INFLUENCE OF MODIFIER AMOUNT ON THE SORPTION PROPERTIES OF CELLULOSIC MATERIAL

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ABSTRACT

During the study, the impact of the amination mixture consumption on the key quality indicators of cellulose filtration material, such as colour and turbidity, was analysed. Additionally, the productivity and selectivity of the material were calculated based on these parameters. Infrared (IR) spectroscopy was used to identify the active groups formed during the preparation of the amination mixture. Experimental results showed that using the modifier in an amount of up to 40 % of the absolutely dry fiber mass leads to a significant increase in the materialapos sorption properties, which substantially improves the filtration process efficiency. However, increasing the modifier amount beyond 50 % results in its deposition on the fiber surface, negatively affecting the productivity and sorption capacity of the filtration material. Such modified cellulose can be utilized in environmentally safe water purification systems, where high sorption properties and stability during filtration are key requirements. This makes modified cellulose materials promising for use in modern water treatment systems, where environmental performance and material efficiency under industrial conditions are of paramount importance.

Keywords: cellulose, modifier, coloration, turbidity, selectivity, productivity.

INTRODUCTION

Clean water is a critically important resource for ensuring the health and well-being of the population. Water contamination by chemicals, pathogens, or physical pollutants poses a serious threat to the health of millions of people worldwide. Issues related to water pollution affect public health and the economy, agriculture, and ecosystems as a whole [1 - 3].

The application of biopolymers as substitutes for synthetic materials in producing filtration materials has become an important strategy within the context of the country's sustainable development concept. In this regard, searching for new chemical compounds (modifiers) for treating cellulose fibers to enhance their sorption properties is a significant area of scientific research [4 - 6].

Cellulose is one of the most common renewable natural biopolymers, characterized by low toxicity, biodegradability, and easy modification [7, 8]. In its pure form, cellulose fibers are insoluble in water and organic solvents; however, their mechanical properties are inferior to synthetic materials. The use of cellulose as a natural polymer to replace synthetic materials in the filtration process contributes to reducing the negative impact on the environment and creates an effective waste disposal system [7 - 9].

To increase the efficiency of water purification, it is necessary to find ways to modify cellulose fibers to impart improved adsorption properties to the material. Using inexpensive, eco-friendly, and accessible materials such as epichlorohydrin and diethylamine for this purpose will enable the production of highly efficient filtration material that can be used in modern water purification systems [10, 11].

Epichlorohydrin is an organic compound often used for the so-called "cross-linking" of polymers. The interaction of epichlorohydrin with the hydroxyl groups of cellulose leads to the formation of epoxy groups and the creation of a three-dimensional network, which improves the mechanical properties of the fiber, its moisture resistance, and chemical stability [12 - 14].

Triethanolamine is an organic compound that plays several key roles in the process of cellulose modification. It acts as a catalyst, accelerating the reaction between cellulose and epichlorohydrin, and helps stabilize the formed epoxy groups. In addition, triethanolamine can interact with cellulose molecules, enhancing their ability to "cross-link" and form stable polymeric compounds [11, 16].

The modification of cellulose fibers with epichlorohydrin and triethanolamine is an important area of research aimed at improving the sorption properties of cellulose material [11, 14].

EXPERIMENTAL

In laboratory conditions, an amination mixture was prepared using triethanolamine (TEA) (LLC "KHIMPRODUKT" TD, Ukraine) and epichlorohydrin (ECH) (Merck Co., Germany). A heat-resistant flask was loaded with 1 mole of triethanolamine (101.9 g), to which 1 N HCl was gradually added in a molar ratio of TEA : HCl = 1 : 1.1. The flask was immersed in a container with cold water for cooling. The contents of the flask were kept for 30 min at room temperature with constant stirring. After that, ECH was added to the reaction flask in an equimolar ratio of 1 : 1 (TEA : ECH = 1 : 1). The pH of the resulting amination mixture was 8 - 8.5. The reaction mixture was then placed in a TS-20 thermostat (MIZMA, Ukraine) at 40°C for 3.5 h. After the interaction between ECH and TEA was completed, the resulting mixture was cooled to room temperature.

To determine the effect of modifier consumption on the sorption properties of cellulose fibers, samples of filtration material with a mass of 80 g m^{-2} were prepared from bleached softwood kraft pulp grade SB-5. The degree of cellulose beating was 91 ± 2°SR (the conditional parameter °SR represents the degree of refining of fibrous semi-finished material). The modifier consumption ranged from 5 to 50 % of the oven-dry fiber mass. The prepared fiber mass was thoroughly mixed and placed in a TS-20 thermostat at a temperature of 40°C for 60 min. Mixing was performed every 10 min to ensure uniform distribution of the modifier in the cellulose mass. The filtration material was formed on synthetic meshes using a LA-1 sheet-forming device (Ukraine). The laboratory membrane samples were then dried and labelled.

The sorption properties of the prepared cellulose material were studied using a static (non-flow) cell. The performance of the cellulose material was evaluated based on changes in the turbidity and coloration of the permeate, alterations in selectivity, and specific productivity. A model solution of sodium humate at a concentration of 100 mg L^{-1}, with an initial coloration of 1632 - 1685 degrees, and a kaolin suspension with a concentration of 1000 mg L^{-1}, were used for these measurements. Filtration was conducted under a pressure of 1 atm for 1 min. Fresh distilled water was used in all experimental studies.

The productivity (transmembrane flux rate) Q was determined (1), $m^3\ m^{-2}\ h^{-1}$.

$$Q = \frac{V}{S \cdot t} \qquad (1)$$

where V - volume of permeate, m^3; S - filtration area, m^2; t - filtration time, h.

The determination of residual coloration and turbidity of the permeate was carried out using a KFK-2 colorimeter (Ukraine). Turbidity was measured at a wavelength of 670 nm, and coloration at 400 nm. The obtained optical density values were converted into units of coloration and turbidity using calibration curve methods.

Selectivity SL for turbidity (coloration) of the membrane was determined using (2), %.

$$SL = \left[1 - \left(\frac{C_2}{C_1}\right)\right] \cdot 100 \qquad (2)$$

where C_1, C_2 - the turbidity (coloration) of the feed solution and permeate, mg dm^{-3} (degrees).

RESULTS AND DISCUSSION

The reaction between triethanolamine (TEA) and epichlorohydrin (ECH) is a key step in the modification of cellulose fibers. During the interaction of TEA with ECH (Fig. 1), epoxy groups are formed,

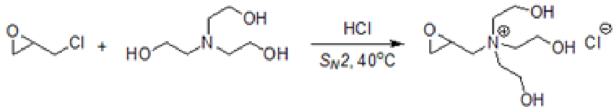

Fig. 1. Quaternization of triethanolamine with epichlorohydrin in an acidic medium.

which contribute to the creation of a three-dimensional network, significantly improving the mechanical properties of the cellulose fibers, their moisture resistance, chemical stability, and enhancing the reactivity of the cellulose fibers. The epoxy groups formed on the surface of the fibers are highly reactive, as they contain an electrophilic center (oxygen and carbon atoms in the ring) that can easily interact with nucleophilic groups such as hydroxyl, amine, or other functional groups present on the fibers.

The formed epoxy groups enable further cross-linking or the introduction of new functional groups, which not only improves the mechanical properties of the fibers but also enhances their ability to chemically interact with other substances. Thus, the formation of epoxy groups significantly increases the reactivity of cellulose fibers, making them more suitable for subsequent chemical modifications.

The quaternization of triethanolamine with epichlorohydrin occurs under conditions of nucleophilic substitution (S_N2) in an acidic medium provided by a 1 N HCl solution. Under these conditions, in addition to the desired transformation, side reactions such as oxirane ring-opening may also occur, leading to the formation of a complex mixture of products that are difficult to identify.

To identify the active groups formed because of the interaction between epichlorohydrin and triethanolamine, the IR spectrum of the aminating reagent was studied (Fig. 2).

In the IR spectrum, the absorption bands at 1361 and 1446 cm^{-1} are attributed to the vibrations of $-CH_3$ and $-CH_2-$ groups, which are part of the 2-hydroxypropyltriethylammonium chloride fragment formed because of the interaction between triethanolamine and epichlorohydrin. The band at 1045 cm^{-1} is attributed to the CH_2–Cl group. The bands at 2885 cm^{-1} indicate the presence of CH_2 groups, while the band at 3261 cm^{-1} corresponds to C-H bond vibrations. The broad intensity bands at 1640 cm^{-1} and 2800 cm^{-1} indicate the presence of ethyl groups in the resulting mixture.

In the studied sample, bands in the intensity range from 1250 to 1020 cm^{-1} indicate the presence of aliphatic amines (C–N). An intensity in the range of

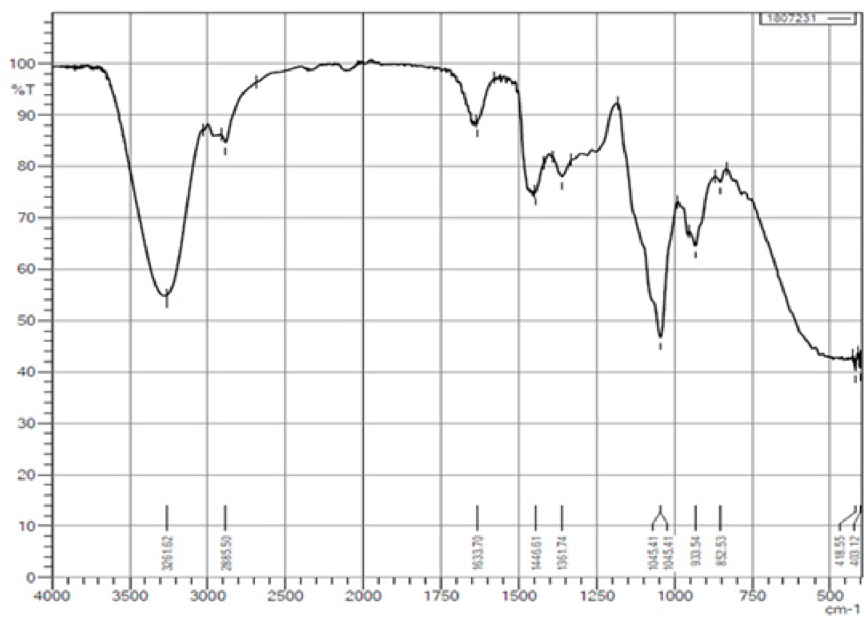

Fig. 2. IR spectrum of quaternized triethanolamine with epichlorohydrin.

840 to 870 cm^{-1} is observed, which characterizes the presence of stretching vibrations of C–N bonds.

The resulting mixture (without isolation of the quaternization product) was used for the modification of cellulose fibers (Fig. 3).

In this case, the O - alkylation reaction of cellulose with the quaternization product of triethanolamine also follows the S_N2 nucleophilic substitution mechanism and is accompanied by the opening of the oxirane ring, resulting in the formation of a macromolecular polyammonium polyhydroxy cellulose derivative. Accurately identifying the structure of the final product, as well as determining the exact number of hydroxyl groups involved in the alkylation process, remains challenging.

The interaction of cellulose fiber with the prepared aminating mixture ensured the uniform distribution of the modifier within the fibrous mass, achieved through regular stirring during the modification process. This significantly improved the sorption properties of the cellulose material, as confirmed by studies using a model solution of sodium humate and a kaolin suspension (Table 1, Fig. 4, 5).

As shown by the obtained research results, the use of a modifier in the amount of 5 - 30 % of the oven-dry fiber mass increases the sorption properties of the cellulose material by 0.3 - 2.4 % compared to the initial sorption of the cellulose fibers. With this amount of modifier, cross-linking with -OH groups do not occur fully, as the modification is carried out in an aqueous medium, where part of the modifier undergoes hydrolysis without participating in the reaction.

At a modifier consumption of 40 % of the oven-dry fiber mass, the material's sorption increases by 13.8 %. However, with a further increase in modifier consumption to 50 %, the sorption properties decrease again. This is because, at 40 % consumption, maximum interaction with –OH groups occur, while additional amounts of modifier lead to the deposition of excess mixture on the fiber surface. This deposition impairs further sorption by reducing the effective sorption surface area.

Fig. 6 shows the dependence of the productivity of the cellulose material on the consumption of the aminating mixture (modifier).

As shown by the productivity values in Fig. 6,

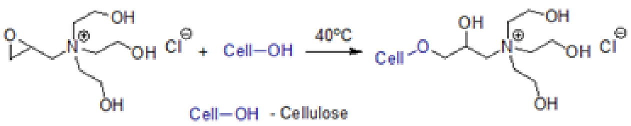

Fig. 3. Reaction of the quaternized derivative of triethanolamine with cellulose.

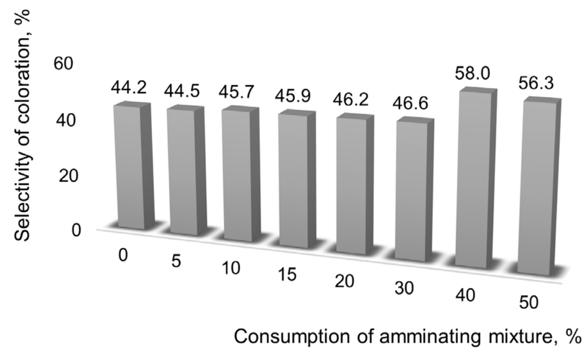

Fig. 4. Dependence of the change in selectivity for coloration on the modifier.

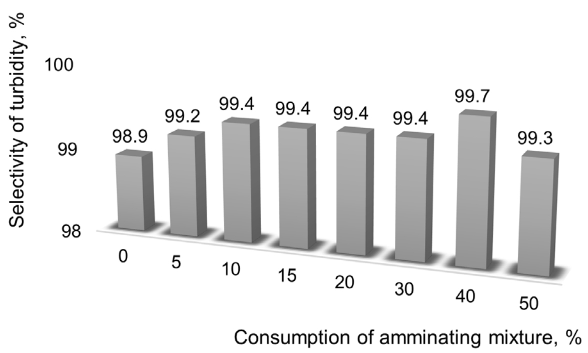

Fig. 5. Dependence of the change in selectivity for turbidity on the modifier consumption.

Table 1. Filtration capacity of cellulose samples with different amounts of modifier.

Modifier consumption, %	0	5	10	15	20	30	40	50
Coloration, degrees	935.0	915.0	906.25	896.0	893.7	893.7	695.0	725.5
Turbidity, mg L^{-1}	0.4	0.3	0.2	0.2	0.2	0.2	0.1	0.1

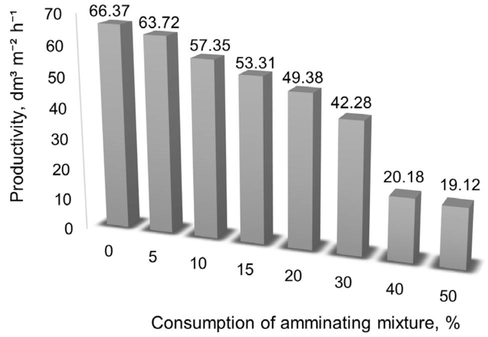

Fig. 6. Dependence of material productivity on the modifier consumption.

increasing the modifier consumption results in a decrease in productivity, indicating the formation of a denser material. This is due to the interaction between the cellulose fibers and the modifier, leading to fiber cross-linking and the formation of a more compact structure. Such a structure reduces the material's permeability, thereby decreasing its productivity but enhancing its mechanical properties.

CONCLUSIONS

Experimental results indicate that modifier consumption below 20 % does not significantly improve the sorption properties of the cellulose material. Increasing the consumption beyond 50 % likely results in the formation of a sediment layer on the fiber surface, reducing the effective sorption area and the material's productivity. The maximum improvement in sorption properties, by 13.8 %, is achieved with a modifier consumption of 40 % of the oven-dry fiber mass.

Authors' contributions: *I.T. made the primary contribution to the manuscript preparation, including the synthesis of scientific data, analysis of the obtained results, and their graphical and textual presentation. She was responsible for structuring the material and ensuring the manuscript's compliance with the journal's requirements. A.H. was responsible for conducting experimental studies, including sample preparation, performing a series of measurements, and processing primary data. Additionally, she translated the manuscript into English and handled the formatting of the reference list.*

REFERENCES

1. Progress on household drinking water, sanitation and hygiene 2000-2022: special focus on gender, New York, United Nations Children's Fund and World Health Organization, 2023, 172.
2. World Health Organization, United Nations Children's Fund, World Bank, State of the world's drinking water: an urgent call to action to accelerate progress on ensuring safe drinking water for all, Geneva, World Health Organization, 2022.
3. S.C. Yadav, Water Pollution: The Problems and Solutions, Science Insights, 44, 2, 2024, 1245-1251.
4. N. Fatema, R. M. Ceballos, C. Fan, Modifications of cellulose-based biomaterials for biomedical applications, Front. Bioeng. Biotechnol., 10, 2022, 1-8.
5. A.M. Elgarahy, M.G. Eloffy, E. Guibal, H.M. Alghamdi, K.Z. Elwakeel, Use of biopolymers in wastewater treatment: A brief review of current trends and prospects, Chinese Journal of Chemical Engineering, 64, 2023, 292-320.
6. G.P. Udayakumar, S. Muthusamy, B. Selvaganesh, N. Sivarajasekar, K. Rambabu, S. Sivamani, N. Sivakumar, J.P. Maran, A. Hosseini-Bandegharaei, Ecofriendly biopolymers and composites: Preparation and their applications in water-treatment, Biotechnol. Adv., 15, 52, 2021, 107815.
7. T. Aziz, A. Farid, F. Haq, M. Kiran, A. Ullah, K. Zhang, C. Li, S. Ghazanfar, H. Sun, R. Ullah, A Review on the Modification of Cellulose and Its Applications, Polymers, 14, 2022, 3206.
8. I.V. Trembus, N.V. Mykhailenko, A.S. Hondovska, Membranes Based on Modified Cellulose Fibers: A Review, Vcheni zapysky TNU imeni V.I. Vernadskoho, Seriia: Tekhnichni nauky, 34, 2, 2023, 40-45.
9. H. Kang, R. Liu, Y. Huang, Graft modification of cellulose: Methods, properties and applications, Polymer, 70, 2015, A1-A16.
10. R. Sun, B. Fang, Y. Lu, X. Qiu, W. Du, Rheology and rheokinetics of triethanolamine modified carboxymethyl hydroxyethyl cellulose, Journal of Dispersion Science and Technology, 39, 7, 2018, 923-928.
11. A.O. Kostyk, O.H. Budishevska, V.B. Vostres, Z.Ya. Nadashkevych, S.A. Voronov, Oderzhannia i kharakterystyka kationnykh krokhmaliv, Chemistry, Technology and Application of Substances, 2, 1, 2019, 159-165.

12. A.U. Inimfon, M.D. Raquel, D.W. Lee, V.H. John, Adsorption properties of cross-linked cellulose-epichlorohydrin polymers in aqueous solution, Carbohydrate Polymers, 136, 2016, 329-340.
13. A. Kumar, Y.S. Negi, Chemical modification of cellulose using epichlorohydrin and its impact on fiber properties, Carbohydrate Polymers, 207, 2019, 558-568.
14. H. Liu, T. Chen, Crosslinking cellulose with epichlorohydrin: A review of methodology and applications, Journal of Applied Polymer Science, 137, 32, 2020, 1-12.
15. A.I. Udoetok, R.M. Dimmick, L.D. Wilson, J.V. Headley, Adsorption Properties of Cross-linked Cellulose-Epichlorohydrin Polymers in Aqueous Solution, Carbohydrate Polymers, 136, 2016, 329-340.
16. P.J. Smith, R.J. Brown, Role of triethanolamine in the stabilization and modification of cellulose fibers, Polymer Chemistry, 9, 12, 2018, 1523-1531.