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Review

Recent Advances in Organic Fouling Control and Mitigation Strategies in Membrane Separation Processes: A Review

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Abstract: Membrane separation processes have become increasingly popular in many industries because of their ability to treat wastewater and purify water. However, one of the main problems related to the processes is organic fouling, which can significantly reduce their efficiency and cause membrane damage. This review provides a summary of the various forms of organic fouling that can occur in membrane separation methods and examines the factors that lead to their development. The article evaluates the progress made in different techniques designed to manage and reduce organic fouling, such as physical cleaning methods, chemical cleaning agents, and modifications to the membrane surface, including ultrasonic and membrane vibration methods. The review also highlights recent advances in emerging 3D printing technology to mitigate membrane fouling. Finally, the review provides a brief summary of the conclusions and future directions for research in the field of organic fouling control and mitigation in membrane separation processes.

Keywords: organic fouling; membrane fouling mitigation; surface modification; membrane cleaning; 3D printing; membrane separation processes

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1. Introduction

Water pollution is a critical problem worldwide, as it leads to the shortage of clean water and has posed a serious threat to public health and the ecosystem [1–5]. Most organic wastewater is generated from various sources, including households, industrial production, paper mills, food production facilities, pharmaceutical industries, and other similar sources. This wastewater contains organic compounds that can be harmful to the environment and human health if not treated properly. Therefore, it is important to develop effective treatment methods to remove these organic compounds from wastewater before it is discharged into the environment [3,4] and are characterized by high loads of organic matter, high acidity or alkalinity [5].

Conventional approaches to eliminating organic pollutants from organic wastewater include sand filtration, coagulation, flocculation, sedimentation, electrodeposition, extraction, precipitation, biological degradation, and ion exchange. They have the drawbacks of operating in successive steps of heterogeneous reactions, or distribution of substances among various phases, which usually require a large area and a lengthy operating period [6,7]. These methods require a high cost of reagents or have a high energy requirement or operational difficulties [8]. The importance of recovering nutrients such as nitrogen (N) and phosphorus (P), for agricultural purposes and for reusing water, is often overlooked [9]. Conventional methods may have limited effectiveness in removing contaminants from wastewater.

Membrane separation processes are gaining popularity due to their many advantages, including high separation selectivity, low energy consumption, and low capital and operating costs. These processes are also environmentally friendly and can be easily scaled up. As a result, membrane filtration is becoming an attractive option for treating organic wastewater and has been widely applied in various industries and municipal wastewater [1,3,4,7,10]. Anaerobic membrane reactors (AnMBRs) are gaining attention as an alternative to conventional anaerobic treatment processes, as they effectively resolve long-term concerns about biomass retention [7]. In addition, membrane separation processes have been applied to treat wastewater from different industries, such as corn starch production [11], and dried potato purée production [12].

Despite intensive research and the promising potential of membrane separation processes, fouling remains a severe problem in membrane filtration and can prevent continuous and large-scale operation of membrane separation processes [13–15]. Numerous studies have been carried out to identify the organic compounds responsible for membrane fouling and to gain a better understanding of the fouling mechanism. However, of the various types of fouling, organic fouling is perhaps the least well-understood when compared to other types of fouling such as biofouling, inorganic fouling, and colloidal fouling. Despite the extensive research that has been conducted, there is still much to be learned about the nature of organic fouling and the factors that contribute to it. More research is needed to develop effective fouling mitigation strategies and to improve the performance and efficiency of membrane-based water treatment processes [13–16].

Organic fouling can increase the costs of membrane separation processes in several ways. Firstly, it can increase the consumption of energy to maintain the required flux. Secondly, it can cause system downtime for cleaning and maintenance, which can further increase costs associated with lost productivity. Thirdly, it can require the use of larger membrane areas to maintain the required flux, which can increase capital and operating costs. Finally, backwashing and cleaning processes can require additional construction, labor, time, and materials, which can further increase costs. To ensure the successful use of membranes, there has to be efficient fouling control and mitigation strategies. Therefore, ongoing research is focused on developing effective and sustainable fouling mitigation strategies to reduce the costs associated with membrane fouling [7,17]. In recent years, researchers have given more attention to preventing and reducing organic membrane fouling [14,15]. The use of three dimension (3D) printing in membrane separation processes is an emerging field and is growing to mitigate fouling [16]. Therefore, the objective of this study is to provide a comprehensive review of the current literature and recent developments related to strategies for controlling and mitigating membrane fouling caused by organic foulants in membrane separation processes. The introduction of 3D printing in fouling mitigation in this review is another novelty.

2. Membrane Fouling, Types and Mechanisms

Membrane fouling is typically considered a major hindrance in membrane filtration processes. It is an unavoidable issue where particles, colloids, macromolecules, and salts that are meant to be filtered end up sticking to and accumulating on the membrane, which is undesired [7,18]. The SEM image of the membrane surface before and after BSA fouling can be indicated in Figure 1.

Membrane fouling is typically characterized by a reduction in permeate flux through the membrane, resulting from increased flow resistance due to various mechanisms. Pore blocking occurs when foulants accumulate in the membrane pores, reducing the effective pore size and limiting the flow of water molecules. Concentration polarization occurs when a concentration gradient develops at the membrane surface, leading to a decrease in permeate flux. This can be caused by the accumulation of solutes or suspended solids on the membrane surface. Cake formation occurs when foulants deposit and form a layer on the membrane surface that raises the resistance to water flow. These mechanisms can occur individually or in combination, leading to complex and heterogeneous fouling behavior. Understanding the mechanisms and characteristics of membrane fouling is critical for developing effective fouling mitigation strategies [19]. For quite some time, membrane fouling has been a significant obstacle that has limited the practical applications of membranes [18].

Membrane fouling can be formed by various types of foulants, which can be identified based on their physical and chemical characteristics [20]. Some common types of foulants include: (1) Organic foulants: These foulants are made up of organic compounds, such as proteins, lipids, carbohydrates, and humic substances. They are often hydrophobic and can cause severe fouling due to their tendency to adsorb onto the membrane surface. (2) Inorganic foulants: These foulants are made up of inorganic compounds, such as calcium carbonate, silica, and metal hydroxides. They can cause fouling by forming scales or precipitates on the membrane surface, reducing the effective pore size and limiting water flow. (3) Biological foulants: These foulants are made up of microorganisms, such as bacteria, viruses, and fungi. They can cause fouling by forming biofilms on the surface of the membrane, which can decrease the permeate flux and increase the risk of membrane damage. (4) Colloidal foulants: These foulants are composed of suspended particles, such as clays, silt, and nanoparticles. They can cause fouling by accumulating on the membrane surface and forming a cake layer or by causing concentration polarization. Identifying the type of foulant is critical to developing effective fouling mitigation strategies that can target specific foulant species.

The accumulation of organic foulants can take on different forms, concentration polarization, gel/cake layer, and physical blocking of pores [17].

The organic fouling mechanism can be further described by four models of filtration, which are represented by equations 1–4 [17,21]. The four filtration models are influenced by various factors, including membrane properties, feed water, and foulant characteristics, and process operating conditions [22,23].

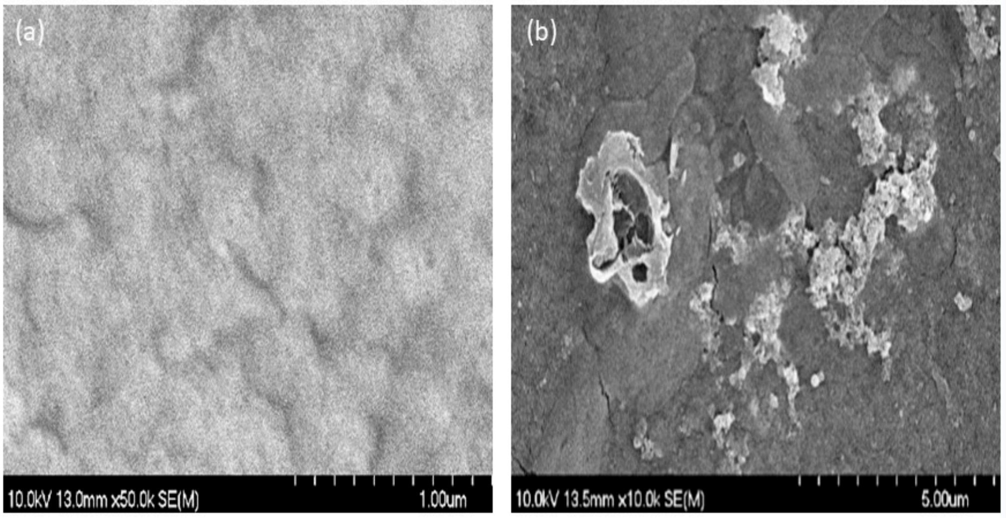


Figure 1. SEM image of (**a**) unused PVDF membrane and (**b**) BSA fouled PVDF membrane [24].

Complete Blocking:

$$J_0 - J = A.V \tag{1}$$

Standard Blocking:

$$\frac{1}{t} + B = J_0.V1 \tag{2}$$

Intermediate Blocking:

$$ln\, J_0 - \ln\ J = C.V \tag{3}$$

Cake Filtration:

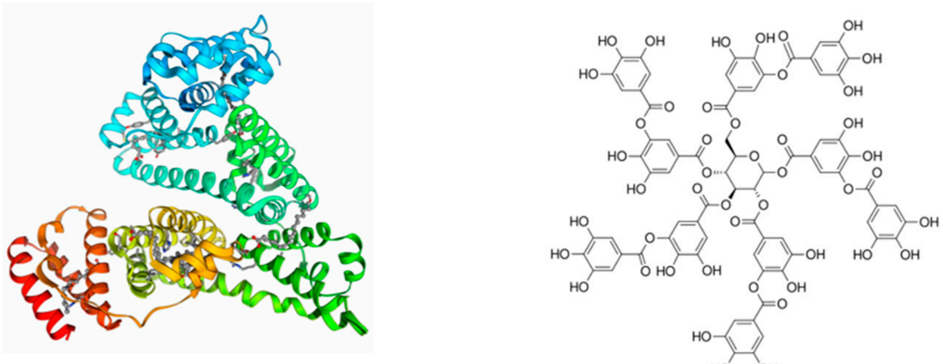
$$\frac{1}{J} - \frac{1}{J_0} = D.V \tag{4}$$

where *J* is the flux (m/s), *t* is the filtration time (s), *V* is the filtration volume (m^3), *A*, *B*, *C* and *D* are constants.

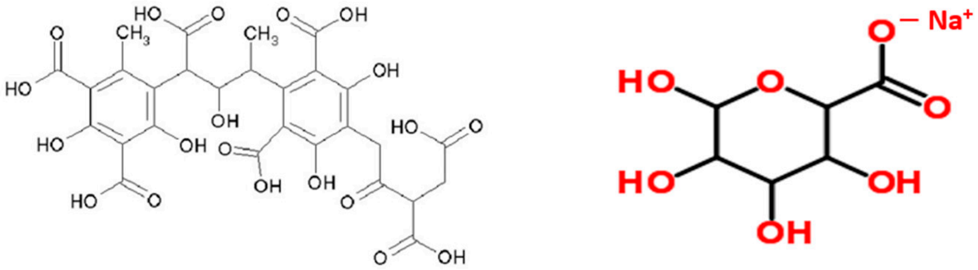
3. Types and Characteristics of Organic Foulants

Organic matter such as raw wastewater organic matter (WOM), effluent organic matter (EOM), and natural organic matter (NOM) can contribute to membrane fouling in membrane separation processes. These organic compounds can include proteins, lipids, amino acids, polysaccharides, colloidal particles, humic and folic acids, and other complex organic molecules. These compounds can accumulate on the membrane surface or inside pores, leading to fouling. The accumulation of organic matter on the membrane surface can also lead to the formation of a biofilm, which can further exacerbate fouling and reduce the efficiency of the membrane separation process. To mitigate organic fouling, it is necessary to understand the characteristics of foulants and develop effective mitigation strategies that can target the specific organic species causing fouling [25].

To simulate and investigate the organic fouling of membranes, various model foulants are commonly used in laboratory experiments. The chemical structures of the model foulants are irregular and random, unlike the well-defined crystalline structure of the inorganic salts, and are indicated in Figure 2. The chemical structures of the model foulants on a membrane surface are influenced by various factors. These include ionic strength, divalent cations, and pH. The initial flux, the velocity of the crossflow, and the pressure can also affect the structure of the fouling layer [25]. By using model foulants, researchers can systematically investigate the fouling behavior of different organic compounds and develop more efficient and sustainable fouling mitigation strategies [25].



(a) Bovine Serum Albumin Molecule (b) Tannic Acid Molecule



(c) Humic Acid Molecule (d) Sodium Alignate Molecule

Figure 2. Chemical structure of model foulants. (**a**) Bovine serum albumin (BSA) (**b**) tannic acid (**c**) humic acid (**d**) sodium alginate adapted from [25].

Organic micropollutants (MPs) are another organic foulant that is receiving more attention in membrane separation processes. They can enter the environment through wastewater discharged from hospitals, households, and the manufacturing industries. These pollutants can be classified into several categories, including pharmaceutical active compounds (PhACs), personal care products (PCPs), pesticides, and industrial chemicals [26].

4. Factors That Influence Organic Fouling

Organic fouling in membrane separation processes can be influenced by several factors [27–29]. These factors include:

4.1. Organic Composition and Concentration in the Feed Solution

Sodium alginate (SA), bovine serum albumin (BSA), Aldrich humic acid (AHA), natural organic matter from the Suwannee River (SRNOM), and octanoic acid (OA) are commonly used to represent different types of organic matter in studies related to water treatment processes. SA is often used to represent polysaccharides, BSA represents proteins, AHA or SRNOM represents terrestrial humic substances, and OA represents fatty acids. Several studies have reported that SA exhibits the greatest potential for membrane fouling among these organic compounds. This can be attributed to the specific interactions between SA and calcium ions (Ca^{2+}), which can result in the formation of unique egg-box-shaped gel structures. These gel structures can adhere strongly to membrane surfaces, leading to fouling [30]. The presence of high organic foulants, mixtures of organic foulants, concentration of monovalent and divalent ions in the feed solution, and draw solutes in the feed water resulted in severe organic fouling behavior [31]. The properties of polysaccharides can also affect the degree of organic fouling potential in water treatment processes. The severity of flux decline, which is a measure of the reduction in water flow rate due to fouling, appears to be related to the molecular weight (MW) and solution viscosity of the organic compounds. Larger molecular sizes of organic matter are likely to reduce the shear force associated with the feed cross-flow velocity, leading to a more pronounced flux decline. For example, a study by Xie et al. [28] found that flux decline was more severe on the order of xanthan (1000–50,000 kDa) > sodium alginate (SA) (200 kDa) > pullulan (75 kDa). Xanthan gum, with its high molecular weight and solution viscosity, showed the greatest fouling potential among these polysaccharides.

The fouling aspect of a hollow fiber ultrafiltration membrane (UF) was investigated using combinations of dissolved organic matter (DOM), including humic acid (HA), bovine serum albumin (BSA), and sodium alginate (SA) representing humic substances, proteins and polysaccharides, respectively. The findings showed a considerable correlation between fouling resistance and the concentration of small molecules in DOMs, as well as the solution's zeta potential, based on statistical analysis. The study found that the impact of small molecules on membrane fouling was more significant compared to the zeta potential of the solution, indicating that the concentration of small molecules in DOMs played a more critical role in determining the fouling behavior of the UF membrane [31]. These findings suggest that controlling the concentration of small molecules in the solution is an important factor in mitigating fouling in UF membrane separation processes.

4.2. Operating Conditions

Operating conditions such as temperature, pressure, and flow rate can also affect organic fouling. Higher temperatures can increase the rate of fouling, while higher pressures can help mitigate fouling. The flow rate can affect the shear stress on the membrane surface, which can impact the extent of fouling.

BSA fouling was significantly pronounced at the pH 4.7 isoelectric point of BSA, where there is a minimum repulsion force between BSA molecules. As the pH moved away from the isoelectric point, the fouling of the membrane became less severe. At pH 3.0, increasing the ionic strength resulted in severe fouling, probably due to compression of the electric double layer (EDL) [32].

The rate of NOM fouling increases with higher ionic strength, pH, and applied pressure due to various mechanisms such as electrostatic repulsion, hydrophobic forces, hydrophobicity, valley blocking, and compaction [33].

Ultrafiltration experiments were conducted on whey proteins at different pH values of 3, 9, and 10. The resulting permeate fluxes were measured as 68 to 85, 91 to 87, and 89 to 125 $\text{Lm}^{-2}\ \text{h}^{-1}$, respectively. However, when the pH was close to the isoelectric points of the major proteins (at pH 4 and 5), the resulting permeate fluxes were lower, ranging from 40 to 25 and from 51 to 25 $\text{Lm}^{-2}\ \text{h}^{-1}$, respectively. These results suggest that the pH of the protein solution plays a significant role in determining the permeate flux during ultrafiltration. When the pH is close to the isoelectric point of the major proteins, the proteins are less soluble and are more likely to aggregate, leading to reduced permeate flux [32]. Therefore, controlling the pH of the protein solution is an important factor in optimizing the performance of ultrafiltration processes for protein separation.

4.3. Membrane Properties

The properties of the membrane, including surface charge, pore size, and hydrophobicity, can also affect organic fouling. Membranes with a higher surface charge or smaller pore size can be more prone to fouling, while more hydrophobic membranes may be more resistant to fouling. The fouling of polyvinylidene fluoride (PVDF) membranes can be significantly affected by their hydrophobicity and pore size. As the hydrophobicity of the PVDF membrane increases, it becomes more prone to organic matter fouling, which tends to adhere more strongly to hydrophobic surfaces [34]. Similarly, as the pore size of the PVDF membrane decreases, it becomes more susceptible to fouling by organic matter, which can become trapped in the smaller pores and accumulate over time. This can lead to a reduction in membrane permeability and an increase in transmembrane pressure required to maintain a constant flow rate [34]. The fouling of membranes in the presence of NOM can be affected by several factors, such as the membrane surface structure and chemical properties. The rate of NOM fouling increases with surface roughness, membrane charge, and hydrophobicity [33].

In an organic fouling simulation study, dextran (DEX), bovine serum albumin (BSA), and Aldrich humic acid (HA) were used as model foulants representing polysaccharides, proteins, and humic substances, respectively. The study found that hydrophobic interaction was the primary mechanism that influenced adsorptive fouling, rather than electrostatic interaction. The results suggested that the hydrophobicity of both the polyvinylidene fluoride (PVDF) membrane microfiltration and the foulant played a significant role in the adsorptive fouling, with the higher hydrophobicity increasing the extent of fouling [35]. The study gives emphasis to the need to consider both membrane and foulant hydrophobicity in developing effective fouling mitigation strategies for membrane separation processes.

4.4. Pretreatment Wastewater

Pretreatment methods such as coagulation or adsorption can affect the concentration and composition of the foulants, which can impact the extent of fouling. Cost-effective pretreatment of wastewater can bring several benefits, such as disinfection, removal of large suspended particles through settling, and reduction of total suspended solids (TSS) in the wastewater. Furthermore, effective pretreatment can also result in a lower fouling propensity of the feed wastewater, which can improve the efficiency and lifespan of the membrane.

Pretreatment techniques may be used to reduce the incidence of membrane fouling in wastewater treatment systems. These methods involve eliminating or altering the compounds responsible for fouling prior to their contact with the membrane surface. Coagulation has been shown to be highly effective in mitigating membrane fouling and is therefore extensively used in multiple industrial sectors for wastewater treatment [36,37].

4.5. Membrane Materials

The choice of membrane material, whether organic or inorganic, can have a significant impact on fouling in membrane-based processes [38]. Organic membranes are typically made from polymers such as cellulose acetate, polyamide, polyethersulfone, or polyvinylidene fluoride. The properties of organic membranes can vary significantly depending on the specific polymer used [34]. Here's how organic membrane materials affect fouling: The surface properties of organic membranes, such as hydrophilicity or hydrophobicity, play a crucial role in fouling. Hydrophilic membranes tend to be less prone to fouling as they repel organic foulants and promote easier cleaning. However, they may be more susceptible to fouling by inorganic foulants such as colloidal particles or minerals. Hydrophobic membranes, on the other hand, can repel organic foulants but may be more prone to fouling by hydrophilic substances. The pore size and distribution of organic membranes influence fouling by determining the size of particles or solutes that can pass through. Membranes with smaller pore sizes are generally more resistant to fouling by larger particles but may be more prone to fouling by smaller molecules that can penetrate the pores. The surface charge of organic membranes affects fouling by influencing the interaction between the membrane and charged foulants. Electrostatic repulsion between similarly charged foulants and the membrane surface can reduce fouling. Membrane materials can be modified to have a positive or negative charge to enhance fouling resistance.

Inorganic membranes are typically composed of materials such as ceramics, metals, or metal oxides (e.g., alumina, titania, zirconia). Inorganic membranes offer distinct characteristics that can influence fouling behavior [37]: Chemical Stability: Inorganic membranes generally exhibit high chemical stability, making them resistant to degradation when exposed to harsh chemical environments. This stability can reduce fouling caused by chemical reactions or exposure to aggressive substances. Inorganic membranes tend to have superior mechanical strength compared to organic membranes. This strength can help withstand physical stresses, such as pressure or cleaning procedures, reducing the likelihood of membrane damage and fouling. The surface roughness of inorganic membranes can impact fouling. Smoother surfaces typically experience less fouling as there are fewer sites for foulants to adhere to. However, excessively smooth surfaces may promote the formation of a thin, dense fouling layer due to reduced hydrodynamic shear forces. Inorganic membranes often exhibit excellent thermal stability, allowing their use in high-temperature processes. This stability can help minimize fouling caused by heat-induced reactions or thermal degradation of foulants. Overall, the choice of membrane material, whether organic or inorganic, should be carefully considered to mitigate fouling. Factors such as surface characteristics, pore size, surface charge, chemical stability, mechanical strength, surface roughness, and thermal stability all play significant roles in determining the fouling behavior of a membrane.

In general, understanding the factors that contribute to organic fouling is critical to developing effective control and mitigation strategies. By optimizing the operating conditions, membrane properties, and pretreatment processes, it is possible to reduce the extent of fouling and improve the performance of membrane separation processes. A summary of factors influencing organic fouling can be indicated in Table 1.

Table 1. A summary of factors influencing organic fouling.

Factors Influencing Organic Fouling	Description	Reference
Organic composition and concentration in the feed solution	The properties of organic compounds, such as their size, molecular weight, hydrophobicity/hydrophilicity, charge, and tendency to form aggregates, can influence their fouling behavior. Certain compounds may have a higher affinity for membrane surfaces or be more prone to fouling the membrane pores.	[28,29,32,37]
Operating conditions	Operating conditions, including transmembrane pressure, crossflow velocity, temperature, and pH, can influence organic fouling. Higher pressures and velocities can help minimize fouling by reducing the deposition of foulants on the membrane surface. Temperature and pH can affect the solubility and aggregation behavior of organic compounds.	[34,35]
Membrane properties	The material and surface characteristics of the membrane, such as surface charge, hydrophilicity/hydrophobicity, roughness, and pore size, can affect the interaction between the membrane and organic foulants. Surface properties that reduce fouling include hydrophilic surfaces and negatively charged membranes.	[33,35,36]
Pretreatment wastewater	The effectiveness of pre-treatment processes, such as coagulation, flocculation, or activated carbon adsorption, in removing or reducing organic foulants before they reach the membrane can impact fouling.	[38,39]

5. Fouling Control and Mitigation Strategies for Organic Fouling

Firstly, the paper discussed physical cleaning methods employed for fouling control in membrane separation processes. This may include techniques such as backwashing, air scouring, and mechanical cleaning, along with their effectiveness and limitations. Secondly, the review will delve into chemical cleaning agents utilized for fouling mitigation. It will explore different types of cleaning agents, their mechanisms of action, and their application in removing organic fouling from membranes. Consideration will be given to the compatibility of these agents with different membrane materials and their environmental impact. Furthermore, the paper will cover surface modifications as a strategy to reduce fouling in membrane separation processes. It will highlight various surface modification techniques, such as hydrophilic/hydrophobic coatings, grafting of functional groups, and nanostructured surfaces. The review will discuss the impact of these modifications on fouling resistance and the underlying mechanisms involved. In addition to conventional approaches, the review will also focus on recent advancements in membrane technology that aim to reduce fouling. This will include the application of emerging techniques such as 3D printing, membrane vibration, and ultrasound treatment. These innovative approaches hold promise for enhancing membrane performance and reducing fouling tendencies.

Finally, the review paper will incorporate recent developments in membrane technology that have shown potential for fouling reduction. It will highlight the advancements in membrane materials, module design, and system optimization strategies that contribute to improved fouling control in organic fouling scenarios.

Many efforts have been made to address the problem of fouling in membrane filtration processes [16]. We can see that there has been a significant amount of publications in the past decade, as indicated by the data presented in Figure 3. There have been more studies on membrane surface modification compared to those of other methods. However, back washing, membrane vibration, chemical cleaning, vibration, ultrasound, air scouring, and 3D printing are also useful to mitigate membrane fouling.

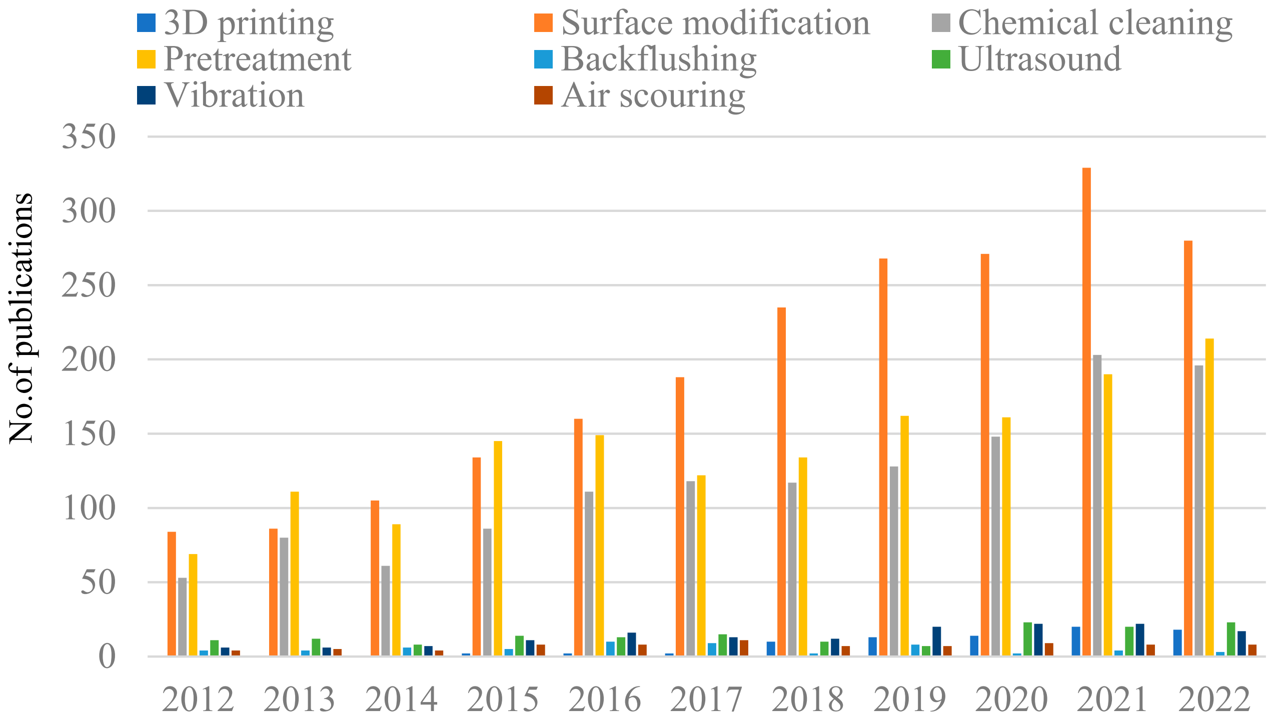


Figure 3. Number of publications related to different approaches for reducing membrane fouling, collected from Web of Science as of 13 July 2023, using the search keywords "membrane AND fouling AND (method)".

5.1. Pre-Treatment Techniques

Pretreatment methods can be used to decrease the occurrence of membrane fouling in wastewater treatment systems. This is achieved by removing or modifying the organic compounds that cause fouling before they reach the membrane surface. Depending on the type of wastewater and foulants, pretreatment may be physical, chemical, and biological processes. Pretreatment can extend the life of the membrane, reduce the need for frequent cleaning or replacement, improve the quality of treated water, and reduce the energy consumption of the treatment system [25]. To combat organic fouling in wastewater treatment systems, various pretreatment techniques have been utilized, for example, oxidation, coagulation, and adsorption have been utilized [2]. Coagulation is considered to be an effective physicochemical technology to control membrane fouling in the treatment of organic wastewater at the industrial level. It is relatively inexpensive, highly efficient, and easy to operate. When coagulants are added to wastewater, the suspended solids and organic matter can be aggregated and settled, thereby reducing the frequency of membrane cleaning and extending the lifespan of the membrane. Coagulation has been widely applied in various industries for wastewater treatment due to its effectiveness in controlling organic fouling [36,37]. The coagulation/flocculation process involves three stages: destabilization, agglomeration, and floc formation.

Coagulants are added to wastewater during the destabilization stage, which causes suspended solids and organic matter to become destabilized and form small clusters. In the agglomeration stage, these clusters combine to form larger aggregates, called flocs. The final stage involves the continued growth of flocs until they are large enough to be removed from wastewater. The efficiency of the coagulation/flocculation process depends on the type and amount of coagulants/flocculants used. The optimal dose of coagulants/flocculants may differ depending on the characteristics of the wastewater being treated. Therefore, the selection and optimization of coagulants/flocculants is crucial to designing and operating coagulation/flocculation processes effectively [37].

Coagulants are capable of neutralizing the negative charges of organic foulants, which reduces the electrostatic repulsion of the electric double layer. This process is called destabilization. Once the particles are destabilized, they begin to develop and gradually aggregate into larger flocs. Eventually, these flocs can be separated from the water phase through free precipitation or air flotation. During free precipitation, the flocs settle at the bottom of the tank due to gravity. In air flotation, the flocs rise to the surface of the water and are skimmed off. This destabilization and floc formation process is a common method of separating organic foulants from wastewater and is widely used in industrial processes [39]. Coagulants and flocculants are often added to wastewater to change its physical state to destabilize charged organic foulants and promote agglomeration. Coagulants typically work by neutralizing the charges on organic foulants, while flocculants help aggregate the particles into larger flocs. By doing so, flocs can be more easily removed from wastewater through sedimentation, flotation, or filtration. The use of coagulants and flocculants is a common and effective method for the treatment of wastewater in many different industries, including municipal wastewater treatment, food and beverage production, and chemical manufacturing.

Coagulants and flocculants commonly applied to control organic fouling can be categorized into various groups depending on their molecular weight and composition. Some examples include low-molecular-weight inorganic coagulants such as ferric chloride and aluminum sulfate, inorganic polymeric coagulants such as polyaluminum chloride (PAC) and polysilicate aluminum chloride (PASiC), synthetic organic polymeric flocculants such as polyacrylamide (PAM) and its derivatives, natural polymeric flocculants such as chitosan, starch, cellulose, and other polysaccharide materials, as well as microbial flocculants [37,40].

Although there have been advances in the development of environmentally friendly and high polymer coagulants/fluids, chemical coagulants/fluids such as PAM, PAC, and PASiC with high polymer content continue to be widely used in real-world scenarios due to their cost-effectiveness and excellent efficiency [37].

In an integrated coagulation membrane filtration process, the coagulants/flocculants commonly used to control organic fouling are inorganic coagulants, for example ferric chloride ($FeCl_3$), aluminum chloride ($AlCl_3$), as well as polymeric ferric chloride (PFC) and polymeric aluminum chloride (PAC) [41], and organic polymer flocculants, including cationic polyacrylamide (P(AM–DAC)), polyacrylamide (PAM)and poly dimethyl diallyl ammonium chloride (PDMDAAC) [37,42]. However, multiple studies have demonstrated that a large amount of inorganic coagulants can lead to the induction of secondary pollution as a result of the presence of residual metal ions. This can have a negative impact on the water ecosystem and pose a threat to vital security [2].

Polyaluminum chloride (PACl), as a conventional aluminum-based coagulant, has two primary disadvantages. First, the cost of disposing of the sludge generated by the use of PACl can be quite high. Second, contamination of the environment with aluminum due to the use of PACl poses a health risk, as it has been associated with the onset of Alzheimer’s disease [43].

However, using synthetic polymers as an alternative to PACl can help reduce sludge volume, but they also pose the risk of secondary pollution. As a result, there has been growing interest in environmentally friendly natural polymers as an alternative. Among these natural polymers, chitosan (CTS) is one of the most promising candidates. CTS is obtained through the deacetylation of chitin and is considered an environmentally friendly alternative to synthetic polymers as a result of its biodegradability and low toxicity. Despite its effectiveness as a coagulant, CTS is not yet widely available commercially due to its high production costs. However, CTS is often used as a coagulant aid to reduce production costs and improve coagulation efficiency [43].

The use of Fe (III) salt, a common coagulant, is often used to reduce fouling in UF membranes. However, it is not effective in removing low-molecular-weight organic compounds. Recently, researchers have discovered that potassium ferrate (Fe (VI)) has performed well in removing organic compounds and mitigating organic fouling [14].

To address the issues associated with the high dosage of inorganic coagulants and the high cost of natural polymers, this study used inorganic/organic hybrid coagulants. Hybrid coagulants were chosen with the aim of reducing the dosage of inorganic coagulants while also improving the coagulation performance [44]. The results of the humic acid (HA) ultrafiltration experiments demonstrated the utilization of hybrid coagulants of PAC/PDMDAAC with viscosities ranging from 0.99 dLg^{-1} to 1.86 dLg^{-1}. This resulted in a significant reduction in organic fouling and an increase in water fluxes [44].

Various studies have suggested that ozone treatment is an effective method of degrading natural organic matter colloidal, also known as biogenic colloids, which are often the primary cause of membrane fouling in water treatment systems [18,34]. On the other hand, pre-ozonation can actually worsen membrane fouling, indicating that the effectiveness of ozone treatment in mitigating fouling may depend on various factors, such as the type of membrane and the characteristics of the water being treated [18]. It is conceivable that the degradation of organic matter, such as biopolymers, through ozone treatment can produce degradation products that are similar in size to the pores of nanofiltration membranes. Alternatively, the resulting degradation products may have substantially different sizes, which can lead to different membrane fouling behaviors.

Generally, the effectiveness of pretreatment to mitigate organic fouling depends on the type and concentration of organic compounds present in the feed water, as well as the specific operating conditions of the membrane system. A combination of multiple techniques may be necessary to achieve optimal organic fouling mitigation.

5.2. Physical Cleaning

The process of removing foulants from the surface of a membrane using hydraulic or mechanical forces is referred to as physical cleaning [45]. There are several physical cleaning methods that are commonly employed, including hydraulic methods such as backwashing and air scouring as well as mechanical methods such as ultrasonic, vibration, and electric fields. Mechanical membrane cleaning involves the use of physical force to remove fouling materials from the surface of a membrane. This can include techniques such as sponge ball cleaning or fluidized particle cleaning, which involve the use of small, abrasive particles to scrub the surface of the membrane and dislodge fouling materials. Mechanical cleaning is often used in conjunction with hydraulic cleaning techniques to maximize the effectiveness of membrane cleaning and prolong the lifespan of the membrane. This type of cleaning is particularly useful for removing stubborn or hard-to-remove fouling materials that may not be effectively removed by hydraulic cleaning alone.

Unlike chemical cleaning, physical cleaning is a quicker process compared to chemical cleaning, typically taking fewer minutes to finish. Chemicals are not required and, consequently, no chemical waste is generated. In addition, physical cleaning is gentler on the membrane. Nevertheless, it is generally less efficient than chemical cleaning. Because nonreversible foulants can be cleaned by chemicals [45]. The first step in physical cleaning is to unwind and dissolve the foulant layer and then directly flush to clean any foulants that are firmly attached to the membrane. Fouling within the pores, cake layer, or gel layer is removed by flushing and back flushing (Figure 3) [25,46]. Proper and controlled physical cleaning can help extend the membrane life by removing accumulated foulants, such as suspended solids, colloids, and particulate matter. Regular physical cleaning prevents the build-up of fouling layers and maintains the membrane's hydraulic performance [45]. However, excessive or harsh physical cleaning can potentially damage the membrane surface, leading to irreversible damage and reduced membrane life [47]. High-pressure backwashing or aggressive scrubbing can cause abrasion, delamination, or deformation of the membrane material. The causes of changes in membrane life, such as fouling, are related to the accumulation of foulants on the membrane surface. Physical cleaning directly addresses this issue by physically dislodging and removing foulants. The action mechanism of physical cleaning technologies involves the application of mechanical forces (e.g., hydraulic pressure or air agitation) to disrupt foulant adhesion and facilitate their removal. The efficiency of physical cleaning methods depends on factors such as the type and nature of foulants, membrane material and configuration, and operational conditions. The following sections elaborate on each physical cleaning technique in more detail.

5.2.1. Backwashing

Backwashing is a physical cleaning technique that involves reversing the flow of filtration, causing the filtered substance to move from the permeate to the feed side. It is a simple process that requires adding pressure from the permeate side [48–50].

The use of backwash in direct membrane filtration of municipal wastewater led to a reduction in the fouling rate and an increase in the porosity of the fouling layer. This was achieved by dislodging foulants from the membrane surface in an indiscriminate manner. In MBR, backwashing proved to be an effective method of reducing membrane fouling, resulting in fewer cake formations and a lower rate of pore fouling [51]. Chemicals may be applied to enhance backwashing cleaning performance [48–50].

Backwashing involves periodically reversing the flow of permeate to the feed side for a short period of time. This process has been found to be effective in reducing fouling. However, the downside is that it results in loss of permeate and increases the processing time, which can be costly for production. Furthermore, reverse washing has been found to modify the pore structure and damage polymeric membranes [16].

5.2.2. Air Scouring

Air scouring can be used in conjunction with filtration to prevent fouling or intermittently to remove accumulated residues. The function of air is to remove foulant from fouled membranes on the walls. This method is most efficient in tubular and flat plate membranes, but its efficacy is lower in spiral-wound and hollow fiber membranes. However, the method poses a risk of protein denaturation in the food or dairy processing industries, and it also consumes a relatively high amount of power [16]. To remove organic fouling from RO membranes, a physical cleaning technique called CO_2 nucleation was used. In this study, sodium alginate, a model polysaccharide, was mixed with different concentrations of Ca^{2+}. It was revealed that CO_2 bubbles for physical cleaning were revealed to be more effective than conventional hydraulic flushing [52].

Aeration can prevent the deposition of particles and increase the growth of microorganisms, resulting in the formation of a thin fouling layer. However, when integrated with backwash, fouling control is improved by a factor of five compared to either method used alone [49].

5.2.3. Vibration and Rotating Membranes

Introducing vibrations can be an effective way to improve the performance of membrane filtration systems. When a membrane is subjected to vibration, it can help create a more turbulent flow regime, which can increase the shear rate and reduce the tendency of particles and other fouling agents to adhere to the membrane surface. The increased shear rate can also help to promote the removal of fouling layers that have already formed on the surface of the membrane, which can improve the overall flux of the membrane. Furthermore, vibration can help promote better mixing of the feed solution, which can help prevent concentration polarization and improve the uniformity of flow across the membrane surface [52]. The vibrational cleaning process works by creating more turbulence and shear forces on the surface of the membrane, which can effectively remove and eliminate any deposits that may have accumulated on the surface.

However, the effectiveness of using vibration to reduce fouling and improve flux depends on several factors, such as the membrane material, the feed solution, and the operating conditions. Therefore, it is essential to evaluate the potential benefits and limitations of vibration in a given application before implementing it in a membrane filtration system.

A study by F. Zhao et al. [25] showed that increasing the vibration frequency improved fouling cleaning efficiency. Vibrating the anaerobic membrane bioreactor mitigated reversible and irreversible fouling during municipal wastewater treatment [53].

Rotating hollow fiber membranes (R-HFM) have been shown to be successful in mitigating fouling in anaerobic membrane bioreactors [54].

Vibrating spacers have been reported to be a highly effective tool in reducing membrane fouling. Studies have shown that 3D spacers are more efficient than their 1D and 2D counterparts in reducing fouling. Additionally, increasing the frequency and amplitude of the vibration can further enhance fouling control. One major advantage of spacer vibration is its energy efficiency, as it consumes less energy than other methods such as gas bubbling [55].

The use of resonance vibration has been found to be an effective means of mitigating membrane fouling during whole milk filtration in a submerged membrane system with hollow polyvinylidene fluoride fibers. Research has shown that the use of resonance vibration can prolong the duration of the filtration by up to 54 times compared to no vibration, even at a pressure of 70 kPa [56].

The uniform shearing vibration membrane (USVM) system has been shown to be highly effective in controlling membrane fouling during filtration, even at a low frequency of 5 Hz. Increasing the frequency of vibration can lead to a significant reduction in both reversible and irreversible fouling [52].

Experiments were carried out on a membrane submerged vertically in 4 gL^{-1} of bentonite solution. The bentonite solution showed that moderate frequency (0–15 Hz) and small amplitude (0–12 mm) vibrations can improve membrane performance. Under both constant permeate flux and constant suction pressure conditions, increasing the vibration frequency or amplitude beyond a certain threshold was found to significantly enhance the membrane's performance. When the membrane was vibrated at an 8 mm amplitude and 8 Hz frequency, it resulted in a more than 90% reduction in the membrane fouling rate compared to no vibration [57].

To enhance the flux of a submerged hollow fiber membrane system, two methods have been employed: imposing rotationally oscillating fluid or transverse oscillating membrane motion. The transverse vibration method generates shear forces and secondary flows, effectively limiting fouling even at low displacements (<5 mm) and frequencies (<21 Hz). This method prevents cake formation by focusing shear forces directly on the surface of the membrane rather than recirculating the bulk fluid [58,59]. However, scale-up remains a concern for vibrating/rotating membranes [16].

5.2.4. Ultrasound

Ultrasound (US) refers to sound waves with frequencies beyond the hearing limit of humans 16 kHz. When microbubbles generated by the US are present, they can create local turbulence and shear effects near the membrane surface, which can disrupt concentration polarization and fouling layers, leading to improved flux [60].

Ultrasound waves result in the collapse of transient bubbles, which create shock waves, microjets, microstreaming, acoustic streaming, and microstreamers. Ultrasound affects membrane filtration in three ways: first, by dislodging deposited fouling materials, second, by improving mass transfer; and third, by enhancing the heat transfer of water [60].

The combination of ultrasound (US) application with membrane filtration has shown encouraging results in minimizing membrane fouling. Applying 20 kHz US has been found to reduce fouling and improve permeate flux. However, the effectiveness of US in reducing fouling decreased significantly as the frequency was increased [61]. In the ultrafiltration of skimmed milk solutions, a frequency of 28 kHz and power intensity of 100 W showed the best permeate flux compared to other configurations, such as skimmed milk solution with US (28 kHz, 50 W), skimmed milk solution with US (28 kHz, 25 W) and skimmed milk solution without US. The use of ultrasound at this frequency and power intensity generated a higher number of bubbles, which proved effective in controlling fouling [62].

Previous studies have reported membrane damage resulting from exposure to ultrasound. Additionally, if the distance between the membrane and the ultrasound actuator is not properly maintained, fouling removal can be ineffective because of nonuniform ultrasonic vibrations. When using ultrasonication as a method to manage membrane fouling, it is crucial to carefully evaluate the lifespan of the membranes. Controlling the negative impact of US on the membrane is critical to the adoption of this approach in the scaling process of the membrane industry's scale-up process [47].

5.3. Chemical Cleaning

Physical cleaning cannot completely remove foulants from the membranes. Therefore, different chemicals are applied in chemical cleaning. These chemicals react with the foulants and enhance their solubility by degrading them to a more soluble form by breaking the chemical structure and bonding between the foulants and the membrane (Figure 4) [25].

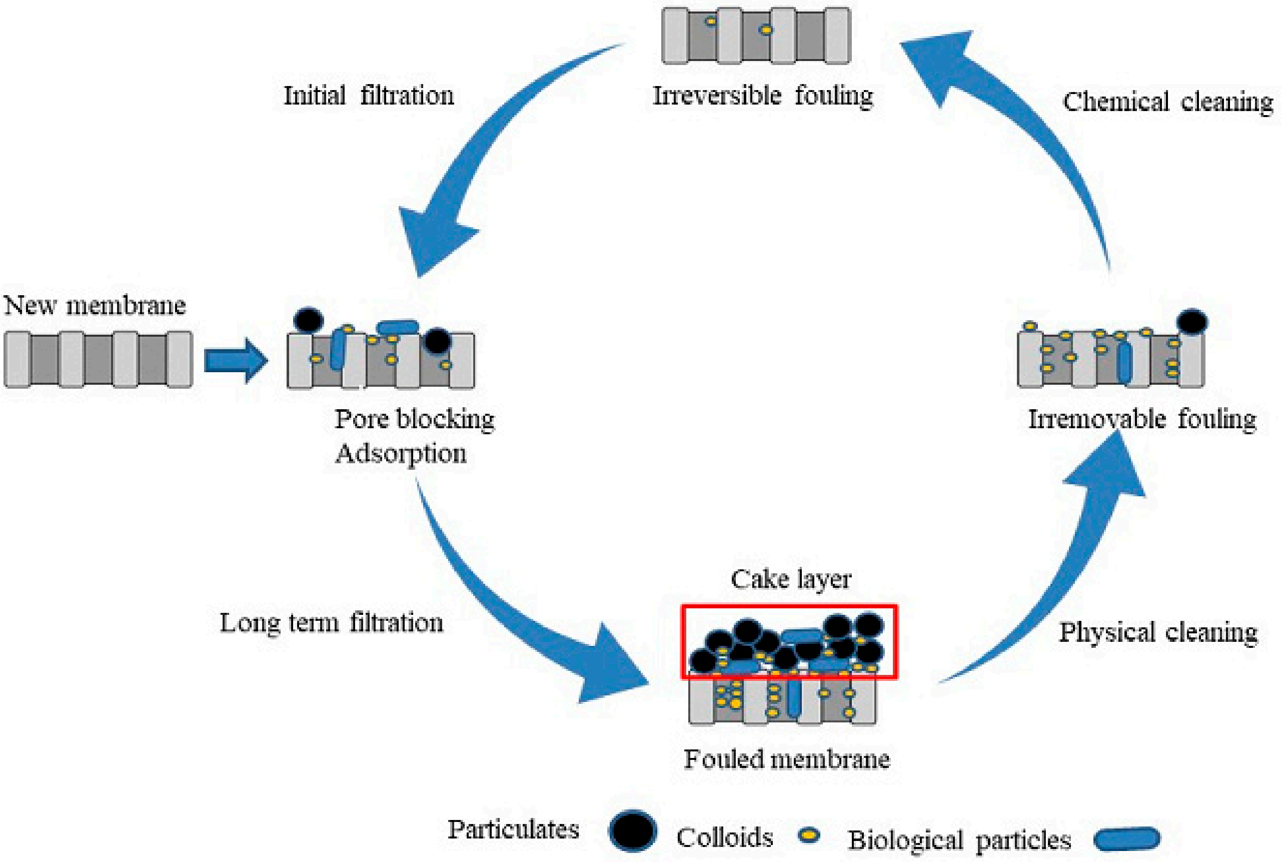


Figure 4. Schematic illustration of membrane fouling and cleaning mechanisms adapted from [25,46].

According to Gul et al. [45], chemical cleaning treatments can be classified into four basic types:

- Clean-in-place (CIP), which involves immersion of fouled membranes in chemicals-in-place.
- "Clean out of place" (COP), which involves soaking fouled membranes in chemicals out of place.
- "Chemical wash" (CW), which involves washing the fouled membrane by the feed stream containing chemicals.
- "Chemical enhanced backwash" (CEB), which combines physical and chemical cleaning techniques.

The effects of chemical cleaning on membrane life are as follows: Chemical cleaning can effectively remove organic foulants, biofilms, scaling, and inorganic deposits from the membrane surface. It can restore the membrane's performance and extend its lifespan by dissolving or chemically altering foulants that are not easily removable by physical cleaning alone. Improper or excessive use of cleaning chemicals can be detrimental to membrane life [63]. Harsh chemicals or incorrect dosing can cause membrane degradation, loss of performance, and accelerated aging. It is essential to follow manufacturer guidelines and employ appropriate cleaning protocols. Changes in membrane life are primarily caused by fouling, scaling, or biofouling. Chemical cleaning targets these issues by chemically breaking down, dissolving, or dispersing foulants. The action mechanism of chemical cleaning technologies involves chemical reactions or dissolution processes that alter the foulant's composition or solubility, making it easier to remove from the membrane surface. Factors such as contact time, temperature, and concentration of cleaning chemicals should be carefully controlled to achieve effective cleaning without causing harm.

Mechanism of Chemical Cleaning

Porcelli and Judd [59] describe the membrane chemical cleaning process as a six-step procedure:

1. Cleaning reagents undergo a bulk reaction, including hydrolysis and other reactions.
2. The cleaning agent is conveyed to the surface of the membrane.
3. The cleaning agent then passes through the foulant layers.
4. Cleaning reactions occur in the fouling layer, leading to solubilization and detachment of the foulants.
5. Suspended foulants and waste cleaning agent are transported to the interface.
6. Waste matter is transported from the retentate side of the membrane to the bulk solution.

As described above, chemical cleaning is a process that involves submerging membranes in a solution containing strong acids, bases, or disinfection agents. This procedure helps restore the initial flux and prepares the membrane for further use. However, a potential drawback of this process is that it can modify the surface of the membrane. In some situations, this can cause holes to form in the skin layer of the membrane, which can reduce its useful life. Thus, it is crucial to assess how chemical cleaning affects the surface of the membrane and take the necessary precautions to prevent any damage [63].

As mentioned earlier, high-concentration gradients of cleaning chemicals, such as 0.1% NaOH and 100 ppm hypochlorite ion (NaOCl) or free chlorine, can be introduced to prevent a decrease in flux caused by organic fouling. This approach can be effective in restoring the initial flux, and almost complete recovery is possible [63].

NaOH is a commonly used chemical for membrane cleaning because of its ability to dissolve slightly acidic natural organic matter (NOM) and break down polysaccharides and proteins into smaller sugars and amides. This is because NaOH contains a hydroxyl group (-OH) that is responsible for these chemical reactions [64]. In addition to its ability to break down NOM and facilitate mass transfer, the -OH group in NaOH can also help expand the NOM molecules, allowing the cleaning agent to reach the membrane surface more easily. However, it is important to control the concentration of NaOH during cleaning to achieve maximum cleaning efficiency, while also considering factors such as cost and membrane integrity. Finding the optimal concentration of NaOH is crucial to achieve efficient cleaning without causing damage to the membrane [64].

NaOCl is a commonly used oxidizing agent for cleaning organically fouled nanofiltration (NF) membranes. However, it is not universally adopted as a cleaning agent due to the potential for damage to certain types of membranes that are not chlorine-resistant. Additionally, the generation of chlorinated organics during the cleaning process can have negative impacts on both human health and the environment. Therefore, it is important to carefully consider the suitability of NaOCl as a cleaning agent for a particular membrane and to explore alternative cleaning methods if necessary [64].

Combining oxidants with alkaline agents can be more effective in removing organic foulants than using oxidizing agents alone. Theoretically, this combination can enhance cleaning efficiency and provide better removal of organic foulants. However, the optimal combination of oxidants and alkaline agents may vary according to the type of membrane and the nature of the foulants and must be carefully evaluated to avoid any potential damage to the membrane. The study reported that when nanofiltration membranes fouled with Aldrich humic acid (AHA) were cleaned at a concentration of 10 mg/L, higher flux recovery, and resistance removal were achieved with the use of sodium hypochlorite (NaOCl) compared to sodium hydroxide (NaOH). This suggests that NaOCl may be a more effective cleaning agent for this type of fouling than NaOH. However, it is important to note that the optimal cleaning agent may vary depending on the type and concentration of the foulants, as well as the type of membrane being used [64].

In a microfiltration study of activated sludge wastewater, the primary types of membrane fouling identified were pore blocking and cake layer. Periodic sonication of the membrane microfiltration module was effective in removing the cake from the membrane surface, resulting in a significant recovery of permeation flux. However, sonication was found to be less effective for removing pore blocking, resulting in a reduced flux recovery. An integrated sonication, backwashing, and chemical cleaning was found to be effective in achieving almost complete flux recovery [19].

In a study in which the effluent from a membrane bioreactor was filtered using nanofiltration (NF), it was found that acid cleaning was effective in removing elements such as P, Mg, Fe, and Ca, while NaOH cleaning was more effective in removing organic and amino acids. These results suggest that the optimal cleaning agent for NF can vary depending on the specific foulants that are being targeted. Careful consideration of the type and concentration of foulants present in the system is necessary to determine the most effective cleaning strategy for NF [65].

Ultrafiltration (UF) is frequently employed during or after biological treatment, with or without additional pretreatment. However, it is often plagued by severe fouling from effluent organic matter (EfOM). EfOM is usually composed of three primary fractions: (i) soluble microbial products (SMPs) produced by microorganisms during the biological treatment process, (ii) natural organic matter (NOM) sourced from drinking water, and (iii) trace amounts of synthetic organic compounds. Among the different cleaning agents tested, the use of an alkali cleaning agent was found to have the greatest impact on the cleaning of EfOM-fouled membranes. This suggests that alkali cleaning agents may be more effective in removing EfOM foulants from UF membranes than other types of cleaning agents. However, the optimal cleaning strategy can vary depending on the specific composition and concentration of foulants present in the system [66].

The five main categories of chemical cleaning agents commonly used for organic fouled membranes are alkaline, Caustic (such as NaOH), disinfectants and oxidants, surfactants, and enzymes [45]. The effectiveness of chemical cleaning of fouled membranes is influenced by multiple factors, including temperature, pH, concentration of cleaning chemicals, contact time with the cleaning solution, and operating conditions such as cross-flow velocity and pressure. To achieve efficient removal of fouling agents from membranes, it is important to carefully control these factors and optimize the chemical cleaning process [67]. The flushing of the membrane with NaOH and DI water was found to reduce the fouling of the membrane by 19.6–70.5%, while the flushing of NaCl removed 13.3–51.5% of organic foulants [68].

5.4. Physio-Chemical Cleaning

In certain cases, physical cleaning alone may not be sufficient to remove certain types of contaminants from a membrane, and a chemical cleaning process may be necessary to restore the membrane's permeability. Currently, a combination of water and air is used to clean MF and UF membranes in the forward or backward direction. However, if these methods are not effective in restoring the flux of the membrane to an acceptable level, chemical cleaning of the membrane becomes necessary [63].

A physical cleaning method can be combined with certain chemical agents to enhance the effectiveness of cleaning. Some researchers have explored the introduction of ultrasound into ethylene diamine tetra-acetic acid (EDTA) and these can be further improved beyond what can be achieved by using chemical or ultrasound separately [25].

The study by Ang et al. [69] showed that disodium ethylenediaminetetraacetate (Na2-EDTA) and sodium dodecyl sulfate (SDS) were effective in cleaning organic fouling. The findings demonstrated that this method was more effective than NaOH cleaning.

Characterization of membrane fouling revealed that the application of osmotic backwashing (OBW) before chemical cleaning resulted in an improvement in water flux of up to 10.8%, as well as an improvement in membrane cleaning efficiency [70].

Initially, hydraulic flushing and backwashing were employed to clean the organic fouling that had built up in the hollow fiber nanofiltration (HFNF) membranes used for processing river water. Both methods were found to be highly effective, achieving more than 90% efficiency, particularly with respect to large molecular weight organic foulants (>1000 Da) in river water. However, the cleaning efficiency decreased over time as a result of the lower cleaning efficiency of low-molecular-weight (LMW) organics. To overcome this, chemically enhanced backwashing (CEBW) was used, using concentrations of 5 ppm and 10 ppm NaOCl, to improve the cleaning efficiency. The results indicated that the fouling of the membrane could be effectively cleaned with CEBW, achieving a removal efficiency of 95% [71].

Membrane fouling in food processing plants is typically addressed through periodic clean-in-place (CIP) operations, which require significant amounts of water, energy, and chemicals. However, microbubble (MB)-assisted cleaning has emerged as a promising technology that can be integrated into current CIP operations to improve their cleaning efficiency while reducing water and chemical usage [72].

5.5. Surface Modification

The low surface energy and hydrophobic nature of commonly used polymeric membranes, such as PVDF membranes, lead to inadequate wetting and are susceptible to organic fouling [73].

Researchers have suggested several surface-modifying materials to address the problem of membrane fouling, such as applying nanoparticles (NPs) in membrane structure as one of the most common methods. Some of the recently applied NPs include TiO_2 [74], zinc oxide [75], Molybdenum sulfide (MoS_2) [76], copper sulfide (CuS) [77], silver (Ag) [78], Cu(II) [79], sulfonated TiO_2 ($STiO_2$) [80], silica [81], cerium oxide/graphene oxide (CeO2/GO) [82], and TiO_2/a-MoSx/Ag (TMA) [83].

Water-stable metal-organic frameworks (MOFs) have garnered significant interest among various types of nanoparticles because of their strong affinity for organic polymers and unique physicochemical properties. These properties include an extremely high surface area, precise control over porosity, and the ability to design their structure in a specific manner [84–86].

In addition to NPs, other hydrophilic materials have been used to decrease fouling and improve membrane performance. These include polyethylene glycol (PEG) [75,87], polyvinylpyrrolidone (PVP) [75,88,89], poly(methyl methacrylate) (PMMA) [87], polyvinyl alcohol (PVA) [90], poly(ethylene glycol) [81]; polyethyleneimine (PEI) [73,91]. quaternary ammonium modified [92], polydopamine (PDA) [89,93], 2-N-propyl sulfonated chitosan (PCS) [94], and bio-based tannic acid (TA) [95].

Antifouling membranes possess certain characteristics such as excellent hydrophilicity, better smooth surface, appropriate membrane charge, and antimicrobial properties. These properties are desirable to reduce or prevent membrane fouling of the membrane [96,97]. Membrane surfaces that exhibit superior hydrophilicity or water-attracting properties can facilitate the formation of a hydration layer. This layer serves as a physical and energy barrier, preventing foulants from adhering to the membrane surface (Figure 5) [96]. In addition, certain antimicrobial additives such as graphene oxide, lipophilic bismuth dimercaptopropanol nanoparticles, silver, titanium, chitosan, copper, selenium, carbon nanotubes, zinc oxide, and aqueous fullerene nanoparticles, have been used to prevent biofouling. These additives work by deactivating microorganisms that adhere to the membrane surface [7,98].

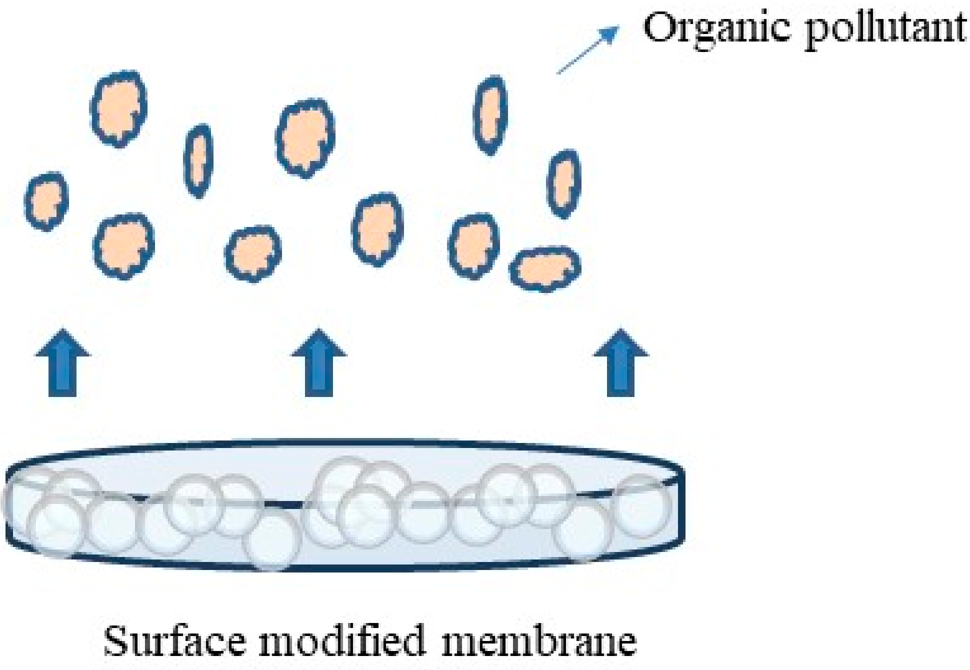


Figure 5. Schematic representation of a surface-modified membrane with an organic pollutant-repellant surface.

A study by Maneewan et al. [7] revealed that ultrafiltration PVDF membrane modified with Tannic acid (TA) and Cu (II) in a 1:3 molar ratio, increased hydrophilicity and introduced some antibacterial properties. The modified membrane exhibited higher permeability after being backwashed, and lower irreversible fouling was obtained on the membrane surface compared to the unmodified membrane.

In order to improve the antifouling property of ultrafiltration PVDF membranes, SiO_2-g-PEGMA nanoparticle-based PVDF membranes were fabricated by the phase inversion technique. The PVDF membrane containing 1% by weight of SiO_2-g-PEGMA NP exhibited a water contact angle of 50.7° and adsorbed 0.05 mg/cm^2 BSA, while the unmodified membrane showed 68.7° and 0.17 mg/cm^2, respectively. The modified PVDF membranes were also tested for antifouling properties and rejection performance using BSA, oil-in-water (o/w) emulsion, and humic acid (HA) ultrafiltration experiments. The modified membrane showed a better flux recovery ratio, and reduced irreversible and total resistance [99].

Various techniques have been explored to improve the antifouling ability and extend the service life of membranes, including blending, surface grafting, and surface coating. Photocatalytic membranes developed via the phase inversion method offer superior porosity due to their unique film structures. The surface of the membranes can further be modified by grafting with inorganic acids such as sulfuric acid, phosphoric acid, and hydrochloric acid and boric acid. This modification enhances the surface protonation of oxygen atoms and promotes the formation of hydroxyl groups and oxygen adsorption. As a result, charge carrier separation is improved and the life of e^-/h^+ pairs is prolonged [20].

In addition to other factors, the in situ self-cleaning performance is a crucial aspect to consider when dealing with the antifouling properties of photocatalytic membranes.

Photocatalytic membrane (PM) has been receiving great attention for membrane cleaning as it avoids the application of chemicals and utilizes ecologically friendly solar energy during industrial wastewater treatment [100–106] When illuminated, • OH radicals and other ROS (reactive oxygen species) generated on the surface of the photocatalytic membrane may degrade the attached pollutants in situ, as shown in Figure 6. Photocatalytic membranes can be modified to prevent the recombination of e^-/h^+ pairs and improve the use of solar energy, which are vital for mitigating membrane fouling [20].

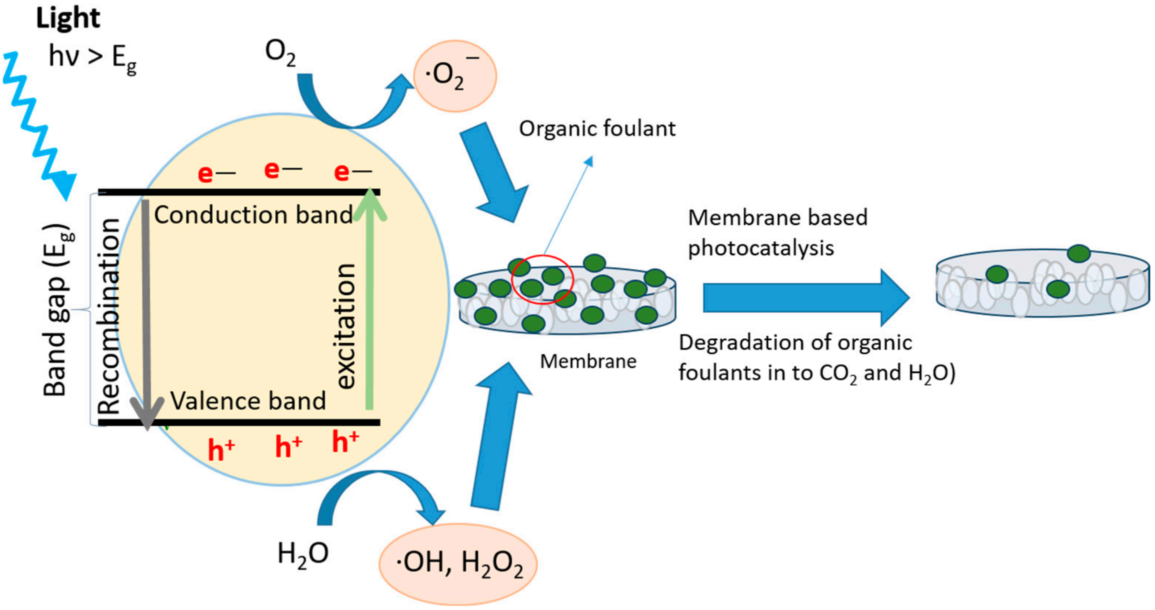


Figure 6. Illustration of membrane-based photocatalysis adopted from X. Wang et al. [20].

5.6. Three-Dimensional (3D) Printing

Additive manufacturing, also known as 3D printing, has various industrial applications, including but not limited to the marine and offshore food industry, biomedical, building and construction, desalination, and water treatment. One of the key benefits of using 3D printing is the ability to create intricate patterns with complex geometry in an effortless manner [107].

In recent times, there has been remarkable progress in applying additive manufacturing for water treatment, as depicted in Figure 7a,b. This is because additive manufacturing offers several benefits, such as improved energy efficiency, outstanding mechanical properties, high printing precision, and fast fabrication with good control over the pore structure and porosity, and that allows for easy regeneration and reuse of the device. Due to such benefits, 3D printing has been increasingly utilized to manufacture membrane module components, such as membrane spacers and membranes, which require intricate geometry while maintaining a high level of precision [108].

Conventional manufacturing methods have limited the optimization of spacer design due to difficulties in producing complex geometries. Today, several types of additive manufacturing technologies, such as 3D printing, have gained interest in membrane applications. The significant advantage of 3D printing for spacer fabrication is that it offers an opportunity for developing spacers with new and complex geometries, providing the freedom to design and optimize the spacer for better mass transfer and reduced fouling. This enables the design of spacers that can better control flow patterns and enhance mixing, resulting in improved mass transfer and reduced fouling. Furthermore, 3D printing enables the fabrication of spacers with customized properties, such as surface roughness and hydrophilicity, to further improve their performance [109].

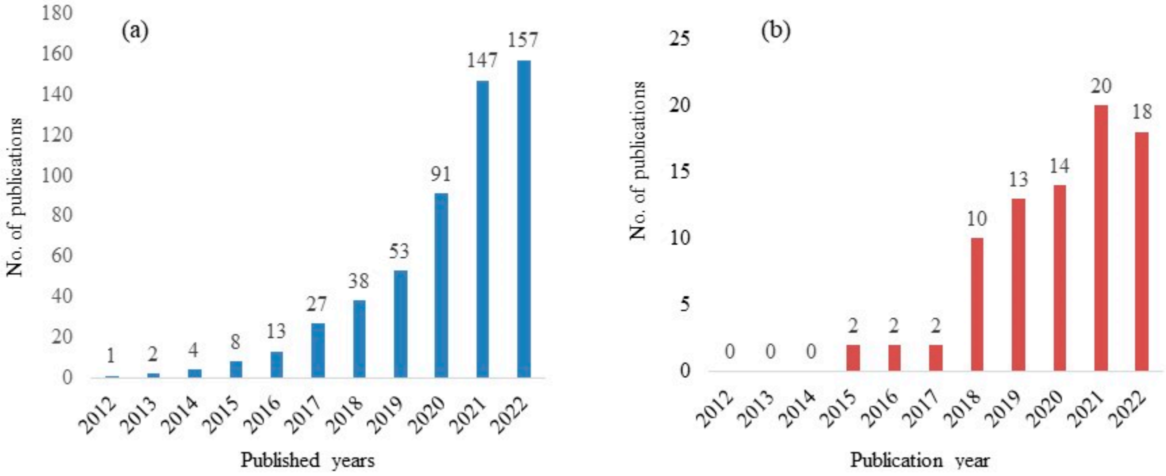


Figure 7. Trends in publication in 2012–2022 with key words of: (**a**) 3D printing and water treatment, (**b**) 3D printing and membrane fouling, and 3D printing, collected from Web of Science as of 13 July 2023.

3D printing also enables the production of shapes that are difficult to create using traditional manufacturing methods. This technique involves the layer-by-layer engineering of freeform objects or the optimization of the orientation and geometry of feed spacers. In recent times, a wide range of materials, such as polymers, composites, novel materials, and metals, can be used in 3D printing [107].

The effectiveness of feed spacers in membrane separation processes is closely linked to the mechanical strength of the spacer and the water flux and fouling resistance performance of the membrane. These properties have a significant impact on membrane fouling performance and can be affected by the materials, methods, and designs used [110]. There are several 3D printing methods available for developing spacers, including liquid-based printing such as Polyjet, stereolithography apparatus (SLA); solid-based printing such as Fused Deposition Modelling (FDM), selective deposition lamination (SDL); and powder-based printing such as selective laser sintering (SLS), electron beam melting (EBM) [111,112]. Different 3D printing techniques have varying precision and critical flux values for feed-spacer fabrication. The highest precision and critical flux can be obtained by Polyjet and FDM, respectively. While the lowest precision and critical flux are obtained by FDM and SLS respectively.

The shape of the 3D-printed feed spacer is critical for optimizing flux. Feed spacers printed by FDM, Polyjet, and SLS methods have anisotropic semi-anisotropic and isotropic surfaces, respectively. Different designs of feed spacers have been proposed for membrane separation processes, including diamond-shaped feed spacers, triply periodic minimal surfaces (TPMS) feed spacers, uniform sinusoidal pattern feed spacers, and hexagonal shape feed spacers [111,113]. The main goal of the feed spacer design is to optimize fluid dynamics and mass transfer within the membrane system. Geometric modifications to feed spacers have been explored to achieve this goal, including variations in internal strand angle, spacer mesh size, and spacer thickness. Additionally, changes to the shape of the feed spacer strands can be made. These modifications aim to reduce the impact of fouling on the membrane system while maintaining the water production rate. The primary focus of feed spacer design is on the impact of spacer geometry on membrane performance, specifically in decreasing fouling and maximizing water production [107].

Based on the level of technological development, several 3D printing techniques have been considered for the preparation of membranes. The 3D printing techniques, including FDM, SLS, and Polyjet, follow a similar printing process. The process starts with the creation of a computer-aided design (CAD) of the custom model. Then, the model is converted into a 3D printer-readable interface, which is followed by the slicing of the model into multiple 2D layers. Finally, the model is made using a 3D printer. This process is illustrated in Figure 8. Post-processing is performed after fabrication [113].

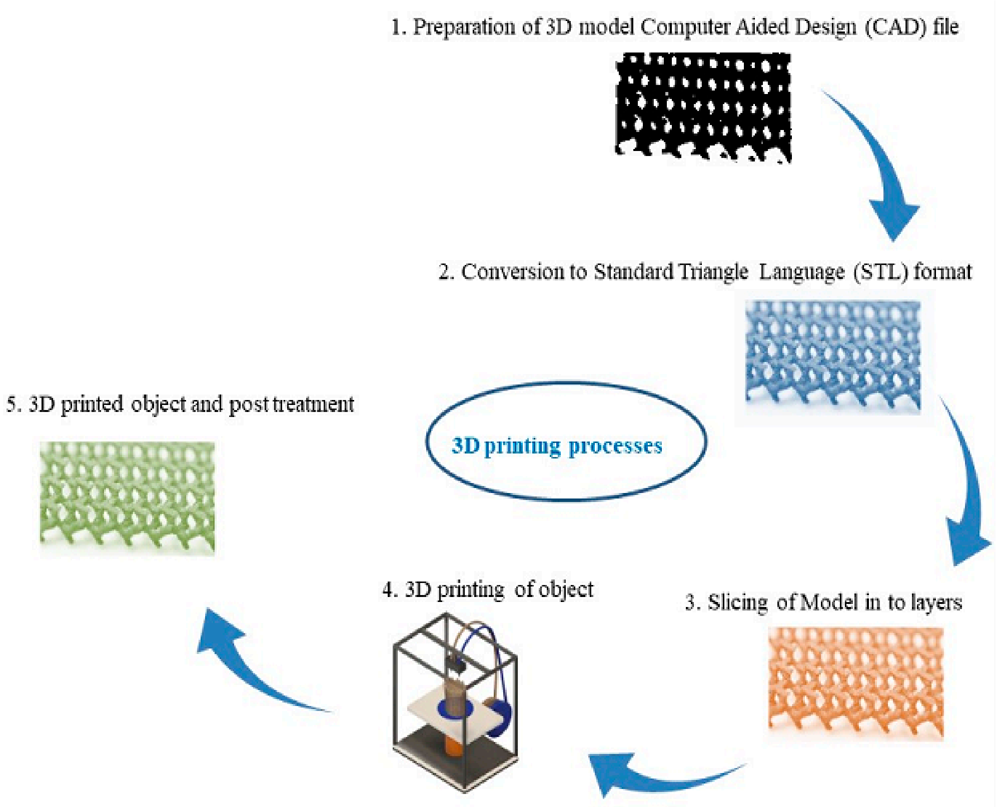


Figure 8. Schematic representation of 3D printing processes adopted from [105].

3D printing materials recently used include a range of options such as photopolymer resins, thermoplastics, Nafion 117, metals, alloys, and ceramics. Some of the commonly used thermoplastics for 3D printing include Nylon 618, Nylon 680, acrylonitrile butadiene styrene (ABS), polylactic acid (PLA), and T-glase. Polypropylene and polystyrene are the most widely utilized thermoplastics [113]. Table 2 provides a concise overview of recent studies, including information on the printing method, spacer design, materials used, applications, and key findings.

Polymeric materials are generally preferred over other 3D printing materials because they are cheaper and more convenient for additive manufacturing. Polymer-based additive manufacturing processes avoid the need for inert gases and/or vacuum conditions, which are needed to control the oxidation of metals at high temperatures. In addition, polymeric materials require lower temperatures for melting and glass transition compared to metals and ceramics, making polymeric material-based additive manufacturing processes more accessible with lower processing temperatures and easier curing and bonding processes during cooling. Recent research has shown that polymer-based additive manufacturing technologies are widely used in the fabrication of membranes and spacers for numerous wastewater treatment applications [114].

The incorporation of surface-patterned microscale and nanoscale polymeric membranes, manufactured using 3D printing, can improve the antifouling properties of membranes during the separation of particles, proteins, and salts [114]. In contrast to polymeric membrane printing, 3D printing of ceramic membranes patterned with surface or line patterned resulted in a significant improvement in flux and antifouling properties, particularly when printed lines were oriented perpendicular to the flow direction in crossflow filtration [107].

Table 2. A concise overview of recent studies, including information on the printing method, spacer design, materials utilized, applications, and key findings.

Printing Method	Spacer Design	Spacer Material	Application	Effect	Reference
SLS	Honeycomb-shaped spacer standard diamond-shaped spacer	Nylon powder	NF	Thinner organic fouling layer is formed in honeycomb-shaped spacers than in standard spacers	[110]
SLS	Triply periodic minimal surfaces (TPMS) spacers	PA 2202 (black) thermoplastic material	RO and UF	TPMS-based feed spacers enhanced flux and reduced fouling with sodium alginate solution	[110]
SLS	TPMS (Gyroid and tCLP) and commercial spacer	Polypropylene	RO	Gyroid spacer exhibited superior fouling mitigation with humic acid solution	[16]
Polyjet	Sinusoidal spacers	-	RO	Sinusoidal spacers performed better in controlling membrane fouling with NaCl solution	[105]
Polyjet	Full-contact hexagonal support horizontal & vertical oriented	Polypropylene (PP)-like material	FO	Better flux and antifouling property were obtained by vertical oriented spacer	[111]
Polyjet	Turbulence promoters or static mixers can	Photosensitive acrylate-based polymer	UF	Kenics mixer improved the flux with humic acid with a photosensitive acrylate-based polymer UF Kenics mixer	[104]
FDM	Three turbulence promoters with different configurations (circular, diamond, and elliptic)	Polyester elastomer	MF	Elliptic promoter enhanced flux by 30–64%. Adding the turbulence promoter significantly mitigated membrane fouling and enhanced filtration flux	[106]
DLP	Helical spacers	Liquid Resin Acrylate Monomer BV-007	UF	Specific permeate flux increased up to 291%. Pressure loss decreased by up to 65%	[106]
DLP	Turbospacer	-	UF	Turbospacer exhibited lower fouling layer & specific energy consumption than conventional spacers	[106]

Woven and non-woven feed spacer configurations are the most commonly used commercial feed spacer [107]. These types of spacers cause dead zones at nodes or strands, where particles begin to deposit. These dead zones are ideal locations for biofouling to occur because they offer a perfect place for microbes to attach and grow. Consequently, the design of the feed spacer, for example, in spiral wound modules (SWMs), is crucial in enhancing mass transfer and preventing fouling in the feed channel [107,109].

Effective feed spacer configurations should minimize the build-up of fouling deposits and reduce concentration polarization by maintaining the solute concentration in the fluid layer in contact with the membrane surface close to the bulk concentration. A new approach to minimizing fouling is to alter the design of the feed spacer. There are several techniques that are being explored to produce mesh-type spacers. These include altered geometry design or three-dimensional printing of feed spacers, the use of electrically conductive spacers, and surface coating [107].

Triply periodic minimal surface (TPMS)-based feed spacers that are 3D printed have demonstrated significant potential in improving both reverse osmosis (RO) and ultrafiltration (UF) membrane processes. They have been found to enhance the flux, decrease the pressure drop, and reduce fouling. These spacers have demonstrated a flux enhancement of 15.5% and 38% in brackish water RO and UF tests with sodium alginate solution, respectively, compared to a commercial feed spacer. This improved performance is attributed to the unique geometry of the TPMS-based spacers, which provide efficient mixing and turbulence in the feed channel, reducing dead zones and minimizing the formation of concentration polarization and fouling. Moreover, 3D printing enables the accurate creation of complex geometries, resulting in custom feed spacers suited to specific applications [109].

A 3D-printed honeycomb-shaped spacer has demonstrated a higher fouling mitigation performance for organic foulants, such as HA, BSA, and TA, compared to a standard diamond-shaped spacer in nanofiltration. The permeate flux of the honeycomb-shaped spacers was 16.0% higher than that of the standard spacers. Nanofiltration with either the honeycomb-shaped spacer or the standard diamond-shaped spacer showed better flux and fouling mitigation performance compared to nanofiltration without a spacer. The improved performance of the honeycomb-shaped spacer is attributed to its geometry, which provides better mixing and turbulence in the feed channel, reducing the formation of dead zones and minimizing concentration polarization and fouling. The use of 3D printing technology allows for the precise fabrication of complex geometries, resulting in customized feed spacers tailored to specific applications [110].

The adoption of 3D printing in spacer design, such as the creation of a skeletal-based gyroid spacer or a sheet-based transverse crossed layer of parallel (tCLP) spacer, has significantly improved the efficiency of membrane distillation (MD). These spacers have demonstrated a better performance in permeate flux and energy efficiency by up to 200% when compared to an empty channel and a 30–70% improvement in flux performance compared to a diamond-shaped commercial spacer. The 3D gyroid spacer has proven to be more effective in mitigating organic fouling, with lower organic mass deposition in comparison to tCLP. This is due to the intricate design of the spacer, which can deter foulants and minimize fouling. The utilization of 3D printing technology allows the manufacture of personalized spacers with complex geometries, promoting the development of optimized spacers that respond to specific membrane processes [16].

Turbospacers have shown better fouling prevention and control in the Forward Osmosis (FO) process of primary effluent from municipal wastewater treatment plants. The Turbospacer design provides better mixing and turbulence in the feed channel, reducing the formation of dead zones and minimizing concentration polarization and fouling. This enhanced performance is attributed to the unique geometry of the Turbospacer, which promotes efficient mixing and flow of the feed solution, reducing the potential for fouling. Additionally, Turbospacers can be customized to specific applications using 3D printing technology, allowing the development of optimized spacers tailored to the FO process of primary effluent from municipal wastewater treatment plants [103].

3D printed mixer geometries, turbulence promoters, or static mixers inserted into the tubular membrane flow channel have been shown to reduce fouling and improve flux by up to 140% during humic acid filtration. Static mixers are devices that are used to mix fluids or gases together by creating turbulence and mixing the fluids as they flow through the device. They are typically made up of a series of stationary blades or channels that cause fluids to mix as they pass through the device. The use of 3D printing technology allows for the precise fabrication of complex geometries, resulting in customized mixers and turbulence promoters tailored to specific membrane processes [104]. Table 3 provides a summary of fouling control and mitigation approaches for organic fouling.

Table 3. A summary table outlining fouling control and mitigation strategies for organic fouling.

Fouling Control Strategy	Description	References
Pretreatment	These methods remove suspended solids, colloidal particles, and microorganisms that contribute to organic fouling. Effective pretreatment reduces the fouling potential by minimizing the presence of foulant precursors and particulate matter in the system.	[5,38–41]
Physical Cleaning	Physical cleaning methods involve mechanical actions to physically remove organic fouling. Techniques include backwashing, air scouring, vibration, rotating membranes, and ultrasound	[48,52,55,56,58,64]
Chemical Cleaning	Chemical cleaning utilizes cleaning agents or solvents to dissolve or dislodge organic foulants. Acidic or alkaline cleaning solutions, detergents, or enzymatic cleaners can be employed based on the nature of the foulants. Chemical cleaning should follow appropriate guidelines, considering material compatibility and safety precautions. It is crucial to select the appropriate cleaning agent for effective removal of organic fouling.	[28,69]
Surface Modification	Surface modification techniques alter the surface properties of materials to make them less prone to fouling. Strategies include applying hydrophilic or non-stick coatings, surface roughening, or incorporating surface-active agents. These modifications discourage organic foulant adhesion, making cleaning or fouling removal easier. Surface modification methods should be selected based on the specific application and material characteristics.	[7,97,112]
3D Printing	3D printing technology allows for the fabrication of complex geometries and customized designs. In the context of fouling control, 3D printing can be utilized to create structures with enhanced fluid dynamics, optimized surface textures, or integrated features that reduce fouling potential. Tailoring the design of components using 3D printing can improve fouling resistance and facilitate easier cleaning.	[106]

6. Conclusions and Future Directions

Understanding the factors that contribute to organic fouling is critical to developing effective control and mitigation strategies. By optimizing the operating conditions, membrane properties, and pretreatment processes, it is possible to reduce the extent of fouling and improve the performance of membrane separation processes.

It should be noted that the fouling potentials of different polysaccharides can vary depending on their specific properties such as MW, structures (such as linear chain, branched chain, etc.) as well as the operating conditions of the water treatment process. Therefore, it is important to carefully examine the properties of the organic matter present in feed water in order to develop effective fouling mitigation strategies.

Membrane processes are influenced by many factors and different processes require different pore sizes and hydrophobicities. As a result, the use of a membrane with lower hydrophobicity and larger pore sizes is suitable. Despite extensive research, the mechanisms underlying organic fouling are not fully understood. More studies are proposed to gain a deeper understanding of the complex interactions between the membrane surface and foulants and to develop predictive models that can help optimize membrane performance.

Organic fouling can cause irreversible damage to the membrane structure, leading to a reduced lifespan and performance. Therefore, more robust membranes that are resistant to fouling and can maintain high performance over long periods of time are needed. Although polymeric membranes are widely used in membrane separation processes, alternative materials, such as ceramic and graphene oxide membranes, have shown promising results in terms of fouling resistance. Further studies are required to discover the potential of these materials in industrial settings.

Selection and effectiveness of fouling control and mitigation approaches may vary depending on the specific application, membrane type, fouling mechanism, and operating conditions. Implementing a combination of these approaches and tailoring them to the specific needs of the system can help effectively mitigate fouling and maintain membrane performance.

Cost-effective pretreatment of wastewater can bring several benefits, such as disinfection, removal of large suspended particles through settling, and reduction of total suspended solids (TSS) in the wastewater. Additionally, effective pretreatment can also result in a lower fouling propensity of the feed wastewater, which can improve the efficiency and lifespan of the membrane. The effectiveness of pretreatment and fouling control techniques to mitigate organic fouling depends on the type and concentration of organic compounds present in the feed water, as well as the specific operating conditions of the membrane system. A combination of multiple techniques may be necessary to achieve optimal organic fouling mitigation.

Although physical and chemical cleaning methods have been proven to be effective in mitigating organic fouling, they can be costly and time-consuming. Therefore, it is very important to develop more efficient and cost-effective cleaning strategies that can be easily implemented in industrial settings.

3D printing offers the flexibility to design and fabricate complex membrane structures; the membranes must be optimized for fouling resistance. Further study is required to fabricate 3D-printed membranes with improved fouling resistance, which can be achieved through modifications to the membrane surface or the incorporation of antifouling agents. The performance of 3D-printed membranes can be affected by various printing parameters, such as layer thickness, printing speed, and nozzle diameter. It is necessary to investigate how these parameters affect membrane performance, including fouling resistance, to optimize the printing process.

The complex geometries of 3D-printed membranes can make cleaning challenging, particularly in industrial settings. Therefore, there is a need to develop in situ cleaning strategies that can effectively remove fouling from the membrane surface. 3D printing offers the potential for rapid and customizable membrane fabrication, but scalability remains a challenge. There is a need to investigate the scalability of 3D printing for membrane fabrication and identify ways to optimize the process for large-scale production. It also offers the ability to fabricate membranes from a wide range of materials, including polymers and ceramics. There is a need to explore the potential of novel materials, such as metal-organic frameworks and graphene oxide, for 3D printing in membrane separation processes and investigate their fouling resistance.

It is important to note that the performance and stability of organic fouling control and mitigation methods can vary depending on the specific membrane material, fouling characteristics, operating conditions, and cleaning protocols employed. It is recommended to conduct pilot-scale or field-scale studies to validate the performance and stability of the cleaning methods under real-world conditions and to optimize cleaning protocols based on the specific fouling challenges encountered. To facilitate the practical implementation of fouling control strategies, future research should include techno-economic analysis and consideration of scale-up aspects. Evaluating the cost-effectiveness, energy efficiency, and scalability of different fouling control approaches will help bridge the gap between research and industrial application, facilitating the adoption of advanced fouling mitigation strategies in large-scale membrane separation processes.

In general, addressing the challenges and exploring future directions will be critical to advancing the field of organic fouling control and mitigation in membrane separation processes.

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Abbreviations

ABS, acrylonitrile butadiene styrene
AHA, Aldrich humic acid
$AlCl_3$, aluminum chloride
AnMBRs, anaerobic membrane reactors
BSA, bovine serum albumin
CAD, computer-aided design
CEBW, chemically enhanced backwashing
CEB, chemical enhanced backwash
CIP, clean-in-place
COP, clean-out-of-place
CTS, chitosan; R-HFM
CW, chemical wash
3D, three-dimension
DEX, dextran
DLP, digital light processing
EBM, electron beam melting
EDL, electric double layer
EfOM, effluent organic matter
EDTA, ethylene diamine tetra-acetic acid;
FDM, fused deposition modeling
$FeCl_3$, ferric chloride
FO, forward osmosis
HA, humic acid;
HFNF, hollow fiber nanofiltration;
LMW, low-molecular-weight;
MB, microbubble
MD, membrane distillation
MF, microfiltration
MOFs, metal-organic frameworks
MPs, organic micropollutants
NaOCl, sodium hypochlorite
NPs, nanoparticles
NF, nanofiltration
NOM, organic matter
Na2-EDTA, disodium ethylenediaminetetraacetate
OBW, osmotic backwashing
PACl, polyaluminum chloride
PAC, polyaluminum chloride
P (AM–DAC), cationic polyacrylamide
PAM, polyacrylamide
PASiC, polysilicate aluminum chloride
PCPs, personal care products
PCS, 2-N-propyl sulfonated chitosan
PDA, polydopamine
PDMDAAC, poly dimethyl diallyl ammonium chloride
PEG, polyethylene glycol
PEI, polyethyleneimine
PhACs, pharmaceutical active compounds;
PLA, polylactic acid;
PM, Photocatalytic membrane;
PVDF, polyvinylidene fluoride
PVA, polyvinyl alcohol
PFC, polymeric ferric chloride
PP, polypropylene; SDL
RO, reverse osmosis
rotating hollow fiber membranes
ROS, reactive oxygen species
SA, sodium alginate
SDL, selective deposition lamination
SDS, sodium dodecyl sulfate
selective deposition lamination
SLA, stereolithography apparatus
SLS, selective laser sintering
NaOH, sodium hydroxide
SWMs, spiral wound modules
TA, tannic acid
tCLP, transverse crossed layer of parallel
TPMS, triply periodic minimal surfaces
UF, ultrafiltration
US, ultrasound
USVM, uniform shearing vibration membrane
WOM, wastewater organic matter

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