Control of Biofouling In Marine Environment – Past, Present And Future

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Abstract: Biofouling is a worldwide phenomenon plaguing mariners and accounting for economic burden on shipping, aquaculture and various other maritime industries. The fouling organisms cause extensive damage to commercially important marine structures causing increased drag of marine surface and submarine vessels incurring increased fuel penalties. . Antifouling is the phenomenon of preventing biofouling. Conventionally the principal protective method against fouling has been the use of antifouling paints. Environmental concerns of high toxicity against non- specific targets including marine flora and fauna have resulted in imposition of worldwide ban on the use of most chemical antifouling formulation including TBT in 2006. Currently, other available approaches are far from ideal and consequently they do not provide a complete or long term answer to this expensive problem. Consequently exploration for alternatives coating has been intensified to bridge the gap. Great deal of attention is being currently focused on identification of nontoxic, environmentally friendly, Natural Product Antifouling agents (NPA).

Key words: Marine environment Biofouling , Antifouling, NPA,

1.INTRODUCTION

The marine realm is one of the major habitats of the biosphere and covers around 70% of the earth's surface. Eighty to ninety percent of all life forms of earth are present only in the oceans. The microbial diversity is enormous in marine habitat. The diverse structure, physiology and metabolism enable microorganisms to survive in this extreme environment. Halophiles are adapted to harsh, hyper-saline conditions. Halophiles and halotolerant microorganisms grow over a wide range of salt concentrations inhabiting natural hypersaline brine in arid, coastal and deep-sea waters as well as in artificial salterns used to mine salt from the sea(1,2). They include both prokaryotic and eukaryotic organisms. It has been estimated that though more than half of the earth's biomass is microbial, they are not obviously conspicuous in natural environment (3,4,5).

In the marine environment the competition for living space is intense and all surfaces living or innate are susceptible to fouling. The colonization of living or non-living surfaces by sessile organisms, plants or animals is an omnipresent phenomenon in aquatic environment . Biofouling in fresh water systems is less pronounced as compared to seawater, which has high salt content and forms a complicated solution, containing majority of the known elements. The process of biofouling generally begins with the formation of a biochemical conditioning film onto which bacteria and other organisms colonize. The macroforms include various eukaryotic organisms like marine invertebrates and algae. Macrofoulers like barnacles, tunicates and bryozoans that frequently occur on the surfaces or submerged waters, impede movement of ships (6,7),. Fouling on ships is significantly detrimental and results in increased drag, surface corrosion, decreased fuel efficiency, loss of speed and an increase in pollution. Submerged structures become corroded, followed by rusting due to the intense actions of the fouling organisms. The prevalence of marine biofouling is naturally higher in the shallower water along the coast. Initially ~2000 species were identified on fouled structures which has been revised and increased to more than 4000 species (8). Microfoulers have the ability to adapt to new situations created by man and can adhere firmly thereby avoiding washing off and initiate fouling. Bacterial colonization of a surface is influenced by the physico-chemical properties of the surface, the biological properties of the bacterium such as surface motility, surface structures like pili production of adhesive molecules, nutrient availability, substratum, sea water chemistry, temperature and exposure time etc (7). Ships are an example of specialized environment that fluctuates frequently due to constant movement of the vessels. Bioforms that adapt and tolerate wide fluctuations in environmental conditions such as temperature, water flow and salinity are only the dominant foulers on ship surfaces (9). The settlement of invertebrate larvae to man made surfaces submerged in marine waters is often associated with damage of materials and increased drag. The vast economic loss resulting due to fouling has justified extensive investigations into its cause and more particularly of practical methods for prevention. Attention has been focused on the exact sequence of events, especially during the initial stages and relationship of one group of organisms to another. In spite of great advances over the years, biofouling control is still a formidable problem in cooling circuits of power plants, ship hulls, oil platforms and other marine structures . In addition to the direct costs, additional expenditures are incurred in the form of expenditure associated with continual inspections by divers, under water cleaning for maintaining of the equipment and cost of application of antifouling agents. Dealing with biofouling alone, costs the shipping and maritime industry over $ 6.5 billion per year (5,10,11).

The process of inhibition of fouling activities is called antifouling. Different approaches apart from periodic cleaning have been adopted for controlling fouling, which include coatings, osmotic stress, radiation, electric systems etc. These approaches are far from ideal and do not provide a complete or long term answer to the

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expensive problem of fouling. The commonly employed chemical approaches to control biofouling include antifouling paints relying upon effective leaching of the toxic substance. Prominent anti-fouling paints contained organotin compounds like Tributylin (TBT), tri-butyl tin oxide (TBTO), tri-butyl tin fluoride (TBTF) tri-phenyl tin lead acetate (TPLA), and copper and zinc based other metallic species, as substitutes. These organotin and copper based paints had devastating impact on the aquatic ecosystems. Coating the surface with antifouling paints release toxic elements such as copper oxidizing biocides like Cl, Br or peroxidases into the water column resulting in environmental pollution (10 12 13). The increased residual concentrations of organic booster biocides in marinas and harbours are of concern as they adversely affect non-target marine forms. Environmental concerns of high toxicity against non- specific targets including marine flora and fauna have resulted in imposition of worldwide ban on the use of most chemical antifouling formulation including TBT . The major environmental impacts of the released biocides on non-target organisms have forced investigations into alternative methods to develop natural environmentally friendly strategies for use in near future. Hence, there is an increasing interest in isolating naturally produced antifouling agents (14,15),

Currently, other available approaches are far from ideal and consequently they do not provide a complete or long term answer to this expensive problem. The self-polishing copolymer (SPC) technique is another prominent strategy which uses both hydrolysis and erosion to control the anti- fouling activity. Controlling the release of antifouling compounds from coating by using either a soluble or insoluble matrix along with addition of booster are being explored. However booster addition can be species specificity or too broad activity influencing non-target organisms in which case concentration of release good control. The other approach is foul release coating lowers the organism ability to attach due to low surface energy. The two major types of foul release coatings are fluoropolymer and silicon based polymer coating. Techniques involving producing microtextured surfaces including moulds and casting, laser abarasios and use of nanoparticles showed that these influence the attachment of fouling organisms significantly and there was a clear correlation between the surface features with type and extent of fouling (12, 16, 17) .

Organisms living in the marine environment have developed strategies to protect themselves from fouling, One of the strategies adopted involve production of chemicals which are mainly secondary metabolites apart from physical and mechanical and behavioral strategies (18). NPA being mostly secondary metabolites, though not essential for living provide several evolutionary advantages including chemical defences from predators in natural environment. . The chemical strategy has attracted the attention world wide as as a cheaper and ecofreindlier alternative as NPA as they usually show diverse biological activities (14,16). Consequently exploration for alternatives coating has been intensified to bridge the existing gap of antifouling agents. Marine microorganisms have been found to produce great diversity of surface bound and or soluble chemicals that inhibit effectively adhesion of invertebrate larvae to various surfaces. The production of secondary metabolites is principle biological antifouling mechanism of marine microorganisms resulting in production Natural Product Antifouling agents (NPA). The important phlya activelyinvestigated for NPA over the last decade include both prokaryotic and eukaryotic organisms like Bacteria, Porifera (sponges), Algae, Cnidaria (e.g. corals), Echinodermata (e.g. sea-urchins), Tunicates (e.g. sea-squirts), Bryozoa etc. More than 250 molecules have been characterized from marine organisms wide range of antifouling efficiency(19,20,21,22). Some have the very promising compounds have been isolated from microorganisms, algae and sponges belonging to the groups of triterpene glycosides, formoside, the halogenated furanone small brominated compounds and several enzymes(23,24), . Of the marine organisms studied world wide, species of *Pseudoalteromonas* and related organisms belonging to γ-Proteobacteria have drawn wide attention. A diverse group of antimicrobial and antifouling substances are produced by *Pseudoalteromonas* species including protein antibiotics, pigments, small brominated compounds and toxins like neurotoxin, tetratoxins which are demonstrated to be target specific on groups of biofoulants (16, 20, 25). Just to consider a few, two classes of compounds, including cell-bound polyanionic macromolecules and small-brominated compounds were found responsible for the biological activity of *P.luteoviolaceae*. Several other inhibitory agents of unknown chemical nature were also observed to be produced by this organism . Bactericidal antibiotic active against methicillin-resistant *S. aureus* was reported from *P.phenolica* (26). Two proteins with molecular masses of approximately 100kDa, another oligomeric 190kDa protein were purified from *P.tunicata* whereas a 200 kDa polysaccharide was purified from *Pseudoalteromonas* strain X153 strain and *Alteromonas sp.* with antifouling activity (27,28). Production of three antifouling compounds has been characterized from *P.tunicata*. D2 strain. These include a thermo-stable, polar, anti-larval compound of <500Da in size, another heat sensitive, polar, antifouling compound of 3-10kDa., and a peptide anti-spore component of 3kDa in size (25 29). Biofilms of the bacterium *P.tunicata* exhibited antifouling activity against invertebrate macrofoulers like *Balanus amphitrite* and *Ciona intestinalis*. The approach of incorporating natural products into antifouling paints has been tried by a number of groups. The coatings exhibited significant protection against marine bacteria, barnacle larvae and algal spores, revealing their application potential. These studies have opened up immense scope of using the microbial biofilms or bacteria immobilized in hydrogels for controlling biofouling (18, 30, 31).

Based on biomolecules being characterized, synthetic molecules can increasingly produced by combinatorial chemistry approaches to synthesize novel compounds or synthetic chemical analogs of the active compound with more suitable bioactive profile. The economics of the chemical production becomes major factor and synthesizing complex chemically becomes limiting. The microbial approach is being considered an inexpensive way to produce large amounts of potentially active biological antifouling agents. The NPA active ingredients characterized are forming the basis of further biotechnological research for heterologous production also. Great deal of attention is being currently focused on identification of nontoxic, environmentally friendlyand have been extensively reviewed(14,16, 18, 23, ,32 33).

Natural biocide paint or coating contains natural substances as the biocide to prevent fouling or hinder fouling process is long term green technology alternative. The combination of copper with the natural compound quebracho tannin has lowered the copper content in paint formulations by a factor of 40 when compared to that found in cuprous oxide paints Burges 13,14,30,34). Alternative to traditional antifouling paints that rely on cytotoxic effects, the new environmentally safe alternatives aim to interfere fouling using enzyme-based paints which target breakdown of adhesive components and catalytic production of repellent compounds *in-situ*.Some of the important classes of enzyme explored for antifouling activity include oxidoreductases, transferases . hydrolases , Lyases, isomerases ligases etc.(23,29 35,36). N -acyl homoserine lactones (AHL) is reported play an important role for quorum sensing an important factor in biofim formation and repelling zoospores of Ulva sp (8). AHL acylases which degrade AHL have been activily pursued in addition to several proteases, glycosylases and oxidoreductases acylase for their antifouling potential as they have been shown to hold potential for broad antifouling effectiveness. Spore adhesion strength and settlement of Ulva zoospores the settlementof Balanusamphitrite cypridlarvae has been shown to be significantly highly inhibited by serine-protease at laboratory ansd field level experiments by incorporating in paints (29, 34, 35)

CONCLUSION

Marine fouling is a world wide phenomenon plaguing mariners accounting for economic burden on shipping, aquaculture and various maritime industries. The currently available approaches are far from ideal and do not provide a complete or long term answer to this expensive problem. In view of the ban imposed on the popularly used antifouling paints due to toxicity on non specific targets including marine flora and fauna, alternative approaches are being rigorously explored. Marine environment is viewed as an answer to this challenging problem. Among the currently viable options, microbial approach appears to be most promising and a less expensive way for development of long term environmental friendly nontoxic natural product antifoulants (NPAs). Biological antifoulants development is still in infancy and being a frontier area in biotechnology has wide implications in maritime industry. To address this challenging task efficiently it is essential to understand marine biodiversity and optimally exploit microorganism/genes pools for benefit of mankind.

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