

# Development of eco-friendly self-polishing antifouling coatings

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Silicates are a well-known class of chemical compounds that are widely used in various sectors of the national economy. Such a wide range of applications of silicon-containing substances is explained by their chemical inertness, thermal stability, and porosity.

The paint and varnish industry are a promising area for the application of silicon-containing compounds. In polymer and coating technology, it has been shown that the addition of SiO<sub>2</sub> or wollastonite to polymer matrices has improved many properties and provided new functions for coatings [1, 2].

In order to find out the respective effect of SiO<sub>2</sub> and calcium hydrosilicate (CH) on the physicochemical characteristics of the coating, different paints were compiled according to different types of fillers and their ratio (Table 1). A bacterial organic extract from *Pseudoalteromonas piscicida* 2202 with antifouling and anticorrosion properties served as an antifouling agent.

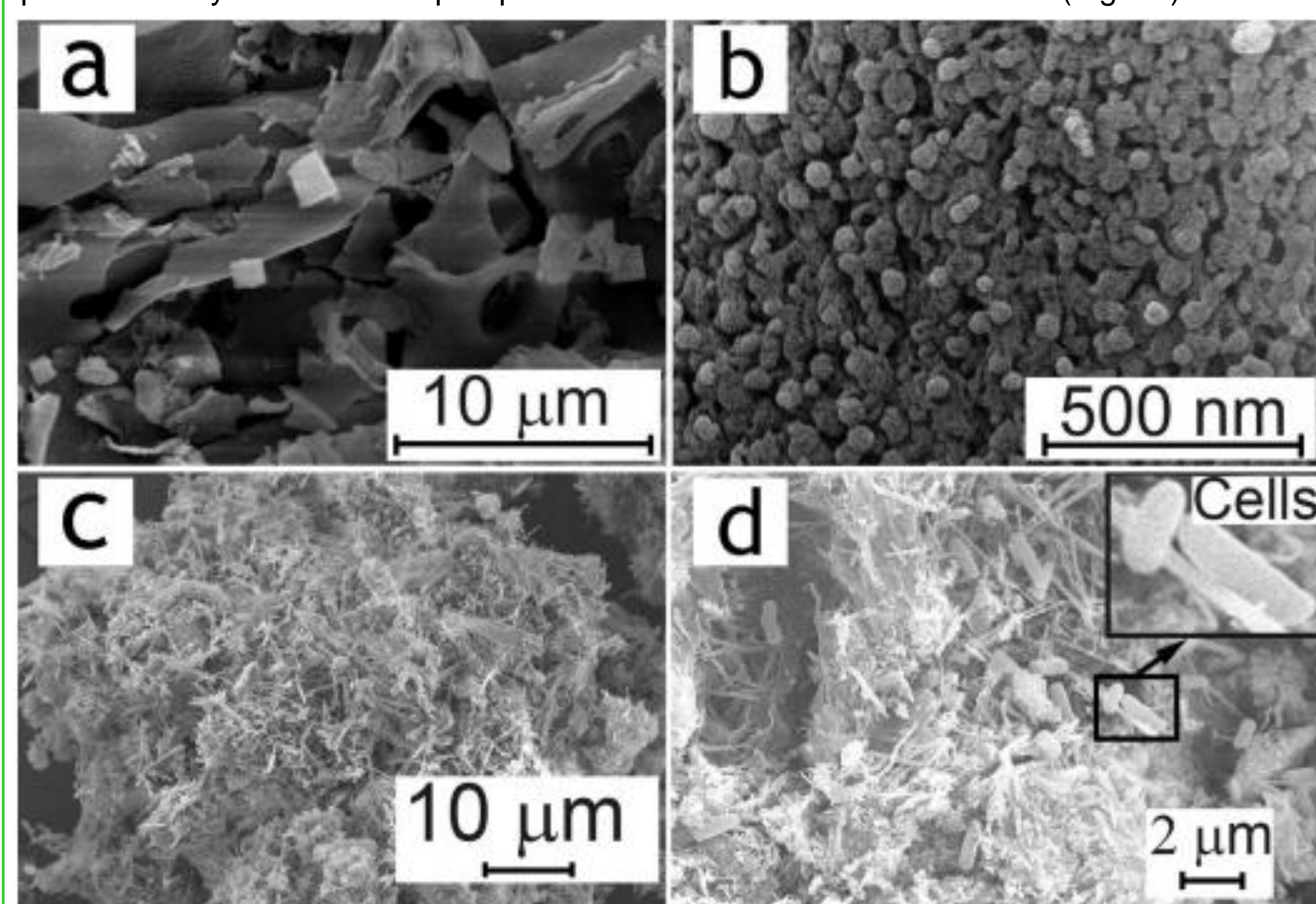
**Table 1.** The composition (g) of different paints under study

Component		Coating		
		№1	№2	№3
Binder	Acrylic copolymer	15	15	15
	Rosin	20	20	20
Pigments	ZnO	20	20	20
	Extract (ml)	10	10	10
Antifoulants	CaCO <sub>3</sub>	10		
	SiO <sub>2</sub> -rh		10	
	CH			10
Solvent	Xylene (ml)	100	100	100

Paints were applied to polycarbonate plates with an automatic applicator to determine the physico-chemical properties and by brush to PVC plates to evaluate the antifouling effectivity in field tests. Painted samples were exposed to seawater on a test bench located in Dam Bay (Vietnam) at a depth of 1.5 m for 9 months. The average temperature and salinity of seawater during the experiments were 28 °C and 32 ‰, respectively.

According to the X-ray data, the specimen SiO<sub>2</sub>-rh is amorphous. The composition of the sample is characterized by SiO<sub>2</sub> content up to 97.4%. In the composition of the sample obtained from technogenic raw materials (CH), there are both amorphous phase and phases of tobermorite Ca<sub>4</sub>Si<sub>6</sub>O<sub>15</sub>(OH)<sub>2</sub>·5H<sub>2</sub>O and xonotlite Ca<sub>6</sub>Si<sub>6</sub>O<sub>17</sub>(OH)<sub>2</sub>. The value of specific surface area for the SiO<sub>2</sub>-rh is 309.6 m<sup>2</sup>/g, for the CH 155.2 m<sup>2</sup>/g. According to the results of thermogravimetric analysis, the amount of water in the samples is about 2.2% for the sample from rice husk and up to 12% for the calcium hydrosilicate.

The SEM images in Fig. 1 show morphological structure of silicon-containing samples. SiO<sub>2</sub>-rh particles are of irregular geometric shape and are characterized by globular micromorphology (Fig. 1a and b). The morphology of the calcium silicate-based sample (CH) is represented by micron-sized (1–40 μm) agglomerates. The agglomerates consist predominantly of needle-shaped particles less than 100 nm in diameter (Fig. 1c).



**Fig. 1** SEM images of silica containing samples: a and b –SiO<sub>2</sub>-rh; c –CH; d –CH with *E. coli* cells

The use of silicate by-products as fillers in antifouling has maintained a balance between antifouling and mechanical strength of the developed coatings. The results of the study showed that the barrier characteristics of coatings can be substantially enhanced by incorporating particles of inorganic filler SiO<sub>2</sub>-rh and CH by reducing heterogeneity and limiting the diffusion path for water. Incorporating these details into self-polishing coatings also offers environmentally friendly solutions by enhancing the integrity and durability of coatings. Improved antifouling performance has been shown in coatings with SiO<sub>2</sub>-rh in combination with a bacterial antifouling extract.

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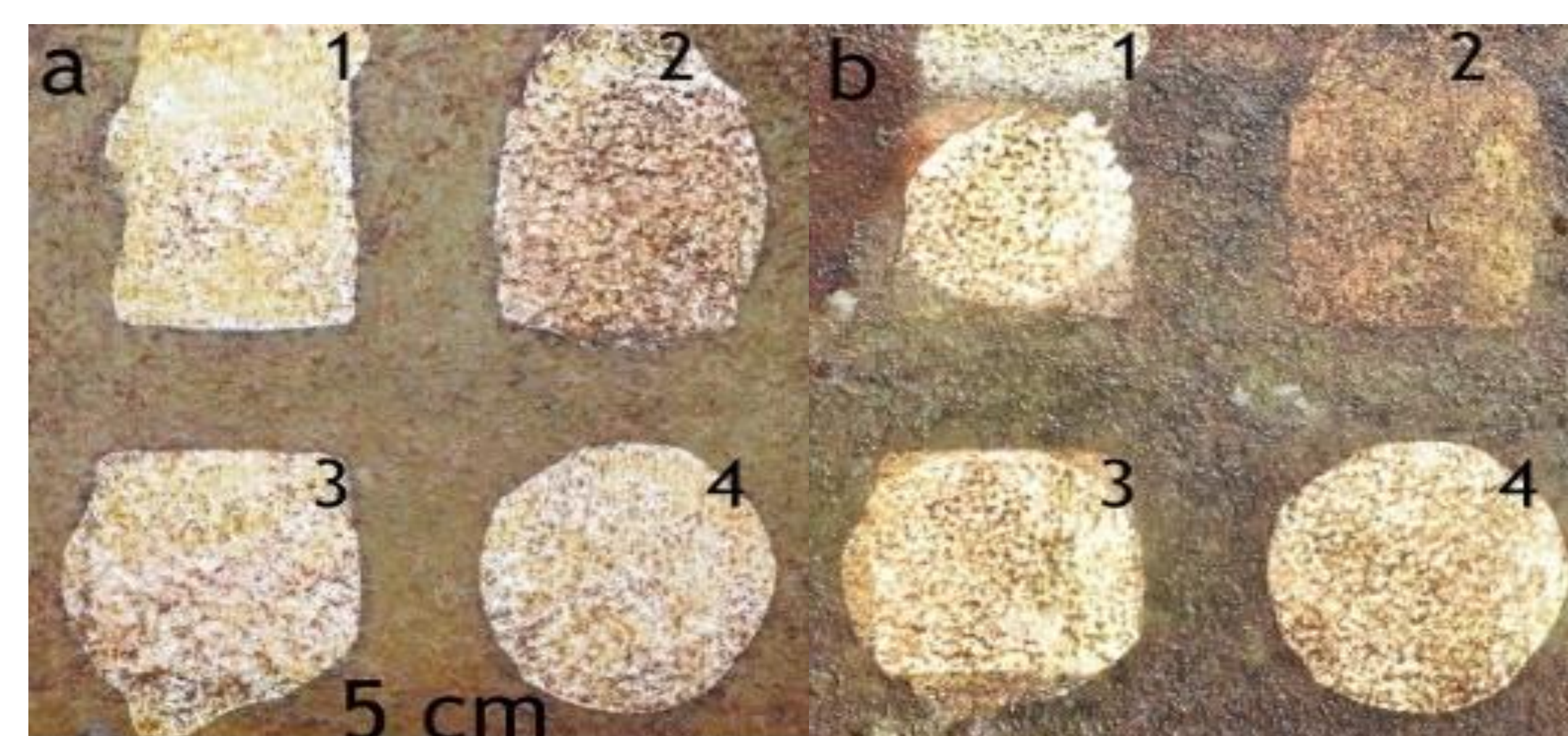
The data in Table 2 show that the silicon-containing particles have an average particle size 2.2 μm for SiO<sub>2</sub>-rh and 0.9 μm for CH and are characterized by negative zeta-potential. The information about the zeta-potential can be very useful in identifying the mechanism of sorption interaction between particles and bacterial cells. The table also presents data on the zeta-potential of bacteria. As the data show, the zeta-potential of *Escherichia coli* and *Bacillus subtilis* strain has negative values.

**Table 2** Zeta-potential and average particle size of test specimens and bacterial cell

Samples	Zeta-potential (mV)	Average size, μm
SiO <sub>2</sub> -rh	-16.6±1.2	2.2
CH	-24.5±1.8	0.9
<i>Escherichia coli</i>	-27.2±1.6	1.7
<i>Bacillus subtilis</i>	-20.2±1.5	4.1

The replacement of widely used calcium carbonate with additives of SiO<sub>2</sub>-rh and calcium hydrosilicate (CH), which make up from 30 to 50 % of the total volume of the filler, has little effect on the water-absorbing properties of the resulting coatings. In this case, the hardness of the coatings increases by more than 1.5 times. Complete replacement of CaCO<sub>3</sub> leads to an increase in water absorption by 20–30 % and an increase in the rate of degradation of the coating by 2 times when using SiO<sub>2</sub> and by 8 times when using CH. Thus, the partial replacement of CaCO<sub>3</sub> by SiO<sub>2</sub>-rh and CH favorably affects the hardness of coatings without affecting their sensitivity to erosion.

Figure 2 shows a panel with areas painted with different coatings after 4 and 9 months of immersion in seawater. Even after 9 months of exposure, only non-adhesive algal slime remains on the surface of the painted areas, while on the surface that is not painted, a layer of macrofouling is formed, consisting of bryophytes and single balanuses. It should be noted that the area of Coating 2 with CH as a filler is more susceptible to fouling than areas 1, 3 and 4 with CaCO<sub>3</sub> and SiO<sub>2</sub>-rh as fillers.



**Fig. 2.** Fouling of immersed panels with various paints (1 and 4 with CaCO<sub>3</sub>, 2 with CH, 3 with SiO<sub>2</sub>-rh) after 4 months (a) and 9 months (b) field tests

It is known that fillers, being an active component of polymer coatings, affect their technical and functional properties. Correct selection of fillers when formulating the coating leads, on the one hand, to significant savings in expensive components (for example, TiO<sub>2</sub> or ZnO), and on the other hand, to an improvement in the physical and mechanical properties of the coating being developed. The use of products obtained from production waste as fillers contributes to the development of environmentally oriented and resource-saving technologies.

The principle of action of self-polishing coatings is based on the continuous hydrolysis of film forming agents. Self-polishing rate of paint films and also biocide release are closely related with water uptake of coatings.

It is known that one of the important factors ensuring the effectiveness of the antifouling coating and its long service life is the controlled release of the active compound (e.g., biocide) from the coating, which is achieved in several ways, one of which is its preliminary adsorption onto carriers. As it was shown by the obtained results, all paint coatings exhibited certain antifouling activities compared to the uncoated panels, which were fouled most heavily by diverse marine organisms. After 9 months of immersion, the filler CH associated with the bacterial extract is not efficient: the paints are colonized rapidly – green algae have settled. In the case of the filler E-SiO<sub>2</sub>-rh, it proved to be more effective in biofouling prevention. It is possible that the different antifouling efficiency of samples E-CH and E-SiO<sub>2</sub>-rh is associated with a different type of bond formed between the mineral particle and the organic extract. According to FTIR data, sample CH forms a strong complex with organic compounds of the extract, in contrast to sample SiO<sub>2</sub>-rh. At the same time, apparently, the active compounds of the extract during interaction with the surface of the sample CH lose their mobility, as well as antifouling properties over time, which explains the short-term antifouling efficiency of the coating with E-CH as a filler.