Production of polymeric membranes based on activated carbons for wastewater treatment

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Abstract: Comprising advanced materials like Polyvinylidene fluoride (PVDF) for mechanical stability and biofouling prevention and Polyvinylpyrrolidone (PVP) for hydrophilicity, these membranes enable selective filtration, retaining larger particles and external contaminants in wastewater treatment. Incorporating activated carbon during manufacturing is a strategic approach to enhance membrane (AC-CO_2 membrane) properties, leveraging its high surface area and adsorption capacity. This study produced mixed polymeric membranes by combining PVDF, PVP, and activated carbon (AC-CO_2), using N-Methyl-2-pyrrolidone (NMP) as the solvent. These membranes were employed for the filtration of phenolic compounds, particularly phenol. In the AC-CO_2 membrane formulation with 1.3g of PVP, 1.15g of PVDF, 8.8 ml of NMP, and 2.5g of AC-CO_2, with thickness variations of 150 μm and 300 μm, approximately 56.77% and 90.35% of 50mg/l of phenol in model wastewater were removed within 5 minutes, respectively, with breakthrough occurring at 15 minutes. Finally, this study developed a hydrophilic membrane with alkaline characteristics and a neutral pH point of zero charge (pH_{PZC}), establishing the feasibility of employing these membranes to treat model wastewater containing phenolic compounds. The prospect of scaling up for practical applications presents a promising avenue for future investigations.

Keywords: Polymeric membrane; activated carbon; industrial wastewater treatment; phenolic compounds;

1. Introduction

Current industrial wastewater treatment (IWWT) systems follow a well-defined sequence of stages[1,2]. Initially, there is the preliminary treatment, which involves the removal of coarse pollutants, such as solids and large-sized materials, through processes such as screening, sieving, sand traps, and flotation, among others[3]. Subsequently, the primary treatment removes suspended solids and some organic matter. This step is followed by secondary treatment, which focuses on the more thorough removal of organic matter in wastewater[4].

However, due to the high organic load often present in wastewater, it becomes necessary to adopt additional treatment alternatives to deal with these effluents effectively. Various treatment approaches are applied to minimize the adverse impacts of this IWWT on the environment, encompassing physical, chemical, and biological aspects[5–7]. These approaches can be implemented in an integrated manner within industrial facilities to treat IWWT completely. Examples of such approaches include membrane filtration[8,9] and adsorption using activated carbon[10,11], which contribute to even more effective purification of this wastewater before its discharge into the natural environment.

A polymeric membrane is a thin layer of synthetic or natural polymers featuring micropores, mesopores, and macropores that enable selective passage of specific substances. This selective capacity renders polymeric membranes attractive for meeting demands across diverse domains[12]. A polymeric membrane can encompass various approaches, preparation methods, and characterization techniques. Yet, all membranes are composed of polymeric materials, such as polyethersulfone (PES)[13], polyacrylonitrile (PAN)[14], polypropylene (PP)[15], polysulfide (PS), polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF), among other polymers. PVDF is a semicrystalline polymer that exhibits solvent resistance. Its chemical resistance to many acids and alkalis imparts thermal stability. At the same time, its amorphous phase provides the flexibility desired in a membrane[16].

PVDF is also renowned for its hydrophobic properties, enabling an effective barrier against the passage of liquid contaminants. Its mechanical attributes ensure the structural stability of the membrane during the filtration process, enhancing the material's durability and lifespan[17]. However, the high hydrophobicity also poses a drawback. Nevertheless, a method that aids the membrane in reducing its hydrophobic character involves grafting hydrophilic polymers onto the hydrophobic surface of the membrane. This approach aims to enhance the membrane interaction capacity with organic compounds and other polar substances in the effluent[18–20].

Polyvinylpyrrolidone (PVP) is hydrophilic, facilitating interactions with water molecules and aqueous solutes, aiding in enhanced adsorption and retention of organic contaminants[21]. Incorporating PVP into membrane production seeks to optimize its water affinity, similar to its ability to retain pollutants in the effluent[22].

As an innovative approach, incorporating other materials into the polymeric membrane matrix, such as AC-CO_2, may improve the filtration capacity. The activated carbon is already utilized in IWWT systems due to its pivotal role in selectively adsorbing organic contaminants, inorganic compounds, metal ions, and dyes in the effluent[23–25]. Due to its high surface area and porosity, activated carbon significantly augments its capacity to remove contaminants and impurities, thus enhancing effluent treatment efficacy[26,27,28].

The primary objective of this study is to fabricate a membrane by combining PVDF and PVP polymers with the addition of AC-CO_2. The purpose of this enhanced AC-CO_2 membrane is to employ it in a filtration/adsorption process to remove phenolic compounds. This amalgamation is designed to leverage the membrane's hydrophobic, hydrophilic, and absorptive characteristics, significantly improving pollutant removal efficiency.

2. Materials and Methods

2.1. Materials

In the experimental setup, the materials were PVDF and PVP as polymers, which THERMO SCIENTIFIC manufactured. As for the solvent, NMP was chosen for AC-CO_2 membrane production.

The research group produced the AC-CO_2 within the laboratory of the Mountain Research Center (CIMO), where exhausted olive pomace underwent slow pyrolysis in an inert atmosphere using nitrogen (N_2), and carbon dioxide (CO_2) was utilized during activation.

Furthermore, for the application of polymeric films at adjustable thicknesses, the Knife film applicator (Elcometer; model 3580/7) was acquired, providing precise control in the research laboratory's AC-CO_2 membrane production processes.

2.2. Methods

2.2.1. Polymeric membranes based on activated carbons production

To produce the membranes, the determined mass of 1.3g of PVP and 2.5g of AC-CO_2 were added to a beaker, followed by 8.8 ml of NMP, and then subjected to ultrasonication for 3 hours to achieve a homogeneous mixture. Subsequently, 1.15g of PVDF was added to form the gel, which was then placed in an agitated bath at 40°C, 200 rpm, for 48 hours. After 48 hours, the material needed to rest for at least 12 hours. After this resting period, the material was spread using the Knife film applicator equipment at thicknesses of 150 μm, 200 μm, and 300 μm. Following the material spreading, the gel was immersed in a coagulation bath of distilled water. This process can be analyzed through the schematic diagram depicted in Figure 1.

Figure 1 - Schematic diagram for AC – CO_2 membrane preparation
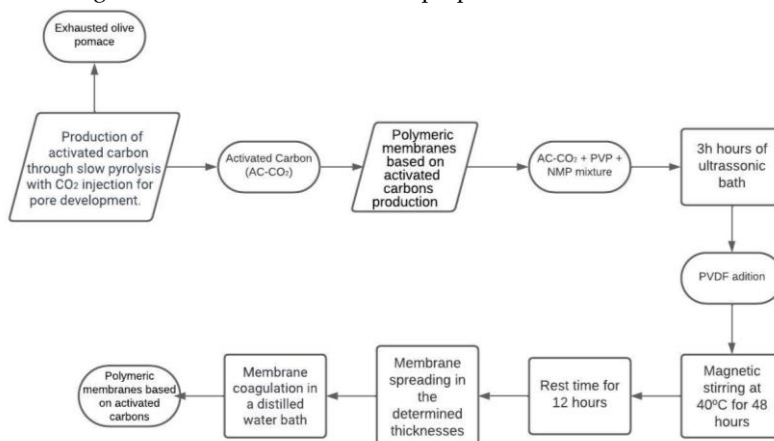
For the filtration process, a setup was assembled (Figure 2), including an HPLC pump with a flow rate of 0.5 ml/min. The inlet was connected to a solution containing the pollutant, in this case, phenol, at a concentration of 50 mg/L, while the outlet was connected to the reactor with the membrane. Samples (2 ml) were collected at intervals of 0, 5, 15, 30, 45, and 60 minutes.
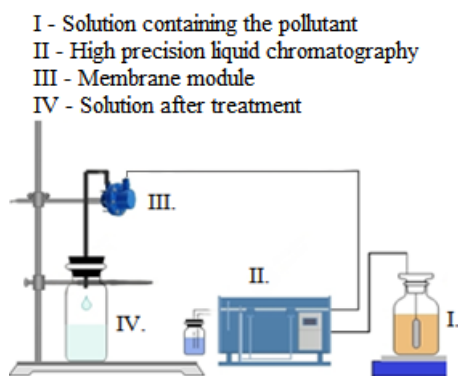

I - Solution containing the pollutant
II - High precision liquid chromatography
III - Membrane module
IV - Solution after treatment

Figure 2. Structural diagram for the AC – CO_2 membrane filtration system.

2.2.2. Characterization techniques

The Fourier-transform infrared spectroscopy (FT-IR) was obtained by Perkin Elmer FT-IR spectrophotometer UATR Two, with a resolution of 4 cm-1 and scan range 4500 – 400 cm-1. The analysis required previous preparation of sample pellets, which was performed by dispersing 1 mg of sample in 100 mg of potassium bromide (KBr). This mixture was pressed into a mold with 8 tons for 3 minutes.

To evaluate acid-base properties, five distinct solutions were prepared (NaCl 0.01 mol/L, HCl 0.02 mol/L, and 0.01 mol/L, NaOH 0.02 mol/L and 0.01 mol/L). Analyzing the acid-base properties of the material offers insights into the adsorption mechanism and the interaction between the adsorbent and the adsorbate, allowing characterization of its basicity or acidity. The acidity of the materials was determined by adding the solid sample (0.2 g) into 25 mL of a 0.02 mol/L NaOH solution and mixing on a magnetic stirrer at 300 rpm for 48 h. The resulting solution was then filtered, and a 20 mL aliquot of the recovered solution was titrated with 0.01 mol/L HCl solution using phenolphthalein as an indicator. For basicity, 0.2 g of the solid sample was added to 25 mL of 0.02 mol/L HCl solution and mixed on a magnetic stirrer at 300 rpm for 48 h. After filtration, 20 mL of the recovered solution was titrated with 0.01 mol/L NaOH solution, using phenolphthalein as an indicator.

The *pH*$_{PZC}$ was determined by preparing up to nine dilutions of 0.01 mol/L NaCl at pH values ranging from 4 to 12 by adding 0.02 mol/L NaOH or HCl. Then, 0.15 g of the solid sample was added to each solution, and each suspension was stirred on a magnetic stirrer at 300 rpm for 24 h. Afterwards, each suspension was filtered, and the pH of each recovered solution was measured. At last, initial and final pH values were plotted to determine the *pH*$_{PZC}$ when the charge in the adsorbent surface was zero.

The contact angle measurement was conducted using the sessile drop technique, which relies on determining the contact angle by measuring the base diameter and height of the droplet[28]. The sample was positioned on a flat base, and then a 5 µl droplet of distilled water was deposited onto the AC-CO$_2$ membrane surface. A photo was captured at the exact moment the droplet made contact with the membrane. The contact angle was subsequently determined using ImageJ software.

3. Results and discussion

3.1. Surface chemistry

The FTIR analysis for the polymeric AC-CO$_2$ membrane and AC-CO$_2$ is depicted in figure 3. Each peak corresponds to the absorption of infrared radiation at a specific frequency, and these peaks are associated with different molecular vibrations, providing information about functional groups and chemical composition.
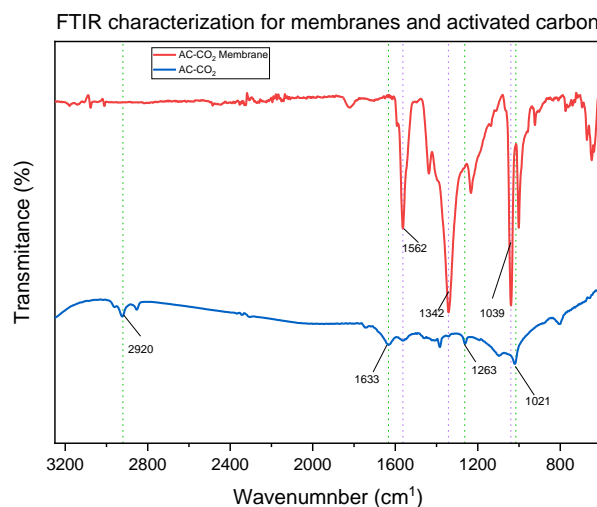
Figure 3. FTIR characterization for AC-CO_2 membranes and AC-CO_2.

The peaks observed in the AC-CO_2 membrane at the wavenumbers of 1562 cm-1 are associated with the variation of C=C stretching in aromatic rings[29,30], indicating the presence of carbonyl-containing groups due to the incorporation of AC-CO_2. The peaks at 1039 and 1342 can also describe the stretching vibrations of the alcohol group in C_6-OH and the secondary alcohol group in C_3-OH[31,32].

In the FTIR spectrum of AC-CO_2, the prominent band at 2924 cm-1 is distinguished by symmetric and asymmetric vibrations of methyl and methylene groups[33]. In the 1633 cm-1 region, it is possible to discern the presence of C=O groups conjugated to an aromatic ring, indicating the formation of carbonyl-containing groups during carbonization and physical activation[31]. The band at 1263 cm-1 can be associated with oxygen-containing functional groups, such as C—O and C=O carboxylic groups, or the in-plane vibration of O-H in the carboxylic group. Conversely, the band at 1021 cm-1 corresponds to the stretching vibration of the C-O group in alcohols, phenols, ethers, or esters[34]. The surface acidity and basicity analysis plays a crucial role in interpreting the surface chemistry of adsorbed materials[35].

The polymeric AC-CO_2 membrane (2.63 mmol/L) and the AC-CO_2 (9.75 mmol/L) exhibited a surface alkalinity. This characteristic is ascribed to groups comprising oxygen on the material's surface, such as carboxylic acids, phenols, and lactonas[35]. It is also associated with a high content of electron-rich sites and a low concentration of electron-withdrawing groups in the basal plane.

The surface charge of polymeric membranes is responsive to pH, resulting in a positive, negative, or neutral charge at specific pH values. The pH at which the net charge on the AC-CO_2 membrane becomes zero is referred to as the zero point of charge (figure 4).
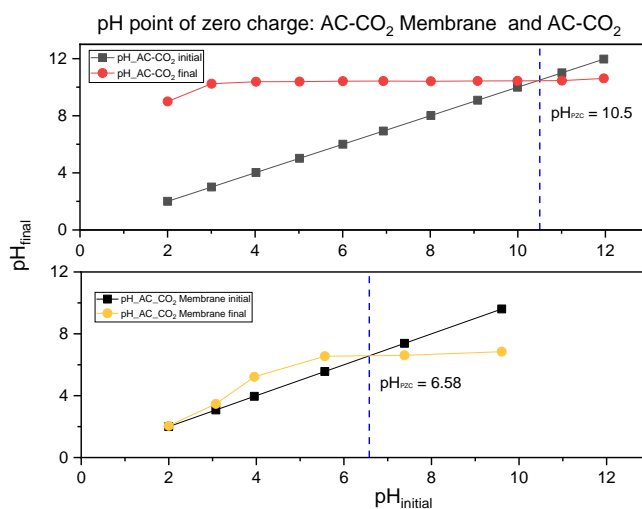
Figure 4. pH_{PZC} of AC-CO$_2$ and AC-CO$_2$ membrane.

Figure 4 illustrates a pH_{PZC} of 6.58 for the AC-CO$_2$ membrane, denoting the particular pH at which the net surface charge nullifies. This finding implies that the AC-CO$_2$ membrane is electrically neutral, displaying a harmonious balance between positive and negative charges[36]. Such information is pivotal for identifying and fine-tuning the membrane's performance in specialized applications, including selective filtration and adsorption[37].

The pH_{PZC} for AC-CO$_2$ was determined to be 10.5, and considering the results obtained from the FTIR analysis, where the presence of alcohols, phenols, ethers, and other compounds with basic characteristics (band at 1021 cm-1), the assigned value of pH_{PZC} is expected, given that this component has basic characteristic [35,38].

The contact angle is a reliable measure of the hydrophilicity and hydrophobicity of a surface, reflecting various wetting situations. For instance, an angle θ of 0° indicates a completely hydrophilic surface, while an angle between 0° < θ < 90° represents a hydrophilic surface. An angle between 90° and 180° signifies a hydrophobic surface, while an angle of 180° indicates an entirely hydrophobic surface. The results obtained from this analysis are presented in table 1.

Table 1. AC-CO$_2$ Contact Angle.

Membrane	Contact Angle	Image
AC-CO$_2$ membrane	56,09±2	

Therefore, since the AC-CO$_2$ membrane exhibited a contact angle below 90º (56.09°), being considered hydrophilic, this result can be attributed to AC-CO$_2$ hydrophilic properties[39]. Activated carbon is known for its ability to interact favorably with water, making surfaces where it is applied more susceptible to wetting by water[40].

Adding AC-CO$_2$ to the membrane can modify its surface properties, increasing the affinity for water and resulting in a lower contact angle, as observed in the value of 56.09. Furthermore, the presence of the PVP polymer in the AC-CO$_2$ membrane matrix contributes to the hydrophilic nature of the membrane.

3.1.1. Phenol Removal through Polymeric Membranes based on activated carbons

The produced AC-CO$_2$ membrane is remarkable for its high mechanical strength and hydrophilic nature, with an intrinsic affinity for aqueous solvents, facilitating the

permeability of water and soluble substances[18]. Furthermore, the AC-CO_2 membrane features suitable active sites for the filtration and adsorption of these pollutants. These characteristics confer practical utility to this material in tackling the targeted pollutant, fostering favorable interactions with the treatment process.

Experiments were conducted with membranes of different thicknesses (150 μm, 200 μm, and 300 μm) to assess the affinity between AC-CO_2 and the polymeric membrane. During these experiments, a solution containing phenol was used as a model contaminant to analyze the interaction between these materials table 2.

Table 2. - Phenol Removal Rate Using Polymeric AC-CO_2 membranes.

Points (min)	150 μm		200 μm		300 μm	
	C (mg/l)	Removal (%)	C (mg/l)	Removal (%)	C (mg/l)	Removal (%)
0	55.96	0	55.33	0	47.41	0
5	24.19	56.78	15.57	71.86	4.57	90.36
15	33.51	40.12	26.68	51.78	34.74	26.73
30	37.83	32.39	36.74	33.61	41.70	12.04
45	40.34	27.90	43.83	20.78	45.30	4.45
60	44.13	21.13	47.18	14.73	47.55	-0.29

Concerning the AC-CO_2 membrane with a thickness of 150 μm, the initial phenol concentration was 55.95 mg/L. In the first 5 minutes, there was a notable reduction of approximately 56.77% in the effluent concentration. Subsequently, a gradual decline in removal efficiency occurred over time, with a tendency to stabilize after 45 minutes of analysis, maintaining approximately 20% removal. This suggests membrane saturation.

The 200 μm AC-CO_2 membrane exhibited an impressive removal rate of 71.86% within 5 minutes of analysis. It continued to effectively eliminate the pollutant over time, displaying higher efficiency than the 150 μm membrane, as highlighted in Table 1. This superior performance indicates a substantial improvement in pollutant adsorption, attributed to the increased contact area between the AC-CO_2 membrane and the permeated stream[41].

Upon evaluation of the 300 μm membrane, a remarkable removal rate of 90.36% was observed in the initial 5 minutes. However, its efficiency gradually declined throughout the analysis due to rapid saturation from the intense initial removal of pollutants[42,43]. This decline is visually depicted in figure 5, clearly illustrating the efficacy of the three membranes in phenol removal.
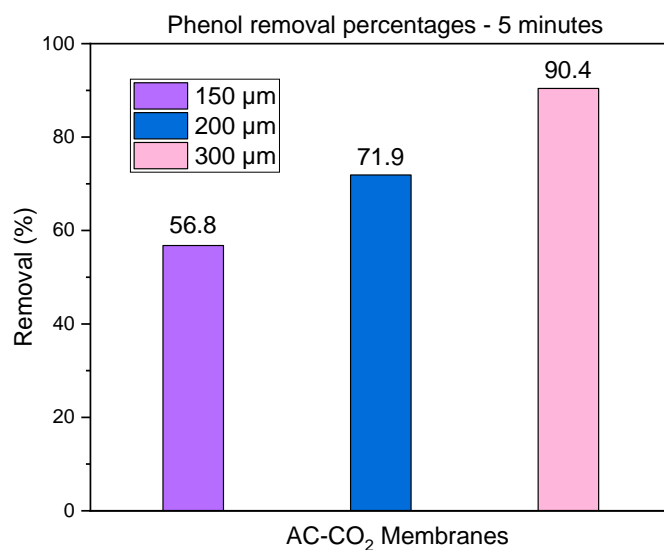
Figure 5. Phenol Removal Using Polymeric Membrane.

Considering all three membranes collectively, the 200 μm AC-CO_2 membrane demonstrated superior efficiency over time, attributed to its larger contact area. It surpassed the performance of the 150 μm AC-CO_2 membrane and fell slightly below that of the 300 μm membrane. By the conclusion of the analysis, the 200 μm AC-CO_2 membrane achieved a significant removal of pollutants, outperforming the other membranes in this regard.

4. Conclusion

The composite polymeric AC-CO_2 membranes have shown promising results, with the incorporation of AC-CO_2 proving to enhance the adsorption of phenolic compounds, using phenol as the model pollutant. In summary, the FTIR analysis highlighted the incorporation of AC-CO_2 into the AC-CO_2 membrane, revealing characteristic peaks indicative of carbonyl-containing groups and various functional groups associated with activated carbon.

The surface analysis indicated a alkalinity of 2.63 mmol/L for the polymeric AC-CO_2 membrane, while AC-CO_2 displayed a 9.75 mmol/. These features are attributed to oxygen-containing groups and electron-rich sites on the material's surface.

The investigation into surface charge revealed a *pH_{PZC}* of 6.58 for the AC-CO_2 membrane, indicating electrical neutrality and a balanced distribution of positive and negative charges, crucial for tailoring the membrane's performance in specific applications.

The contact angle analysis demonstrated the hydrophilic nature of the AC-CO_2 membrane (56.09°), enhanced by the presence of the PVP polymer, making the AC-CO_2 membrane more susceptible to wetting by water.

Finally, the comparative analysis of membranes with different thicknesses showed that the 200 μm AC-CO_2 membrane outperformed in phenol removal, emphasizing the critical role of AC-CO_2 membrane thickness in influencing pollutant removal and the need to optimize contact areas for enhanced treatment efficacy.

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