

# CELLULOSE-BASED WASTE STRUCTURE AND CHEMICAL COMPOSITION IMPACT ON THE ADSORPTION OF PHARMACEUTICALS

Marija Vukčević<sup>1\*</sup>, Marina Maletić<sup>2</sup>, Nataša Karić<sup>2</sup>, Biljana Pejić<sup>1</sup>,  
Katarina Trivunac<sup>1</sup>, Aleksandra Perić Grujić<sup>1</sup>

<sup>1</sup> University of Belgrade, Faculty of Technology and Metallurgy, Belgrade, Serbia

<sup>2</sup> Innovation Center of Faculty of Technology and Metallurgy, Belgrade, Serbia

\* e-mail: marijab@tmf.bg.ac.rs

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**Abstract:** In an attempt to reuse fibrous textile waste, and at the same time to reduce its quantity, waste hemp and flax fibers, and cotton yarn were used as cheap and sustainable adsorbents for the removal of pharmaceuticals from water. In order to improve their adsorption properties, waste fibers, and yarn samples were modified using 18% NaOH solution. Morphology, surface chemistry, and structural characteristics were examined through scanning electron microscopy, Fourier transform infrared spectroscopy, degree of surface crystallinity, and crystallinity index. Adsorption properties were analyzed through the determination of iodine sorption and water retention, as well as, the adsorption of selected sedatives. Modification with 18% NaOH increased the content of amorphous areas in examined fibers and yarn samples, improving their adsorption characteristics. Utilization of both unmodified and modified samples enables fast and highly efficient removal (adsorption efficiency ranging from 75 to 100%) of sedatives from water, making waste hemp and flax fibers and cotton yarn samples promising adsorbents for water treatment.

**Keywords:** cotton, hemp, flax, alkali modification, adsorption, sedatives.

## UTICAJ STRUKTURE I HEMIJSKOG SASTAVA CELULOZNOG OTPADA NA ADSORPCIJU FARMACEUTIKA

**Apstrakt:** U cilju smanjenja količine vlaknastog tekstilnog otpada, kao i njegove ponovne upotrebe, u ovom radu je ispitana mogućnost primene otpadnih vlakana konoplje i lana i pamučnog prediva, kao jeftinih i održivih adsorbenata za uklanjanje lekova iz vode. Izvršena je hemijska modifikacija otpadnih vlakana i prediva 18% rastvorom NaOH, da bi se poboljšala adsorpciona svojstva materijala. Morfologija, hemija površine i strukturne karakteristike korišćenih materijala ispitane su skenirajućom elektronskom mikroskopijom, infracrvenom spektroskopijom sa Furijeovom transformacijom, kao i određivanjem stepena površinske kristaliničnosti i indeksa kristalnosti. Adsorpciona svojstva su analizirana kroz vrednosti sorpcije joda i sposobnosti zadržavanja vode, kao i određivanjem adsorpcionih kapaciteta ispitivanih materijala za uklanjanje odabranih sedativa. Prime-njeni alkalni tretman dovodi do povećanja sadržaja amorfne oblasti u ispitivanim uzorcima vlakana i prediva, poboljšavajući njihove adsorpcione karakteristike. Dobijeni rezultati su pokazali da primena nemodifikovanih i modifikovanih otpadnih vlakana konoplje i lana i pamučnog prediva omogućava brzo i visoko efikasno uklanjanje (efikasnost adsorpcije u opsegu 75 - 100%) sedativa iz vode.

**Ključne reči:** pamuk, konoplja, lan, alkalna modifikacija, adsorpcija, sedativi.

## 1. INTRODUCTION

Pharmaceuticals production and consumption have rapidly increased with the development of medicine and population growth. The total number of pharmaceutically active compounds was determined to be 11,926, of which 713 compounds were detected in wastewater [1]. Water-soluble and pharmacologically active organic micropollutants or pharmaceutically active compounds have attracted much attention worldwide. As with most organic micropollutants, the origin of pharmaceutical pollution is anthropogenic, and they are continuously released into wastewater or directly into the environment. In addition to the fact that people use different drugs for their health in their daily lives, drugs are also used in veterinary medicine for treating animal diseases [2].

There are many different ways in which pharmaceutical compounds reach surface and groundwater, as well as water bodies, in concentrations from sub- $\mu\text{g/L}$  to more than  $\mu\text{g/L}$  [3]. Some of the most important sources are effluents from the pharmaceutical industry, with high concentrations of pharmaceuticals due to discharges directly from factories; urban wastewater; inadequate disposal of expired or unused drugs; agricultural and livestock waste, especially livestock, because in large intensive livestock farms animals are fed food containing drugs, but also due to the application of untreated animal wastes as a soil supplement [2]. Pharmaceutical products, even at very low concentrations, can be biologically effective causing harmful effects, such as ecotoxicity (acute and chronic toxicity, genotoxicity, and carcinogenicity); pharmacological effects (hormone and immune system interference) and antimicrobial resistance, which is one of the greatest public health challenges of the 21<sup>st</sup> century [4, 5].

Pharmaceutical products are one of the most important classes of environmental pollutants, due to their strong hydrophilicity and low biodegradability, which makes them hard to remove from water using traditional water treatment approaches. Conventional wastewater treatment methods are not designed to completely eliminate pharmaceuticals from water [6].

All the mentioned facts point to the need to provide a long-term solution based on sustainable techno-economic and ecological principles. In addition to avoiding the direct disposal of pharmaceutical products into the environment, a potential solution may be using efficient and inexpensive adsorbents to purify polluted water. Adsorption is considered a simple and fast method with low energy and operating costs, without the creation of toxic by-products that would

cause secondary pollution. In recent years the new materials are developed and proposed as biosorbents for the removal of pharmaceutical products in adsorption-oriented processes. These biosorbents can be in the form of living organisms (e.g. fungi, bacteria, algae and yeasts) and dead biomass (e.g. sawdust, bark, peat, natural fibers such as flax, hemp, cotton, plants, and other organic substances such as polysaccharides or biopolymers) [7].

Cotton, flax and hemp fibers are classified as ecologically and economically acceptable materials and good candidates as substitutes for commercial adsorbents for wastewater treatment. Hemp, flax, and cotton waste fibers from the textile industry are interesting materials for use in wastewater treatment processes because at the same time, their added value is found and the problem of safe disposal is solved. The chemical composition of these fibers, such as moisture content, macromolecular network with numerous hydroxyl groups that can form intra- and intermolecular bonds, as well as specific physical, mechanical, and thermal properties [7, 8], allow their design, i.e. modification in the direction of achieving high removal efficiency of organic and inorganic pollutants from wastewater. There are several chemical methods that can improve the physico-chemical and structural properties of waste fibers, and one of the simplest and fastest methods is a modification with NaOH [9]. Modification with 18 % NaOH was applied in this work to improve the adsorption properties of the waste flax and hemp fibers, and cotton yarn. The influence of applied treatment on the physico-chemical, structural, and adsorption properties of fibers and yarn samples was examined. Unmodified and modified materials were used for the adsorption of bromazepam, lorazepam, and diazepam from water, and the influence of initial pH value, contact time, and different sedative concentrations on adsorption was investigated.

## 2. EXPERIMENTAL

### 2.1. Material preparation

Waste hemp (H) and flax (F) fibers were obtained from ITES Odzaci (Serbia), and Banja Luka (Republic of Srpska, Bosnia and Herzegovina), respectively, while waste cotton (Cott) yarn was obtained from the factory SIMPO Dekor Vranje (Serbia). In order to change the adsorption characteristics of fibers and yarn, the modification with an 18% NaOH solution was performed. Fibers and yarn samples were soaked in sodium hydroxide solution for one hour at room temperature. After modification, samples were neutralized with 1 % acetic acid, washed with deionized water, and dried

overnight at 60°C. Modified samples are denoted as  $H_{al}$ ,  $F_{al}$ , and  $Cott_{al}$ .

## 2.2. Material Characterization

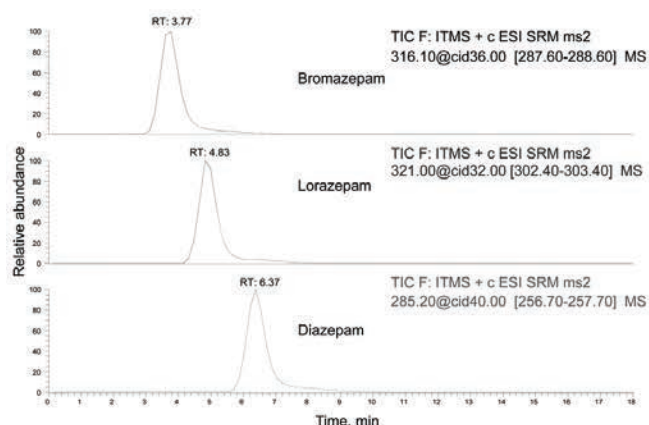
The content of chemical components ( $\alpha$ -cellulose, hemicelluloses, lignin) in the structure of starting and modified materials was determined by the sequential removal of specific components from the structure of the fibers and yarns, as it was described in the literature [10].

The influence of alkali treatment on the morphological characteristics of fibers and yarn samples was examined by scanning electron microscopy (SEM JEOL JSM-6610LV).

Spectra obtained by Fourier transform infrared spectroscopy (Nicolet™ iS™ 10 FTIR Spectrometer, ThermoFisherScientific), in the range of 400-4000  $cm^{-1}$ , were used to determine the content of functional groups present on the surface of tested samples. From the intensity of characteristic bands present in FTIR spectra, the degree of surface crystallinity ( $C_i$ ) [11] can be assessed as a ratio of the intensity of bands at 1368  $cm^{-1}$  and 2885  $cm^{-1}$  ( $I_{1368}/I_{2885}$ ), which are related to the in-the-plane C-H bending and C-H symmetrical stretching in cellulose and hemicelluloses, respectively [12].

The Schwertassek method, based on the sorption of iodine onto fibers and yarn samples and the determination of unadsorbed iodine by titration with sodium thiosulfate solution, was used to determine the iodine sorption values (ISV) [13]. The content of crystalline phase within the structure of fibers and yarn samples, marked as crystallinity index ( $X_K$ ), is calculated from the obtained ISVs using the following equation:

$$X_K = 100 - \left( \frac{ISV}{412} \cdot 100 \right), \% \quad (1)$$



**Figure 1:** Mass chromatogram of selected sedatives and gradient of mobile phase

The ability of tested samples to retain water was examined by the standard centrifuge method (ASTM D 2402-01 2001) and given as water retention value (WRV).

## 2.3. Adsorption of sedatives

The adsorption of selected sedatives (bromazepam, lorazepam, diazepam) from aqueous solution was performed in a batch system, with constant shaking (170 rpm), at room temperature. For all adsorption experiments, the concentration of adsorbent was 2  $g/dm^3$ . The influence of the initial pH of the aqueous solution (the concentration of each sedative was 500  $\mu g/dm^3$ ) on adsorption capacities was tested by setting the initial pH to 2, 4, 6, and 8. Additionally, the adsorption of sedatives onto unmodified and modified fibers and yarn samples was performed without the pH adjustment (measured initial pH was 5.5). To examine the effect of contact time on adsorption from 500  $\mu g/dm^3$  sedative solution, at specified time intervals (5, 15, 30, 60, 120, and 180 minutes), the sedative concentration was measured using liquid chromatography with tandem mass spectrometry (HPLC-MS/MS). The influence of initial concentration was examined using a sedative solution with different concentrations (250, 750, 1000, and 1250  $\mu g/dm^3$ ). Obtained experimental results were analyzed by theoretical models: pseudo-first (PFO) [14] and pseudo-second (PSO) [15] order kinetic models, as well as Langmuir [16] and Freundlich [17] adsorption isotherms.

### HPLC-MS/MS analysis

The analyte was separated on a reverse-phase column of the Surveyor HPLC system (Thermo Fisher Scientific, USA). The mobile phase gradient is shown in the table embedded in Figure 1. For the detection and quantification of selected sedatives, an ion trap mass spectrometer (LCQ Advantage, Thermo Fisher Scientific, USA) was used, and a mass chromatogram of tested sedatives is given in Figure 1.

Gradient of mobile phase

t, min	Flow rate, $cm^3/min$	Water, %	Methanol, %	10% acetic acid, %
0	0.5	38	60	2
8.00	0.5	0	98	2
15.00	0.5	0	98	2
15.01	0.9	0	100	0
18.00	0.9	0	100	0
18.01	0.5	38	60	2
20.00	0.5	38	60	2

### 3. RESULTS AND DISCUSSION

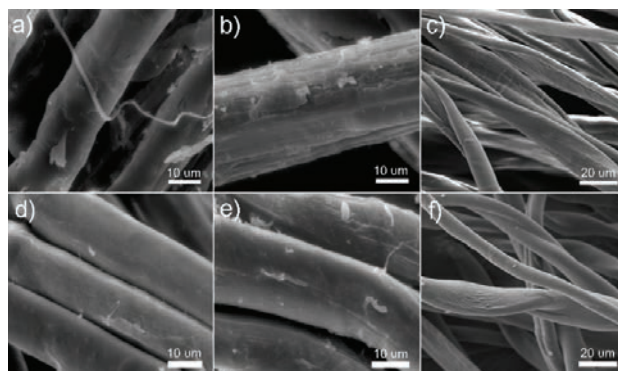
#### 3.1. Material Characterization

Applied treatment with 18% NaOH leads to the removal of hemicelluloses from interfibrillar regions, partial removal of lignin from the secondary fiber wall (especially in lignocellulosic fibers), as well as a certain shortening of macromolecular cellulose chains. A decrease in hemicelluloses and lignin content, as a consequence of modification, is given in Table 1. These structural changes lead to a change in the supramolecular structure of fibers in favor of increasing the content of amorphous areas. The increase in the content of amorphous areas in modified samples is visible from better iodine sorption and an increase in ISV, and consequently, a decrease in the degree of fiber crystallinity ( $X_{kr}$ ) (Table 1). On the other hand, the degree of surface crystallinity (Ci) increases after the treatment with NaOH. With the removal of lignin and hemicelluloses from the fiber structure during modification, cellulose chains become more available on the surface of the fibers. Having in mind that cellulose has a higher degree of crystallinity than hemicelluloses, the higher surface availability of cellulose results in an increase in surface crystallinity.

The values obtained for water retention (Table 1) follow different trends for all examined samples: WRV decreases after flax modification, increases for modified cotton, and retains almost the same in the case of hemp fibers. Generally, water is retained in the micropores and microcracks of the fibers, which are most abundant in lignin in the case of lignocellulosic fibers (F and H). As can be seen from Table 1, a more significant decrease in lignin content after hydroxide treatment is observed for flax fibers, compared to the hemp fibers. The higher content of lignin in both the unmodified and alkali-treated hemp fibers provides the presence of micropores and microcracks, in which water is retained by capillary action, leading to the highest WRV values. In the case of cotton fibers, which

usually contain a small portion of lignin, the ability to retain water can be conditioned by the presence of cellulose hydroxyl groups that bind water by hydrogen bonds. Although modified cotton fibers have the lowest lignin content, a significant increase in WRV for the Cott<sub>al</sub> sample can result from the highest content of  $\alpha$ -cellulose. Also, a yarn form, in which the cotton samples are present, i.e. the degree of twisting of the cotton yarn, can be the reason for such values of water retention.

The morphologies of examined samples are shown in Figure 2. Unmodified flax (Figure 2a) and hemp fibers (Figure 2b) are characterized by a rough surface, while spirally twisted cotton fibers (within the yarn structure) are characterized by a smoother surface. Applied alkali treatment led to the removal of hemicelluloses from interfibrillar regions, resulting in the pronounced fibrillation and separation of elementary fibers in the fiber structure of samples F and H. For the modified cotton sample only a relative peeling of the surface of the fibers is visible on the Figure 2f.



**Figure 2:** Scanning electron microscopy of a) F, b) H, c) Cott, d) F<sub>al</sub>, e) H<sub>al</sub>, and f) Cott<sub>al</sub>

The type of surface functionalities of examined samples and changes in surface chemistry resulting from the modification were analyzed using FTIR spec-

**Table 1:** Chemical composition and characteristics of examined fibers and yarn samples

Sample	Chemical composition			ISV, mgI <sub>2</sub> /g	$X_{kr}$ , %	Ci	WRV, %
	$\alpha$ -cellulose	hemicelluloses	lignin				
F	75.8	7.84	4.03	118	68.2	0.981	39.9
F <sub>al</sub>	92.8	2.89	2.18	149	63.7	0.991	31.8
H	78.2	10.7	6.06	161	60.8	0.963	60.0
H <sub>al</sub>	79.7	3.60	5.41	212	48.5	0.988	61.5
Cott	93.9	2.09	2.16	85.7	79.2	0.979	33.1
Cott <sub>al</sub>	97.9	1.14	0.90	100	75.9	0.984	43.8

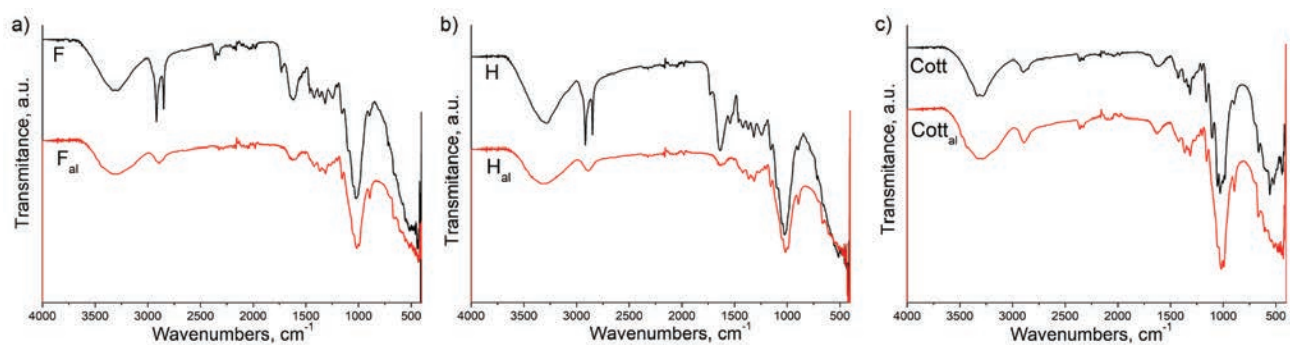


tra. The broadband, observed around  $3300\text{ cm}^{-1}$  for all samples, is assigned to the stretching vibration of the O-H bond in hydroxyl groups. In this wavenumber area, on the spectra of modified samples, two shoulders ( $3478\text{ cm}^{-1}$  and  $3436\text{ cm}^{-1}$ ) attributed to hydroxyl groups in cellulose II and to the specific hydrogen bonds, were observed [18]. The FTIR spectra of examined fibers and yarn samples display two peaks at  $2850\text{ cm}^{-1}$  and  $2920\text{ cm}^{-1}$  that can be assigned to the symmetrical and asymmetrical vibrations of the C-H bond in methyl and methylene groups of cellulose, and hemicelluloses [19]. The visible changes in intensities of these two peaks, observed after modification, are the consequence of hemicelluloses removal. The band near  $1730\text{ cm}^{-1}$ , attributed to C=O stretching of carbonyl or ester groups of hemicelluloses [19, 20], decrease in intensity for modified hemp and flax fibers and disappears for modified cotton yarn sample. The bands in the region  $1000\text{--}1370\text{ cm}^{-1}$ , related to the C-O and C-C stretching in polysaccharides, cellulose, and hemicelluloses, behave in a similar way. Also, the band at  $890\text{ cm}^{-1}$  indicates the presence of a glucopyranose ring in the structure of all examined samples. Obtained results of FTIR analysis also confirmed that applied modification induces changes in the distribution of hemicelluloses in the structure of tested fibers and yarn samples.

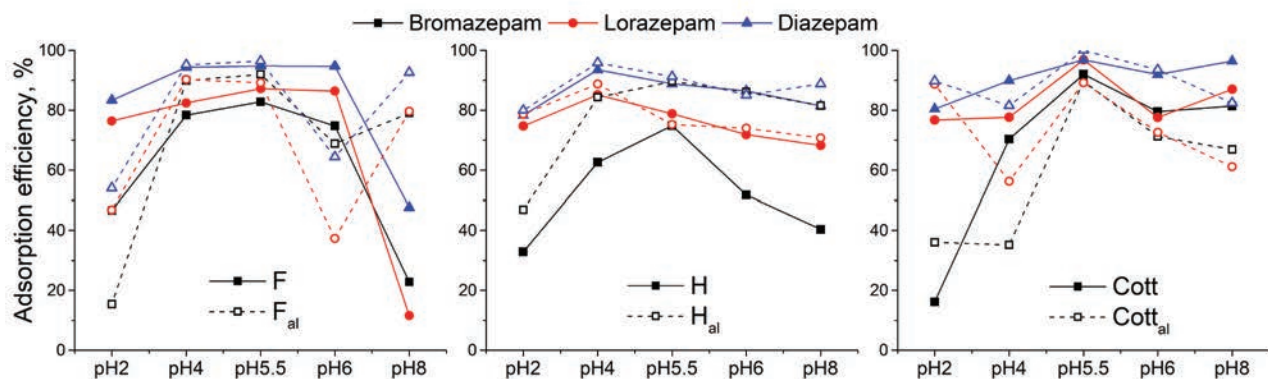
### 3.2. Adsorption of sedatives

The initial pH value of the adsorbate solution is one of the parameters that could affect the adsorption efficiency, since the ionization of surface groups, which can act as active sites for adsorption, depend on the pH of the solution. The highest adsorption efficiency of examined samples was obtained for initial pH values ranging from 4 to 6 (Figure 4). The variations in surface chemistry induced by alkali treatment led to the highest influence of initial pH on adsorption efficiencies for modified samples. Generally, all examined samples showed good adsorption efficiency in solution without pH adjustment (the measured pH of the starting sedative solution was 5.5), and this pH value was chosen for further adsorption experiments.

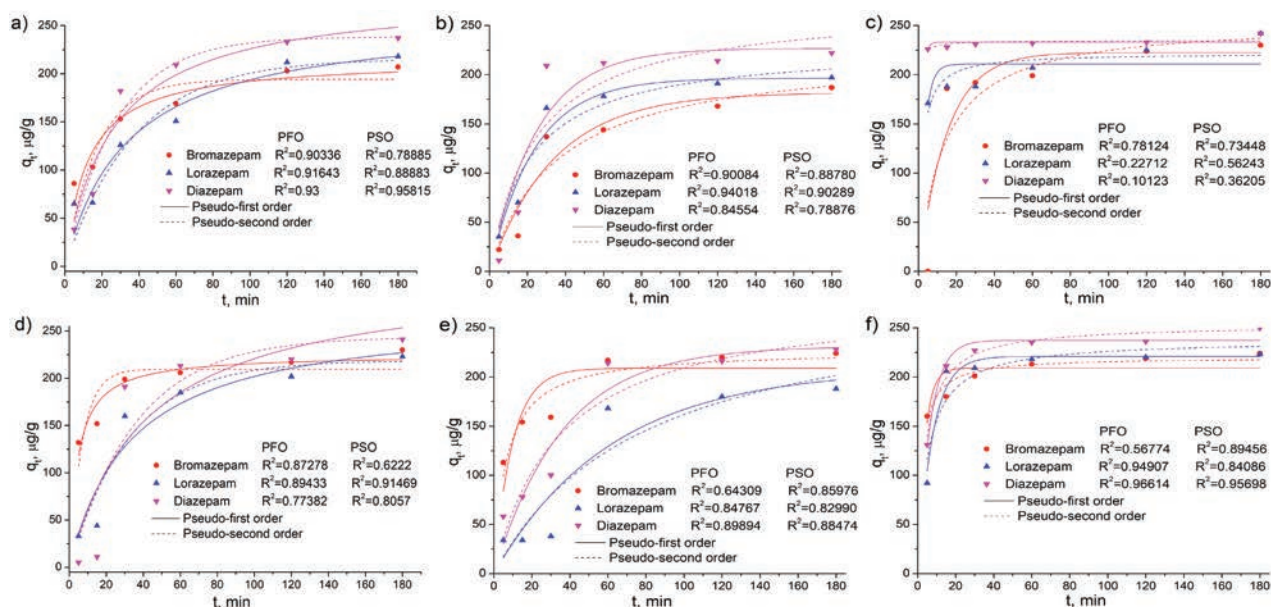
The influence of contact time on adsorption is shown in Figure 5. All samples have shown relatively high adsorption capacities with equilibrium adsorption reached in 60 minutes for flax and hemp samples and 15 and 30 minutes for Cott and Cott<sub>al</sub>, respectively. Sedative adsorption onto lignocellulosic samples seems to be controlled by the slow diffusion of adsorbate through the porous fiber matrices since rough surface, presence of micropores and microcracks, along with the fibrillation of lignocellulosic



**Figure 3:** FTIR spectra of unmodified and alkali-modified a) flax and b) hemp fibers, and c) cotton yarn



**Figure 4:** Adsorption capacities of examined samples as a function of initial pH value



**Figure 5:** The influence of contact time on adsorption and fitting of experimental data with PFO and PSO models for a) F, b) H, c) Cott, d)  $F_{al}$ , e)  $H_{al}$ , and f)  $Cott_{al}$

fibers, especially modified ones, require a longer time to establish the equilibrium adsorption. On the other hand, adsorption onto cotton samples with relatively smooth and unporous surfaces occurs through external adsorption, providing fast removal of sedatives from an aqueous solution.

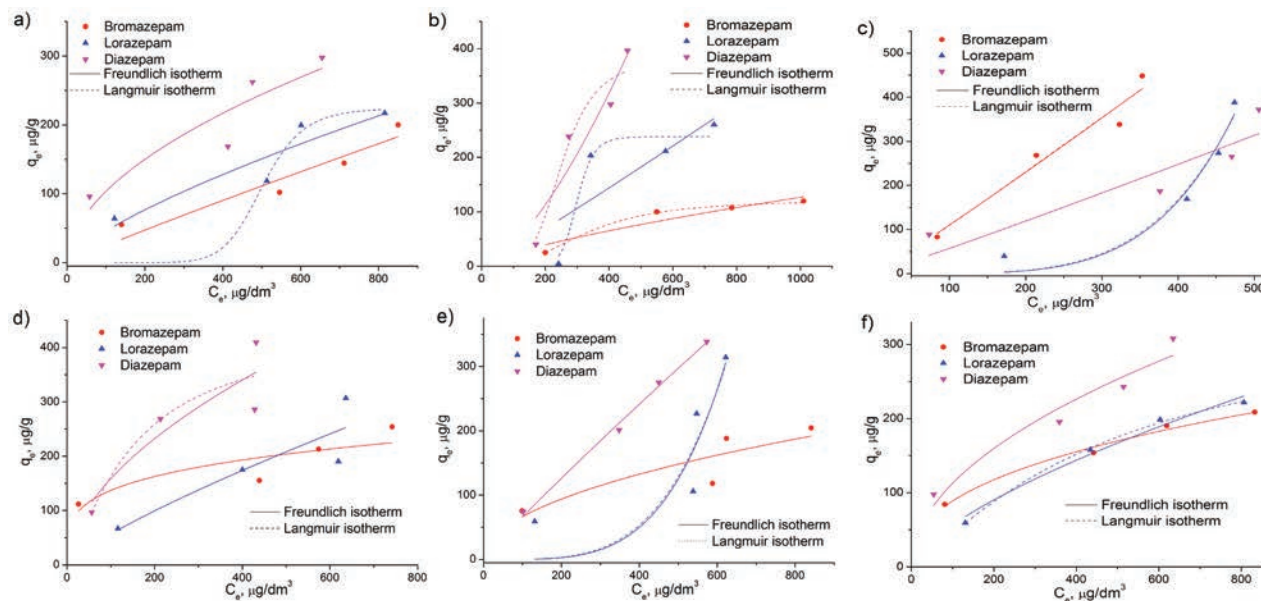
Experimentally obtained data were analyzed by pseudo-first (PFO) and pseudo-second (PSO) order kinetic models, and obtained kinetic parameters are

given in Table 2. Based on the comparison of experimentally obtained and calculated adsorption capacities and correlation coefficients ( $R^2$  values given in Figure 5), it has been noted that neither of these two kinetic models fully described the adsorption of sedatives onto examined materials. Therefore, it can be assumed that sedative adsorption occurs through a complex mechanism that includes both chemisorption and physisorption.

**Table 2:** Kinetic parameters for adsorption of sedatives onto examined samples

Sedative*		F	$F_{al}$	H	$H_{al}$	Cott	$Cott_{al}$
Pseudo-first order							
$q_{e,cal}$ µg/g	B	215	225	182	209	223	209
	L	259	269	196	208	211	221
	D	284	311	227	231	233	237
$k_1$ , min <sup>-1</sup>	B	$8.3 \times 10^{-2}$	$2.2 \times 10^{-1}$	$2.9 \times 10^{-2}$	$1.0 \times 10^{-1}$	$6.7 \times 10^{-2}$	$2.7 \times 10^{-1}$
	L	$2.9 \times 10^{-2}$	$3.0 \times 10^{-2}$	$4.2 \times 10^{-2}$	$1.6 \times 10^{-2}$	$3.2 \times 10^{-1}$	$1.3 \times 10^{-1}$
	D	$3.9 \times 10^{-2}$	$2.4 \times 10^{-2}$	$4.0 \times 10^{-2}$	$2.7 \times 10^{-2}$	$6.9 \times 10^{-1}$	$1.5 \times 10^{-1}$
Pseudo-second order							
$q_{e,cal}$ µg/g	B	194	210	225	227	255	220
	L	216	219	230	291	222	238
	D	238	244	271	282	235	253
$k_2$ , g µg <sup>-1</sup> min <sup>-1</sup>	B	$3.0 \times 10^{-4}$	$6.8 \times 10^{-4}$	$1.3 \times 10^{-4}$	$6.7 \times 10^{-4}$	$2.9 \times 10^{-4}$	$2.1 \times 10^{-3}$
	L	$1.2 \times 10^{-4}$	$1.4 \times 10^{-4}$	$2.1 \times 10^{-4}$	$4.3 \times 10^{-5}$	$2.4 \times 10^{-3}$	$8.0 \times 10^{-4}$
	D	$1.5 \times 10^{-4}$	$1.1 \times 10^{-4}$	$1.5 \times 10^{-4}$	$1.0 \times 10^{-4}$	$1.8 \times 10^{-2}$	$9.7 \times 10^{-4}$
$q_{e,exp}$ µg/g	B	207	230	187	224	230	224
	L	218	223	197	188	242	223
	D	237	241	222	228	242	250

\*B-bromazepam, L-lorazepam, D-diazepam



**Figure 6:** Langmuir and Freundlich isotherm for sedatives adsorption onto a) F, b) H, c) Cott, d)  $F_{al}$ , e)  $H_{al}$ , and f)  $Cott_{al}$

Figure 6 shows the influence of the initial concentration of the sedative solution on the adsorption capacities of all tested samples. Adsorption capacities constantly increase with the initial concentration of

sedative, without reaching the characteristic plot of adsorption isotherm, which led to the very high values of Langmuir maximal adsorption capacities ( $Q_0$ ) (Table 3).

**Table 3:** Isotherm parameters for adsorption of sedatives onto examined samples

Sedative*		F	$F_{al}$	H	$H_{al}$	Cott	$Cott_{al}$
Langmuir isotherm							
$Q_0$ , µg/g	B	162863	55382	122	47980	5178	12638
	L	224	34326	238	11728	17162	348
	D	102618	437	381	45395	289848	96864
b	B	$2.0 \times 10^{-06}$	$8.0 \times 10^{-04}$	$1.5 \times 10^{-07}$	$1.4 \times 10^{-4}$	$1.3 \times 10^{-04}$	$1.1 \times 10^{-03}$
	L	$7.2 \times 10^{-27}$	$4.0 \times 10^{-05}$	$2.6 \times 10^{-29}$	$1.9 \times 10^{-13}$	$1.4 \times 10^{-14}$	$6.1 \times 10^{-04}$
	D	$8.7 \times 10^{-05}$	$1.6 \times 10^{-03}$	$3.7 \times 10^{-12}$	$1.9 \times 10^{-05}$	$1.5 \times 10^{-06}$	$1.1 \times 10^{-04}$
$R^2$	B	0.68353	0.28970	0.98292	0.29368	0.86263	0.96831
	L	0.17470	0.35924	0.88704	0.27057	0.86804	0.99537
	D	0.53500	0.54426	0.83142	0.98466	0.43979	0.83528
Freundlich isotherm							
$K_f$ , $\mu g^{1-1/n} L^{1/n} g^{-1}$	B	0.332	44.034	0.841	6.749	0.838	13.940
	L	1.537	1.389	0.258	0	0	2.570
	D	8.899	12.603	0.041	0.895	0.440	11.150
1/n	B	0.936	0.247	0.726	0.497	1.060	0.402
	L	0.738	0.806	1.056	4.107	4.655	0.672
	D	0.533	0.550	1.496	0.934	1.057	0.502
$R^2$	B	0.84189	0.64513	0.83943	0.64705	0.93124	0.98437
	L	0.79811	0.67971	0.48484	0.64269	0.93964	0.97521
	D	0.76769	0.73785	0.85588	0.99244	0.72003	0.91782

\*B-bromazepam, L-lorazepam, D-diazepam

According to the isotherm parameters given in Table 3, sedative adsorption behavior at equilibrium can be described by Freundlich isotherm for all examined samples, except for unmodified hemp fibers. Experimental data obtained for unmodified hemp fibers fit well with the Langmuir isotherm model, indicating the most homogenous distribution of active sites on the surface of the H sample.

#### 4. CONCLUSION

Through the utilization of textile fibrous waste as adsorbents in water treatment, this kind of waste gains a new life in the value chain, making the process of textile production more sustainable. Accordingly, this work was focused on the use of waste hemp and flax fibers, and cotton yarn, as adsorbents for the removal of pharmaceuticals from sedative class from water, as well as on the influence that fiber structure may have on its adsorption properties. Heterogeneous chemical composition and the presence of components of non-cellulosic origin in the fiber structure, along with the presence of fibrillation, cracks, and cavities on the surface of the fibers are key factors that affect the efficiency of waste fibers as adsorbents. Modifications in surface chemistry and chemical composition induced by applied alkali treatment improved the adsorption properties of hemp and flax fibers and cotton yarn. Utilization of both unmodified and modified samples enabled fast and highly efficient removal (adsorption efficiency ranging from 75 to 100%) of sedatives from water, making waste hemp and flax fibers and cotton yarn promising adsorbents for water treatment.

#### Acknowledgment

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#### REFERENCES

- [1] Femina Carolin, C., Senthil Kumar, P., Janet Joshiba G., Vinoth Kumar, V. (2021). Analysis and removal of pharmaceutical residues from wastewater using membrane bioreactors: a review, *Environmental Chemistry Letters*, 19, 329–343.
- [2] Ortúzar, M., Esterhuizen, M., Olicón-Hernández, D.R., González-López, J., Aranda, E. (2022). Pharmaceutical pollution in aquatic environments: A concise review of environmental impacts and bioremediation systems, *Frontiers in Microbiology*, 13, 869332.
- [3] BIO Intelligence Service (2013), Study on the environmental risks of medicinal products, Final Report prepared for Executive Agency for Health and Consumers.  
[https://ec.europa.eu/health/system/files/2016-11/study\\_environment\\_0.pdf](https://ec.europa.eu/health/system/files/2016-11/study_environment_0.pdf), available: 26.04.2023.
- [4] Sayadi, M.H., Trivedy, R.K., Pathak, R.K. (2010). Pollution of pharmaceuticals in environment, *Journal of Industrial Pollution Control*, 26, 89–94.
- [5] Desai, M., Njoku, A., Nimo-Sefah, L. (2022). Comparing Environmental Policies to Reduce Pharmaceutical Pollution and Address Disparities, *International Journal of Environmental Research and Public Health*, 19, 8292.
- [6] Bello, M.M., Raman, A.A.A. (2019). Synergy of adsorption and advanced oxidation processes in recalcitrant wastewater treatment, *Environmental Chemistry Letters*, 17, 1125–1142.
- [7] Morin Crini, N., Loiacono, S., Placet, V., Torri, G., Bradu, C., Kostić, M., Cosentino, C., Chanet G., Martel, B., Lichtfouse, E., Crini, G. (2019). Hempbased adsorbents for sequestration of metals: a review, *Environmental Chemistry Letters*, 17, 393–408.
- [8] Amaducci, S., Scordia, D., Liu, F.H., Zhang, Q., Guo, H., Testa, G., Cosentino S.L. (2015). Key cultivation techniques for hemp in Europe and China, *Industrial Crops and Products*, 68, 2–16.
- [9] Noori, A., Lu, Y., Saffari, P., Liu, J., Ke, J. (2021). The effect of mercerization on thermal and mechanical properties of bamboo fibers as a biocomposite material: A review, *Construction and Building Materials*, 279, 122519.
- [10] Pejić, B., Vukčević, M., Kostić, M. (2020). Hemp Fibers in Serbia: Cultivation, Processing and Applications, in *Sustainable Agriculture Reviews 42*, Springer Nature Switzerland AG, Cham.
- [11] De Farias, J.G.G., Cavalcante R.C., Canabarro B.R., Viana H.M., Scholz S., Simão R.A. (2017). Surface lignin removal on coir fibers by plasma treatment for improved adhesion in thermoplastic starch composites, *Carbohydrate Polymers*, 165, 429–436.
- [12] Dai, D., Fan, M. (2011). Investigation of the dislocation of natural fibres by Fourier-transform infrared spectroscopy, *Vibrational Spectroscopy*, 55 (2), 300–306.
- [13] Vukčević, M. M., Maletić, M. M., Pejić, B. M., Karić, N. V., Trivunac, K. V., Perić Grujić, A. A. (2023). Waste hemp and flax fibers and cotton and cotton/polyester yarns for removal of methylene blue from



- wastewater: Comparative study of adsorption properties, *Journal of the Serbian Chemical Society*, 88 (6), 669–683.
- [14] Lagergren, S. (1898). About the Theory of So-Called Adsorption of Soluble Substances. Kungliga Svenska Vetenskapsakademiens, *Handlingar* 24, 1-39.
- [15] Ho, Y. S., McKay, G. (1999). Pseudo-second order model for sorption processes, *Process Biochemistry*, 34 (5), 451–465.
- [16] Langmuir, I. (1918). The Adsorption of Gases on Plane Surface of Glass, Mica and Olatinum, *Journal of the American Chemical Society*, 40, 1361–1403.
- [17] Freundlich, H.M.F. (1906). Over the Adsorption in Solution, *The Journal of Physical Chemistry*, 57 384–470.
- [18] Lazić, B. D., Pejić, B. M., Kramar, A. D., Vukčević, M. M., Mihajlovski, K. R., Rusmirović, J. D., Kostić, M. M. (2018). Influence of hemicelluloses and lignin content on structure and sorption properties of flax fibers (*Linum usitatissimum* L.), *Cellulose*, 25 (1), 697–709.
- [19] Zhang, H., Ming, R., Yang, G., Li, Y., Li, Q., Shao, H. (2015). Influence of alkali treatment on flax fiber for use as reinforcements in polylactide stereocomplex composites, *Polymer Engineering and Science*, 55 (11), 2553–2558.
- [20] Sawpan, M. A., Pickering, K. L., Fernyhough, A. (2011). Effect of various chemical treatments on the fibre structure and tensile properties of industrial hemp fibres, *Composites Part A: Applied Science and Manufacturing*, 42 (8), 888–895.

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