Nanomaterials and Nanotechnologies for Marine and Membrane Antifouling Applications

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Abstract: The major responsibility of the marine industry includes the global transportation of goods, materials, and people. To cater the longstanding challenges like degradation of materials and biofouling, it has embraced nanotechnology solutions. Nano-technology offered numerous products such as nano-ZnO, nano alumina, and nano silica, etc. to deal with corrosion in a cost-effective manner. Similarly, to address the biofouling in the aquatic environment, hybrid nanocomposites of organic-inorganic materials, photocatalytic nanomaterials, metal and metal oxide nanomaterials (nanoparticles, nanowires, nanorods), etc. are employed as viable agents to create non-toxic or low-toxic antifouling coatings. On the other hand, membrane separation technology plays a significant role in various industries including water treatment plants, food, medicine, pharmacy, biotechnology, etc. in addition to the domestic arena for the purification of drinking water. Such a wonderful technology is being totally disturbed by a troublesome problem and a predominant barrier called membrane fouling, which drastically limits the commercialization of the membranes and the whole membrane industrial technology as well. Hence, this review exclusively throws light on the role of nanomaterials and nanotechnologies developed for the prevention of fouling that occurs on submerged structures and membranes as well and to give possible solutions with increased resilience against challenges to come.

Keywords: Nanomaterials, nanocomposites, marine, membrane, anti-fouling, anticorrosion.

1. INTRODUCTION

Nanotechnology has brought in a myriad of changes in the twenty-first century, utilizing the novel characteristics, phenomena, and functions that matter exhibits when examined at the nanoscale dimensions. The physico-chemical and biological characteristics of materials differ fundamentally and significantly from those of individual atoms and molecules or bulk matter at this level [1]. The surface free-energy and plasma resonance effect are a major impact in nanotechnology. Consequently, nanoscale materials have a high surface area/volume ratio, resulting in a larger interfacial area between the macromolecular binder and the nanoparticle [2]. The utilization of nano-sized and sub-micron-sized materials is the method of choice now a days for enhancement in barrier properties for protective coatings and painting that were the traditional methods to slow down the degradation and biofouling.

1.1. Biofouling

Biofouling has been the subject of several investigations. Especially, the post-monsoon period has the highest amount of biofouling build-up, followed by the pre-monsoon period, while the monsoon season has the least amount of fouling activity. The necessity to preserve ship hulls against marine fouling dates back to man's use of ships as a mode of transportation, as evidenced by the following list of antifouling chemicals used before the mid-nineteenth century [3]. Mussels, barnacles, and algae may significantly increase ship weight up to several tonnes in a short period of time by settling on ship hulls, resulting in increased resistance during transport and higher fuel consumption - even on long hauls [4]. Around the seventh century BC, the earliest attempts to employ anti-biofouling methods were made. To avoid fouling, arsenic and sulphur-and-oil coatings were employed about the fifth century BC, and the Romans and Greeks concealed lead sheathing with copper nails in the third century AD. Although lead casings were the most popular anti-fouling method, their usage exacerbated the corrosion of steel components, leading to the prohibition of lead sheathings [5]. All the above findings revealed that the substrata surface energy, followed by the surface roughness R, had a significant impact on the most common fouling organisms viz., barnacles, mussels, oysters, and tubicolous polychaetas adhesion found in the coastal environment, with a total of 8 species belonging to various groups. Seasonal variations in the proximate composition of ascidians from Palk Bay were also reported by Ananthan [6].

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The idea behind the earliest antifouling paints, which appeared in the mid-nineteenth century, was to disperse a strong toxicant in a polymeric binder. Other paints with binders based on other bituminous materials and natural resins, which were diluted with turpentine spirit, benzene, or naphtha, followed. However, because the pigments in these paints, which were applied directly to the ship hull, caused corrosion on the first steel hulls, a primer capable of preserving the hull was quickly developed. Later in 19th and 20th century, copper and mercury compounds were embedded in rosin to combat corrosion and fouling in addition to enhance the mechanical characteristics. But the performances were relatively inefficient and had led to apprehensions on health and safety [7].

In 1990s, the majority of anti-fouling methods are based on the application of protective coatings based on Tributyltin (TBT), which are well-known for their effectiveness and flexibility. But it was realized later that a long-term release of toxic TBT caused severe destruction to aquatic life and also the maritime industry across the world lost billions of amounts due to biofouling of marine installations. But most of coatings are based on toxic inorganic and organic biocides that leach out of the coating and kill biofouling organisms besides killing of non-targeted marine species that get accumulated in the marine waters. Hence, these were banned by the International Maritime Organization (IMO). On the other hand, the non-toxic antifouling coating techniques are very costly and are not as effective as traditional biocides. Hence, there is an utmost need to explore novel solutions through nanotechnology.

2. ANTI-FOULING COATINGS FOR BIOFOULING PREVENTION

2.1. Enzymatic AF Coatings

Enzymatic AF coatings are those in which enzymes play an important role in biofouling prevention. Over the last 20 years, the application of enzymes in AF coatings has been widely researched [8]. On the basis of enzymatic methods, the AF impact is divided into two types: direct and indirect AF. The application of biocidal or adhesive degrading enzymes is referred to as direct enzymatic AF, whereas indirect enzymatic AF refers to the enzymatic production of biocides from substrates found in saltwater or coating components [9].

Enzymatic activity for AF coating applications is classified into two groups in the literature. The presence of hydrolytic enzymes may reduce the adhesion strength of settled algal spores to the substrate surface, according to this study. Enzymatic adhesive breakdown in AF coatings has also been the subject of several patent applications [10]. However, the efficient application of direct AF coating based on a single or a few enzymes and a proper methodology for indirect AF coating have not yet been explored.

2.2. Electrolyte Deposited Coatings

In this technique, modification of material surface is done by physical alteration through electrodeposition or by creating micropatterns. A number of studies have taken use of the electrolytic coating's potential for biofouling prevention. Metallic surfaces are extremely durable, and some are biofouling resistant. The coatings were non-wetting despite being impinged with zirconia particles stabilized with yttria and occasionally subjected to UV radiation and very high/low temperatures, as the TO coatings, which are naturally super hydrophilic, were changed to super hydrophobic [11]. Anti- biofouling and anti-corrosive nickel matrix–silver nanoparticles were created and characterized for use in the aquatic environment.

On copper, two Ni–Ag composite coatings with compositions of Ni–0.25 at. percent Ag and Ni–0. 75 at. percent Ag was electrodeposited. The impacts of silver nanoparticles on biofouling, Ni passivation, and electrochemical corrosion of these composite coatings have been highlighted. Silver nanoparticles contained in a nickel-induced galvanic passivation matrix were discovered during anodic polarization in around 3.5 percent sodium chloride, enhancing the potential of using composite coatings for passivation. When exposed to sulfate- reducing bacteria, these composite coatings demonstrated excellent biofouling resistance by preventing the production of biofilms.

The amount of silver nanoparticles included in the composite coatings lowered the amount of bio-film. The corrosion resistance of the coatings was reduced due to biofilm. When incorporated into an appropriate metal matrix, anti-microbial nanoparticles can protect substrates against biofouling [12]. In the cathodic polarisation AF application, a conductive PPy/resin covering with commendable electrochemical anti-fouling properties was created. The anti-fouling impact was enhanced under substantially lower cathodic voltage, resulting in increased anti-fouling efficacy. This revealed that the Ag/TNT with the least amount of silver and adorned with Ag nanoparticles had the least amount of biofilm development caused by the bacteria Halomonas Pacifica [13].

2.3. Marine AF Coatings

Some marine biological compounds with anti-pollution properties have been found in recent years. The structure-activity link of suber-gorgic acid (SA) was investigated in depth, and it was discovered that both the ketone carbonyl and the double bond are required components for antifouling action [14]. On this premise, established AF benzyl esters and methylene chains were added to SA to create novel SA derivatives. The antifouling test findings reveal that all benzyl esters of SA have an antifouling activity that is similar to or stronger than SA with unsubstituted benzyl rings. The findings also demonstrate that the AF impact of SA derivatives with methylene chains is inferior to that of SA and that the effect of methylene chain length on the antifouling effect of SA derivatives is dependent on the functional group at the methylene chain's opposite end. Further research on the effects of this sort of AF chemical on non-target marine species is required [15]. However, the AF active functional groups demonstrated in the studies have some utility for antifouling chemical research. The antifouling active functional groups, on the other hand, have been shown in tests to have particular characteristics to defend themselves against diseases or parasites, marine creatures have developed a variety of biological methods to interact with microbes in nature. Interfering with bacterial QS with marine biological secretions can successfully prevent the development of bacterial biofilms, making it harder for other species to adhere [16].

Tintillier *et al.*, [17] discovered four novel tetrabromotyrosine compounds from the marine sponge Pseudoceratina sp. 2081 that have AF and quorum sensing inhibition characteristics. They investigated the antifouling properties of six different extracts. They have a focused mechanism of action on bacteria and microalgae, affecting sole adhesion rather than growth. AF properties have been discovered in indole derivatives present in bryozoans and ascidians. However, the impact of antifouling coatings with added indole derivatives is weak due to the uncontrolled release rate of indole derivatives in antifouling coatings. The coating was studied in the maritime environment using dynamic simulation tests and static immersion measurements. Furthermore, indole derivatives hinder the development of marine algae by disrupting the calcium ion balance in algal cells and lowering the amount of cellular Ca^{2+}. The essence of a biological enzyme is protein, which is simple to degrade, does not pollute the environment, and does not harm marine life, making a biological enzyme with antifouling properties an excellent anti-foulant [18].

Bacillus velezensis, a marine proteolytic bacterial strain, was isolated from sea muck and shown to generate a protease that inhibited barnacles, diatoms, and mussels. Currently, these marine biological anti-foulants are difficult to acquire in significant quantities from the ocean and are difficult to chemically synthesize at an affordable cost, making them challenging to economically mass-produce to some extent. However, developing a more ideal anti-foulant requires examining its antifouling process using chemical techniques and investigating the activities of different groups [19].

2.4. Low Surface Energy Anti-Fouling Coatings

Foul-release coatings with low surface energy and no toxic biocides may be used to control fouling [20]. The need for fuel-efficient and low-emission coatings has driven the expansion of the marine coatings industry in recent years. Foul-release technology, which also saves a lot of fuel, is especially beneficial for huge cargo ships that use a lot of it. Many businesses are devoting time and resources to producing environmentally friendly goods such as low-friction coatings, metal-free antifouling coatings, and so on.

They can either be silicone or fluoride based. Silicone does not prevent marine biofouling, but it does minimize the amount of fouler that adheres to the material. Although silicone has low surface energy, its adherence to the substrate material is poor [21]. Fluorocarbon resin, on the other hand, has a high resistance to water and oil, as well as weather, stain, chemical, and solvent, among other things. As a result, it appears to be an ideal material for anti-biofouling coatings.

Fluoride has great chemical resistance and endurance, but it is prohibitively costly. Silicone- based anti-fouling paint and fluoride-based anti-fouling paint are two forms of AF paint. In 1972, an American researcher successfully created silicone-based anti-fouling paint and received a patent. Silicone has a low surface energy, yet its adherence is poor [22]. As a result, in the future, it will be required to increase the silicone's enhanced adherence. Fluorocarbon resin is a sort of good material for super weather-resistant, anticorrosive, and architectural paint because it has high weather resistance, water and oil resistance, stain resistance, chemical resistance, and solvent resistance, among other things [23].

2.5. Studies on Green AF

The majority of AF research in India has focused on green AF technologies to combat biofouling [24]. Water soluble and organic extracts from two Gorgonian coral species have antifouling properties. The bioactive potential of sea grasses such as Cymodocea serrulata and Syringodiumi soetifolium, which grow abundantly along the Thoothukudi coast, was investigated, and their antifouling activities against marine biofilm producing bacteria were examined [25]. Streptomyces filamentous, a marine actinomycetes, was shown to be a promising source for the creation of environmentally benign antifouling chemicals. The researchers were successful in discovering marine actinomycetes from India's southeast coast, which have yet to be utilized for AF chemicals [26].

2.6. Other Alternatives

Following the invention of TBT-based paints, the research of such systems was partly abandoned, but it was restarted after the first restrictions against them. Initially, the success of these systems was dependent on the production of harmful compounds on the ship's surface, mostly chlorine [27]. Due to a considerable voltage drop across the surface, steel corrosion issues, cathodic chalk development, and early coating aging, some of these systems, particularly those requiring high voltages, do not have great efficiencies. Furthermore, the production of organo-chloro by-products causes local contamination, and they are frequently incapable of attaining a uniform dispersion of pollutants [28].

The electrochemical oxidation of the intracellular material is caused by direct electron transfer between an electrode and the microbial cells in these systems. To avoid using high potentials, Okochi and Matsunaga suggested using ferrocene derivatives as redox mediators to prevent chlorine production. Matsunaga *et al*. utilized conductive paint electrodes to deliver 1.2V saturated calomel electrode potentials, which killed the bacteria entirely, and a negative potential to remove them from the electrode [29]. Although the reduction does not appear to be sufficient for ship hulls, the low prices and absence of harmful effects may make it helpful for anti-fouling in medical applications. Wang *et al*. [30] had good findings in their investigation of the influence of microsecond electric fields producing an electric breakdown of the outer cell membranes of biofouling organisms despite utilizing hazardous chemicals. Regrettably, these systems are limited to single-use applications. The majority of these concepts have only been tested on a small number of marine species, mostly marine bacteria, thus their efficacy in real-world fouling conditions is yet unknown. When it comes to the usage of piezoelectric coatings, Gerliczy and Betz claim that "most marine species" do not settle on these vibrating surfaces [31]. Ultraviolet radiation is frequently employed in seawater pipe systems for sanitation, but its fast attenuation and expensive costs preclude it from being utilized on large exterior surfaces. Swain also mentions several attempts to utilize radioactive coatings [27].

Nippon Paint Marine (NPM), a coating company located in Japan, has introduced FASTAR, a self-polishing antifouling paint with a unique nano-domain resin structure designed to reduce the impact of seawater temperatures, vessel speeds, and other external variables on coating performance. When the polishing rate is low, AF performance becomes less dependable. According to NPM, this is not the case with FASTAR. When compared to conventional hull coatings, it significantly reduces the time and film thickness required for application. “FASTAR is a sophisticated self-polishing AF paint,” said Makoto Nakagawa, Marketing General Manager of Nippon Paint Marine. Ship owners expect antifouling to work effectively and predictably. FASTAR does this by lowering total capital and operating costs.

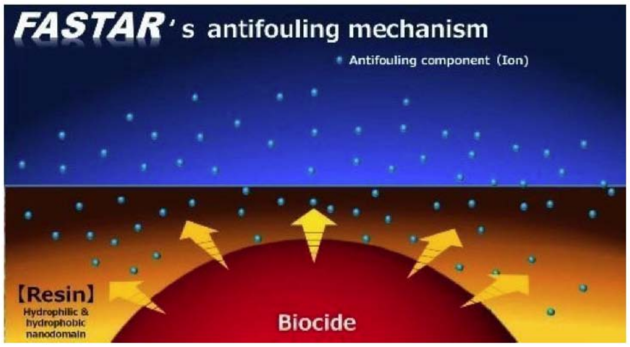

Figure 1: Fastar’s AF mechanism [32].

FASTAR comes in four different versions: FASTAR I & II, and FASTAR XI & XII, the latter two of which include Nippon Paint's hydro-gel technology and are found to be effective. The optional addition of the hydro-gel, according to Nippon Paint Marine, would provide FASTAR XI & XII the same 8% decrease in fuel consumption and CO_2 as the company's proven A-LF-Sea series, which has been installed on over 3,300 vessels since its market launch [32].

Understanding how AF systems function, starting at the nanoscale and scaling up to future commercial implementations, will be possible thanks to research on nanoscale interfacial characteristics of various surfaces and how organisms adhere [24]. The goal of AMBIO of the European Union was to investigate and create various nano-structured surfaces to prevent marine fouling organisms from adhering to them. Many bulk characteristics important to AF, "non-stick" surfaces, including surface energy, charge, conductivity, porosity, roughness, wettability, friction, physical and chemical reactivity, are controlled by nano-structuring of a coating. The interfacial area imparts novel structural arrangements to the molecular scale, giving new characteristics that are intermediate between those of the organic and inorganic components, and is responsible for effective stress transmission between composite components. Nanomaterials have a greater elastic modulus and mechanical strength than traditional composite materials due to surface or interface energy effects [33]. Biocidal coatings typically kill bacteria and fungi by gradually releasing biocide from the dried film. Unfortunately, this mechanism is also responsible for the biocide's eventual deactivation; once the biocide has leached or washed out of the coating, all protection against microorganisms has been lost. Consequently, biocidal action typically lasts approximately 18 months, and even shorter in hot, humid conditions, after which a fresh coating must be placed to restore antifungal protection. As a result, a novel biocidal coating system with extended biocidal activity must be developed by integrating biocide additives on a nano-particulate medium utilizing modern nanoparticle technology. Some of the examples of biocides are Michelia champaca leaf, neem oil and nontoxic chemical biocide as they possess certain essential qualities such as biodegradability, low toxicity, simple accessibility, and cost-effectiveness [3]. Nano- containers with the potential to release encapsulated active biocides in a controlled manner can be used to create a new class of self-repairing multifunctional coatings, which not only have functionality but also have quick feedback activity in reaction to changes in the local environment. The active biocides are only released when they are triggered, which prevents the active component from leaking out of the coating and improves coating longevity [34].

Copper oxide (CuO) is used in ship paint in quantities ranging from 26 to 76 percent by weight. In this case, 5 wt. percent CuO nano-containers are adequate to provide even better outcomes, resulting in a substantial decrease of copper in the paints and reduced copper pollution. Bromosphaerol's usage in paints is a significant success since it is a natural substance that is compatible with the sea environment; thus, authorization to use it in paints is required. Another significant advancement in current technology is the enhanced coating's capacity to self-heal owing to the integration of nano-containers. The inclusion of nano- containers increases the contact angle by modifying the surface [35].

3.3. Membrane Fouling

Membrane fouling is the process of adsorption of colloidal particles, or deposition of macromolecules such as proteins and various salts on the surface of the membrane or the pore walls or inside the pore structure, which severely affects membrane life and its filtration parameters such as permeation flux, separation efficiency and change in selectivity [36]. It is

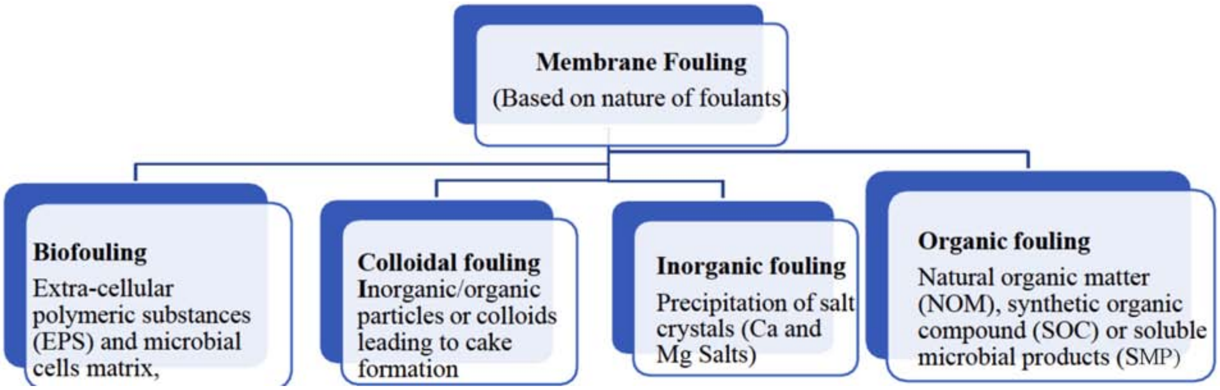

Figure 2: Types of membrane fouling based on the nature of foulants.

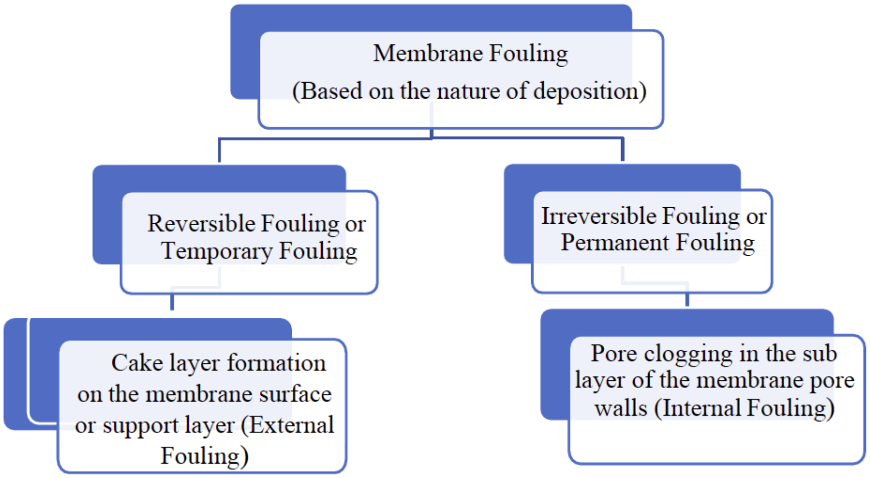

Figure 3: Types of membrane fouling based on the nature of deposition.

classified based on the nature of foulants present in the water feed. The following flow chart describes the various type of fouling that occurs.

Based on the nature of deposition, it is further classified into reversible or temporary fouling and irreversible or permanent fouling [37].

In comparison, internal fouling is less reversible than external fouling. The foulants deposited within the support layer can be efficiently removed by the developed backwash method. However, the same is not possible with respect to the internal fouling of foulants in the sub layer of membrane pore walls. Hence these prevention methods such as cleaning or back- washing can only remove reversible fouling. The irreversible fouling or internal fouling prevention and control are still a complicated process and extensive research is still going on in this field. Researchers believe that it is possible only by modification in membrane preparation techniques [38]. According to Elimelech *et al.*, [39] the membrane surface is the critical functional layer, which determines the fouling ability of the membranes. Thus, we understood that membrane surface modification plays a more significant and more directive role in the prevention of fouling that occurs both on the surface layer and the inner layer of the membranes [40]. To address this problem, the modification strategies are also facilitated in two ways as given below.

The external modification or surface modification implies coating hydrophilic components onto the membrane surface either physically or chemically. Internal modification is done by either blending the casting solution with other polymers or additives in different concentrations and ratios or by reactive functional modification (amination, sulfonation, chloro-sulfonation, etc.). Surface modification modifies the membrane surface into hydrophilic, photocatalytic, cationic, anionic and also amphiphilic in some cases. Upon discussing the advantages of both the methods, internal modification is easier to obtain enhanced antifouling performance of the membrane; however, the highly preferred one is surface modification since it ensures higher efficiency and larger selectivity besides being very expensive due to complicated experimental operations and additional chemicals involvement during the process.

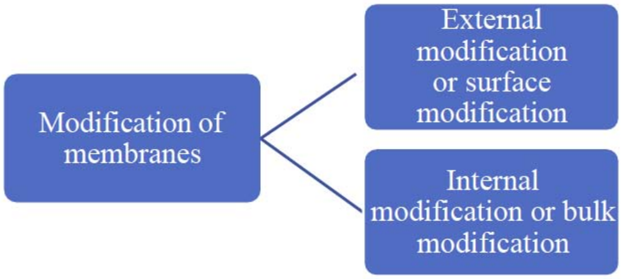

Figure 4: Types of membrane modification.

Hence membrane scientists and researchers came out with numerous modification strategies to control membrane fouling and to impart improved antifouling properties. It includes the incorporation of various nanomaterials into well-known conventional polymers like PVDF, PES, PSf, and PVC with the nanoparticles (NPs) either in the membrane matrix or surface, the utilization of new monomers, the development of novel fabrication methodologies and also the membrane surface modification through physico-chemical methods [41]. The major advantages of this technology are high separation efficiency, operation flexibility, easy access, less energy requirement and affordable cost.

Since this chapter exclusively deals with the role of nanomaterials and their technological applications for membrane fouling prevention, let us first understand nanocomposite membranes and their AF properties. Nanocomposite membranes are of two types:

1. Mixed matrix nanocomposite membranes and
2. Thin-film nanocomposite membranes.

Several researchers worked on both mixed-matrix nanocomposite membranes and thin-film nanocomposite membranes separately. The aim of such studies is to impart the anti-fouling property by improving the hydrophilicity so that the foulants are repelled and washed away from the membrane surface during the filtration. In the first type, nanomaterials are uniformly dispersed into polymer dope solution before membrane casting, which is otherwise called as nanoparticles-blend membranes or nanoparticles-entrapped membranes. In the second type, nanoparticles are allowed to self-assemble onto the surface of the membranes and also in their inner pores by dip-coating technique or they are made to deposit by applying pressure [36].

3.1. Antifouling (AF) of Mixed Matrix Nanocomposite Membranes

Taghaddosi *et al.* [42] fabricated nano clays embedded Poly propylene (PP) membranes containing 0, 0.5, 1, 1.5 and 2 wt.% nanoparticles by using the thermally induced phase separation (TIPS) method in the presence of PP-g-MA (PP-grafted maleic anhydride) as a compatibilizer. They examined the antifouling properties of the fabricated nano clay embedded PP membranes by filtration of BSA protein solution under trans-membrane pressure of 1.5 bar as a common solution model. Modified membranes with 1.5 wt. % nano clays revealed efficient flux recovery and rejection compared to the other concentrations of nano clays. They also analyzed the fouling mechanisms by Hermia and combined fouling models which displayed the improvement in AF performance of the membranes in the presence of nano clay particles.

A series of symmetric flat sheet halloysite nanotube-ferri-hydrates (HNT-HFO) (0.5, 1.0, 1.5 and 2.0 wt.%) -embedded PES membranes were fabricated by using the immersion precipitation phase inversion technique with methyl-2-pyrrolidone (NMP) as the solvent [43]. The flux recovery ratio of the membranes increased with the increased loading of nanocomposite, which clearly demonstrates the improved AF ability of such nanocomposite membranes. Interestingly, the modified membranes showed a high oil rejection percentage throughout the filtration process, with a 9% difference in comparison to the pristine PES.

Lawrence Arockiasamy *et al.* [44] fabricated hollow fiber membranes by phase inversion technique using PPSu (polyphenylsulfone) and SPPSu (Sulfonated polyphenylsulfone) with nanoparticle titanium oxide (TiO_2).

They evaluated the AF performance of the said membranes using BSA as a model protein at pH 7. It was observed that neat PPSu was highly prone to

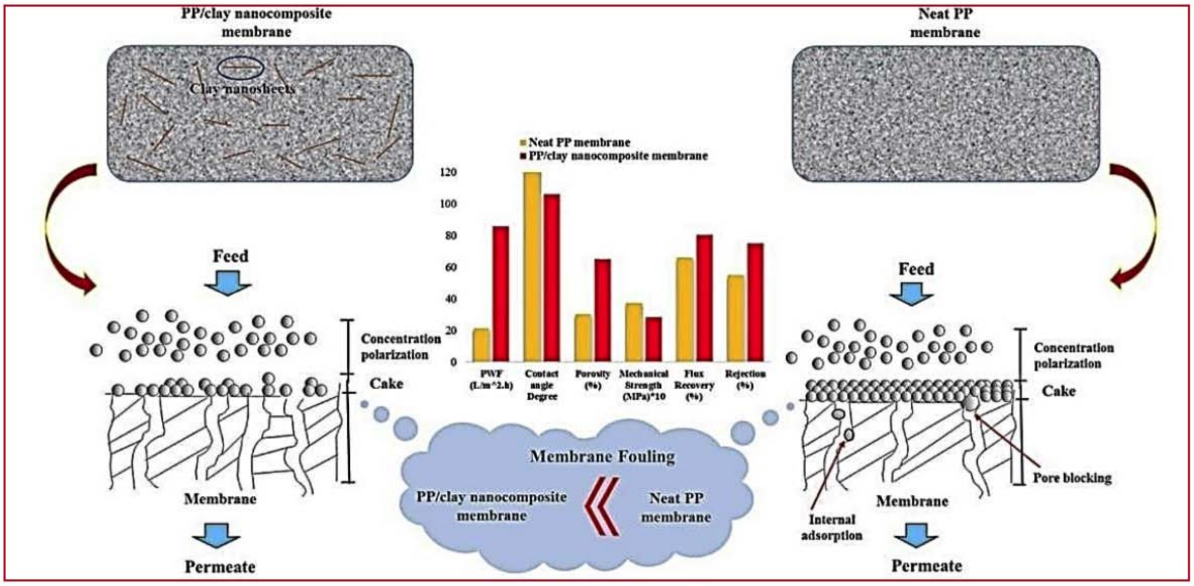

Figure 5: AF performance of Nano clay particles embedded PP membranes.

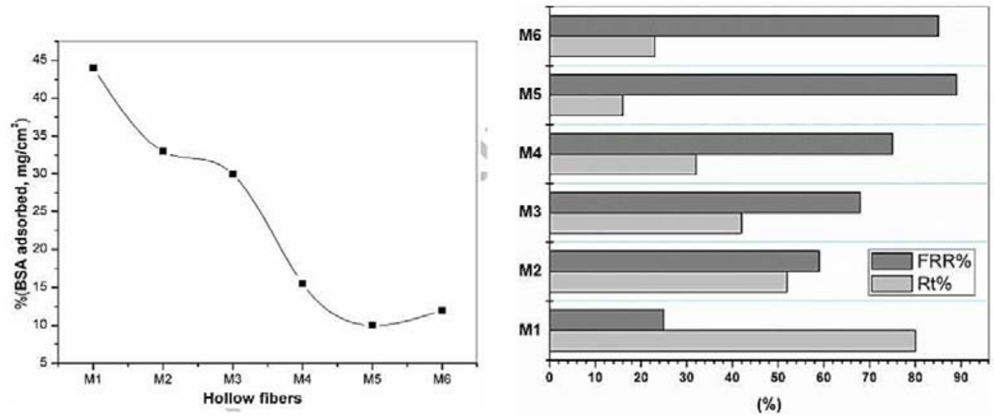

Figure 6: FRR and Rt.% of PPSu and PPSu hollow fiber membranes.

fouling due to its hydrophobic nature and absence of charges in the polymer backbone, whereas SPPSu membrane showed reduced protein adsorption. This substantiates that the incorporation of the negatively charged sulfonic group with increased hydrophilicity in the polymeric matrix repels the negatively charged protein of the membranes. Observations were also made with the addition of water soluble hydrophilic additive PEG 600 and loading of nanoparticle TiO_2 in the PPSu and SPPSu hollow fiber membranes. These additions strongly form hydrated layer and encumbers the protein adsorption of the SPPSu. The Flux Recovery Ratio (FRR) value for TiO_2 embedded SPPSu andit blends were found to be high at 85% due to their hydrophilic ability.

Farahani *et al.* [45] picked four different nano particulates—clay, MWCNTs-COOH, SiO_2 and TiO_2 to improve the morphology and performance of PVDF ultrafiltration membranes with PVP as a pore former and NMP as a solvent by means of the non-solvent induced phase separation method. Five different loadings of each nano-particulate were embedded in the dope solution. As the nano particulates concentration was increasing in the dope, the membrane porosity and mean pore size was also increasing, while the hydrophilicity of the membranes increased and then decreased. The increase in porosity and hydrophilicity both resulted in a remarkable improvement in water flux as shown by the clay/PVDF MMM (0.5- Clay) with 187% higher PWF as compared with pristine PVDF membrane. The Flux recovery ratio was significantly enhanced with the addition of all the nano particulates, and thus, the MMMs showed superior AF properties than their pristine membrane counter parts.

Out of the four different nanoparticles used in this study, 0.2 wt.% MWCNTs-COOH nano particulate was suggested as the best one for the modification of PVDF

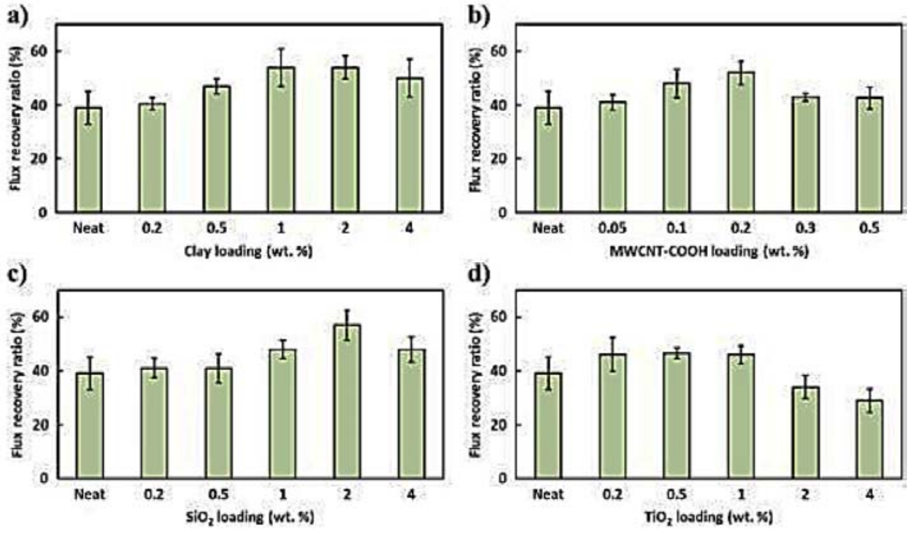

Figure 7: Flux recovery ratio (FRR, %) of the pristine and (**a**) Clay/PVDF, (**b**) MWCNTs- COOH/PVDF, (**c**) SiO2/PVDF, and (**d**) TiO_2/PVDF MMMs.

membrane as it showed the ultimate performance with a 135% PWF improvement with 100% BSA rejection and 33% FRR enhancement.

3.2. AF by Thin Film Nanocomposite Membranes

Lee and Huang *et al.* [46] synthesized thin-film nanocomposite (TFN) polyamide membranes using trimesoyl chloride as solvent by interfacial polymerization by embedding the silica particles of various sizes 50, 200, and 500 nm. The AF behavior of TFC (pristine thin film composite), TFN50, TFN200, and TFN500 in a total of six cycles was observed. At the end of each cycle, the pure water flux for TFN membranes was found to be always superior than that of TFC. This major advantage of TFN over TFC is the improved membrane hydrophilicity. In spite of very high surface roughness of TFN membranes, the AF performance was found to be appreciable due to the dominating hydrophilic ability. While cleaning, more BSA was removed from TFN membranes than from pristine TFC membranes.

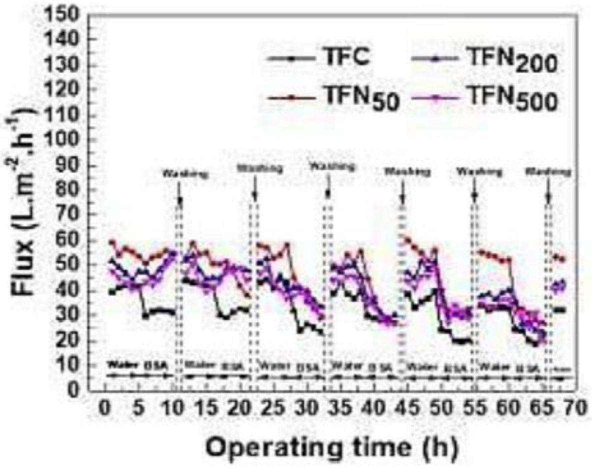

Figure 8: AF behavior of TFC, TFN_{50}, TFN_{200}, and TFN_{500}.

Babak Rajaeian *et al.* [47] developed a series of TFC membranes by coating a surface-modified porous poly (vinylidene fluoride) (PVDF) support with poly (vinyl alcohol) (PVA) doped solution containing TiO_2 nanoparticles. On the surface of TiO_2, an endothermic carboxylation reaction using chloro-acetic acid was done to improve the interfacial adhesion of nanoparticles in the PVA blend. The fouling characteristics of the said membranes demonstrate a significantly improved antifouling performance. The carboxylated TiO_2 nanocomposite membranes showed the lowest total fouling value than other membranes. It was observed that the carboxylated TiO_2 nanoparticles had a lower hydrophilic surface than the pure nanoparticles and hence the hydrophobic interaction between BSA protein and the unreacted acid groups on the surface of modified TiO_2 led to greater adsorption of BSA molecules. But it was found that the outer surface of the membranes modified with inorganic nanoparticles was far less reactive to BSA molecules than the one coated with PVA alone. This was substantiated by the reduced number of active sites penetration of the protein molecules through the polymer chains.

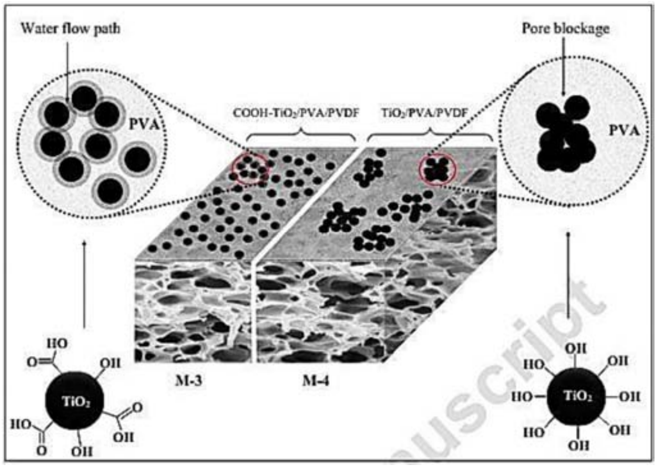

Figure 9: Schematic illustration of agglomeration of TiO_2 within the PVA, leading to lower rejection of solutes.

3.3. Metal Oxide Nanocomposite AF Membranes

In the recent development of membrane materials with unique characteristics, one of the most versatile and effective methodologies is the modification of membranes through the incorporation of metal oxide nanoparticles into polymeric membranes. More specifically TiO_2 is one such ideal and most viable nanoparticles with unique properties such as a large surface-to-volume ratio, strong reactivity and photocatalytic properties to be incorporated into polymeric the matrix as a hydrophilic filter offering a promising platform for various applications. Following is the Table that highlights the various studies of membrane modification by TiO_2 [48].

3.4. Photocatalytic Nanomaterials Imparting Membranes with AF and Self-Cleaning Properties

The surface parameters such as roughness, surface pore size, surface free energy were the dominating factors that can influence and prevent fouling initially by the PVDF/TiO_2 MMM's membranes than hydrophilicity. Hence the observed results revealed that fine X500 TiO_2 nanoparticles had the low tendency of aggregation and the lowest fouling tendency (14.69% of RFR)

Table 1: Enhancement of Antifouling Shown through Membrane Modification by TiO_{2+} [48]

S. No.	Membrane incorporated with NPs	% TiO_2	Method of synthesis	Property enhanced	Time	Temperature
1	PVDF/TiO_2	2%	Phase inversion	Show flux reduction, and antifouling	24 h	40 ˚C
2.	PES/PI–TiO_2 NPs	0.01– 0.03%	Solution casting	Antifouling	15 min	160 W UV lamp
3.	PVDF–TiO_2		Low temperature hydrothermal method	Antifouling	6 h	UV light
4.	PES–TiO_2	1–4%	Casting solution	Antifouling	3 h	25 ˚C
5.	SPES/TiO_2	7.82%	Phase inversion	Antifouling	10 min	24 ± 1 ˚C
6.	PAA/PVDF/TiO_2	0.05%	Grafting and self-assembling	Antifouling	15 min	160 W UV lamp
7.	PVDF/TiO_2, PAN/TiO_2, PSF/TiO_2	1%	Phase inversion	Antifouling	1 min	-
8.	PES/TiO_2	1.94%, 2.34%, 3.75%	Phase inversion	hydrophilicity and antifouling	10 min	Room temperature
9.	PVDF/PAA/TiO_2 –		Sol–gel	Dye degradation and antifouling	24 h	32 ˚C
10	Reverse osmosis membrane/TiO_2	0.001%, 0.003%, 0.005%	Sol–gel	Antifouling/self- cleaning	10 min	UV radiation
11	Cellulose (top layer) On a mixed polyethylene/polypropylene non-woven support)/TiO_2	0.01– 0.03%	Photo- induced phase separation	Hydrophilicity, membrane permeation and antifouling	30 min	160 W UV lamp

parallelly maintaining a high flux recovery ratio (78.24%). In addition, studies also reveal that the photocatalytic activity of TiO_2-embedded PVDF membranes in degrading the absorbed Humic Acid (HA) induced by UV irradiation consequently increased membrane- cleaning efficiency. IFRR(UV) data of X500 TiO_2-embedded PVDF membranes showed UV-cleaning capacity (15.30% of IFRR(UV)). This in turn, in the history of photolysis, created a more uniform dispersion with a lot more active sites and a very high surface charge carrier transfer rate. Thus, the research paved the way to produce metal-based membranes with a top notch combination of performance properties such as anti-fouling, de-fouling and UV-cleaning capability [49].

We understood that TiO_2 in polymer matrix not only improves the hydrophilicity but also endows the membranes with the self-cleaning ability [50]. However, we have certain limitations in TiO_2 due to its settling down at the bottom of the polymer membrane bulk due to its relatively higher density. To address this issue, Sun *et al.* [50] developed PES-TiO_2@Ni composite membranes by magnetic field assisted phase inversion method in which the magnetic MNPs were successfully embedded onto the top layer of the membrane. The said membrane exhibited 5 times higher flux and a higher rejection of BSA (95.85%) than that of the pristine PES membrane. It also possessed splendid antifouling and self-cleaning abilities.

Q. Liu *et al.* [51] fabricated four different PVDF based ultrafiltration membranes (PVDF, PVDF-TiO_2, PVDF-Activated Carbon (AC) and PVDF-TiO_2-AC) by the NIPS method and compared them with each other. It was observed that the addition of AC effectively improved the fouling resistance than TiO_2 and the irreversible fouling of the PVDF-AC membrane significantly decreased from 40% to 25%. The study also proves that AC could be a potential new type of nanomaterial for developing high performance membranes with the ability to construct the AF liquid membrane interfaces for advanced water purification. Similar performances were observed with ZnO nanoparticles too. Hong *et al*. [52] developed PVDF-ZnO composite membranes. It was established that the addition of ZnO nanoparticles caused a smaller water contact angle with very good hydrophilicity resulting in enhanced antifouling ability. The hydrophilic ZnO nanoparticles promoted larger cavities with looser sub-layer and higher membrane flux. Additionally, ZnO nanoparticles were good photochemical catalysts having the photocatalytic self-cleaning ability with 93% washing efficiency to PVDF membrane. Liang and

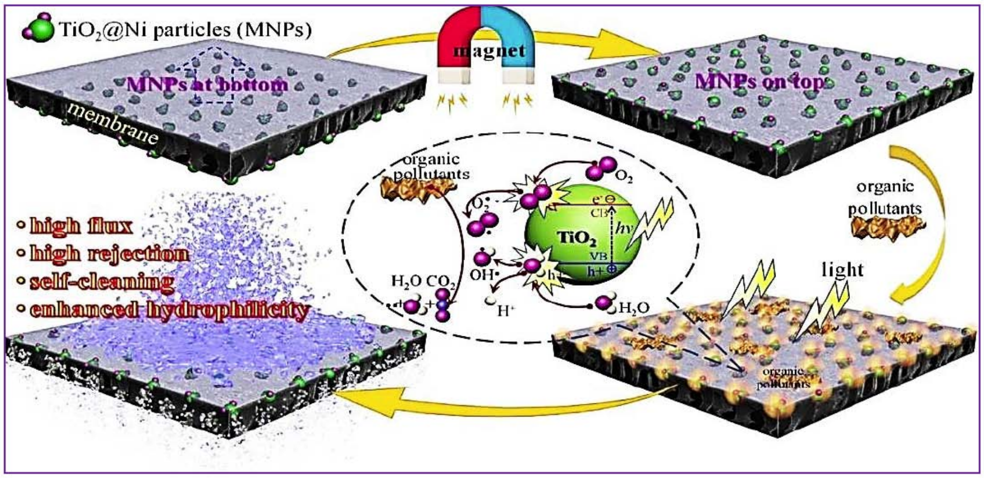

Figure 10: AF and self-cleaning abilities of TiO_2@Ni nano particles [50].

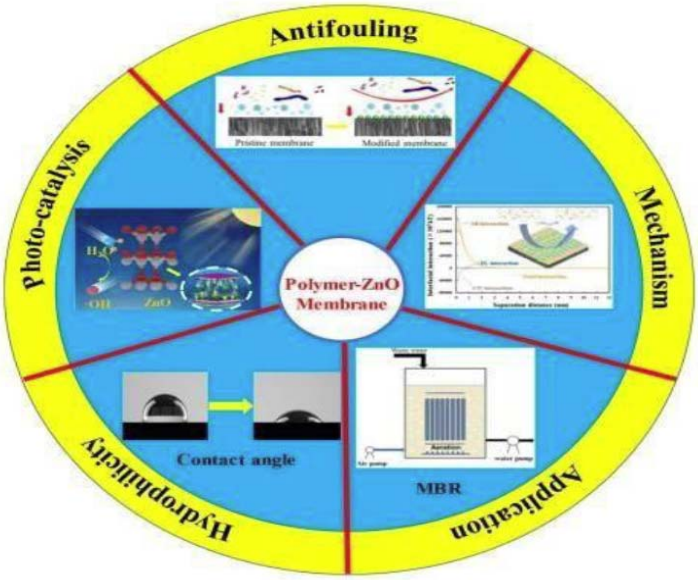

Figure 11: Polymer – ZnO nanoparticles in antifouling processes [54].

Zhang *et al.* [53] also studied and reported a similar combination of ZnO nanoparticles with PVDF to prepare nanocomposite membranes and proved that ZnO nanoparticles have an obvious advantage in anti-irreversible fouling and showed the minimum adsorption capacity compared neat PVDF membranes.

Li *et al.* [55] was the first to have synthesized 10nm ZnO nanoparticles by sol–gel method and then introduced into PES polymer membranes. They investigated the fouling behavior with three model solutions of organic foulant mediums. The PES-ZnO composite membranes possessed 83% flux recovery rate to the mixture solution of sodium alginate (SA), HA and BSA, which established that the PES-ZnO composite membranes are the ideal solution for water purification.

Mahlangu *et al*. [56] used one of the most popular materials Graphene oxide (GO) and combined it with ZnO. As the GO–ZnO nanocomposites were impregnated in the membrane, the membrane and organic matters had the same type of charges, which led to the repulsion at the interface thereby promoting solute rejection. Furthermore, the composite membrane possessed enhanced hydrophilicity, permeability, and antifouling ability to the pristine membrane. Pintilie *et al*. [57] studied the effects of addition of both ZnO and TiO_2 on the polysulfone (PS) membranes. During their investigations, they proved that ZnO nanoparticles had a very good replacement for TiO_2 nanoparticles in the modification process. They also established that out of the three nanocomposite blend membranes of PS-ZnO, PS- TiO_2 and PS - ZnO–TiO_2 hybrid, the latter exhibited more efficient and also comparable and better performance than the other two combinations.

3.5. Bio-Inspired AF Nanomaterials

Soria *et al.* [58] used polydopamine (PDA) to firmly bind a combination of nanoparticles 0.03%wt ZnO nanoparticles and (TiO_2, ZnO) (1:2 and 2:1) ratio on thin film composite (TFC) membranes by two methods 1) co-deposition (one step) and 2) binding (two-step method). The membranes obtained by the binding method (TiO_2, ZnO) showed practical anti-bio fouling properties and the same combination also enhanced the photocatalytic ability of the fabricated membranes to remove dyes from the solution. Feng *et al.* [59] developed hydroxyapatite nanotubes (HANTs) via bio-inspired PDA/PEI co-deposition designed ultrafiltration membranes by combining polysulfone with carboxyl groups. The membrane performance was greatly enhanced by the synergistic effects of both the polymer and the nano-fillers through this novel strategy of HANTs@PDA/PEI and PSF-COOH-30% combo to result in increased hydrophilicity and number of pores. Also, the presence of the carboxyl group in the matrix greatly increased the antifouling properties of membranes for BSA and HA through electrostatic repulsion between membranes and foulants, which in turn increased the compatibility of HANTs@PDA/PEI. The very high value of pure water flux and flux recovery ratio (90%) confirmed that this membrane potential can be exploited for continuous water treatment.

3.6. Carbon Based AF Materials

The incorporation of carbon-based nanomaterials in to the polymeric membrane structure is highly aimed at tuning the water permeability and antifouling resistance along with excellent solute rejection efficiency. Next to CNTs, GO is another type of carbon-based nanomaterial, which has received huge attention due to its abundant oxygen-containing functional groups that could contribute to high membrane hydrophilicity, filtration performances and adsorption capability against metal ions. The unmodified CNTs are difficult to distribute uniformly throughout the membrane matrix due to their intrinsic aggregation (hydrophobicity) by van der Waals force between them. Hence, almost all the researchers have functionalized/modified CNTs to make them chemically active, soluble as well as hydrophilic and also to utilize them for antifouling purposes. Moreover, the functional groups present in GO pave the way to develop and fabricate functionalized GO and Graphene based materials for various applications. An overview of the performances of the CNT-based composite membranes is shown in Table **2**.

CNTs and GO are shown to be highly potential materials to be used for many industrial membrane applications by enhancing their permeation flux, surface hydrophilicity and apparently reducing fouling propensity and mechanical strength of the NCMs. However, the Commercialization of carbon-based nanocomposite membranes is still in the infancy stage of research [63].

3.7. Metal Organic Frameworks (MOF) in AF

The MOF-based FO/RO/NF/UF membranes have the following remarkably enhanced membrane properties along with high tuneable porosities,

- Accessible large surface areas,
- High hydrophilicity
- Reduced membrane fouling and
- Enhance membrane selectivity
- Enhanced roughness and

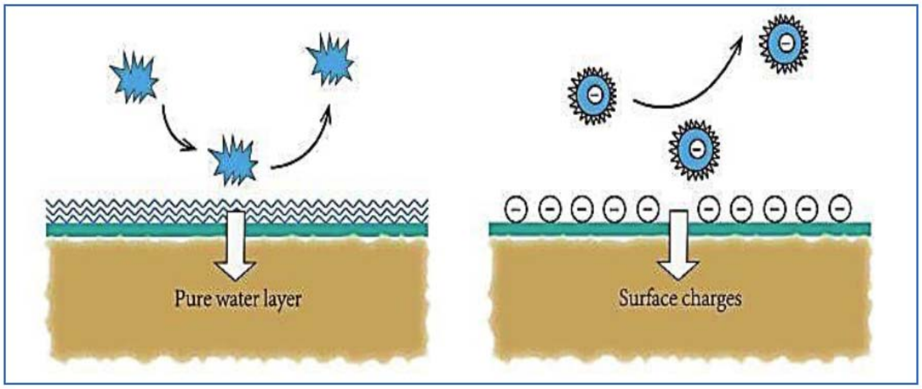

Figure 12: Schematic illustration of AF mechanisms: (**a**) hydration layer, (**b**) electrostatic repulsion [59].

Table 2: Enhancement of Antifouling Shown through Membrane Modification by CNT [60]

S. No.	Membrane type	Carbon based material	Method of synthesis	Property enhanced
1	Polysulphone (PSF)	MWCNTs	phase inversion method	AF property
2.	Poly(arylene ether sulfone) (PAES) and sulfonated copolymer (S-PAES)	MWCNTs	Non-solvent- induced phase separation method	AF property
3.	Polyacrylonitrile (PAN)	MWCNTs	Phase inversion method	Membrane surface hydrophilicity
4.	(3-chloro-2- hydroxypropyl)-(5,5-dimethylhydantoinyl-1- methyl)-dimethyl ammoniumchloride (CDDAC)	MWCNTs	Grafting	Membrane surface hydrophilicity, AF property
5.	Polyaniline (PANI)/Polyethersulfone (PES)	MWCNTs	-	Water permeability, 80% rejection of Natural organic matter (NOM)
6.	PVDF	GO	-	Membrane AF resistance
7.	3-aminopropyltriethoxysilane (APTES)	GO	-	Water flux, BSA rejection, and AF resistance
8.	PSF	SiO_2-GO nano-hybrid particles	-	Membrane water permeability, BSA rejection, as well as AF properties
9.	PVDF	Fe_3O_4-GO nanocomposite	magnetic field induced casting and a phase inversion technique	Highly hydrophilic with robust resistance to fouling

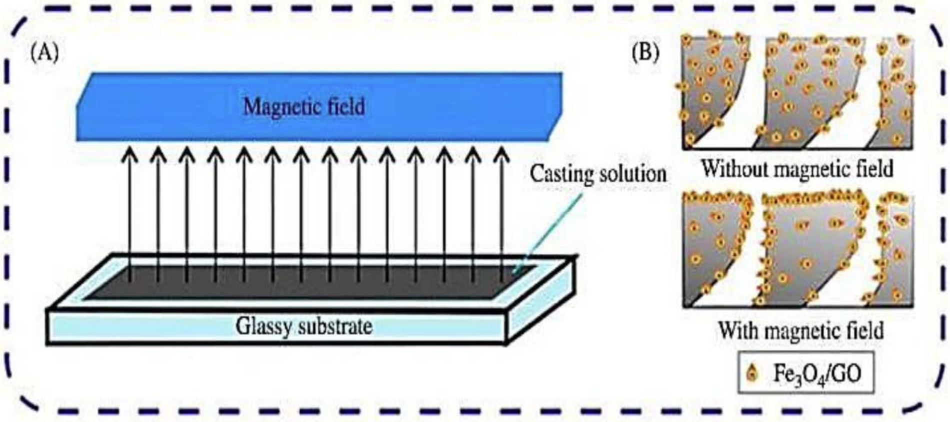

Figure 13: The distribution of Fe_3O_4-GO nanoparticles within the membrane matrix with and without magnetic field effects [61].

- High durability of membranes,
- Extended large-scale industrial applications

However, the cost of MOFs could limit the large-scale application. Hence more practical approaches associated with low cost and indigenous raw materials are to be explored and employed to fabricate novel MOF membranes in the future [64].

During the recent decade, the usage of microcapsule-based technologies has gotten a lot of attention. Microencapsulation technology is an effective AF nanotechnology that uses water- soluble resin to create AF agent nanopowder, which is then formulated into the paint. It's a technique in which a coating surrounds microscopic particles or droplets to create miniature capsules with a variety of beneficial characteristics. The micro-encapsulated anti-fouling chemical can provide a longer and more effective AF effect while also lowering environmental impact [65]. The aesthetic recovery along with the rapid release of the healing ingredient from the microcapsules are the two advantages. Although the healing ingredient is locally exhausted after a single injury event, this microcapsule-based method might be easily applied to various polymer systems. The benefits of this technique include extending the material's service life and lowering the cost of repair or replacement of a damaged component [66].

Table 3: Enhancement of Antifouling Shown through Membrane Modification by Carbon Based Material [63]

S. No.	Membrane type	Carbon based material	Property enhanced
1	PSf (Poly sulphone)	dodecyl amine (DDA)-functionalized MWNTs	Compatibility and interfacial adhesion between the PSf matrix and the inorganic nanotubes, 0.5 wt.% DDA-MWNTs significant improvement in permeability and fouling resistance with the highest flux recovery of 83%, with the reduced irreversible fouling resistance of 17% and the lowest total flux loss of 29% [62].
2.	PES Nanocomposites	SiO_2, cloisite 30B clay, TiO_2, hydroxyl-functionalized MWCNTs(MWCNTs-OH), carboxyl-functionalized MWCNTs (MWCNTs-COOH)	Hydrophilicity porosity, water permeation flux and antifouling properties
3.	Poly(piperazine amide) Thin Film Nanocomposites (TFNMs)	Sulfonated MWCNTs (S-MWCNTs)	Surface hydrophilicity and better antifouling ability to BSA,with 91.2% water flux recovery ratio
4.	PVDF UF	Polypyrrole (PPy)-coated oxidized and raw MWCNT	Higher hydrophilicity (smaller contact angles), pure water flux and antifouling properties
5.	RO TFNMs with Trimesoyl chloride (TMC) and m- phenylenediamine (MPD)	amine-functionalized MWCNTs ($MWCNT-NH_2$)f	Increased fouling resistance, hydrophilicity and the negative charge density of the membrane surface, and membrane surface roughness reduced.
6.	Polypyrrole NF TFNMs	PPy-coated oxidized and raw MWCNT	High permeation flux and improved antifouling properties.
7.	PA TFNMs	GO nano-sheets	Improved water permeation flux and fouling resistance
8.	PSf NCM	polyethylene glycol (PEG)-functionalized CNTs (PEGCNTs),	Fourfold increase in pure water and protein solution permeability and improved fouling resistance
9	PES NCM	GO (nano-ribbons or nano-sheets)	Organic matter rejection (59%), maximum water permeation flux and fouling resistance (30% Improvement).

Table 4: Enhancement of Antifouling Shown through Membrane Modification by MOF [64]

S. No.	Membrane type & Separation technique	Metal organic framework	Property enhanced
1.	TFN Polyamide membrane, Forward Osmosis (FO)	2D MOF(copper1,4-benzenedicarboxylate)nano filter	Water flux and antifouling ability without reducing the selectivity
2.	Polysulfone TFN membranes, reverse osmosis	HKUST-1 ($Cu_3(BCT_2)$)	Water flux and antifouling
3.	Polyether sulfone and cellulose-acetate-	MOF-5	Porosity, pore size, water permeation, and antifouling behavior increased and hydrophobicity decreased
4.	Cellulose acetate	HKUST-1/reduced GO	Excellent water flux, removal, and antifouling performance for methylene blue and Congo red (89% and 80%, respectively).
5.	Polyether sulfone UF membranes	UiO-66 nanoparticles attached to hydrophilic GO nano-sheet layers	High AF and water purification performance
6.	Polyether sulfone membranes	Cu tere-phthalate@GO	Superior AF behavior
7.	Polyether sulfone membranes	All negatively charged MOF@GO	Better AF behavior increasing the lifespan of the membrane
8.	TFN	Porous MOF (copper 1,4-benzenedicarboxylate nano sheet	water permeability and a clear AF tendency with reduced hydrophobicity and biocidal action of the membranes
9.	TFN	GO – Ag-MOF membrane	Anti-bio fouling and antifouling behaviors of the membranes
10.	Poly(sulfobetaine methacrylate)/ Polysulfone	UiO-66	Highly improved water permeance and AF tendency

The microcapsule shell and encapsulation method are chosen based on the physical characteristics of the core and the desired application. Polymeric materials are embedded with microcapsules carrying a self-

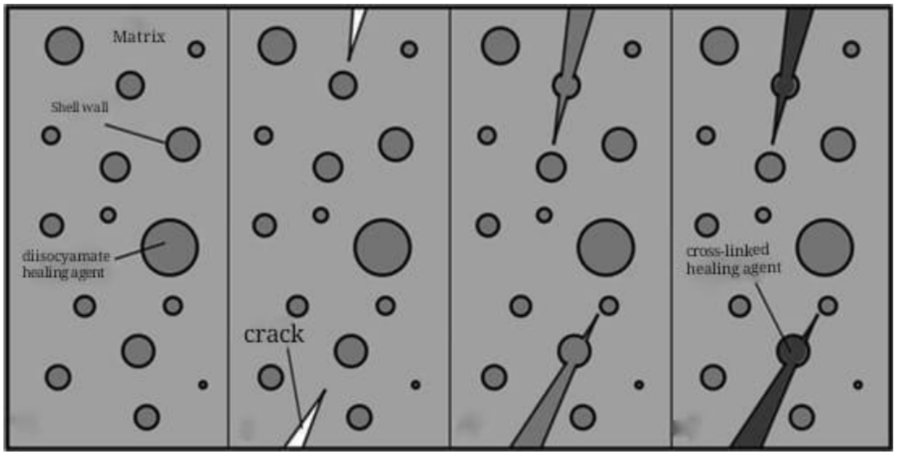

Figure 14: Schematic illustration of self-healing process [67].

healing ingredient. When a crack in the polymer matrix is caused by an external force, such as a sudden physical impact or stretch, some of these microcapsules along the crack line rupture, and the liquid curing agent flows into the cracks and reacts with the catalyst or the matrix itself to form a solid that fills the gaps. The healing agents can be monomers, dyes, catalysts, or hardeners, and they're encapsulated to match the chemistry of the matrix and applications [68].

These healing agents act as adhesives, gluing the polymeric matrix together from inside the system. Interfacial polymerization, in situ polymerization, extrusion, and sol-gel techniques are some of the processes used to make these microcapsules [69]. Because it is the simplest process and does not require expensive equipment, in situ polymerization was the most often utilized approach among these techniques. In situ polymerization was used to create the shells of microcapsules.

Commercially, this technique has been utilized to make a variety of microcapsules. The yield and size of the microcapsules can be affected by a number of processing factors. The core/shell weight ratio, emulsifier type and concentration, pH, and stirring speed during microencapsulation are all factors to be considered [70].

Shi *et al*. [77] used an in-liquid drying method to encapsulate the non-toxic AF chemical sodium benzoate in polystyrene microcapsules. The sodium benzoate might progressively leak from the AF coating matrix, according to the findings. While the reaction temperature fell or the amount of dispersion agent and stirring speed increased, the polymer particle size decreased.

Saravanan. P, *et al*. [78] prepared APTES-TiO_2, an epoxy resin with nanoscale fillers that provides an outstanding mix of characteristics, including improved dimensional stability, mechanical and electrical capabilities, and durability. The influence of various inorganic nanoparticles (1, 3, 5, and 7 wt. percent) filler loading concentrations towards corrosion and fouling resistance characteristics were investigated. Electrochemical impedance and static immersion experiments evaluated the corrosion and fouling resistance of these coatings. After 30 days in a 3.5 percent NaCl solution, a nano-hybrid coating (3 wt. percent APTES-TiO_2) demonstrated corrosion resistance of up to 108 U cm^2, suggesting good corrosion resistance. If the addition of APTES-TiO_2 is greater than 3 wt.%, regrettably, the excess addition creates an uneven distribution of APTES-TiO_2 in the coating film, which may have resulted in pore development on the coating's surface.

3.8. Membranes with Graphene Oxide (GO) Incorporation

By refilling SnO_2-GO nanoparticles into PVDF and using delay phase conversion technology, Chen, Z.*et al*., [72] created a unique full sponge-like porosity SnO_2-GO/PVDF membrane with remarkable photocatalytic antifouling capabilities. The SnO_2-GO/PVDF membrane had the ideal morphology, including high porosity and pore size, low surface roughness, and a consistent sponge pore structure, which resulted in the improved separation and antifouling performance. The rejection rate of SnO_2-GO/PVDF membranes was 97.2 percent under high flux (363.2 L m 2 h 1), compared to 64.0 percent for primitive PVDF membranes under high flux (201.2 L m 2 h 1), indicating better membrane structure and

Table 5: Enhancement of Antifouling Shown through Membrane Modification by GO

Author	Material	Method	Observations	Inference
[71]	Polyaniline/p-phenylenedia mine-functionalize d graphene oxide (PANI- PGO)	Ultrasonic- assisted in situ polymerization technique with different PGO loadings (x = 0.05–0.4 g).	After 192 hours of immersion in a 3.5 wt. percent NaCl solution, E/PANI–PGO (0.2) performed 5.15 times better than E/PANI–PGO (0.05). The E/PANI–PGO (0.4) coating has a lower corrosion resistance than the E/PANI–PGO (0.2) coating. E/PANI–PGO (0.1) and E/PANI–PGO (0.2) are found to exhibit the best antifouling properties after three months.	Findings reveal that E/PANI–PGO (0.2) had the highest corrosion resistance of all the coatings.
[72]	SnO_2- graphene oxide/polyvin ylidene fluoride (SnO_2- GO/PVDF)	Delay phase conversion method.	The rejection rate of SnO_2-GO/PVDF membranes was 97.2 percent under high flux (363.2 L m -2 h -1), compared to 64.0 percent for primitive PVDF membranes under high flux (201.2 L m -2 h -1). When compared to GO/PVDF and SnO_2/PVDF membranes, photodegradation efficiency rose 75.5 percent and 43.3 percent, respectively, while photodegradation kinetics accelerated 209.8 percent and 126.8 percent	The photodegradation on efficiency indicates that the combination of GO and SnO_2 had a synergism and enhanced the inductive function of photocatalysis and self-cleaning capacity.
[73]	Bi_5O_7I/Zwitt erion Fluorinated Polymers (Bi_5O_7I/ ZFP)	Ultrasonic vibration was used with a mass ratio of Bi_5O_7I powders of 1%.	Bi_5O_7I/ZFP-2 had the greatest inhibition rates against E. coil and S. aureus, reaching 99.09 percent and 99.66 percent, respectively. The positive and negative ions found in ZFP films can attract molecules, forming a thermodynamic hydration barrier that keeps fouling organisms away.	Thus, the resultant optimized Bi_5O_7I/ZFP composite film exhibited an excellent diatom anti- settling performance and a high antibacterial.
[74]	Epoxy-based polyaniline–graphene oxide nano-sheets (PANI-GON)	Modified Hummers'- in situ polymerization technique.	Epoxy/PANI-GON coatings are more resistant to corrosive environments than epoxy and/or epoxy/PANI coatings. After 192 hours in a 3.5 wt. percent NaCl solution, the coating resistance (Rc) of epoxy/PANI-GON (12 wt. percent) was 7.9 times greater than epoxy/PANI-GON (3 wt. percent) epoxy/PANI-GON (6 and 12 wt. percent), had the lowest and maximum antifouling behavior after three months of immersion in simulated seawater including microorganisms	The epoxy/PANI- GON (12 wt.%) coating has the greatest resistance.
[75]	ZnO and ZnO-GO Nanoparticles	sol-gel technique with various percentages of ZnO (1, 2, 3 wt.%) and ZnO-GO (0.1, 0.3, 0.6 wt.%) nanoparticles.	All of the membranes containing nanoparticles showed enhanced membrane characteristics. HA rejection rose from 52 percent for the P0 membrane to 99 percent for the ZG3 membrane. In comparison to other GO-Nano hybrids GO the ZnO-GO composite is more hydrophilic.	Membranes ontaining 2 wt.% ZnO and 0.6 wt.% ZnO- GO performed the best and also has shown better hydrophilicity, permeability, and porosity, as well as a higher HA rejection rate and superior antifouling and antibacterial control.
[76]	SiO_2/Polyvin ylchloride (PVC)	phase- inversion technique with various nano- SiO_2 particle loading (0–4 wt. percent).	With the addition of nano-SiO_2, a hydrophilic layer was generated on the surface and cross section of the modified membrane. This hydrophilic layer efficiently prevents the adsorption or adhesion of hydrophobic substances. Increased viscosities, adverse degassed effect, and film-formation performance were observed in casting solutions with a nano-SiO_2 loading rate of 3 wt. percent or higher	The membrane with a 1.5 wt.% nano-SiO_2 dosage had higher AF performance and better abilities against protein absorption and bacterial adhesion

increased hydrophilicity due to the addition of SnO_2-GO. After a compliant test, the performance of the SnO2-GO/PVDF membrane showed good recovery and excellent repeatability.

Chung *et al*., 2017 [75] examined ZnO and ZnO-GO nanoparticles using sol-gel technique with various percentage of ZnO (1, 2, 3 wt.%) and ZnO-GO (0.1, 0.3, 0.6 wt.%) nanoparticles. The greatest membrane performance was found in membranes containing 2 wt.% ZnO and 0.6 wt.% ZnO-GO. Due to the polar properties of ZnO and the presence of hydroxyl, carbonyl, and epoxy groups in GO, both types of nanoparticles were hydrophilic in nature. These two membranes showed substantial improvements in hydrophilicity, permeability, and porosity, as well as a higher HA rejection rate and superior antifouling and antibacterial control. To some extent, the strong antibacterial capacity of these nano hybrid membranes appear to be an ideal option for contributing to or overcoming biofouling concerns in brackish water or seawater desalination applications. Zhao, X., *et al*. [79] proposed a polyphenol-metal manipulated nano-hybridization method to fabricate a CNT@CS/TA-FeOOH nano hybrid membrane. The permeability of the constructed CNT@CS/TA-FeOOH nano hybrid membrane was above 8000 Lm-2h-1bar-1. Based on the synergy of hydration-induced antifouling mechanism and photo-induced self-cleaning mechanism, the CNT@CS/TA-FeOOH nano-hybrid membrane demonstrated high separation efficiency above 99 percent, high permeate flux above 4000 Lm-2h-1bar-1, and desirable flux recovery capability above 97 percent when used to separate various oil/water emulsions.

4. ANTIFOULING COLONIZATION

The main factors that affect the AF colonization are the effect of environmental parameters and the effect of substrate. Salinity, temperature, pH, nutritional elements, flow rate, dissolved gases, and sun radiation are all environmental factors that impact the colonization of marine life [80]. The presence of oxygen in rosin-based paints may cause dissolved copper to be oxidized, resulting in partial re-precipitation of copper carbonate, copper chloride, copper hydroxide or copper sulphide, the last anion being produced by biological activities. Fouling organisms' settling is further influenced by the substrate's surface energy, roughness, porosity, and other characteristics. Hydrophobic fouling organisms are thought to cling to hydrophobic materials, while hydrophilic organisms prefer to stick to hydrophilic substrates [81].

In general, bryozoans settle on low-energy substrates, while barnacles settle on high-energy surfaces. Cypris larvae of the barnacle B. prefers to land on surfaces with low wettability or surface energy, whereas Amphitrite prefers to settle on surfaces with high wettability [82]. Ulva spores have been shown to bind poorly to hydrophilic surfaces and to cling more firmly to hydrophilic surfaces. The roughness and porosity of surfaces submerged in a marine environment are also important factors in fouling organism settling [83].

The imperfections of the surfaces expand the area of colonization and, as a result, the number of adhesion sites. Several studies have found that valleys in rough surfaces result in a secure mechanical lock between the organisms and the substrate, a phenomenon known as thigmotactic fouling organisms have investigated the effect of substrate composition on fouling and found that a decrease in the substrate's C = N or C = P ratio might have a substantial impact on biomass median particle size at steady state, resulting in a reduced membrane fouling rate [84].

5. CHALLENGES

The obscuration of structures, the development of microenvironments that may encourage corrosion, physical obstruction, weight loading, and increased hydrodynamic loading are all negative impacts of marine biofouling on offshore facilities. Salinity, temperature, nutrition levels, flow rates, and light levels are the primary factors that influence biofouling. The creation of a research programme to examine the colonization of such submerged buildings has resulted from the shift toward deep-water oil and gas extraction. Increases in water depth were shown to cause changes in the physical and chemical environment that were less conducive to the growth of fouling populations [85].

The temperature of seawater varies from –2°C to 30°C, which has a significant impact on enzyme catalytic activity and stability. Furthermore, if the temperature is too high, each enzyme will break down, shortening the lifespan of the enzymatic antifouling coating. As a result, striking a balance between efficacy and longevity will be a big issue. Another critical step for effective application will be the creation of a suitable coating matrix to encapsulate the enzymes [86]. Furthermore, the distribution of enzymes and their quantity should be thoroughly examined, since soluble enzymes will quickly create a thick leaching layer. In conclusion, there are no convincing hypotheses to explain differences in AF performance caused by changes in surface zeta potential, topography, or wettability in the majority of instances. As a result, several trials examining diverse factors are insufficient for resolving the biofouling issue [87].

Photosynthetic fouling species, such as barnacles, sea anemones, sponges, tubeworms, and bryozoans, are replaced by suspension and filter-feeding organisms. Because deep water habitats lack firm substrates, colonizing organisms are drawn to man-made structures such as subsea production systems. Fouling may be a serious concern for long-term submerged buildings since it occurs in deep water but at a slow rate. A deeper understanding of these communities' biodiversity and settlement patterns will aid in the development of tailored AF protection [88].

The projected influence of global warming on biofouling communities has recently been examined, with the major results being that calcium-dependent organisms may be replaced by non-calcareous species, with a predominance of UV-resistant species that can withstand low salinity [89]. AF coatings should now be routinely screened against more soft-bodied species such as tunicates, sponges, and algae in order to be proactive about prospective community changes [90]. Because biofouling is a complicated biochemical problem rather than a pure physical problem, detailed information on the adhesion mechanism is necessary.

6. SCOPE AND PERSPECTIVES

TBT-based solutions will soon be phased out, and shipping firms will be forced to rely on new tin-free biocide-based AF treatments. Traditionally, the latter has been divided into two classes based on the features of their binder system. In theory, the best suitable alternative for TBT-SPC products should be found in paints with similar chemical properties. This is the foundation for what is referred to as acrylic-based tin-free "self-polishing" paints in this article.

However, the performance of TBT-based paints is more complicated than simply attaching a hydrolysable pendant group to an acrylic backbone. Furthermore, it was found that the presence of co-binders, additives, pigments, and other possible paint components has a significant impact on the performance of chemically active AF paint systems. Following the progression illustrated in the patents, it is clear that businesses selling acrylic-based "SP" paints have had to modify their products over time to address various issues with their paints [91].

The absence of scientifically backed data provided by the various firms feeds these suspicions. Similarly, the so-called rosin-based tin-free “SP” paints, which are improved traditional rosin- based systems that claim to have solved all of the drawbacks associated with both traditional soluble matrix technology and modern CDP systems and achieved the "SP" mechanism [83]. As a result of this, and the lack of scientific evidence on the relationship between reaction mechanisms (also unknown) and antifouling performance in commercially available tin-free AF paints, it is more reasonable to classify existing products based on performance parameters, which are, after all, the most important ones. All of the major businesses commercializing tin- free “SP” AF coatings were asked to give data supporting the self-polishing behavior of their products as a first step toward characterizing the AF performance of existing commercial goods.

Due to confidentiality and properitery concerns, the various firms have supplied very little comprehensive data, therefore the statistics in this study frequently lack scientifically desired properties (e. g. experimental uncertainty). Although tests comparable to those used to develop the figures in this work may be used to infer the performance of AF paints, gaining a fundamental understanding of their processes under various situations would considerably simplify the product optimization process.

The findings indicate that having a deep understanding of a system (TBT-SPCs) may lead to the construction of mathematical models that can accurately represent the performance of that system. After the model has been confirmed to represent the paint's primary processes, it may be used to improve coating performance by examining the impacts of changes in pigment type and content, retardant concentration, and biocide type on polishing rates, biocide release rates, and leached layer thickness [92].

The development of such a model might also assist to reduce the time it takes to design new AF products using standard empirical approaches. This might be achieved, for example, by combining short-term rotational tests with response engineering studies to give empirical inputs for the model, which could then replicate the paint's whole lifetime in only a few minutes. It goes without saying that accurate AF paint performance models would be an useful tool for more rationally screening new ideas based on comparable mechanisms of action. The model might be used to determine the features that the new AF product should have in order to achieve the desired outcome [93].

Systems that are overly susceptible to environmental changes, which have been found to impact the performance of AF paints, might be eliminated early in the development phase. For example short tests could be conducted in various seawater conditions to input the model, which would then be capable of quickly predicting the AF performance of the paint in any conceivable fouling situation [94].

Potentially stricter limitations on the release rate of active compounds from AF products in the near future may highlight the benefits of having trustworthy paint models for the design and optimization of coatings with precisely regulated biocide release mechanisms. The same can be said for the commercialization of AF products based on chemically active non-toxic compounds, such as those extracted from marine creatures, which is unquestionably one of the most important study areas. The demand for more ecologically acceptable TBT-based product replacements has prompted a deeper investigation into the adhesion processes and biological features of the fouling process. While there are several commercial fouling-release systems on the market, the development of an effective solution solely based on natural biocides appears to be a long way off [91].

Further study on AF coatings is needed in areas such as: (i) photo-curing AF coatings while adhering to strict maritime rules, which minimizes VOC emissions, environmental impact, and maintenance costs. (ii) Developing self-healing coatings that will provide AF coatings with better performance and a longer lifespan. (iii) Developing new fluoro-based polymers and hybrid foul-release coatings to increase foul release coatings' effectiveness against slime fouling [95].

7. CONCLUDING REMARKS

Biofouling causes the majority of significant disasters in the maritime and membrane sectors, which exacerbates fuel loss, drag resistance, maintenance costs, and severe environmental consequences. Owing to the above said reasons, the high-performance nanocomposite material for marine and membrane AF is the topic of interest and need of the hour for our present generation. The continuous research on new nanomaterials and exploration of synthetic polymers will certainly create huge scope for such novel materials with improved performances and specific end-use in marine and membrane AF applications. As a result, the widespread usage of biocidal AF coatings has resulted in a slew of environmental problems, prompting the shipping industry to enact stringent regulations. This has led to the adoption of an environmentally acceptable method of biofouling prevention in the form of a coating that is either sprayed on or applied using electrolytic deposition techniques.

On the one hand, covering surfaces with compounds such as nano-AF paints have been shown to effectively minimize biofouling over time. However, the longevity of these paints is still an issue, since repainting will be necessary frequently, making this option extremely costly and unsustainable in the long term. Electrolytic deposition of nano-composite coating, on the other hand, appears to be a more sustainable option, particularly if the composite contains natural materials as one of its elements.

Nontoxic biocide/natural AF agents derived from neem oil, are readily accessible. The goal of nano-zeolite is to extend the life of biocides and antifouling agents by protecting them from direct contact with enzymes and microorganisms while allowing for regulated biocide dispersion from the polymer to the fouling environment. The developed nano-hybrid coatings with anticorrosive and AF efficiencies were assessed using conventional test techniques to determine their applicability and efficiency in a variety of situations. EIS studies, salt spray tests, and immersion testing were used to assess the panels corrosion resistance. Antifouling tests were used to assess the fouling resistance of these coatings, which involved immersing coated specimens in salt water for 180 days on India's east coast.

Corrosion and fouling experiments clearly reveal that the chemical biocide Pandol and natural products employed as biocide resulted in a lower fouling rate than a coating without a biocide. It may be inferred that natural ingredients and Pandol might be employed as an efficient antifouling biocide in nano-hybrid coatings instead of the presently used conventional epoxy coatings for improved performance and lifespan. In terms of corrosion resistance, the nano- hybrid coating without biocide demonstrated the highest level of resistance.

Because they have strong antibacterial capabilities and because their specific surface area is big, the usage of "nanomaterials" is very efficient in preventing bacterial adherence and biofilm development. Using electrolytically deposited nanocomposites from anti-biofouling natural materials in biofouling prevention has received little attention so far. Biofouling on substrates has been effectively mitigated with substances such as nano-AF paints over time. However, the lifetime of these paints is still an issue, since repainting will be necessary frequently, making this option extremely costly and unsustainable in the long term. So, innovation and invention are like two sides of the golden coin, which are highly essential in nanotechnology for the fabrication of high-performance materials to prevent marine and membrane fouling processes to get a proper insight into the characteristics of materials at the nanoscale.

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