

Application of Emerging Ecofriendly Antifouling Paints: A Need and Challenge

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SUMMARY

Metallic antifouling coatings are hazardous to the environment. Copper is commonly employed in AF formulations since TBT-based AF coatings were banned. However, there is mounting evidence that the copper produced by these coatings has serious consequences for the marine ecosystem. Because natural antifoulants are less toxic, effective at low concentrations, biodegradable, have broad spectrum antifouling activity, and their effects are reversible, they have been advocated as one of the best replacement possibilities for metallic based AF coatings.

INTRODUCTION

Any natural or manmade structure exposed to seawater is immediately fouled by micro and macro fouling organisms. Bio fouling is a fast, dynamic and complex issue in the shipping or transportation industry. Marine bio fouling alludes to the colonization and settlement of fouling organism such as plants, green growth, or little creatures on the outer layer of submerged substrates, which typically truly influences the ordinary activity of boats and submerged structures. The predominance of marine bio fouling is naturally higher in the shallower water along the coast. At first 2000 species were distinguished on fouled structures which has been revised and increased to more than 4000 species of marine fouling organisms including soft (algae and anemones) and hard (barnacles, mussels) fouling species. They shift extraordinarily with various topographical areas and distinctive ecological conditions, including salinity, temperature, nutrition, flow velocity, and solar radiation intensity. In general, the process of bio fouling starts with the adsorption of organic molecules on the recently submerged metal surfaces, which is the development of micro-fouling, then the bacteria, diatoms, and other microorganisms accumulate, attached to an extracellular film of polymeric substances. Such biofilms foster quickly on surfaces in a matter of soaking hours, increasing in thickness and structural complexity as time passes. Bio fouling in fresh water systems is less articulated when contrasted with seawater, which has high salt content and forms a complicated solution, larger part of the known components. Adhesion process of fouling organisms usually has four principle stages:

- The first stage is the adsorption of organic and inorganic macromolecules after immersion: the primary film.
- The second stage is the transport of microbial cells to the surface, and the immobilization of microscopic organisms.
- In the third stage (combination), bacterial binding to the substrate is combined through extracellular creation polymers, shaping a microbial film on the surface.
- In the fourth stage, a more complicated community is created with the presence of multicellular species, microalgae, residues, sediments on the surface. After this stage, larger marine invertebrates like mussels, barnacles, and macro algae join the surface and forming macro fouling.

Biofouling's effects on the marine industry

Different types of resistance that has an impact on ship efficiency based on ship profile (Tanker ships, Container ships). Air, Wave-making, Appendages, and Frictional are the types of resistance. An increase in frictional resistance, which leads to a reduction in ship speed, is one of the effects of marine fouling on ships and the environment. The following are some of the negative effects of ship hull bio fouling: (i) Higher fuel consumption because bio fouling increases frictional resistance, making the hull rougher and the ship heavier. In order to maintain the appropriate vessel speed, it also slows the vessel's speed by 10% and increases fuel consumption by around 40%. Increased fuel use owing to bio fouling contributes to hazardous emissions, with estimates ranging from 38 to 72 percent increase in carbon dioxide and sulphur dioxide emissions by 2020. (ii) Because marine bio fouling necessitates more frequent and lengthier dry-docking operations, hull maintenance is more expensive and time demanding. Furthermore, these cleaning operations discharge a vast amount of harmful compounds into the water. (iii) Corrosion of the ship hull as the protective coating surface deteriorates due to

metabolic and other biological processes. As a result, the hull's surface is more prone to corrosion and discoloration. The colonization of hulls has been related to two significant environmental pollutions: gas emissions into the atmosphere (CO₂, CO, SO₂, and NO_x) and the spread of potentially alien species. Historically, hull fouling was the most common vector of species translocation, in which organisms stuck to the hulls in one region and were moved across oceanographic borders during the voyage, either coming off naturally in a new habitat or after the ship's hulls were cleaned. Non-indigenous species in an environment have the potential to threaten biodiversity as well as social and economic interests.

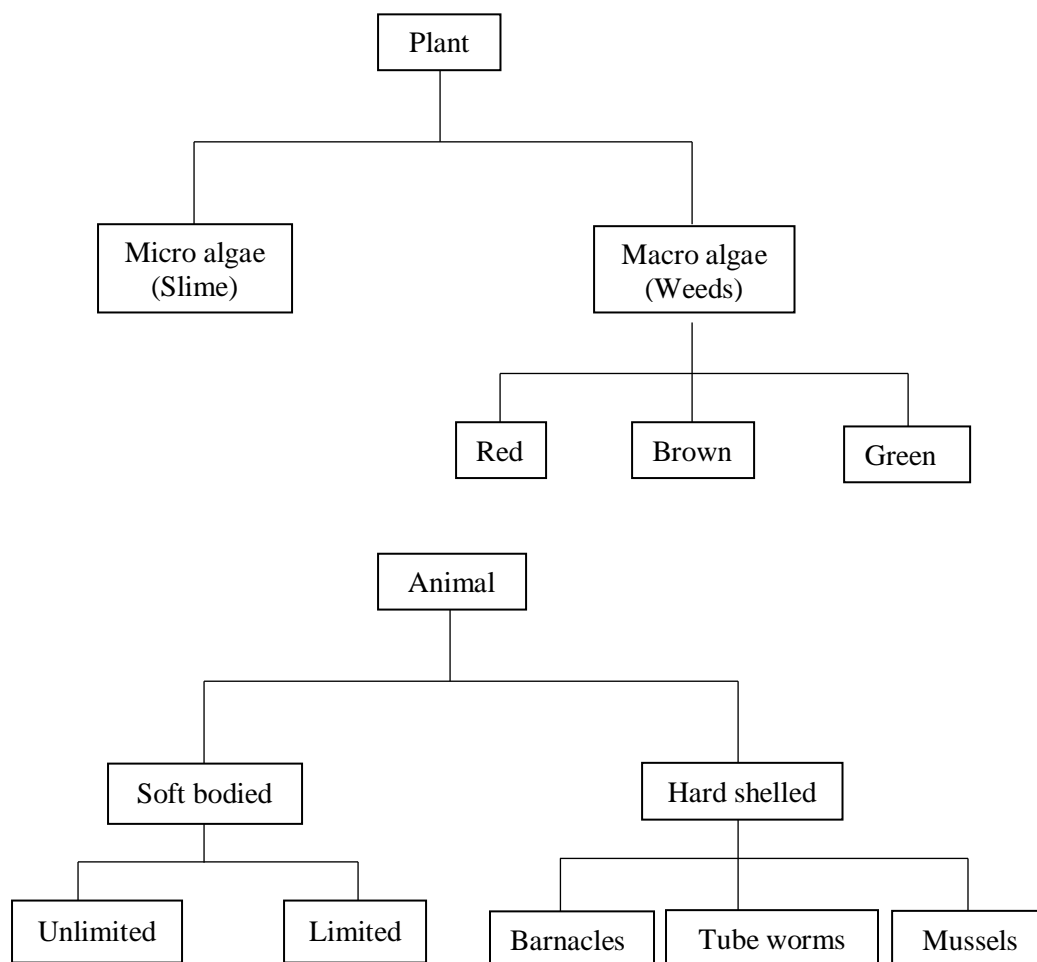


Fig. 1. Classification of marine fouling organism

Biofouling Prevention on Ships

Antifouling technology has a long and illustrious history. For more than 2,000 years, humans have battled marine fouling. The most effective technique to avoid biofouling is to choose the right material for the building that will be immersed in water. Scraping the hulls of ships is one of the first means of fixing the problem in the shipping industry. According to literature, the earliest ancient Greeks wrapped the hull in asphalt, wax, tar, and other materials for antifouling treatment. Anti-coating has been discovered to be the most effective strategy for controlling the formation of bio fouling on submerged surfaces. The first attempt to control bio fouling goes back to the Greek and Roman civilizations, 700 BC, when copper or lead sheathing was employed to protect wooden boats from the growth of marine organisms on man-made surfaces. Ships were manufactured of steel around 1860, but copper sheathing could not be employed because electrolyte action increased hull deterioration. As a result, different techniques of protecting ships became necessary, resulting in the development of contemporary paint systems. In recent decades, the dominant technique for controlling the effects of bio fouling organisms has been to apply a protective organic layer comprising particle biocides. According to the mechanism used to release the biocide, these paints can be divided into three categories: soluble matrix, insoluble matrix or contact paint, and

self-polishing paints. Until the 1960s, the most effective antifouling compounds were based on alkyl tins, particularly tributyl tin (TBT), which was previously thought to be a permanent answer to the problem of marine bio fouling.

Ecological consequences of anti-fouling paints

The chemicals of tributyltin (TBT) and triphenyltin (TPT) were highly toxic for many aquatic organisms and which have been shown to infect the food chain and remain in the environment. In the 1990s, self-polishing TBT paints were used on 70% of the world's maritime fleet, accounting for two-thirds of the overall antifouling market. Unfortunately, the most popular antifouling coating also proved out to be the most harmful, with a lifespan of up to five years. Excessive use of this biocide in the environment resulted in oyster population shell thickening and gastropod imposex. Furthermore, their bioaccumulation and biomagnification in the marine food chain have raised serious concerns. As a result of the restriction issued by the International Maritime Organization (IMO) in 2001, TBT antifouling coatings were banned worldwide after 2008. Although copper and organic booster biocides combined with copolymers have been frequently employed as quick replacements to TBT, most of these biocides should be considered interim treatments rather than true TBT substitutes due to their ecotoxicity, durability, and expense.

The Need for development of novel non-toxic antifouling agents

Toxic biocides and metal-based anti-fouling coatings have been offered as alternatives to marine natural products for managing bio fouling. TBT-replacement antifouling coatings must therefore be environmentally friendly while also having a lengthy service life. In this context, natural product antifoulants have been presented as one of the finest viable solutions. They are less toxic, effective at low concentrations, biodegradable, having broad range antifouling action, and their effects are reversible, compared to conventional harmful biocides. Additionally, they have evolved through millions of years within the system. Terpenoids, steroids, carotenoids, phenolics, furanones, alkaloids, peptides, and lactones make up the majority of natural product antifoulants discovered thus far. Sponge, soft corals, seaweeds, sea grasses, tunicates, bryozoans, mangroves, and microbes are among the principal categories of species from which they have been separated.

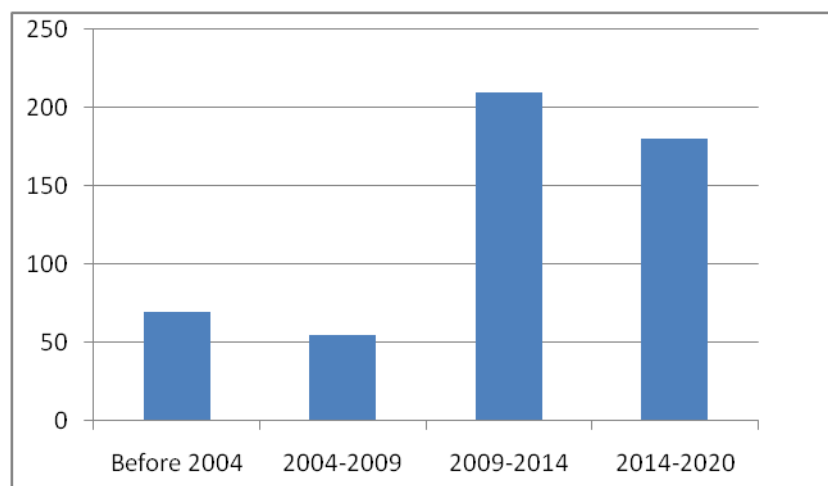


Fig.2. Number of anti-fouling natural products isolated from a marine source before May 2020

According to statistics, 3,129 different types of marine natural chemicals were found from algae between 1965 and 2012. There are approximately 1,658 different types of natural chemicals isolated from Rhodophyta plants, accounting for 53% of the total and ranking first. In second place, approximately 1,213 natural chemicals derived from Ochrophyta plants account for 39 percent of the total. Only 258 species of Chlorophyta are extracted, accounting for 8% of the total. The antifouling efficacy of nemertinepyridyl alkaloids from marine Haplomertines against the barnacle *B. Amphitrite* larvae is strong. *Nerita albicilla* and *N. oryzarum*, two marine

mollusks from Tuticorin, demonstrated broad spectrum inhibitory action against biofilm bacteria. The fouling diatoms *Navicula subinflata* and *N. crucicula* were suppressed by a methanol extract of *Holothurialeucospilota*. *H. scabra* crude extract had antifouling efficacy against the limpet *Patella vulgata*. Zosteric acid, derived from the seagrass *Zostera marina*, has been discovered to prevent both micro- and macrofouling organisms. The potential of antifouling characteristics against marine biofilm forming bacteria was examined in sea grasses of *Cymodocea serrulata* and *Syringodium isoetifolium* found commonly along the Thoothukudi coastal area. Biofilm-forming bacteria such as *Micrococci sp.*, *Aeromonas sp.*, *Pseudomonas sp.*, *Flavobacterium sp.*, *Cytophaga sp.*, and *Enterobacter sp.* were evaluated using extracts from seaweeds *Ulvalactuca*, *Caulerpa pascaliiformis*, *Padinaboergeseni*, *Caulerpa sp.*, and *Chaetomorpha linoides*.

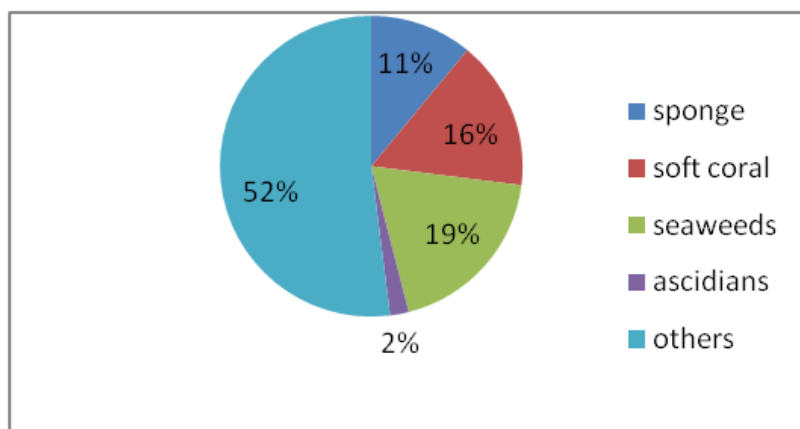


Fig 3. Natural product antifoulants isolated from marine sources

Bacteria obtained from sponges and algae, *Pseudoalteromonas luteoviolacea*, *P. tunicata*, and *P. aurantia*, suppressed the growth of other bacteria present in the maritime environment that cause biofouling. *Pseudoalteromonas sp.* strain Y produces water-borne algicidal chemicals that kill *Chatonella*, *Gymnodium*, and *Heterosigma* planktonic algae. *P. tunicata*, a marine bacterium, produces antialgal chemicals that prevent *Ulvalactuca* spores from settling. Some NPA-based antifouling paints have previously been commercialised, such as 'Sea Nine-211,' 'Netsafe,' and 'Pearlsafe.' Similarly, analogues of furanone isolated from Australia were used to create 'Netsafe' and 'Pearlsafe.'

CONCLUSION

Natural materials produced from marine organisms are used as active components in coatings meant to prevent fouling organisms from growing and settling. These chemicals are being used as "environmentally friendly and anti-bio fouling agents. By collecting effective antifouling components from marine microorganisms and aquatic plants, natural antifouling agents are viewed as the most optimal. Biological antifoulants are still in infancy stage, but as a frontier area in biotechnology, they have far-reaching ramifications in the maritime industry. Among the currently possible possibilities, the microbial approach looks to be the most promising and cost-effective method for developing long-term environmentally safe nontoxic materials.

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