No. 131/24, 48–58
ISSN 2657-6988 (online)
ISSN 2657-5841 (printed)
DOI: 10.26408/131.04

Submitted: 15.04.2024
Accepted: 19.05.2024
Published: 30.09.2024

CHARACTERISTICS OF THE SORPTION PROPERTIES OF DRIED HEMP

Julia Ziajka
Gdynia Maritime University, Morska 81-87, 81-225 Gdynia, Poland,
ORCID 0009-0008-8318-9617, e-mail: j.ziajka@sd.umg.edu.pl

Abstract: The study is aimed at assessing the sorption properties of dried hemp (Cannabis sativa L.), which determines the storage stability of the raw material. The statistical and desiccator method was used, with the BET equation used to mathematically interpret the course of the water vapor sorption isotherms. Based on the study, it was found that product IV had the best sorption properties - dried hemp with the lowest degree of fragmentation and non-decarboxylated. Product IV was characterized by the highest water absorption capacity and the highest values of the BET equation parameters (6.13 g/100 g d. m. for the capacity of the monomolecular layer and 215.3 m^2/g for the specific sorption surface).

Keywords: fibre hemp (Cannabis sativa), water activity, sorption isotherm, sorption properties.

1. INTRODUCTION

Industrial hemp (Cannabis sativa L.) is an annual plant in the hemp family. Naturally found in areas of Asia, it is now crop-grown worldwide. It gained popularity due to its high fibre content, which is used to make textiles. Currently, industrial hemp is used as a raw material in the pharmaceutical and cosmetic industries due to the presence of 61 chemical compounds known as cannabinoids [Mańkowska et al. 2015]. Cannabinoids are compounds that can alleviate the feelings of pain, reduce stress, eliminate the occurrence of anxiety, and relax the body [Chang et al. 2021]. Terpenes extracted from hemp are valuable additives in food and cosmetics as they have anti-inflammatory, anticancer, and antioxidant properties. The combination of terpenes with cannabinoids improves pain treatment, inflammation, depression, anxiety, and bacterial infections [Chang et al. 2021]. Hemp products, including dried hemp, have antiseptic properties; therefore, they can be used as medicines during food poisoning, against nosocomial infections and they are effective against antibiotic-resistant bacterial strains [Nissen et al. 2010].

Additionally, they are used as insecticides [Bedini et al. 2016; Górski, Sobieralski and Siwulski 2016], fungicides [Wielgusz, Heller and Byczyńska 2012], and herbicides [Synowiec et al. 2016].

Hemp products are used for plant disease and pest preventatives [Górski, Sobieralski and Siwulski 2016]. However, the quality of dried hemp, and thus all the beneficial properties of hemp products, may deteriorate during transport. From a medical point of view, the high quality of the raw material (dried hemp) is crucial for the effective levelling of disease symptoms, the effectiveness of treatment, and, from an industrial point of view, the high quality of dried hemp is an essential parameter for the finished product. It is therefore essential to understand the behaviour of dried hemp during storage and transport.

Determining the sorption properties makes it possible to characterise the behaviour of dried hemp during the above-mentioned situations under different environmental conditions. Therefore, it is important to make the best use of the knowledge gained to minimise the quality lost from the dried product, the deterioration of the active substances it contains [Challa and Kiran 2020], as well as to increase the stability of the finished products [Chasiotis et al. 2022].

The study aimed to characterise the sorptive properties of dried hemp, which determines the storage stability of the product, and to understand the importance of the sorption properties as quality determining factors. The behaviour of the products in environments with different humidities, such as absorption and desorption, affects the physicochemical and organoleptic properties, resulting in a reduction in product quality. It can also decrease the product's safety and result in its rotting. The results of this study can be used as grounds for further research as it contains information necessary for the additional use of the health-promoting properties of dried hemp by the cosmetics and pharmaceutical industries, as well as to improve the conditions of the raw material transport.

2. MATERIAL AND METHODS

The research material was dried hemp sourced from different hemp oil manufacturers. The raw material samples were characterised by different sources and origins, different degrees of fragmentation, and cannabinoid profiles. Products I to III were decarboxylated dried hemp (subjected to higher temperatures to convert the acidic forms of cannabinoids into neutral forms), while product IV was non-decarboxylated (raw product). Product I was CBD dried hemp imported from Croatia, product II was CBD dried hemp imported from Lithuania, product III was CBD dried hemp imported from Italy, and product IV was raw dried hemp imported from Lithuania. The chemical composition of the dried hemp was similar, with 100 g of dried hemp containing, approximately, 28 g of fat, 31 g of carbohydrates, 23 g of fibre, and 30 g of protein. The differences were observed in the chemical composition, yet they were not significant. Products I to III contained 0.1–0.2% of tetrahydrocannabinol and approximately 12% of cannabidiols. Product IV (non-decarboxylated raw product) contained approximately less than 1% of

tetrahydrocannabinol acid and less than 15% of cannabidiolic acid. Unfortunately, further analysis of the chemical composition was not performed.

The initial water content of samples I–IV was determined using the thermal drying method at a temperature of 105°C in an SML dryer. Samples (3 for each product) of approximately 2 g were placed in glass weighing containers and then in the dryer. After the drying process, the samples were placed in a desiccator and brought to room temperature. The initial water content (X_p) was calculated using equation 1:

$$X_p = \frac{m_1 - m_2}{m_2 - m} \cdot 100 \quad (1)$$

where:

X_p – initial water content [%],
m – mass of weighing container [g],
m_1 – mass of weighing container with the sample BEFORE drying [g],
m_2 – mass of weighing container with the sample AFTER drying [g].

Water activity was measured using an AquaLab Series 3 model TE (AquaLab Series 3 model TE, Decagon Devices, Inc, Ullman USA), characterised by an accuracy of ±0.003. Each sample was placed in a plastic cuvette and then sealed. The measurement using the AquaLab involved determining the thermodynamic equilibrium of the relative air humidity in the laboratory cell using a dew point sensor, which was equivalent to determining the water activity of the tested samples. For each product, 3 reruns were made.

Table 1. Water activity of saturated salt solutions

Salt	Water activity at 293 K (20°C)
NaOH	0.07
LiCl	0.11
CH_3COOH	0.22
$MgCl_2$	0.33
K_2CO_3	0.43
$Mg(NO_3)_2$	0.55
$NaNO_2$	0.69
NaCl	0.76
$(NH_4)_2SO_4$	0.81
$BaCl_2$	0.92

Source: [Tyszkiewicz 1987].

The sorption isotherms were determined using the static-eccentric method, in the water activity range $a_w = 0.07/0.92$. The equilibrium establishment time of the system was 80 days. Samples (3 for each product) were placed in hygrostats containing sature salt solutions, see Table 1. The test sample was approximately 2 g of the tested product. The samples were placed in a weighed measuring vessel with a diameter of 15 mm. Hygrostats with a water activity higher that 0.69 contained crystalline thymol to protect the tested products from microbiological contamination. Based on the initial weight of the product and the increments or decrements in water content, the equilibrium water content was calculated and the sorption isotherms were plotted.

In order to mathematically describe the empirically determined sorption isotherms, the Brunauer, Emmet, and Tellet (BET) equation was transformed, see equation 2.

$$V = \frac{V_m C a_w}{(1-a_w)[1+(C-1)a_w]} \tag{2}$$

where:

a_w – water activity [-],
V – equilibrium water content [g H_2O/100 g d.m.],
V_m – monolayer capacity [g H_2O/100 g d.m.],
C – energy constant [Ocieczek and Skotnicka 2017; Paderewski 1999].

In the next research stage, knowing the volume of water vapor adsorbed at a temperature below the boiling point and the so-called water settling area, the specific surface area of the adsorbent was calculated based on equation 3.

$$a_{sp} = \omega \frac{V_m}{M} N \tag{3}$$

where:

a_{sp} – sorption specific surface area [m^2 /g d.m.],
v_m – monolayer capacity [g /100 g d.m.],
N – Avogadro number [$6{,}023 \cdot 10^{23}$ molecules/mol],
M – water molecular mass [18,015 g/mol],
ω – water setting surface, [[$1{,}05 \cdot 10^{-19}$ m^2/molecule] [Paderewski 1999].

The results were processed statistically using Statistica 13.3. The following methods were used to test statistical hypotheses: one-way analysis of variance (ANOVA): parametric Fisher-Snedecor F test, combined with post-hoc analysis used the least significant difference (LSD) test. Additionally, basic statistical measures, such as arithmetic mean and standard deviation, were calculated.

3. ANALYSIS OF THE RESULTS

Table 2 presents the water content of the dried hemp samples.

Table 2. Water content in individual samples of dried hemp

Product	Water content [g/100 g d.m.]	
	x	SD
I (Croatia)	9.72[a]	0.0003
II (Lithuania)	10.58[c]	0.0005
III (Italy)	14.54[d]	0.0003
IV (Lithuania RAW)	10.45	0.0080

X – mean, SD – standard deviation, n = 3. Different letter symbols next to the mean values indicate significant differences between the means in the LSD test, $p<0.05$.

Source: own study.

The study found that product III had the highest water content, at 14.54 g/100 g d.m., see Table 2. The significant difference between the water contents of the products may indicate improper storage or irregularities that occurred during the drying process. The lowest water content was obtained for product I at 9.72 g/100 g d.m. For products II and IV, the values oscillated at a similar level, 10.58 g/100 g d.m. and 10.45 g/100 g d.m., respectively.

Based on the literature analysis, the obtained results for dried hemp were at a similar level to the obtained data: 10.90 g/100 g d.m. for lemon balm [Argyropoulos, Alex and Muller 2011] and 7.19 g/100 g d.m. and 8.99 g/100 g d.m. for marjoram [Ruszkowska and Newerli-Guz 2017]. The percentage water content of dried hemp should not exceed 15% by weight of the product [https://vapomaniak.pl/ile-suszu-jest-w-suszu-jak-wybierac-susz-konopny/].

The percentage water content in the tested samples of dried hemp varied around 9–13%. The limit of 15% water content was not exceeded, which indicates that the products were protected against the development of bacterial microflora. At the same time, the parameters obtained fluctuated around 10–11%, which, according to Odoula, is the best value for dried hemp [Odoula et al. 2023]. Based on different tests (such as ANOVA and LSD), statistically significant differences were found in the water content between all hemp samples.

Table 3 shows the water content of samples I–IV.

Table 3. Water activity in individual samples of dried hemp

Product	Water activity [-]	
	x	SD
I (Croatia)	0.6134^{b}	0.005
II (Lithuania)	0.6313^{c}	0.004
III (Italy)	0.7503^{d}	0.007
IV (Lithuania RAW)	0.5387^{a}	0.006

x – mean, SD – standard deviation, n = 3. The different letter symbols next to the mean value indicate significant differences between the means in the LSD test, $p<0.05$

Source: own study.

It was observed that the distribution was normal for p-values<0.05.

Product III had the highest water activity, with a value of $a_w = 0.7503$ (Tab. 3). The lowest water activity for the given dried hemp samples was $a_w = 0.5387$ (Tab. 3) for product IV. The values obtained for products I and II were very similar, at $a_w = 0.6134$ and $a_w = 0.6313$, respectively.

Given the small number of sources describing the water activity of dried hemp, the results could not be compared with other literature works [Oduola, Lutra and Griffiths 2022]. Taking into account the type of material and the intended use of the hemp dried, the water activity should be $0.55< a_w <0.65$ to prevent the growth of microbial flora [Carter 2021]. Trials I and II were within the specified range (Tab. 3). Product III exceeded the permissible limits of the value range – $a_w = 0.7503$, see Table 3.

In addition, the obtained dried hemp water activity values coincide with the dried hemp water activity proposed by Oduola as the water activity to extend the shelf life without quality loss [Oduola, Lutra and Griffiths 2022]. Based on the tests carried out (such as ANOVA and LSD), statistically significant differences were found in the water content between all dried hemps.

Figure 1 shows the course of the sorption isotherms of the hemp dried samples tested (I–IV) in the water activity range $a_w = 0.07–0.92$.

The sorption isotherms were classified as type II isotherms, according to Brunauer's classification [Brunauer, Emmet and Teller 1938]. It was noted that the desorption process for products I and II occurred in an environment where $a_w = 0.07–0.55$, for product III in an environment where $a_w = 0.07–0.75$, and for product IV in an environment where $a_w = 0.07–0.44$. The adsorption process occurred in aqueous environments with a higher water activity. The dried hemp samples absorbed water, which can lead to microbial growth, as well as degradation of the active constituents-cannabinoids.

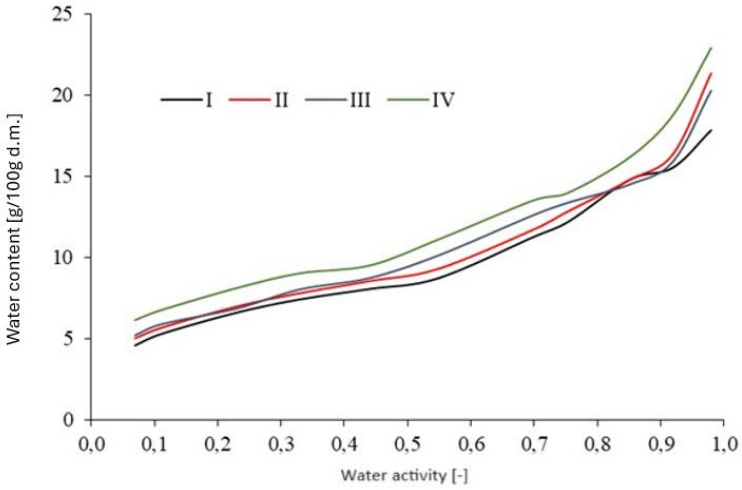

Fig. 1. Sorption isotherm determined for the tested dried hemp I-IV, in the range of water activity a_w = 0.07–0.92 over an 80 day period

Source: own study.

The curves obtained have a sigmoidal shape and can be compared to the isotherms obtained by Argyropoulos [Argyropoulos, Alex and Muller 2011] for lemon balm. The dried hemp and lemon balm herbs showed relatively small amounts of water at low relative humidity conditions. For example, the water content for lemon balm herb at a 40% relative humidity was approximately 8.52 g/100 g d.m. [Argyropoulos, Alex and Muller 2011], while for dried hemp at the same relative humidity, the result for sample II reached a very similar value, of about 8.53 g/100 g d.m. The results obtained are at a similar level to the values obtained by Oduola – about 8.5 g/100 g d.m. at a relative humidity of 40% [Oduola, Lutra and Griffiths 2022]. Based on the sorption isotherms of the dried hemp samples, the parameters of the BET equation were determined, see Table 4.

Table 4. Parameters of the BET equation

Product	v_m	c_e	R^2
I (Croatia)	5.13	77.08	0.9984
II (Lithuania)	5.37	114.56	0.9984
III (Italy)	5.46	124.99	0.9997
IV (Lithuania RAW)	6.13	289.80	0.9987

Source: own study.

It was found that the highest monolayer capacity, v_m, was characterised by product IV (Lithuania RAW) at 6.13 g/100 g d.m. (Tab. 4), while the lowest value was obtained for sample I at 5.13 g/100 g d.m. (Tab. 4). Based on the obtained values of the monolayer capacity, it can be assumed that product IV was characterised by high storage stability. Monolayer capacity is a significant parameter of product quality, and its value determines the amount of water that the product can absorb. This is determined by the number of available polar sites for water vapour and is influenced by the presence of ingredients rich in polar sites and their physical state [Ocieczek, Ruszkowska and Palich 2012]. The energy constant (c) is a parameter describing the difference between the enthalpy of desorption of the monolayer and the enthalpy of the liquid absorbent [Paderewski 1999]. The lowest value was obtained for product I at 77.08 and the highest for product IV at 289.8. These values indicate that a physical sorption process was taking place. The differences in values may be due to the degree of fineness of the products (product I had the highest degree of fineness). It is also possible that the decarboxylation process itself may have affected the sorption properties of the products. The test results for product IV (RAW-type dried imported from Lithuania) differed the most from those of the other products. This was the only product not subjected to the decarboxylation process.

Comparing the results with the literature data: v_m = 4.75 g/100 g d.m. for lemon balm [Argyropoulos, Alex and Muller 2011] and 5.22–5.86 g/100 g d.m. for marjoram [Ruszkowska and Newerli-Guz 2017], it was noted that the capacity of the dried hemp monolayer was at a similar level as for products of the same type.

Based on the parameter v_m for the individual dried samples, the specific surface area of sorption was determined (Tab. 5).

Table 5. Structural characteristics of the tested products estimated based on the parameters of the BET equation

.

Product	Specific surface area of sorption [m^2/g]
I (Croatia)	180.3
II (Lithuania)	188.6
III (Italy)	191.9
IV (Lithuania RAW)	215.3

Source:own study.

The highest value of sorption area was achieved by product IV, while the lowest value was achieved by product I. The values obtained for dried hemp samples were much higher than for other hemp products produced from the raw material, at 36.24 m^2/g for hemp plaster, 80.80 m^2/g for hemp mortar and 88.77 m^2/g for hemp wool [Collet et al. 2008]. This may be due to the intended use of the products, other processing and the fineness of the products.

4. CONCLUSIONS

1. The dried hemp sorption isotherms obtained during the study were classified as type II sorption isotherms, according to Brunauer's classification.
2. Product III (dried hemp CBD imported from Italy) had the highest water activity, while product IV (RAW dried hemp imported from Lithuania) had the lowest water activity. Their storage stability parameters did not show statistically significant differences, which may indicate the multivariate nature of the storage stability parameters of dried hemp.
3. Product IV (dried hemp RAW imported from Lithuania) had the smallest degree of fineness and better sorption properties.
4. Product IV (RAW-type dried hemp imported from Lithuania) had the highest monomolecular layer capacity, the largest specific sorption area, and the highest sorption isotherm, characterised by the longest storage life. Based on the results, product IV is the most valuable for producers.
5. The initial water content of the dried hemp determined its sorption properties. The best storage stability parameters were characterised by the product with the lowest water content (product I, dried CBD from Lithuania). This dried product reacted the least to changes in ambient humidity and had the smallest specific sorption area.
6. The parameters of the decarboxylation process (120°C for 45 minutes) destroyed the structure of dried hemp. Judging by the results of the research, the decarboxylation process (that is responsible for converting the acidic forms of cannabinoids into neutral forms and improving the medicinal properties) caused a change in the sorption properties of dried hemp. Although the chemical composition of dried products was not compared to fresh ones, it is possible that the denaturation of proteins and changes in the carbohydrates' structure could affect the sorption properties of dried hemp.
7. The information gained during the research will provide valuable information for further improvement of the processing and transport, allowing the preservation of the medicinal and nutritional properties of the raw material. The disadvantages include the lack of knowledge of the detailed chemical composition of dried hemp before and after the decarboxylation processes, which makes it impossible to precisely determine the impact of chemical compounds present in the raw material on its sorption properties. The advantage, however, is knowing the possible relationships between the decarboxylation process and the storage stability of the product, which can be confirmed in further research. If such a relationship exists, the process parameters can be manipulated to ensure the best product quality.

REFERENCES

Argyropoulos, D., Alex, R., Muller, J., 2011, *Equilibrium Moisture Contents of a Medicinal Herb (Melissa officinalis) and a Medicinal Mushroom (Lentinula edodes) Determined by Dynamic Vapour Sorption*, Procedia Food Science, vol. 1, pp. 165–172.

Bedini, S., Flamini, G., Cosci, F., Ascrizzi, R., Benelli, G., Conti, B., 2016, *Cannabis sativa and Humulus lupulus Essential Oils as Novel Control Tools Against the Invasive Mosquito Aedes albopictus and Fresh Water Snail Physella acuta*, Industrial Crops and Products, 2016, vol. 85, pp. 318–323.

Brunauer, S., Emmet, P.H., Teller, E., 1938, *Adsorption of Gases in Multilayer's*, Journal of the American Chemical Society, vol. 60, pp. 309–319.

Carter, B., 2021, *The Role of Water Activity in Cannabis Quality and Safety*, Cannabis Sciences,

Challa, R., Kiran, S., 2020, *Drying Kinetics and the Effects of Drying Methods on Quality (CBD, Terpenes, and Color) of Hemp (Cannabis sativa l.) Buds*, Dalhousie University Halifax, Nova Scotia, Canada, pp. 12–37.

Chang, C., Wongso, I., Putnam, D., Khir, R., Zhongli, P., 2021, *Effect of Hot Air and Infrared Drying on the Retention of Cannabidiol and Terpenes in Industrial Hemp (Cannabis sativa L.)*, Industrial Crops and Products, vol. 172.

Chiasiotis, V., Tsakirakis, A., Termentzi, A., Machera, K., Filios, A., 2022, *Drying and Quality Characteristics of Cannabis sativa L. Inflorescences under Constant and Time-Varying Convective Drying Temperature Schemes*, Thermal Science and Engineering Progress, vol. 28.

Collet, F., Bart, M., Serres, L., Miriel, J., 2008, *Porous Structure and Water Vapour Sorption of Hemp-Based Materials*, Construction and Building Materials, vol. 22, no. 6, pp. 1271–1280.

Górski, R., Sobieralski, K., Siwulski, M., 2016, *The Effect of Hemp Essential Oil on Mortality Aulacorthum solani Kalt. and Tetranychus urticae Koch.*, Ecological Chemistry Engineering, vol. 23, pp. 505–511.

https://vapomaniak.pl/ile-suszu-jest-w-suszu-jak-wybierac-susz-konopny/ [accessed 17-03-2024].

Mańkowska, G., Luwańska, A., Wielgus, K., Bocianowski, J., 2015, *Ocena zawartości kannabinoidów wybranych odmian konopi Cannabis sativa L*, Biuletyn Instytutu Hodowli i Aklimatyzacji Roślin, vol. 277, pp. 79–86.

Nissen, L., Zatta, A., Stefanini, I., Grandi, S., Sgorbati, B., Biavati, B., Monti, A., 2010, *Characterization and Antimicrobial Activity of Essential Oils of Industrial Hemp Varieties (Cannabis sativa L.)*, Fitoterapia, vol. 81, pp. 413–419.

Ocieczek, A., Ruszkowska, M., Palich, P. 2012, *Porównanie właściwości sorpcyjnych wybranych rodzajów skrobi*, Bromatologia i Chemia Toksykologiczna, vol. XIV, no. 3, pp. 1018–1023.

Ocieczek, A., Skotnicka, M., 2017, *Porównanie właściwości sorpcyjnych grzybów suszonych w kontekście ich stabilności przechowalniczej*, Problemy Higieny i Epidemiologii, vol. 98, no. 3, pp. 296–301.

Oduola, A.A., Bruce, R.M., Shafiekhani, S., Atungulu G.G., 2023, *Impacts of Industrial Microwave and Infrared Drying Approaches on Hemp (Cannabis sativa L.) Quality and Chemical Components*, Food and Bioproducts Processing, vol. 137, pp. 20–27.

Oduola, A.A., Lutra, K., Griffiths, G., 2022, *Determination of Moisture Sorption Isotherms of Industrial Hemp (Cannabis sativa L.) Flower and Leaf Composite Powders*, Industrial Crops and Products, vol. 186.

Paderewski, M., 1999, *Procesy adsorpcyjne w inżynierii chemicznej*, WNT, Warszawa.

Ruszkowska, M., Newerli-Guz, J., 2017, *Evaluation of the Quality and Stability of the Storage of Marjoram (Origanum Majorana l.) Based on the Characteristics of the Sorption Properties*, Zeszyty Naukowe Akademii Morskiej w Gdyni, no. 101, pp. 43–52.

Synowiec, A., Rys, M., Bocianowski, J., Wielgusz, K., Byczyńska, M., Heller, K., Kalemba, D., 2016, *Phytotoxic Effect of Fiber Hemp Essential Oil on Germination of Some Weeds and Crops*, Journal of Essential Oil Bearing Plants, vol. 19, pp. 262–276.

Tyszkiewicz, S., 1987, *Aktywność wody produktów spożywczych. Definicja. Metoda bezwzględnego pomiaru. Wzorce*, Przemysł Spożywczy.

Wielgusz, K., Heller, K., Byczyńska, M., 2012, *The Assessment of the Fungistatic Effect of Hemp Essential Oil as Seed Dressing, Depending on the Composition*, Journal of Research and Applications in Agricultural Engineering, vol. 57, pp. 183–187.