Bulgarian Chemical Communications, Volume 57, Special Issue D (pp. 37-40) 2025 DOI:10.34049/bcc.57.D.MAEP4

Stage filtration of wastewater from rose processing

M. Miteva[1]*, A. Dobreva[2]

[1] *Faculty of Technical Sciences, Burgas State University "Prof. Dr. Assen Zlatarov", Burgas, Bulgaria*
[2] *Department of Aromatic and Medicinal Plants, Institute for Roses and Aromatic Plants, Agricultural Academy, Kazanlak, Bulgaria*

Revised: September 09, 2025

Membrane processes are applied in different industrial sectors, including treating wastewater to restore its quality. Ultrafiltration polyacrylonitrile membranes with molecular weight cut-off of 1 kDa (UF1) and 25 kDa (UF25) were used individually in a single-stage process and sequentially in a two-stage ultrafiltration process, with the aim to purify wastewater from hydrodistillation of oil-bearing roses. Wastewater contains mainly non-volatile phenolic compounds and is considered as a biopollutant.

In a single-stage operation the permeability of the UF1 membrane was 13 $l/m^2.h$, and that of the UF25 was 20 $l/m^2.h$ with a rejection of 58% on the total polyphenols, decreasing from 11.3 mg GAE/ml to 6.6 mg GAE/ml. In a two-stage process, the UF25 membrane retains the values, while the permeability of UF1 increases to 28 $l/m^2.h$ and reaches a rejection of the total polyphenols up to 91%, with their concentration decreasing to 1.02 mg GAE/ml.

The use of membranes in a two-stage ultrafiltration mode increases the efficiency of the process. The concentrated and separated polyphenols in the retentate and permeate from the second stage were-microbiologically purified, which provided an opportunity for their direct application in food, pharmaceutical, cosmetic, etc. products and additives.

Keywords: membrane processes, oil-bearing roses, industrial wastewater, recovery of bio-resources

INTRODUCTION

The modern trends in the implementation of a circular economy promote the development of technological models that rely on the reuse of waste products and the extraction of resource components [1]. Membrane technologies have shown effectiveness in water purification and extracting of biologically active components, making them a potential solution for this approach [2]. The agro-industrial sector's rose processing on a large volume generates significant amounts of by-products, including solid and liquid waste streams [3, 4].

The treatment of wastewater from the hydrodistillation of oil-bearing rose flowers is important for protecting ecosystems and preventing water pollution, as it reduces the risk of eutrophication [5]. Purifying and restoring the quality of wastewater is primarily achieved through conventional methods [6-10]. According to the principles of sustainable development and the goals of bioeconomics, it is necessary not only to recycle wastewater but also to extract biologically active components with high potential for added value [11, 12]. Recovering these resources will reduce waste-related costs and generate additional income. Membrane processes such as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) effectively purify wastewater from various sources, retaining substances that act as pollutants, including microorganisms, organic matter, poly- and oligomeric compounds. High concentrations of these substances can lead to reversible and irreversible membrane fouling negatively impacting permeability and operational longevity [13, 14]. These undesirable effects can be overcome by utilizing various membranes and processes in combination or hybrid form, revealing their potential [15-17]. In ultrafiltration, porous membranes are predominantly used, typically polymeric, with various structures and morphologies [18]. These membranes determine the molecular weight limits that can be retained by the membrane [19, 20]. The most commonly available polymer membrane brands are produced using the phase inversion method [21, 22].

When selecting a membrane, the user considers the practical assessment of its performance based on operating characteristics such as permeability and selectivity [23-25]. These values are interdependent and involve a compromise. Modifying membranes through changes in parameters like phase inversion can enhance their properties [26]. Choosing a

---

* To whom all correspondence should be sent:
Email: *rmkpetrovi@abv.bg*

membrane can be challenging because two membranes with the same molecular weight cut-off (MWCO) from different manufacturers may have different pore sizes and operating characteristics. Additionally, membranes exhibit varying capabilities and behaviors based on the qualitative and quantitative composition of the fluid [27].

This study aims to investigate the ultrafiltration treatment of wastewater after hydrodistillation of oil-bearing roses using polyacrylonitrile membranes with molecular weight cut-offs of 1 kDa (UF1) and 25 kDa (UF25). These membranes will be used separately in a single-stage process and sequentially in a two-stage ultrafiltration process.

Implementing these processes can lead to more efficient resource utilization and enhance environmental sustainability.

EXPERIMENTAL

The wastes were collected after distillation of fresh rose flowers from *Rosa damascena Mill. f. trigintipetala Dieck* (R.D.). The process was used for obtaining essential oil at semi-industrial processing line at the Institute of Roses and Aromatic Plants (IRAP) in Kazanlak, Bulgaria. The plantations were grown according to established technology in the experimental field of the Institute. The liquid waste was stored at a temperature of -20°C until its membrane filtration and was pre-filtered through standard filter paper.

PAN membranes were formed from a solution of polyacrylonitrile with MWCO of 25 kDa using a solvent – N,N-dimethylformamide (DMF) and with a MWCO of 1 kDa using as solvents dimethyl sulfoxide (DMSO) and DMF, products of Fluka, Germany. The homogeneous polymer solutions were filtered through a textile filter and after deaeration were drawn as a film onto a calendered polyester substrate attached to a glass plate. The polyester mat brand FO-2403, manufactured by Viledon Filter, Germany, has a density of 100 ± 5 g/m^2 and a thickness of 2 ± 0.1 nm. The plate was immersed in a laboratory bath with distilled water at a temperature of 25 ± 1°C for non-solvent induced phase separation (NIPS). During NIPS, PAN coagulates to form a porous membrane, which is then intensively washed with water until the solvent is completely removed. The washed membrane is then subjected to heat treatment in distilled water in the temperature range of 60 – 90°C.

The membranes were tested in a laboratory installation with a cylindrical module for horizontally installing of round flat membranes. The volume of the membrane filtration module with perpendicular pressure supply is 500 ml. The tests were conducted with a filtration volume of wastewater of 400 ml resulting in up to a 75% reduction.

The values of the permeability (*J*, l/m^2.h) and rejection (*R*, %) of the PAN membrane at different pressures were calculated by the following equations:

$$J = V/(S.\tau), l/m^2.h \qquad (1)$$

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;

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

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 total phenolic content (TPC) was determined by the Folin-Ciocalteu assay [28]. The results were evaluated as gallic acid equivalent (mg GAE/ml) by linear regression equation of the calibration curve – y = 2.5x+0.108 and R^2 = 0.9893 at 765 nm. The calibration curve was constructed using various concentrations of gallic acid ranging from 0.02 to 0.10 mg/ml.

RESULTS AND DISCUSSION

The formed membranes are a composite structure consisting of an asymmetric porous PAN layer supported by a polyester backing [29]. This structure contributes to the mechanical resistance of the membrane, with its specific morphology designed to ensure the passage rate of liquid matches the driving force and selectively retains the composition of the filtered liquid based on the MWCO.

The membranes were used separately in a barofiltration process, with pressure applied above the wastewater and on the membrane, respectively. The results for the permeability of the membranes versus filtration volume are presented in Figure 1, demonstrating better functionality in terms of permeability for the UF25 membrane compared to UF1.

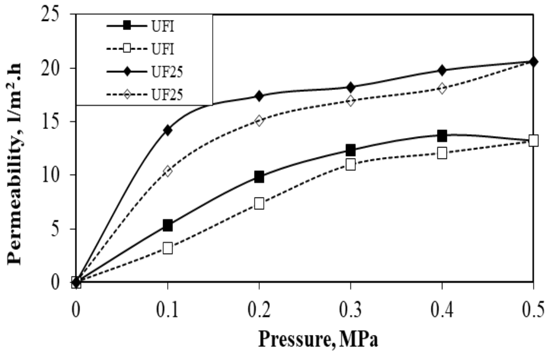

Fig. 1. Hysteresis curves of wastewater flux permeability in a single-stage filtration process

The permeability of UF25 sharply increases to 14.21 l/m^2.h at 0.1 MPa, then smoothly reaches 20.60 l/m^2.h at the maximum applied pressure of 0.5 MPa. For UF1, the permeability smoothly increases from 5.28 l/m^2.h at 0.1 MPa to 13.7 l/m^2.h at 0.4 MPa, with a slight decrease at 0.5 MPa. This decrease suggests a challenging flow, likely due to increase in the concentration of retained components in the interface with the membrane surface [30, 31].

Therefore, we can assume that 0.4 MPa is the effective limit working pressure for this membrane. The different behavior of the membranes is determined by the specifics of the structural morphology, which is a result of the thermodynamic conditions during their formation [32]. The course of the curves depends on the pores actively occupied during the filtration process. Even at low pressure, pores with a larger opening diameter are permeable, while pores with a smaller diameter gradually become active as pressure increases. The linear dependence of permeability on pressure shows a hysteresis area, which corresponds to the deformation reaction of the membrane structure during operation. The hysteresis area is visually similar for both membranes at the same mechanical load magnitude. However, the area between 0.1 and 0.3 MPa is noticeably larger for UF25 due to the greater asymmetry in the pore structure of the membrane [33].

Individually applied in a single-stage wastewater filtration process, the rejection values of UF1 and UF25 are shown in Figure 2. The values for the two membranes vary based on the applied pressure and molecular weight limit of retention, while maintaining the same qualitative and quantitative composition of the filtered material. The retention of the membranes was assessed against the determined analytical total polyphenol content of 11.3 mg GAE/ml in the wastewater.

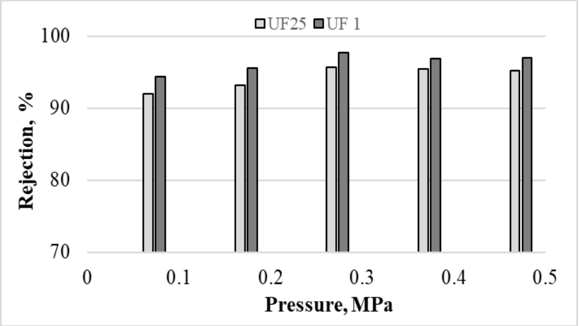

Fig. 2. Membrane rejection of TPC from the wastewater

The rejection of UF1 was consistently higher than that of UF25 at all pressures. Both membranes showed peak rejection values for polyphenolic components at 0.3 MPa. At this pressure, UF25 had a rejection rate of 95.75%, while UF1 had a rejection rate of 97.7% (Fig. 2). This translates to polyphenols passing through the UF25 membrane at 0.48 mg GAE/ml and only 0.25 mg GAE/ml through UF1. Consequently, 10.82 mg GAE/ml were eliminated from the wastewater using the UF25 membrane, and 11.05 mg GAE/ml with the UF1 membrane. The membrane rejection percentage values in the two-stage process are outlined in Table 1.

Table 1. Rejection of the two-stage ultrafiltration process at 0.3 MPa

Membrane type	Stage R, %	Final R, %
UF 25	95.75	99.02
UF 1	77.08	

The results were obtained at a system pressure of 0.3 MPa, which was determined to be optimal for both membranes in a single-stage filtration. In the two-stage filtration, the rejection of UF25 in the first stage is identical to the values obtained in the single-stage filtration (Fig. 2). However, during the second stage of filtration with UF1, a rejection value of 77.08% is obtained, which is lower compared to both the rejection value obtained with single-stage filtration using UF1 and that obtained with UF25. This is due to the lower concentration of TPC after the first stage, which was used in the calculations according to equation 2. As a result of the achieved rejection in the joint operation of the membranes in the two-stage filtration, the final rejection value increases to 99.02%, with only 0.11 mg GAE/ml of polyphenols passing through to the final permeate. The permeability of the UF1 membrane also increases, and its structural deformation decreases, as seen in the decreasing hysteresis area in Figure 3.

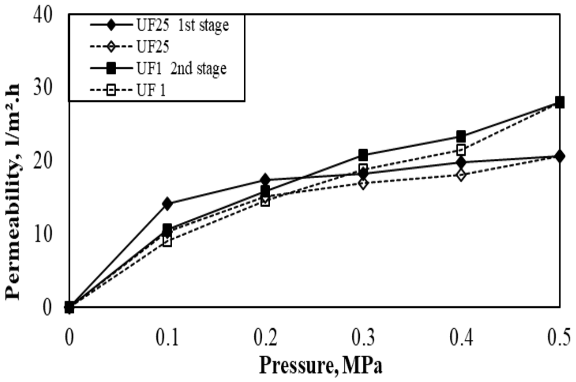

Fig. 3. Hysteresis curves of wastewater flux permeability in a two-stage filtration process

The composition of P1 is lightened in terms of the amount of TPC, which we believe is one of the main reasons for the almost twofold increase in permeability of the UF1 membrane, reaching 28 l/m^2.h at a pressure of 0.5 MPa. By conducting membrane filtration as a two-stage process with the sequential passage of wastewater flow through the UF25 and UF1 membranes, optimization of the process is achieved by utilizing the potential of UF1 nd improving the quality of the wastewater in terms of polyphenol composition.

CONCLUSIONS

The use of a two-stage membrane filtration approach, in which wastewater passes sequentially through UF25 and UF1, allows for maximum utilization of rejection of UF1 and results in the restoration of the polyphenol profile of the treated waters. The performance characteristics of the membranes were determined, and it was established that when applied sequentially in a two-stage ultrafiltration process and depending on the mode conditions, the permeability of the UF1 membrane increased from 13.2 to 28 l/m².h, while its structural deformation decreased.

It was found that more effective purification of industrial wastewater (up to 99.02%) is achieved in the two-stage ultrafiltration process with TPC rejection. The TPC in the purified water decreases from 11.3 mg GAE/ml to 0.11 mg GAE/ml, providing an opportunity for their valorization through the resulting retentate.

Acknowledgement: *This study was financially supported by the Burgas State University through the Scientific Research Sector – Project number 478/2024.*

REFERENCES

1. A. P. M. Velenturf, P. Purnell, *Sustain. Prod. Consum.*, **27**, 1437 (2021).
2. K. Czuba, A. Bastrzyk, A. Rogowska, K. Janiak, K. Pacyna, N. Kossińska, M. Kita, P. Chrobot, D. Podstawczyk, *Sci. Total Environ.*, **791**, 148266 (2021).
3. A. Slavov, I. Vasileva, L. Stefanov, A. Stoyanova, *Rev. Environ. Sci. Biotechnol., 16*, 309 (2017).
4. N. T. Dintcheva, E. Morici, *Molecules,* **28**(7), 3165 (2023).
5. Ö. Uysal, K. Ekinci, *J. Environ. Manag.,* **295**, 113089 (2021).
6. Y. Avsar, U. Kurt, T. Gonullu, *J. Hazard. Mater.,* **148** (1–2), 340 (2007).
7. Z. Sabahi, F. Farmani, E. Mousavinoor, M., *Moein, Sci. World.,* **2020**, 5409493, 6 (2020).
8. J. A. Silva, *Sustainability*, **15**(14), 10940 (2023).
9. T. M. Galal, A. Majrashi, H. M. Al-Yasi, E. A. Farahat, E. M. Eid, E. F. Ali, *Agriculture,* **12**(9), 1319 (2022).
10. E. Mutegoa, *Discov. Water., 4*, 69, (2024).
11. T. Ronzon, R. M'Barek, *Sustainability,* **10**(6), 1745 (2018).
12. https://ec.europa.eu/enrd/sites/default/files/enrd_publications/publi-enrd -rr-28_bg_2021.pdf
13. N. AlSawaftah, W. Abuwatfa, N. Darwish, G. Husseini, *Water,* **13**(9), 1327 (2021).
14. V. O. Mkpuma, N. R. Moheimani, H. Ennaceri, *Algal. Res.,* **61**, 102588 (2022).
15. M. A. Abdel-Fatah, A. Amin, H. Elkady, Membrane-Based Hybrid Processes for Wastewater Treatment, Elsevier, 2021, p. 341.
16. D. S. Rajendran, E. G. Devi, V. S. Subikshaa, P. Sethi, A. Patil, A. Chakraborty, S. Venkataraman, V. V. Kumar, *Clean. Techn. Environ. Policy*, **27**, 649 (2025).
17. E. Jalilnejad, P. Sadeghpour, K. Ghasemzadeh, Current Trends and Future Developments on (Bio-) Membranes, Elsevier, 2020.
18. J. Jia, M. Rui, X. Cheng, H. Liang, *Aqua Water Infrastruct. Ecosyst. Soc.*, **72** (12), 2408 (2023).
19. K. Castro, R. Abejón, *Membranes,* **14**(8), 180 (2024).
20. F. J. Ansari, H. A. Tafti, A. Amanzadeh, S. Rabbani, M. A. Shokrgozar, R. Heidari, J. Behroozi, H. Eyni, V. N. Uversky, H. Ghanbari, *Biochem. Biophys. Rep.*, **38**, 101668 (2024).
21. B. S. Johann, W. Fei, M. Michael, V. J. Lisičar, S. Andreas, U. Mathias, N. Britta, B. Stéphan, *Front. Sustain.*, **4,** 2023 (2023).
22. T. A. Geleta, I. V. Maggay, Y. Chang, A. Venault, *Membranes,* **13**(1), 58 (2023).
23. M. Al-Maas, A. Hussain, J. M. Matar, D. Ponnamma, M. K. Hassan, M. A. A. Al-Maadeed, K. Alamgir, S. Adham, *J. Water Process Eng.*, **43**, 102185 (2021).
24. V. A. Maske, A. M. Kokate, P. A. More, R. S. Salunkhe, A. P. More, *Polym. Bull.,* **81**, 16415 (2024).
25. M. Miteva, D. Christova, *MATEC Web Conf.*, **387,** 05003 (2023).
26. G. V. Theodorakopoulos, D. S. Karousos, E. P. Favvas, A. D. Gotzias, *ChemPlusChem*, **89**, e202300766 (2024).
27. L. R. Sahu, D. Yadav, D. Borah, A. Gogoi, S. Goswami, G. Hazarika, S. Karki, M. Borpatra Gohain, S. V. Sawake, S. V. Jadhav, S. Chatterjee, P. G. Ingole, *Polymers,* **16**(23), 3240 (2024).
28. V. Hellwig, J. Gasser, *Phytochem. Rev., **19***, 1539-1546, (2020).
29. R. W. Baker, Membrane Technology and Applications (2nd edn.), Chichester, John Wiley & Sons Ltd., 2004.
30. O. T. Majekodunmi, S. M. Hashmi, *Sci. Rep.,* **12,** 22587 (2022).
31. W. Yi, D. Y. Kim, H. Jin, S. Yoon, K. Hyun Ahn, *Sep. Purif. Technol.,* **359**(2), 130428 (2025).
32. T. Ahmad, L. M. Rehman, R. Al-Nuaimi, J.-P. B. Boross de Levay, R. Thankamony, M. Mubashir, Z. Lai, *Chemosphere,* **337**, 139430 (2023).
33. St. Petrov, M. Miteva, *Int. J. Sci. Res.,* **3**(5), 145 (2012).