Sustainable Marine Structures
https://ojs.nassg.org/index.php/sms

ARTICLE

Effects of Antifouling Technology Application on Marine Ecological Environment

Liangcheng Liu[1] Ge Wang[2] Junyi Song[1] Bipu Hu[1*]

1. Department of Chemistry and Biology, College of Science, National University of Defense Technology, Changsha, 410073, China
2. Institute of Special Services, Naval Research Academy, Beijing, 102442, China

ARTICLE INFO

Article history
Received: 08 September 2021
Accepted: 10 January 2022
Published Online: 25 January 2022

Keywords:
Biological contamination
Antifouling technology
Marine ecological environment
The risk assessment

ABSTRACT

Resolving the contradiction between Marine economic development and Marine ecological environment protection has become an unavoidable and sharp problem. The uncontrolled use of Marine antifouling technology will bring uncontrollable and even irreversible damage to the Marine biosphere, which will lead to ecological disaster and threaten the survival of human beings. Therefore, it is an urgent task to find antifouling technology with lower environmental toxicity under the premise of considering economy. More attention should be paid to the long-term impact of mature and new technologies on the Marine ecological environment. This paper introduces the development status of antifouling technology, its influence on Marine ecological environment and puts forward the design strategy of comprehensive biological fouling prevention and control technology.

1. Introduction

With the increasing frequency of human marine activities and the construction of large-scale marine projects, marine fouling organisms will seriously threaten the safe and stable operation of marine facilities and cause greater economic losses. Humans have tried to explore marine antifouling technology by means of poisoning, coercion, avoidance, stripping and cleaning. At present, there is no antifouling technology that has the advantages of low cost, high efficiency, persistence, broad spectrum and environmental friendliness. Developing more green antifouling technology has become the world consensus.

The importance of marine environmental protection is self-evident, and the marine environmental pollution caused by economic development is increasingly prom-

*Corresponding Author:
Bipu Hu,
Department of Chemistry and Biology, College of Science, National University of Defense Technology, Changsha, 410073, China;
Email: 1508422574@qq.com

DOI: http://dx.doi.org/10.36956/sms.v4i1.438

inent. The Maritime Environment Protection Committee (MEPC) of the International Maritime Organization (IMO) has been committed to energy conservation and emission reduction of ships, improving the International Convention for the Prevention of Pollution from Ships and other conventions [1]. On March 3, 2011, China submitted its accession to the International Convention on The Control of Harmful Anti-Fouling Systems on Ships to the International Maritime Organization and took effect on June 7, 2011 [2]. In building a modern legal system for marine ecological and environmental protection, China has revised the Marine Environmental Protection Law four times, and issued more than 100 supporting regulations, departmental rules and local legislation. The widespread use of antifouling technology is one of the marine pollution sources that can not be ignored, and its impact on the marine ecological environment has attracted more and more attention of policy makers and scientific research institutions.

2. Application Status of Antifouling Technology

2.1 Harm of Fouling of Marine Organisms

Fouling of marine organisms mainly involves the formation of organic membranes by adsorption of organic molecules on the substrate, and the formation of biofilm by attachment reproduction of microorganisms [3]. Then, spores of algae, small fouling animals and larva of large benthic fouling organisms will attach and grow, and eventually form a large number of stable biological communities. In the development process of biological fouling from the early, middle and late stages, there is the phenomenon of attachment succession in the fouling community. In the end, micro and large fouling organisms usually form the fouling together, and it is often manifested as the aggregation and attachment phenomenon of some dominant fouling organisms, such as barnacles and mussels. However, in the actual environment, the formation process and apparent phenomena of defilement biomes are very complex and diverse, which are affected by various factors such as environment and competition between species, and are complicated with environmental conditions such as sea area, season, temperature and surface characteristics of materials [4].

The fouling of marine organisms mainly involves the formation of organic membranes by absorbing organic molecules on the substrate, and then the biofilm is formed by the attachment and reproduction of microorganisms. Then the spores of algae, small fouling animals and larva of large benthic fouling organisms will attach and grow, and eventually form a large number of stable biological communities. In the development process of biological fouling from the early, middle and late stages, there is the phenomenon of attachment succession in the fouling community. In the end, micro and large fouling organisms usually form the fouling together, and it is often manifested as the aggregation and attachment phenomenon of some dominant fouling organisms, such as barnacles and mussels. However, in the actual environment, the formation process and appearance of defilement community are very complex and diverse, which are affected by various factors such as environment and competition between species, and have complex relationship with environmental conditions such as sea area, season, temperature and surface characteristics of materials.

Barnacles, mussels, worms and other representatives of large Marine fouling organisms have both can secrete powerful underwater adhesion glue and the characteristics of calcium have hard shell, able to withstand high speed water erosion, the population is dominant in the community, the harm to Marine underwater installations, the largest is the main factors of ship sailing resistance increase [5]. Therefore, it has become the main research object in the field of marine pollution prevention. The most critical link for the occurrence of biological fouling is that larvae or algal spores are easy to attach themselves to underwater fixed facilities or anchored ships with relatively smooth water flow [6]. Biological fouling will increase the ship's sailing resistance, the most serious can increase the shaft power 84%, and accelerate the shell corrosion; The flow of seawater is reduced by blocking the seawater pipeline; Blocking aquaculture cage mesh and production reduction; Signal and transmission failures affecting underwater detection equipment. In freshwater basins, the main fouling organism is the Limnoperna fortunei [7], which is the most harmful to water transport projects, water conservancy projects and inland river navigation.

2.2 Principles of Marine Antifouling Technology

According to the scientific principle of antifouling technology, it is classified and introduced [8].

Physics-based antifouling technology has little impact on the environment, but it has great limitations in use and high energy consumption. Once physical conditions cannot be maintained, biological fouling will occur immediately. Mechanical removal refers to the removal of fouling organisms attached by underwater dynamic machinery instead of divers. Marine static facilities need continuous use. Cleaning before the ship docks can prevent biological invasion, and cleaning before leaving the port can timely prevent the development of early fouling and reduce treatment costs. Increasing flow rates and creating turbulence both work by creating a flow environment that adheres to the surface of the substrate and makes it difficult for the plankton larvae to attach; Increasing the surface temperature of the attached substrate will cause the larva to escape, and the fouling organisms will die and fall off at the temperature that can not survive. The reduction of oxygen concentration is mainly aimed at the use of closed pipes. When oxygen concentration is lower than a certain value, the larva will lose its motor ability and cannot attach, and will cause the death of the attached contaminated organisms. Ultrasonic vibration makes it difficult for plankton larvae to attach and causes the shedding of early fouling organisms through the high-frequency vibration attached to the substrate [9]. Uv antifouling refers to the direct exposure of diode radiation or the embedding of the diode on the substrate of the high permeability UV coating. Uv radiation will cause DNA, RNA and protein denaturation, so that the fouling organisms lose their attachment ability or die [10].

Antifouling technology based on chemical principle has environmental toxicity, mainly divided into direct release antifouling agent and antifouling coating. The former is the early use of heavy metal ions or highly toxic pesticides as antifouling agents to kill a large range of contaminated organisms, and has been banned [11]. The latter has the advantages of high efficiency, broad spectrum, durability and low cost, and is the main antifouling technology means at present. Antifouling coating can be divided into biodegradable coating, fouling release coating (FRC) and self-polishing coating (SPC) according to the technical principle. Biodegradable coatings are mainly polyester polymer materials which can be degraded by biology and environment. The continuous degradation makes the contaminated organisms lose the binding site and desorption, but the service life is short because of continuous degradation. Fouling desorption coating is a kind of polymer material represented by silicone and fluoropolymer, which is difficult for fouling organisms to attach and easy to desorption due to its low surface energy and low modulus. However, its service life is limited by mechanical strength and underwater adhesion between substrate. The cations in seawater can be replaced by antifouling agent after hydrolyzing the polyacrylate silane ester resin base material in the self-polishing coating, so that the antifouling agent is released slowly, but the porosity will gradually increase. Humans have tried to screen antifouling agents by extracting antifouling active substances from marine animals, plants and microorganisms in large quantities, but high production cost, difficult grafting and easy degradation are the biggest limiting factors.

The antifouling technology based on biological principle mainly adopts biological suppression to limit the fouling of organisms by predation of natural enemies. This approach remains in the theoretical stage, because changing the stable abundance of organisms in the ecosystem or introducing alien species may cause secondary ecological disasters, and it is difficult to limit the activity range of the removal organisms, and the effect is slow. The removal organisms themselves are also affected by environmental changes. Bionical anti-fouling technology in recent years become a hot research topic, human through material micro-nano structure design and simulation of Lotus Leaf [12], Salvinia natans All, Sea anemones, Shark, fur animals, Andrias and so on antifouling mechanism [13], the structure has the characteristics of low surface energy, low modulus, in subsequent studies found creatures and antifouling secretion metabolic stop loss of anti-fouling ability of structure, Such technologies therefore need to address issues such as the high cost of manufacturing materials and the simulation of dynamic life processes.

3. Environmental Effects of Marine Antifouling

3.1 Current Situation of Marine Pollution

Due to its huge volume and strong self-purification capacity, the ocean is regarded as a “sea containing all kinds of pollution” by human beings. Ocean warming, acidification and accumulation of toxic substances are the most significant characteristics of its pollution [14], and the pollution of the upper coastal waters and tidal flats is the most serious. Direct economic losses mainly come from the reduction of aquaculture and fishing [15]. The exploitation and utilization of fossil fuels leads to the overload emission of greenhouse gases such as carbon dioxide, methane and nitrous oxide [16], which is the basic cause of global climate warming and ocean warming. Ocean warming will bring global ecological problems such as glacier melting and release of ancient viruses, land area shrinking due to sea level rise, irreversible degradation of coral reefs and other ecosystems [17]. Excessive fossil fuel use releases acidic gases such as Carbon dioxide, sulfur dioxide and Nitrogen oxides, which dissolve in water, causing ocean acidification and hindering the growth of calcareous skeletal shells of organisms such as crustaceans, coelenterates and mollusks. Toxic substances accumulate in water due to their stable chemical properties and most of them can be enriched in organisms, such as heavy metal ions, radioactive substances and microplastics, etc. Oil pollution will cause large-scale death of plankton and decrease of dissolved oxygen in water [18]. Therefore, marine pollution will bring about the compression of human living space and the destruction of food supply chain and other problems that threaten human existence.

Marine underwater facilities are one of the main sources of pollution. Nuclear power plants and nuclear-powered vessels will cause radioactive pollution [19]. Oil exploitation, transportation and ship navigation will produce oil pollution. There are also industrial emissions of heat sources, ship navigation noise and other physical pollution and solid and liquid waste pollution.

3.2 Effects of Antifouling Coating Active Substances on Marine Environment

The polyester polymer materials in biodegradable coating are degraded into esters with low toxicity in water without forming residues [20]. It is worth mentioning that artificial synthesis of bacterial toxin butenolide extracted from Fusarium can block the fouling of biological attachment signal pathway rather than poison to achieve antifouling effect. The antifouling effect of the defiled-desorption coating depends on the physical properties of its material surface [21]. It does not release toxic substances. After the expiration of its life, the coating is scraped off for harmless treatment. The most harmful component to the marine ecological environment is the antifouling agent in the antifouling agent release coating [8]. Most antifouling agents are used in combination with cuprous oxide and organic biocides. Copper ions exist stably in free state in seawater and are difficult to be mineralized and precipitated. They accumulate in the environment and are enriched in the biological food chain. Long-term use will threaten the breeding of marine organisms and human food safety. Pyridinthione (PT) in the biocide will degrade to pyridine 1-ox-2-sulfonic acid with low toxicity in a short time [22], and the isothiazolinone derivative (DCOIT) can be rapidly oxidized and degraded to low toxicity in water, and finally converted to non-toxic substances without residue [23]. Irgarol 1051 (2-methyl sulfur-4-tert-butylamino-6-cyclopropyl amino-S-triazine) degrades slowly in water but is easy to photolysis [24]. It is most toxic to marine plants and has little effect on animals and bacteria. Antifouling agent release of antifouling paint in the base material and auxiliary materials of the pollution is small, the base material component polyacrylate silane ester resin, the main chain fracture hydrolyzed into low toxicity acrylate single molecule and is slowly degraded, will not remain as microplastics; Xylene in excipients is a class 3 carcinogen, which can degrade slowly in water and volatilize photodecomposition easily. It is not a persistent pollutant. N-butanol has a stronger paralyzing effect than ethanol, and it is not the main pollutant.

3.3 Impact of Other Antifouling Technologies on the Marine Environment

Physical antifouling has no residual harm, no environmental toxicity for fouling organisms, but the need for high energy consumption to maintain physical conditions may produce greater secondary pollution. High temperature antifouling requires a heat source to maintain the temperature of the base surface. Therefore, the continuous release of heat will increase the water temperature near the facility, causing the temperature stress effect on the surrounding aquatic organisms, and may affect the facility itself or the operator due to heat conduction. Because ultrasonic vibration can be widely spread in water, it may cause neurotic disorder of ultrasonic sensitive marine organisms such as dolphin, grouper, black bass and drum shrimp. Although there is no residual harm, the radiation area is wide, and it will also affect the precision instrument components and operators of facilities. Ultraviolet radiation causes nearby plankton die and biological exposed skin burns, a wide range of radiation attenuation in the water and won't cause pollution and no residue, but the extensive use of diode produces electronic garbage disposal costs and maintenance costs of circuit may be higher, so only apply to small underwater detection equipment.

In chemical antifouling, electrolysis of seawater produces hypochlorite ions and chlorine gas [25], which can directly kill plankton microorganisms, destroy the mucus on the body surface of fish and lead to electrolyte metabolism disorder in the body. Although non-toxic chloride ions can be rapidly converted, the electrochemical corrosion of the substrate will be accelerated, and energy consumption is also high. Analog enzymes, although they consume no energy, remain in the conceptual stage and are not discussed here. Bionic antifouling materials mostly do not release toxic substances, but the leakage of silicone oil from the porous structure will also cause oil pollution.

4. Management of the Use of Marine Antifouling Technology

4.1 Risk Assessment of Marine Antifouling Technology

Because the pollutants produced by immersion of antifouling coating have the characteristics of long half-life, accumulation and enrichment, strong toxicity and uncontrollable, the vast majority of laws and standards restricting the use of antifouling technology in the world are formulated for antifouling coating. The United States enacted the Toxic Substances Control Act (TSCA) in 1976; In 2006, THE European Union issued the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), and in 2012, a new biocide regulation BPR-Biocidal Products Regulation replaced the original biocide directive BPD-Biocidal Products Directive. In

2017, China also issued national standards such as Risk Assessment Method for Marine Environment of Antifouling Active Substances used in Ship Antifouling Bottom Systems and Risk Assessment Method for Marine Environment of Ship Antifouling Bottom Systems Using Antifouling Active Substances.

The risk assessment procedure of antifouling coatings is firstly to screen substances [26], quantify the release rate and establish exposure scene model to obtain the predicted environmental concentration (PEC) to complete the exposure assessment. Then collect hazardous information for toxicity assessment and obtain environmental effect threshold (PNEC) to complete the risk assessment; Finally, all the information is integrated to carry out risk characterization to obtain risk entropy and form a risk assessment report. In recent years, the regulatory procedures for risk assessment and control of antifouling coatings have been basically and increasingly improved. The problem that needs to be solved is to perfect the model database of each sea area exposure scenario and construct various functional laboratory microcosmic models. In addition, the impact of other antifouling technologies on the marine ecological environment, especially precious and endangered species, should also be included in the evaluation scope.

4.2 Design Strategy of Marine Antifouling Technology

The biggest factor limiting new environmentally friendly antifouling technologies is cost control, and copper-containing antifouling paints are still dominant in the short term. It should be noted that the environmental toxicity of copper is much lower than TBT and other organotin antifouling agents, but the minimum effective permeability is more than 10 times of the latter. The cumulative effect of long-term use is uncontrollable and irreversible, which is obviously not a long-term solution. The AFS has banned organotin since 2008, and this year, the 76th Session of the International Maritime Organization's Marine Environmental Protection Committee (MEPC) adopted the AFS amendment. Use of Cybutryne (2-tert-butamino-4-cyclopropyl-6-methanethio-1,3, 5-triazine) in antifouling bottom systems will be prohibited from 1 January 2023. The leaching rate of copper ion is limited by the Technical Requirements for Environmental Marking Products - Antifouling Paints for Ships formulated by the Ministry of Environmental Protection of China. All over the world, the regulation of existing antifouling agents and the access of new antifouling agents will only become more stringent, and it is necessary to continue to look for antifouling agents with lower environmental and biological toxicity. Low cost bionic degradable antifouling agent and antifouling coating with dynamic surface matching use, forming multi-mechanism long-term static antifouling is an important direction of antifouling coating development.

The ultimate goal of antifouling is to achieve zero emissions only through physical structure and material surface properties. But in the real sense of the present environment-friendly antifouling technology has a variety of congenital defects, we can develop antifouling strategies through the macro level. To establish a database of the changing rules and characteristics of the fouling community in different seasons and sea areas, and to formulate a comprehensive anti-fouling strategy according to the dominant fouling organisms. On the premise of meeting the discharge standards, the pollutants discharged into the ocean are screened as antifouling agents, and local enrichment and discharge are carried out in antifouling parts to achieve antifouling effect, and the pollutants are reused. Comprehensive anti-pollution technology strategy should be considered in an overall way to find a balance between economic cost and risk management, so as to achieve lower overall toxicity and less consumption of pollutants produced by anti-pollution.

5. Conclusions

A large number of species extinction, seabed desertification, abnormal climate change, deterioration of coastal water quality, frequent fishing disasters have rung the alarm bell for human beings. Let us realize that it is urgent to solve the irreversible pollution problem, and we should comprehensively reduce the pollution caused by marine pollution prevention from multiple dimensions such as technological research and development, rational use, legal supervision and so on. Oceans connect all continents. Only by making joint efforts to protect and sustainably utilize oceans and marine resources can we maintain our common "blue granary" and "blue medicine storehouse". This is the only way for human civilization to continue to grow and flourish.

References

[1] Aldo, Ch., 2019. The IMO initial strategy for the reduction of GHGs from international shipping: A commentary(Article). International Journal of Marine and Coastal Law. 3, 482-512.

[2] Hassan, C.A.S.H., 2016. The Impact of Implementing the International Convention on the Control of Harmful Anti-fouling Systems in Ships (AFS Convention) on the Marine Environment. Shipbuilding and ocean engineering. 1, 57-63.

[3] Culver, C.S.A.B., Johnson, L.T.C., Page, H.M.B., et al., 2019. Integrated Pest Management for Fouling Organisms on Boat Hulls. North American Journal of Fisheries Management.

[4] Dürr, S.P.W.D., Wahl, M., 2004. Isolated and combined impacts of blue mussels (Mytilus edulis) and barnacles (Balanus improvisus) on structure and diversity of a fouling community. Journal of Experimental Marine Biology and Ecology. 2, 181-195.

[5] Farkas, A., Degiuli, N., Martić, I., 2020. The impact of biofouling on the propeller performance. Ocean Engineering. 108376.

[6] Liang, Ch., Strickland, J., Ye, Z.H., et al., 2019. Biochemistry of Barnacle Adhesion: An Updated Review(Review). Frontiers in Marine Science.

[7] Wei, L., Xu, M.Zh., Zhang, J.H., et al., 2020. Survival and attachment of biofouling freshwater mussel (Limnoperna fortunei) to environmental conditions: potential implications in its invasion, infection and biofouling control. Limnology. 2, 245-255.

[8] Tian, L., Yin, Y., Bing, W., et al., 2021. Antifouling Technology Trends in Marine Environmental Protection. J Bionic Eng. 18(2), 239-263.

[9] Salta, M., Goodes, L.R., Maas, B.J., 2018. Bubbles versus biofilms: A novel method for the removal of marine biofilms attached on antifouling coatings using an ultrasonically activated water stream(Article). Surface Topography: Metrology and Properties. 3, 1-18.

[10] Ryan, E., Turkmen, S., Scopus Preview Benson, S.D., 2020. An Investigation into the application and practical use of (UV) ultraviolet light technology for marine antifouling(Article). Ocean Engineering. 107690.

[11] Amara, I., Miled, W., Slama, R.B., et al., 2018. Antifouling processes and toxicity effects of antifouling paints on marine environment. A review. Environmental Toxicology & Pharmacology. 115-130.

[12] Carve, M., Scardino, A., Shimeta, J., 2019. Effects of surface texture and interrelated properties on marine biofouling: a systematic review. Biofouling. 35(6), 597-617.

[13] Tian, L., Yin, Y., Bing, W., et al., 2021. Antifouling Technology Trends in Marine Environmental Protection. J Bionic Eng. 18(2), 239-263.

[14] Dobretsov, S., Coutinho, R., Rittschof, D., et al., 2019. The oceans are changing: impact of ocean warming and acidification on biofouling communities. Biofouling. 35(5), 585-595.

[15] Yigit, U., Ergun, S., Bulut, M., et al., 2017. Bio-economic efficiency of copper alloy mesh technology in offshore cage systems for sustainable aquaculture. Indian Journal of Geo-marine Sciences. 10, 2017-2024.

[16] Man, L., Feng, K.Sh., Zheng, H., et al., 2021. Supply chain effects of China's fast growing marine economy on greenhouse gas emissions. Environmental Research Letters. 5, 54061.

[17] Bradley, D.E., Andersson, A.J., Cyronak, T., 2014. Benthic coral reef calcium carbonate dissolution in an acidifying ocean. Nature Climate Change. 11, 969-976.

[18] Jin, Ch.H., Xu, Y.P., 2021. Risk Analysis and Emergency Response to Marine Oil Spill Environmental Pollution. IOP Conference Series: Earth and Environmental Science. 12070.

[19] M-Navarrete, J., Espinosa, G., I-Golzarri, J., et al., 2014. Marine sediments as a radioactive pollution repository in the world. Journal of Radioanalytical and Nuclear Chemistry. 299(1).

[20] Ma, Ch.F., Zhang, W.P., Zhang, Zhang, G.Zh., et al., 2017. Biodegradable Polymers; Studies in the Area of Biodegradable Polymers Reported from Hong Kong University of Science and Technology (Environmentally Friendly Antifouling Coatings Based on Biodegradable Polymer and Natural Antifoulant). Journal of Engineering.

[21] Hu, P., Xie, Q.Y., Ma, Ch.F., et al., 2020. Silicone-Based Fouling-Release Coatings for Marine Antifouling. Langmuir : the ACS journal of surfaces and colloids. 36(9).

[22] Zhi, Y.S., Jung, J.H., Jang, M., et al., 2019. Zinc Pyrithione (ZnPT) as an Antifouling Biocide in the Marine Environment—a Literature Review of Its Toxicity, Environmental Fates, and Analytical Methods. Water, Air, & Soil Pollution: An International Journal of Environmental Pollution. 230(4).

[23] Heloísa, B.G.A., Da-Silveira-Guerreiro, Juliana, Z.S., 2021. Molecular and biochemical effects of the antifouling DCOIT in the mussel Perna perna. Comparative Biochemistry and Physiology, Part C. 239.

[24] Zhang, A.Q., Zhou, G.J., Lam, M.H.W., et al., 2019. Toxicities of the degraded mixture of Irgarol 1051 to marine organisms. Chemosphere. 565-573.

[25] Gaw, Sh.L., Sarkar, S., Nir, S., et al., 2017 Electrochemical Approach for Effective Antifouling and Antimicrobial Surfaces(Article). ACS Applied Materials and Interfaces. 31, 26503-26509.

[26] Karina-Lotz-Soares-A, C., Sergiane-Caldas-Barbosa, C., Ednei-Gilberto-Primel, C., et al., 2021. Analytical methods for antifouling booster biocides determination in environmental matrices: A review. Trends in Environmental Analytical Chemistry. e108.