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PHYSICOCHEMICAL PROBLEMS OF MATERIALS PROTECTION

Biocorrosion, Biofouling, and Advanced Methods of Controlling Them

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Abstract—Microbiologically influenced corrosion (MIC) and biofouling in the marine environment are two main mechanisms of marine corrosion. The present review summarizes the results of recent studies and demonstrates that both MIC and marine biofouling are closely related to biofilms on the surface of materials formed by marine microorganisms and their metabolites. As a result, to prevent the emergence of MIC and biofouling, it is important to control microorganisms in biofilms or to prevent adhesion and formation of biofilms. The present review describes research approaches involving the use of new materials and innovative technologies in combination with traditional chemicals to achieve longer-lasting effects with the least environmental pollution due to the emerging synergistic effect.

Keywords: biocorrosion, microbiologically influenced corrosion, biofouling, aerobic bacteria, anaerobic bacteria, sulfate-reducing bacteria, iron-oxidizing bacteria, biocide, synergist, self-polishing coatings

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INTRODUCTION

Corrosion is a global problem that affects a wide range of industries and municipal services, such as shipping, oil refineries, construction, sewerage, and systems for drinking-water supply, as well as the maintenance of historical buildings and sculptural monuments. One of the main reasons for the destruction of various materials is the biocorrosion and biodegradation of materials resulting from the microorganism vital activity. The idea that microorganisms participate in the destruction of materials was suggested as early as in 1910 [1]. Different terms have been used to describe the corrosion caused by microorganisms—"biocorrosion," "microbial corrosion," "microbiologically influenced corrosion" [2], etc. All these concepts are very similar in meaning. Biocorrosion and microbial corrosion usually indicate that microbes serve as the main cause of corrosion. Microbiologically influenced corrosion (MIC) entails the effect of not only the microbes themselves, but also of their metabolites on corrosion. Formulating the concept of "biocorrosion" more precisely, one can say that biocorrosion is the result of electrochemical reactions affected or stimulated by microorganisms that are often present on materials in the form of biofilms. Thus, the concepts of MIC and biocorrosion have very similar meanings. Theoretical studies on biocorrosion of metallic and composite materials are comprehensively presented in [3–6].

Important objects that are most acutely affected by biodeterioration are sea vessels, harbor installations, water passages and pipelines, heat exchangers, oil and gas platforms on the shelf, navigation and underwater equipment, hydraulic structures, etc. The most aggressive degraders of materials are microorganisms—bacteria and fungi. They account for more than 40% of all biodeteriorations. The damage caused by microorganisms amounts to tens of billions of dollars annually [4, 7–9]. However, in a number of cases, microbes can inhibit or protect against corrosion [10].

Biocorrosion can be considered as a separate type of destruction, but most often biological corrosion processes proceed in parallel with others, for example, with marine, soil, atmospheric corrosion, and corrosion in electrolytes and aqueous solutions. The most common corrosion types that cause significant damage to the national economy are atmospheric and soil corrosion. Thus, the study of their developmental laws and the improvement of methods of protection are not

Abbreviations and notation: MIC, microbiological corrosion; SRB, sulfate-reducing bacterium; NRB, nitrate-reducing bacterium; IOB, iron-oxidizing bacterium; MOB, manganese-oxidizing bacterium; EET, extracellular electron transfer; SOB, sulfur-oxidizing bacterium; TBT, tributyltin; ZnPT, zinc pyrithione; DCOIT, Sea-Nine 211 biocide; PEG, polyethylene glycol; EPS, extracellular polymer substance.

losing importance [11–14]. Marine corrosion and soil corrosion are the most destructive types [15, 16]. Biological corrosion, depending on the microorganism type, is divided into bacterial and mycological ones and can be also of a mixed type [17–21]. Bacterial corrosion occurs most often [22–24], and it is also the most destructive type. The danger of bacterial corrosion consists in the fact that bacteria reproduce rapidly and easily adapt to changes in physical, chemical, and biological environmental conditions [25].

Studies have shown that microbiological corrosion and marine biological fouling are the two main components of marine corrosion caused by a complex marine environment and marine organisms.

The marine environment is an extremely aggressive environment for metals and other materials used in the marine industry [26]. First, seawater itself is an electrolyte with high corrosion activity. Second, in an ocean environment, marine organisms form complex communities on solid objects and affect them simultaneously, leading to corrosion of materials [27].

According to foreign specialists, corrosion causes damage to the economy of developed countries amounting to 3–3.5% of the value of gross national product, whereas losses in metal reach 20% [28]. According to incomplete assessments, the total damage to the world economy from biodeteriorations and marine fouling is estimated about US$50 billion per year. Marine biofouling proceeds due to undesirable colonization and accumulation of marine microorganisms, plants, and animals on material surfaces immersed in an aquatic environment and has a huge adverse effect on the infrastructure and equipment serviced in marine industries [29–32]. Marine fouling increases the weight and roughness of ship hulls, which increases the friction resistance and thereby causes additional fuel consumption.

The present review considers the mechanisms of microbiological corrosion and biofouling along with methods to prevent and control them.

MICROBIOLOGICAL CORROSION

At present, significant attention is paid to microbiologically influenced corrosion or (for simplicity) microbiological corrosion (MBC). At the same time, the main interest of researchers is caused by specific microbes as the main cause of corrosion and not by other corrosion factors, such as related chemical transformations (formation of CO_2, hydrogen sulfide, etc.). MBC comprises the corrosion of materials initiated directly by the vital activity of microorganisms and/or their metabolites [33, 34]. Most of the economic losses in the marine industry are caused by MBC. According to statistics, it accounts for about 20% of total economic losses [35].

Bacteria the vital activity of which proceeds in oxygen-containing environments are classed as "aerobic," while those that live in oxygen-free environments are "anaerobic." In natural environments, aerobic and anaerobic microorganisms live together. At the same time, the living conditions of anaerobic bacteria can be often created by the activity of aerobic bacteria. MBC is often produced by a mixture of anaerobic sulfate-reducing bacteria (SRBs) or nitrate-reducing bacteria (NRBs) and aerobic metal-oxidizing bacteria [36–40]. The corrosion process results from the use by SRBs and NRBs of elemental iron Fe^0 as an energy source [41, 42]. Experiments have shown that Fe^0 can serve as the only energy source for some SRB and NRB, which use metals as electron donors. Aerobic metal-oxidizing bacteria can be divided into two main groups: iron-oxidizing bacteria (IOBs) and manganese-oxidizing bacteria (MOBs) [43, 44]. Aerobic IOBs are easy to detect in the waters of oil fields, and they are usually considered corrosive microorganisms that contribute to MBCs.

Sulfate-Reducing Bacteria

Sulfate-reducing bacteria are the most studied bacteria in MBC conditions. SRBs are related to chemolithotrophic and chemo-organotrophic bacteria, which number 220 species and use sulfate as an electron acceptor [45–47]. SRBs are anaerobic, which means that they do not require oxygen for growth and activity [40]. This allows SRBs to survive under extreme conditions. These bacteria reduce sulfate to sulfide. The electrochemical reaction proceeds inside a biofilm, in which iron interacts with water and SRBs. As a result, hydroxyl groups (OH^-) are formed, which contribute to the reaction proceeding. SRBs are active in the pH range from 4 to 9.5 and can tolerate pressures up to 500 atm [45, 47]. Figure 1 shows the MBC process resulting from SRBs on an iron surface.

As was already noted, SRBs usually use sulfate as an electron acceptor. However, some SRB strains can also use sulfur, thiosulfate, or even CO_2 as oxidizing agents.

According to the literature data, the mechanism of corrosion induced by SRBs can be described using the cathodic-depolarization theory. However, other theories describing this process are currently known. According to the cathodic-depolarization theory, the electrochemical reaction proceeds on two parts: anode and cathode. On the anode site, iron reacts into the ionic form (Fe^{2+}). Fe^{2+} ions are separated from the surface while losing electrons moving to the cathode part. Concave areas ("pits") are formed on the anode due to the separation of iron ions. Then, iron ions react with sulfide (S^{2-}) from SRBs to form iron sulfide (FES), which is a coproduct. On the cathode part, the electrons move to the surface and react with hydrogen ions (H^+) with the formation of hydrogen gas (H_2). Due to the biofilm nature, water particles are ionized to hydroxide (OH^-) and hydrogen ions. Hydrogen ions decrease the pH level within the biofilm limits to

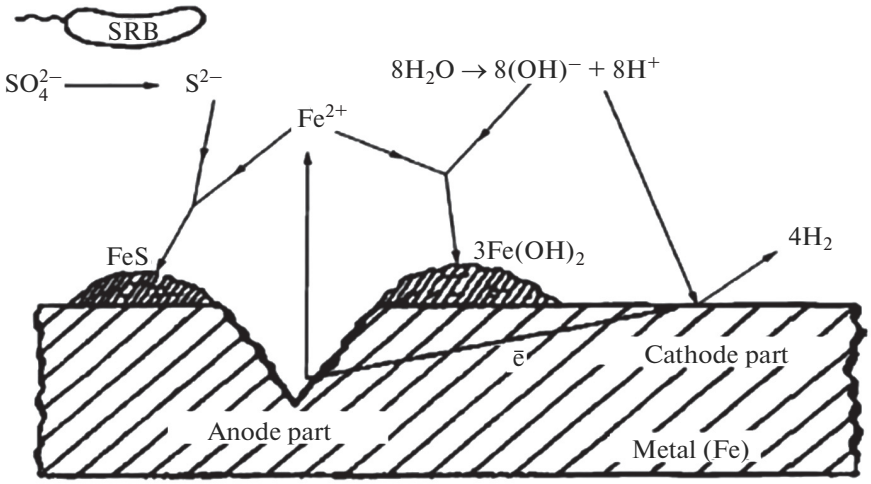


Fig. 1. Schematic representation of the cathodic depolarization theory caused by SRBs [48].

the acidic level. Hydroxide reacts with iron ions to form iron hydroxide ($Fe(OH)_2$) or rust. Scheme 1 shows electrochemical reactions proceeding inside the biofilm formed by SRBs on the iron surface [46, 49].

Anode: $4Fe \rightarrow 4Fe^{2+} + 8e.$

Water dissociation/ionization: $8H_2O \rightarrow 8H^+ + 8OH^-.$

Cathode: $8H^+ + 8e \rightarrow 8H.$

Cathodic depolarization resulting from SRBs: $SO_4^{2-} + 8H \rightarrow S^{2-} + 4H_2O.$

Corrosion products: $Fe^{2+} + S^{2-} \rightarrow FeS$; $3Fe^{2+} + 6OH^- \rightarrow 3Fe(OH)_2.$

Overall reaction: $4Fe + 4H_2O + SO_4^{2-} \rightarrow 3Fe(OH)_2 + FeS + 2OH^-.$

Scheme 1.

One should note that the oxidation of insoluble elemental iron proceeds outside SRBs, while the reduction of sulfate proceeds inside SRBs [45]. Thus, electrons released upon iron oxidation must be transferred through the cell wall into the SRB cytoplasm to participate in the sulfate reduction. To explain how electrons cross the cell wall of an SRB, the term "extracellular electron transfer" (EET) was introduced [50]. There are two main types of EET—direct and indirect electron transfer [51, 52]. When "sitting" cells are attached to the metal directly, cytochrome C is used for electron transfer. On the other hand, in the case in which "sitting" cells are close to the iron surface, conductive nanowires (pili) are released that bind microorganisms to the iron surface.

One should also note that, on the contrary to the case of the corrosion of NRBs, the corrosion of SRBs proceeds with more difficulties due to the release of H_2S. It can be concluded that their main metabolite is hydrogen sulfide—a strong stimulator of steel corrosion [53]. There are several hypotheses about the mechanism of anaerobic corrosion of steel, iron, aluminum, and their alloys under the effect of SRBs. One of the hypotheses is that, at a high content of iron sulfide in the medium, it forms a galvanic pair with iron in which sulfide is the cathode, while iron (the anode) is subjected to corrosion [6].

Another hypothesis suggests that a high concentration of H_2S resulting in the formation of iron sulfide actually passivates the iron surface against further corrosion [2]. Whether the FeS film causes corrosion resulted from SRB [54] or, on the contrary, passivates the iron surface is a debatable question. First of all, S^{2-} is not an electron acceptor, but a reduction state for the sulfur element. This means that the FeS film, in the best case, serves as a conductive mineral film between the iron and the biofilm, which can affect the adhesion of the biofilm to the iron surface. In addition, the assumption of the participation of the FeS film as a cause of SRB corrosion cannot explain why NRB are corrosive, if in the case of these bacteria no sulfide is formed at all.

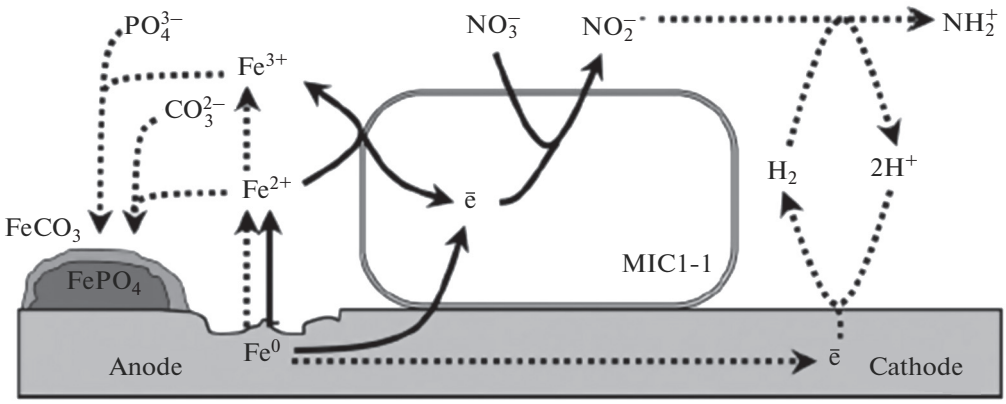


Fig. 2. The proposed model of Fe corrosion caused by NRB *Prolixibacter* sp. MIC1-1. Solid lines represent biotic processes; dotted lines represent abiotic chemical transformations [64].

Nitrate-Reducing Bacteria

Nitrogen is one of the basic elements of all forms of life and is necessary for the production of amino and nucleic acids [55]. Bacteria use nitrate as an alternative electron acceptor instead of oxygen and reduce it to N_2 in anaerobic reduction–oxidation processes [55, 56]. NRBs are mostly heterotrophic and often anaerobic with the ability to switch between oxygen and nitrate respiration depending on environmental conditions [57].

Metal corrosion in the presence of NRBs proceeds as follows: nitrate and iron form a redox pair. Metallic iron (Fe^0) is oxidized to divalent iron (Fe^{2+}) or divalent iron is oxidized to trivalent one (Fe^{3+}) with accompanying reduction of nitrate to nitrogenous compounds with a lower oxidation degree (for example, NH_4^+, N_2) [58]. A number of works have showed that chemical reduction of nitrates could occur in the presence of metallic (Fe^0) or divalent iron and that copper catalyzed this reaction [59–62]. It was determined that the chemical reduction of nitrate with Fe^{2+} iron occurs spontaneously in the pH range of 7.0–8.8 [62, 63].

In [64], the corrosion process caused by *Prolixibacter* sp. MIC1-1 NRBs was studied. It was determined that the main corrosion products formed in anaerobic conditions of the *Prolixibacter* sp. MIC1-1 culture were $FePO_4$ and $FeCO_3$. This indicates that Fe^0 was oxidized to both Fe^{2+} and Fe^{3+} ions. The oxidation of Fe^0 to Fe^{3+} ions under anaerobic conditions is unusual, since divalent iron (Fe^{2+}) compounds were usually detected as corrosion products in the case of SRBs and methanogens [41, 65]. The authors proposed the following mechanism of corrosion caused by *Prolixibacter* sp. MIC1-1. This strain oxidizes Fe^0 mainly to Fe^{2+} ions, as in the case of other aggressive microorganisms. Fe^{2+} ions can then be additionally oxidized to Fe^{3+} ions. Iron oxidation reactions are followed by the reduction of nitrate either to nitrite or to NH_4^+ ions. The proposed model of Fe^0 corrosion caused by NRB *Prolixibacter* sp. MIC1-1 NRBs is shown in Fig. 2.

Iron-Oxidizing Bacteria

Iron (Fe) has been long recognized as a potential energy source for bacteria, and mentions of bacteria as organisms that feed on iron can be dated to the mid-1800s [66, 67]. However, the understanding of the process of iron oxidation remained unclear for a long time. Only in the 1990s did the first review works dedicated to iron-oxidizing bacteria (IOBs) appear [68].

IOBs are bacteria that oxidize iron as a result of their metabolism, whereas many of them can use the electrons captured as a result of this process as their only energy source for growth. Of all potential energy sources, the oxidation of Fe(II) yields the lowest Gibbs free energy (G^0) for cellular metabolism. The amount of energy that a bacterium can extract from the $Fe^{2+} + 0.25O_2 + H^+ \rightarrow Fe^{3+} + 0.5H_2O$ reaction is equal to 29 kJ mol^{-1} [69]. However, if Fe(III) deposits in the form of iron hydroxide (rust), as it proceeds at neutral pH [$Fe^{2+} + 0.25O_2 + 2.5H_2O \rightarrow Fe(OH)_3 + 2H^+$], then the energy output doubles. In addition, the energy yield is estimated to increase up to 90 kJ mol^{-1} at the oxidation of Fe(II) at low oxygen partial pressures [68, 70].

Bacteria can be lithotrophic or heterotrophic depending on where they receive their energy and carbon from.

Lithotrophic microorganisms receive energy from the oxidation of divalent iron to trivalent iron and use this energy to consume carbon dioxide (CO_2) as the main carbon source in the cell. Heterotrophic Fe oxidation is related to microbes that actively catalyze the Fe(II) oxidation but do not receive energy from this

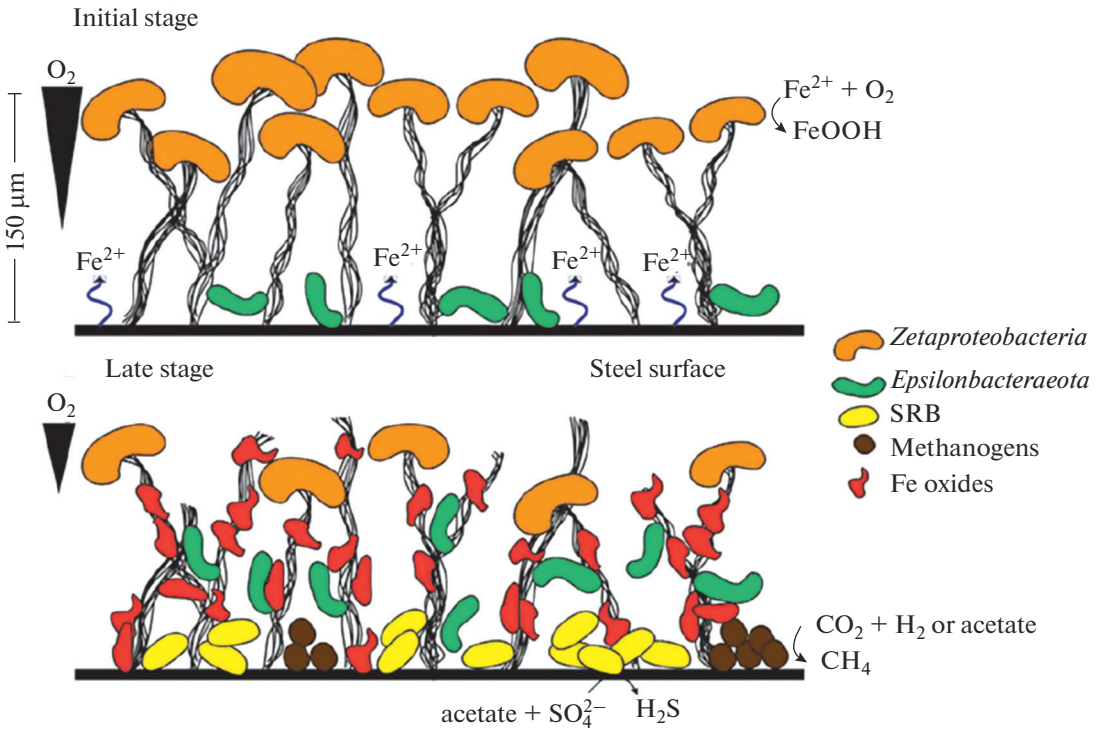


Fig. 3. Schematic model of steel fouling in a marine environment in the presence of *Zetaproteobacteria* [72].

process and do not consume CO_2, using instead an organic substrate as a source of carbon and energy. Examples of this process are organisms (such as *Leptothrix discophora* and *Sphaerotilus natans*), which produce proteins or enzyme systems that actively catalyze the oxidation of Fe but do not receive any energy benefits from this [66, 71].

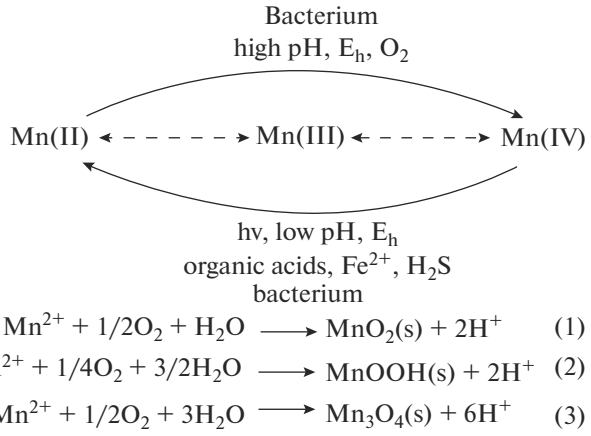
The main role of IOBs in MBC is to develop ecological associations within a larger microbial community or microbiome responsible for MBC. These associations may be more significant for the process than direct physiological interactions between the IOBs and the metal surface. Thus, based on a number of studies, it can be postulated that the most important role played by IOBs is in the early colonization of steel surfaces in combination with the production of three-dimensional biofilm [71].

In [72], a model was suggested based on detailed studies of the early phases of colonization of steel by pure *Zetaproteobacteria* cultures (Fig. 3). Based on this model, at an early stage of colonization of steel surfaces subjected to the impact of O_2, *Zetaproteobacteria* attach and grow from the surface, taking advantage of the release of Fe(II) from steel. *Epsilonbacteraeota* bacteria have also been detected at the early stages of biofilm formation, although their overall role in this process is not clear. As the biofilm on the steel surface grows and ages, anoxic regions develop, probably, due to the consumption of O_2 by both lithotrophic and heterotrophic bacteria, with the latter group growing on an organic substrate inside a biofilm. These areas offer opportunities for anaerobes (such as SRBs and methanogens), which, in turn, grow and develop a more mature microbiome that accelerates the corrosion process. In this model, at the initial stage, the number of IOBs may decrease, although the surfaces of iron oxides that they leave behind facilitate the colonization process by other microbes.

Thus, considering the overall complexity of the MBC process from the point of both microbial and physicochemical factors, the effect of IOBs is of a situational, rather than unambiguously negative or positive, nature.

Manganese-Oxidizing Bacteria

MOBs are widespread in nature and they are easy to detect in drinking water supply systems [73, 74]. MOBs are characterized by the ability to catalyze the oxidation of Mn(II) to Mn(IV) followed by the deposition of manganese dioxide (MnO_2) [44, 75]. Biogenic manganese oxides often interact with different metals. Mixed oxides of Fe and Mn are among the most common in nature. Manganese oxides are considered strong oxidizing agents [76] capable of oxidizing various organic and inorganic compounds [77]. The oxidation of Mn(II) to Mn(IV) is thermodynamically favorable under aerobic conditions with a negative free energy of about 16 kcal/mol [78–80]. How-



$$Mn^{2+} + 1/2O_2 + H_2O \longrightarrow MnO_2(s) + 2H^+ \quad (1)$$

$$Mn^{2+} + 1/4O_2 + 3/2H_2O \longrightarrow MnOOH(s) + 2H^+ \quad (2)$$

$$3Mn^{2+} + 1/2O_2 + 3H_2O \longrightarrow Mn_3O_4(s) + 6H^+ \quad (3)$$

Fig. 4. Scheme of Mn(II) oxidation reaction [78].

ever, the high activation energy of Mn(II) oxidation makes it very stable in most aqueous media [78, 79]. The activation-energy barrier can be overcome by increasing the pH (Fig. 4) or by adding Mn-binding components, including Mn oxides themselves, which are excellent Mn(II) chelators [79]. The catalysis of Mn(II) oxidation by Mn oxides (autooxidation) makes it difficult to distinguish between chemically and microbiologically catalyzed Mn oxidation, especially in natural environments where organic chelators and Mn oxide particles are abundant [78].

Biofilm Formation

During the corrosion process, SRBs and IOBs interact with each other, forming biofilms on metal surfaces. Under natural conditions, microorganisms can exist either in the form of planktonic (free-floating) cells or in the form of biofilms. According to current beliefs, 95–99% of microorganisms in natural habitats exist in the form of biofilms. Biofilms play a very important role in MBC [35, 54], and, in the process of development, they goes through a number of stages [37]. At the first stage, the adhesion or sorption of microorganisms to the substrate surface from the environment proceeds, an adsorbed film is created. This stage is reversible, since the sorbed cells can return to the planktonic form of existence. At the second stage, planktonic microorganisms migrate to the surface of the material attracted by the adsorbed film. The third stage consists in the final attachment of cells to the surface and is termed "fixation." At this stage, microbes release extracellular polymers, which provide strong adhesion, and planktonic microorganisms attach to active sites on the surface of the material and turn into "sitting" microorganisms. At the fourth stage, "sitting" microorganisms grow and produce metabolites with the formation of biofilms. At the fifth stage, microbes secrete extracellular polymers that provide strong adhesion. In this case, microcolonies—separate clusters of sorbed cells—are formed. At this stage, the cells actively divide, while the secreted matrix holds the entire colony together. Finally, the microcolonies merge and a mature biofilm is formed, which initiates corrosion. In the course of time, the stability of biofilms decreases, and then some of them fall off, thus forming heterogeneous biofilms. Many studies have shown that the composition of biofilms affects the corrosion of materials. Heterogeneous biofilms produced by the deposition of unstable biofilms create local corrosion of materials and accelerate it [38, 81–83]. The reason that heterogeneous biofilms cause local corrosion can be explained using the theory of oxygen concentration [84]. When heterogeneous biofilms emerge on the surface of the material, areas with dense biofilms prevent the spread of oxygen to them, and aerobic bacteria in biofilms contribute to the destruction of oxygen under biofilms. Both of these processes lead to the creation of areas with a low oxygen concentration. Consequently, these areas serve as anode portions for corrosion of the material. At the same time, areas with less dense biofilms or without biofilms and with higher oxygen concentrations serve as cathode portions for the oxygen reduction reaction and electron consumption.

Other Corrosive Bacteria

In addition to SRBs and NRBs, there are other corrosive microorganisms, for example, sulfur-oxidizing bacteria (SOBs). Neutrophilic (preferring a neutral medium) SOBs, such as *Thiobacillus* spp. and *Thiomonas* spp., oxidize sulfides and other sulfur compounds ($S_2O_3^-$ and S^0) to sulfuric acid and polythionic acids, thereby reducing the pH to about 3.5–5.0 [85–87]. The rate of bacterial oxidation of sulfides can be millions of times higher than the rate of conventional chemical oxidation. At pH 5.0 and below, acidophilic SOBs (such as *Acidithiobacillus thiooxidans*) continue to oxidize sulfur, producing a large amount of sulfuric acid, which decreases the pH down to 1.0–2.0 [88, 89]. H_2SO_4 reacts with the cement matrix, leading to the formation of gypsum ($CaSO_4 \cdot 2H_2O$) and ettringite ($3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}32H_2O$) [90]. These sulfate-containing salts produce internal cracks in the concrete and, ultimately, to the destruction of the structure [91].

Acid-forming bacteria are able to metabolize organic compounds (e.g., ethanol, lactate, aromatic hydrocarbons, and even CO_2) and produce organic and inorganic acids. These produced acids can increase the rate of corrosion, cause cracking of pipelines, or serve as nutrients for some other aggressive microbes, such as SRBs [92, 93]. Some acid-forming bacteria involved in bioleaching are aerobic [94]. Organic acids can accelerate corrosion, if acid corrosion is more active than oxygen-corrosion inhibition resulting from an aerobic acid biofilm. Some materials

(such as stainless steel) are resistant to oxygen corrosion due to their thin and dense passivating films of metal oxide. However, these mineral films can also be destroyed by biofilms. Acetic acid produced by *Acetobacter aceti* has been reported to accelerate the corrosion of stainless steel by destroying the protective chalky film formed at the cathodic polarization [93, 95]. The main causes of internal corrosion of carbon-steel gas pipelines are *Clostridia* and *Butyribacteria* [93, 95]. In general, the resulting organic acids accelerate corrosion by producing additional cathode reagents, binding metal ions and destroying the passivating film and passivation obstacles, which in total accelerates the dissolution of the metal [96]. Acetobacteria are aerobic bacteria that can oxidize ethanol into acetic acid during aerobic fermentation. It was found that they accelerated the pitting corrosion of steel and copper alloys due to the formation of acetic acid in its vaporous form and at the dissolution in an aqueous solution [97]. Bacteria of the genus *Acidithiobacillus* increase the rate of corrosion of metals and alloys by producing inorganic acids: their metabolism products such as sulfuric acid at the oxidation of thiosulfate [98].

Aerobic mucus-producing bacteria are commonly found in marine environments. The biofilm formed by these bacteria is characterized by a patchy distribution on metal surfaces. These bacteria remove oxygen from the areas under the biofilms through respiration, which results in the creation of areas with low oxygen concentrations. Consequently, these areas, as already noted, become anodic (relative to places with a large amount of oxygen), which results in local oxygen corrosion. Areas with a less dense biofilm or without it and with higher oxygen concentrations serve as cathode portions for oxygen recovery during electron consumption [99]. This corrosion process is known as the "release of caustic metabolites."

Anaerobic Biocorrosion

There are at least three different types of anaerobic biocorrosion based on anaerobic metabolism [2]. Type I is caused by electrogenic microbes such as SRBs (and microbes using molecular hydrogen H_2 as an electron carrier). They attack carbon steel, stainless steel, and some other base metals that are electron donors and have sufficiently negative reduction potentials. The process of reducing an oxidant (such as a sulfate anion) occurs with the participation of enzyme catalysis in the cytoplasm of the microbe cell. Type II is caused by enzymatic microbes, such as acidic bacteria that secrete caustic metabolites. These microbes act on the metal surface extracellularly. Enzymatic metabolism does not require external electron acceptors and is accompanied by the formation of a large amount of organic and mineral acids. The reduction of a proton at a sufficiently acidic pH can be combined with the iron oxidation to form a thermodynamically favorable reduction–oxidation reaction, which does not slow down kinetically. This process is not different from the effect of organic acids (for example, acetic acid) in common chemical corrosion [94]. The mechanisms of biocorrosion of types I and II are considered as electrochemical. Type III biocorrosion can be determined as a microbial attack on an organic substance (such as polyurethane) in order for microbes to use organic carbon [100]. This type of nonelectrochemical corrosion is better known as "biodegradation." Here, microbes can be both aerobic and anaerobic. In addition, there can be other types of biocorrosion, especially in open reservoirs with dissolved oxygen as a possible electron acceptor.

Other Corrosive Bacteria

Fungi play a huge role in the biocorrosion process (mycological corrosion). This type of biocorrosion is a special case of biodegradation of materials [101]. The species diversity of fungi and their high adaptability to living conditions lead to the fact that the volume of materials damaged by them is significantly higher than that of materials damaged by bacteria. It is known that, during the growth process, fungi release large amounts of organic acids (acetic, oxalic, citric, glutaric, etc.), which cause corrosion of various materials. For example, *Serpula lacrymans* fungus leaches calcium, sulfur, silicon, and iron from mineral materials and plaster [102].

Fungi related to *Aspergillus, Penicillium, Chrysosporium merdarium, Talaromyces flavus, Saccharomyces, Paecilomyces parvus*, and *Cladosporium herbarum* genera are distinguished as the most corrosive [103–105]. *Aspergillus niger* is one of the most common types of fungi [106]. Some studies have shown that *A. niger* can contribute to the corrosion of titanium, carbon steel, and magnesium alloy in eutrophic media [106–108]. According to some studies, oxalic acid, citric acid, and some other organic acids produced by *A. niger* can cause metal corrosion [107, 109–112]. However, it is still unclear which of them play a key role in the process of corrosion of aluminum alloys. In addition, the corrosion of aluminum alloys induced by *A. niger* is even stronger than in sodium-chloride solution [113]. In [114], the corrosion behavior of Al and Zn in a humid atmosphere in the presence of *A. niger* was studied. It has been shown that *A. niger* acts either as a corrosion accelerator or as an inhibitor, depending on the metal it colonizes. It was shown in [106] that *A. niger* significantly accelerated the corrosion of AZ31B magnesium alloy at the initial stages and, then, the acceleration weakens. Adsorption of *A. niger* on the magnesium alloy contributed to the development of pitting corrosion.

Other microorganisms can also cause corrosion. For example, algae can produce oxygen in a biofilm as a result of photosynthesis during the daytime and convert it into carbon dioxide at night. They can acceler-

ate the corrosion process, causing changes in metal surfaces under conditions of dissolved oxygen [115]. There are three different types of algae in the cooling water: blue-green (cyanobacteria), green, and diatom. The following species are most the common: *Chlorella*, *Phomidium*, and *Cyclotella* [103, 116, 117].

In [118, 119], the methods by means of which algae can contribute to corrosion were considered. Algae are able to change their habitat by changing the pH—the oxygen concentration in the local area of the electrolyte—producing metabolites that make the electrolyte more aggressively corrosive. The results showed that photosynthetic algae could increase the pH to higher than 10 and, while decomposing, decrease the pH to lower than that of the surrounding seawater.

When immersed in natural seawater, various surface films (including mucus) form on the metal surface. Mucus is a viscous secretion produced by algae that spreads over the surface as they move. The spread of mucus is often inhomogeneous and contributes to corrosion.

Algae-covered surfaces create favorable conditions for bacterial growth [119]. This is an indirect mechanism of the effect of algae on corrosion. SRBs are among the bacteria that can thrive in decomposing algae. As was already noted, SRBs accelerate corrosion in different ways—by producing toxic hydrogen-sulfide gas; by the formation of iron sulfide, which causes pitting corrosion; and by the reduction of sulfates to corrosive sulfide. However, a number of works report that algae can play a useful role in preventing corrosion. In particular, *Hydroclathratus clathratus* algae have been shown to act as inhibitors of acid corrosion of mild steel [120].

In fact, any microorganisms capable of damaging the mineral passivating layers on metal surfaces can cause corrosion. These microorganisms do not need to release an oxidizer on their own if there is already an oxidizer such as CO_2 and oxygen.

Stone Corrosion

In addition to metals, other materials can also undergo biocorrosion. Biofilms on concrete, stone, and marble are visible as a colored mucous layer or a dry crust. Microbial communities can directly cause physical and chemical destruction of historical buildings and art objects [121, 122]. Moreover, mucous biofilms retain moisture, which can cause mechanical stress in the structure of the material during freeze–thaw cycles.

Different groups of microorganisms are involved in the stone corrosion. According to a number of authors, mycelial fungi of the *Penicillium*, *Aspergillus*, *Trichoderma*, and *Cephalosporium* genus predominate on the surface of stone building materials.

In this case, biodeteriorations were mainly reduced to debonding of the constituent components as a result of exposure to mineral or organic acids along with enzymes and due to chemical reactions between cement stone and the metabolic by-products of microorganisms [123].

At the stone–air interface, the presence of light can lead to the growth of phototrophs, such as algae and cyanobacteria [124]. Fungi can penetrate into the stone and produce extracellular enzymes and metabolites that cause chemical and physical damage [125, 126]. Acids produced by bacteria dissolve carbonaceous stone [3].

Corrosion can also occur at the stone–soil interface, including in building foundations and sewer systems. Concrete sewer systems can be seriously damaged by microorganisms, such as *Acidothiobacilli* spp., which produce sulfuric acid that reacts with the calcite binder material of concrete [3, 127].

The corrosion of carbonate stone is chemically simple, but the overall process is complicated by a number of factors related to the porosity of the material—by the presence of microorganisms, moisture content, and the tendency of the stone to "breathe."

In addition, carbonate stone is not chemically homogeneous, and the constantly present transition metals and noncarbonate minerals complicate the representation of corrosion. Despite this, the conceptual picture of corrosion is rather simple. In the presence of a significant amount of atmospheric SO_2 and high humidity (or the presence of water), dissolved SO_2 is oxidized to SO_4^{2-} in solution and, thereafter, calcite transforms into gypsum. The latter, being characterized by significant water solubility, can be easily washed out in a stream. In addition, the stone can undergo splitting as the cementing matrix weakens or as the weakened crystal structure itself undergoes cycles of wetting and drying, thawing and freezing [128].

If the sulfur content in the atmosphere is minimal or completely absent, microorganisms colonize on and inside the stone and generate oxalate ions. The resulting calcium oxalates then form a weak protective surface layer.

Attempts to alleviate the corrosion of carbonate stone are reduced to two approaches: the use of protective agents to repel water and reactive compounds and the impregnation of the stone pores with inert materials [129, 130]. Further studies of protective materials are required to preserve stone structures. For new constructions, carbonate stone must be selected only with full knowledge of its physicochemical properties and corrodibility, as well as the possibilities of using protective agents at the initial stage and throughout the entire service life [128].

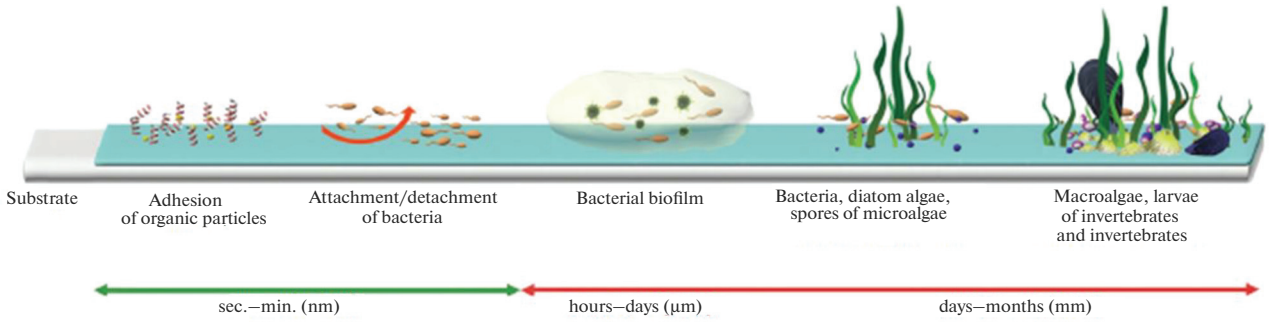


Fig. 5. Scheme of the marine fouling process [131].

Marine Biofouling

Marine biofouling is a serious global problem, the solution of which will have a huge impact for both the marine economy and the marine industry. Long-term studies have led to the general opinion that marine biofouling, along with MBC, is closely related to biofilm and includes the following stages [32]: (1) an initial adsorbed film is formed on the surface immersed in the marine environment; (2) bacteria and other microorganisms adhere to the adsorbed film and gradually transform into a biofilm, releasing extracellular polymeric substances consisting of proteins and polysaccharides used for fixing micro- and macroorganisms; (3) marine organisms, such as diatoms, larval spores, and microalgae, accumulate on the surfaces of materials, since the biofilm can provide them with nutrients; (4) and larvae of marine macroorganisms (such as mollusks) settle and grow on the surfaces of materials (Fig. 5). This general fouling process illustrates the interrelation between microorganisms and macrofouling agents [131]. Macrofouling is the main result in this scheme. Microorganisms, in turn, contribute to biofouling by creating conditions and accumulating nutrients that they provide to attract new organisms**.** The activity of microorganisms can regulate the formation of macrofouls, while their accumulation, in turn, can provide some protection against the destruction of microorganisms and biofilms. However, it should be taken into account that there are more than 4 thousand fouling organisms in the ocean, as well as the fact that different marine environments can lead to different dominant fouling organisms and different biological interactions.

There are differences and similarities between microbiological corrosion and biofouling. The differences are as follows.

• MBC is a corrosion process occurring at the micro level while biofouling is a process of deposition and accumulation of fouling conducting at the macrolevel.

• Organisms related to MBC are represented by different microorganisms, while organisms related to biological fouling include both different microorganisms and macrofouling plants and animals.

• MBC causes direct damage to materials, while biofouling damage is broader and more complex in various areas.

The similarities between MBC and biofouling include the following.

• MBC and biofouling start with the formation of an initially adsorbed film on the surface of the material. This stage is reversible, since the sorbed cells can return to a planktonic form of existence.

• MBC and biological fouling are closely related to biofilms created by marine microorganisms sorbed by the initial film.

• The similar origins of MBC and biological fouling results in similar protective (prevention) strategies. If a method can destroy the formed biofilms and prevent the formation of new biofilms, then it will be able to eliminate or prevent the development of MBC and biofouling at the same time.

Scientific Approaches to Microbiological Corrosion and Biofouling Protection

As was already noted, the presence of a biofilm is the main condition for the emergence of MBC and biofouling. In the case of MBC, biofilms are directly involved in the corrosion process. For marine biofouling, biofilms are the main factor, attracting most types of polluting organisms to deposition and grow on the surface of the material. As a result, to eliminate MBC or marine biofouling, it is required to control the activity of microorganisms in biofilms or prevent the formation of biofilms and adhesion of marine organisms. One of the main ways to protect materials (metals and alloys, concrete, etc.) from biocorrosion and biofouling is the use of protective coatings [132].

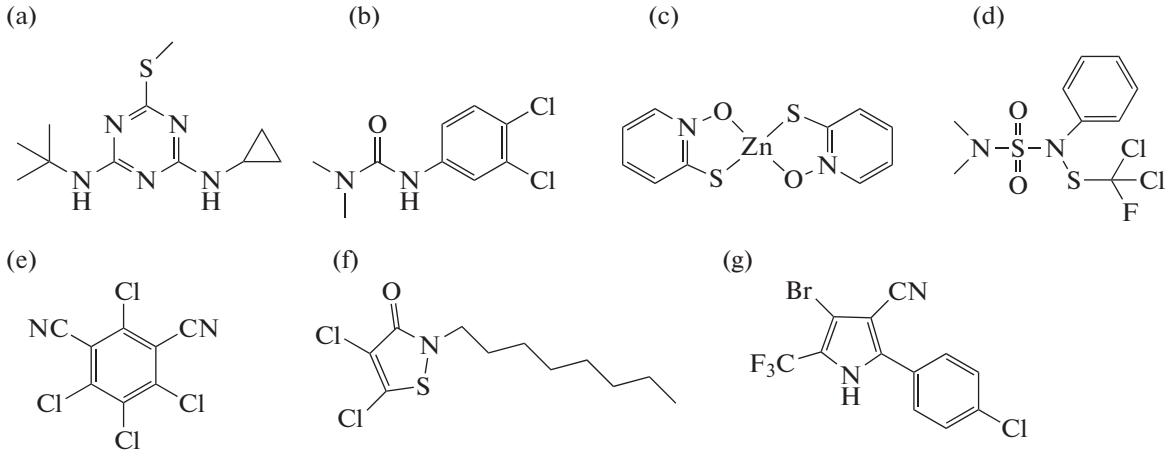


Fig. 6. Structures of biocides for antifouling coatings: (a) Irgarol 1051, (b) Diuron, (c) zinc pyrithione, (d) dichlofluanide, (e) chlorothalonil, (f) Sea-Nine 211, and (g) ECONEA (tralopyryl).

To solve the problem of biofouling, antifouling coatings containing tributyltin (TBT) have been commercialized since the 1960s. These materials were characterized by durability at a low cost of production and were able to effectively prevent fouling of a hull for 5 years. However, tin-containing coatings releasing harmful substances into the environment are characterized by high toxicity to marine organisms [29, 131, 133, 134]. Over time, sufficient amounts of TBT compounds were released into the ocean for irreversible damage to be done to the environment [30, 135]. These adverse effects have led to restrictions on their use in many countries [136–138]. Based on the recommendations of the International Convention, the use of TBT as biocides within the composition of antifouling coatings has been prohibited since September 2008 [29, 139].

This led to the gradual dominance of self-polishing coatings without the addition of biocides. In addition, polymer resins based on acrylic copolymers were used, in which TBT was replaced with copper (I) oxide as a biocide [140, 141]. Although Cu_2O is less toxic than tin compounds, it can negatively affect the marine environment. The massive accumulation of copper ions in the marine environment is related to the use of copper-containing antifouling coatings on ships [142, 143]. In addition, the cost of raw materials for antifouling coatings constantly increases worldwide [144]. Therefore, the development of highly effective and environmentally friendly antifouling coatings is required.

After the prohibition of tributyltin in antifouling paints, many alternative biocides were introduced to prevent the colonization and growth of marine organisms on ship hulls. Currently, the following compounds are known as biocides for antifouling coatings: Irgarol 1051 (*N*-2 methylthio-4-tert-butylamino-6-cyclopropylamino-*s*-triazine), Diuron (1-(3,4-dichlorophenyl)-3,3-dimethyloxetane), zinc pyrithione, dichlofluanid (*N*,*N*-dimethyl-*N*'-phenyl-*N*'-fluorodimethylthiosulfamide), chlorothalonil, Sea-Nine 211 (4,5 dichloro-2-*n*-octyl-4-isothiazolin-3-one), and ECONEA (tralopyril) (Fig. 6).

Irgarol 1051 and Diuron, which act as photosynthesis inhibitors, were among the first biocides to replace tin-containing compounds. Irgarol 1051 (S-triazine biocide) is a highly specific and effective inhibitor of photosynthesis of algae with very low water solubility, which provides good antifouling properties for coatings. However, currently, their use in the compositions of antifouling coatings in a number of countries is very limited. It is believed that Irgarol 1051 is difficult to decompose in a natural marine environment, with a half-life period from 100 to 350 days [145–148]. Diuron is less stable in seawater, with a half-life period of 14 days. However, when used as a component in coating compositions, the half-life period increases significantly [149]. For the first time, environmental pollution with Irgarol 1051 was reported in 1993 when a biocide (conc. 1700 ng/L) was found in the waters (Cote d'Azur) of France [145, 150]. Since 1993, a content of Irgarol 1051 in waters has been repeatedly reported. Diuron is extremely dangerous for the aquatic ecosystem, highly toxic to algae (in particular, green algae *Scenedesmus vacuolatus*), and moderately toxic to aquatic plants such as duckweed [151]. One of the metabolites of Diuron, which is formed when it is eroded in an aqueous medium, is the toxic 3, 4-dichloraniline, which is characterized with genotoxic properties. According to certain data, 3, 4-dichloraniline is able to accumulate in living organisms. Another metabolite of Diuron is 3, 4-dichlorophenol. This substance is characterized with reproductive toxicity, irritates the mucous membranes, and affects the kidneys, liver, and immune system.

Some European countries have restricted or completely prohibited the use of these biocides due to their adverse environmental effects. The use of Diuron has been prohibited as an active component in antifouling coatings in the Netherlands [152], Sweden [153], and—along with Irgarol 1051—in the United Kingdom [154, 155] and Finland [156]. Moreover, in Sweden, Irgarol is allowed only for vessels of a length of >25 m [157], but is gradually being obsoleted [156]. The use of Irgarol 1051, Diuron and dichlofluanide is also restricted in Denmark [153, 156, 158, 159].

Zinc pyrithione (ZnPT) is one of the most popular biocides used in antifouling coatings. This biocide is a zinc complex with two pyrithione ligands, in which Zn^{2+} ions are bound to oxygen and sulfur atoms. ZnPT is widely used as an algicide, bactericide, and fungicide [140, 160–162]. Its action is based on the destruction of the membrane's transport capacity by blocking the proton pump, which supplies energy to the transport mechanism. ZnPT can be introduced into an antifouling coating as an independent biocide, but it is introduced more often as a mixture with other biocides, for example, with zinc dithiocarbamate, Sea Nine 211, or copper thiocyanate of a concentration of up to 7% [163]. ZnPT decomposes rapidly in an aqueous medium, mainly by photolysis. However, when ultraviolet light cannot penetrate due to water turbidity or great depth, ZnPT can accumulate in an undissolved form, having a continuous toxic effect on the marine environment. At the moment, there is insufficient information on the biodegradation and hydrolysis of ZnPT in a marine environment. In addition, due to its toxic effects on a wide range of marine organisms, it is recommended to control the use of ZnPT and test thoroughly the level of ZnPT in the environment [160].

Dichlofluanide is a halogenated sulfonamide derivative from the group of aryl dichlorofluoromethylthio-containing fungicides. This fungicide acts as an inhibitor of thiol-containing enzymes by means of formation of disulfide bridges [164]. Dichlofluanide is rapidly hydrolyzed in water with the formation of *N*'-dimethyl-*N*-phenylsulfamide [165] with a half-life period in seawater of less than 20 h [145, 148, 166]. The biocide is moderately toxic to invertebrates. Dichlofluanide is less toxic than are other antifouling agents, although some studies have revealed some of its toxic effects [167–169], such as embryotoxicity in sea urchin *Glyptocidaris crenularis* [170, 171]. Unfortunately, there are no data on its toxicity to other aquatic species.

Chlorothalonil is attributed to the fungicides of the chloronitrile class. The toxicity of this pesticide to aquatic invertebrates is not completely clear. Certain studies show that chlorothalonil is most toxic in the early stages of development for three species of marine invertebrates: *Paracentrotus lividus*, *Ciona intestinalis*, and *Mytilus edulis*, causing embryotoxicity, larval inhibition, and mortality [172]. Chlortalonil is also toxic to fish; LD_{50} after 96-h exposure varies in the range from 8.2 to 110 μg/L, depending on the type and conditions of exposure. It can accumulate in fish tissues [151].

For the first time, the Sea-Nine 211 biocide (DCOIT) was introduced as an antifouling compound in 1996 [173]. At present, Sea-Nine 211 is one of the commercial antifouling agents widely used worldwide. The manufacturers of the Sea-Nine 211 biocide declare its environmental safety mainly because of its declared rapid destruction in the marine environment. However, a number of studies show that the kinetics of decomposition of DCOIT depend on seawater as well as on factors such as temperature, sunlight and pH. This means that the DCOIT released from the coating will not be deactivated as rapidly as stated by the manufacturer [174].

Studies of the toxicity of this biocide have shown that algae, crustaceans, and fish are very sensitive to this biocide, their survival rate begins to decrease even at low concentrations (from 2 to 4 μg/L) [151]. Sea-Nine 211 is toxic to a wide range of aquatic organisms. For example, the accumulation of Sea-Nine 211 was detected in the waters of Spain at a level of 3700 ng/L. Due to the different decomposition rates and high toxicity, the use of DCOIT as an antifouling agent can cause irreversible damage to the marine ecosystem. Ships the protective coatings of which contain Sea-Nine 211 and dichlofluanide are prohibited from entering the waters of some European countries [153].

Tralopyryl (ECONEA) was relatively recently registered as a biocide for antifouling coatings (2014, [175]), becoming a potential new environmental pollutant. Tralopyryl is recommended as an antifouling agent for the control of biofouling by shells, hydroids, mussels, oysters, and polychaetes and has been commercialized under the trade name ECONEA® (Janssen PMP, Belgium). According to the literature data, tralopyryl undergoes degradation very quickly in a marine environment. Its half-life period is 3 h at 25°C and 15 h at 10°C, respectively [176, 177]. Due to its recent introduction, there is very little information about its toxicity in the literature. Tralopyryl is known to be toxic to sea urchins, as well as to *C. japonicus*, *P. depressus*, and *H. pulcherrimus*. In [178], it was shown that tralopyryl was highly toxic and leads to abnormal development of veliger larvae with LD_{50} 3.1 μg/L. Oliveira et al. [179] reported that tralopyryl significantly inhibited the amount of ATP and the growth of *C. reinhardtii*. In addition, tralopyryl is also highly toxic for zebra danio embryos, with an LD_{50} value of 5 μg/L, and changes the protein content involved in energy metabolism, cytoskeleton, cell differentiation, cell division, and mRNA splicing [179, 180].

In view of the above, there is a current trend toward the development and creation of nontoxic or low-toxicity bioresistant coatings based on a polymer matrix and different kinds of nontoxic additives that prevent

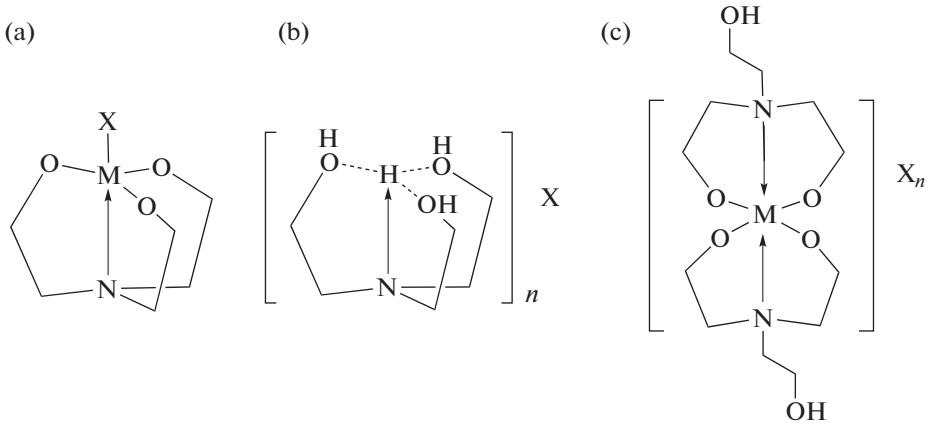


Fig. 7. The main representatives of the atrane class: (a) metallatranes (M = Si, Ge, etc., X-OAlk, Alk, Hal, etc.), (b) protatranes (X-protic acid anion), and (c) hydrometallatranes (M = Co, Cu, Ni, etc., X is the protic-acid anion).

the process of biocorrosion and biofouling. In recent years, due to the development of nanotechnology, new opportunities have emerged for the invention of materials with unique soft biocidal properties. Their advantage consists in environmental friendliness, prolonged action, and the ability to inhibit the development of aggressive microbial communities without changing the properties of the material itself or improving them. As soft biocidal additives that do not have a destructive effect on the environment, polymer compounds are used—for example, those based on guanidine, chloromethyl derivatives of aromatic hydrocarbons with pyridine, etc., phthalocyanines, porphyrins, and chlorophyll analogues, which are photosensors that, under effect of sunlight, produce reactive oxygen species that inhibit the development of bacteria and fungi [181–183]. Titanium dioxide in the form of anatase also has a photosensitizing effect, and its aqueous suspensions are currently being actively tested for protection of stone [184–186].

As soft biocides, it is promising to use intracomplex compounds of hydroxyalkylamines—atranes. Atranes are characterized by a unique tricyclic structure containing a donor–acceptor transannular bond N → E (Fig. 7). Extensive studies in the field of atranes began for the first time in Russia under the supervision of Acad. M.G. Voronkov. Pharmacological and biochemical studies of atranes based on silatranes, germatranes, protatranes, and hydrometallatranes have shown that they are low-toxic substances and have a wide range of useful biological effects (immunomodulatory, adaptogenic, antitumor, anti-inflammatory, etc.) [187–191]. In [192], the possibility of using compounds of the atrane class as soft biocides in the compositions of protective coatings based on silicon rubber and polymethylphenylsiloxane was shown for the first time. Coatings based on polymethylphenylsiloxane showed high biostability, both with and without a biocidal additive. The development of microorganisms on their surface was limited only by inoculate droplets and local zones along the edge of the plates. However, a coating with a biocidal additive based on the triethanolammonium salt of salicylic acid (3 wt %) demonstrated the highest biostability.

In [193], the process of biofouling of paint coatings of six different compositions based on a vinyl chloride copolymer with vinyl acetate with the additive of epoxy-diane resin under the natural conditions of the White Sea was studied. Compounds of the atrane series—protatranes and hydrometallatranes with a total content of 2 wt %—were used as soft biocides. However, the biofouling process was recorded on all the studied plates. The basis of fouling was associated with the attached forms, with the most widespread of them being scyphistomas (the polypoid stage) of *Aurelia aurita* and *Cyanea* sp. jellyfishes, *Mytilus edulis* mussel, and hydroid *Obelia longissima*. The authors attributed the development of biofouling on the surface of coatings to an insufficient (low) concentration of biocides and their leaching from coatings.

The most popular trend at present is the combination of both biocidal and antifouling agents with new polymer matrices, chemicals, and innovative technologies, which, due to a synergistic effect, results in a decrease in the content of biocides and the achievement of a better bactericidal effect. Bactericidal synergist is one of the most common chemical agents used: it can destroy biofilms transforming "sitting" bacteria into planktonic ones and, thus, enhancing the bactericidal effect of a traditional biocide [194, 195].

In the case of marine biofouling, the antifouling agent is mainly used to control the activity of microorganisms in biofilms or to prevent their adhesion and formation of biofilms. Generally, antifouling is introduced into polymer binders used in so-termed "antiadhesive coatings." The most popular binders currently used in the marine industry are self-polishing copolymers (mainly acrylic polymers), to the molecules of which antifouling molecules are attached

[196]. In self-polishing copolymers, the side groups (such as silyl ones) can undergo hydrolysis with the formation of a hydrophilic surface, which is then polished by a stream of water, thus washing out the "adherent" foul. Here, antifouling reagents are released and allow controlling the activity of microorganisms in biofilms [197, 198]. However, surface renewal does not proceed rapidly enough in the absence of a strong water stream, so that most self-polishing coatings have poor resistance to marine biofouling under static conditions. Moreover, slow erosion of the surface and constant water absorption can cause coatings swelling negatively affecting the mechanical and antifouling characteristics.

In [199–203], diblock copolymers of tret-butyldimethylsilylmethacrylate and methyl methacrylate with a controlled microstructure were developed for antifouling coatings, which demonstrate a more controlled erosion rate and antifouling efficiency than coatings based on traditional copolymers [200].

In [204], approaches to the formation of coatings, to the surface or matrix of which an antimicrobial agent (biocide) was "bound," were considered. One of the main methods for obtaining an antimicrobial surface involves a two-step approach. At the first stage, the surface is treated to obtain functional groups amenable to chemical addition. At the second stage, the biocide interacts with the functional groups of the surface, which results in its covalent binding. In the case of polymers with functional groups, additional modification of the surface is not required. In some cases, surface functionality is created in the presence of a biocide, and the reaction proceeds immediately. The main methods of surface modification include the plasma-treatment, plasma-deposition, irradiation, and chemical methods.

The aforementioned methods either transform existing groups of surfaces into reactive centers or introduce new functional groups to the surface. The nature of the functional groups depends on the substrate used. Oxygen-containing centers are usually formed for metals and polymers based on hydrocarbons (such as polyolefins), while nitrogen-containing groups are formed for polyamides and other nitrogen-containing polymers. Plasma (i.e., glow discharge) surface treatment leads to the emergence of free radicals, hydroxyl, amino, and peroxide functional groups. Plasma surface treatment results in a reaction on the outermost molecular layers of the surface. By means of argon plasma, the surfaces of silicone rubber [205, 206], polyethylene terephthalate [207], cellulose [207], and materials were modified for antimicrobial binding. In addition, polyethylene was functionalized by the same means using helium-plasma treatment [208]. Argon and helium plasma generates free radicals on the surface. These reactive particles can interact directly with the corresponding materials or transform into hydroxyl and peroxide groups when exposed to air or oxygen. A related form of plasma surface treatment is plasma deposition. This method introduces functional groups by exposing the surface to ionized vapors of the deposited material. Plasma deposition of propanal monomer was used to create a thin polymer coating with aldehyde surface groups on the surface of a contact lens made of hydroxyethylmethacrylate [209].

Another method of surface modification consists in the use of radiation or an electron beam. Ionizing radiation is usually used to create free radicals on the surface, which react in the presence of the corresponding functional groups. Hu et al. [210] modified the polyester surface using ^{60}Co as a γ radiation source for further addition of biocides.

Although plasma and beam treatments are excellent methods, they often require sophisticated instrumentation or special technological capabilities to create the corresponding surfaces. Traditional chemical methods can be also used to modify the surface with functional groups for subsequent binding of antimicrobial agents. An approach based on the oxidation of surface groups by means of hydrogen peroxide, a mixture of sulfuric acid with hydrogen peroxide and other reagents is often used. In addition to oxidation, an approach based on the hydrolysis of bonds inside these materials using acid or alkaline reagents is often used [204].

Surface treatment by flame and crown discharge are also used to create functional groups. Both methods work by the chemical oxidation mechanism. Flame treatment uses an open flame to oxidize surface groups while crown discharge treatment (also known as air plasma) uses high voltage to ionize air in the gap between the electrode and the surface to be treated. These methods are cost-effective and very common for increasing the wettability, adhesion and surface energy of polymer materials, especially of polyolefins. However, they are nonspecific in relation to the types of polar groups obtained [204].

Cationic biocides based on quaternary ammonium salts bound to the surface of alkoxysilane and successfully released on the commercial market by Dow Corning were used among the first antimicrobial agents. The biocide shown in Fig. 8a had a broad antimicrobial effect, which did not decrease after repeated successive rinses, which indicated its "binding" to the coating surface. Then, a broad range of compounds with a similar structure were tested for antimicrobial activity.

It has been suggested that the antimicrobial mechanism of effect of cationic biocides occurs through the destruction of the cell membrane [211, 212]. It was assumed that the adsorption of negatively charged cells took place on cationic surfaces, which facilitates the antimicrobial activity of the latter.

Epoxides comprise one of the common classes of compounds used in the paint and varnish industry

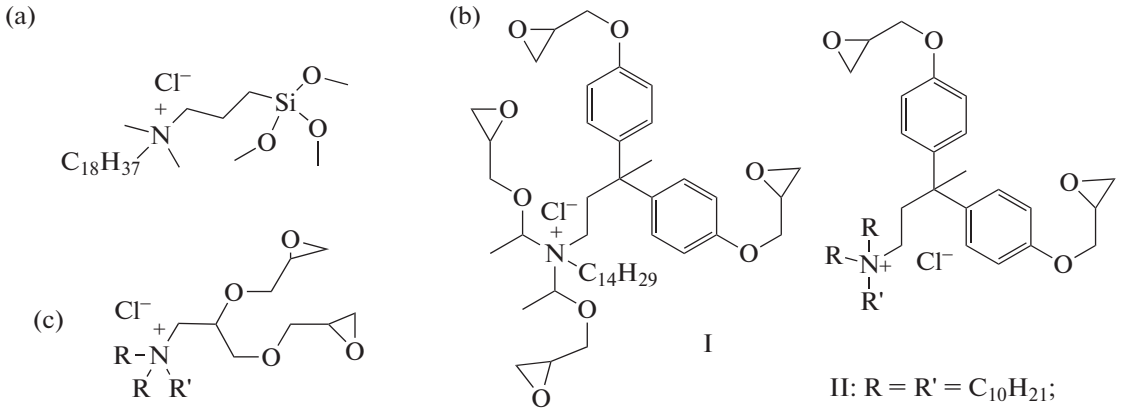


Fig. 8. The structure of some cationic biocides [204].

[204]. In [213], the antifungal character of epoxy resins based on bisphenol A with bound carbendazim and thermally cured isophorone diamine was studied. In [214], quaternary ammonium salts (Figs. 8b, 8c) bound to an epoxy matrix were used as biocides.

Silva et al. [215] demonstrated the efficiency of an antifouling composition based on a polyurethane and silicone matrix, to the surface of which biocides (Irgarol 1051 and ECONEA) were covalently attached using an isocyanate linker. Coatings based on polydimethylsiloxane demonstrated the best antifouling properties with both one biocide (ECONEA) and two biocides with their total content of no more than 0.6 wt %. The test samples remained practically pure after exposure for more than 1 year in the Atlantic Ocean (coast of Portugal).

Many antimicrobial compounds have an effect on microorganisms by specific biochemical ways that require chemical penetration into the cell. A significant problem at the binding of noncationic biocides to surfaces is the maintenance of activity in the bound state. Binding of the biocide probably changes the mechanism of its antimicrobial effect. In addition, a constant problem for all attached biocides is the decrease in activity observed at the proceeding microbial contamination or fouling. A layer of dead cells or protein rapidly deactivates contact activity.

In the literature, an approach is known for encapsulating biocides or corrosion inhibitors in different inert nanomaterials (nanocontainers), which are subsequently dispersed into a polymer matrix. Encapsulation of biocides in a nanovoid is an interesting and innovative strategy for controlling the release of biocides and decreasing their concentration. This approach allows the biocide to be retained in the matrix, preventing its leaching and simultaneously providing an environmentally safe and moderate release. Generally, nanomaterials with a large pore volume and a large surface area are used to encapsulate compounds using either the method of physical adsorption or physicochemical interaction after the surface functionalization stage [216, 217]. During physical adsorption, nanoparticles for example, SiO_2 are used as frameworks, on which a biologically active compound is adsorbed. This method is relatively simple and enables one to load nanoparticles with different types of biocides depending on the solvent. However, it has a significant disadvantage—rapid leaching of biocides from the surface [218, 219]. When using the second approach based on physicochemical interaction, the nanoparticle surface is functionalized to bind to the biocide. This approach enables one to increase the leaching time. However, it is more complex, time-consuming, and specific for each class of biocides. In [220], the approach of encapsulation/incorporation of environmentally safe biocides into inert nanosystems (nanocontainers) based on silicon dioxide was considered. In [221, 222], this approach was tested on the example of a commercial corrosion inhibitor—2-mercaptobenzothiazole encapsulated in nanocapsules of mesoporous silicon dioxide.

Due to the global problem of biocide toxicity, recent studies were focused on environmentally safe technologies, such as the use of hydrophilic and hydrophobic antifouling coatings [223].

Hydrophilic antifouling coatings do not allow or significantly delay the attachment of marine biofouls to the hulls of marine vessels due to their supersmooth surface. To make the surface hydrophilic, chitosan was used in [224–226] to treat nanoparticles, for example, such as copper (I) and zinc oxides. Coatings with introduced chitosan-modified nanoparticles exhibited excellent antifouling efficiency for 30 days without environmental damage. In [227], the antifouling effect of the polyurethane coating was improved by introducing zinc-oxide nanoparticles modified with polyaniline into their composition by increasing hydrophilicity and wetting, which led to a significant decrease of biofilm on the surface compared to unmodified polyurethane coating. Polyethylene glycol (PEG) is often used to increase the hydrophilicity of coatings. The surface of PEG is characterized by resistance to protein adsorption and antiadhesion properties to marine fouling organisms [228]. PEG is a neutral hydrophilic polymer consisting of repeating oxyethylene groups ($-CH_2CH_2O-$). Due to its unique structure, PEG can participate in the formation of hydrogen bonds with water, which provides a high degree of hydrophilicity and good solubility in water. PEG is commonly used as a hydrophilic segment of amphiphilic polymers. In [229], PEG-modified SiO_2 nanoparticles were obtained which were introduced into acrylic–polyurethane coatings, which enables to reduce the contact angle of wetting to 38.7°.

Recently, the use of hydrogels in antifouling coatings has attracted increasing attention on the part of researchers. A hydrogel has a form of a network of cross-linked polymer chains that are hydrophilic. The three-dimensional solid state is the result of hydrophilic polymer chains held together by cross-linking bonds.

As a rule, hydrophobic coatings contain fluorine-containing and silicon compounds characterized by a high wetting angle and low surface energy. The deposited micro- and macrofouls are loosely attached to the surface of these coatings and are removed mechanically at the movement of the vessel [230]. Hydrophobic coatings serve as an environmentally safe alternative to traditional antifouling coatings with a long service life. Hydrophobic and superhydrophobic materials have a number of unique properties: water resistance; corrosion resistance; and resistance to biofouling, to inorganic, and, in some cases, to organic pollutants. Near the hydrophobic surface of such materials, the sliding of the liquid flow is facilitated [231]. To obtain materials with high contact angles, the combined effect of surface roughness and chemical structure should be used. At present, the following methods are actively used to make the surface hydrophobic: polymerization of the coating from a solution with the formation of a spongy phase; plasma etching of the polymer surface, chemical-vapor deposition of ordered structures with subsequent treatment with hydrophobic materials, electrodeposition and electrochemical deposition of nanoparticles and films with subsequent treatment by hydrophobic materials, the use of template methods to create roughness with subsequent removal of the template and treatment with hydrophobic materials, etc.

However, the main disadvantage of hydrophobic and superhydrophobic coatings consists in the aging and degradation processes which result in a hydrophobicity decrease. One of the reasons for the decrease of coating hydrophobicity in operation in open air is related to atmospheric pollution. Generally, as a result of deposition of dust and chemical substances of organic nature on the surface, its hydrophilicity is significantly enhanced [231]. It was shown [232] that, under the effect of the sea wave and impurities suspended in it, the roughness of the superhydrophobic coating was damaged and the contact angle decreased from 151° to 70° after 35 days of the experiment.

Temperature-switched wetting observed in a number of systems having a lower critical dissolution temperature can be used to control biofouling of surfaces [231]. The most studied polymer with this property is poly(*N*-isopropylacetamide). The wetting transition is related to a change in the conformation of polymer molecules grafted to the surface. It was shown [233] that this conformational transition with increasing temperature causes a change in the contact angle of the surface from 63° to 93°. By applying a texture in the form of micrometer-sized grooves, one can achieve a transition from superhydrophobicity to superhydrophilicity with a very small hysteresis of contact angle. The system can withstand multiple switching of wetting modes without coating degradation.

The development of coatings with a dynamic surface is another approach to obtaining the antifouling coatings. A dynamic surface related to a changing surface that is constantly regenerated in seawater and, consequently, decreases the adhesion of biofouls [234, 235]. Coatings with a dynamic surface based on a polyester–polyurethane matrix modified with biodegradable polymers such as polyester and polyester–acrylate are known [223]. Such biodegradable polymers were used as linkers that controlled the release rate of environmentally safe antifouling agents and demonstrated excellent antifouling effect with controlled renewability [236, 237].

The mechanism of release of antifouling substances includes two stages: biodegradation and erosion (destruction from the surface). Under the effect of environmental factors (heat, light, and chemical substances), the polymer undergoes degradation with changes in properties, such as tensile strength, color, shape, etc. [238, 239]. The physical erosion processes can be represented as heterogeneous or homogeneous. At heterogeneous erosion (or surface erosion), the polymer is corroded only on the surface and, at the

same time, retains its physical integrity during destruction. Most polymers undergo homogeneous erosion—this means that hydrolysis occurs uniformly throughout the polymer matrix [240, 241].

The authors of [242] revealed that polyurethane based on a copolymer of caprolactone and glycolide demonstrates high decomposition rates, which increase along with the increasing glycolide content. Testing in seawater for 3 months for polyurethane with 10 mol % glycolide showed the best antifouling properties without any antifouling agent. This indicates that the decomposable polymer itself is effective in antifouling.

It was also mentioned in [196] that the decomposable polymer is more effective for antifouling coatings than the traditional self-polishing copolymer. Its constant surface renewal rate in seawater releases antifouling more stably, which can extend the service life of coatings and reduce environmental pollution. It can be concluded that the combination of an effective antifouling agent with a decomposable polymer binder with a dynamic surface can become a potential method of preventing marine biofouling.

The destruction of the polymer creates a changing dynamic surface that prevents permanent bacterial adhesion due to a decrease of the adhesive strength. The process of biodegradation of the polymer occurs throughout the immersion in seawater since hydrolytic and enzymatic degradation always occurs [236]. At the same time, biodegradable polymers can undergo enzymatic and hydrolytic splitting of the main polymer chain resulting in the formation of oligomers or small molecules, which, after a certain period of time, transform into carbon dioxide and water. One should mention that the biodegradable sections of polymers comprise very small particles and, therefore, do not have a negative impact on the environment [223].

To sum up, both MBC and biofouling in the marine environment are a consequence of the adhesion and growth of marine microorganisms on the surface of materials and the formation of biofilms plays an important role in the occurrence and proceeding of these processes. Studies have shown that biofilm is difficult to remove from the surface of the material. In order to eliminate "sitting" bacteria growing in biofilms, it is necessary to use high concentrations of biocides, which are significantly higher than for bacteria in the planktonic state [243, 244].

The External Electric Field in Biocorrosion Protection

In [245], it was suggested for the first time that extracellular polymeric substances (EPS) consisting of proteins and polysaccharides and being metabolites of microorganisms that protect bacteria from antibacterial drugs participate in the binding of biocides before they reach target cells. This is caused by the fact that the exopolysaccharide contained in an EPS is charged and has ion-exchange properties. Based on this hypothesis, the authors of [246] suggested that the destruction of charges on an EPS could significantly facilitate the penetration of biocides into target cells. It was also revealed that some industrial biocides may have an enhanced effect against *P. aeruginosa* biofilms in a weak electric field with a low current density. However, the nature of the mechanisms remains unclear to the end, but it can be the result of electroporation, electrophoresis, iontophoresis, etc. The authors of [247] also studied the combined effect of an electric field and a biocide on the destruction of biofilms of SRBs. The results showed that the additional electric field does not virtually affect the formation of biofilms, but, at the same time, damages the structure of the formed biofilms and contributes to both mass transfer of biocides into biofilms and desorption of calcium and magnesium ions from biofilms. These regularities lead to the emergence of an effective synergistic effect of an external electric field with biocides. Taking into account the positive effect of an external electric field on the destruction of biofilms, some electroactive materials that could themselves create a microelectric field (for example, piezoelectric materials) can be considered as potential materials for preventing MBC and biological fouling.

Conductive Polymers

Due to the electrical activity of biofilms on the surfaces of materials in the marine environment, conductive polymers are considered as potential materials for preventing marine corrosion and biofouling. Studies of the anticorrosive properties of conductive polymers began with works [248, 249], where it was first discovered that an electrodeposited polyaniline film on stainless steel could significantly decrease the rate of corrosion of steel in a sulfuric-acid solution. The corrosion resistance of various conductive polymers (such as polyaniline, polypyrrol, polythiophene, and their derivatives) was studied in [250–255]. Most of these studies have focused on traditional mechanisms of corrosion protection of metals, such as the formation of a passivating layer on the metal surface, an increase in the corrosion potential of the metal, and a decrease in the corrosion rate. Recently, more and more researchers have begun to pay attention to the possibility of using conductive polymers to prevent MBC and biofouling. In this context, additional research was conducted and the following concepts were put forward.

(a) Adjustment of the pH values of the conductive polymer coating to stabilize it in the acidic range in order to prevent the adhesion and growth of microorganisms and marine organisms adapted to alkaline seawater on the surface of the material [256].

(b) Conductive polymers can be used as an anode, while parts of metals that are exposed to seawater can

be used as a cathode. When a weak current is applied between these two electrodes, surface seawater is electrolyzed to sodium hypochlorite and, then, forms an ionic membrane that can damage the cellular tissues of fouling organisms. It should be noted that the concentration of sodium hypochlorite in seawater is rather low so its formation does not significantly affect the environment [256, 257].

(c) Conductive polymers with a conductivity above 10^9 S/cm can be used as the main coating matrix without using current [258]. In [259], this possibility was demonstrated on the example of polyaniline. Polyaniline has been shown to have good antifouling properties in the marine environment without the use of additional electric current. The antifouling effect of polyaniline is enhanced by the use of biocides such as copper(I) oxide or dichlorodiphenyltrichloroethane (synergistic effect). Recent studies [260] have shown that the conductive polymer polypyrrol is able to change the hydrophobicity of its surface under the effect of an electric current. This indicates that polypyrrol can create an electrically controlled amphiphilic surface to prevent adhesion of marine microorganisms.

The presented studies have demonstrated that conductive polymers are promising polymer matrices for the development of anticorrosive and antifouling coatings.

CONCLUSIONS

Microbiological corrosion and biofouling of materials are the two main causes of marine corrosion, causing damage to and failure of equipment and structures serviced in the marine environment. Strategies for preventing MBC and biofouling are mainly focused on controlling the activity of microorganisms in biofilms, their adhesion, and the formation of biofilms. New materials and technologies, in combination with traditional biocides or antifouling agents, due to their synergistic action, can decrease their content and, at the same time, achieve a better bactericidal effect. At the same time, there is no clear understanding of the toxicological background for currently used antifouling substances, which requires conduction of additional studies of their adverse effects and mechanisms of effect on marine organisms, especially after prolonged exposure. In addition, since antifouling agents and biocides are conventionally used simultaneously, their combined effect remains unstudied and poses a potential risk to the health of the marine ecosystem. Another uncertainty of particular concern is that most environmental agencies have not included antifouling agents and biocides in a regular monitoring program to study their presence in the marine environment. If we had a complete understanding of the destruction, contamination, and toxicity of these compounds, it would be possible to control and regulate accurately their use. This, in turn, would lead to the advancement of the antifouling industry forward and, ultimately, would make it possible to reveal optimal antifouling substances that are both effective and environmentally safe.

To develop a highly effective antifouling system, the selection of a biocidal nanocomposite has a significant effect on the hydrophobicity/hydrophilicity of the coating. Compared to traditional biocides, the nanocomposite biocide is released in smaller quantities and demonstrates excellent antifouling characteristics. In addition, the approach based on the use of a biodegradable polymer in combination with an environmentally safe antifouling agent demonstrates long-term protection against biofouling, as well as making it possible to control the release of the antifouling substance due to the constant renewability of the surface.

The trend in the development of methods to control MBC and biofouling is to search for methods and materials that have high efficiency, long service life, a simple implementation process, and a low cost and are safe for the environment. The scientific approaches presented in the review have demonstrated the prospects for controlling biocorrosion and biofouling. Hopefully, that synergistic effect of chemicals, materials, and innovative technologies will constitute a very important in the field of marine corrosion and fouling protection in the future.

A promising area of advanced materials science consists in the development of multifunctional coatings with a dynamic surface along with environmentally safe biocides with a controlled release rate in order to provide effective protection of marine equipment from the main problem of modern materials science—biological fouling.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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