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USE OF MODIFIED MINERAL SORBENT FOR CELLULOSE MEMBRANE OPERATION

The article examines the prospects of using modified bentonite as a sorption material in cellulose membranes for water purification. Thermal and acid modification of natural bentonite was conducted to improve its adsorption properties. IR spectroscopy methods were used to analyze the structural changes in bentonite after the modification process. Changes in the intensity of functional groups were observed, indicating partial destruction of the crystal lattice. Analysis of adsorbent material fixation showed that the material is actively retained on the surface of cellulose fibers. The cellulose membranes were manufactured using miscanthus cellulose obtained through oxidative-organosolvent delignification of plant raw material stems. The cellulose was modified with an aminating mixture containing epichlorohydrin : triethanolamine in a 1:1 ratio. The impact of using natural and modified bentonite on cellulose membrane performance was demonstrated. The sorption properties and productivity of the obtained membranes were evaluated during the filtration of model solutions of sodium humate and kaolin. It was established that membranes made from modified miscanthus fiber with internal filler addition showed improved residual permeate color indicators compared to material made from conventional modified oxidative-organosolvent cellulose. Specifically, when using modified cellulose with the addition of natural and calcined bentonite, the residual color of the model solution was 528.15 and 480.2 degrees, respectively, which is 4.6% and 13.3% more effective. Conversely, using acid-modified bentonite as a filler in membrane manufacturing deteriorates permeate quality due to the formation of a porous material structure and particle deposition on the fiber surface, which inhibits sorption. The obtained results demonstrate the potential for applying modified cellulose membranes in water treatment technologies.

Keywords: bentonite, organosolvent cellulose, thermal treatment, acid modification, selectivity, productivity

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ВИКОРИСТАННЯ МОДИФІКОВАНОГО МІНЕРАЛЬНОГО СОРБЕНТУ ДЛЯ РОБОТИ ЦЕЛЮЛОЗНИХ МЕМБРАН

У статті розглянуто перспективи використання модифікованого бентоніту як сорбційного матеріалу у складі целюлозних мембран для очищення води. Проведено термічну та кислотну модифікацію природнього бентоніту з метою покращення його адсорбційних властивостей. Методами ІЧ-спектроскопії проаналізовано структурні зміни бентоніту після процесу модифікації. Показано зміну інтенсивності функціональних груп, що свідчить про часткове руйнування кристалічної решітки. Аналіз з дослідження фіксації адсорбуючих матеріалів показав, що матеріал активно затримується на поверхні целюлозних волокон. Целюлозні мембрани було виготовлено на основі целюлози з міскантусу, одержаної окисно-органосольвентним способом делігніфікації стебел рослинної сировини. Целюлозу було модифіковано амінуючою сумішшю, яка містить епіхлоргідрин : триетаноламін у співвідношенні 1 : 1. Показано вплив використання бентоніту природнього та модифікованого на роботу целюлозних мембран. Оцінено сорбційні властивості та продуктивність отриманих мембран у процесі фільтрування модельних розчинів гумату натрію та каоліну. Встановлено, що мембрани, виготовлені з модифікованого волокна з міскантусу та з додаванням наповнювача внутрішньомасно, показують покращені показники залишкової кольоровості перміату порівняно з матеріалом виготовленим зі звичайної модифікованої окисно-органосольвентної целюлози. Зокрема, при використанні модифікованої целюлози з додаванням природного та випаленого бентоніту залишкова кольоровість модельного розчину становить 528.15 та 480.2 градусів, відповідно, що на 4.6% та 13.3% ефективніше. Використання в якості наповнювача кислотно-модифікованого бентоніту при виготовлені мембран, навпаки, погіршує якість перміату за рахунок утворення пористої структури матеріалу та осіданні частинок на поверхні волокна, що перешкоджає сорбції. Отримані результати демонструють потенціал застосування модифікованих целюлозних мембран у водоочисних технологіях.

Ключові слова: бентоніт, органосольвентна целюлоза, термічна обробка, кислотна модифікація, селективність, продуктивність

Formulation ofthe problem

Water pollution is one of the most pressing environmental problems of our time, directly affecting the state of the environment, human health, and industrial processes. The increasing level of anthropogenic pressure, particularly the discharge of industrial and domestic wastewater, leads to the accumulation of toxic organic and inorganic pollutants in water systems, including heavy metals, pharmaceutical compounds, and dyes. The implementation of effective, environmentally safe, and economically viable water treatment methods is an urgent scientific and practical task [1].

One of the most promising approaches to solving this problem is the use of adsorption technologies based on natural sorbents. Traditionally, activated carbon is used for water purification; however, its production is energy-intensive and accompanied by a significant environmental burden. In this regard, a relevant research direction is the development of alternative sorption materials using natural minerals and biopolymers [2-4].

Special attention is paid to materials that are environmentally safe, economically advantageous, and easily renewable. Promising and safe natural materials for membrane manufacturing include coal, bentonite, perlite, xylite, and cellulose [3].

Bentonite is a natural aluminosilicate mineral characterized by high specific surface area, developed porous structure, and the ability to absorb heavy metal ions and organic contaminants. The basic structure of bentonite includes two tetrahedral layers of silicon dioxide (Si^{4+}) and an octahedral layer of aluminum oxide (Al^{3+}). This clay mineral has a permanent negative charge that arises from the isomorphic substitution of Al^{3+} for Si^{4+} in the tetrahedral layer and Mg^{2+} for Al^{3+} in the octahedral layer. This negative charge is naturally compensated by exchangeable cations (Na^{+}, Ca^{2+}) in the interlayer space. Bentonite has high cation exchange capacity, significant swelling, and large specific surface area, which provides high adsorption capacity for ionic or polar compounds. Its application in adsorption processes and membrane technologies can significantly improve purification efficiency through ion exchange mechanisms and interlayer sorption [4, 5].

Cellulose is the most abundant biopolymer, possessing unique mechanical properties, biodegradability, and potential for functionalization. The use of resource-efficient technologies for cellulose production opens new prospects for creating environmentally friendly membrane materials. Oxidative-organosolvent methods remain the most economical and environmentally friendly approaches for plant raw material delignification [6-8].

Oxidative Organosolv Cellulose exhibits high brightness, low residual lignin content, and enhanced structural characteristics, making it a promising material for the development of filtration membranes. The combination of bentonite and cellulose in the form of composite materials allows for the creation of new materials with improved adsorption properties and mechanical stability [5].

The scientific significance of this research lies in expanding knowledge about the modification of bentonite and its interaction with cellulose matrices for the creation of sorption membranes. The practical value of the work consists in the development of innovative materials that can be applied in water purification systems adhering to sustainable development principles, reducing reliance on synthetic polymers, and minimizing the use of toxic chemical reagents.

Analysis of recent sources

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Among the wide range of adsorbents, activated carbon is the most commonly used due to its microporous structure and significant specific surface area (500-1500 m^2/g), which ensures the effective removal of various organic pollutants, including aromatic compounds, dyes, and phenolic derivatives [9].

Among aluminosilicate minerals, bentonite is of particular scientific and practical interest due to its high sorption capacity for heavy metal ions and organic contaminants. Experimental studies demonstrate that thermochemical modification and acid activation of bentonite materials lead to a significant increase in surface active centers, enhancing their adsorption capacity and catalytic activity [10-11].

Natural zeolite minerals, particularly clinoptilolite, find wide application in ion exchange processes and adsorption purification of aquatic environments. Modifying their surface through acid treatment or metal cation intercalation allows for increased selectivity towards specific contaminants, such as ammonium nitrogen and heavy metal ions, as confirmed by the results of systematic studies [12-14].

Intensification of sorption processes and modification of natural sorbents is a priority vector of scientific and technological research. Thermal activation of materials leads to the formation of a developed micro- and mesoporous structure, while acid modification enhances the reactivity of surface functional groups. The application of targeted chemical functionalization allows for optimizing the selectivity of sorbents towards specific types of pollutants [10-11].

Presenting main material

Modification of natural materials is aimed at optimizing their structural and sorption characteristics. Physico-chemical modification methods for natural sorbents include thermal, chemical, and combined treatments, which lead to significant changes in their surface properties

For the study, natural bentonite (manufacturer: Italy) was used—a light gray clay mineral with an average particle size of 5–10 μm.

For the thermal modification of bentonite, a 25 g sample of natural clay was used, which was subjected to calcination in a muffle furnace at a temperature of 800 ± 10 °C for 90 minutes.

The acid-thermal modification method of bentonite involved treating a 25 g sample of natural bentonite in 200 ml of a 1N acetic acid solution until a pH of 5 was achieved. Next, 400 ml of a 0.1N sodium acetate solution was added to the mixture, followed by the gradual addition of 100 ml of a 35% hydrogen peroxide solution.

The obtained mixture was maintained in a thermostat at a temperature of 60 ±2 °C for 7 hours. After the thermal treatment, the mixture was centrifuged for 5 minutes at 5000 rpm to precipitate the bentonite. The resulting precipitate was dried at a temperature of 120 ±10 °C. The dried acid-modified bentonite was then subjected to additional calcination in a muffle furnace at 800 ±10 °C for 90 minutes. Following the thermal treatment, the modified bentonite was ground in a ceramic mortar to obtain a homogeneous fine-disperse fraction.

To assess the structural changes in bentonite under the influence of modification, IR spectral analysis was conducted on samples of natural, thermally treated, and acid-modified bentonite (Fig. 1)

The spectra of the studied clays show bands characteristic of bentonites, specifically 3712 (3102 - 3580) H - OH, 112 (131) Si - OH, 1002 (1079) Si - O - Si, and 471 (484) cm^{-1}. The broad band at 3102 - 3580 cm^{-1} is associated with the stretching of - OH bonds in structural hydroxyl groups and water molecules present in the bentonite. This band is more pronounced in the calcined bentonite. The presence of hydroxyl Si - OH groups accounts for the chemical activity of the bentonite itself. The bands at 806, 691, and 471 cm^{-1} correspond to quartz impurities. Changes in the intensity of these groups may indicate partial disruption of the crystalline lattice of bentonite clay.

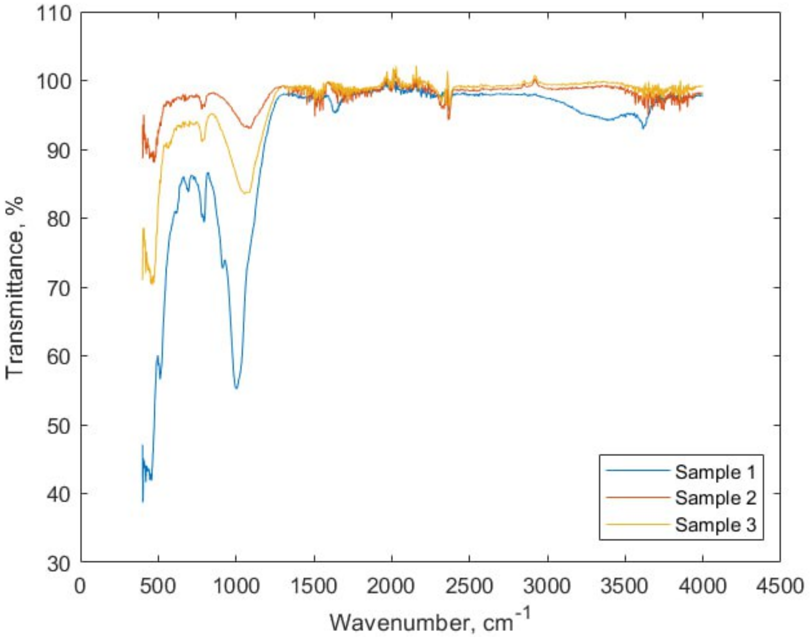


Figure 1. IR Spectrum of Bentonite and Its Modifications:
Sample 1 – Natural Bentonite; Sample 2 – Calcined Bentonite; Sample 3 – Acid-Modified Bentonite

To determine the sorption properties of modified bentonite clays, cellulose membranes were fabricated from modified oxidative-organosolv cellulose derived from Miscanthus giganteus. The oxidative-organosolv cellulose from Miscanthus was previously ground to 92 ± 2°SR, modified with an aminating mixture containing epichlorohydrin and triethanolamine in a 1 : 1 ratio, and the bentonite clay content was 25% of the absolute dry (abs. dry) fiber weight. The filtration material was cast on synthetic meshes using a sheet-forming machine with a mass of 80 g/m². Subsequently, the laboratory samples of cellulose membranes were dried and labeled.

The membrane performance was tested at a pressure of 1 atm, with samples taken every 1 minute. Filtration was conducted in a non-flow cell using model solutions of sodium humate at a concentration of 100 mg/dm³ and an initial color range of 1625.0 - 1726.75 degrees, as well as a kaolin solution with an initial turbidity of 32 mg/dm³. The results of color selectivity are shown in Fig. 2, residual turbidity in Table 1, and productivity in Fig. 3.

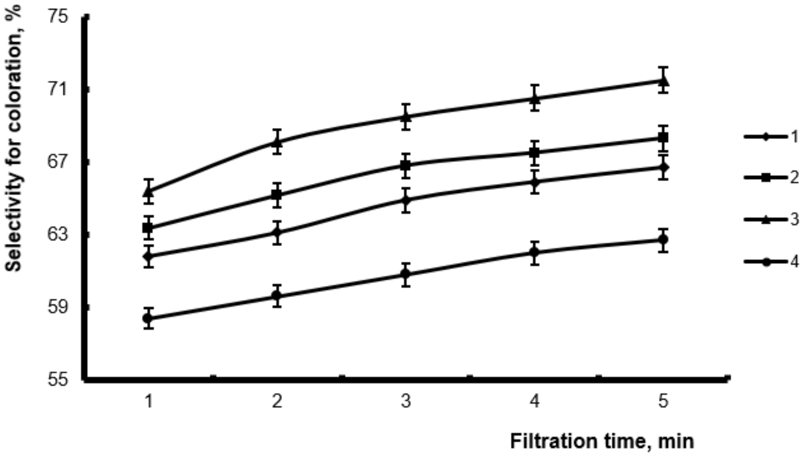


Figure 2. The effect of filtration duration on the color selectivity of cellulose membranes:
♦ – modified cellulose; ■ – with natural bentonite; ▲ – with calcined bentonite; ● – with acid-modified bentonite

Table 1

Residual turbidity of the kaolin solution filtered through miscanthus cellulose membranes with modified bentonites

Filtration Time, min	Residual Turbidity, mg/dm³			
	Modified cellulose	Modified cellulose with natural bentonite (25% of abs. dry fiber weight)	Modified cellulose with calcined bentonite (25% of abs. dry fiber weight)	Modified Cellulose with Acid-Treated Bentonite (25% of abs. dry fiber weight)
1	0.25	0.4	0.85	1.1
2	0.25	0.35	0.25	0.75
3	0.1	0.1	0.15	0.5
4	0.1	0.1	0.1	0.2
5	0.1	0.1	0.1	0.1

As shown in Fig. 2, the change in the coloration selectivity of the permeate reflects the degree of removal of dissolved substances from the surface of the filtration material. The highest selectivity is achieved when using a membrane made from modified cellulose with the addition of thermally calcined bentonite. Thermal activation enhances the adsorption properties by removing water and hydroxyl groups from the bentonite structure, thereby providing access to surface centers with a negative charge.

The determination of residual turbidity for all types of membranes showed a significant reduction in turbidity after just 1 minute of filtration. The residual turbidity values are within 0.1 mg/dm^3 for all types of membranes studied.

Fig. 3 shows the relationship between the productivity of membranes fabricated from modified miscanthus cellulose combined with natural, calcined, and acid-modified bentonite and the duration of filtration. With increasing filtration time, the productivity of the membranes decreases due to pore blockage by colloidal particles present in the sodium humate solution and the compaction of the fibrous structure of the membrane. The highest productivity is observed during the first minute of operation for the membrane made from modified cellulose with the addition of thermally treated bentonite, which can be attributed to the higher porosity of the resulting material compared to the others. In contrast, the material made from modified cellulose without fillers has a less porous structure, resulting in a membrane productivity that is 1.9 - 2.4 times lower than that of the membrane incorporating thermally treated bentonite.

To verify the fixation of adsorbing materials on the surface of the cellulose membrane, images of samples were obtained using Scanning Electron Microscopy (SEM). These samples were made from miscanthus cellulose and bleached softwood kraft pulp (ground to 92 ± 2 °SR) with the addition of thermally modified bentonite (Fig. 4).

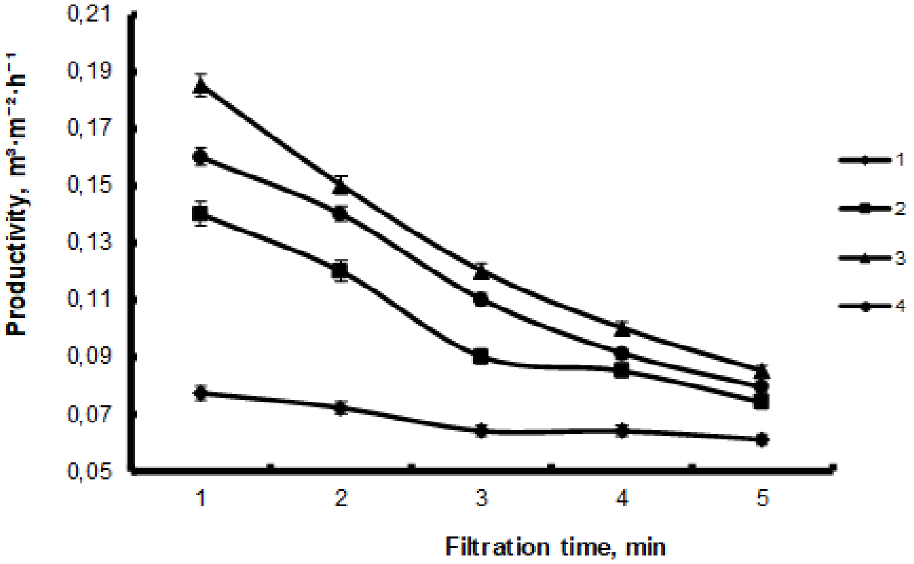
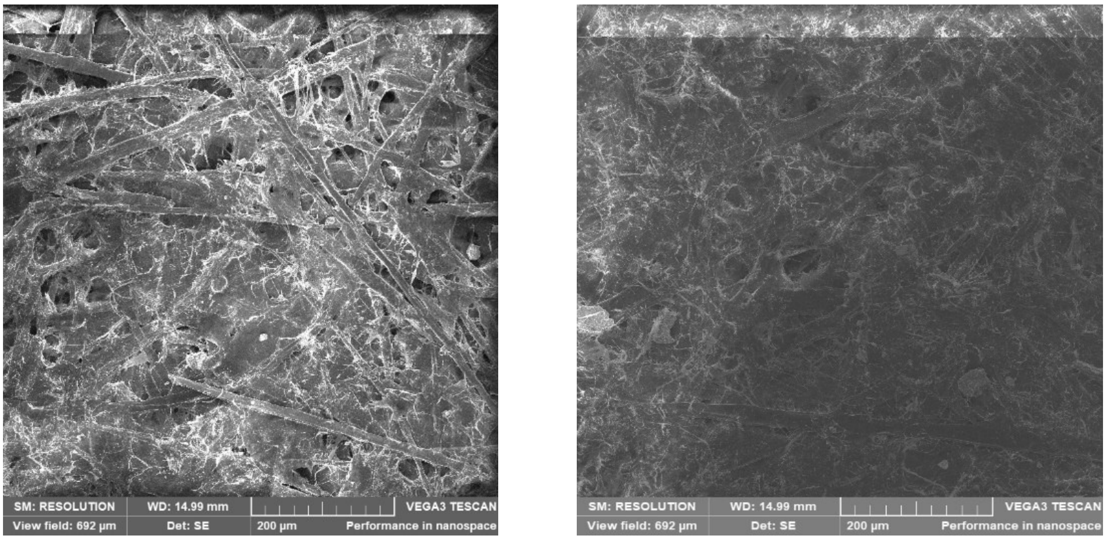


Figure 3. The effect of filtration duration on the productivity of cellulose membranes: ♦ – modified cellulose; ■ – with natural bentonite; ▲ – with calcined bentonite; ● – with acid-treated bentonite.

As seen from the images, the adsorbing material is fixed both on the surface of the fibers and trapped in the pores between them. Consequently, this leads to an increase in the thickness and mass of the membrane itself, as well as a reduction in density.



a) **b)**

Figure 4. SEM Micrographs of Modified Cellulose Membranes with Thermally Treated Bentonite: a) –Oxidative-Organosolv Cellulose from Miscanthus; b) – Bleached Softwood Kraft Pulp.

Conclusions

Studies on the modification of natural bentonite using thermal and acid-thermal methods have been conducted, enhancing its sorption characteristics. IR spectroscopic analysis confirmed structural changes in the bentonite after treatment, specifically an increase in the number of active centers on the surface. Composite cellulose membranes were developed based on organosolv cellulose from Miscanthus giganteus, modified with an aminating mixture, incorporating modified bentonite as a sorption filler.

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