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DEVELOPMENT OF POLYMERIC MEMBRANES WITH CARBON ADDITIVES FOR REMOVAL OF PHENOL

Abstract. This study presents the synthesis and application of polymeric mixed matrix membranes (MMMs) incorporating activated carbon (AC) derived from extracted olive pomace for removal of phenol from aqueous solutions. MMMs were fabricated by dispersing AC in a PVDF/PVP/NMP matrix, followed by phase inversion. Characterization revealed improved surface porosity and structural asymmetry in the membranes, which were ascribed to AC. Continuous flow experiments using phenol (50 mg L^{-1}) as a model pollutant, which are very common in olive mill wastewater, demonstrated that membranes containing AC achieved up to 90% removal within 60 minutes in continuous mode, significantly outperforming pristine membranes. The results indicate that incorporating bio-based AC into polymer membranes improves adsorption capacity and filtration efficiency, offering a promising route for sustainable wastewater treatment and inspiring further research in this field.

Keywords: activated carbon, mixed matrix membranes, phenol adsorption.

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Introduction. Polymeric mixed matrix membranes (MMMs) have emerged as one of the most promising and versatile technologies for advanced wastewater treatment [1-3], combining the processability and flexibility of polymeric membranes with the enhanced separation and adsorption capabilities of inorganic or carbon-based fillers [4]. This hybrid design enables improvements in permeability, selectivity, antifouling resistance [5], and mechanical strength, addressing the limitations of conventional membranes. Among the various fillers explored, activated carbon (AC) derived from agro-industrial residues stands out for its cost-effectiveness, high surface area, and strong affinity for a wide range of pollutants [6,7], particularly phenolic compounds [8] commonly found in industrial effluents.

The olive oil extraction process generates significant by-products, particularly olive pomace (OP) and olive mill wastewater (OMWW) [9]. For the two-phase continuous extraction system (standard in Portugal), about 1.1 cubic meters (1,100 liters) of OMWW are generated per ton of olives milled [10]. About 50 kg of pomace is generated per ton of olives milled [11]. OMWW is a highly pollutant effluent due to its high organic load, phytotoxic phenolic compounds, and limited biodegradability [8,12-14]. Its disposal poses serious environmental risks, such as soil contamination [15], inhibition of plant growth [16], pollution of surface and groundwater [17], and disruption of aquatic ecosystems due to the leaching of phenolic substances [18].

To address these issues, this study focuses on valorizing extracted olive pomace (EOP), a by-product of oil extraction, by producing AC via slow pyrolysis with injection of CO_2, which enhances porosity development. The resulting activated carbon, rich in surface area and functional groups, is known for its high affinity toward phenolic compounds. By incorporating this bio-based activated carbon into polymeric membranes, this study aims to fabricate mixed matrix membranes with improved adsorptive and filtration properties. These membranes are designed to retain and remove phenol from aqueous solutions, simulating the effluent contaminated with phenol, a representative phenolic compound of OMWW.

Materials and methods. *Chemicals and apparatus.* The raw materials and reagents employed in this study include: Olive pomace, provided by Mirabaga – Food Industry and Commerce S.A; Carbon Dioxide (CO_2), provided by Air Liquide; Distilled water; Sodium chloride (NaOH – 98%), provided by Labkem; Hydrochloric acid 37% (HCl), supplied by AnalaR Normapur; 1-Methyl-2-pyrrolidone (C_5H_9NO), provided by Thermo scientific; Polyvinylpyrrolidone $(C_6H_9NO)n$, supplied by Thermo scientific; Polyvinylidene Fluoride($-CH_2CF_2-$)n, provided by Thermo scientific; Phenol Crystallized (C_6H_6O), supplied by Panreac.

Synthesis of the materials. AC was synthesized according to procedures described in previous studies [6]. Incorporating 2.5 g of AC, the sample was subjected to ultrasound with 0.7 g of PVP and 7.2 g of NMP for 3 hours to achieve a homogeneous mixture. Subsequently, 0.3 g of PVDF was added to the resulting gel, which was then placed in an agitated bath at 40°C, 200 rpm, for 48 hours. This procedure enabled the formation of polymeric membranes with controlled incorporation of AC, ensuring a uniform distribution of the material and providing desirable characteristics for its application. After 48 hours, the material must rest for at least 12 hours. Following the resting phase, the prepared gel was cast into films of 150 , 200 , and 300 μm of thickness using a precision blade applicator. After the material was spread, the gel was immersed in a coagulation bath containing distilled water. The resulting membrane was denoted AC_membrane.

Characterization techniques. The characterization techniques were performed according to reported in previous studies [6,17]. The textural properties of the polymeric membranes were gathered upon analysis of N_2 adsorption-desorption isotherms at 77 K, obtained in a Quantachrome NOVATOUCH LX^4 adsorption analyzer equipped with long cells with a bulb and outer diameter of 9 mm. Scanning electron microscopy (SEM) was employed to investigate the surface morphology and microstructure of the membrane samples that were analyzed using a FEI Quanta 400 SEM with a resolution of 4 nm. The elemental composition in the solid phase was determined using a CHNS Flash 2000 analyzer (Thermo Fisher Scientific, Massachusetts, USA), equipped with a thermal conductivity detector (TCD). To determine the point of zero charge (pH_{PZC}), NaCl (0.01 mol L^{-1}) solutions were prepared, and their pH was adjusted between 4 and 12. 0.15 g of the solid sample was then introduced into each prepared solution and agitated at 300 rpm at a constant temperature of 25°C for 24 hours, after this time the mixtures were filtered, and the pH values were taken. The point of zero charge (pH_{pzc}) was established by analyzing the variation between the initial and final pH values, enabling the determination of the pH at which the adsorbent surface reaches electrical neutrality.

Polymeric mixed matrix membranes in a continuous system. A continuous system was employed to assess the effectiveness of the polymeric membranes in pollutant treatment, utilizing a reactor coupled with an HPLC pump. In the experiments, a pollutant, specifically phenol at a concentration of 50 mg L^{-1}, was placed in a container with an inlet directly connected to the pump. The pump, operating at a flow rate of 0.5 mL min^{-1}, fed the pollutant through the reactor inlet and passed it through the polymeric membrane installed in the reactor. Samples (2 mL) were collected during filtration at 0, 5, 15, 30, 45, and 60 minutes. The treated wastewater was collected for subsequent HPLC analysis.

Research results and discussion. *Characterization of the materials.* Figure 1 displays the adsorption isotherms of N_2 at 77 K for the AC_membrane and the membrane itself, along with the results obtained for the BET surface area. The isotherm for AC_membrane Figure 1 (a) shows an isotherm of Type IV with H3 hysteresis, typical of mesoporous materials with slit-like pores [19]. The measured surface area was 47 m^2 g^{-1}, significantly lower than the pure AC, likely due to partial pore blockage or encapsulation by the polymer matrix during membrane formation. Nonetheless, incorporating activated carbon enhances the porosity compared to the pristine membrane.

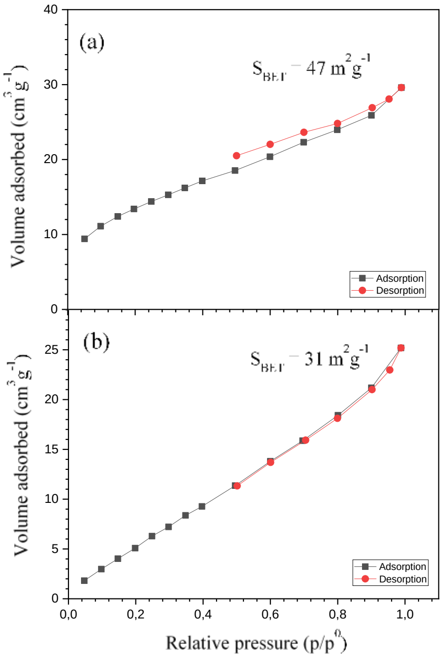

Fig. 1. N2 adsorption-desorption isotherms at 77 K for (a) AC_membrane and (b) membrane

The pristine membrane Figure 1 (b), also displays an isotherm of Type IV, with a much smaller hysteresis loop and lower adsorbed volume [20]. The BET surface area of 31 m^2 g^{-1} suggests a low degree of porosity, primarily mesoporous, likely originating from the intrinsic structure of the polymer blend used. These results demonstrate that adding AC to the membrane matrix significantly improves the textural properties, particularly the surface area and pore structure, which are essential for enhanced adsorption performance in wastewater treatment applications.

The hydrophilicity of the surface of the polymeric membranes was evaluated by measuring the contact angle with water. According to the data presented in Table 1, it can be observed that all membranes had a hydrophilic surface. Singh *et. al*. [21] suggest that hydrophilic membranes, which have high chemical resistance, could be considered for use in wastewaters and in the processing of food and pharmaceuticals.

The pH_{PZC} values of the membranes with and without activated carbon were 7.2 and 7.3, respectively, indicating minimal variation between the two formulations. This small difference suggests that the surface charge characteristics are predominantly dictated by the polymeric matrix, rather than by the presence of additives. Such behavior is commonly observed in membranes where the polymer phase remains dominant in defining surface properties, including charge distribution and interfacial interactions. The near-neutral pH_{PZC} values also imply that, under typical operating conditions, the membranes are likely to exhibit low surface charge, which can reduce electrostatic repulsion between the membrane and neutral or weakly charged species.

Table 1

Contact angle and pH_{PZC}

Samples	pH_{PZC}	Contact Angle (º)
AC_membrane	7.2	56±2
Membrane	7.3	54±2

The morphology of polymeric membranes, in their pure form and after the addition of AC, was evaluated by SEM. The manufacturing technique involves casting polymers together with the solvent, resulting in asymmetric structures that promote molecule separation and selective transport. Furthermore, it can be observed that the inner part of the membrane contains macropores, which contribute to its mechanical structure and stability, as illustrated in the SEM images shown in Figure 1.

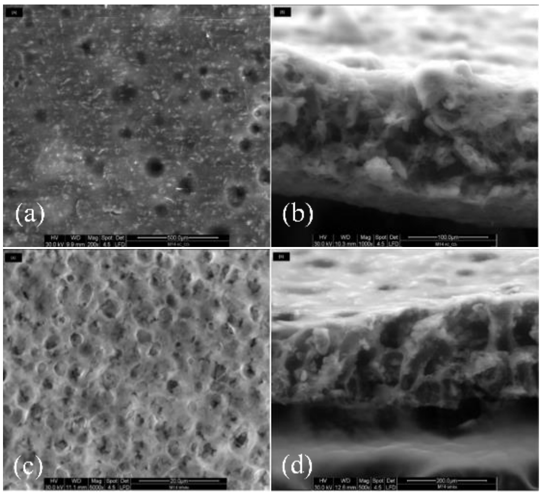

Fig. 1. SEM images of (a) and (b) polymeric membrane with incorporation of AC, and (c) and (d) the pristine polymeric membrane

The incorporation of AC into the composition of the membrane has resulted in an increase in the presence of pores, both on the surface and within. It is important to note that the membrane is asymmetric due to the production process (phase inversion), resulting in a dense surface and a porous internal structure. According to Hwang *et. al.* [22], the incorporation of AC into the polymeric solution confers to the membrane selective and adsorptive properties, which can enhance adsorption and increase the number of active adsorbent sites. This facilitates selecting a broader range of particles and improvement of the filtration characteristics.

Continuous system experiment with simulated olive mill wastewater. A range of thicknesses (150, 200 and 300 μm) was selected to enhance adsorption differentiation and evaluate the comparative adsorption performance between the AC_membrane and the pristine polymeric membranes. During these analyses, a solution containing phenol (50 mg L^{-1}) was employed as a model wastewater in a continuous system, thereby assessing the interaction between the materials. The results are presented in Figure 2.

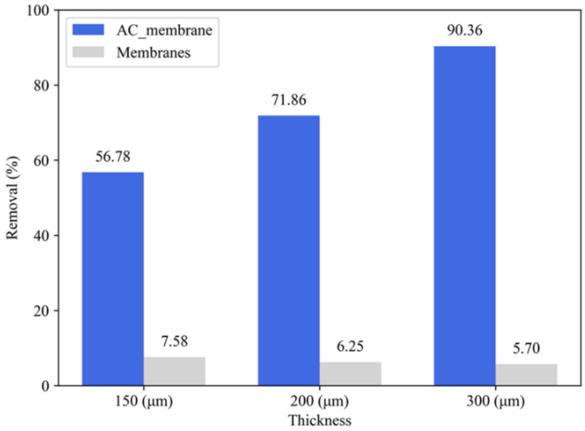

Fig. 2. Percentage of phenol removal for AC_membrane and pristine membrane with different thicknesses

Membranes incorporating AC and control membranes without activated carbon were tested with three different thicknesses. All thicknesses of AC_membrane achieved phenol removal efficiencies exceeding 50% within one hour; notably, the membrane with a thickness of 300 μm reached the highest removal efficiency of 90%. In contrast, all the control polymeric membranes demonstrated significantly lower performance across all thicknesses. These findings underscore the critical role of AC incorporation in enhancing pollutant removal, as described in the work of Ferreira *et. al.* [6] on gallic acid removal using the same biomass precursor for the synthesis of AC, where a capacity of 314 mg g^{-1} was achieved, primarily due to the increased availability and distribution of active adsorption sites on the surface of the membrane.

The experimental results showing improved phenol removal efficiency with increasing thickness of AC_membranes are consistent with membrane transport and adsorption mechanisms reported in literature. Roman *et al.* [23] found that thicker ion-exchange membranes (300–600 μm) exhibited 20–40% higher diffusion coefficients for neutral organic micropollutants, attributed to reduced surface resistance effects. The transport enhancement associated with increased membrane thickness is linked to higher bulk-to-surface energy ratios, which promote deeper adsorbate penetration into the membrane matrix. This supports the superior performance observed for the 300 µm AC_membrane tested in the present study.

However, exceeding optimal thickness ranges, as seen in cases like 2 wt% AC loaded PDMS membranes [24], can lead to decreased free volume and reduced permeability due to filler agglomeration. This suggests that the 300 µm thickness observed in this study represents an optimal balance between maximizing adsorption capacity and minimizing transport limitations.

Conclusion. In conclusion, this study underscores the significant potential of polymeric mixed matrix membranes incorporating bio-derived activated carbon as a viable and effective solution for removing phenolic contaminants from aqueous systems. The successful integration of activated carbon synthesized from extracted olive pomace enhanced the membranes' porosity and adsorption capacity. It significantly improved their performance in continuous flow treatment, achieving up to 90% phenol removal in one hour. The observed improvements in adsorption efficiency demonstrate the critical role of AC in increasing the number and accessibility of active sites within the membrane matrix. The physicochemical characterization further confirmed that the modified membranes maintained desirable surface properties, structural asymmetry, and chemical stability, essential for scalable and long-term environmental applications. These findings establish a foundation for developing sustainable membrane technologies based on agro-industrial waste valorization. Future studies focused on membrane regeneration, long-term operational stability, and performance under complex effluent conditions.

References

1. Shi W., Xu C., Cai J., et al. Advancements in material selection and application research for mixed matrix membranes in water treatment // Journal of Environmental Chemical Engineering. – 2023. – Vol. 11. – P. 111292.
2. Xu X., Song H., Xiong S., et al. A new route to mixed matrix membranes: Atomic layer deposition of TiO2 on membrane-forming polymers followed by nonsolvent-induced phase inversion // Separation and Purification Technology. – 2025. – Vol. 366. – P. 132737.
3. Dechnik J., Gascon J., Doonan C.J., et al. Mixed-Matrix Membranes // Angewandte Chemie – International Edition. – 2017. – Vol. 56. – P. 9292-9310.
4. Chen M., Zhou J., Ma J., et al. Merging polymers of intrinsic microporosity and porous carbon-based zinc oxide composites in novel mixed matrix membranes for efficient gas separation // Green Energy & Environment. – 2025. – Vol. 10. – P. 203-213.
5. De Guzman M.R., Andra C.K.A., Ang M.B.M.Y., et al. Increased performance and antifouling of mixed-matrix membranes of cellulose acetate with hydrophilic nanoparticles of polydopamine-sulfobetaine methacrylate for oil-water separation // Journal of Membrane Science. – 2021. – Vol. 620. – P. 118881.
6. Ferreira A.P., Baldo A.P., Silva A.S., et al. Enhancing single and multi-component adsorption efficiency of pharmaceutical emerging contaminants using bio waste-derived carbon materials and geopolymers // Journal of Water Process Engineering. – 2025. – Vol. 75. – P. 107914.
7. Wong S., Ngadi N., Inuwa I.M., et al. Recent advances in applications of activated carbon from biowaste for wastewater treatment: A short review // Journal of Cleaner Production. – 2018. – Vol. 175. – P. 361-375.
8. Mu'azu N.D., Jarrah N., Zubair M., et al. Removal of phenolic compounds from water using sewage sludge-based activated carbon adsorption: A review //

International Journal of Environmental Research and Public Health. – 2017. – Vol. 14.
9. Ammari M., Amakdouf H., Zoufri I., et al. Fixed-bed column adsorption of olive mill wastewater using clinker: Optimization via response surface methodology // Results in Engineering. – 2025. – Vol. 26. – P. 104863.
10. Duarte J.C., Santori F., Ribeiro B., et al. Wastes: Solutions, Treatments and Opportunities: Proceedings of the 1st International Conference OLEICO+ project: olive mill wastes and the sustainability of the olive oil industry in Europe.
11. Doula M.K., Moreno-Ortego J.L., Tinivella F., et al. Olive mill waste: recent advances for the sustainable development of olive oil industry // Olive Mill Waste: Recent Advances for Sustainable Management. – 2017. – P. 29-56.
12. Solomakou N., Goula A.M. Treatment of olive mill wastewater by adsorption of phenolic compounds // Reviews in Environmental Science and Biotechnology. – 2021. – Vol. 20. – P. 839-863.
13. Yu L., Han M., He F. A review of treating oily wastewater // Arabian Journal of Chemistry. – 2017. – Vol. 10. – P. S1913-S1922.
14. Ahmad T., Belwal T., Li L., et al. Utilization of wastewater from edible oil industry, turning waste into valuable products: A review // Trends in Food Science & Technology. – 2020. – Vol. 99. – P. 21-33.
15. Environmental Impact of Olive Oil Processing // EcoMENA. – [Electronic resource]. – Acess mode: https://www.ecomena.org/olive-oil-wastes/. Date of access: 9 June 2025.
16. Yaakoubi A., Aganchich B., Meddich A., et al. Land spreading of olive mill wastewater (OMW): Biodegradation of organic matter and polyphenols in soil and effect on the activity of the total soil microflora // Water Practice and Technology. – 2024. – Vol. 19. – P. 297-310.
17. Ferreira A.P., Natal A.P.S., Baldo A.P., et al. Response surface method-driven design of experiments for the synthesis of fly ash-based geopolymers in the gallic acid optimized removal from wastewater // Chemical Engineering Journal Advances. – 2025. – Vol. 21. – P. 100703.
18. Parida K.M., Pradhan A.C. Removal of phenolic compounds from aqueous solutions by adsorption onto manganese nodule leached residue // Journal of Hazardous Materials. – 2010. – Vol. 173. – P. 758-764.
19. Dragan G., Kutarov V., Schieferstein E., et al. Adsorption hysteresis in open slit-like micropores // Molecules. – 2021. – Vol. 26. – P. 5074.
20. Donohue M.D., Aranovich G.L. Classification of Gibbs adsorption isotherms // Advances in Colloid and Interface Science. – 1998. – Vols. 76–77. – P. 137-152.
21. Singh R. Introduction to membrane technology // In: Membrane Technology and Engineering for Water Purification. – 2015. – P. 1-80.
22. Hwang L.L., Chen J.C., Wey M.Y. The properties and filtration efficiency of activated carbon polymer composite membranes for the removal of humic acid // Desalination. – 2013. – Vol. 313. – P. 166-175.
23. Roman M., Roman P., Verbeke R., et al. Non-steady diffusion and adsorption of organic micropollutants in ion-exchange membranes: Effect of the membrane thickness // iScience. – 2021.
24. Gonçalves A., Cren C., Windmoller D., et al. Activated carbon-loaded polydimethylsiloxane membranes for the pervaporation of 1-butanol from aqueous solutions // Materials Research. – 2019. – Vol. 22. – P. 20180573.

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ФЕНОЛДЫ ЖОЮ ҮШІН КӨМІР ҚОСПАЛАРЫ БАР ПОЛИМЕРЛІК МЕМБРАНАЛАРДЫ ӘЗІРЛЕУ

Аңдатпа. Бұл зерттеуде зәйтүн сығындысынан алынған активтелген көмірді (AC) енгізу арқылы полимерлі аралас матрицалы мембраналардың (MMM) синтезі мен қолданылуы қарастырылды. MMM үлгілері AC-ті PVDF/PVP/NMP матрицасына диспергирлеу және фазалық инверсия арқылы дайындалды. Сипаттау нәтижелері мембраналардың беткі кеуектілігі мен құрылымдық асимметриясының артқанын көрсетті, бұл AC-тің болуымен түсіндіріледі. Фенолды (50 мг/л) модельді ластаушы ретінде қолданған үздіксіз ағымдық тәжірибелер, ол зәйтүн майын өндіретін зауыттардың ағынды суларында жиі кездеседі, мембраналардың AC қосылған нұсқалары 60 минут ішінде 90%-ға дейін жою тиімділігіне жеткенін көрсетті, бұл бастапқы мембраналарға қарағанда әлдеқайда жоғары. Нәтижелер био-негізді активтелген көмірді полимерлі мембраналарға енгізу адсорбция қабілетін және сүзу тиімділігін арттыратынын көрсетеді, бұл тұрақты ағынды суларды тазартудың перспективті бағытын ұсынып, осы саладағы одан әрі зерттеулерге түрткі болады.

Тірек сөздер: активтелген көмір, аралас матрицалы мембраналар, фенол адсорбциясы.

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РАЗРАБОТКА ПОЛИМЕРНЫХ МЕМБРАН С УГЛЕРОДНЫМИ ДОБАВКАМИ ДЛЯ УДАЛЕНИЯ ФЕНОЛА

Аннотация. В данной работе представлены синтез и применение полимерных мембран смешанной матрицы (MMM), содержащих активированный уголь (AC), полученный из жмыха оливок, для удаления фенола из водных растворов. MMM были изготовлены путем диспергирования AC в матрице PVDF/PVP/NMP с последующей фазовой инверсией. Характеризация выявила улучшенную поверхностную пористость и структурную асимметрию мембран, что обусловлено присутствием AC. Непрерывные эксперименты с фенолом (50 мг/л) в качестве модельного загрязнителя, характерного для сточных вод оливковых мельниц, показали, что мембраны с AC достигали до 90% удаления за 60 минут в непрерывном режиме, что значительно превышает эффективность исходных мембран. Результаты свидетельствуют о том, что введение био-углерода в полимерные мембраны повышает их адсорбционную способность и эффективность фильтрации, предлагая перспективный путь для устойчивой очистки сточных вод и стимулируя дальнейшие исследования в этой области.

Ключевые слова: активированный уголь, мембраны смешанной матрицы, адсорбция фенола.