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Mining and Metallurgy
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PROCEEDINGS

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Editors:
Ljubiša Balanović
Dejan Tanikić

18-21 October 2023, Bor Lake, Serbia

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PREFACE

On behalf of the Organizing Committee, it is a great honor and pleasure to welcome all esteemed participants of the 54th International October Conference on Mining and Metallurgy (IOC 2023), scheduled to take place at the picturesque Bor Lake, Serbia, from October18th to 21st 2023.

The collaborative efforts of the University of Belgrade, the Technical Faculty in Bor, and the Mining and Metallurgy Institute Bor have meticulously organized this year's IOC. Our focus remains unwavering on showcasing the latest research findings and advancements in geology, mining, metallurgy, materials science, technology, environmental protection, and other engineering disciplines. Our primary objective is to foster a dynamic environment where academics, researchers, and industry professionals can come together to share their knowledge, experiences, and innovative ideas while exploring opportunities for collaborative research endeavors.

Our conference agenda is rich and diverse, encompassing plenary sessions, engaging invited lectures, technical presentations, enlightening oral and poster sessions, informative technical tours, a diverse exhibition, and memorable social gatherings. At the heart of this event lies our strong commitment to sustainable development within the mining and metallurgy sector. We are dedicated to exploring ecologically conscious methodologies, responsible resource extraction practices, and cutting-edge technologies that reduce the industry's environmental impact and enhance the well-being of local communities.

The conference proceedings comprise 129 papers authored by individuals from universities, research institutes, and industries in 22 countries. We are proud to welcome participants from Bosnia and Herzegovina, Bulgaria, Canada, China, Croatia, Germany, Greece, India, Iran, Kazakhstan, Libya, North Macedonia, Montenegro, Morocco, Romania, Russia, Slovakia, South Africa, Spain, Turkey, United States, and, of course, Serbia.

We are excited to host the 8th International Student Conference on Technical Sciences (ISC 2023) as part of IOC 2023. This event offers students from Serbia and the wider region a unique chance to showcase their research and discuss the future of their fields with experts.

We sincerely thank the Ministry of Science, Technological Development, and Innovation of the Republic of Serbia for their generous financial support. In addition, we express our profound gratitude to all our sponsors, exhibitors, and friends of the Conference for their contributions and unwavering support for playing a pivotal role in ensuring the success of IOC 2023.

We would like to express our heartfelt thanks to all authors, committees, reviewers, speakers, and chairpersons for their invaluable contributions in shaping IOC 2023.

We look forward to welcoming you to the 55th International October Conference on Mining and Metallurgy (IOC 2024), which will be held in October 2024.

On behalf of the 54th IOC Organizing Committee,

Prof. dr Ljubiša Balanović

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MODIFIED HYBRID CELLULOSE MEMBRANE FOR NICKEL(II) IONS REMOVAL FROM INDUSTRIAL WASTEWATER

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Abstract

Nickel pollution of water induces several problems for the environment. The purpose of this paper was to investigate the adsorption of Ni^{2+} ions on fabricated biomembranes. The proposed adsorbent was prepared from epoxy and amino-functionalized waste cellulose fibers, able to participate in cross-linking with amino acid lysine - wCell/Mn-Fe_LDH. The prepared material underwent preliminary structural characterization by Fourier-transform infrared spectroscopy. In a batch system, the influence of pH, contact time, temperature, and initial concentration on adsorption efficiency was investigated. The effectiveness of the membrane was demonstrated by acceptable adsorption capacities of 40.49 mg g^{-1} obtained for Ni^{2+} at 45°C. The kinetic study, using the Weber-Morris model, indicates intraparticle diffusion as the rate limiting step. Adsorption mechanism physisorption was proposed based on thermodynamic behaviors. The outcomes demonstrated that environmentally friendly sustainable technology has been successfully developed.

***Keywords**: water treatment, wCell/Mn-Fe_LDH, adsorption, environmental engineering.*

1. INTRODUCTION

The total environment, including the air, water, and soil, is widely distributed with a transition element nickel. Nickel might originate from both anthropogenic activity and natural sources. Industries, the use of liquid and solid fuels, as well as municipal and industrial waste, may all contribute to nickel contamination of the environment. Consequently, exposure to nickel can have several adverse effects on people, including allergies, kidney and heart problems [1]. Although it can exist in some oxidative states, the +2 oxidation state (Ni^{2+}) is the most prevalent [1]. Water pollution by nickel under the special attention of researchers.

Treatment of wastewaters can be performed by utilizing different processes like photocatalysis [2], adsorption [3], electrochemical oxidation [4] and so on. Among them, adsorption poses the most viable and economical way to solve problems in this area. Various materials are employed during different probes, but hybrid (combination of organic/inorganic) materials show the best results. Due to their numerous uses in catalysis, energy conversion and storage, medicine delivery, environmental cleanup, and carbon dioxide preservation, layered double hydroxides (LDH) are a diverse class of materials [5]. On the other hand, one of nature's most plentiful and eco-friendly polymers is cellulose [6]. Crude cellulose exhibits a poor level of adsorption ability. Because of this, it has been common practice to chemically or physically modify cellulose to increase its capacity to bind heavy metals [7]. A combination of LDH and cellulose derivate can be the solution for before mentioned issues.

The main objective of the present study was to develop a novel wCell/Mn-Fe_LDH adsorbent with high affinity toward metal ions (+2 oxidation state). Determination of the ability to remove Ni(II) as a model pollutant by varying process conditions, during adsorption tests, was performed.

2. EXPERIMENTAL

2.1 Synthesis of biobased membrane

All acquired chemicals for synthesis were p. a. grade without needing further purification (all obtained from Merck). Preparation of membranes was done according to Perendija et al. [1] with deposition of Mn-Fe_LDH [8] onto the surface of wCells.

2.2 Structural characterization

Preliminary structural properties (the presence of organic and inorganic bond in materials) were obtained by Fourier-transform infrared spectroscopy (FTIR). FTIR spectra were collected with a Nicolet™ iS™ 10 FT-IR Spectrometer (Thermo Fisher SCIENTIFIC) with Smart iTR™ Attenuated Total Reflectance (ATR) Sampling accessories. The spectra were recorded in the range 4000-500 cm^{-1}, in 20 scans mode, and at a resolution of 4 cm^{-1}.

2.3 Adsorption experiments

Adsorption tests were carried out by adding 1, 2, 3, 4, 5, 7.5, and 10 mg of adsorbent to an 8 cm^3 vial of standard Ni^{2+} solutions with Ci = 7.55 mg dm^{-3}. Adsorptions were conducted at 25, 35, and 45 °C and pH 7. Atomic absorption spectrometry (AAS) was used to determine the amounts of Ni^{2+} ions (Perkin Elmer AAnalyst 300). Similar to the equilibrium study, the kinetic study was carried out by altering the contact time: 1, 5, 15, 30, 45, 60, 75, and 90 minutes at 25, 35, and 45 °C.

Using Eq. (1), the adsorption capacity was determined:

$$q = \frac{(C_i - C_f)}{m} V \qquad (1)$$

where q is the adsorption capacity in mg g^{-1}, C_i and C_f are the initial and final concentrations of ions in the solution in mg dm^{-3}, V is the volume of solution in dm^{-3}, and m is the mass of the adsorbent in g.

3. RESULTS AND DISCUSSION

3.1 Structural characterization of prepared material

Preliminary structural characterization of fabricated material is presented in Figure 1. ATR-FTIR scans of precursors and finally obtained membrane are depicted together in Figure 1.

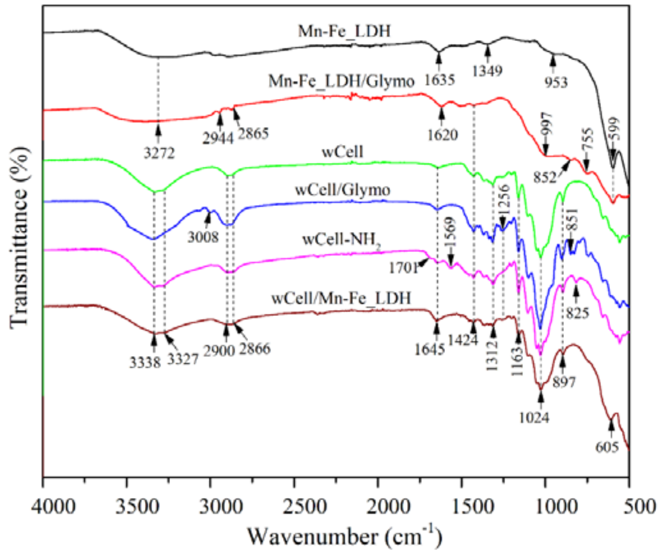

Figure 1 - FTIR spectra of membrane constituents and wCell/Mn-Fe_LDH membrane

The wCell/Mn-Fe_LDH membrane's FTIR spectrum shows the existence of all constituent functionalities that were included during cross-linking and Mn-Fe_LDH deposition. A peak at 605 cm^{-1} confirms that Mn-Fe_LDH successfully covered the surface.

3.2 Adsorption results

Removal of Ni^{2+} ions from water solution was described by the Langmuir model. Results in Table 2 for Ni^{2+} demonstrate that qm decreases as temperature rises. The strong connections between the functional groups on the adsorbent surface and the adsorbate were shown by the high values of the Langmuir constant (K_L), which measures adsorption affinity.

Table 1 - The results of non-linear fitting using Langmuir isotherm for Ni^{2+} adsorption onto wCell/Mn-Fe_LDH membrane

Langmuir model	T (°C)	q_m (mg g^{-1})	K_L(dm^3 mg^{-1})	K_L (dm^3 mol^{-1})	R^2
Ni^{2+}	25	42.68±1.45	6.289±0.097	369120.2±5693.2	0.999
	35	41.68±1.54	5.538±0.10	325017.5±5927.5	0.998
	45	40.49±1.64	4.775±0.11	280273.9±6339.2	0.999

Thermodynamic parameters are shown in Table 2.

Table 2 - Calculated thermodynamic parameters for Ni^{2}+ adsorption onto wCell/Mn-Fe_LDH membrane

	$\Delta G^{\ominus}$ (kJ mol^{-1})			$\Delta H^{\ominus}$ (kJ mol^{-1})	$\Delta S^{\ominus}$ (J mol^{-1} K^{-1})	R^2
T (K)	298	308	318	-10.85	103.63	0.996
	-41.73	-42.81	-43.80			

At all temperatures, negative Gibbs free energy ($\Delta G^{\ominus}$) values demonstrate the spontaneity of adsorption onto wCell/Mn-Fe_LDH (Table 2). The exothermic nature of the whole process is mirrored by lower energy Ni^{2+} electrostatic interactions with surface functions, on the other hand. The increasing randomness of the entire system at the established equilibrium state and the high survivability of the examined processes are both indicated by positive entropy change ($\Delta S^{\ominus}$).

Table 3 - PSO model parameters and activation energy (Ea) for the adsorption of Ni^{2+} ions onto wCell/Mn-Fe_LDH membrane at 25, 35, and 45 °C

Ion	T (°C)	q_e (mg g^{-1})	k_2 (g (mg min)$^{-1}$)	R^2	Ea (kJ mol^{-1})
Ni^{2+}	25	52.22±1.34	0.00190±0.00052	0.997	21.26
	35	50.33±1.22	0.00246±0.00048	0.998	
	45	48.59±0.99	0.00325±0.00018	0.999	

The diffusion-controlled processes i.e., ion exchange/complexation are characteristic for the values of *E*a between 8 and 40 kJ mol^{-1} [9] and according to the results from Table 3, the diffusion is a rate-controlling step.

4. CONCLUSION

FTIR analysis of obtained composite membrane wCell/Mn-Fe_LDH showed the presence of functionalities that enable very high adsorption affinity towards cation species. Correlating the equilibrium adsorption results with Langmuir adsorption isotherm model give fine fitting results, and these experiments also showed that adsorption process is exothermic and spontaneous. Kinetics of adsorption process showed that process is in higher order of reaction (third order or higher) which is expected for such kind of materials (composites with complex chemical structure). Performing continuous measurements of adsorption capacity as a function of contact time on different temperatures provided the data needed to determine activation energy of the adsorption process. Obtained value of only 21.26 kJ mol^{-1} indicate that adsorption process is very fast due to very low activation energy barrier. In current study we utilized this membrane as an adsorbent of nickel (II) ions and the results we obtained showed that this composite membrane may be perspective choice for cation pollutants diminution.

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