

Development of Antifouling Strategies for Marine Applications

Subjects: [Microbiology](#) | [Materials Science, Coatings & Films](#)

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Marine biofouling is an undeniable challenge for aquatic systems since it is responsible for several environmental and ecological problems and economic losses. Several strategies have been developed to mitigate fouling-related issues in marine environments, including thermal stress, osmotic shock, deoxygenation, and the development of marine coatings using nanotechnology and biomimetic models, as well as the incorporation of natural compounds, peptides, bacteriophages, or specific enzymes on surfaces.

biofilms

antifouling surfaces

marine biofouling

marine coatings

1. Introduction

Marine biofilm development is a complex and dynamic process comprising several organisms and interactions, which can be affected by different factors, from surface properties to environmental parameters and microbial content [\[1\]\[2\]\[3\]\[4\]](#). Indeed, biofilms are a common feature on all aquatic submerged surfaces, contributing to marine biofouling, which is responsible for several detrimental impacts on shipping efficiency, aquaculture industries, equipment corrosion, and maintenance, as well as disturbances in ecosystems [\[5\]\[6\]\[7\]](#). Since cell adhesion and biofilm formation are primordial steps to macrofouling, the most promising marine biofouling mitigation approach is delaying and controlling microfouling events [\[8\]\[9\]](#).

Even though the schematic conceptual biofilm developmental model based on five stages (reversible attachment of planktonic cells, irreversible attachment, biofilm maturation by the development of microcolonies and high extracellular polymeric substance (EPS) production, maturation of the biofilm, and dispersal/detachment) has been widely generalized to describe all biofilms [\[10\]](#), this model does not necessarily describe the complexity of biofilms in the real world, including industrial, clinical, and natural settings as marine environments. Indeed, this model was recently reviewed by the scientific community, which proposed a most inclusive model involving three major events: aggregation, growth, and disaggregation [\[11\]](#). Therefore, although no developmental model accurately represents biofilm formation for all microorganisms, numerous *in vitro* systems have been designed to study biofilm formation and development to better mimic real conditions [\[12\]\[13\]](#). Moreover, some of these *in vitro* studies are posteriorly validated and/or confirmed by *in situ* studies in real marine environments [\[14\]](#). The advantages and limitations of both study types must be considered when choosing the most appropriate method.

There is a pressing need to develop novel antibiofilm surfaces to manage concerns associated with marine fouling and comply with the increasingly strict and demanding legislation in this area [\[15\]\[16\]](#). Some of these policies involve

banning biocides or antifouling paints due to their high persistence and toxicity on non-target marine organisms [17], as well as providing guidelines for the control and management of ship biofouling to minimize the transfer of invasive aquatic species [18]. Several marine coatings have been developed and tested under *in vitro* and/or *in situ* assays. Advancements in polymer science, nanotechnology, and the progress of innovative surface models inspired by nature are expected to significantly impact the improvement of antifouling methodologies, contributing to the development of a new generation of environmentally friendly marine coatings.

2. Marine Biofouling

Marine biofouling is a dynamic natural process that comprises both microfouling and macrofouling events. Although the diversity and prevalence of fouling organisms depend on geographic location, seasonal variations, and different interactions [19], microfouling includes forming a conditioning film over the submerged surface, the adhesion of microfouler organisms (mainly bacteria, cyanobacteria, and diatoms), followed by biofilm development. In turn, macrofouling implies the attachment and settlement of soft fouler organisms, such as algae, corals, sponges, anemones, tunicates, hydroids, and additional marine invertebrates (e.g., larvae of brine shrimp), as well as barnacles, mussels, bryozoans, and tubeworms (hard fouler organisms) (Figure 1) [19][20].

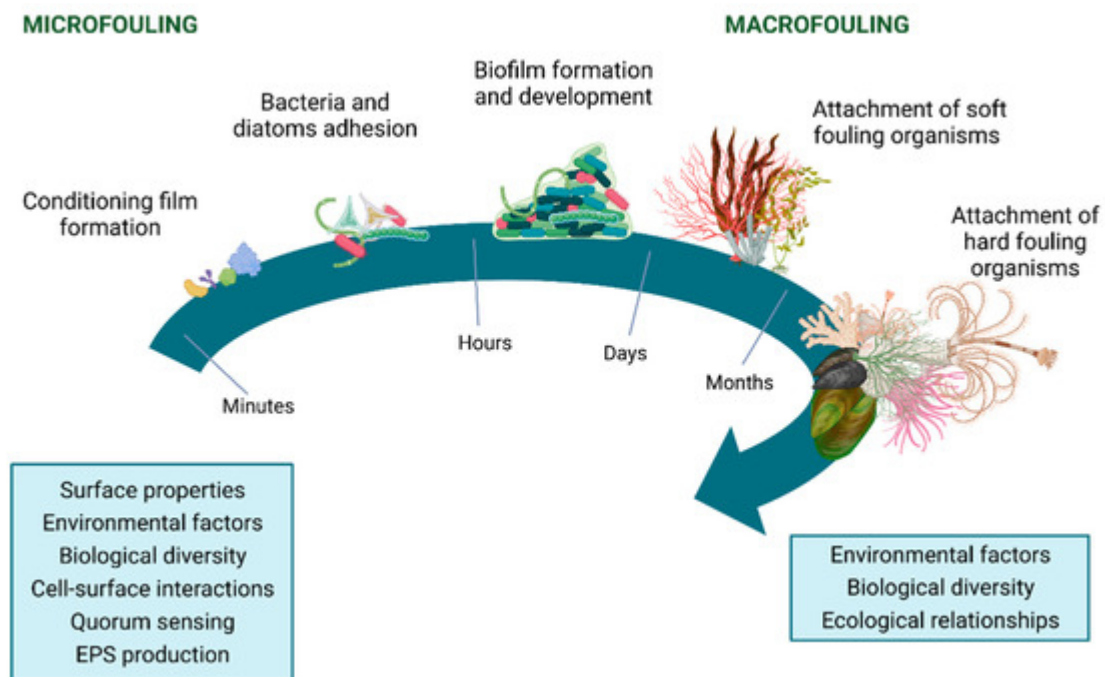


Figure 1. Representation of the marine biofouling process and the main parameters/factors that affect microfouling and macrofouling events. Microfouler organisms include mainly marine bacteria, cyanobacteria, and diatoms, while macrofouler organisms comprise algae, corals, sponges, anemones, tunicates, hydroids, and additional marine invertebrates (soft macrofouler organisms), as well as barnacles, mussels, bryozoans, and tubeworms (hard macrofouler organisms). This image was created with the software BioRender (<https://biorender.com/>).

After the first minutes of immersion, the physicochemical properties of the submerged surface may be modified by the formation of a film comprised of inorganic and organic molecules from the surrounding environment, including glycoproteins, proteoglycans, and polysaccharides, which make the surface more wettable. The adhesion of these molecules provides nutrition and attachment points for organisms, affecting the adhesion and biofilm formation by microfouler organisms [21]. By a reversible process caused by different weak forces [22], as well as due to the bacterial organelles which promote cell attachment to the surfaces [23], the first cells adhere to the conditioning film surface. The irreversible adhesion of microfouler organisms and biofilm formation are driven by different types of physicochemical interactions with the surface, by the secretion of EPS from cells [21], and by quorum-sensing (QS) phenomena [24][25]. Biofilm development and maturation proceed with a greater production of EPS, which acts as a glue, having a significant impact on the cohesion and the protection of biofilms against environmental alterations and predation, as well as on the promotion of genetic information exchange [26][27]. Indeed, the EPS matrix may account for 50% to 90% of the biofilm composition, depending on the species present, the stage of biofilm development, and the environmental conditions [28]. The remaining percentage corresponds to the embedded organisms. The influence of biofilms on the settlement of macrofouling organisms is modulated by the spatial and temporal heterogeneity of marine environments, which suffer variations in terms of hydrodynamics, surface energy, topography, hydrophobicity, nutrients, and organic matter availability, as well as biological dispersal and aggregation at the microhabitat level [29][30]. Moreover, biological factors and ecological relationships such as parasitism, mutualism, commensalism, competition, and predation may affect macrofouling events (**Figure 1**).

The effects of marine biofouling involve an increase in direct costs either for maintenance or cleaning procedures, as well as indirect costs resulting from the efficiency loss of maritime industries. Additionally, issues related to human health, marine ecology, and the environment are also a matter of concern (**Figure 2**). The effect of marine biofouling on aquatic ecosystems is important as it disturbs species richness and genetic diversity [31]. Although several guidelines are discussed and implemented for the management of marine invasive species [5][18][32], the invasion of exotic species from different geographic areas continues to present a negative impact on global biodiversity since novel interactions between exotic and native species can be established, affecting predation and competition events [31][33]. Indirectly, marine biofouling contributes to climate change, environmental pollution, and global warming due to air pollution and greenhouse gas emissions promoted by the increased hydrodynamic drag and friction of vessels and ships [34]. Additional environmental and health-related problems involve the contamination of aquaculture facilities, such as fish cages and shellfish sites, the possibility of cyanobacterial blooms from benthic mat proliferations, and water contamination by the accumulation of toxins produced by some fouler organisms [6]. The economic impact of marine biofouling on industrial activities such as heat exchangers, water desalination stations, marine transport, aquaculture, gas, and oil industries remains relatively high. The direct economic costs of managing marine biofouling in the aquaculture industry are estimated to be around 10% of production costs [35]. The impacts on aquaculture infrastructures include the increased disease risk for marine animals, as well as human health effects due to biofoulers and associated pathogens, modified hydrodynamics in and around the cage affecting oxygen levels, water quality, and the cage's volume and stability, increased weight, and physical damage that culminate in substantially reduced productivity [6]. In turn, in marine transport, around 35–50% of costs are concerned with increased fuel consumption [36], and in the gas and oil industry, about 20–30%

are material corrosion costs [37]. In addition to the material corrosion of different facilities and infrastructures and costs related to cleaning, paint removal, and repainting, marine biofouling can prompt increased maintenance operations on submerged equipment. Moreover, specific areas of the vessels are highly prone to accumulating biofouling since they are often hidden, are difficult to inspect and treat, and can rapidly lose antifouling protection [38]. Examples of these niche areas include the internal pipework of vessels, dry-docking support strips, bow thrusters, rudders, and propeller shafts [39]. Additionally, a decrease in the precision of measurements on submerged devices, such as electrochemical and optical sensors, may also be promoted by the formation of a biofilm on the optics of these devices [40].

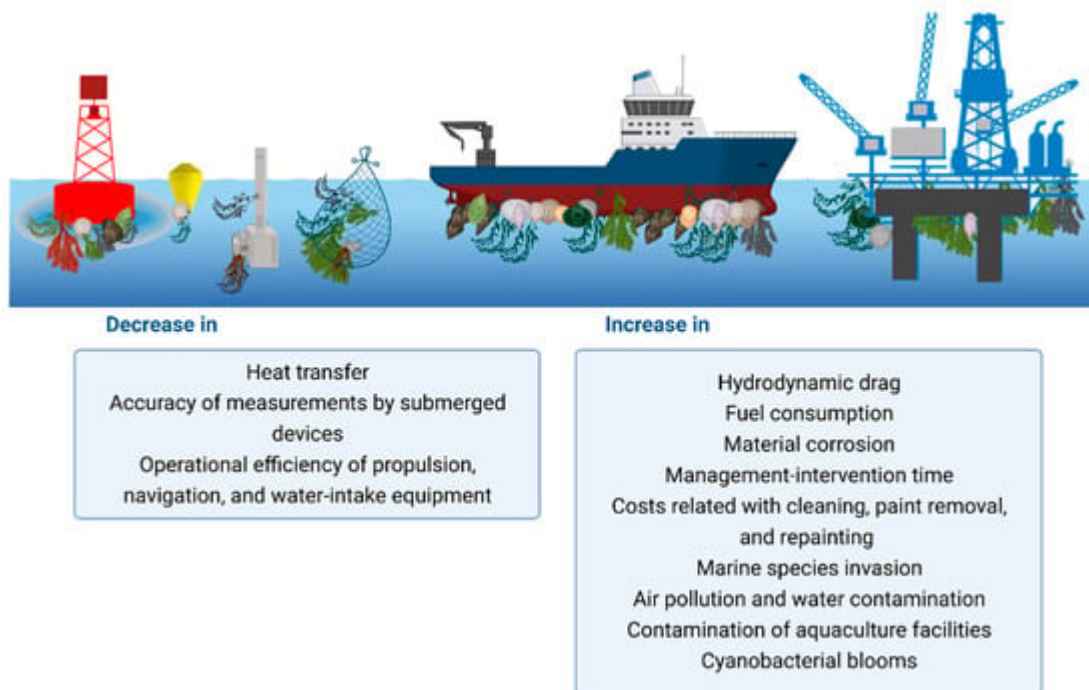


Figure 2. Main consequences of marine biofouling. This graphic representation shows the major effects of marine biofouling on submerged devices/equipment, such as sensors, buoys, cameras, aquaculture facilities, ships, and oil and gas platforms. This image was created with the software BioRender (<https://biorender.com/>).

3. Marine Antifouling Strategies

Several strategies have been used to mitigate the effects of marine biofouling. These approaches can prevent and/or delay biofilm development and the attachment of macrofoulers, comprising antimicrobial, antibiofilm, and antifouling surfaces [41], or control already established biofilms and fouling communities (Figure 3, Table 1). Control methodologies involve using bacteriophages, enzymes, QS inhibitors, disinfectants, additional treatment methods, and cleaning technologies [38][42][43][44][45] (Figure 3). A range of criteria should be evaluated to select the most suitable marine antifouling strategy, including effectiveness, safety, biosecurity, compatibility with the materials of devices/equipment, and feasibility. First, effectiveness implies evaluating the activity, concentration, or intensity spectrum of antifouling activity and required exposure time. The antifouling strategy must be safe for the environment (ecotoxicological safety) and operators, as well as not exacerbate the biosecurity risk of releasing and

establishing non-indigenous species. Moreover, the antifouling strategy should be compatible with the equipment itself to avoid damaging systems or other components of the devices/equipment. It should also be cost-effective and fulfill infrastructure requirements [38].

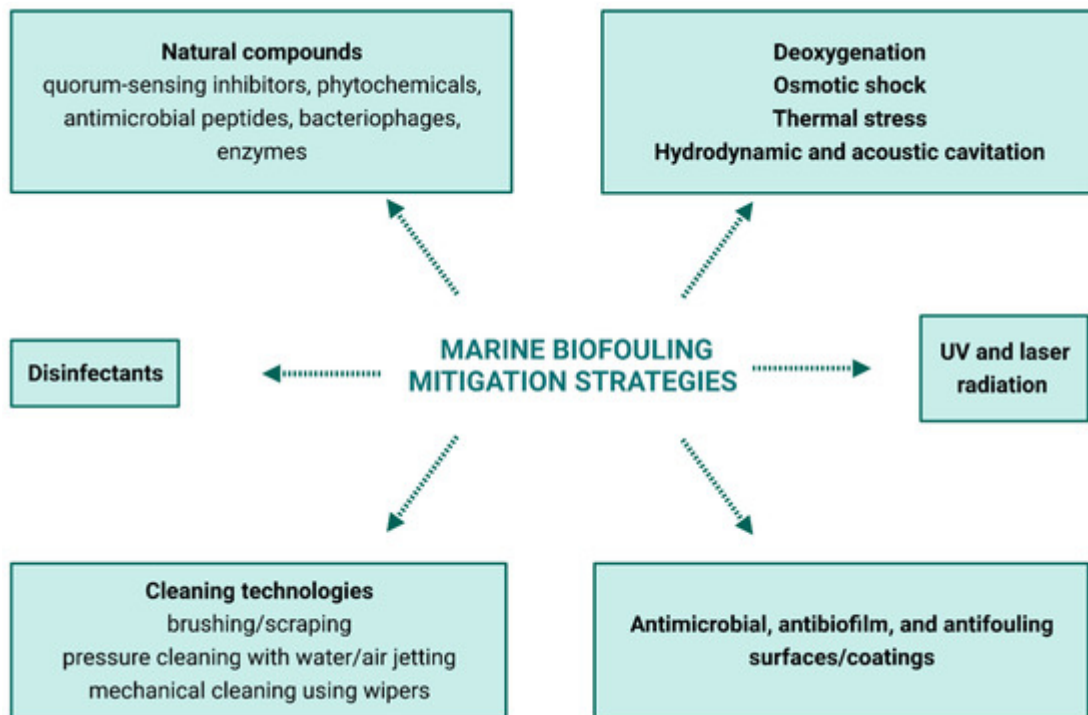


Figure 3. Preventive and control methodologies to mitigate marine biofouling effects.

Antifouling paints containing arsenic, zinc, tin, and mercury were commonly used as the initial strategy to deal with marine biofouling [46][47] until their toxicity on the surrounding marine environment was demonstrated [48][49][50]. Indeed, in the 1960s, coatings incorporating a tributyl tin (TBT)-based biocide were the first to present robust effectiveness with a relatively low production cost. However, several findings indicated the negative impacts of TBT-based compounds related to their persistence and toxicity, showing adverse effects on non-target marine organisms. Several governments restricted its use, and the International Maritime Organization decided to ban the use of this type of biocide in the manufacturing of antifouling paints in 2003 and the presence of these paints on ship surfaces from 2008 [17].

Therefore, further biofouling treatments have been applied, including thermal stress, osmotic shock, deoxygenation, UV and laser radiation, and hydrodynamic and acoustic cavitation [38][44][45][51]. The most commonly available cleaning technologies are brushing, scraping, pressure cleaning with water/air jetting, or mechanical cleaning using wipers [33][38][44][45][51][52]. These mitigation strategies vary in their effectiveness in removing biofouling organisms and in their suitability for use on different marine surfaces. For instance, although the intensity of cavitation erosion of submerged surfaces depends on the material properties of the surface, liquid temperature, and the distance from the edge of the working tool to the fouling which should be removed, cavitation technology allows lower surface damage compared to brush-based technologies [53]. Moreover, nowadays, the cleaning of boats, ships, and additional moveable marine equipment such as cages and nets can be performed in a dry-dock

or by in-water cleaning technologies [44][53]. Although in-water biofouling approaches can be cheaper than onshore activities, they may present higher chemical contamination and biosecurity risks, e.g., the application of underwater technology may increase the recolonization of surrounding surfaces [54].

Enzymes have also been proposed as an alternative to traditional antifouling compounds since they can act on the breakdown of adhesive components and the catalytic production of repellent compounds *in situ* [42]. A broad spectrum of aquatic disinfectants, such as Triple7 EnviroScale Plus[®] (citric acid: 30–60%; lactic acid: 30–60%), Descalex[®] (sulfamic acid: 60–100%), NALCO[®] 79125 Safe Acid (sulfamic acid: 60–100%), and Rydlyme[®] (hydrogen chloride: <10%), has been demonstrated to effectively control biofouling, being one of the most widespread treatments for cleaning and disinfecting marine equipment and devices [43][55][56]. They can be applied through the immersion of equipment into disinfectant solutions or spray applications since these disinfectants are available in powder and/or tablet form. TernoRens[®] Liquid 104 cleansing fluid (5–15% citric acid and <10% phosphoric acid) was formulated to remove mussels, barnacles, and additional marine organisms and is marketed as environmentally friendly. Likewise, Barnacle Buster[®] (85% phosphoric acid) is promoted as a safe, non-toxic, and biodegradable marine growth removal agent [38]. In the peroxygen family, Virkon[®] Aquatic is 99.9% biodegradable and breaks down to water and oxygen [57]. It is one of the very few U.S. Environmental Protection Agency registered disinfectants labeled specifically for use in aquaculture facilities against aquatic bacterial, fungal, and viral pathogens, and is available through aquaculture suppliers such as Syndel in North America [58][59]. In turn, in the European Community, Antec International Limited indicates that the compound is registered as a disinfectant only for professional use. Due to the restrictive legislation, which requires several risk studies before registration and marketing authorization, the global costs of the development of new biocides or new antifouling coatings incorporating biocides have increased [17]. These costs reactivated the development of non-toxic approaches, including novel antifouling surfaces in which some natural compounds can be incorporated. Although the choice of the correct strategy depends on the cost and application possibilities, antifouling coatings are probably the most cost-effective method for boats and other submerged devices and equipment [60][61].

Table 1. Currently employed marine biofouling strategies, their advantages, and limitations.

Marine Biofouling Strategy	Description	Advantages	Limitations	Reference
Antimicrobial, antibiofilm, antifouling surfaces/coatings	Includes compounds (nanoparticles of copper, zinc, silver, immobilized molecules that become active upon contact, light-activated molecules) able to – kill or reduce the growth of foulers (antimicrobial)	– Probably represent the most cost-effective method against marine biofouling	– Coatings must be inert and transparent when applied to sensors requiring electrochemical or optical transduction	[45][61][62][63][64][65][66]

Marine Biofouling Strategy	Description	Advantages	Limitations	Reference
	<ul style="list-style-type: none"> – decrease the ability to form and develop biofilms (antibiofilm) – reduce the adhesion/attachment of fouler organisms (antifouling) 			
Natural compounds	<p>Includes QS inhibitors, phytochemicals, peptides, bacteriophages, or specific enzymes which</p> <ul style="list-style-type: none"> – degrade adhesives used for settlement – disrupt the biofilm matrix – interfere with intercellular communication 	<ul style="list-style-type: none"> – Most of them can be incorporated on surfaces/coatings. – May be isolated from natural resources 	<ul style="list-style-type: none"> – Compounds need to be produced in significant amounts 	[42] [67] [68] [69] [70] [71] [72]
Disinfectants/chemical treatments	<p>Mechanisms of action of disinfectants depend on the type/class but include the</p> <ul style="list-style-type: none"> – damage and loss of the structural integrity of the cell wall and cytoplasmic membrane – leakage of intracellular components and cell lysis – inhibition of cellular metabolism/replication 	<ul style="list-style-type: none"> – Compared to oxidizing treatment agents, non-oxidizing chemical treatment agents, such as quaternary ammonium compounds, can be more specific 	<ul style="list-style-type: none"> – Insufficient information is available to accurately determine efficacy against all relevant biofouling taxa – Most of the chemical compound concentrations need to be actively 	[38] [43] [44] [58] [59]

Marine Biofouling Strategy	Description	Advantages	Limitations	Reference
	<ul style="list-style-type: none"> denaturation of cellular constituents 		<ul style="list-style-type: none"> monitored because their efficacy depends on different factors 	
Cleaning technologies	<p>Commonly employed before other treatments and include physical removal by</p> <ul style="list-style-type: none"> brushing scraping pressure cleaning with water/air jetting mechanical cleaning using wipers 	<ul style="list-style-type: none"> May be performed in a dry-dock or in water Present fewer toxicological and environmental risks 	<ul style="list-style-type: none"> Associated with high maintenance costs and reduce the commercial operation time of ship hulls Not entirely feasible when applied to sensors with sensitive components 	[38][45]
UV and laser radiation	<p>Radiation leads to the formation of toxic by-products</p>	<ul style="list-style-type: none"> A cheaper and more reliable application of UV radiation is likely to be a powerful approach Requires low maintenance 	<ul style="list-style-type: none"> Incorporation into sensors has not been practical due to the high energy requirements Can be better suited as a pretreatment rather than a final strategy against marine biofouling 	[44][45]

Marine Biofouling Strategy	Description	Advantages	Limitations	Reference
			<ul style="list-style-type: none"> - Difficult to apply to large, submerged structures 	
Thermal stress	Heating seawater to above the thermal tolerance of biofouling organisms	<ul style="list-style-type: none"> - Well-suited for application to internal pipework, given the confined spaces and relatively small total volumes to be treated - Resilient taxa can render it nonviable in 2 h or less - It poses few risks to operators and is unlikely to harm vessel components at or below 60 °C - Fewer toxicological and environmental risks are presented 	<ul style="list-style-type: none"> - It is only fitted to confined spaces - It requires continual monitoring of water temperature to ensure lethal conditions are maintained throughout the process 	[38]
Deoxygenation	Reducing dissolved oxygen concentrations to below the tolerance of biofouling organisms by wrapping fouled surfaces with impermeable plastic	<ul style="list-style-type: none"> - It enables vessels to be treated <i>in situ</i>, preventing the expense of 	<ul style="list-style-type: none"> - It can take several weeks to kill resilient fouling taxa - 	[38][73][74][75]

Marine Biofouling Strategy	Description	Advantages	Limitations	Reference
		<ul style="list-style-type: none"> removing boats from the water - Fewer toxicological and environmental risks 	<ul style="list-style-type: none"> Absolute anoxic conditions may be required to expose all taxa to lethal conditions 	
<p>Hydrodynamic cavitation</p> <p>Acoustic cavitation (by ultrasonic irradiation)</p>	<p>Hydrodynamic mode—cavitation is produced by pressure variations obtained using the geometry of the system, creating velocity variation</p> <p>Acoustic cavitation—the pressure variations in the liquid are accomplished using sound waves, usually high-intensity ultrasound (16 kHz–1 MHz), which creates high liquid shear forces that prevent the settlement of organisms on the submerged surfaces</p>	<ul style="list-style-type: none"> - They seem to have no adverse effects on marine life 	<ul style="list-style-type: none"> - It may be limited by energy costs - The installation of ultrasonic treatment systems is expensive - Further research is required to optimize operating parameters accounting for the effects of acoustic treatments on coating integrity and the influence of pressure waves on the viscoelastic properties of biofilms 	<p>[44][45][76][77]</p>

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Marine Biofouling Strategy	Description	Advantages	Limitations	Reference
Osmotic shock	Reducing salinity interferes with the osmotic balance of marine organisms	<ul style="list-style-type: none"> Fewer toxicological and environmental risks associated 	<ul style="list-style-type: none"> It is unlikely to be effective within acceptable timeframes Some marine bivalves can survive weeks in freshwater 	[38]

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