Ultrafiltration for Sustainable Biodiesel Purification. Part 2 – Fouling Mechanisms and Modelling Approaches

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Review
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Abstract

Membrane-based ultrafiltration (UF) has emerged as a sustainable alternative to conventional wet and dry washing for biodiesel purification, offering low energy consumption and zero-waste potential. However, industrial adoption of UF is primarily hindered by membrane fouling, caused by the deposition of glycerol, soaps, and catalyst residues, which leads to flux decline and increased operational costs. This manuscript provides a comprehensive review of fouling mechanisms, including pore blocking and cake formation, and evaluates predictive frameworks such as Hermia's and resistance-in-series models to optimise filtration performance. Strategies to mitigate fouling are critically discussed, ranging from physical and chemical cleaning protocols to advanced surface modifications. Specifically, the integration of hydrophilic coatings, plasma treatments, and photocatalytic TiO_2 nanoparticles is analysed for their ability to enhance antifouling properties. Furthermore, the review explores process intensification through membrane reactors and hybrid systems (*e.g.*, UF-nanofiltration), highlighting their role in improving conversion rates and resource circularity. While UF requires higher initial capital investment compared to traditional methods, its long-term economic and environmental benefits make it a superior choice for high-quality biodiesel production. This study concludes by identifying key research gaps in membrane longevity and the scale-up of hybrid purification technologies.

Keywords

Membrane fouling mechanisms, Hermia's modelling, surface modification, biodiesel purification, process intensification

1 Introduction

Membrane-based ultrafiltration (UF) has attracted considerable attention as a sustainable alternative to conventional biodiesel purification methods, particularly wet washing and dry washing.[1] Its main advantages include reduced water consumption, lower wastewater generation, mild operating conditions, and compatibility with continuous processing. These characteristics make UF particularly attractive for developing more environmentally acceptable downstream processing routes in biodiesel production. However, despite these benefits, broader industrial implementation of UF remains limited by membrane fouling.[2–4] Fouling results from the accumulation or adsorption of impurities such as glycerol, soaps, residual catalysts, free fatty acids, unreacted glycerides, and colloidal species on the membrane surface or within membrane pores. This leads to a gradual decline in permeate flux, an increase in transmembrane pressure (TMP), reduced separation efficiency, more frequent cleaning requirements, and a shorter membrane lifetime.[5] Consequently, fouling is not only a technical limitation but also an economic and environmental challenge that directly affects the long-term feasibility of UF-based biodiesel purification.[4] Although numerous studies have addressed membrane application in biodiesel purification, the available literature remains fragmented regarding fouling mechanisms, modelling approaches, cleaning strategies, membrane surface modification, and scale-up considerations. Most studies focus on specific membrane materials, individual operating conditions, or selected purification efficiencies, while fewer works provide a critical connection between fouling behaviour, predictive modelling, process stability, and industrial applicability. Therefore, a systematic analysis of fouling-related limitations is needed to define the current state of the field and identify the key challenges that must be addressed before wider industrial implementation.

This manuscript is the second part of a two-part overview of ultrafiltration for sustainable biodiesel purification. Part

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1 covers biodiesel production methods, purification technologies, UF principles, membrane materials, operating modes, and general process limitations. This paper focuses on fouling mechanisms and modelling approaches.

Particular attention is given to Hermia's models, resistance-in-series analysis, cleaning strategies, antifouling surface modifications, membrane reactors, hybrid systems, and scale-up challenges. The aim of this overview is to analyse membrane fouling mechanisms and modelling approaches relevant to UF-based biodiesel purification, and to evaluate their implications for process optimisation, membrane lifetime, and industrial implementation.

2 Membrane fouling mechanisms and modelling approaches

Crude biodiesel produced by transesterification typically contains impurities such as glycerol, soaps, free fatty acids, methanol, and catalyst residues. These components interact with the membrane depending on their physicochemical properties, the membrane material, and the hydrodynamic conditions. The principal fouling mechanisms include:[6]

(1) *Pore blocking*: Particulate matter or macromolecules obstruct the entrance or interior of membrane pores, reducing the effective filtration area.
(2) *Adsorptive fouling*: Polar impurities such as glycerol and soaps adhere to the membrane surface or internal pores through hydrophobic or electrostatic interactions.
(3) *Cake layer formation*: Retained particles accumulate on the surface, forming a resistive layer that further reduces permeate flux.
(4) *Gel layer formation*: When emulsified or colloidal species reach a critical concentration near the membrane, they form a dense, viscous layer that significantly restricts flow.

The dominant mechanism depends on the filtration configuration and operating parameters, particularly the mode of filtration (dead-end or cross-flow), which significantly influences hydrodynamics and fouling development.[7] In dead-end filtration, the feed stream is applied perpendicular to the membrane surface, forcing all solutes either through or onto the membrane. As there is no shear force to remove deposited material, foulants rapidly accumulate on the surface, causing a steep decline in flux. The primary fouling mechanisms are pore blocking in the early stages and cake layer formation in later stages.[8] This mode is simple, compact, and cost-effective, making it suitable for small-scale or batch biodiesel purification. However, the main drawbacks are rapid flux decline, frequent cleaning requirements, and limited operational stability. In contrast, cross-flow filtration introduces the feed tangentially to the membrane surface, generating a shear force that continuously removes part of the deposited material. This hydrodynamic effect reduces cake compaction and delays the onset of severe fouling.[9] The system can operate under steady-state conditions, where the rate of deposition equals the rate of removal. Although cross-flow systems require higher energy input for circulation and a more complex setup, they provide better fouling control, higher and more stable flux, and longer membrane lifetime, which are advantageous for continuous industrial biodiesel purification.[10]

Mathematical modelling of fouling provides a framework to predict flux decline, identify dominant fouling mechanisms, and design strategies for fouling mitigation.[11] Two common modelling approaches are Hermia's fouling models and the resistance-in-series model. Hermia[12] developed a general expression that relates the rate of flux decline to time and identifies four different fouling mechanisms based on the constant n (Eq. 1):

$$\frac{\mathrm{d}^2 t}{\mathrm{d}V^2} = k \cdot \left(\frac{\mathrm{d}t}{\mathrm{d}V} \right)^n \tag{1}$$

where t is the filtration time (s), V is the permeate volume (m^3), *k is the fouling constant, whose units depend on n, and n is the dimensionless model index representing the fouling mechanism*. Integrating this general equation under constant pressure yields the following specific relationships for each fouling type, expressed in terms of permeate flux, J (Table 1). Although Hermia's models are widely used due to their simplicity and ability to distinguish between idealised fouling mechanisms, their application to biodiesel purification should be interpreted with caution. Crude biodiesel is a chemically complex and often heterogeneous system, and fouling may result from simultaneous adsorption, pore narrowing, pore blocking, emulsion deposition, and cake formation. Therefore, assigning the entire filtration process to a single Hermia mechanism may oversimplify the actual fouling behaviour. For this reason, Hermia's models are most useful as comparative diagnostic tools rather than complete mechanistic descriptions. Their value lies in identifying the dominant fouling tendency under specific experimental conditions and comparing the relative suitability of different membranes or operating regimes. However, for process design and scale-up, Hermia analysis should ideally be combined with resistance-in-series modelling, cleaning-recovery data, and long-term filtration experiments.

Another widely used approach is the resistance-in-series (RIS) model, which relates the overall flux decline to the total hydraulic resistance[13] (Eq. 2):

$$J = \frac{\Delta p}{\mu \cdot \left(R_\mathrm{m} + R_\mathrm{f} \right)} \tag{2}$$

where J is the permeate flux ($m^3\ m^{-2}\ s^{-1}$), Δp is the transmembrane pressure (Pa), μ is the viscosity of the permeate (Pa·s), R_m is the intrinsic membrane resistance (m^{-1}), and R_f is the fouling resistance (m^{-1}) (the sum of reversible and irreversible resistances). The fouling resistance term can be further divided into reversible resistance, associated with cake layers removable by hydraulic cleaning, and irreversible resistance, due to adsorptive or pore-blocking phenomena. Monitoring these resistances provides valuable insights into the nature and reversibility of fouling in biodiesel purification systems. Modelling fouling behaviour allows prediction of membrane performance under various operational conditions. By integrating Hermia's equations and RIS models, engineers can evaluate how variables such as TMP,[14] feed concentration, or flow velocity affect fouling rates. For example, high TMP may initially increase flux but accelerate fouling through compaction of cake layers. Similarly, higher cross-flow velocity enhances shear stress, reducing reversible resistance and stabilising flux.

Moreover, advanced computational fluid dynamics (CFD)[15] and data-driven models such as artificial neural networks (ANNs)[16] are increasingly used to simulate mass transfer, predict fouling behaviour, and optimise cleaning cycles. By coupling experimental data with predictive models, biodiesel purification processes can be fine-tuned for maximum flux recovery, reduced downtime, and extended membrane longevity.

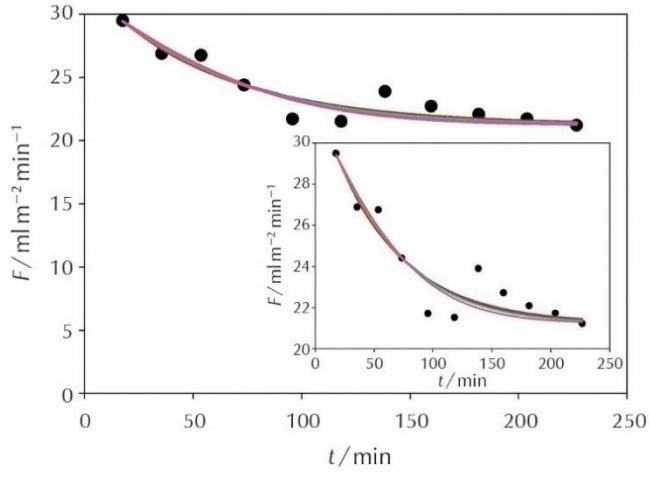


Fig. 1 – Dynamic change in permeate flux during biodiesel purification in the integrated system (experimental data obtained from the authors) (Hermia model: — complete pore blocking, — standard pore blocking, — intermediate pore blocking, — cake formation, ● experimental data)

Slika 1 – Dinamička promjena protoka permeata tijekom pročišćavanja biodizela u integriranom sustavu (eksperimentalni podatci autora) (Hermia model: — potpuno blokiranje pora, — standardno blokiranje pora, — srednje blokiranje pora, — stvaranje filtarskog kolača, ● eksperimentalni podatci)

For example, Fig. 1 shows the dynamic change in permeate flux observed during the experimental removal of glycerol from biodiesel using a polyethersulfone (PES) membrane. The results indicate a clear decrease in permeate flux over time. All four fouling mechanisms showed good agreement with the experimental data. For each mechanism, the corresponding model constant k was estimated. The applicability of each Hermia fouling model was evaluated using the coefficient of determination (R^2) and the root mean square error (RMSE) (Table 2). Although all four Hermia models demonstrated reasonable agreement with the experimental data, the obtained fitting parameters suggest that cake formation was the most representative fouling mechanism under the investigated conditions. The relatively similar R^2 values obtained for all four mechanisms indicate that flux decline cannot be attributed exclusively to a single fouling mechanism. This suggests that fouling during biodiesel ultrafiltration is probably governed by overlapping mechanisms. Nevertheless, based on the overall trend of flux decline and the physical nature of biodiesel impurities, cake formation appears to be the most plausible dominant mechanism during the later stages of filtration.

3 Membrane cleaning strategies in ultrafiltration of biodiesel

Membrane fouling remains the most critical operational challenge in biodiesel ultrafiltration, as the deposition of glycerol, soaps, free fatty acids, catalysts, and colloidal particles on or within membrane pores reduces flux, increases TMP, and shortens membrane lifetime. Efficient cleaning strategies are therefore essential to maintain long-term productivity and ensure the economic feasibility of filtration systems. Cleaning procedures generally aim to remove reversible fouling (*e.g.*, cake layer, loosely adhered solutes) and mitigate irreversible fouling (*e.g.*, adsorption, pore blocking) without damaging the membrane structure.[17] Cleaning approaches can be broadly classified as physical, chemical, and biochemical (enzymatic), with the choice of cleaning method determined by the properties of the foulant and the membrane material.[18–20] In biodiesel purification, glycerol and soaps are the dominant foulants; these hydrophilic compounds adhere strongly to hydrophilic membranes, while hydrophobic fatty acids and residual oils more commonly affect hydrophobic membranes. Therefore, membrane selection and cleaning strategies must be considered together.

Physical cleaning techniques such as ultrasonic irradiation,[21,22] hydraulic backwashing,[23,24] and air sparging remove[25] reversible fouling by inducing shear force and disrupting the cake layer on the membrane surface.[26]

Table 1 – Hermia's fouling models[12]
Tablica 1 – Hermijini modeli čepljenja[12]

Model Model	Equation Jednadžba	Description Opis
Complete pore blocking, $n = 2$ Potpuno blokiranje pora, $n = 2$	$J = J_0 \cdot e^{-k \cdot t}$	In complete pore blocking, each particle arriving at the membrane fully seals an open pore, reducing the total number of active pores available for filtration. This mechanism dominates during the initial filtration stage, when pore entrances are still accessible, and leads to a rapid decline in flux. Kod potpunog blokiranja svaka čestica koja stigne na membranu potpuno zatvara otvorenu poru, smanjujući ukupan broj aktivnih pora dostupnih za filtraciju. Taj mehanizam dominira tijekom početne faze filtracije, kad su ulazi u pore još uvijek dostupni i dovodi do brzog smanjenja gustoće toka tvari.
Intermediate pore blocking, $n = 1$ Srednje blokiranje pora, $n = 1$	$\frac{1}{J} = \frac{1}{J_0} + k \cdot t$	In intermediate pore blocking, particles randomly deposit on the membrane surface, with some blocking pores and others settling on already deposited particles. This mechanism represents a transitional phase between pore blocking and cake formation, resulting in a moderate rate of flux decline. Kod srednjeg blokiranja pora čestice se nasumično talože na površini membrane, pri čemu neke blokiraju pore, a druge se talože na već istaloženim česticama. Taj mehanizam predstavlja prijelaznu fazu između blokiranja pora i stvaranja filtarskog kolača, što rezultira umjerenim smanjenjem gustoće toka tvari.
Standard pore blocking, $n = 1.5$ Standardno blokiranje pora, $n = 1{,}5$	$\frac{1}{\sqrt{J}} = \frac{1}{\sqrt{J_0}} + k \cdot t$	Standard pore blocking occurs when particles or solutes penetrate the pores and deposit along the inner walls, gradually decreasing the effective pore volume without fully blocking the pores. This typically occurs in membranes with pore sizes larger than the foulant molecules. Standardno blokiranje događa se kad čestice ili otopljene tvari prodru u pore i talože se duž unutarnjih stijenki, postupno smanjujući efektivni volumen pora, bez potpunog blokiranja pora. To se obično događa u membranama s porama koje su veće u odnosu na čestice onečišćenja.
Cake formation, $n = 0$ Stvaranje filtarskog kolača, $n = 0$	$\frac{1}{J^2} = \frac{1}{J_0^2} + k \cdot t$	Cake formation occurs after the surface pores are mostly covered, and additional particles accumulate to form a porous layer, known as the cake, on the membrane surface. This external layer increases hydraulic resistance but can sometimes act as a secondary filtration medium, improving permeate quality. Stvaranje filtarskog kolača događa se nakon što su površinske pore uglavnom prekrivene, a dodatne čestice se nakupljaju i formiraju porozni sloj, poznat kao filtarski kolač, na površini membrane. Taj sloj povećava hidraulički otpor, ali ponekad može djelovati kao sekundarni filtracijski medij, poboljšavajući kvalitetu permeata.

Table 2 – Applicability of the fouling model and individual mechanisms (experimental data obtained from the authors)
Tablica 2 – Primjenjivost modela čepljenja i pojedinačnih mehanizama (eksperimentalni podaci autora)

	Mechanism Mehanizam			
	complete pore blocking potpuno blokiranje pora	standard pore blocking standardno blokiranje pora	intermediate pore blocking srednje blokiranje pora	cake formation stvaranje filtarskog kolača
k	0.0171 ± 0.0024	0.0874 ± 0.0119	0.4473 ± 0.061	11.817 ± 1.770
R^2	0.883	0.882	0.882	0.881
RMSE	0.902	0.907	0.915	0.937

Backwashing is commonly used in polymeric dead-end configurations, while air sparging increases shear intensity in cross-flow systems, especially when treating highly viscous biodiesel streams. These methods are most effective when applied before significant pore blocking occurs.

In cases of irreversible fouling, chemical cleaning is required.[17,27] Alkaline surfactants (*e.g.*, NaOH with sodium dodecyl sulphate) effectively remove soaps and glycerol residues, while acidic agents (*e.g.*, citric or nitric acid) dissolve catalyst deposits and metal ions. Organic solvents (*e.g.*, ethanol, hexane)[28] may be used to remove hydrophobic species, though excessive use is discouraged due to environmental and safety concerns. Care must be taken to prevent swelling or degradation of polymeric membranes; thus, chemical cleaning protocols must be membrane-specific. In the study by *Sokač et al.*[28] the polyethersulfone (PES) membrane was removed after each cycle of biodiesel ultrafiltration and washed with 70 % ethanol. A total of four cycles were performed, continuing until a pronounced decline in permeate flux was observed. The experimental flux profile, along with the standard blocking model, is presented in Fig. 2.

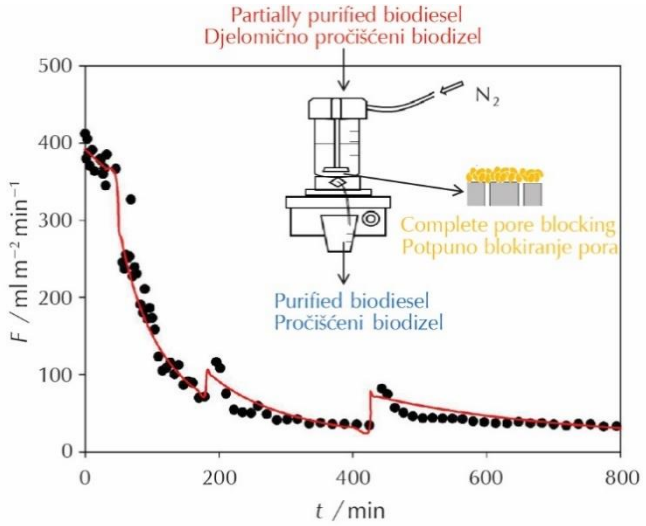


Fig. 2 – Permeate flux for semi-continuous biodiesel ultrafiltration using a PES membrane (▬ complete pore blocking model, ● experimental results)

Slika 2 – Protok permeata kod polukontinuirane ultrafiltracije biodizela uporabom PES membrane (▬ model potpunog blokiranja pora, ● eksperimentalna mjerenja)

Enzymatic cleaners, particularly lipases, provide a selective and environmentally friendly method for degrading residual triglycerides and glycerides. They are effective at mild pH and low temperatures, making them suitable for sensitive polymeric membranes. Although still relatively expensive, enzymatic cleaning can reduce chemical exposure, prolong membrane lifetime, and be incorporated into closed-loop cleaning systems for green biodiesel production.[17] To optimise system performance, a combined strategy is often used, starting with physical cleaning to remove reversible fouling, followed by tailored chemical or enzymatic cleaning for persistent contaminants. Proper scheduling of cleaning cycles based on fouling models (*e.g.*, Hermia or RIS models) can further reduce downtime and extend membrane operational life. A summary of cleaning methods usually used for biodiesel ultrafiltration membranes is presented in Table 3.

From a practical perspective, membrane cleaning should be assessed not only by immediate flux recovery, but also by membrane compatibility, chemical consumption, wastewater generation, safety, and long-term membrane stability. Physical cleaning methods are attractive because they reduce chemical use and operational costs, but they are mainly effective against reversible fouling. Chemical cleaning is more efficient for irreversible fouling, but repeated exposure to alkaline, acidic, or organic cleaning agents may damage polymeric membranes, cause swelling, alter pore structure, or shorten membrane lifetime. In biodiesel purification, cleaning strategies must therefore be adapted to both membrane type and foulant composition. For polymeric membranes, mild solvent or alkaline cleaning may be suitable, but aggressive solvents should be avoided due to possible polymer degradation. Ceramic membranes tolerate harsher cleaning conditions and higher temperatures, but their higher capital cost must be justified by longer operating lifetime and improved cleaning recovery. Enzymatic cleaning represents a promising, environmentally friendly alternative, particularly for triglyceride- and glyceride-rich deposits, but its wider use is currently limited by enzyme cost, slower cleaning kinetics, and the need for process-specific optimisation. Thus, the most realistic industrial approach is likely to involve combined cleaning protocols, where physical cleaning is applied regularly to remove reversible deposits, while chemical or enzymatic cleaning is used periodically to control irreversible fouling. Such cleaning schedules should be supported by fouling models and flux-recovery monitoring to avoid unnecessary downtime and excessive chemical consumption.

4 Membrane surface modification for antifouling performance

While membrane selection plays a critical role in biodiesel ultrafiltration, the intrinsic surface properties of the membrane often determine fouling severity, particularly when processing biodiesel streams rich in glycerol, soaps, and free fatty acids. Surface modification has therefore emerged as a key strategy to enhance antifouling properties by altering hydrophilicity, charge, roughness, and catalytic activity without compromising permeability or mechanical stability (Fig. 3).

Table 3 – Overview of membrane cleaning methods and their characteristics[17,19,29–31]
Tablica 3 – Pregled metoda čišćenja membrana i njihovih karakteristika[17,19,29–31]

Cleaning type Vrsta čišćenja	Typical agent/process Tipično sredstvo/proces	Target foulants Ciljana onečišćenja	Advantages Prednosti	Limitations/impact Nedostatci/utjecaj
Physical cleaning Fizikalno čišćenje	Backwashing, air sparging Povratno ispiranje, propuhivanje zrakom	Cake layer (glycerol-soap complexes); suspended solids Sloj filtarskog kolača (glicerol-sapunski kompleksi); suspendirane tvari	Low cost; no chemicals; reduces reversible fouling Niska cijena; bez upotrebe kemikalija; smanjuje reverzibilno čepljenje	Ineffective against adsorption and internal pore blocking Neučinkovito protiv adsorpcije i unutarnjeg začepljenja pora
Chemical alkaline cleaning Kemijsko alkalno čišćenje	NaOH, Na_2CO_3, alkaline surfactants NaOH, Na_2CO_3, alkalne površinski aktivne tvari	Soaps, glycerol, fatty acid salts Sapuni, glicerol, soli masnih kiselina	High effectiveness on main glycerol-soap deposits Visoka učinkovitost na glavnim naslagama glicerol-sapun	May cause swelling of polymeric membranes; requires wastewater handling Može uzrokovati bubrenje polimernih membrana; zahtijeva obradu nastalih otpadnih voda
Chemical acidic cleaning Kemijsko kiselo čišćenje	Citric acid, nitric acid Limunska kiselina, dušična kiselina	Catalyst residues (Na^+, K^+), metal ions Ostatci katalizatora (Na^+, K^+), metalni ioni	Removes scaling and catalyst contaminants Uklanja kamenac i onečišćenja od katalizatora	Corrosive; unsuitable for frequent use on sensitive membranes Korozivno; neprikladno za čestu primjenu na osjetljivim membranama
Solvent cleaning Čišćenje otapalima	Ethanol, *n*-hexane Etanol, *n*-heksan	Residual oils, FAME, hydrophobic deposits Zaostala ulja, FAME, hidrofobne naslage	Compatible with biodiesel components; fast Kompatibilno s komponentama biodizela; brzo	Environmental concerns; fire hazard; may degrade polymer structure Utjecaj na okoliš; opasnost od požara; može razgraditi strukturu polimera
Enzymatic cleaning Enzimsko čišćenje	Lipases Lipaze	Triglycerides, glycerides Trigliceridi, gliceridi	Mild operating conditions; biodegradable; preserves membranes Blagi radni uvjeti; biorazgradivo; čuva membrane	Higher cost; slow process Veći trošak; spori proces

Modified membranes are designed to weaken foulant-surface interactions and reduce the adhesion of contaminants, thereby delaying flux decline and extending operational lifetime (Table 4).[32,33]

One approach to modifying membrane surface chemistry is the application of *hydrophilic coatings*.[34,35] Glycerol and soaps have high polarity and a strong affinity for hydrophilic UF membranes. Paradoxically, increasing hydrophilicity through surface coatings can reduce fouling, as water molecules preferentially adsorb to the membrane, forming a hydration barrier that prevents direct contact with foulants. Poly(ethylene glycol) (PEG), polyvinyl alcohol (PVA), and graphene oxide (GO) are among the most studied hydrophilic modifiers. PEG and PVA create dense hydration layers that repel polar impurities, while GO nanosheets provide additional benefits, including mechanical reinforcement, high surface area, and resistance to oxidation. Cold plasma (*plasma surface modification)* treatment offers a solvent-free approach to adjust membrane surface chemistry by introducing charged and oxygen-containing functional groups (*e.g.*, −COOH, −OH). This process improves hydrophilicity and allows partial etching of surface pores, reducing surface roughness where contaminants typically anchor. Plasma-modified polyvinylidene fluoride (PVDF), PES, and polysulfone (PSF) membranes have shown enhanced resistance to cake formation by soap-glycerol complexes. As fouling begins with adsorption at micro-roughness features, smoothing *via* plasma reduces initial pore blocking and delays the transition from pore fouling to cake filtration.[36,37]

Coating membranes with photocatalytic TiO_2 nanoparticles enables self-cleaning,[38] whereby UV or visible light activates reactive species that degrade organic contaminants.

Table 4 – Overview of membrane surface modification methods for fouling reduction[42–48]
Tablica 4 – Pregled metoda modifikacije površine membrane za smanjenje čepljenja[42–48]

Modification type Vrsta modifikacije	Typical materials Tipični materijali	Targeted foulants Ciljana onečišćenja	Main advantages Glavne prednosti	Modification limitations Glavni nedostatci
Hydrophilic coatings Hidrofilni premazi	PEG, PVA, GO PEG, PVA, GO	Glycerol, soaps, polar impurities Glicerol, sapuni, polarne nečistoće	Forms hydration barrier; reduces adsorption; mechanically reinforces membrane (GO) Stvara hidratacijsku barijeru; smanjuje adsorpciju; mehanički ojačava membranu (GO)	Coatings may leach over time; requires periodic renewal Premazi se s vremenom mogu ispirati; zahtijeva periodično obnavljanje
Plasma modification Modifikacija plazmom	O_2/air plasma treatment of PVDF, PES, PSF Obrada PVDF, PES, PSF plazmom iz O_2/zraka	Initial pore-blocking compounds; glycerol-soap complexes Tvari koje uzrokuju početno blokiranje pora; kompleksi glicerol-sapun	Solvent-free process; smooths roughness; reduces initial pore fouling Postupak bez otapala; zaglađuje hrapavost; smanjuje početno onečišćenje pora	Effect may diminish without post-treatment; equipment cost Učinak se može smanjiti bez naknadne obrade; cijena opreme
TiO_2 nanoparticle coating (catalytic) Premaz od nanočestica TiO_2 (katalitički)	TiO_2-coated PVDF or ceramic membranes PVDF ili keramičke membrane obložene TiO_2	Triglycerides, glycerides, fatty acids Trigliceridi, gliceridi, masne kiseline	Photocatalytic self-cleaning; degrades organics; reduces irreversible fouling Fotokatalitičko samočišćenje; razgrađuje organske tvari; smanjuje nepovratno čepljenje	Requires UV/visible activation; added material cost; nanoparticle leaching concerns Zahtijeva UV/vidljivu aktivaciju; dodatni trošak materijala; problemi s ispiranjem nanočestica
Zwitterionic modification Zwitterionska modifikacija	Sulfobetaine, carboxybetaine polymers Sulfobetain, karboksibetain polimeri	Soaps, FFAs, ionised species Sapuni, FFA, ionizirane tvari	Strong hydration layer; excellent resistance to soap adsorption; best stability in high-FFA feeds Jak hidratacijski sloj; izvrsna otpornost na adsorpciju sapuna; najbolja stabilnost u sirovinama s visokim udjelom FFA	Synthesis cost; limited commercial membrane availability Troškovi sinteze; ograničena komercijalna dostupnost membrana
Organic-inorganic hybrid membranes Organsko-anorganske hibridne membrane	PVDF-TiO_2, PES-SiO_2, PAN-GO PVDF-TiO_2, PES-SiO_2, PAN-GO	Mixed hydrophobic and/or hydrophilic foulants Miješane hidrofobne i/ili hidrofilne tvari koje uzrokuju čepljenje	Improved mechanical strength, thermal stability, and antifouling Poboljšana mehanička čvrstoća, toplinska stabilnost i otpornost na čepljenje	Higher fabrication complexity; membrane scalability is still emerging Veća složenost izrade; uvećanje mjerila još je u razvoju

In biodiesel streams, TiO_2 coatings have been shown to be effective in removing adsorbed glycerides, fatty acids, and residual triglycerides, which are otherwise resistant to conventional chemical cleaning.[39] The catalytic activity breaks down hydrophobic components, reducing irreversible fouling and allowing *in situ* surface regeneration without harsh chemicals. TiO_2-modified ceramic and PVDF membranes are particularly promising for continuous biodiesel production requiring minimal downtime. *Zwitterionic polymers*, such as sulfobetaine and carboxybetaine, contain both positive and negative charges, forming strong hydration layers via electrostatic interactions with surrounding water molecules. These hydrated surfaces sterically repel organic contaminants and exhibit exceptionally low adsorption, even in complex biodiesel matrices. Unlike simple hydrophilic coatings, zwitterionic layers resist binding by multivalent soaps and ionized free fatty acids, which are major contributors to gel layer formation. As a result, zwitterionic membranes have demonstrated superior antifouling performance under high-soap biodiesel feed conditions and maintain stable flux without rapid increases in TMP.[40,41]

Although surface modification offers significant potential for improving antifouling performance, its practical implementation in biodiesel purification remains challenging. Many reported modifications are evaluated under controlled laboratory conditions, often using model solutions rather than actual crude biodiesel streams. However, real biodiesel contains variable concentrations of glycerol, soaps, alcohol, catalysts, free fatty acids, and glycerides, which may affect coating stability and antifouling

efficiency. Hydrophilic coatings can reduce adsorption by forming hydration layers, but coating stability and possible leaching during long-term operation remain important concerns. Plasma treatment is attractive because it is solvent-free and can modify surface chemistry without adding a separate coating layer, but the induced surface properties may partially decay over time. TiO_2-based photocatalytic membranes may enable self-cleaning, but their implementation requires light activation, stable nanoparticle immobilisation, and prevention of nanoparticle release into the product stream. Zwitterionic and hybrid organic-inorganic membranes show strong antifouling potential, but their cost, fabrication complexity, and limited commercial availability currently restrict industrial use. Therefore, future studies should move beyond short-term flux tests and include long-term filtration, repeated cleaning cycles, coating stability, membrane regeneration, and economic assessment. Without such data, it remains difficult to determine whether advanced surface modifications can be translated from laboratory-scale membrane development to industrial biodiesel purification.

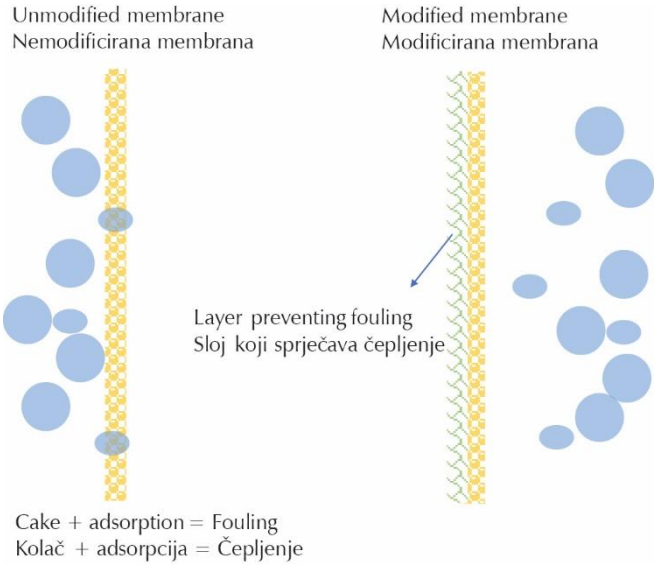


Fig. 3 – Comparative fouling scheme: a) unmodified *vs.* b) modified membrane

Slika 3 – Usporedna shema čepljenja: a) nemodificirana *vs.* b) modificirana membrana

5 Process design and scale-up considerations

Although membrane technology is well known, fouling mechanisms are characteristic of each system, making them a technical challenge to overcome, especially on an industrial scale. Fouling mechanisms are important for identifying the relationship between operational parameters and the phenomena that limit mass transfer, ensuring the process is conducted under conditions that minimise fouling and, consequently, increase the efficiency of membrane filtration.[49] In addition, models can help predict the performance of the ultrafiltration process, size equipment, and plan membrane cleaning cycles to ensure long-term reliability and efficiency. Furthermore, ultrafiltration in biodiesel production involves significant economic and operational considerations, which are presented in Table 5.

Engineers aiming for large-scale biodiesel production seek to design facilities that enhance output by reducing energy consumption, increasing reaction rates, minimising wasted energy and costs related to waste products, improving purification steps, reducing equipment size, and increasing safety and operational simplicity. These challenges can be addressed by employing novel reactors, such as coupled reaction/separation reactors.[52] A membrane reactor is an innovative system in which chemical reaction and membrane separation are carried out simultaneously (Fig. 4).[50,52] The concept of using a membrane reactor in biodiesel production was first proposed by *Dubé et al.*[53] Their results demonstrated the high potential of membrane reactors for removing impurities after biodiesel production.

As shown in Fig. 4, the ultrafiltration membrane in a reactor plays two main functions: first, it enables the transesterification of oil to produce biodiesel; second, it separates impurities such as glycerol from the product without the use of water or adsorbents. The main advantages of producing biodiesel in membrane reactors are reduced separation costs, higher conversion, and high purity and quality of biodiesel.[52] The economic viability of biodiesel production is increasingly dependent on purification technology, where capital costs, operational expenditures, and waste disposal fees dominate downstream processing. Although conventional wet washing remains widespread due to its low equipment cost and simplicity, it incurs high recurring expenses associated with water consumption, chemical use, wastewater treatment, and extended processing times. In contrast, UF requires a higher initial investment but offers long-term cost savings through reduced energy consumption, lower consumable use, and minimised waste generation.

Table 5 – Summarised considerations for industrial biodiesel ultrafiltration systems[1,28,50,51]
Tablica 5 – Sažeta razmatranja za industrijske sustave ultrafiltracije biodizela[1,28,50,51]

	Considerations/Gledišta
Economic considerations Ekonomska gledišta	– high initial cost for ultrafiltration system (modules, pumps) – membrane material (ceramic membranes are more expensive than polymer membranes) – requires instrumentation for process monitoring – visoki početni troškovi za ultrafiltracijski sustav (moduli, pumpe) – materijal membrane (keramičke membrane su skuplje od polimernih membrana) – potrebna je instrumentacija za praćenje procesa
Operational considerations Operativna gledišta	– low energy requirement – membrane cleaning (performed by chemicals) and replacement (the life-time for ceramic membrane is 5–10 years, and for polymeric membranes 1–5 years) – UF systems are mostly automated, but the presence of qualified engineers or technicians is important – niski energetski zahtjevi – čišćenje (provodi se kemikalijama) i zamjena (vijek trajanja keramičke membrane je 5 – 10 godina, a polimernih membrana 1 – 5 godina) – UF sustavi su uglavnom automatizirani, ali je važna prisutnost kvalificiranih inženjera ili tehničara
Environmental considerations Ekološka gledišta	– high quality biodiesel and a small amount of wastewater – low environmental footprint – visokokvalitetni biodizel i mala količina otpadnih voda – nizak utjecaj na okoliš

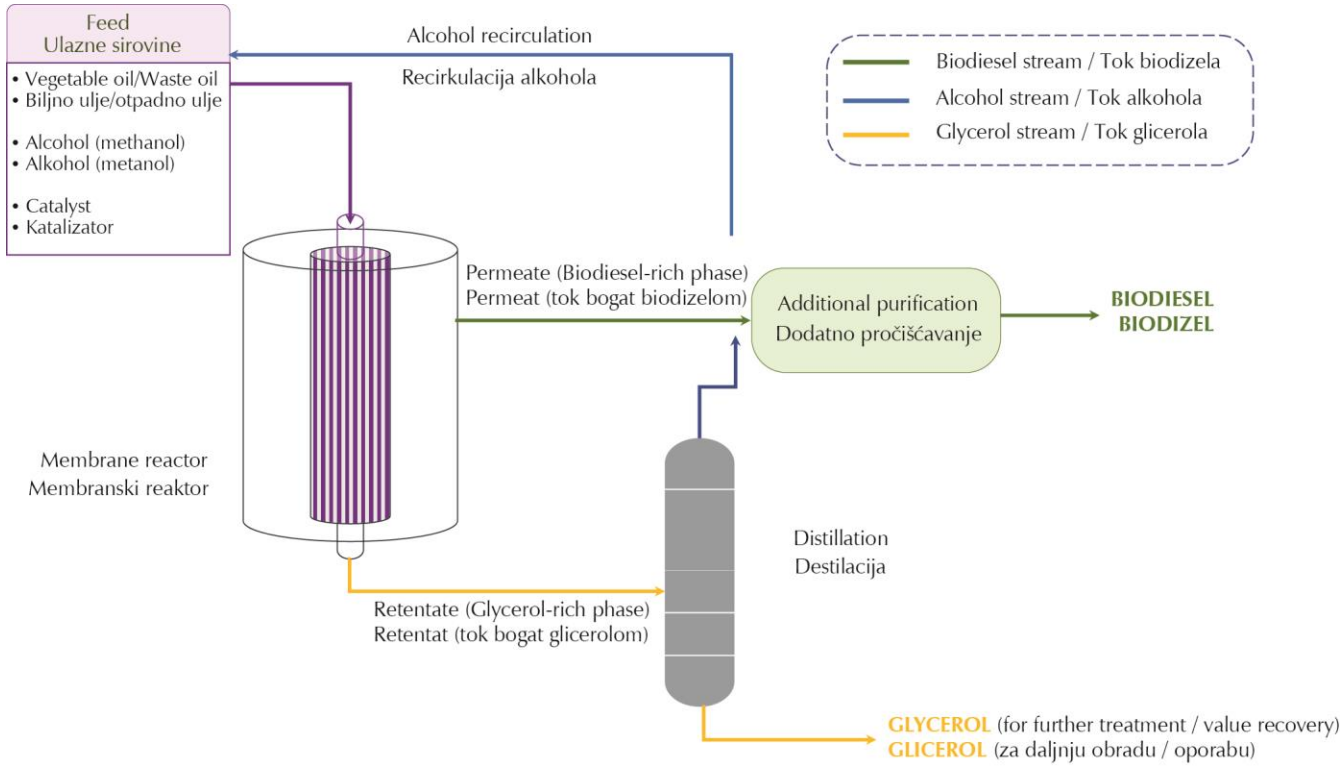


Fig. 4 – Schematic process of biodiesel production and purification in a membrane reactor
Slika 4 – Shematski prikaz procesa proizvodnje i pročišćavanja biodizela u membranskom reaktoru

Despite these advantages, membrane reactors are not yet widely implemented in industrial biodiesel production. Their practical application remains limited by several challenges, including membrane fouling under reaction conditions, catalyst compatibility, pressure control, membrane replacement cost, and the complexity of simultaneously optimising reaction and separation. In addition, long-term operation may be affected by the accumulation of glycerol, soaps, residual catalysts, and partially converted glycerides, which can reduce membrane permeability and compromise process stability. Another limitation is that membrane reactors require more complex process control than conventional transesterification followed by separate purification. Parameters such as reaction conversion, membrane selectivity, TMP, flow rate, alcohol-to-oil ratio, catalyst concentration, and impurity removal must be optimised simultaneously. This increases design complexity and may require advanced monitoring and automation. Therefore, although membrane reactors are promising for process intensification, their current role should be considered mainly as an emerging technology rather than a fully established industrial solution. For this reason, hybrid systems may be more realistic in the near term. UF can be integrated as a polishing step after transesterification, or combined with nanofiltration, adsorption, alcohol recovery, or solvent extraction to achieve complete impurity removal. Such hybrid configurations may offer a more flexible route towards industrial implementation because they allow each unit operation to target a specific group of contaminants.

6 Future perspectives

Future research on UF-based biodiesel purification should progress from short-term laboratory demonstrations to long-term, process-relevant validation. Although many studies report promising flux, glycerol retention, or antifouling performance, direct comparison remains difficult due to differences in feed composition, membrane material, pore size, TMP, temperature, filtration mode, and analytical methods. Establishing more standardised testing protocols would improve comparison between studies and support more reliable membrane selection. A key research direction is the development of membranes with improved resistance to organic solvents, soaps, glycerol, and free fatty acids. Hybrid organic-inorganic membranes, surface-modified polymeric membranes, and low-cost ceramic membranes are particularly promising, but their performance should be evaluated under realistic biodiesel purification conditions, including repeated cleaning cycles and long-term operation. Another important direction is the integration of modelling tools into process optimisation. Hermia's models and resistance-in-series analysis provide useful information on fouling behaviour, but they should be combined with CFD, statistical modelling, and data-driven approaches to improve prediction of flux decline, cleaning intervals, and membrane lifetime. Such integrated modelling frameworks may support the transition from empirical membrane testing to rational process design. Finally, pilot-scale studies are needed to evaluate the economic and environmental feasibility of UF and hybrid membrane systems. Particular attention should be given to membrane replacement frequency, cleaning agent consumption, energy demand, wastewater generation, product quality, and compatibility with existing biodiesel production plants. These aspects will ultimately determine whether UF can become a widely implemented purification technology or remain limited to specialised applications.

7 Conclusion

This review analysed membrane fouling mechanisms, modelling approaches, cleaning strategies, antifouling surface modifications, and scale-up considerations relevant to UF-based biodiesel purification. The analysis shows that membrane fouling remains the main limitation preventing wider industrial implementation of UF, despite its clear environmental advantages over conventional wet and dry washing. Fouling in biodiesel UF is governed by complex interactions between membrane properties, feed composition, operating conditions, and filtration configuration. Although pore blocking, adsorption, cake formation, and gel-layer formation can be described separately, real biodiesel systems often involve overlapping mechanisms. Therefore, single-mechanism models should be interpreted carefully. Hermia's models are useful for identifying dominant fouling tendencies, while resistance-in-series models provide additional insight into reversible and irreversible hydraulic resistance. However, reliable process design requires combining modelling with experimental validation, cleaning-recovery analysis, and long-term operational data.

Cleaning methods and surface modification are essential for extending membrane lifetime. Physical cleaning is effective for reversible fouling, while chemical and enzymatic cleaning are necessary for more persistent deposits. Advanced surface modifications, such as hydrophilic coatings, plasma treatment, TiO_2-based photocatalytic layers, zwitterionic polymers, and organic-inorganic hybrids, offer promising antifouling properties; however, their long-term stability, scalability, and economic feasibility have not been sufficiently demonstrated for biodiesel purification. From an industrial perspective, UF is unlikely to fully replace conventional purification methods in the near future. Its most realistic application is as part of integrated or hybrid purification systems, where UF is combined with nanofiltration, adsorption, alcohol recovery, or membrane reactors. These approaches could reduce water

consumption, minimise waste generation, and improve process continuity.

Overall, future progress will depend on the development of more durable and economically viable membranes, standardised fouling evaluation protocols, integrated modelling approaches, and pilot-scale validation under realistic biodiesel production conditions. In this context, fouling analysis should be regarded not only as a diagnostic tool but also as a central element in the design of sustainable and industrially applicable biodiesel purification processes.

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SAŽETAK

Održivo pročišćavanje biodizela ultrafiltracijom. 2. dio – Mehanizmi čepljenja i modeliranje procesa

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Membranska ultrafiltracija (UF) pojavila se kao održiva alternativa procesima mokrog i suhog pranja koji se primjenjuju kao konvencionalni postupci za pročišćavanje biodizela. Za razliku od tih uobičajenih pristupa pročišćavanju biodizela, UF odlikuje niska potrošnju energije i zanemariva količina otpada koji pri procesu nastaje. Međutim, industrijsku primjenu UF-a u pročišćavanju biodizela ponajprije ograničava čepljenje membrana, uzrokovano taloženjem glicerola, sapuna i ostataka katalizatora, što dovodi do smanjenja protoka kroz membrane i povećanja operativnih troškova. Ovaj rad daje sveobuhvatan pregled i analizu mehanizama čepljenja, uključujući začepljenje pora i stvaranje filtarskog kolača te vrednuje prediktivne okvire poput Hermijina modela i modela serijski vezanih otpora koji se primjenjuju kod optimiranja filtracijskih performansi membrana. Strategije za smanjenje čepljenja pora kritički se razmatraju, u rasponu od fizičkih i kemijskih procesa čišćenja do naprednih procesa koji uključuju površinsku modifikaciju membrana. Posebno se analizira integracija hidrofilnih prevlaka, plazma-tretmana i fotokatalitičkih TiO_2 nanočestica zbog njihova potencijala u smanjenju čepljenja pora. Nadalje, analizirana je intenzifikacija procesa kroz uporabu membranskih reaktora i hibridnih sustava (npr. UF-nanofiltracija), pri čemu je istaknuta njihova uloga u povećanju konverzije i održivosti resursa. Iako UF zahtijeva veća početna kapitalna ulaganja u usporedbi s tradicionalnim metodama, njegove dugoročne ekonomske prednosti i minimalan utjecaj na okoliš čine ga superiornim izborom za proizvodnju biodizela visoke kvalitete. Pregled primjene UF-a za pročišćavanje biodizela završava s analizom ključnih istraživačkih izazova povezanih s trajnošću membrana i povećanjem mjerila kod hibridnih tehnologija.

Ključne riječi

Mehanizmi čepljenja membrana, Hermijin model, površinska modifikacija, pročišćavanje biodizela, intenzifikacija procesa

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