Nanoparticles in marine antifouling coatings: a case study

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Abstract. The problem of fouling of hydraulic structures, marine structures, ships and vessels has been acute since the beginning of the era of navigation. The formation of a biofilm of fouling reduces the speed of the vessel, worsens its controllability, increases fuel consumption, shortens the service life of hydraulic structures and increases the load on them. Many methods have been proposed to control fouling. One of the most promising coatings is considered to be based on the use of nanoparticles of biologically active metals and their oxides. The paper discusses various strategies for using nanoparticles to combat biofouling. The paper also presents preliminary results of a study of the antifouling efficiency of coatings modified with nanoparticles of metal oxides Fe-ZnO, ZnO, CuO. The study was carried out by exposing plates with experimental compositions at the sea test site in the Sevastopol Bay for a year, starting from August 2020. The species composition of a separate group of microperiphyton - microalgae - on plates with experimental coatings in the first two months of exposure, as well as the result of photographic fixation of the state of the surface of the plates from the point of view of macro-fouling, was investigated.

1. Introduction

Any object or structure located in the marine environment experiences many negative impacts. Firstly, this is a dynamic impact from the marine environment, secondly, rapid corrosion, and thirdly, the impact from micro- and macroorganisms attached to the surface of the substrate and their metabolic products. This leads to an increase in the load on hydraulic structures, worsens the sailing properties of ships and vessels. Fouling inside pipelines and various structures also leads to a deterioration in their performance [1-2].

There are many ways to combat fouling [3]:

- Mechanical cleaning of the surface from build-ups.
- Special physical methods of fighting fouling (transmission of current pulses, ultrasonic waves, ionizing radiation, etc.).
- Application of special compounds with anti-fouling properties.

Mechanical processing requires a lot of labor, often special engineering structures (docks, caissons, diving bells), which are not always available. Special means of struggle also require the organization of special technical devices and are unsafe for the personnel operating this equipment or working on the structure.
The application of special coatings is historically the first way to combat the fouling process. The development of scientific and technological progress has led to the creation of various anti-fouling compounds, the main idea of which was the introduction of a certain amount of biocide into its composition (a substance that causes the death of target aquatic fouling organisms). At the same time, the coatings used do not meet all the demands of practice from the point of view of the balance between their environmental safety and efficiency. Biocides have significant side effects on “off-target” accompanying marine organisms [4]. Antifouling paints release compounds of heavy metals, which, obviously, pollutes the marine environment, especially in the areas of anchorage of ships [5]. In this regard, the relevance of the development of new highly effective coatings that prevent marine biofouling of ships and hydraulic structures, on the one hand, and low-toxic for the environment, on the other, is still relevant.

Today, the main trend in the development of world science in this direction is the development of new, less toxic, but effective coatings for the prevention of biological growth, based on the use of nanoparticles of biologically active metals and their oxides [6]. The introduction of nanoparticles can lead to a modification of the rheological and adhesion properties of the coating, their antimicrobial and, in general, biotoxic effect, proven in laboratory conditions, allows to consider them as a promising alternative to the traditional biocidal components of antifouling coatings [7].

Currently, there are several strategies for applying nanotechnology to the development of anti-fouling coatings. The first of them is based on the creation of a nanorelief of coatings with predetermined useful mechanical and hydrophobic properties. In particular, the creation of superhydrophobic (contact angle with a water drop > 150°) nanoscale surfaces have shown anti-fouling efficiency for the example of target organisms (Ulva rigida, Polysiphonia sphaerocarpa, Amphibalanus amphitrite, and some others) [8]. Certain regularities were established between the surface parameters (wettability indicators and surface free energy) of xerogels synthesized from aminopropylsilyl-, fluorocarbonsilyl-, and hydrocarbonsilyl-containing precursors and their anti-fouling efficiency using the example of the target fouling Ulva [9]. The combination of superhydrophobicity and surface nano-roughness characteristics can provide significant antifouling properties of nanocoatings [10].

The second strategy for using nanotechnology is based on the idea of microencapsulation of anti-biofouling agents and obtaining a biocidal nanopowder. In microencapsulation technology, the target biocide substance is incorporated into drops of a water-soluble resin with a controlled release rate of the biocide, which stabilizes the antifouling effect of the coating [11]. This achieves a double effect: prolonging the action of the anti-fouling agent and reducing the impact on the environment. Technologically, in the process of microencapsulation, the size of the nanocontainers of particles can be varied depending on the temperature of the polymerization reaction, on the amount of the dispersing agent and the stirring speed [12].

The third strategy is based on the direct use of metal nanoparticles and their oxides as an anti-fouling agent. The motivation for this is their less harm to the environment. For example, zinc oxide nanoparticles are less toxic than copper, copper oxides, silver, and metallic zinc [13]. The action of zinc oxides (ZnO) and, to a greater extent, titanium dioxide (TiO2) is based on their photocatalytic activity. As a result of this process, the generation of reactive oxygen species (ROS) occurs when the material is illuminated with light of a certain wavelength and the slow release of toxic metal ions. There are other examples as well. When using nanoparticles of vanadium pentoxide (V2O5), hypobromous acid HOBr (a strong oxidizing agent) and active oxygen are released in water, causing serious damage to marine organisms - bacteria, shells and macroalgae [14]. The toxic effect of V2O5 is limited to a thin microlayer near the fouling attachment surface, and therefore has a minimal impact on the environment. Within the framework of the third strategy, the most promising type of nanoparticles are nanostructures containing two components - biologically active metals and/or metal oxides [15].

Our research is also aimed at solving this scientific problem. This paper presents preliminary results of evaluating the antifouling efficiency of commercial paints modified with metal nanoparticles Fe-ZnO, ZnO, CuO. As noted in [16], the effectiveness of the anti-fouling coating and the release of metals with subsequent accumulation in the ecosystem strongly depend on the coating formulation and the state of
the aquatic environment. On the one hand, the formulation of commercial paints is not available and is a trade secret, on the other hand, a simple substitution of a standard biocide for a new agent (nanoparticles) can disrupt the adhesion and viscous properties of the coating, especially during the preparation process. Therefore, we decided to modify the commercial composition by introducing an insignificant number of nanoparticles to establish only a qualitative effect. The paper presents preliminary results of exposure of plates with a modified antifouling coating in natural conditions of the marine environment.

2. Materials and methods
Metal nanoparticles in three versions were introduced into the standard antifouling coating: Fe-ZnO, ZnO, CuO. For the synthesis of nanoparticles, an innovative technology of electric explosion of wires of corresponding metals in an oxygen-containing atmosphere was used [17]. Varying the parameters of electroexplosive synthesis and oxygen content in the working gas makes it possible to obtain multicomponent nanoparticles with different contents of oxide and metal phases and dispersed composition. Preliminary experiments with the indicated nanocompositions on test microorganisms (V. cholera, E. coli, K. pneumonia, S. aureus, C. albicans, and P. aeruginosa) showed a high biological activity of these substances [17]. We tested these trains at the offshore test site in the Sevastopol Bay. Four formulations were used in the study: a standard commercial paint and varnish coating "Bioplast-52" (as a control) and three modifications with three types of nanoparticles introduced. The standard coating formulation contains 35% by mass of copper oxide Cu₂O. It was experimentally found that when 10% of the mass fraction of the biocide was replaced by the indicated nanoparticles, the paint retained its rheological properties at a satisfactory level for application to test plates made of Plexiglass.

In the course of the work, a regular analysis of the composition of microalgal component of biofilm and photographic recording of the surface of the experimental plates were carried out at different times from the beginning of exposure to the sea. The analysis of fouling microalgae was carried out four times during the exposure period of the plates: three days after the beginning of the exposure, two weeks later, three weeks later, and two months later. The study of the composition of microalgae in the initial suspension was carried out using in vivo preparations. Microscopic examination and photographing of cultures were carried out using a Levenhuk 740T biological microscope at a magnification of x 400. The obtained images were processed in the Adobe Photoshop CC 2018 program.

3. Results and discussion
As studies by other authors have shown, the process of fouling occurs in several stages. Almost immediately after the immersion of any object in the marine environment, a primary film is formed on it from macromolecules: polysaccharides, lipids and proteins. It is a substrate for the attachment of various heterotrophic microorganisms, micromycetes and microalgae. At the next stage, macro-fouling begins to attach to this film of micro-fouling. Research shows that preventing the first stage of fouling is nearly impossible; during the formation of a community of macro-fouling at the third stage, it already indicates the ineffectiveness of the coating. Thus, an objective comparative assessment of the effectiveness of the anti-fouling composition can be performed according to the second stage - the intensity and composition of the microbiological colonization of the substrate [18].

Table 1. The results of photographic recording of the anti-fouling coating state.

| Month    | Control | FeZnO   | ZnO    | CuO  |
|----------|---------|---------|--------|------|
| August 2020 | ![Image](image1) | ![Image](image2) | ![Image](image3) | ![Image](image4) |
Studies of the species composition of microalgae on plates with the studied compositions were carried out. On the third day after the installation of the coated plates, fouling was weak on all samples; microscopic examination of the washings revealed mainly various small forms of dinophytic algae (Dinophyta), diatoms (Bacillariophyta) and microcolonies of cyanobacteria (Cyanoprokaryota) were found in insignificant amounts. On the 14th day of exposure of the plates, microalgal fouling, as in the previous case, was mainly represented by various forms of dinophytic algae. Some representatives of diatoms were found, but only on plates coated with (Fe-Zn)O. Dinophytic algae also dominated in the microalgal fouling of the plates on the 21st day of installation; however, an increase in the occurrence of diatoms was noted. Filamentous cyanobacteria belonging to the order Oscillatoriales were also detected on plates with (Fe-Zn)O and ZnO additives. Two months after the plates were installed, various forms of dinophytic algae, which are representatives of the genera *Prorocentrum*, *Amphidinium*, *Scrippsiella*, *Gambierdiscus*, and some others, developed on their surface. By that time, however, the occurrence of diatoms had significantly increased, especially representatives of such genera as *Rhizosolenia*, *Navicula*, *Amphora*, *Nitzschia*, *Pleurosigma*. In general, Dinophyta dominates among all other representatives of the algal flora at all stages of the formation of microalgal phytoperiphyton.

The work also carried out photographic recording of the surface for visual control of the surface condition and the transition of the fouling process to the third stage (settlement of macrohydrobionts). The results of these observations are shown in table 1. From the analysis of these data, it can be concluded that even after a year of exposure in the marine environment, the surface of the experimental plates is covered only with a layer of micro-fouling, without the appearance of macro-fouling. The photo also shows that the physical and mechanical state of the surface remains good, which gives grounds for cautious optimism about the possibility of using the studied or similar compositions as a new effective means to combat the fouling process. In the first two months of exposure, the composition modified with CuO nanoparticles showed the best anti-fouling activity. A year later, the best qualities were demonstrated by the composition with ZnO nanoparticles.

In future work, we plan to develop a simple formulation (based on epoxy resin) with introduced bimetallic nanoparticles as the only anti-fouling agent for a comparative assessment of their effectiveness in comparison with standard commercial coatings. The second task of further research will be to assess the level of side toxicity of formulations with nanoparticles for the environment.

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[Table 1]

| Date       | Image 1 | Image 2 | Image 3 | Image 4 |
|------------|---------|---------|---------|---------|
| September 2020 | ![Image 1](image1.png) | ![Image 2](image2.png) | ![Image 3](image3.png) | ![Image 4](image4.png) |
| October 2020   | ![Image 1](image1.png) | ![Image 2](image2.png) | ![Image 3](image3.png) | ![Image 4](image4.png) |
| July 2021      | ![Image 1](image1.png) | ![Image 2](image2.png) | ![Image 3](image3.png) | ![Image 4](image4.png) |
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