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HEMP FIBERS AGAIN IN SERBIA: OLD FIBERS – NEW APPLICATIONS

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ABSTRACT: *This paper attempts to summarize the historical facts about the cultivation and use of hemp in the world, and especially in Serbia, with a special emphasis on the research and new application brought by the renaissance of hemp production at the end of the 20th century. Hemp (*Cannabis Sativa L.*) as one of the oldest cultivated plants represents a renewable and sustainable source of fibers, mainly for textile production. Due to their specific chemical composition, structure and properties, such as high specific strength, non-toxic, biocompatible and biodegradable nature, hemp fibers become ideal candidates for a wide range of applications. Being lignocellulosic, hemp can be used alone, or as combined with different kinds of polymers to provide a wide range of useful composites in textiles, construction, automotive industry, and soil conservation. Also, hemp fibers have proven to be efficient biosorbents and suitable precursors for the production of low-cost carbon materials for adsorption applications.*

Keywords: *Hemp fibers, application, modification, carbonization, adsorption, water purification.*

POVRATAK KONOPLJE U SRBIJU: STARA VLAKNA – NOVA PRIMENA

Savez inženjera i tehničara tekstilaca Srbije



APSTRAKT: U ovom radu su sumirane istorijske činjenice o gajenju i upotrebi konoplje u Srbiji i svetu, sa posebnim osvrtom na istraživanja i nove primene sa renesansom konoplje krajem 20. veka. Konoplja (*Canabis Sativa L*) je jedna od najstarijih gajenih biljaka, i predstavlja obnovljiv i održiv izvor vlakana, uglavnom za tekstilnu industriju. Zbog svog specifičnog hemijskog sastava, strukture i svojstava, kao što su visoka specifična čvrstoća, netoksičnost, biokompatibilnost i biorazgradivost, vlakna konoplje imaju visok potencijal za primenu u različitim oblastima. Sama, ili kao kompozit u kombinaciji sa različitim vrstama polimera, konoplja nalazi primenu u oblastima tekstila, građevinarstva, automobilske industrije, očuvanja životne sredine. Takođe, vlakna konoplje su se pokazala kao efikasni biosorbenti i pogodni prekursori za proizvodnju jeftinih ugljeničnih adsorbenata za prečišćavanje vode od organskih i neorganskih zagađujućih materija.

Ključne reči: Vlakna konoplje, primena, modifikacija, karbonizacija, adsorpcija, prečišćavanje vode.

1. INTRODUCTION

Through the human history, hemp (*Cannabis sativa L.*) was cultivated for its seeds and fibers. Seeds were used for the production of oil, medicines and food, while hemp fibers were utilized for ropes, textiles, and paper production. According to the ancient writings, hemp was grown in China at 2700 BC, and arrived in Europe about 2000–2200 years ago. The oldest piece of hemp textile found, dates from 8000 BC, and the oldest piece of paper made from hemp is over 2000 years old. It is known that up to the 19th century hemp paper was used for printing, even the Gutenberg Bible was printed on this kind of paper. Hemp seed oils were used for a wide range of applications, from cooking to cosmetics, while extracts of hemp were used to treat a wide range of diseases [1, 2].

Many historical sources from the period of the Nemanjić dynasty (12th century) testify about the cultivation of hemp in the area of today's Serbia. The growing, production and processing of hemp become a traditional part of agriculture in Serbia, and first it was widespread in the Province of Vojvodina. At the end of the 18th century, the colonists from Northern Italy came to the Bačka region and transferred the skill of growing and processing hemp to the local population. First, small manufactories for hemp processing were formed, which later grew into industrial production. The first organized production of hemp ropes was established in 1884, in Stojkovac, near Leskovac. After that in 1907 a factory for the cultivation of hemp and production of ropes was opened in Odžaci, which have already become a biggest center and stock marketplace for hemp production in Europe [3, 4].

The beginning of the cheap and efficient production of chemical fibers, along with the prohibition of hemp due to the hallucinogenic properties of *Canabis Indica*, led to the suspension of industrial hemp production after 1925,



However, in the 1990s, due to ecological trends and considerable exhaustion of raw material sources, the attention of the industrial and scientific community turned towards renewable and biodegradable raw materials, prompting the beginning of an unexpected, worldwide return to the almost forgotten bast fibers, among them hemp [2, 3]. Hemp is an annual plant that grows in temperate climates, without agrochemicals, and with an optimum fiber yield of more than 2000 kg/ha. Currently, hemp is the subject of a European Union subsidy for non-food agriculture, and a considerable initiative for its further development in Europe is underway [5]. The hemp leading producers are France, the Democratic People's Republic of Korea, China, the Netherlands, and Poland with 78% of the hemp world production, according to The Food and Agricultural Organisation's statistics for 2020. year [6].

After the Second World War, on the territory of Serbia (in former Yugoslavia) hemp research and production were enhanced by the establishment of the Research Station for Hemp, Hops, and Sorghums at the Institute of Field and Vegetable Crops in Novi Sad in 1952. Hemp production in Serbia started using mainly Italian seeds. Although, during the 1960s interest in hemp production decreased, and the program on hemp and the bast fiber research was almost stopped, the Italian seeds were used for selecting the first domestic cultivar called “Novosadska konoplja”, which was officially registered in 1967 [7, 8]. In the line with the European trends and growing interest in biocompatible and environmentally friendly materials, after the 1990s Serbia is experiencing increased hemp production. In accordance with this, three varieties of hemp (“Marina”, “Helena”, and “Diana”) have been registered in Serbia in 2002 [9].

2. APPLICATIONS OF HEMP

Owing to the high utilization of almost all parts of the hemp plant, there has been an exponential increase in the use of hemp for various applications. Different applications of hemp plants are presented in Figure 1.

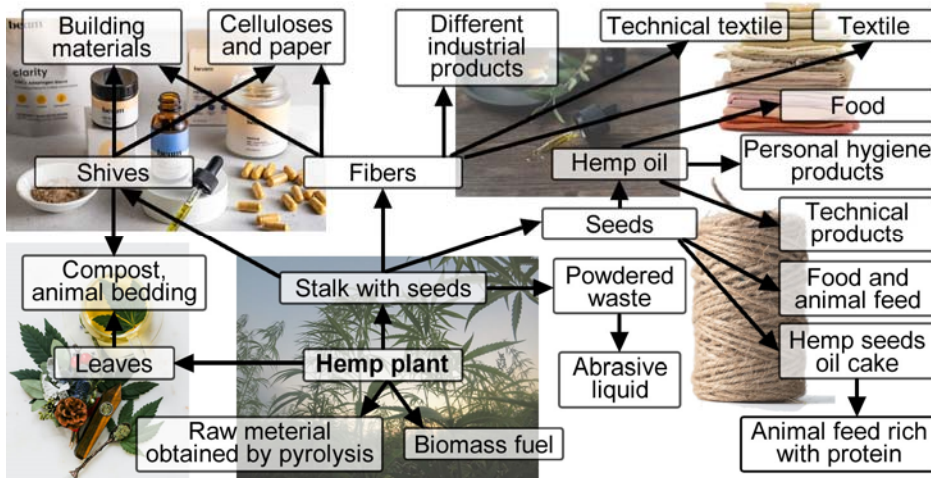


Figure 1: Different application of hemp plants

From the economic aspect, hemp products, which can be found on the market, are divided into two groups. The first group is high value-added products, such as oil and healthy food; knitted and woven textiles, which can be used for draperies, carpets, clothes, etc.; and technical textiles and fibers as a reinforcing component of composites. The second group includes medium and small value-added products: pulp and paper, building materials, alcoholic beverages, fodder, animal bedding, and biomass fuels. Hemp seed oil is superior to the other types of oil due to its specific composition. Hemp oil contains omega-3, and omega-6 derivatives of gamma-linolenic acid (GLA) in a high concentration of 1.7% or even 2-3%. This oil is widely used in the cosmetics and pharmaceutical industries as an ingredient in shampoos or skincare products due to its ability to penetrate as many as three layers of the skin [10, 11]. Lately, hemp oil has been used as an immunomodulator in the field of medicine for the treatment of different diseases. Hemp-based foods are very rich in essential minerals, and proteins, containing all eight essential amino acids. Lately, hemp has also been used to make beer.

As a textile fiber, hemp is used in the clothing industry for the production of comfortable, biocompatible, and environmentally friendly products, due to its extraordinary properties as antimicrobial properties, extremely quick absorption of humidity accompanied by quick drying, good thermal and electrical properties (increased heat of sorption and low static electricity charges), outstanding tenacity (50–90 cN/tex), lack of allergenic effects, biodegradability, and protection against UV radiation [11-13]. Long hemp fibers can be spun and woven to make the linen-like fabric used in clothing, home furnishing textiles, and floor coverings. In Europe, hemp fibers are used mainly in the special paper industry.

Good physico-mechanical properties of hemp fibers (high values of breaking strength, and low density) contribute to the successful use of these fibers as reinforcing



components in the production of technical textiles and molded thermoplastics in the automobile industry. Today, fiber composites, based on hemp, flax, wood, etc., are applied in the automotive industry, for the production of non-structural parts such as interior panels, parcel shelves, etc. German researchers have developed the production of coatings for car interiors, based on PP and hemp, at far lower prices than the panels that were previously used. Shaped and pressed hemp parts are far lighter, more fire-resistant in collision situations, and can be recycled. Practically all major vehicle manufacturers around the world now use natural fiber composites in various applications. Flax, hemp, sisal, and other natural fibers are used to make up to 50 components in Mercedes-Benz A-, C-, E- and S-Class [14]. Hemp processing yields also the woody core part (shives) and short and entangled fibers as a by-product that can be used in insulation products, fiberboard, and erosion control mats, while the fibrous core can be blended with lime to make strong lightweight concrete.

3. RESEARCH OF HEMP FIBERS IN SERBIA

The growing need for biocompatible and environmentally friendly materials has led to an increase in the popularity and usage of industrial hemp to obtain a wide range of new products, followed by the increase in scientific research in the field of hemp production, characterization, and application. The necessity for research in this field was recognized by the Ministry of Science and Environmental Protection of the Republic of Serbia, who, for the first time in 2002, provided funds for it through the project “Development of agrocellulosic fibers and fibrous materials based on domestic naturally available bio-renewable resources (hemp) for the needs of the textile and high-quality paper industry”. The successful implementation of this project was followed by a series of other projects, financed by the relevant Ministry, and related to the production, modification, and characterization of hemp fibers and their applications in conventional and new ways. Investigations conducted within these projects have resulted in the improvement of a method for determination of the hemp fibers' chemical composition, and development of a new method for measuring the hemp fibers breaking strength, as well as the development of new modification procedures for improving the sorption characteristics of hemp fibers, followed by expanding the range of their applications to the biosorbents, and raw materials for carbon adsorbents.

Broadening the scope of use of hemp fibers is primarily conditioned by the chemical composition and the structure of these fibers. For that reason, the first hemp fibers studies in Serbia were directed toward determining their chemical composition and its influence on the structure and properties of hemp fibers. Methods and procedures for determining the chemical composition of hemp fibers, already developed elsewhere, did not provide accurate data on the content of the components. The team of researchers working within the mentioned project adopted a procedure for chemical composition analysis based on sequential removal of individual components from hemp fibers' structure, which was in accordance with the Soutar and Bryden research [15].

The scheme for determining the chemical composition of hemp fibers is given in Fig. 2.

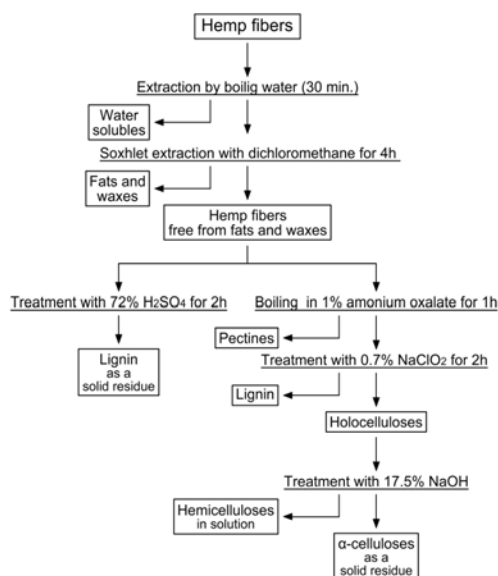


Figure 2: Procedure for determining the chemical composition of hemp fibers through the sequential removal of individual components from hemp fibers' structure [16]

The proposed procedure was applied to several hemp fiber samples (Institute of Field and Vegetable Crops of Novi Sad and ITES Odzaci, both from Serbia) that have been obtained from different varieties of the hemp plant species; the determined chemical composition was as follows: 67.10-79.10 % cellulose, 10.41-12.28 % hemicelluloses, 1.39-12.81 % pectin, 4.68-6.13 % lignin, 1.5-1.82 % water solubles and 0.23-1.59 % fats and waxes [16].

In an effort to characterize the hemp fibers' tensile properties, the team of researchers from Serbia met with a lack of an adequate standardized method for determining breaking strength. Namely, the method for breaking strength determination on a single technical hemp fiber, developed until then, gave precise results after 200 measurements of breaking force with a high coefficient of variation [17]. This problem was overcome by measuring the breaking strength on hemp fiber bundles of different fineness (bundles containing different numbers of fibers) and lengths. The influence of measuring conditions on the tensile properties of hemp fibers was investigated, and the original method that is based on the use of tenacity of 500 tex fiber bundle extrapolated to zero-tensile length, was developed. This new method for measuring the breaking strength of hemp fibers required much less time and skill, and at the same time, the values obtained for flat bundle tenacity show a high correlation with values measured on single fibers [11, 17].



The use of hemp fibers for different applications resulted in the necessity for further fiber processing and modification of its mechanical and sorption properties. The team of researchers from Serbia used the dielectric-barrier discharge (DBD) in air and atmospheric pressure for the modification of hemp fibers. The source of DBD was developed in the Laboratory of Quantum Optics of the Faculty of Physics in Belgrade (Serbia) as a device prototype with plane-parallel geometry, for the continuous plasma modification or treatment of textile materials. A relatively short DBD treatment leads to changes in the surface without changes in the bulk properties. The plasma oxidation increased the content of various hydrophilic functional groups on the fiber surface and thereby improved sorption properties (moisture content, capillarity, wetting time, and adsorption capacity). In this way, fibers of high hydrophilicity, improved chemisorption, biocompatibility, and adhesive properties can be obtained [18, 19].

Different chemical modification methods are also used to increase the adsorption capacity of hemp fibers intended as biosorbents for heavy metal adsorption. Applied alkali and oxidative treatments affect the chemical composition of hemp fibers by selective removal of hemicelluloses and lignin, respectively, changing in that way the morphology, fiber structure, and surface chemistry.

Changes in the chemical composition that occurred during the alkaline treatment affect the structure of hemp fibers, leading to the disruption of the hydrogen bond network, conversion of cellulose I into cellulose II, and an increase in the amorphous cellulose content at the expense of crystalline cellulose. Additionally, alkaline treatment increases the surface roughness and separates the fiber bundles making hemp fibers finer and more flexible. Oxidation of hemp fibers by sodium chlorite progressively removes lignin from the hemp fibers structure, leading to fiber liberation and increased fiber fineness, along with the changes in the surface chemistry by increasing the number of available carboxyl groups, which can represent active sites for adsorption. Therefore, the hemp fibers obtained as waste from the Serbian textile industry were used as environmentally and economically friendly materials for the removal of heavy metals. Obtained biosorption capacities were: 3.86 mg/g for Zn^{2+} , 6.63 mg/g for Cd^{2+} , and 15.54 mg/g for Pb^{2+} removal. Applied chemical modification significantly increases the fiber adsorption capacities due to the differences in the chemical composition, fiber structure, degree of crystallinity, fibrillar orientation, and specific surface area, i.e. the presence of micropores and microcracks [20, 21].

Despite the satisfactory performance of hemp fibers biosorbent in water purification, activated carbons are known to be more efficient in adsorbing a greater amount of pollutants, although its large-scale application is limited by the high cost. Being lignocellulosic material, hemp fiber contains cellulose, hemicelluloses, and lignin, which are rich in carbon, and therefore our team of researchers utilized waste hemp fibers as a low-cost and renewable precursor for biocarbon sorbents production [22]. Figure 3 shows the scheme of activated biocarbon production, starting with waste hemp fibers as

raw material. Following optimal production parameters (highlighted in red in Figure 3) microporous activated biocarbons with a high specific surface area ($S_{BET} = 2192 \text{ m}^2/\text{g}$) and amount of surface oxygen groups (11.258 mmol/g) were obtained [23].

Carbonized and activated hemp fibers were used in water purification for the adsorption of heavy metals and pesticides. Compared to the adsorption capacities of hemp fibers as biosorbents, carbonized hemp fibers have proved to be much more efficient in heavy metal removal, showing the adsorption capacities of $25.6 - 27.7 \text{ mg/g}$ for Zn^{2+} , $16.7 - 19.1 \text{ mg/g}$ for Cd^{2+} and $28.4 - 46.6 \text{ mg/g}$ for Pb^{2+} [22].

Also, it was shown that activated hemp fibers have good adsorption properties toward pesticides. Due to the good adsorption properties toward heavy metals and pesticides, along with the strong antimicrobial effect, the examined materials were successfully used as filter materials in water purification. Activated hemp fibers were successfully applied as a solid-phase sorbent for the preconcentration of pesticides from water, and for the same pesticides, recoveries obtained by these cartridges were even higher than recoveries obtained by commercial ones [23].

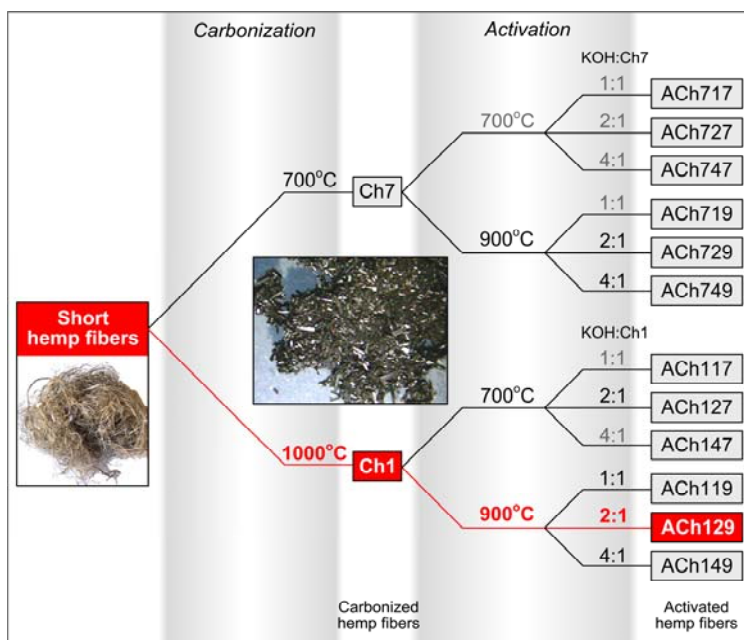


Figure 3: The scheme of activated biocarbon production

4. CONCLUSION

Although hemp cultivation in Serbia has not yet reached a satisfactory level, there are ambitious plans in the scientific community for its revitalization in terms of new applications. The production of innovative hemp-based materials is becoming an



important area of research in Serbia, as hemp offers a unique combination of high physical and specific chemical properties, producing a variety of high-value products with a low impact on the environment. Disposal of such products does not pose a problem, as is the case with synthetic materials, i.e. they can be composted to improve soil structure, or incinerated with no emission of pollutants, releasing no more carbon than the fiber crops absorbed during their lifetimes. Based on the rich and long-lasting history of hemp in this region, it is expected that hemp will easily become a major crop in Serbia once again.

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