Comprehensive review of chemical cleaning in polyvinylidene fluoride/graphene oxide-based membrane for oilfield-produced water treatment

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The high demand for oil results in an oilfield-produced water (OPW) production increment. The management of OPW presents a significant environmental and industrial challenge, attributed to its intricate composition, which encompasses hydrocarbons, suspended solids, and salts. Polyvinylidene fluoride (PVDF)/graphene oxide (GO)-based membranes, represent effective options for oil-water separation, attributed to their enhanced mechanical strength, hydrophilicity, and resistance to fouling. Maintaining the durability and performance of these membranes requires effective chemical cleaning strategies to mitigate fouling issues. This review discusses the fouling mechanism that takes place in OPW treatment, reviews chemical cleaning of the membranes utilized in OPW treatment, and compares the chemical cleanability of PVDF/GO-based membranes. The findings indicate that the chemical cleaning process of PVDF/GO-based membrane can be aligned with that of the PVDF membrane. The incorporation of GO in PVDF-based membranes can mitigate membrane fouling. The use of chemicals can be decreased as fouling decreases. This mitigates potential harm to the membrane during the chemical cleaning procedure, particularly when employing chemicals that are susceptible to resulting in damage. When the fouling is reduced, the chemicals used can be reduced, hence reducing the potential damage to the membrane during the chemical cleaning process, especially when using chemicals prone to causing damage. This study analyses recent developments and proposes future directions to optimize the cleaning process, enhancing the sustainability and operational efficiency of PVDF/GO-based membranes in OPW treatment applications.

Keywords: Chemical cleaning; PVDF/GO-based membranes; OPW treatment.

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1. Introduction

Oilfield-produced water (OPW) is currently challenging in its disposal process. The content of hazardous materials, such as toxic gases, methane (CH_4), nitrous oxide (N_2), carbon dioxide (CO_2) [1], high salinity [2], hydrocarbons [3], organic compounds, heavy metals, and naturally occurring radioactive materials [4], makes it difficult for OPW to be disposed of. These OPW can harm living things such as animals, plants, and even humans [5-7]. Therefore, the treatment of OPW is very crucial.

Membrane technology is currently one of the most widely developed technologies for treating OPW, especially in its function to separate oil and water. This technology offers several compelling advantages, including high separation efficiency, low energy consumption, potential to enable water reclamation and reuse [1,8]. In its application, polymer-based membranes are extensively developed for oil-water separation, categorized according to their wettability properties. Both hydrophilic and hydrophobic polymers can be employed as the primary material for membrane manufacturing, as they allow the achievement of high-level and stable filtration. Even so, hydrophobic polymers have been widely utilized because of their superior mechanical strength and chemical resistance over an extended duration when compared to hydrophilic polymers [9]. In OPW treatment that emphasizes water reuse and in cases involving oil in water emulsion treatment, it is essential to utilize a membrane with hydrophilic properties to achieve optimal results [10-12].

Polyvinylidene Fluoride (PVDF) is a polymer commonly used as a membrane material due to its excellent properties. It possesses high mechanical strength, including strong tensile strength and resistance to pressure [13,14]. It is ideal for maintaining membrane continuity under high pressure during filtration. Additionally, PVDF exhibits broad chemical compatibility, allowing it to interact with various solvents used in membrane manufacturing [15]. However, PVDF is hydrophobic. Graphene oxide (GO) nanocomposite material can be utilized to enhance the hydrophilicity of the PVDF membrane. GO possesses an oxygen chain functional group that can enhance hydrophilic properties [16]. GO has a large surface area per unit mass. It is advantageous for membrane applications as it provides a greater interface for interactions with target substances [17]. Venault *et al*. (2018) [18] reported that, the incorporation of GO into PVDF membranes via the vapor-induced phase separation (VIPS) technique significantly enhanced separation efficiency of GO-infused membranes compared to pure PVDF, particularly in complex oils like diesel or soybean oil. Cui et al. (2021) [19] additionally developed crosslinked modified PVDF/GO membranes exhibiting resistance to acid, alkali, and salt, achieving efficient oil-water emulsion separation with high rejection rates (> 99%) and fluxes (> 145 L $m^{-2}h^{-1}$). Although the PVDF/GO membranes do not allow oil to pass through the membrane, membrane fouling is still possible [20]. Over time, oil droplets can adhere to the membrane surface, especially if they have an affinity for the membrane material. Moreover, this problem can even lead to the end of the membrane's lifespan, making it ineffective for further use [21].

Multiple treatments have been established to address membrane fouling issues, including pre-treatment, physical, chemical, and biological cleaning. Nonetheless, these different methods possess both advantages and disadvantages contingent upon the type of membrane employed. Pre-treatment aims to reduce fouling by minimizing particles or organic matter in the feed prior to membrane filtration. However, this method often entails high initial costs and may not consistently yield effective results [22]. Physical cleaning effectively addresses less fouling, such as removable physical deposits. However, this method poses a risk of membrane damage, is ineffective for complex fouling, and lacks time efficiency. For instance, backwashing is incompatible with reverse osmosis membranes and dead-end cell testing procedures due to their unidirectional feed [23,24]. Biological cleaning is an environmentally beneficial method for the removal of biofouling. However, its effectiveness diminishes with other types of fouling, controlling challenges and more expenses [25]. Chemical cleaning is efficient for various types of fouling and demonstrates effectiveness regarding time and labour. The primary concern in employing this method should be the selection of chemicals that optimize cost efficiency while minimizing the risk of membrane damage due to unsuitable chemicals [26]. Collaboration among pre-treatment, physical, biological, and chemical cleaning methods may be advantageous, contingent upon the specific type of fouling and the membrane employed [27]. Alternatively, the ease and efficiency of chemical cleaning can be employed with various modifications.

Based on Fang *et al*. work, periodic chemical cleaning processes have been successfully carried out on gravity-driven ceramic membranes to remove organic fouling due to extracellular polymeric (EPS). The used cleaning agents were ascorbic acid, sodium hypochlorite (NaClO), and sodium hydroxide (NaOH) with backwash and soak additional processes. Although the functional layer was temporarily biologically damaged, the impact on water quality decreased over time [28]. Meanwhile, research by Xiao *et al*. used radical-based membrane cleaning technology with a peroxymonosulfate (PMS)/hydroxylamine (NH_2OH)/ferrous ion (Fe^{2+}) system, which was capable of producing high amounts of hydroxyl radicals (HO.) as a chemical agent. The results showed the recovery and improvement of membrane performance with a simultaneous increase in flux of 181% 219% of the initial value. Although the flux increased, the ability of the membrane to filter remained significantly unchanged [29]. In the following, chemical cleaning can also be carried out in combination with membrane pre-coating. Research by Li *et al*. combined calcium carbonate ($CaCO_3$) pre-coating and citric acid cleaning. This combination was effective for cleaning ceramic nanofiltration membranes without a backwash and reduces dependence on chlorine, allowing efficient and safe permeability recovery for long-term operation [30].

In addition, maintaining superhydrophilicity can be challenging in harsh environments [31]. Exposure to high temperatures, acidic or basic solutions, and organic solvents can degrade the membrane's surface properties, diminishing its effectiveness [32,33]. Consequently, an appropriate design is essential for the application of chemical cleaning, particularly with PVDF/GO-based membranes. This article seeks to pinpoint the appropriate chemical cleaning method in the application of PVDF/GO-based membranes. The problem of fouling and chemical compatibility remains a critical issue in modern approaches to membrane technology when the membranes are used in severe conditions. By identifying effective cleaning strategies, this work contributes to the development of sustainable and long-lasting OPW treatment processes.

2. Fouling mechanisms in OPW treatment

Prior to understanding the types of membrane fouling caused by OPW, it is necessary to recognize the characteristics of OPW. The characteristics of OPW vary depending on the geological formation, production techniques, and stage of the well's lifecycle [2,34]. Table I shows the general characteristics of OPW. The COD, TOC, TDS, and TSS levels in OPW are greater in comparison with domestic wastewater or natural water. Consequently, OPW necessitates specialized treatment before discharge or reuse, primarily to comply with environmental standards. Various types of OPW can produce various types of fouling, which can be classified into organic, inorganic, biofouling, and emulsion fouling. Understanding the various fouling sources on the membrane will help direct an effective chemical cleaning process.

2.1. Organic Fouling

Organic matter is the cause of fouling that most often occurs on membranes that perform treatment at OPW [38]. Usually,

TABLE I. OPW general characteristics.

Parameter	Values [35]	Values [36]	Values [37]	Values [1]
Density (kg/m^3)	1014–1140	1014–1140	–	–
pH	4.3–10	4.3–10	–	5.18–8.9
Chemical Oxygen Demand (COD) (mg/L)	1220	1200–2600	1220–2600	–
Total Organic Carbon (TOC) (mg/L)	0–1500	1500	0–1500	< 0.1 & $> 11{,}000$
Total Dissolved Solids (TDS) (mg/L)	–	100–400,000	100–400,000	1000–40,000
Total Suspended Solids (TSS) (mg/L)	1.2–1000	1.2–1000	1.2–1000	1.2–1000
Metals (mg/L)	0.001–97,000	–	–	–
Salinity (mg/L)	–	–	5,000–300,000,000	–

ally, organic membranes will settle or adsorb on the surface or pores of the membrane, causing fouling. Oils and fats, dissolved hydrocarbons, protein surfactants, carbohydrates, polysaccharides, acids, and organic ingredients from emulsions are the substances that contribute most to organic fouling [37,39]. The primary foulants contributing to the organic fouling of nanofiltration membranes comprised fulvic acid-like compounds, along with polysaccharides and protein-like molecules recognized in the literature [40]. Factor analysis indicated that low molecular weight organic compounds contributed to organic fouling. Organic fouling is a complex process in which three main types of foulants are involved simultaneously [40].

2.2. Inorganic fouling

Inorganic constituents are significant as they not only contribute to settling but can also interact synergistically with biofouling and organic fouling, resulting in the formation of a dense cake layer [38]. Inorganic fouling is caused by the deposition of inorganic compounds on the surface or pores of the membrane during the filtration process. The causative components include scaling compounds such as calcium carbonate ($CaCO_3$), calcium sulphate ($CaSO_4$), and barium sulphate ($BaSO_4$); iron derived from Fe^{2+} ions oxidized to Fe^{3+}, and various types of salts [1,41]. Inorganic fouling mechanisms can occur through crystal precipitation caused by ions in water that exceed their solubility, particle deposition due to small particles trapped in membrane pores, and chemical reactions [42].

2.3. Biofouling

Biofouling is a fouling that can cause no less serious problems than organic and inorganic fouling. This fouling is caused by the growth of microorganisms on the membrane surface [43]. These microorganisms can form biofilms, which are complex layers consisting of microbial cells and a sticky extracellular matrix [44]. The biofouling process on the membrane is affected by three factors: microbes, surface structure, and the feed.

2.4. Impact of fouling on membrane performance

The effects of fouling on membrane processes encompass flux decline, structural damage to membranes, disruption of conventional transport mechanisms, elevated feed and differential pressures, increased energy consumption, and the necessity for frequent cleaning [25,43]. These factors negatively influence membrane plant operations and reduce membrane lifespan. Additionally, feed characteristics such as temperature, pH, dissolved organic and inorganic matter, shear forces, and flux are relevant considerations [44].

Different types of fouling, including organic, inorganic, and biofouling, can interact with one another in the development of fouling, depending on the morphology of the fouling layer. This form of fouling is illustrated in Fig. 1. Cake layer fouling occurs when a dense layer forms on the membrane surface. Pore-blocking fouling occurs when particles or molecules enter and obstruct the membrane pores. Internal fouling typically results from organic compounds or biofilms that infiltrate the system [45,46]. This form of fouling poses greater cleaning challenges and necessitates intricate chemical cleaning methods. This fouling significantly obstructs water flow, necessitating increased pressure for drainage. This makes chemical cleaning essential to restore performance and extend membrane life.

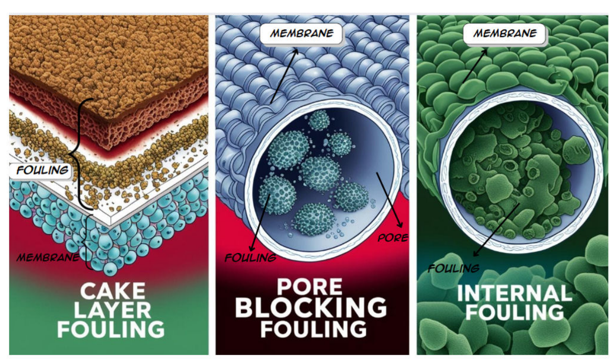

FIGURE 1. Fouling types based on the morphology.

TABLE II. Chemical cleaning agents for PVDF-based membranes.

Membrane types	Materials	Chemical types	Foulant types	Method in chemical cleaning process	Sources
Membrane bioreactors	PVDF membranes	sodium hypochlorite (NaClO)	Irreversible foulant	–	[54]
		triethyl phosphate (TEP)	Recalcitrant, irrecoverable foulants		
Full scale membrane bioreactors	PVDF membranes	0.5% NaClO	Irrecoverable foulants	Immersed for 2 hours	[55]
		1.5% citric acid	Irrecoverable foulants		
PVDF membranes fabricated via non-	PVDF membranes hydrochloric acid	19.767 mg/L of scaling	Calcium	Batch soaking	[56]
solvent induced phase separation (NIPS) and		3.000 mg/L sodium hypochlorite	Acid cleaning		
thermally induced phase separation (TIPS)	sodium hydroxide	39,452 mg/L cleaning	Alkaline oxide		
Flat-sheet ultra-filtration membrane	PVDF membrane	sodium hypochlorite	Organic foulant, biofouling control	Soak in chemical cleaning for one hour	[57]
		ethylenediaminetetra acetic acid (EDTA)	Humic and allergenic foulant		
		dodecyl trimethyl ammonium chloride (DTAC)	Lipid, humic acid, polymethyl acrylate (PMA)		
Hollow-fiber Ultrafiltration membrane	PVDF membrane	anionic surfactant [sodium dodecyl sulfate (SDS) and sodium dodecylbenzene sulphonate (SDBS)]	Irreversible foulant	Soaking for 10 minutes	[58]
		cationic surfactant [(cetyltrimethylammonium bromide (CTAB)]			
		non-ionic [Tween 85 (T-85)]			

3. Chemical cleaning strategies in membranes for OPW treatment

Chemical cleaning is essential on membranes used for OPW treatment. As discussed earlier, OPW can cause complex fouling during filtration. The mechanism of chemical cleaning depends on the type of fouling that occurs on the membrane. This will affect the type of chemical and the method used in chemical cleaning. The details of the relationship between the type of fouling and the chemical agent are as follows [26,40,44]: In organic fouling, caustic cleaning agents such as sodium hydroxide (NaOH) are usually used to remove polysaccharides, microbial foulants, hydrolysis, and solubilization. Inorganic fouling is usually treated with acid-cleaning agents such as citric acid and hydrochloric acid (HCl). While biofouling usually uses oxidizing agents such as hydrogen peroxide (H_2O_2) or sodium hypochlorite (NaOCl) to kill microbes. In addition, some alkalis play a role in the alteration of surface charges and decrease in the number of bonds between the foulant and the membrane surface. While surfactants are for dispersion, emulsifying, and surface conditioning. As for methods on organic fouling and inorganic fouling, it is usually done by cleaning in place (CIP) in stages where the removal of organic fouling is firstly done without removing the membrane from the system [47]. Meanwhile, biofouling, which is included in heavy fouling, can usually be done by soaking cleaning [47]. In addition to the type of fouling, membrane compatibility is also an important factor to consider [45]. Thus, it is necessary to study it specifically. It is essential to determine an appropriate strategy for chemical cleaning to mitigate negative implications [26], including the elevated costs of chemicals, potential membrane damage from excessively harsh substances, and the environmental repercussions of the chemicals employed.

3.1. Chemical cleaning strategies in membranes based on PVDF

PVDF is one type of polymer that is widely used as a membrane material for OPW treatment. It is due to its outstanding anti-oxidation activity, high thermal stability, high organic selectivity, excellent chemical resistance as well as mechanical and membrane forming strength [48]. Because it has good chemical and mechanical resistance, this membrane is quite resistant to chemical cleaning processes. PVDF-based membranes can withstand chemical agents with a PH range of 2-12 and are not easily degraded by surfactants. In addition, it also has high thermal stability with a range of 60-80°C. However, in the chemical cleaning process, PVDF can be degraded if exposed to strong oxidizers such as NaOCl or H_2O_2 in high concentrations or for a long time [49,50]. However, Table II shows that most of the chemical cleaning on the PVDF-based membrane has NaOCl as the chemical agent. Moreover, In Zhang's (2017) research [51] pure PVDF membranes with aged PVDF that has been subjected to NaOCl have flux recovery values that are not much different, in the type of fouling caused by Bovine serum albumin (BSA) and humic acid (HA) where the type of fouling is dominated by blocking the cake layer. However, when the membrane was only challenged by HA solution, the aged PVDF membrane showed a lower flux drop at the fouling stage, indicating an improved anti-fouling ability, which could be attributed to the enhanced surface hydrophilicity. In addition, all three commercial PVDF hollow fiber membranes (SMM-1010, MEMCOR® CS II, and ZeeWeed 500) showed good chlorine resistance, and their pure water permeability after HA fouling can be recovered by more than 80% [52]. The use of NaOCl on PVDF-based membranes can be optimal in alkaline conditions with a PH of 10 [52]. Jia et al. propose that the inclusion of radical scavengers in chemical cleaning processes using NaOCl may enhance membrane longevity, especially in facilities treating source waters with minimal natural scavengers [53]. Furthermore, the integration of chemical agents and enzymes in chemical cleaning strategies for biofouling mitigation can yield greater results [26]. Other various types of chemicals that can be used on PVDF-based membranes can be seen in Table II.

Besides NaOCl, NaOH is also widely used in cleaning membranes. The average pore diameter of PVDF membranes exhibited a modest increase when subjected to a 5% NaOH cleaning solution. The mechanical integrity of the PVDF membranes was completely compromised in the 4 wt.% NaOH solution at 70°C due to an increase in NaOH concentration and treatment temperature, leading to a reduction in elongation and crystallinity. Likewise, elevating the NaOH concentration may lead to the degradation of PVDF, resulting in an enlarged pore size. Nonetheless, the pore size of the PVDF membrane remained unaltered following the application of the chemical cleaning agent [59]. In addition, Rabuni's work suggests that the usage of NaOCl as compared to NaOH causes a more detrimental effect on the stability of the PVDF membrane [50].

Besides that, anionic, cationic, and non-ionic surfactants as cleaning agents for PVDF were compared as well. Anionic surfactants demonstrated superior cleaning efficiencies relative to cationic and non-ionic surfactants at equivalent concentrations, attributable to the synergistic effects of electrostatic repulsion of emulsified oil particles and the reemulsification of oil particles within the fouling layer [58]. Based on this, the utilization of appropriate chemical agents and procedures tailored to the specific impurities in PVDF membranes can enhance OPW treatment efficiency.

4. Compatibility of chemical cleaning with PVDF/GO-based membrane

The chemical strategies in GO-based membranes depend on the polymer used in the membrane fabrication. The incorporation of GO into the PVDF membrane enhances its hydrophilicity, thereby minimizing fouling [16]. In the research conducted by Zhang *et al*. in comparison to pure PVDF, a two-dimensional nanocomposite membrane (NCM) enhanced with GO and g-C3N4 modified with nitrogen defects (DCN) diminished unrecoverable fouling by 29.6% [60]. In addition, GO-based membranes also have high reusability. Baig *et al*. [10] demonstrated that ceramic membranes incorporating graphene oxide maintained over 90% efficiency after 10 cycles, and Tan *et al*. [61] indicated that PVDF-GO-phytic acid membranes achieved 99% efficiency. This shows that GO-based membrane in OPW treatment has the potential for reusability.

Although the incorporation of GO into PVDF-based membranes can reduce the risk of fouling, in its function for OPW treatment the tendency of high viscosity can still cause the risk of fouling [62,63]. Hence, chemical cleaning is still necessary for this kind of membrane.

Chemical cleaning methods commonly applied to PVDF membranes, such as cleaning with NaOCl, NaOH, or surfactants, are also applicable to PVDF/GO membranes. This is because although modified with GO, the main matrix of the membrane remains PVDF thus having good chemical resistance [64,65]. GO-based membrane has good thermal and chemical stability. Chemical stability is the ability of a membrane material to maintain its structural integrity and functional properties when exposed to various chemical environments, so it enhances long-term membrane performance [62]. Meanwhile, thermal stability is the ability of a membrane to withstand temperature variations without undergoing significant physical or chemical changes, so it affects the method of membrane manufacturing [62]. This indicates that the chemical resistance of PVDF/GO-based membranes may surpass that of pure PVDF-based membranes. Nonetheless, the stability of GO during rigorous cleaning must be kept in consideration. Excessively forceful cleaning, such as the use of high concentrations of NaOCl or elevated temperatures, may provide a risk of slight degradation of GO functional groups [66,67]. Although the procedure is the same, the cleaning effectiveness on PVDF/GO membranes tends to be higher due to the more hydrophilic and antifouling surface properties. Zhao et al.'s investigation have shown that the PVDF/GO composite membrane exhibited consistent permeability, reduced cleaning frequency, and a filtration duration three times greater than that of the PVDF membrane [68]. In addition, Embaye et al. developed PVDF membranes modified with GO to improve the efficiency and stability of the Membrane Distillation-Crystallisation (MDCr) process on hypersaline solutions. The PVDF-GO membrane exhibited excellent antifouling properties with a reduction in biofilm formation of up to 60% for E. coli and 90% for S. aureus, as well as a significant decrease in protein fouling compared to the unmodified PVDF membrane. Thus, chemical cleaning for PVDF/GO membranes aligns with hydrophilic PVDF membranes [69].

Besides, the addition of GO can also be explicitly done as a cleaning agent as in the research of Jurkuyeh *et al*. [71] for heavy metal removal from aqueous solution, Chen *et al*. [71] used in wastewater purification, and Lai *et al*. [72] used for enhanced water separation. As for the addition of GO which has reduced fouling, it can help the chemical cleaning process with a reduced role (see Fig. 2). This reduction can be adjusted to the type of fouling that occurs on the membrane

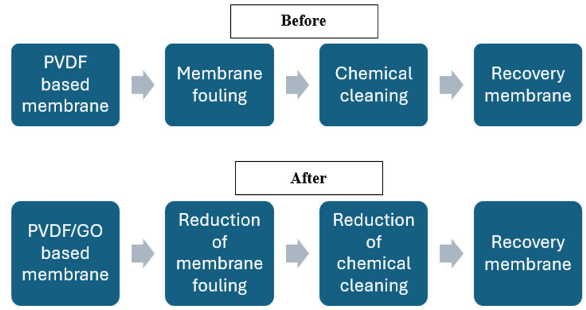

FIGURE 2. Schematic diagram of before and after condition of PVDF and PVDF/GO-based membrane.

caused by OPW [26]. This can help reduce the risk of membrane damage in the chemical cleaning process. In addition, more research is required to determine the extent of reduction in the chemical cleaning process for PVDF/GO-based membranes.

5. Conclusion and outlook

The fouling mechanism in OPW treatment is contingent upon types of fouling, including organic, inorganic, and biofouling. The form of the fouling layer influences the interaction among various types of fouling during its advancement. The chemical cleaning process depends on the specific type of fouling present on the membrane. This will affect the type of chemical and the technique employed in the chemical cleaning process. Organic and inorganic fouling is often addressed by Clean-in-Place (CIP) procedures, whereas biofouling is generally mitigated by soaking. The chemical cleaning of the PVDF-based membrane predominantly employs NaOCl, NaOH, and anionic surfactants as chemical agents. The integration of GO into PVDF membranes enhances fouling resistance, chemical stability, and reusability, making them highly effective for OPW treatment. Reducing fouling diminishes the need for intensive chemical cleaning, hence extending membrane lifespan and improving operational efficiency. However, further investigation is required to assess the extent of chemical cleaning decrease and its long-term implications on PVDF/GO-based membranes.

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