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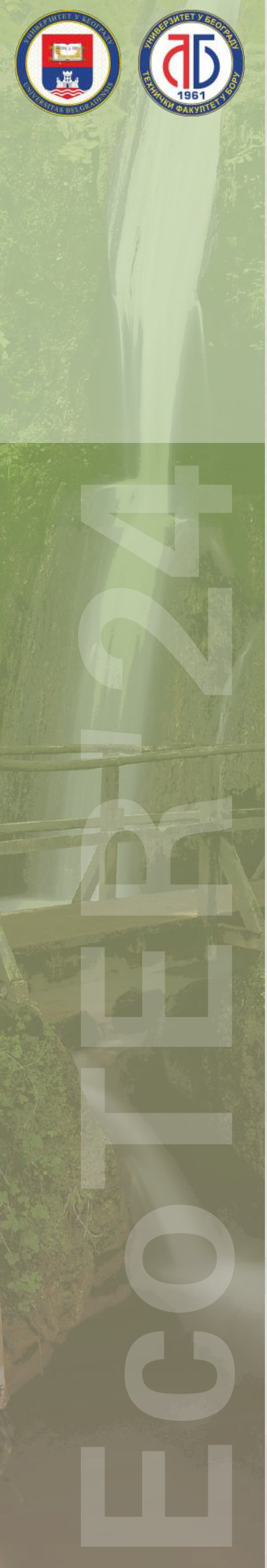

31st International conference

Ecological Truth & Environmental Research

Editor
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PREFACE

The 31st international conference Ecological Truth & Environmental Research – EcoTER'24 focuses on showing the latest research findings and innovations in the field of ecology, environmental protection and sustainable development. The conference will be held in Sokobanja (Serbia) in hotel Sunce in the period of 18–21 June 2024.

The aim of the conference is to connect the experts in various fields in order to transform attitudes and behaviors in everyday practices, as well as in the industry and economy sector which is essential for achieving the desired changes that our society must undergo.

The 31st international conference Ecological Truth & Environmental Research – EcoTER'24 is organized by the University of Belgrade, Technical Faculty in Bor, and co-organized by the University of Banja Luka, Faculty of Technology; the University of Montenegro, Faculty of Metallurgy and Technology – Podgorica; the University of Zagreb, Faculty of Metallurgy – Sisak; the University of Pristina, Faculty of Technical Sciences – Kosovska Mitrovica and the Society of Young Researchers – Bor.

These Proceedings encompass 119 papers from the authors coming from the universities, research institutes and industries in 15 countries: Brazil, Norway, USA, Spain, Austria, Libya, Italy, Israel, Slovenia, Croatia, Romania, Bulgaria, Montenegro, Bosnia and Herzegovina, North Macedonia, and Serbia. It is a great honor and pleasure to cordially wish a warm welcome to all the participants of the conference.

As a part of this year's conference, the 6th Student Section – EcoTERS'24 will be held. We appreciate the contribution of the students and their mentors who have also participated in the conference and hope that students will continue to explore and to be curious, since education is a never-ending process, and knowledge is continuously growing.

The organization of the EcoTER'24 conference has been financially supported by the Ministry of Science, Technological Development and Innovation of the Republic of Serbia.

The support of the Donors and their willingness and ability to cooperate has been of great importance for the success of the EcoTER'24 conference. The organizing committee would like to extend their appreciation and gratitude to the Platinum donors of the conference – Serbia ZiJin Copper doo Bor and HBIS SERBIA, to the Gold donor of the conference – Elixir Group, as well as to the Silver donor of the conference – Serbian Chamber of Engineers.

We would like to express our sincere appreciation to all the authors who have contributed to the Proceedings. We would also like to express our gratitude to the members of the scientific, organizing and honorary committees, reviewers, speakers, chairpersons and all the conference participants for their support of the EcoTER'24. Sincere thanks go to all the people who have contributed to the successful organization of the EcoTER'24.

Prof. Snežana Šerbula,

President of the scientific and organizing committee

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CELLULOSE BASED MEMBRANE FOR CATIONIC POLLUTANTS REMOVAL FROM WATER

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Abstract

This study focuses on the removal of cation and cationic dye from wastewater by adsorption on a bio-based adsorbent. Cellulose bio-based membrane, CMTA, was obtained by cross-linking of amino-modified cellulose fiber (CF-A) and tartaric acid (TA) using L-lysine as a cross-linker. The properties of the prepared membrane were examined through FTIR and SEM techniques, and pHpzc and porosity determination. The effect of pH, initial concentration, temperature, and contact time on the adsorption efficiency was studied in a batch system. Results from the adsorption study proved CMTA adsorbs of Crystal violet (CV) dye and Ni^{2+} cation ion with high adsorption capacities of 285.01 mg g^{-1} and 54.35 mg g^{-1}, respectively, fitted to the Langmuir isotherm. The kinetic study and thermodynamic parameters determination indicate spontaneous and diffusion-controlled processes.

Keywords: bio-based membrane, batch adsorption study, cation and cationic dye, environmental protection.

INTRODUCTION

Pollution from various industrial sectors (waste water, soil, air), influence sharp increase and disturbs human health and the environmental [1]. Heavy metals, textile dyes, plastics, cosmetics, and rubber are widely used and belong to the group of the most dominant pollutants. Crystal violet (CV) dye has been widely used as a dye in textiles, veterinary medicine, and medical solutions as a mutagenic and bacteriostatic agent, but it has harmful effects due to its carcinogenic and mutagenic nature. They influence the cell division process and cause long-lasting damage to the eyes [2,3]. The heavy metals are toxic, carcinogenic, and not biodegradable. Nickel causes brain and spinal cord damage, and its presence in water and soil has an impact on crop yields and aquatic resources [4].

Among many technologies as filtration, coagulation, oxidation, and sedimentation, adsorption is the most commonly used and effective method. Bio-based adsorbents as membranes are mostly used because they are environmentally acceptable, renewable, and harmless to nature and the living world [3]. Cellulose as a material is a natural, renewable, biodegradable, and non-toxic polymer. Hydroxyl groups in the structure are easily functionalized with other given functional groups, increasing their hydrophilicity, physical stability, and adsorption efficiency.

In the present study, bio-based membrane (CMTA) was prepared, characterized and their examine for effectiveness in the removal of CV and Ni^{2+} ions from water solutions. The isotherms, thermodynamics, and kinetics of pollutants removal onto the CMTA were studied.

MATERIALS AND METHODS

Materials

All chemicals: Tartaric acid (TA), L-Lysine, *N*'-diisopropylcarbodiimide (DPCA), 4-dimethylaminopyridine (DMAP), dimethyl sulfoxide (DMSO), lithium chloride (LiCl) dimethylformamide (DMF), nickel standard 1000 mg dm^{-3} and crystal violet (CV) are of *p.a.* quality, and supplied from Sigma Aldrich. The synthesis of ethyl 4-chloro-4-oxobutanoate (CPC) was performed according to the procedure described previously [5]. Cellulosic material from waste tobacco boxes was provided by Naša Kuća (Belgrade, Serbia). Adjustment of pH was accomplished with 0.1M NaOH and 0.1M HNO_3 (Sigma Aldrich).

Preparation of membrane

The cellulose based membrane preparation (Figure 1a) was performed by cross-linking of amino functionalized cellulosic fibers with tartaric acid similarly to the procedure given in recent literature [6]. The cellulose fibers (CF) from waste paper was prepared by swelling, using DMSO/LiCl system, and aftre performing functionalization with CPC and L-Lysine to obtain amino-modified cellulose fiber (CF-A) [7]. In a subsequent step 10 g of CF-A were soaked in 30 mL of tartaric acid (TA) solution (0.2 mol in 20 mL of DMF) and mixed using a planetary stirrer (at 60 rpm) for 5 min. After that 2.5 g of DPCA (0.0156 mol) and 0.25 g of DMAP (10 mol.% with respect to DPCA) were added and continued with mixing for 20 min and then continuously heated at 100°C for 3 h. The obtained material was filtered (to remove excess of DMF), washed with ethanol, and pressed at room temperature between two porous plates (90 μm pore) with a load of 20–30 kN to obtain a membrane CMTA (thickness 4 mm).

Characterization and adsorption method

The structural and morphological characterization, pH_{PZC}, and porosity were performed using Fourier transform infrared spectroscopy (FTIR) (Nicolet iS10 spectrometer, Thermo Scientific, Sweden, in the transmission mode and range 4000–500 cm^{-1}), Scanning Electron Microscopy (SEM) (Tescan Mira3 XMU Field, operated at 20 kV, Czech Republic), pH meter (HI-2210-02 Bench Top, HANNA instruments, Hungary) according to procedure described [7], image analysis (Image-Pro Plus software), and dry-wet weight method [7], respectively. Adsorption of CV dye and Ni^{2+} ions was done in a batch system at different temperatures (25°C, 35°C, and 45°C), mixing of 1, 2, 3, 4, 5, 7.5, and 10 mg of CMTA with 10 cm^{-3} of solution CV dye (C_i=20.0 mg dm^{-3} and pH 7) and 10 cm^{-3} of Ni^{2+} ions solution

(C_i=7.55 mg dm^{-3} and pH 7). The process of attaining of adsorption equilibrium for dye removal was monitored for 120 min at a wavelength of 590 nm, using the UV-Vis Spectrophotometer 1800 (Shimadzu, Japan). The concentrations of ions Ni^{2+} were measured by atomic absorption spectrometry (AAS) using a Perkin Elmer AAnalyst 300 (United States). The adsorption capacity was calculated using the equation given in the work of Muna *et al*. [7].

RESULTS AND DISCUSSION

The result of the dry-wet weight method and the image analysis (Image-Pro Plus software, Media Cybernetics) revealed that the porosity of the membranes was about 54.8% and had an average pore diameter of about 4.2 µm.

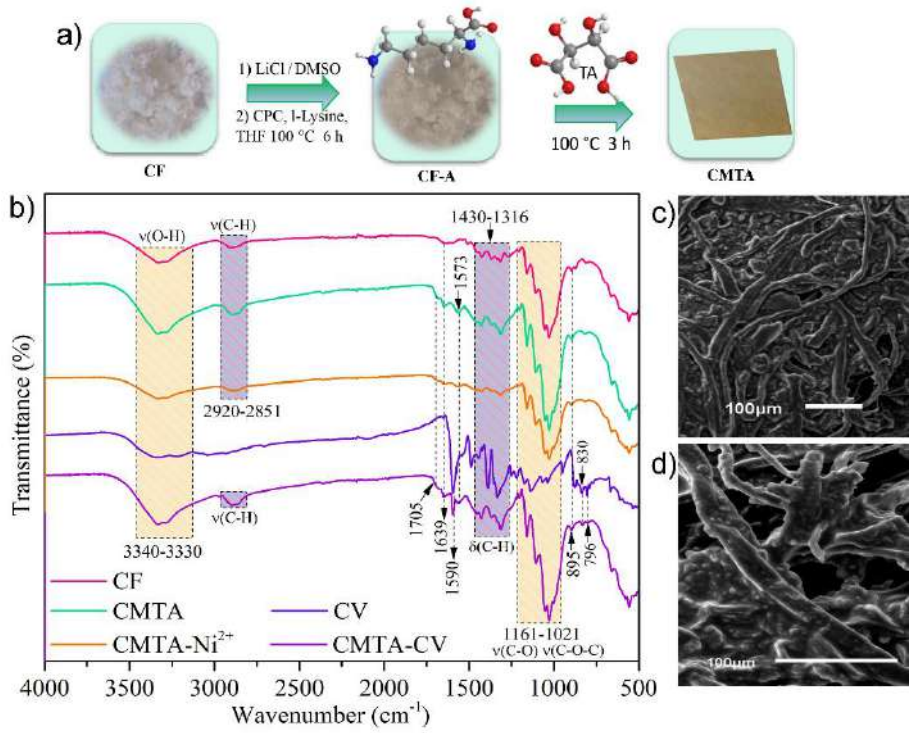

Figure 1 *a) Preparation of CMTA; b) FTIR spectra of membrane before and after adsorption with CV and Ni^{2+}; c) SEM image of CF; d) CMTA*

The FTIR spectra, presented in Figure 1b, confirmed successfulness of CMTA membrane preparation. FTIR spectra of CF show characteristic bonds for cellulose. The peaks at 3340–3330 cm^{-1}, 1639 cm^{-1} refer to the stretching vibration and bending vibration of O-H group, respectively, and ones in the range from 1161 to 1021 cm^{-1} were assigned to asymmetric/symmetric vibrations of C-O, C-O-C groups of polysaccharide structure. Stretching and bending vibration of C-H groups are observed in 2920–2851 cm^{-1} and 1430–1316 cm^{-1} regions. After amino modification with lysine and cross-linking with tartaric acid, obtained CMTA show peaks from cellulose and small peaks at 1705 cm^{-1} and 1573 cm^{-1} corresponding to overlapped ester, carboxylic and the amide group, respectively, which confirmed successful modification. A new peaks at 1592, 830 and 796 cm^{-1} in the spectra

CMTA-CV corresponding to N-H and =CH out-of-plane deformation vibration of the aromatic ring from CV dye. In the spectrum of CMTA-Ni^{2+} the decrease of peak intensity, due to electrostatic interaction of Ni^{2+} with negative charges at the adsorbent surface, was observed.

SEM images (Figures 1c and 1d) indicate the change of cellulose surface after modification and the surface of obtained membranes gives the adsorbents with a highly porous morphology in relation to unmodified CF.

The determined pHpzc value of CMTA of 6.3 indicate that CMTA has a negative surface at pH > pH_{PZC} which is beneficial condition for effective removal of cationic pollutants. The results of adsorption data fitting, determined using Langmuir adsorption models as described in the recently published work Muna *et al.* [7], are given in Table 1.

Table 1 *Results of Langmuir isotherm models for CV and Ni^{2+} ions adsorption onto CMTA*

Pollutant	t (°C)	q_m (mg g^{-1})	K_L (dm^3 mg^{-1})	R^2
CV	25	285.01	20.557	0.999
	35	291.90	32.149	0.999
	45	298.84	57.205	0.999
Ni^{2+}	25	54.35	7.6984	0.998
	35	56.36	9.5170	0.998
	45	58.39	12.061	0.999

The data from Table 1 show that adsorption capacity (q_e) and Langmuir constant (K_L) increases with increasing temperature, indicating a high affinity of CMTA surface sites for cationic pollutants removal.

Results of the adsorption study at 25, 35, and 45°C, fitted using Van't Hoff Equations [7], have been used for calculation of thermodynamic parameters presented in Table 2.

Table 2 *Calculated Gibbs free energy ΔG^{Θ}, enthalpy (ΔH^{Θ}), and entropy (ΔS^{Θ}) for CV and Ni^{2+} adsorption onto CMTA*

Pollutant	ΔG^{Θ} (kJ mol^{-1})			ΔH^{Θ} (kJ mol^{-1})	ΔS^{Θ} (J mol^{-1} K^{-1})	R^2
	25°C	35°C	45°C			
CV	-49.47	-52.28	-55.50	40.29	300.84	0.99
Ni^{2+}	-42.23	-44.19	-46.25	17.69	200.92	0.99

Thermodynamic data indicate feasible and spontaneous adsorption processes with the participation of both physisorption and chemisorption [8], as well as and an endothermic nature of the adsorption processes.

Additionally, the results in Table 3 show that the best correlation of experimental data was obtained using the PSO model of the equation. This result indicates that the rate depends on both adsorbate and surface functionalities concentration and diffusion-controlled processes (Table 4).

Table 3 *Pseudo-first, PSO and second-order model parameters for the adsorption of CV and Ni^{2+} on CMTA*

Pollutant	Model parameters	Pseudo-first	PSO	Second order	E_a (KJ mol^{-1})
CV	q_e	76.92	189.98	189.98	9.60
	k (k_1, k_2)	0.06086	0.00160	0.00568	
	R^2	0.994	0.999	0.950	
Ni^{2+}	q_e	54.11	79.61	79.61	16.37
	k (k_1, k_2)	0.04823	0.00080	0.00574	
	R^2	0.974	0.993	0.949	

Table 4 *Kinetic parameters of the Weber-*Morris *(W-M), Dunwald-Wagner (D-W), and Homogenous Solid Diffusion Model (HSDM) models for the adsorption of CV and Ni^{2+} onto CMTA*

Model	Model parameters	CV	Ni^{2+}
Weber-Morris (W-M) (Step 1)	k_{p1} (mg g^{-1} min$^{-0.5}$)	13.272	12.166
	C (mg g^{-1})	97.89	8.89
	R^2	0.995	0.979
Weber-Morris (W-M) (Step 2)	k_{p2} (mg g^{-1} min$^{-0.5}$)	0.59651	0.47721
	C (mg g^{-1})	177.06	61.65
	R^2	0.997	0.997
Dunwald-Wagner (D-W)	$K \times 10^{-2}$	2.4972	1.3937
	R^2	0.938	0.921
Homogenous Solid Diffusion Model (HSDM)	$Ds \times 10^{-11}$	2.71	1.83
	R^2	0.933	0.894

CONCLUSION

The aim of the present study was focused on development of a new bio-based membrane (CMTA), characterization and investigation of its adsorption efficiency. The adsorptive potential was studied concerning Ni^{2+} and CV dye removal in the batch system. Thermodynamic parameters indicate the spontaneous and endothermic character, while kinetic data confirmed participation of both adsorbate and membrane surface functionalities in an adsorption step. Diffusional models indicate that intra-particle diffusion govern overall process.

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