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RECEIVED 27 February 2023

ACCEPTED 17 April 2023

PUBLISHED 01 May 2023

CITATION

Carrier AJ, Carve M, Shimeta J, Walker TR,
Zhang X, Oakes KD, Jha KC, Charlton T
and Stenzel MH (2023) Transitioning
towards environmentally benign marine
antifouling coatings.
Front. Mar. Sci. 10:1175270.
doi: 10.3389/fmars.2023.1175270

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Transitioning towards environmentally benign marine antifouling coatings

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Marine biofouling has been an issue since antiquity whose solutions have a history of negative environmental impact. The development of environmentally sustainable solutions is paramount as society is becoming more conscious of anthropogenic impacts on the global ecosystem, particularly the global oceans. Herein we include a brief overview of common strategies in the development of sustainable marine antifouling coatings in terms of their efficacy, durability, and environmental impact. We discuss technical challenges to the development of sustainable antifouling coatings; barriers and incentives to their market uptake; and advocate the necessity of multi-stakeholder collaboration, including scientists, engineers, industry groups, and regulators, toward the development of marketable and sustainable antifouling coating solutions.

KEYWORDS

biofouling, sustainability, microplastics, standardization, incentives

Introduction

Marine biofouling and its effect on hull integrity and hydraulic resistance have been a concern for seagoing vessels since antiquity; even today, biofouling poses significant negative economic and environmental effects, not only in the context of marine shipping but also in any situation where substrates are immersed in aqueous environments, such as aquaculture infrastructure ([Woods Hole Oceanographic Institution and United States Navy Dept. Bureau of Ships, 1952](#)). Given the economic, e.g., increased fuel use and maintenance, and environmental, e.g., increased carbon dioxide emissions and transportation of invasive species, costs, much work has gone towards developing fouling-resistant coatings.

Biofouling occurs as a stepwise process initiated by the adsorption of dissolved macromolecules and followed by the adhesion of microorganisms that excrete extracellular

polymeric substances forming a biofilm slime (microfouling), which acts as an anchor for the adhesion of larger sessile organisms (macrofouling). Antifouling (AF) strategies can target fouling at any of these stages, the most famous being biocidal tributyltin (TBT)-based coatings developed in the 1960s that were subsequently phased out and banned by the International Maritime Organization (IMO) in 2001 when their high persistence and unselective toxicity in the environment was discovered (Updegraff and Davis, 1965; Cooksley and Parham, 1966; Antizar-Ladislao, 2008; Gipperth, 2009). The need for effective AF coatings nonetheless persists, and research continues toward suitable replacements.

Strengths and challenges of contemporary coatings

To date, a major motivation in AF coating development is the production of more sustainable materials with good efficacy and minimal off-target impact (Yebra et al., 2004; Chambers et al., 2006; Banerjee et al., 2011; Callow and Callow, 2011). Copper-based coatings rapidly replaced TBT (Ranke and Jastorff, 2000), but there is some concern regarding the ecotoxicity of copper in marine environments (Gu et al., 2020). As such, research activity is largely focused on using degradable synthetic organic or natural-product-based biocides, photocatalytic surfaces, or biocide-free coatings that exploit surface chemistry to reduce adhesion or dislodge adhered organisms.

Organic and natural product biocides are potentially biodegradable alternatives to copper, reducing their long-term impact when leached into the environment (Armstrong et al., 2000; Bhatnagar and Kim, 2010; Qian et al., 2010; Ma et al., 2017; Ferreira et al., 2020). However, there are challenges involved in their application and regulatory pressures appear to disfavor any biocidal coatings (Aldred and Clare, 2008; Banerjee et al., 2011; Almeida and Vasconcelos, 2015). Natural products may not be easily available or affordable depending on whether they are extracted in sufficient quantities from commercially available species or if there is a scaled total synthesis. Synthetic organic biocides have an advantage in this respect, but the off-target acute and chronic ecotoxicity of biocides need to be evaluated before regulatory approval. Food safety must be considered when used in aquaculture or infrastructure applications where coatings may leach into food or water supplies.

A popular mechanism for dosing these biocides is through the slow degradation of self-polishing polymeric coatings (Ma et al., 2017; Pan et al., 2022). These coatings can be engineered to manage their dosing rate and longevity. These have the advantage of a continuously renewing surface that maintains its properties over the coating lifetime. Naturally, these coatings have a limited lifetime as they are designed to slough off protected surfaces, and their applications may be limited to seasonal use, e.g., on fishing or aquaculture equipment that is removed seasonally where coatings can be reapplied. These coatings will enter their receiving environment faster than more durable coatings, so attention should be given to the impact and degradability of these oligomers or microplastics. Polyethylene glycol and biodegradable

esters, e.g., poly(lactic acid), are promising matrix materials in this regard.

Another alternative that results in the localized destruction of microbes are photocatalytic coating materials (Scandura et al., 2016; Liu et al., 2022). Photocatalysts use light to generate powerful free-radical oxidants that eradicate bacteria and can also mineralize near-surface organic pollutants. Although these seem to be a straightforward solution to fouling, they suffer from some challenges. Photocatalysts are typically UV-active, and UV light is strongly attenuated by water so deeper structures receive less protection. The efficacy is also modulated by season and latitude. Novel photocatalysts that can either directly use or upconvert more readily available visible or near-infrared light are promising alternatives (Richards et al., 2021). For efficacy, these photocatalysts are typically in the form of nanoparticles, which also have environmental concerns and they may not be environmentally benign (Marcone et al., 2012), and depending on the matrix they are embedded in, may accelerate the physical deterioration of the coating through photodegradation, reducing coating longevity and accelerating the deposition of microplastics in the marine environment. Detailed studies into the interaction of photocatalysts with their matrix, the free radicals involved, and their environmental fate (particularly for newer, less well studied, photocatalysts) may promote their durability, efficacy, and sustainability.

Other biocide-free coatings rely on novel surface chemistry and physical effects that retard fouling adhesion or promote fouling release (FR) (Yang et al., 2014; Hu et al., 2020). The most common strategies include using amphiphilic coatings with both superhydrophilic and superhydrophobic phases (Krishnan et al., 2008; Park et al., 2010; Galli and Martinelli, 2017), using biomimetic or “bioinspired” coatings that have multiple (micro or nano) scales or surface topographies (Statz et al., 2006; Schumacher et al., 2007; Wong et al., 2011; Kirschner and Brennan, 2012; Carve et al., 2019; Selim et al., 2020; Jin et al., 2022), and using low-surface-energy FR coatings (Dobretsov and Thomason, 2011; Martinelli et al., 2012) containing silicones (Galhenage et al., 2016; Selim et al., 2017; Hu et al., 2020) and/or fluororous phases (Gudipati et al., 2005; Xiao et al., 2013). These coatings minimize microbial adhesion through physical effects and benefit from the application of shear forces, making them most suitable for non-stationary applications. These coatings benefit from regular grooming to dislodge slime or macrofouling to maintain their efficacy (Tribou and Swain, 2010). The lack of biocidal components provides a clear benefit regarding ecotoxicity, but these coatings still face challenges. Abrasion resistance is a concern, especially for biomimetic coatings where a loss of topographical structure results in a loss of function (Liu et al., 2023). These can be difficult to apply on large scales, with self-assembly strategies being critical to their practical adoption (Su et al., 2021). Self-assembled micro- and nanostructures can form either during curing/drying or in contact with water. FR coatings are less technically demanding during application, but silicone and fluororous phases may eventually be deposited as persistent non-degradable particulate matter. Innocuous or degradable alternatives to fluororous phases can make this strategy more sustainable and highly competitive in the marketplace.

Biomimetic coatings and marine natural product biocides are both examples of exploiting natural AF products and mechanisms for human endeavours. It stands to reason that other biomass-derived materials may contribute to effective, sustainable, and biodegradable coating materials. Waxy compounds derived from, or mimicking leaf cuticles produce slick surfaces (Ma et al., 2011) and chitosan, which is derived from marine biomass waste, has known antibacterial properties (Yang et al., 2011). Such materials can be components of zero waste economies in coastal communities and support local fisheries using their own upgraded waste products (Ubando et al., 2020).

Although these strategies appear more sustainable and responsible than using non-selective and persistent inorganic biocidal coatings, their complete cradle-to-grave life cycles should be assessed to estimate their long-term impacts. An often-overlooked concern regarding any coating materials, whether they contain biocidal compounds or not, is their ultimate fate in the environment. Coatings degrade over time, either intentionally in the case of self-polishing coatings or unintentionally through normal aging and abrasion. Additionally, coated equipment, such as fishing gear, may become lost or discarded at sea. In any case, coatings will find their way into the environment where they will contribute to the micro/nanoplastic waste problem currently plaguing our watercourses and oceans. Apart from their impact on ocean life through ingestion, bioaccumulation, and a general decrease in water quality (Peters et al., 2018; Park et al., 2020; Dibke et al., 2021), microplastic particles have a high surface area-to-volume ratio and act as effective mobile vectors and reservoirs for hydrophobic chemical compounds. AF coating microplastics also potentially contain biocides and other active ingredients, which may extend their impacts in areas they are applied most often, e.g., harbours, fishing grounds, and seawater intakes (Soroldoni et al., 2018).

Biofouling is a serious issue that requires immediate action. While numerous creative solutions are available, stakeholders must take a careful and thoughtful approach to their selection and implementation. The economic cost, application complexity, durability, and resource use of each solution must be weighed against their potential benefits. Equally important is the long-term impact of these solutions on our planet's ecosystem. We must consider the potential consequences of their widespread use and eventual accumulation in oceans to prevent another ecological disaster, like TBT contamination, from occurring. It is our responsibility to act now and ensure that we are taking the most effective and responsible measures to address biofouling. By carefully considering the advantages and disadvantages of each solution and prioritizing their long-term impact on our planet, we can work towards a more sustainable future.

Discussion

Despite the tremendous efforts of small and medium-sized enterprises and academic researchers, there are still very few viable alternatives to inorganic biocidal coatings available on the market today. Scientists, engineers, industry groups, consumers,

and regulators must work together to identify and address the key barriers that are preventing the development and implementation of novel coatings. There are several significant challenges that must be overcome, including a complex regulatory environment, a lack of standardized evaluation methods, and limited access to high-quality performance data for comparison. The cost and availability of raw materials, such as marine natural product biocides, also pose a significant challenge. In addition, there is a pervasive sense of inertia, which can hinder progress and discourage innovation. The belief that currently available solutions are sufficient creates a barrier to change.

To address these challenges, we must collaborate to develop a program of incentives and barriers that encourage the adoption of sustainable AF solutions and establish standards and evaluation methods that allow for accurate performance data comparison. We must identify actionable pathways toward marketable and sustainable AF solutions. With the right collaborative efforts and strategic implementation, we can overcome these barriers and create a better, more sustainable future.

Technical challenges

The development of novel AF coatings requires an objective standard method for evaluating coating efficacy. Without one, competing technological solutions cannot be directly compared for different uses. For example, infrastructure, such as floating docks, buoys, and water inlets, are not exposed to the same shear forces as ocean-going vessels and do not similarly benefit from FR strategies.

Although there is a great deal of work by academics to develop standard laboratory methods to assess AF efficacy under static (Ribeiro et al., 2008) and hydrodynamic conditions (Swain et al., 2007; Nolte et al., 2018), and under potentially accelerated time frames and/or with high throughput (Cassé et al., 2007; Webster et al., 2009; Stafslie et al., 2012; Pansch et al., 2017) to compliment field assessments (Rittschof et al., 2008; Zhang et al., 2013; Stafslie et al., 2016), current ASTM standard methods (D01 Committee, 2020a; D01 Committee, 2020b), which were last updated in 2020 and represent a consensus of producers, consumers, scientists, and engineers, are still highly subjective and involve visual inspection of coated panels submerged in natural seawater. As seawater composition varies with geography and season (Swain et al., 2000), such tests lack reproducibility under varying cases and limits their effectiveness in providing accurate and reliable data. Moreover, they presume a biocidal effect whereas FR coatings are better assessed via adhesion testing (Swain and Schultz, 1996). Testing is also generally over short time scales and cannot capture the effects of aging on coated surfaces (Webster et al., 2009). Therefore, a critical research gap exists in evaluating the long-term efficacy of AF coatings in relevant environments, including establishing long-term compatibility with different substrates, e.g., steel and plastic. ASTM methods are widely used in industry, and consensus regarding better standards would improve communicating reproducible efficacy data. These research questions are best addressed through pilot studies where the coatings will be exposed to realistic operating conditions

for target applications (Bellas Bereijo and Beiras Garcia-Sabell, 2010; Callow et al., 2014; Guerin and Clare, 2018). Additionally, the long-term ecological impact should be addressed on a smaller scale to minimize the potential for deleterious effects on the environment. However, such testing is challenged by local regulations regarding what can be intentionally introduced to natural waters. Such realistic long-term tests can be supplemented by small-scale aquarium models of the receiving environment. To address the variation of fouling based on environment, application, and season, standardized model systems must address the speciation, nutrient profiles, temperature, and photoperiods relevant to each application.

Laboratory efficacy data should also be supplemented with economic feasibility studies and the practical application for desired uses, e.g., complex layer-by-layer syntheses of hierarchical structures on panels at the lab scale may never be practically applicable on large ocean-going vessels and rare marine natural products may never be economically viable in large-scale applications. Questions regarding scale-up, cost-effectiveness, and commercialization potential require contributions from engineers and industry groups that can evaluate the practicability of laboratory-scale ideas and determine whether additional funding investment is worthwhile. The establishment of relevant standards and participation by stakeholders at all levels can ensure the best use of research funding towards the overall goal of economically viable, practical, and effective sustainable AF solutions.

Finally, cradle-to-grave life cycle analyses are essential to determine if a technology is sustainable, rather than just assuming it must be if it does not include currently deleterious components. Inert coatings may have long-term persistence and any coating applied to a submerged surface will find its way into the environment. Modern AF coatings can reduce the monetizable fuel and maintenance costs, and their environmental impacts have been widely explored in the literature, but subsequent studies of their impacts on ecosystem services, both monetizable and environmental value, should be performed. The impact of coatings should be well understood early rather than after several decades when any potential problems become difficult to resolve. Sustainability must be necessarily forward-looking. Our future economies, environment, and health depend on it.

Barriers and incentives to market uptake

Although our current reliance on biocidal coatings requires urgent action, inertia among stakeholders has slowed progress. The lack of viable replacements allows current manufacturers to continue profiting while avoiding regulation. Conversely, small market entrants struggle to compete due to large financial and time barriers, with few competitors on the horizon. Incentives, such as grants, commercial research and development, and public-private ventures, that encourage the development and application of effective, sustainable solutions to overcome these barriers can bring alternatives to the market. New benign technologies can rapidly gain market share as older materials face regulatory pressure. Thus, the long-term incentive for investment in innovative and sustainable AF solutions is strong as their market share would be supported by strong barriers to entry, i.e., regulatory

approval and intellectual property protection. Incentivizing the development and adoption of sustainable AF solutions is a sound investment. For example, public investment in research and development helps fund the creation of new and effective solutions, whereas tax credits or rebates for consumers can encourage the adoption of sustainable coatings while incentivizing collaborative partnerships to help resolve technical challenges and lead to more effective solutions.

The establishment of industry standards for both efficacy and sustainability can impart consumers with a clear understanding of competing products, allowing manufacturers to provide direct comparisons in a more competitive marketplace. Additionally, independent certification programs provide confidence for consumers, helping to increase demand. Finally, pilot projects, education, and awareness campaigns can effectively demonstrate the efficacy and sustainability of products and attract new consumers. By investing in sustainable AF solutions and providing the necessary incentives, we can create a cleaner and healthier future for our oceans and rivers, while supporting the economies that rely on these environments.

Disincentivizing the use of current biocidal coatings will rely on regulatory pressure, as was used for TBT-based coatings. Regulators, however, hesitate to act because there are few viable alternatives available on the market, and industries remain dependent on biocidal coatings. The development of commercially viable and marketed sustainable alternatives will enable regulators to act, give consumers alternatives, and disincentivize the use of older, less sustainable materials.

Outlook

A ban on biocidal coatings, and their current environmental impact, will have a delayed effect as previously applied coatings come out of service, making the timely development of novel active coatings critical for regulators, global marine shipping, and related industries. This presents many challenges as novel active agents must demonstrate both sufficient AF activity for industrial applications and minimal environmental impact to meet various regulatory agency standards, a time-consuming and expensive process.

Considering the critical concern for time-to-market, disruptive technologies using marine natural products and their derivatives, among other low environmental concern materials, present promising alternatives to established biocidal compounds now facing regulatory pressure. The overall life-cycle assessment of these products, in combination with their effects on their proposed application, must also be considered. Do the economic and environmental benefits of reduced fuel use, greenhouse gas emissions, and faster shipping cycles overcome any drawbacks of the manufacture, application, and ultimate disposition of coating materials in the environment? It is essential to understand the technical gaps in reducing and eliminating marine debris and toxic pollutants arising from marine AF coating applications to create a framework for coating technology development and a roadmap to support the development of innovative commercially viable coatings and standards.

There is an urgent need to address the environmental impact of AF coatings. The development of novel active coating modalities is a critical step toward achieving sustainability in the marine industry. Together we can create innovative, commercially viable coatings that are environmentally sustainable and meet the needs of the marine industry. By doing so, we can minimize the environmental impact of AF coatings and preserve the health of our shared marine ecosystems.

Data availability statement

The original contributions presented in the study are included in the article/supplementary material. Further inquiries can be directed to the corresponding author.

Author contributions

AC coordinated the perspective manuscript and prepared the first drafts of the synopsis and manuscript. All authors contributed to the article and approved the submitted version.

Funding

AC, XZ, and KO have received funding from the Natural Science and Engineering Research Council of Canada (NSERC) Discovery Development grants, Canada Research Chairs program, the Canada Foundation for Innovation John R. Evans Leaders Fund, and the Cape Breton University Research Innovation Scholarship Exploration program. TW has received funding from the NSERC Discovery grant program. KJ was an industrial partner

with Cape Breton University in obtaining funding from NSERC Alliance Missions, Mitacs Accelerate, the Information and Communications Technology Council, and the National Research Council (Canada). KJ has also received funding from Canada's Ocean Supercluster. TC and MS received funding from the UNSW Faculty of Science Industry Network Seed Fund.

Acknowledgments

KJ acknowledges multiple discussions and insightful feedback on the topic from Eric Siegel of the Ocean Startup Project and Ocean Frontier Institute.

Conflict of interest

KJ is a founder of Kavacha, a company working in the field of marine antifouling coatings. TC is a Director of Ecozean Pty Ltd., which has developed an anti-fouling coating for aquaculture.

The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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