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Hellio (2010) J. Sci. Hal. Aquat., **2**:35-41

Research paper

The potential of marine biotechnology for the development of new antifouling solutions

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Received 19/03/2010; accepted 22/03/2010; published on-line 26/03/2010
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Abstract

Biofouling is the undesirable colonisation of man-made surfaces by microorganisms, macroalgae and invertebrates, leading to subsequent biodeterioration costing the shipping industry millions of Euros every year worldwide. Since the ban of TBT-based paints due to high level of toxicity, new environmentally friendly formulations are under development. Many research teams focus now on a promising line of research inspired by biomimetic solutions and marine biotechnology: marine natural antifoulants and microtexturing of surfaces.

Keywords: antifouling; biomimetism; environment; marine biotechnology.

Résumé

Le biofouling est défini comme la colonisation (par des micro-organismes, algues et invertébrés) non désirée des surfaces immergées, résultant en la bio-détérioration du substrat. Ce phénomène biologique naturel et récurrent coûte des millions d’euros chaque année à l’industrie maritime. Depuis l’interdiction du TBT en raison d’une forte toxicité envers les organismes non-cibles, de nouvelles formulations plus respectueuses de l’environnement sont recherchées. Des solutions à ce problème pourraient être trouvées en faisant appel aux stratégies développées par les organismes marins fixes et/ou dépourvus de défenses physiques. Ces processus sont actuellement étudiés dans le but d’élaborer de nouveaux procédés utilisables pour la protection des surfaces immergées et non nocives pour l’environnement. Deux axes majeurs de recherches sont aujourd’hui en cours d’investigation: les molécules bioactives et les études topographiques.

Mots clefs: antifouling; bio-mimétisme; environnement; marine biotechnologie.

1. Biofouling: a definition

Biofouling is the undesirable colonisation of man-made surfaces by microorganisms (bacteria, fungi, yeasts, and microalgae), macroalgae and invertebrates, leading to subsequent biodeterioration. In the marine environment, this bioprocess affects surfaces such as pipes, water intake systems, desalination devises, probes and sensors, ship’s hulls, building materials and filters (Hellio & Yebra, 2009).

Marine biofoulers are divided into three groups: primary, secondary and tertiary colonizers (Fig. 1).

Primary colonizers are microorganisms (mainly bacteria and microalgae) which will settle first on the surface. They can be considered as pioneering organisms and will be found on unprotected surfaces after less than few hours immersion. These organisms have been linked to biocorrosion which is a result of synergistic interactions, between the metal surface, abiotic corrosion products, and microbial cells and their metabolites (Beech and Sunner, 2004). The latter include organic and inorganic acids and volatile compounds, such as ammonia and hydrogen sulfide. Severe biocorrosion can lead to stress corrosion cracking and/or pitting corrosion, especially with the ballast tanks being viewed as a critical area of potential weakness. In that case, the biofilm and its associate biocorrosive compounds represent a severe health and safety hazard for immersed structures. Moreover, microfoulers have been proven to be responsible for 1-2 % augmentation in ships hulls frictional drag resulting in fuel penalty and augmentation of gas emission (Schultz, 2007).

Secondary macrofoulers comprises protozoa and spores of macroalgae, and, will account for an frictional drag increase of up to 10 % (Schultz, 2007). Significant technical and environmental damages of man-made structures are linked to algal fouling. Algal development on structures such as aquaculture nets, buoys and marine blazes can result in such a weight increase that they can consequently sink (Lebret *et al*., 2009). Algal fouling on hulls is very abundant because ships move between different areas with different biological, physical and chemical properties and are always in the photic zone (Chambers *et al*., 2006). The algal biomass develops mostly in well-aerated areas such as stem, waterline, propeller and rudder blade. Algal fouling on ships hulls and ballast waters has been linked to the introduction of new species which can potentially become invasive (Gollasch, 2006).

Tertiary colonisers are hard macrofoulers which will settle on unprotected man-made surfaces after 2-3 weeks immersiom. A great variety of organisms have been observed on surfaces the main ones being, mussels, tubeworms and bryozoans. Their presence will lead to a dramatic increase of frictional drag up to 40 % increase and in some cases to the damage of ships hulls.

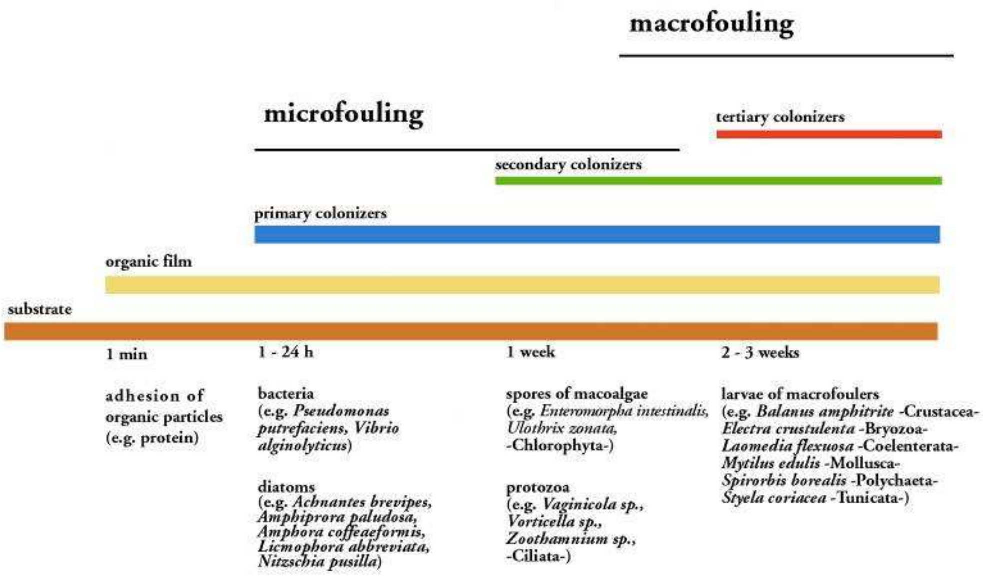

Figure 1. *Simplified temporal structure of biofouling settlement (adapted from Yebra et al., (2004)).*

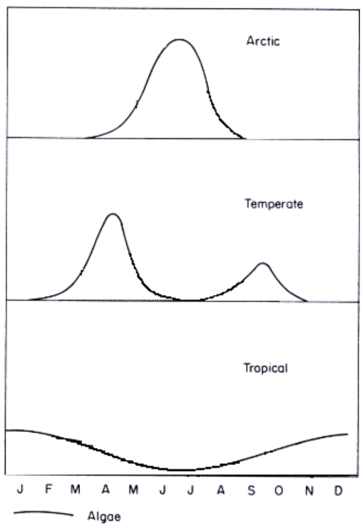

Figure 2. *Representation of algal density cycle in three different systems: Arctic, Temperate, and Tropical (Adapted from Cushing (1975)).*

The biodiversity of biofoulers varies according to the environmental conditions (light, nutrients, temperature, salinity, flow rates) and the geographical location. Tropical and sub-tropical areas are subjected to minor variation of water temperature and levels of lights and thus will face a high pressure of fouling due to the continuous reproduction period of macroalage and invertebrates. At the opposite, temperate and cold areas will face seasonal fouling pressure with a peak during spring/summertime when temperature and light levels are at their maximum values (Fig. 2).

2. Detrimental effects of biofouling

Fouling costs the shipping industry millions of euros every year worldwide due to vessels being out of service in order to have fouling removed, costly repairs and man hours lost. The first obvious effect is the increase frictional drag, thus slowing down the vessel in the water and leading to increased fuel consumption to maintain the same speed. Additionally, engine equipment must labour harder, increasing wear, stress and fatigue. These adverse effects will be significantly increase when the ships route is via tropical/sub-tropical zones and lead to significant increase in the cost of maritime transportation, which in terms of tonnage as it handles about 90 % of the global exchange of goods (Rodrigue, 2006). The major trading routes are going via tropical and/or sub-tropical areas (Fig. 3) and consequently ships will face at some point of their voyage some very high fouling pressure.

***Figure 3**. Major international maritime trading routes.*

Another detrimental effect of biofouling on ship's hulls is the increased emissions of gas (CO_2, CO, SO_2 and NOx) into the atmosphere correlated with the augmentation of fuel consumption. Considering that at a given time most vessels are relatively near shore, this implies that consequently the principal amount of gas emitted is along the coastline mainly in the Northern Hemisphere, along the West and East coast of the United States, in Northern Europe and in the North Pacific (Rodrigue, 2006).

Another significant environmental damage which is linked to the colonisation of man-made surfaces is the species translocation from a geographical zone to another one during the ship voyage either falling off naturally in a new habitat or after the cleaning of the ship's hulls (Minchin & Gollasch, 2003). For example, Williams & Smith (2007) estimated that 277 species of algae have been introduced in new environment with a total of 408 introductions. Among these, only 60 % of the introduction vectors are known and 77 species were reported to be introduced by ship hull transport. Marine macroalgae are a significant component of marine alien taxa (Schaffelke *et al*. 2006) and invasions can result in an alteration of the environment through modification of the habitat, or competition with indigenous species, resulting in important ecological (competition with native biota, effect on higher trophic level), evolutionary (change of ecosystem processes, genetic effects), economic and societal (cost of loss of ecosystem functions, impacts on environmental amenity and on human health, management costs) impacts (Lebret *et al*. ,2009; Schaffelke & Hewitt, 2007).

3. The history of antifouling research

From the dawn of maritime history, the growth of marine organisms on man-made surfaces has been one of the most important problems faced by the shipping industry. The first boats hulls were made of wood and were prone to decay by marine borers (*Teredo sp.*, *Bankia sp.*, *Lyrodus sp.*, *Limnoria sp.*, and *Sphaeroma sp.*) and microorganisms (bacteria and fungi). The first attempt to control biofouling goes back to the Greek and Romans civilization, 700 BC, when copper or lead sheating was used to protect wooden boats (Jones, 2009).

Around 1860, ships were built of steel; however copper sheating could not be used because electrolytic action did accelerate the corrosion of the hull (Jones, 2009). This gave rise to the need for alternative methods to protect ships and the dawn of modern paints systems (Fig. 4). During the 1960s the chemical industry developed extremely efficient AF paints using organotin compounds: tributyltin (TBT) and triphenyltin (TPT). The performance of these paints was even further improved when the release rate of organotins could finally be control thanks to the development of self-polishing polymer paints (Yebra *et al*., 2004). However, the deleterious effects of TBT released by AF paints were first highlighted in Arcachon Bay (France) at the end of the 1970s. Organotin belong to the most toxic pollutants so far for aquatic life. These chemicals have been proven to contaminate the food chain and to be persistent in the environment and have been fully banned since September 2008.

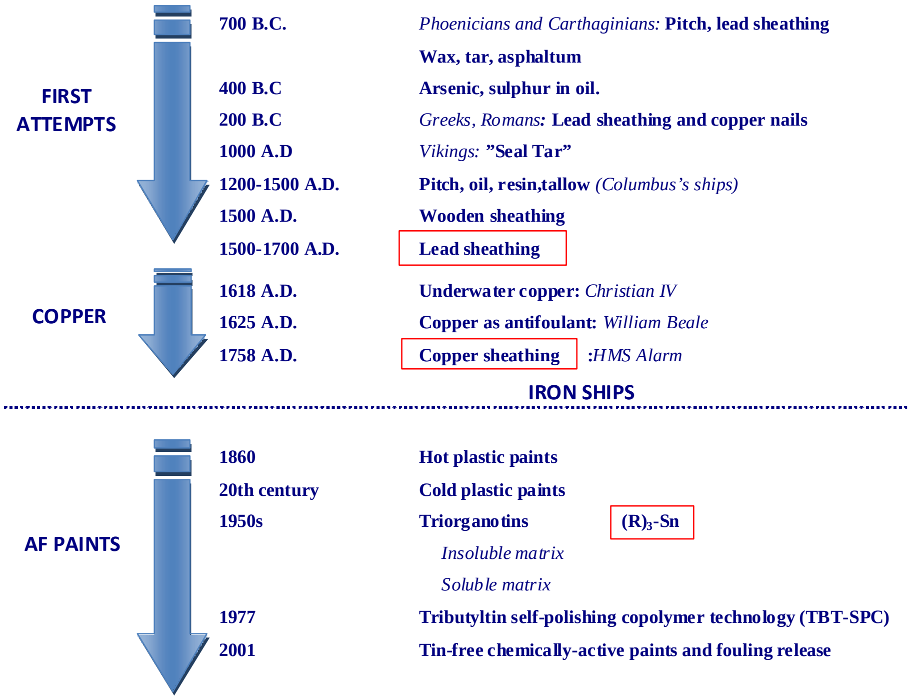

Figure 4. *Chronogram of the development of antifouling technologies (Hellio & Yebra, 2009).*

4. Current antifouling coatings and perspectives

At the moment, 18 different compounds only are used for biocides-based coating and are classified as biocides. The introduction of potential new biocide is regulated by the Biocidal Products Directive 98/8/EC which require major testing of a new active substance before marketing authorisation. This has result in a dramatic increase of costs for development which include for example not only preparing agreed protocols and placing studies but 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 (Marechal & Hellio, 2009). Since the ban of TBT-based paints (September 2008, AFS Treaty), new formulation have been developed containing high levels of copper and herbicides such as Irgarol 1051, diuron, chlorothalonil, dichlorofuanid and zineb. These paints were first classified as environmentally friendly due to the facts that the active compounds were non-toxic towards non-target species and highly biodegradable when released in the water column. However, there are now significant evidences of a widespread of these compounds in many countries (Europe, North America and Japan) with sizeable concentrations in marinas and harbours (Turner *et al*., 2009) and these compounds may face a ban within the next years. In order to be proactive, there is a real need for the continuous development of new non-toxic AF formulations. The industrial requests for new coatings developments are as follow: minimal length of activity: 5 years durable and resistant to damage, repairable, low maintenance, easy to apply, hydraulically smooth, compatible with existing anticorrosion coating, cost effective, non-toxic to non-target species, and, effective at port and sea (Ralston & Swain, 2009). So far no new compound with such properties has been discovered despite a massive effort of research. After exploring a wide range of potentialities, many research teams focus now on an interesting and promising line of research which is inspired by biomimetic solutions and marine biotechnology. Indeed, most marine organisms are prone to biofouling, and colonisation of their surfaces can lead to dramatic stress. Organisms that settle on the body surface of other organisms are called the epibionts, at the opposite of the basibionts, which are the hosts. Epibiosis refers to the assemblage of epibionts on a basibiont. Epibiosis is a typically aquatic phenomenon. The threat of fouling is omnipresent and the list of fouled species is long. Several hundred epibiotic associations have already been noted. This complex association of species will affect the fitness of both the basibionts and the epibionts (Wahl, 2008). On the other hand, a great number of marine organisms do keep their body surface largely clean of epibionts - though it is unlikely that there are many sessile species which are not occasionally (seasonally, locally, or on the level of 'weakened' individuals) subject to epibiosis. Any potential basibiont, *i.e*. the majority of sessile, relatively long-lived organisms, must either defend itself against fouling or tolerate epibiosis. A better understanding of epibiosis avoidance would help to the design of new AF solutions. Marine organisms have developed natural AF strategies which can be classified in four groups: chemical, physical, mechanical and behavioural (Ralston & Swain, 2009). They are reported on Annex (Table 1 and 2). It is of interest to note than none of the marine organisms do use a single AF solution. The first three are of great interest for new AF developments and have been the basis of biotechnological research respectively on marine natural antifoulants and microtexturing of surfaces. However, even if researchers are focusing on single solutions, the best solutions would certainly be a mixture of these technologies (de Nys & Guenther, 2009).

Marine naturals products had been extensively studied for their potential antifouling bioactivities. Soft, Fixed or slow moving, organisms showing no epibionts have been selected for bioassay-guided fractionation and purification procedures. To be selected as a new promising AF compound, the new products need to have an effective concentration $EC_{50} < LC_{50}$ (Dahms & Hellio, 2009). From the literature, it appears that the best sources for AF compounds are organisms such as sponges, corals and macroalgae and/or their associated microflora and/or symbionts (Clare, 1998; Fusetani, 2004). Around 200 molecules with variable degrees of AF activities have been isolated and characterized (Hellio *et al*., 2009). However, it has been regularly highlighted that the active compounds are quite often produced by the associated microflora on the surface of the organisms, which confers a great advantage in term of potential large scale production. It is indeed less costly to produce a compound via microbial biotechnology than trying to elucidation a synthesis route. A limitation to the use of secondary metabolites within paint formulation is that they are usually rapidly breakdown when released in the environment, thus their incorporation in paint a formulation is very challenging. The best method developed so far is to use microencapsulation to ensure a control of the release rate (Price *et al*., 1992).

Regarding microtexturing of surfaces, studies has focus on marine organisms apparently deprived of physical and chemical defences, such as molluscan shells, crustose coralline algae, marine mammal and shark skin (Scardinio, 2009). Methods have been developed to reproduce these microtextured surfaces (laser abrasion, photolithography, moulds & casting, and nano-particles). Preliminary laboratory and field tests showed a slow down on the colonisation but not a full inhibition. This was explained by the fact that fouling organisms (at the attachment phase) vary significantly in shape and size and that attachment points are crucial for the success of the settlement and are correlated to the size of the surface features. This complexity limits the effectiveness of surfaces to a restricted range of fouling organisms. Researchers are now developing multiple scales of topography with the goal of achieving broader deterrents effects (Schumacher *et al*., 2007). Biomimetics models can enable an understanding of which microtextures have the best deterrence property.

5. Conclusions

Despite many years of intense research, no solution as efficient as TBT-based paints has been discovered. Many efforts are now focus on biomimetism for the development of new paints. The best solutions would certainly be a mixture of development of new surfaces topographies reducing the pace of the surface colonisation associate to a control release of bioactive compounds. However, in order to develop better solutions, we need to gain more understanding on the organisms' adhesion strategies as well as on the interspecies relationships in benthic communities.

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Annex 1

Table 1. *Natural antifouling mechanisms and their human equivalents and how they relate to Navy requirement. + = positive; X = negative; n/a = not applicable; ? = unclear or dependent on specifics. Despite experience with many of these methods, there are still many questions. The answers depend on which specific human surrogate is used for comparison (reproduce from Ralston & Swain, 2009).*

	Chemical	Physical	Surface renewal	Grooming	Behavior	Combination	
Equivalent	Biocides	Foul release	Self-polishing	Hull cleaning	Dry storage	Biocide containing self-polishing	Compliant silicone with oil
Life span	X	X	X	+	+	?	X
Durability	?	?	+	+	+	+	X
Repairable	+	?	+	?	+	+	?
Maintenance	+	?	+	X	+	+	?
Application	+	?	+	+	?	+	X
Smooth	?	?	+	?	+	+	+
Compatible	+	+	+	+	+	+	+
Cost	?	?	?	?	X	+	X
Environment	?	+	+	?	+	?	+
In port	+	?	X	+	+	?	X
Underway	+	+	+	X	X	+	+

Table 2. *Marine taxa and their antifouling strategies Y=yes, it is used; N= not used or not reported used; ? = unclear if it is used (reproduce from Ralston & Swain, 2009).*

Taxon	Chemical	Physical	Mechanical surface renewal	Mechanical grooming	Behavioral	Combination
Echinoderm	Y	?	N	Y	N	Y
Bryozoan	?	N	N	Y	N	?
Sponge	Y	Y	N	N	N	Y
Soft coral	Y	Y	Y	N	N	Y
Stony coral	Y	Y	Y	?	N	Y
Crustacean	N	?	Y	Y	Y	Y
Bony fish	Y	?	?	N	Y	Y
Shark	?	Y	?	N	?	?
Dolphin	Y	Y	Y	N	Y	Y