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VEGETABLE WASTE IN FREEZING PROCESS AS A HIGH QUALITY MATERIAL FOR FREEZE-DRYING®

Odpady warzywne z procesu mrożenia jako wysokiej jakości surowiec do liofilizacji®

We would like to thank mgr Monika Szczęsna, whose research carried out in the master thesis was used to prepare this publication.
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Key words: vegetable, freeze-drying, anthocyanin, polyphenol, sorption properties, colour, sugars, thermal properties.

The article of the study was to investigate selected physical and chemical properties of freeze-dried vegetables which were rejected as a waste of freezing process due to non-compliance with the size criterion. Cauliflower, carrot, yellow bean, potato and onion were freeze-dried with registration of drying kinetics and next sugars, anthocyanin and polyphenols content were determined, rehydration and sorption properties as well as colour, water activity and content and thermal properties. It was shown that obtained samples were characterized typical properties for freeze-dried vegetables and may be used as an e.g. component of freeze-dried vegetable mix or innovative food product.

Słowa kluczowe: warzywa, liofilizacja, antocyjany, polifenole, właściwości sorpcyjne, barwa, cukry, właściwości termiczne.

Celem artykułu było przedstawienie zbadanych wybranych właściwości fizykochemicznych warzyw liofilizowanych, które zostały odrzucone jako odpad z procesu mrożenia z powodu niespełnienia kryterium wielkości. Liofilizowano kalafior, marchew, żółtą fasolę, ziemniak i cebulę z rejestracją kinetyki suszenia, a następnie oznaczono zawartość cukrów, antocyjanów i polifenoli, właściwości rehydratacyjne i sorpcyjne, a także barwę, aktywność wody oraz zawartość i właściwości termiczne. Wykazano, że otrzymane próbki charakteryzowały się właściwościami typowymi dla warzyw liofilizowanych i mogą być wykorzystywane m.in. jako składnik liofilizowanej mieszanki warzywnej lub innowacyjnego produktu spożywczego.

INTRODUCTION

Diet rich in vegetables, which contain significant amounts of bioactive phytochemicals, may provides desirable health benefits such as reduce the risk of chronic diseases, what was confirmed in investigations. More and more countries encourage the consumption of vegetables to prevent various diseases, e.g. cancer, cardiovascular disorders [38, 47]. This protective effect may be connected with its against diseases initiated by free radicals, which results from the presence of compounds with antioxidant properties, e.g. polyphenols, anthocyanins [60]. More than 8,000 phenolic compounds

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have been isolated from various natural products, including flavonoids and phenolic acids. Polyphenolic compounds can be divided in terms of the structure of the basic carbon skeleton into: phenolic acids, flavonoids. The content of phenolic compounds in products foods varies greatly and depends on a number factors. Depending on the technological processing the phenolic content of processed foods is different from fresh foods [21]. The greatest amounts of polyphenols are found in [50]: cruciferous vegetables (red cabbage, broccoli); onion vegetables (onion, garlic); root vegetables (red beet); nightshade vegetables (red pepper). Vegetables provide adequate amount of many vitamins and minerals for humans. They are rich source of carotene, ascorbic acid, riboflavin, folic acid and different minerals [19], but they have short shelf live because of they contain a large proportion of water. The widely used technique for vegetable preservation is drying [52]. Appropriate drying technique should maintain food qualities such as flavour, texture, functionality and high nutritional content, but also chemical compounds including the content of phenolics [40], protection of vitamins or carotenoids [51].

During the process of freezing vegetables, some of the raw materials are largely rejected because they do not meet the shape or size criteria. Then they become waste, which in terms of quality are wholesome vegetables and can be successfully used, for example, in the production of multi-vegetable freeze-dried snacks [14] or as a component of freeze-dried vegetable mix.

The aim of the research was to assess the selected chemical and physical properties of freeze-dried vegetables. The same vegetables were used to obtain innovative vegetable bars with hydrocolloids [14]. The scope of this work include investigations of total polyphenol, flavonoids and sugars content, sorption isotherms and hygroscopic properties, colour, water content and activity, as well as thermal properties for freeze-dried onion, carrot, yellow bean, potato and cauliflower. During the freeze-drying process, the kinetics of freeze-drying was registered.

MATERIALS AND METHODS

The research material were rejected frozen vegetables: cauliflower, onion, potato, yellow beans and carrots, stored in a chest freezer (Electrolux EC4200A0W1, Sweden) at the temperature of -18°C in ziplock bags. They were rejected in the course of the production of frozen vegetables due to their improper shape or uneven colour. Vegetables were varied in terms of shape. The freeze-drying was carried out in a Christ ALPHA 1-16 freeze dryer (Germany) at the temperature of the heating shalves of the freeze dryer 30°C for 24 h, under the presure of 63 Pa, safety pressure of 137 Pa. During the freeze-drying process, the kinetics of freeze-drying was determined. Until the tests, the freeze-dried vegetables were stored in barrier packages, limiting the access of oxygen, moisture and light, and stored in controlled conditions (temperature 25°C, humidity RH 50%) in a climatic chamber.

Water activity of freeze-dried vegetables was measured by HygroLab Rotronic Company apparatus with accurancy of ±0,001, at a temperature 25±0.5°C, according to the manufacturer's instruction. Water content was determined in a WAMED SUP 65 W/G convective dryer (Poland) for 24 hours at the temperature of 60°C [16]. Colour measurement was done for the thawed and freeze-dried vegetables with the use of Chroma – Meter CM-5 Minolta Company (Austria) [12].

The colour indicators were calculated with the use of the following formula:

ΔE – relative colour difference index

$$\Delta E = \sqrt{(L^{*0} - L^{*})^2 + (a^{*0} - a^{*})^2 + (b^{*0} - b^{*})^2}$$

where: L^* – lightness coefficient [dimensionless value]

a^* – red colour coefficient [dimensionless value]

b^* – yellow colour coefficient [dimensionless value]

L^{*0}, a^{*0}, b^{*0} – colour coefficients for thawed vegetables (relate to) [dimensionless value].

Total polyphenols content was determined by the Folin-Ciocalteu method, using gallic acid standard [42]. To determine the content of total flavonoids, the spectrophotometric method was used, based on the measurement of the absorbance of colored complexes formed between flavonoid compounds with aluminum chloride [43]. The liquid chromatography method with refractive index detection was used to determine sugars [56]. In order to determine the hygroscopic properties of the dried material, the method proposed by Nowacka & Witrowa-Rajchert [44] was used. Determination of sorption isotherms was performed using an automatic gravimetric water sorption analyzer (AQUADYNE DVS-2HT QUANTAHROME INSTRUMENTS) according to the manufacturer's instruction. To describe the water sorption isotherms of freeze-dried vegetables four mathematical models (Oswin [31], Lewicki [32], Peleg [32], GAB [31]) were considered based on R2 correlation coefficient; MRE mean relative error; RSS residual sum of squares and SEE error of water content estimation [10, 13]. The structure of vegetables after freeze-drying was determined with the use of a scanning electron microscope TM-3000 HITACHI [11]. From freeze-dried vegetables a piece about 1-2 mm were cut out across the sample. Structural changes were determined at 100x magnification. TGA and DTG curves were registered with the use of Thermogravimeter TGA/DSC 3+LF (Mettler Toledo Company, Poland). 5-6 mg of every sample were put in aluminium Pan 40 µl and were heated at a rate of 5°C/min with gas flow N2 50 ml/ min, in the temperature range of 30-600 ℃. Statgrafics Plus, version 4.1. MS Excel 2010 (Microsoft) was used in the following statistical analysis. For the obtained results pooled standard deviations were calculated. Homogeneous groups were determined using the Tukey's test, with a significance level of $\alpha = 0.05$.

RESULTS AND DISCUSSION

Figure 1 presents kintetics of the freeze-drying process for yellow bean, cauliflower, potato, carrot and onion. The u/u0 is the ratio of water content during drying to initial water content before drying [61]. All samples were freeze-dried in the same conditions. On the basic of obtained drying curves it was shown that most of samples obtain similar drying kinetics. Only cauliflower freeze-drying curve indicates that this vegetable characterize lower drying rate. It may be also connected with the higher initial water content for cauliflower than for other investigated vegetables. On freeze-drying process different factors influence, such as drying temperature, chamber pressure, and sample thickness [3]. In the case of analysed samples, different structure and shape of the vegetable: cubes for potato, onion and carrot, florets for cauliflower, pieces for yellow bean may have influence on drying kinetics (Figure 1). Similar drying rate obtained Lin et al. [35] for sweet potato with the use of far-infrared freeze-drying and Wang et al. [59] for freeze-dried potato. Reyes et al. [54] obtained lower freeze-drying rate for carrot than results presented on Figure 1, but authors indicated that samples which were quick frozen obtained higher drying rate than samples slow-frozen, which might be due to a more open structure obtained by quick freezing.

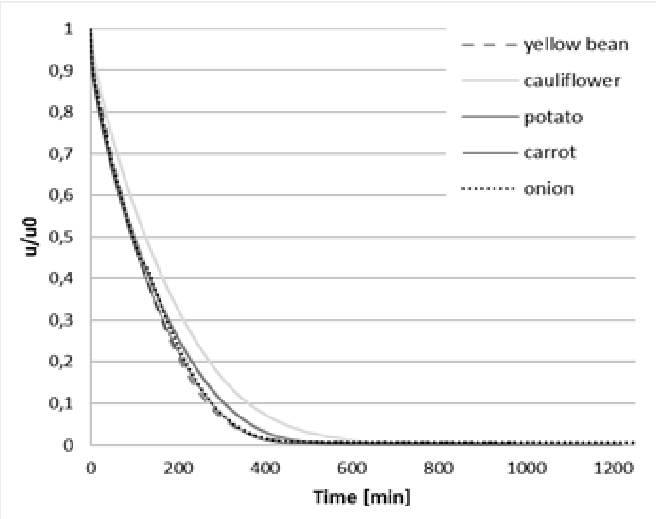


Fig. 1. Kinetic curves of freeze-dried vegetable waste.
Rys. 1. Krzywe kinetyki liofilizacji odpadów warzywnych.

Source: Own study

Źródło: Opracowanie własne

Freeze-dried vegetables obtained low water content in the range of 0.005–0.023 g H_2O/kg (Table 1). The lowest value was shown for freeze-dried potato. Between onion and carrot, as well as yellow bean and cauliflower differences were statistically insignificant. Guine & Barroca [24] obtained similar water content value for freeze-dried onion. Baloch, Xia & Sheikh [4] measured moisture content of raw and cabined dried cauliflower and indicate that this vegetable should be preserved as soon as possible. Cui et al. [15] obtained higher value of moisture content for freeze-dried carrot, but differences may be connected with e.g. different drying conditions, or samples size. Water activity of freeze-dried vegetables was also on low level, in the range of 0.088–0.126 (Table 1). In most cases differences were statistically significant. The value lower than 0.60, ensures complete inhibition of microbial growth in food products [25]. Choi et al. [9] showed that for sweet potato the drying process reduced the water activity (a_w) by accumulation of sugars during processing, what increased the final product shelf-life due to the prevention of microbial growth. Rajkumar et al. [52] obtained significant higher value of a_w for carrot (0.422), but they conducted freeze-drying process in temperature 45°C.

Table 1. Water content and water activity for freeze-dried vegetable waste
Tabela 1. Zawartość i aktywność wody w liofilizowanych odpadach warzywnych

Sample	Water content [g H_2O/kg]	Water activity
yellow bean	(b)0.018±0.000	(a)0.088±0.001
cauliflower	(b)0.019±0.001	(b)0.117±0.005
potato	(a)0.005±0.000	(d)0.100±0.003
onion	(c)0.023±0.001	(c)0.126±0.004
carrot	(c)0.023±0.000	(cd)0.099±0.006

Abbreviations: Value are mean (n=2) ± standard deviation (P < 0.05). The means with the same letter (abcd) in the lines are not significantly different according to ANOVA and Tukey's multiple comparison tests.

Oznaczenia: Wartości to średnia (n=2) ± odchylenie standardowe (P < 0,05). Średnie z takimi samymi literami (abcd) w wierszach, nie różnią się znacząco według testów wielokrotnych porównań ANOVA i Tukeya.

Source: Own study

Źródło: Opracowanie własne

Colour retention of dried vegetables can indicate retention of the pigments and nutrients such as carotenoids, flavonoids, phenols [17]. Natural colour compounds determine the colour of vegetables and they may be oxidized during the preservation processes especially when high temperature and oxygen is used [36]. In particular carotenoids become rapid decomposition in the presence of oxygen [23]. Carrot is reach in caretonoids, which are organic pigments naturally occure in chloroplasts and chronoplasts [28]. The α- and β-carotene constitute over 90% of all carotenoids and have to be protect before thermal destruction, because degradation of carotenoids affects not only the colour of food products, but also their nutritive value and flavour [34]. Even that freeze-drying is recognized as a method, which protect sensitive compounds the absolute colour difference parameter (ΔE) calculated for freeze-dried vegetables indicates drying influence on colour changes (Figure 2). Freeze-dried vegetables obtained ΔE in the range of 16.5–27.1 units. The highest colour changes were observed for potato, and only for this sample differences were statistically significant in comparison to the other vegetables. The colour of potatoes is a very important criterion strictly related to consumer perception and acceptance [48]. Pedreschi et al. [49] argue that for potato colour change is mainly due to the Maillard reaction, which depends on the amino acids, proteins and content of reducing sugars at the sample surface, which can be sensitive for the temperature and time of drying. Cooking step before freeze-drying leads to a Maillard reaction, and characteristic golden brown zones may be achieved [8]. Such pre-treatment before freeze-drying was used for potato and yellow bean. Pedreschi et al. [49] for freeze-dried potato chips obtained ΔE parameter at the level about 13, but as reference sample raw potato was used.

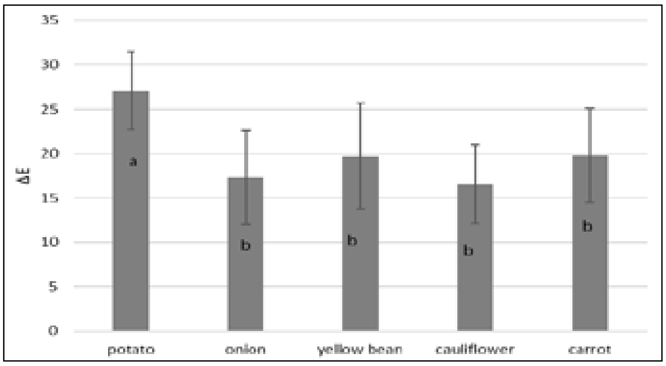


Fig. 2. The absolute colour difference of freeze-dried vegetable waste. Value are mean (n=2). The means followed with the same letter (abcd) are not significantly different according to ANOVA and Tukey's multiple comparison tests.

Rys. 2. Bezwzględna różnica barwy liofilizowanych odpadów warzywnych. Średnie (n=2) opisane takimi samymi literami (abcd) nie różnią się znacząco, według testów wielokrotnych porównań ANOVA i Tukeya.

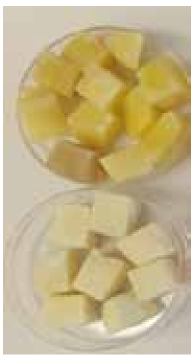
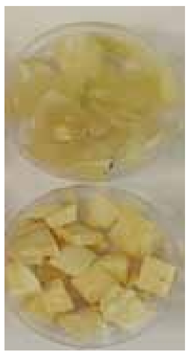
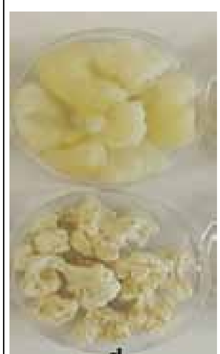
Source: Own study

Źródło: Opracowanie własne

Mokrzycki & Tatol [39] indicated that when the value of ΔE is below 2.0, trained observers would notice the difference, while when this values is over 3.5, a clear difference in colour is noticed even by average observers. For all freeze-dried vegetables this parameter was above 3.5, so differences in comparison to thawed samples are visible for average observers. It may be connected with the highest increase of potato lightness coefficient after freeze-drying (Table 2). It was also observed on photos made for thawed and freeze-dried samples. Statistically significant increase of lightness coefficient (L*) was observed for all vegetables as an effect of porosity increase (not presented in this publication) in freeze-dried samples. Structure changes during drying process may influence on perception of colour of dried products which may be different from that of raw vegetables [33]. Colour coefficients value obtained for freeze-dried carrot are lower than presented by Reyes et al. [54]. Ren et al. [53] showed that fresh onions were characterized by L* coefficient at 74.24 units and after freeze-drying this parameter increased to the range of 80.8–93.74 units, but investigations were conducted for samples after pre-treatment as blanching and ultrasounds, which could influence on this index. Also freezing and next thawing could caused that onion obtained lower lightness coefficient value than in Ren et al. [53] research. Negi & Roy [41] confirmed such a statement for dehydrated carrots,

Table 2. Photos and colour coefficients of thaved and freeze-dried vegetable waste

Tabela 2. Zdjęcia i współczynniki barwy rozmrożonych i liofilizowanych odpadów warzywnych

Colour coefficient	Vegetable									
	Potato		onion		yellow bean		cauliflower		carrot	
	thaved	freeze-dried	thaved	freeze-dried	thaved	freeze-dried	thaved	freeze-dried	thaved	freeze-dried
Lightness coefficient (L*)	[a]52.26 ±2.04	[b]77.72 ±4.49	[a]46.39 ±1.54	[b]60.77 ±6.50	[a]50.08 ±4.38	[b]67.72 ±6.76	[a]55.47 ±2.59	[b]71.15 ±4.47	[a]34.28 ±2.72	[b]53.65 ±5.76
Red colour coefficient (a*)	[a]-1.75 ±0.54	[a]-2.14 ±0.48	[a]-3.92 ±0.21	[b]0.33 ±1.18	[a]-5.40 ±0.46	[b]-2.27 ±1.17	[a]-3.27 ±0.20	[b]-1.80 ±0.24	[a]25.43 ±2.75	[a]23.75 ±1.29
Yellow colour coefficient (b*)	[a]23.86 ±2.31	[b]14.70 ±0.83	[a]15.61 ±1.52	[b]23.10 ±2.07	[a]19.74 ±1.92	[b]27.00 ±2.59	[a]9.00 ±1.78	[b]13.88 ±0.82	[a]33.57 ±3.33	[a]32.64 ±2.84
Photos of thawed and freeze-dried samples										

Abbreviations: Value are mean (n=10) ± standard deviation (sd) ($P < 0.05$). The means with the same letter ([abcd]) in the lines are not significantly different according to ANOVA and Tukey's multiple comparison tests conducted to comparison between thawed and freeze-dried samples.

Oznaczenia: Wartości to średnia (n=10) ± odchylenie standardowe (sd) ($P < 0,05$). Średnie z takimi samymi literami ([ab]) w wierszach, nie różnią się znacząco, zgodnie z testami wielokrotnych porównań ANOVA i Tukeya, przeprowadzonymi w celu porównania między próbkami rozmrożonymi i liofilizowanymi.

Source: Own study

Źródło: Opracowanie własne

which quality does not only depend on the drying method and conditions, but also on the other operations before and after drying. Increase of red (a*) and yellow (b*) colour coefficients for most of investigated vegetables may be connected with formation of colour compounds occured as an effect of nonenzymatic browning during drying [53, 58].

The thermal pre-treatment as blanching, boiling or freezing may reduce antioxidant activity and total phenolic content of vegetables [57]. Maskan [36] indicated that colourless polyphenols as an effect of enzymatic browning may change colour of vegetable during eg. drying process. The lack of oxygen access and a lower freeze-drying temperature may contribute to a better preservation of the quality indicators of the dried material. Less damage to the permeability of cell membranes is also important, since water is removed from the material by the gradual movement of the ice front from the surface to the interior [18].

In most cases of freeze-dried vegetables significant decrease of total polyphenol content (TPC) was observed from 15 to 59% (Figure 3). Only for carrot increase of investigated parameter after freeze-drying was observed (83%), while Witrowa-Rajchert et al. [61] showed for carrot with purple roots after the freeze-drying of material frozen at temperature of -20°C an almost 10% reduction of polyphenol content. Ren et al. [53] indicated that the yellow colour coefficient [b*] was correlated to total polyphenol content of hot-air dried samples, but such correlation of the colour coordinates with the bioactive compounds was not shown in freeze-drying. For freeze-dried onion Ren et al. [53] obtained TPC on the level of 9.21±0.82 of gallic acid equivalents per dry weight. Fabisiak et al. [18] indicated that losses of polyphenols can be contributed with the presence of polyphenol oxidase, which participates in oxidation substances containing polyphenolic compounds. The optimal thermal operation for this enzyme is temperature 40°C. Freeze-drying process was conducted in the temperature of heating shelves 30°C, what could influence on polyphenol content reduction.

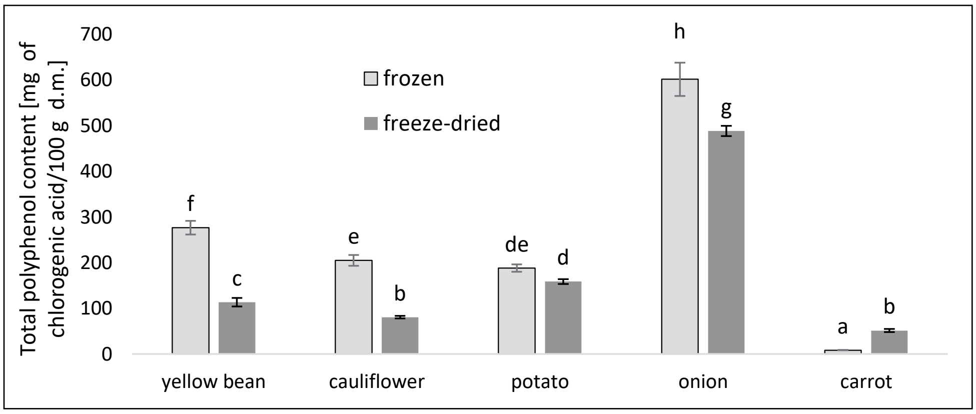


Fig. 3. Total polyphenol content of freeze-dried vegetable waste Value are mean (n=2). The means followed by same letter (abcd) are not significantly different according to ANOVA and Tukey's multiple comparison tests.

Rys. 3. Całkowita zawartość polifenoli w liofilizowanych odpadach warzywnych. Średnie (n=2) opisane takimi samymi literami (abcd), nie różnią się znacząco według testów wielokrotnych porównań ANOVA i Tukeya.

Source: Own study

Źródło: Opracowanie własne

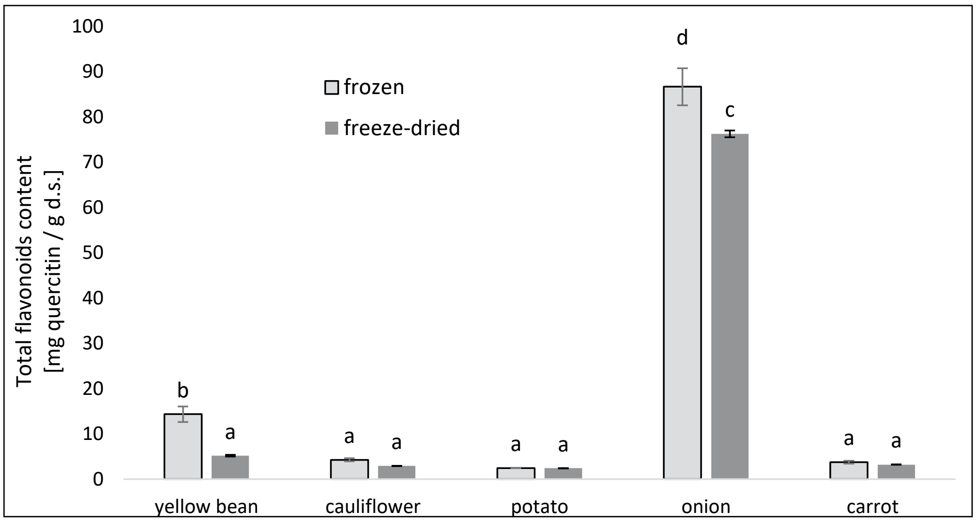


Fig. 4. Total flavonoids content of freeze-dried vegetable waste. Value are mean (n=2). The means followed by same letter (abcd) are not significantly different according to ANOVA and Tukey's multiple comparison tests.

Rys. 4. Całkowita zawartość flawonoidów w liofilizowanych odpadach warzywnych. Średnie (n=2) opisane takimi samymi literami (abcd), nie różnią się znacząco według testów wielokrotnych porównań ANOVA i Tukeya.

Source: Own study

Źródło: Opracowanie własne

It was shown that freeze-drying proces decreased total flavonoid content (TFC) of freeze-dried vegetables, but only for yellow bean and onion differences were statistically significant (Figure 4). It was also indicated that for cauliflower, potato and carrot investigated parameter was on the level below 5 mg quercetin/g d.s., for yellow bean thawed and freeze-dried, respectively, 14 and 5 mg quercetin/g d.s., whereas for onion 87 and 76 mg quercetin/g d.s. Ren et al. [53] indicated that TFC of freeze-dried onion was on the level 4,10±0,08 mg of quercetin equivalents/g d.s.

It was shown that freeze-dried vegetables were differ in sugars content (Figure 5). In freeze-dried onion and carrot total sugar content was the highest ~60±1%. Freeze-drying process decreased

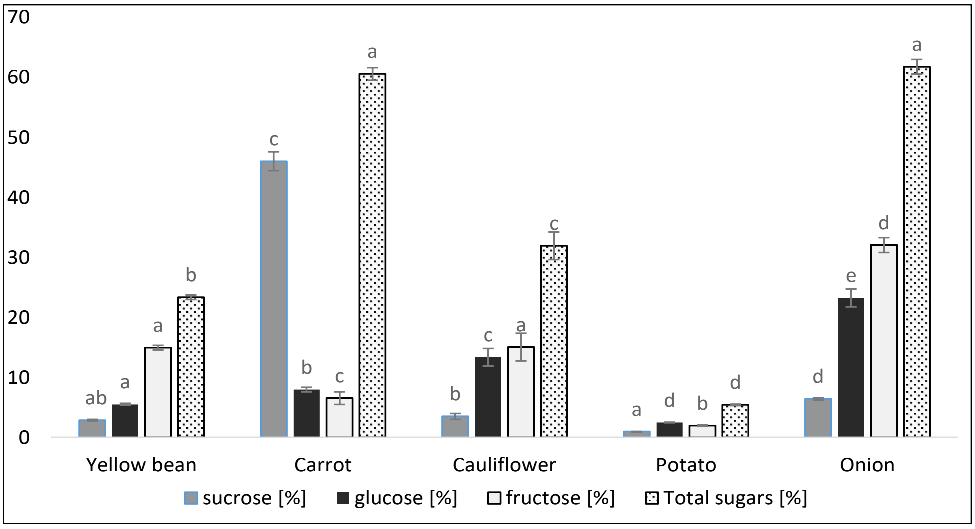


Fig. 5. Sugars content in freeze-dried vegetable waste. Value are mean (n=2). The means followed by same letter (abcde) are not significantly different according to ANOVA and Tukey's multiple comparison tests.

Rys. 5. Zawartość cukrów w liofilizowanych odpadach warzywnych. Średnie (n=2) opisane takimi samymi literami (abcde), nie różnią się znacząco według testów wielokrotnych porównań ANOVA i Tukeya.

Source: Own study

Źródło: Opracowanie własne

reducing sugars content. For carrot, glucose and fructose content was equal 8.25±0.37% and 6.68±0.16% respectively, while Leong & Oey [30] shown that for fresh carrot, reducing sugars were on 15±0.43%. For freeze-dried potato reducing sugars content were on the level 2.48±0.04% and 1.96±0.15% respectively (glucose and fructose), while Lati et al. [29] shown that fresh potato obtained reducing sugars 1.6%. Differences may be connected with different variety of vegetables.

It was shown that freeze-dried vegetables were differ in internal structure (Figure 6). Freeze-dried onion and yellow bean were characterised in porous structure, but for onion structure was more uniform, while for yellow bean closer to the center of the sample bigger open pores were shown. For potato and carrot structure was more closed and uniform. Similar structure for carrot obtained Reyes et al. [54]. The structure of cauliflower was delicate, porous, with small pores and present bigger open spaces. Similar structure obtained Cui et al. [15] for freeze-dried carrot. Bhatta et al. [5] argue that if the freezing step is properly done at adequate low temperatures (without ice crystals destroying/weakening the cell walls), cellular materials are better prepared to save structure during the freeze-drying. Mechanical properties and structural strength may be more important in keeping product integrity than glass transition temperature.

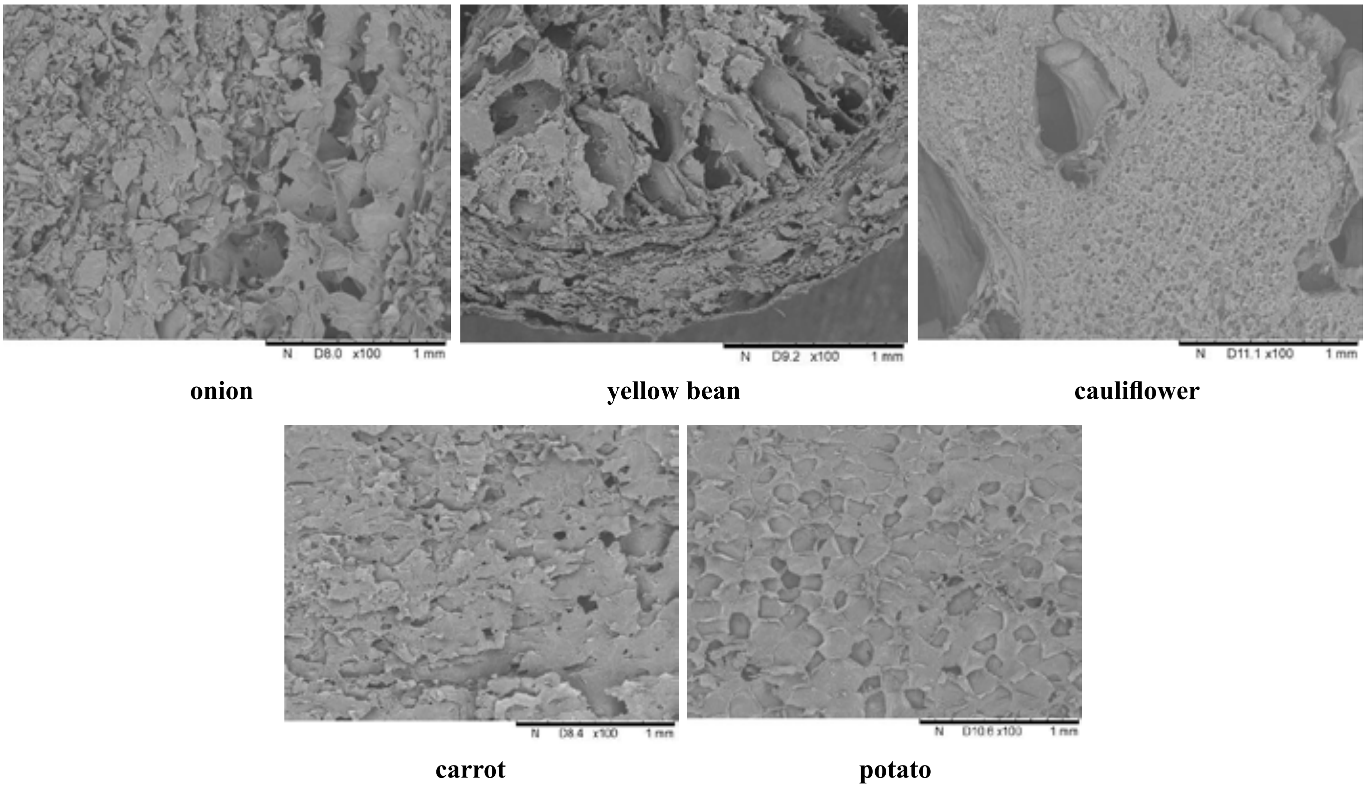


Fig. 6. The structure of freeze-dried vegetable waste. Magnification 100x.

Rys. 6. Struktura liofilizowanych odpadów warzywnych. Powiększenie 100x.

Source: Own study

Źródło: Opracowanie własne

The dried food peaces should have a short preparation time ~5–15 min [6]. The degree of damage caused by dehydration determines the extent of water binding and holding. Rehydydration should be fast and may be respected as the method to measure the degree of changes in the material in the drying process [62], but even if the rehydration was run for a very long time dehydrated material does not completely return to its form before drying, because irreversible changes in the structure of a plant tissue occure [61].

For most of freeze-dried vegetables rehydration process characterized a gradual water content increase, and after 24 hours stabilization was observed while the intracellular spaces of vegetables became saturated (Figure 7). All samples were rehydrated in high degree, almost threefold increase in water content was observed. Freeze drying removes water through sublimation, keeping the shape of the raw material very well, creating a porous structure, which increases the rehydration degree and rate of rehydration [26]. The exception was the sample of freeze-dried potato, which was characterized by an almost 4 times higher increase in water content. For potato, water was rapidly absorbed from the beginning of the process. Futhermore, Ghosh & Gangopadhyay [22] obtained high rehydration capacity for freeze-dried potato. It may be connected with presence of gelatinised starch in dried potato, which strongly absorbed water. Witrowa-Rajchert & Lewicki [62] argue that during rehydration water was absorbed by gelatinised starch and swelling of the material was observed from the beginning of rehydration process. The dried starch with numerous amorphous domains became well hydrated. Lower rehydration ratio for potatos obtained Wang et al. [59], but they conducted rehydration for freeze-dried potato chips, not cubes.

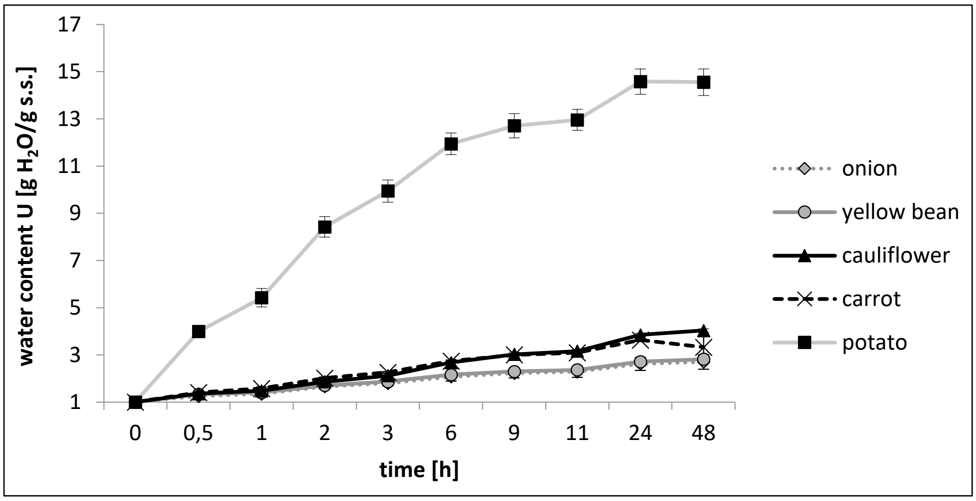


Fig. 7. Rehydration properties of freeze-dried vegetable waste.
Rys. 7. Właściwości rehydracyjne liofilizowanych odpadów warzywnych.
Source: Own study
Źródło: Opracowanie własne

The quality characteristics for dried foods may be predicted by moisture sorption isotherm determination [63]. Very often the BET (Brunauer-Emmett-Teller) equation is used to describe multilayer sorption isotherms, but the range of water activity is limited to 0.05–0.35 [1], so more often others modified kinetic and empirical models are used (Table 3). On the sorption isotherm models the type and composition of foods have influence [2]. Regardless of the vegetable type, freeze-dried samples exhibited a sigmoidal sorption curve as a function of water activity (Figure 8) and were classified as type II based on the classification of Brunauer, Emmett Teller [7].

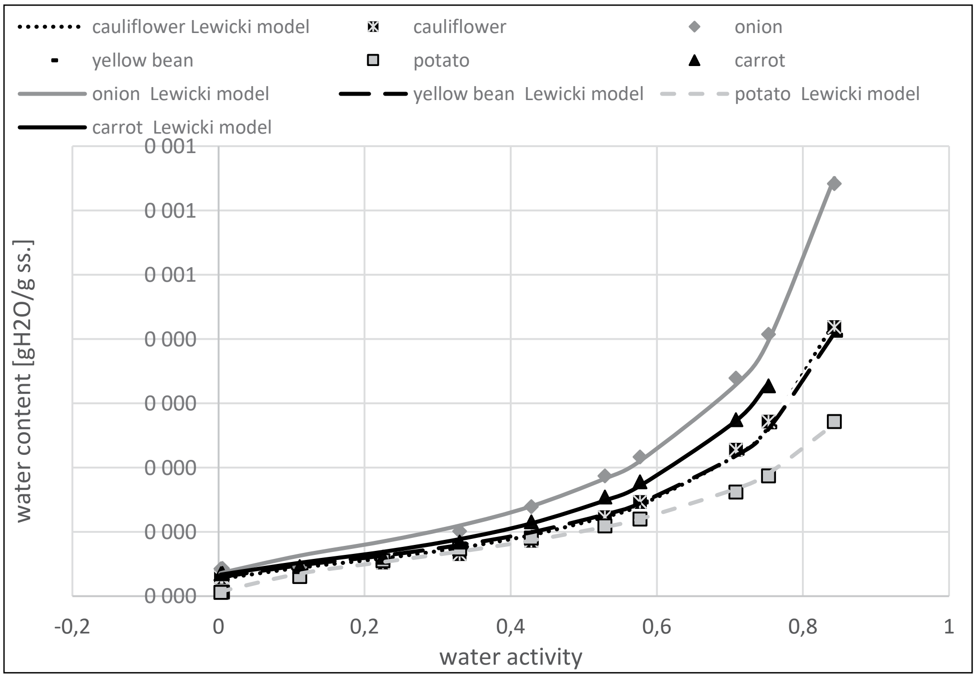


Fig. 8. Water vapour adsorption isotherms for freeze-dried vegetable waste.
Rys. 8. Izotermy sorpcji pary wodnej liofilizowanych odpadów warzywnych.
Source: Own study
Źródło: Opracowanie własne

Oh, Lee & Hong [45] obtained the same type of sorption isotherms for sweet potato. This is also in agreement with results for potato investigated by McMinn & Magee [37]. Four models were tested to describe the sorption equilibrium isotherms of freeze-dried vegetables and Lewicki's model was chosen as the best on the basis of fitting parameters (Table 3).

Table 3. Parameters of fitting water vapor sorption models for freeze-dried vegetable waste

Tabela 3. Parametry dopasowania modeli sorpcji pary wodnej dla liofilizowanych odpadów warzywnych

Cauliflower				
Model Coefficient	GAB	Lewicki	Peleg	Oswin
RSS	0.002	0.0005	0.0005	0.002
MRE	23.26	8.22	7.50	23.16
SEE	0.044	0.023	0.023	0.043
R^2	0.987	0.997	0.996	0.988
Onion				
Model Coefficient	GAB	Lewicki	Peleg	Oswin
RSS	0.004	0.002	0.003	0.003
MRE	21.029	12.618	15.55	20.76
SEE	0.060	0.038	0.053	0.059
R^2	0.990	0.996	0.992	0.991
Yellow bean				
Model Coefficient	GAB	Lewicki	Peleg	Oswin
RSS	0.002	0.0001	0.001	0.002
MRE	20.223	4.334	9.603	22.032
SEE	0.042	0.012	0.027	0.045
R^2	0.995	0.999	0.995	0.986
Potato				
Model Coefficient	GAB	Lewicki	Peleg	Oswin
RSS	0.0001	0.0001	2.8708E-05	0.0002
MRE	14.704	6.168	11.283	7.602
SEE	0.012	0.011	0.005	0.014
R^2	0.998	0.998	0.994	0.997
Carrot				
Model Coefficient	GAB	Lewicki	Peleg	Oswin
RSS	0.002	0.0002	0.0001	0.002
MRE	22.635	5.568	3.302	22.579
SEE	0.048	0.015	0.012	0.048
R^2	0.976	0.998	0.999	0.976

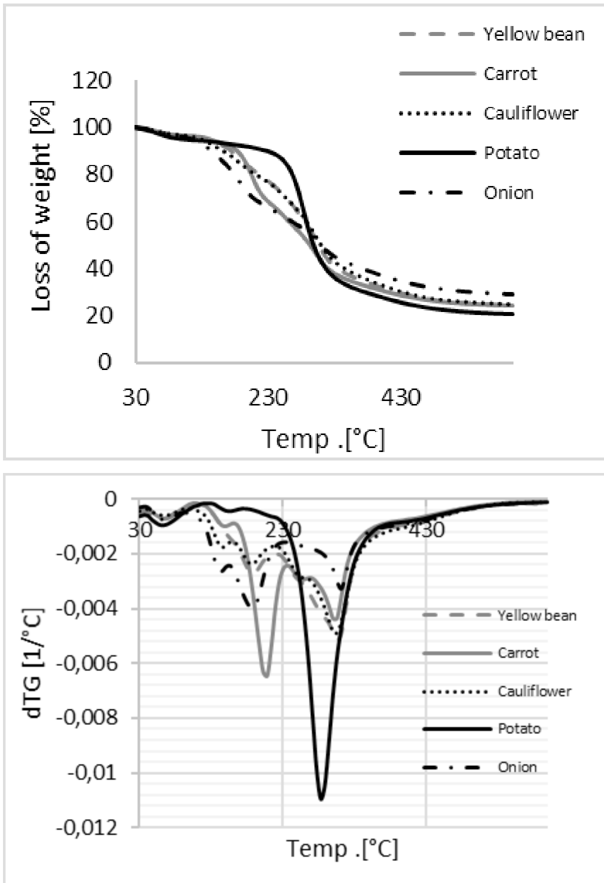
Abbreviations: Designations in methodology of determination of water vapour adsorption isotherms.

Oznaczenia: Oznaczenia w metodyce wyznaczania izoterm adsorpcji pary wodnej.

Source: Own study

Źródło: Opracowanie własne

The lowest sorption properties obtained from freeze-dried potato, while the highest cauliflower and onion (Figure 8). The obtained water sorption isotherms of the freeze-dried vegetables are typical of products with e.g. high sugar content which absorbs a relatively small volume of water at low water activity and a larger volume of it when the water activity is higher [46]. As expected, the obtained equilibrium moisture content values show an increase with increasing water activity. The freeze-dried vegetables analysed in this work show a sharp increase in sorption capacity above 0.529 water activities, which is typical for high-sugar fruit materials [27]. Freeze-dried vegetable also contain sugars what may influence on such course of sorption curves. The chemical composition, the type of components and the structure of the investigated samples may influence differences in the moisture content [11].



a)

b)

Fig. 9. TGA (a) and DTG (b) curves for freeze-dried vegetable waste.

Rys. 9. Krzywe TGA (a) i DTG (b) liofilizowanych odpadów warzywnych.

Source: Own study

Źródło: Opracowanie własne

Using thermogravimetry (TGA), the loss of weight (Δm) during sample heating can be recorded and the changes presented on the TGA curve (Δm = ∫ (T)). The rate of weight change (dm / dt) is also recorded, yielding a differential thermogravimetric curve (DTG): as a function of temperature (dm / dt = ∫ (T)) [20]. In the course of the TGA (Figure 9a) and DTG (Figure 9b) curves, three characteristic stages can be determined. In most cases for freeze-dried vegetables the most intensive loss of weight (about 60%) was observed in the temperature range of 130-440°C (Figure 9a). The TGA curves of freeze-dried yellow-bean show three general regions of weight loss (30–139.25°C, 139.25–334.75°C, and 334.75–599.25°C). For freeze-dried carrot regions, those regions were in the temperature range of (30–122°C, 122–334.75°C, 334.75–599.25°C), for freeze-dried cauliflower (30–122°C, 122–346.25°C, 346.25–599.25°C), freeze-dried potato (30–173.75°C, 173.75–352°C, 352–599.25°C) and freeze-dried onion (30–122°C, 122–426°C, 426–599.25°C). For potato at a temperature of 283°C the elongatd peak was observed on DTG curve (Figure 9b), which may indicate a strong gas adsorption of decomposition products on the surface of the newly formed phase [55].

SUMMARY

The article assessed whether the vegetable waste from freezing process may be used as a full quality product for freeze-drying. Most of investigated vegetables obtained similar drying curves, exept cauliflower which drying rate was the lowest, but for all samples water activity and content was low, what indicates that samples are microbiologically safe. After freeze-drying colour of vegetables significantly changed in comparison to thawed samples. In most cases a significant decrease in total polyphenol content was observed and only for carrot an increase in the investigated parameter was shown after freeze-drying. Freeze-drying process decreased total flavonoid content, but in most cases insignificantly.

Freeze-dried vegetables differed in internal structure. For onion, yellow bean and cauliflower structure was porous, more delicate, whereas for potato and carrot, it was more closed and uniform. Freeze-dried samples obtained a sigmoidal sorption curves, classified as type II and described by Lewicki's model. The lowest sorption properties obtained freeze-dried potato, while the highest cauliflower and onion probably as an effect of structure. Rehydration process of freeze-dried vegetables indicated gradual water content increase, and after 24 h stabilization was observed. Freeze-dried potatoes was characterized by an increase in water content almost four times higher as an effect of high starch content.

PODSUMOWANIE

W artykule oceniono, czy odpady warzywne z procesu zamrażania mogą być wykorzystane jako pełnowartościowy produkt do liofilizacji. Większość badanych warzyw uzyskała podobne krzywe suszenia, z wyjątkiem kalafiora, którego szybkość suszenia była najniższa, ale dla wszystkich próbek zarówno aktywność jak i zawartość wody była niska, co wskazuje, że próbki są bezpieczne mikrobiologicznie. Po liofilizacji barwa warzyw istotnie zmieniła się w porównaniu z próbkami rozmrożonymi. W większości przypadków zaobserwowano znaczne obniżenie zawartości polifenoli ogółem i tylko w przypadku marchwi wykazano wzrost badanego parametru po liofilizacji. Proces liofilizacji obniżył całkowitą zawartość flawonoidów, ale w większości przypadków tylko nieznacznie.

Warzywa liofilizowane różniły się budową wewnętrzną. W przypadku cebuli, fasoli żółtej i kalafiora struktura była porowata, delikatniejsza, natomiast w przypadku ziemniaka i marchwi bardziej zwarta i jednolita. Próbki liofilizowane uzyskały sigmoidalne krzywe sorpcji, sklasyfikowane jako typ II i opisane modelem Lewickiego. Najniższe właściwości sorpcyjne uzyskał ziemniak liofilizowany, natomiast najwyższe kalafior i cebula – prawdopodobnie był to efekt wpływu struktury. Proces uwadniania warzyw liofilizowanych wykazał stopniowy wzrost zawartości wody, a po 24 godzinach nastąpiła stabilizacja. Liofilizowane ziemniaki charakteryzowały się prawie 4-krotnie większym wzrostem zawartości wody w wyniku wysokiej zawartości skrobi.

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