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Bio-inspired antifouling approaches: the quest towards non-toxic and non-biocidal materials

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Biofouling is an undesirable process in which organisms and their by-products encrust a surface. Antifouling solutions are of great importance since biofouling has negative effects on numerous species, ecosystems, and areas including water treatment facilities, health-care systems, and marine devices. Many useful solutions have been developed in the last few decades. However, with the emergence of environmental issues, the search for new promising non-toxic materials has expanded. One approach tries to mimic natural antifouling surfaces and relies on mechanisms of action derived from nature. Since these materials are based on natural systems, they are mostly biocompatible and more efficient against complex fouling. In this review, we cover the latest advances in the field of antifouling materials. We specifically focus on biomaterials that are based on the chemical and physical behavior of biological systems.

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Introduction

Biofouling is an undesirable process in which organisms and their by-products encrust a surface. It begins with the adsorption of organic molecules such as polysaccharides and proteins on surfaces and continues with the accumulation of other organisms from surrounding areas [1]. In hospitals, these organisms may consist of pathogenic bacteria that form an ordered network on the surface, termed biofilm. The biofilm enables the bacteria to corporate and acquire resistance to antibiotics [2•]. In marine environments, organisms such as mussels and barnacles accumulate on marine devices and lead to their deterioration and to the alteration of ship flow rates [1,2•,3••,4]. On water treatment devices, such as membranes, the accumulation of organisms damages their function [5]. Overall, since biofouling is a widespread phenomenon with negative effects on many areas of our lives, there is a high demand for materials that resist fouling. These materials are termed antifouling materials [1].

The first antifouling materials to be designed were coatings incorporating chemically active compounds (Figure 1). These coatings released chemicals [1,2•,3••,4], biocidal nanoparticles, such as silver or copper [6], and different antibiotics [7]. These biocides either eradicate the organisms that are in proximity to the surface or degrade the foulants and metabolites that have already settled on it. However, this methodology either harms the natural fauna of the surrounding environment or leads to antibiotics-resistant bacterial strains [8].

A more ecological solution mimics the defense mechanisms found in nature (Figure 1) [1]. Thus, some efforts have focused on developing coatings that imitate natural antifouling surfaces such as the skin of the shark [9]. Other approaches combine natural products such as molecules extracted from plants, marine organisms, bacteria or fungi that interfere with the chemical cues of the foulants [2•,3••,10•]. In addition, compounds that adhere to the surface via biological linkers [11–13] and alter its energy or features have also been explored [1,2•,14]. In general, these natural solutions inhibit either the attachment or growth of the organisms. Therefore, the bioaccumulation is prevented in advance.

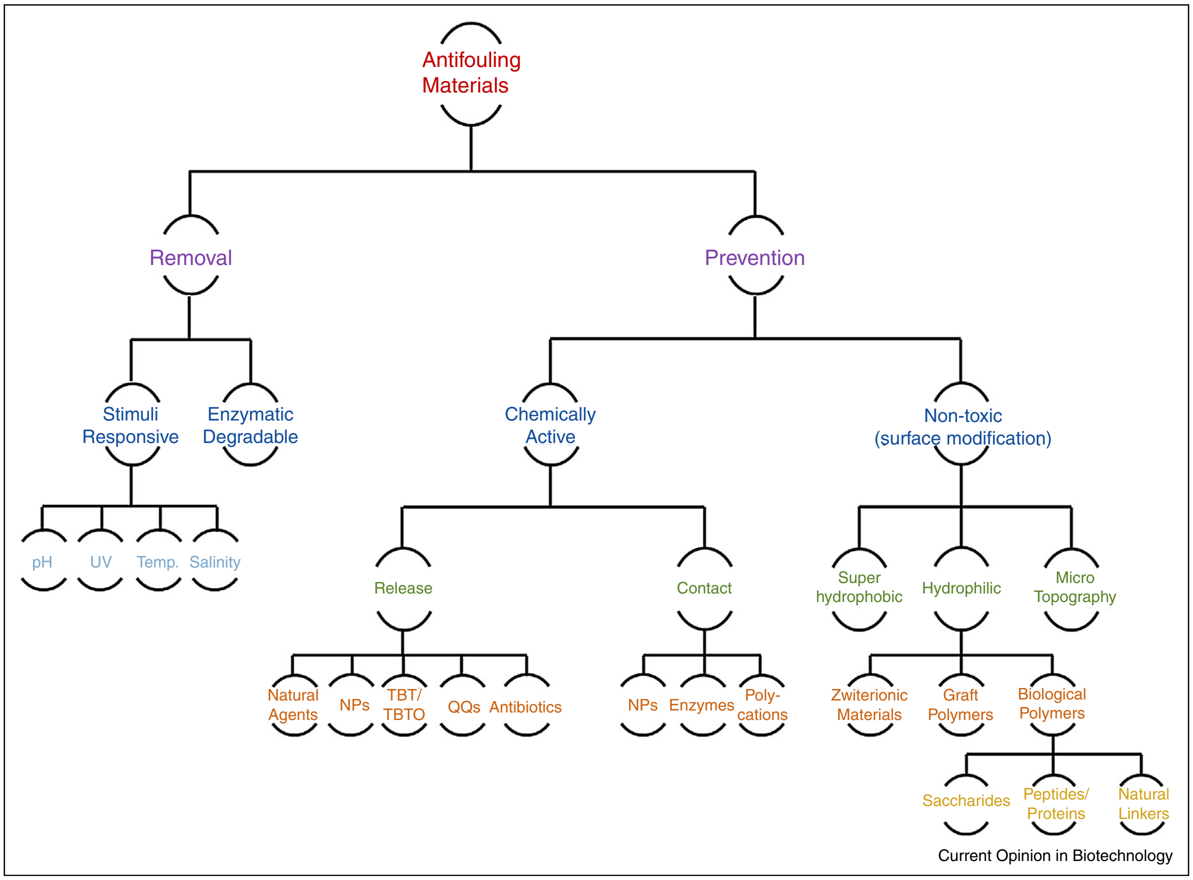
This review will focus on recent approaches that are inspired by or mimic natural surfaces and materials.

Surface topography as a strategy for antifouling

The topography of a surface dictates its roughness and wettability. These features have been found to affect bioadhesion either by inhibiting or promoting it [15,16]. Many plants and marine organisms possess a unique micro/nanotopography that protects them from colonizing organisms [4,9]. The motivation is to mimic these topographies in order to fabricate surfaces with antifouling activity (Figure 2).

The skin of the shark was one of the first topographic models to be investigated [1]. The unique morphology of this skin consists of patterned dermal denticles covered by riblets (Figure 2f). This morphology allows the

Figure 1



A schematic overview of mechanisms for developing antifouling materials. On the left are approaches to remove accumulated biomass. On the right are approaches to prevent the adsorption in advance.

formation of small vortices, along the body of the shark, which reduce the drag flow, and prevent microorganisms from settling on the skin [17••]. The small grooves between the riblets also prevent the macro-organisms from settling. The spacing between the grooves reduces the surface area to which organisms can adhere. Moreover, by flexing its denticles, the shark controls the formation of vortices, resulting in a change of flow, faster movement and enhanced resistance to fouling [17••]. In 2006, Brennan and his colleagues presented, for the first time, a surface that mimics the skin of sharks (Figure 2i) [18]. The surface was fabricated by soft lithography using polydimethylsiloxane (PDMS) [19,20]. It was effective against marine foulers and reduced their settlement significantly. Based on this design, Brennan established a company for fabricating micro-patterned antifouling surfaces, which he named Sharklet AF$^{\mathrm{TM}}$ [18].

The skin of the Pilot Whale can also resist fouling using a topography composed of nanometer-size pores surrounded by nanoridges [21]. Cao *et al.* fabricated surfaces mimicking the skin of the Pilot Whale using polyelectrolyte layer-by-layer spray coating [22]. The poly(acrylic acid) (PAA)/polyethyleneimine (PEI) multilayers' surface topography and roughness resemble those of the skin of the whale (Figure 2j) and can easily be controlled by altering the pH of the applied PEI solution. The more the topography resembeled the whale skin's the better the antifouling activity was.

Another interesting topography is that of the lotus leaf. The lotus leaf exhibits phenomenal superhydrophobic and self-cleaning characteristics [17••,23]. These characteristics originate from the surface roughness of the leaves. The surface consists of dense microbumps that are hydrophobic in nature (Figure 2e). This topography minimizes the energy of the surface, resulting in lower adhesion to the surface [17••]. Inspired by the lotus leaf, Pokroy and his colleagues attained new surface roughness by thermal deposition of paraffin and fluorinated waxes on various surfaces (e.g., copper, glass, and silicon) [23,24]. The different waxes formed well-oriented crystalline layers, with defined nanotopographies (Figure 2k). These new surface topographies exhibited superhydrophobic