XX JUBILEE INTERNATIONAL SCIENTIFIC CONGRESS

WINTER SESSION

08 - 11.03.2023, BOROVETS, BULGARIA

МЕЖДУНАРОДЕН КОНГРЕС - МАШИНИ. ТЕХНОЛОГИИ. МАТЕРИАЛИ
MTM 2023
INTERNATIONAL CONGRESS - MACHINES. TECHNOLOGIES. MATERIALS

MACHINES. TECHNOLOGIES. MATERIALS 2023

PROCEEDINGS

VOLUME I
MACHINES
MATERIALS

ISSN 2535-0021 (PRINT)
ISSN 2535-003X (ONLINE)

SCIENTIFIC-TECHNICAL UNION OF MECHANICAL ENGINEERING - INDUSTRY 4.0
BULGARIA

XX JUBILEE INTERNATIONAL CONGRESS
WINTER SESSION
"MACHINES.TECHNOLOGIES.MATERIALS"
08–11.03.2023 BOROVETS, BULGARIA

PROCEEDINGS

YEAR VI, ISSUE 1 (25), BOROVETS, BULGARIA 2023

VOLUME I
MACHINES. MATERIALS.

ISSN 2535-0021 (PRINT)
ISSN 2535-003X (ONLINE)

PUBLISHER:

**SCIENTIFIC TECHNICAL UNION OF MECHANICAL ENGINEERING
INDUSTRY-4.0**

108, Rakovski Str., 1000 Sofia, Bulgaria
tel. (+359 2) 987 72 90,
tel./fax (+359 2) 986 22 40**,**
office@mtmcongress.com
www.mtmcongress.com

INTERNATIONAL EDITORIAL BOARD

C O N T E N T S

MACHINES

MATERIALS

Physico-chemical characterization of the corn silk by DTA-TGA, SEM-EDS and FTIR analysis

Milan Gorgievski [1*], Dragana Božić [2], Miljan Marković [1], Nada Štrbac [1], Vesna Grekulović [1], Kristina Božinović [1], Milica Zdravković [1]
University of Belgrade Technical Faculty in Bor, Vojske Jugoslavije 12, 19210 Bor, Serbia[1]
Mining and Metallurgy Institute Bor, Zeleni bulevar 35, 19210 Bor, Serbia[2]
mgorgievski@tfbor.bg.ac.rs

Abstract: *In this paper, the results of the DTA-TGA, SEM-EDS, and FTIR analysis of the corn silk are presented. The DTA-TGA analysis shows that the decomposition of corn silk has several stages which are manifested with corresponding peaks on obtained DTA-TGA curves. SEM-EDS analysis was performed before and after the adsorption of copper ions. It has shown that untreated corn silk has a non-uniform structure, consisting of channels and cavities of irregular orientation, which facilitates the penetration of the water phase into the adsorbent structure, and incorporation of copper ions in the internal active sites. After the adsorption of* Cu^{2+} *ions, the structure becomes more compact, and uniform, as a result of the incorporation of copper ions into the molecular structure of the corn silk. FTIR analysis shows that ion exchange is not the dominant mechanism of binding copper ions to the active sites in the molecular structure of the corn silk, but also chemisorption and physical adsorption is present.*

Keywords*: CORN SILK, CHARACTERIZATION, DTA-TGA, SEM-EDS, FTIR, COPPER IONS*

1. Introduction

Water pollution with heavy metals is a significant environmental problem all over the world. Most of these pollutants are not biodegradable and tend to accumulate in living organisms. Their toxicity, along with their non-biodegradability makes the polluted wastewater purification an initial concern [1].

Conventional methods for wastewater purification include ion exchange, chemical precipitation, membrane processes, electrolysis, etc [1, 2]. Among these wastewater treatment methods, sorption has shown good prospects, thanks to its economic feasibility, and environmental-friendly nature [2].

The use of waste biomass, including agricultural by-products, as adsorbents for wastewater purification, has been very popular in the scientific world in the past decade. This process is often referred to as biosorption. The main advantages of the biosorption process are the low-cost, biodegradability, efficiency, ease of operation and simplicity of design, and abundance of potential biosorbents. Further, this process can remove/minimize the different types of pollutants, and thus it has wider applicability in water pollution control [2, 3].

Corn silk (*Stigma maydis*) has been used for thousands of years as a folk medicine in many parts of the world for the treatment of edema as well as for cystitis, gout, kidney stones, nephritis, diabetes mellitus, and prostatitis [4].

Corn silk is a by-product of corn after deep processing, and is one kind of crop waste, widely available in large quantities. Corn silk, whose components are significantly different from maize stalk, maize corncob, and maize leaf, mainly contains cellulose. However, corn silk is constituted of lignin and cellulose and there are a large number of oxygen-containing functional groups, such as hydroxyl groups, carboxyl, and carbonyl on its surface classifying it as a potential adsorbent for metal ions [1, 5]. However, there are only a few papers dealing with metal removal by raw or modified corn silk [1, 6].

In this study, SEM-EDS, DTA-TGA, and FTIR analysis of corn silk, as a potential adsorbent for copper ions biosorption is given. The SEM-EDS and FTIR analysis was performed on samples before and after the biosorption process.

2. Materials and methods

Corn silk was collected from the local cornfields near the city of Bor (Serbia). Collected samples were firstly washed, ground, then sieved through a set of laboratory sieves, and the sieve fraction (−1 + 0.4) mm was analyzed for potential use as an adsorbent for copper ions biosorption.

A synthetic Cu^{2+} solution of an initial concentration of 0.2 g dm^{-3} was used for the adsorption experiments, to obtain a corn silk sample after the biosorption process for the SEM-EDS and FTIR analysis.

The SEM-EDS analysis was performed on a VEGA 3 LMU TESCAN scanning electron microscope, coupled with an integrated energy-dispersive X-ray detector X-act SDD 10 mm^2 (Oxford Instruments).

The DTA-TGA analysis was performed on a simultaneous DSC-DTA-TGA device (SDT-Q600), under an inert atmosphere (nitrogen).

The FTIR analysis of the corn silk samples before and after the biosorption process was performed on a BOMEM MB-100 (Hartman & Braun Michelson) FTIR spectrometer.

3. Results and discussion

3.1 SEM-EDS analysis of corn silk

Based on a large number of results from scientific research in which the SEM analysis of different biosorbents was performed, the corn silk was analysed before and after the biosorption process. On the basis of the SEM analysis, in which the surface of the samples was observed, certain differences in the structure of the surface before and after the biosorption process were noted. The surface morphology of the corn silk samples before and after the biosorption process is shown in Figure 1.

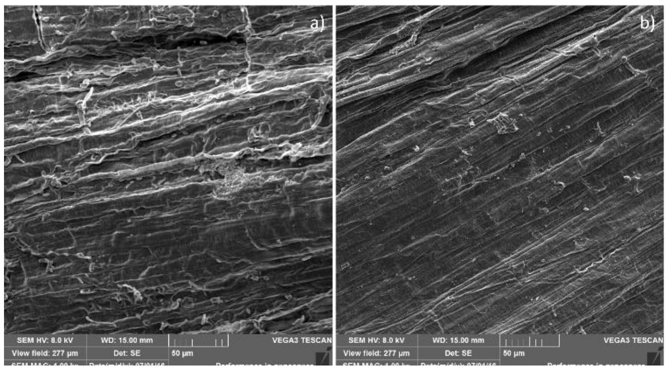

Figure 1. *SEM micrographs of the corn silk samples before (a) and after the biosorption of copper ions (b)*

Figure 1a shows a micrograph of the surface of untreated corn silk. Macro-pores and cavities can be seen in the image. The presence of macro pores and larger cavities facilitate the movement of the aqueous phase through the corn silk structure and promotes internal diffusion. The cavities and macro-pores of untreated corn silk have a chaotic and irregular orientation, and their openings are also irregularly shaped, as can be seen in Figure 1a. It is assumed that metal ions through these pores easily penetrate into the structure of the adsorbent where they are adsorbed on numerous internal active sites [6]. Similar morphological changes in biosorbents were observed by other authors using SEM analysis in their works [7, 8].

After the biosorption process, a change in the morphology of the surface is noted (Figure 1b), compared to the untreated sample. Figure 1b shows a relatively uniform structure of the corn silk sample. The change in morphology is manifested as a compact cellulosic structure, where no pores are observed, and the surface has become rough [9]. The given changes in the morphology of the sample lead to the conclusion that the adsorption of copper ions is related to chemical changes on the surface of corn silk.

The EDS spectra of corn silk samples before and after the biosorption process are shown in Figure 2. As can be seen from Figure 2a, pointed on the alkali and alkali earth metal ions, the EDS spectrum before the biosorption of copper ions shows a high content of Ca, K, and Mg. After the biosorption process, the K peaks decreased with the disappearance of Ca and Mg peaks, and peaks for Cu were observed (Figure 2b). Hence, it could be assumed that the ion-exchange mechanism occurs between Ca^{2+}, Mg^{2+}, K^{+}, and Cu^{2+} ions [10].

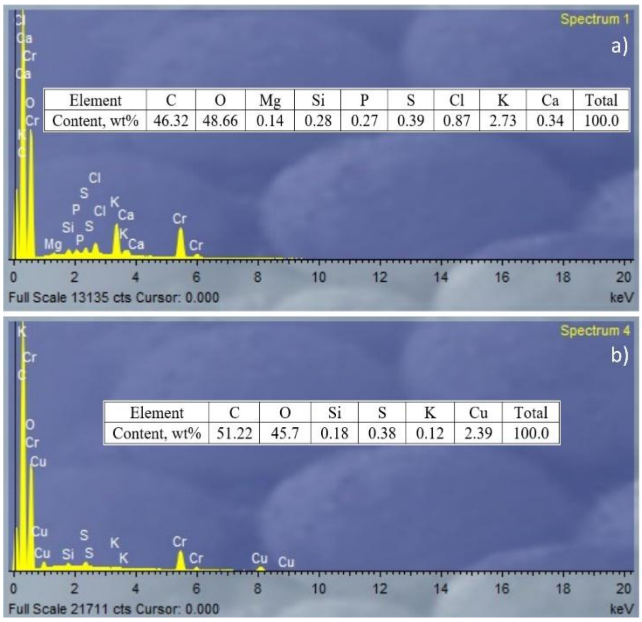

Figure 2. *The EDS analysis of the corn silk samples before (a) and after the biosorption of copper ions (b)*

3.2 DTA-TGA analysis of corn silk

The DTA-TGA analysis of corn silk was performed in order to determine the thermal stability of the biosorbent. 4 mg of corn silk was heated at a constant rate of 10 ^{o}C/min in the range from 20 ^{o}C to 900 ^{o}C, and the obtained results are shown in Figure 3.

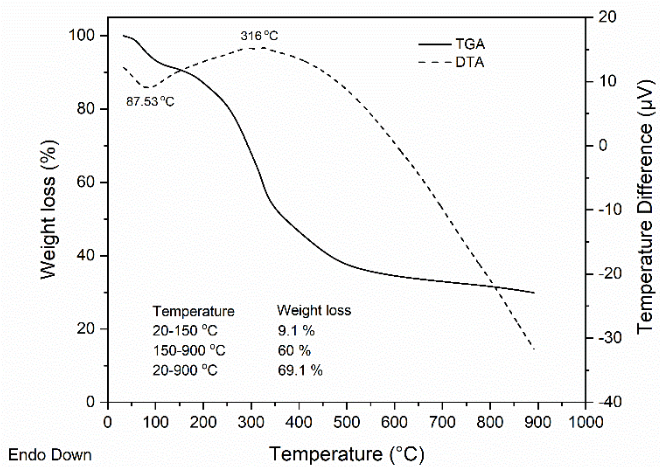

Figure 3. *The DTA-TGA analysis of the corn silk sample*

Figure 3 shows the DTA and TGA profiles of corn silk. The TGA curve shows a weight loss of 9.1 % in the temperature range from 20 to 150 ^{o}C, as a result of the loss of physically bound water within the sample. This process is followed by an exothermic peak on the DTA curve with a minimum of 87.53 ^{o}C. Further, in the range from 150 to 900 ^{o}C, the TGA curve shows a weight loss of about 60 %, which can be contributed to the degradation of the lignocellulose components present in the corn silk sample, and the formation of volatile products like CO, CO_2 and others [10, 11]. This change is followed by an exothermic peak on the DTA curve, with a maximum of 316 ^{o}C. The total weight loss, in the temperature range from 20 to 900 ^{o}C, was 69.1 %.

3.3 FTIR analysis of corn silk

FTIR spectroscopy is an instrumental method used to determine the functional groups in the adsorbent responsible for ion exchange with metal ions from the solution. The FTIR analysis of the corn silk samples was performed in the spectral range from 4000-400 cm^{-1}, with a resolution of 2 cm^{-1}. The obtained results are shown in Figure 4.

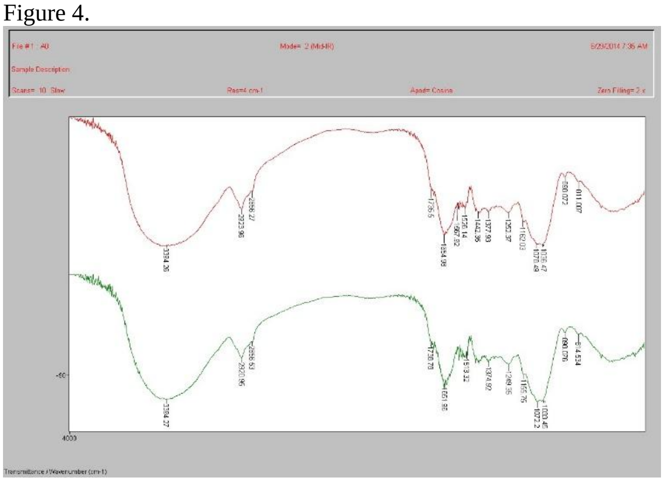

Figure 4. *FTIR spectra of the corn silk samples before (green band) and after the biosorption of copper ions (red band)*

The obtained FTIR spectra before and after the biosorption process do not show significant shifts in the terms of wavelengths, which suggests that ion exchange is not the dominant mechanism of binding copper ions to the active sites in the molecular structure of the corn silk, but also chemisorption and physical adsorption is present.

4. Conclusions

The characterization of corn silk, as a potential adsorbent for copper ions biosorption is presented in this work. The SEM-EDS analysis was performed on corn silk samples before and after the biosorption of copper ions. The SEM analysis showed a change in the surface morphology of the corn silk samples after the biosorption process. The macro-pores and cavities, present on the SEM image before the biosorption process, disappeared, and the structure of the corn silk sample became more uniform and compact. The change in the morphology of the sample occurred as a result of the incorporation of the copper ions inside the structure of the corn silk.

DTA-TGA analysis was performed on a corn silk sample to determine its thermal stability. The sample was heated at a constant rate of 10 ^{o}C/min, from 20 ^{o}C to 900 ^{o}C. The obtained results showed a total weight loss of 69.1 % in the analysed temperature range indicating the degradation of the lignocellulose components in the sample.

The FTIR analysis was performed on samples before and after the Cu^{2+} ions biosorption. The obtained FTIR spectra showed no significant shifts in the terms of wavelengths. This led to the conclusion that ion exchange is not the dominant mechanism of binding copper ions to the active sites in the molecular structure of the corn silk, but also chemisorption and physical adsorption is present.

5. Acknowledgment

The research presented in this paper was done with the financial support of the Ministry of Education, Science and Technological Development of the Republic of Serbia, within the funding of the scientific research work at the University of Belgrade, Technical Faculty in Bor, according to the contract with registration number 451-03-68/2022-14/200131.

6. References

1. H. Yu, J. Pang, T. Ai, L. Liu, *J. Taiwan. Inst. Chem. Eng.* **62** (2016), 21-30.
2. G. Tan, H. Yuan, Y. Liu, D. Xiao, *J. Hazard. Mater.* **174** (2010), 740-745.
3. A. Bhatnagar, M. Sillanpää, *Chem. Eng. J*. **157** (2010), 277-296.
4. Q.-L. Hu, L.-J. Zhang, Y.-N. Li, Y.-J. Ding, F.-L. Li, *Int. J. Phys. Sci*. **5(4)** (2010), 321-326.
5. H. Yu, J. Pang, M. Wu, Q. Wu, C. Huo, *Anal. Sci.* **30** (2014), 1081-1087.
6. M. Petrović, T. Šoštarić, M. Stojanović, J. Petrović, Č. Lačnjevac, K. Trivunac, S. Stanković, *Zaštita Materijala* **57** (2016), 480-487.
7. J. O. Ighalo, A. G. Adeniyi, *SN Appl. Sci.* **2** (2020), Ar, No 509.
8. D. Božić, M. Gorgievski, V. Stanković, M. Cakić, S. Dimitrijević, V. Conić, *CICEQ* **27** (2021), 21-34.
9. M. Petrović, T. Šoštarić, M. Stojanović, J. Milojković, M. Mihajlović, M. Stanojević, S. Stanković, *J. Taiwan. Inst. Chem. Eng.* **58** (2016), 407-416.
10. P. M. K. Reddy, P. Verma, C. Subrahmanyam, *J. Taiwan. Inst. Chem. Eng.* **58** (2016), 500-508.
11. H. Yang, R. Yan, H. Chen, D. H. Lee, C. Zheng, *Fuel* **86** (2007), 1781-1788.