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Research Paper

Eco-Friendly Antifouling Membranes from Cigarette Filters Modified with Tannic Acid and Ferric Chloride for Oil Emulsion Separation

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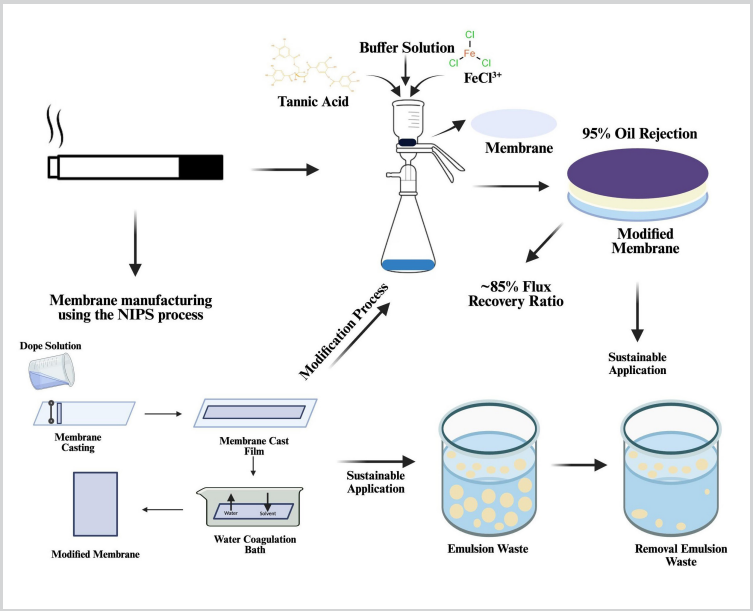
Keywords

Oil-in-water emulsion
Cigarette filter membrane
Tannic acid
Antifouling modification
Wastewater treatment
Ferric chloride
Green membrane technology

Highlights

- A green membrane was developed using cigarette filter waste and modified with tannic acid and ferric chloride through vacuum-assisted coating.
- Surface modification significantly enhanced hydrophilicity, reducing water contact angle from 62.5° to 58.3°.
- Modified membranes exhibited high oil rejection efficiency (>95%) and excellent antifouling performance across various oil-in-water emulsions.
- Flux recovery ratio (FRR) reached up to 85.1%, indicating strong resistance to irreversible fouling.
- Statistical analysis confirmed pesticide emulsions caused the highest total fouling, while used oil emulsions were the hardest to clean.
- The integration of waste valorization and bio-based additives supports circular economy and sustainable wastewater treatment strategies.

Graphical abstract



Abstract

Emulsified mixtures of oil and water frequently originate from industrial, agricultural, and automotive sources, representing a major environmental concern. This study develops an eco-friendly, low-cost membrane solution using cigarette filter waste as a base material, enhanced with surface modifications using tannic acid and ferric chloride. Membranes were fabricated through the non-solvent-induced phase separation technique and modified via vacuum-assisted coating. Characterization demonstrated that the modified membrane had improved hydrophilicity, indicated by lower water contact angles and increased resistance to irreversible fouling. The surface-modified membranes demonstrated greater hydrophilicity and superior oil rejection efficiency exceeding 95% across all emulsion types and exhibited excellent antifouling properties, with flux recovery ratios of up to 85%. SEM, EDS, and FTIR analyses confirmed the formation of hydrophilic metal–polyphenol coordination layers on the membrane surface. Unlike our earlier work, which mainly reported the fabrication and preliminary performance of cigarette filter-based membranes, this study extends the investigation to multiple wastewater types (industrial, agricultural, and automotive) and introduces statistical analysis of fouling behavior to validate membrane versatility and sustainability potential. These enhancements resulted in improved separation efficiency and extended operational longevity. The bio-modified, waste-derived membrane offers a sustainable and competitive solution, emphasizing the integration of waste valorization and green surface chemistry toward advanced antifouling membrane technologies.

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1. Introduction

The widespread occurrence of oil–water emulsions in industrial as well as household effluents has become a serious issue for environmental sustainability. These emulsions originate from numerous sources, including oil spills, petrochemical discharges, food and metal processing industries, agricultural runoff, automobile maintenance facilities, and household wastewater [1]. Collectively, these sectors contribute large volumes of oily wastewater containing dispersed and stabilized oil droplets, often stabilized by surfactants, which significantly hinder separation processes [2]. Their persistence in aqueous environments leads to the contamination of freshwater resources, which adversely affects both aquatic ecosystems and human health. The persistent stability of emulsified oil droplets and the inefficiency of traditional separation techniques highlight the pressing need for advanced treatment methods to manage these complex wastewater systems. Efficient removal of these emulsions is not only essential for environmental protection but also for the recovery of clean water for reuse, particularly in regions experiencing water scarcity or intensive industrial activities [3].

These oil emulsions, whether originating from household kitchen waste, vehicle repair and washing stations, agrochemical applications, or industrial effluents, pose similar challenges due to the presence of finely dispersed oil droplets with high stability [4]. The widespread occurrence of these emulsions across diverse sectors intensifies the need for universally adaptable treatment technologies. Traditional approaches such as coagulation–flocculation, adsorption, and biological treatments are commonly employed; nevertheless, their effectiveness is limited when dealing with wastewater that contains persistent oil emulsions [3]. Coagulation is often ineffective against submicron oil droplets, especially when surfactants are present, while adsorption methods, though effective for certain types of oils, frequently suffer from limited adsorption capacity and the generation of secondary waste [5]. Biological treatments may degrade organic pollutants, but can be inhibited by oil toxicity or high surfactant concentrations [6]. As such, these conventional processes are frequently constrained by low efficiency, operational instability, and maintenance costs, particularly when applied to wastewater from household, automotive, agricultural, or industrial origins [7].

In contrast, membrane-based separation technologies provide a promising alternative, offering high oil rejection efficiencies and operational flexibility. By employing size exclusion and selective permeability, membranes can separate emulsified oil droplets without the need for chemical destabilization. Their modularity and compatibility with existing treatment infrastructures further enhance their attractiveness for large-scale application in mixed-source wastewater treatment [8]. Recent developments in membrane surface engineering especially those utilizing superhydrophilic and underwater superoleophobic surfaces have significantly improved membrane resistance to fouling while maintaining high flux rates [9]. These advanced membranes are highly adaptable, allowing optimization for various feed compositions, including emulsions from domestic greywater, automotive wash-off, agro-industrial drainage, and oily industrial discharge [10].

Cellulose acetate (CA) has traditionally been employed as a polymer matrix for membrane fabrication due to its favorable hydrophilicity, ease of processing, and biodegradability. The tunable nature of its porous structure, combined with its compatibility with various chemical modifications, makes it an ideal candidate for oil-water separation membranes [11]. Cellulose acetate (CA) membranes enhanced with nanomaterials or functional additives have shown superior mechanical strength, better filtration efficiency, and enhanced resistance to fouling, rendering them promising candidates for oily wastewater treatment in multiple industrial applications [12].

In recent years, researchers have turned to alternative and sustainable sources of cellulose acetate, particularly waste cigarette filters, which are mainly composed of CA fibers. Cigarette butt waste is one of the most ubiquitous forms of litter worldwide, contributing significantly to urban and aquatic pollution. Repurposing this waste into membrane material aligns with the principles of circular economy and green engineering by transforming an environmental pollutant into a high-value filtration medium [13], [14]. Nevertheless, processing cigarette filters into usable membranes poses challenges related to contaminant removal, reproducibility, and mechanical performance of the resulting materials.

To improve the applicability of cigarette filter-derived membranes in large-scale application, implementation of antifouling strategies are essential. Bio-based surface modification using polyphenols such as tannic acid, combined with ferric chloride ($FeCl_3$), has proven to be an effective approach. These compounds form metal–phenol coordination layers that increase surface hydrophilicity and inhibit the adhesion of hydrophobic oil droplets and organic foulants [15]. Membranes coated with tannic acid–Fe complexes have shown higher flux recovery ratios and longer operational stability compared to unmodified variants, making them ideal for continuous treatment of oil-emulsified wastewater from diverse sources [16].

Several studies have demonstrated the potential of tannic acid and Fe-based coatings to enhance membrane surfaces by introducing hydroxyl and metal-complex groups that act as a barrier against irreversible fouling. However, such antibacterial and hydrophilicity with the use of tannic acid (TA) and iron ions (Fe^{3+}) as multifunctional coating agents is a cutting-edge strategy for surface modification of ultrafiltration membranes [17].

Furthermore, studies that apply these techniques across a broad spectrum of wastewater sources, including domestic, automotive, agricultural, and industrial remain rare, despite the urgent demand for such comprehensive treatment solutions. In contrast to our preceding publication [15], which mainly focused on membrane fabrication and initial antifouling observations, the present work significantly extends the research scope. It evaluates the membrane's performance against diverse oily wastewater sources, applies quantitative statistical analyses (ANOVA and Tukey HSD) to assess fouling mechanisms, and discusses the broader sustainability and circular economy implications. These additions collectively establish the distinct novelty and broader impact of this study.

The present study addresses these gaps by developing membranes fabricated from waste cigarette filters and enhancing them through surface coating with tannic acid and $FeCl_3$. The study specifically targets the purification of oil-contaminated wastewater derived from a wide range of human activities, including household greywater, vehicle washing effluents, agricultural runoff, and industrial oil-laden waste streams. By evaluating the physicochemical properties, permeability, selectivity, and antifouling behavior of these modified membranes, the study aims to demonstrate a sustainable, low-cost solution suitable for diverse emulsion separation applications. The distinctive contribution of this study is integration of waste-derived polymeric materials and environmentally benign antifouling agents to create membranes that are not only effective across various wastewater categories but also aligned in accordance with green chemistry concepts and the circular economy. The scope includes membrane fabrication through the non-solvent-induced phase inversion technique, surface functionalization using a vacuum-assisted coating process, and performance testing under simulated oily wastewater conditions that reflect of real-world contamination scenarios. Through this research, this study adds to the progress of antifouling membrane technology tailored for broad-spectrum wastewater treatment.

2. Methodology

This study focused on developing and evaluating antifouling membranes made from cigarette filter waste, both with and without modifications using tannic acid and ferric chloride ($FeCl_3$). The membranes were designed for separating oil-in-water emulsions from industrial, agricultural, and automotive wastewater. Two types of membranes were examined: M0, the unmodified version, and M1, the modified version treated with tannic acid and $FeCl_3$. Membrane formation employed the non-solvent-induced phase separation (NIPS) approach to achieve phase inversion, while the surface modification employed a vacuum-assisted coating method, as established in prior research (Luthfiana et al., 2025) Characterization and performance evaluation included analyses of morphology, structure, hydrophilicity, porosity, and antifouling properties. The separation efficiency of each membrane was tested against three types of emulsions that simulate real-world oily wastewater conditions.

2.1. Materials and Reagents

The primary raw material used was cigarette butt filters (CBFs), which consist of 97% cellulose acetate. Dimethylacetamide (DMAc, ≥99%) served as the solvent to dissolve the cellulose acetate from the filters. Tannic acid ($C_{76}H_{52}O_{46}$, analytical grade) and ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) were used as bio-based antifouling additives in the surface coating process. Additional reagents included Tris chloride and sodium hydrogen phosphate ($Na_2HPO_4 \cdot 2H_2O$) as buffering agents to stabilize the additive solution.

For the oil emulsion test, three artificial emulsions were created to represent oily wastewater from industrial, agricultural, and automotive sources. Refined palm oil simulated industrial waste, pesticides represented agricultural runoff, and used engine oil was selected to model automotive waste. Each emulsion contained sodium dodecyl sulfate (SDS) at a concentration of 0.15% to enhance stability.

2.2. Membrane Fabrication via Non-Solvent Induced Phase Separation (NIPS)

The process of membrane preparation utilized a refined NIPS protocol like Fig. 1, commonly employed for creating porous cellulose acetate membranes with adjustable separation properties. Cigarette butt filter (CBF) were dissolved in DMAc to create a 15% (w/w) polymer solution. This solution was continuously continuously mixed at ambient temperature for 24 hours to achieve full dissolution. Following one hour of degassing to eliminate entrapped air, the polymer solution was spread on a clean glass substrate using a casting knife adjusted to a specific gap that determined the final membrane thickness.

Immediately following casting, the membrane film was immersed in a coagulation bath of distilled water at room temperature. This immersion initiated solvent-nonsolvent exchange, resulting in phase separation and the formation of a porous asymmetric membrane structure. The membrane was then thoroughly washed in distilled water to eliminate any residual solvent and stored in water at room temperature prior to modification.

Two membrane configurations were evaluated: M0 (unmodified cigarette filter membrane) and M1 (modified with tannic acid and $FeCl_3$). Both configurations underwent the same fabrication processes but differed in surface treatment. Their performance was tested against three types of oil-in-water emulsions, simulating wastewater compositions from industrial, agricultural, and automotive sources. This evaluation framework facilitated a thorough investigation of membrane behavior across various practical applications.

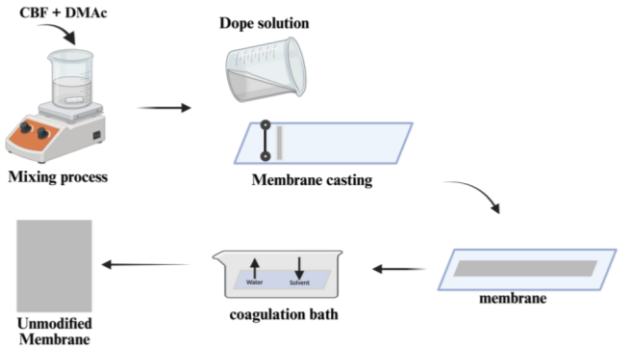


Fig. 1. Mechanism membrane Fabrication via Non-Solvent Induced Phase Separation (NIPS).

Table 1
Membrane Composition and Modification Status.

Membrane Code	Cigarette Filter (%)	Tannic (mmol)	Acid	$FeCl_3$ (mmol)
M0	15	0.0		0.0
M1	15	2.4		3.7

This methodological framework combines established membrane fabrication techniques with environmentally friendly surface modifications, assessing the resulting materials under conditions that mimic real-world oily wastewater challenges. The application of the non-solvent-induced phase inversion (NIPS) method combined with vacuum-assisted surface coating presents a sustainable approach to developing high-performance membranes for complex emulsion separation tasks.

2.3. Surface Modification via Vacuum-Assisted Coating

M1 membrane was modified using vacuum-assisted coating with tannic acid and $FeCl_3$ shown Fig. 2, chosen for its effectiveness in evenly applying antifouling layers to porous supports. A coating solution was prepared, comprising 2.4 mmol tannic acid and 3.7 mmol ferric chloride within a buffered solution of Tris-chloride and Na_2HPO_4 to ensure a stable pH. The membranes were placed in a vacuum filtration apparatus, and 25 mL of the coating solution was applied to each surface. The vacuum pump was activated to draw the solution through the membrane, promoting the adherence of additive molecules and forming a bio-coating through Fe^{3+}–tannic acid coordination complexes. This modification aimed to enhance hydrophilicity and reduce organic fouling by utilizing the antioxidant and complex-forming properties of tannic acid.

2.4. Characterization of Membrane Properties

2.4.1. Morphological Analysis and Elemental Composition (EDS)

The surface and cross-sectional structures of the M0 and M1 membranes were examined through scanning electron microscopy (SEM, JEOL JSM-7500). Samples were freeze-fractured in liquid nitrogen to obtain clean cross-sections and were then sputter-coated with a thin layer of Au–Pd to improve conductivity. SEM images allowed for the evaluation of surface pore distribution and the effects of additive coating on membrane topography. Energy-dispersive X-ray spectroscopy (EDS) was conducted alongside SEM to identify elemental differences between the unmodified and modified membranes, specifically detecting iron (Fe) and chlorine (Cl).

2.4.2. Functional Group Identification

Attenuated total reflectance Fourier-transform infrared (ATR-FTIR) spectroscopy (PerkinElmer) was used to identify chemical functionalities on the membrane surfaces. The spectral data were collected within the wavenumber range of 650 to 4000 cm^{-1}.

2.4.3. Water Contact Angle

The hydrophilicity of the membrane surfaces was measured using static water contact angle (WCA) assessments with a goniometer (DropMaster 300, Tokyo, Japan). A 5 µL droplet of deionized water was placed on the membrane surface, and the angle between the droplet and the surface was measured. Lower angles indicated greater hydrophilicity and improved resistance to fouling.

2.5. Performance Evaluation

2.5.1. Pure Water Flux (PWF)

PWF was measured using a cross-flow membrane module at a transmembrane pressure of 1 bar and a temperature of 25 °C, with deionized water as the feed. Permeate samples were collected every 10 minutes for a total duration of 60 minutes. The flux (J) was calculated as the volume of water per unit area per time. This baseline test evaluated the impact of the antifouling coating on water transport properties.

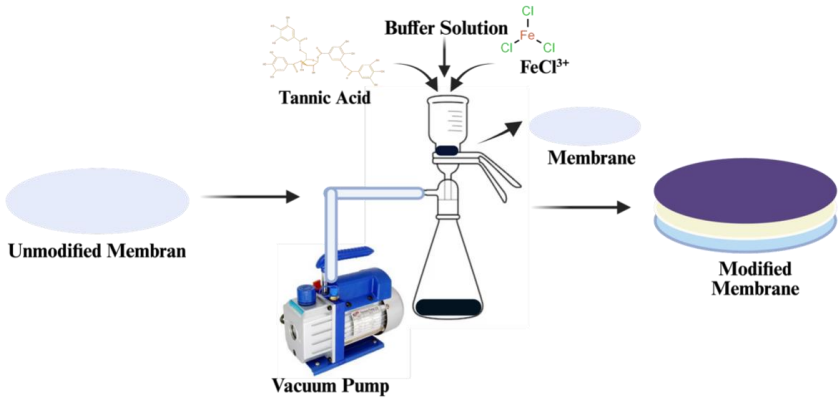


Fig. 2. Mechanism Surface Modification Via Vacuum Filtration.

2.5.2. Oil Emulsion Filtration and Selectivity

Three emulsions were prepared using distilled water and sodium dodecyl sulfate (SDS), consisting of crude palm oil (representing industrial and agricultural applications) and used motor oil (representing automotive applications). After 2 hours of vigorous stirring, the emulsions were filtered through the membranes. The oil concentration in the permeate was analyzed using UV–Vis spectrophotometry (Shimadzu UV-1700) at specified wavelengths. The rejection rate (R%) was calculated as the difference in oil concentration between the feed and permeate, providing insights into membrane effectiveness across different emulsion types.

2.5.3. Antifouling Performance

Antifouling behavior was assessed through a three-stage flux measurement: (1) initial PWF (Jwi), (2) flux during emulsion filtration (Jha), and (3) PWF after backwashing (Jwi+1). Membranes underwent backwashing with deionized water for 10 minutes between stages. The flux recovery ratio (FRR) and fouling indices (total, reversible, irreversible) were calculated using standardized equations. Higher FRR values indicated improved fouling reversibility and surface resilience.

3. Results

3.1. Membrane Characterization

3.1.1. Membrane Morphological Structure

The SEM analysis Fig. 3 shows significant differences in surface morphology between unmodified (M0) and modified (M1) membranes. M0 has irregular, widely distributed pores, while M1 features a smoother, more uniform surface with finer, denser pore structures. These differences align with previous findings that surface morphology significantly impacts separation performance in oil-water systems by affecting wettability and fouling resistance [18] . The application of tannic acid and $FeCl_3$ via vacuum-assisted coating created a cross-linked surface layer, reducing surface defects and enhancing water affinity [19].

Complementary EDS spectra Fig. 4 confirmed the elemental differences between M0 and M1. M0 primarily exhibited peaks for carbon and oxygen, while M1 displayed additional signals for iron (Fe) and chlorine (Cl), indicating the successful incorporation of $FeCl_3$ into the membrane matrix. This supports previous findings that the coordination complex between Fe^{3+} ions and phenolic groups in tannic acid improves membrane structure and chemistry [20].

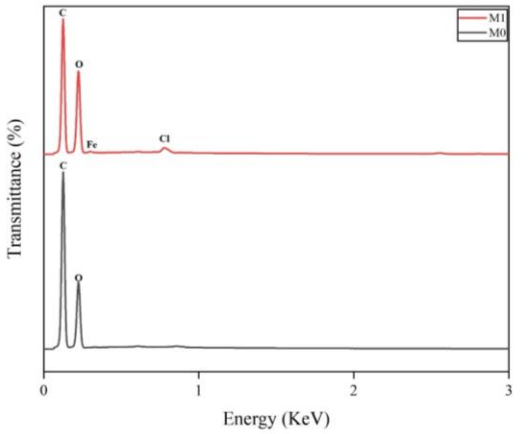


Fig. 4. EDS spectra of M0 (unmodified) and M1 (modified) membranes.

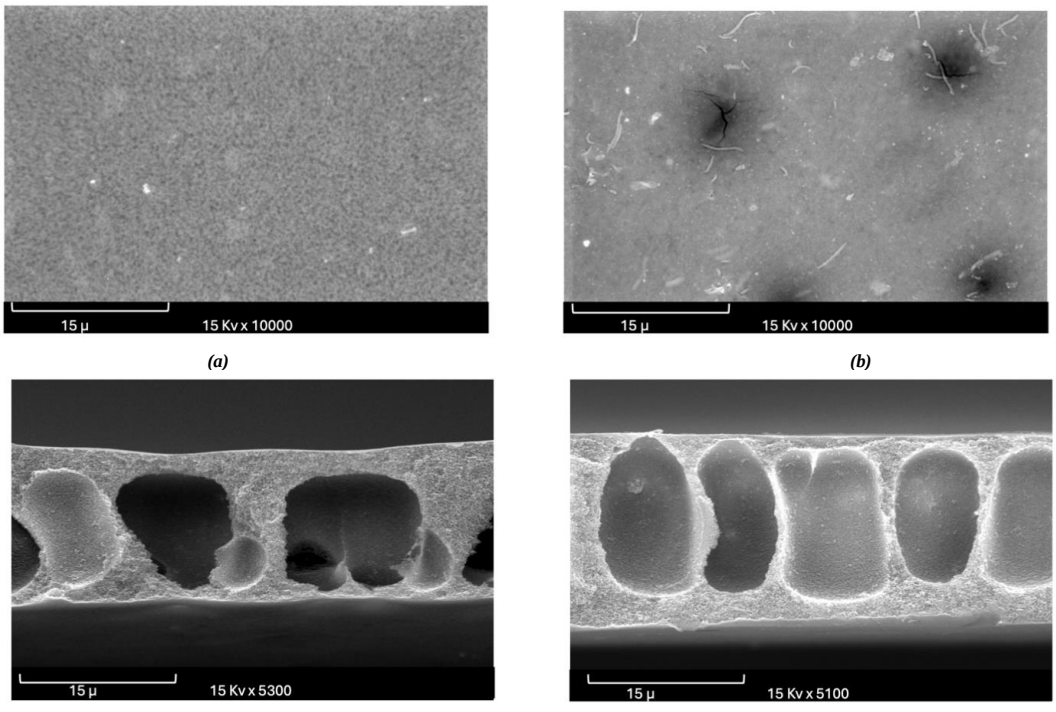


Fig. 3. SEM micrographs and EDS spectra of M0 (unmodified) and M1 (modified) membranes (a) surface of M0 Membrane (b) Surface of M1 Membrane (c) Cross-section Of M0 Membrane (d) Cross-section Of M1 Membrane.

Table 2
Chemical elemental composition of the membrane surface.

Membrane code	Atomic Weight C	O	Cl	Fe
M0	63.658	36.342	0.00	0.00
M1	57.842	41.321	0.237	0.601

3.1.2. Functional Group Analysis of the Membranes

FTIR spectra in Fig. 5 confirm the successful modification of the membranes. Both M0 and M1 displayed characteristic peaks of cellulose acetate: C=O at approximately 1750 cm^{-1}, C–O at around 1220 cm^{-1}, and C–O–C at about 1050 cm^{-1}. In M1, new peaks emerged between 1500–1600 cm^{-1} (C=C from aromatic rings) and 580–600 cm^{-1} (Fe–O stretching), indicating the presence of tannic acid and $FeCl_3$. These findings support the model of molecular interactions where TA and Fe^{3+} ions form chelate complexes on the membrane surface [15].

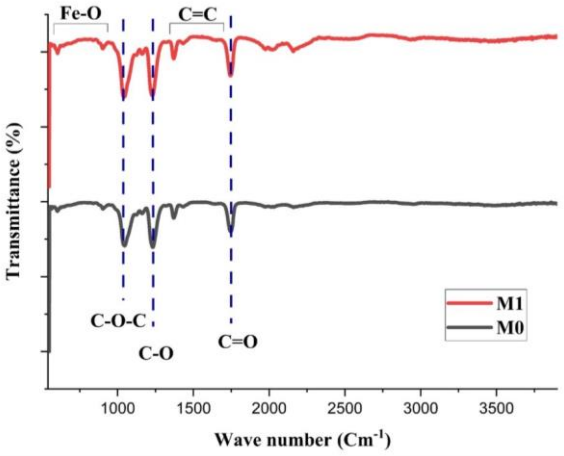


Fig. 5. FTIR spectra of M0 (unmodified) and M1 (modified) membranes showing functional groups.

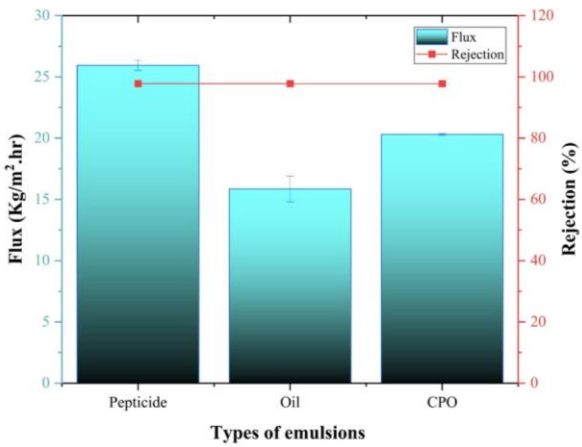


Fig. 7. Flux and oil rejection (%) of M1 (modified) membrane across different emulsion types.

3.1.3. Hydrophilicity of the Membranes

Water contact angle data in Fig. 6 showed a decrease when comparing M0 and M1 with the corresponding values of 62.5 ± 0.8° and 58.3 ± 0.6° respectively. This minor yet significant as proven from analysis of variance reduction demonstrates increased surface hydrophilicity due to the introduction of hydroxyl-rich tannic acid and Fe^{3+} complexation [21]. As established in earlier works, enhanced hydrophilicity facilitates greater water flux and reduces membrane fouling propensity [22].

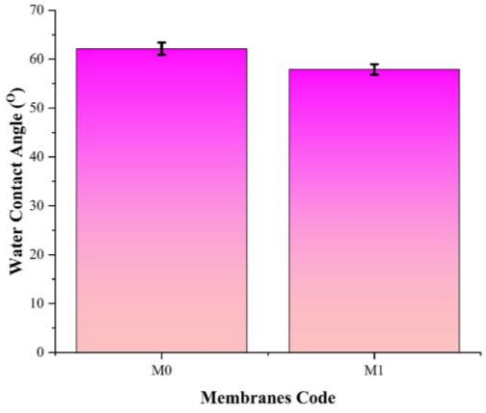


Fig. 6. Water contact angle values of M0 (unmodified) and M1(modified) membranes.

3.1.5. Water Flux and Oil Rejection Performance

The Fig. 7 presents the membrane performance results for three emulsion types: pesticide, used oil, and crude palm oil (CPO). Among the tested samples, M1 demonstrated superior water permeability, achieving 26.5 kg/m²·h for the pesticide emulsion and 20.3 kg/m²·h for CPO. The used oil emulsion had a lower flux of approximately 15.6 kg/m²·h, primarily due to its higher viscosity and tendency to foul. M1 also demonstrated consistently high oil rejection rates, exceeding 95% for all emulsion types. This suggests that although surface modification slightly reduced porosity, it created a selective layer that enhanced rejection efficiency. These findings align with previous studies indicating that tannic acid–Fe coatings can improve flux while maintaining oil rejection rates above 90% [15].

3.2. Membrane Performance

3.2.1. Antifouling Performance: Flux Recovery Ratio

Fig. 8 presents the FRR values for the M1 membrane. The M1 membrane demonstrated excellent antifouling performance, achieving FRR values of 85.1% for CPO emulsion, 77.4% for pesticide, and 60.8% for used oil. These results significantly exceed the recovery rates of standard cellulose acetate membranes, indicating that the hydrophilic surface layer of the M1 membrane effectively prevents irreversible foulant adhesion [23].

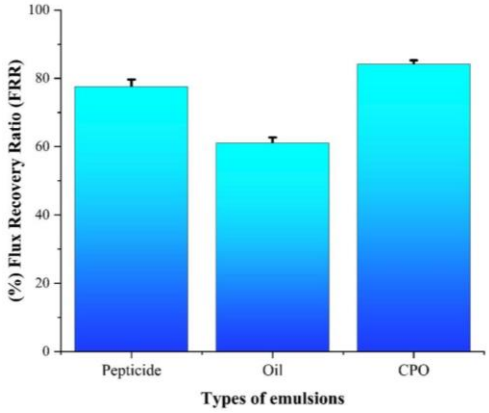


Fig. 8. Flux recovery ratio of M1 (modified) membrane for various emulsion types.

3.2.2. Reversible and Irreversible Fouling Ratios

Collectively, Fig. 9 shows the fouling partitioning into reversible (RR) and irreversible (RIR) components. M1 exhibited a dominant RR component for pesticide emulsion at approximately 54%, followed by CPO at around 47% and used oil at about 32%. The lower RIR values indicate that most fouling was weakly bound and could be removed through simple backwashing. These results are consistent with literature suggesting that hydrophilic, bio-modified membranes are less prone to irreversible fouling [23].

These results confirm the effectiveness of cigarette filter-based membranes functionalized with tannic acid and ferric chloride to effectively separate oil emulsions from various wastewater sources. The combination of waste-derived membrane materials and eco-friendly antifouling coatings paves the way for sustainable wastewater treatment technologies.

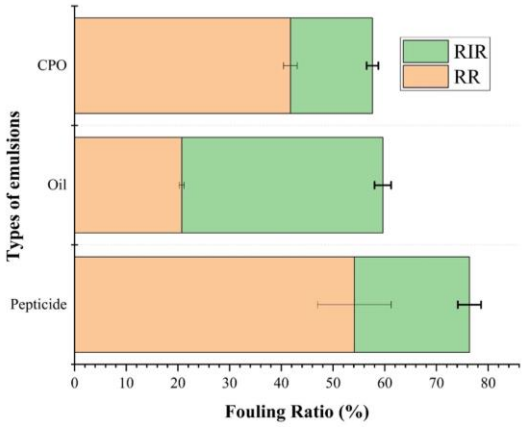


Fig. 9. Reversible (RR) and irreversible (RIR) fouling ratios of M1 (modified) membranes across emulsion types.

4. Discussion

It is important to note that the valorization of cigarette filter waste in this study does not aim to incentivize tobacco consumption. Instead, it represents an environmental remediation approach by converting an already existing, hazardous, and non-biodegradable waste into a functional material. This approach is consistent with the concepts of a circular economy and environmental responsibility by mitigating pollution rather than promoting cigarette production or use.

The results of this study highlight the significant impact of surface modification and base material on membrane performance, particularly in the separation of oil-in-water emulsions in wastewater from industrial, agricultural, and automotive sectors. The incorporation of bio-derived additives, namely tannic acid and ferric chloride, is crucial for enhancing surface morphology, chemical composition, and hydrophilicity, which together improve separation efficiency and fouling resistance [24].

The SEM and EDS analyses results Fig. 3 showed that the vacuum-assisted deposition of tannic acid and $FeCl_3$ created a dense, uniform surface layer on the M1 (modified) membrane, which was not present on the unmodified M0 membrane. This finding supports the notion that membrane surface morphology directly influences filtration efficiency [25], noted that smoother and more uniformly coated surfaces reduce oil droplet adhesion by minimizing crevices that can trap contaminants. The presence of iron and chlorine peaks in the EDS spectrum confirmed the successful incorporation of $FeCl_3$, which is essential for forming Fe-phenol complexes with tannic acid, thereby strengthening the antifouling layer [24].

The Fourier Transform Infrared (FTIR) spectra shown in Fig. 5 offered additional structural evidence, showing spectral shifts that indicate successful chemical bonding. The Fe-O and aromatic C=C peaks observed in M1, absent in M0, confirm the interaction between tannic acid and $FeCl_3$ [26]. This supports the antifouling mechanism proposed in previous studies, wherein phenolic compounds establish a chelating network with metal ions, enhancing surface hydrophilicity and reducing foulant adhesion [27]. This characteristic is vital to the separation process, as it not only enhances water permeation but also discourages oil adhesion [28].

The long-term stability of the tannic acid-Fe^{3+} (TA-Fe) coordination layer depends on both chemical and mechanical resilience under continuous operation. Chemically, Fe-phenolic complexes remain stable in neutral to mildly acidic environments (pH 5-7) but may degrade under alkaline or oxidative conditions, leading to partial Fe oxidation or hydrolysis of phenolic bonds that reduce surface hydrophilicity [17]. Mechanically, shear stress from crossflow operation and transmembrane pressures up to 2 bar can induce micro-delamination, especially in areas of non-uniform coating thickness, making adhesion strength to the cellulose acetate substrate critical for long-term durability [27]. In real wastewater containing surfactants, salts, and suspended solids, these foulants can compress or abrade the TA-Fe layer, accelerating surface wear. To maintain structural integrity, non-oxidative and mild-pH cleaning solutions are recommended to minimize degradation of both the TA-Fe layer and the cellulose acetate support (Wu et al., 2019). Durability can be assessed by monitoring water contact angle stability, Fe-O stretching bands at 580-600 cm^{-1} in FTIR spectra, Fe signal retention in EDS, and flux recovery ratio (FRR) constancy during repeated operation [27] [22]. These observations provide a practical and evidence-based framework for evaluating the coating's robustness under dynamic wastewater treatment conditions.

Performance data Fig. 7 demonstrated that M1 outperformed M0 in terms of flux and oil rejection across all tested emulsions. The highest flux was observed for the pesticide emulsion, followed by crude palm oil (CPO) and used oil, a trend likely influenced by variations in oil viscosity and droplet size. These results align with previous research showing that surface-modified membranes with tannic and ferric chloride exhibit no significant difference in performance [15].

To evaluate the effect of emulsion type on membrane fouling behavior, a one-way ANOVA was performed, followed by Tukey's HSD post hoc analysis for two key performance indicators: RT and FRR.

The ANOVA results for RT indicated a statistically significant difference among the three emulsion types ($F = 25.29$, $p = 0.0132$). The subsequent Tukey test revealed that the pesticide emulsion resulted in significantly higher total fouling compared to both CPO and used oil emulsions. The mean RT for the pesticide emulsion (78.38%) was notably higher than that for CPO (57.61%) and used oil (59.64%), with differences exceeding the HSD threshold of 10.25%. However, the difference between CPO and used oil was not statistically significant. These results indicate that emulsions from pesticide runoff present a greater fouling challenge, likely due to their surfactant content or fine colloidal particles that adhere more strongly to the membrane surface [29].

Table 3
Analysis of Variance (Anova) of Total Fouling Ratio (RT) on the emulsion variation.

Groups	Count	Sum	Average	Variance
CPO	2	115.22127	57.610635	12.0944932
Pepticide	2	156.752008	78.376004	16.5197058
Oil	2	119.27362	59.63681	2.48537972

Table 4
Results of One-Way ANOVA on Total Fouling Ratio (RT).

Source Of Variation	Sum Of Square (SS)	df	Mean Square (MS)	F Value	P Value	
Between Groups	524.308885	2	262.154443	25.2885525	0.01324991	Significant
Within Groups	31.0995787	3	10.3665262			

Table 5
Tukey HSD Table for Total Fouling Ratio (RT).

Group 1	Group 2	Mean Group 1	Mean Group 2	Difference	HSD Threshold	Significant (Yes/No)
CPO	Pesticide	57.6106	78.376	20.7654	10.2466	Yes
CPO	Oil	57.6106	59.6368	2.0262	10.2466	No
Pepticide	Oil	78.376	59.6368	18.7392	10.2466	Yes

Table 6
Analysis of Variance (Anova) of Flux Recovery Ratio (FRR) on the emulsion variation.

Groups	Count	Sum	Average	Variance
CPO	2	168.280513	84.1402567	2.60434878
Pepticide	2	155.170058	77.5850289	8.67795197
Oil	2	122.192639	61.0963196	5.10313966

Table 7
Results of One-Way ANOVA on Flux Recovery Ratio (FRR).

Source Of Variation	Sum Of Square (SS)	df	Mean Square (MS)	F Value	P Value	
Between Groups	563.914392	2	281.957196	51.623366	0.0047447	
Within Groups	16.3854404	3	5.46181347			Significant

Table 8
Tukey HSD Table for Flux Recovery Ratio (FRR).

Group 1	Group 2	Mean Group 1	Mean Group 2	Difference	HSD Threshold	Significant (Yes/No)
CPO	Pepticide	84.1403	77.585	6.5552	7.4375	No
CPO	Oil	84.1403	61.0963	23.0439	7.4375	Yes
Pepticide	Oil	77.585	61.0963	16.4887	7.4375	Yes

The ANOVA analysis for the flux recovery ratio (FRR) indicated significant differences between groups ($F = 51.62$, $p = 0.0047$). Tukey's HSD test showed that both crude palm oil (CPO) and pesticide emulsions resulted in significantly higher FRR values compared to used oil, indicating better fouling reversibility. Specifically, FRR values were 84.14% for CPO and 77.59% for pesticide emulsions, both significantly greater than the 61.10% for used oil, with mean differences exceeding the HSD threshold of 7.44%. However, the difference between CPO and pesticide emulsions was not statistically significant. These results suggest that used oil creates more persistent foulant layers, likely due to its high viscosity and complex hydrocarbon structure, which reduces the membrane's flux recovery even after cleaning [30].

The statistical analyses of both the total fouling ratio (RT) and FRR clarify the membrane's fouling behavior under different oily emulsion conditions. The pesticide emulsion had the highest total fouling (RT = 78.38%), significantly greater than both CPO (RT = 57.61%) and used oil (RT = 59.64%). This indicates that the pesticide emulsion, likely containing surfactants and hydrophilic-hydrophobic complexes, promotes extensive foulant deposition on the membrane surface [29].

In contrast, the lowest FRR was observed for the used oil emulsion (FRR = 61.10%), significantly lower than CPO (84.14%) and pesticide emulsion (77.59%). This suggests that while used oil does not cause the highest total fouling, it forms a more persistent and less reversible fouling layer, making removal more challenging even after hydraulic cleaning. Conversely, CPO resulted in the lowest RT and the highest FRR, indicating it is the least severe in terms of both fouling intensity and reversibility [31].

The pesticide emulsion poses the most significant issue regarding overall fouling accumulation, while used oil presents the greatest challenge for membrane cleaning and recovery. These findings highlight the importance of developing tailored antifouling strategies based on total fouling loads and the degree of fouling reversibility for different wastewater types.

Optimization of coating thickness and uniformity plays a critical role in balancing antifouling performance and permeability. A higher Fe^{3+}: tannic acid ratio or longer coating duration produces denser hydrophilic layers that enhance fouling resistance but may slightly reduce flux due to increased hydraulic resistance. Conversely, thinner or non-uniform coatings may preserve higher permeability but can develop localized fouling or delamination. Therefore, precise control of coating parameters including Fe^{3+}: TA ratio, vacuum pressure, and deposition time is essential to achieve an optimal balance between selectivity and flux [22]. Moreover, the vacuum-assisted coating technique adopted in this study is scalable for large-area membrane production because it is solvent-free, energy-efficient, and suitable for continuous roll-to-roll processing, offering a sustainable pathway toward industrial fabrication [32].

Although the modified membrane exhibited consistent antifouling behavior across various wastewater emulsions, achieving a universal one-size-fits-all configuration remains challenging. The observed differences in fouling intensity and reversibility indicate that membrane performance is highly dependent on oil composition, surfactant type, and fluid viscosity. Such variations can be more effectively managed by adjusting structural parameters such as the Fe^{3+}-tannic acid (TA) ratio and pore-size distribution, which influence the compactness of the metal-phenolic layer, hydrophilicity, and overall selectivity. Understanding these interdependencies is essential for achieving balanced permeability and fouling resistance suitable for specific wastewater types.

5. Conclusion

This study successfully demonstrated the fabrication and surface modification of cellulose acetate membranes derived from cigarette filters using tannic acid and ferric chloride. The modified membrane exhibited improved hydrophilicity, strong antifouling resistance, and oil rejection exceeding 95% across industrial, agricultural, and automotive wastewater emulsions. SEM, EDS, and FTIR analyses confirmed the formation of a hydrophilic metal-phenolic coordination layer that enhanced surface wettability and fouling reversibility. The results verified that cigarette filter waste can be effectively upcycled into functional membrane materials, contributing to both environmental remediation and circular economy principles.

While the present work establishes a strong proof of concept, the broader sustainability and practical viability of this approach require further contextual consideration. The long-term stability of the tannic acid-Fe^{3+} coating, its oxidation resistance, and membrane reusability represent key indicators of environmental durability. In real wastewater applications, the presence of diverse foulants and complex matrices may alter fouling and cleaning dynamics. Moreover, the antifouling enhancement arises from the metal–phenolic deposition mechanism, where understanding the layer structure, bonding, and uniformity is critical for process reproducibility. Finally, assessing the overall environmental footprint through a life-cycle perspective would provide quantitative insight into the true sustainability of this waste-derived membrane technology.

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Declaration of generative AI

During the preparation of this work, the authors used artificial intelligence tools, specifically Sci-Space AI were utilized to assist in retrieving relevant references and improving the grammatical and stylistic clarity of the manuscript during its preparation. All decisions regarding reference selection, data interpretation, and scientific content remain solely the responsibility of the author.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Credit authorship contribution

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N. Arahman: Methodology, Validation.
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