






Polymeric Membranes for Industrial Wastewater Treatment: A Review

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ABSTRACT

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The industrial sector often generates wastewaters contaminated with various pollutants, contingent upon the industry type such as textile, food, petroleum, tannery and others. These pollutants pose a real threat to public health and the environment, so their removal is necessary to minimize their harmful effects. Many treatment methods are used to remove these pollutants by physical, chemical and biological techniques. Among these methods, the membrane separation process is the most efficient and less cost. This review addresses the types of industrial water treatment methods, membrane filtration systems, and how to overcome the challenges facing the membrane technology. The main disadvantage of membrane process, which cause a decrease in membrane performance and increase the maintenance cost, is fouling problems. Many strategies can be employed to minimize fouling, such as grafting polymers with hydrophilic additives, applying hydrophilic coatings, using negatively charged membranes to decrease the adsorption rate of organic matter and microbial attachment, or utilizing plasma treatment to enhance surface charge or hydrophobicity. The addition of hydrophilic additives is more effective than the other methods because of its flexibility and reliability.

1. INTRODUCTION

The inadequate management and direct release of industrial wastewater into water bodies bring about the degradation of the ecological gadget and detrimental effects on human property-being over both immediate and extended periods [1]. The ramifications of this effect extend beyond the contamination of aquatic assets and the discount of useable water resources, encompassing the drawback of meals materials and the escalation of purification charges.

Therefore, various techniques have been employed to address this case, such as flocculation, adsorption, membranes and so on. Among these techniques, membrane technology has garnered good sized interest recently. The primary technological benefits of this technique, comparing to traditional separation approaches, include the technique feasibility, excessive separation efficiency, and reduced electricity consumption and chemical additive requirements [2].

2. LITERATURE REVIEW

Vaidh et al. [3] explored the impact of loading WO_3 NPs into a polysulfone (PSF) matrix at varying weights (0 to 2 wt.%) on the membrane's performance used in landfill leachate treatment with an amount of 12,420 ppm. To assess the membranes' self-cleaning (SC) ability, they were

subjected to radiation. The findings indicated that the landfill leachate achieved a significant reduction in chemical oxygen demand (COD) of 77.45% when subjected to irradiation with a loading of 2 wt.% nanoparticles, compared to a reduction of 54.91% without irradiation. Additionally, the flux recovery ratio (FRR%) increased to 64.9% after irradiation, in contrast to 59.96% before irradiation. Membranes containing 2 weight percent of NPs demonstrated superior pure water flow compared to membranes without radiation. Furthermore, the hydrophilicity of these membranes improved, resulting in a decrease in contact angle from around 67 degrees for the regular membrane to approximately 37.9 degrees.

To assess the membranes' SC ability, they were subjected to radiation. The findings demonstrated that the landfill leachate achieved a significant reduction in COD when treated with a 2 wt.% loading of NPs. The COD removal efficacy increased to 77.45% after irradiation, compared with 54.91% without irradiation. Additionally, the flux recovery ratio (FRR%) enhanced to 64.9% after irradiation, in contrast to 59.96% before irradiation.

Rathna et al. [4] examined the effectiveness of a PSF matrix modified with WO_3 and polyaniline (PANI) nanoparticles, ranging from 0 to 2 wt.%, for treating landfill leachate with a concentration of 12,420 ppm. The membranes were manufactured using a phase inversion procedure. The findings demonstrated that the hydrophilicity of the modified membranes improved after irradiation. The best contact angle was about 37.9 degrees with a loading of 2 wt.% NPs,

compared to 73.7 degrees for the clean membrane. Under the influence of UV light, increasing the proportion of WO_3 to PANI NPs resulted in enhanced antifouling characteristics, while raising the proportion of WO_3 to PANI NPs improved the elimination of COD from synthetic membranes.

Han et al. [5] created a composite membrane made of GO/TiO₂-PVDF using a phase inversion method. The researchers noted that the membrane modified with GO/TiO₂ effectively prevented the passage of bovine serum albumin (BSA) and significantly boosted the flow rate of pure water by 208% compared to the original membrane. Under UV irradiation ($\lambda=365$ nm), the photocatalytic activity of the membranes modified with GO/TiO₂, TiO₂, and GO was enhanced. The rejection rates for BSA (1000 ppm) were 46%, 53%, and 80% for the corresponding modifications. The FRR% of the (GO/TiO₂-PVDF) membranes improved from 71.1% in the absence of irradiation to 82.1% in the presence of irradiation.

Ursino et al. [6] created a nanocomposite membrane (Nanoc-M) using a phase inversion procedure. The membrane is made of a PVDF matrix that has been modified with immobilized silver (Ag) and nanoparticles of TiO₂ (0.01, 0.03, and 0.06 wt.%). Based on the statistics, the membrane hydrophilicity was enhanced, as shown by a decrease in the contact angle from 83 degrees for the pristine membrane to 56.5 degrees for the membrane with 0.06 wt.% of NPs. Under visible light exposure, the authors observed a significant rise in the FRR% values, increasing from 45.27% in the original membrane to 97.21% in the modified membranes. The rejection of BSA rose from 63.43% for the original membrane to 89.8% for the membrane modified with 0.06 wt.% Ag-TiO₂.

Islam et al. [7] fabricated a Nanoc-M using the phase inversion approach. The membranes consist of a matrix composed of cellulose acetate-polyurethane, with the addition of ZnO at concentrations of 0.1 and 0.2 wt.%. The membranes' photocatalytic activity was assessed for the reduction of reactive orange dye and reactive red (100 ppm) under sun irradiation. They discovered that the pure water flow for the modified membranes increased from 66.21 to 93.12 L/m² h. It was found that the duration of irradiation had a positive impact on the rate of dye degradation. The modified membranes exhibited the greatest rate of dye degradation.

Chi et al. [8] investigated the effects of incorporating various amounts of silver-modified graphite carbon nitride (Ag/g-C₃N₄), ranging from 0.1 to 1 wt.%, into the PES matrix. They utilized the phase inversion approach to construct the membranes. The researchers found that the hydrophilicity and filtration characteristics of the membrane improved with the addition of Ag/g-C₃N₄, with the best improvement achieved when 1 gram of nanoparticles (NPs) was loaded. Furthermore, it was observed that the antifouling and SC capabilities of the membranes improved when subjected to visible light ($\lambda = 400$ nm) irradiation, specifically against BSA at a concentration of 1000 ppm.

Ouaddari et al. [9] assessed the effectiveness of a PES matrix mixed with ZnO (0.1, 0.5, and 1 wt.%) coated multiwalled carbon nanotubes (MWCNTs). The results demonstrated that the optimal efficiency occurs when 1 wt.% of NPs is loaded, with the membrane's hydrophilicity, in terms of contact angle, measuring 55.6°, compared to 68.3° for the pristine membrane. Additionally, at 0.5 wt.% NPs loading, following UV irradiation, the best antifouling capacity (FRR%) against a powdered milk solution (8000 ppm) was achieved. The membranes' rejection was evaluated using 30

ppm direct red 16 dyes, and for every membrane, the rejection performance exceeded 90%.

Anan et al. [10] used phase separation to create artificial photocatalytic membranes made of TiO₂ and PSF polymer. Bisphenol A (10 ppm) was utilized to assess the efficacy of the photocatalytic membranes. According to the findings, the removal rate of bisphenol after being exposed to visible light was nearly 90.78%.

Fua et al. [11] investigated the efficacy of a PSF matrix that included nitrogen-doped graphene/titania (NRGT) nanocomposites, which were produced using the phase inversion technique with a concentration of 0.5 wt.%. They found that adding NRGT to the PSF membrane enhanced both the rate of photocatalytic activity and pure water flow, regardless of whether the radiation source was UV or solar. The methylene blue solution (50 ppm) exhibited clearance efficiencies of 80.6% and 77.5%, respectively. When exposed to radiation, the flux recovery ratio (FRR) levels were higher than in the dark. Under UV and sunlight irradiation, the FRR for NRGT-PSF was 94.6% and 90.1%, respectively.

Hoseini et al. [12] produced a modified PES matrix by incorporating cobalt-doped titania (Co/TiO₂) via the phase inversion procedure. According to the results, the presence of 1.34 weight percent of Co/TiO₂ in the PES matrix improved the flow and rejection of membranes when subjected to visible light. Specifically, the membranes showed a 53% increase in flow and a 25.3% increase in 2, 4-dichlorophenol rejection at a concentration of 40 ppm.

Argurio et al. [13] incorporated photocatalytic zinc oxide nanoparticles (ZnO NPs) into a matrix of PES using the phase inversion procedure. The amounts of ZnO NPs used were 5, 7, 9, 11, 13, 15, 17, and 19 wt.%. The membrane performance was assessed in terms of the degradation of 10 ppm methyl orange dye. They found that the membranes' photocatalytic activity increased when subjected to UV light, with a 17 wt.% loading of nanoparticles resulting in the complete breakdown of the dye.

Arif [14] examined the impact of incorporating N, Pd doped TiO₂ into a PSF matrix at different weight percentages (0.5, 1, 2, 4, and 7 wt.%). The researchers manufactured the membranes using a phase separation procedure. The membrane's photocatalytic activity was assessed by measuring its ability to degrade eosin yellow dye (100 ppm) under visible light radiation. They demonstrated that during irradiation, the dye disintegrated by up to 92% when 7 wt.% NPs were loaded, compared to just 67.3% decomposition when pure PSF was used.

Yu et al. [15] produced Nanoc-Ms utilizing the phase inversion technique of a PSF matrix that had been modified with mesoporous graphitic carbon nitride/titanium dioxide (mpg-C₃N₄/TiO₂). The study examined the photocatalytic efficiency of solar light in decomposing the antibiotic sulfamethoxazole (SMX). The investigation showed that the neat mpg-C₃N₄ (0.2% NPs) had varying levels of SMX elimination (14%, 33%, and 49%) depending on the amount of polymer and the presence of 0.2% mpg-C₃N₄/TiO₂ membranes. The membrane with 1% mpg-C₃N₄/TiO₂ exhibited superior water permeability and optimal photodegradation efficacy compared to the mpg-C₃N₄-loaded membrane.

Liu et al. [16] examined the impact of incorporating 2 grams of graphite carbon nitride/silver phosphate (g-C₃N₄/Ag₃PO₄) on the PVDF matrix's resistance to 10 ppm of rhodamine B dye. The membranes were produced using the phase inversion

approach. The findings indicated that after fouling, the flow and FRR% of the PVDF membranes enhanced with $g\text{-C}_3\text{N}_4/\text{Ag}_3\text{PO}_4$ were able to return to elevated levels. The results demonstrated that the Nanoc-Ms ($g\text{-C}_3\text{N}_4/\text{Ag}_3\text{PO}_4$)-PVDF exhibited a removal efficacy of 97% against the dye when subjected to visible light. In comparison, the plain PVDF membrane had a removal effectiveness of 41%, while the $g\text{-C}_3\text{N}_4$ -PVDF membrane had a removal effectiveness of 85%.

Zangeneh et al. [17] examined the phase inversion process and synthesized performance membranes. The membranes were made of a PES matrix integrated with (K-B-N-TiO₂) metal-nonmetal dopings at concentrations of 0.1, 0.5, and 1 wt.%. The biologically treated palm oil mill effluent (POME) at a concentration of 1000 ppm was used to test the separation performance. A fouling agent of 8000 ppm was mixed with a milk powder solution to assess the antifouling ability. The FRR% increased to approximately 95.4% with 0.5 NPs wt.% loading, compared to 48% for the neat membrane. The color and COD elimination of POME were approximately 98% and 90%, respectively. The antifouling test results revealed that the FRR% increased from 48% to 71.7% with 0.5 NPs wt.% loading before exposure to visible light; however, after exposure to visible light, the magnitudes enhanced under UV irradiation compared to visible irradiation light.

Dolatshah et al. [18] produced a photocatalytic membrane by adding boron-doped TiO₂-SiO₂/CoFe₂O₄ nanoparticles at concentrations of 0.1, 0.5, and 1 wt.% to a PES polymer. The highest pure water flow and fouling resistance rate (FRR%) were observed when the amount of nanoparticles was 0.5 wt.%. The effectiveness of the membranes was evaluated by directly measuring their ability to reject 16 dyes at a concentration of 50 ppm. During the experiment, the antifouling ability of the modified membranes was assessed against a milk powder solution with a concentration of 8000 ppm. The findings indicated that the fouling resistance rate (FRR%) was greater when the membranes were exposed to UV light compared to washing with water or using visible light. Furthermore, it was shown that the elimination of the dye reached an impressive 98% when the loading of nanoparticles was at 0.5 wt.%. The photocatalytic activity was evaluated using the optimal membrane loading of 0.5 wt.% nanoparticles to assess the efficiency of removing biologically treated POME with a concentration of 1000 ppm (COD). Based on the findings, the removal of COD was 100% and 98% when visible light was present and absent, respectively.

Zakeritabar et al. [19] produced a Nanoc-M consisting of ZrO₂-SnO₂ by including PSF polymer at amounts of 0.1, 0.25, and 0.5 wt.%. The efficacy of membranes was assessed in the treatment of wastewater with medicines. The study showed that the membranes experienced less fouling when exposed to radiation and exhibited photocatalytic breakdown of pharmaceutical wastewater, leading to effective and durable treatment. Following exposure to radiation, the permeability of the membranes exhibited a significant increase as compared to the original, unaltered membrane. Furthermore, the greatest pharmaceutical wastewater flow rate was attained when a modified membrane, subjected to UV light, included 0.5 wt.% NPs. Under UV irradiation, the membrane hydrophilicity increased, where the reducing contacting angle from 62.33° for the clean membrane to 45.97° for membranes treated with 0.5wt.% nanocomposite. Additionally, these modified membranes' degrading efficiency, COD elimination, and FRR% increased to 90, 57.1, and 68.5%, respectively.

Grylewicz and Mozia [20] examined the effects of adding

titania nanoparticles (NPs) to the surface of functionalized halloysite nanotubes (HNTs) in a matrix of polyvinyl chloride. The photocatalytic activity of the produced membranes was evaluated by subjecting them to UV light ($\lambda=254$ nm) and testing their ability to degrade dyes, particularly rhodamine B (RB) and methylene blue (MB) dyes, at concentrations of 20 ppm. The loaded membranes with 2 and 3 wt.% NPs, according to the researchers, decomposed MB dye by up to 27.19% and 42.37%, respectively, while for RB dye, the degradation was up to 30.78% and 32.76%, respectively.

Heng [21] created a Nanoc-M by altering the phase inversion process of the PVDF matrix using 0 to 2 wt.% titania nanotubes. The application of the photocatalytic membranes was examined with brilliant green (BG) dye, yielding a contact angle of 70.2° at 1.5 wt.% nanotube loading, compared to 86.2° for the clean membrane. According to the research, the BG dye can degrade by up to 42% at 1.5 wt.% nanotube loading following UV irradiation (253.7 nm), as opposed to 13% in the absence of a manufactured membrane. Additionally, a high fouling resistance (FFR%) was achieved at 1.5 wt.% nanotube loading after adding 100 ppm of BSA solution to the filter system to evaluate antifouling capabilities.

Wu et al. [22] created Nanoc-Ms, which are composed of a modified PSF matrix that includes N-doped graphene, TiO₂, and activated carbon. The degradation of methyl orange (MO) dye at a concentration of 30 ppm was investigated under both UV and daylight conditions. Compared to polysulfone modified with TiO₂ and polysulfone enhanced with a clean membrane and activated carbon, the findings demonstrated that the degradation of the dye was 95.2% and 78.1% under UV and sunlight, respectively. Han et al. [23] produced a PVDF matrix doped with CuFe₂O₄ nanocrystals. Under visible light, the membranes' ability to catalyze reactions was evaluated using Congo red dye at a concentration of 14 ppm. The results indicated that even after five cycles, the membranes maintained their enhanced SC capacity, with 95% of the dye decomposed. The PVDF membrane incorporated with CuFe₂O₄ nanocubes exhibited a high rejection rate (99%) and high water flux (40 L/m² h) in terms of flux performance and rejection.

Zangeneh et al. [24] examined the effects of adding C, N, and S triple-doped TiO₂-ZnO NPs to a PES matrix at concentrations of 0.1, 0.5, and 1 wt.%. According to the research, when comparing the modified NP membranes to the clean membrane, both hydrophilicity and flux increased. The effectiveness of the membranes was assessed in relation to the rejection of Direct Red 16 dye (30 ppm). The findings demonstrated that membranes with 0.5 and 1 weight percent NP load achieved 99 percent dye rejection, while the neat membrane's FRR% magnitude was 52.4%. In contrast, the membrane with 0.5 weight percent NP load had an FRR% of 88.9%. Under visible light irradiation, the photocatalytic activity of the membranes was investigated in biologically treated POME at a concentration of 1000 ppm. The findings revealed that membranes with 0.5 wt% exhibited the optimum photocatalytic activity and anti-biofouling properties. Under visible light irradiation (400 nm), the FRR% increased to 99% compared to 67% for the neat membrane.

George and Luo [25] created polyarylether sulfone matrix photocatalytic membranes that were modified with TiO₂ nanotubes (TNTs) at concentrations of 1, 3, and 5 wt.% for separating polyacrylamide (1000 ppm). The findings demonstrated that, in contrast to non-fluorinated hybrid membranes (TNTs/PES-CH₃-COOH), the retention rate in

fluorinated (TNTs/PES-F-COOH) hybrid membranes efficiently withstood degradation in the photocatalytic process. By increasing the amount of TNTs (from 0 to 5 wt%), the pure water flux enhanced from 499 to 936 L/m² h, and the flux recovery ratio (FRR) rose from 40 to 80 percent after solar light irradiation for the (5 g TNTs)/polyarylether sulfone membrane.

Li et al. [26] examined the properties of Fe₃O₄/g-C₃N₄/PVDF membranes (FCMs) produced by the magnetically induced freezing casting process. They decided to load nano Fe₃O₄ using g-C₃N₄ sheets. According to the study, 1% of the particles were induced onto the membrane surface by a magnetic field. The researchers attributed the membranes' increased ability to absorb visible light to the presence of more active zones on their surface, as well as the Macroporous structure, which facilitates light penetration. The FCM also featured high porosity and flux. After five cycles, the membranes' fouling resistance and photocatalytic performance remained above 90%. In 150 minutes, FCMs demonstrated a 97.8% removal efficiency against RhB (5 ppm).

Boopathy et al. [27] assessed the effectiveness of sulfonated graphene oxide/ZnO (SGZ) integrated into a PES matrix. According to the research, the membranes' hydrophilicity increased when treated with SGZ. Under ultraviolet (UV) light, the membranes' photocatalytic activity was evaluated using crystal violet dye. When crystal violet (10 ppm) was present, the membranes' photocatalytic efficacy was approximately 92.3% higher than that of ZnO and sulfonated graphene oxide (SGO) membranes. The flux recovery ratio (FRR%) in the membranes without irradiation increased from 73.2% to roughly 88.7% following radiation.

Shaku [28] created a photocatalytic membrane by combining a PES matrix with hyperbranched polyethyleneimine (HPEI) customized with different concentrations of TiO₂ (0.05, 0.1, 0.5, and 1 wt.%). HPEI was employed to immobilize the TiO₂. The performance of the membranes was evaluated by testing their ability to remove methyl orange at a concentration of 10 parts per million (ppm). The findings demonstrated enhanced degradation of dyes in membranes treated with 0.5 wt.% photocatalysts upon exposure to UV irradiation, in comparison with the unmodified membrane.

Gao et al. [29] examined the photocatalytic efficiency of a PVDF matrix that was modified with g-C₃N₄ in degrading rhodamines (ranging from 5 to 100 ppm) under visible light irradiation. The results indicated that Rhodamine (6G) and Rhodamine (B) were both rejected at a rate of 96 percent. Moreover, the degradation rates of Rhodamine (B) and Rhodamine (6G) dyes during visible light exposure were approximately 80 and 85 percent, respectively.

Zakeritabar et al. [30] produced Nanoc-Ms using the phase inversion method. The membranes were made of a PSF matrix that was modified with varying amounts (0.25, 0.5, 0.75, and 1 wt. percent) of cerium fluoride (CeF₃) nanoparticles. Wastewater containing pharmaceuticals was treated using these membranes. The researchers found that the modified membranes exhibited improved antifouling properties, flux, and hydrophilicity. The results showed that organic contaminants in pharmaceutical wastewaters could be effectively broken down by photocatalytic CeF₃ nanoparticles in the membranes under UV irradiation. At 0.75 wt.% CeF₃-PSF, the degradation efficiency exceeded 97%, and the amount of COD removed was greater than 65 percent,

compared to 75 and 31 percent for the untreated membrane.

Bouziane Errahmani et al. [31] produced photocatalytic Nanoc-M using the phase inversion technique. The membranes consist of a PVDF/PMMA matrix that has been modified with TiO₂ (2.5% and 5 wt.%). The performance of the membranes was assessed using Tartrazine and Congo red dye as contaminants, with an initial concentration of both pollutants set at 20 ppm. They found a 99 percent rejection rate for Congo red dye and an 81 percent rejection rate for Tartrazine.

Huang et al. [32] found that when exposed to visible light, the g-C₃N₄ nanosheet coated on the Bi₂MoO₆ (SCB) surface, with a concentration of 1 wt.% combined with a polysulfone matrix, could enhance the photocatalyst performance for BSA degradation (1000 ppm). The membrane demonstrated exceptional antifouling properties, with a fill rate ratio of 82.53 percent and a BSA rejection rate of 94.77%. They discovered that the (rGO/TiO₂-PPSU) membranes could incorporate (rGO) and (TiO₂). The membrane showed significant photodegradation in response to a 15 ppm concentration of phenazopyridine hydrochloride (PhP) under both visible and ultraviolet light. The FRR% of the membrane demonstrated improved flow due to enhanced SC properties, which performed well against photocatalytic degradation and exhibited better SC under the influence of visible light.

2.1 Industrial wastewater

Contaminated water produced as a result of industrial operations and processes is referred to as industrial wastewater. This water contains harmful pollutants, chemicals, and contaminants. Thus, to safeguard the environment and the general public's health, these pollutants need to be properly identified and treated [33]. Therefore, various physical, chemical, microbiological, and toxicity tests must be carried out. These tests include color, odor, turbidity, COD, biochemical oxygen demand (BOD), total dissolved solids (TDS), total suspended solids (TSS), heavy metal analysis, the presence of harmful microorganisms (bacteria, viruses, or parasites), and biological assays to evaluate the toxicity of the wastewater [34]. By combining the results obtained from these tests, the actual contaminants present in industrial wastewater can be easily identified, and the suitable treatment method can be specified.

2.2 Treatment methods of wastewater

Many processes are applied for wastewater treatment, including biological, chemical, physical, and mixed methods. Physical techniques include filtration, flotation, adsorption, and precipitation. Membrane separation is considered a sophisticated technique for treating wastewater. During this procedure, the wastewater flows through the pores of the membrane. If the size of the solute exceeds the membrane pore size, it will become trapped; otherwise, it will permeate through the membrane [35].

Chemical techniques involve several methods such as oxidation, chemical reduction, electrolysis, chemical precipitation (flocculation and coagulation), neutralization, and ion exchange. These procedures are quite effective at removing dyes. Although wastewater treatment technologies are efficient, they are costly and not economically appealing. Additionally, the excessive use of chemicals in these processes leads to difficulties in disposing of sludge, and electrical

energy is also necessary for their implementation [36].

Biological methods such as phytoremediation, bioremediation, and mycoremediation involve the use of fungi, bacteria, yeast, algae, and other microorganisms. Biological approaches provide distinct benefits, including their environmentally benign nature, cost-effectiveness, and ability to remove organic material. The biological treatment of wastewater is effective at eliminating organic pollutants. However, it has certain drawbacks, including the generation of substantial quantities of sludge, the potential toxicity of leachate, which can affect the efficacy of microbial degradation, and the presence of residual chemical compounds even after treatment. Additionally, some processes associated with biological wastewater treatment may be costly to operate.

The primary obstacle in combination methods is achieving thorough decontamination. Therefore, it is necessary to use a multi-step treatment method to achieve optimal outcomes. The choice of wastewater treatment methods is determined by the anticipated impact of the effluent on the specific environment in which it will be discharged [37].

2.3 Membrane manufacturing methods

Membrane technology has a short but impactful history. The synthesis of asymmetric membranes, which serve as the basis for the majority of commercially available membranes today, was first accomplished in the 1960s. During that period, membranes were not deemed suitable for any kind of application. In the subsequent decades of the 1970s and 1980s, membrane technology saw significant growth and was widely believed to have the potential to address all separation and even reaction-related challenges. Currently, the use of membrane technology for the treatment of wastewater is gaining increasing interest because it offers reliable removal of pollutants without generating any hazardous by-products. This method is feasible, has high separation efficacy, and consumes minimal energy [38]. Membranes may serve as superior alternatives to conventional treatment techniques due to their exceptional efficiency in removing contaminants, which aligns with stringent environmental regulations.

Membrane technology encompasses the scientific and technical methods that facilitate or impede the movement of components, species, or materials across membranes. It encompasses the mechanical separation procedures used to separate gas or liquid streams [39].

From a worldwide standpoint, membranes have emerged as viable alternatives to traditional separation methods in industrial-scale operations. Membranes can be installed at several locations within a manufacturing plant, and they can also be effectively integrated with other separation processes, resulting in the development of hybrid technologies. This technology has formidable capabilities.

Membranes are often regarded as the most advanced technology currently available in numerous fields related to processing and waste management. Nevertheless, several options within the latter category remain pricier compared to the less eco-friendly alternatives that still comply with regulations.

Membranes have been utilized to expedite the movement or exclusion of substances across different media, as well as to physically segregate liquid and gas streams. Filtration occurs when the pores of a membrane are smaller than the diameter of the undesirable material, such as a hazardous bacterium, leading to the removal of environmental contaminants. Membrane technology is frequently utilized in industries

including food, biotechnology, pharmaceuticals, metals and chemicals processing, and water treatment [40].

The technology of membranes finds applications in several sectors, such as water treatment for both home and industrial water supplies, as well as in chemical, metallurgy, beverages, pharmaceuticals, food, biotechnology, and other processes for separation [41]. Membrane-based separation methods have been very influential in purifying contaminated wastewater. Membrane technology is used to purify, separate, and collect CO₂, CH₄, and absorb H₂SO₄ from biogas. Moreover, membrane techniques may be used to extract pure H₂ from various industrial processes for diverse uses. Membranes have the potential to be utilized for the absorption of CO₂ and other noxious gases to mitigate the release of hazardous emissions in current industrial facilities that handle exhaust gases [42]. Ultimately, the captured CO₂ may be utilized as a carbon source to grow microalgae, which could then be used to produce valuable compounds. Additionally, this process could be combined with advanced membrane-based technologies to achieve a sustainable industry.

2.4 Membrane filtration systems

There are many types of membranes, such as electro dialysis (ED), reverse osmosis (RO), nanofiltration (NF), UF, and microfiltration (MF), each with different characteristics, as shown in Figure 1. Membrane technologies, such as microfiltration and ultrafiltration, are increasingly being utilized in current urban water systems for wastewater rehabilitation. These technologies effectively remove particulate matter. Additionally, RO and nanofiltration have been employed to eliminate dissolved contaminants, as seen in several studies [43]. Immersed membranes of microfiltration and ultrafiltration are very effective for pretreating RO systems. They can remove a broad variety of dissolved substances, making them essential components of modern membrane filtration systems.

To ensure disinfection and obtain drinkable water, membrane-based systems require supplementation with UV-oxidation treatments. In this study, researchers are exploring nanotechnology principles to develop membranes with enhanced performance, reduced fouling properties, increased hydraulic conductivity, and greater selectivity in rejecting or transporting substances. The main reasons for the failure of these systems are membrane fouling and clogging [44].

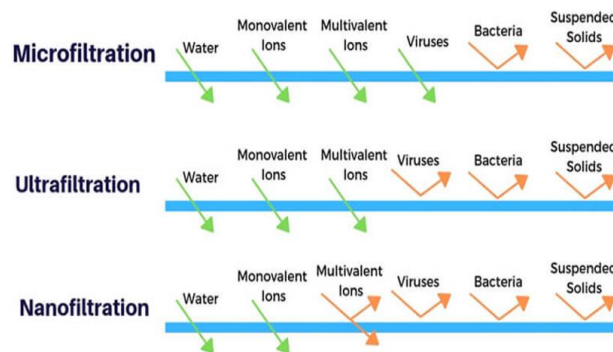


Figure 1. Some of membranes types with their characteristics [45]

2.5 UF

UF was a purification technique that employs an extremely

narrow membrane to separate solid particles from dissolved substances. The ultrafiltration membrane selectively excludes particles with diameters ranging from 103 to 106 Daltons, thereby preventing the passage of protein, silt, smog, pathogens, viruses, endotoxins, germs, and other undesirable particles. UF effectively eliminates several types of colloidal particles found in water, as well as some highly dissolved impurities. Additionally, this treatment eliminates any cloudiness or haziness in the water.

UF is considered one of the most effective membrane systems for treating wastewater since its several benefits, including low operational pressure, relatively low energy consuming, simplicity of operation, and scalability.

UF was a water purification method that effectively eliminates detrimental particles, germs, and viruses, resulting in clean and potable water. During this procedure, the water is compelled to traverse a membrane with a pore size of 0.02 micron. This membrane selectively permits the passage of pure water and minerals while blocking other substances.

The majority of UF systems utilize a hollow fiber membrane for efficient water filtration. Nevertheless, UF systems are incapable of eliminating TDS, fluoride, or salts that may be present in water. UF is a very effective technique used for pretreating desalination, RO, and wastewater reclamation processes. It is also used in the production of drinking water. UF is a kind of membrane filtration that utilizes forces including pressure or amount gradients to achieve separation via a semipermeable membrane. The retentate contains suspended particles and solutes with high molecular weight, whereas the permeate (filtrate) consists of water and solutes with low molecular weight that have passed thru the membrane [46].

UF and microfiltration are similar in that they both rely on particle capture or size exclusion to separate substances. Membrane gas separation differs fundamentally from other methods by separating gases based on variations in absorption levels and diffusion speeds. UF membranes are characterized by the Molecular Weight Cut-Off (MWCO) of the membrane utilized. UF may be used either in dead-end or crossflow mode.

Most membranes of the UF are made of various polymeric materials involving polyvinylidene fluoride (PVDF), polyacrylonitrile (PAN), polyether sulfone (PES) and PSF [47].

UF membranes have been used since the 1980s to remove color, adsorbable organic halides (AOX), COD, and BOD from caustic effluents. Adnan et al. provide a comprehensive assessment of the history, research, development, and uses of membranes methods, involving as MF, NF, UF, and RO, in various sectors of the pulp and paper industry.

Various research was done to investigate the use of UF membrane technology in the treatment of black liquor with the purpose of recovering valuable organic substances. Most of these uses are still in the experimental phase. UF membrane technology may be used to raise the amount of solids of weak black liquor to a level above 30 percent. The drawbacks of using the membrane method for black liquor pre-evaporation are outlined:

1. Significant decrease in the rate at which fluid passes through a membrane and the resulting issues with clogging.
 2. Operated in very alkaline circumstances
 3. The capital and operational expenditures are exorbitant.
- Efficient fouling prevention and effective cleaning procedures are crucial for the successful use of membrane

technology in large-scale black liquor focus processes [48].

2.6 Reverse osmosis process

The fundamental premise of this process is that the large molecules of the solute are unable to permeate through it, causing them to remain on the side that is under pressure. The unpolluted solvent, however, is permitted to traverse the membrane [49]. During this process, the solute molecules become more concentrated on one side of the membrane, while the opposite side becomes more diluted. Moreover, the levels of the solutions also vary to a certain extent. Reverse osmosis occurs when the solvent moves across the membrane in the opposite direction of the concentration gradient. It essentially undergoes diffusion from a region of higher concentration to a region of lower concentration.

Osmotic pressure refers to the minimum pressure required to stop the movement of solvent across a semipermeable barrier. Consequently, the solvent particles on the side of the solution move across the semipermeable membrane towards the region with a lower concentration of solute once the side of the solution with a high solute concentration is subjected to a pressure greater than the osmotic pressure [50].

The process of transporting solvents in the opposite direction over a semipermeable membrane is referred to as reverse osmosis. It is crucial to remember that the pressure exerted on the solution side must exceed the osmotic pressure for the process of reverse osmosis to occur. Since reverse osmosis uses a membrane with the smallest pore size to filter water extensively, it is the most effective and efficient method of water filtration. The undamaged membrane rejects pyrogen materials, viruses, and bacteria. In this regard, the quality of RO water is similar to that of distilled water [51].

2.7 Nano filtration

NF is a filtration membrane process that operates on a scale between UF and RO. It uses a selectively permeable membrane with a pore size typically ranges 1 to 10 nm to separate and remove particles, ions, and dissolved molecules from a liquid stream.

The nanofiltration process is mainly used for water treatment and purification, as well as in various industrial applications.

From the structure viewpoint, nanofiltration membranes are thin, composite structures made of polymer materials. They have a dense layer that acts as a barrier to larger particles and ions while allowing smaller ions and molecules to pass through.

The mechanism of Nanofiltration separation is dependent on charge interactions and size exclusion [52]. The membrane's pore size allows the selective separation of particles and ions dependent on their charge characteristics and size. It can effectively remove divalent ions, involving magnesium and calcium, and accepting the passing of smaller monovalent ions, involving chloride and sodium.

Nanofiltration typically operates at lower pressures compared to reverse osmosis, but higher pressures than ultrafiltration. The operating pressure based on the specific application and the feeding solution properties [53].

2.8 MF

MF is a membrane-based separation technique used to

eliminate particles with a mean molecular weight more than 400kDa. This is achieved by utilizing membranes with pore diameters ranging from 0.1 to 1.0 μm , while working at pressures below 2 bar (Figure 2). It is frequently utilized in combination with many other separation procedures, including ultrafiltration.

MF is used for the purpose of purifying, concentrating, or segregating suspended particles, colloids, and macromolecules from a solution. Furthermore, MF processing is extensively utilized in treatment of wastewater applications, as well as in the separation of plasma from blood for medicinal and commercial purposes [54]. Within the biotechnology sector, MF is utilized for several purposes including cell recycling and harvesting, the separation of recombinant proteins from cellular waste, and the process streams purification. MF is commonly utilized in the food and dairy business, pharmaceutical sector, and for treating oil and latex emulsions. MF is involved in the management of municipal wastewater on a wide scale, treatment of hazardous industrial waste effluent, and removal of contaminants from drinkable water [55].

During the MF process, the feed stream is directed tangentially to the surface of the membrane to avoid the production of cake and subsequent fouling. Membrane fouling, produced by suspended particles in the input stream, frequently constrains the effectiveness of crossflow microfiltration. The permeate flow diminishes with time due to the accumulation of trapped particles on and inside the membrane. The buildup of cells, cell debris, or other particles on the surface of the membrane (cake formation or external fouling) can typically be reversed. However, the adsorption and deposition of small particles or macromolecules within the internal pore structure is frequently permanent. In membranes with significant fouling, the reduction in the area or number of functional pores may lead to filtrate fluxes that are lower than those reported in UF. Tomczak and Gryta [56] conducted a study where they filtered fermentation broth (*Escherichia coli*) using a 100 kD UF membrane and a 0.2 μm MF membrane. They observed that the fall in flux was much higher with the MF membrane compared to the UF membrane. Additionally, the ultimate fluxes achieved with the MF membrane were lower than those achieved with the UF membrane.

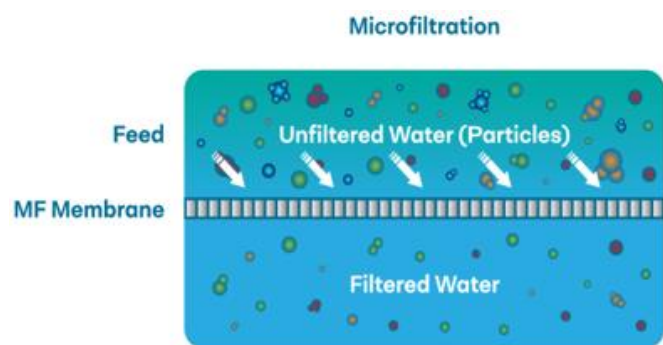


Figure 2. Microfiltration process

3. MEMBRANES PROBLEMS

3.1 Fouling

A significant disadvantage of polymeric membranes is their vulnerability to fouling caused by their inherent hydrophobic

nature. Membrane fouling is a prevalent issue that may occur in several membrane filtering processes. This phenomenon occurs when particles or chemicals in the feed solution adhere to the surface or pores of the membrane. The fouling agents may be classified into several categories: scaling (mineral deposits), organic (humics, polyelectrolytes, oils), biological (fungi, bacteria), and colloidal (flocs, clays) [57].

Fouling leads to the obstruction or blockage of the membrane, resulting in a decrease in its performance and a reduction in its effectiveness. Fouling creates an additional obstacle that results in reduced membrane permeability under a constant applied pressure, ultimately decreasing the membrane's lifespan. Moreover, the occurrence of membrane fouling may lead to a significant reduction in flux and have a detrimental impact on the quality of the generated water. Membrane fouling results in increased operational pressure, higher pressure consumption, frequent chemical cleaning, and a reduced membrane lifespan.

The fouling process is influenced by factors such as the hydrophobicity of the surface, the distribution and size of the pores, the material of the membrane, the amount and size of the feed, the types of components, and the operating conditions. In cases of severe fouling, it may be necessary to use highly concentrated chemical cleaning agents or to replace the membrane altogether [58]. This leads to an escalation in the operational expenses of a treatment facility.

3.2 Fouling kinds

Fouling is categorized as organic, inorganic, or colloidal/bio-colloidal. Inorganic fouling occurs when the concentration of inorganic salts, including calcium sulfates, sodium sulfates, carbonates, and others, exceeds the solubility thresholds of the solvents. This results in the formation of solid deposits on the membrane surface or within its pores [59]. Fouling caused by natural organic matter (NOM) occurs when substances such as proteins, humic acid, and polysaccharides deposit on the surfaces of membranes, as shown in Figure 3.

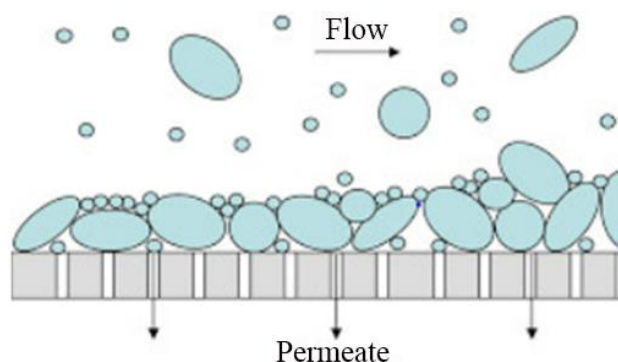


Figure 3. Membrane fouling by natural organic matters (NOM)

Colloidal fouling refers to the occurrence of fouling caused by the deposition of colloids and the suspension of micro or nanoparticles. There are three categories of colloids: organic colloids, which include proteins and natural organic matter; inorganic colloids, which consist of iron oxides, silica, hydroxides, heavy metals, and iron; and bio-colloids, which include bacteria, viruses, and other microorganisms.

Fouling may be categorized as irreversible or reversible, depending on the degree of adhesion between particles and the

membrane surface [60]. Reversible fouling is caused by the deposition of contaminants on the membrane surface and can be separated more readily than irreversible fouling using physical methods such as flushing and backwashing. Irreversible fouling is considered a type of permanent fouling that occurs when foulants tightly bind to the membrane and clog its pores during filtration. To eliminate this type of fouling, chemical agents are required [61]. At the molecular level, secondary forces, such as Van der Waals forces, hydrogen bonds, and dipole-dipole attractions, are the essential adhesion forces among surfaces in fouling.

3.3 Control of membrane fouling

Fouling can be minimized through several strategies, such as:

-Surface modification by grafting, plasma treatment, and the deposition of hydrophilic coatings. Grafting hydrophilic polymers can be achieved through chemical or radiation-induced graft polymerization to create a hydrophilic layer on the membrane's surface, decreasing the adsorption of organic matter and microbial attachment. Plasma treatment can be used to introduce polar functional groups on the membrane's surface, increasing hydrophilicity and surface charge, which can inhibit the adhesion of foulants [62, 63]. Coatings such as polyethylene glycol (PEG), zwitterionic polymers, or silica-based materials can be deposited on the membrane's surface to improve hydrophilicity and decrease fouling [64].

-Using positively charged membranes, which can repel cationic foulants, such as proteins, and reduce their adsorption on the membrane surface [65].

-Incorporating anti-fouling additives, such as nanoparticles (e.g., silver, titanium dioxide) or enzymes, can disrupt the formation of biofilms and reduce fouling [66].

-Optimizing the pore distribution and size can minimize the passage of foulants through the membrane, thereby reducing internal fouling [67].

-By using a suitable cleaning technique, membranes can be cleaned through chemical, biological, or physical approaches. Physical cleaning methods for removing contaminants from surfaces involve water jets, sponges, gas scouring, and backflushing using pressurized air or permeate. Biological cleaning employs biocides to eliminate all living germs, while chemical cleaning utilizes bases and acids to remove foulants and pollutants [68].

-The operating parameters during membrane filtration are crucial, as they can influence the fouling situations that occur throughout the filtering process. For example, crossflow filtration is often preferred over dead-end filtration due to the turbulence it generates during the filtering process. This turbulence results in a thinner film of deposited material, which helps reduce fouling, such as the tubular squeeze effect. Air scours can be used in some applications to enhance turbulence on the membrane's surface [69].

-Pretreating wastewater and modifying its properties may effectively decrease membrane fouling [70].

3.4 Polymeric membranes

Polymeric membranes are the preferred option in the membrane separation industry due to their cost-effectiveness, strong mechanical properties, specific part affinity, controllable pore size, flexibility, and compact installation requirements. In addition, membranes have the capability to

include nanomaterials such as CNTs and metal/metal oxide to enhance their overall functionality. Enhancing both the retention capacity and permeability of polymeric membranes simultaneously is a difficulty. One way to enhance the characteristics of the membrane is by incorporating additives into the polymer solution, which leads to significant variations in the membrane structure [71]. Applying positive charges to UF membranes might enhance their efficiency in purifying wastewaters that include cationic colors and heavy metal ions often found in the printing and textile sectors.

Putting positive charges onto UF membranes can improve their performance in treating wastewaters containing cationic dyes and heavy metal ions from the textile and printing industries.

Polymeric membranes are commonly utilized in different separation processes, involving water treatment, gas separation, and bio-separation [72].

3.5 Requirements for the polymeric membrane for industrial wastewater treatment

Chemical resistance: To survive exposure to a variety of industrial wastewater elements, such as acids, bases, organic solvents, and other pollutants, polymeric membranes should have exceptional chemical resistance. This guards against fouling and deterioration while ensuring the membrane's long-term integrity [73].

Mechanical strength: High operating pressures are frequently used in industrial wastewater treatment procedures, which put a lot of mechanical stress on the membranes. As a result, polymeric membranes need to be strong enough and long-lasting enough to bear these pressures without breaking or deforming [74].

Thermal stability: In certain industrial operations, wastewater streams may have temperatures that range from room temperature to very high. For polymeric membranes to retain their separation effectiveness and structural integrity throughout the whole temperature range encountered during wastewater treatment, they must have strong thermal stability [75].

Hydrophilicity or hydrophobicity: Polymeric membrane surface properties have a significant role in regulating fouling potential. By encouraging water permeability and decreasing the adherence of organic and inorganic foulants, hydrophilic membranes have the tendency to resist fouling. Hydrophobic membranes, on the other hand, might be chosen in some situations when fouling by organic or greasy materials is an issue [76].

MWCO and pore size: The size range of the target pollutants to be eliminated determines the pore size of membrane and MWCO selection. For instance, UF membranes are usually used to remove suspended particles, colloids, and macromolecules; on the other hand, NF and RO membranes were utilized in removing dissolved salts and have lower pore sizes [77].

Selectivity and rejection efficiency: While permitting the flow of water or desired components, membranes employed in wastewater treatment should have excellent selectivity and rejection efficiency for the target contaminants. By doing this, contaminants are effectively removed and treated water that satisfies the necessary quality criteria is produced. The membranes rejection turned into calculated the use of the following equation:

where, C_p and C_f represent the amount of the permeate and

feed (mg/L), respectively [78].

$$\text{Rejection \%} = \frac{C_f - c_p}{C_f} \times 100\%$$

Anti-fouling properties: One of the most frequent problems in wastewater treatment is membrane fouling. Smooth surfaces, charge modification, and hydrophilic coatings are examples of anti-fouling polymeric membranes that can assist reduce fouling by lowering foulant adherence and making it easier to remove foulants during cleaning procedures [79].

Compatibility with cleaning and sterilization procedures: Cleaning and maintenance are frequently necessary for the membranes used in industrial wastewater treatment systems. The chosen polymeric materials ought to function well and not significantly deteriorate when exposed to standard cleaning agents and sterilizing techniques [80].

Should have excessive pure water flux (J). Pure water flux has been identified by the following formula:

$$J = \frac{W}{t \times A}$$

where, J is denoted as kg/h m², the weight of permeate flux (W) is represented as kg, the experiment time (t) is measured in hours, and the membrane's active region (A) is denoted as m² [81].

3.6 The essential required tests for polymeric membranes for industrial wastewater treatment

Polymeric membranes are frequently employed to isolate impurities from water during industrial wastewater treatment. To assess the effectiveness and suitability of polymeric membranes for this application, several crucial tests are carried out, such as:

Filtration efficiency: This test assesses the membrane's capacity to hold on to colloidal particles, suspended solids, and other impurities. It entails putting test particles with a known concentration across the membrane and calculating the effectiveness of particle removal [82].

Permeability and flux are two different concepts: Permeability describes how easily water molecules can move through a membrane, whereas flux describes how quickly water can permeate through a barrier. The evaluation of the membrane's fouling propensity and water treatment capability depends on these factors [83].

Potential for fouling: When impurities build up on the membrane's surface, the membrane's ability to function is diminished. Several tests, including fouling index measures, can be used to assess the membrane's long-term effectiveness and identify its fouling susceptibility [84].

Chemical compatibility: This test evaluates how resistant the membrane is to swelling or chemical breakdown when exposed to the chemical makeup of wastewater. It assists in ascertaining whether a given industrial effluent stream is compatible with the membrane [85].

Mechanical sturdiness and robustness: The membrane must be robust enough to endure the operational circumstances, including cleaning procedures and pressure variations. The membrane's overall durability, tear resistance, and tensile strength are assessed through mechanical testing [86].

Chemical cleaning efficiency: To keep membrane performance intact and eliminate fouling, periodic cleaning is required. Chemical cleaning experiments assess how well different cleaning solutions remove fouling and restore permeability to the membrane [87].

Long-term stability and aging: Membranes should have strong resistance to deterioration and long-term stability. Accelerated aging tests allow evaluation of the membrane's stability and durability under operating settings by simulating the membrane's performance over a lengthy period [88].

Testing for water quality: One crucial factor is the quality of the treated water. To guarantee compliance with regulatory norms, it is crucial to test the permeate for the removing of contaminants, involving heavy metals, organic compounds, or pathogens [89].

3.7 Evaluating of filtration efficiency

When evaluating the filtration efficiency of a system, there are several key indicators to consider in addition to care, respect, and truth. Here are some factors that can be used to assess the performance of a filtration system.

Particle removal efficiency: This is a measure of the system's ability to remove particles of a certain size from the air or fluid being filtered. It is typically expressed as a percentage, with higher percentages indicating better filtration efficiency [90].

Filtration speed: The speed at which a filtration system can process air or fluid is an important consideration, particularly in applications where high flow rates are required [91].

Filter life: The time length that a filter could effectively remove particles before it needs to be replaced is an important factor in evaluating filtration efficiency [92]. Longer filter life can help reduce maintenance costs and downtime.

Energy efficiency: The amount of energy required to operate a filtration system can have a significant impact on its overall efficiency and cost-effectiveness. Energy-efficient filters can help reduce operating costs and minimize environmental impact [93].

Filtration capacity: The amount of air or fluid that a filter can process before it becomes saturated with particles is another important factor to consider. A filter with a high filtration capacity can help reduce the frequency of filter changes and maintenance [94].

Particle size distribution: The size distribution of particles in the air or fluid being filtered can affect filtration efficiency. Filters that are designed to remove particles of a specific size range may be more effective than those that are designed to remove particles of all sizes [95].

Pressure drops: The drop of pressure across a filter could affect filtration efficiency and energy consumption. A filter with a low-pressure drop can help reduce energy costs and improve filtration performance [96].

4. CONCLUSIONS

For greater than 5 a long time, polymeric membranes have been used to treat the economic wastewater of numerous sectors, such as chemical industries, refineries, meals and beverage, textile enterprise, pharmaceutical industry and so on.

The predominant problem going through membranes is the fouling, wherein the accumulated impurities above the

membrane surface causes reduction of permeate flux, which ends up in increasing the working pressure.

Compared with the opposite membrane types, polymeric membranes possess many benefits. These membranes have excessive elimination charges of a huge spectrum of impurities, which includes natural compounds, heavy metals, vitamins and suspended solids. Also, they operate at lower pressures compared to standard techniques, resulting in saving the energy consumption.

There are many techniques adopted to enhance the overall membranes performance, along with the usage of decided on polymeric materials (have high permeability, better selectivity, and enhanced fouling resistance), contain nano fillers into the polymer matrix to beautify membrane performance or editing the floor chemistry of membranes to lessen fouling and improve the hydrophilicity.

For the purification of commercial wastewater, UF approach gives a few wonderful blessings over the other filtration strategies, which include excessive elimination efficiency (with traditional rejection charge extra than ninety%), lower fouling tendency (Fouling may be eliminated by using cleaning and backflushing) and high flux, permeate pleasant and productiveness. As a result, these membranes yield water with low ranges of impurities, rendering it suitable for unique water reuse initiatives.

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