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APPLICATION OF POLYVINYL ALCOHOL TO IMPROVE THE FILTRATION PROPERTIES OF CELLULOSE MEMBRANES

Pollution of water resources by organic, biological, and inorganic substances is one of the most pressing environmental issues of today. Ultrafiltration membranes ensure the effective removal of viruses, bacteria, colloidal particles, and macromolecules, and play a key role in water purification technologies. However, the use of synthetic polymeric materials in membrane production poses a disposal problem due to their non-biodegradable nature.

This study investigates the potential use of a cellulose-based filtration material derived from annual plants, specifically Miscanthus giganteus stems. The cellulose was obtained via an oxidative organosolv delignification method using hydrogen peroxide and glacial acetic acid. An environmentally friendly reagent citric acid was employed as a catalyst. Prior to membrane formation, the cellulose fibers were treated with an amination mixture containing epichlorohydrin and triethanolamine in a 1:1 ratio. Various amounts of polyvinyl alcohol, ranging from 10% to 40% by the weight of absolutely dry fiber, were added to the cellulose pulp, which enabled the formation of a stable hydrophilic matrix with enhanced mechanical properties. The study examines the effect of polyvinyl alcohol content on the physicomechanical characteristics of the membranes, such as bursting resistance, breaking force, and wet strength. Optimization of technological parameters was carried out based on a full factorial experimental design.

The research results showed that the optimal polyvinyl alcohol content is 20% of the absolutely dry fiber weight, which ensures a balance between coloration selectivity and productivity filtration process. Thus, the use of polyvinyl alcohol for the modification of cellulose membranes derived from organosolv miscanthus cellulose contributes to enhancing their efficiency and environmental sustainability in water treatment technologies.

Keywords: polyvinyl alcohol, organosolvent cellulose, fiber modification, mechanical properties, selectivity, productivity

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ВИКОРИСТАННЯ ПОЛІВІНІЛОВОГО СПИРТУ ДЛЯ ПОКРАЩЕННЯ ФІЛЬТРУВАЛЬНИХ ВЛАСТИВОСТЕЙ ЦЕЛЮЛОЗНИХ МЕМБРАН

Забруднення водних ресурсів органічними, біологічними та неорганічними речовинами є однією з найбільш актуальних екологічних проблем сучасності. Ультрафільтраційні мембрани забезпечують ефективне видалення вірусів, бактерій, колоїдних частинок та макромолекул та відіграють важливу роль у технологіях очищення води. Проте використання синтетичних полімерних матеріалів у виробництві мембран створює проблему їх утилізації у звязку з нездатністю до біорозкладності.

У даній роботі досліджено можливість використання целюлозного фільтрувального матеріалу, отриманого з однорічних рослин, а саме стебел міскантусу. Целюлозу було отримано окисно-органосольвентним способом делігніфікації, з використанням пероксиду водню та льодяної оцтової кислоти. В якості каталізатора використано екологічно безпечний реагент, а саме лимону кислоту. Попередньо целюлозні волокна було оброблено амінуючою сумішшю, яка містить епіхлоргідрин та триетаноламін у їх співвідношенні 1:1. В целюлозну масу додавали різні витрати полівінілового спирту від 10% до 40% від маси абсолютно сухого волокна, що забезпечує утворення стабільної гідрофільної матриці з високими механічними показниками. У роботі розглянуто вплив витрати полівінілового спирту на фізико-механічні характеристики мембран, такі як опір продавлюванню, руйнівне зусилля та вологоміцність. Проведено оптимізацію технологічних параметрів на основі повного факторного експерименту.

Результати досліджень показали, що оптимальна витрата полівінілового спирту становить 20 % від маси абсолютно сухого волокна, що забезпечує баланс між селективністю по кольоровості та продуктивністю процесу фільтрації. Таким чином, використання полівінілового спирту для модифікації целюлозних мембран отриманих з органосольвентної целюлози з міскантусу сприяє підвищенню їхньої ефективності та екологічності у водоочисних технологіях.

Ключові слова: полівініловий спирт, органосольвентна целюлоза, модифікація волокна, механічні показники, селективність, продуктивність

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Formulation of the problem

Pollution of freshwater by organic, biological, and inorganic substances is among the most critical environmental challenges of the 21st century [1–2]. Ultrafiltration membranes play a key role in modern water treatment technologies, ensuring the effective removal of viruses, bacteria, colloidal particles, and macromolecules [2–4]. However, the majority of membranes are produced from synthetic polymeric materials, which, although resistant to physicochemical degradation, are non-biodegradable in the natural environment. This contributes to the accumulation of plastic waste and intensifies its negative impact on ecosystems [4].

This necessitates the development of filtration materials based on environmentally friendly and biodegradable substances. Cellulose is the most abundant natural polymer and possesses several advantages, including high strength, thermal stability, hydrophilicity, and biodegradability. Particular attention is given to cellulose derived from annual plants (such as straw, flax, corn, and miscanthus), which represents a low-cost, annually renewable, and widely available raw material that promotes the advancement of resource-efficient technologies [5–10].

Analysis of recent sources

Recent studies have demonstrated that cellulose-based materials can be effectively used in the fabrication of filtration membranes with enhanced mechanical and sorption properties [5, 8, 11-12]. Additional functionality of such systems is provided by polyvinyl alcohol (PVA) a hydrophilic synthetic polymer that is biocompatible, non-toxic, and biodegradable, with its structural formula shown in Fig. 1. PVA is a water-soluble polymer with pronounced hydrophilic and film-forming properties, attributed to the presence of hydroxyl groups and C–C bonds in its macromolecular chain [13].

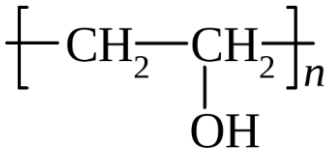

Fig.1. Structural formula of polyvinyl alcohol [13]

Composites based on PVA and cellulose exhibit improved stability and form a homogeneous structure, while maintaining high permeability and selectivity of the filtration material [14-19].

Thus, the development of ultrafiltration membranes based on cellulose derived from annual plants and polyvinyl alcohol represents a promising research direction that combines purification efficiency with environmental safety.

Formulation of the article's goals

The aim of this study is to investigate the effect of polyvinyl alcohol content on the physicomechanical and filtration properties of a modified cellulose membrane fabricated from organosolv miscanthus-derived cellulose.

Presenting main material

Oxidative organosolv cellulose derived from miscanthus was used in this study. It was obtained using acetic acid and hydrogen peroxide, with citric acid serving as a catalyst, which enabled the effective removal of lignin and hemicelluloses [20]. The cellulose was refined to a beating degree of 94 ± 2 °SR and modified with an amination mixture consisting of epichlorohydrin and triethanolamine in a 1:1 ratio. The dosage of the amination mixture was 40% relative to the absolutely dry fiber weight. The prepared fibrous pulp was thoroughly mixed with the amination mixture and placed in a TS-20 thermostat at 40 °C for 60 minutes. Stirring was performed every 10 minutes to ensure uniform distribution of the aminating agent throughout the cellulose mass.

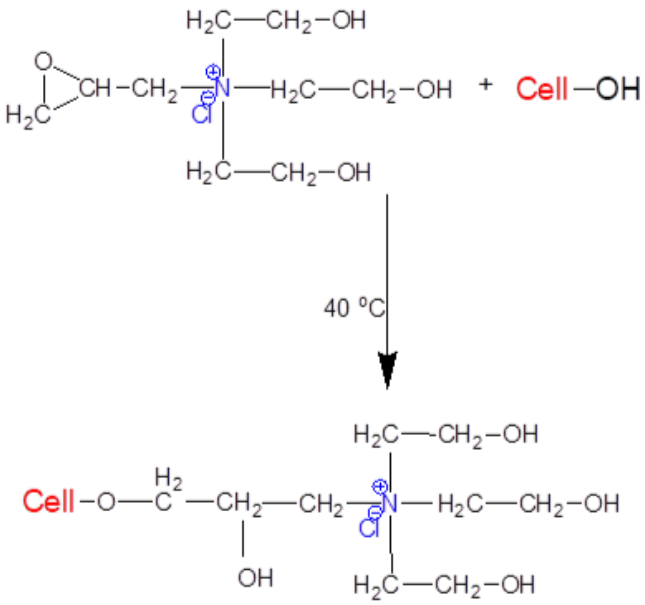

Fig.2. Reaction of cellulose with the aminating mixture

Following fiber modification, and prior to the fabrication of the filtration material using an LA-2 sheet-forming device, polyvinyl alcohol (PVA) was introduced into the fiber suspension at dosages ranging from 10% to 40% based on the oven-dry fiber weight. The mixture was homogenized through thorough agitation to ensure uniform incorporation of PVA within the cellulose fiber network.

The obtained samples of the filtration material were evaluated for mechanical strength and filtration performance using a non-flow (dead-end) filtration cell with a model solution of sodium humate at a concentration of 100 mg/dm³. The initial color intensity of the solution ranged from 1642 to 1688 degrees.

The results of the study on the physicomechanical properties of the filtration material are presented in Fig. 3.

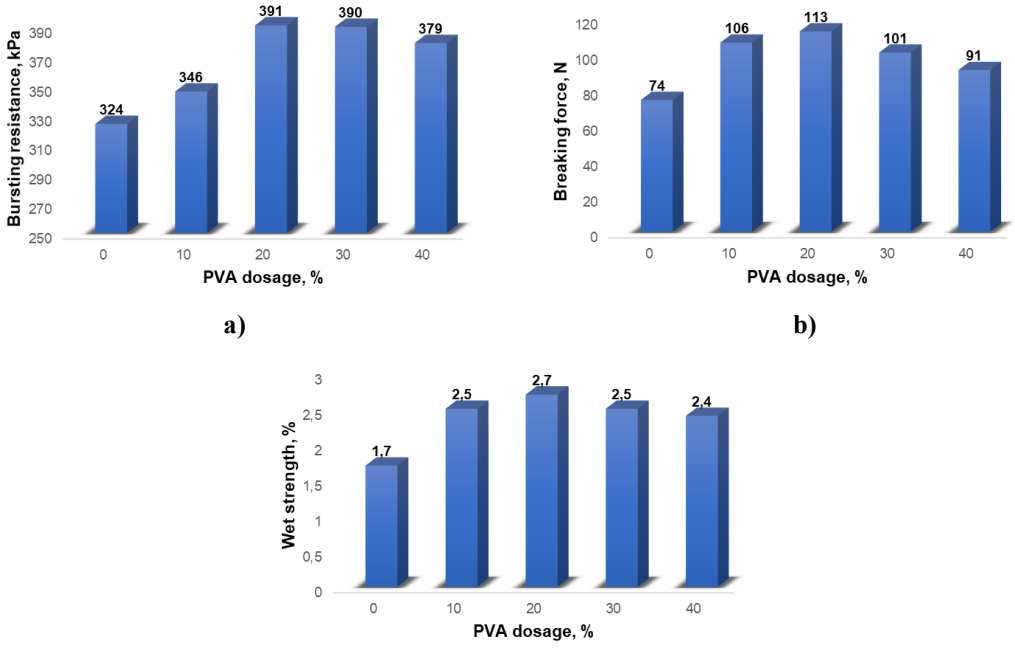

Fig.3. Effect of PVA dosage on the strength characteristics of the filtration material: a) – bursting resistance; b) – breaking force; c) – wet strength of the cellulose membrane

As shown in Fig. 3(a), increasing the PVA dosage in the material composition leads to a 17% increase in bursting resistance compared to the corresponding material without PVA. This effect can be attributed to the formation of additional bonds between PVA molecules and the modified cellulose fibers, which enhances the mechanical stability of the membrane.

An increase in PVA dosage also results in improved breaking force, as shown in Fig. 3(b). This can be attributed to the formation of a uniform matrix by PVA, which effectively binds the fibers and enhances their mechanical strength. A similar trend with increasing PVA content is observed for the wet strength of the cellulose material (Fig. 3(c)). This behavior can be explained by the hydrophilic nature of PVA, which promotes water retention within the membrane structure while simultaneously providing resistance to mechanical stress under wet conditions.

Based on the filtration of the model sodium humate solution through the cellulose membranes, the color selectivity and membrane productivity were determined (Fig. 4).

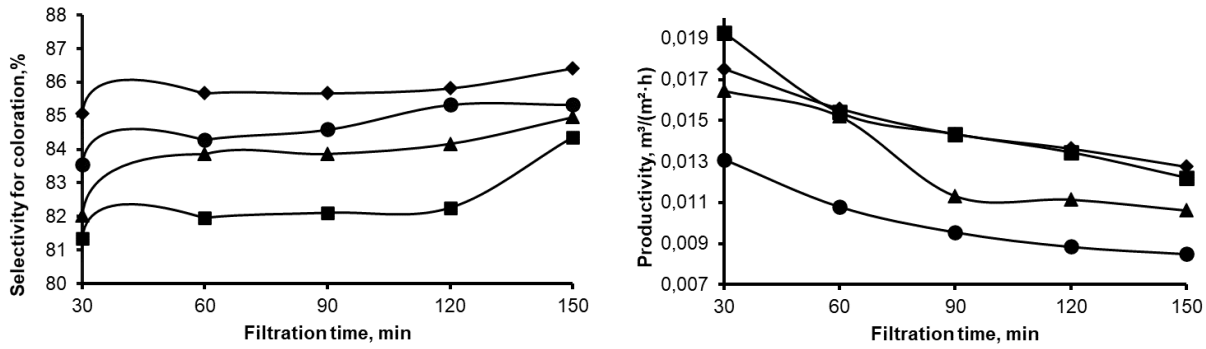

Fig.5. Effect of PVA dosage on a) selectivity for coloration; b) productivity of the filtration material: ■ – 10%, ♦ – 20%, ▲ – 30%, ● – 40%.

As shown in Fig. 4(a), increasing the PVA dosage up to 20% of the absolutely dry fiber weight leads to an increase in selectivity for coloration. This can be attributed to enhanced intermolecular interactions between the fibers and PVA molecules, resulting in a denser membrane structure that improves contaminant retention. However, a further increase in PVA dosage to 30–40% leads to a slight decrease in selectivity, which may be due to oversaturation of the fiber suspension with polymer. This, in turn, can result in the formation of an excessive polymer film on the membrane surface, thereby reducing its filtration performance.

Figure 4(b) illustrates that increasing the PVA content up to 20% results in a noticeable decrease in membrane flux. A further increase to 30-40% (based on oven-dry fiber weight) leads to a continued decline in performance, which can be attributed to the densification of the membrane matrix and a concomitant reduction in pore size, ultimately limiting the membrane's permeability.

To derive mathematical relationships between the quality indicators of the filtration process and the effect of PVA dosage on the properties of the filtration material, a full factorial experiment of the 2^2 type was conducted. The key technological parameters considered as independent variables influencing filtration performance were: PVA dosage, % (x_1), and filtration time, min (x_2). The following parameters were selected as optimization criteria: Y_1 – residual coloration of the permeate, degrees; Y_2 – volume of filtered permeate, mL.

Statistical processing of the experimental data resulted in the following regression equations, which adequately describe the dependence of the output variables on the selected technological factors:

- Mathematical model for the residual coloration of the permeate (degrees):

$$Y_1 = +250 - 10.74 \cdot x_1 - 16.55 \cdot x_2 + 0.87 \cdot x_1 \cdot x_2 + 26.212 \cdot x_1^2 - 0.42857 \cdot x_2^2$$

- Mathematical model for the volume of filtered permeate (mL):

$$Y_2 = +74.814 - 14.58 \cdot x_1 - 16.4 \cdot x_2 + 3.6 \cdot x_1 \cdot x_2 - 7.2 \cdot x_1^2 + 8.5714 \cdot x_2^2$$

The optimal point x_i (opt) corresponds to the factor levels at which the best values of Y_i are achieved. In natural units, the optimal values of the factors are: x_1 (PVA dosage) = 20%, x_2 (filtration time) = 120 minutes.

Analysis of the obtained regression equations indicates that the main process factors, x_1 and x_2, have negative linear coefficients. Therefore, increasing the PVA dosage (x_1) and the filtration time (x_2) leads to improvements in the specified permeate quality indicators. Moreover, filtration time (x_2) has a more significant impact on permeate quality than PVA dosage (x_1).

The permeate quality indicators calculated using the obtained regression equations at the optimum point are as follows: residual coloration Y_1 = 237.93 degrees; permeate volume Y_2 = 69.52 mL. The optimal values of color selectivity and permeate flux are achieved at a PVA dosage of 20% based on the absolutely dry fiber weight, which ensures both effective filtration performance and mechanical stability of the material.

Conclusions

The use of polyvinyl alcohol contributes to the improvement of the filtration properties of cellulose membranes derived from miscanthus-based cellulose. It was determined that the optimal PVA dosage is 20% of the absolutely dry fiber weight, which enhances the physicomechanical properties and improves the overall filtration performance.

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