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Review

Research Progress of Marine Anti-Fouling Coatings

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Abstract: The extended immersion of ships in seawater frequently results in biofouling, a condition characterized by the accumulation of marine organisms such as barnacles and algae. To combat this issue, the application of anti-fouling coatings to the hull surfaces of vessels has emerged as one of the most effective strategies. In response to the increasing global emphasis on environmental sustainability, there is a growing demand for anti-fouling coatings that not only demonstrate superior anti-fouling efficacy but also adhere to stringent environmental standards. The traditional use of organotin-based self-polishing anti-fouling coatings, known for their high toxicity, has been prohibited due to environmental concerns. Consequently, there is a progressive shift toward the development and application of environmentally friendly anti-fouling coatings. This paper reviews the toxicity and application limitations associated with conventional anti-fouling coatings. It provides a comprehensive overview of recent advancements in the field, including the development of novel self-polishing anti-fouling coatings, low surface energy coatings, biomimetic coatings, and nanostructured coatings, each leveraging distinct anti-fouling mechanisms. The paper evaluates the composition and performance of these emerging coatings and identifies key technical challenges that remain unresolved. It also proposes a multi-faceted approach to addressing these challenges, suggesting potential solutions for enhancing the effectiveness and environmental compatibility of anti-fouling technologies. The paper forecasts future research directions and development trajectories for marine anti-fouling coatings, emphasizing the need for continued innovation to achieve both environmental sustainability and superior anti-fouling performance.

Keywords: fouling; anti-fouling paint; anti-fouling mechanism; self-polishing; bionic paint

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1. Introduction

The marine environment is home to a vast diversity of species, with over 4000 marine fouling organisms identified, including algae, mollusks, bacteria, and microorganisms [1]. As shown in Figure 1, these organisms tend to adhere to the ship's hull and propeller surfaces, causing biofouling, which increases sailing resistance and power consumption. This, in turn, leads to increased emissions of harmful gases, impacts the vessel's maneuverability, and may even cause the failure of instruments submerged in seawater [2,3]. Furthermore, the transportation of these organisms to new regions by ships poses significant risks to local ecological systems [4]. Anti-fouling coatings have thus become a prevalent and effective strategy for mitigating these issues. These coatings typically comprise resins, pigments, anti-fouling additives, solvents, and fillers [5].

Early anti-fouling coatings for ships typically relied on toxic metal compounds, such as copper oxide, or organic biocides, like tributyltin (TBT), to inhibit the attachment of marine organisms. However, these chemical substances have had severe adverse effects on marine ecosystems. Although TBT has been banned, the widespread use of biocides like copper oxide continues to result in the accumulation of copper ions in the marine environment, disrupting aquatic ecological balance. The increasing stringency of environmental regulations has made the development of non-toxic, low-pollution anti-fouling coatings an urgent necessity [6].

Recently, researchers have enhanced traditional cuprous oxide formulations by incorporating nano-sized cuprous oxide, which extends effectiveness and improves storage stability [7]. Innovations such as soft-template and self-template methods have led to the synthesis of cuprous oxide hollow microspheres, which boost anti-fouling performance and reduce the amount of cuprous oxide needed [8]. Furthermore, polyvinylpyrrolidone-cuprous oxide (PVP-Cu_2O) microcapsules, created using sodium sulfite reduction and single-condensation methods, have been shown to enhance anti-fouling coatings when used with polyurethane/epoxy resin (PU/EP). These coatings exhibit improved dispersibility and lower release rates of the anti-fouling agent, reaching 11.5 $\mu g \cdot cm^{-2} \cdot d^{-1}$ [9]. While these advanced cuprous oxide coatings offer notable improvements in long-term anti-fouling and antibacterial properties, their stability can be compromised by environmental factors such as high temperatures, humidity, and salinity. Compared to eco-friendly coatings based on nanotechnology and biomimetic materials, cuprous oxide anti-fouling agents may still pose environmental risks, as the released cuprous oxide can potentially harm marine ecosystems. To address this issue, future research must focus on the development of environmentally friendly anti-fouling technologies. For instance, anti-fouling strategies based on physical or biomimetic approaches, such as superhydrophobic surfaces or bioinspired structural surfaces, may offer new pathways for achieving non-toxic coatings. Additionally, the use of natural substances, such as extracts from marine organisms, represents a significant research direction, as these materials may exhibit excellent anti-fouling properties while being harmless to the environment.

Meanwhile, the study by Farkas et al. [10,11] indicates that anti-fouling coatings with a certain degree of roughness significantly impact the resistance and power requirements of ships. Specifically, the surface roughness of anti-fouling coatings increases frictional resistance when ships move through water, necessitating greater power consumption to maintain the same speed. This increased power demand leads to higher fuel consumption, which not only elevates operational costs but also results in increased emissions of greenhouse gases (such as carbon dioxide) and pollutants (such as sulfur oxides and nitrogen oxides). Additionally, higher surface roughness of anti-fouling coatings enhances the adhesion rate of marine fouling organisms, making the hull and propellers more prone to biofouling. This biofouling further exacerbates the surface roughness of the hull, increasing the ship's resistance and creating a vicious cycle. To address this issue, the design of anti-fouling coatings should aim to reduce surface roughness while maintaining their anti-fouling efficacy, in order to achieve fuel savings and carbon dioxide emission reductions.

Despite the significant progress made in anti-fouling coating technology for ships over the past few decades, critical challenges persist in areas such as environmental sustainability, long-term effectiveness, multifunctionality, and the reduction in coating roughness. This paper reviews recent advances in marine anti-fouling coatings, provides a concise overview of the historical development and anti-fouling mechanisms of various coatings, identifies current challenges, and proposes potential solutions. Additionally, it projects future challenges and research directions, offering novel insights into the advancement of environmentally friendly anti-fouling technologies.

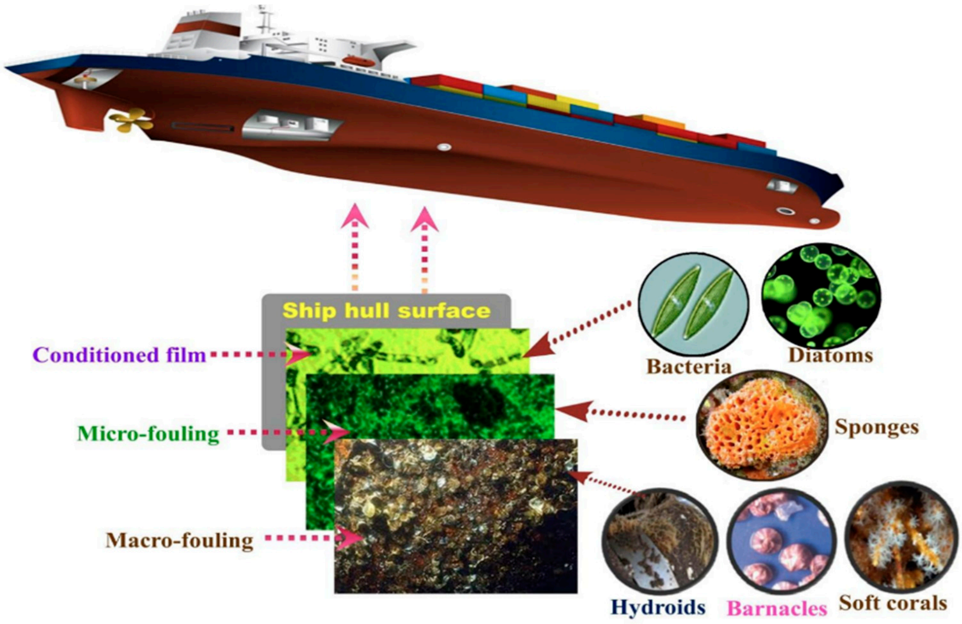


Figure 1. Hull surface fouling process and main fouling organisms [12].

2. Self-Polishing Anti-Fouling Coatings

Self-polishing anti-fouling coatings are a type of marine coating with unique chemical properties. Their mechanism involves the hydrolysis of certain chemical bonds, such as ester or metal–oxygen bonds, within the coating matrix when exposed to seawater. This hydrolytic reaction gradually erodes the coating on the hull surface, releasing embedded toxic substances, such as copper ions, or biocides into the surrounding water. The released copper ions, which possess broad-spectrum biotoxicity, can disrupt the metabolic functions of algae, bacteria, and small marine organisms, thereby preventing biofouling. As the coating degrades, a fresh, smooth surface is continuously exposed in a layer-by-layer manner, ensuring the coating remains effective throughout its service life [13].

Historically, organotin self-polishing anti-fouling coatings, particularly those based on TBT copolymers, demonstrated high efficacy but were also highly toxic, resulting in significant marine pollution. In response to these environmental concerns, the International Maritime Organization (IMO) mandated a complete ban on TBT use starting in January 2008 [14]. To address these issues, recent research has focused on developing environmentally friendly alternatives, including tin-free self-polishing coatings, additive-based formulations, and biodegradable self-polishing anti-fouling coatings.

2.1. Tin-Free Self-Polishing Anti-Fouling Coating

Tin-free self-polishing anti-fouling coatings are made using hydrolyzable resins as the base material, with copper oxide, zinc oxide, and other biocides as active substances [15]. Through chemical modification, these coatings utilize the hydrolysis reaction of the polymer matrix to gradually release anti-fouling agents, thereby preventing the adhesion of marine biofilms and achieving anti-fouling effects.

Sun Baoku et al. [16,17] developed an innovative anti-fouling formulation by integrating an eco-friendly acrylic resin with bactericidal functional groups and the broad-spectrum biocide Tralopyri in a 3:5 mass ratio. This formulation achieved an impressive antibacterial efficacy of approximately 93.4%. By incorporating only 12% biocide, the formulation balances cost-effectiveness with high performance, demonstrating significant potential to replace traditional Cu_2O-based self-polishing anti-fouling coatings. Shallow-sea immersion tests validated its superior anti-fouling capabilities, highlighting its effectiveness in reducing copper emissions and its potential benefits for marine environmental protection. 1,2-benzisothiazolin-3-one (BIT) is a commonly utilized antimicrobial agent with broad-spectrum antimicrobial properties. Incorporating BIT into anti-fouling coatings disrupts microbial metabolic processes, thereby inhibiting their growth and proliferation, which consequently reduces biofouling. Dong et al. [18] synthesized BIT-allyl methacrylate (BM) and zinc methacrylate (ZM) functional monomers and co-polymerized them with methyl methacrylate (MMA) and butyl acrylate (BA) to create a series of BIT acrylate anti-fouling resins. Field tests conducted in coastal waters demonstrated that the BIT-zinc methacrylate resins exhibited excellent anti-fouling performance against marine bacteria, algae, and barnacle larvae, alongside notable self-polishing properties. This development presents a promising strategy for designing stable and durable anti-fouling resins. Despite these advancements, tin-free self-polishing anti-fouling coatings face challenges in maintaining effectiveness across both seawater and freshwater environments. In seawater, the release rate of copper increases with salinity, resulting in higher copper discharge from anti-fouling agents with elevated cuprous oxide content. Conversely, copper-based anti-fouling agents show limited efficacy in freshwater, rendering their application redundant [19]. This suggests that biocides in freshwater environments may lead to unnecessary copper release, contributing to metal pollution and exacerbating the environmental impact. Consequently, further research is required to address these issues by reducing copper release rates in seawater and minimizing biocide use in freshwater environments.

2.2. Additive Self-Polishing Anti-Fouling Coating

Antibacterial agents are chemicals with bactericidal or bacteriostatic properties. Adding the right number of antibacterial agents to anti-fouling coatings can effectively enhance their antibacterial performance and reduce toxicity. Organic antibacterial agents, known for their broad-spectrum effectiveness and high efficiency, are among the most studied, including quaternary ammonium salts, chlorophenols, and heterocyclic compounds [20].

As illustrated in Figure 2, Hu et al. [21] synthesized indole derivatives containing carbon–carbon double bonds using 5-Cl/NO_2-indole as a starting material. These derivatives were incorporated into zinc acrylate resin through N-acylation reactions. The resulting zinc acrylate resin was then combined with polycaprolactone (PCL) and integrated into an acrylic urethane lacquer (AUL) to develop a novel indole-based self-polishing anti-fouling coating. The study demonstrated that the coating exhibited antibacterial rates of 92.79% against the typical Gram-negative bacterium *Escherichia coli* and 99.71% against the Gram-positive bacterium *Staphylococcus aureus*. Additionally, it showed inhibitory rates of 90.35% and 79.74% against *Nitzschia closterium* and *Phaeodactylum tricornutum*, respectively. The inclusion of PCL also contributed to an extended service life of the coating. Zuena et al. [22] developed composite coatings using tetraethoxysilane (TEOS) as a matrix, with the addition of nano-TiO_2 imparting unique self-cleaning and anti-fouling properties. Miriam et al. [23] explored eco-friendly anti-fouling additives derived from plant extracts, specifically cycloartenone extracted from Tillandsia tenuifolia L. At a concentration of 4.241 $\mu g/cm^2$, cycloartenone inhibited mussel attachment by 50%, demonstrating enduring anti-fouling efficacy at low concentrations without environmental harm. This high growth rate of Tillandsia tenuifolia further supports the sustainability of utilizing natural products as anti-fouling agents.

Incorporating organic and natural antibacterial agents as additives in anti-fouling coatings can significantly enhance anti-fouling efficacy. Zhao Bo et al. [24] demonstrated the use of guanidine-based diethylpropion acid (DMG) as a chain extender in fluorinated polyurethane, resulting in a coating with exceptional anti-fouling performance. The polyurethane exhibited a dual functionality with antibacterial properties in the upper layer and hydrophobic characteristics in the lower layer, as depicted in Figure 3. Similarly, An Xuelian et al. [25] developed a novel capsaicin derivative via the reaction of N-hydroxymethylacrylamide with aromatic compounds through Friedel–Crafts alkylation. This compound showed inhibition rates exceeding 80% against marine Pseudomonas and marine yellow bacteria. When incorporated into anti-fouling coatings alongside chlorothalonil, it demonstrated notable anti-fouling effectiveness.

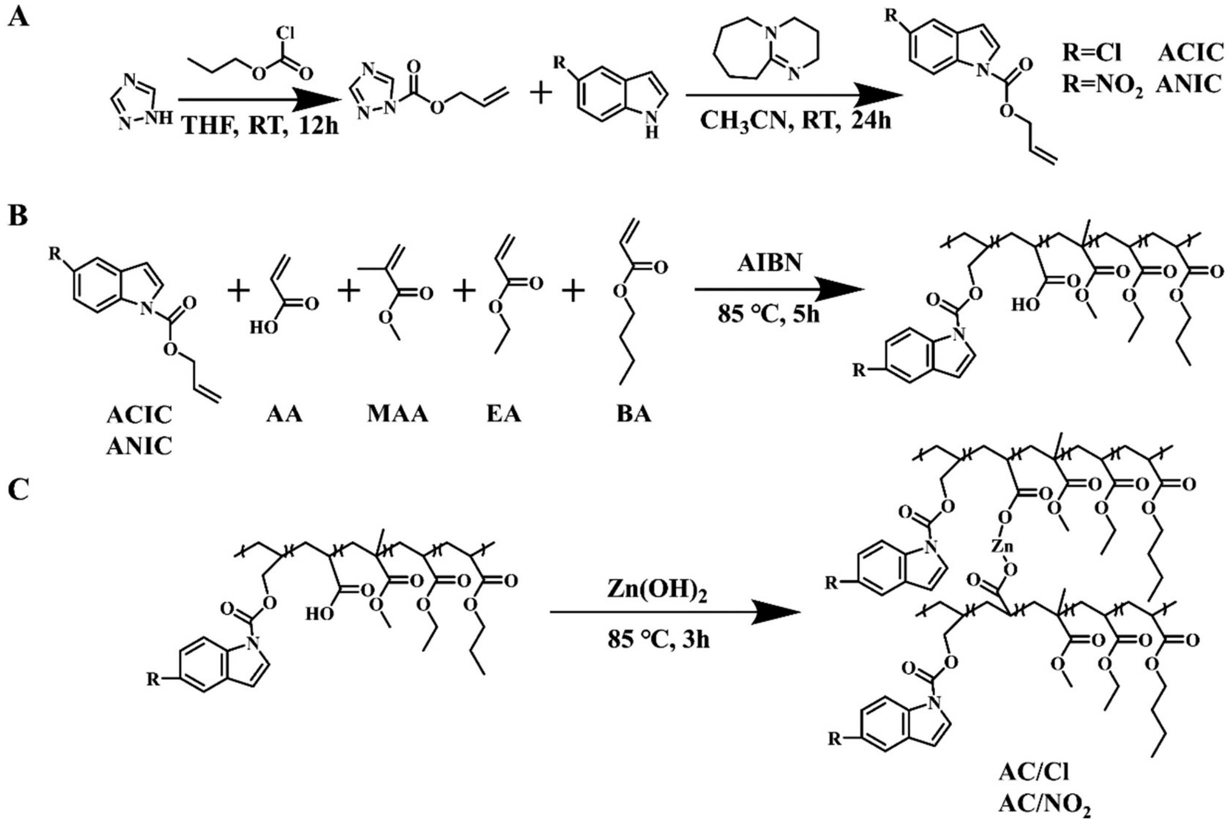


Figure 2. Synthesis of zinc acrylate resins containing different indole derivatives. (**A**) Synthesis of 5-Cl/NO_2-indole-carboxylate; (**B**) Synthesis of a prepolymer containing 15% indole derivatives; (**C**) Synthesis of Indole-free Zinc Acrylate Resin and Novel Zinc Acrylate Resin [21].

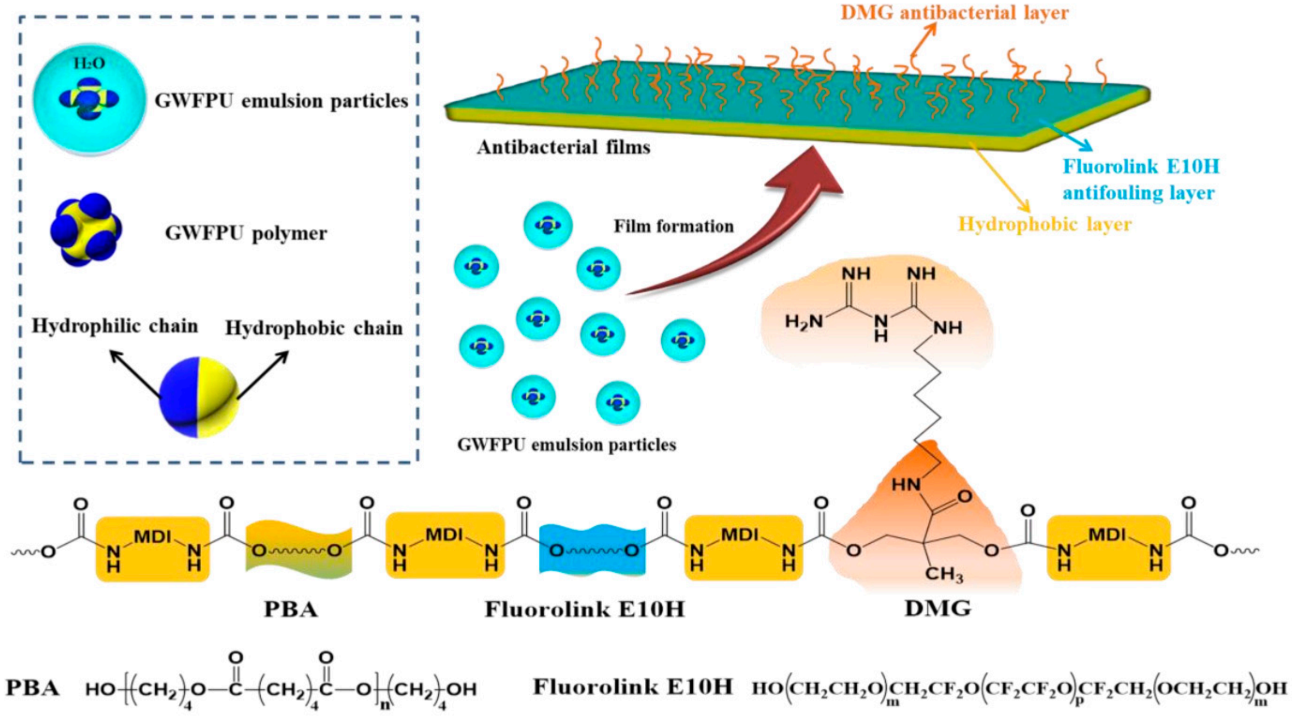


Figure 3. The schematic of antibacterial and anti-fouling waterborne fluorinated polyurethane (GWFPU1~4) films containing DMG and the corresponding chemical structure [24].

Ferreira et al. [26] developed an anti-fouling coating by reacting diisocyanate-functionalized bromopyrrole nitrile with polysiloxane. This innovative coating demonstrated significant antibacterial activity, effectively inhibiting Gram-positive bacteria, including multi-drug-resistant *Staphylococcus aureus*. Field tests conducted with real-sea panels revealed that the biocide-containing coating maintained superior cleanliness compared to control coatings, highlighting its exceptional anti-fouling performance, as illustrated in Figure 4.

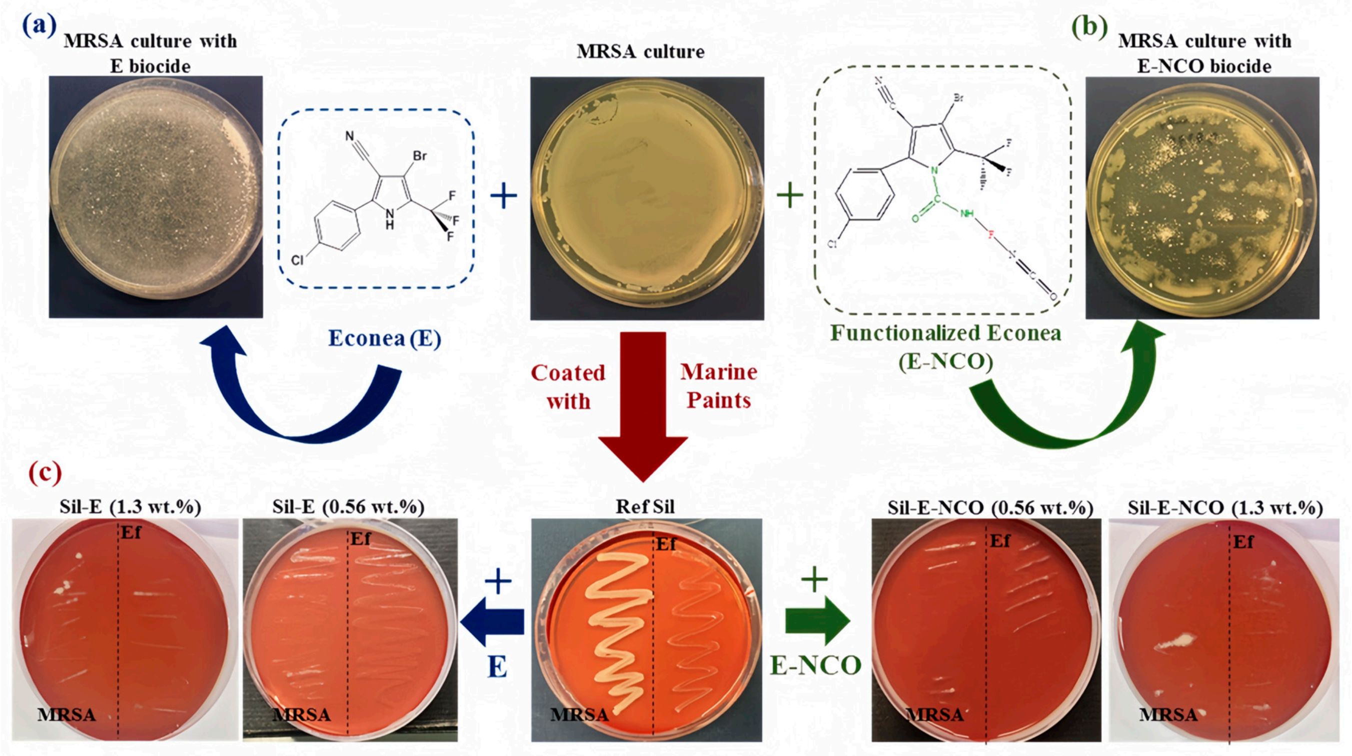


Figure 4. Antimicrobial assessment of biocides and coatings against Methicillin-resistant *Staphylococcus aureus* (MRSA-ATCC 33591) and *Enterococcus faecalis* (Ef-ATCC 29212) bacteria: (**a**) Econea biocide (E); (**b**) functionalized Econea (E-NCO), where F represents the molecular structure of the diisocyanate compound; and (**c**) polydimethylsiloxane (PDMS)-based coatings (Ref Sil) containing incorporated Econea (Sil-E) and grafted Econea (Sil-E-NCO) at different biocides contents, 0.56 and 1.3 wt %. [26].

The incorporation of organic antimicrobial agents can significantly enhance the anti-fouling properties of coatings. However, their antimicrobial efficacy often remains constrained, and their compatibility with the coating matrix is frequently suboptimal. Additionally, some of these additives may contribute to environmental pollution. To address these challenges, there is a pressing need to develop non-toxic composite antimicrobial agents that can surpass the limitations of single agents. Enhancing the compatibility between antimicrobial agents and the matrix can be achieved through advanced surface modification techniques and optimization of the preparation process.

2.3. Biodegradable Self-Polishing Anti-Fouling Coatings

Biodegradable anti-fouling coatings represent an environmentally friendly and sustainable solution for marine biofouling, leveraging surface chemistry and biodegradable materials to deliver persistent anti-fouling and anti-adhesion performance on ship surfaces. These coatings gradually release low concentrations of active ingredients, which enhances ship performance, reduces fuel consumption, and minimizes marine environmental pollution [27,28]. Sha et al. [29] developed a self-polishing anti-fouling polymer utilizing methyl acrylate-eugenol. The hydrolysis of the phenolic ester group transforms the resin from hydrophobic to hydrophilic, enabling the gradual release of natural, non-toxic eugenol into seawater for self-polishing. Laboratory evaluations with bacteria, marine diatoms, and purple mussels demonstrated that the polymer, composed of methyl acrylate-eugenol, hexafluorobutyl methacrylate, methyl methacrylate, butyl methacrylate, and methoxyethyl methacrylate (EMFP), exhibited exceptional antibacterial and anti-algal properties, effectively reducing the initial adhesion of fouling organisms, as shown in Figure 5. Dai et al. [30] developed a novel series of zinc-polyurethane copolymers featuring zinc cations in a polymer salt form, which are capable of ion exchange with sodium in seawater. As the ion exchange reaction proceeds, the zinc-polyurethane copolymer becomes soluble and is gradually leached out by seawater. Despite a decrease in adhesion after prolonged immersion in seawater, the zinc-based polyurethane coatings maintained strong adhesion (>5.2 MPa). Marine field tests confirmed that these zinc-polyurethane anti-fouling coatings were highly effective in preventing marine biofouling for over 12 months.

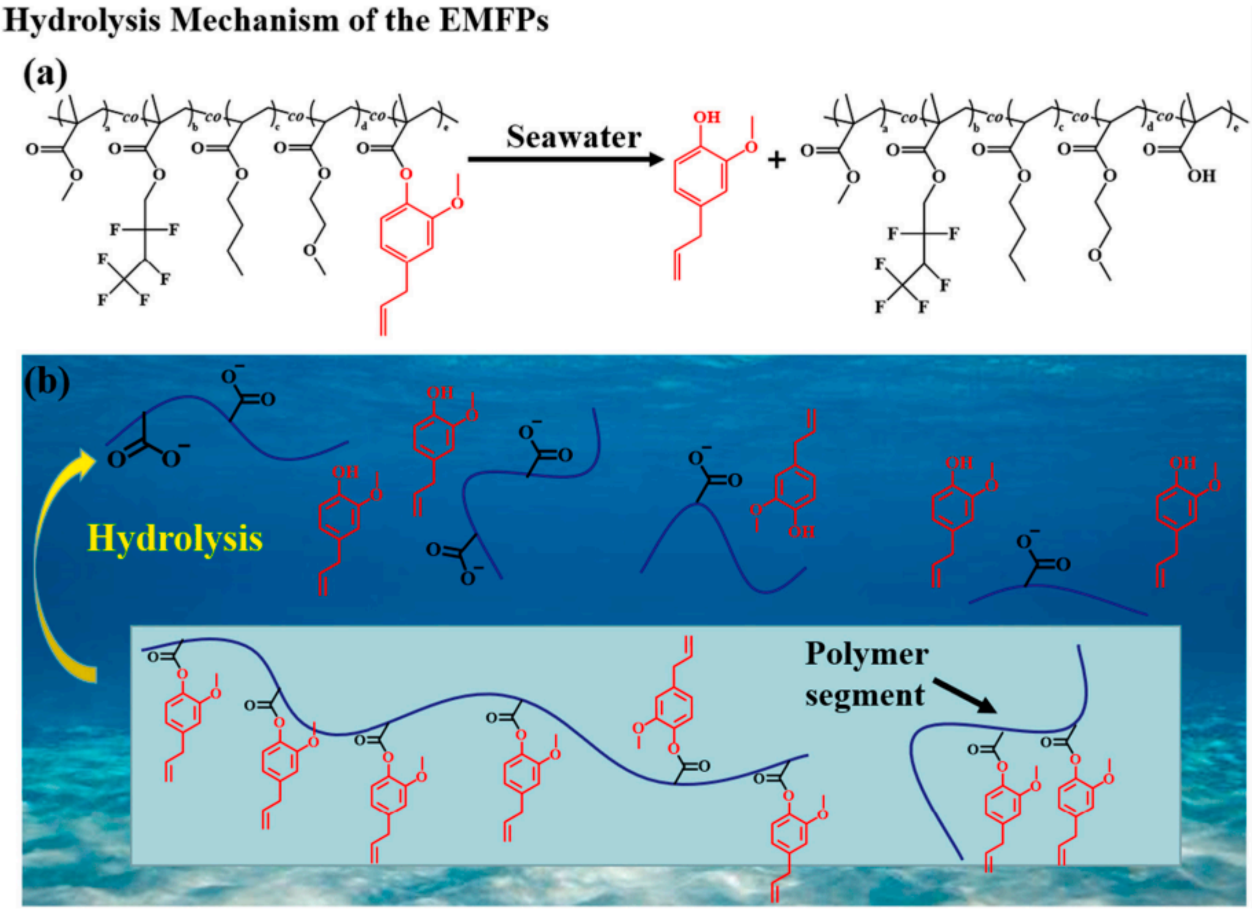


Figure 5. Hydrolysis mechanism of the EMFPs: (**a**) Hydrolysis reaction equation and (**b**) hydrolysis schematic illustration [29].

Despite the rapid advancements in biodegradable anti-fouling coatings, several challenges persist, particularly in addressing the complexity of marine environments, enhancing resistance to pollution, improving durability, and reducing costs. Therefore, the design of biodegradable anti-fouling materials should incorporate multiple mechanisms to achieve optimal performance. One promising approach involves integrating large-scale anti-fouling or resistance-reducing components into degradable polymers, thereby creating multifunctional dynamic surfaces. Additionally, extending the lifespan of biodegradable polymers can be achieved by incorporating degradable polymers with hydrolyzable bonds onto the surfaces of silicon-based foul-release coatings (FRCs). This method facilitates the development of advanced polymers with tailored properties. Crucially, precise control over the chemical bonding between the degradable polymer and the FRC surface is essential for effective material design and functionalization. By leveraging the benefits of both material types, it is possible to produce coatings with enhanced mechanical properties, superior chemical resistance, and improved biocompatibility.

3. Low Surface Energy Anti-Fouling Coatings

Low surface energy anti-fouling coatings are a type of marine coating designed to prevent biofouling by reducing the adhesion between the coating surface and marine organisms [31]. These coatings are characterized by a very low surface free energy, typically less than 25 J/m^2. The molecular structure of the coating surface significantly diminishes van der Waals forces, hydrogen bonding, and other physicochemical interactions between the fouling organisms (such as bacteria, algae, and mollusks) and the coating, effectively slowing down their attachment and preventing biofouling, thus enhancing surface cleanliness [32]. Figure 6 illustrates the anti-fouling mechanism of low surface energy coatings. These coatings usually exhibit strong hydrophobicity, or even superhydrophobicity, with water contact angles exceeding 90° for hydrophobic materials and surpassing 150° for superhydrophobic surfaces. The micro- or nano-scale roughness of these surfaces reduces the contact area between water droplets and the solid surface, further decreasing the adhesion of fouling organisms. Bayer found that an optimal bioadhesion resistance is achieved when the surface energy of the coating is in the range of 22 to 24 J/m^2 [33]. Furthermore, high-performance low surface energy coatings require additional properties such as flexible chain segments, sufficient coating thickness, and a smooth surface finish to maximize their anti-fouling effectiveness [34].

Research on low surface energy anti-fouling technology dates back to the early 20th century, with the first patent for silicone waterproof coatings issued in the United States. Despite their promise, these coatings faced limitations due to prolonged curing times and suboptimal adhesion quality, which restricted their widespread use. Silicone-based low surface energy coatings have been developed through two main approaches: first, by synthesizing new silicone polymer resins to improve adhesion and weather resistance, and second, by incorporating various functional groups or modifying the silicone resin structure to enhance anti-fouling properties, weather resistance, and adhesion. For instance, the siloxane bonds in the main chain of silicone polymers confer exceptional hydrophobicity and weather resistance [35]. However, achieving a balance between anti-fouling performance and mechanical properties remains a significant challenge. Fluorinated anti-fouling coatings have largely concentrated on fluorinated acrylates and perfluoropolyethers, often utilizing other resins as carriers to leverage their unique atomic properties for enhanced hydrophobicity [36]. The incorporation of fluorinated groups and perfluoropolyethers into silicone-based polymers has proven effective in achieving strong anti-fouling properties. A comparative analysis of these approaches is presented in Table 1.

Table 1. Comparison of Advantages and Disadvantages of Low Surface Energy Anti-Fouling Coatings.

Types of Anti-Fouling Coatings	Research Direction	Advantages	Disadvantages
Silicone low surface energy anti-fouling coatings	Addition of small molecule silicone oil	Enhanced mechanical properties and anti-fouling properties of the coating, environmentally friendly, non-toxic	(1) The need to balance the mechanical properties of coatings with anti-fouling properties. (2) Lack of broad spectrum. (3) Poor anti-fouling performance at low speeds or under stationary conditions.
	Improvement of the coating matrix	Relatively small modulus of elasticity, non-toxic, environmentally friendly	
Organic fluorine low surface energy anti-fouling coatings	Fluorinated acrylic resins	Low surface energy, low friction, reduced fouling bio-adhesion	High processing costs and complex preparation
	Perfluoropolyether polymers	Better suppleness and lower coefficient of friction	

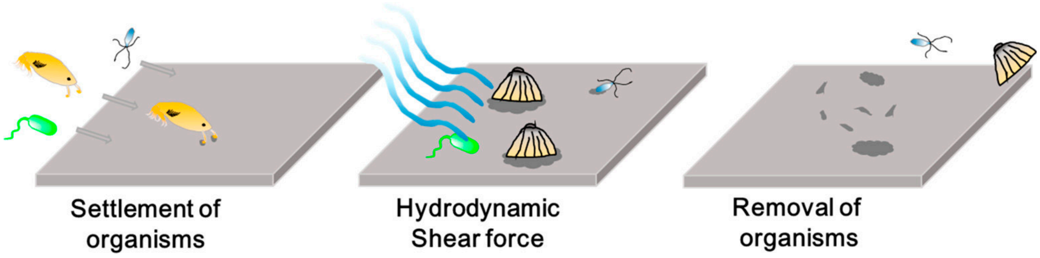


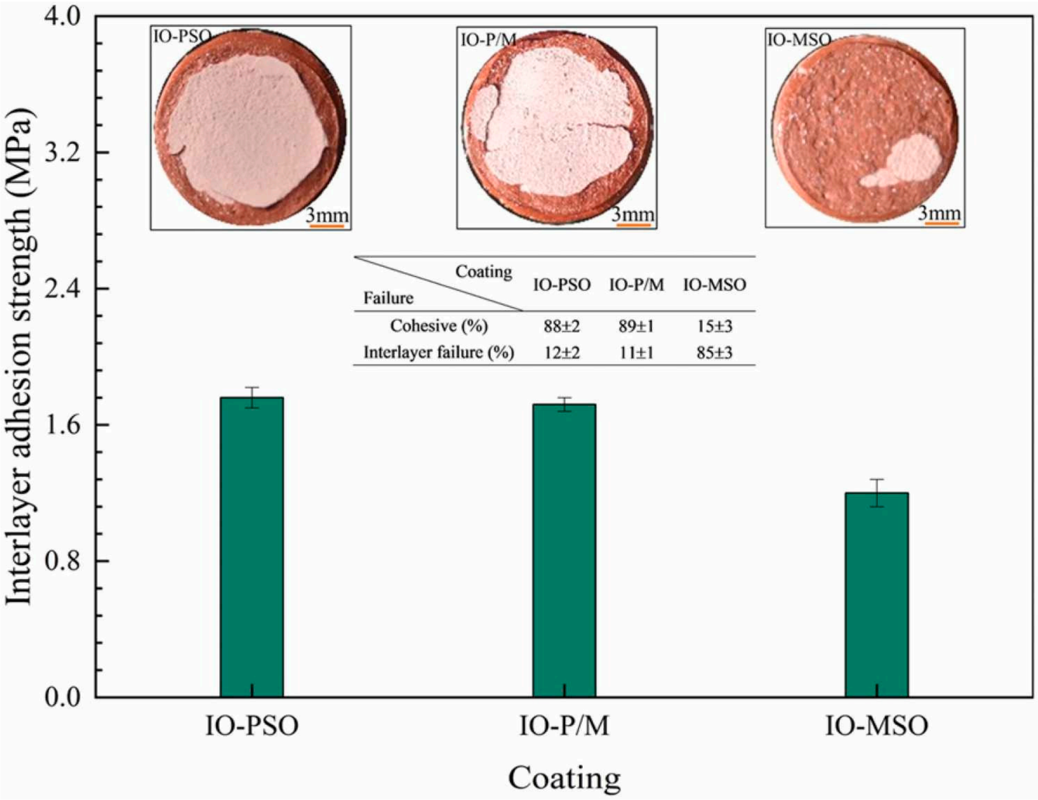
Figure 6. Schematic diagram of action principle of low surface energy anti-fouling coating [37].

3.1. Silicone Anti-Fouling Coatings

Silicone materials are known as fouling-release materials due to the high bond energy and significant bond angles of Si–O bonds, making the Si–O–Si backbone very stable with excellent weather resistance. The methyl groups in their side chains enhance the water resistance of silicone coatings and reduce the surface energy [38]. Current research strategies for silicone anti-fouling coatings include incorporating small molecule silicone oils and optimizing the coating matrix.

Silicone oils, specifically linear polydimethylsiloxane products, migrate from within the coating to the surface during a vessel's journey, creating a smooth oil film. This film helps in easily removing contaminants by water flow, thereby preventing fouling. Chen et al. [39] developed Fe_2O_3/PDMS coatings utilizing phenylmethyl silicone oil (PSO), methyl silicone oil (MSO), and their mixture. Their results, as illustrated in Figures 7–9, demonstrated that coatings incorporating PSO exhibited a higher leaching rate in air and superior properties in terms of hydrophobicity, interlayer adhesion strength, antibacterial activity, and drag reduction compared to those containing MSO. Through field testing, it was clearly observed that the adhesion strength of the IO-PSO coating was superior to that of the IO-P/M coating. After one month of immersion, no large biofouling organisms were present on the surfaces of both the IO-PSO and IO-P/M coatings, with only a layer of sludge observed. However, after 3 to 4 months of immersion, large biofouling organisms began to adhere to the IO-PSO coating. Notably, all attached fouling organisms could be removed through manual cleaning. After 4 months of immersion in seawater, the adhesion strength between the fouling organisms and the IO-P/M coating was relatively low, and at this point, the coating itself was damaged when subjected to shear forces as the fouling organisms detached. Yang et al. [40,41] incorporated high concentrations of PSO into polydimethylsiloxane (PDMS) coatings. Their findings revealed that PSO-modified silicone coatings significantly enhance anti-fouling performance by decreasing the adhesion factor (RAF). Specifically, the removal rate of bacteria increased from 17.74% to 55.56%, while the removal rate of diatoms improved from 22.46% to 52.79%. However, the inclusion of PSO negatively impacts the mechanical properties of the coating. To address this trade-off between anti-fouling performance and mechanical strength, inorganic nano-additives may be employed.

Current research on silicone-based low surface energy anti-fouling coatings predominantly addresses specific types or limited classes of marine fouling organisms, resulting in a lack of broad-spectrum efficacy. These coatings primarily depend on seawater flushing to remove biofouling, which leads to suboptimal performance at reduced ship speeds or when stationary, thereby constraining their practical application [42]. Future research should aim to improve the broad-spectrum properties of these low surface energy coatings and develop novel formulations specifically tailored for low-speed or stationary conditions through the incorporation of modified substances.



Coating Failure	IO-PSO	IO-P/M	IO-MSO
Cohesive (%)	88±2	89±1	15±3
Interlayer failure (%)	12±2	11±1	85±3

Figure 7. Multiple interlayer adhesion strength of the coatings [39].

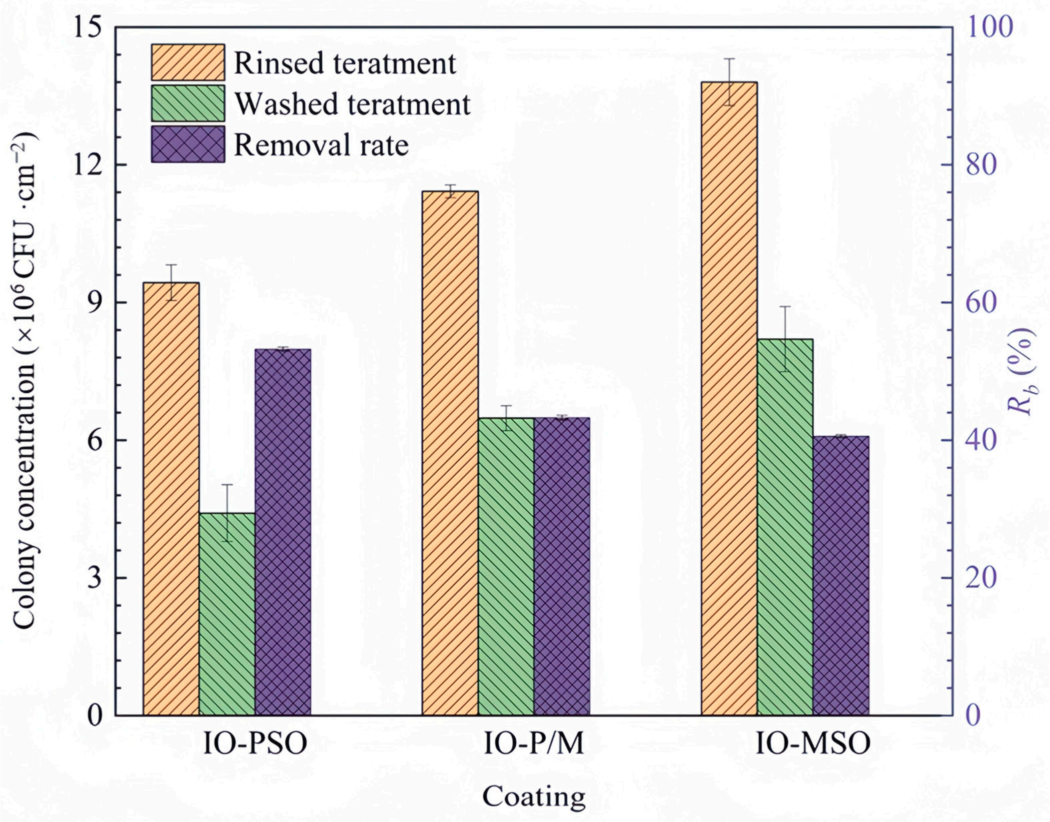


Figure 8. Colony concentration and removal rate of the coatings [39].

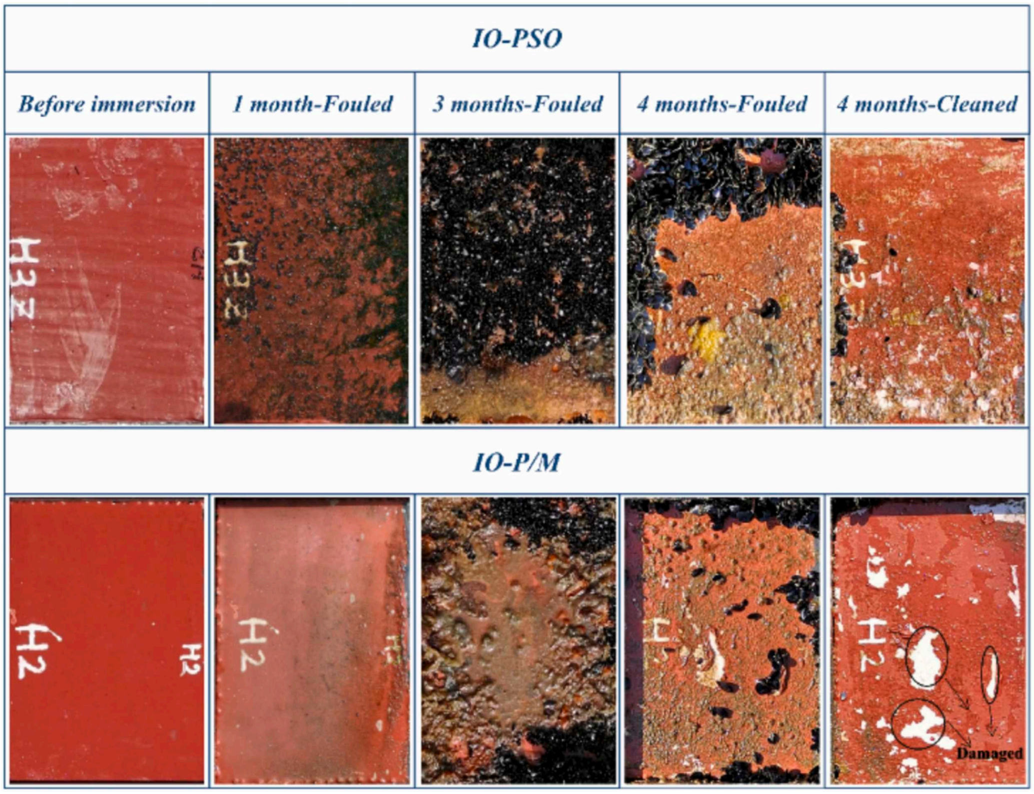


Figure 9. Photos of test panels immersed in marine environment (coating IO-MSO knocked off by the ships) [39].

3.2. Organic Fluorine Low Surface Energy Anti-Fouling Coatings

Fluorine atoms, characterized by high electronegativity, short C–F bonds, and substantial bond energy, effectively shield C–C bonds by occupying the interstitial spaces, thereby preserving their integrity. This results in fluorinated resins demonstrating exceptional chemical stability, heat resistance, and hydrophobicity. Nonetheless, polytetrafluoroethylene (PTFE) coatings, despite their porous structure, exhibit inadequate anti-fouling performance [43,44].

Current research primarily focuses on fluorinated acrylates and perfluoropolyether polymers. Zhang et al. [45] developed an underwater self-stratifying interpenetrating polymer network coating composed of fluorocarbon resin/polyacrylate (F/PAA-X, F/PBA-X). This coating, characterized by a surface enriched with fluorinated segments and micro-wrinkle structures, effectively lowers surface energy while providing exceptional anti-fouling and anti-icing properties, as illustrated in Figure 10. Yang et al. [46] synthesized a novel fluorosilicone polymer (FS-SS) incorporating disulfide bonds and vinyl groups, initiated by thiol radical reactions under UV light. This curing approach resulted in a fluorosilicone resin coating with superior hydrophobicity (minimum surface energy of 21.54 mN/m), low roughness (Ra values ranging from 2.24 nm to 12.2 nm), and high-temperature resistance, as depicted in Figure 11. Cheng et al. [47] developed a dual-functional coating with low surface energy, exhibiting both anti-fouling and anticorrosive properties, by incorporating a fluorinated crosslinked polysilazane preceramic polymer. The coating achieves a surface-free energy (SFE) below 30 mJ/m^2 and offers additional antibacterial protection. The inclusion of perfluoro surfactants in fluid polymers with polar groups creates a stable monolayer on the polymer surface, maintained during curing, which significantly lowers the critical surface tension of the base material and imparts notable low surface energy characteristics to the paint film. Song et al. [48] synthesized the copolymer poly (furan dimethacrylate-co-adipic acid butylene glycol ester) (PBAF) using menthone monomer and fluorine free-radical polymerization techniques. This coating demonstrates 98.2% antimicrobial resistance against *Escherichia coli* and 92.3% against *Staphylococcus aureus*, showcasing strong antibacterial and anti-fouling properties. Moreover, the PBAF coating is environmentally friendly and stable over extended periods, as illustrated in Figure 12.

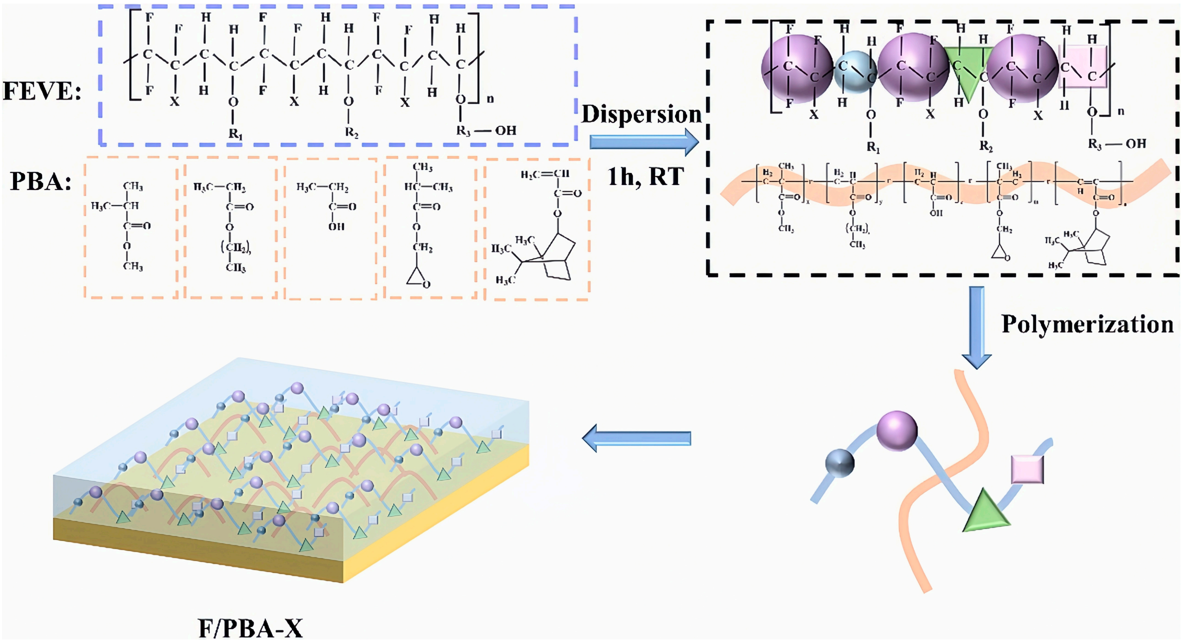


Figure 10. Design of F/PBA-X of an interpenetrating polymer network [45].

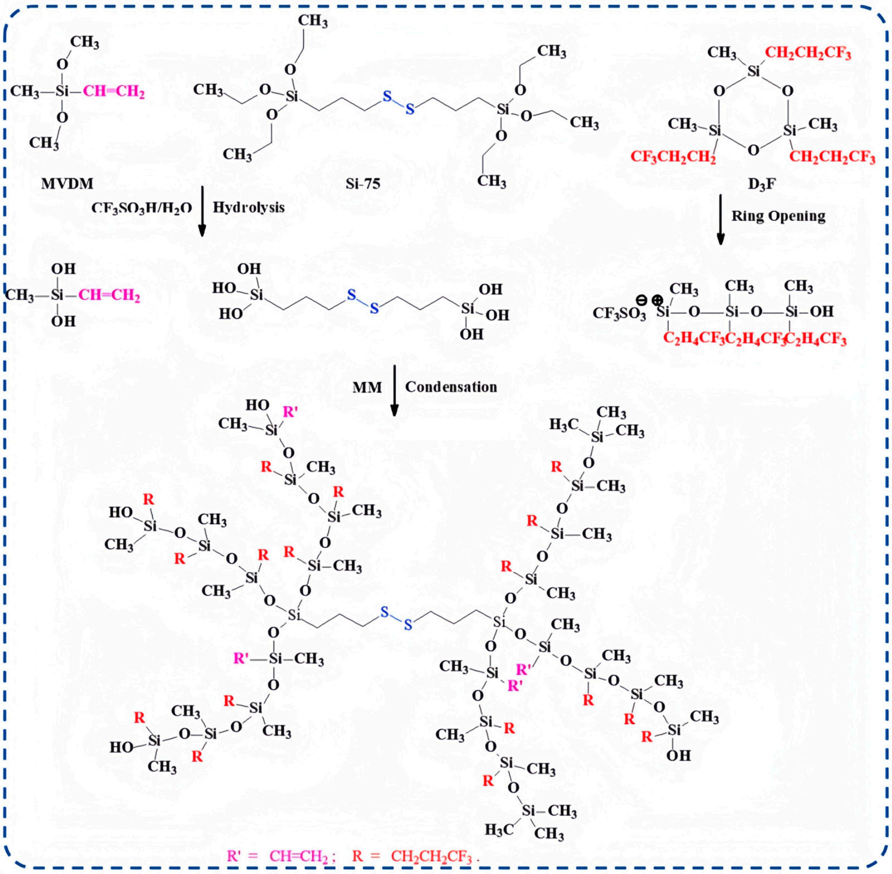


Figure 11. *Cont.*

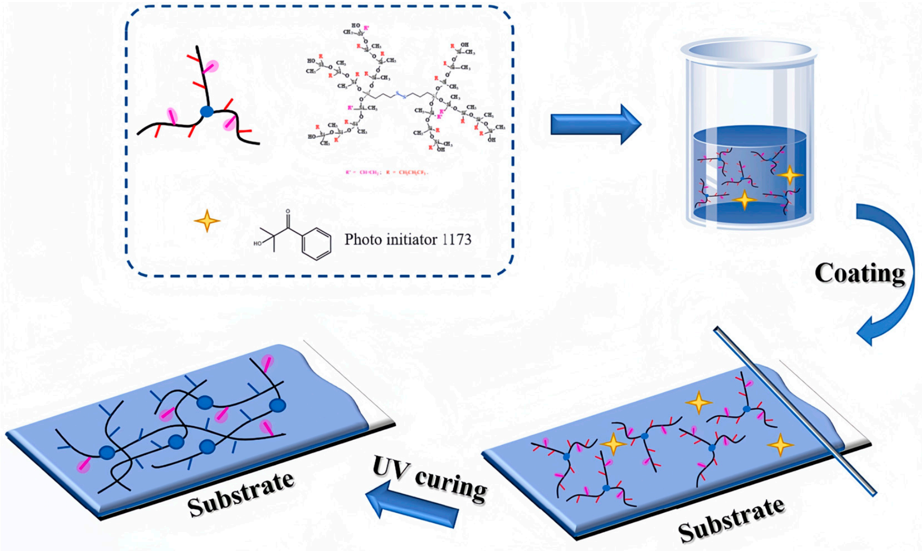


Figure 11. The synthesis of pathway of FS-SS and schematic diagram of the preparation of fluorosilicone coatings [46].

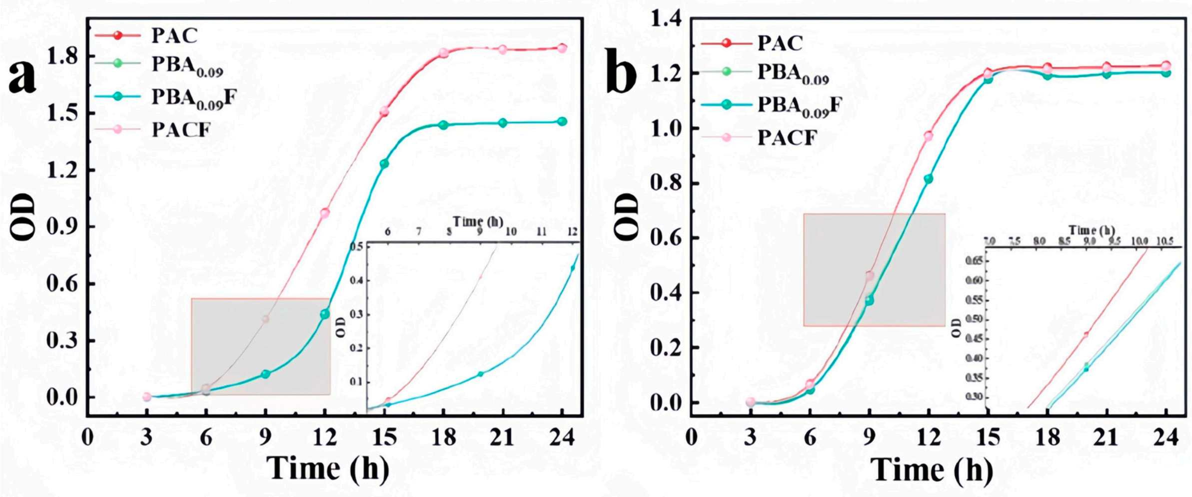


Figure 12. OD600 test of (**a**) *E. coli* and (**b**) *S. aureus* versus different samples [48].

The development of fluorine-based anti-fouling coatings, akin to their silicone-based counterparts, encounters substantial challenges. While fluororesins offer corrosion resistance, low surface energy, and anti-adhesion properties, their application is impeded by processing difficulties, high costs, and poor adhesion to substrates. Recent research seeks to address these issues by utilizing fluorosilicone as the base material for novel low surface energy anti-fouling coatings. These coatings are primarily structured with siloxane chains and incorporate $–CF_3$ groups in the side chains, which provide strong surface affinity and ensure precise orientation. This macromolecular design combines the high elasticity and excellent flow properties of linear polysiloxanes with the ultra-low surface energy of $–CF_3$ groups [49]. Silicon fluororesins, thus, merge the advantageous features of both silicone and fluorine resins, delivering superior anti-fouling performance. Despite their proven effectiveness, the complex production process and high cost currently limit their broader application in anti-fouling and drag reduction.

4. Biomimetic Anti-Fouling Coatings

Biomimetic anti-fouling coatings, or microstructured surface coatings, function by emulating the microstructures observed on biological surfaces, thereby disrupting the physical adhesion of marine organisms. Numerous marine species, including dolphins, sharks, and shellfish [50], exhibit remarkable anti-fouling properties owing to their distinctive surface microstructures. By engineering polymers that replicate these biological features, superior anti-fouling performance can be attained in biomimetic coatings. Surface chemical modification also plays a crucial role in bioinspired anti-fouling coatings. Researchers incorporate antimicrobial agents or other active components into the materials, which reduce microbial growth by mechanisms such as disrupting bacterial cell walls and interfering with cellular metabolism, thereby preventing the formation of biofouling [51]. The effectiveness of bioinspired anti-fouling coatings stems from the synergistic interaction of multiple mechanisms, including the effects of physical structure and chemical property adjustments. These mechanisms work together to help bioinspired coatings maintain excellent anti-fouling performance across various environments.

4.1. Terrestrial Plant-Based Biomimetic Anti-Fouling Coatings

Inspired by Nepenthes, which secretes mucus to form a repellent smooth layer, Ware et al. [52] incorporated silicone oil into wrinkled polymer surfaces to replicate the plant's lubrication mechanism. Bacterial adhesion tests revealed that this approach could reduce bacterial adhesion by up to 99%. Nonetheless, improvements are needed in the coating's surface morphology and the stability of the biomimetic mucus. In contrast, Jin E et al. [53] employed room-temperature vulcanized silicone rubber (RTV-2) to emulate the mucous gel layer and porous structure of soft corals, resulting in a transparent, porous coating with a clear top layer and a porous bottom layer. The addition of seven organic anti-fouling agents yielded a coating that effectively inhibited Pseudomonas fluorescens and Bacillus subtilis, with inhibition rates of 69.67% and 63.54%, respectively, after three weeks of dynamic testing. This approach demonstrates that incorporating live coral structural features into anti-fouling coatings enhances their performance.

Inspired by the radiating micro-fuzzy hairs on the surface of *Salvinia molesta*, Zhou Kai et al. [54] employed the principles of underwater three-phase contact and the adhesive properties of polydopamine (PDA) to develop a novel superhydrophobic surface. This surface emulates the *Salvinia natans* morphology, featuring hydrophilic microstructures at the tips and high adhesive properties. The resulting surface achieved a contact angle of 155.5° ± 0.7° and a rolling angle of just 6.0° ± 1.4°. The underwater solid/liquid/gas three-phase contact line influences the PDA adhesion sites, while the oxygen content within the nano-scale grooves of the structure enhances PDA adhesion.

The lotus leaf surface is renowned for its exceptional superhydrophobic properties and resistance to biological fouling [55,56]. Jiang et al. [57] demonstrated the synergistic antibacterial effect of the lotus leaf's super-repellency to bacterial culture media and its mechanical bactericidal activity against attached bacteria, through the study of its bacterial repellency and the physical rupture caused by nanotubes. Compared to conventional superhydrophobic surfaces, this type of surface can significantly extend its efficacy under harsh conditions without inducing any potential antimicrobial resistance.

4.2. Marine Bio-Based Biomimetic Anti-Fouling Coatings

Shark skin is distinguished by its rough surface, adorned with dermal denticles or rib-like structures, which confer remarkable anti-fouling and drag-reduction properties [58]. Dolphin skin, on the other hand, exhibits sinusoidal grooves aligned perpendicular to or across the direction of water flow [59]. These microstructured surfaces are critical in preventing or reducing the attachment of barnacles, algae, and bacteria.

Mo et al. [60] developed a fish-scale-like micro/nanostructured surface by modifying a PDMS coating on a phenylmethylsilicone oil (PSO) substrate with a monolayer of polystyrene (PS) microsphere arrays. This PSO/PDMS-PS coating outperformed both unstructured PSO/PDMS and conventional silicone coatings in terms of antiadhesion activity against marine bacteria and the benthic diatom Navicula sp. Furthermore, the presence of PS microspheres substantially reduced the release rate of PSO, extending the coating's service life, with a sustained release efficiency reaching 23.2% (see Figure 13).

Lin et al. [61] fabricated a shark-skin-like surface using a polymer blend of PDMS, PVA, and methacryloyloxyethyl phosphorylcholine (PMPC), which effectively resisted *E. coli* adhesion. Dundar et al. [62] replicated shark-skin-like micro/nanostructures on a PET substrate using Norland optical adhesive and incorporated titanium dioxide nanoparticles (TiO_2 NPs) with photocatalytic antibacterial properties to create a superhydrophobic nano-coating (see Figure 14). The addition of TiO_2 NPs increased the contact angle from 30° to 100°. With 90 wt % TiO_2 NPs, the coating's hardness and modulus rose significantly from 0.28 MPa and 4.8 MPa to 0.49 GPa and 16 GPa, respectively, and reduced *E. coli* adhesion by approximately 70% compared to a smooth coating with the same chemical composition, demonstrating notable antibacterial efficacy. As shown in Figure 15, Qin et al. [63] improved a flexible polyurethane (PU) coating by incorporating snake holes (OST) to form a PUx/OSTy composite coating inspired by dolphins. This composite demonstrated drag reduction rates ranging from 8.20% to 12.65% at flow speeds between 1 and 6 m/s. Both dynamic and static anti-fouling tests revealed that the coating effectively inhibited green algae and diatoms, with efficiencies reaching up to 98.4% and 97.5%, respectively, highlighting its superior anti-fouling performance.

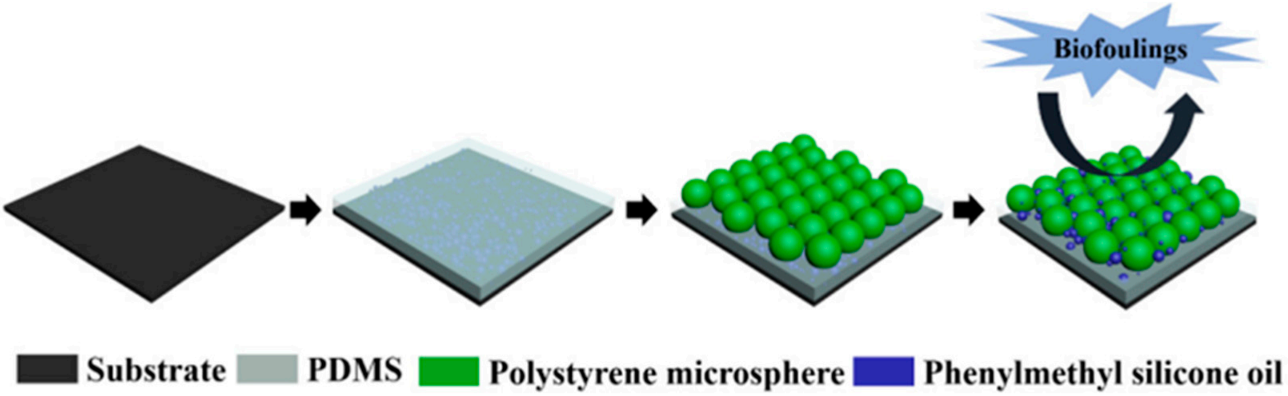


Figure 13. A schematic illustration of the fabricating process of phenylmethylsilicone oil/polydimethylsiloxane-polystyrene (PSO/PDMS-PS) composite coating [60].

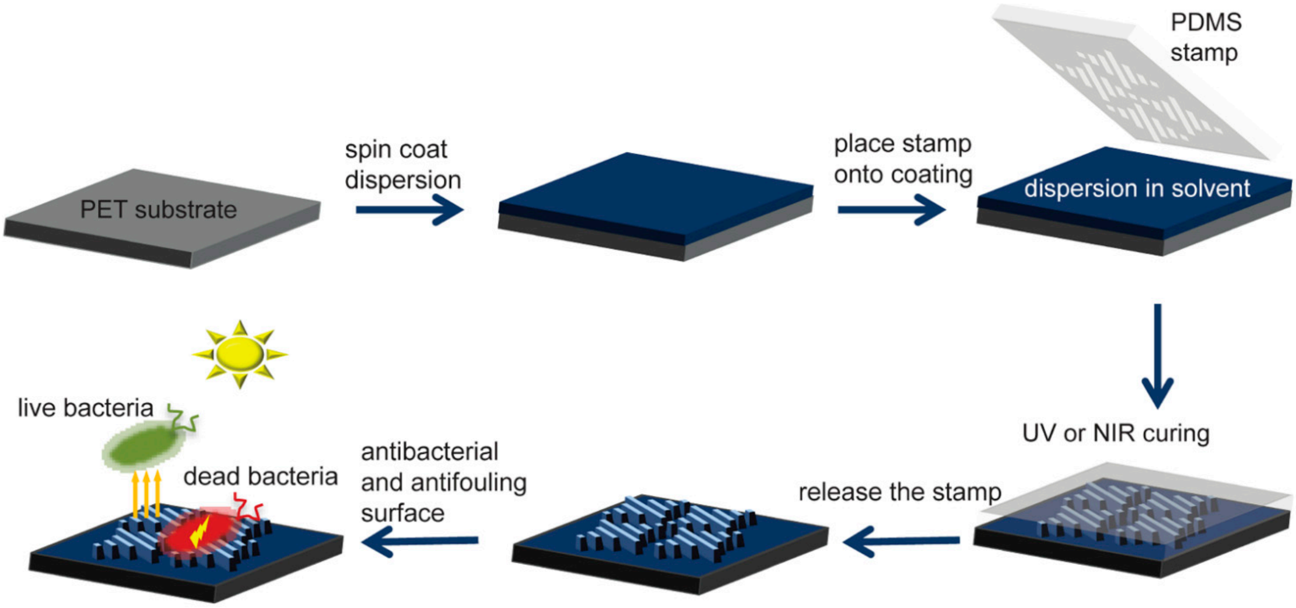


Figure 14. Preparation technology of bionic shark skin pattern [62].

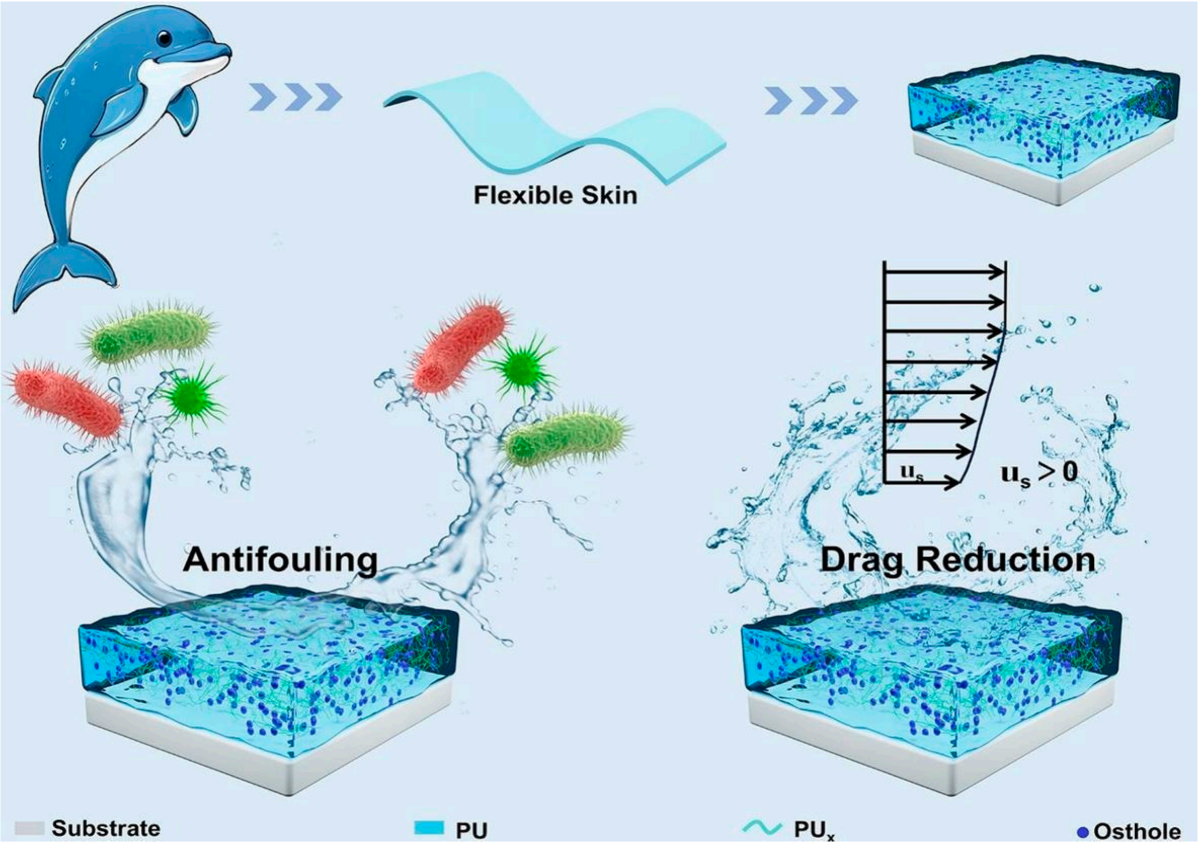


Figure 15. Dolphin-inspired anti-biofouling and drag-reducing PUx/OSTy coatings with different flexibilities [63].

Biomimetic anti-fouling coatings offer an eco-friendly alternative by eliminating the need for biocides and avoiding the release of toxic substances into seawater. Despite their environmental benefits, these coatings face challenges due to the complexity of their surface microstructures, limited mechanical strength, and difficulties in repair, which often result in suboptimal performance in real marine conditions. Addressing these issues through the development of self-healing capabilities and cost-effective production methods presents significant opportunities for improvement. Advances in microelectromechanical systems (MEMS) and laser repair technologies suggest that biomimetic anti-fouling coatings hold considerable promise for future applications.

5. Nano-Anti-Fouling Coating

Nanomaterials in anti-fouling coatings, such as nanosilver, can gradually release active ingredients with antibacterial properties. These active particles create an antibacterial environment on the coating surface, inhibiting the growth of marine organisms. By controlling the chemical properties of the coating surface and the release rate of the active substances, a sustained anti-fouling effect is achieved [64,65]. Based on different anti-fouling mechanisms, these can be divided into two main categories as shown in Table 2.

Table 2. Comparison of advantages and disadvantages of nano-anti-fouling coatings.

Coating Category	Anti-Fouling Mechanisms	Advantages	Disadvantages
Release-type Nano-Anti-Fouling Coating	The release of nanoparticles and ions kills bacterial cells and inhibits the growth of soiled materials	Enables controlled release and better anti-fouling at lower concentrations	(1) The slow release of anti-fouling agents leads to the gradual loss of anti-fouling activity. (2) The anti-fouling mechanism of some nano-anti-fouling agents is still unclear.

Table 2. *Cont.*

Coating Category	Anti-Fouling Mechanisms	Advantages	Disadvantages
Nanocomposite anti-fouling coatings	Multiple anti-fouling strategies work synergistically	(1) Improve the adhesion, hardness, finish, and aging resistance of the coating. (2) The formed micro- and nanocomposite structures can improve the hydrophobicity of the samples and obtain the self-cleaning effect.	High processing costs and complex preparation

5.1. Release-Type Nano-Anti-Fouling Coating

Release-type nano-anti-fouling coatings represent a cutting-edge fusion of nanotechnology and controlled release mechanisms. These advanced coatings leverage nanoparticles to deliver anti-fouling agents effectively. The nanoparticles or released antimicrobial ions penetrate microbial cells, induce the generation of reactive oxygen species (ROS), and disrupt microbial activity, thereby mitigating biofouling [66,67].

Among various antimicrobial agents, silver (Ag) stands out for its broad-spectrum efficacy. Silver ions exhibit potent antimicrobial activity through multiple mechanisms, including inhibition of proton motive force (PMF), disruption of the respiratory electron transport chain, and alteration of cell membrane permeability, ultimately leading to cell death. Notably, the bactericidal effectiveness of silver nanoparticles (AgNPs) is significantly enhanced by their surface effects [68]. In nanocomposite anti-fouling coatings, silver nanoparticles serve as the primary active component. These coatings are formulated with organic polymers as the matrix, organic solvents to modulate viscosity, and various fillers and additives [69]. Johurul et al. [70] synthesized silver nanoparticles using pomegranate leaf extract and evaluated their antibacterial properties. The preparation process is shown in Figure 16. The results demonstrated that these nanoparticles, produced with guava-mediated synthesis, exhibited substantial antibacterial activity against both Gram-positive (*Staphylococcus aureus*) and Gram-negative (*Escherichia coli*) bacteria. Li Xiaoyu et al. [71] developed a nanosilver anti-fouling coating incorporating acrylic resin and rosin as film-forming agents, with xylene and n-butanol as solvents. This coating demonstrated impressive sterilization rates of 99.6% against Bacillus subtilis and 99.4% against Arthrobacter chlorophenolicus after 24 h of exposure. During ship navigation, the coating's released silver nanoparticles effectively eliminated bacteria on the hull surface, thereby preventing biofouling and fulfilling the protective role for ship hulls [72,73].

The integration of silver nanoparticles (AgNPs) into coating surfaces has emerged as a promising strategy for anti-fouling applications. However, challenges such as nanoparticle aggregation and uncontrolled release during AgNP synthesis currently limit their broader applicability [74]. To address these issues, Song et al. [75] employed a novel approach by coating Fe_2O_3 nanorods with 1H,1H,2H,2H-perfluorododecyltriethoxysilane (FSA) and subsequently applying FSA-modified SiO_2 particles onto the Fe_2O_3 nanorod array (designated as HPC@Fe_2O_3). This multi-step modification mimics the complex nanostructures observed in insect compound eyes. The resulting array demonstrated exceptional superhydrophobicity, with a contact angle of 175° and a sliding angle of 3.5°. This study underscores the potential of chemical surface modification in enhancing nanoparticle dispersion and imparting novel functional properties to materials.

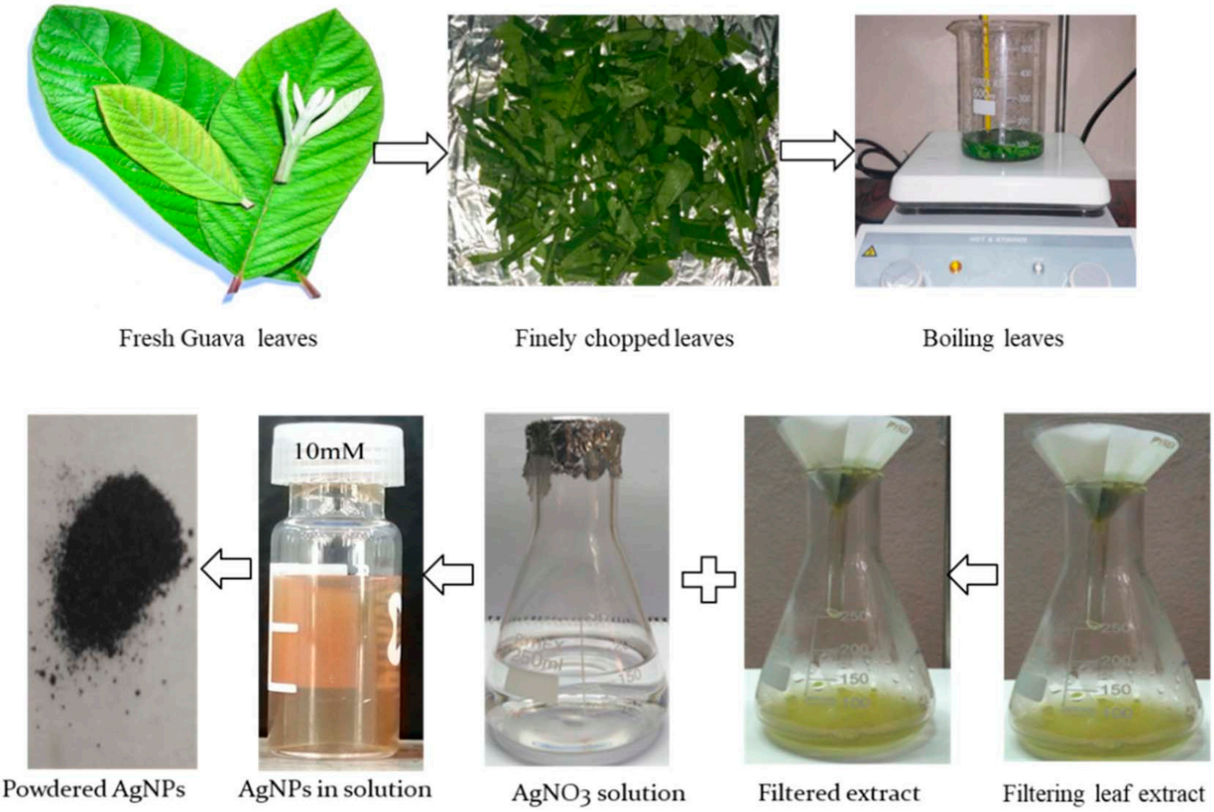


Figure 16. Schematic representation for the synthesis of *P. guajava* leaf-extract-mediated AgNPs [70].

5.2. Nanocomposite Anti-Fouling Coatings

Nanocomposite anti-fouling coatings are advanced materials that operate at the nanometer scale, combining a base material with nanoparticles and additives. These coatings integrate anti-fouling agents, including silver nanoparticles, titanium dioxide nanoparticles, and silica nanoparticles, within a resin matrix. The unique attributes of nanoparticles—such as their high surface area, strength, exceptional dispersion, and stability—significantly enhance both the anti-fouling performance and environmental benefits of these coatings. PDMS is commonly employed in nanocomposite anti-fouling materials due to its thermal resistance, UV stability, hydrophobicity, and inherent anti-fouling properties. Research has focused extensively on the formulation of PDMS nanocomposites, incorporating inorganic nanofillers like Al_2O_3, ZnO, and Ag. By meticulously controlling the size, type, and morphology of these fillers, the anti-fouling efficacy and mechanical stability of the coatings can be markedly improved [76].

Salas et al. [77] developed a copper selenide (CuSe NP) nanocomposite anti-fouling coating by incorporating CuSe nanoparticles modified with gum arabic into a water-based acrylic polymer matrix. The release of selenium ions facilitates strong adhesion of the coating to metal substrates. Antimicrobial assays revealed that the coating effectively inhibits the growth of *Escherichia coli* and *Candida albicans*. In a separate study, Jiang et al. [78] employed free-radical polymerization to synthesize a linear fluorinated copolymer (L-SF) from 3-mercaptopropyl trimethoxysilane (MPTES) and 1H,1H,7H-perfluorooctyl methacrylate (DFMA). The results are depicted in Figures 17 and 18. This copolymer was condensed with α, ω-dihydroxy dimethylsiloxane, tetraethyl orthosilicate (TEOS), and inorganic nanoparticles to produce a superhydrophobic coating with continuous micro/nanostructures. α, ω-Dihydroxy polydimethylsiloxane is a dihydroxy compound containing siloxane groups, imparting hydrophobic characteristics to the polymer. TEOS is utilized to form a siloxane network, which enhances the structural integrity of the coating, while the incorporation of inorganic nanoparticles promotes the integration with other components, leading to the formation of a micro/nanostructured surface, further reinforcing the hydrophobic properties. Experimental results indicate that the coating achieved a water contact angle of 162°, a sliding angle of 2°, and an adhesion strength exceeding 2 MPa across various substrates. It also demonstrated a 97.8% antibacterial rate against *Staphylococcus aureus*, highlighting its superior hydrophobicity and anti-fouling performance.

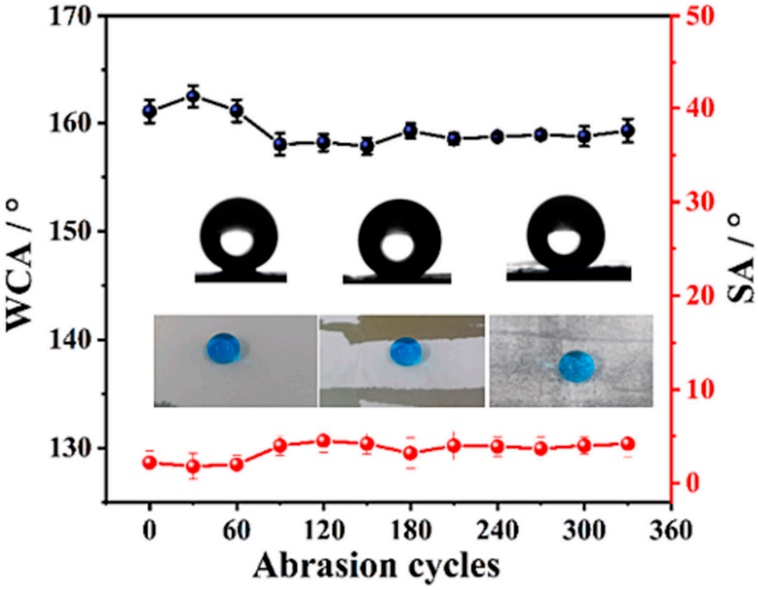


Figure 17. Variation in WCAs and SAs of the PDMS-20%SiO_2-16%TiO_2 coating with wear cycles [78].

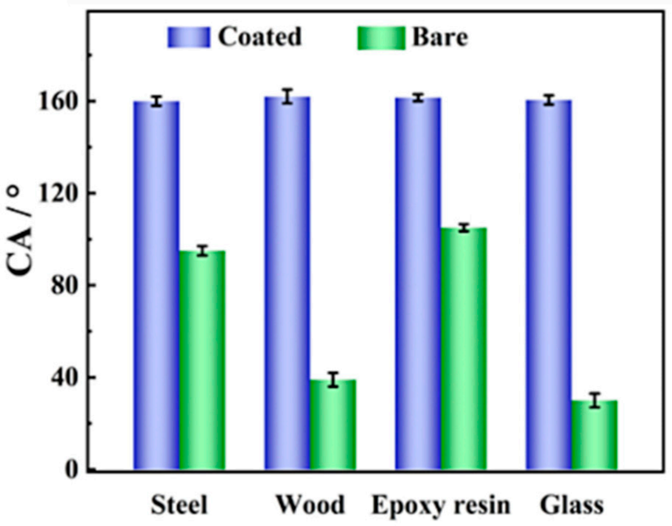


Figure 18. Ground adhesion and WCAs of water droplets on carbon steel, wood, epoxy resin plate, and glass plate [78].

Organometallic frameworks (Fe-MOFs) are prized for their cost-effectiveness and non-toxic properties, reducing the reliance on harmful heavy metals such as copper and tin, which can be detrimental to marine ecosystems Chang et al. [79] developed a composite anti-fouling agent (Fe_3O_4@Fe-MOF@Ag) by integrating silver nanoparticles into magnetic Fe-MOFs via co-precipitation and hydrothermal methods. As illustrated in Figure 19, the anti-fouling mechanism involves magnetic treatment, which facilitates the mobilization of AgNPs-containing magnetic fillers to the coating surface. This process enhances the efficacy of the anti-fouling agents within the coating, leading to superior anti-fouling performance.

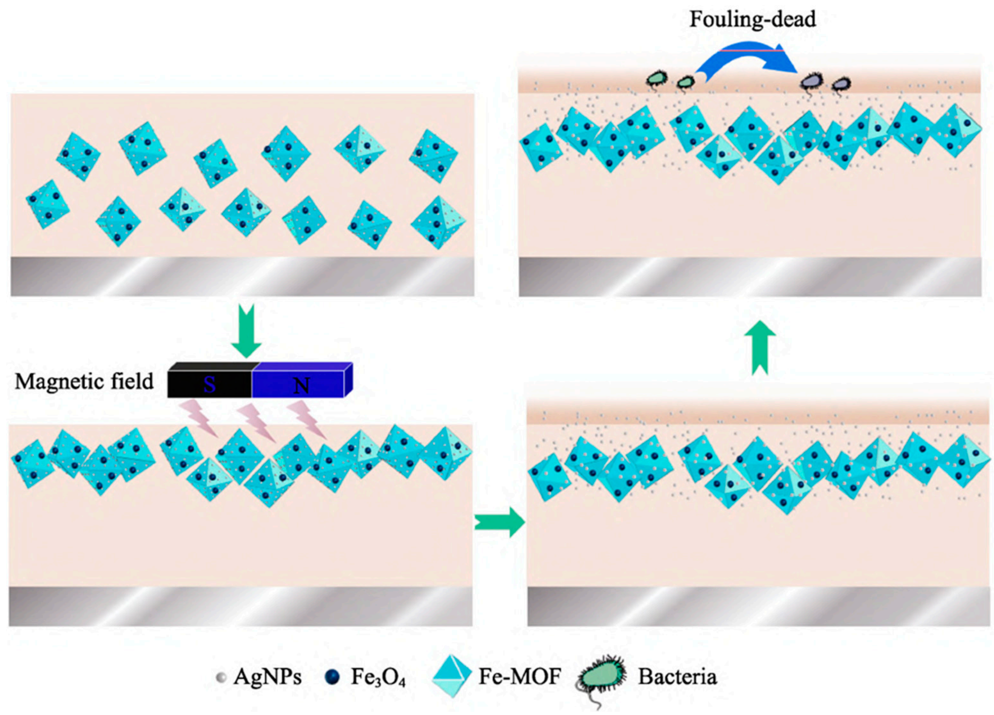


Figure 19. Antibacterial mechanism of Fe_3O_4@Fe-MOF@Ag-PDMS composite coating [79].

Nanotechnology-based composite coatings can utilize multiple anti-fouling strategies concurrently. Despite advances in understanding the micro-scale roughness and nano-scale structures of these materials, challenges remain in achieving stable dispersion within coatings and ensuring the long-term stability of nanoparticles. By optimizing dispersion techniques, coating formulations, and incorporating high-performance dispersants, the uniform distribution of nanoparticles in the matrix can be improved. Furthermore, selecting nanoparticles compatible with the base material is crucial for maintaining the storage stability of the coating, thus ensuring enduring anti-fouling efficacy.

6. Conclusions and Prospects

This paper begins with an in-depth analysis of marine biofouling mechanisms, emphasizing recent advancements in anti-fouling technologies. It explores the effectiveness and limitations of self-polishing coatings, low surface energy coatings, biomimetic coatings, and nano-coatings. The paper critically evaluates the advantages and drawbacks of each type. Conclusively, the future prospects for the application of anti-fouling coatings in ships and the relevant regulatory framework were discussed.

(1) Despite significant advancements in resins and biocides, self-polishing coatings continue to grapple with high production costs, limited anti-fouling durations, and constrained strategies. Future research should prioritize optimizing coating components, developing novel eco-friendly biocides, and harnessing nanotechnology alongside biological anti-fouling methods to enhance performance, environmental sustainability, and durability.

The regulatory policy for self-polishing coatings is primarily governed by the 2001 International Convention on the Control of Harmful Anti-fouling Systems on Ships (AFS Convention), which explicitly prohibits the use of toxic organotin compounds, such as tributyltin (TBT), as active ingredients in self-polishing anti-fouling coatings. The European Union's Registration, Evaluation, Authorization, and Restriction of Chemicals (REACH) regulation imposes strict requirements for the registration, evaluation, and authorization of chemicals used in self-polishing anti-fouling coatings, ensuring that they do not cause irreversible damage to aquatic ecosystems. In the future, the regulatory framework will need further improvement to keep pace with the rapid development of self-polishing coating technology and its potential environmental impacts [80,81].

(2) Low surface energy materials have proven effective in reducing marine organism attachments, thereby decreasing cleaning and maintenance frequency. Compared to traditional coatings, these materials are non-toxic, environmentally friendly, and exhibit prolonged durability. Nonetheless, challenges such as long-term stability in harsh marine environments and efficacy against a broad spectrum of species persist. Future research should focus on creating self-cleaning anti-fouling coatings utilizing biocompatible materials to achieve enhanced, eco-friendly, and durable anti-fouling performance.

The current regulatory framework for low surface energy anti-fouling coatings is also based on the International Maritime Organization's (IMO) AFS Convention and the EU's REACH regulation. While the environmental friendliness of these coatings has led to their widespread use globally, chemical regulatory standards vary across countries and regions, and assessments of their long-term ecological impact and degradation by-products remain insufficient. Therefore, future regulatory frameworks must enhance environmental monitoring and assessment of low surface energy coatings to address the potential impacts of these new materials.

(3) Biomimetic anti-fouling coatings present a promising approach by leveraging specific antibacterial functional groups to inhibit fouling. However, these coatings remain in the early stages of development. Issues such as the low conversion efficiency of synthetic biomimetic agents and substantial challenges in practical applications due to process constraints hinder progress. Future research will need to deepen the understanding of biomimetic anti-fouling mechanisms, develop innovative solutions, and employ artificial intelligence to optimize coating design and performance prediction, thereby addressing current limitations.

The regulatory framework for existing bio-inspired anti-fouling coatings is still being refined, with international and regional marine environmental protection regulations serving as its foundation, complemented by national technical standards. However, the main challenge in the current regulatory framework is the lack of sufficient empirical data and monitoring mechanisms to assess the long-term ecological impact of bio-inspired anti-fouling coatings. Therefore, future regulatory frameworks may need to incorporate more comprehensive scientific assessment mechanisms to address the emerging environmental concerns associated with bio-inspired anti-fouling coatings.

(4) Release-based nano-anti-fouling coatings hold significant potential for preventing marine biofouling. However, nanoparticles can be released during the manufacturing and application processes, leading to cumulative toxic effects on the marine environment. Numerous studies have demonstrated the potential toxicity of nanoparticles, and their possible disruption of the marine food chain has drawn considerable attention from environmental scientists. Additionally, uncertainties surrounding the release rate and high production costs pose challenges to the practical application of nano-coatings. Future research should focus on optimizing the distribution and stability of nanoparticles to achieve efficient and controlled anti-fouling coatings. Surface modification and functionalization of nanomaterials will be essential to reduce their mobility and toxicity in the environment. Regulatory measures on nano-coatings are still evolving. Although the International Maritime Organization (IMO) and the European Union's REACH regulation have imposed strict limits on the chemical components in some coatings, specific regulatory measures for nanomaterials are not yet well developed [82,83].

As more research uncovers the long-term environmental impact of new anti-fouling coatings, regulatory frameworks will be further refined. In the future, the life cycle analysis of coatings, including their production, use, and degradation, may become a key focus of regulation. Additionally, deeper international cooperation will foster global regulatory alignment for environmentally friendly coatings, ensuring the sustainable development of marine environments. Overall, new anti-fouling ship coatings show great promise in reducing toxic emissions and protecting marine ecosystems, but their potential long-term environmental impacts still require further empirical research. With the rapid advances in materials science, chemistry, and bioengineering, future anti-fouling coatings will likely be characterized by low toxicity, biodegradability, and environmental friendliness, with the development of synergistic anti-fouling technologies as the primary direction.

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