Chapter 10
Antibiofilm, Antifouling, and Anticorrosive Biomaterials and Nanomaterials for Marine Applications

Mani Jayaprakashvel, Mnif Sami, and Ramesh Subramani

Contents

M. Jayaprakashvel (✉)
Department of Marine Biotechnology, AMET Deemed to be University,
Chennai, Tamil Nadu, India

M. Sami
Laboratory of Molecular and Cellular Screening Processes, Centre of Biotechnology of Sfax,
Sfax, Tunisia

R. Subramani
School of Biological and Chemical Sciences, The University of the South Pacific,
Suva, Republic of Fiji

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Abstract Formation of biofilms is one of the most serious problems affecting the integrity of marine structures both onshore and offshore. These biofilms are the key reasons for fouling of marine structures. Biofilm and biofouling cause severe economic loss to the marine industry. It has been estimated that around 10% of fuel is additionally spent when the hull of ship is affected by fouling. However, the prevention and control treatments for biofilms and biofouling of marine structures often involve toxic materials which pose severe threat to the marine environment and are strictly regulated by international maritime conventions. In this context, biomaterials for the treatment of biofilms, fouling, and corrosion of marine structures assume much significance. In recent years, due to the technological advancements, various nanomaterials and nanostructures have revolutionized many of the biological applications including antibiofilm, antifouling, and anticorrosive applications in marine environment. Many of the biomaterials such as furanones and some polypeptides are found to have antibiofilm, antifouling, and anticorrosive potentials. Many of the nanomaterials such as metal (titanium, silver, zinc, copper, etc.) nanoparticles, nanocomposites, bioinspired nanomaterials, and metallic nanotubes were found to exhibit antifouling and anticorrosive applications in marine environment. Both biomaterials and nanomaterials have been used in the control and prevention of biofilms, biofouling, and corrosion in marine structures. In recent years, the biomaterials and nanomaterials were also characterized to have the ability to inhibit bacterial quorum sensing and thereby control biofilm formation, biofouling, and corrosion in marine structures. This chapter would provide an overview of the biomaterials from diverse sources and various category of nanomaterials for their use in antibiofilm, antifouling, and anticorrosion treatments with special reference to marine applications.

Keywords Antibiofilm · Antifouling · Anticorrosion · Biomaterials · Nanomaterials · Marine structures

10.1 Introduction

Bacteria are unicellular microorganisms present in almost all ecosystems in our planet. They usually exist in two different formats such as planktonic forms and biofilms. Planktonic forms are free-living bacteria which exist either individually or collectively as a colony, whereas in biofilms, bacteria live in communities within an extracellular matrix made of exopolysaccharides produced by the same bacteria itself. According to Flemming et al. (2016), bacterial biofilms are the emergent form of bacterial life. The life of biofilms is entirely different from that of planktonic forms. Biofilms are demonstrating various emergent properties such as communal mutualism, capture of space, and nutrition. The biofilms also demonstrate extended survival as a community by exhibiting resistance to antibiotics. By forming biofilms, bacteria evade the environmental challenges such as drying, washing action of water, and air (Roberts et al. 2013).

The biofilms, upon maturation, can cause serious changes in the metallic properties of substrates in which they form microcolonies. Thus, beyond the electrochemical influences on metal corrosion, biofilm-induced corrosion is also found naturally. Moreover, biofilms on solid surfaces in aquatic environments make the attachment of macrofouling organisms easier. This makes all structures in aquatic environment more prone to biofouling. Thus, biofilms can cause serious environmental, medical, industrial, and economic impacts by inciting various diseases, biocorrosion, and biofouling (Videla and Characklis 1992). Three sectors, viz., medical, food industry, and shipping industry, are the most affected by the biofilms. The biofilms in human and animals, both on internal organs and medical implants, cause serious challenge to the medical sector. In various industries, more specifically in food, beverage, and dairy industries, biofilms are of serious concern. In ships, the biofilms on external surfaces, propellers and piping systems, cause serious problems such as lowering fuel efficiency and weakening the strength of metals and also form the foundation for the biofouling. Thus, the economic losses due to biofilms in shipping are many fold higher than any other industry.

Marine environment is a diverse environment wherein different ecosystems are existing. Each of the ecosystems in marine environment is unique. Marine environment has all extremities of temperatures, pH, atmospheric pressure, tidal action, wind, salinity, nutrients, etc. Hence, the organisms living in the marine environment are so dynamic in producing new and potential biomolecules to face all these extremities as adaptation. The centuries-long continued research on the terrestrial environment has yielded millions of metabolites and thousands of bioactivities. However, due to the fast-evolving microbes, especially in the fields of control and treatment of biofilms, biocorrosion, and biofouling, we are in salient need of alternative and new molecules to develop alternative strategies. Since the terrestrial bioresources are having the disadvantage of finding previously reported molecules or bioactivities, we need alternative bioresources for the exploration of new molecules. Marine bioresources, especially, marine microorganisms, are so diverse and hence could offer themselves as potential choice for the exploration of novel biomolecules with potent biological functions. Thus, this chapter would emphasize on the role of marine microorganisms for the production of antibiofilm, antifouling, and anticorrosion metabolites. Besides, the nanotechnology is revolutionizing almost all branches of scientific research. The role of nanotechnology in improving the prevention and control strategies for the successful management of biofilms, biocorrosion, and biofouling is also emphasized in this chapter.

10.2 Antibiofilm Compounds

10.2.1 The Biology of Biofilms

Biofilms are multicellular communities of bacteria colonized together in a self-produced extracellular matrix, usually made of exopolysaccharides (López et al. 2020). Biofilms are architecturally unique arrangement of bacteria to evade environmental stresses. Researchers have concluded that in natural environment, bacteria survive in solid surfaces majority through the formation of biofilms (Costerton and Lewandowski 1995). In an ecological perspective, biofilms are communities of bacteria, which live in an interdependent mutualistic relationship among multiple bacterial genera as well. Their association as a biofilm community is more complex. However, they exhibit coordinated functions to survive as a biofilm on solid surfaces (Davey and O'Toole 2000).

Biofilms largely consist of water (more than 90%) only, like any other living system. Most of the biofilms contain microbial cells, nucleic acids (DNA and RNA), polysaccharides, proteins, and water. Biofilm forming bacteria exhibit different strategies for formation of biofilms. The strategies are different due to difference in environment and species involved. Formation of bacterial biofilms usually comprises four steps (Parsek and Singh 2003; Jamal et al. 2015; Jamal et al. 2017).

10.2.1.1 Bacteria Adhere to Solid Surfaces

The bacterial cells which are planktonic make initial adhesion with solid surfaces. The locomotion appendages of bacteria such as flagella, pili, and fimbriae are helpful in establishing initial cell adhesion with solid surfaces. A solid-liquid interface promotes the biofilm formation. This attachment is found to be reversible

10.2.1.2 Formation of Microcolonies

After successful initial attachment with solid surfaces, bacteria regulate their physiological and metabolic activities to form microcolonies. The microcolonies thus formed may have single species or also have multiple species depending on the nature of environment.

10.2.1.3 Formation of 3D Matrix with Exopolymers

All the biofilms are encompassed inside an extracellular matrix. The extracellular matrix is largely composed of exopolysaccharides. However, proteins and DNA are also present in minor quantities.

10.2.1.4 Maturation of Biofilms

Once bacterial biofilms are protected with extracellular matrix, they form water-filled channels for the distribution of nutrients. These channels act as circulatory systems to transport nutrients in and dispose wastes out. The biofilm forming bacteria are having programmed mechanisms for stopping the exopolysaccharide protection at certain point of time, after which the planktonic bacterial cells are released into the environment.

The different processes involved in the biofilm formation in general are depicted in Fig. 10.1.

10.3 Biofilm Forming Bacteria: Medical Implications

Though many genera of bacteria are capable of producing biofilms, the following few bacterial genera are studied extensively for biofilm formation. These bacteria are also highly significant in view of industrial, medical, and environmental safety.

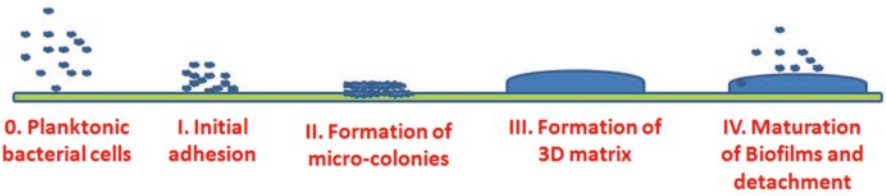

Fig. 10.1 Summary of basic processes involved in microbial biofilm formation

10.3.1 Escherichia coli

E. coli is one of the most widely studied facultatively anaerobic bacterium. Most of the strains of the *E. coli* are active colonizers in the gastrointestinal tract of human and animals. Because of their ability to form infectious biofilms in both internal systems and environmental systems, *E. coli* is assumed to be one of the model organisms in biofilm studies (Beloin et al. 2008). *E. coli* was also found associated as a normal flora in gut as a commensal. It was also reported to cause serious infectious biofilms in the intestine. They also form biofilms in medical devises and implants. Because of their high versatility and resistant mechanisms, antibiotic treatment for the control of *E. coli* is still a hurdle.

10.3.2 Pseudomonas aeruginosa

Pseudomonas aeruginosa is a Gram-negative ubiquitous bacterium. It is also regarded as most notorious opportunistic pathogen in animals and human. *P. aeruginosa* are reported to form biofilms in internal organs, medical devices, and medical implants. They are also involved in the nosocomial infections. The biofilm forming *P. aeruginosa* are quite difficult to be managed by the immune system and antibiotic therapy (Mulcahy et al. 2014). Biofilm forming *P. aeruginosa* are causing cystic fibrosis, a most dangerous lung biofilm infection in humans (Rasamiravaka et al. 2015). Besides, *Pseudomonas* was also found associated with biofilms of food industry (Amina and Bensoltane 2015).

10.3.3 Staphylococcus aureus

Staphylococcus aureus is a Gram-positive nonmotile bacterium yet forms biofilms. Strains of *S. aureus* are known for their biofilms in wounds and medical implants and can cause multiple chronic infections. There are several highly antibiotic-resistant strains reported (Lister and Horswill 2014) Because of their antibiotic resistance and sturdy biofilms, *S. aureus* produce stable and recurrent internal infections with huge mortality rate. The biofilms of *S. aureus* are associated with several infections in many internal organs such as the bones, teeth, gums, sinus, and eyes; chronic wound infections; etc. (Archer et al. 2011).

10.3.4 Streptococcus epidermidis

Streptococcus epidermidis is also found associated with infectious biofilms in humans. They cause biofilms in medical devices also.

10.3.5 Streptococcal Biofilms

Streptococcus is a versatile genera of Gram-positive bacteria which are found to establish biofilms in internal tissues and tooth surfaces of humans (Suntharalingam and Cvitkovitch 2005). *Streptococcus pyogenes* (group A streptococci, GAS) is a serious pathogen which causes biofilm-mediated infections in the skin and mucosal membranes. Several antibiotic-resistant GAS were also reported to cause bacterial pharyngitis in children by the formation of biofilms (Conley et al. 2003; Fiedler et al. 2015).

10.3.6 Enterobacter cloacae

Enterobacter cloacae is a Gram-negative bacterium found in the intestines of humans and animals. They cause severe infections such as nosocomial infections, respiratory tract infection, urinary tract infections, endocarditis, skin and soft tissue infections, osteomyelitis, and ophthalmic infections by forming biofilms. They also cause biofilms in food industries and also cause food spoilage (Jamal et al. 2015; Cai et al. 2018; Zurob et al. 2019).

10.3.7 Klebsiella pneumoniae

Klebsiella pneumoniae is a Gram-negative pathogenic bacteria. It causes biofilms and results in urinary tract infections (UTI), pneumonia, and soft tissue infections. It also causes meningitis (Vuotto et al. 2017).

10.4 Biofilms in Industrial Sector

Bacteria such as *Salmonella* spp., *Listeria* spp., pathogenic *E. coli*, *Campylobacter* spp., *Bacillus cereus*, and *S. aureus* are found to produce biofilms in various facets of the food industry. Since they are also pathogenic, they cause food contamination. They cause huge loss to the food industry especially in the dairy, seafood processing, meat processing, beverages, and ready-to-eat food industries (Laxmi and Bhat 2018; Giaouris and Simoes 2018; Srey et al. 2013). Most of the biofilm forming bacteria are highly resistant to the mechanical washing and chemical disinfection processes followed in food industries (Shi and Zhu 2009a, b). The prevention and control of biofilms in food industries needs careful understanding of the exact steps involved in biofilm formation. The identification of biofilm site is the foremost need to design prevention or control strategy: use of proper sanitation methods, appropriate food preservatives, antibiofilm enzymes, organosilanes, probiotics, phage therapy, extracts from aromatic plants, inhibitors of quorum-sensing system, bacteriocins, and nanomaterials (Kregiel 2014, Meireles et al. 2016; Merino et al. 2019; Lamas et al. 2018). Besides bacteria, yeasts such as *Rhodotorula mucilaginosa*, *Candida krusei*, *Candida kefyr*, *and Candida tropicalis* were also reported to have formed biofilms in beverage industries and are best controlled by the usage of effective disinfectants such as sodium hypochlorite on the ultrafiltration membranes (Tarifa et al. 2018).

Bacteria such as *Pseudomonas*, *Campylobacter*, *Salmonella*, *Enterobacter*, *Proteus*, *Citrobacter*, *E. coli*, *Klebsiella*, *Staphylococcus*, and *Listeria* were found associated with infectious biofilms that cause huge contamination, spoilage, and economic losses to the food (seafood, meat, poultry) processing industries (Wang et al. 2016a, b; Wang et al. 2017a, b, c; Li et al. 2017; Pang et al. 2019; Wang et al. 2019). Biofilm formation in dairy industry is one of the major concern of quality dairy products. Biofilm forming bacteria such as *Bacillus* spp., *Pseudomonas* spp., *Klebsiella* spp., *Listeria* spp., and *Staphylococcus* spp. were reported to form biofilms in different parts of the dairy manufacturing plants (Grutsch et al. 2018; Bremer et al. 2018). While it is envisaged that controlling biofilms through frequent cleaning would cost more and also limit the amount of product that can be manufactured (Bremer et al. 2018), alternate strategies such as use of sanitizers (Tang et al. 2010), phytochemicals (De Oliveira et al. 2018), and biopolymers (Felipe et al. 2019) were attempted for the control of biofilms in dairy industries.

Biofilms are also formed in unusual entities such as hemodialysis units (Pasmore and Marion 2008), spent nuclear fuel pools (Sarro et al. 2005, 2007), paper and board machines (Kolari et al. 2003), fluidized bed reactors (Jordening et al. 1992), and gas industry pipelines (Zhu et al. 2003). There are some new approaches such as use of ultrasound and electroporation, use of chemicals to hydrolyze exopolymers, physical disruption of biofilm adhesion, and use of phytochemicals that are tested globally. However, these attempts are mostly in experimentation level and needed much precision to be upscaled to suit the large industrial systems (Murthy and Venkatesan 2008; Xu et al. 2017; Wang et al. 2019).

10.5 Biofilms in Aquatic Ecosystems

In natural aquatic ecosystems, bacteria, diatoms, and protozoa form biofilms. These biofilms are complex and dynamic. They are usually developed on all exposed interfaces of the aquatic ecosystems. Their diversity, composition, and effects vary from nature of the ecosystems (Neagu et al. 2017). The complexities of microbial biofilms in aquatic environment are very large yet poorly understood. These biofilms have important consequences for the performance of aquatic environments and the ecological responses (Besemer 2015). Metagenomic analysis of biofilm forming bacteria revealed that the genes responsible for biofilm formation in aquatic environment are conserved across wide range of bacteria and most of these genes are identical to that of pseudomonads (Anupama et al. 2018). The major consequence of biofilms in aquatic ecosystems is that they could accumulate toxic pollutants such as pesticide residues. Through a recent study, Fernandes et al. (2019) have concluded that some of the biofilms formed in the aquatic ecosystems tend to accumulate the herbicide glyphosate in the polluted waters. Antibiotic resistance genes (ARG) were also found conserved in biofilms of aquatic ecosystem. This is very serious that these ARG can be transferred to other bacteria in the same ecosystem by horizontal gene transfer; thereby it can increase the risk of overpopulation of antibiotic-resistant pathogens (Proia et al. 2016). *Legionella pneumophila*, an upcoming waterborne pathogen, also develops as biofilms in industry and domestic appliances and spread through aerosols that arise from reclaimed water sources. *Legionella* are found associated with infectious biofilms in reclaimed water from wastewater treatment plants, cooling towers, spray irrigation, and toilet flushing and pose serious health risks (Caicedo et al. 2019; De Giglio et al. 2019). Biofilms in the river beds are also reported to influence the river bed structure and function. They were reported to reduce the river bed erosion and maintain the flow of stream channels (Piqué et al. 2016). However, in most cases, river biofilms and sediments are reported to be the main reservoirs for infectious pathogens. This appears to be a serious risk for the public health (Mackowiak et al. 2018).

10.6 Biofilms in Marine Environment

Marine environment is a dynamic environment where the living organisms face a constant stress. Besides heavy salinity, temperature fluctuation, strong tidal and wave actions, dynamic pressure across water columns, and nutritional selectivity, the microorganisms especially marine bacteria have conquered the sea and established their survival on solid marine surfaces through biofilms. Biofilm formation not only is advantageous for the biofilm forming bacteria but also favors ecological and biogeochemical functions in the changing marine environment. Among various marine ecosystems, intertidal systems are highly fluctuating ecosystems. The microorganisms that form biofilms in these intertidal ecosystems are forming a protective microenvironment to alleviate the physical and chemical stress faced by the other organisms. Especially, the exopolysaccharide matrix of the marine biofilms functions as a solid surface for cells to carry out diverse physiological functions such as biogeochemical cycle, nutrient mobilization, and evading environmental stresses such as salinity, temperature, UV irradiation, and desiccation (Decho 2000). However, bacterial biofilms in marine environment result in the formation of biofouling and biocorrosion, which are deleterious to the environment and also causes huge economic loses to the marine industry. They also serve as reservoirs for pathogenic microbes and resistant genes (Wahl et al. 2012; Salta et al. 2013a, b, c; Dang and Lovell 2016). Biofilm forming bacteria colonize almost all possible marine structures in the seawater. Biofilms, also termed as microfouling in marine environment, are affecting both natural and artificial marine structures. Marine structures such as nets, offshore oil platforms and pipelines, ship hulls, ballast tank, and piping systems are greatly affected by biofilms which eventually allow higher organisms such as barnacles and mussels (termed as macrofoulers) to cause biofouling (Salta et al. 2013a, b, c). Marine biofilms have direct deleterious effects in various marine-related economic activities such as shipping, offshore oil rigs, desalination plants, aquaculture, and other industries (De Carvalho Carla 2018). The detailed review by de Carvalho Carla (2018) emphasizes that biofilms in marine environment could be deleterious to the marine environment in addition to the huge economic losses it causes to various industrial sectors (aquaculture, maritime transport, oil and gas industry, desalination plants) associated with the marine environment. It is rightly envisaged by many authors that the biofilms in any environment can be prevented effectively than be controlled totally. Nurioglu et al. (2015) have given an overview of various methods used for the prevention of biofilms and biofouling. They have summarized that paints and coatings such as copper, arsenic, tin, and mercury are used to prevent microbial adhesion. However, these biocides cause more environmental damage than the benefits. Now, the preventive paints and coatings are now done with fluorine and silicon-based materials or their combinations. Natural compounds, enzymes, nanomaterials, graphene, and ultrasonic waves have also been used for the prevention of marine biofilms (Armstrong et al. 2000a, b; Kristensen et al. 2008; Fabrega et al. 2011; Silva et al. 2019; Kurzbaum et al. 2019). However, considering the complexity in controlling the marine biofilms, alternative strategies or works on improvising the existing methods are still warranted.

10.7 Antibiofilm Metabolites from Marine Organisms

Marine environment covers almost 70% of the Earth's surface. The earlier life on Earth has also originated from the seas. So, the oceanic environment is having enormous diversity than its terrestrial counterpart. The biological diversity in the World Oceans accounts for about 95% of the total biodiversity (Qasim 1999; Subramani and Aalbersberg 2012). It appears that the emphasis has been shifted to marine environment for the search of novel metabolites with newer bioactivities. Because, it has been envisaged that research over centuries has completely studied the terrestrial bioresources, and hence, chances for getting newer metabolites from these bioresources are very limited (Subramani and Aalbersberg 2012). The marine environment is now becoming the focus of researchers worldwide as it harbors diverse bioresources. These bioresources produce a battery of novel metabolites, which often have unique structure, function, and applications with highest efficiency. Hence, marine organisms are collected, extracted, and fractionated to develop compounds for novel therapeutic and industrial applications (Gallimore 2017). Many of the marine organisms such as microorganisms, sponges, and seaweeds have been experimented for getting novel bioactive metabolites with antibiofilm potential. Among these organisms, marine microorganisms are becoming the promising source of effective metabolites with antibiofilm activity. The microbial metabolites are found to inhibit the biochemicals involved in biofilm formation. They also inhibit the initial attachment, biofilm development, and the quorum sensing among the biofilm forming bacteria (Adnan et al. 2018).

The published literature on the production of antibiofilm compounds from marine organisms is so enormous. Marine organisms such as seaweeds (red seaweeds and brown seaweeds), microalgae, cyanobacteria, crab shells, sponges, soft corals, fungi, bacteria, and actinomycetes have produced an array of antibiofilm metabolites. Metabolites such as sesquiterpenes, fucoidan and other polysaccharides, chitosan, ianthellin, brominated tyrosine, lectins, surfactants, enzymes, culture filtrates, and other uncharacterized compounds have been produced by these marine organisms against various biofilm forming bacteria. These organisms and antibiofilm metabolites have exhibited antibiofilm activities against biofilm forming bacteria by various mechanisms such as antimicrobial activity, destabilization of plasma membrane, inhibition of initial attachment, affecting virulence factors, inhibition of swarming motility, inhibition of quorum sensing, affecting cell surface hydrophobicity, inhibition of resistance characters, and cell wall degradation. The complete details such as the name of marine organisms that exhibited antibiofilm activity, the compounds they produced, the biofilm forming bacteria they inhibited, and the mechanisms of biofilm inhibition are summarized in Table 10.1.

10.8 Nanotechnology and Antibiofilm Strategies

Biofilms are complex microbial communities formed in diverse systems including marine structures. These biofilm forming bacteria are highly evolving in nature so that they could be able to develop resistance against traditionally used biocides. The biofilm forming bacteria are also developing resistance to the antibiotic metabolites synthesized for the control and prevention of biofilms. Hence, alternative strategies are always in search for the prevention and control of biofilms. Several new approaches such as inhibition of quorum sensing (QS), enzymatic disruption, use of natural products, paints coasted with bactericides, nanotechnology, and bioelectric approach have been attempted globally as an alternative strategy for the prevention

Table 10.1 Marine organisms, which produced antibiofilm compounds

Marine organism	Antibiofilm compound	Target biofilm organism	Possible mechanism/ implication	References
Marine brown alga *Halidrys siliquosa*	Algal methanolic extract	*Staphylococcus*, *Streptococcus*, *Enterococcus*, *Pseudomonas*, *Stenotrophomonas*, and *Chromobacterium*	Antimicrobial nature	Busetti et al. (2015)
Red seaweed, *Laurencia dendroidea*	Elatol, sesquiterpene	*Leishmania amazonensis*	Destabilization of the plasma membrane	Santos et al. (2010)
Seaweed, *Chondrus crispus*	Extract of the seaweed	*Cobetia marina* and *Marinobacter hydrocarbonoclasticus*	Affected bacterial attachment	Salta et al. (2013a, b, c)
Fucus vesiculosus, seaweed	Fucoidan	*Streptococcus mutans* and *S. sobrinus*	Antimicrobial activity	Jun et al. (2018)
Marine brown alga *Halidrys siliquosa*	Partially fractionated methanolic extract	*Staphylococcus aureus* MRSA	Antimicrobial nature	Busetti et al. (2015)
Cyanobacteria *Westiellopsis prolifica*	Acetone extract	*Bacillus subtilis*, *Shigella* sp., *Proteus* sp.	Antimicrobial activity	Al-TmimiG et al. (2018)
Portunus sanguinolentus, crab shells (biowastes)	Chitosan	*Staphylococcus aureus*	Reducing the staphyloxanthin pigment, a characteristic virulence feature of the pathogen	Rubini et al. (2018)
Aiolochroia crassa, sponge	Ianthellin	Six different marine biofilm forming bacteria	Inhibition of initial attachment	Kelly-Quintos et al. (2005)
Soft coral, *Eunicea* sp.	Batyl alcohol (1) and fuscoside E peracetate (6)	*Pseudomonas aeruginosa* ATCC 27853 and *Staphylococcus aureus* ATCC 25923	Specific biofilm inhibition with lower antimicrobial effect	Díaz et al. (2015)
Aiolochroia crassa, sponge	Brominated tyrosine	Six different marine biofilm forming bacteria	Inhibition of swarming	Kelly-Quintos et al. (2005)
Aplysina fulva, marine sponge	Mucin-binding lectin	*Staphylococcus aureus*, *S. epidermidis*, and *Escherichia coli*	Reduce the biomass biofilm	Carneiro et al. (2019)

Marine organism	Antibiofilm compound	Target biofilm organism	Possible mechanism/ implication	References
Marine-associated fungi	Mevalonolactone	*Staphylococcus epidermidis*	Interfere with the adherence and biofilm formation	Scopel et al. (2014)
Marine-derived fungus of *Emericella variicolor*	Sesterterpenes	*Mycobacterium smegmatis*	Antimicrobial activity	Arai et al. (2013)
Coral-associated bacterium *Bacillus horikoshii*	Cell-free extracts	*Streptococcus pyogenes*	Quorum-sensing inhibition properties and cell surface hydrophobicity reduction properties	Thenmozhi et al. (2009)
Marine bacterium *Pseudoalteromonas* sp. strain 3J6	Culture filtrates	*Paracoccus* sp. 4M6 and *Vibrio* sp. D01	Impaired biofilm formation	Dheilly et al. (2010)
Marine bacterium *Vibrio* sp. QY101	Bacterial exopolysaccharide (A101)	*Pseudomonas aeruginosa* and *S. aureus*	Inhibits initial adhesion and the development of complex architecture	Jiang et al. (2011)
Bacillus cereus, deep-sea bacterium	Amylase enzyme	*Pseudomonas aeruginosa* and *Staphylococcus aureus*	Inhibition of complete biofilm formation	Vaikundamoorthy et al. (2018)
Sponge-associated strain of *Bacillus licheniformis*	Polysaccharide; α-D-galactopyranosyl-(1→2)-glycerol-phosphate	*Escherichia coli PHL628* and *Pseudomonas fluorescens*	Reduced the initial adhesion and biofilm development	Sayem et al. (2011)
Marine Actinomycetes *Streptomyces, Nocardiopsis, Micromonospora*	Supernatants	*E. coli and S. aureus*	Prevented bacteria to develop biofilms and resistance	Leetanasaksakul and Thamchaipenet (2018)
Actinomycetes *Nocardiopsis* sp.	Pyrrolo[1,2-a] pyrazine-1,4-dione, hexahydro-3-(2-methylpropyl)	*Proteus mirabilis* and *E. coli.*	Cell wall degradation in treated cells of the bacteria	Rajivgandhi et al. (2018)

and control of biofilms (Sadekuzzaman et al. 2015). Use of microbial metabolites from the marine bioresources, which are certainly new and novel, is one of the effective alternative strategy for prevention and control of biofilms. In addition to that, nanomaterials are also found as an efficient alternative (De Souza et al. 2014). Because of the highest heterogeneous nature of the biofilm, the biofilm forming bacteria develop multiple resistance mechanisms (Mah and O'Toole 2001). Hence, multiple and combination of control and prevention strategies are the present need.

The nanomaterials such as nanospheres, liposomes, dendrimers solid lipid nanoparticles, polymeric nanoparticles, and polymeric micelle have been used for the control of biofilms (Kasimanickam et al. 2013; De Souza et al. 2014; Mohankandhasamy and Lee 2016). Singh et al. (2017) have reviewed recent articles published on the biofilm control using nanomaterials. They have emphasized the role of nanomaterials and nanostructures in treating biofilms by interfering with quorum sensing. Biologically synthesized silver nanoparticles were reported to reduce biofilm formation by marine bacteria (Inbakandan et al. 2013). The bacterial biofilms in a natural marine environment were negatively affected by the silver nanoparticles (Fabrega et al. 2011). Biosurfactants such as rhamnolipid are coated with metal nanoparticles such as silver and iron oxide nanoparticles to enhance their antiadhesive and antibacterial activity against *S. aureus* (Khalid et al. 2019). Gold nanoparticles functionalized with proteolytic enzyme were found to have dual role such as antimicrobial and biofilm disruption in *Pseudomonas fluorescens* biofilms (Habimana et al. 2018). Similarly, chitosan nanoparticles were also functionalized by adding antibiotic (oxacillin) and enzyme (DNase) to reduce the thickness of exopolysaccharide matrix and number of viable cells in *Staphylococcus aureus* biofilms (Tan et al. 2018). Studies done across the globe have indicated that nanotechnology coupled with antibiofilm metabolites from marine bioresources could be an effective strategy for the prevention and control of biofilms.

10.9 Antifouling Compounds

The aggregation of undesired organic molecules and marine fouling organisms such as microorganisms, algae, plants, animals, and their by-products on human-made structures in the marine industry causes serious technical and economic complications globally (Callow and Callow 2011; Schultz et al. 2011). The accumulation of biofoulers on marine vessels can increase vessel's hydrodynamic volume and friction up to 60% (Vietti 2009a) resulting in drag increase affecting the vessel's speed by up to 10%, which could also elevate fuel consumption and thereby greenhouse gas emissions (Vietti 2009a, b). Several antifouling methods have been applied to combat biofouling worldwide (Magin et al. 2010; Shan et al. 2011). Metal-based compounds such as tributyltin and cuprous oxide and synthetic organic biocides Igarol and diuron have widely been used to control marine biofouling (Yebra et al.

2004). However, most of these antifoulants showed toxicity on nontarget species and possibly contaminate the marine environment, leading to bans and stringent rules on their use in antifouling coatings (van Wezel and van Wlaardingen 2004; Yebra et al. 2004; Guerin et al. 2007; Wang et al. 2016a, b). Therefore, effective and eco-friendly antifouling agents are desperately needed.

10.10 Fouling Organisms

Biofouling causes serious problems to marine industry products and aquaculture development leading to severe economic loss and also creates multiple ecological issues worldwide (Wang et al. 2017a, b, c). An estimate has found that over 4000 different biofouling organisms may be present in the marine environment (Shan et al. 2011). Among them, majorities are primarily living in shallow water along the coast and harbors, those that afford rich nutrients (Wang et al. 2017a, b, c). Generally, in biofouling, marine adhesion organisms are of two types. The first of these microfoulers or biofilm organisms are marine bacteria, algae, and protozoa (Shan et al. 2011). Biofilms are ubiquitous in nature, as long as the natural and artificial surfaces are in contact with the water. The second category is macrofoulers such as barnacles, bryozoans, and tubeworms (Shan et al. 2011). Among these two, macrofoulers such as barnacles, mussels, polychaete worms, bryozoans, and seaweed are associated with more severe forms of biofouling in marine environments (Yebra et al. 2004).

10.11 Mechanism of Biofouling Process

Biofouling is accumulation of different organisms, a complex process, and common problem worldwide on man-made objects immersed in the waters (Shan et al. 2011). The series of phases involved in the biofouling process are as follows:

1. The initial short-term phase is when the surface submerged in the water adsorbs organic molecules such as protein, polysaccharide, and proteoglycan, forming the primary film which provides adhesive surface aiding attachment of microorganisms; those are sessile in this conditioned layer (Shan et al. 2011; Maureen and Robert 1994).
2. Microbial attachment on the substratum leads to the next phase in the formation of biofilm which is development of microfoulers (includes microalga and bacteria) that adhere to the surface (Shan et al. 2011).
3. Colonization of microorganisms in biofilm involves adsorption and adhesion. In this process, the adsorption is reversible while adhesion is irreversible. The reversible adsorption is generally ruled by physical effects such as Brownian

motion, electrostatic interaction, gravity, water flow, and van der Waals forces (Fletcher and Loeb 1979; Walt et al. 1985; Per et al. 2004; Chambers et al. 2006; Shan et al. 2011). However, irreversible adhesion is primarily governed through biochemical effects such as secretion of extracellular polymeric substances (EPS). Diatoms are the most important contributors for biofilm formation in marine ecosystems (Shan et al. 2011). Lewin (1984) reported that exclusively microfouling can increase up to 18% fuel consumption and reduce at least 20% sailing speed.

4. In this phase, larvae or spores of macrofoulers attach to the surface of the biofilm and then develop into a complex biological community. Generally, larvae of bryozoan members (Maki et al. 1989), polychaetes (Lau et al. 2003), and some other biofoulers (Hung et al. 2005) involve in the development of complex biological community (Shan et al. 2011).
5. In the last stage, attachment of marine invertebrates such as barnacles, mussels, and macroalgae develops a more complex community.

Focusing on inhibition of physical reactions may be easier to control biofouling rather than the biochemical reactions (Shan et al. 2011). However, it is very difficult to prevent biofilm formation and eventual biofouling as adhesion of diatoms and bacteria is very hard to disrupt (Yebra et al. 2004; Shan et al. 2011).

10.12 Natural Products as Antifouling Agents

In past years, several physical, mechanical, chemical, and biological methods were applied for the prevention of marine biofouling (Abarzua et al. 1999). Antifouling coatings containing heavy metals such as Cu, Pb, Hg, and As and organotins such as tributyltin (TBT) were generally used to control biofouling (Omae 2003;

Qian and Fusetani 2010; Qi and Ma 2017). However, owing to marine ecological protection and high toxicity of these antifouling coatings, they were banned globally (Rittschof et al. 2001; Faÿ et al. 2007; Qi and Ma 2017). Therefore, nontoxic or less toxic and environment-friendly antifouling coating is urgently needed. Marine natural products can be a better alternative for the chemicals commonly used in antifouling coatings. Marine organisms such as sponges, soft corals, ascidians, seaweeds, and microorganisms especially symbiotic microbes produce metabolites that demonstrate potential antifouling properties (Satheesh et al. 2016; Qi and Ma 2017; Wang et al. 2017a, b, c; Dahms and Dobretsov 2017). The secondary metabolites derived from marine organisms are nontoxic or low toxic to the marine ecological environment and degradable and showed high efficiency against biofouling (Qi and Ma 2017).

10.13 Antifouling Natural Products from Marine Microorganisms

10.13.1 Bacteria

Recently, natural products from the marine realm are in spotlight for the discovery of antifouling compounds (Wang et al. 2017a, b, c). Many antifouling compounds have been reported so far from seaweeds and marine invertebrates (Qian et al. 2015). However, the major issue for the commercialization of these natural products from macroorganisms in the marine sectors was found to be limited supply as coating material (Wang et al. 2017a, b, c). Interestingly, microbial-derived extracts and natural products are the particular target in the spotlight of marine natural products because of the probability of supplying perpetual quantities of antifouling compounds through fermentation and genetic engineering of the producing organisms and the potential of source renewal (Dobretsov et al. 2006, 2013; Satheesh et al. 2016; Wang et al. 2017a, b, c). The metabolites of marine organisms especially microorganisms with antifouling properties have been proved as effective inhibitors against fouling organisms with low and nontoxic properties (Qian and Fusetani 2010).

Marine microorganisms produced various natural products belonging to polyketides, lactones, nucleosides, peptides, phenyl ethers, fatty acids, steroids, benzenoids, alkaloids, and terpene antifouling agents (Wang et al. 2017a, b, c). Table 10.2 summarizes some marine bacteria reported for producing antifouling compounds. Members of *Bacillus* and *Streptomyces* are the top antifouling metabolite producers. Importantly, symbiotic bacteria associated with various marine organisms showed rich potential for searching for the antifouling compounds. To mention a few, two fatty acids reported from marine *Shewanella oneidensis* showed effective inhibition of germination of green alga *Ulva pertusa* spores (Bhattarai et al. 2007). A promising nontoxic antifouling diterpene isolated from *Streptomyces cinnabarinus* exhibited significant activity against the diatom *N. annexa* and the marine macroalga *U. pertusa* (Cho and Kim 2012). The steroids obtained from the filamentous bacterium *Leucothrix mucor* significantly inhibit the attachment of biofilm forming bacteria *Pseudomonas aeruginosa* and *Alteromonas* sp. (Cho 2012). Ubiquinones from sponge-derived *Alteromonas* sp. showed effective inhibition on larval settlement of *B. amphitrite* at lower concentrations (Kon-ya et al. 1995). The seaweed-derived *Streptomyces praecox* afforded environment-friendly diketopiperazines displaying strong inhibition of zoospore settlement of the seaweed *U. pertusa* and growth of the diatom *N. annexa* (Cho et al. 2012).

10.13.2 Fungi

Several marine fungi produced diverse chemical groups of antifouling metabolites (Table 10.3). Among the various fungi, *Aspergillus* species produced large amount of antifouling metabolites (Table 10.3). Bisabolane-type sesquiterpenoids from

Table 10.2 List of few marine bacterial strains reported for antifouling activity

Bacterial strain	Source	Antifouling compound	Target fouling organism	References
Pseudovibrio denitrificans	Ascidian	Diindol-3-ylmethanes	Larval settlement of *B. amphitrite* and the bryozoan *Bugula neritina*	Wang et al. (2015)
Bacillus sp.	Sponge, *Aplysina gerardogreeni*	Culture extracts	Prevent biofilm formation	Aguila-Ramírez et al. (2014)
Bacillus sp.	Sponge	Culture extracts	Anti-diatom activity	Jin et al. (2013)
Streptomyces violaceoruber	Seaweed	Butenolides	*Ulva pertusa*	Hong and Cho (2013)
Streptomyces praecox	Macroalga	Diketopiperazines	Active against the marine seaweed *Ulva pertusa* and fouling diatom	Cho et al. (2012)
Bacillus cereus	Sponge, *Sigmadocia* sp.	Culture extracts	Strong microalgal settlement inhibitory activity	Satheesh et al. (2012)
Streptomyces cinnabarinus	Seaweed rhizosphere sediment	Lobocompactol	Macroalga *U. pertusa* and the diatom *N. annexa*	Cho and Kim (2012)
Leucothrix mucor	Red algae	Steroids	Larval settlement of *B. amphitrite* and diatoms	Cho et al. (2012)
Bacillus sp.	Seagrass	Culture extracts	Activity against biofilm forming activity	Marhaeni et al. (2011)
Pseudoalteromonas haloplanktis	Ascidian	Culture extracts	Spore germination of *Ulva pertusa*	Ma et al. (2010)
Streptomyces albidoflavus	Deep-sea sediments	Butenolides	Larval settlement of *Balanus amphitrite*	Xu et al. (2010); Dickschat et al. (2005; 2010)
Streptomyces sp.	Deep-sea sediment	12-Methyltetradecanoic acid	*Hydroides elegans* larvae	Xu et al. (2009)
Shewanella oneidensis	Seawater	2-Hydroxymyristic, cis-9-oleic acid	*Ulva pertusa* spores	Bhattarai et al. (2007)

(continued)

Table 10.2 (continued)

Bacterial strain	Source	Antifouling compound	Target fouling organism	References
Pseudoalteromonas tunicata	Macroalga *Ulva australis*	Culture extracts	Settlement of *Bugula neritina*	Rao et al. (2007)
Vibrio sp.	Macroalga	Water-soluble macromolecules	Larval attachment of the polychaete *Hydroides elegans*	Harder et al. (2004)
Marine cyanobacterium *Kyrtuthrix maculans*	Exposed to sheltered rocky shores	Maculalactone A	Naupliar larvae of the barnacles *B. amphitrite, Tetraclita japonica*, and *Ibla cumingii*	Brown et al. (2004)
Pseudomonas sp.	Nudibranchs	Culture extracts	Larval settlement of *B. amphitrite*	Burgess et al. (2003)
Acinetobacter sp.	Ascidian, *Stomozoa murrayi*	6-Bromoindole-3-carbaldehyde	Larval settlement of *B. amphitrite*	Olguin-Uribe et al. (1997)
Alteromonas sp.	Sponge, *Halichondria okadai*	Ubiquinones	Larval settlement of *B. amphitrite*	Konya et al. (1995)

Aspergillus sp. (Li et al. 2012), a novel benzenoids from *Ampelomyces* sp. (Kwong et al. 2006), aspergilone A from *Aspergillus* sp. (Shao et al. 2011a, b), and eurotiumides A–D from *Eurotium* sp. (Chen et al. 2014) are the antifouling compounds that are of particular interest as those displayed activity against the larval settlement of *B. amphitrite* at minimum concentrations. Pestalachlorides obtained from marine-derived *Pestalotiopsis* sp. exhibited high antifouling potential against larval settlement of *B. amphitrite* and demonstrated no toxicity (Xing et al. 2016). The marine *Xylariaceae* sp. produced two antifouling compounds such as dicitrinin A and phenol A acid. Dicitrinin A showing significant effect against the attachment of *B. neritina* larvae and less toxicity than phenol A acid (Nong et al. 2013). Sterigmatocystin and methoxy sterigmatocystin isolated from marine *Aspergillus* sp. strongly inhibit the larval settlement of *B. amphitrite* with the EC_{50} values <0.125 μg/mL and are able to paralyze the larvae at effective concentration (Li et al. 2013; Wang et al. 2017a, b, c). Alkaloids reported from *Scopulariopsis* sp. demonstrated potent antilarval settlement activity at lower concentrations, and they were nontoxic, therefore suggesting that alkaloids are promising antifoulants (Shao et al. 2015).

Table 10.3 List of few marine fungal strains reported for antifouling activity

Fungal strain	Source	Antifouling compound	Target fouling organism	References
Sarcophyton sp.	Soft coral	Amibromdole	Larvae of *B. amphitrite*	Xing et al. (2016)
Pestalotiopsis sp.	Marine-derived	Pestalachlorides E and F	Larval settlement of *B. amphitrite*	Xing et al. (2016)
Scopulariopsis sp.	Gorgonian coral	Alkaloids	Larval settlement of barnacle *B. amphitrite*	Shao et al. (2015)
Eurotium sp.	Gorgonian coral	Eurotiumides A–D	Larval settlement of *B. amphitrite*	Chen et al. (2014)
Aspergillus terreus	Gorgonian coral *Echinogorgia aurantiaca*	Territrem and butyrolactone derivatives	Larval settlement of *B. amphitrite*	Nong et al. (2013)
Cochliobolus lunatus	Sea anemone	Cochliomycins D–F	Larval settlement of *B. amphitrite*	Liu et al. (2014)
Xylariaceae sp.	Sea gorgonian corals *Melitodes squamata*	Dicitrinin A and phenol A acid	Larval settlement of *B. neritina*	Nong et al. (2013)
Aspergillus sp.	Marine-derived	Sterigmatocystin and methoxy sterigmatocystin	Larval settlement of *B. amphitrite*	Li et al. (2013)
Aspergillus elegans	Soft coral *Sarcophyton* sp.	Phenylalanine derivatives and cytochalasins	Larval settlement of *B. amphitrite*	Zheng et al. (2013)
Aspergillus sp.	Gorgonian coral	Polyketides	Antifouling activity	Bao et al. (2017)
Aspergillus sp.	Sponge *Xestospongia testudinaria*	Sesquiterpenoids	Larval settlement of *B. amphitrite*	Li et al. (2012)
Aspergillus sp.	Gorgonian coral	Aspergilone A	Larval settlement of *B. amphitrite*	Shao et al. (2011a, b)
Cochliobolus lunatus	Gorgonian coral	Cochliomycins	Larval settlement of *B. amphitrite*	Shao et al. (2011a, b)
Letendraea helminthicola	Sponge	3-Methyl-*N*-(2-phenylethyl) butanamide and cyclo(D-Pro-D-Phe)	Antifouling activity	Yang et al. (2007)
Ampelomyces sp.	Biofilm developed on the glass slides submerged in Hong Kong waters	3-Chloro-2,5-dihydroxybenzyl alcohol	Larval settlement of *B. amphitrite* and *Hydroides elegans*	Kwong et al. (2006)

10.14 Antifouling Compounds from Marine Macroorganisms

10.14.1 Invertebrates

Marine invertebrates especially sponges, gorgonians, and soft corals are the prominent resources for producing antifouling compounds. Qi and Ma (2017) summarized a total of 198 antifouling compounds obtained from sponges, gorgonians, and soft corals which mostly belong to chemical classes such as diterpenoids, sesquiterpenoids, prostanoids, alkaloids, and steroids. To summarize a few, kalihinenes and kalihipyrans were obtained from the marine sponge *Acanthella cavernosa*, showing strong antifouling activity against *B. amphitrite* larvae (Okino et al. 1996a, b). Sesquiterpenes and phenol derivatives from the sponge *Myrmekioderma dendyi* showed activity against *B. amphitrite* larvae at nontoxic concentrations (Tsukamoto et al. 1997). Antifouling sesquiterpenoids and subergorgic acid isolated from a gorgonian *Anthogorgia* sp. and *Subergorgia suberosa* showed strong inhibition against the larval settlement of *B. amphitrite* larvae at $EC_{50} < 7.0$ μg/mL and 1.2 μg/mL, respectively (Qi et al. 2008; Chen et al. 2012). Cembranoid epimers obtained from the Caribbean gorgonian *Pseudoplexaura flagellosa* inhibited the bacterial biofilm maturation of *Pseudomonas aeruginosa*, *Vibrio harveyi*, and *Staphylococcus aureus* without inhibiting the bacterial growth (Tello et al. 2011). Steroids from sponge *Topsentia* sp. exhibited antifouling activity without toxicity against *B. amphitrite* larvae (Tsukamoto et al. 1997). However, antifouling pyrrole-derived compounds oroidin and mauritiamine that were isolated from the sponge *Agelas mauritiana* showed moderate activity against larval metamorphosis of *B. amphitrite* (Feng et al. 2013). Interestingly, aaptamine and isoaaptamine alkaloids derived from the sponge *Aaptos aaptos* showed antifouling activity against zebra mussel attachment (Diers et al. 2006). Number of antifoulants are reported from marine invertebrates; however, their mode of action is still unknown. However, it is interesting to note that antifoulants from marine invertebrates inhibit both microfoulers such as bacteria and diatoms and macrofoulers such as *B. amphitrite*, *B. albicostatus*, *B. improvises*, *B. neritina*, *Mytilus edulis*, *Psychotria viridis*, and *Halocynthia roretzi* (Qi and Ma 2017).

10.14.2 Macroalgae

Marine macroalgae are well-known for producing various commercial products such as cosmetics, various groups of antibiotics, and cytotoxic agents. Notably, several marine macroalgae constantly clean over decades of time suggesting their potential in antifouling properties (Dahms and Dobretsov 2017). Both the three major algal groups (green, brown, and red algae) were reported for antifouling compound production; however, green algae incurred less attention, while brown algae are being explored globally for antifouling compounds. In contrast, research on green algae for discovery of antifoulants has recently increased (Dahms and Dobretsov 2017). Organic extracts of seaweed *Ulva reticulata* showed moderate antifouling activity, and later chemical characterization of those extracts revealed that those metabolites have potential antibiofilm molecules (Prabhakaran et al. 2012). The compounds 3-bromo-5-(diphenylene)-2(5*H*)-furanone and β-carotene isolated from green algae *U. rigida* and *Ulva* sp., respectively, exhibited significant antifouling activity (Grosser et al. 2012; Chapman et al. 2014). Methanolic extracts of a brown alga *Padina tetrastromatica* displayed strong antibacterial, anti-diatom, and anti-mussel properties (Surest et al. 2014). Similarly, nonpolar extracts of native and invasive *Sargassum* spp. (Schwartz et al. 2017) and ethanol and dichloromethane extracts of *Sargassum muticum* (Silkina et al. 2012) inhibited the growth and attachment of diatoms. A total of six chromanol compounds were isolated from *Sargassum horneri*. These compounds effectively inhibited the settlement of the larvae of *M. edulis* (mussel) with an EC_{50} of 0.11–3.34 μg mL^{-1}. They also inhibited the zoosporic settlement of *U. pertusa* with an EC_{50} of 0.01–0.43 μg mL^{-1} and the diatom *N. annexa* with an EC_{50} of 0.008–0.19 μg mL^{-1} (Cho 2013). Besides, fatty acid derivatives especially docosane, hexadecanoic acid, and cholesterol trimethylsilyl ether from red algae showed rich antifouling activities (Dahms and Dobretsov 2017). The ethanol and dichloromethane extracts from a red alga *Ceramium botryocarpum* were studied for growth inhibition of marine diatoms. The ethanol fraction of *C. botryocarpum* extracts was most efficient with growth of an EC_{50} 5.3 μg mL^{-1} with reversible diatom growth effect (Silkina et al. 2012). Polyether triterpenoids such as dehydrothyrsiferol and saiyacenols B and C isolated from the *Laurencia viridis* showed high inhibitory activity against marine biofouling organisms (Cen-Pacheco et al. 2015). Furthermore, omaezallenes, a newly discovered natural product from the red alga *Laurencia* sp., effectively inhibit the fouling marine organism (Umezawa et al. 2014). It is no doubt that marine macroalgae harbor rich amount of biofouling compounds; however, extraction, isolation, and commercialization are critical, expensive, and laborious.

10.15 Development of Marine Natural Product-Based Antifouling Treatments

The consequence of metal-based antifouling coatings in the marine sectors has been the subject of serious controvert on the ecology of the marine environment (Foster 1994). Tributyltin (TBT) is a chemical antifoulant, most widely used in the antifouling coatings especially in paints, which accumulates in marine sediments contaminating numerous marine species (Stewart and Thompson 1997; Hashimoto et al. 1998; Fisher et al. 1999) due to which some countries have banned the use of TBT (Burgess et al. 2003). Currently, copper and herbicide and 2-methylthio-4-tert-butyl-amino-6-cyclopropylamino-*s*-triazine (Irgarol®)-based paints are widely used as an alternative to TBT; however, copper and Irgarol also showed toxicity to several marine species (Claisse and Alzieu 1993; Batley et al. 1994; Thomas 2001; Gibbon 1995). Marine natural products can be an alternative for the chemicals as it is environment-friendly and effective in antifouling coatings (Willemsen and Ferrari 1993; Armstrong et al. 2000a, b; Burgess et al. 2003). Price et al. (1994) added sea pansy extracts into commercially available paint and found to be effective for only a short duration in the ocean. Later on, researchers used sponge extracts (Willemsen and Ferrari 1993) and gorgonian extracts (Bakus et al. 1994) in paints which successfully inhibited the barnacle settlements and tube worms. A paint added with culture extract of marine *Pseudomonas* sp. strain NUDMB50-11 exhibited excellent activity to inhibit the settlement of barnacle larvae *B. amphitrite* and algal spores of *Ulva lactuca* (Burgess et al. 2003). The extracellular compounds produced by a tunicate-derived *Pseudoalteromonas tunicata* exhibited strong inhibition against settlement of invertebrates and algal spores, growth of microbes, and surface colonization by diatoms (Holmstrom and Kjelleberg 1999; Burgess et al. 2003). Therefore, it is evident that number of epibiotic bacteria have the potential of producing biomolecules which can be incorporated into paints that retain their antifouling activity (Burgess et al. 2003).

10.16 Biological Synthesis of Nanoparticles

Nanotechnology is now playing crucial role in the contemporary technical world and applied science for designing, synthesizing, and exploiting small structures for a number of applications in medicine and life sciences (Dahms and Dobretsov 2017; Prasad et al. 2016, 2018a, b). Besides, nanoparticles have been applied in several processes such as wastewater treatment, industrial catalysis, chemical and biological sensors, agriculture and food industries, and modern electronic components such as wireless electronic logic and memory systems (Pugazhendhi et al. 2015; Dahms and Dobretsov 2017; Prasad et al. 2017a, b). Metal nanoparticles including silver, gold, and platinum have been applied in various fields of medicine, pharmaceuticals, and bioelectronics (Shankar et al. 2016; Aziz et al. 2014, 2015, 2016). Recently, metal and metal oxide nanoparticles and nanostructures have also been used in the antifouling activities (Yang et al. 2016a, b; Sathe et al. 2016; Al Naamani et al. 2017). Among the other metal oxide nanoparticles, zinc oxide nanoparticles are of particular interest due to it being inexpensive and colorless and their UV blocking properties (Al Naamani et al. 2017). Zinc oxide is a natural product employed in food processing and agriculture (Reddy et al. 2007) and recently used as a potential source as antimicrobial, antibiofilm (Dhillon et al. 2014), and antifouling agents with enhanced physical properties (Malini et al. 2015; Abiraman et al. 2016; Al Naamani et al. 2017). However, the most widely used nanoparticle is silver due to its size, shape, and broad applications including antifouling activity (Muthukumar et al. 2015; Yang et al. 2016a). Biological synthesis of nanoparticles using seaweeds is getting momentum in recent years which is environment-friendly, less cost-intensive, and less energy-consuming with reliable production method and antifouling applications. Al Naamani et al. (2017) developed nanocomposite chitosan-zinc oxide nanoparticle hybrid coatings that showed antibiofilm and anti-diatom activity against *Navicula* sp. and antibacterial activity against *Pseudoalteromonas nigrifaciens*. Biocompatible and functionalized silver nanoparticles synthesized from an aqueous extract of a macroalga *Enteromorpha compressa* are employed as a reducing and stabilizing agent displayed strong antimicrobial and anticancer activity which may potentially be applied in antifouling approach (Ramkumar et al. 2017). Green synthesis of metal nanoparticles could be a promising source in antifouling applications.

10.17 Anticorrosion Metabolites

Seawater covers more than 70% of the globe's surface. It contains many mineral salts, dissolved gases including oxygen (O_2), bacteria and other unicellular or multicellular organisms, and suspended solids and sediments that sometimes give it a high degree of turbidity. Seawater is therefore not simply a solution of sodium chloride. Thus, the sulfate ions arrive, in order of importance, after the Na^+ and Cl^- ions and are strongly involved in the mechanisms associated with the marine corrosion of steels and other metals. The chemical and biological specificities of seawater make it a particularly aggressive environment with regard to many materials, steels and others.

10.18 The Problem of Corrosion of Marine Structures

Corrosion is the set of phenomena of destruction or alteration of a solid body in contact with a fluid external medium. Such a definition brings together, of course, the most diverse phenomena, materials, and environments (Phull and Abdullahi 2017). The disorders observed on the metallic structures of harbor, fluvial, and seaside infrastructures are mainly caused by the corrosion phenomenon which manifests itself differently on the metallic parts according to the zones of exposure (splashing, tidal, immersion, etc.).

In general, the calculation of the lifetime of a metallic structure in an aquatic site takes into account a loss of thickness due to the uniform corrosion of the order of 0.1 mm/year; localized corrosion rates of the order of cm/year were recorded at some sites. The areas considered to be the site of this degradation deserve special attention and protection (Phull and Abdullahi 2017).

10.19 Corrosion Types and Damages

In desalination system, where seawater is used, corrosion of metals is of two types: general and localized corrosion. Both corrosions will bring great harm to the service life of equipment and safety of operation systems. Corrosion in the seawater primes to even significant economic losses, such as productivity loss, loss of end product, loss of efficiency, and product contamination. Even more serious, corrosion in the seawater leads to catastrophic major accidents, such as contamination of potentially toxic materials, causing pollution to the environment, and may also pose severe threat to the public health (Hou et al. 2018).

10.20 Corrosion Main Characteristics

According to seawater characteristics and metal corrosion law, the behavior of corrosion in sea is shown as four corrosion characteristics:

1. When dissimilar metals contact, anode metal may cause significant galvanic corrosion damage, which ascribed to the seawater has good conductivity and small corrosion resistance.
2. Since seawater has vast amount of chlorine, passive metals are prone to suffer localized corrosion in seawater, such as "pitting corrosion, crevice corrosion, and stress corrosion," and prone to suffer "erosion corrosion" in the high-velocity seawater.
3. Any factor of increasing limiting diffusion current density could aggravate metal corrosion.
4. According to the contact style of metal and seawater, the sea could be categorized into five zones: atmospheric zone, splash zone, tidal zone, immersion zone, and sea area. The metal corrosion in these areas is quite different, and the most serious corrosion appears in splash zone (Hou et al. 2018).

10.21 Living Organisms that Contribute to Corrosion in Marine Environment

During the corrosion process, the biological factor is likely to intervene to induce or accelerate the phenomenon. The corrosion is then called biocorrosion, biodeterioration of materials, or corrosion influenced (or induced) by microorganisms (MIC, microbially influenced corrosion). The ISO 8044 (1999) defined the terms "microbial corrosion" and "bacterial corrosion" as the interactions between living microorganisms and the material. In general, microorganisms would not directly use the materials as a source of nutrients. However, the drastic modification of the conditions on the surface thereof, under the influence of microbial metabolism, is likely to induce or accelerate its degradation.

10.22 Concept of Bacterial Metabolism

The prokaryotes, especially bacteria, that are generally associated with the biocorrosion processes of steels or other metals are mainly involved in sulfur and iron cycles: they use as terminal acceptor of electron a compound derived from sulfur or iron. The main groups from these metabolisms such as those of sulfate-reducing, thiosulfate-reducing, and sulfo-oxidant bacteria and more concisely bacteria using iron for their metabolism are also presented in the following sections.

10.23 The Microflora Linked to the Sulfur Cycle

The sulfur cycle is a major and complex life cycle. In nature, both parts of the sulfur cycle, aerobic and anaerobic, are usually overlaid and complement each other. In anaerobiosis, the sulfur cycle is entirely microbial. Sulfide comes from the reduction of sulfates by sulfate-reducing bacteria (SRB), the decline of primary sulfur by sulfate-reducing bacteria, the decline of thiosulfates by thiosulfate-reducing bacteria, and bacterial decomposition of sulfur-containing proteins. The sulfide is subsequently oxidized by the anoxygenic phototrophic bacteria that use it as an electron donor for their photosynthesis. Under aerobic conditions, the cycle is only partly biological, and the sulfide can be oxidized by aerobic chemilithotrophic bacteria (Caumette et al. 1986). The group of sulfate-reducing bacteria is slightly detailed below.

10.24 Sulfate-Reducing Bacteria (SRB)

Sulfate-reducing bacteria (SRB) are those that have been and are still the most studied in the field of the biocorrosion of steels and other metals (Beech and Gaylarde 1999). They are considered among the most harmful and are present in many cases of accelerated corrosion of metal structures. They are particularly involved in the accelerated corrosion of low-water port infrastructure (Pedersen and Hermanson 1991). Most recent studies, however, agree that bacterial consortia should be given a key role, particularly between microorganisms that are sulfurogenic and sulfo-oxidant (Pedersen and Hermanson 1991). From a morphological and physiological point of view, sulfate-reducing bacteria represent a complex and varied group of anaerobic bacteria (Rabus et al. 2002.) Within sulfurous microorganisms, sulfate-reducing bacteria were found to form the most important microbial group. They generally belong to the domain of *Bacteria* except of three species of the genus *Archaeoglobus* that belong to the domain of *Archaea*. Among *Bacteria*, the most described are *Desulfovibrio* with forty-one species and *Desulfotomaculum* with twenty species (Ralf et al. 2002).

10.25 The Microflora Linked to the Iron Cycle

The iron cycle consists of the transformation of iron (II) into iron (III) and vice versa. These operations take place under different physicochemical conditions (pH, temperature, etc.) in an abiotic or biotic way. The reduction or oxidation of iron by microorganisms plays a significant role in this cycle. Microorganisms associated with iron metabolism are the second most frequently cited group in biocorrosion phenomena of steels. It contains iron-reducing bacteria (IRB) and iron-oxidative bacteria (IOB). The IRB group is described below.

10.26 Iron-Reducing Bacteria (IRB)

IRBs form a metabolic group in which species can be phylogenetically distant (Lonergan et al. 1996). The described strains belong in their majority with δ-Proteobacteria and more precisely with the genera *Geobacter*, *Desulfuromonas*, and *Pelobacter*. However, some of the γ-Proteobacteria such as *Shewanella* spp. and *Geovibrio ferrireducens* also belong to the IRB (Caccavo et al. 1996). IRBs are divided into two groups according to their ability to completely oxidize organic matter to CO_2. This oxidation is coupled with the reduction of iron (III) contained in minerals (ferrihydrite, goethite, hematite). Some of these minerals are also produced by iron corrosion in the marine environment. Therefore, the presence of IRB could locally modify the rust layer, which would initiate the creation of anodic zones and induce a difference in electrochemical potential conducive to the development of a localized corrosion process (Lee and Newman 2003).

10.27 Compounds or Metabolites from Marine Organisms with Anticorrosive Potential

Recently, it has been demonstrated that incorporating bacteria into a protective coating of metals against marine corrosion is the solution devised at Sheffield Hallam University (Great Britain). It has been shown to be effective in preventing biocorrosion on an aluminum alloy. Moreover, some extracellular enzymes from marine organisms showed anticorrosive activity. This is the case of protease from the marine bacterium *Bacillus vietnamensis*. In fact, it has been projected that Cu ions coordinated with proteolytic enzymes and bonded with H_2O molecules which results in reduction in the oxygen availability in the environment, thereby preventing the corrosion of the copper-based alloys (Moradi et al. 2019).

Steel corrosion is a global problem in the marine environment. Many inhibitory treatments have been applied to alleviate the degradation of metallic constituents. Many of those methods are not cost-effective and not environment-friendly as well. Liu et al. (2018) presented a novel and "green" method which uses marine bacterium *Pseudoalteromonas lipolytica* for the prevention of steel corrosion in seawater. In this method, the marine bacterium would produce a biofilm over the steel and forms a hybrid form of film over the steel; thereby the steel is getting prevented from corrosion. The bacterium used in the study is capable of transitioning from a biofilm status to biomineralized film state which is crucial for its enduring anticorrosion potential. By forming a biomineralized film, the bacteria overpowers the volatility of biofilm defense on corrosion (Liu et al. 2018).

10.28 Anticorrosive Biomaterials in Industrial Applications

Biomaterial, one of the most interesting fields of modern science, deals with the biologically derived materials or substances that are used within a biological system. Although according to the sources two types are there yet in terms of several advantageous properties, natural biomaterials are far more important than synthetic biomaterials. Among the natural sources, the newest one and also the most potent one identified to be is the marine environment. The most undiscovered part of the Earth, the marine environment is the powerhouse of millions of undiscovered species generating the greatest biodiversity zone. Biomaterials from various marine organisms like sponges, ascidians, crustaceans, sessile organisms, corals, actinobacteria, seaweeds, and fungi have been reported. Development of new strategies coupled with chemical synthesis method could pave the way for future discovery in this actively growing field (Aritra Saha et al. 2014). Many studies were done to develop biomaterials with anticorrosive activities. As examples, a hybrid pigment based on acetylacetonate was tested for its effect on the protection of corrosion in an epoxy-ester polymeric coating. The results obtained exhibited that the epoxy-ester coating protection performance was significantly improved by adding zinc acetylacetonate (Palimi et al. 2018). On the other hand, the incorporation of plant extract in epoxy paint could increase its anticorrosive properties. This is the case of the *Gracilaria edulis* extract (Rajan et al. 2016).

10.29 Nanotechnology and Corrosion Control

Studies across the globe over the years have concluded that the nanotechnology has chiefly contributed for the management of metal corrosion through recent advancements in the cutting-edge technology. Nanotechnology, wherein materials of nanosize are employed, is having the scope for reinventing other and fresher technologies that are more effective than those used nowadays (Wansah et al. Wansah et al. 2014). The processes of nanocrystallization and modification of nanoscale chemical composition have revolutionized the field of nanotechnology. This has prompted the nanotechnology to be used in corrosion management (Shi et al. 2010). Nanoparticles are much smaller than the micro-sized particles and are not covered in the spectrum of visible light (400–700 nm) which are transparent to the human eye. They may contain very few aroms and molecules and may be arranged in two or three dimensions (Liu and Shi 2009). In addition to many applications, nanotechnology is also applied in the management of metal corrosion because of the formation of metal nanocomposites in thin-film coatings of metallic surfaces. Nickel-, silica-, and aluminum-based nanocomposites/nanomaterials and nanostructures were used in the management of metallic corrosions (Lekka et al. 2005). Titanium-based technologies are also developed for the prevention of corrosion in metallic steel through the formation of multilayer nanofilms (Shen et al. 2005). There have been many review articles published on the recent trends in the use of nanotechnology and about various nanomaterials for the management of metallic corrosion (Saji and Thomas 2007). Thus, the immensely effective nanotechnology can be effectively used for the prevention and control of corrosion of metallic particles in marine environment with cost-effectiveness and ecological friendliness.

10.30 Conclusion

Biofilms, biocorrosion, and biofouling are important biological processes that cause severe economic losses in many industries. The prevention and control strategies used conventionally for the management of the bioprocesses are becoming ineffective as the organisms operating these bioprocesses are fast evolving and develop resistance rapidly. Marine bioresources are potential sources for the exploration of novel bioactive metabolites with antibiofilm, anticorrosion, and antifouling properties. The nanoparticles functionalized with biomaterials from marine and other bioresources are considered as most desired alternative strategy for the eco-friendly and sustained prevention and control strategy for the management of biofilms, biocorrosion, and biofouling.

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