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Abstract: Highly hydro and oleophobic materials applied to needs of the marine environment represent a relatively young field achieving growing interest as innovative solution, where technological and ecological aspects allow to be merged, taking into account the limitations imposed by international laws in terms of environmental protection. In this work a superhydrophobic (SH) coating for seawater applications has been characterized and tested in both laboratory and field conditions, since investigations in real seawater are crucial to evaluate the behaviour of SH surfaces because of a complexity not reproducible in laboratory. Taking into account the real conditions where the surface can operate oleophobicity can be investigated in presence of organic and inorganic pollution. The amphiphobic surface has been also studied to simulate those applications where the surface undergoes to thermal stress like pipelines and desalination plants affected by biofouling. The preliminary wearing test shows the effective resistance to a continuous low velocity impact of micrometric particles of the coating investigated here. Finally, time durability in field tests has been studied as a function of immersion angle in real seawater environment to investigate the role of the coating on early stages of biofilm growth.

To: Dr. Reinhard Miller

Special Issue Managing Guest Editor

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Genova, February 20<sup>th</sup> 2106

Dear Dr, Miller,

please find enclosed the manuscript of the article "AMPHIPHOBIC COATINGS FOR ANTIFOULING IN MARINE ENVIRONMENT" by

*Francesca Cirisano, Alessandro Benedetti, Libero Liggieri, Francesca Ravera, Eva Santini and Michele Ferrari*

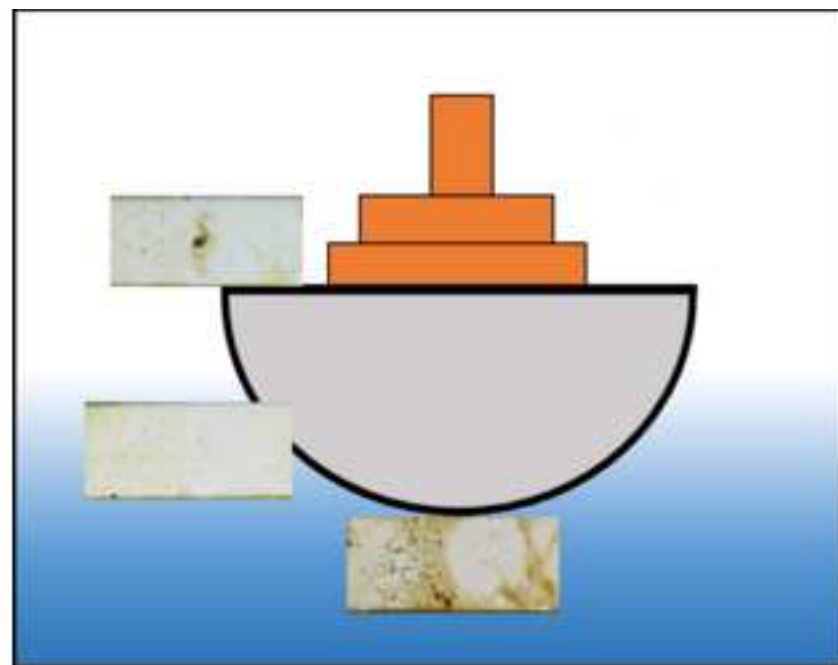
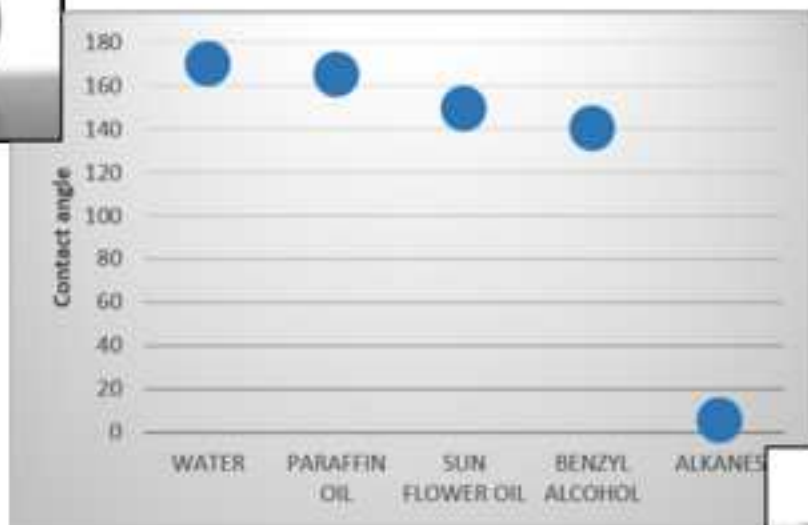
According to reviewers we have taken into account all the comments integrating them into the text as attached and the text was revised accordingly.

We add an image as a support information as requested by a reviewer.

With kind regards

Michele Ferrari

### Paraffin oil



### Alkanes



## HIGHLIGHTS

- Easy preparation and application of amphiphobic coating for marine environment
- Wearing and temperature resistance for longer term application
- Easy removability of early stages biofilm for antifouling

## **AMPHIPHOBIC COATINGS FOR ANTIFOULING IN MARINE ENVIRONMENT**

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## 1. INTRODUCTION

The contact of seawater with materials causes major, undesired chemical-physical alterations like mainly change in surface topography and chemical composition induced by the growth of biological layers at solid-liquid interfaces (the so-called biofouling) holding to corrosion phenomena and drag reduction of vessels. The resulting effects are the enhancement fuel consumption during navigation and material deterioration. These effects regard ship hulls and materials used in other applications like marine sensor, pipelines in power or desalination plants, inducing high maintenance costs regarding different maintenance procedures [1,2].

In this direction, it is important to develop innovative solutions merging technological and ecological aspects taking into account limitations imposed by international laws in terms of environment protection [3–5]. In this respect, superhydrophobic materials applied to marine environment are a relatively young field achieving growing interest [6,7].

A superhydrophobic surface shows extraordinary non-wetting properties due to the simultaneous existence of specific topographical patterns (micro-nano roughness) and low surface energy compounds [8,9]. As a matter of fact, this kind of surfaces exhibit large water contact angle (CA),  $CA > 150^\circ$ , and low sliding angle (SA),  $SA < 5^\circ$ . Water drops easily roll off the surface producing a self-cleaning action [10]: while moving they easily remove dust and dirt particles.

Thus, superhydrophobic surfaces (SHS) can act as a protecting defence against water in different applications such as antifouling coatings, membrane for oil separation, waste-water treatments, optical windows including anti-corrosion [11,12], anti-fouling [13] and drag reduction for ship's hull [14,15], anti-bacteria of medical equipment [16,17] and anti-water condensation and heat transfer [18].

For applications in real seawater, a superhydrophobic coating has to survive long-term exposures to water, sand impact, mechanical scratch/abrasion and fouling growth. The aspect of the fouling growth has been addressed in our previous work, dealing with a facile fabrication of a superhydrophobic surface [19] and its preliminary characterization. In particular, we had investigated the behaviour of the SHS in a real seawater environment and the corrosion behaviour evidencing the evolution within 3 weeks of electrochemical parameters and surface wettability [20,21].

Biofouling is a process consisting in biocolonization of surfaces immersed in natural seawater. Macromolecules adsorb within minutes/hours determining the formation of the so called 'conditioning film' [22]. This layer contributes to further bacteria and diatoms adhesion (days)

constituting the biofilm, followed by the subsequent arrival and colonization of macro organisms (macrofouling) [23,24].

Along with the formation of biological layers, in real seawater environments mechanical wearing like abrasion by suspended particles can be regarded as another possible source of damage occurring on topographical patterns of a SH surface. The integrity of micro–nano textured topography is essential for the presence of air pockets in the Cassie-Baxter non-wetting state [25]. The physical damage of this structure can lead to undesired progressive pinning of water droplets and, eventually, to the loss of superhydrophobicity.

In addition, surfaces are often easily wetted by oily liquids, leading to organic contamination and loss of water repellence. To avoid this problem an oleophobic/superoleophobic surface is preferred [26–28], and, regarded in combination with the superhydrophobicity, as a more suitable solution for a wider use in many fields.

The preparation of surfaces with such behaviour is a wide research topic [29–31], nevertheless, many of these coatings require a too expensive preparation, exhibit very short lifetime and often are limited to small surface, reducing their use for a real employ. Some works are devoted to the durability of these surfaces with different techniques: abrasion by sand paper [32], sand particle impacting [33], continuous drop impact [34] and immersion in solution [35] are referred. Nevertheless, in general, the investigation of surface robustness was limited to a short time (minutes, hours) [31] [36].

This work is devoted to the investigation of a coating for underwater/seawater applications as a possible tool to control biofouling growth and friction drag. The coating was easily prepared by spray allowing the possibility to use it for applications that require frequent maintenance. Characterization was performed by CA measurements, profilometry and water bouncing, laboratory investigations were performed including wettability tests after thermal treatment and wearing tests, in order to emphasize the oleophobic behaviour. Finally, the growth of biofouling growth and its removability has been studied in seawater exposing the samples to the natural photoperiod up to 4 weeks with different angles.

## 2. MATERIALS AND METHODS

### □ Surface preparation and characterization

The surfaces were prepared by a mixed organic-inorganic coating, fluoropolymer blend and fumed silica nanoparticles, as described elsewhere [37]. High purity grade water, produced by a MilliQ (Milli-Pore) ion-exchange purifier with a microfiltration stage, was utilized for the contact angle (CA) measurements. The coating was applied on a glass substrate by spraying a dispersion

of silica particle/fluorinated polymer coating on the substrate. The spray was used at the distance of 5 cm at the pressure of 3 bar.

For the evaluation of wetting properties of the surface, CA measurements were carried out by the ASTRAview tensiometer (developed at CNR–IENI [38]) at room temperature. In order to check the homogeneous deposition of the film data were collected in at least 3 different positions of the surface.

The surface structure of samples was investigated with 3D Confocal and Interferometric Profilometry (Sensofar S-NEOX, Spain) in order to evaluate the roughness. The profilometry was chosen to permit large surfaces scan, such as the samples used in this work and for its ease of use.

The as prepared surface was tested to study its oleophobicity. For this purpose different organic liquids, hexane, paraffin oil, benzyl alcohol, sun flower oil, petroleum and lubricant were used. These solvents were chosen for their different properties such as viscosity or surface tension and as example of a real possible contaminant. In addition, the samples have been studied observing the impact of water bouncing on the SH surface with the use a camera Fujifilm Finepix HS10 (1000 fps). A stainless steel capillary, with a diameter of 0.21 mm, was connected to a syringe to produce water drops of about 5 mm<sup>3</sup> from a height of 25 mm (tip to surface).

The amphiphobic behaviour was tested with thermal treatment and immersion in stirred solution with suspended solids, in order to understand the behaviour in conditions more similar to a real employ.

#### □ Thermal treatment

The thermal test was performed in a furnace in air atmosphere. The temperature was increased at a constant rate of 5°/min up to 200 °C and maintained constant for 60 hours. Successively, the samples were extracted from the furnace and cooled down at room temperature. Furthermore a cyclic test was done. The samples were heated until 200°C for 2 hours, then cooled at T room and repeated for 10 times. The temperature of 200°C [39] was selected in order to avoid the thermal decomposition of the fluoropolymer. This test was also a possible accelerated aging test for application where is required a thermal treatment

The CA was measured on each sample by ASTRAview tensiometer in order to verify possible alterations of the topography induced by the thermal treatment

#### □ Wearing test and durability

In order to evaluate the coating resistance in contact with suspended solids, the samples have been tested with an abrasion test that was set up for this kind of experiment. For this purpose, the test could be assumed as alternative to classical tribologic experiment, being less invasive



for the evaluation of abrasion resistance. This test was performed to simulate an aquatic, aggressive and non-static environment. To obtain this environment, a dispersion of micrometric diatomaceous earth (DE) in deionized water with or without 3,5 wt% NaCl was used. The concentration of DE dispersion (0,5 g/l) was chosen in order to have more suspended particles with respect to a real seawater environment where a water can be defined transparent with a suspended solid concentration of 20 mg/l while turbid when the concentration is over 40 mg/l [40]. Such a dispersion could be regarded as an accelerated, non-destructive aging method. The samples were placed vertically and were immersed for a half in a glass beaker with the dispersion and were monitored constantly. The liquid was maintained to the selected level. The stirring rate was chosen to simulate the continuous contact with fluids containing dispersed solids transported at modest speeds (by natural convection or currents). Two dispersion speeds of 2,5 knots corresponding to «light air» conditions and 3,80 knots corresponding to «light breeze» conditions [41] have been used.

To investigate different aggressive conditions the tests were performed in DE aqueous dispersion with and without NaCl. In the first case was considered the effect of the abrasion itself, separating any other potential influence, in the second case was reproduced a real sweater

Finally, the coverage degree of biofouling was studied immersing the coated samples together to reference plain glass surfaces for one month in a 200 l seawater mesocosm exposed to the natural photoperiod with 3 different angles. The angle of 0° was intended for the sample facing the sun with its SH surface (being parallel to the water surface), 180° facing the bottom of the mesocosm, and 90° in the middle. Pictures of the samples were achieved weekly. The aim of this test was to study the degree of the biofouling coverage in function of the immersion angle. To evaluate the self-cleaning behaviour at the end of each immersion period, the samples were gently extracted from the seawater and half of the fouled surfaces were cleaned with weak water pressure (household manual water sprayer). The collected pictures were used to calculate the percentage of the area not covered by the biofouling. The analysis was done by working on the contrast between the SH zones (contact angle measurements) and the no more SH zones. According to the adjustment of various filters a 'binary image was obtained, the histogram was calculated and from it, based on the number of white or blacks pixels, the percentage of the total area still SH was acquired. The analysis was performed using the ImageJ software (National Institutes of Health, Bethesda, Maryland, USA) [Rasband, W.S. (1997–2008) ImageJ. US National Institutes of Health, Bethesda].

#### □ Exposure environments

Immersion tests were held during summer 2015 in the MARECO CNR-IENI sea marine station in Bonassola (44°11'0.37"N, 9°35'2.73"E, Italy, Mediterranean Sea), a small village close to Cinque Terre (UNESCO human world heritage), far from pollution sources by harbours and heavy anthropic activities. The period of choice has been summertime in order to test the samples under the highest biological activity. The natural seawater mesocosm where samples were immersed are the same described in [19]. The main features are resumed as follows: the seawater renewal rate was 5 l/min rate, the environmental parameters monitored at a rate of 0.1 Hz in the tanks were the photosynthetic active radiation (PAR,  $\mu\text{E m}^{-2} \text{s}^{-1}$ ), bulk seawater temperature (T, °C) and the dissolved oxygen concentration (DO,  $\text{mg L}^{-1}$ ).

### 3. RESULTS and DISCUSSION

- Surface characterization

CA measurements were performed before and after heating, wearing and field tests. Before the treatments, the silica particle/fluorinated polymer coating resulted in  $\text{CA}=170^\circ$ , with hysteresis  $<5^\circ$ .

3D Confocal and Interferometric profilometry was performed on the surface in order to characterize the roughness before and after each test. These measurements revealed a topography based on two roughness scales accounting for the superhydrophobic behaviour of the SH surface: a primary rough structure of 100-200 nm coupled with a second finer one of 50 nm (medium value). On the same sample, drop impact experiment was performed as well. The data showed a number of bounces equal or slightly larger than 10. These data are in agreement with the study performed by Colin R. [42] and suggest that the superhydrophobicity of the prepared surface depends on two-scale roughness coupled with the chemical composition.

In addition, the impact experiment could be an interesting and indirect method to evaluate the microstructure of the sample. From these preliminary bouncing results, it was possible to observe that the SHS produced a substantial friction reduction, a key feature for reducing fuel consumption during navigation.

As a result of these tests, it was decided to study this SH surface in more critical conditions and real environments. The surface was therefore investigated paying attention on oleophobicity, wearing, temperature resistance and biofouling growth, in consideration of possible industrial application.

- Oleophobicity

The surface with different organic liquids was tested. The acquired data are reported in table 1. It was evident that for paraffin oil the surface was superoleophobic and for sunflower oil and benzyl alcohol was highly oleophobic, while hexane, petroleum and lubricant completely wetted the surface. In particular, it was interesting to observe that even organic liquids completely wetting the surface can easily be removed by a weak water pressure leaving the surface still superhydrophobic with a kind of self-cleaning properties. In these cases, the observation of the coating at profilometer after organic liquid deposition has showed that the roughness was not altered by the organic liquids. This result suggest to that the organic liquid wetting the surface do not adsorbe on the coating and appears to be insoluble to these organic liquids. The highly repellence to such different liquids supports a potential use for amphiphobic applications.

- Thermal treatment

The coating was went to under two different thermal treatments. The first was heating the sample in a furnace for 60 hours at 200°C consecutivly in order to investigate its wetting behaviour after long thermal treatment, the other was a cyclic test where the samples were heated at 200°C for 2 hour and cooled repeating 10 times to study the resistance to thermal stress. CA was measured each time after cooling. It resulted that the surface remains amphiphobic until 200°C in both tests. Roughness measurements also showed that treatment did not alter this property.

This result suggests that for real applications the impact of high temperatures does not represent a threat. In particular, this could be of interest as aging test for application like desalinization plants, where T does not typically overcome 110°C [43].

- Investigation in simulated and real seawater environments

- Wearing resistance

Aim of this investigation was to verify the abrasive effect of suspended particles as a potential effect on wettability property, considering that diatoms size is on the order of  $\mu\text{m}$ .

Resistance to abrasion of the coating was tested in a simulated environment with micrometric siliceous water dispersion (diatomaceous earth) with or without salt under continuous stirring. The coating was tested in both solutions. After the test in each dispersion for two time windows and two speed, the immersed part of the sample was still superhydrophobic ( $CA > 170^\circ$ ) and oleophobic. In particular, the roughness of the immersed and not immersed parts were not distinguishable basing on the profilometry investigation (Fig. 1).

At present, relating to suspended particles only, the coating was able to preserve its amphiphobicity after a continuous exposition to the abrasive agent. Furthermore, after these preliminary results the coating shows resistance also in a salted abrasive dispersion. These findings forecast possible applications of this coating on surfaces continuously exposed to water flow containing dispersed solids like in pipelines for fluids transport.

– In field test

The influence of immersion angle on the fouling growth and the removability of biological colonization was investigated immersing samples in a natural seawater mesocosm during summer 2015. The environmental parameters of the tanks resembled values reported in [19], being the same mesocosm, in the same season, in the same place. The samples were prepared spraying the amphiphobic dispersion on not yet dried undercoat, as suggested in [19], where relatively better performances were obtained in terms of biocolonization retard vs. application of SH spray on dried undercoat. Immersion periods were 7, 14 and 28 days at 0° (facing the sunlight), 90°, and 180° (facing the bottom of the mesocosm) with respect to the water surface (Fig. 2). The aim of this test was to simulate the different inclinations on a ship hull during early stages (few weeks) of immersion. As a first outlook, it was decided to restrict the temporal window within weeks timeframe since initial stages of biofouling formation were demonstrated to exert important effects [20].

After 28 days of immersion, a soft and thin fouling layer was grown on all coated samples (Fig. 3). It is worth noting the significant fouling coverage area on the plain reference surface, we report (Fig.4) the comparison between immersed samples at 28 days at 90° representing the most fouled situation as shown in Fig.5. The presence of the coating seems to be a delay factor for the early stages of the biofilm formation. Half of the coated surface was then washed in order to macroscopically estimate the cleaning degree, and, on the washed part water CA was measured.

The CA data are reported in table 2. It is possible to observe that the samples remained superhydrophobic until 14 days when immersed at 0° and 90°. Differently, when immersed at 180°, they remained superhydrophobic until 4 weeks. The data are reported as a range since the surfaces after the tests were locally not homogeneous. The data regarding the percentage of not fouled area after 28 days as a function of immersion angles were obtained using the software ImageJ and are reported in Fig. 5. The figure shows 2 curves, one (dashed line) is the not fouled surface on not washed part, the other (continuous line) is the clean area on washed part.

It has to be specified that for inclinations of 0° and 90°, the homogeneous fouling coverage allowed the cleaned fraction of washed surface to be evaluated. For the sample exposed at

180°, large parts of the immersed area were not covered even after 28 days. As consequence, the graph presented in Fig. 5, including data referring to all the angles, should be interpreted as the capacity of the SH coating to actually inhibit the biofouling colonization.

It was evident that after 4 week of immersion the angle providing the best resistance against the fouling growth was 180°. At this inclination angle the coating presented large areas still not colonized and still superhydrophobic, while for the other 2 angles colonization appeared extended and it was  $CA < 150^\circ$  (only some sporadic points were SH). These results are in agreement with previous study about air trapping in SHS [41]. To support this result, laboratory test with induced bubble confirm that at 180° the air plastron remain trapped under the surface respect to the 90° tilt position where the bubble coalescence is significantly reduced because the induced bubble were collected at the sample border. (See Support Information)

As a matter of fact, on samples exposed with 0° and 90° orientations, clean areas corresponding to the presence of air bubbles were much more modest.

Regarding the investigation in simulated and real sea water we can observe that depending only on the environment after 4 weeks of immersion the samples had different behaviour. After 4 weeks of continuous DE impact in the lab test the coated sample remains SH, while the immersed samples in a real sea water lost (on the majority of the sample area) the superhydrophobicity after 2 weeks not as a consequence of abrasion but probably because the adsorption of material. This phenomenon could be explained by the adsorption of biological materials released by Diatoms during their settlement [20] (Fig. 6).

#### 4. CONCLUSIONS

The amphiphobic properties of a mixed organic-inorganic coating have been investigated in this work. The highly water repellence was maintained under different stress conditions and different environments and also the oleophobic/superoleophobic character results in a promising feature for marine applications for its easy preparation. For these reasons, the work has been carried out both in lab and real seawater environment, which represents a complex and challenging system.

The coating tested with various organic liquids has shown that the surface had a oleophobic/superoleophobic behaviour with most of the liquids and kept the superhydrophobic character after removal of the more wetting liquids.

Non-destructive wearing tests simulating the effect of concentrated suspended solids dispersion at different speeds result in a not altered surface roughness maintaining the amphiphobic character.

Long and short time cyclic thermal treatment do not affect the coating properties suggesting a potential application in plants under constant or periodic heating conditions.

When the samples were studied in natural seawater mesocosm they had a different behaviour against biofouling growth as a function of the sample tilting simulating potential different orientation of an immersed surface. The spontaneous biological pressure over SH coating performance is important within weeks. In particular, we emphasized that SH surface modification by biological processes was delayed by exposition angle with SH surface facing parallel the bottom.

In case of naval applications further investigations in natural seawater to achieve knowledge and extend SH lifetime are necessary and still needed.

Further investigations should improve the coating durability over longer time observations in order to provide a more reliable system in case of surfaces, which can undergo to shorter time maintenance.

In seawater applications where the biological impact is relatively less aggressive or controlled (e.g. in power or distillation plants), features like oleophobicity, thermal and mechanical resistance of the investigated coating represent encouraging premises for applications exploiting seawater in pipelines.

In the framework of a collaboration with CNR Institute for Marine Sciences in Genova [20], experiments are ongoing in Genova harbour seawater, considerable as a quite heavy polluted area of reference.

### **Acknowledgements**

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## Figure captions

**Fig. 1.** 3D profilometer image of a SH coating (scanning area of 2.3 mm<sup>2</sup>) and its profile after 40 days of immersion. The left side of the image respect the red line is the immersed part of the sample.

**Fig. 2.** Schematic representation of the samples arrangement in the seawater mesocosm exposed to the natural photoperiod. The grey part is the SHS.

**Fig. 3.** Coated samples after 28 days of immersion on which was applied the SH coating on not completely dry undercoat paint. For all the clean part is on the right.

**Fig . 4.** Comparison between plain (a) and coated (b) surface at 90° after 28 days of immersion

**Fig. 5.** Graph of trend of the % of area not covered by macrofouling as a function of the exposure angle. 0°, 90°, 180° are the degree of tilt of the SH surface respect the water surface, with 180° the angle facing the bottom of the mesocosm (■ washed; ● not washed).

**Fig. 6.** SEM image (2500 X) about diatoms settlement phenomena on coated sample immersed in natural seawater.

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## Tables

	Contact angle
Paraffin oil	165°
Sun flower oil	149°
Benzyl alcohol	140°
Hexane	5°
Petroleum	<5°
Lubricant	<5°

Table 1. Contact angles with selected organic liquids.

Tilt Days	0°	180°	90°
7	>160°	>160°	>160°
14	>160°	>160°	>160°
28	40°< $\theta$ <60°	>160°	70°< $\theta$ <80°

Table 2. Behaviour of the surfaces as a function of tilt angle and days of immersion.

Figure1

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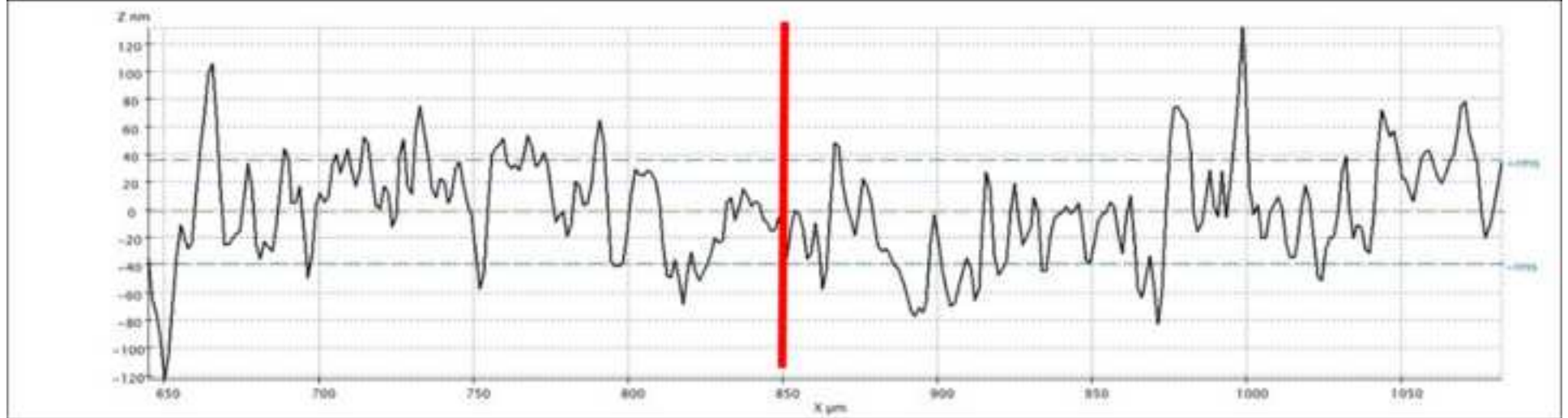
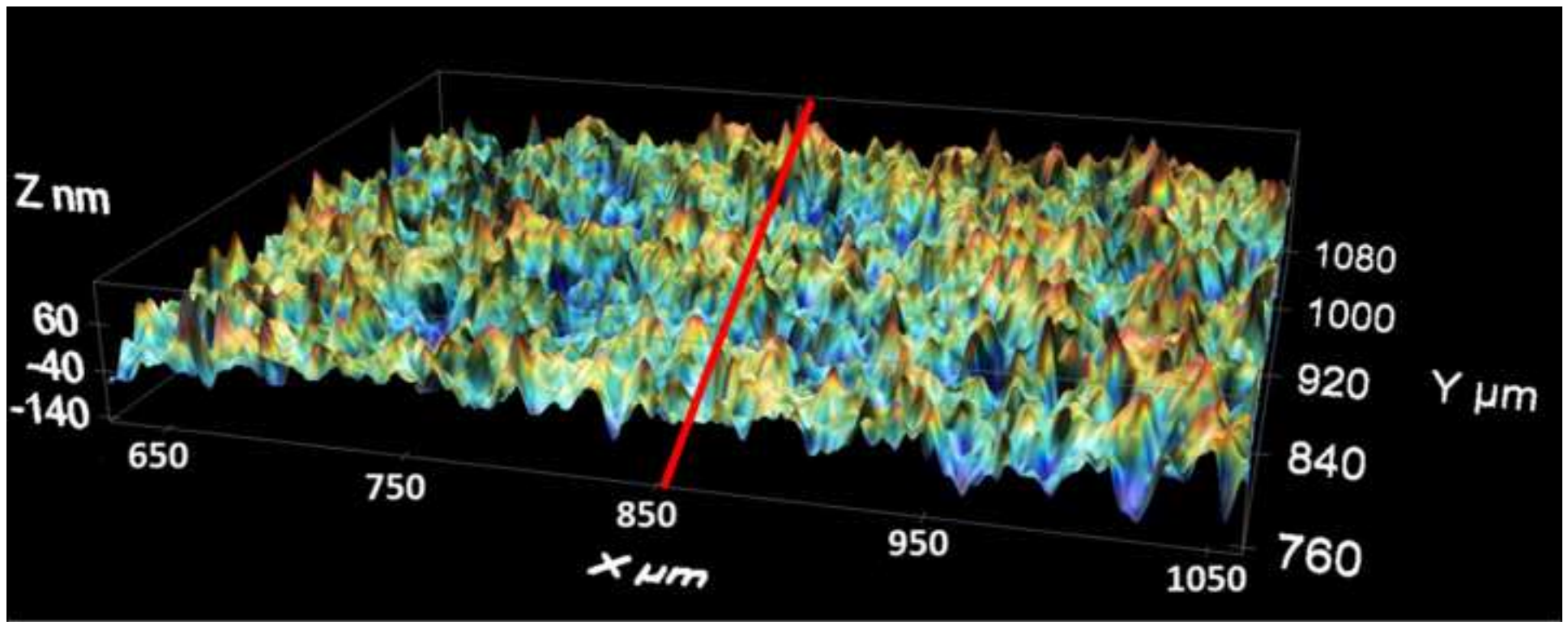


Figure2  
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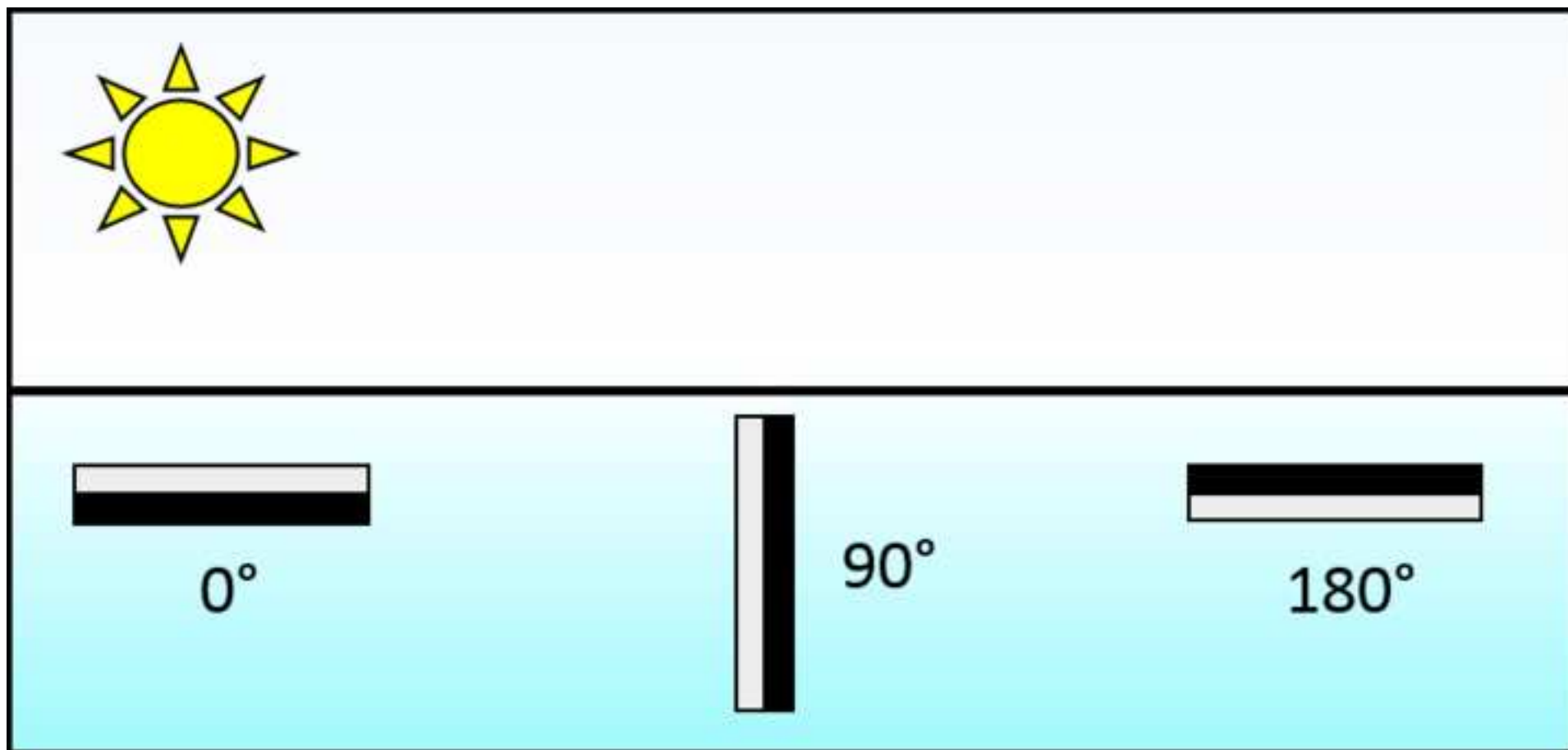


Figure3

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**0° 28 days**



**90° 28 days**



**180° 28 days**

Figure4

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**a)**



**b)**

Figure5  
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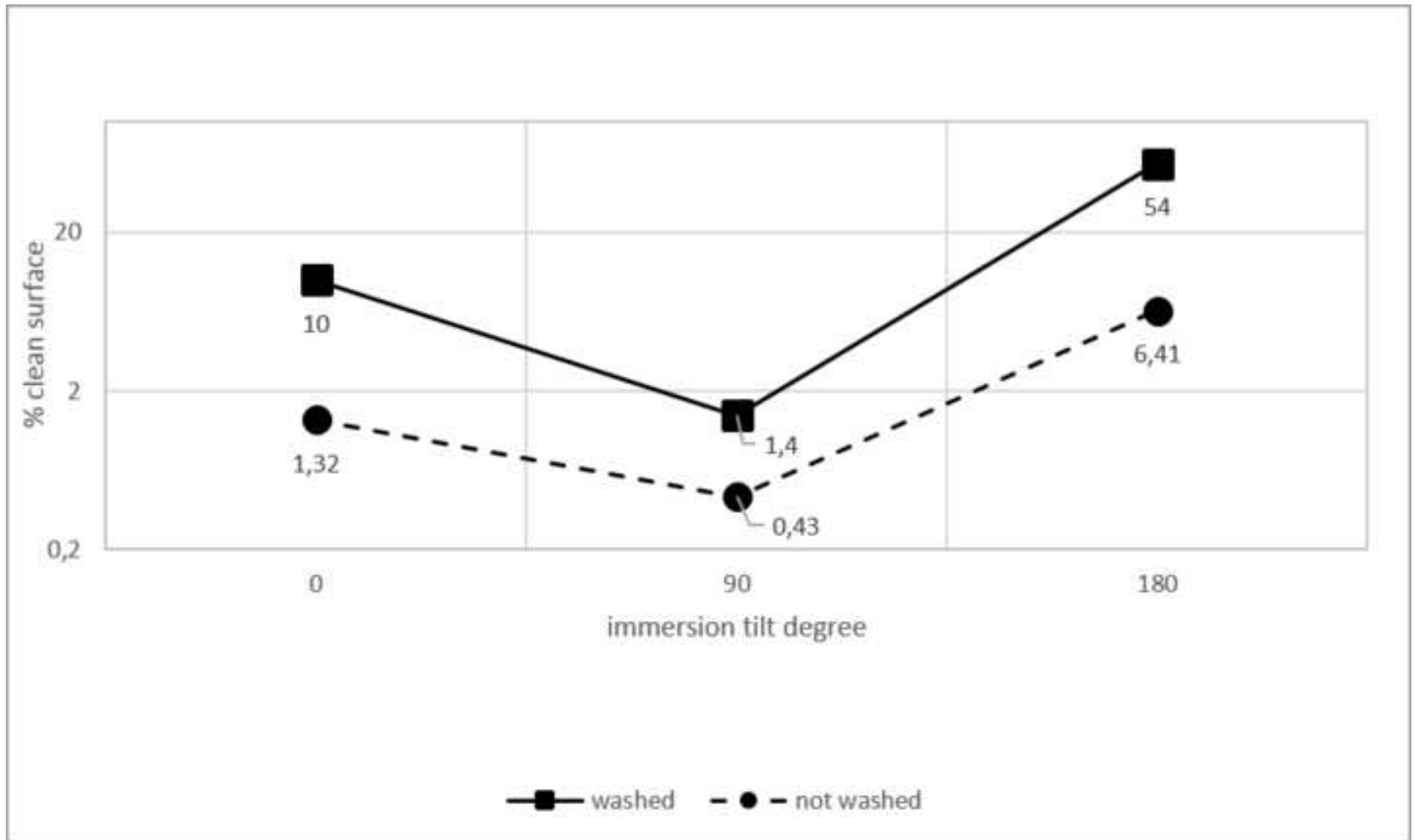
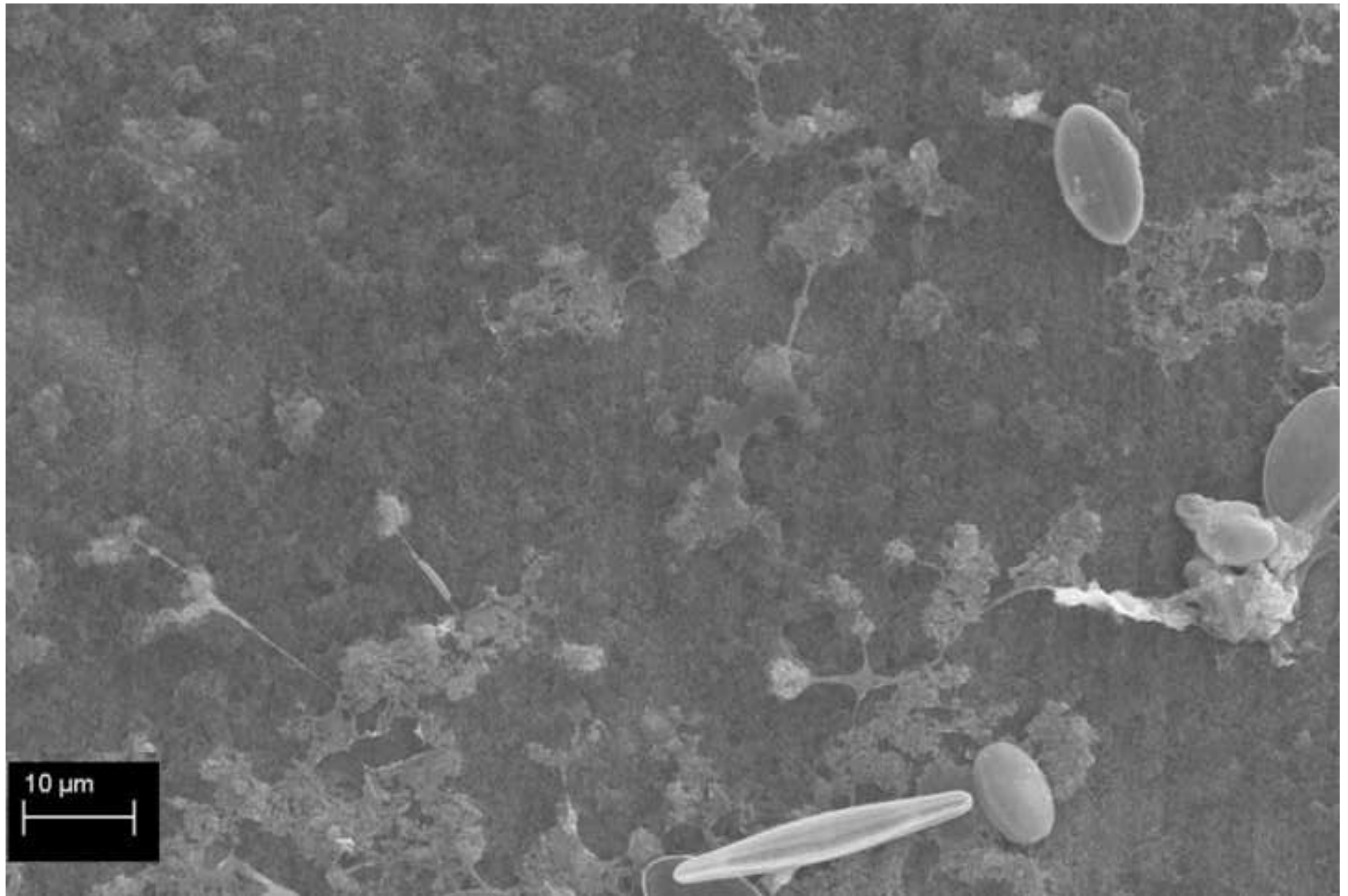




Figure6  
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**Supplementary Material**

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## **AMPHIPHOBIC COATINGS FOR ANTIFOULING IN MARINE ENVIRONMENT**

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### **ABSTRACT**

Highly hydro and oleophobic materials applied to needs of the marine environment represent a relatively young field achieving growing interest as innovative solution, where technological and ecological aspects allow to be merged, taking into account the limitations imposed by international laws in terms of environmental protection.

In this work a superhydrophobic (SH) coating for seawater applications has been characterized and tested in both laboratory and field conditions, since investigations in real seawater are crucial to evaluate the behaviour of SH surfaces because of a complexity not reproducible in laboratory. Taking into account the real conditions where the surface can operate oleophobicity can be investigated in presence of organic and inorganic pollution. The amphiphobic surface has been also studied to simulate those applications where the surface undergoes to thermal stress like pipelines and desalination plants affected by biofouling.

The preliminary wearing test shows the effective resistance to a continuous low velocity impact of micrometric particles of the coating investigated here.

Finally, time durability in field tests has been studied as a function of immersion angle in real seawater environment to investigate the role of the coating on early stages of biofilm growth.