METHOD FOR DEGRADATION OF COLORED ELUENTS AFTER DESORPTION FROM CHEMICALLY FUNCTIONALIZED CELLULOSIC MATERIAL

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Abstract

In this study, a method for the removal and degradation of colored eluents after desorption from chemically functionalized cellulosic materials was developed. Waste hemp fibers were transformed into an efficient cellulosic adsorbent through a two-step process involving delignification and subsequent quaternization with betaine hydrochloride-urea (QDHF-BHU). The fibers were first subjected to delignification, followed by quaternization using the synthesized Deep Eutectic Solvents (DES), betaine hydrochloride-urea. The adsorbent was evaluated for the removal of anionic dyes, including Metanil Yellow (MY) and Congo Red (CR), in a batch adsorption system. Structural and chemical characterization of the modified fibers was performed using Scanning Electron Microscopy (SEM), Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR), porosity measurements, and point of zero charge (pHpzc) analysis. Pore size was determined through image analysis and the dry-wet weight method. The adsorption process was found to be endothermic and spontaneous, achieving high adsorption capacities (qm) at 25°C, with the optimal pH for adsorption being 7. Kinetic studies indicated that the adsorption followed both pseudo-first-order (PFO) and pseudo-second-order (PSO) models. After adsorption, the desorbed dyes were subjected to photocatalytic degradation using zinc oxide as a catalyst, with high and rapid decolorization efficiency, particularly for Metanil Yellow. The photocatalytic process ensured that the treated water posed minimal environmental risk.

This work demonstrates the application of green chemistry principles in the functionalization of waste lignocellulosic materials and the subsequent degradation of colored eluents, offering an eco-friendly and efficient method for water purification and wastewater treatment.

Keywords: *waste hemp, anionic pollutants, adsorption process, photodegradation method, Deep eutectic solvents*

1. INTRODUCTION

The contamination of surface and groundwater with synthetic organic dyes represents one of the major environmental challenges in water pollution control. Anionic dyes such as Congo Red (CR) and Metanil Yellow (MY) are widely used in textile, pharmaceutical, and food industries, and are characterized by high chemical stability, toxicity, and potential carcinogenicity (Forgacs et al. 2004). Their removal from wastewater using conventional methods (e.g., coagulation, flocculation, chlorination) is often inefficient and environmentally undesirable. In contrast, adsorption has emerged as a simple, selective, and energy-efficient method for the elimination of dyes from aqueous systems (Rafatullah et al. 2010). Recently, increasing attention has been paid to the use of plant-based waste materials such as hemp fibers, agricultural residues, cotton, and straw for wastewater treatment. These lignocellulosic materials are rich in cellulose, hemicelluloses, lignin, pectins, fats, and waxes, and due to the presence of active surface sites, they offer great potential for adsorption processes. For instance, hemp fibers typically contain 67.0-78.3% cellulose, 5.5-16.1% hemicelluloses, 2.9-3.3% lignin, and 0.8-2.5% pectins (Liu et

al. 2017, Knežević et al. 2024). Naturally occurring functional groups such as hydroxyl (–OH) and carboxyl (–COOH) enable efficient interactions with various pollutants. However, the adsorption performance of these materials can be significantly enhanced through chemical modification. One modern, environmentally friendly, and increasingly adopted approach for cellulose functionalization involves the use of deep eutectic solvents (DES) as a green alternative to traditional chemical reagents.

DES are mixtures of two or more components that form a stable liquid phase with a melting point lower than that of the individual constituents. They are usually composed of hydrogen bond donors and acceptors, and are characterized by their biodegradability, low toxicity, non-volatility, and simple preparation. Among various DES systems, betaine hydrochloride–urea-based DES stands out as a particularly effective and sustainable option for cellulose modification. Betaine, a natural quaternary ammonium compound found in plants and animals, is known for its ability to form strong hydrogen bonds, which contribute to the stability and functional versatility of DES systems (Liang et al. 2020, Mnasri et al. 2022). In this study, waste hemp fibers were modified using a two-step process involving delignification and subsequent quaternization with a DES composed of betaine hydrochloride and urea, resulting in a highly efficient adsorbent (QDHF-BHU). The modified material was tested for its ability to remove CR and MY from model dye solutions under batch adsorption conditions. The fibers were characterized by scanning electron microscopy (SEM), attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR), porosity analysis, point of zero charge (pHpzc), and pore size measurements. The adsorption process was further evaluated using kinetic and thermodynamic modeling.

Following the adsorption phase, the dyes desorbed from the fiber surface were subjected to photocatalytic degradation using ZnO under UV irradiation. This additional step enabled further removal of pollutants and significantly reduced the ecotoxicological potential of the treated effluents. The combination of adsorption, desorption, and photocatalytic degradation presented in this work offers an integrated and sustainable approach for efficient wastewater treatment. In comparison to previous studies that relied solely on adsorption or oxidative degradation (Gupta et al. 2023), this research contributes to the advancement of innovative green technologies for the treatment of dye-contaminated effluents through the utilization of waste biomaterials and principles of green chemistry.

2. MATERIALS AND METHODS

2.1. Materials

Recycled materials, specifically waste hemp fibers, were sourced from KONOBETON in Novi Sad, Serbia. All chemicals utilized in this research were of analytical quality and used as provided. The following chemicals were obtained from Sigma Aldrich, Germany: DMSO, TBAOH, urea (NH_2CONH_2), betaine hydrochloride ($C_5H_{12}ClNO_2$), and zinc oxide (ZnO). The dyes Metanil yellow and Congo red were acquired from Merck. To adjust the pH, 0.1 M NaOH and 0.1 M HNO_3 (Sigma Aldrich) were used. Working dye solutions of the required concentrations were prepared before each experiment by proper dilution of powder with deionized water. Deionized water was supplied from a Milli-Q water purification system (Simplicity® Water Purification System, Millipore Corporation, USA).

2.2. Methods

Structural and chemical characterization of the modified fibers was performed using:

- Scanning Electron Microscopy (SEM) with Tescan Mira 3 XMU FEG equipment with a Schottky field emission gun operated at 20 kV, Czech Republic.
- Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR) Nicolet™iS™10 FT-IR Spectrometer (Thermo Fisher SCIENTIFIC) with Smart iTR™ Attenuated Total Reflectance (ATR), United States of America. The resolution of scans was 4 cm-1, while the number of scans was 20.

- Porosity measurements and fibers diameters using the Software Image-Pro Plus 6.0 (Media Cybernetics). Also, porosity was determined using the gravimetric method ("dry-wet mass"), following the procedure described in the literature (Koromilas et al. 2019)
- The point of zero charge (pHpzc) was obtained using a pH meter (HI-2210-02 Bench Top, HANNA instruments, Hungary), with an instrument accuracy of 0.01. A series of pH solutions ranging from 2 to 12 was created using KNO_3 solutions at concentrations of 0.1, 0.01, and 0.001 M, respectively. After allowing the solutions to equilibrate for 24 hours by adding the same quantity of sorbent (100 mg) to the same amount of electrolyte (50 mL), the pH value was measured again and taken as the final.
- The process of establishing the adsorption equilibrium of dyes on the prepared material was monitored using a UV-Vis spectrophotometer 1800, Shimadzu, Japan.

Photodegradation products of Congo red and Metanil yellow were identified using mass spectrometry (MS). The MS analysis was conducted with a linear ion trap mass spectrometer LTQ XL (Thermo Fisher Scientific, Waltham, US) employing the electrospray ionization (ESI) technique in negative mode. The optimal ESI parameters were as follows: capillary temperature (220 ºC), capillary voltage (-38.5 kV), sheath gas (19 au), and auxiliary gas (17 au). Mass spectra were recorded in the m/z range of 50-1000.

ZnO was subjected to X-ray diffraction investigation on two distinct diffractometers employing a Bragg-Brentano geometry. The Ital Structure APD2000 diffractometer was used for the preliminary investigations, which used CuKα radiation over a 2θ range of 5 to 80°. Additional measurements were performed using CuKα radiation with a wavelength of λ=1.54178 Å on a SmartLab Rigaku diffractometer, which likewise used Bragg-Brentano geometry. At 40 kV and 30 mA, the X-ray tube was in operation. Diffraction data were gathered using a scan speed of 2°/min and a step size of 0.02° throughout a 2θ range from 6 to 80°.

The pHpzc (standardized abbreviations) were obtained following the procedure in our previous work (Knežević et al. 2023).

2.3. Preparation of the waste hemp fibers as adsorbent (QDHF-BHU)

Waste hemp fibers were transformed into a cellulosic adsorbent via a two-step modification process, involving initial delignification followed by quaternization using betaine hydrochloride-urea as a deep eutectic solvent (DES). In the first step, the hemp fibers were subjected to delignification using a solvent system based on dimethyl sulfoxide (DMSO). According to (Sirviö and Lakovaara 2021) a mixture of DMSO and an aqueous solution of tetrabutylammonium hydroxide (TBAOH) offers high solvency power and facilitates mild delignification and cellulose alkalization, leading to effective fiber purification and defibrillation. Following delignification, the fibers were quaternized using a synthesized DES composed of betaine hydrochloride and urea. The DES was prepared by mixing betaine hydrochloride and urea in a molar ratio of 1:4 in a three-neck round-bottom flask. The mixture was heated to 100 °C and stirred until a homogeneous liquid was formed. After cooling, 5 g of delignified hemp fibers were added to the DES, maintaining a fiber-to-DES mass ratio of 2.5:100. The resulting suspension was stirred at 100 °C for 4 hours. Upon completion of the reaction, the modified fibers were washed in several cycles-initially with warm water, followed by cold water-to remove residual solvents and unreacted components. The purified fibers were then left to air-dry at room temperature for 24 hours.

2.4. Adsorption and desorption experiments

Adsorption isotherm data were obtained through batch experiments in which varying amounts of QDHF-BHU (up to 10 mg) were added to 10 mL of dye solution with an initial concentration of 10 mg L^{-1}. The experiments were conducted at two different temperatures (25 °C and 45 °C) over a maximum contact time of 120 minutes. The residual dye concentrations were determined spectrophotometrically using a UV-Vis spectrophotometer (UV-1800, Shimadzu, Japan) at specific wavelengths: 436 nm (MY) and 498 nm (CR). The eluent was separated from the adsorbent by centrifugation using an LLG mini centrifuge (uniCFUGE5, LLG Labware, Germany) at 10,000 rpm for 10 minutes.

The adsorption behavior of the investigated system was evaluated through equilibrium, kinetic, and thermodynamic studies. The most commonly used isotherm models, Langmuir and Freundlich, were

applied to analyze the adsorption equilibrium (Knežević et al. 2023). The Langmuir model assumes that maximum adsorption occurs when a saturated monolayer of adsorbate molecules forms on the adsorbent surface, with no further movement of adsorbate in the surface plane and constant adsorption energy. In contrast, the Freundlich isotherm accounts for surface heterogeneity and describes the exponential distribution of active sites and their corresponding energies (Veličković et al. 2023).

Kinetic studies were conducted to gain insight into the possible adsorption mechanism and to determine the rate of adsorbate-adsorbent interaction. The adsorption data were evaluated using linear least-squares methods, based on pseudo-first-order and pseudo-second-order kinetic models (Foo and Hameed 2010, Vafakhah et al. 2016, Benjelloun et al. 2021).

Thermodynamic parameters, including changes in Gibbs free energy ($\Delta G°$, kJ mol^{-1}), enthalpy ($\Delta H°$, kJ mol^{-1}), and entropy ($\Delta S°$, J mol^{-1} K^{-1}), were calculated using the Van't Hoff equations to assess the spontaneity and heat changes associated with the adsorption process (Lima et al. 2019)

The chemical structure of the removed dyes is shown in Fig. 1.

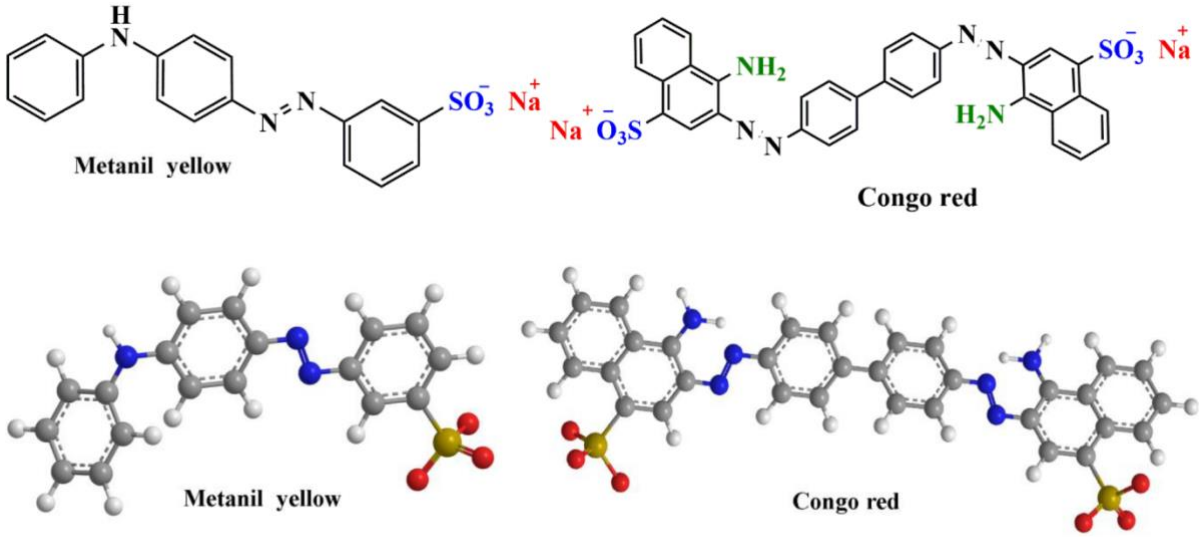

Fig. 1. Chemical structures of dyes 2D and 3D model

To assess the reusability of the adsorbent, desorption experiments were carried out over five consecutive cycles. In each cycle, 200 mg of the spent sorbent was immersed in 50 mL of 4 wt.% NaOH solution for 240 minutes. After each cycle, the desorbed dye in the supernatant was quantified using a UV-Vis spectrophotometer.

The adsorbent regeneration efficiency was calculated with the following equation 1 : (Khan et al. 2021)

$$(\%RE) = {q_r}/{q_0} \times 100 \quad (1)$$

Where q_0 and q_r represent the adsorbents' adsorption capabilities (mmol g^{-1} or mg g^{-1}) before and after the desorption stage, respectively.

2.5. Photodegradation procedure

Following the desorption of dyes from the sorbent surface, the resulting dye-containing effluents were subjected to photocatalytic degradation under UV light using a commercial ZnO catalyst. This approach was employed for the removal of anionic dyes MY and CR as a cost-effective and efficient method for wastewater treatment (Sun et al. 2019). The progress of the photodegradation process was monitored by

UV-Vis spectroscopy, with the efficiency assessed by tracking the decrease in absorbance at 436 nm and 498 nm, corresponding to the maximum absorption wavelengths of MY and CR, respectively. Degradation kinetics were evaluated by applying zero-, first-, and second-order kinetic models (Gaur et al. 2023). Initially, higher dye concentrations were used, but the solutions were subsequently diluted to 20 mg L^{-1} to reduce the reaction time. X-ray diffraction (XRD) analysis of the ZnO catalyst was performed after multiple degradation cycles to assess structural stability, while the degradation products of CR and MY were identified using mass spectrometry (MS).

The degradation kinetics were investigated using zero, first, and second-order kinetics, with the following equations (2-4) (Rabeie and Mahmoodi 2023)

$$C - C_0 = -k_0 t \tag{2}$$

$$\ln\left(\frac{C}{C_0}\right) = -k_1 t \tag{3}$$

$$\frac{1}{C} - \frac{1}{C_0} = k_2 t \tag{4}$$

Where C_0 and C are the concentrations of the studied dye at the beginning and end of time t, and k_0, k_1, and k_2 are the rate constants for zero, first, and second orders, respectively.

3. RESULTS AND DISCUSSION

3.1. SEM and FTIR analysis

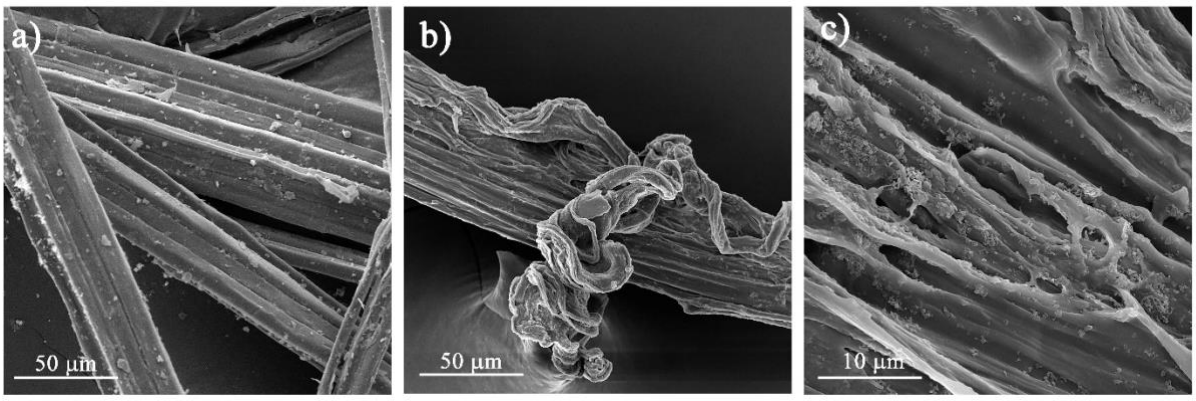

Fig. 2. SEM micrographs of (a) nonmodified fibers and (b, c) QDHF-BHU

Figure 2a shows the morphology of nonmodified fibers, which appear relatively smooth, with a compact surface and minimal porosity. The fiber surface does not show significant irregularities or structural damage, indicating a preserved and unaltered microstructure typical of natural cellulosic materials. In contrast, Figures 2b and 2c show QDHF-BHU modified fibers, which display pronounced surface roughness and noticeable morphological changes. The modified fibers have a more disrupted and porous surface, with visible cracks, folds, and increased specific surface area. The effect of the solvent can be observed, which disintegrates the fiber structure and creates a fluffy appearance, along with a few undissolved fibers with damaged structure. The observed morphological transformation increases the availability of active sites, contributing to improved adsorption capacity and reactivity in further applications such as pollutant removal.

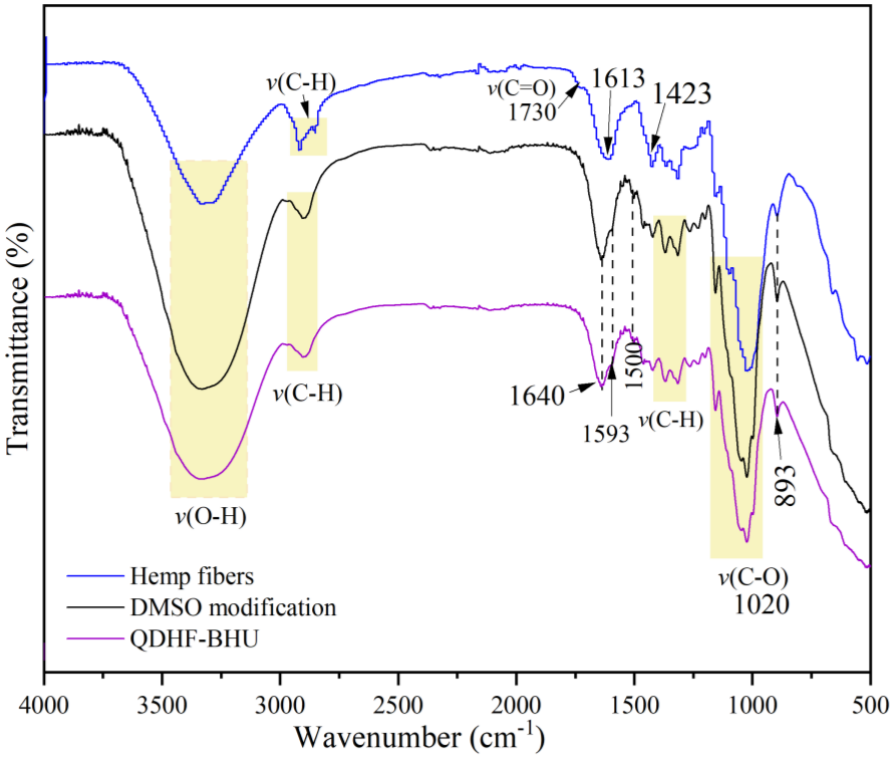

Fig. 3. FTIR spectra of hemp fibers, modified with DMSO and synthesized DES

The presence of distinctive functional groups in the hemp fiber samples before and after modification is confirmed by FTIR analysis, which also shows that the fiber surface has undergone chemical change. A wide absorption band at about 3400 cm^{-1} dominates the spectra of all materials, and this is explained by the stretching vibrations of O–H bonds (*ν*(O–H)), which are typical of the hydroxyl groups found in cellulose, hemicellulose, and lignin. The band shows the asymmetric stretching of C–H bonds (ν(C–H)) from methylene groups, which is common for aliphatic components, at about 2920 cm^{-1}. The band at 1730 cm^{-1} assigned to strechig vibrations of ester groups in hemp fibers, during the modification process disappears, indicating on the succesuful proces delignificaations (Viscusi et al. 2020). The bound water or the deformation of -OH groups may be linked to a weaker band in the 1640 cm^{-1} area. Asymmetric and symmetric bending vibrations of NH_3^+, and C–H bending of CH_3 and CH_2 groups linked to $\equiv N^+$-vibrations were identified as the causes of the new peaks that formed at 1593 -1500, and 1450-1315 cm^{-1} when the modifying agents reacted with hemp fibers. Changes in the strength and structure of this band reveal structural variations in the polysaccharide environment of the fibers. The stretching of C-O bonds (*ν*(C-O)), which is characteristic of alcohols, ethers, and esters, is responsible for an intense signal in the region around 1020 cm^{-1}.

The successful surface modification of the fibers with DMSO is confirmed by comparing the spectra of the modified and unmodified samples, which show variations in the intensity and location of these distinctive bands. The functional characteristics of the fibers, including their enhanced hydrophilicity, reactivity, and potential for future application in the field of pollutant adsorption, may be directly impacted by these modifications.

3.2. Adsorption and desorption analysis

The pHpzc of QDHF-BHU was determined to be 7.35, indicating that its surface carries no net charge at this pH due to an equal presence of positively and negatively charged functional groups. At this point, electrostatic interactions with ionic species in the surrounding medium are minimized, making this parameter crucial for predicting the material's adsorption performance under different conditions.

Using the gravimetric method, the porosity of the modified fibers was determined based on the ratio of the dry and wet mass of the sorbent (Imdad and Dohare 2022), yielding a value of 71%. This high porosity indicates favorable conditions for the flow of pollutant solutions through the sorbent structure, enabling more efficient binding of contaminant molecules and contributing to the overall adsorption capacity of the material.

The adsorption results were used to calculate the adsorption capacity at different temperatures. Table 1 shows the results of the Freundlich and Langmuir models.

CR	***Langmuir***			***Freundlich***		
	q_m (mg g^{-1})	K_L(L mg^{-1})	R^2	K_F (mg g^{-1}) (L $mg^{-1})^{1/n}$	1/n	R^2
25°C	343.3	0.992	0.9965	141.9	0.452	0.9832
45°C	346.3	2.375	0.9966	193.3	0.366	0.9377
MY	***Langmuir***			***Freundlich***		
	q_m (mg g^{-1})	K_L(L mg^{-1})	R^2	K_F (mg g^{-1}) (L $mg^{-1})^{1/n}$	1/n	R^2
25°C	238.4	1.901	0.9991	128.8	0.358	0.9075
45°C	256.5	4.431	0.9982	171.2	0.295	0.8425

Table 1. Linear adsorption isotherm model parameters at two temperatures

Adsorption data for the dyes Congo red (CR) and Methyl yellow (MY) at 25 °C and 45 °C revealed that the Langmuir model provides a better fit to the experimental results compared to the Freundlich model, as evidenced by the high determination coefficients (R^2 > 0.9966 for CR and R^2 > 0.9982 for MY). The Langmuir model assumes monolayer adsorption of adsorbate molecules onto a surface with homogeneously distributed active sites, whereas the Freundlich model describes multilayer adsorption on a heterogeneous surface. According to the Langmuir model, the maximum adsorption capacity (q_m) increased with temperature for both dyes (from 343.3 to 346.3 mg g^{-1} for CR and from 238.4 to 256.5 mg g^{-1} for MY), along with the Langmuir affinity constant (K_L), indicating the endothermic nature of the process. The higher q_m value for CR quantitatively confirms its greater adsorption capacity (C_o = 10 mg L^{-1}) compared to MY, which can be attributed to its higher specific surface area and porous structure, providing a larger number of active binding sites.

The values of the Freundlich parameter n within the range of 1 to 10 suggest a favorable adsorption process for these anionic species. Freundlich parameters show an increase in adsorption capacity (K_F) and a decrease in 1/n values with rising temperature, indicating more favorable adsorption at higher temperatures. However, lower R^2 values, particularly at 45 °C (R^2 = 0.9377 for CR and R^2 = 0.8425 for MY), indicate a weaker correlation with this model. The results confirm that the adsorption of CR and MY onto the tested material occurs as a homogeneous monolayer, consistent with the assumptions of the Langmuir isotherm. The trend of adsorption values on the synthesized sorbent shows a correlation with the removal efficiencies of the same pollutants using the sorbent derived from choline chloride and urea (Knežević et al. 2024).

Kinetic rate law equations were applied to fit the experimental data, including the pseudo-second-order model (Ho and McKay), the pseudo-first-order model (Lagergren), and the Elovich model, all evaluated using the linear least-squares method (Table 2).

Models	Parameters	CR		MY	
		25 °C	45 °C	25 °C	45 °C
Pseudo-first order	q_e (mg g^{-1})	23.078	22.21	30.89	14.97
	k_1 (min^{-1})	0.0787	0.0752	0.0775	0.0266
	R^2	0.9592	0.9064	0.6770	0.3051
Pseudo-second order	q_e (mg g^{-1})	64.04	62.74	86.85	72.62
	k_2 (g mg^{-1} min^{-1})	0.0069	0.0081	0.0006	0.0015
	R^2	0.9998	0.9959	0.9349	0.9960
Elovich	a (mg g^{-1} min^{-1})	271.5	2030	9.361	14.97
	β (g mg^{-1})	0.1121	0.1552	0.0049	0.0579
	R^2	0.9617	0.9400	0.9752	0.9872

Table 2. The kinetic parameters for CR and MY adsorption onto QDHF-BHU

The pseudo-first-order model showed a poor fit to the experimental data. The low determination coefficients, especially for MY (R^2 = 0.6770 at 25 °C and 0.3051 at 45 °C), indicate that this model does not reliably describe the adsorption process, particularly at lower temperatures. In contrast, the pseudo-second-order model, which assumes that adsorption occurs through chemical interactions (chemisorption) between QDHF-BHU and the dye molecules, showed a much better agreement with the data. The high R^2 values (0.9064-0.9998) confirm its suitability for describing the adsorption kinetics of both dyes. Moreover, the rate constant (k_2) values revealed faster adsorption for CR (0.0069 g mg^{-1} min^{-1}) than for MY (0.0006 g mg^{-1} min^{-1}), likely due to greater accessibility of active sites on the adsorbent surface. The Elovich model, commonly used for systems with heterogeneous surfaces, also fitted the data well (R^2 = 0.9400-0.9872). High initial adsorption rates (a), particularly for CR at 45 °C (2030 mg g^{-1} min^{-1}), indicate a strong initial interaction between dye molecules and the adsorbent. These results suggest that the heterogeneous surface and rich functional group content of the adsorbent play an important role in the adsorption process.

Pollutant	ΔG^{Θ} (kJ mol^{-1})		ΔH^{Θ}	ΔS^{Θ}	R^2
	25 °C	45 °C	(kJ mol^{-1})	(J mol^{-1} K^{-1})	
CR	-43.28	-48.49	34.42	260.6	0.9999
MY	-44.89	-50.15	33.36	262.5	0.9999

Table 3. Calculated thermodynamic parameters of removal CR and MY at two temperatures

The thermodynamic analysis of CR and MY dye (Table 3) adsorption reveals that the process is both spontaneous and endothermic. The negative values of standard Gibbs free energy ($\Delta G° < 0$) at 25 °C and 45 °C (ranging from -43.28 to -50.15 kJ mol^{-1}) indicate the favorable and spontaneous nature of adsorption, with spontaneity increasing at higher temperatures. The positive standard enthalpy values ($\Delta H°$ = 34.42 kJ mol^{-1} for CR and 33.36 kJ mol^{-1} for MY) confirm that the process requires heat input, which is consistent with the observed enhancement of adsorption capacity with increasing temperature. The high positive values of standard entropy ($\Delta S° \approx 261$ J mol^{-1} K^{-1}) suggest increased disorder at the sorbent-adsorbate interface, likely due to the release of water molecules or other solvated species during adsorption (Foo and Hameed 2010). The elevated entropy values further imply improved stability of

surface complexes and greater adsorption capacity. The high correlation coefficients (R^2 > 0.999) confirm the reliability of the obtained thermodynamic parameters.

The regeneration of the QDHF-BHU adsorbent was achieved by washing with a 4 wt. % NaOH solution at room temperature for 4 hours. After elution, the used adsorbent was thoroughly rinsed with deionized water until a neutral pH was reached, followed by drying at room temperature for 6 hours. This regeneration method enabled effective removal of the adsorbed anionic dyes from the sorbent surface, due to the neutralization between the adsorbed dye and hydroxide ions, as well as the formation of a concentration gradient that facilitated desorption. After five successive adsorption-desorption cycles, the dye removal efficiency of the QDHF-BHU adsorbent showed a slight decrease, retaining approximately 85% of its initial capacity for MY, while for CR, the capacity declined to around 79% (Figure 4). These results indicate good regenerative adsorption properties of the synthesized sorbent, making it suitable for repeated use in the removal of anionic pollutants from aqueous media.

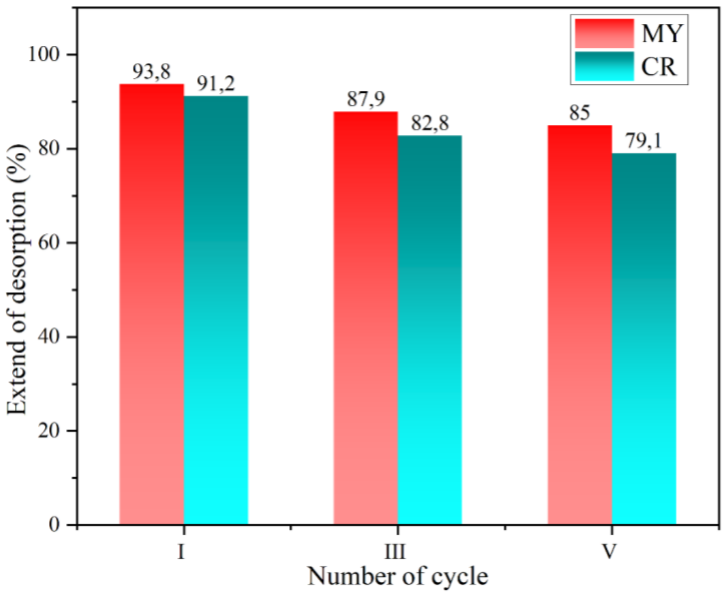

Fig. 4. Reusability study of QDHF-BHU in five cycles for anionic pollutants removal using 4 wt. % NaOH

3.3. Photocatalytic assays of dyes MY and CR

Photocatalytic tests of MY and CR were performed at initial pollutant concentrations of 20 mg L^{-1}, at room temperature, over a period of 6 hours. Absorption spectra obtained by UV-Vis spectroscopy were analyzed at 436 nm and 498 nm (λmax for MY and CR, respectively) to monitor the efficiency of the photocatalytic process. The XRD pattern of the ZnO catalyst after three photodegradation cycles, is presented in Fig. 5.

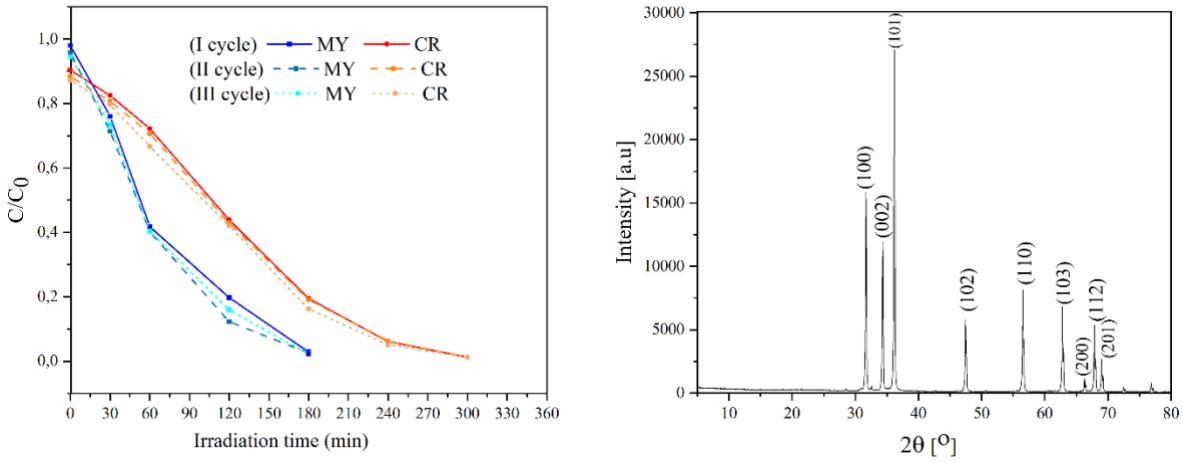

Fig. 5. Effect of photodegradation process during 6h and XRD patterns of ZnO after degradation processes

The results demonstrate that MY and CR were almost completely degraded in a lengthy period, at 180 and 300 minutes, respectively. The catalyst effect on dye degradation was 97.2% for MY (180 min) and 98.8% for CR (300 min), respectively. Using modified ZnO catalysts results in a higher proportion of dye degradation (Yuliasari et al. 2022, Gaur et al. 2023). The lower molecular weight of MY with the same photocatalyst dose is directly proportional to the availability of active sites on the photocatalyst's surface, which increases its efficiency.

The results of the employed catalyst regeneration tests revealed that the catalyst's regeneration ability did not decline considerably after three cycles. After three cycles, the regeneration efficiency maintained above 97% (100%, 98%, and 97%, respectively). As a result, the catalyst displayed good regeneration capabilities, as evidenced by XRD examination of the catalyst following desorption. Table 4 presents the kinetic constants and correlation coefficients. The results show that dye degradation with the commercial catalyst follows first-order kinetics. Table 4 shows that first-order kinetics has a greater correlation coefficient (R^2) compared to zero-order and second-order kinetics.

Pollutant	Zero order		First order		Second order	
	k_0 (mg min^{-1} L^{-1})	R^2	k_1 (min^{-1})	R^2	k_2 (L mg^{-1} min^{-1})	R^2
MY	0.1325	0.9509	0.0242	0.9686	0.0112	0.7756
CR	0.0640	0.9512	0.0152	0.9431	0.0119	0.6135

Table 4. Degradation kinetics constants of MY and CR solution with ZnO at 25 °C

X-ray diffraction (XRD) was used to verify the different stages of ZnO catalysts. By the peaks seen for syntesized ZnO before the photodegradation process, the XRD peaks at 31.64°, 34.39°, 36.19°, 47.48°, 56.49°, 62.77°, 66.30°, 67.86°, and 68.96° were determined to be (100), (002), (101), (102), (110), (103), (200), (112), and (201) reflections, respectively. The sharper and more intense diffraction peaks show that the product has a fine crystalline structure. The photodegradation products were analyzed using MS analysis. All identified species with m/z values of 416, 401, 325, and 222, corresponding to the degradation products of CR dye, are consistent with previous findings reported by (Bhaumik et al. 2015, Yao et al. 2022). Similarly, the species with m/z values of 369, 351, 276, and 156 related to the degradation of MY dye are in agreement with the results of (Sleiman et al. 2007) indicating the effectiveness of the ZnO catalyzed degradation method for these dyes.

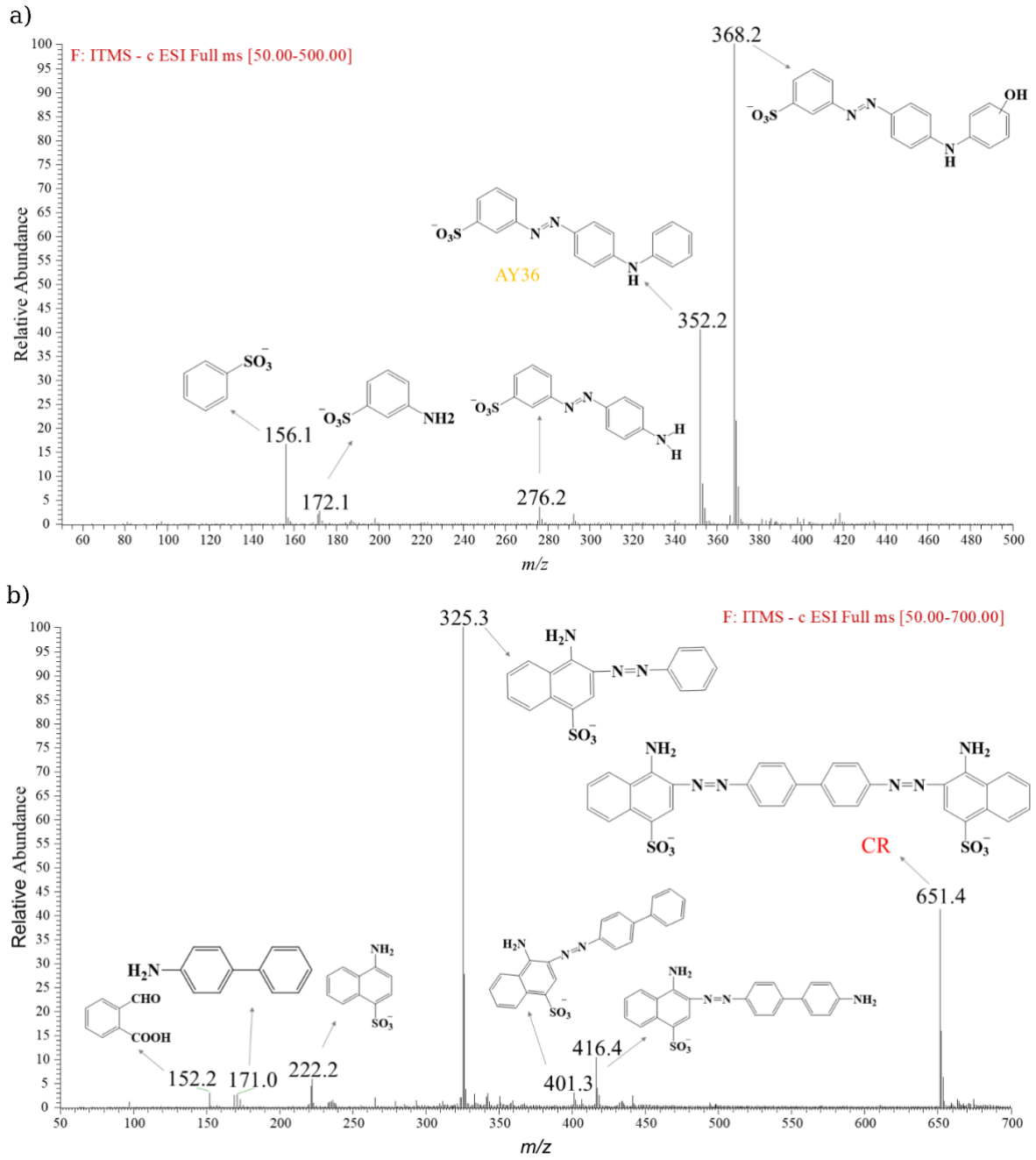

Fig. 6. MS spectra of (a) MY and (b) CR dye solution after degradation treatment with catalyst (Knežević et al. 2024)

4. CONCLUSIONS

This study presents an environmentally friendly and efficient approach for the removal and degradation of MY and CR using chemically functionalized waste hemp fibers. The synthesized adsorbent (QDHF-BHU), obtained through delignification followed by quaternization with betaine hydrochloride and urea, showed excellent performance in batch adsorption experiments. Maximum adsorption capacities reached 238.4 mg g^{-1} for MY and 343.3 mg g^{-1} for CR at 25 °C, indicating high affinity toward both dyes. The adsorption process was spontaneous and endothermic, with $\Delta G°$ values ranging from –50.15 to –43.28 kJ mol^{-1}, and followed both pseudo-first-order and pseudo-second-order kinetic models, suggesting a complex adsorption mechanism. Based on the comparison, it can be concluded that the

pseudo-second-order model best describes the adsorption kinetics of CR and MY dyes, suggesting that chemisorption is the dominant adsorption mechanism. After desorption, the dyes eluents were successfully degraded using ZnO catalysis**,** achieving up to 97.2% decolorization of MY within 180 minutes of irradiation. The results of the employed catalyst regeneration tests revealed that the catalyst's regeneration ability did not decline considerably after three cycles. After three cycles, the regeneration efficiency maintained above 97%. These findings confirm the potential of QDHF-BHU as an effective and sustainable adsorbent, and the combined adsorption-photodegradation system as a promising strategy for advanced wastewater treatment based on green chemistry and circular economy principles.

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