MODIFICATION OF CELLULOSE-BASED WASTE MATERIALS FOR REMOVAL OF METHYLENE BLUE FROM WASTEWATER

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ABSTRACT
Different natural fibers and yarns (hemp, flax, and cotton), obtained as a waste from textile industry, were used for the removal of methylene blue from aqueous solution. In attempt to increase the adsorption efficiency, examined fibers and yarn were modified by sodium hydroxide solution. Characterization of examined samples was performed by scanning electron microscopy and Fourier transform infrared spectroscopy. It was shown that applied modification caused the differences in the distribution of hemicelluloses in the structure of examined fibers and fibers in yarn, inducing the changes in morphology and surface chemistry. These changes slightly improved the adsorption properties of hemp fibers, while in the case of cotton yarn modification had a negative effect on methylene blue adsorption. Nevertheless, adsorption efficiency of these waste fibers and yarns highly increase with the pH of the solution, enabling their utilization for methylene blue removal from wastewaters.

INTRODUCTION
Intensive growth of world population along with the frequent changes in clothing fashion trends and furniture industry lead to the excessive consumption of textiles to meet human needs. Also, there is a growing demand for clothes made from comfortable, biodegradable, biocompatible and ecological fibers. Therefore, after quite a long period of intensive application of synthetic fibers, natural fibers take precedence over the synthetic ones, especially in regard to comfort and ecological properties. As the result of increased production in textile industry, the amount of solid textile waste (in the form of short and entangled fibers, natural or synthetic yarns, pieces of clothing etc.) considerably increases. The reckless disposal of textile wastes can cause serious soil, water and air pollution, and it is of great significance to find a new way to reuse these wastes, rather than their commutation.

In the recent years, attention has been devoted to the utilization of different waste materials, as cheap and efficient sorbents for removal of organic and inorganic pollutants from wastewater [1, 2]. The application of these biosorbents for purification of waste and drinking water is a very cost-effective method that can be used as an alternative for adsorption on commercially available activated carbons. Due to the specific structure, heterogeneous chemical composition, and surface functional groups, natural fibers as biosorbent offer an effective way to decrease the concentration of pollutants in wastewaters [3, 4].

In this paper, we report on utilization of different natural fibers and yarns (hemp, flax, and cotton), readily available in large quantities as a waste from textile industry, as an adsorbents for removal of methylene blue from wastewater. To increase the adsorption efficiency, natural fibers and yarns were modified, using cheap and simple treatment of mercerization. Mercerization implies soaking the cellulose fibers in a dilute solution of sodium hydroxide (NaOH), resulting in the dissolution of hemicellulose and rearrangement of microfibrils in a more compact manner.

METHODS

The fibers used as a starting material in this investigation were short flax fibers (L) obtained from Banja Luka (Republic of Srpska, Bosnia and Herzegovina) [5], and short hemp fibers (K) obtained from ITES Odzaci (Serbia) [6], while waste cotton yarn (P) was obtained from textile factory SIMPO Dekor Vranje (Serbia) [4].

Waste fibers and yarn (approximately 1 g), were immersed in 50 ml of 18% NaOH solution. Chemical modification was performed with constant stirring (150 rpm), at room temperature for 60 minutes. After chemical treatment, fibers and yarn were neutralized with 1% acetic acid solution, washed with distilled water and dried at 60 °C overnight. The modified flax and hemp fibers, and cotton yarn are labeled as L_{mod}, K_{mod} and P_{mod}, respectively.

The morphological characteristics of examined samples were assessed by scanning electron microscopy (Mira3, Tescan and SEM JEOL JSM-6610LV). FTIR spectra of the samples, within a range of 400-4000 cm^{-1}, were recorded using a Nicolet™ iS™ 10 FT-IR Spectrometer (Thermo Fisher Scientific).

Adsorption efficiency of unmodified and alkali modified fibers and yarn to remove methylene blue (MB) were tested in batch system with constant shaking at room temperature. The influence of initial pH value on adsorption efficiency was examined by adjusting the initial pH (2, 4, 6, 8 and 10), and adsorption onto 0.02 g of examined samples was performed from 20 cm^3 of methylene blue solution (20 mg/dm^3). Adsorption kinetics was examined by soaking 0.1 g of unmodified and modified samples in 100 cm^3 of MB solution (20 mg/dm^3), and concentration of MB was measured in defined period of time (5, 15, 30, 60, 120 and 180 minutes) by UV/Vis spectrophotometer.

RESULTS AND DISCUSSION

The structure and surface morphology of unmodified and alkali modified samples are shown in Figure 1. The changes in morphological characteristics of samples L and K, induced by applied chemical treatment, are visible in Figures 1d, and 1e. Removal of hemicelluloses from the structure of L and K, induced by mercerization, led to the formation of new open spaces between distinctly liberated elementary fibers in the structure of L_{mod} and K_{mod}. On the other hand, modification of P sample caused only a relative peeling of yarns' surface (Figure 1f).

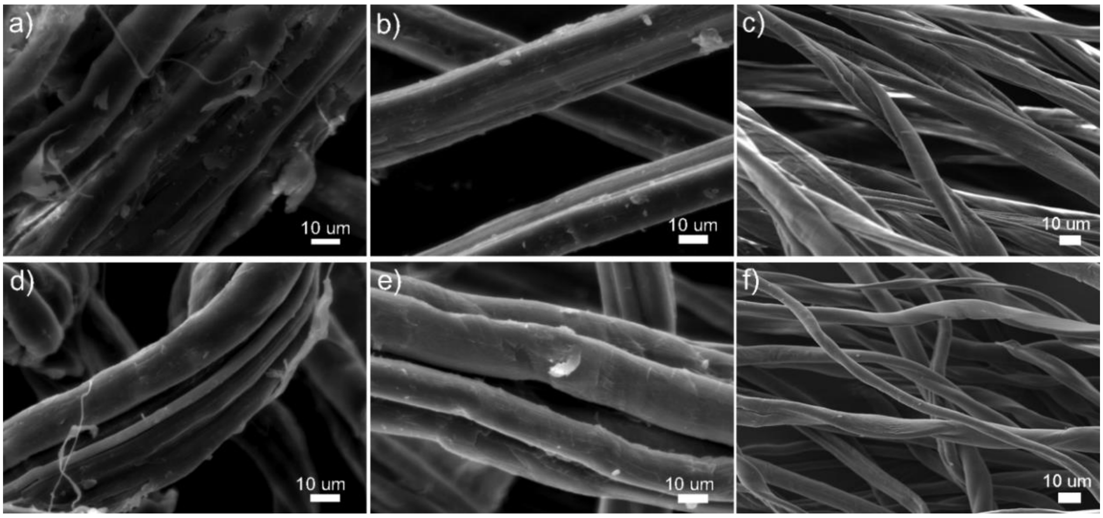

Figure 1. SEM photographs of a) L, b) K, c) P, d) L_{mod}, e) K_{mod}, and f) P_{mod}

FTIR spectra for all samples (Figure 2) show a broad band around 3300 cm^{-1}, originating from stretching of O-H bond in hydroxyl groups. Spectra of modified samples also show two shoulders at 3478 cm^{-1} and 3436 cm^{-1}, attributed to hydroxyl groups in cellulose II, and to the specific hydrogen bonds between O(3)H and O(5), respectively [5]. Peaks at 2850 cm^{-1} and 2920 cm^{-1} originate from the symmetrical and asymmetrical vibrations of C-H bond in methyl and methylene groups of cellulose, and hemicelluloses [7] in the structure of examined fibers and yarns. The changes in FTIR spectra in this wavenumber region, observed for modified samples, originate from hemicelluloses removal by applied mercerization. Also, as a consequence of modification, the peak near 1730 cm^{-1}, attributed to C=O stretching of carbonyl or ester groups of hemicelluloses [7, 8], decreases in intensity for samples L_{mod} and K_{mod}, and disappears for sample P_{mod}. The similar behavior is observed for the bands in the region 1000-1370 cm^{-1}, which are related to the C-O and C-C stretching in polysaccharides, cellulose, and hemicelluloses. The peak around 890 cm^{-1} indicates the presence of glucopyranose ring in the structure of all examined samples. Results of FTIR analysis also showed that applied modification cause the changes in the distribution of hemicelluloses in the structure of examined fibers and yarn.

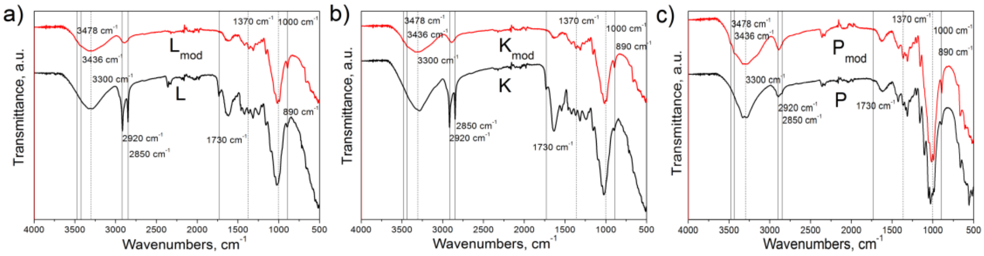

Figure 2. FTIR spectra of unmodified and modified a) flax fibers, b) hemp fibers, and c) cotton yarn.

The influence that applied modification has on adsorption properties of flax and hemp fibers, and cotton yarn, was examined through the adsorption of methylene blue. The solution pH value can be a critical factor that affects adsorption of MB on examined samples through the ionization of surface oxygen containing groups, which represents the binding sites for adsorption. The effect of pH was investigated by varying the initial values of pH solution from 2 to 10, and obtained results are shown in Figure 3. The initial pH of solution has considerable influence on the amount of MB adsorbed. Removal efficiency of methylene blue in the case of P and P_{mod} increases from 5 % on pH 2, to the 50 % on pH 10, while in the case of unmodified and modified L and K samples, removal efficiency increases with the pH even more, up to 75 %. Being the biopolymers, examined fibers and yarns, consist mainly from cellulose and hemicellulose chains, which, at higher pH may get negatively charged, and enhance the adsorption of positively charged dye through electrostatic forces of attraction.

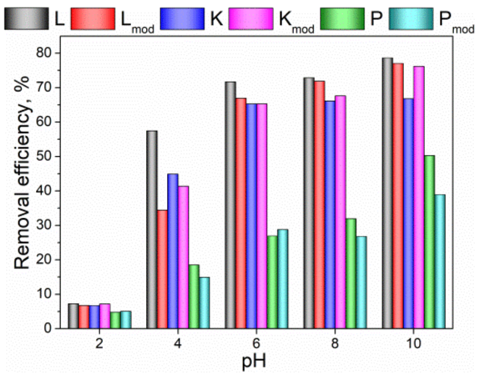

Figure 3. Influence of initial pH on removal efficiency of MB

The increase in adsorption capacities with an increase of contact time is noticeable for all tested samples (Figure 4). Unmodified and modified fibers samples (L, L_{mod}, K and K_{mod}) showed higher adsorption capacities, and higher rates of adsorption (Figure 4a and 4b) than yarns samples (P and P_{mod}) (Figure 4c), most likely due to the different form of samples, i.e. larger contact surface and easier adsorption on the samples in the form of fibers, than in form of yarns. Applied modification has different influence on adsorption capacities: no effect in the case of flax fibers, slight increase for hemp fibers, and negative effect for cotton yarns. Experimental data were examined by the pseudo-first and pseudo-second order kinetic models (Figure 4). Adsorption of methylene blue onto examined fibers and yarns better fits with pseudo-second order kinetic model, suggesting that adsorption process is characterized by chemisorption.

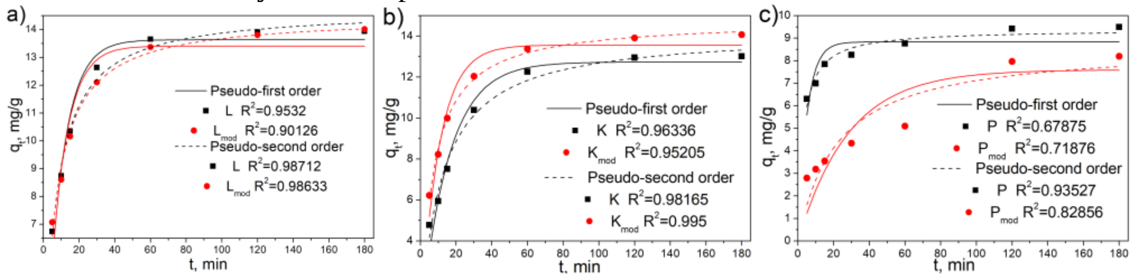

Figure 4. Effect of time on MB adsorption onto unmodified and modified a) flax fibers, b) hemp fibers, and c) cotton yarn.

CONCLUSION

Different natural fibers and yarns (hemp, flax, and cotton), readily available in large quantities as a waste from textile industry, were chemically modified and used as an adsorbents for removal of methylene blue from wastewater. Applied chemical modification caused the differences in the distribution of hemicelluloses in the structure of examined fibers and fibers in yarn, inducing the changes in morphology and surface chemistry. These changes slightly improved the adsorption properties of hemp fibers, while in the case of cotton yarn modification had a negative effect on methylene blue adsorption. Nevertheless, adsorption efficiency of these waste fibers and yarns highly increase with the pH of the solution, enabling their utilization for methylene blue removal from wastewaters. Results obtained in this work showed that waste natural fibers and yarns may be used as sustainable and renewable low cost biosorbent.

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REFERENCES

[3] B. Dhir, Environ. Sci. Pollut. Res., 21 (2014) 1614.
[4] M. Fawzy, M. Nasr, H. Nagy, S. Helmi, Environ. Sci. Pollut. Res., 25 (2018) 5875.
[5] W. Yuan, J. Cheng, H. Huang, S. Xiong, J. Gao,J. Zhang, S. Feng, Ecotoxicol. Environ. Saf., 175 (2019) 138.
[6] S. Mihajlović, M. Vukčević, B. Pejić, A. Perić-Grujić, M. Ristić, K. Trivunac, J. Nat. Fibers, (2021) https://doi.org/10.1080/15440478.2021.1993414.
[7] B. D. Lazić, B. M. Pejić, A. D. Kramar, M. M. Vukčević, K. R. Mihajlovski, J. D. Rusmirović, M. M. Kostić, Cellulose 25 (2018) 697.
[8] M. M. Vukčević, A. M. Kalijadis, T. M. Vasiljević, B. M. Babić, Z. V. Laušević, M. D. Laušević, Microporous Mesoporous Mater., 214 (2015) 156.
[9] H. Zhang, R. Ming, G. Yang, Y. Li, Q. Li, H. Shao, Polym. Eng. Sci., 55 (2015) 2553.
[10]M. A. Sawpan, K. L. Pickering, A. Fernyhough, Composites, Part A., 42 (2011) 888.