An evaluation of whether bio-inspired antifoulants are the solution to biofouling

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Abstract

Biofouling, the undesirable accumulation of marine organisms on submerged surfaces, has been recognised as an obstacle for centuries, and, to combat this, antifoulants were developed. Despite this, a concrete solution that benefits both the economy and the environment is yet to be made. Since the first antifouling methods, progress has been made in environmentally friendly antifouling coatings, however, these antifoulants still have negative consequences for the surrounding environment. Recently, there has been a push for using nature-inspired antifoulants to combat this problem. Examples include simulating the microtopography of organisms, extracting natural antifouling compounds, and interference with quorum sensing. An evaluation of the literature revealed that, although bio-inspired products are not ready for commercial production, there are some promising outcomes. Therefore, I conclude that the most effective way to increase the economical viability of bio-inspired antifoulants is to ban biocide-based paints with high release rates. In addition, with increased research and field experiments, it is possible that bio-inspired antifoulants can revolutionise the antifouling market.

Introduction

Biofouling, from a human perspective, is the undesirable accumulation of micro-organisms, plants, algae, and animals on a submerged surface (IMO, 2019). For humans, biofouling is undesirable as it has both economic and ecological impacts such as additional hydrodynamic drag for ships, corrosion, and translocation of species (Callow and Callow, 2002). As a result, managing biofouling can be very expensive; the US Navy alone spends approximately one billion dollars a year as a consequence of biofouling (Callow and Callow, 2002). The number of fouling species is relatively small as they must tolerate a wide range of abiotic factors (Yebra *et al.,* 2004). Despite this, biofouling has successfully introduced many invasive species that can create ecological problems. Currently, the most popular and effective way to manage biofouling is using biocide-based antifoulants. Biocides can leach into the environment and impact marine non-fouling organisms causing olfactory and chemoreceptive damage (Cato and Walmsley, 2010). Therefore, a more environmentally friendly antifouling technique is required to protect these immersed surfaces to limit both economic and environmental impacts.

Biofouling

Biofouling can be divided into two stages: micro-fouling and macro-fouling. The former process is when a biofilm is created and this facilitates the latter process. Micro-fouling initiates when dissolved organic matter, such as proteins and carbohydrates, begins to adhere to an unprotected submerged surface, thus creating a biofilm. Following this, the secretion of extracellular polymeric substances allows for the settlement of rapidly growing bacteria and diatoms (Figure 1; Yebra *et al.,* 2004). Arguably, biofilms could be defined as the root of all biofouling as this assemblage of cells is usually the first permanent colonisation of a surface and therefore integral in aiding the adhesion of microorganisms. Furthermore, biofilms provide protection from abiotic changes, predation, toxins and control nutrient diffusion within the colony thus allowing microorganisms to flourish within this environment (Flemming *et al.,* 1996; Costerton *et al.,* 1995).

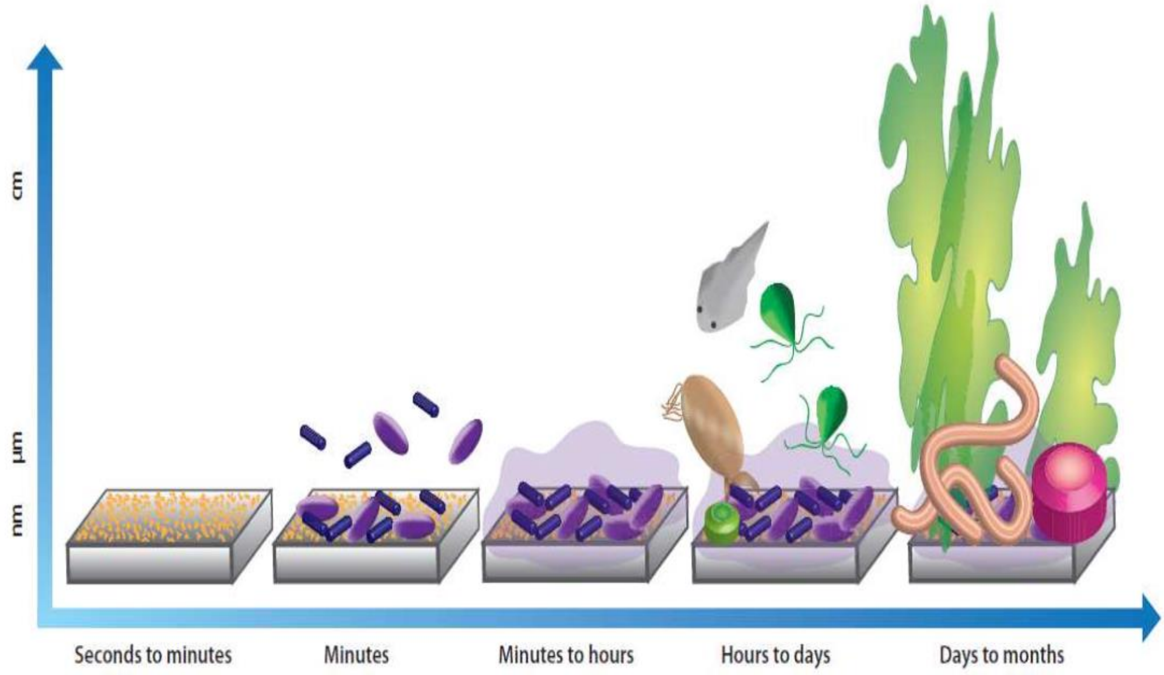

Figure 1: The process in which biofouling occurs from a diagram by Delauney and Compère (2009). Initially micro-fouling occurs where microorganisms attach to a surface and create a biofilm. Following this, a complex community of macro-foulers is able to form, dominated by invertebrates and macro-algae. It is important to remember that this schematic is simplified and linear succession does not always occur.

After the biofilm has developed, further macro-fouling is facilitated. The type of fouler is dependent on substrate, season, competition, and predation levels as fouling is such a dynamic process (Callow and Callow, 2002). This more mature fouling community has large growth rates, little substrate preference, and tolerance to a wide range of abiotic factors (Yebra *et al.,* 2004). Macro-foulers all adhere differently to surfaces; for example, adult barnacles use a combination of hydrophobic proteins crosslinked by cysteine residues (Callow and Callow, 2002). Alternatively, the adhesive proteins secreted by blue mussels are largely composed of 3,4-dihydroxy-L-phenylalanine (DOPA). The variety of adhesives used by organisms and their tenacity, despite changing physical conditions, are a few of the challenges that must be combated when designing an effective antifouling technique.

Biofouling is predominantly a problem for shipping; however, it can also create problems for both tidal renewable energy projects (Loxton *et al.,* 2017) and aquaculture (Edwards, Pawluk and Cross, 2014). As well as the obvious economic cost biofouling creates for these industries, there can also be environmental costs. The hydrodynamic drag created by foulers increases fossil fuel consumption which can result in air emissions increasing up to 40% (Frost, 1989). Therefore, if antifouling paints were not applied, there could be a significant rise in greenhouse gas emissions. The creation of biofilms is problematic too as they provide the infrastructure through which invasive species are introduced. Between 1995 and 2002, 20 new species were introduced in the North Sea by either biofouling or ballast water; since then and 2009 the number of introduced species has over doubled (Hewitt *et al.,* 2009). Therefore, it is evident that biofouling is a clear vector for the translocation of species and must be managed to control invasive introductions, which have been recognised as one of the greatest ecological and economic threats to the marine environment (Callow and Callow, 2002).

As you can see, from a human perspective, biofouling is seen as a problem, However, ecologically speaking, biofouling can increase biodiversity while biofilms can aid biological processes such as coral settlement (Erwin *et al.,* 2008). Additionally, epibiotic biofilms on marine organisms can create a barrier from the surrounding physical environment, which can be detrimental to some marine organisms but beneficial to others. Organisms can benefit from biofilms as they can repel pathogens which limits infectious diseases (Wahl *et al.,* 2012). On the contrary, many organisms rely on their body surface for multiple exchange processes and if a thick biofilm is created it can decrease fitness (Wahl *et al.,* 2012). Additionally, biofouling can be a problem for larger marine organisms. Whelks on juvenile green turtles can account for 20% of their total weight, thus slowing them down, increasing drag, damaging the carapace and increasing energy expenditure (Lezama *et al.,* 2013).

Antifouling

The need for a universal antifoulant, that is able to combat a range of fouling organisms with varying adhesives, is clear. To prevent biofouling, antifouling techniques must be applied before surfaces are submerged as there is a lack of warning signs. Therefore, once the biofouling has started, it is often too late to prevent it (Flemming, 2002). Antifouling paints are designed to alter the chemical reactions and diffusion rate of biofoulers. This process depends on the type of biofouler and the seawater conditions (Kiil *et al.,* 2003). Previously, antifouling paints used biocides which killed microorganisms; however, these techniques included the environmentally harmful tributyltin (TBT). TBT is lipid-soluble so is taken up into cells where it inhibits respiration and photosynthesis by stopping the necessary ATP transfer for these processes (Callow and Callow, 2002). Over 20 years ago it was estimated that 70% of all shipping fleets used TBT-based paint (Champ*,* 2001). Many studies have concluded the detrimental effects that TBT has on the environment, including weakened immunological defences in fish (IMO, 2019) and stunted shell growth in oysters, *Crassostrea gigas* (Evans *et al.,* 1995). TBT was an effective antifoulant that was economically beneficial and prevented the introduction of invasive species but at a significant cost for the environment. Therefore, all antifouling paints releasing TBT were banned by the International Maritime Organisation (IMO) in 2003.

Current antifoulants include biocidal coatings or foul-release coatings. However, neither antifoulant is sufficiently effective, economic nor environmentally-friendly enough to dominate the antifouling market. Research within this field has increased so that a sustainable solution to biofouling can be discovered. Nonetheless, a universal eco-friendly solution has not yet been developed. In this essay the following research questions will be addressed; can bio-inspired antifoulants be the universal solution to biofouling? If not, what research needs to be done to push forward the development of these antifoulants? Literature has been assessed to highlight the problems with current antifouling techniques, the gaps within research and to discover whether bio-inspired antifouling techniques could be a realistic solution to biofouling. An evaluation of bio-inspired antifoulants will be made and the next steps to revolutionise the antifouling market will be proposed.

Current antifoulants

Biocidal antifoulants work by releasing biocides, which can be either copper, zinc, or silyl acrylate-based (Pei and Ye, 2015). Most biocidal antifoulants are cuprous oxide-based as they are the most efficient against algal fouling (Amara *et al.,* 2018). Biocidal coatings are popular antifoulants, they are not a perfect solution but, currently, are the most efficient antifoul coatings. In a study evaluating the release rates of various copper and zinc biocide-based antifouling paints, it was discovered that there was no significant difference in efficiency between low copper release paints compared to paints with release rates 4 to 6 times higher (Lagerström *et al.,* 2020). This suggests that an unnecessary amount of copper is being leached into the surrounding environment. Antifouling paints release up to 113,000 tons of biocides yearly (Ivče *et al.,* 2020) resulting in the bioaccumulation of biocides which can be of particular concern for species of high trophic levels, such as predators. Zinc pyrithione, a common antifouling compound, can cause spinal deformities in the embryos of Japenese medaka fish, *Oryzias latipes* (Goka, 1999). In extreme cases, where water flow is minimal and boat density is large, marine organisms can suffer directly from biocides. For example, seagrass *Zostera marina,* studied within a marina, was found to have reduced photosynthetic capacity of photosystem II, which can reduce their efficiency and create stress (Scarlett *et al.,* 1999). Therefore, biocides are still an environmental concern thus their use is regulated by the EU Biocidal Products Regulation (EU Parliament and Council, 2012).

Foul release coatings are a more environmentally friendly antifoulant, as they are based on the physical properties of fouling organisms, and work by minimising the adhesive strength of organisms alongside vessel movement (Schultz *et al.,* 1999). The coating is smooth which reduces the friction coefficient so flow across the surface is facilitated which inhibits fouling (Anisimov *et al.,* 2014). Foul release coatings can be either organic fluorine or silicone. Fluorine-based coatings have a strong electronegativity and low polarizability, making them hydrophobic and chemically stable (Gao *et al.,* 2017). In comparison to an unprotected surface, protein adsorption is reduced by 45-75% and cell attachment is reduced by 70-90% (Xu *et al.,* 2017). Despite this, fluoropolymers are difficult to create and expensive so there is a lack of organic, fluorine, foul-release coatings on the market (Gu *et al.,* 2020). In light of this, there has been an expansion into the research of silicone-based foul release coatings. These non-toxic silicone-based coatings have good desorption capabilities and usually have a poly (dimethylsiloxane) base that provides low surface energy (Gu *et al.,* 2020). Despite this, a recent review highlighted their problems; low mechanical strength, low adhesion, and low foul resistance performance (Hu *et al.,* 2020). Evidently, foul release coatings do not come without their complications, however, they significantly reduce fouling and should not be overlooked as an antifoulant.

Bio-inspired antifoulants

A relatively new approach to the antifouling industry is the use of nature to inspire novel antifouling techniques. One of the earliest examples of bio-inspired antifouling was discovered in 2000, when De Rossi and Ahluwalia created dynamic antifouling patterns inspired by fish stripes. Bio-inspired antifoulants can be based on physical traits, chemical properties or stimuli responses seen in nature (Kirschner and Brennan, 2012). Mimicking and modifying these natural antifouling traits could provide the solution to biofouling. Firstly, physical characteristics that are being translated into antifouling will be discussed. Following this, natural chemical extracts that can be used in antifouling and stimuli response-based antifouling will be explored. Finally, the potential use of organisms themselves as antifoulers will be evaluated.

Topography based antifoulants

The general aim of topography based antifouling solutions are to reduce attachment points for microorganisms (Ralston and Swain, 2009). These techniques involve altering surface microtopography which determines how easy bio-adhesion is as it controls both the surface roughness and wettability (Blossey, 2003). Terrestrial-inspired antifoulants include those based on the microstructure of lotus leaves, rice leaves, and butterfly wings. A comparison experiment between the aforementioned terrestrial antifoulants revealed that lotus leaves were the most effective removers of inorganic fouling (Bixler and Bhushan, 2015). Lotus leaves have a superhydrophobic structure (Barthlott and Neinhuis, 1997), resulting in a surface with low adhesion and low surface energy that prevents fouling (Bixler and Bhushan, 2015). Previous research by Bhushan *et al.* (2009) showed lotus leaves remove 99% of contaminants and significantly reduce drag in both laminar and turbulent flow. Nevertheless, the durability of superhydrophobic structures, like the lotus leaf, is low (Zhao *et al.,* 2014) and the hydrophobic effect does not work on immersed surfaces (Flemming, 2011). Therefore, the lotus effect cannot be translated into an applicable antifoulant, at least not for submerged surfaces. Another recent terrestrial antifoulant was found by Liu *et al.* (2018) within *Nerium oleander*, a subtropical shrub. Cardenolides were isolated from *N. oleander* that effectively inhibited barnacle settlement, however, they were mildly toxic to other non-target organisms (Liu *et al.,* 2018). If these cardenolides are to undergo wide-scale implementation, additional research needs to be done on their toxicity. Generally, research is more focused on marine-based antifoulants as there is a lack of documentation of terrestrial antifoulants (Zhou *et al.,* 2009), resulting in less research.

Aquatic organisms also have antifouling characteristics, such as modified microtopography. The microtopography of elasmobranchs has been particularly studied as a possible bio-inspired antifoulant (Carman *et al.,* 2006; Bixler and Bhushan, 2015; Dundar Arisoy *et al.,* 2018). Elasmobranchs, such as sharks, are covered in dermal denticles that are diamond-shaped with longitudinal rib patterns, often referred to as riblets, which can reduce hydrodynamic drag and fouling by ectoparasites. Early experiments revealed that bio-inspired riblet patterns could reduce drag up to 10% (Bechert *et al.,* 1997). More recently Bixler and Bhushan (2015) replicated the impact riblets have on incoming vortices, the results concluded that the riblet lifts and reduces the size of the vortex, ultimately leading to a small surface contact area and lower drag. These characteristics are ideal for antifouling as the small surface area and lifted vortex reduces the area of contact for the adhesive and the associated interaction forces.

Efimenko *et al.* (2009) proposed that antifouling microtopography structures with the same length pattern are not sufficient enough to prevent biofouling, due to the vast range of fouling organisms, therefore hierarchical structures were proposed as an alternative solution. The first hierarchical Sharklet antifouling surface (Figure 2) was developed by Carman *et al.* (2006). Results from this study showed that *Ulva sp*. settlement decreased by 86% and that the surface worked on a multitude of other organisms including diatoms and cyprids. However, a study by Reddy *et al.* (2011) evaluated that although 55% of *Escherichia coli* could be removed by Sharklet patterns, after a sufficient amount of time bacteria will accumulate on the surfaces again. Therefore, Reddy *et al.* (2011) concluded that microtopography alone is an insufficient solution to biofouling. It is important to bear in mind that many physical and chemical reactions occur on the surface of shark skin that could contribute to its antifouling properties so merely simulating the microtopography is unlikely to have a significant reduction in fouling.

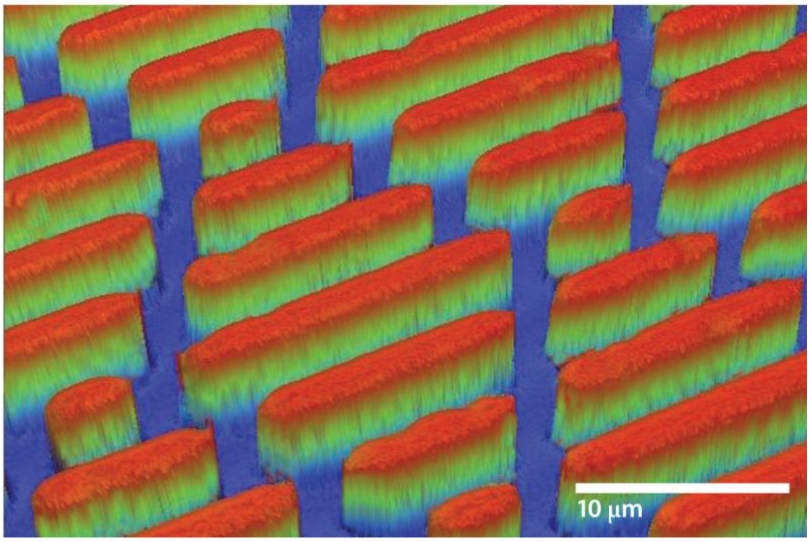

Figure 2: A white light optical profilometry image of the Sharklet pattern created by Carman *et al.* (2006). The multi-feature topography consists of a combination of 4, 8, 12, and 16 micrometre length and 2 micrometre wide rectangular ribs.

Dundar Arisoy *et al.* (2018) incorporated both microtopography and chemical antifoulants by combining antifouling sharkskin patterns with antibacterial titanium dioxide nanoparticles. These antifouling sharkskin patterns are stamped onto Polyethylene terephthalate substrate, also known as PET, which is dispersed in titanium dioxide nanoparticles (Dundar Arisoy *et al.,* 2018). This PET substrate is then cured for 10 seconds using near-infrared irradiation (Dundar Arisoy *et al.,* 2018). This creates a durable surface that decreases microbial attachment and inactivates attached microorganisms. After only one hour of UV light exposure, over 80% of *E. coli* is removed on all photocatalytic shark skin surfaces, being approximately 70% more efficient than smooth surfaces (Figure 3; Dundar Arisoy *et al.,* 2018). Even with only 10% titanium dioxide incorporated into the chemical matrix, over 80% of both *E. coli* and *Staphylococcus aureus* were removed. This is a promising material design that could be scaled up to control biofouling, however, field experiments are needed to confirm the effectiveness of this design as a universal antifoulant.

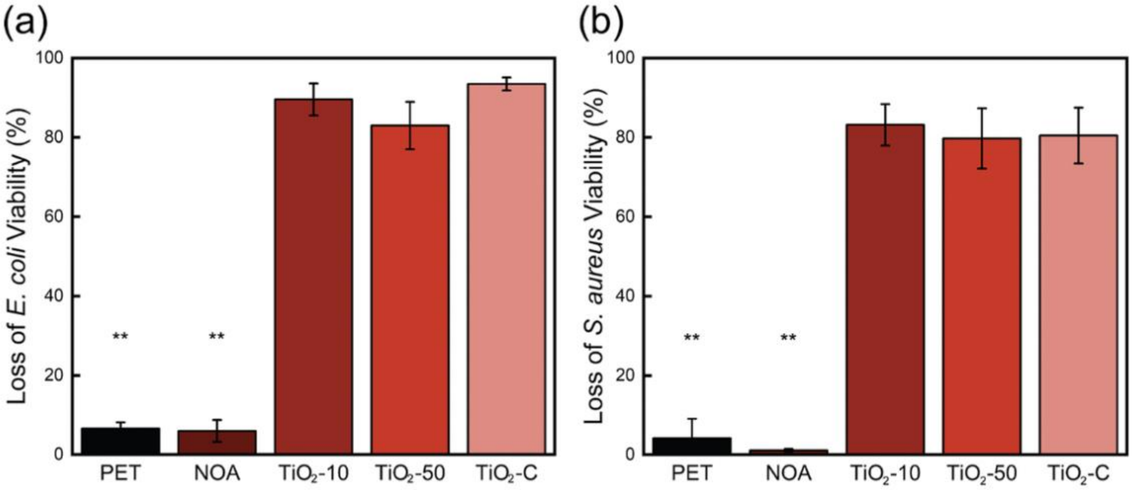

Figure 3: The percentage reduction in the bacterial attachment (± Standard Error) for **a)** *Escherichia coli* and **b)** *Staphylococcus aureus* in two control conditions: PET (polyethylene terephthalate) and NOA (Norland Optical Adhesive). These control conditions were compared to the photocatalytic shark skin pattern with various titanium dioxide concentrations and nanoparticles. The ** denotes 99% significance between the control substrates and photocatalytic shark skin pattern (Dundar Arisoy *et al.,* 2018).

As well as the aforementioned Dundar Arisoy *et al.* (2018) study, Munther *et al.* (2018) developed a micro-moulded silicone with a height gradient placoid scale pattern that reduced *E. coli* settlement by 75%. In addition, when the surface was put under extreme wear, the degraded surface still created a 56% reduction in *E. coli* settlement (Munther *et al.,* 2018). Both of the aforementioned coatings have promising potential and have had initial success in reducing settlement of micro-foulers. The next steps that need to be taken, in order to develop these coatings, are field experiments as this will allow exposure to a variety of foulers and abiotic factors. To encourage the development of coatings such as these, projects such as the Advanced Nanostructured Surfaces for the Control of Biofouling (AMBIO) are in place. With the assistance of AMBIO, it may be possible that these nanostructured coatings could reach large-scale implementation.

Chemical based antifoulants

Marine mussels use adhesive proteins to bond to underwater surfaces, the main bio-adhesive within this is DOPA. DOPA is very adaptable and can resist protein fouling (Statz *et al.,* 2006), adhere to many substrates, as well as tolerate a variety of abiotic conditions (Bazaka *et al.,* 2015). Modified surfaces with DOPA and poly(ethylene glycol) resisted fouling from diatoms, *Navicula perminuta,* and macro-algae, *Ulva linza* (Statz *et al.,* 2006). A series of other DOPA-inspired chemical antifouling coatings have been tested (Statz *et al.,* 2005; Rodriguez-Emmenegger *et al.,* 2013; Ham *et al.,* 2013; Maity *et al.,* 2014). Examples of modifications to DOPA-inspired antifoulants include the addition of a pentapeptide anchor that improves adsorption of DOPA (Statz *et al.,* 2005) or the incorporation of a fluorine-based tripeptide that reduces biofilm formation (Maity *et al.,* 2014). These modified DOPA-inspired coatings have had some success but were only tested on a very limited range of species. Recently, Qi *et al.* (2018) developed a, DOPA-inspired, multifunctional antifouling coating that effectively repelled both *E. coli* and *S. aureus*. Despite this, there is a common trend within these DOPA-inspired coatings that are only being tested on a limited range of species, therefore, judgement should be reserved on their effectiveness until they are faced with a larger variety of foulers.

The antifouling properties of sponges were first isolated by Bakus *et al.* (1983) and, since then, many other useful antifouling compounds have been found within sponges. Researchers from Sweden found a strong inhibitory effect on cyprid (*Balanus improvises*) settlement when extracting agelasine D from sponges (Sjögren *et al.,* 2008). With the addition of 0.24 µM agelasine D, settlement can be reduced over 80% and if this concentration is increased by a factor of 100 there is no cyprid settlement (Figure 4; Sjögren *et al.,* 2008). Additionally, agelasine D prevented settlement without causing any larval mortality (Sjögren *et al.,* 2008). These results suggest that this antifoulant would have little ecotoxicity so is worth pursuing further research on. Another natural antifouling chemical is oroidin that can be extracted from sponges of the Agelasidae family. After structure-activity relationship analysis, it led to the design of dihydroroidin which inhibits the formation of *Halomonas pacifica* biofilms both *in vitro* and when incorporated into marine paint (Melander *et al.,* 2009). Additional testing is required to see whether similar effects are seen on other biofilms and macro-foulers. However, this initial research is promising and could, with continuing field experiments on a larger range of foulers, lead to an effective antifouling technique.

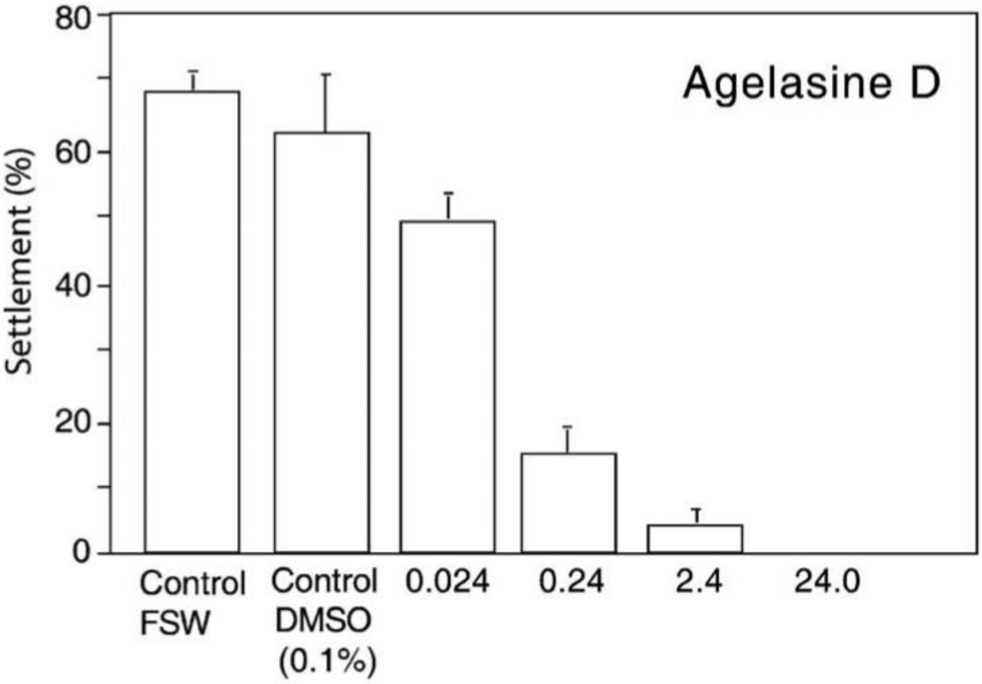

Figure 4: Percentage settlement of *Balanus improvises* (± Standard Error) in two control conditions, compared to varying concentrations of agelasine D: 0.024 µM, 0.24 µM, 2.4 µM or 24 µM. Graphic from Sjögren *et al.,* 2008.

Another way to prevent biofouling is by inhibiting quorum sensing, which prevents the formation of biofilms. Quorum sensing is important for bacterial communication and gene expression so inhibiting this process could be a non-toxic antifouling technique (Nir and Reches, 2016). Hellio *et al.* (2002) determined that red algae produced more valuable antifouling compounds compared to brown seaweeds. This led to the discovery of furanones which are secondary metabolites extracted from red algae, *Delisea pulchra,* that have natural antifouling properties (De Nys *et al.,* 2006). Furanones are able to inhibit bacterial colonisation and biofilm formation through interference with quorum sensing (Steinberg *et al.,* 1997). Dworjanyn *et al.* (2006) revealed that furanones deterred *Ulva* sp. settlement by 90%. In this study *Ulva* sp. was used as an assay organism as it is an abundant fouling organism (a common trend throughout the literature). Furanones are clearly a promising bio-inspired antifoulant as over 200 furanone-based polymer coatings have been synthesised (De Nys *et al.,* 2006). Advances in research of the controlled release of furanones has led to the development of some commercially available antifouling paints, thus proving bio-inspired antifoulants have the potential to revolutionise the antifouling market. Although furanone extraction has proved the most successful seaweed antifouling compound, there are many more that have been investigated over the years (see summary table 3 in review paper Raveendran and Mol, 2009). With increased screening and isolation of antifouling compounds, there could be many more antifoulants available to study for possible commercial application.

Recently, Muras *et al.* (2021) conducted successful field experiments where *Bacillus licheniformis* methanol cell extract was incorporated into 5% of self-polishing paint and caused fouling to reduce by 30%. The coating has low ecotoxicity and was particularly successful at inhibiting biofilm formation and bryozoan settlement (Muras *et al.,* 2021). Despite this, the antifouling capabilities of this coating decrease with exposure and impacts of this coating on hard foulers is relatively unknown. It is encouraging to see field experiments of bio-inspired antifoulants, however, as fouling is only reduced by 30%, field research should be focused on more successful antifoulants.

Stimuli response antifoulants

Self-polishing paints themselves are based on physical processes seen within biology (Kiil *et al.,* 2001). The polymers within the paint hydrolyse then dissolve in contact with seawater, thus leaving a foul-free surface. Pilot whales exhibit similar self-cleaning mechanisms by removing small patches of skin cells by enzymatic digestion (Baum *et al.,* 2002). Coatings that swell or contract in response to variation in pH have also been developed. This dynamic coating consists of a hydrogel-actuated polymer microstructure and is inspired by the embedded dermal denticles within sharks (Zarzar *et al.,* 2011). Recently, a pH-sensitive polymer brush coating has been developed that is able to transition between antibacterial and antifouling traits in response to pH (Xu *et al.,* 2020). At this moment, pH dependent coatings have only been tested in the lab against very few foulers, thus further field experiments are required to discover whether they are an effective antifouling coating. Despite this, Xu *et al.* (2020) had significant reductions in protein adsorption, bacterial and microbial attachment as well as microalgae attachment. Therefore, this coating has several promising outcomes and a push for field experiments should be made.

Oil resistant, hierarchically structured topographies have been developed that are inspired by the grass carp (*Ctenopharyngodon idella*). The interplay between rigid nano clays and flexible poly-Nisopropylacrylamide (pNIPAm) hydrogel stabilises trapped water on the hierarchical structure and creates a low adhesion surface (Lin *et al.,* 2010). Stimuli response antifoulants have also been implemented in other areas of science. Chen *et al.,* (2021) used similar oil-resistant antifouling coatings, specifically zwitterionic silanes, to create a foul free surface that could be used in optical sensors and other biomedical equipment to reduce contamination. These oil resistant coatings appear to in the very early stages of development and are less researched than pH dependent coatings. Therefore, more research needs to be done until it is clear whether oil resistant coatings could be universal antifoulants. Other stimuli response coatings can be temperature-dependent, Cordeiro *et al.* (2010) used a pNIPAm based system with a modified, low critical solution temperature for marine waters. The low critical solution temperature allows the surface to easily switch from hydrophobic to hydrophilic states which creates changes in the surface energy and wettability thus aiding the removal of micro-organisms (Fu *et al.,* 2004). Nevertheless, the Cordeiro *et al.* (2010) thermo-responsive coating did not show any significant reduction in adhesive strength of diatoms (*N. perminuta*). Therefore, as there are other bio-inspired antifouling techniques with more significant fouling potential, research into thermo-responsive coating should be reduced.

Organism antifouling

A sustainable and less intrusive way to manage biofouling is using marine organisms themselves. This method has been tested using Caribbean spider crabs on an abandoned SeaStation cage which revealed that the spider crabs were more effective at removing biofouling than manual scrubbing, and removed 90% of fouling on the structure in four weeks (Zeinert *et al.,* 2021). Despite this, it is unclear whether this technique could be scaled up to target larger infrastructure. Additionally, it would not be applicable on moving structures such as ships which is one of the main reasons antifoulants were developed. Within the shellfish industry, alongside other techniques, sea stars and crabs selectively control fouling by predation (Bourque and Myrand, 2006). This technique is very sustainable; however, it must be closely monitored to ensure shellfish stocks themselves are not predated (Watson *et al.,* 2009). Application will be difficult as there must be considerable fouling to ensure a constant food source and limit the number of escaping organisms. Zeinert *et al.* (2021) ran studies on an inactive aquaculture cage and reported fish mortalities as well as significant reduction in fouling. Therefore, it is unlikely that this technique could be used in aquaculture due to predation of non-target organisms. This technique cannot be considered a universal antifouling technique and will only be applicable in niche situations with almost constant monitoring.

Discussion

Currently, no nature-inspired sustainable antifoulant is sufficiently effective and inexpensive enough to replace biocide-based antifouling paints. Biocide-based antifouling paints are the most efficient antifouling products on the market. However, to limit impacts to the environment, a ban on high release biocide-based antifouling paints, which aren’t significantly more effective (see Lagerström *et al.,* 2020), would currently be the easiest change to implement into the antifouling market to reduce environmental impacts.

As previously highlighted, foul release silicone coatings have been the focus of much research. One advantage of these coatings is their ability to save in fuel consumption (Lejars *et al.,* 2012), thus adding economic value to the coating. It is possible that a new generation of silicone-based foul release coatings will be generated. Recently, a superhydrophobic poly (dimethylsiloxane) was developed by Selim *et al.* (2018) which significantly reduced bacteria, yeast, and fungi settlement. Although this coating has a clear antifouling capacity, diatom settlement, expense, a complicated application process and stationary fouling are still problems that need to be addressed (Gu *et al.,* 2020; Lejars *et al.,* 2012). Hu *et al.* (2020) also carried out promising work on organic-inorganic hybrid functional silicone foul release coatings that have optimal foul release performance and mechanical properties. However, this still requires further research and field experiments before a full analysis on antifouling potential can be made. Additionally, there is a clear trend throughout the literature where research on potential ecotoxicity of these coatings is minimal (Hu *et al.,* 2020, Selim *et al.,* 2018). Lack of toxicity within these coatings has been proved (Feng *et al.,* 2012), as well as analysis into potential metallic ecotoxicity of these coatings (Piazza *et al.,* 2018). Despite this, a full analysis into the ecotoxicity of all active compounds within foul release coatings has not yet been made. Therefore, it is clear that at this time silicone-based foul release coatings, despite their potential eco-friendly properties, are not a universal solution to biofouling and cannot yet replace biocide-based paints. To promote the development of these coatings, increased field experiments and ecotoxic research needs to be carried out.

At the moment a lot of focus has been given to furanone antifoulants and microtopography-based antifouling techniques. However, bio-inspired research is relatively new meaning researchers still lack a full understanding of the possibilities. Nevertheless, some bio-inspired paints have been commercialised: Sea Nine-211, Netsafe, and Pearlsafe (Jacobson and Willingham, 2000). The latter two antifouling paints were both developed based on furanones. The problem with furanone use for antifouling is that extraction and purification are very expensive and time-consuming. However, Dahms and Dobretsov (2017) believe it will soon be possible to transfer genes for the production of secondary metabolites, such as furanones. Therefore, more productive organisms, where metabolites are easily extractable, could be used to obtain antifouling components and the whole process would become cheaper and more productive. However, further research on the degradation capacity and toxicity levels of these compounds still needs to be done before their large-scale application (Dahms and Dobretsov, 2017). Furanone-based antifouling techniques could be a solution to biofouling as there are already effective commercialised paints that have been developed and innovative ideas to increase the efficiency of these products.

The shift in bio-inspired antifouling products is now moving towards microorganisms due to the concern of overexploitation of secondary metabolites (Satheesh *et al.,* 2016). The use of micro-organisms in antifouling is a great solution as they can be rapidly cultivated. Holmström and Kjelleberg (1999) produced five compounds based on bacteria (*Pseudoalteromonas tunicata*) that inhibited surface colonisation. More than 50 genomes of the genus *Pseudoalteromonas* have been sequenced to aid the development of a novel antifoulant (Wang *et al.,* 2015). Another bacteria-based self-polishing paint recently underwent successful field experiments (Muras *et al.,* 2021). Field experiments are relatively unusual for bio-inspired antifoulants. Therefore, this is a promising development that suggests bio-inspired antifoulants are more realistic solution then they have previously been acknowledged to be. Despite this, microorganisms are not a perfect solution either as they are difficult to synthesise chemically (Yang *et al.,* 2006) and isolation of microbes could create a bottleneck as they rely on their hosts for survival (Satheesh *et al.,* 2016). Another challenge facing microbe-based antifouling applications is that microbes rapidly break down thus reducing the durability of any antifouling paint developed (Ralston and Swain, 2009).

In regards to microtopography based antifouling techniques, there has been a lot of recent work inspired by sharks. Studies have shown that microtopography based antifouling techniques reduce in effectiveness when mechanical wear is apparent (Munther *et al.,* 2018). Therefore, if implicated, these surfaces would require replacing. One advantage for the Dundar Arisoy *et al.* (2018) shark-based design is that the modified surface can be produced easily on a large scale, thus giving it a commercial advantage. Microtopography based bio-inspired antifoulants have been largely successful, however most have only demonstrated significant antifouling potential on a few species. Therefore, a push for research on a wider range of both micro and macro foulers is necessary. As concluded by Reddy *et al.* (2011) microtopography based antifouling techniques alone are not sufficient enough to combat biofouling. Further research on the combination of microtopography and chemical antifoulants, like the Dunday Arisoy *et al.* (2018) design, could be the future for bio-inspired antifoulants.

The progress within this area of research, that has been heavily researched for over a decade, is still relatively low. This is due to the array of challenges associated with creating an effective, economic, eco-friendly antifoulant that can combat a variety of foulers and tolerate a range of abiotic factors. However, as discussed above, there are many successful bio-inspired antifoulants that have promising outcomes. Additionally, there are plenty of antifouling compounds that can be sourced from nature that have not been discussed within this review. Ascidians, seagrass, mangroves, and echinoderms are a few of the many other species that have been studied for bio-inspired antifouling solutions that have not been considered (see Raveendran and Mol, 2009). A common trend throughout the literature is successful lab trials that are not followed by any field experiments. Bio-inspired antifoulants show significant reductions in colonising bacteria, however, there is a vast range of micro and macro foulers within marine waters that cannot all be tested in the labs. Field experiments are more applicable as they expose the antifoulant to a more dynamic environment and subsequently test it's full antifouling capacity. Without a push for continuing *in-situ* research, bio-inspired antifouling coatings will remain an unfeasible idea rather than a reality.

Conclusion

At this moment in time, there are no efficient environmentally friendly antifoulants that are able to replace biocide-based antifouling coatings. Despite this, with increasing research and funding, there are some promising solutions both bio-inspired and foul release. The first step in increasing sustainability in the antifouling market is banning biocide-based antifoulants with unnecessarily elevated biocide release rates. Proceeding this, increased research needs to be done on foul release coatings; primarily on their ecotoxicity to ensure they are a sustainable alternative. Finally, a push for field experiments on bio-inspired antifoulants needs to be made to encourage their development. There are many promising bio-inspired antifoulants that would value from more *in-situ* research, such as furanone extraction, microbial antifouling compounds, and microtopography simulation. Additionally, it is possible that a combination of bio-inspired techniques could be a viable solution to antifouling. Before any large-scale commercial application, a full analysis of the effects of these bio-inspired coatings on the surrounding environment will need to be conducted. Bio-inspired antifoulants could be the solution to biofouling in the future but, if this target is to be achieved, there needs to be a push for increased research.

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