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MEMBRANE TREATMENT OF WASTE WATER FROM THE HYDRODISTILLATION OF OIL-BEARING ROSES

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ABSTRACT

Bulgarian rose oil is world famous for its high quality. Obtaining it makes the cultivation and processing of oil-bearing rose crops an important agricultural branch. There are more than 200 species of roses in the world, and in Bulgaria the species with the greatest agricultural importance are *Rosa damascena* Mill. f. trigintipetala Dieck. and *Rosa alba* L. Their qualitative composition is relatively constant and includes, in addition to essential oil, a variety of polyphenols, vitamins, and minerals. Products from the processing of the rose flower are: rose oil, rose absolute, rose concrete, rose water and others from secondary processing. Hydrodistillation is the technological method for obtaining rose oil, but it generated huge amount of biocontaminated wastewater. The retention of the organic components will satisfy the ecological criteria for the purity of wastewater and will create an opportunity for full-fledged use of their bioactive properties. The developed conventional methods are not sufficiently precise, cost-effective and environmentally friendly. Membrane technology and ultrafiltration processes have proven their technological and economic efficiency for purification, separation, concentration and decontamination of various liquid products. The aim of the study is to investigate the possibility of applying composite polyacrylonitrile membranes for the purification of wastewater from the hydrodistillation of oil rose flower and separated into the waste components. The membranes used were found to remove more than 60% of total organics and separate more than 70% of polyphenolic compounds.

Keywords: *Roses, Waste waters, Polyphenols content, Membrane filtration, Ultrafiltration.*

INTRODUCTION

Membrane technology includes processes that differ in purpose, driving force, equipment, etc. The common element for these processes is the semipermeable barrier or the membrane. Key to membrane technology are baromembrane processes - microfiltration, ultrafiltration, nanofiltration, reverse osmosis, in which the driving force is the difference in pressure before and after the membrane

(Mulder, 1991; Baker, 2004; Othman *et al*., 2022). Each of these processes has specific selective capabilities and a range of applied pressures and requires suitable membranes. Polymer membranes are the conventional choice. A classic method of obtaining them is non-solvent induced phase separation (NIPS) (Dong *et al*., 2021; Irfan *et al*., 2017). The physicochemical stability of polyacrylonitrile (PAN) makes it preferred for forming ultrafiltration (UF) membranes (Irshad and Zhiping, 2023; Yang *et al*., 2023). UF membranes used in different industrial applications and water treatment processes (Shoshaa *et al*., 2023; Aani *et al*., 2020). The provision of water resources suitable for drinking, domestic and industrial needs and satisfying the legal requirements for the quality of waste water are the driving force for the search for effective technical, economic and ecological solutions. In this regard, baromembrane processes and, in particular, ultrafiltration are an opportunity to restore the quality of waste water from various production activities. Waste water from the processing of plant crops has a predominantly organic composition, which in most cases significantly exceeds the legally defined norms. According to their qualities, they are able to change the organoleptic properties of water and even make it toxic. Released untreated into bodies of water can lead to oxygen depletion, causing eutrophication of water bodies, and colored and cloudy ones affect photosynthesis. Used for irrigation and fertigation, waste water can have adverse effects on the life activity of various organisms and soil qualities, and if applied for long period, can also affect groundwater qualities (Ramos *et al*., 2023). The oil-bearing rose is an industrial crop, the flower of which is mainly processed by hydrodistillation. The process generates liquid waste in huge amount of, which is waste waters with a rich and diverse content of polyphenols, minerals, essential oil components (Ilieva *et al*., 2022; Dobreva *et al*., 2013; Erdal and Munduz, 2017; Todorova *et al*., 2022). The aim of the study is to investigate the possibility of applying composite polyacrylonitrile membranes for the purification of wastewaters after extracting of rose oil and separated into the waste components. A large part of the pollutants in this residues are suitable for treatment, through processes of chemical and biological oxidation and various physicochemical methods (Eliane *et al*., 2014; Raks *et al*., 2018; Avsar *et al*., 2007). Membrane processes offer quality treatment of waste water from the processing of various plants, but under significantly more favorable conditions (Pérez *et al*., 2022; Ezugbe *et al*., 2020; Othman and Rathilal, 2022).

MATERIALS AND METHODS

The raw material was fresh rose flowers from *R.damascena* Mill. and *R.alba* L., grown in the experimental field of the Institute for Roses and Aromatic Plants (IRAP), Kazanlak, Bulgaria. The plantations are part of the collection of oil-bearing roses, grown according to the established technology of the institute. The liquid wastes were collected after distillation of the available semi-industrial processing line to obtain essential oil during the harvest season of 2022. A flat composite membrane with a molecular weight cut-off of 15 kDa was formed by the phase inversion method from a homogeneous 17 wt% PAN solution. It is obtained from fibers of the ternary copolymer poly(acrylonitrile–methylacrylate–2-acryloamide–2-methylpropanesulphonic acid) produced by LUKOIL Neftochim Burgas Co., Bulgaria. The polymer solution was cast on a calandered polyester matt brand FO-2403 from Velidon Filter (Germany) attached on a glass plate, after that was placed in a bath of distilled water to carry out the process of phase inversion. The formed membrane was washed intensively with water and subjected to thermal fixation at T=60°C in distilled water. Tests with the membrane were carried out with a laboratory cell SM 165-26 ("Sartorius", England). The object of the filtration are two types of waste water from the distillation respectively from the genotypes of damask (*R.D.*) and white (*R.A.*) roses, described above. The waters are stored at T= -20°C and pre-filtered through standard filter paper. The permeability (J, l/m^2.h) and rejection (R, %) of the PAN membrane was determined at pressures in the range 0.1 - 0.5 MPa. The values are calculated by the following equations:

$$J = \frac{V}{S \cdot \tau}, \ l/m^2.\ h \qquad \textbf{(1)}$$

where: J –flux permeate through the membrane, l/m^2.h; V - volume of permeated flux, l; S - effective area of tested samples, m^2; τ – record time, h;

$$R = \frac{C_2 - C_1}{C_2}.100, \% \qquad \textbf{(2)}$$

where: R- rejection of the membrane, %; C_2- concentration of retained matter in the feel, g/l; C_1- concentration in the permeate, g/l.

The content in waste water, permeate (filtrate) and retentate (concentrate) of the organic matter (TOC) was determined by the permanganate oxidizability method and the results were expressed as equivalent to potassium permanganate (mgEm $_{KMnO_4}$) (BDS 17.1.4.16:1979). The total flavonoids (TFC) was determined according to the method described by Kivrak et al. (2009) as quercetin equivalents (mgQeE). The concentration of flavonoids was calculated by the equation of the standard curve y=2.8575.x+0.21476, R^2 = 0.9737 at λ=410 nm. Prepared standard solutions with a quercetin concentration in the range of 10 - 100 mg/ml were used to construct a standard curve.

RESULTS AND DISCUSSION

The technological characteristics of the membrane are provided by its structure and morphology. The permeability of 17 wt% PAN membrane and the behavior of the structure according to the mechanical effect of changing pressure were initially tested against water. The pressure was changed stepwise by increasing and then decreasing in steps of 0.1 MPa. Permeability was determined at each pressure applied perpendicular to the membrane surface. Based on the results, a hysteresis curve was constructed as *J*=f(*P*) (Figure 1A). With an increase in pressure, the mechanical load on the polymer structure increases and vice versa, and the change in the hysteresis area corresponds to the degree of deformation. The permeability also increases and at 0.5 MPa maximum exploitation of the pore structure is achieved in laboratory conditions.

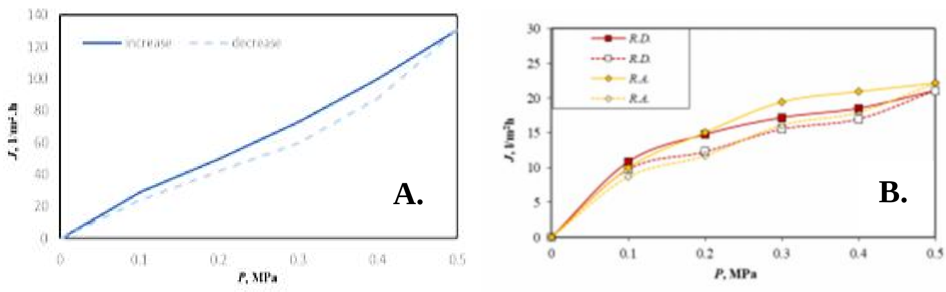

Fig. 1. Hysteresis curves of water flux permeability (A.) and waste water flux permeability (B.) through 17 wt% PAN membrane

The water permeability of the membrane reaches 131 $l/m^2.h$ at 0.5 MPa, with very good mechanical stability and reversible structural deformation. The change in the hysteresis area is apparently insignificant, expanding in the region 0.3-0.4 MPa.
UF is a type of membrane filtration in which hydrostatic pressure forces a liquid against a semi-permeable membrane. Suspended solids and high molecular weight solutes are retained while water and low molecular weight solutes pass through the membrane (Kumar *et al*., 2013). Production waste water was used in the membrane process after pre-filtration through a paper filter to eliminate solid plant residues. The filtration cell was charged with waste water with an initial volume of 200 ml. This was done successively with the waste water from *R.D.* and *R.A.*. Ultrafiltration was carried out until a reduction of 75% of the initial volume. The pressure was applied under the same conditions as in the membrane water permeability test. The waters were investigated for the content of TOC and TFC (Table 1).

Table 1. Contents of waste water from the hydrodistillation of oil-bearing roses.

waste water	**TOC**, mgEm $_{KMnO4}$/ml	**TFC**, mgQeE/ml
R.D.	15.80	7.80
R.A.	16.43	1.58

During ultrafiltration, the mechanical behavior of the membrane with respect to both investigated objects was stable in the entire range of applied pressure shows the permeability of the waste water flow through the membrane (Figure 1 B). The change in the hysteresis area is more noticeable when treating the *R.A.* waste water, with the flux permeability also being slightly larger. Corresponding differences stand out at pressures of 0.3 and 0.4 MPa, and at the highest pressure the permeabilities almost equalize.
The membrane exhibited the highest rejection of total flavonoids at a pressure of 0.1 MPa, which was 92% for the waste water from *R.D* and 89% respectively for those from *R.A.* (Figure 2). In terms of total organic matter at the same pressure, the rejection at the waste water of *R.A.* reaches 68% and is slightly higher than the waste water of *R.D.*, where it is 64%. In both cases, the process takes place with a low permeability not exceeding 11 l/m^2.h. As the degree of initial volume reduction increases, the retentates become an additional separation barrier. This helps keep rejection values high along with the growing permeability as pressure increases.

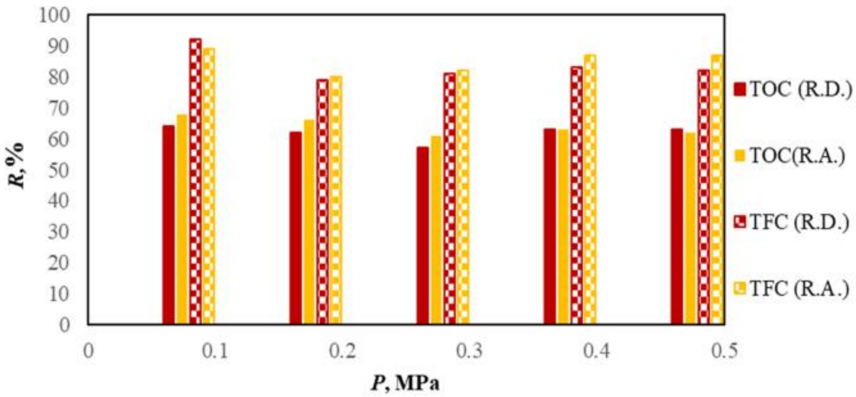

Fig. 2. Membrane rejection of the waste water composition.

At the highest experimental pressure, the permeability was 21 l/m^2.h of the hydrodistillation waste water of *R.D.* and 22 l/m^2.h of *R.A.*, with rejection respectively of 62 % and 63 % to total organics and 82 % and 87 % relative to the established amounts of total flavonoids. This trend should be preserved during membrane treatment of the studied objects in real conditions, which is a very good representation of the PAN membrane, according to the technological conditions of the ultrafiltration process.

CONCLUSIONS

The presented results show that a 17 wt% polyacrylonitrile membrane is structurally stable at pressures from 0 to 0.5 MPa applied in the ultrafiltration process to industrial waste water from the hydrodistillation of flower from essential oil crops *Rosa damascena* Mill. f. trigintipetala Dieck and *Rosa alba* L. It was found that the permeability of the treated waste water flow through the membrane reaches 22 $l/m^2.h$ with retention of up to 68% of the amount of the total organic composition and up to 92% of the polyphenolic compounds from the flavonoid group. It has been proven that the proposed membrane is suitable for ultrafiltration treatment of wastewater from the hydrodistillation of rose oil flower, and in a next step it can be tested in semi-industrial conditions for the purification or recovery of bioactive substances.

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