



A Chemical Engineering Perspective on Fouling Mechanisms in Long-Term Operation of Membrane Bioreactors

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Article Info

ISSN (online): 2582-7138

Volume: 03

Issue: 02

March-April 2022

Received: 02-03-2022

Accepted: 07-04-2022

Page No: 662-680

Abstract

Membrane bioreactors (MBRs) have emerged as a leading technology for high-quality wastewater treatment by combining biological degradation with membrane filtration. However, their long-term performance is critically hindered by membrane fouling, which increases energy consumption, reduces permeate flux, and necessitates frequent cleaning or replacement. This study presents a chemical engineering perspective on the fouling mechanisms that dominate during prolonged MBR operation. It classifies fouling into reversible and irreversible forms, including organic, inorganic, particulate, and biofouling, and emphasizes the role of foulant-membrane interactions at the molecular level. The formation and evolution of the fouling layer are examined through mass transfer limitations, adsorption dynamics, and physicochemical interactions such as electrostatic attraction, van der Waals forces, and hydrogen bonding. Special attention is given to extracellular polymeric substances (EPS) and soluble microbial products (SMP) as key contributors to gel layer development and pore blockage. The study explores how operational parameters such as hydraulic retention time (HRT), sludge retention time (SRT), aeration intensity, and flux loading affect fouling rates and compositions. Advanced characterization techniques including Fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and atomic force microscopy (AFM) are highlighted for diagnosing fouling morphology and chemistry. Additionally, modeling approaches based on mass transport equations, resistance-in-series frameworks, and fouling kinetics are discussed to provide predictive insights into membrane lifespan and cleaning cycles. Strategies for fouling mitigation are evaluated from a process design standpoint, including dynamic membrane operation, membrane surface modification, and chemically enhanced backwashing. This chemical engineering approach reveals the interdependence between biological processes and physical transport phenomena in fouling behavior. By understanding the mechanistic basis of long-term fouling, the study informs the design of more resilient and energy-efficient MBR systems. Ultimately, the findings contribute to optimizing membrane selection, operational regimes, and maintenance protocols, ensuring the sustainable deployment of MBRs in both municipal and industrial wastewater treatment applications.

DOI: <https://doi.org/10.54660/IJMRGE.2022.3.2.662-680>

Keywords: Membrane Bioreactor, Membrane Fouling, Chemical Engineering, EPS, SMP, Long-Term Operation, Fouling Mitigation, Wastewater Treatment, Adsorption Dynamics, Mass Transfer

1. Introduction

Membrane bioreactor (MBR) technology has emerged as a transformative advancement in modern wastewater treatment, offering a hybrid solution that integrates conventional biological processes with membrane filtration. This synergy allows for the simultaneous removal of organic matter, nutrients, and suspended solids, delivering high-quality effluent suitable for reuse or discharge into sensitive receiving environments.

MBR systems have gained widespread adoption across municipal and industrial sectors due to their ability to achieve superior treatment performance within a compact footprint, making them particularly attractive in urban areas and facilities with space constraints. By decoupling the hydraulic retention time from the sludge retention time, MBRs enable enhanced control over biomass concentrations, resulting in increased process efficiency, better sludge characteristics, and reduced reactor volumes compared to traditional activated sludge systems (Ajayi, *et al.*, 2020, Ikeh & Ndiwe, 2019, Orieno, *et al.*, 2021).

Despite these advantages, the long-term operation of MBRs remains hindered by one critical and persistent issue: membrane fouling. Over time, the accumulation of particulate matter, colloids, microbial products, and dissolved organics on membrane surfaces leads to a decline in permeability, increased transmembrane pressure, and higher energy consumption. Fouling not only compromises operational efficiency but also necessitates frequent cleaning and membrane replacement, thereby escalating operational costs and reducing the economic viability of the technology (Bristol-Alagbariya, Ayanponle & Ogedengbe, 2022, Ogunwole, *et al.*, 2022). Various types of fouling including biofouling, organic fouling, inorganic scaling, and colloidal fouling interact in complex ways, often influenced by operational parameters such as sludge characteristics, membrane material, hydrodynamics, and chemical environment. As such, understanding the mechanisms of fouling from a chemical engineering standpoint is vital for developing predictive models, designing fouling-resistant membranes, and formulating mitigation strategies.

The objective of this paper is to provide a detailed chemical engineering analysis of fouling mechanisms in MBR systems during long-term operation. Through an examination of the physicochemical interactions at the membrane interface, the transport phenomena within the fouling layer, and the thermodynamics of foulant deposition, this work seeks to elucidate the underlying processes that govern membrane fouling (Gianni, Lehtinen & Nieminen, 2022; Helo & Hao, 2022). By bridging fundamental principles with practical insights, the paper aims to support the design and operation of more resilient, cost-effective, and sustainable MBR systems for wastewater treatment applications.

2. Methodology

The methodology for this conceptual analysis integrates systematic literature review techniques with domain-specific engineering insights. The first step involved identifying the core problem: long-term fouling in membrane bioreactors (MBRs) and the necessity for an engineering-based understanding. A systematic literature search was conducted using databases such as Scopus, ScienceDirect, and Google Scholar with keywords including “membrane fouling,” “MBRs,” “biofouling,” “chemical engineering,” and “long-term operation.” The inclusion criteria were peer-reviewed publications that specifically addressed MBR performance, fouling characterization, and chemical mitigation approaches.

Relevant data were extracted from studies that aligned with these criteria, including mechanisms such as organic fouling, inorganic scaling, and biofouling. Particular attention was given to studies that applied or referenced chemical engineering modeling, such as mass transfer equations, fouling kinetics, and thermodynamic interactions. The

chemical framework was drawn from foundational insights, including diffusion limitations, solute-membrane interactions, and the role of operational stressors in fouling intensification.

Next, the identified fouling mechanisms were comparatively analyzed, with factors like pH, temperature, crossflow velocity, and feed composition considered as modifying parameters. The insights from Adeoba *et al.* (2018–2019) regarding discriminatory classification and system variability were leveraged to frame a system-level understanding of heterogeneity in operational responses. Studies like Gkotsis *et al.* (2014) and Jabbari *et al.* (2019) provided essential details for benchmarking against newer insights from Adewoyin (2021, 2022) and Agho *et al.* (2022) on structural and operational system degradation.

Finally, a conceptual framework was developed linking fouling types to operational variables, integrating both empirical data and mechanistic models. This framework offers a clearer visualization of how each type of fouling evolves under prolonged operation and identifies the leverage points for chemical intervention and design optimization. Research gaps, particularly in real-time modeling and predictive chemical dosing, were identified for future exploration.

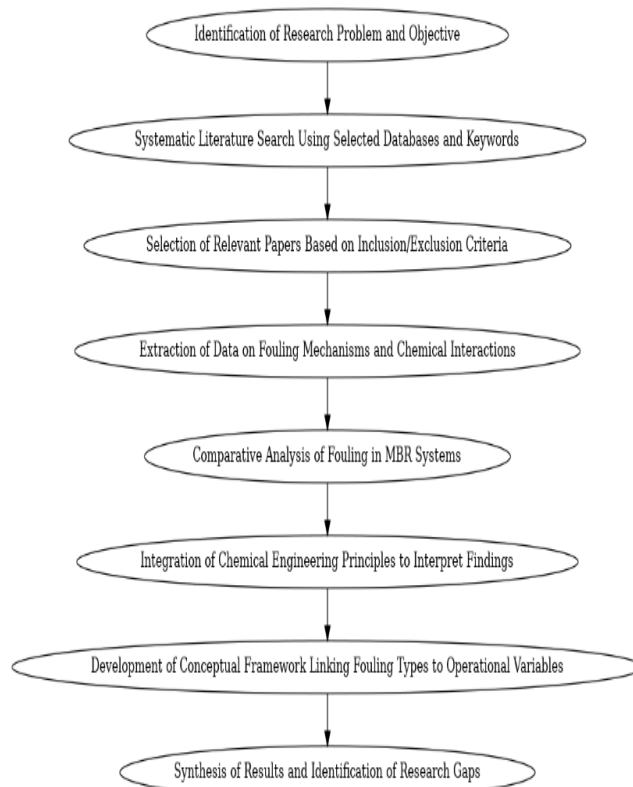


Fig 1: Flow chart of the study methodology

2.1 Classification of membrane fouling

Membrane fouling remains a fundamental challenge in the long-term operation of membrane bioreactors (MBRs), directly influencing system efficiency, operational cost, and membrane lifespan. From a chemical engineering perspective, understanding the classification of membrane fouling is critical to developing effective mitigation and cleaning strategies. Fouling can be broadly categorized into reversible and irreversible forms, with further subclassification based on the nature of the foulants: organic,

inorganic, particulate/colloidal, and biological. This classification allows for systematic analysis of the physicochemical interactions and transport phenomena that govern fouling behavior under real operating conditions (Al-Besher & Kumar, 2022; Djeflal, Siewert & Wurster, 2022; Tardieu, 2022).

Reversible fouling refers to the accumulation of material on the membrane surface or within its pores that can be removed through physical cleaning methods such as backwashing, relaxation, or low-pressure flushing. This type of fouling tends to involve loosely attached particulates or biofilm precursors that have not yet developed strong adhesion or undergone chemical transformation (Daraojimba, *et al.*, 2021, Egbumokei, *et al.*, 2021, Sobowale, *et al.*, 2021).

Reversible fouling, although disruptive, can often be managed with minimal chemical input, making it more tolerable in regular operations. In contrast, irreversible fouling is more tenacious, resulting from strong adsorption, chemical bonding, or structural entrapment of foulants within the membrane matrix. These deposits typically require chemical cleaning agents or, in severe cases, membrane replacement. Irreversible fouling leads to permanent permeability decline and is considered the most detrimental to long-term membrane performance (Androustoupoulou, *et al.*, 2019; Kankanhalli, Charalabidis & Mellouli, 2019). Figure 2 shows the operational factors affecting membrane fouling in AnMBRs presented by Jabbari, *et al.*, 2019.

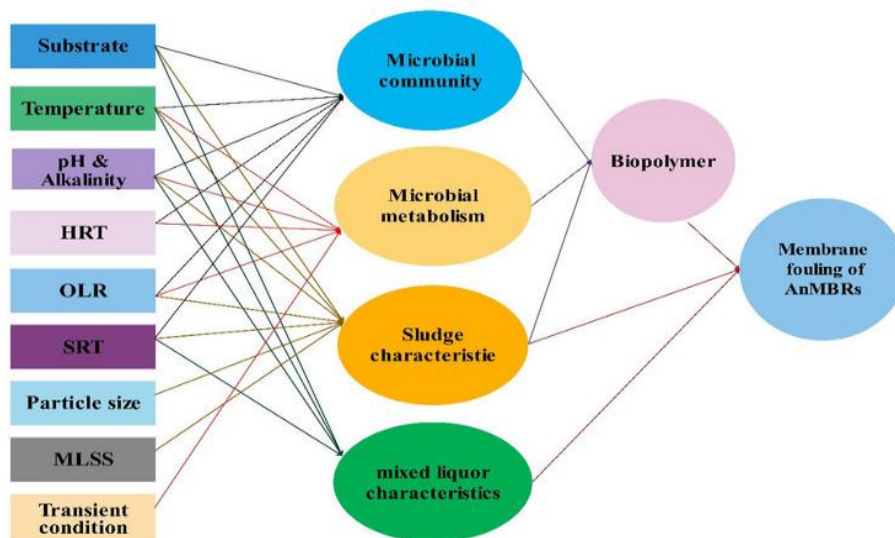


Fig 2: The operational factors affecting membrane fouling in AnMBRs (Jabbari, *et al.*, 2019).

Among the different types of fouling, organic fouling is a major contributor in MBR systems due to the abundance of natural and synthetic organic matter in wastewater. Humic substances, proteins, polysaccharides, and surfactants can adsorb onto membrane surfaces or penetrate pores, forming a dense cake layer or clogging internal channels. The fouling potential of organic compounds is influenced by their molecular weight, hydrophobicity, and charge characteristics (Onyeke, *et al.*, 2022, Orieno, *et al.*, 2022, Ozobu, *et al.*, 2022). For instance, proteins and polysaccharides, especially those derived from extracellular polymeric substances (EPS) and soluble microbial products (SMP), exhibit strong fouling tendencies due to their sticky nature and ability to form gel-like structures. These compounds can also interact synergistically, creating complex matrices that are more difficult to remove than individual components. Chemical engineers must consider the thermodynamic affinity between organic foulants and membrane materials, including hydrogen bonding, electrostatic attraction, and van der Waals forces, to understand fouling progression and select appropriate anti-fouling coatings or pretreatment processes (Chukwuma, *et al.* 2022, Johnson, *et al.*, 2022, Ogunwole, *et al.*, 2022).

Inorganic fouling, or scaling, is another significant issue in long-term MBR operation, particularly in systems treating

hard water or industrial effluents rich in minerals. Common scaling agents include calcium (Ca^{2+}), magnesium (Mg^{2+}), phosphate (PO_4^{3-}), carbonate (CO_3^{2-}), and sulfate (SO_4^{2-}), which can precipitate as salts such as calcium carbonate, calcium phosphate, and magnesium hydroxide. These precipitates form crystalline deposits on membrane surfaces and within pores, causing flux decline and increased transmembrane pressure (Akintobi, Okeke & Ajani, 2022, Ezeanochie, Afolabi & Akinsooto, 2022). Inorganic scaling is often pH-dependent and can be exacerbated by high recovery rates or temperature fluctuations. For instance, calcium carbonate scaling is more likely to occur at higher pH levels, while phosphate precipitation is influenced by the presence of multivalent cations and temperature. From a modeling perspective, mass transfer limitations, local supersaturation conditions, and nucleation kinetics must be incorporated to predict scaling behavior accurately. Preventive measures such as pH adjustment, anti-scalant dosing, and softening of feedwater are commonly used to manage inorganic fouling, but these add operational complexity and cost (Adeoba, 2018, Imran, *et al.*, 2019, Orieno, *et al.*, 2021). Membrane Bioreactors (MBR) fouling mechanisms for operation at constant flux presented by Gkotsis, *et al.*, 2014 is shown in figure 3.

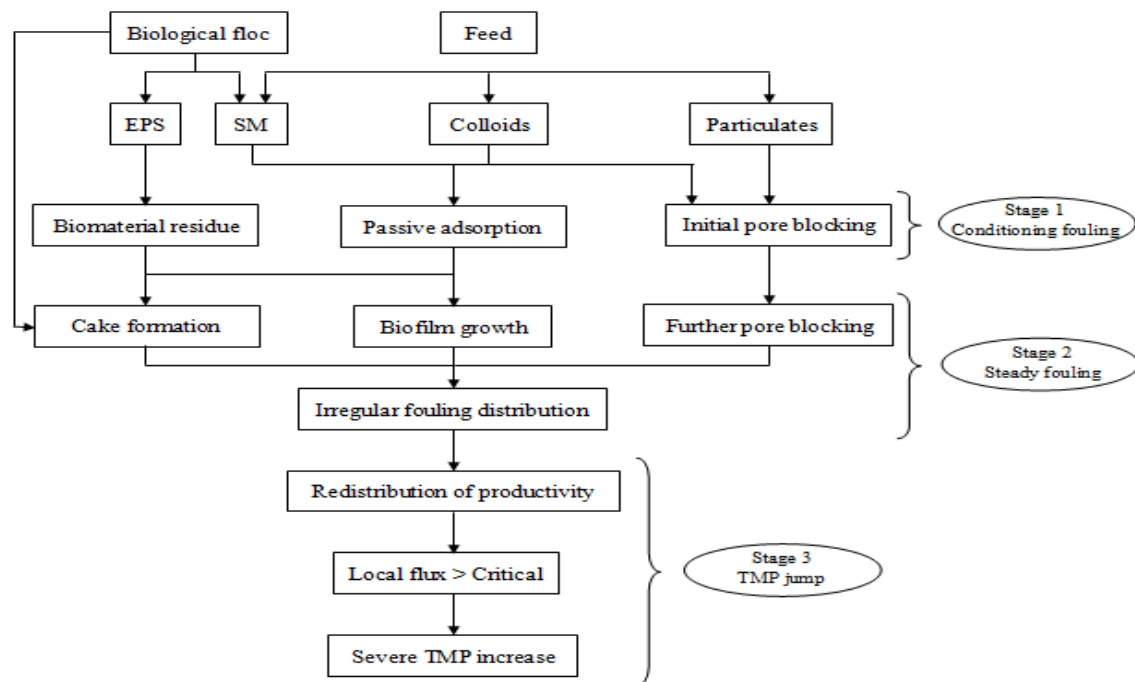


Fig 3: Membrane Bioreactors (MBR) fouling mechanisms for operation at constant flux (Gkotsis, *et al.*, 2014).

Particulate and colloidal fouling involves the deposition of suspended solids and colloidal matter that escape prior treatment stages. These materials may include clay particles, silt, metal oxides, or fine organic aggregates. Their small size allows them to accumulate on the membrane surface, forming a dense cake layer that hinders water permeability. Unlike organic fouling, which is driven largely by adsorption, particulate fouling is governed by physical filtration and cake layer formation mechanisms (Ojika, *et al.*, 2021, Okolo, *et al.*, 2021, Onukwulu, *et al.*, 2021). The extent of fouling depends on particle size distribution, concentration, zeta potential, and hydrodynamic conditions in the reactor. In MBR systems, shear forces generated by air scouring or cross-flow filtration play a key role in dislodging particles and mitigating cake build-up. However, when particles are highly deformable or adhesive, such as in the case of colloidal microbial debris, they can still penetrate into membrane pores and cause irreversible blockage. Understanding the deposition dynamics, cake layer compressibility, and permeability resistance is essential for optimizing cleaning cycles and aeration strategies (Adepoju, *et al.*, 2022, Onoja, Ajala & Ige, 2022).

Biofouling, a uniquely complex and persistent form of fouling, arises from the microbial colonization of membrane surfaces and the subsequent formation of biofilms. This process begins with the attachment of planktonic

microorganisms, followed by the secretion of EPS and the development of a mature, structured microbial community. Biofilms act as barriers to water flow and facilitate the accumulation of organic and inorganic foulants, further exacerbating membrane resistance (Agho, *et al.*, 2021, Ezeanochie, Afolabi & Akinsooto, 2021). Moreover, biofilms can harbor pathogenic organisms and contribute to system instability through biomass sloughing or clogging. The chemical and structural heterogeneity of biofilms makes them particularly resistant to physical and chemical cleaning. Effective control of biofouling requires a multidisciplinary approach, combining microbial ecology, surface chemistry, and hydrodynamics. From a chemical engineering standpoint, the focus is on understanding the transport of nutrients and antimicrobial agents within the biofilm matrix, the adhesion forces between microbial cells and membrane materials, and the influence of operational parameters on biofilm growth dynamics (Egbuhuzor, *et al.*, 2021, Isi, *et al.*, 2021, Onukwulu, *et al.*, 2021). Strategies such as periodic cleaning with biocides, optimization of hydraulic shear, and the use of anti-adhesive membrane surfaces are employed to manage biofouling, but their long-term efficacy remains an area of active research. Jabbari, *et al.*, 2019 presented in figure 4, Overview of membrane fouling types, mechanisms and the required cleaning techniques.

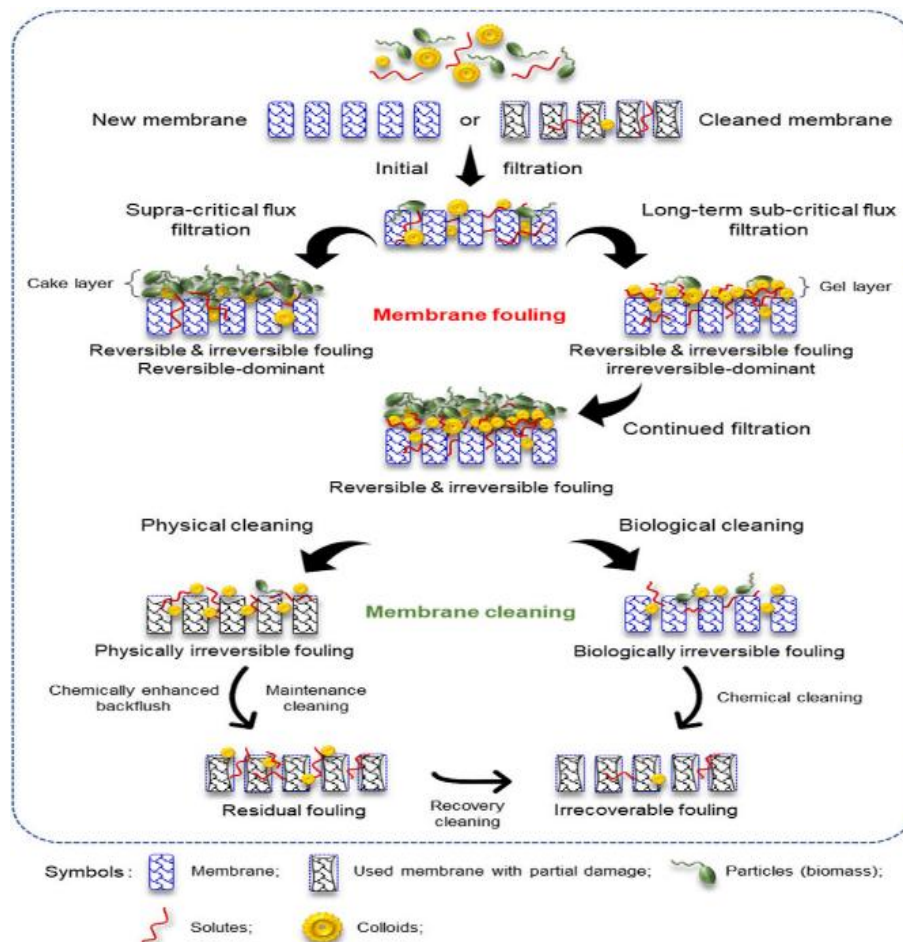


Fig 4: Overview of membrane fouling types, mechanisms and the required cleaning techniques (Jabbari, *et al.*, 2019).

Each type of fouling presents distinct mechanisms and challenges, yet they often occur simultaneously and interact in synergistic or antagonistic ways. For example, biofouling may enhance the retention of organic and inorganic compounds, leading to a composite fouling layer with highly heterogeneous properties. Similarly, scaling may create rough surfaces that facilitate microbial attachment, or organic matter may serve as a matrix for crystal growth (Daraojimba, *et al.*, 2022, Elete, *et al.*, 2022, Okolo, *et al.*, 2022). These interactions complicate fouling diagnosis and necessitate an integrated analytical framework to capture the full complexity of membrane fouling in MBRs.

In conclusion, the classification of membrane fouling into reversible and irreversible forms, and into specific foulant categories such as organic, inorganic, particulate, and biological, provides a foundational framework for understanding the long-term performance limitations of membrane bioreactors (Onukwulu, *et al.* 2021, Taeihagh, 2021). A chemical engineering perspective that emphasizes molecular interactions, transport phenomena, and system thermodynamics is essential for elucidating fouling mechanisms and guiding the development of effective mitigation strategies. As MBR technology continues to evolve and expand, addressing the multifaceted nature of membrane fouling remains a priority for ensuring sustainable, high-efficiency wastewater treatment.

2.2 Role of Extracellular Polymeric Substances (EPS) and Soluble Microbial Products (SMP)

Extracellular polymeric substances (EPS) and soluble

microbial products (SMP) play a central role in the fouling mechanisms encountered during the long-term operation of membrane bioreactors (MBRs). These substances, produced and released by microbial communities in activated sludge systems, are major contributors to membrane fouling, particularly due to their complex chemical composition, high molecular weight, and strong affinity for membrane surfaces. From a chemical engineering perspective, understanding the behavior of EPS and SMP is essential to unraveling the physical, chemical, and interfacial phenomena that underlie membrane fouling and to designing strategies for its mitigation (Standardisation, 2017; Truby, 2020).

EPS are high-molecular-weight biopolymers secreted by microorganisms and are typically found in the vicinity of microbial flocs. They form a protective matrix that maintains microbial structure, facilitates nutrient exchange, and provides resistance to environmental stress. EPS are broadly classified into two categories: bound EPS, which are tightly associated with cell surfaces and microbial aggregates, and loosely bound EPS, which are more loosely attached and may disperse into the bulk liquid (Adewoyin, 2021, Isi, *et al.*, 2021, Ogunnowo, *et al.*, 2021). SMP, on the other hand, consist of cellular metabolic byproducts and lysis products that remain dissolved or colloidal in the surrounding liquid phase. While EPS are predominantly structural and localized, SMP are soluble and dispersed, making them more mobile and reactive within the MBR environment.

The chemical composition of EPS and SMP includes a diverse range of organic compounds such as polysaccharides, proteins, nucleic acids, lipids, humic substances, and uronic

acids. Polysaccharides and proteins are the dominant components and are largely responsible for the fouling behavior due to their abundance and functional groups. Polysaccharides contain hydroxyl and carboxyl groups, which contribute to strong hydrogen bonding and electrostatic interactions with membrane materials (Bristol-Alagbariya, Ayanponle & Ogedengbe, 2022, Onukwulu, *et al.*, 2022). Proteins, with their variable amino acid side chains, can engage in both hydrophilic and hydrophobic interactions depending on their tertiary structure and the surrounding pH and ionic strength. The heterogeneity in EPS and SMP composition leads to a wide range of physicochemical behaviors that affect their interaction with membrane surfaces and their contribution to fouling.

One of the most critical fouling pathways associated with EPS and SMP is pore blocking. Due to their size and conformational flexibility, these substances can infiltrate membrane pores and accumulate within the internal structure of the membrane. This internal fouling reduces effective membrane porosity and increases resistance to flow, leading to a decline in permeate flux and a rise in transmembrane pressure. Pore blocking is particularly problematic in membranes with larger pore sizes or in systems where SMP concentration is high, such as during biomass decay or shock loading events (Attah, *et al.*, 2022, Elele, *et al.*, 2022, Nwulu, *et al.*, 2022). The tendency of SMP to enter and remain in membrane pores is governed by their hydrodynamic radius, charge density, and molecular configuration, all of which are affected by operational conditions such as pH, ionic strength, and shear forces.

In addition to pore blocking, EPS and SMP contribute to the formation of a dense, viscous gel layer on the membrane surface, often referred to as the cake layer. This layer acts as an additional filtration barrier, further restricting water flow and exacerbating energy consumption due to increased pressure requirements. The gel layer is primarily composed of high-molecular-weight polysaccharides and proteins that form a hydrated network capable of trapping suspended solids, colloidal particles, and additional biomolecules (Afolabi & Akinsooto, 2021, Ogundipe, *et al.*, 2021). This layer is not only a physical obstruction but also a chemically active zone where further fouling can be catalyzed through reactions such as cross-linking, precipitation of salts, and biofilm formation.

The adhesion and stability of the EPS/SMP-derived gel layer are strongly influenced by interfacial interactions between the biopolymers and the membrane surface. Hydrogen bonding is a key mechanism, particularly between the hydroxyl, carboxyl, and amine groups in the EPS/SMP matrix and polar functional groups on membrane surfaces such as hydroxyl (–OH), carboxyl (–COOH), and sulfonic (–SO₃H) groups. These interactions enhance the affinity of EPS for the membrane and contribute to the formation of a stable fouling layer that is difficult to remove through physical cleaning (Agho, *et al.*, 2022, Ezeafulukwe, Okatta & Ayanponle, 2022).

Hydrophobic interactions also play a significant role, especially when hydrophobic membrane materials such as polyvinylidene fluoride (PVDF), polypropylene (PP), or polyethylene (PE) are used. Proteins and lipids in EPS and SMP often possess nonpolar regions that can adsorb onto the hydrophobic portions of the membrane, leading to strong and irreversible attachment. This hydrophobic attraction not only increases the fouling potential but also affects the

configuration of the fouling layer, making it more compact and less permeable (Daraojimba, *et al.*, 2022, Kanu, *et al.*, 2022, Okolo, *et al.*, 2022). The balance between hydrophobic and hydrophilic interactions is a function of the surface properties of both the membrane and the foulants, and it is sensitive to environmental factors such as temperature, pH, and salt concentration.

Electrostatic interactions further govern the adsorption and deposition of EPS and SMP on membrane surfaces. Both the foulants and the membranes typically carry surface charges that depend on the chemical composition and the pH of the medium. For instance, many EPS components carry a net negative charge due to the presence of carboxyl and phosphate groups. When the membrane surface also exhibits a negative charge, electrostatic repulsion may reduce foulant attachment. However, the presence of multivalent cations such as Ca²⁺ and Mg²⁺ can neutralize these charges and act as bridging agents, enhancing fouling by facilitating aggregation and adhesion (Ojika, *et al.*, 2021, Onaghinor, *et al.*, 2021, Sobowale, *et al.*, 2021). This phenomenon is often observed in systems with high hardness or in cases where salts are used in the treatment process.

The aggregation behavior of EPS and SMP is also central to their fouling capacity. Under certain ionic conditions, these substances can self-associate or form complexes with other colloids and solutes, resulting in floc-like structures that deposit more readily on the membrane surface. These aggregates exhibit viscoelastic properties and can deform under shear, making them resilient to cleaning processes. Their composition and behavior can also evolve over time due to microbial activity, oxidation, or interaction with cleaning agents, further complicating fouling management (Ajayi, *et al.*, 2021, Odio, *et al.*, 2021, Onukwulu, *et al.*, 2021).

From a modeling and process optimization perspective, understanding the roles of EPS and SMP is essential for predicting membrane fouling rates and designing appropriate control strategies. Chemical engineering models often incorporate empirical or mechanistic descriptions of EPS/SMP transport, adsorption, and reaction kinetics, providing a basis for simulating long-term membrane performance. Variables such as the rate of EPS production, the degradation kinetics of SMP, and their interaction coefficients with membrane surfaces are critical inputs for these models (Adeoba & Yessoufou, 2018, Oyedokun, 2019). In conclusion, EPS and SMP are among the most influential foulants in membrane bioreactor systems, driving both reversible and irreversible fouling mechanisms. Their complex composition, high reactivity, and propensity for interfacial interactions result in pore blocking, gel layer formation, and the promotion of biofilm development (Adepoju, *et al.*, 2022, Okolie, *et al.*, 2022). A detailed chemical engineering analysis of these substances including their transport behavior, surface chemistry, and thermodynamic affinities is essential for developing predictive fouling models and effective mitigation strategies. As MBR technology continues to evolve, managing the impacts of EPS and SMP remains central to achieving sustained, high-efficiency, and cost-effective wastewater treatment.

2.3 Physicochemical fouling mechanisms

Physicochemical fouling in membrane bioreactors (MBRs) is a complex and multifaceted phenomenon that significantly

impacts the long-term efficiency and sustainability of membrane filtration systems. From a chemical engineering perspective, understanding the fundamental mechanisms of fouling particularly those driven by the physicochemical interactions between the foulants and the membrane surface is crucial to designing more efficient, fouling-resistant membranes and optimizing system performance (Adepoju, *et al.*, 2021, Okolie, *et al.*, 2021, Sobowale, *et al.*, 2021). Fouling mechanisms in MBRs arise from a variety of factors, including the adsorption dynamics of organic and inorganic materials, mass transfer limitations, and the thermodynamic and kinetic processes governing the accumulation of foulants. In addition, the inherent properties of the membrane material itself, such as hydrophilicity, surface charge, and roughness, play a significant role in determining the extent and nature of fouling.

The adsorption of foulants onto the membrane surface is one of the primary mechanisms contributing to membrane fouling. The nature of this adsorption is influenced by the physicochemical properties of both the membrane and the foulant. Organic compounds, proteins, polysaccharides, microbial cells, and other dissolved or particulate matter in wastewater tend to interact with membrane surfaces through a combination of van der Waals forces, hydrogen bonding, electrostatic forces, and hydrophobic interactions (Adewoyin, 2022, Elete, *et al.*, 2022, Nwulu, *et al.*, 2022). Adsorption dynamics can be modeled using adsorption isotherms, such as Langmuir or Freundlich models, which describe the relationship between the concentration of foulants in the bulk liquid and their concentration on the membrane surface. However, adsorption is often a dynamic process where foulants continuously adsorb and desorb depending on the operational conditions, leading to the formation of a reversible or irreversible fouling layer.

One of the most important factors that influence the adsorption of foulants is the membrane material itself. Membranes are typically made from polymers such as polyvinylidene fluoride (PVDF), polyethersulfone (PES), or polypropylene (PP), each with distinct surface properties that affect fouling behavior. The hydrophilicity or hydrophobicity of the membrane surface plays a critical role in its interaction with foulants. Hydrophilic membranes tend to repel hydrophobic organic substances but can attract hydrophilic compounds like proteins and polysaccharides (Akintobi, Okeke & Ajani, 2022, Kanu, *et al.*, 2022, Onukwulu, *et al.*, 2022). Hydrophobic membranes, on the other hand, tend to adsorb hydrophobic foulants more readily, creating a favorable environment for fouling. The charge of the membrane surface also influences the type of foulants that adsorb. For example, positively charged membranes can attract negatively charged particles or organic molecules, while negatively charged membranes may attract positively charged species, such as certain types of proteins or cations. The roughness of the membrane surface is another critical factor affecting fouling. A rough surface provides more surface area for foulants to accumulate, and the microstructural characteristics of the membrane (such as pore size and pore distribution) further influence the amount of foulant deposition. Membranes with smoother surfaces may reduce fouling by minimizing surface area for adsorption; however, this must be balanced with other performance characteristics such as flux and permeability (Edwards, Mallhi & Zhang, 2018, Tula, *et al.*, 2004, Vindrola-Padros & Johnson, 2022). The topography of the membrane surface

also affects the formation of a fouling cake or gel layer, as rougher surfaces may promote the deposition of particulate matter, leading to thicker and more difficult-to-remove fouling layers.

Mass transfer limitations and concentration polarization are also key contributors to physicochemical fouling. As water passes through the membrane, the concentration of foulants at the membrane surface increases relative to the bulk solution, creating a concentration polarization layer. This layer acts as a resistance to mass transfer, limiting the rate at which foulants are carried away from the membrane surface. The buildup of concentrated foulants at the surface accelerates adsorption and further exacerbates the fouling process. In systems with high fouling potential, such as those treating high-strength industrial wastewater, concentration polarization can significantly increase the rate of membrane fouling (Bristol-Alagbariya, Ayanponle & Ogedengbe, 2022, Onukwulu, *et al.*, 2022). The extent of concentration polarization is influenced by factors such as the flow velocity, cross-flow velocity, and turbulence in the system. Inadequate flow conditions, especially in regions of low shear stress, can lead to stagnant zones where fouling is most pronounced.

Mass transfer limitations also affect the ability to effectively clean the membrane. In systems where backflushing, air scouring, or chemical cleaning is used, fouling layers can become tightly bound to the membrane surface if mass transfer limitations hinder the removal of foulants. For instance, fouling by organic materials such as proteins or polysaccharides may lead to the formation of a gel-like layer that is difficult to dislodge. The high resistance to flow associated with such fouling layers can also increase transmembrane pressure (TMP), further complicating cleaning procedures (Adeoba, *et al.*, 2018, Omisola, *et al.*, 2020). Therefore, understanding the dynamics of concentration polarization and the associated mass transfer limitations is critical for designing more efficient membrane cleaning strategies and optimizing operating conditions.

Thermodynamic and kinetic modeling plays a vital role in understanding foulant accumulation and predicting fouling behavior over time. Thermodynamic models help describe the equilibrium between foulants in the bulk solution and those adsorbed on the membrane surface, providing insight into the adsorption isotherms and the driving forces behind the accumulation process. The enthalpy and entropy changes associated with foulant adsorption can indicate whether the process is driven by favorable entropic or enthalpic interactions (Ajiga, Ayanponle & Okatta, 2022, Noah, 2022, Ogundipe, Sangoleye & Udokanma, 2022). Kinetic models, on the other hand, help predict the rate at which fouling will occur based on the concentration of foulants, the membrane surface area, and the environmental conditions such as temperature and pH. These models can be used to estimate the long-term effects of fouling and to predict when cleaning or replacement will be necessary. By incorporating these models into operational strategies, chemical engineers can optimize the timing of cleaning cycles and predict the lifespan of membranes.

One of the major challenges in dealing with physicochemical fouling is the presence of multiple foulant types simultaneously. Organic, inorganic, and microbial foulants often accumulate together, forming complex fouling layers with varying properties. The interaction between these different types of foulants can create synergistic effects, leading to faster fouling than would be predicted by

considering each foulant type independently (Onaghinor, *et al.*, 2021, Orieno, *et al.*, 2022, Sobowale, *et al.*, 2022). For example, organic foulants such as proteins and polysaccharides may interact with inorganic salts, leading to the formation of composite foulant layers that are more difficult to remove. Similarly, microbial biofilms can trap organic and inorganic foulants, creating a heterogeneous fouling layer that exhibits both physical and chemical resistance to cleaning.

In conclusion, the physicochemical mechanisms of fouling in membrane bioreactors are a multifaceted challenge that involves the complex interactions between membrane surfaces and foulants in wastewater. Adsorption dynamics, mass transfer limitations, concentration polarization, and the physicochemical properties of the membrane material all contribute to the development and progression of fouling. From a chemical engineering perspective, understanding these mechanisms is crucial for optimizing membrane performance, designing more fouling-resistant membranes, and developing effective cleaning and mitigation strategies. As MBR technology continues to be employed in wastewater treatment, particularly in decentralized applications, ongoing research into the physicochemical aspects of fouling will be essential to ensuring the long-term sustainability and cost-effectiveness of these systems.

2.4 Operational factors affecting fouling

The long-term operation of membrane bioreactors (MBRs) is heavily influenced by a variety of operational factors that affect the fouling mechanisms encountered during filtration processes. Fouling, as a critical challenge in MBR systems, results in a gradual decline in performance, with increased energy consumption, reduced permeate flux, and increased operational costs due to the need for frequent cleaning and membrane replacement. These operational factors, which encompass both hydraulic and operational parameters, significantly influence the extent and severity of fouling in MBRs, impacting both reversible and irreversible fouling processes. From a chemical engineering perspective, understanding how these factors contribute to fouling allows for the optimization of system design and operation to enhance the longevity and efficiency of MBR systems in wastewater treatment.

One of the most significant operational factors affecting fouling in MBRs is the flux loading, which is directly related to the transmembrane pressure (TMP). Flux refers to the rate at which water passes through the membrane, and it is typically measured as the volume of permeate per unit area of membrane surface per unit of time. As the flux increases, the volume of water treated per unit time also increases, but this comes at the cost of an increased TMP. TMP is the pressure difference between the feed and permeate sides of the membrane and is a key indicator of the membrane's resistance to flow (Ajayi, *et al.*, 2020, Ofori-Asenso, *et al.*, 2020). A high TMP indicates that the membrane is facing greater resistance due to the accumulation of foulants on the surface or within the pores.

In membrane filtration processes, TMP is closely linked to fouling because as foulants accumulate on the membrane surface, the resistance to flow increases, causing the TMP to rise. When the system operates at high flux loading, the increased fouling rate can be exacerbated, leading to rapid permeability decline and more frequent cleaning cycles. Chemical engineers must consider the balance between high

flux loading, which improves system throughput, and the associated increase in fouling and TMP (Bristol-Alagbariya, Ayanponle & Ogedengbe, 2022, Nwulu, *et al.*, 2022). High flux loading may be appropriate in short-term operations, but over extended periods, it accelerates fouling and leads to higher energy consumption and more maintenance, making it less viable for long-term operation without careful management of TMP and fouling.

Hydraulic retention time (HRT) and sludge retention time (SRT) are two additional operational factors that play a crucial role in fouling behavior in MBR systems. HRT is the average time that wastewater remains in the reactor, while SRT represents the average time that the activated sludge remains in the system. Both parameters influence the microbial community in the bioreactor, and consequently, the production of extracellular polymeric substances (EPS), which are major contributors to fouling (Francis Onotole, *et al.*, 2022). In general, longer HRTs allow more time for pollutants to be degraded by microorganisms, leading to a reduction in the organic load on the membrane. However, excessive HRT can lead to an accumulation of EPS, as the longer the sludge remains in the system, the more extracellular materials are produced by microbial metabolism.

Similarly, SRT influences the microbial composition and activity in the bioreactor. A longer SRT promotes the growth of slow-growing microorganisms that are more efficient in breaking down pollutants but also tend to produce more EPS, which can lead to an increased fouling potential. Shorter SRTs, on the other hand, may result in a lower accumulation of EPS, but they could reduce the efficiency of biological treatment and increase the organic loading on the membrane (Ogunyankinnu, *et al.*, 2022, Kolade, *et al.*, 2022). Thus, chemical engineers must carefully optimize both HRT and SRT to achieve a balance between effective treatment and manageable fouling. Proper adjustment of these parameters can reduce the rate of fouling by controlling the microbial dynamics in the reactor.

Aeration rate is another important operational factor that directly affects fouling in MBRs. Aeration serves multiple functions in MBR systems, including supplying oxygen for aerobic microorganisms, promoting mixing in the bioreactor, and preventing the formation of cake layers on the membrane surface by creating shear forces. The impact of aeration rate on fouling is highly dependent on the shear forces generated, which can influence the adhesion of foulants to the membrane surface (Ilori & Olanipekun, 2020). Higher aeration rates create greater shear forces that can help keep the membrane surface clean by physically dislodging foulants and preventing the formation of a stable fouling layer. However, excessive aeration can also lead to turbulence that disturbs the microbial community or leads to the breakage of biofilms, which could result in the release of more soluble microbial products (SMP) into the system. This increase in SMP can exacerbate fouling by providing additional organic matter for adsorption to the membrane.

Conversely, insufficient aeration can lead to biofilm accumulation and an increased rate of irreversible fouling. Without sufficient mixing or shear, particles, organic matter, and microorganisms can accumulate and adhere to the membrane surface, leading to the formation of a gel-like fouling layer. Aeration must, therefore, be optimized not only for maintaining aerobic conditions but also for minimizing the adverse effects of excessive shear on microbial activity

while effectively mitigating fouling (Ajibola & Olanipekun, 2019; Olanipekun & Ayotola, 2019).

The impact of cleaning cycles and fouling reversibility is another critical factor in the long-term operation of MBRs. Membrane cleaning is essential to restore permeability and reduce TMP, especially in systems that experience high levels of fouling. The frequency and type of cleaning, whether it involves physical methods such as backwashing or chemical cleaning with acids, alkalis, or detergents, significantly influence the longevity of the membrane and the overall performance of the MBR system. In terms of fouling reversibility, some fouling layers are more easily removed than others (Olanipekun, 2020; West, Kraut & Ei Chew, 2019). Reversible fouling, often caused by the adsorption of particulate matter or soluble organic compounds, can typically be mitigated with regular cleaning cycles or by controlling operational parameters such as aeration or flux loading. Irreversible fouling, such as that caused by biofilm formation or the deposition of inorganic scaling, may require more aggressive cleaning methods or even membrane replacement in extreme cases.

The effectiveness of cleaning cycles depends on the nature of the fouling layer, the cleaning technique employed, and the duration of membrane operation. Over time, the cleaning process may become less effective, particularly for irreversible fouling. If cleaning cycles are not properly managed, the fouling layer can become more compacted and harder to remove, leading to a further increase in TMP and a decrease in the overall flux (Belot, 2020; Olanipekun, Ilori & Ibitoye, 2020). Chemical engineers must, therefore, consider the cleaning efficiency when optimizing operational parameters and incorporate strategies for minimizing irreversible fouling, such as by adjusting flux loading, HRT, and aeration rate to reduce the formation of biofilms and scale.

In conclusion, the long-term operation of MBRs is significantly influenced by a variety of operational factors that contribute to fouling mechanisms. Flux loading, TMP, HRT, SRT, aeration rate, and cleaning cycles all play a critical role in determining the fouling rate and, consequently, the system's overall performance and operational costs. Balancing these parameters is key to minimizing fouling and ensuring the sustainable operation of MBR systems (Kolade, *et al.*, 2021; Ramdoo, *et al.*, 2021). A comprehensive understanding of how these factors interact allows chemical engineers to optimize MBR design and operation, helping to extend the life of the membrane and reduce operational costs while maintaining high treatment efficiency. Future research and advancements in process control and monitoring will be critical in further improving the management of fouling in MBR systems, enabling their wider application in wastewater treatment, particularly in decentralized and resource-constrained settings.

2.5 Analytical and diagnostic techniques

The effective operation of membrane bioreactors (MBRs) is highly contingent upon the understanding and management of fouling, which remains one of the most significant barriers to the long-term success of these systems. Fouling in MBRs involves the accumulation of organic, inorganic, and microbial materials on the membrane surface, leading to increased resistance to flow, reduced permeate flux, and higher operational costs due to the need for frequent cleaning and membrane replacement. To optimize MBR performance,

chemical engineers have developed various analytical and diagnostic techniques to understand fouling mechanisms better, characterize fouling layers, and monitor fouling progression in real-time. These techniques provide crucial insights into the nature of the foulants, their interactions with the membrane surface, and the impact on overall system performance.

One of the primary tools used in the analysis of fouling is Fourier-transform infrared spectroscopy (FTIR). FTIR provides a non-destructive way to identify the chemical composition of foulants on the membrane surface by detecting vibrations in molecular bonds. This technique is invaluable for identifying organic foulants such as proteins, polysaccharides, lipids, and other soluble microbial products (SMP), which are key contributors to fouling in MBRs (Akan, *et al.*, 2019; Ezenwa, 2019). By examining the characteristic absorption bands in the infrared region, FTIR enables chemical engineers to quantify specific types of organic materials that accumulate on the membrane surface. For example, the presence of amide I and II bands in the FTIR spectrum indicates the presence of proteins, while carbohydrate-related vibrations are associated with polysaccharides. Understanding the composition of these foulants allows for more targeted strategies to mitigate fouling, such as optimizing operational parameters or modifying the membrane material to reduce the affinity for specific foulants.

Scanning electron microscopy (SEM) is another critical tool for studying fouling in MBR systems. SEM provides high-resolution imaging of the membrane surface, allowing researchers to observe the morphology and structure of the fouling layer. With the ability to magnify images up to several million times, SEM reveals the detailed surface topography and pore blocking characteristics, offering insights into how foulants accumulate over time. SEM images can show the growth and development of biofilms, the aggregation of particulate matter, or the formation of a cake layer on the membrane surface (Otokiti, *et al.*, 2022; Oyewola, *et al.*, 2022). This visual information is essential for understanding the physical characteristics of the fouling layer, such as its thickness, uniformity, and adherence to the membrane surface. Furthermore, SEM can be coupled with energy-dispersive X-ray spectroscopy (EDX) to obtain elemental composition data, enabling the identification of inorganic foulants such as salts and metal oxides that contribute to scaling in MBR systems.

Atomic force microscopy (AFM) is another powerful technique used to characterize fouling on the nanoscale. Unlike SEM, which requires a vacuum environment, AFM operates in ambient conditions and provides detailed topographical maps of the membrane surface at extremely high resolution (up to nanometer-scale resolution). AFM uses a sharp tip to scan the membrane surface, and the deflection of the tip is measured to produce a three-dimensional surface profile. This allows for the characterization of the roughness, elasticity, and surface energy of the fouling layer (Ochinawata, 2019; Negi, 2021; Otuoz, Hunt & Jefferson, 2021). By assessing the changes in the surface properties of the membrane, AFM can provide insights into how fouling affects membrane permeability and how the fouling layer evolves under different operational conditions. AFM is particularly useful for studying the viscoelastic properties of biofilms, as it can provide data on the stiffness and mechanical properties of microbial communities growing on

the membrane surface. Additionally, AFM can be used to study the interactions between the membrane surface and foulants at the molecular level, helping to identify the forces involved in adhesion and fouling.

Quantifying the composition of foulants and changes to the membrane surface is critical for developing effective fouling mitigation strategies. In addition to FTIR, SEM, and AFM, several other techniques can be used to evaluate the fouling layer's characteristics and its impact on membrane performance. For example, X-ray photoelectron spectroscopy (XPS) provides surface-sensitive chemical analysis, enabling the determination of elemental composition and the chemical states of the materials adsorbed on the membrane surface (Ijeomah, 2020; Qi, *et al.*, 2017). This technique is particularly useful for investigating the interactions between organic foulants and metal ions, which are common in industrial wastewater. XPS can help to identify whether fouling is driven by the adsorption of organic compounds or the precipitation of inorganic materials, providing valuable information for selecting appropriate cleaning strategies.

Furthermore, the characterization of the fouling layer's effect on membrane performance is often carried out by measuring changes in water flux over time, transmembrane pressure (TMP), and the resistance to filtration. The increase in TMP is directly related to the development of fouling on the membrane surface, and real-time monitoring of TMP provides an indication of the fouling rate and the need for cleaning (Babatunde, 2019; Olukunle, 2013; Danese, Romano & Formentini, 2013). By correlating TMP data with fouling composition and surface changes observed through techniques like FTIR, SEM, and AFM, chemical engineers can develop more accurate models for predicting fouling behavior and determining when to perform maintenance.

Real-time fouling monitoring is increasingly becoming an essential tool for managing fouling in MBR systems. Traditional methods for assessing fouling rely on periodic sampling and post-treatment analysis, which can provide valuable information but fail to capture the dynamic nature of fouling during continuous operation. Modern fouling monitoring tools, such as online sensors for turbidity, total organic carbon (TOC), and optical fouling sensors, offer the advantage of continuous, in-situ monitoring of fouling progress (Lu, 2019; Simchi-Levi, Wang & Wei, 2018). These sensors provide real-time data on changes in water quality and fouling potential, allowing operators to adjust operational parameters such as flux, aeration rate, and chemical dosing in response to detected fouling.

One promising development in real-time fouling monitoring is the use of ultrasonic sensors to detect fouling in MBRs. These sensors emit high-frequency sound waves and measure the attenuation of the signal as it passes through the membrane and fouling layer. Changes in the signal attenuation correlate with the thickness and density of the fouling layer, providing real-time feedback on fouling progression (Qrunfleh & Tarafdar, 2014; Wang, *et al.*, 2016). This technology allows for early detection of fouling, enabling operators to take corrective actions before significant performance degradation occurs.

Another emerging trend in fouling monitoring is the use of machine learning and artificial intelligence (AI) to analyze the vast amounts of data generated by sensors. AI algorithms can process data from multiple sources, including TMP measurements, online sensors, and fouling characterization

techniques, to predict fouling rates and optimize cleaning schedules (Mwangi, 2019; Zohuri & Moghaddam, 2020). Machine learning models can be trained to recognize patterns in fouling behavior and adjust operational parameters in real-time to minimize fouling while maintaining treatment efficiency. These advancements in fouling monitoring technology enable more proactive management of membrane systems, reducing the frequency and severity of fouling-related issues.

In conclusion, the analytical and diagnostic techniques available for characterizing and monitoring fouling in membrane bioreactors provide invaluable insights into the mechanisms that govern fouling behavior and its impact on membrane performance. Techniques such as FTIR, SEM, AFM, and XPS enable detailed characterization of the fouling layer's composition, structure, and interactions with the membrane surface, helping chemical engineers to identify the causes of fouling and develop effective mitigation strategies. Real-time monitoring tools and the integration of AI-based systems further enhance the ability to manage fouling in MBRs by providing continuous, actionable data (Dong, *et al.*, 2020; Tien, *et al.*, 2019). As membrane bioreactor technology continues to evolve, the development of more advanced diagnostic and monitoring techniques will play a crucial role in improving the sustainability, efficiency, and cost-effectiveness of wastewater treatment systems.

2.6 Modeling Approaches

Modeling fouling mechanisms in membrane bioreactors (MBRs) is a critical aspect of chemical engineering research and practice, providing insights into the behavior of fouling layers over time and offering tools for system optimization and long-term performance prediction. Fouling is a complex and dynamic phenomenon, and understanding how it develops under various operational conditions can help in designing more efficient MBR systems, reducing the frequency of cleaning cycles, and extending membrane lifespan. Various modeling approaches are used to represent the accumulation of foulants, their impact on membrane performance, and to predict the long-term effects of fouling on the system (Duan, Edwards & Dwivedi, 2019; Tien, 2017). These models play a crucial role in providing quantitative understanding and guiding operational decisions in MBR systems.

The resistance-in-series model is one of the simplest and most commonly used approaches for describing fouling in membrane filtration systems, including MBRs. This model assumes that the total resistance to filtration (transmembrane pressure or TMP) is the sum of resistances from various components, including the clean membrane resistance, the fouling layer resistance, and the resistance due to concentration polarization. Each component of the system adds a resistance that impedes the flow of water through the membrane (Javaid, *et al.*, 2022; Richey, *et al.*, 2022). The resistance-in-series model treats each resistance as independent of the others, which means that the total resistance is the sum of individual resistances, and the overall TMP is directly related to the fouling layer's buildup.

The model assumes that the membrane's resistance to flow is constant and that the fouling resistance changes over time, increasing as foulants accumulate. By monitoring TMP and understanding the relationship between TMP and fouling resistance, engineers can estimate fouling accumulation rates and make informed decisions regarding cleaning schedules.

This model, however, is limited by its simplification of the fouling process (Korteling, *et al.*, 2021; Zhang & Lu, 2021). It does not account for the complex interactions between foulants, the physical structure of the fouling layer, and the effect of operational conditions such as shear forces, temperature, and chemical concentrations. Despite its simplicity, the resistance-in-series model is valuable for providing a basic framework for evaluating membrane performance and the need for maintenance in the early stages of fouling development.

Fouling rate and transport-based models offer a more detailed and dynamic approach to understanding fouling in MBRs. These models incorporate mass transfer principles, recognizing that fouling is not just a static accumulation of materials but also a dynamic process driven by the movement of foulants from the bulk solution to the membrane surface. The rate of fouling is influenced by several factors, including the concentration of foulants in the feedwater, the flow conditions in the reactor, the properties of the foulants, and the characteristics of the membrane surface (Jarrahi, 2018; Terziyan, Gryshko & Golovianko, 2018). In transport-based models, the rate of fouling is typically described by a set of differential equations that govern the movement of solutes toward the membrane surface. The rate of fouling depends on the flux of foulants to the membrane, which is governed by diffusion and convection.

These models are often used to predict how the fouling layer forms and evolves over time, taking into account the transport of both organic and inorganic compounds, the effect of concentration polarization, and the influence of shear forces generated by aeration or cross-flow filtration. One common approach is to use a combination of convective-diffusive transport equations and fouling kinetics to model the accumulation of foulants on the membrane surface. The modeling process typically requires empirical data to determine key parameters such as fouling rate constants, diffusivity, and the effect of hydrodynamic conditions (Affognon, *et al.*, 2015; Misra, *et al.*, 2020). By integrating these parameters into the model, engineers can estimate the rate at which fouling develops under different operating conditions and predict when the membrane will require cleaning or replacement.

In addition to fouling rate and transport models, predictive models for long-term fouling behavior are becoming increasingly important in the design and operation of MBRs. Long-term fouling behavior is highly complex and depends on a variety of factors, including the composition of the wastewater, the operational conditions of the MBR, and the membrane material properties. Predictive models are designed to forecast how fouling will develop over extended periods, taking into account the long-term changes in the system and providing insights into when membrane replacement or system modifications may be necessary (Akande & Diei-Ouadi, 2010; Morris, Kamarulzaman & Morris, 2019).

Predictive models typically incorporate both short-term fouling behavior, which is influenced by the immediate operational conditions, and long-term effects, such as changes in membrane permeability, fouling layer consolidation, and biofilm maturation. These models often use data from real-world operations or laboratory-scale experiments to calibrate parameters and simulate the fouling process over extended timeframes. Some predictive models are based on machine learning algorithms or artificial

intelligence, which can learn from vast amounts of operational data and refine their predictions over time (Ahiaba, 2019; Hodges, Buzby & Bennett, 2011). These data-driven models are capable of handling complex interactions that may be difficult to capture using traditional deterministic approaches.

One key advantage of predictive models is that they enable engineers to simulate different operational scenarios and evaluate how various adjustments to parameters such as flux, aeration rate, HRT, or SRT affect long-term fouling rates. By incorporating real-time data into the predictive model, operators can adjust system parameters proactively, reducing fouling and extending the life of the membrane (Jagtap, *et al.*, 2020; Sibanda & Workneh, 2020). For instance, predictive models can forecast when to adjust aeration rates to reduce biofouling or when to alter flux loading to prevent excessive particulate deposition. Additionally, predictive models can help optimize cleaning schedules, ensuring that cleaning occurs only when necessary, minimizing the wear and tear on the membrane and reducing chemical usage.

However, one of the challenges with predictive models is their reliance on high-quality data. Accurate predictions require detailed input data on feedwater composition, membrane properties, and operational parameters, which can be difficult to obtain or measure in real-time. Furthermore, the complexity of fouling mechanisms, especially when multiple foulants are involved, makes it challenging to model all aspects of fouling behavior (Chaudhuri, *et al.*, 2018; Stathers & Mvumi, 2020). While predictive models can provide valuable insights into long-term fouling, they need continuous refinement and validation with real operational data to improve their accuracy and reliability.

Overall, modeling approaches for fouling in membrane bioreactors are essential for understanding and mitigating the challenges posed by fouling in long-term operation. The resistance-in-series model provides a simple framework for assessing the impact of fouling, while fouling rate and transport-based models offer a more detailed, dynamic approach that incorporates mass transfer principles. Predictive models, incorporating both short- and long-term fouling behaviors, provide invaluable insights into how fouling will develop over time and how operational strategies can be optimized to minimize fouling and extend membrane life (Khalifa, Abd Elghany & Abd Elghany, 2021; Nahr, Nozari & Sadeghi, 2021). As MBR technology continues to be adopted for wastewater treatment, further advancements in modeling techniques, particularly those based on machine learning and real-time data integration, will be critical for improving fouling management and ensuring the sustainability and efficiency of these systems. Through a combination of empirical research, model refinement, and advanced monitoring tools, chemical engineers can continue to develop more effective strategies to reduce fouling, enhance membrane performance, and lower operational costs in membrane bioreactor systems.

2.7 Fouling mitigation strategies

Fouling mitigation in membrane bioreactors (MBRs) remains a significant challenge that directly affects the performance, longevity, and operational cost of the system. Membrane fouling is a complex process that involves the accumulation of organic, inorganic, and microbial matter on the membrane surface or within its pores, leading to an increase in resistance to flow and a decrease in permeate flux. Over time, this

fouling can result in higher transmembrane pressure (TMP), frequent cleaning cycles, and even membrane replacement (Alam, *et al.*, 2022; Kumar, *et al.*, 2022). As membrane bioreactors are increasingly used for high-efficiency wastewater treatment, particularly in decentralized and industrial applications, the development of effective fouling mitigation strategies is critical for enhancing their operational efficiency and sustainability. A combination of surface modification techniques, dynamic operational strategies, chemical cleaning protocols, and integration with pretreatment or hybrid systems can offer a comprehensive approach to managing fouling.

One of the most effective strategies to reduce fouling is membrane surface modification. The surface properties of the membrane, such as hydrophilicity, charge, and roughness, play a crucial role in determining the extent of fouling. Hydrophobic membranes tend to attract organic foulants more readily, while hydrophilic surfaces can help repel organic compounds but may still experience fouling due to microbial attachment (Das Nair & Landani, 2020; Krishnan, Banga & Mendez-Parra, 2020). Membrane surface modification techniques aim to enhance the membrane's resistance to fouling by altering these surface properties.

One approach to membrane surface modification is coating, where a thin layer of materials, such as polymers or nanoparticles, is applied to the membrane surface. These coatings can increase the membrane's hydrophilicity, reduce surface roughness, or introduce functional groups that hinder the adhesion of foulants. For example, coatings made from polyethylene glycol (PEG) are widely used due to their ability to improve surface hydrophilicity and reduce the fouling potential by preventing protein adsorption (Balana, Aghadi & Ogunniyi, 2022; Raja Santhi & Muthuswamy, 2022). Another effective technique is grafting, where functional groups or polymers are chemically bonded to the membrane surface. Grafted membranes can exhibit improved resistance to fouling by providing a more stable surface that repels or reduces the adhesion of fouling agents such as proteins, polysaccharides, and microbial biofilms. These surface modifications not only enhance the antifouling properties of the membrane but also improve the overall performance of the MBR system by maintaining higher permeate flux over extended periods.

In addition to surface modification, dynamic operational strategies offer a valuable tool for mitigating fouling. These strategies focus on optimizing operational parameters such as flux, hydraulic retention time (HRT), sludge retention time (SRT), and aeration rate to minimize fouling during membrane operation. One widely used dynamic strategy is flux stepping, which involves varying the permeate flux over time rather than maintaining a constant rate. Flux stepping can help manage fouling by reducing the rate of foulant accumulation on the membrane surface (Dauvergne, 2022; Lin, Lin & Wang, 2022). By temporarily lowering the flux during periods of higher fouling potential, such as during startup or when treating wastewater with high concentrations of organic or particulate matter, the fouling rate can be slowed. After the fouling layer begins to stabilize, the flux can be increased again, maintaining high treatment efficiency while controlling fouling.

Relaxation, another dynamic operational strategy, involves periodically halting filtration to allow the fouling layer to "relax" and partially detach from the membrane surface. During the relaxation phase, the buildup of foulants on the

membrane is alleviated, and the fouling layer becomes less compact. This reduction in fouling resistance can result in a lower TMP, improving system performance and extending the operational life of the membrane. The relaxation period can be optimized based on the fouling characteristics and operational conditions, but it is most effective when combined with periodic backwashing or aeration (Shah, Li & Ierapetritou, 2011; Urciuoli, *et al.*, 2014).

Additionally, optimizing aeration rates during filtration can help mitigate fouling by applying shear forces to dislodge fouling material. Proper aeration is crucial because excessive aeration can disrupt the microbial community or increase the release of soluble microbial products (SMP) into the system, while insufficient aeration can lead to biofilm formation and particulate deposition. By carefully balancing the aeration rate, operators can reduce the formation of a stable fouling layer and minimize fouling potential (Kuang, *et al.*, 2021; Sircar, *et al.*, 2021).

Chemical cleaning and backwashing protocols are essential tools for mitigating fouling in MBR systems. While dynamic operational strategies can reduce the rate of fouling, they cannot eliminate the need for cleaning. Over time, fouling will accumulate to a point where cleaning is necessary to restore membrane performance. Chemical cleaning involves using various cleaning agents, such as acids, alkalis, and detergents, to break down and remove fouling materials from the membrane surface. Common chemical cleaning agents include sodium hydroxide (NaOH), phosphoric acid (H_3PO_4), citric acid, and chlorine-based solutions. Alkaline cleaning agents are often effective for removing organic fouling and microbial biofilms, while acidic solutions can help dissolve inorganic scale deposits (Koroteev & Tekic, 2021; Yigitcanlar, *et al.*, 2021). Detergents or surfactants can be added to facilitate the removal of organic matter, especially in the case of SMP.

Backwashing is another widely used cleaning method, particularly in systems where particulate fouling is prevalent. During backwashing, the flow of water is reversed through the membrane, allowing the accumulated particles to be flushed off the surface. Backwashing can be more effective when combined with intermittent aeration or physical agitation, which helps dislodge fouling material from the membrane (An, Wilhelm & Searcy, 2011; Kandziora, 2019). However, backwashing is most effective for reversible fouling, such as that caused by particulate matter or loosely bound organic compounds. For irreversible fouling, chemical cleaning methods are often required to fully restore membrane performance.

The frequency and intensity of cleaning cycles depend on the nature of the fouling and the operational conditions of the MBR. Overzealous cleaning or using harsh chemicals can degrade the membrane material and reduce its lifespan, making it crucial to optimize cleaning protocols to balance fouling removal and membrane durability. Moreover, excessive cleaning cycles can lead to increased chemical consumption, waste generation, and operational costs, further emphasizing the need for preventive strategies and effective fouling management (An, Wilhelm & Searcy, 2011; Kandziora, 2019).

Finally, integrating pretreatment or hybrid systems with MBRs can significantly reduce fouling and improve system performance. Pretreatment systems, such as dissolved air flotation (DAF), chemical coagulation, or sedimentation, can be used to remove large particles, oils, and suspended solids

from the influent before it enters the MBR. This reduction in particulate matter decreases the fouling potential of the wastewater and extends the life of the membrane (Yue, You & Snyder, 2014; Oyedokun, 2019). Hybrid systems that combine MBRs with other filtration or treatment technologies, such as ultrafiltration (UF) or reverse osmosis (RO), can also enhance fouling resistance by providing additional filtration stages that reduce the overall fouling load on the MBR membrane.

In conclusion, the mitigation of fouling in membrane bioreactors is crucial for maintaining system performance and extending the life of the membrane. A multifaceted approach that includes membrane surface modification, dynamic operational strategies, chemical cleaning and backwashing, and integration with pretreatment or hybrid systems offers a comprehensive solution to the fouling challenge. By carefully selecting and optimizing these strategies, chemical engineers can design more efficient, sustainable MBR systems capable of handling diverse wastewater treatment needs while minimizing the operational costs associated with fouling (De Almeida, dos Santos & Farias, 2021; Yigitcanlar, Mehmood & Corchado, 2021). Through continued innovation and research, these strategies can be refined to ensure that MBR technology remains a viable and cost-effective solution for wastewater treatment in both industrial and municipal applications.

3. Conclusion, future perspectives and research needs

The long-term operation of membrane bioreactors (MBRs) is significantly influenced by the challenge of fouling, which impairs membrane performance and increases operational costs. Through a chemical engineering perspective, a deeper understanding of the fouling mechanisms whether due to organic matter, inorganic scaling, microbial biofilms, or particulate deposition has been essential in optimizing MBR design and operation. This includes the development of effective fouling mitigation strategies such as surface modifications, dynamic operational adjustments, and advanced cleaning protocols. Despite these advances, the long-term sustainability of MBR systems remains a subject of active research, particularly as new technologies and methodologies emerge to address the persistent issue of fouling.

Future perspectives in MBR technology will undoubtedly be shaped by the increasing focus on smart membranes and real-time fouling prediction. The concept of smart membranes, integrated with sensors and responsive coatings, holds great potential in revolutionizing fouling management. These membranes can be designed to detect fouling events as they occur and adjust their properties or operational parameters to counteract the fouling process. Real-time fouling prediction, through the use of advanced monitoring tools, will allow operators to anticipate fouling before it becomes a serious issue, thereby minimizing downtime and reducing the frequency of maintenance or cleaning. This will be achieved by incorporating real-time data on feedwater quality, TMP, and other operational parameters, feeding them into predictive models that can forecast fouling progression and provide actionable insights for system optimization.

The integration of artificial intelligence (AI) and process automation will also play a pivotal role in the future of MBR technology. AI-driven systems, leveraging machine learning algorithms, can analyze vast amounts of data to identify patterns and optimize operational strategies autonomously.

By continuously learning from real-time data, AI can provide dynamic adjustments to system parameters such as flux, aeration rates, and cleaning schedules, ensuring that fouling is minimized while maintaining treatment efficiency. Automation, when paired with AI, will enable the MBR systems to operate with minimal human intervention, improving both efficiency and cost-effectiveness. This integration of AI and automation can lead to more reliable MBR systems, enhancing their viability for decentralized wastewater treatment applications, where operational flexibility and remote monitoring are crucial.

Another area that warrants further attention is the lifecycle analysis and sustainability considerations of MBR systems. As MBR technology continues to evolve, the environmental and economic sustainability of membrane operations must be assessed holistically. This includes not only the energy and chemical consumption associated with cleaning and maintenance but also the environmental impact of membrane production and disposal. Research into biodegradable or more easily recyclable membranes, as well as energy-efficient cleaning methods, could help mitigate the ecological footprint of MBR systems. Furthermore, lifecycle assessments that include both the direct costs of operation and the indirect costs associated with fouling, such as increased energy consumption and reduced membrane lifespan, will be crucial for developing more sustainable wastewater treatment solutions.

In summary, significant progress has been made in understanding the key fouling mechanisms in MBRs and developing strategies to mitigate their effects. Membrane surface modifications, dynamic operational strategies, and advanced cleaning protocols have proven effective in addressing fouling in various stages. However, continued research is needed to refine these strategies and integrate them with cutting-edge technologies such as smart membranes, AI, and process automation. Chemical engineering contributions to MBR optimization will continue to be integral to overcoming fouling challenges, ensuring that MBR systems remain reliable, cost-effective, and sustainable in the face of increasing wastewater treatment demands.

Ultimately, the future of MBR technology lies in enhancing the long-term reliability and cost-effectiveness of these systems. By focusing on smarter, more responsive systems, integrating real-time monitoring and predictive modeling, and embracing sustainable practices, the MBR technology will continue to evolve as a viable solution for wastewater treatment. The development of these advanced technologies, along with a holistic approach to system design, will enable MBRs to meet the increasing global demand for efficient, sustainable, and resilient wastewater treatment. The research needs in this field are vast and varied, and they will require collaboration across disciplines, including material science, process engineering, and data science, to bring about the next generation of membrane bioreactor technologies.

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