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CHEMICAL VERSUS NATURAL BIOCIDE COMPOUNDS - MINIREVIEW ON ANTIFOULING COATINGS

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ABSTRACT

Marine biofouling is an old problem, known and studied for centuries, since the beginning of navigation. The accumulation of marine biofouling begins on the submerged portion of an ocean-going vessel or on any installation (equipments, pipes, platforms, etc.) within minutes of contact with seawater. Over time, this accumulation increases the ship's resistance, leading to increases in the physical resistance of the ship in the water, with negative consequences on fuel consumption and greenhouse gas emissions, high maintenance costs (due to corrosion), and a negative impact on the marine environment (due to the release of toxic bioactive compounds into the environment and the transfer of invasive species). These environmental issues were identified and recognized by the IMO, which in the early 1990s, through the Marine Environment Protection Committee (MEPC), adopted a resolution recommending that member governments adopt measures to eliminate TBT-based antifouling paints. These recommendations have led to the identification, development, and application of new antifouling technologies that could provide the maritime industry with a significant potential opportunity with an innovative, cost-effective, and efficient approach to the effects of marine biofouling. Our study aimed to make a small incursion in time, through the specialized literature on methods used to combat marine fouling, to highlight new research approaches to the identification and use of natural biocides to replace chemical ones. The targeting of research directions towards the identification of the most environmentally friendly antifouling compounds, in particular natural marine compounds, has been a focus of international researchers in recent years. To achieve this goal, going back to nature is currently the best option, as it could provide us with very effective models for research and development of antifouling coatings. In the development and modeling of new antifouling paints, the influence of the physical-chemical parameters of seawater (pH, salinity, temperature) on the chemical components (active groups) of the biocides used should not be ignored. The aim of this study is to highlight the importance of developing new antifouling paint technologies using biodegradable, non-toxic, and environmentally friendly compounds according to international legislation. In recent years there has been an increasing emphasis in research studies on the combination of natural biocides (obtained through the valorization of marine wastes) with natural or synthetic hydrogels whose action is to minimize the attachment of marine fouling.

Keywords: antifouling, environmentally friendly, bioactive compounds, natural biocides

AIMS AND BACKGROUND

Biofouling is a natural marine process consisting of the growth of micro and macro aquatic organisms on submerged surfaces like ship hulls, floating platforms, or all offshore marine equipment (Bighiu *et al*., 2017). The evolution and development of fouling on surfaces immersed in water involves 3 stages. The first one consists of the adsorption of inorganic compounds and organic macromolecules, such as polysaccharides and proteins from the marine environment, known as molecular fouling. The second stage, called microfouling, is determined by primary and secondary colonization. The primary colonizers represented by bacteria and diatoms are adsorbed by the conditioning layer through physical bonds. At the same time, these colonizers can adhere to the adhesion film by creating certain types of extracellular polysaccharides. The secondary colonizers of the microfouling are represented by spores of macroalgae and protozoa, which make up the microfilm, whose mass develops non-linearly Liu *et al*., 2023; Selim *et al*., 2017). The third stage of biofouling, macrofouling, is determined by the attachment of macro-organisms (aquatic plants and animals) to the microfilm and can be soft or hard fouling (Selim *et al*., 2017), (Fig. 1).

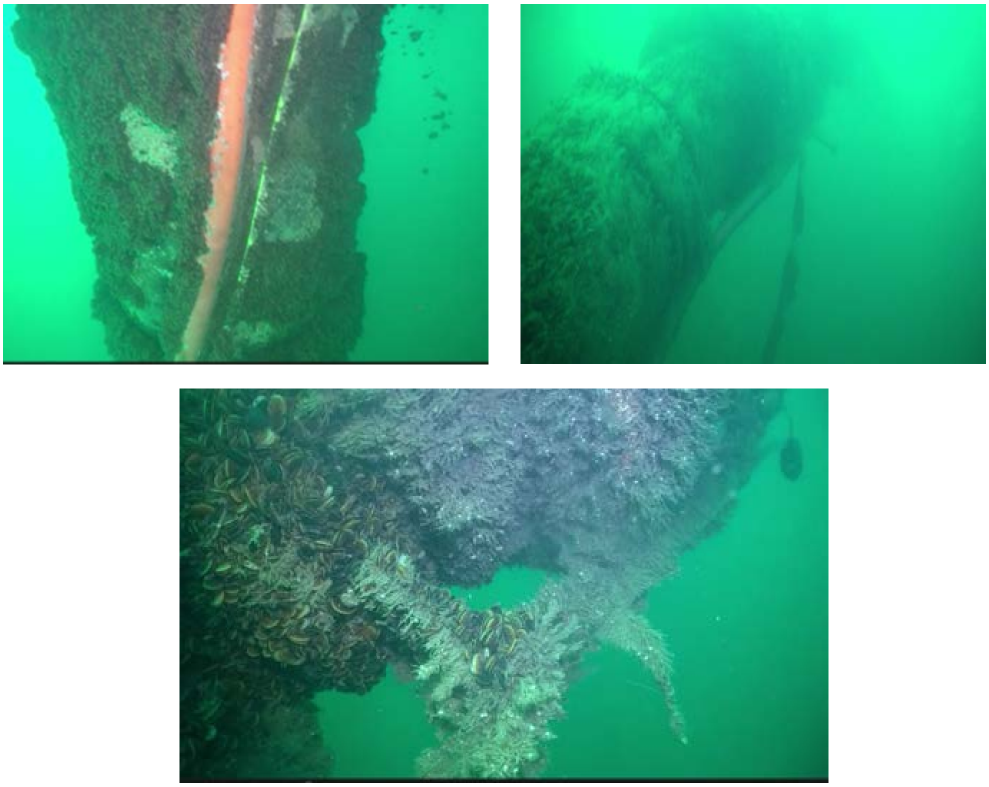

Fig. 1. Different development stages of biofouling from living work from single point mooring (SPM) Midia Năvodari (25 m depth) (original photos)

EXPERIMENTAL

A lot of studies showed serious economic and environmental loss impacts are caused by biofouling development on the ship hulls (Selim *et al*., 2017; Gu *et al*., 2020; Jin *et al*., 2022). From an economic point of view, this increased biofouling on ship hulls leads to corrosion, damaged propellers, increased resistance, high fuel consumption, and high maintenance costs. On the other hand, an increase in fuel consumption affects greenhouse gas emissions, with influences on global warming (Jin *et al.*, 2022). At the same time, biofouling is responsible for the transfer of invasive species in local marine environments, as a result of their presence on the hull of ships, this problem is considered an important environmental concern from the point of view of pollution (Chakraborty, 2019). An example, in this case, is the appearance of the marine snail, *Rapana venosa* in the Pontic basin in the middle of the last century, where this exotic intruder has long since become a widespread mollusk and an integral part of the seabed biocenosis. As a strong invader and a strong competitor in the local food chain, in time, this organism has affected the populations of mussels and oysters in the Black Sea (Jensen, 2023).

Historically, there has been a special concern regarding the development of paint and antifouling coatings for maritime ships. As a result, there is a lot of information in the literature data about the use of lime and certain chemical compounds such as arsenic, mercury, silver, copper, and organotin compounds (Li et al., 2023; Jin *et al*., 2022; Jones & Ross, 2018). In time, these contaminants have proven to be very toxic both for micro/macro-organisms of the fouling type and for the marine ecosystem. In the middle of the last century, highly effective antifouling paints based on organotin compounds were developed. Among them, the best known are tributyltin fluoride (TBTF) and tributyltin oxide (TBT) due to their increased fungicidal action by inhibiting the growth of fouling organisms at low concentrations and with oxidative stress phenomena (Parisi *et al.*, 2022; Galvão *et al*., 2021). At the beginning of the 1990s, the use of organotin compounds was banned, due to their high toxicity, which affected the populations of mussels, and oysters, caused sex changes in marine snails, the behavior of fish, etc. (Amara *et al*., 2018). Thus, the maritime industry has adapted to the new requirements, by developing new technologies, friendly to the environment, less toxic, and affordable.

Moreover, in 1989, the IMO recognized the harmful effects of organotin compounds on the marine environment. In 1990, the IMO's Marine Environment Protection Committee (MEPC) adopted an international resolution recommending that all states adopt measures to prohibit the use of TBT-based antifouling paints on ships with non-aluminum hulls and less than 25 m with a leakage rate of more than four micrograms of TBT per day [1].

The purpose of this minireview is to underline the importance of developing new painting technologies, using biodegradable, non-toxic, and marine-friendly compounds, based on international legislation.

Interaction between Antifouling Coatings and Marine Environment

Worldwide, more than 4000 types of marine fouling species are registered, the vast majority of which are found especially in shallower waters, in coastal or harbors areas, loaded with nutrients. These marine species are of two categories: the first category, known as biofilm, includes microfouling organisms such as bacteria and diatoms. The second category, called macrofouling, includes species of seaweed, barnacles, mussels, polychaetae worms, and bryozoan (Cao *et al*., 2011; Yebra *et al.*, 2004).

Antifouling biocides are active chemical compounds, which have the role of destroying, controlling, or preventing the action of any organism considered harmful to the environment. Its effectiveness is determined by a series of physicochemical factors, the type of biocide as well as its chemical interaction with salt water (Jin *et al*., 2022; Parisi *et al*., 2022). In the development of antifouling coatings, more emphasis is placed on the interaction between the physical-chemical parameters of seawater and the active substances in the composition of antifouling paints (AF) (Fig. 2). Thus, recent research has been oriented toward the study of identifying the performance of new coating technologies, based on the possible reactions between the biocides in AF (incorporated in a polymer matrix) and seawater salts, conditioned by certain physical-chemical parameters of seawater. At the same time, the control over the thickness of the layer depleted of biocides is considered, due to a low interaction between the polymer matrix and the salts in the seawater, which will lead to the gradual release of the biocide in the water mass (Cao *et al*., 2011).

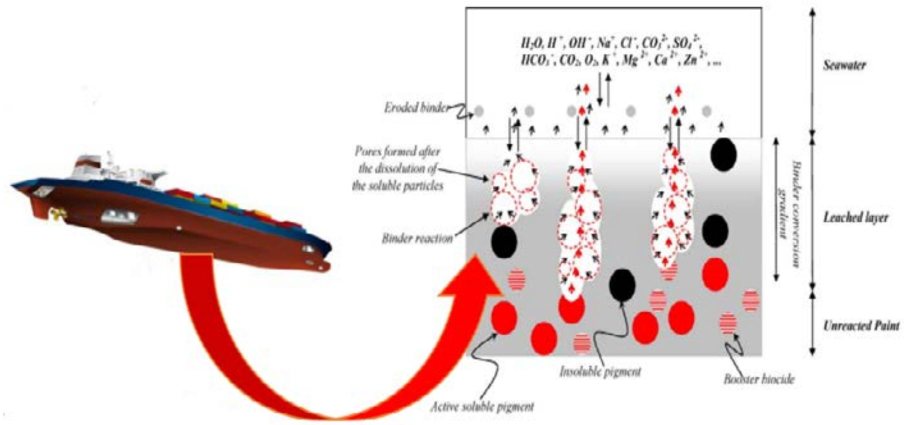

Fig. 2. Interaction between biocide-based antifouling system exposed and sea water, adapted from (Yebra *et al*., 2004)

Parameters such as pH, temperature, seawater salts, dissolved gases (O_2, N_2, CO_2), geographical area as well as the toxicity of biocides released into the environment and their interaction with environmental parameters are taken into account in the development of new AF technologies. Data from the literature showed that salinity is an important factor in the dissolution of biocide particles based on copper. Because seawater is an oxidizing medium, copper complex compounds are quickly oxidized to Cu^{2+} (which is the main biocidal active form) derived from cuprous oxide (Cu_2O) (Pourhashem *et al*., 2022; Almeida *et al*., 2007), according to the below reactions:

$$\frac{1}{2}CuO(s) + H^{+} + 2Cl^{-} \rightarrow 2CuCl_2{}^{-} + \frac{1}{2}H_2O \quad (1)$$

$$CuCl_2{}^{-} + Cl^{-} \leftrightarrow CuCl_3{}^{2-} \quad (2)$$

Also, the reaction of some components of the rosin-type binders, as well as the release reactions of the components obtained by the cleavage of the groups in the paints based on organotin-type are influenced by the salinity of the seawater (Yebra *et al*., 2004). At the same time, the kinetics of chemical reactions, the release rates of biocides in water, their dissolution, and transport rates are influenced by the high values of the seawater temperature. There are numerous studies regarding the influence of seawater pH on the solubility and release of biocidal active chemical groups from AF paints (based on rosin, TBT or Cu_2O). There are numerous studies regarding the influence of seawater pH on the solubility and release of biocidal active chemical groups from AF paints (based on rosin, TBT, or Cu_2O). The higher the seawater pH, the higher the release rate (Cao *et al.*, 2011; Almeida *et al*., 2007; Yebra *et al*., 2004). The presence of dissolved oxygen in surface waters can influence the oxidation reactions of Cu (I) dissolved in rosin-based AF paints, leading to the obtaining of compounds based on Cu (II), such as copper (II) chloride, copper (II) carbonate, copper (II) hydroxide, or even copper (II) sulfide, the latter chemical is obtained through biological processes (Yebra *et al.*, 2004). Information on water salinity values, copper concentration in the paint, and environmental temperature are not to be neglected in order to calculate a rough estimate of the copper release rate into the environment with an antifouling effect (Lagerström *et al.*, 2020).

Taking into account such aspects, it is very important that in the identification, modeling, and development of new AF paint technologies, the interaction of the active groups in biocides with environmental factors should be taken into account.

Past and Present of Chemical Antifouling Coatings

Since ancient times, humanity has been interested in developing anti-fouling protection technologies for sailing ships and wooden boats. The first written testimonies about the first attempts at AF technologies were provided by the ancient Mediterranean civilizations: Phoenicians, Carthaginians, Greeks, and Romans, (Almeida *et al*., 2007; Jin *et al*., 2022; Van Kerk & Luijten, 2007). Thus, the attestations of the time showed that for antifouling protection of wooden hulls, around 200 BC hot tar, animal hair and grease were used. Also, as an antifouling measure, the use hundreds of years ago of thin lead plates to cover the wooden parts of ships is attested. During the Middle Ages, sailing ships were sheathed with copper or brass, and at the end of the 18th century, substances such as arsenic, sulphur, and mercury were used to protect the hulls of ships (Dafforn *et al*., 2011).

Starting in the 20th century, the US Navy developed an antifouling coating based on rosin with copper oxide and mercuric oxide, which could resist in water for 18 months. In the middle of the last century, research studies by van der Kerk's team laid the basis for a new, highly effective AF technology based on organotin compounds (TBT) (Jin *et al*., 2022; Van Kerk & Luijten, 2007). However, over time it was discovered that these compounds had a negative impact on the marine environment, due to toxic effects and bioaccumulation in crustaceans, fish, mammals, and even humans. In addition, TBT degrades slowly and its accumulation in the environment can persist for months to decades. This has led to international awareness, and countries such as the UK (1987), USA (1988), Canada (1989), and Australia (1989) have banned the use of TBT-based biocides in AF paints on commercial ships through their legislation (Jin *et al*., 2022). Nowadays, organotin compounds from AF coatings have been replaced with biocides based on metal compounds. Of these, the most recognized in terms of low toxicity and low negative impact on the aquatic environment are those based on copper and zinc. Although copper is a trace element present in nature and essential for the proper functioning of biological organisms, due to its physical-chemical properties, at certain concentrations it becomes dangerous for the marine environment, because it accumulates in sediments and can disrupt the biological functions of marine organisms (Illuminati *et al*., 2019; Selim *et al*., 2018).

In the early 2000s, following an evaluation of the harmful effects of TBT on the aquatic environment, the International Maritime Organization (IMO) proposed a ban on the use of TBT-based antifouling paints from 1 January 2003 and a ban on the use of these paints on ships' surfaces from 1 January 2008. According to the Anti-Fouling Systems (AFS) convention, parties of the convention are required to prohibit and/or restrict the use of harmful antifouling systems on ships flying their flag, as well as on vessels not entitled to fly their flag but operating under their authority, as well as at all vessels entering a port, shipyard or offshore terminal of a Signatory Party. It should be noted that in 2021, the Marine Environment Protection Committee (MEPC) adopted amendments to include controls on the use of the Cybutryne-based biocide in AF coatings. This Cybutryne is known as a biocide, xenobiotic and environmental contaminant. Due to its toxicity, ships are prohibited from using this biocide in AF systems starting from January 1, 2023 [2, 3]. These measures have opened the way for further research to develop new environmentally friendly antifouling coatings.

Alternative Techniques to Antifouling Coatings

Over the years, along with the development of AF technologies, several alternative techniques have emerged. They were divided according to Swain's study (1998) into electrical, chemical, radiation, surface treatment, and thermal techniques. According to the Aghapour Aktij *et al.*, 2020 study currently the most common antifouling cleaning techniques are mechanical, hydraulic, chemical, and electrical methods, each of them with its advantages and limitations. Ultrasonic vibration techniques applied to ships in the middle of the last century were partly ineffective from the point of view of AF protection and on the other hand very expensive. The use of isotopes of type ^{60}Co, ^{204}Tl, and ^{91}Y was effective from the antifouling point of view only for high-intensity radiation, which made it not used because of its danger.

The injection of biocide solutions into crude oil and then applied to the hulls of ships were not reliable alternatives from the point of view of AF protection, as well as the impact on the environment and the high costs.

Alternatives regarding the use of AF coatings based on Teflon and silicone rubber could not be applied due to their non-adherence on the ship's hull. The use of electrical techniques, based on electric current, electric pulses, or electrolysis of seawater with the formation of biocidal molecules based on ozone, chlorine, ammonia, or bromine compounds, or electrolytically generated oxygenated water are all examples of alternative techniques to the methods of antifouling paint (Almeida *et al.*, 2007). Piezoelectric coatings, acoustic radiation, UV radiation, or magnetic fields can also be included in the category of alternatives to antifouling paints (Yadav&Kumar, 2023; Grilli *et al*., 2022, Almeida *et al*., 2007) [2].

The polyvalent metallic salts of pyrithione (e.g., zinc and copper salts), known as metal-based biocides could be considered alternative strategies in developing new AF coatings. They proved to have an interesting action in reducing fouling, being successfully used as algicides, fungicides, and bactericides in naval paints (Porhashem *et al*., 2022).

RESULTS AND DISCUSSION

Bioactive Compounds Based on Natural Designs for Antifouling Applications

The orientation of research directions toward the identification of antifouling compounds as friendly as possible to the environment, especially natural marine compounds, represents a target of researchers at the international level, in recent years. To achieve this goal, returning to nature is currently the best option, as it could provide us with very effective models for the research and development of antifouling coatings. The new coatings must be broad-spectrum, environmentally friendly, and prevent the attachment and formation of biofilm on the hulls of ships in operation. Also, these antifoul coatings must not leak into the environment and must be as durable as possible over time. Nowadays, researchers' efforts have focused on identifying and creating new coatings that can imitate the surfaces of various animals or plants that have developed these types of antifouling surfaces over time, due to natural environmental stresses [3].

To create new environmentally friendly coatings with high durability over time, Jin *et al*., 2022 identified in their study several nature-inspired surface designs (Jin *et al*., 2022). Thus, starting from the surface pattern of certain plants (*Lotus* leaves) and animals (shark) that have developed over time micro/nanostructure surfaces with antifouling protection, the researchers attempted to create similar, synthetic patterns with superhydrophobic or weakly adhesive properties [3] (Selim *et al*., 2020). Studies have shown that these microstructures form a physical barrier at the surface of the organism for the surface substrate that can resist biofouling organisms from attaching, but at the same time reduce water resistance due to the air trapping effect (Jin *et al*., 2022; Barthlott *et al*., 2016). The self-healing and antifouling properties due to these microstructures allowed the adaptability of each organism to its habitat.

A new applied strategy in combating biofouling could be using natural foulants of bioactive compounds similar to those released by some species of corals and sponges (Tian *et al*., 2020; Jin *et al*., 2020).

Aquatic organisms, such as fish, that live in an environment rich in microbes and are in permanent contact with their environment are vulnerable to the pathogenic invasion of different species of microorganisms. As a result, the hydrogel or epidermal mucus secreted by fish can be considered a multifunctional material, with a very important role not only in protection and lubrication but also in respiration, ionic and osmotic regulation, feeding, etc. (Yan *et al*., 2022; Seo *et al*., 2021). Most research studies have shown that the antifouling activity of this natural epidermal hydrogel secreted by fish is due to the presence of a group of antimicrobial polypeptides, with amphipathic-helical structures, which by their nature can interact strongly with the phospholipid membranes of microorganisms (Liu *et al*., 2023). The creation of synthetic hydrogels, similar to the epidermal mucus produced by fish, could be a new target for the development of new antifouling capacities, friendly to the environment and resistant over time.

Some marine organisms, such as dolphins and sharks, have rubber-like skin, which under the action of the hydrodynamic forces of water, can become unstable. For this reason, the epiderma of these marine mammals is not conducive to the attachment of fouling microorganisms, due to the dynamics and environmental characteristics. The creation of this type of dynamic structure similar to the antifouling surfaces of dolphin and shark skin (epiderma) could revolutionize today's modern antifouling technologies (Jin *et al*., 2022).

Because traditional antifouling methods use toxic biocides, which have developed over time negative effects on the marine environment, the creation of new eco-friendly biocides for the environment and sustainability in time has become a wish for researchers in the naval industry. Applying the principle "from nature for nature", a multitude of natural antifoulants types have been discovered in recent years (Jin *et al*., 2022; Saha *et al*., 2017). Thus, natural antifouling models produced by various organisms or the creation of chemically similar structures to natural antifouling compounds appeared as possible alternatives. However, these approaches present certain impediments in environmental engineering applications because, on the one hand, the collection of organisms producing natural antifoulants could affect their natural environment, and on the other hand, the extraction process of these compounds is expensive and complicated. As a result, nowadays, research is oriented towards identifying and finding alternatives, either of the type of developing aquaculture based on the growth of source organisms or of synthesizing synthetic analogs (Jin *et al.*, 2022).

Literature data have shown that in nature there is a diversity of marine invertebrates, from which natural biocide compounds with antifouling activity could be extracted: sesquiterpenes, steroids, indoles, alkaloids, diterpenes, sterols, terpenoids and polyketides (Liu *et al.*, 2023; Tian L. *et al.*, 2022). From marine invertebrates, research studies by Tian L. *et al.*, 2020, and Tian W. *et a*l., 2022 on coral and sponge species that contain organic extracts with antifouling action showed that these extracts can have specificity for certain fouling organisms. Thus, it can be concluded that natural, individual organic compounds cannot be used in naval applications. Instead, the tests performed with multi-compounds proved a good antifouling activity.

The bioactive compounds extracted from red algae, brown algae and green algae, known as macroalgae with antifouling activity, have been intensively studied in the last 30 years (Nys *et al*., 1995; Chapman *et al*., 2014; Pereira *et al*., 2021). Thus, in their studies, Pereira *et al*., (2021) identified in algal extracts specific lipids (sterols), as well as hexadecanoic, dodecanoic, octadecanoic, and tetradecanoic acids, which could be associated in this activity. Likewise, the bromoform type compounds, dibromo acetic acid, dibromochloromethane, bromo-chloroacetic acid, tribromoethanol, and dibromoacrylic acid, which exhibited a high antifouling capacity, cannot be neglected either (Pereira *et al*., 2021).

Nowadays there is an increased interest in understanding how micro/macro marine organisms interact with each other and how they adapt in marine ecosystems. Research studies in recent years have proposed AF strategies to be inspired by the chemical defense mode of marine organisms. The chemical compounds secreted by them can be proposed as alternatives to biocides and metal-based AF paints, for biofouling control. To survive in the marine environment, from the point of view of physical-chemical and biological conditions (temperature, pressure, salinity, oxygen content, viruses, parasites, etc.), defense against predators, competition for space and food with other organisms, and prevent external surfaces from fouling attack, invertebrates produce their own chemical defense compounds. By studying the chemical structures of these bioactive compounds, as well as the biosynthesis mechanisms, similar, friendly compounds with antifouling action can be produced or synthesized.

The studies of Torres, & De-la-Torre (2021) highlighted a new class of natural marine products called butanolides, with high AF activity. Of these, the 2-furanone fraction, isolated from a marine strain of *Streptomyces*, presented an interesting AF activity (Gomez-Banderas, 2022; Pan *et al.*, 2019). Starting from this discovery, Peiyuan *et al*., 2017 synthesized a modified butanolide, which was incorporated into paint and then tested in the field and showed both high AF activity and low toxicity (EC50=0.02 μg/L) (Gomez-Banderas, 2022; Peiyuan *et al.*, 2017).

An interesting antifouling (AF) activity was observed with hydrophilic polymers of the polyethylene glycol type, zwitterionic polymers (Su *et al.*, 2021), in the form of hydrogel [3]. Hydrogels have increasingly obtained the interest of researchers in the last time due to the intrinsic properties amenable to various applications. Their biocompatibility, the ability to release water-soluble compounds from the polymer network, and the versatility in modeling the physicochemical properties allow the generation of new biomaterials with applications in the field both of pharmaceutical and engineering environments protection. Hydrogels are defined as macromolecular supports for obtaining controlled/sustained release systems of bioactive compounds and are classified into two main categories: natural hydrogels and synthetic hydrogels. At the same time, they appear in the form of films, sponges and solid particles, depending on the type of crosslinking (chemical or physical). Hydrogels are composed of polymer networks, reticulated, elastic, with highly hydrophilic properties, able to swell, absorb and retain impressive amounts of water or other liquids. In general, hydrophilic monomers are used for the preparation of hydrogels, but hydrophobic monomers are also successfully used when materials with specific properties are desired. Hydrogels from natural sources (agar, cellulose, chitosan, alginate) are preferred in applications that require high cell adhesion, precisely due to the intrinsic characteristics of polysaccharides, such as: biodegradability and biocompatibility. Polyethylene glycol (PEG), polyvinyl alcohol (PVA), polyacrylamide (PAM), polyurethanes (PU), and polymethyl methacrylate (PMMA) are known as synthetic hydrogels, obtained by physical or chemical crosslinking methods with successfully used as new marine AF coatings (Jin *et al*., 2022; Bignotti *et al*., 2021; Selim *et al*., 2017;). Hydrogels based on PEG are known as non-adherent materials to cell and protein fouling. This is due to the hydrophilic structure of PEG, its electrostatically neutral charge, and its non-toxicity. In addition, the AF performance of PEG is due to the formation of hydrogen bridges with water, which leads to the maximization of the hydrophilic surface and the minimization of attractive forces with fouling. However, there are also disadvantages regarding the use of PEG-based hydrogels, due to the decomposition of AF coatings over time, as a result of the rapid auto-oxidation process of PEG in the presence of oxygen. By cause of, the use of PEG-ZnO nanocomposites significantly reduces fouling attachment, which is why they are successfully recommended in AF coatings (Jin et al., 2022; Pourhashem *et al*., 2022; Zhang *et al*., 2022).

One of the brand leaders in producing high-quality AF coatings, Hempel has developed the best fuel-saving hull ship coating, regardless of the sailing conditions or the vessel's sailing speed. This new technology, *Hempaguard*, does not allow the biofilm to attach to the ship's hull, regardless of whether the boat has very long periods of inactivity or its speed is low, thanks to the combination of *Actiguard* technology based on silicone-hydrogel, with the controlled biocidal release. The results of the application of this new technology led to an average fuel economy of 8 %, over the entire docking interval, according to the company's statistics [4].

It cannot be ignored in the identification of new marine antifouling strategies by using chitosan, known as a bioactive, biodegradable, biocompatible, odorless, and non-toxic material. Chitosan is the only alkaline polysaccharide in nature, mainly of by marine origin and depending on its main characteristics (molar mass Mw and deacetylation degree DD), possesses antimicrobial properties against a number of bacteria, fungi and algae (Sathiyaseelan *et al*., 2023; Bakshi *et al*., 2019; Al-Naamani *et al*., 2019). In their research, Al-Naamani *et al*., 2019 studied the AF effect of chitosan solutions with medium molar mass, which were applied as a coating on acrylic plastic surfaces immersed in a salty aqueous environment loaded with micro/macro-organisms of fouling type. The obtained results showed that chitosan is proper to be used as a coating component to prevent marine micro- and macro-fouling (Al-Naamani *et al*., 2019).

CONCLUSIONS

Nowadays, fouling represents a major hazard for the naval industry, due to the effects produced: high fuel consumption, with high greenhouse gas emissions, resistance to the ship's progress, high maintenance costs, and negative impact on the marine environment. At the same time, biofouling is responsible for the transfer of invasive species to local marine environments, because of their presence on the hull of ships, which represents a major threat to the environment. In order to prevent and control biofouling contamination, by applying eco-friendly technologies, naval industries spend billions of dollars.

Since the beginning of navigation, humanity has been concerned with the identification, development, and use of protective technologies to cover the AF of ships. However, it was discovered that the substances used as biocides in AF coatings (arsenic, sulfur, mercury, copper, organotin compounds, etc.) had a negative impact on the marine environment, due to toxic effects and bioaccumulation in crustaceans, fish, mammals, and even humans. Thus, at the international level, legislation and legal regulations have imposed a ban on the use of organotin compounds (TBT compounds) in AF-type coatings on ships. In the future, research and application of AF technologies will be directed in such a way that their efficiency will be on a broad spectrum, to be non-polluting, non-toxic, biodegradable, and low-cost.

Despite chemical biocides used in AF technologies are relatively efficacious, the identification and use of antifouling agents based on natural biocides are considered one of the most effective ways to reduce and prevent marine pollution, being currently considered a global public concern. The development of science and technology has taken the problem of marine antifouling to a new stage of knowledge. Today, there is a better understanding and knowledge of the control of contact surface characteristics such as low resistance, low adhesion, wetting (hydrophobicity or hydrophilicity), and microtextured surface patterns, which are designed to reduce the accumulation and attachment of biological fouling. Nature has been, is, and will be a source of inspiration for the development of AF technologies.

Data from the literature showed that in nature there is a diversity of marine invertebrates, from which natural biocidal compounds could be extracted that could be used in antifouling coatings: sesquiterpenes, steroids, indoles, alkaloids, diterpenes, sterols, terpenoids, and polyketides.

An interesting AF activity is developed by using natural (agar, cellulose, chitosan, alginate) and synthetic (PEG, PMMA, PVA, etc.) hydrogels in the marine industry. A number of AF coatings analyzed in this paper are based on the naturally inspired, such as natural antifouling agents, the chemical defense mode developed by marine organisms, the creation of a type of dynamic structure similar to the antifouling surfaces of dolphin and shark skin (epidermal), and hydrogel antifouling coatings, which have the advantages of antifouling performance while remaining non-toxic and environmentally harmless, etc. Nevertheless, these AF coatings present disadvantages of high cost and poor stability. Consequently, in the future it is necessary to focus on further research into the anti-fouling mechanism of natural biocides produced by plants and animals, to find effective, broad-spectrum and non-polluting antifouling coatings.

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