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Application of Me-PAN nanocomposite membrane in two-stage ultrafiltration of industrial wastewater

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Membrane technologies and processes present a viable technological solution to address modern industrial and ecological challenges related to water resources. In this, the potential application of polyacrylonitrile (PAN) membranes and PAN membranes modified with a surface-deposited Fe-Cr-Ni nano layer (Me) was explored in the ultrafiltration process. These membranes were tested individually and in combination for the purification of industrial wastewater resulting from the hydrodistillation of oil-bearing roses, which contained 15.80 mgEm$KMnO_4$/ml of total organics. The transport and separation characteristics of the membranes were analyzed based on pressure changes and their structural morphology response. The permeability values ranged from 19 l/m^2.h for the unmodified membrane to only 3.7 l/m^2.h for the metallized membrane. The process was optimized using a combined approach, where ultrafiltration was conducted sequentially and continuously in two stages: 1. Ultrafiltration through a PAN membrane to obtain permeate (P1); 2. Ultrafiltration of P1 using the Me-PAN membrane to obtain permeate (P2). It was found that in the two-stage ultrafiltration process, the permeability remained the same for the first stage, but increased to 13 l/m^2.h at 0.5 MPa for the second stage. The total organics content in P2 was reduced to 1.74 mgEm$KMnO_4$/ml, resulting in a 89% rejection and purification of the wastewater. This not only rehabilitated the treated wastewater but also provided an opportunity for the targeted utilization of the separated unique and valuable bio-resources present in the wastewater from the oil-bearing roses processing.

Keywords: Ultrafiltration, metal nano layer coating, nanometalized polymer membrane, nanocomposite membrane, industrial wastewater treatment, recovery of bio-resources

INTRODUCTION

Membrane separation technology and its capabilities have been implemented in industry on the largest scale through the baromembrane processes of microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). This is due to their simplicity and accessibility, capital profitability, ease of maintenance and control, technological and ecological efficiency, and the possibility to use them in hybrid processes. Pressure-driven membrane processes are implemented for separation, purification, concentration, and disinfection of liquid systems of various natures and origins, and also provide an opportunity for the rehabilitation of substances and resources. The areas of application of these processes are related to potable and wastewater treatment in pharmaceutical, biotechnological, food-processing industries, as well as in processes of renewable energy storage and conversion [1]. What is common to the baromembrane processes in addition to the driving force is the semipermeable membrane, which, apart from being a key element, is also a specific selective barrier. Conventional membranes used in these processes are synthetic, preferably made of polymer materials. Each of the processes has its specific requirements towards the membrane properties, which are permeability and rejection [2]. As technological challenges to ensure quality water resources increase, so does the demand for and exploitation of UF processes and membranes [3]. PAN membranes have proven their effectiveness in ultrafiltration process. Moreover, they are also an object that allows for manipulation of their properties by means of various modification techniques. Using such an opportunity, selective structural control of the membranes is purposefully achieved, with a significant effect on their performance [4-6]. An innovative approach to PAN-membranes modification is the fixation of a metal coating on the active membrane surface. Various methods of metal coating deposition can be used, the choice depending on the properties of the host polymer matrix, the type of metal, the preliminary modification of the polymer surface, the mechanism

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and conditions of applying the coating [7, 8]. Surface morphology of the PAN membrane can be easily controlled by the use of vacuum metallization [9]. The process consists of magnetron sputtering of a metal (or metals) in a vacuum environment with subsequent mechanical deposition on the chemically activated polymer surface of the membrane. Metallized membranes are a promising option for achieving sustainability in water systems treatment [10, 11]. Applied alone or in combination with other types of membranes, they can increase the efficiency of membrane technologies [12]. The aim of the present work is to conduct a laboratory study of the application of polyacrylonitrile and surface metallized polyacrylonitrile membranes in an ultrafiltration process for treating industrial wastewater–obtained as a result of oil-bearing rose hydrodistillation.

Studying the process of ultrafiltration, which uses membranes with different properties, will clarify their application potential for the purification of bio-contaminated industrial wastewater and recovery of bio-resources, as well as the peculiarities in the particular membrane behavior and the adaptation of the process conditions to the object under treatment [13, 14]. The development and introduction of sustainable technologies will allow the industry to become more environmentally friendly by facilitating waste materials recycling and utilization of resources [3, 15].

EXPERIMENTAL

The PAN membrane used in the experiment had a molecular weight cut-off (MWCO) of 25 kDa and was formed from a polyacrylonitrile solution in dimethyl sulfoxide (DMSO) solvent, a product of Fluka, Germany. After filtration and deaeration, a film was drawn from the polymer solution onto a calendered polyester substrate attached to a glass plate. The polyester mat brand FO-2403, produced by Velidon Filtren, Germany, has a density of 100 ± 5 g/m^2 and a thickness of 2 ± 0.1 nm. Within 15 sec of pouring the solution, the plate was immersed in a lab bath of distilled water at a temperature of 25 ± 1°C. Through the method of phase inversion in a water coagulation bath non-solvent induced phase separation (NIPS), an asymmetric membrane structure was formed, which was then thoroughly washed with water until the solvent was completely removed.

Pieces of the membrane with an area of 100 cm^2 were prepared for modification by depositing a metallizing layer after preliminary activation of the membrane surface with alkaline solutions of $SnCl_2.2H_2O$. The metal coatings were obtained in a vacuum installation BUP-5 (Russia), by sputtering a flat target made of iron-chromium-nickel alloy with dimensions ø 100 × 10 mm, at a target (M)/substrate (N) distance L_{M-N} = 180 mm and specific sputtering power Np = 5.4 W/cm^2. Magnetron deposition of the iron-chromium-nickel alloy was carried out with an initial vacuum in the working chamber Pn= 1.10^{-3} Pa, Ar working gas medium of 99.99 % purity, working pressure in the chamber Pp = 4.10^{-2} Pa and coating deposition time (exposure time) of 25 s. After the deposition process was completed, the membranes were cooled to normal temperature.

The efficiency of the membranes and membrane processes was studied based on the parameters of rejection and permeability. Rejection is expressed as a retention parameter and characterizes the separation ability. Permeability is characterized by a parameter called flux through the membrane. The values were calculated by the following equations:

- *Rejection*:

$$R = \frac{C_2 - C_1}{C_2} . 100, \ \% \tag{1}$$

where C_2 – concentration of the retained substance in the flow over the membrane, kg/m^3; C_1- concentration of the same substance in the flow through the membrane kg/m^3;

- *Permeability*:

$$\mathrm{J} = \mathrm{V}/(S.\tau), \mathrm{l/m^2.h} \tag{2}$$

where V – volume of the liquid which passed through the membrane, l; S – membrane effective area, m^2; τ – time, h.

The membrane-treated object was industrial wastewater, a by-product of hydrodistillation of oil-bearing rose flowers in Bulgarian rose oil production, provided by the Institute of Roses, Essential and Medical Cultures (EMLK), Kazanlak. The quantitative content of total organic matter in the hydrodistilled wastewater and in the permeate (filtrate) was determined by the method of permanganate oxidizability and presented as a potassium permanganate equivalent (mgEm $KMnO_4$) [16].

RESULTS AND DISCUSSION

UF PAN membranes are formed and used as polymer composites. The membrane structure is supported by a polymer substrate made of various types of polymers. A composite asymmetric structure is created (Fig. 1), in which the supporting porous polymer aids in to the mechanical stability when external pressure is applied to achieve an ultrafiltration process.

The membrane is then further modified as a metal-polymer nanocomposite, also incorporating a functional metal layer of chromium-nickel alloy

[17]. Consequently, the modified membrane gains new properties.

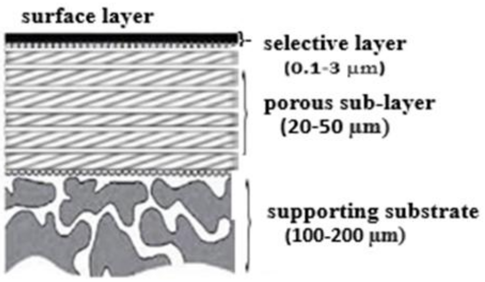

Fig. 1. Schematic diagram of an asymmetric composite membrane in-depth

The membrane metalized in the experiment for 25 min, and the non-modified one were individually used in a membrane process, carried out in a laboratory research barofiltration installation. The filtration focused on bio-contaminated wastewater from the rose flowers of the *Rosa damascena* Mill. f. trigintipetala Dieck (R.D.) variety, with a total organic content of 15.80 mgEm $KMnO_4$/ml. The permeability results, as shown in Figure 2, pertain to the wastewater and illustrate the minimal effectiveness of the modified membrane in this particular approach.

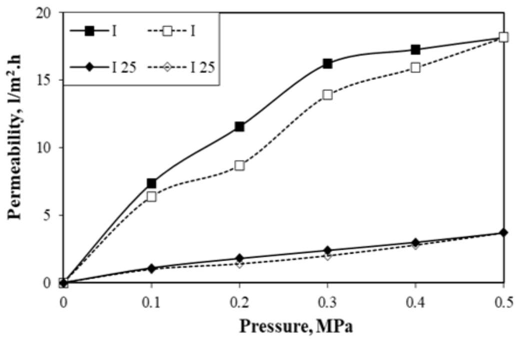

Fig. 2. Hysteresis curves of permeability for a PAN membrane and a metallized membrane for 25 min

The permeability of the two types of membranes differs not only in the range, with the non-modified membrane reaching up to 19 $l/m^2.h$ and the metallized one only reaching 3.7 $l/m^2.h$, but also in the response of the structural morphology to pressure changes. This difference is due to the unique characteristics of the selective layer of the metallized membrane, which consists of many small and similarly sized pore openings. This is supported by AFM visualization [17] and the minimal change in permeability values with increasing force impact from applied pressure (Fig. 2). The expectation that smaller sized pores would be included in the process with each 0.1 MPa step is not confirmed. Despite the extended metallization time, the mechanical stability of the membrane was maintained in the processing of a real object. We can assess this by visually comparing the shape and size of the hysteresis areas (Fig. 2), which provide an indication of the material's mechanical behavior under cyclic loading [18]. An explanation for the unsatisfactory results is that during ultrafiltration, the solvent passes preferentially through the membrane, causing an increase in viscosity of the retentate and pre-concentration of dissolved substances in the boundary layer of the membrane. Consequently, the driving force and process speed decrease, which is a prerequisite to the formation of aggregates in the retentate and eventually their precipitation on the membrane surface, reducing its effective area [19]. For the process to function properly, it is necessary to optimize the correlation between membrane properties and fluid concentration.

Based on the results obtained, a combined treatment approach was implemented for wastewater to enhance the efficiency of the ultrafiltration process and explore the potential of the metal-polymer membrane. The process involved two stages. The first stage included ultrafiltration of the wastewater through the PAN-membrane. The second stage involved subjecting the permeate from the first stage (P1) to ultrafiltration through the metal-polymer membrane to obtain the final permeate (P2) for the two-stage process. It was observed that the permeability of the metallized membrane to P1 differed when compared to direct filtration of wastewater through the same membrane (Fig. 2).

The graphical representation in Figure 3 illustrates the permeability change in the two-stage process. Permeability values are expected to increase with increasing pressure. During the first stage, when the PAN-membrane is used, the permeability values remain the same. However, when the metallized membrane is used, the permeability values increase from 3.7 $l/m^2.h$ for normal ultrafiltration to 13 $l/m^2.h$ for the two-stage ultrafiltration at 0.5 MPa.

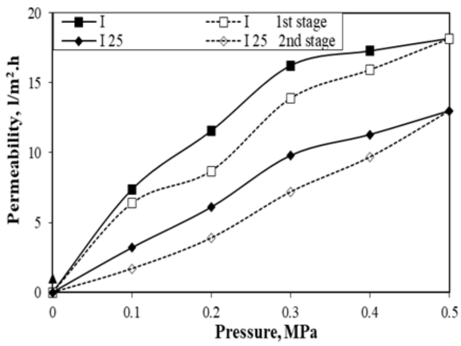

Fig. 3. Hysteresis curves of the PAN membrane permeability relative to wastewater for the 1[st] stage and of the Me-PAN membrane relative to permeate P1 for the 2[nd] stage of a two-stage ultrafiltration process.

In the first stage, the PAN-membrane shows the same rejection rate as in individual ultrafiltration (Table 1) and releases wastewater with a decrease to 8.85 mgEm $KMnO_4$/ml of total organics.

The lower concentration of organic matter in P1 compared to the initial concentration is the reason for the facilitation of the flow passage. This assumption is based on the specific processes occurring on the surface of a metal-polymer membrane during its individual use.

Table 1. Rejection of the two-stage ultrafiltration process relative to the total organics (mgEm $KMnO_4$/ml) when treating wastewater from *Rosa Damascena* hydro-distillation

Membrane	Stage *R*, %	Final *R*, %
I	56	89
I25	75	

As a result, the permeability of the metal-polymer membrane to P1 significantly increases at all pressure levels (as shown in Fig. 3) with a rejection rate of 75%. The total organics content in the final filtrate P2 after the two-stage ultrafiltration treatment is only 1.74 mgEm $KMnO_4$/ml, and the total rejection achieved is 89%.

CONCLUSIONS

The potential of applying both a PAN membrane and a surface-modified Me-PAN membrane in an ultrafiltration process for the purification of industrial wastewater from oil-bearing rose hydrodistillation was investigated.

The performance characteristics of the membranes were determined, showing that when used sequentially in a two-stage ultrafiltration process and depending on the operating conditions, the permeability of the Me-PAN membrane increased from 3.7 l/m^2.h to 13 l/m^2.h.

It was demonstrated that more effective purification of industrial wastewater is achieved in the two-stage ultrafiltration process with the retention of bioorganic substances up to 89%. The total organic substance content in the purified water decreases from 15.80 mgEm $KMnO_4$/ml to 1.74 mgEm $KMnO_4$/ml, providing an opportunity for their valorization through the resulting retentate.

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