

ORIGINAL SCIENTIFIC PAPER

Hemp membranes with anionic functionalization for efficient removal of cationic pollutants

Ljubica Vasiljević¹ | Nataša Knežević² | Milena Milošević³ | Miloš Veličković⁴ | Aleksandar Marinković⁴

¹University of East Sarajevo, Faculty of Technology Zvornik, Karakaj 34A, 75400 Zvornik, Republic of Srpska, Bosnia and Herzegovina

²University of Belgrade, "VINČA" Institute of Nuclear Sciences – National Institute of the Republic of Serbia, Mike Petrovića Alasa 12–14, 11351 Belgrade, Serbia

³University of Belgrade, Institute of Chemistry, Technology and Metallurgy – National Institute of the Republic of Serbia, Njegoševa 12, 11000 Belgrade, Serbia

⁴University of Belgrade, Faculty of Technology and Metallurgy, Karnegijeva 4, 11000 Belgrade, Serbia

Correspondence

Ljubica Vasiljević

Email: ljubicav09@gmail.com

Abstract

The primary aim of this study is to develop a membrane from treated waste hemp fibers using a dimethyl sulfoxide/tetra-n-butylammonium hydroxide (DMSO/TBAOH) solvent system and citric acid (CA) as an efficient adsorbent for the removal of cations and cationic dyes from water. The bio-renewable membrane (cHM) was prepared at the appropriate molar ratio of functional groups, which provided multiple functionalities for the effective removal of cationic pollutants. The formed lignocellulosic cHM adsorbent was characterized in terms of its physico-chemical, structural, and morphological properties through point of zero charge (pH_{PZC}), porosity, Scanning Electron Microscopy (SEM), and Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR) measurements. Pore size was determined using image analysis and the dry-wet weight method. The effects of pH, initial concentration, temperature, and contact time on adsorption were studied in batch adsorption experiments. The membrane demonstrated high adsorption capacities for cationic pollutants, with values of 398.7 mg g^{-1} for Safranine O (SO), 370.60 mg g^{-1} for Methylene Blue (MB), and 445.4 mg g^{-1} for Crystal Violet (CV), following Langmuir model fitting at 25°C . The adsorption process was found to be endothermic, spontaneous, and efficient, highlighting the membrane's potential for water purification. The kinetic parameters of the adsorption process were fitted to both pseudo-first-order and pseudo-second-order models. The five adsorption-desorption cycles yielded effluent waters rich in desorbed pollutants. Photocatalytic degradation of the desorbed dyes using commercial TiO_2 as a catalyst, along with the chemical precipitation of cations into solid form, resulted in treated water that met current legislative standards. Biodegradability tests of the spent membrane confirmed its environmentally safe disposal after 85% degradation. This work demonstrates the application of green chemistry in transforming waste biomass into a high-performance adsorbent for wastewater treatment, offering an eco-friendly technology for water purification.

Keywords: hemp fibers, cationic pollutants, sustainable technology, adsorption process, biodegradability

1. INTRODUCTION

In the modern aspect of the environment, the search for sustainable and efficient solutions for waste management represents the biggest challenge. One of the most pressing global issues is the effective management of industrial and urban wastewater, which is often laden with various pollutants, including toxic cationic dyes. The growing demand for innovative, sustainable solutions to address these pollution challenges drives research towards

more environmentally friendly and cost-effective technologies. Among these, the application of natural and waste-derived materials for pollutant removal stands out due to their easy accessibility, low cost, biodegradability, and minimal environmental footprint (Perkumienė, Atalay, Safaa, & Grigienė 2023).

Hemp fibers, as an agricultural byproduct, have recently garnered significant attention for their potential in environmental remediation. The use of waste hemp

fibers, chemically modified to enhance their adsorption properties, aligns with the principles of green chemistry, which aims to reduce the use of hazardous substances and encourage the use of renewable resources. Specifically, the synthesis of membranes from hemp fibers for the removal of cationic pollutants, such as organic dyes like Safranin O (SO), Crystal Violet (CV), and Methylene Blue (MB), marks a significant step forward in addressing water pollution issues. These dyes, widely used in textile and industrial processes, are not only visually unappealing but are also toxic and persistent in aquatic ecosystems, posing significant health and environmental risks.

The main objective of this research is to explore how waste hemp fibers, treated and modified through environmentally friendly processes, can be transformed into high-performance adsorbents. The study demonstrates the integration of green chemistry principles to convert these waste biomaterials into effective membrane filters capable of capturing cationic pollutants. This approach highlights the potential of such membranes for wastewater purification processes, offering a sustainable and scalable alternative to conventional treatment methods that often rely on synthetic and nonrenewable materials.

A critical aspect of this study is the treatment of waste hemp fibers using the dimethyl sulfoxide/tetra-n-butylammonium hydroxide (DMSO/TBAOH) system (Sirviö & Lakovaara 2021), which facilitates delignification of the fibers. This treatment increases the surface area of the fibers and improves their adsorption properties, making them more effective in capturing cationic pollutants. Following this, the fibers were treated with citric acid, allowing them to be formed into membranes. Citric acid (CA), a natural crosslinking agent, not only enhances the durability of the membranes but also introduces carboxyl groups that can interact with pollutant molecules, thus improving the adsorption capacity. In a batch adsorption system, kinetic and equilibrium studies of SO, MB, and CV dye removal were performed under varying conditions such as adsorbent dosage, temperature, contact time, and pH. The adsorption process was analyzed using several isotherm models, including the Langmuir and the Freundlich models (Hamdaoui & Naffrechoux 2007) to better understand the adsorption mechanisms and the capacity of the hemp membranes. To ensure the longevity and reusability of the developed membranes, desorption cycles were conducted, followed by photocatalytic degradation of the effluents containing cationic dyes. TiO_2 catalysts were employed for this purpose, an established technology known for its efficiency and environmental compatibility in wastewater treatment (Murgolo, De Ceglie, Di Iaconi, & Mascolo 2021). This additional step further emphasizes the sustainable nature of the approach, as it not only extends the life of the adsor-

bent but also ensures that harmful pollutants are broken down into less hazardous substances.

Furthermore, the membrane biodegradability was assessed after their exhaustion, providing additional evidence for the environmental sustainability of this technology. By ensuring that the exhausted materials can degrade naturally without contributing to long-term environmental waste, this research underscores the potential for a fully circular wastewater treatment process. Additionally, the transformation of cationic pollutants in the effluent water through chemical precipitation into solidified form contributes to the overall reduction of environmental harm, making the treated effluents safer for disposal or reuse. In summary, this research not only advances the field of membrane technology by demonstrating the effective use of waste hemp fibers for cationic pollutant removal but also highlights the importance of natural materials in the development of sustainable waste management practices. By utilizing renewable resources, environmentally benign processes, and focusing on pollutant recovery and material biodegradability, this study contributes to the growing body of knowledge aimed at reducing the environmental impact of industrial processes.

2. EXPERIMENTAL PART

2.1. Materials

All the chemicals used in this study were of analytical grade and used as received. The following chemicals were supplied from Sigma Aldrich: dimethyl sulfoxide (DMSO), tetra-n-butylammonium hydroxide (TBAOH), citric acid (CA), and sodium chloride (NaCl). The dyes: Methylene Blue (MB), Crystal Violet (CV), and Safranin O (SO) were purchased from Merck. Adjustment of pH was accomplished with 0.1 M NaOH and 0.1 M HNO_3 (Sigma Aldrich). Waste hemp fibers were obtained from KNOBETON, Novi Sad, Serbia.

2.2. Chemical modification and characterization of hemp membrane

After washing the fibers in distilled water (HF), a chemical modification was performed using the DMSO/TBAOH system to defibrillate and form a membrane (cHM) by cross-linking using citric acid in a mass ratio of 1:0.45 (100 g cHM:450 mL of CA solution) according to our research (Knežević et al. 2023). The treated material was pressed between porous aluminum plates (pore size 0.2 mm) in a press-cast assembly with a load of 20 kN to (numerical range) 30 kN and reheated (100 °C) for 4 h to obtain a compact material (thickness 4 mm, mass 380 mg) as a result of cross-linking reactions.

The structural and morphological characterization of nontreated fibers and the synthesized membrane was investigated by recording the FTIR spectra and SEM micrographs.

2.3. Adsorption-desorption experiments

Data on the adsorption isotherm were obtained by performing the following experiment: by varying the mass of cHM (from 1 mg to (numerical range) 10 mg) was mixed with a solution of dye with an initial concentration of 45 mg L^{-1} to (numerical range) 50 mg L^{-1} in a volume of 10 mL at three temperatures (25°C , 35°C , and 45°C) for a maximum of 120 min. The concentration of dye solutions was determined at 590 nm for CV, 525 nm for SO, and 664 nm for MB using a UV-Vis spectrophotometer 1800, Shimadzu, Japan. The adsorption capacity was calculated using the methodology given in the work Knežević et al. (2023).

To evaluate the efficiency of the adsorption process, desorption of the used sorbent was conducted over 5 cycles. The desorption test was performed by immersing 400 mg of sorbent in 100 mL of 0.5 M NaCl solution. Each cycle lasted 120 minutes. The resulting effluent was analyzed using a UV-Vis spectrophotometer (Blanco et al., 2023).

The pH_{PZC} was obtained following the procedure in our previous work (Knežević et al. 2023).

The disposal of the dye solution after desorption was achieved by photodegradation, facilitated by a commercial TiO_2 catalyst, in the final stage of disposal, following the procedure from the literature (Knežević et al. 2024). Subsequently, the exhausted membrane underwent biodegradability testing, further substantiating the sustainability of the developed technology. A soil sample was collected from an agricultural field in the village of Bečmen, Surčin.

3. RESULTS AND DISCUSSION

3.1. Characterization of materials

The morphology of HF, cHM, and catalyst TiO_2 was examined using Scanning Electron Microscopy (SEM), Figure 1 (a–c).

In Figure 1(a), one can observe the ordered structure of the nontreated fibers, which were then treated with DMSO/TBAOH and CA to obtain a greater number of active sites for contaminant binding. The effect of CA is reflected in the twisting, distortion, and tight binding of fibers, generally changing the morphology of the fiber. SEM analysis of the membrane Figure 1(b) provides evidence of the successful production of the membrane, with

the formation of bonds between the pretreated fibers. Figure 1(c) depicts a picture of the previously synthesized catalyst used in the photocatalytic process (Dey & Mehta 2020).

The image analysis (Image-Pro Plus software) and the result of the dry-wet weight method (Perendija et al. 2020) revealed very similar porosity results. The obtained porosity value was about 61.3%, with an average pore diameter of about $6.2 \mu\text{m}$.

The Fourier Transform Infrared Spectroscopy (FTIR) was used to follow the success of membrane preparation, Figure 2. Both HF and cHM samples on FTIR spectra include a wide band, about 3326 cm^{-1} as a result of hydroxyl group stretching vibrations. The symmetric and asymmetric stretching vibrations of the C–H bond in the methyl and methylene groups of the lignocellulosic structure appeared at 2910 cm^{-1} to (numerical range) 2848 cm^{-1} (Vukčević et al. 2023), while bending vibration appeared between 1423 cm^{-1} and 1317 cm^{-1} .

Methoxy group vibrations of syringyl and guaiacyl molecules from lignin are responsible for a small band at 1365 cm^{-1} . Stretching vibration of the C=O ester groups in hemicellulose and lignin was found at 1731 cm^{-1} in the spectrum of dHF (Viscusi, Barra, & Gorrasi 2020). Cross-linking with citric acid leads to peak shifting to 1709 cm^{-1} in the spectrum of cHM (Pimpang, Sumang, & Choopun 2018). The small peak at 1647 cm^{-1} can be attributed to O–H bending vibration in cellulose. The intensive band at 1610 cm^{-1} in spectrum HF and bands about 1500 associated with C=C stretching vibrations of the aromatic ring from lignin. The symmetric/asymmetric vibrations of C–O–C, C–O, and C–O groups in cellulose, hemicellulose, and lignin appeared in the 1247 cm^{-1} to (numerical range) 1020 cm^{-1} region. From the spectra of cHM after dyes adsorption, significant amount of both dyes adsorbed, which are deduced from increase intensity of and small shift peaks at 1594–1500 due to introduction NH groups from dyes as well as =CH out-of-plane deformation vibrations between 876 cm^{-1} to (numerical range) 500 cm^{-1} region were observed.

3.2. Adsorption-desorption studies

The pH_{PZC} value of cHM is 6.9, indicating that at this pH, cHM has an equal amount of negative and positive surface groups, resulting in a neutral net surface charge. This balance suggests that cHM will exhibit minimal electrostatic interactions with charged species in solution around this pH, making it an important parameter for understanding its adsorption behavior in different environments.

The cHM adsorption capacity at different temperatures was determined using the adsorption findings. Ta-

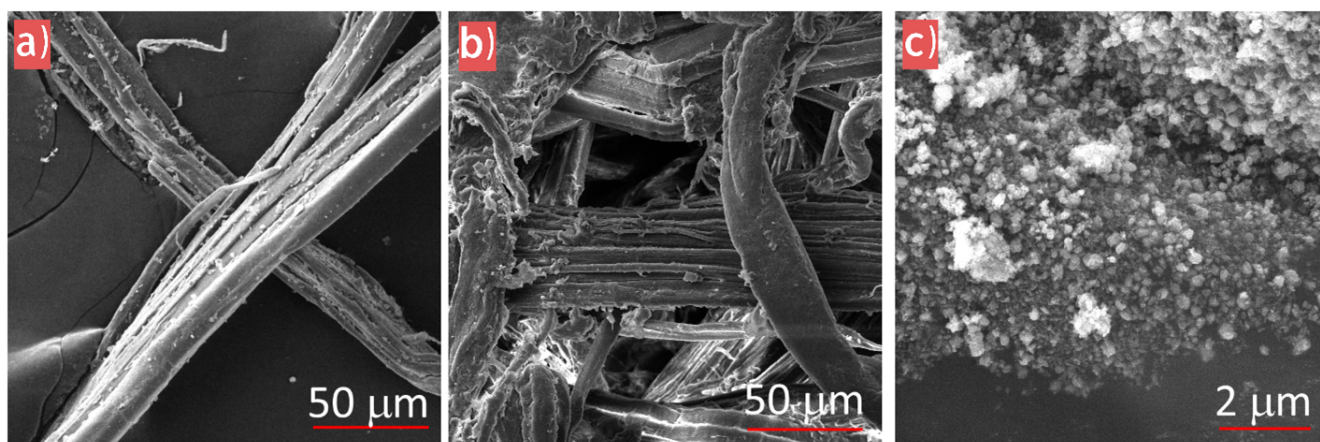


Figure 1. SEM micrographs of (a) HF, (b) cHM, and (c) TiO_2 .

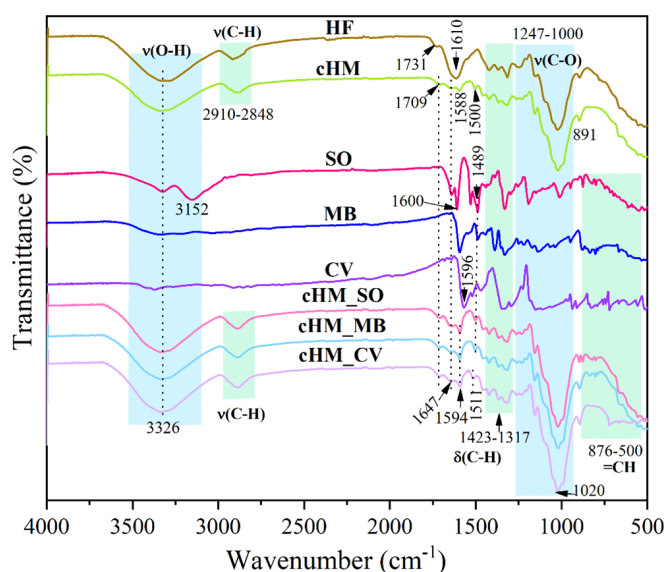


Figure 2. FTIR spectra of nontreated fibers (HF) and synthesized membrane (cHM).

ble 1 presents the findings from the Freundlich and Langmuir model equations given in the work Knežević et al. (2023).

From the data in Table 1, all adsorbents showed high adsorption capacities. With increasing temperature, an increase in adsorption capacities was observed for all dyes. The strong interactions between functional groups on the surface of the adsorbent and the adsorbate were confirmed by high values of the Langmuir constant (K_L). The Freundlich constant (K_F) and the value of parameter n confirm good adsorptivity and indicate high reactivity of the adsorption sites of cHM. For cHM, the Freundlich model shows a better linear fit with higher R^2 values from 0.991 to 0.997, indicating that sorption occurs in multiple layers on a heterogeneous surface. Based on the Langmuir model, maximum adsorption capacities

at 25 °C were determined, with values of 398.7 mg g^{-1} for Safranin O (SO), 370.60 mg g^{-1} for Methylene Blue (MB), and 445.4 mg g^{-1} for Crystal Violet (CV). During the 120 minute investigation of the adsorption properties of the cHM sorbent, each dye reached equilibrium after a certain period. The dye CV achieved its maximum adsorption capacity after 30 minutes, MB after 60 minutes, and SO after 90 minutes.

Thermodynamic parameters Gibbs free energy ($\Delta G^\ominus$), enthalpy ($\Delta H^\ominus$), and entropy ($\Delta S^\ominus$) (Table 2) obtained by using van't Hoff equations (Knežević et al. 2023) represent an important step in the understanding of the adsorption process. The negative value of $\Delta G^\ominus$ and positive values of $\Delta H^\ominus$ and $\Delta S^\ominus$ indicate that adsorption is spontaneous and endothermic.

The thermodynamic data reveal that the processes of dye removal are spontaneous with the pronounced disorder at the adsorbent/adsorbate surface. The differences in $\Delta H^\ominus$ arise mainly from structural characteristics, charge distribution, and availability of positive charges for interaction with negatively charged adsorption sites at cHM.

The results of kinetic parameters, adsorption rate and constants, were determined using pseudo-first-order (PFO; Lagergren model) and pseudo-second-order (PSO) equations (Knežević et al. 2023) by the linear least-squares method. The coefficient of determination (R^2) analysis indicates that the PSO model was the most suitable for describing the kinetic data (Table 3), suggesting that the adsorption is controlled by chemical interaction (Benjelloun, Miyah, Akdemir Evrendilek, Zerrouq, & Lairini 2021).

Examining the effect of temperature change on the kinetics of adsorption processes, the activation energy (E_a) obtained for the adsorbed dyes is $5.135 \text{ kJ mol}^{-1}$ for CV, $4.041 \text{ kJ mol}^{-1}$ for MB, $5.853 \text{ kJ mol}^{-1}$ for SO.

Table 1. Obtained parameters for Langmuir and Freundlich adsorption isotherm for all pollutants adsorption onto cHM

Pollutant	T (°C)	Langmuir			Freundlich		
		K_L (dm ³ mg ⁻¹)	q_m (mg g ⁻¹)	R^2	K_F (dm ³ mg ⁻¹)	$1/n$	R^2
SO	25	1.370	398.7	0.939	214.9	0.625	0.991
	35	1.375	408.3	0.929	222.7	0.6334	0.992
	45	1.381	412.8	0.922	226.6	0.639	0.992
MB	25	1.542	434.9	0.961	222.4	0.541	0.996
	35	1.665	436.9	0.961	232.8	0.540	0.996
	45	1.811	438.7	0.960	244.4	0.540	0.996
CV	25	2.192	445.4	0.977	231.2	0.409	0.997
	35	2.323	445.6	0.978	235.8	0.407	0.997
	45	2.451	446.0	0.979	240.4	0.406	0.997

Table 2. Thermodynamic parameters of pollutants removal using cHM

Pollutant	$\Delta G^\ominus$ (kJ mol ⁻¹)			$\Delta H^\ominus$ (kJ mol ⁻¹)	$\Delta S^\ominus$ (J mol ⁻¹ K ⁻¹)	R^2
	25 °C	35 °C	45 °C			
SO	-42.41	-43.83	-45.21	0.32	143.2	0.827
MB	-42.45	-44.07	-45.72	6.36	163.7	0.997
CV	-43.93	-45.55	-47.17	4.40	162.1	0.999

These results indicate that the rate depends on adsorbate and surface functionalities concentration, while the low E_a values (<40 kJ/mol) indicate the physisorption and diffusion-controlled processes (Knežević et al. 2023).

The desorption results showed a high desorption power of this pollutant when using NaCl as a desorption agent. The highest degree of desorption was recorded with CV, namely 85.76% after the third cycle. After the five cycles, the maximum desorption was: 76.2% for MB, 72.2% for SO, and 81% for CV (Figure 3).

3.3. Stabilization of desorbed pollutants

The success of the biodegradability test (Soil Burial Test; AATCC Test Method 30-1993) of the exhausted membrane is reflected in its complete decomposition after 85 days. The mass of the membrane varied from day to day. In the beginning, the decrease was slower, but at 85 days the mass decreased by 93.9%, which can be considered as a completely degraded membrane (Figure 4).

According to photodegradation studies, MB, SO, and CV virtually completely degraded in 90, 95, and 110 minutes, respectively. When the catalyst was used, the dyes degraded at rates of 70.5%, 68.5%, and 62.1% after 30 minutes for MB, SO, and CV dyes, respectively, and nearly completely at 96% after 90 minutes for MB, 94.1% after 95 minutes for SO, and 92% after 110 minutes for CV (Figure 5).

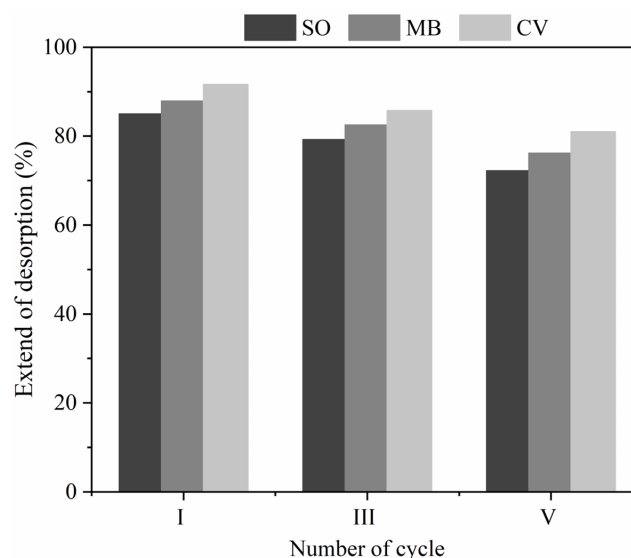
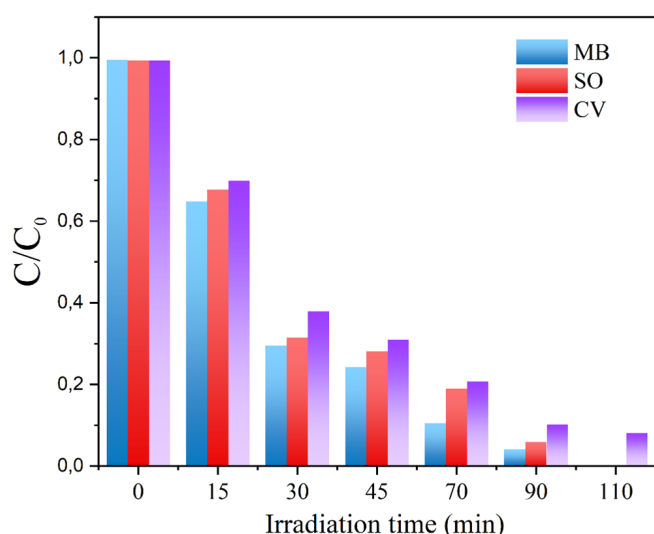
**Figure 3.** Reusability study of cHM in five cycles for cationic pollutants removal ($C_i = 40$ mgL⁻¹, $T = 25$ °C, desorption time: 120 min).

Table 3. PFO and PSO model parameters and activation energy (E_a) for the adsorption of pollutants onto cHM at 25 °C

Adsorbate	Model parameters	Pseudo-first order	Pseudo-second order
SO	q_e (mg g ⁻¹)	11.94	282.8
	k_1 (min ⁻¹); k_2 (g mg ⁻¹ min ⁻¹)	0.0422	0.0049
	R^2	0.392	0.999
MB	q_e (mg g ⁻¹)	46.09	366.5
	k_1 (min ⁻¹); k_2 (g mg ⁻¹ min ⁻¹)	0.0663	0.0026
	R^2	0.789	0.999
CV	q_e (mg g ⁻¹)	105.35	420.05
	k_1 (min ⁻¹); k_2 (g mg ⁻¹ min ⁻¹)	0.1546	0.0031
	R^2	0.963	0.999

**Figure 4.** Biodegradability test of cHM before and after 85 days.

4. CONCLUSION

**Figure 5.** Photodegradation of SO, MB, and CV dyes under optimal conditions.

A treatment process involving dimethyl sulfoxide/tetra-n-butylammonium hydroxide (DMSO/TBAOH) achieved defibrillation, thereby increasing the surface area of the sorbent. Analysis of the structure, morphology, and surface chemistry of cHM, in addition to its porosity (61.3%) and pore size, indicates its suitability for cation removal. Exceptional adsorption capacities were observed for a variety of pollutants, with the Langmuir model fitting the experimental data well. The Freundlich model shows a better linear fit with higher R^2 values, indicating that sorption occurs in multiple layers on a heterogeneous surface. Furthermore, the efficient applicability of cHM in water treatment, together with its low endothermic and spontaneous equilibrium, highlights its potential to address water pollution challenges. The study also highlights the use of TiO₂ as a catalyst for photocatalytic degradation (95%; 90 min) which further improves water quality. Moreover, the biodegradability test confirms an environmentally friendly solution for membrane disposal. Overall, this study highlights the application of green chemistry in the transformation of waste biomaterial into an effective adsorbent for water treatment.

ACKNOWLEDGMENTS

This work was supported by the Ministry of Science, Technological Development and Innovation of the Republic of Serbia (Contract No. 451-03-136/2025-03/200017, 451-03-136/2025-03/200026, 451-03-136/2025-03/200135).

REFERENCES

- Benjelloun, M., Miyah, Y., Akdemir Evrendilek, G., Zerrouq, F., Lairini, S. (2021). Recent Advances in Adsorption Kinetic Models: Their Application to Dye Types. *Arabian Journal of Chemistry* 14, 103031. <https://doi.org/10.1016/j.arabjc.2021.103031>
- Dey, S., Mehta, N.S. (2020). Synthesis and applications of titanium oxide catalysts for lower temperature CO oxidation. *Current Research in Green and Sustainable Chemistry* 3, 100022. <https://doi.org/10.1016/j.crgsc.2020.100022>
- Hamdaoui, O., Naffrechoux, E. (2007). Modeling of adsorption isotherms of phenol and chlorophenols onto granular activated carbon Part I. Two-parameter models and equations allowing determination of thermodynamic parameters. *J Hazard Mater* 147, 381–394. <https://doi.org/10.1016/j.jhazmat.2007.01.021>
- Knežević, N., Milanović, J., Veličković, Z., Milošević, M., Vuksanović, M.M., Onjia, A., Marinković, A. (2023). A closed cycle of sustainable development: Effective removal and desorption of lead and dyes using an oxidized cellulose membrane. *Journal of Industrial and Engineering Chemistry* 126, 520–536. <https://doi.org/10.1016/j.jiec.2023.06.041>
- Knežević, N., Vuksanović, M.M., Banjanac, K., Pantić, K., Veličković, Z., Cvijetić, I., Marinković, A., Milošević, M. (2024). Cationic waste hemp fibers-based membrane: Case study of anionic pollutants removal through environmentally friendly processes. *J Environ Manage* 371, 123174. <https://doi.org/10.1016/j.jenvman.2024.123174>
- Murgolo, S., De Ceglie, C., Di Iaconi, C., Mascolo, G. (2021). Novel TiO₂-based catalysts employed in photocatalysis and photoelectrocatalysis for effective degradation of pharmaceuticals (PhACs) in water: A short review. *Curr Opin Green Sustain Chem* 30, 100473. <https://doi.org/10.1016/j.cogsc.2021.100473>
- Perendija, J., Veličković, Z.S., Cvijetić, I., Rusmirović, J.D., Ugri-nović, V., Marinković, A.D., Onjia, A. (2020). Batch and column adsorption of cations, oxyanions and dyes on a magnetite modified cellulose-based membrane. *Cellulose* 27, 8215–8235. <https://doi.org/10.1007/s10570-020-03352-x>
- Perkumienė, D., Atalay, A., Safaa, L., Grigienė, J. (2023). Sustainable Waste Management for Clean and Safe Environments in the Recreation and Tourism Sector: A Case Study of Lithuania, Turkey and Morocco. *Recycling* 8, 56. <https://doi.org/10.3390/recycling8040056>
- Pimpang, P., Sumang, R., Choopun, S. (2018). Effect of concentration of citric acid on size and optical properties of fluorescence graphene quantum dots prepared by tuning carbonization degree. *Chiang Mai Journal of Science* 45, 2005–2014.
- Sirviö, J.A., Lakovaara, M. (2021). A Fast Dissolution Pretreatment to Produce Strong Regenerated Cellulose Nanofibers via Mechanical Disintegration. *Biomacromolecules* 22, 3366–3376. <https://doi.org/10.1021/acs.biomac.1c00466>
- Viscusi, G., Barra, G., Gorrasi, G. (2020). Modification of hemp fibers through alkaline attack assisted by mechanical milling: effect of processing time on the morphology of the system. *Cellulose* 27, 8653–8665. <https://doi.org/10.1007/s10570-020-03406-0>
- Vukčević, M., Maletić, M., Pejić, B., Karić, N., Trivunac, K., Perić-Grujić, 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, 669–683. <https://doi.org/10.2298/JSC221213015V>