* (0.951) and *SG* (0.871), were found very satisfactory and showed the good fitting of the model to experimental results.

Optimization of the OT is performed using Standard Score Analysis, to ensure optimal processing conditions (with as low as possible immersion time) yielding an acceptable product quality (with high *WL* and low *SG*), and a high throughput capacity. The optimum OT conditions for celery leaves, dehydrated in sugar beet molasses solution are obtained at immersion time of 5 h, solution concentration and temperature of 80% and 20°C. The analysis of dissimilarities in *WL* and *SG* between the samples was investigated by means of PCA (diagram on Fig. 1). PCA diagram shows the superiority of molasses solution compared to ternary solution, which is evident by the position of points 1, 2 and 3, and the direction of DEI vector. More appropriate WL values were observed after more immersion time (points 3 and 6, according to direction of WL vector), while more acceptable SG values were noticed for lesser immersion time (points 1 and 2, according to the direction of SG vector). Euclidean distances were used as the measure of proximity between different samples, used to draw the CA dendrogram (Fig. 2).

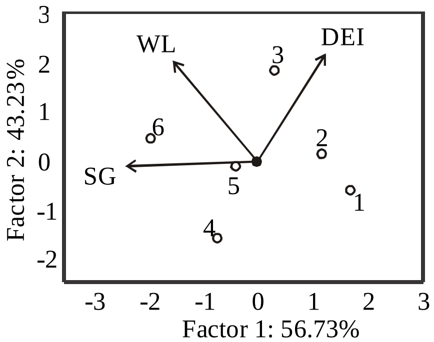

Fig. 1. PCA biplot diagram

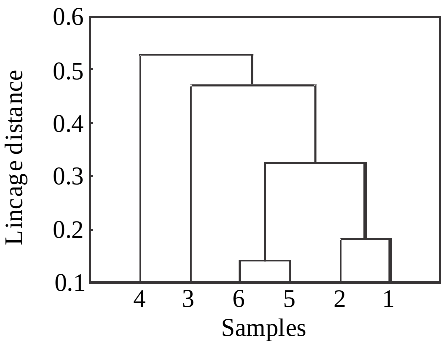

Fig. 2. CA dendogram

CONCLUSION

On the basis of presented results it can be concluded that both solutions are satisfying osmotic mediums, taking into account the considerable loss of water during both processes. Optimal solution for drying celery leaves was sugar beet molasses and optimum process parameter was immersion time of 5 h. The predicted responses for the optimum dehydration conditions in sugar beet molasses were: *WL* about of 0.49 and *SG* about 0.16 g/g i.s.w. (*DEI*=3.10, *SS*=0.69). Despite the fact that sugar beet molasses proved to be more effective osmotic solution, its use is justified also from environmental and economic aspects, because molasses is side product of sugar industry. Since both osmotic treatments carried out at room temperature, without the need of extra input of energy, it can be concluded that this is energy and economically favorable method of preservation.

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