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ASSESSMENT OF THE EFFICIENCY OF CELLULOSE MEMBRANES WITH CARBON ADSORBENT APPLICATION

Introduction

Water pollution is a highly pressing issue today. Water purification is a critically important process for ensuring human health, preserving ecosystems, and achieving sustainable development. Due to human activities, a significant amount of contaminated wastewater is discharged into water bodies, altering the natural composition of water and directly impacting the functioning of ecosystems. Therefore, there is a substantial need for effective water treatment solutions [1, 2].

Membrane technologies for water purification are currently considered the most efficient and energy-saving solutions. A wide variety of materials, both organic and inorganic, are used in membrane fabrication. The most commonly used materials include polyamide, polysulfone, polyvinyl chloride, polysulfonamide, ceramics, graphite, and others. These materials differ in their efficiency, selectivity toward various types of contaminants, and are characterized by complex manufacturing processes [3].

Among the most widely used materials for membrane production, cellulose stands out as a readily available, cost-effective, efficient, and environmentally friendly option. The use of cellulose significantly simplifies the membrane fabrication process, thereby substantially reducing production costs.

Formulation of the problem

Despite technological advancements, the percentage of polluted water is not decreasing; on the contrary, it continues to grow. Therefore, modern water treatment technologies demand the use of so-called «green» materials, such as activated carbon, bentonite, zeolite, clinoptilolite, and palygorskite. These materials demonstrate high adsorption and ion-exchange capacities for contaminants of both organic and inorganic origin [4]. The purification of polluted water using such materials involves a combination of processes, including physical and chemical sorption, ion exchange, and precipitation [4].

To enhance the sorption properties of such materials for compounds present in polluted water, they undergo mechanical, thermal, or chemical treatment. This treatment not only improves their adsorption capacity but also enhances their physicochemical properties by removing impurities from the native materials that hinder the sorption of substances [5].

Analysis of recent research and publications

Modern water treatment technologies face substantial challenges due to the ongoing rise in pollution levels of water resources. Natural sorbents are of particular interest, as they exhibit significant potential owing to their high adsorption and ion-exchange capacities for the removal of various types of pollutants.

Activated carbon remains one of the most widely used sorbents in water treatment due to its high specific surface area and efficiency in removing organic compounds such as dyes, phenols, and other organic substances [5–6]. The modification of activated carbon through chemical or thermal treatment enhances its sorption properties, tailoring it to specific application conditions.

Among clay minerals, bentonite exhibits high efficiency in the removal of heavy metals and organic compounds. Research has shown that thermal and acid activation of bentonites promotes an increase in the number of active sites on their surface, thereby enhancing their adsorption capacity and catalytic properties [7–8]. Zeolites, particularly clinoptilolite, are widely used for ion exchange and adsorption due to their framework structure. The modification of zeolites with acids or metals enhances their selectivity toward specific contaminants, such as ammonium or heavy metals, as confirmed by numerous studies [9–11].

Palygorskite, as a fibrous mineral, effectively removes a wide range of organic and inorganic compounds due to its high surface activity. Its modification through thermal or acid treatment enhances its sorption properties and reduces the presence of impurities that limit adsorption [12–14].

The modification of natural sorbents is a key approach to enhancing their efficiency. Thermal treatment increases porosity, acid activation improves the activity of surface groups, and chemical modification imparts specific selectivity to the sorbents [7–8].

Overall, modern research highlights the significant potential of natural sorbents in addressing water pollution challenges. Further development of methods for their modification and adaptation to water treatment conditions can enhance the efficiency of existing technologies and contribute to ensuring environmental safety.

Presentation of the Main Material

The application of activated carbon as part of cellulose membranes primarily improves the organoleptic properties of water (odor, color, and taste). This material contains a large number of micropores capable of retaining a significant amount of impurities due to molecular attraction forces.

A promising method for polluted water treatment is solid-phase oxidation based on MnO_2. Manganese dioxide is an active oxidizing agent [15]:

$$MnO_2\downarrow + 4H^+ + 2\bar{e} = Mn^{2+} + H_2O;\ E^\circ = +1{,}23\ V.$$
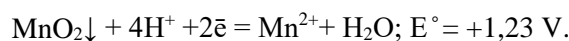
The study investigated the process of MnO_2 deposition on activated carbon.

Coconut-based activated carbon was used for the research, with the following characteristics: the pore area of 1 g of coconut carbon is 1000–1200 m², and the granule size ranges from 0.9 to 1.5 mm.

The modification of carbon was carried out using a $KMnO_4$ solution with varying concentrations from 0.015 to 0.035 meq/dm³ under neutral pH conditions and at a temperature of 18±2 °C. The process duration ranged from 15 to 135 min with constant stirring.

At the end of the modification process, the residual concentration of the $KMnO_4$ solution was determined by titration with sodium oxalate solution. Additionally, the mass of adsorbed MnO_2 was calculated (Fig. 1).

MnO_2 deposits on the surface of the carbon through a redox reaction, where $KMnO_4$ acts as the oxidizing agent and the carbon serves as the reducing agent. During the reaction, the permanganate ion breaks C-C bonds, resulting in the formation of manganese dioxide within the pores of the carbon [15]:

$$MnO_4^- + 4H^+ + 3\bar{e} = MnO_2\downarrow + 2H_2O;\ E^\circ = +1{,}69\ V.$$
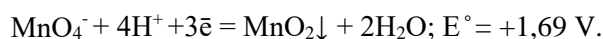
With an increase in the contact duration between the carbon sorbent and permanganate, the amount of MnO_2 deposited in the carbon pores increases. Based on the observed dependencies, it can be concluded that the deposition degree of MnO_2 on activated carbon ranges from 13 % to 30 %, depending on the modification duration and the initial concentration of the $KMnO_4$ solution.

To determine the optimal conditions for the modification of activated carbon, mathematical processing of the experimental data was performed. A full factorial experiment of the 2^2 type was used for the mathematical analysis of the results. [16, 17]. The technological parameters influencing the efficiency of the carbon modification process were considered as variables (x_i): x_1 – modification duration, min; x_2 – potassium permanganate solution concentration, meq/dm³.
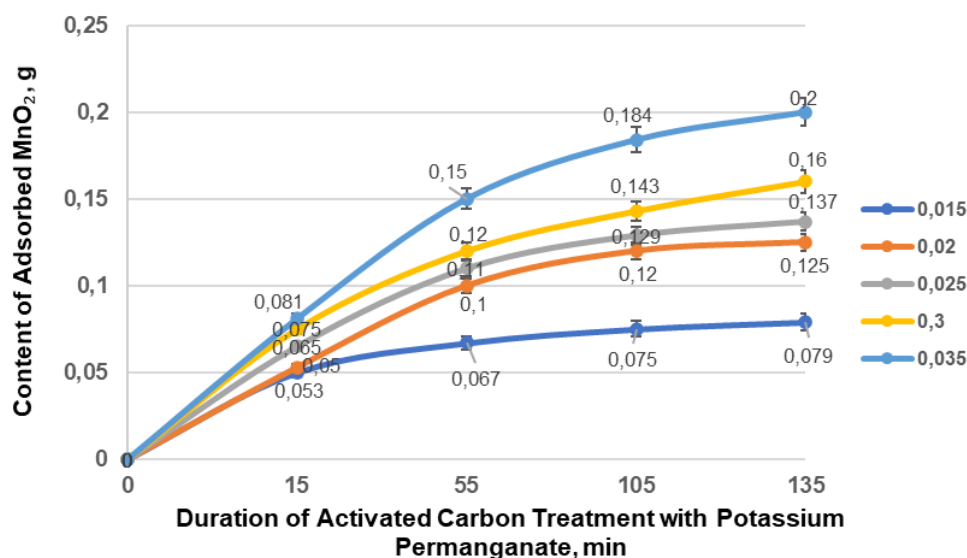
Fig. 1. Dependence of the MnO₂ content adsorbed in carbon pores on the duration of its treatment
with KMnO₄ at different concentrations

The optimization parameters were selected as follows: Y_1 – specific adsorption, mg/g; Y_2 – amount of deposited permanganate, g; Y_3 – amount of deposited manganese dioxide, g.

Using the derived statistical regression equations for Y_1–Y_3, multicriteria optimization was performed using the Gauss-Seidel method. A compromise region for conducting the activated carbon modification process was identified and is presented in Fig. 2.

$$Y_1= -519,14 - 20,3 \cdot x_1 + 1,44925 \cdot x_2 + 579,36 \cdot x_1 \cdot x_2 + 0,029403 \cdot x_1^2 - 4,13876 \cdot x_2^2;$$

$$Y_2= -3,2605 - 0,11736 \cdot x_1 + 839,79 \cdot x_2 + 3,4955 \cdot x_1 \cdot x_2 + 0,00015607 \cdot x_1^2 - 24013 \cdot x_2^2;$$

$$Y_3 = -1,8001 - 0,064764 \cdot x_1 + 463,46 \cdot x_2 + 1,9281 \cdot x_1 \cdot x_2 + 8,6295 \cdot x_1^2 - 13251 \cdot x_2^2.$$
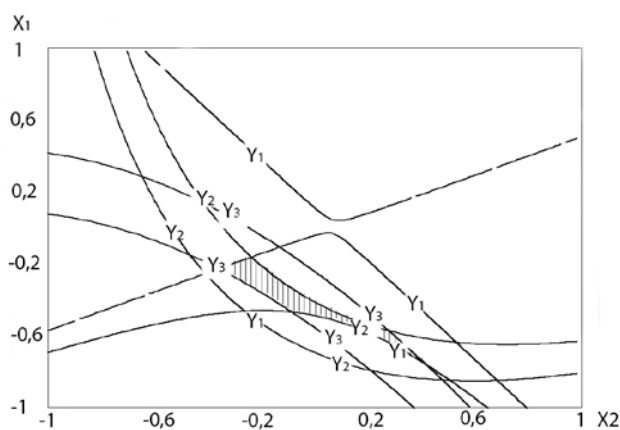

Fig. 2. Compromise region for the modification of activated carbon with a potassium permanganate solution

The optimal point is observed under conditions where the factor values are: processing duration x_1 = 55 min and potassium permanganate solution concentration x_2 = 0.02 meq/dm³. Regression equation analysis indicates that the modification duration negatively affects the activated carbon modification process, particularly the specific adsorption parameter. In contrast, an increase in the potassium permanganate solution concentration positively influences the quality indicators of the modification process.

The modified carbon was ground into a fine fraction and subsequently used for the fabrication of cellulose membranes.

The authors of studies [18–21] established that the delignification processes of non-woody plant stems using cooking solutions based on peracids are highly selective. Experimental results demonstrated the potential of using miscanthus stems for the production of cellulose for various applications [22].

To obtain fibrous semi-finished products from miscanthus stems for subsequent use in the production of filtration materials, a system comprising acetic acid, water, and hydrogen peroxide was utilized [18]. The delignification process of plant raw materials was performed using a solution containing glacial acetic acid and water in a mass ratio of 75:25 vol. %. The solution was supplemented with 50% hydrogen peroxide and 0.5 % citric acid, calculated based on the absolute dry weight of the raw material. The process was conducted at a temperature of 100±2°C for 180 minutes, with a liquor-to-solid ratio (LSR) of 10:1 [18].

Peracetic acid was formed in situ during the cooking process using a hot preparation method. To evaluate the strength characteristics and to produce membranes, the resulting fibrous semi-finished product was refined to a beating degree of 60±2° SR. Laboratory cellulose samples were prepared with a basis weight of 80 g/m².

As a result of the research, cellulose was obtained from miscanthus stems with a yield of 62.4 % and a residual lignin content of 1.84 % based on the absolute dry weight of the raw material.

The key performance indicators for cellulose, intended for the production of laboratory samples of filtration materials–primarily used under wet conditions and elevated pressure–are wet strength and burst resistance. These indicators largely depend on the strength of inter-fiber bonds and fiber flexibility. Fig. 3 illustrates the physical and mechanical properties of the obtained cellulose compared to softwood kraft cellulose, which is currently the most commonly used material for cellulose membrane production.

The experimental data show that miscanthus cellulose lags behind bleached softwood kraft cellulose in wet strength by 33.3 %. However, in terms of burst resistance and breaking length, miscanthus cellulose demonstrates superior performance, with improvements of 32.5 % and 23 %, respectively. Therefore, it can be considered a suitable base material for the production of filtration materials.
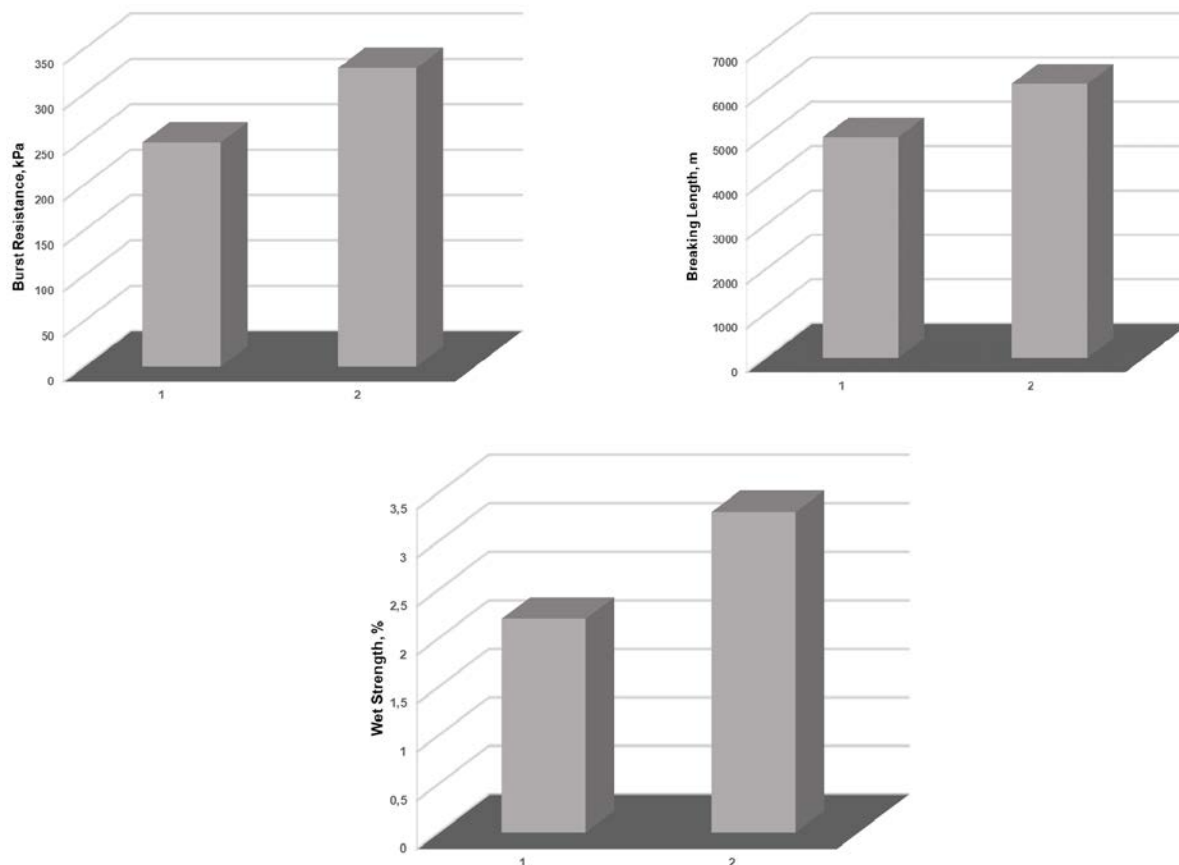
Fig. 3. Strength characteristics of cellulose:
1 – bleached softwood kraft cellulose; 2 – oxidative-organosolv cellulose from miscanthus

The fibrous semi-finished product was preliminarily refined to a beating degree of 91±2 °SR. The filtration material was produced with a basis weight of 80 g/m². For membrane fabrication, modified activated carbon obtained under the defined optimal conditions was used: treatment duration of 55 minutes and potassium permanganate concentration of 0.02 meq/dm³. The prepared modified carbon was directly added to the sheet-forming mold in an amount equal to 25 % of the oven-dry fiber mass. The performance efficiency of the filtration material was tested under a pressure of 1 atm. The research results are presented in Figs. 4 and 5.

Experimental results showed that the turbidity selectivity during the filtration of a kaolin solution with a concentration of 100 mg/dm³ for 5 minutes was in the range of 99.1–99.6 % for the membrane made from modified cellulose and 98.2–98.8 % for the similar membrane containing a carbon adsorbent. Such high selectivity indicates that the membrane is capable of retaining the majority of suspended particles in the suspension. The slightly lower turbidity selectivity for membranes containing the carbon adsorbent is likely due to their lower density (Table 1), which can be attributed to the presence of adsorbent particles between the cellulose fibers, facilitating the passage of colloidal particles. The membrane density was calculated using Equation 1:

$$\rho = \frac{m}{h}. \qquad (1)$$

where: m – mass of 1 m² of the membrane, g; h – thickness of the membrane, µm.

Table 1

Structural parameters of cellulose membranes

Membrane Type	Mass of the membrane, g	Thickness, μm	Density, g/cm³
Modified cellulose fiber from Miscanthus	2.8214	104	0.86
Modified cellulose fiber from Miscanthus with added carbon adsorbent	3.3058	334	0.32
Modified cellulose fiber from Miscanthus with added calcined bentonite	3.3074	302	0.35
Modified cellulose fiber from bleached softwood kraft pulp	2.8412	109	0.83
Modified cellulose fiber from bleached softwood kraft pulp with added natural bentonite	3.1028	228	0.43
Modified cellulose fiber from bleached softwood kraft pulp with added acid-activated bentonite	3.1216	300	0.33

Further research demonstrates that membrane density will directly influence both the efficiency and productivity of membrane operation.

Experimental data show that the membrane produced with the addition of a carbon adsorbent exhibits lower color selectivity compared to its counterpart made from modified cellulose (Fig. 4). It was established that during the first minute of filtration, the selectivity of the membrane containing the carbon adsorbent is 32.2 % lower. However, after 5 minutes of operation, the selectivity for the removal of soluble substances differs by only 11.7 %. This is attributed to greater fiber compaction over time due to the effect of pressure on the membrane with the carbon adsorbent, which results in increased filtration selectivity for soluble substances.

Regarding productivity, the membrane containing the carbon adsorbent is characterized by a higher filtration rate, which gradually decreases over time. For instance, during the first minute of filtration, the productivity of the membrane with the carbon adsorbent is 70.8 % higher compared to the cellulose membrane made with the addition of a modifier. However, after 5 minutes, the productivity rapidly decreases, and the difference between the two membranes is reduced to 44.5 % (Fig. 5). This can be explained by the lower initial density of the membrane and the rapid fiber compaction under pressure, which affects the filtration process.
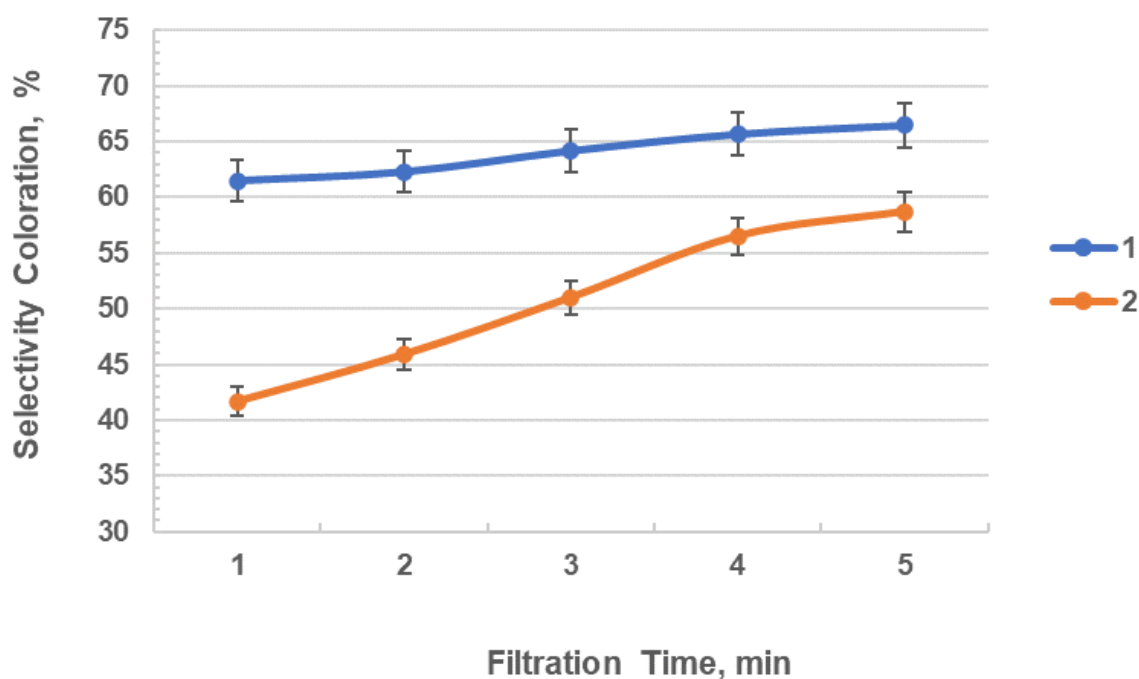

Fig. 4. Effect of filtration duration on the selectivity coloration of the permeate for miscanthus cellulose membrane:
1 – modified cellulose; *2* – modified cellulose with added activated carbon
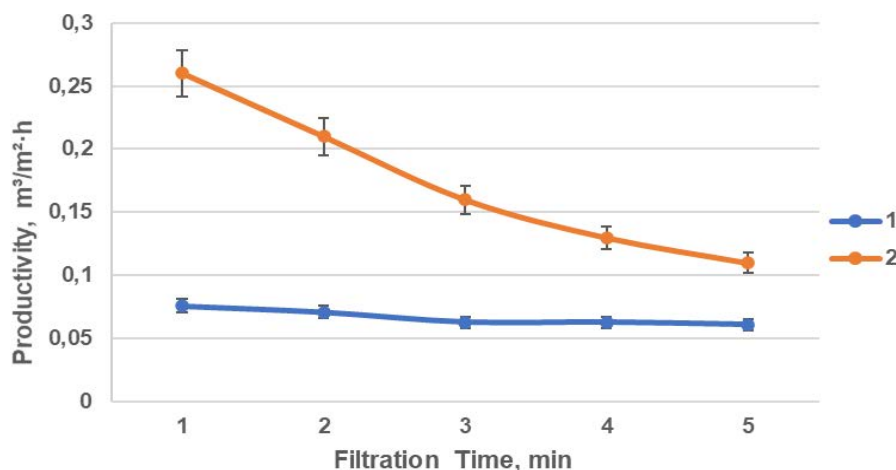
Fig. 5. Effect of filtration duration on the productivity of miscanthus cellulose membranes:
1 – modified cellulose; *2* – modified cellulose with added activated carbon

Conclusions

A methodology for modifying activated carbon with a potassium permanganate solution was proposed. Using a full factorial experiment, optimal treatment conditions were established: a duration of 55 minutes and a potassium permanganate solution concentration of 0.2 meq/dm³.

The incorporation of a carbon-based adsorbent into the structure of modified cellulose membranes leads to an increase in selectivity by 19–21 % compared to filtration material obtained from organosolv miscanthus-derived cellulose. However, due to the reduced structural integrity and packing density of the membrane containing the carbon sorbent, its productivity decreases by 35–73 % relative to the analogous material without adsorbent addition.

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Трембус І. В. Гапонюк А. С.
ОЦІНКА ЕФЕКТИВНОСТІ РОБОТИ ЦЕЛЮЛОЗНИХ МЕМБРАН З ВИКОРИСТАННЯМ ВУГЛЕЦЕВОГО АДСОРБЕНТУ

Стаття присвячена отриманню з окисно-органосольвентної целюлози з міскантусу фільтрувального матеріалу з використанням вуглецевого адсорбенту для очищення води від завислих частинок, що зумовлюють її каламутність. Запропоновано методику модифікації активованого вугілля розчином перманганату калію. Проведено дослідження з окиснення вугілля розчином KMnO$_{4за}$ концентрації від 0,015 до 0,035 мг-екв/дм^3, тривалістю в межах 15–135 хв. Експериментально встановлено, що ступінь осідання MnO$_2$ на активованому вугіллі коливається від 13 до 30 % в залежності від тривалості модифікації та початкової концентрації розчину KMnO$_4$.

Розраховано рівняння регресії, які адекватно описують експериментальні дані і можуть бути використані в якості математичної моделі процесу окиснення активованого вугілля. Методом багатокритеріальної оптимізації умов процесу визначено компромісні області проведення окиснення вугілля. З використанням повного факторного експерименту було встановлено оптимальні умови обробки вугілля, які відповідали тривалості 55 хвилин та концентрації розчину перманганату калію 0,2 мг-екв/дм^3.

В результаті процесу делігніфікації стебел міскантусу в системі оцтова кислота - пероксид водню - лимонна кислота було отримано окисно-органосольвентну целюлозу з виходом – 62,4 % та вмістом залишкового лігніну – 1,84 % від маси абс. сух. сировини та високими показниками міцності. В подальшому отримана целюлоза використовувалася в якості основи водоочисних мембран.

Показано вплив використання адсорбуючого матеріалу на селективність і продуктивність целюлозного фільтрувального матеріалу. Додавання вугільного адсорбенту збільшує продуктивність мембран. Визначено, що мембрани виготовлені з модифікованого целюлозного волокна з міскантусу, що містять в своєму складі адсорбуючі матеріали придатні для використання у процесах ультрафільтрації.

Ключові слова: модифікація; активоване вугілля; целюлоза; міскантус; продуктивність; селективність; фільтрувальний матеріал

Trembus I., Haponiuk A.
ASSESSMENT OF THE EFFICIENCY OF CELLULOSE MEMBRANES WITH CARBON ADSORBENT APPLICATION

The article focuses on the production of a filtration material from oxidative-organosolv cellulose derived from miscanthus, utilizing a carbon adsorbent for water purification from suspended particles causing turbidity. A methodology for modifying activated carbon with a potassium permanganate solution was proposed. Studies were conducted on the oxidation of carbon with KMnO$_4$ solutions at concentrations ranging from 0.015 to 0.035 meq/dm^3, with durations between 15 and 135 minutes. Experimental results established that the deposition degree of MnO$_2$ on

activated carbon ranges from 13 % to 30 %, depending on the modification duration and the initial KMnO₄ solution concentration.

Regression equations were calculated, which adequately describe the experimental data and can be used as a mathematical model for the process of activated carbon oxidation. Using multicriteria optimization, compromise regions for conducting the carbon oxidation process were determined. A full factorial experiment established the optimal conditions for carbon treatment, corresponding to a duration of 55 minutes and a potassium permanganate solution concentration of 0.2 meq/dm³.

As a result of the delignification process of miscanthus stems in the acetic acid–hydrogen peroxide–citric acid system, oxidative-organosolv cellulose was obtained with a yield of 62.4 % and a residual lignin content of 1.84 % based on the absolute dry weight of the raw material, along with high strength characteristics. The cellulose obtained was subsequently used as a base material for water purification membranes.

The impact of using adsorptive material on the selectivity and productivity of cellulose filtration material was demonstrated. The addition of carbon adsorbent increases the productivity of membranes. It was determined that membranes made from modified cellulose fibers derived from miscanthus, containing adsorptive materials, are suitable for use in ultrafiltration processes.

Keywords: modification; activated carbon; cellulose; miscanthus; productivity; selectivity; filtration material