

Hybrid custom-tailored sol-gel derived microsccaffold for biocides immobilization



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ABSTRACT

The present paper regards the development of silica-epoxy matrices, in the form of functional spherical microsccaffolds with controlled morphology, comprising an immobilized biocide, for antifouling purposes. The microsccaffolds herein presented were obtained from sol-gel processing combined with a microemulsion technique, using as Si precursors, tetraethylorthosilicate (TEOS) and 3-glycidioxy propyl trimethoxysilane (GPTMS) to be further loaded with biocide Ecomea[®], which has been approved in 2014 by EU Regulator (BPR) as a safe biocide. Biocide immobilization is proposed to be carried out by chemical grafting mainly between the microsccaffolds' oxirane ring and the secondary amino groups of the biocide Ecomea[®], as well as by physical entrapment within the “worm-like” morphology and multimodal pore size distribution of the microsccaffolds. The presence of Ecomea[®] within the microsccaffolds was confirmed by Fourier transformed infrared spectroscopy (FTIR), thermogravimetric analyses and scanning electron microscopy (SEM-EDX) and it was found to be nearly constant over the time when those are immersed in artificial seawater, while under mild agitation. The biocidal effect of the Ecomea[®] loaded silica-epoxy spherical microsccaffolds was assessed by microbiological tests, exhibiting an effective activity against *Staphylococcus aureus* bacteria, by contact mode, even after exposure to turbulent saline water. These microsccaffolds were designed for enabling a more environmental friendly anti-fouling strategy, able to combine a more efficient, long-lasting antifouling performance for water-immersed applications, together with non-toxic properties, being, therefore, a promising and attractive alternative to the actual conventional releasing strategies.

1. Introduction

Marine biofouling is a result from organisms' spontaneous colonization through adhesion and growth onto surfaces that are in contact with water [1]. It is one of the most serious problems in water-immersed structures as for example in ships' hulls, desalination systems and oil rigs [1–3]. Regarding ships' hulls, the adhesion of marine organisms causes high maintenance costs, increased corrosion and extra fuel consumption, of the order of 40% [2–4]. Greater fuel consumption results in SO₂ and CO₂ emissions [4]. These issues translate into economical, but also environmental damage [1]. The most common measure to prevent biofouling is the incorporation of biocides into coating formulations. The excellent antifouling tributyltin based paints (TBT) were discovered and commercialized in the early 1960s, showing high effectiveness and versatility. However, it has been shown that TBT adversely affects the environment, due to its slow degradation [6],

leading to the appearance of malformations in many biospecies [4,6]. The Marine Environmental Protection Committee (MEPC) of the International Maritime Organization (IMO) has indeed recommended the ban of its use [4]. As a replacement of TBT, coatings with copper compounds have been used for antifouling purposes, such as cuprous oxide (Cu₂O) and copper thiocyanate (CuSCN). However, several algal species have shown physiological tolerance to copper and therefore it has to be combined with booster biocides, such as Diuron[®] and Irgarol[®] 1051 [7–9]. Moreover, the premature leakage of these biocides, as well as their degradation, are a major problem for many of these coatings, leading to a decrease of their useful lifetime [9]. Bioaccumulation of heavy metals in the internal organs of marine life [2,5] is another concern and, therefore, there is a need for a more environmental friendly anti-fouling strategy, able to combine a more efficient, long-lasting antifouling performance, together with non-toxic properties.

A promising solution that has recently been investigated is the

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development of microcapsules, with encapsulated biocide, to be added to the antifouling coating's formulation. This method enables the decrease of the biocide degradation, as the encapsulation provides protection against the external environment and controlled the release of the biocide into the ocean, prolonging the biocidal activity in these coatings [9–11].

The work reported in this paper extends the study developed by the team on the synthesis of scaffolds with different morphologies, organic functionalities and a wide porosity range [12–15], being part of a Technology Platform on Microencapsulation and Immobilization. In this work, silica-epoxy hybrid microscaffolds, capable of enclosing and grafting Ecomea[®], were developed. Ecomea[®], [1H-pyrrole-3-carbonitrile, 4-bromo-2-(4-chlorophenyl)-5-trifluoromethyl], was recently approved in 2014 by EU Regulator (BPR) as a safe biocide [16]. It is a metal-free antifouling agent that does not tend to accumulate in the marine environment, and exhibits a fast degradation in seawater. Also, Ecomea[®] is highly effective at controlling a wide range of invertebrate fouling organisms at significantly reduced usage levels [17]. The developed hybrid scaffolds were synthesized through sol-gel processing combined with microemulsion technique, using as Si precursors, tetraethylorthosilicate (TEOS) and 3-glycidyloxy propyl trimethoxysilane (GPTMS). Hybrid sol-gel compounds, which have been called “organically modified silica” (“Ormocil”), are of great interest due to their potential of combining properties of both organic and inorganic components. Organic compounds offer structural flexibility, as the inorganic materials provide stability, robustness and chemical resistance [18]. The processing technique used in this work is one of the most effective and economical methods for the synthesis of silica matrices, enabling the achievement of inorganic and hybrid structures with controlled microstructure, at relatively low processing temperatures [19–22]. In contrast with encapsulated biocides already described in the literature, the scaffolds in this work are firstly synthesized, followed by the loading (impregnation) with Ecomea[®], assisted by low vacuum conditions. This procedure allows to have the unloaded scaffolds, which can be loaded with many other chemical species (including biocides), depending on the application. In this sense, there is no need to optimize the synthesis for each impregnated compound and to subject the compound to the synthesis' process conditions. In the present work, the entrapped Ecomea[®] is mainly located at the (large) surface area of the scaffolds and is partially grafted onto it, aiming at a permanent and durable antifouling, or antibacterial effect by contact. In this work we have investigated the i) possibility to use silica scaffolds with glycidyloxy (epoxy) organic functionality for the immobilization of Ecomea[®] in order to obtain biocidal scaffolds, for antifouling purposes, ii) the identification and quantification of entrapped, or immobilized Ecomea[®] species and iii) the activity of the Ecomea[®] loaded scaffolds against microorganisms.

2. Experimental section

2.1. Materials and methods

2.1.1. Materials

The Si precursors tetraethyl orthosilicate (TEOS, with 99% purity) and 3-glycidyloxy propyl trimethoxysilane (GPTMS, with purity higher than 98%) were purchased from Dow Corning. Decahydronaphthalene (a mixture of cis and trans isomers, with 99% purity), also named decalin and the surfactant Span 80, sorbitan monooleate (with 99% purity) were obtained from Merck KGaA. N-hexane (with 99% purity), used for the filtration and washing step, was purchased from LabChem and Ecomea[®], the biocide to be immobilized, was received from Janssen PMP. All chemicals were used as received, without further purification.

2.1.2. Microscaffolds' synthesis

The microscaffolds referred in this work were synthesized via a microemulsion preparation, followed by sol-gel hydrolytic polycondensation of the Si precursors, TEOS and GPTMS.

The water-in-oil (W/O) emulsion system was obtained through vigorous stirring of the oil phase (O), composed of a solution of SPAN 80 in decalin, with deionized water, the aqueous phase (W), with an Ultra-Turrax (IKA T25 digital ULTRA TURRAX, Germany).

An aqueous mixture of acidified water and TEOS was stirred at 100 rpm, at room temperature, for 1 h, in order to proceed with the precursor's hydrolysis. Afterward, the pre-hydrolyzed solution was added dropwise to the emulsion solution and mixed with a mechanical stirrer, at 600 rpm, for 1 h, at room temperature. The temperature was then increased in steps of 5 °C, from 65 °C to 95 °C, until the formation of spherical particles was achieved.

Afterward, the scaffolds were filtrated and extensively washed with n-hexane, to avoid any particle aggregation. The scaffolds were dried at 100 °C, for 1 h, and stored in a moisture-free environment.

2.1.3. Impregnation process

In order to proceed to the scaffolds' impregnation with Ecomea[®], a solution of Ecomea[®] in ethyl acetate, at 15 wt%, was prepared. The impregnation process was conducted using a low vacuum system, to further assist the loading process. Firstly, the scaffolds were subject to 10 min under vacuum before being soaked in the previously prepared Ecomea[®] solution, in order to remove residual moisture and air from the scaffold's pores. The scaffolds were then soaked in the Ecomea[®] solution and sonicated for 30 min, before being subject to 1 h under vacuum. The resulting loaded scaffolds were dried at 120 °C for 1 h, with an additional goal of further promoting the reaction between the scaffolds' matrix and the Ecomea[®] molecule. The proposed reaction scheme for the Ecomea[®] grafting on the oxirane ring from the scaffold (derived from GPTMS) is shown in Fig. 1. The loaded scaffolds were filtrated and washed using ethyl acetate and stored in a low moisture environment, so that just the grafted, or effectively immobilized biocide within the scaffold would remain in the loaded sample. The scaffolds impregnated with Ecomea[®] will be referred throughout this work as E SCs, while the reference, i.e. the scaffolds not submitted to the impregnation process,

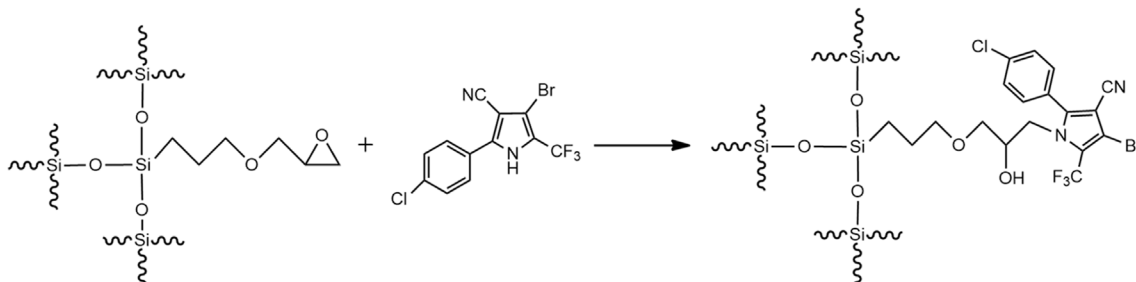


Fig. 1. The oxirane ring opening reaction between Ecomea[®] and the glycidyloxy group (derived from GPTMS) present on the scaffold's matrix (proposed mechanism).

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