A Study on Natural antifoulants and Ecofriendly fouling release coatings Techniques: A Review

Study of various antifouling techniques available in the industry.

1Tejas Nitin Ingole, 2Sankalpa Sanjeevkumar Ithape, 3Ganesh Shivaji Janrao, 4Suyash Sanjay Khot
5Parag Vilas Kulkarni, 6Atharva Gadekar, 7Prof. Yeshashree Pankar, 8Dr. Satchidanand Satpute

Abstract: Antifouling systems generally refer to dealing with the undesirable accumulation of marine biological organisms on surfaces for e.g. ships hulls, sea-platforms which are in contact with seawater. This natural phenomenon offer a large number of economic problems to the marine industry to deal with. The Traditional approaches utilize metal ions especially copper to prevent such biological contamination but it is proved to harm the environment and the ecosystem. Later the use of tributyltin-based coatings made the conditions worst as it is highly toxic in nature. After the ban on use of tributyltin in antifouling coatings , the emphasis is now on the use of nontoxic and/or ecofriendly natural materials which do not negatively affect the environment. This is a review which focuses on the natural antifouling techniques and the synthetic fouling release coatings which are environmentally benign. A lot of biologically extracted antifouling agents are also studied in this review which exhibits a biomimetic approach. The mechanism of marine biofouling and factors affecting it is also overlooked in this study.

Index Terms - Antifouling; Biofouling; Antifouling agents; Antifouling coatings.

I. INTRODUCTION

The maritime industry plays an important role in shaping a nations GDP and generates a lot of revenue, employment, and access to resources. It provides actuation to the global ecommerce, fuel trade, navel defense activities, food supply chain and so on. This industry has the highest exposor to the harsh and tough marine conditions and has to tackle the problems like corrosion, weathering and the most economically demanding one which is biofouling. Due to continuous encounter of the Container ships, bulk carriers, tanker ships, passenger ships etc. with the marine ecology, these ship hulls develop an unwanted growth of marine organism which is referred to as biofouling.

Along with the shipping and transportation industry, other key sectors are negatively impacted by biofouling. For example, The power generation industry is reported to face reduction in efficiency and maintenance due to the accumulation of biofouling in the cooling systems of some nuclear reactors. Other studies have shown that the colonization of barnacles on marine current turbines has a detrimental effect on turbine efficiency. Another study showed that offshore wind power plants offer atypical substrates for fouling assemblage in terms of orientation, depth range, structure and surface texture, and thus efficiency can be affected. Biofouling can also severely affect wave energy plants by having a negative impact on material, weight, shape and efficiency. Biofouling is further responsible for a significant gain in weight of static structures in aquaculture and sometimes cause mechanical failure. Fouling organisms growing on immersed manmade surfaces can also trigger biocorrosion, and transport of biofoulers may promote the spread of nonindigenous species.[3]

In this context, antifouling is basically a strategic application to prevent the adherence of micro-organisms and macro-organisms to surfaces. Corrosion prevention systems create a physical barrier, such as paint, to prevent or slow the ingress of water and oxygen. Over the years, antifouling paints have played a variety of important roles, from preventing marine life to acting as a barrier against corrosion on metal ship hulls. In recent years, several antifouling and anticorrosion paints have been synthesized [1]

Following are the major categories of fouling:

i. Macromolecules and other organic substances, such as fouling, accumulate (proteins, polysaccharides, carbohydrates, lipids, etc.).

ii. Inorganic fouling, which frequently results from crystallization or corrosion processes, is the precipitation of inorganic material, such as salts and metal oxides.
Particulate fouling is the buildup of particles (e.g., colloidal particles) The term "biofouling" refers to the settling and accumulation of biological materials, which produces conditioning films (macromolecules) that can develop into biofilms (microorganisms) and result in macroscopic biofouling (macro-organisms). Composite fouling is the term used to describe fouling that involves multiple foulants or fouling mechanisms.[2]

There are a few approaches used in antifouling systems. The first of these is resistance to fouling: prevents the adhesion of proteins, algae and/or bacteria, often attributed to the formation of a highly hydrated surface, as this provides a physical barrier and d free energy to fouling, the second is the release of fouling: allows low adhesion of contaminants to the surface, while facilitating the easy removal of adsorbed contaminants through the application of limited shear or a mechanical force (for example via a water jet or an external trigger). And the third is fouling-degrading: degrades adsorbed organic matter via oxidants and/or kills (adherent) bacteria and other microorganisms through the action of bactericidal functionalities.[2]

II. MECHANISM OF MARINE FOULING

Marine biofouling occurs through the unwanted colonization and accumulation of marine microbes, flora and fauna on the surfaces of submerged materials, with significant adverse effects on marine industry infrastructure and equipment. Marine biofouling increases hull weight and roughness, increases drag resistance, and increases fuel consumption. It also initiates or accelerates corrosion of metal and concrete structures, increasing the risk of failure of ship equipment and structures. Seawater pipes used in coastal industry and cages used in aquaculture attract biofouling, reducing equipment efficiency and seafood production. Additional onboard biofouling organisms migrate to other seas where they do not occur naturally, disrupting ecosystems. Therefore, marine biofouling is a serious problem that needs to be prevented and solved for both the marine economy and the marine environment. Previous research has focused on the formation and growth of biofilm-related marine biofouling, as shown, comprising the following steps: An absorbed film quickly forms on the submerged surface due to the adsorption of proteins, glycoproteins and polysaccharides; Bacteria and other microorganisms adhere to the absorbed film and gradually grow into a biofilm by secreting extracellular polymeric substances (EPS) composed of proteins and polysaccharides to envelop and fix them; Marine organisms such as diatoms, larvae and spores of microalgae accumulate on the surface of materials because the biofilm can provide them with nutrients; Larvae of marine microorganisms such as barnacles settle and grow on the surfaces of materials as macrofouling. This common formation process for most biofouling organisms illustrates the relationship between microorganisms and macrofouling such as mussels and barnacles. Macrocouling are the primary constituents and ultimate results of biofouling formation while microorganisms are the cause of biofouling formation as they create the proper colonization sites and conditions and provide nutrients to attract new organisms. Microbial activity can regulate macrofouling, while macrofouling accumulation can protect microbes and biofilms from elimination.[10]

The timeline of biofouling growth can be broken down into the following crucial stages, as displayed. First, when the substrate has been submerged in seawater, Organic Carbon Residue (OCR) will instantly adhere to the wet substrate surface and quickly create a conditioned coating. These OCRs' chemical make-up is mostly determined by the ions, glycoproteins, humic acids, and fulvic acids present in the liquid phase. Second, a few hours later, bacteria and other microorganisms are adsorbed on the conditioned film to create a biofilm under the influence of electrostatic force and van der Waals force. Bacteria and other microorganisms are encouraged to adhere to the conditioned film by water flow, Brownian motion, sedimentation, and convective motion. Extracellular Polymeric Substances (EPS), which are made up of polysaccharides, proteins, and nucleic acids, allow bacteria and other microbes to cling to surfaces. Early biofilm formation is a crucial catalyst for later adhesion of additional complex organisms. Third, about 7 days later, a few protists, single-celled algae spores, and marine biological larvae clung to the surface of the biofilm, providing food for the development of sizable biological fouling populations. Finally, after about a month, a more sophisticated biological fouling community has developed on the substrate surface below saltwater. [11]

III. NATURAL ANTIFOULANTS

Marine organisms are an ideal source for isolating natural antifouling agents as they produce and release chemicals that inhibit microbial growth to gain a competitive advantage. Studies have been conducted to extract natural products with antifouling properties from marine organisms such as algae, invertebrates, and microorganisms. Algae are a potential source for research on natural antifoulants as they can produce antifoulants. Another study separated the active components of three macroalgae in methanol and tested the antifouling activity of the extracts. t connection, ornata and S. polycystum reduced fouling organisms on nylon mesh in a 3-month field test. The most important antifouling chemicals are most likely fatty acids, phytosterols, and terpenoids. It is the most meaningful way to verify the antifouling effect of the coating. Field tests should be conducted in waters with high pollution pressure. Therefore, the results may indicate a lasting lasting antifouling effect. Although some antifouling agents can show promising results in laboratory tests, results in the natural environment are conflicting. Some marine bacteria are known to produce active organic compounds that can protect them from their counterparts. Several species of bacteria isolated from sponges have been shown to secrete bioactive metabolites. These compounds have been extracted and about half have been shown to be effective in controlling bacterial and microalgae growth. Ethanol and dichloromethane extracts from 5 macroalgae species and methanol extracts from 2 sponge species were used for antifouling tests. A 40-day field trial showed that extracts from the macroalgae Sargassum horridum and sponge Haliclona caerulea were used as antifouling agents in coatings to reduce biofouling by up to 32%. Quorum sensing (QS) inhibition has been proposed as a powerful antibacterial and antifouling method. QS is involved in cell communication in bacterial colonies. Bacteria detect population density by the concentration of small signaling molecules and regulate gene expression accordingly. QS has been shown to promote bacterial
attachment and biofilm formation. In one study, high-yield screening strains were established and 78 natural products from various sources were screened for quorum absorbance. Of these, about a quarter were expressed as QS inhibitors, and seven active compounds were selected for reporting based on LuxR and LasR. Kojic acid performed the best, confirming its resistance to bacterial and algal growth in mesocosmos experiments. It has also been reported that furanones, particularly halogenated furanones, can disrupt various QS signaling pathways. Butenolides are another promising antifouling agent that has been extensively studied. First synthesized in 2009, it is structurally similar to antifouling compounds produced by marine actinomycete species. It has advantages such as high biodegradability and low toxicity to non-target organisms. The mechanism by which butenolides prevent attachment of various scab organisms disrupts key pathways of energy metabolism. Butenolides were incorporated into poly(ε-caprolactone)-based biodegradable polyurethanes to form biodegradable coatings and exhibited antifouling ability for at least 3 months. The optimal formulation of the butanolid antifouling coating was then described, and the coating demonstrated antifouling properties over a 6-month test period under the best conditions. Corals are also a source of natural anti-fouling agents because they live on the ocean floor and produce chemicals to survive under fouling and competitive pressures. Two of the 13 chemicals showed antifouling effects against Balanus amphitrite and Bugula neritina.

A. Extraction of antifoulants from natural sources

The extraction process is the step of separating the desired natural product from the raw material. H. sponges include various methods that can be used to obtain crude extracts. Crude extracts are known to consist of a complex mixture of various metabolites, including alkaloids, terpenoids, peptides and quinones. Extraction processes can be divided into two categories: traditional extraction methods and emerging technologies based on energy or mechanisms. Conventional extraction methods mainly consist of extraction using solvent or solid-liquid extraction. In Soxhlet, the sample is boiled with a solvent with or without stirring for a period of time, whereas in maceration, the sample is immered in a solvent with occasional stirring. These techniques are examples of viable solid-liquid extraction methods. These methods have been widely practiced for a long time. However, the use of these techniques is time-consuming, requires large amounts of solvent, compounds are lost during the concentration process due to volatilization, and harsh conditions such as high temperatures and waste solvents can lead to compound hydrolysis which has some drawbacks. May cause environmental pollution. The solvents used in these techniques consist of a single solvent or a mixture of solvents with a wide range of polarities. For example, methanol, ethanol, trichloromethane, acetone, and water can be used as solvents individually or together with a mixture of organic solvents such as ethanol and acetone.

IV. Non-ecofriendly Antifoulants coatings

A. Effects of copper leaching

- Copper (Cu) is a trace metal essential to marine life, but is toxic in high concentrations. The global ban of tributyltin-containing AF paints subsequently led to increased Cu concentrations in ports and coastal waters, leading to increased use of copper-based antifouling (AF) paints. Worldwide, it is estimated that approximately 1.5×107 kg of copper-containing AF paints end up in seawater each year. As a result, copper becomes a potential threat to marine life. Numerous biometric experiments have been performed on mussels, clams, sea urchins and fish to study the toxic effects of Cu on marine organisms. On the other hand, the knowledge of the effects of Cu on barnacle larvae is still limited.
- This research clearly shows that:
  - Cypriot settlements are more vulnerable to copper than Cyprus mortality.
  - Nauplius II is the most sensitive larval stage.
  - With increasing copper concentration, the phototaxis of Nauplius II showed a decreasing trend, while the ammonia excretion rate initially increased; followed by a decreasing trend.
  - The Nauplius II ammonia removal rate is the most sensitive indicator of copper and can serve as an indicator for monitoring copper contamination. [5]

B. Zinc Leaching

Zinc is readily leached from used antifouling paint particles under a variety of environmental conditions. Qualitatively, the extent of metal release is largely consistent with the mechanisms governing the release of Zn from oxidized and acrylic pigments. However, under certain conditions, the increase in Zn leaching with decreasing temperature is attributed to complex reaction kinetics and the presence of calcium carbonate in the paint matrix. Clearly, more research is needed on the ecological and biological impact of color fragments in estuaries and coastal environments with high boating activity. [6]
V. SILICON BASED ANTIFOULING COATINGS

Fouling release coatings and fouling resistant coatings make up the bulk of the latter (FRC). Anti-fouling coating can prevent adhesion of marine organisms. Typically, hydrophilic polymers such as poly(ethylene glycol) (PEG) and those based on zwitterions are used to make them. They generally swell under marine conditions, which reduces their mechanical properties and limits their use. FRCs cannot prevent biofouling, but due to their low surface free energy (SFE), the interface contact between the organisms and the coated surface is weak, so fouling organisms can be removed from water by mechanical washing and ship navigation. It can be easily removed by shear force. In addition to low SFE, low modulus is important for FR performance. Hard soils such as barnacles can be removed from surfaces with a low modulus of elasticity. In fact, elasticity makes the surface malleable or dynamic, making it more difficult for microorganisms to land or colonize the surface. The theory of dynamic surface antifouling (DSA) can be used to explain this mechanism. [18]

Improved Fouling Resistance i.e. amphiphiles, zwitterions, quaternary ammonium salts (QAS), and antifouling agents all help silicone-based FRCs avoid fouling under static conditions. It has been introduced as The hydrated layer and sterically excluded bulk effect of PEG-based amphiphiles confers resistance to protein and cell adhesion. There have been several initiatives to incorporate them into marine antifouling coatings. The development of the slippery silicone coated Biomimetic FRC was motivated by the fact that many organisms have built-in ability to resist dirt. Silicone oil and other liquids are added to his silicone-based FRC to mimic the behavior of slime released by organisms such as pitcher plants and fish. A weak surface layer created by the silicone oil's ability to migrate to the interface between coatings helps detach biofouling. Silicon substrates were prepared with thiol termination as previously described. Briefly, a silicon wafer was divided into 1 cm × 1 cm bits. The wafer was cleaned with piranha solution and hydrated with NH4F/HF(aq) solution at room temperature. The substrate was then chlorinated using benzyl peroxide in anhydrous benzene in a saturated PC15 solution. The chlorinated substrate was then immersed in NaSH-DMF solution for surface thiolation after surface chlorination. [18]

Self-Healing Polymer was recently developed for coatings, wearable technology, and soft robots that mimic natural creatures. Self-healing marine antifouling coatings are expected to improve stability and durability in long-term applications. It is well known that PDMS elastomers are susceptible to mechanical damage and cross-linked structures impede spontaneous healing. Recently, Liu et al. We have developed a self-healing polyurea antifouling coating based on PDMS. The high-density hydrogen bonding of polyurea was thought to be responsible for its self-healing power. Cut elastomers were allowed to cure in air or seawater for 48 hours at room temperature, as indicated. Ultimate strength obtained from tensile tests showed a self-healing efficiency of over 90%. Self-healing effectiveness can be enhanced by adding the organic antifouling agent 4,5-dichloro-2-n-octyl-4-isothiazolin-3-one (DCOIT). 10% DCOIT was 100%. It is understandable. The self-healing effect is enhanced when polyurea chains are combined with her DCOIT, which acts as a plasticizer. Moreover, the PDMS polyurea coating exhibited an adhesion strength of above 1 MPa, depending on the DCOIT level. DCOIT can be released through the polymer at a controlled and slow rate. Due to DCOIT’s hydrophobicity and chemical affinity for urea groups, it is retained within the polymer matrix, but gradually migrates to the surface and dissolves in salt water. As a result, it exhibited excellent antifouling performance even after 180 days of immersion in still water. This is the first known report of a self-healing marine antifouling coating. Other self-healing systems based on metal ligand coordination or boronate ester linkages can also be used to generate marine antifouling coatings. [18]

VI. BIOMIMETIC ANTIFOULING SURFACES

Biomimetics uses chemical, physical, mechanical, or behavioral effects to study the structure of biological systems and processes as a template or source of inspiration for the design and construction of environmentally friendly materials and technologies, and manipulation studies.

The ability of marine organisms to resist dirt is thought to be a result of skin patterns, which can influence surface roughness, wettability, surface energy, and other properties. No biocide release is required to replicate the natural antifouling surface microstructure, resulting in less potential damage to marine ecosystems. Therefore, biomimetic microstructured coatings are one of the emerging research topics and have attracted much attention recently. Rough microstructures can have antifouling mechanisms that reduce the surface area that fouling organisms come into contact with them.

On the other hand, if the surface texture is smaller than the soiled organism, the surface pattern has better antifouling properties. On the other hand, if the surface texture is larger than the soiled organism, more dirt will accumulate on the surface. Fowler's adherence increases and adherence decreases with structures of an order of magnitude smaller than fouling organisms. Scardino and de Nys studied nudibranch, sharkskin, echinoderm, and other biomimetic antifouling surfaces. In fact, marine life is not the only source of inspiration. Terrestrial organisms also provide valuable templates.

VII. TESTING FOR THE LEACHING RATE OF FOULING RELEASE COATINGS

The experimental protocol developed proved to be an efficient tool for comparing the potential release of active ingredients from leaching of biocide-free coating products without the use of self-polishing methods. The applied leaching protocol (surface/volume ratio and prolonged immersion time) allowed us to emphasize the release of bioactive components from the tested silicone FRCs and to determine the ecotoxicological impact. I was. Although not representative of real-world environmental exposures, the leaching protocol employed emphasized the differences between the tested coatings. Also, using a sensitive model organism and choosing two endpoints (acute and behavioral) allowed us to obtain significant results. After the first color aging period (24 h, T0), the effects of both selected endpoints showed percentages significantly different from controls for all pure (100%) coating leaching. A sharp drop in response was observed for coatings 3, 4, and 5, even starting from an aging time (T1) of 7 days. Only larvae exposed to the leaching products of Coating 1 showed a significant response even after extended paint aging times (14 and 30 days). Moreover, Coating 1 was the only one that showed a significantly different response than controls, even after 30 days of his aging (behavioral endpoint
only) and also for diluted (50%) exudates. Coating 2 The toxic effect of exudate persisted after 14 days of aging, showing no significant difference between undiluted (for both endpoints) exudate and diluted (for inhibiting flotation rate only) exudate controls. No reaction was detected in larvae after 2 and 3 months (T4 and T5, respectively) for all coatings. Figures 2 and 3 in the figure clearly show the reduction in toxic effects due to leaching of the coating. Coating 1 is the product that releases the toxicant at longer immersion times compared to the other products tested, and Coating 5 shows the lowest release potential. Furthermore, the graph shows the difference in sensitivity between the two endpoints, indicating that the toxic effect disappears after different immersion times for immobilization and changes in swimming speed.[22]

VIII. OUR SUGGESTION

Most of the Antifouling coatings are using Copper ions which harm the environment by killing the organisms dead. Try different types of antioxidants as the constituents of antifouling paints. This reduces the grip of the organisms and eventually prevents them attaching to the hull of the ships. Add silicone-based compound to the coating as an additive. These silicone-based coatings are hydrophobic and produce smooth surfaces, which make it difficult for marine organisms to the coated surface. After studying a lot of chemical properties and composition of various market available antifouling paints we have come up with a different paint composition which is as follows:

Table 1. Proposed composition of antifouling coating.

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Constituent Compound</th>
<th>% By mass</th>
<th>Purpose to serve in the composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Antioxidants</td>
<td>20</td>
<td>Prevent the of growth micro-organisms</td>
</tr>
<tr>
<td>2</td>
<td>Xylene</td>
<td>21</td>
<td>Solvent</td>
</tr>
<tr>
<td>3</td>
<td>Methylisobutylketone</td>
<td>5</td>
<td>As a solvent for rains</td>
</tr>
<tr>
<td>4</td>
<td>Base polymer</td>
<td>7.5</td>
<td>Binder (acrylic polymers)</td>
</tr>
<tr>
<td>5</td>
<td>Rosin</td>
<td>7.5</td>
<td>Provides consistency</td>
</tr>
<tr>
<td>6</td>
<td>Barium sulphate</td>
<td>35</td>
<td>Provides durability (filler)</td>
</tr>
<tr>
<td>7</td>
<td>Anhydrous ferric oxide</td>
<td>1</td>
<td>Prevent corrosion and rusting of metals and also resist blistering, cracking and peeling</td>
</tr>
<tr>
<td>8</td>
<td>Oxidized polyethylene wax</td>
<td>1</td>
<td>Disperse pigment efficiently, prevent pigment and carrier from gathering, avoid protrusion in the process of painting.</td>
</tr>
<tr>
<td>9</td>
<td>Amide wax</td>
<td>2</td>
<td>Reduce gloss but impart a satin texture to the coating.</td>
</tr>
</tbody>
</table>

VI. RESULTS AND DISCUSSION

Silicone-based FRC is environmentally friendly, chemically stable, and has drag-reducing properties. However, their applications are limited due to their low mechanical strength, poor adhesion to substrates, and poor fouling resistance. The addition of nanofillers or chemical modification with epoxies and urethanes can improve the tensile or adhesive strength of FRCs, but usually reduces the elasticity of FRCs, thus reducing their ability to release fouling. Addition of liquids such as amphiphiles and silicone oil improves stain resistance but reduces mechanical strength. Functionalizing FRCs with zwitterions, quaternary ammonium salts, and antifouling agents can effectively improve their antifouling properties, but increase their swelling or elastic modulus in marine environments. A surface-enriched, non-leaching strategy is a good way to optimize the FR performance and mechanical properties of silicone-based FRC. Self-healing FRCs can function even when damaged, but their mechanical properties are often not high enough. Organic-inorganic hybrid functional silicone is a combination of silicone elastomer and inorganic particles with antifouling groups. They can have excellent flame retardant performance and mechanical properties at the same time, representing a new generation of his FRC.
Each technique considered in this review has its own strengths and weaknesses. Antifouling coatings are the most suitable and practical solution for combating fouling. Our research shows that our proposed coating composition can be used in industry. In this review, we learned that adding antioxidants instead of copper ions is more environmentally friendly and good for marine biodiversity. Real ocean environments are difficult to replicate in simulations. Cost can be reduced by changing the quality of paint components.

VII. ACKNOWLEDGMENT
This review paper is prepared with the help of the references attached below and due credits are given to those authors.

REFERENCES