(BIO)FOULING AND ANTIFOULING MEASURES

Biofouling and antifouling: new approaches to the development of sustainable protection technologies

The development of antifouling systems has a long history but the last decade has seen an increase in the focus on environmentally acceptable alternatives. This paper highlights the latest research strategies dedicated to the development of new non-toxic antifouling technologies

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Biofouling as a technological problem

Biological fouling, usually termed biofouling, can be defined as the undesirable accumulation of micro- and macro-organisms on artificial surfaces immersed in water.

Biofouling has been described as a four-step sequential ecological process. The first two steps, which produce a microbial biofilm, occur similarly whether on a surface in the sea or on a catheter in a hospital room. The following two steps are unique to aquatic habitats and involve the attachment of unicellular and multicellular eukaryotes to an inorganic or living surface. The multi-step process results from the web of interactions in the initial biofilm and subsequent community of colonizers, culminating in the establishment of a mature community composed of prokaryotes, fungi, protists and adult invertebrates.

Biofouling assemblages on artificial substrates are a complex phenomenon resulting from several processes, the rate and extent of which are influenced by numerous physical, chemical and biological factors in the immediate proximity of the surface, and cannot be defined as distinct and univocal entities (Figure 1).

From the initial adsorption of organic molecules, to the colonisation by microorganisms, to the development of complex and diverse sessile assemblages, biofouling affects most man-made surfaces, resulting in significant economic costs.

Fouled ships, for instance, need 40% more fuel in order to maintain the same speed. This leads to a global cost of about $ 7.5 billion per year and to related environmental issues due to 20 million tons of CO_2 more, that are emitted annually. The US Office of Naval Research estimated that the periodically cleaning and restoring of ship hulls cost to the US Navy about $1000 million per year [2].

The costs of biofouling are clearly not limited to ship hulls nor to the marine environment. Control of fouling in water intakes, piping systems and desalinisations plants (Figure 2) cost over $15 billion per year [3]. In food industry, the formation of fouling layer within food processing equipment for pasteurization and sterilization costs to the US industrial community about $10 billion per year [4]. Biofilm-associated infections extend hospital stays of an average of about three days and it is estimated that up to 65% of nosocomial infections are biofilm-based

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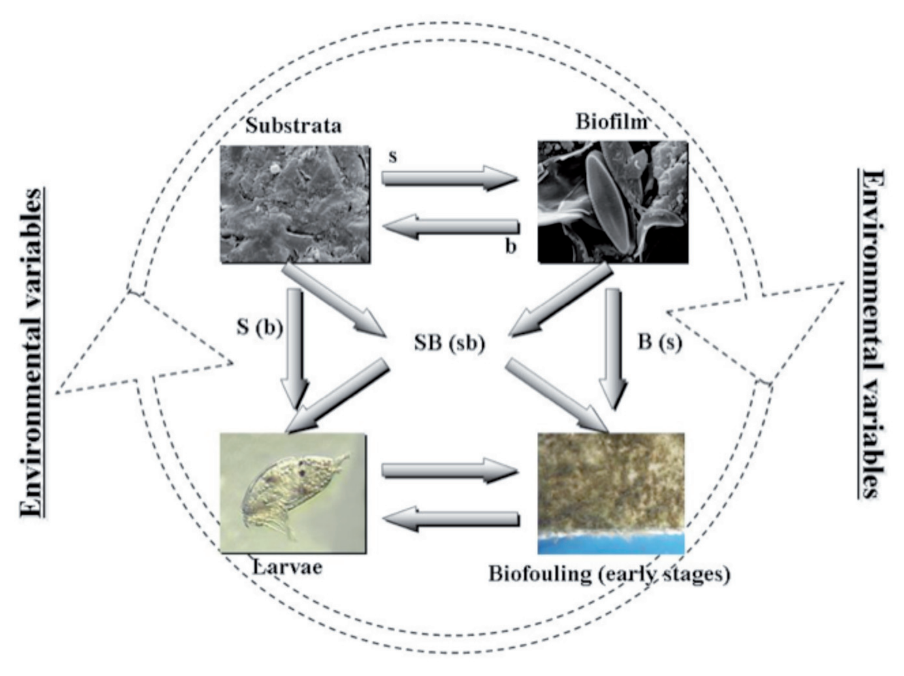

FIGURE 1 Preliminary model of interactions between larvae, biofilm and substratum during settlement process. The role of subtratum and biofilm on settlement S, B is indirectly modulated by their mutual relationships (s, b). In natural conditions, these interactions can be changed by other chemical, physical and biological (environmental) variables [1]

with an associated treatment cost in excess of $1 billion per year. Up to 82% of nosocomial bacteremias are the result of bacterial contamination of intravascular catheterizations [5]. AF technologies are necessary in order to avoid the colonisation of surfaces by biofoulers and consequently the high costs relative to transport delays, hull repairs, cleaning of desalination units and biocorrosion (estimated at 150 billion USD per year) [6].

Biocide-based antifouling coatings: the past

During the ‘60s, the chemical industry developed efficient AF paints using organotin compounds as biocides: tributyltin (TBT) and triphenyltin (TPT). During the late 1970s, the AF research and development efforts were mainly focused on the successful TBT-based, self-polishing, copolymer systems. Unfortunately, these biocides were highly toxic for many aquatic organisms

FIGURE 2 Biofouling colonization residual inside cooling water system [1]

FIGURE 3 The hull of a ship protected with biocide-based antifouling coatings *(Photo of M. Faimali)*

and have been proven to contaminate the food chain and to be persistent in the environment.

TBT has been described as one of the most dangerous substances ever deliberately introduced into the marine environment. As a consequence of different environmental diseases observed by researchers between the late ‘70s and the beginning of the ‘80s, the use of self-polishing coatings containing organotins compounds has been restricted by European Community since December, 1989. The total ban on the presence of TBT-based antifoulings on ships hulls in EU ports came into effect on 1st January, 2008. As a consequence of the ban, in the last few decades a great deal of attention has been devoted to find alternative antifouling technologies [7].

Following the ban of TBT-based products in AF paints, alternatives containing high amounts of copper (Cu)-based compounds were developed. As it is about ten times less toxic than TBT, cobiocides, also called boosters, were used to enhance the AF performance of copper-based coatings [8].

All these compounds vary in terms of their mode of action, environmental persistence, and toxicological properties. Several reviews have been published presenting an overview of the biocides used in AF paints and their specific fate and effects in the environment [9,10-14].

As a consequence of the growing investigations on its toxicity, the release rate of Cu-based soluble species from AF paints has been regulated in several areas, for example, Sweden and the U.S. States of Washington and California [7].

Copper and many of the so-called “booster biocides” have come under increasing scrutiny and local legislation and restriction in as much as the same way and to the same degree than TBT did.

The key property of a good AF biocide with respect to the environment is that it is effective in preventing fouling of the painted surface without persisting at concentrations greater than those that can cause detrimental environmental effects [12].

In order to identify potential candidates able to possess these characteristics in recent years, using a biomimetic approach, the possibility of exploiting marine natural product antifoulants (NPAs) utilized by marine organisms (e.g., sponges, corals, and macroalgae) to prevent them from colonization by other marine organisms has been investigated [15-17].

To date, purification of active products has yielded ca. 200 molecules with some degree of AF activity against a wide range of marine fouling organisms, assayed mainly through laboratory tests [17].

The challenge of finding a natural product which fulfills the required criteria of low toxicity, broad spectrum activity, and ease of production has yet to be realized, and is the main reason why they have not been so far successfully commercialized.

Also the idea of using enzymes, catalytically active proteins omnipresent in nature, for developing new enzyme-based coatings has received increased interest in recent years [18,19].

Enzymes can degrade the fouling organism or its bio-adhesive, or produce other biocidal compounds. Direct enzymatic AF covers the application of "biocidal" or adhesive-degrading enzymes, whereas indirect enzymatic AF is based on enzymatic generation of biocides from substrates present in the seawater or coating-ingredients [20]. In several cases, concepts as well as short-term AF activity in coatings have been proven, but long-term efficiency toward all fouling organisms remains to be reported.

Changes of strategy in the development of antifouling technologies

Furthermore, the definitive failure of the "chemically active strategy" in Europe has been catalyzed by the fact that the predisposition of biocidal compounds (synthetic and/or natural origin) to cause environmental adverse effects has received in recent years, a greater attention, and biocide containing AF paints are currently regulated and require approval.

In the European Union and its member states, the EU Biocidal Products Directive (BPD) regulates all biocide products that are placed on the market. The BPD sets the stage for all businesses selling biocidal products, and each of these businesses will have to deal with the BPD's requirements for documentation. From 1st September, 2013, the Biocidal Products Regulation (BPR) will replace the BPD and henceforth regulate all biocidal products in the European Union. The BPR will introduce new procedures for all EU countries and authorities now require testing of new active substance prior to marketing authorization [21].

The total costs have to be taken into account, for example, not only by preparing agreed protocols and placing studies but also by monitoring studies, analysis of the results, risk assessments based on exposure scenarios, dossier preparation, registration costs, task force participations, legal fees, etc., as well as management activities of the directive and associated registration.

For the development of new biocides, the estimated costs are as follows: toxicity studies on active substances: € 1–3M, environmental studies & ecotoxicity: € 0.6–4M, formulation studies: > € 1M, risk assessments/ exposure scenarios expertise needed > € 1M, dossier preparation: € 0.1–0.25M, registration fees: € 0.1–0.2M, task forces: € 0.05–0.2M [22].

The very high costs and long times for the registration process almost totally limit the development of new biocides, regardless of their potential AF efficacy and environmental compatibility.

The awakening of the global environmental awareness in the form of legislative measures has completely changed the way AF research is conducted nowadays.

Author(s) [Ref]	Title	Year
Yebra, DM; Kiil, S; Dam-Johansen, K [23]	Antifouling technology – past, present and future steps towards efficient and environmentally friendly antifouling coatings	2004
Chambers LD et al. [24]	Modern approaches to marine antifouling coatings	2006
Almeida, E, Diamantino, TC, De Sousa, O [25]	Marine paints: The particular case of antifouling paints	2007
Maréchal JP, Hellio C [22]	Challenges for the development of new non-toxic antifouling solutions	2009
Grozea, CM, Walker, GC [26]	Approaches in designing non-toxic polymer surfaces to deter marine biofouling	2009
Magin CM, Cooper SP, Brennan AB [27]	Non-toxic antifouling strategies	2010
Cao S et al. [28]	Progress of marine biofouling and antifouling technologies	2011
Callow JA, Callow ME [29]	Trends in the development of environmentally friendly fouling-resistant marine coatings	2011
Kirschner CM, Brennan AB [30]	Bio-Inspired Antifouling Strategies	2012
Lejars M, Margaillan A, Bressy C [7]	Fouling Release Coatings: A Nontoxic Alternative to Biocidal Antifouling Coatings	2012

TABLE 1 Selection of scientific papers related to the new trends of antifouling technology

An overview of the main papers that in recent years have addressed the changes in the strategy of research in the field of antifouling technologies are summarized in Table 1.

Non-toxic antifouling coatings: the future

Within the context of worldwide pressure for legislation limiting the use of biocides, and ever-increasing fuel prices, there is now a real need for the continuous development of new non-toxic AF formulations and an interesting and promising line of research is inspired by biomimetic solutions.

Nature provides examples of antifouling surfaces that emphasize the importance of both chemical and physical concepts. Physical cues, such as surface roughness and fluid hydrodynamics, can act singularly or in concert with surface chemistry to enhance or inhibit the attachment of organisms to a surface. Chemical cues, especially surface energy, influence not only the ability of an organism to initially attach to a surface, but also the degree of fouling-release from the surface once adhesion has been established.

They are many examples from natural fouling-resistant organisms, which can serve as a basis for new scientific investigations but two general (non-exclusive) strategies are typically followed in the design of novel, non-biocidal, non-fouling surfaces and are now considered to be the most promising environmentally-friendly, antifouling technology [23].

- *Engineered Microtopographical Surfaces,* in which the objective is to deter the recruitment stages of fouling organisms from attaching in the first place.
- *Fouling Release Coatings (FRC)*, which do not prevent organisms from attaching, but the interfacial bond is weakened so that attached organisms are more easily removed by the hydrodynamic shear forces.

These two general approaches are not mutually exclusive and in fact the distinction is overly simplistic. In both cases the objective is to achieve the desired re-

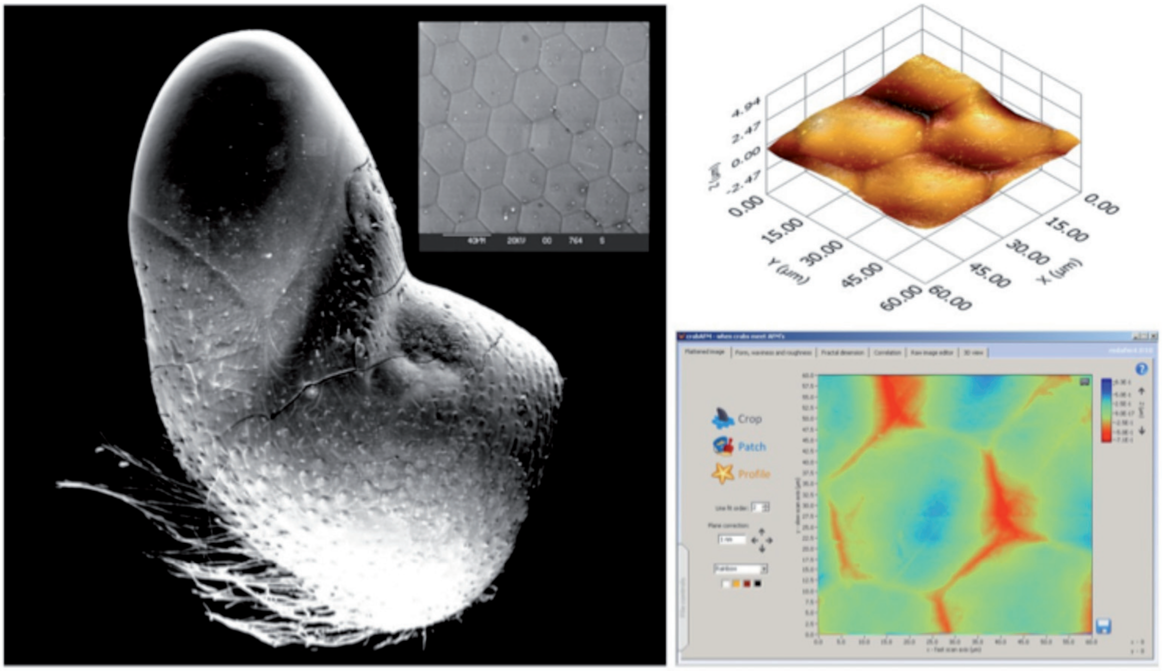

FIGURE 4 Microtopography of the eye surface of the crab Carcinus maenas
Source: SEM image and elaboration: G. Greco - ISMAR-CNR, [30])

sult through the manipulation of the physicochemical properties of coating materials (for example, elastic modulus, frictional coefficient) [29].

Some of the most promising strategies that define a new era of antifouling technology have been inspired by nature and can be summarized in two main approaches [31]:

- *Bio-inspired chemical/physical strategies:* antifouling surface material and topography inspired by natural antifouling surface (eg., shells of mollusks and crabs and skin of marine mammals and sharks).
- *Bio-inspired stimuli-responsive strategies:* surface self-cleaning mechanism inspired by the skin of marine mammals and fishes that have the capability to respond to stimuli in the environment.

At this point, no single technology has been demonstrated to be universally effective and one way forward will be to design 'multifunctional smart coatings' combining chemical, physical, and stimuli-responsive strategies in order to develop the best non-toxic antifouling solutions. ●

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