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STUDY PROPERTIES OF POLYSULFONAMIDE MEMBRANE

In this work, the properties of the polysulfonamide membrane UPM-20 were studied for the purpose of further purification of contaminated water from suspended fine particles and dissolved impurities that cause turbidity and color of water. The influence of pressure from 1 to 5 atmospheres and filtration time from 20 to 100 minutes on specific productivity, selectivity and turbidity and color values of the permeate was shown. It was found that for all pressure values there are three periods in the filtration process of the model sodium humate solution: a sharp change, a slow decrease in parameters and no significant changes in permeate parameters. An increase in pressure and an increase in the duration of the sodium humate filtration leads to a decrease in the productivity index from 87 to $2.7 \text{ m}^2/(\text{m}^3 \cdot \text{h}) \cdot 10^2$. The selectivity of the membrane in terms of color and turbidity was calculated. It is shown that the highest selectivity for color is in the range of 95.2 to 96% for filtration at a pressure of 5 atmospheres and a duration of 80–100 minutes; respectively, for selectivity for turbidity, this indicator is 97.2 % for sodium humate filtration at a pressure of 5 atmospheres and a process duration of 90 minutes. A mathematical model of the filtration process of the model solution, sodium humate, was constructed using the Python programming language and the Matplotlib library for constructing mathematical dependencies. It was found that the purification of sodium humate on the UPM-20 membrane follows a non-linear dependence. Mathematical equations were obtained that adequately describe the dependence of the output variables on the selected technological factor of the filtration process. It is shown that these equations are in the form of a third-order polynomial, a cubic model, which can be used to describe the process of sodium humate filtration using the UPM-20 membrane at different pressures, from 1 to 5 atmospheres.

Key words: UPM-20 membrane, humate solution, filtration, specific productivity, selectivity, permeate, turbidity, color, mathematical model

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ДОСЛІДЖЕННЯ ВЛАСТИВОСТЕЙ ПОЛІСУЛЬФОНАМІДНОЇ МЕМБРАНИ

В роботі було проведено дослідження властивостей полісульфонамідної мембрани УПМ-20 з метою подальшого очищення забруднених вод від зважених дрібнодисперних частинок та розчинених домішок, що обумовлюють каламутність і кольоровість води. Показано вплив тиску від 1 до 5 атмосфер та тривалості процесу фільтрування від 20 до 100 хвилин на показники питомої продуктивності, селективності та значення каламутності і кольоровості перміату. Встановлено, що для всіх значень тиску притаманна наявність трьох періодів проходження процесу фільтрації модельного розчину гумату натрію: різка зміна, повільне зниження параметрів та без значних змін в показниках перміату. Зростання тиску і збільшення тривалості фільтрування гумату натрію призводить до зниження показника продуктивності від 87 до 2,7 м²/(м³·год)·10². Розраховано показники селективності мембрани за кольоровістю і каламутністю. Показано, що найбільша селективність за кольоровістю знаходиться в межах від 95,2 до 96 % для фільтрування за тиску 5 атмосфер, тривалістю 80–100 хвилин, відповідно для селективності за каламутністю даний показник для фільтрації гумату натрію становить 97,2 % за тиску 5 атмосфер, тривалості процесу 90 хвилин. Було побудовано математичну модель процесу фільтрування модельного розчину – гумату натрію за допомогою мови програмування Python і бібліотеки Matplotlib для побудови математичних залежностей. Встановлено, що очишення гумату натрію на мембрані УПМ-20 відбувається за нелінійною залежністю. Отримано математичні рівняння, що адекватно описують залежності вихідних змінних від обраного технологічного чинника процесу фільтрування. Показано, що ці рівняння мають вигляд полінома третього порядку, це кубічна модель, що може бути використана для опису процесу фільтрування гумату натрію з використанням мембрани УПМ-20 за різного тиску – від 1 до 5 атмосфер.

Ключові слова: мембрана УПМ-20, розчин гумату, фільтрація, питома продуктивність, селективність, перміат, каламутність, кольоровість, математична модель.

Formulation of the problem

More than 100 different materials for membrane production are known nowadays [1]. The main problem during purification with using membranes is to choose membrane which will be possible to work according tasks and conditions of separation method as much as possible. The progress of membrane separation usage is closely related to development various technologies which connected with production membranes with separate characteristics like porous structure and surface properties [2].

Analysis of recent research and publications

New technologies of formation porous polymer membranes make possible to create various specialized membranes thereby expanding and deepening fields of membrane technologies application [3, 4]. Polymer membranes have high chemical and thermal stability, low specific resistance and high mechanical properties [5, 6]. It is worth noting that issue of membrane formation is closely related to patterns and features mass transfer studies through porous polymer membranes surfaces. Polysulfones (PSF), polyethersulfones (PES), polysulfonamides (PSA) are very important polymers for membrane production (Fig. 1) [2]. It should be noted that they have high chemical and thermal stability at their glass transition temperature (PSF – T = 190 °C; PES – T = 230 °C, PSA – T = 288 °C) [3, 4]. Therefore, these polymers are widely used as basic materials for ultrafiltration membranes manufacture as well as substrates for composite membranes. So, aromatic polysulfone usage is promising field for functional polymers and membranes production based on them due to high film-forming properties [7].

Polysulfonamide membranes for ultrafiltration purification UPM-20 type have become widely used. Polysulfonamide (PSA) is type of aromatic co-polyamide and an organic high-temperature resistant material which have special molecular structure. PSA have excellent properties in terms of heat resistance, dimensional stability, high temperature resistance and fire resistance [8].

UPM-20 membranes consist of three different layers of polymeric materials namely aromatic polysulfone and thermoplastic materials which provide their strength and durability. Mixture of polyethylene terephthalate (PED) and polypropylene (PP) are polymeric thermoplastic materials which used for UPM-20 membrane production Fig. 2. [8]. Average pore size in UPM-20 membrane is 20 nm and thickness is 150 µm. These material is very strong and resistant to various types of contaminants and chemicals.



Fig. 2. UPM 20 polysulfonamide membrane model

Fillers and stabilizers can be used as additional substances for this type membrane production. Carbonate filler, namely calcium carbonate, is usually included in UPM-20 membranes. It gives mechanical strength and tear resistance for them [9].

Stabilizers are added to UPM-20 composition to ensure their resistance to ultraviolet radiation and other factors that can cause material destruction over time. In general, UPM-20 membranes are very effective materials for water purification due to their complex structure [10]. They are used in filter systems where water is passed through a membrane which ensures the screening of impurities.

UPM-20 can be used both for cleaning drinking water and for cleaning water from industrial and chemical pollution. The usage of UPM-20 membranes in filter systems make possible to effectively purify water from various types of pollutants, including bacteria, viruses, chemical compounds and other substances [11].

The purpose of the work was to evaluate cleaning properties of UPM-20 membrane at pressures from 1 to 5 atm using simulation of cleaning process on example model solution of sodium humate.

Presenting main material

The research of membrane samples was carried out on laboratory setup in non-flow installation (Fig. 3) at different pressure and during experiment each membrane was changed to new one for research reliability. Working surface of membrane is 11.3•10-3 m². The efficiency of purification through membrane was evaluated by values of permeate turbidity, color, residual turbidity, concentrate color, selectivity variable and specific productivity.



Fig. 3. Laboratory installation for studying operational membranes properties

The turbidity of original solution was 170 mg/dm³; chroma 1940 degrees. Filtration was carried out under pressure from 1 to 5 atm. Permeate was sampled at regular intervals every 10 min. Filtration continued until stabilization of monitored parameters, namely the volume and specific productivity (transmembrane flow rate) γ , which was determined by formula, m³/(m²-hour):

$$Y = \frac{\Delta V}{S\Delta t} \tag{1}$$

where ΔV – permeate volume, m³;

S – filtering area, m²;

 Δt – filtering time, hours.

Residual color and turbidity determination of permeate was carried out on KFK-2 calorimeter. Turbidity was determined at wavelength at 670 nm, chroma at 400 nm. The obtained values of optical density were translated into chroma and turbidity units using graduation graphs method.

The selectivity φ according to turbidity (color) of UPM-20 membrane was determined by formula, %:

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

where C_1 , C_2 – turbidity (color) of the original solution and permeate, mg/dm³ (degree).

The mathematical model construction of filtering process was carried out using Python programming language using the sklearn library for calculation and Matplotlib for constructing relevant dependencies [12–15].

As a result of the research (Fig. 4) it can be seen that each pressure value is characterized by presence of three periods of filtration process. The first period is characterized by sharp change, the second one by slower decrease in membrane parameters. As for the third period, it is characterized by almost constant process without significant changes in permeate parameters. The sharpest decrease is observed in the first 20 minutes in permeate characteristics for all pressures. During this period the material structure is maximally compacted and pores in membrane are clogged under the action of pressure.

The filtration process have stabilized after 80 minutes which can be observed from membrane performance values. Sharp drop in this indicator which happened at the beginning of the process indicates that membrane structure is compacted under pressure, porosity of sample decreases, pores in membrane become clogged and productivity decreases accordingly. It can also be assumed that pressure increasing contributes to increasing content of bound water in pores which in such conditions has higher viscosity. This also leads to decreasing in permeability in membrane material.

Membrane selectivity is important aspect during investigating membrane filtering capabilities in terms to color and turbidity. The residual color and turbidity changes of permeate is shown in Fig. 5.

The lowest residual color of permeate for UPM-20 membrane is observed in pressure of 5 atm. Permeate color remains almost unchanged after entering constant filtration mode for all investigated pressures. Pressure and duration increasing during filtration process leads to decreasing in turbidity of permeate.



Fig. 4. Dependence of specific productivity on filtration duration of concentrate at different pressures

Pressure increasing leads to selectivity increases both in terms to color and turbidity (Fig. 6. (a) and (b)).



Fig. 5. Permeate color (a) and turbidity (b) dependence on filtration duration at different pressures

The best results of selectivity in terms to color were obtained for pressure 5 atm and was equal to values in range from 95.2 to 96% (filtration duration from 80 to 100 minutes). Selectivity in terms to turbidity has the highest indicators for sodium humate filtration at pressure 5 atm with duration 90 minutes and has value 97.2%.

Sampling every 10 minutes and permeate turbidity are important parameters for evaluating effectiveness of filtering process and for these parameters mathematical models were built (Fig. 7).

The dependence of experimental studies data and prediction values of mathematical model which were built using linear regression method were shown in Fig. 7 [16]. Humate purification on membrane occurs according to non-linear dependence. Non-linear equations were constructed for each studied parameter at different pressures (x – filtration duration, min.; Y1 – filtration volume, ml; Y2 – turbidity ml/l; R² – approximation reliability) to confirm this model.



Fig. 6. Selectivity dependence in terms to color (a) and turbidity (b) of permeate on filtration duration at different pressures

Mathematical model of sodium humate filtration process:

$$Y(x) = a_0 + a_1 x + a_2 x^2 + a_3 x^3$$
(3)

This is curve equation of third degree or which has third degree polynomial form with respect to variable Y. This is typical cubic model example that can be used to describe sodium humate filtering process through UPM-20 membrane at pressure from 1 to 5 atm.

As a result of experimental data mathematical processing equations that describe dependence of output variables on selected technological filtering process factor were obtained:

a) Mathematical model based on volume indicator for filtering at 1 atm.

 $Y_1 = 61.583 - 1.219x + 0.0199x^2 - 0.000106x^3$ (R₂ = 0.9299)

Mathematical model based on the turbidity index for filtering at 1 atm.

$$Y_2 = 16.983 - 0.576x + 0.00955x^2 - 4.924 \cdot 10^{-5}x^3$$
 (R₂ = 0.9572)

b) Mathematical model based on volume indicator for filtering at 3 atm.

 $Y_1 = 168.952 - 3.371x + 0.0366x^2 - 0.000139x^3 (R_2 = 0.9758)$

Mathematical model based on the turbidity index for filtering at 3 atm.

 $Y_2 = 16.556 - 0.216x + 0.000985x^2 + 1.684 \cdot 10^{-6}x^3 (R_2 = 0.9567)$

c) Mathematical model based on volume indicator for filtering at 5 atm

$$Y_1 = 184.0476 - 3.833x + 0.0339x^2 - 9.596 \cdot 10^{-5}x^3$$
 (R₂ = 0.9852)

Mathematical model based on the turbidity index for filtering at 5 atm.

 $Y_2 = 15.212 - 0.405x + 0.00666x^2 - 3.636 \cdot 10^{-5}x^3$ (R₂ = 0.9933)

It can be concluded that in case of pressure increasing the volume at the initial point of filtration namely in first 10 minunes the biggest. This indicates that UPM-20 membrane pores are not blocked at the beginning of humate purification process. The coefficient α_1 decreases in case of bigger pressure value which indicates decreasing in permeate volume during further filtering due to clogging pores in UPM-20 membrane with pollutants from concentrate. Filtering process continues with non-linear dependence, so pores in UPM-20 membrane become clogged with increasing filtration duration.

Similar dependence is observed during permeate turbidity index determining. Value of coefficient a_0 shows that pressure increasing in filtration process has slight effect on permeate turbidity value. Coefficient a_1 for 5 atm. has smaller value than at 1 and 3 atm which indicates filtering efficiency at high pressures and at the same time coefficients a_2 and a_3 have low values due to nonlinear dependence presence only at the beginning of sodium humate purification process.



Fig. 7. Dependence of permeate volume (a) and turbidity (b) on duration filtering at different pressures: 1-1 atm; 2-3 atm; 3-5 atm

Conclusions

Conducted studies of filtering properties polysulfonamide membrane UPM-20 using model solution of sodium humate showed that membrane performance decreases with increasing process pressure and duration. Membrane selectivity increases to 96.0 and 97.2% respectively in terms of permeate color and turbidity. The efficiency of removing contaminants through membrane stay better with pressure increasing but at the same time with decreasing in membrane performance.

The construction of mathematical model of filtration process was carried out. A nonlinear dependence of filtration process was obtained. Results indicates that effectiveness UPM-20 membrane under stable conditions, constant pressure have high degree of permeate purification.

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