

BIOFOULING IN THE MARINE ENVIRONMENT: MECHANISMS, IMPACTS, AND MODERN SOLUTIONS. A BRIEF REVIEW.

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Abstract

Biofouling in the marine environment is a complex biological process that leads to serious economic and ecological effects for the marine industry and ecosystems. It begins with the adhesion of microorganisms and the formation of a biofilm, which facilitates the attachment of larger organisms and leads to an increase in the weight and hydrodynamic resistance of the vessels. These changes cause significant costs related to fuel, maintenance and operation of marine facilities. In addition, biofouling increases environmental risks, including contamination from biocides and carrying invasive species, which poses a threat to local ecosystems. This article examines the mechanisms of biofouling, economic and ecological impact, as well as global technologies to combat it, including innovations in biocidal and non-biocidal coatings. Achieving efficient and environmentally sound solutions remains a key challenge for the future of the maritime industry.

Keywords: biofouling, marine environment, antifouling, coatings, surface modification.

INTRODUCTION

Biofouling in the marine environment is a complex process that affects multiple aspects of the maritime industry and ecosystems. It involves the attachment and growth of bacteria, algae, mussels, crustaceans, and other marine organisms on various surfaces submerged in saline water bodies. From an economic perspective, this process leads to significant costs related to the maintenance of vessels and marine infrastructure. The present article examines the mechanisms of biofouling in the marine environment, its impact on the environment and the maritime industry, and modern approaches to combat the negative effects resulting from this natural biological process.

EXPOSITION

Mechanisms of Biofouling in the Marine Environment

The biofouling process begins immediately after a structure is submerged in seawater, influenced by various factors in

the aquatic environment such as temperature, salinity, pH, availability of nutrients, and more. Biofouling gradually develops from microfouling to macrofouling and progresses through four main stages, with the first two stages of the process considered reversible [1-9].

- A conditioning biofilm, formed as a result of the physical and chemical attachment of organic and inorganic materials.

- A bacterial biofilm of bacteria, yeast, and diatoms, which serves as a feeding and attachment medium for subsequent colonization by larger fouling organisms.

- A "slime layer" biofilm made up of microorganisms, such as spores of macroalgae, fungi, protozoa, etc.

- Surface colonization by the larvae of macrofouling organisms.

It is considered that the first two stages of the process are reversible.

Impact of Biofouling on the Maritime Industry

Biofouling leads to decreased vessel efficiency, increased weight, and hydrodynamic resistance. This results in higher fuel consumption, increased operational costs, maintenance and cleaning expenses for the hull, additional docking fees, labor costs, and losses stemming from reduced overall economic efficiency due to the vessel being out of service for prolonged periods. Furthermore, biofouling can lead to accelerated wear and tear of engine systems and other mechanical components of vessels [9 - 12].

Impact of Biofouling on the Environment

In environmental terms, the consequences of biofouling are significant. Increased fuel consumption leads to atmospheric pollution through the emission of harmful substances such as carbon dioxide (CO₂), which contributes to global warming, sulfur oxides (SO_x), which cause acid rain in coastal areas, nitrogen oxides (NO_x), and other greenhouse gases, as well as fine particulate matter [6, 13, 14].

Moreover, fouling of the hull can result in the transport of invasive species, which can harm fisheries, aquaculture, marine and port infrastructure, and pose a potential threat to local ecosystems and human health [3].

Finally, the pollution caused by antifouling agents and coatings should also be noted. The release of biocides from the ship's hull can be harmful to most marine organisms at concentrations higher than physiological levels.

Due to its significant environmental footprint, biofouling is increasingly subject to strict international and national legal regulations and control. Efforts to limit it are intensifying in light of the growing environmental, economic, and health risks it poses [5, 6, 15].

Historical Accounts of Biofouling Prevention

The prevention of biofouling in the field of seafaring has its roots in antiquity when sailors began seeking solutions to combat

the accumulation of organisms on ship hulls. As early as ancient Egypt, Greece, and Mesopotamia, natural materials such as wax and animal fat were used to reduce biofouling. In the 18th century, metallic coatings, such as copper plates, began to be used, proving effective against marine organisms due to the antimicrobial properties of the metal. More recently, in the 20th century, various metal alloys with high corrosion resistance and strong antifouling properties, primarily based on copper, nickel, tantalum, niobium, cobalt, chromium, titanium, and others, have been widely used [2, 8, 16].

Copper and copper alloys, due to their biocidal qualities, have been widely applied in the construction of various marine structures, with bronzes and copper-nickel alloys being the most commonly used materials in marine environments [17 - 19]. The antimicrobial, antibacterial, and antioxidant properties of silver have been known and utilized for thousands of years [20 - 22]. The antimicrobial properties of copper and silver are determined by the biological activity of their ions (Cu⁺ and Ag⁺) [9, 23, 24].

Modern Trends in the Development of Antifouling Coatings

Protective coatings that form a relatively thin film and serve as a barrier between the aggressive external environment and the reactive base material of the structure are considered the most effective and cost-efficient method for preventing biofouling on marine facilities [19]. However, the main challenge lies in developing coatings that not only withstand harsh external conditions but also provide effective and long-lasting protection while remaining environmentally friendly [5, 6, 15].

Modern antifouling coatings, according to their mode of action on fouling organisms, can be classified into two main categories: biocidal and non-biocidal.

The antifouling action principle of biocidal coatings involves the release of biocides into the marine environment from a

water-soluble matrix, with the aim of inhibiting the growth or destroying fouling organisms or preventing their attachment. The most commonly used biocides in antifouling paints are Tributyltin (TBT), Chlorothalonil, Dichlofluanid, Sea-Nine 211, Diuron, Irgarol 1051, and Zinc Pyrithione. Following the ban on tributyltin (TBT), copper and copper compounds with one or more “booster biocides,” typically heavy metals, became the main component of biocidal antifouling coatings. Unfortunately, the use of biocides in the aquatic environment has proven harmful, as they have toxic effects on non-target marine organisms [2, 5 – 8, 15, 25 - 27].

Currently, the primary technologies for biocidal antifouling include polymeric coatings with controlled depletion of biocides (CDP) and self-polishing copolymers (SPC). In CDP, biocides such as copper and zinc are gradually leached into the water through the slow dissolution of a rosin agent, while in SPC, biocides are released through hydrolysis, creating a polishing effect [1, 28, 29].

Non-biocidal coatings, considered environmentally safe due to the absence of toxic biocides, are based on surface modification to deter the attachment of organisms or to aid in the release of fouling [5, 8, 9, 30, 31]. They also involve the use of biologically derived components such as natural antifouling products (NPA), biomimetic strategies, and microbial corrosion inhibitors (MIC) [2, 5, 25, 32, 33].

Modern technologies offer innovative materials and surface structures to combat biofouling:

- **Hydrophobic Coatings** – Special polymer or composite coatings with hydrophobic properties that repel water from the surface and can reduce the adhesion of microorganisms and other biofouling species.

- **Micro- and Nano-structured Low-friction Surfaces** – These have smooth surfaces enriched with nanoparticles or

nanostructures that reduce friction with water, improve the hydrodynamic properties of the surface, and prevent the fouling of algae and other biological organisms.

- **Slippery Coatings** – The SLIPS technology uses nano/microstructured substrates to retain a lubricating liquid, creating a stable and inert “slippery liquid film” on the material’s surface [6].

- **Anti-corrosion Coatings** – These protect surfaces from corrosion, which can disrupt hydrodynamic properties and lead to the accumulation of fouling species.

- **Conductive Coatings** – Biofouling is affected by integrating conductive agents into the coatings [6].

- **Photocatalytic Coatings** – The primary principle of photocatalytic disinfection involves the absorption of photons and electron excitation in the metal semiconductor oxide under UV light. The electron-hole pairs participate in a series of oxidation chemical reactions with adsorbed species like water and oxygen, generating highly reactive oxygen species (ROS) [34, 35].

- **Thin-film Metal Coatings with Nanocomposites** – The trend is towards creating nanomaterials based on the use of naturally occurring, non-toxic, biodegradable, and biocompatible materials. Due to their small size, comparable to the diameter of viruses and most biological macromolecules, and their high surface-area-to-volume ratio, nanoparticles possess greater bactericidal efficiency at low concentrations [20, 23, 24, 36].

Silver nanoparticles integrated into a metal matrix attract the most interest due to their high disinfection capacity and significantly lower cost compared to other noble metals [34, 36].

The use of thin-film metal coatings with micro- or nanoparticles of semiconductor metal oxides, possessing strong photocatalytic properties such as titanium dioxide (TiO₂) or zinc oxide (ZnO), is also gaining attention [34, 37, 38].

CONCLUSION

Biofouling in the marine environment represents a significant challenge that affects not only the economic aspects of the maritime industry but also the ecological sustainability of marine ecosystems. The development of biofouling, starting from the initial adhesion of microorganisms, leads to serious economic losses, increased operational costs, and even environmental consequences, such as atmospheric pollution and the spread of invasive species.

Historically, the "battle" against this problem has led to the development of various technologies, including biocidal and non-biocidal coatings aimed at minimizing the negative effects of biofouling.

Modern innovations in protective coatings, such as hydrophobic and photocatalytic solutions, offer promising approaches to addressing this complex biological process. Despite the advancements, finding effective and environmentally safe solutions that provide long-term protection for marine structures remains a challenge.

REFERENCE

- [1] D. M. Yebra, S. Kiil, and K. Dam-Johansen, "Antifouling technology-past, present and future steps towards efficient and environmentally friendly antifouling coatings," *Prog Org Coat*, vol. 50, pp. 75–104, 2004, doi: 10.1016/j.porgcoat.2003.06.001.
- [2] E. Almeida, T. C. Diamantino, and O. De Sousa, "Marine paints: The particular case of antifouling paints," *Prog Org Coat*, vol. 59, pp. 2–20, 2007, doi: 10.1016/j.porgcoat.2007.01.017.
- [3] C. Hellio and D. M. Yebra, "Introduction," *Advances in Marine Antifouling Coatings and Technologies*, pp. 1–15, 2009, doi: 10.1533/9781845696313.1.
- [4] "(PDF) Current and Future Trends in Marine Antifouling Coatings and the Study of Energy Efficiency Benefits for a Naval Fleet." Accessed: Apr. 05, 2024. [Online]. Available: https://www.researchgate.net/publication/331207510_Current_and_Future_Trends_in_Marine_Antifouling_Coatings_and_the_Study_of_Energy_Efficiency_Benefits_for_a_Naval_Fleet
- [5] J. E. Gittens, T. J. Smith, R. Suleiman, and R. Akid, "Research review paper Current and emerging environmentally-friendly systems for fouling control in the marine environment," 2013, doi: 10.1016/j.biotechadv.2013.09.002.
- [6] L. Li, H. Hong, J. Cao, and Y. Yang, "Progress in Marine Antifouling Coatings: Current Status and Prospects," *Coatings* 2023, Vol. 13, Page 1893, vol. 13, no. 11, p. 1893, Nov. 2023, doi: 10.3390/COATINGS13111893.
- [7] V. Matranga and I. Corsi, "Toxic effects of engineered nanoparticles in the marine environment: Model organisms and molecular approaches", doi: 10.1016/j.marenvres.2012.01.006.
- [8] M. S. Selim et al., "Recent progress in marine foul-release polymeric nanocomposite coatings," Jun. 01, 2017, Elsevier Ltd. doi: 10.1016/j.pmatsci.2017.02.001.
- [9] S. Kumar, F. Ye, S. Dobretsov, and J. Dutta, "Nanocoating Is a New Way for Biofouling Prevention," *Frontiers in Nanotechnology*, vol. 3, p. 771098, Nov. 2021, doi: 10.3389/FNANO.2021.771098/BIBTEX
- [10] S. Liu, A. Papanikolaou, A. Bezunartea-Barrio, B. Shang, and M. Sreedharan, "On the effect of biofouling on the minimum propulsion power of ships for safe navigation in realistic conditions," *Biofouling*, vol. 37, no. 2, pp. 194–205, 2021, doi: 10.1080/08927014.2021.1890044.
- [11] M. P. Schultz, J. A. Bendick, E. R. Holm, and W. M. Hertel, "Economic impact of biofouling on a naval surface ship," *Biofouling*, vol. 27, no. 1, pp. 87–98, Jan. 2011, doi: 10.1080/08927014.2010.542809.
- [12] D. A. Jones, "Principles and Presentation of Corrosion - D.A. Jones," ISBN 0 -13-359 993-0, p. 572, Jan. 1996, Accessed: Apr. 04, 2024. [Online]. Available: https://www.academia.edu/74928103/Principles_and_Presentation_of_Corrosion_D_A_Jones
- [13] "Environmental Performance: IMO Agreement on Technical Regulations to Reduce Ships' CO2 | International Chamber of Shipping." Accessed: Apr. 04, 2024. [Online]. Available: <https://www.ics->

- shipping.org/shipping-fact/environmental-performance-imo-agreement-on-technical-regulations-to-reduce-ships-co2/
- [14] “Marine Propeller Market Size, Share | Growth Report, 2022-2029.” Accessed: Apr. 05, 2024. [Online]. Available: <https://www.fortunebusinessinsights.com/marine-propeller-market-103074>
- [15] V. Tornero and G. Hanke, “Chemical contaminants entering the marine environment from sea-based sources: A review with a focus on European seas,” 2016, doi: 10.1016/j.marpolbul.2016.06.091.
- [16] S. Kiil, C. E. Weinell, D. M. Yebra, and K. Dam-Johansen, “Marine biofouling protection: design of controlled release antifouling paints,” *Computer Aided Chemical Engineering*, vol. 23, pp. 181–238, Jan. 2007, doi: 10.1016/S1570-7946(07)80010-1
- [17] “(PDF) Copper-Nickel Alloys for Seawater Corrosion Resistance and Anti-Fouling - A State of the Art Review.” Accessed: Apr. 25, 2024. [Online]. Available: https://www.researchgate.net/publication/254544596_Copper-Nickel_Alloys_for_Seawater_Corrosion_Resistance_and_Anti-Fouling_-_A_State_of_the_Art_Review
- [18] “Copper Nickel: Resistance to Corrosion and Biofouling.” Accessed: Apr. 25, 2024. [Online]. Available: https://www.copper.org/applications/marine/cuni/properties/biofouling/resistance_to_corrosion_and_biofouling.html
- [19] A. Wang, K. De Silva, M. Jones, P. Robinson, G. Larribe, and W. Gao, “Anticorrosive coating systems for marine propellers,” *Prog Org Coat*, vol. 183, p. 107768, Oct. 2023, doi: 10.1016/j.porgcoat.2023.107768.
- [20] T. Bruna, F. Maldonado-Bravo, P. Jara, and N. Caro, “Silver Nanoparticles and Their Antibacterial Applications,” *Int J Mol Sci*, vol. 22, no. 13, Jul. 2021, doi: 10.3390/IJMS22137202.
- [21] M. Jayaprakash and S. Kannappan, “An overview of a sustainable approach to the biosynthesis of AgNPs for electrochemical sensors,” *Arabian Journal of Chemistry*, vol. 15, no. 12, p. 104324, Dec. 2022, doi: 10.1016/J.ARABJC.2022.104324.
- [22] T. Yetim, “An investigation of the corrosion properties of Ag-doped TiO₂-coated commercially pure titanium in different biological environments,” *Surf Coat Technol*, vol. 309, pp. 790–794, Jan. 2017, doi: 10.1016/J.SURFCOAT.2016.10.084.
- [23] E. N. Petrinskaya, D. A. Rogatkin, and E. V. Rusanova, “COMPARATIVE CHARACTERISTICS OF ANTIBACTERIAL EFFECT OF SILVER AND NANOSILVER IN VITRO,” *Almanac of Clinical Medicine*, no. 44–2, pp. 221–226, Jun. 2016, doi: 10.18786/2072-0505-2016-44-2-221-226.
- [24] “Антибактериальные свойства и механизм бактерицидного действия наночастиц и ионов серебра.” Accessed: May 20, 2024. [Online]. Available: <https://cyberleninka.ru/article/n/antibakterialnye-svoystva-i-mehanizm-bakteritsidnogo-deystviya-nanochastits-i-ionov-serebra/viewer>
- [25] K. A. Dafforn, J. A. Lewis, and E. L. Johnston, “Antifouling strategies: History and regulation, ecological impacts and mitigation”, doi: 10.1016/j.marpolbul.2011.01.012.
- [26] I. Amara, W. Miled, R. Ben Slama, and N. Ladhari, “Review or Mini-review Antifouling processes and toxicity effects of antifouling paints on marine environment. A review,” 2017, doi: 10.1016/j.etap.2017.12.001.
- [27] K. Takahashi, “Release Rate of Biocides from Antifouling Paints,” in *Ecotoxicology of Antifouling Biocides*, Tokyo: Springer Japan, pp. 3–22. doi: 10.1007/978-4-431-85709-9_1.
- [28] M. Lagerström, E. Ytreberg, A.-K. E. Wiklund, and L. Granhag, “Antifouling paints leach copper in excess-study of metal release rates and efficacy along a salinity gradient,” *Water Res*, vol. 186, p. 116383, 2020, doi: 10.1016/j.watres.2020.116383.
- [29] C. Bressy, A. Margailan, F. Faÿ, I. Linossier, and K. Réhel, “Tin-free self-polishing marine antifouling coatings,” *Advances in Marine Antifouling Coatings and Technologies*, pp. 445–491, Jan. 2009, doi: 10.1533/9781845696313.3.445.
- [30] N. Misdan, A. F. Ismail, and N. Hilal, “Recent advances in the development of (bio)fouling resistant thin film composite membranes for desalination,” *Desalination*, vol. 380, pp. 105–111, Feb. 2016, doi: 10.1016/J.DESAL.2015.06.001.

- [31] A. J. Scardino and R. de Nys, "Mini review: Biomimetic models and bioinspired surfaces for fouling control," *Biofouling*, vol. 27, no. 1, pp. 73–86, Jan. 2011, doi: 10.1080/08927014.2010.536837.
- [32] M. Lejars, A. Margailan, and C. Bressy, "Fouling release coatings: A nontoxic alternative to biocidal antifouling coatings," *Chem Rev*, vol. 112, no. 8, pp. 4347–4390, Aug. 2012, doi: 10.1021/CR200350V/ASSET/CR200350V.FP.PNG_V03.
- [33] P. Y. Qian, Y. Xu, and N. Fusetani, "Natural products as antifouling compounds: recent progress and future perspectives.," *Biofouling*, vol. 26, no. 2, pp. 223–234, 2009, doi: 10.1080/08927010903470815.
- [34] H. Chakhtouna, H. Benzeid, N. Zari, A. el kacem Qaiss, and R. Bouhfid, "Recent progress on Ag/TiO₂ photocatalysts: photocatalytic and bactericidal behaviors," *Environmental Science and Pollution Research*, vol. 28, no. 33, pp. 44638–44666, Sep. 2021, doi: 10.1007/S11356-021-14996-Y.
- [35] K. H. Leong, L. C. Sim, S. Pichiah, and S. Ibrahim, "Light Driven Nanomaterials for Removal of Agricultural Toxins," pp. 225–242, 2016, doi: 10.1007/978-3-319-48009-1_9.
- [36] R. I. Dovnar, S. M. Smotryn, S. S. Anufrik, T. M. Sakalova, S. N. Anuchin, and N. N. Iaskevich, "ANTIBACTERIAL AND PHYSICO-CHEMICAL PROPERTIES OF SILVER AND ZINC OXIDE NANOPARTICLES," *Journal of the Grodno State Medical University*, vol. 20, no. 1, pp. 98–107, Mar. 2022, doi: 10.25298/2221-8785-2022-20-1-98-107.
- [37] P. M. Leukkunen et al., "Synergistic effect of Ni–Ag–rutile TiO₂ ternary nanocomposite for efficient visible-light-driven photocatalytic activity," *RSC Adv*, vol. 10, no. 60, pp. 36930–36940, Oct. 2020, doi: 10.1039/D0RA07078E.
- [38] M. Zayed, S. Samy, M. Shaban, A. S. Altowyan, H. Hamdy, and A. M. Ahmed, "Fabrication of TiO₂/NiO p-n Nanocomposite for Enhancement Dye Photodegradation under Solar Radiation," *Nanomaterials*, vol. 12, no. 6, p. 989, Mar. 2022, doi: 10.3390/NANO12060989/S1.