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Transitioning to nontoxic antifouling paints

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Transitioning to nontoxic antifouling paints

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Abstract

Purpose – The purpose of this paper is to reduce the amount of copper in antifouling paints by using eugenol as an additive. Biofouling leads to deterioration of any submerged material. The most widespread method for control is the application of cuprous oxide antifouling paints which are toxic. First of all, the paper describes the effect of eugenol on larvae of Balanus amphitrite (fouling organism) under laboratory conditions and then the preparation, application and performance of different types of antifouling paints in field trials.

Design/methodology/approach – Three types of soluble matrix antifouling paints were prepared with different pigments. The first one containing 16 per cent v/v copper, the second with 1.6 per cent copper and the third with 1.6 per cent copper + 2 per cent eugenol.

Findings – After 12 months of immersion in Mar del Plata harbour paints containing 1.6 per cent copper + eugenol and 16 per cent copper were the most effective. Although these formulations showed a similar performance, copper + eugenol-based paint contains 90 per cent lesser copper than a traditional copper-based formulation.

Originality/value – The use of antifouling paints with copper + eugenol combination as pigment is a promising alternative due to its performance, low cost and reduction in copper leaching to environment.

Keywords Copper, Organic compounds, Antifouling paints, Marine biology, Micro-organisms

Paper type Research paper

Introduction

In the aquatic environment, all immersed substrate (natural or artificial) is immediately colonized by a succession of organisms known as biofouling. This phenomenon can result in a great loss of function and effectiveness for both cruising ships and static constructions (Chambers *et al.*, 2006; Pinori *et al.*, 2011). It is well-established that biofouling on ships increases the surface roughness of the hull; it causes increased frictional resistance and fuel consumption, and decreased top speed and range (Lewthwaite *et al.*, 1985; Leer-Andersen and Larsson, 2003; Schultz *et al.*, 2011).

The use of antifouling paints is a commonly used method to prevent organism settlement. However, most of these coatings incorporate biocides which are toxic to marine ecosystem. In this sense, organotins were not only the most effective antifouling agents known, but also among the most toxic biocides ever introduced because they are not readily degraded in the natural environment and because they act on both target and non-target organisms (Qian *et al.*, 2010). The ban on harmful substances in antifouling paints requires the development of new antifouling strategies; consequently, development of alternative compounds should be encouraged (Yebra *et al.*, 2004). It is clear that alternatives should be as effective as conventional paints, but of lower toxicity and friendly to the environment. However, a complete change towards non-toxic antifouling coatings implies a gradual reduction in copper content in conventional coatings still in use. Although copper is an essential element for the normal growth of organisms, high concentrations can be lethal (Voulvoulis *et al.*, 1999). The copper used in antifouling paints has harmful effects not only on the fouling community organisms but also on non-target species such as fish, macro and micro algae, diatoms and bivalves, among others (Chapman, 1978; Brooks and Mahnken, 2003; Andrade *et al.*, 2004; Lim *et al.*, 2006; Munari and Mistri, 2007; Falasco *et al.*, 2009). In addition, several cases of copper bioaccumulation in marine organisms, such as urchins, lobsters and oysters, have been reported (Claisse and Alzieu, 1993; Chou *et al.*, 2000, 2003; Radenac *et al.*, 2001).

In this context, the search and identification of natural products that can be combined with small quantities of copper to be included as antifouling pigment is a promising alternative.

Essential oils extracted from plants are widely used in folk medicine, food preservation, cosmetic and pharmaceutical industries (Pascual *et al.*, 2001; Burt, 2004; Edris, 2007; Kamatou *et al.*, 2012). Although these compounds have natural origin, some of them could be obtained by laboratory synthesis, and this is an advantage from the point of view of their availability.

In this study, antifouling properties of eugenol were evaluated under laboratory and field trials. This compound is a clear to pale yellow oily liquid common in certain essential oils, especially clove, nutmeg and cinnamon. It is slightly

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soluble in water and in organic solvents too (Bhuiyan *et al.*, 2010; Mallavarapu *et al.*, 1995) (Figure 1).

Eugenol is commonly used as flavouring and in perfumery industry. It has antiseptic, antimicrobial and insecticidal properties, and it is also used as a local anaesthetic in dentistry and as a anticorrosive agent (Enan, 2001; Vázquez *et al.*, 2001; Chaieb *et al.*, 2005; Braga *et al.*, 2007; Kamatou *et al.*, 2012). It is important to remark that this compound is degraded in the environment by photolysis and biodegradation (Tadasa, 1977; Rabenhorst, 1996; Isman, 2000; Overhage *et al.*, 2002; Amat *et al.*, 2005; Kadakol and Kamanavalli, 2010). Particularly, antimicrobial properties of eugenol suggest that it could interfere on natural fouling succession (Bhattarai *et al.*, 2007).

The aim of the present paper is to evaluate antifouling properties of eugenol in laboratory tests and then formulate marine coatings with low copper content and eugenol as an additive. The employment of low copper content in marine coating formulations would reduce the input of contaminants not only to water and sediments but also to the biota.

Experimental

Materials

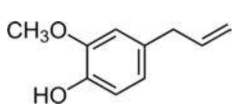
Bioassays were carried out using *Balanus amphitrite* nauplii and cyprids larvae. The barnacle *B. amphitrite* is a typical species of fouling organisms at Mar del Plata harbour, Argentine (38°08′17′′S, 57°31′18′′W). It is considered one of the most successful and aggressive species as a consequence of its calcareous exoskeleton (Koryakova and Korn, 1993).

Methods for laboratory tests

For toxicity test, the effect of each eugenol solution was tested using *B. amphitrite* nauplii II. Larvae were collected from adults 2-4 hours before starting bioassays. Toxicity tests were realized by adding 30 nauplii into crystallizing vessels containing 30 ml of either eugenol solutions between 0.015 and 1.5 μM or filtered seawater as control. The number of swimming nauplii and phototactic response were recorded after exposure to solutions for 24 hours at 22 ± 2°C. The lethal concentration for 50 per cent of nauplii (LC_{50}) is used to identify toxic compounds and it was determined using Probit analysis. Non-swimming larvae were regarded as dead (Rittschof *et al.*, 1992).

For the settlement test, newly metamorphosed cyprids were maintained in filtered seawater for four days at 6°C before being used in settlement assays (Rittschof *et al.*, 1992). Twenty cyprids were introduced into crystallising vessels with 30 ml of each eugenol solution for 24 hours at 22 ± 2°C. When larvae did not swim or close their valves or if their appendages were extended and they did not respond when touched with a metal probe, they were counted as inactive cyprids. Concentrations used for the bioassays were the same as those used for the toxicity test.

Figure 1 Eugenol structure



The percentages of swimming, inactive and settled individuals were determined by counting under a dissecting microscope, and the results are expressed as a proportion of the total number of larvae in the vessel. Settlement data for EC_{50} (concentrations of eugenol solutions causing settlement inhibition in 50 per cent of experimental organisms) were obtained by normalizing settlement values to control prior to analysis. EC_{50} was determined by Probit analysis.

In the laboratory, toxic compounds are not differentiated from narcotic compounds, and for this reason, larvae were placed in seawater to determine if they recovered. After a 24-hour exposure to eugenol solutions, nauplii and cyprids were transferred to clean seawater to determine whether the effects observed were temporary or permanent.

All experiments were performed as five replicates and controls. As the data obtained were normally distributed (Shapiro-Wilk's normality test), they were analysed by analysis of variance (ANOVA) and Tukey pairwise comparison tests. The level of significance was set at p less than 0.05.

Methods for field tests

Paints were prepared at laboratory scale in a ball mill (1L jar). Colophony (WW rosin) was used as binder and oleic acid as plasticiser. The operating conditions of the ball mill were chosen so as to achieve an efficient dispersion. The ball mill was loaded with the vehicle (binder + plasticizer + solvents) followed by pigments and were dispersed during 24 hours (Table I).

Sandblasted acrylic tiles (8 × 12 cm^2) were used for field trials. Paints were applied by brush on tiles previously de-greased with toluene. Three coats of paint were applied and allowed to dry for 24 hours between each application, resulting in a final dry thickness of 100 ± 5 μm. Then, coated panels were hung in a marina in Club de Motonáutica at Mar del Plata harbour to a depth of 50 cm below the water line. Painted panels and controls were sampled after 12 months immersion, and fouling cover percentage was evaluated under a stereomicroscope (Foster *et al.*, 1991). A series of unpainted acrylic tiles was used to establish fouling community development. All treatments were performed by triplicate and were statistically analysed by ANOVA and Tukey pairwise comparison tests. The level of significance was set at p less than 0.05.

Results and discussion

Laboratory tests

Toxicity test performed with nauplii of *Balanus amphitrite* showed a marked inhibitory effect of eugenol, with LC_{50} =

Table I Paint composition expressed as volume percentage

Components	PCI	PCII	Cu + eugenol
Cuprous oxide	16.0	1.6	1.6
Calcium carbonate	11.0	25.4	23.4
Eugenol	–	–	2.0
Colophony	27.0	27.0	27.0
Oleic acid	6.0	6.0	6.0
Solvents (xylene/white spirit) (4:1)	40.0	40.0	40.0

0.094 μM after 24 hours of exposure (Figure 2). All organisms exposed to different concentrations of eugenol recovered normal activity when they were transferred to clean seawater, i.e. the inhibitory effect was temporary.

The anti-settlement activity of eugenol was evaluated by exposure of cyprids for 24 hours. Significant differences on cyprids settlement percentage for all assayed concentrations versus control were detected (ANOVA test, $p < 0.05$). The eugenol threshold molarity which inhibited larval settlement was 0.015 μM and the EC_{50} value obtained was 0.023 μM (Figure 3).

The therapeutic ratio (TR), LC_{50}/EC_{50} is a way of expressing the effectiveness of the compound in relation to its toxicity. It is calculated to determine whether settlement inhibition is due to toxic action or some other mechanism (Vitalina *et al.*, 1991; Rittschof *et al.*, 1994). From the perspective of potency for use in an antifouling coating, the desired target ratio should be greater than 1.0 (Rittschof *et al.*, 2003). Eugenol is of particular interest because it shows good anti-settlement activity at concentrations that were not acutely toxic to barnacle larvae, with a TR = 4.09, thus satisfying the abovementioned criterion. Additionally, the effect can be reversed by the removal of larvae from the eugenol solutions, demonstrating that eugenol acts through a nontoxic mechanism.

Figure 2 Inhibition of *B. amphitrite* nauplii II after a 24-hour exposition in eugenol solutions. Bars indicate mean ± SE

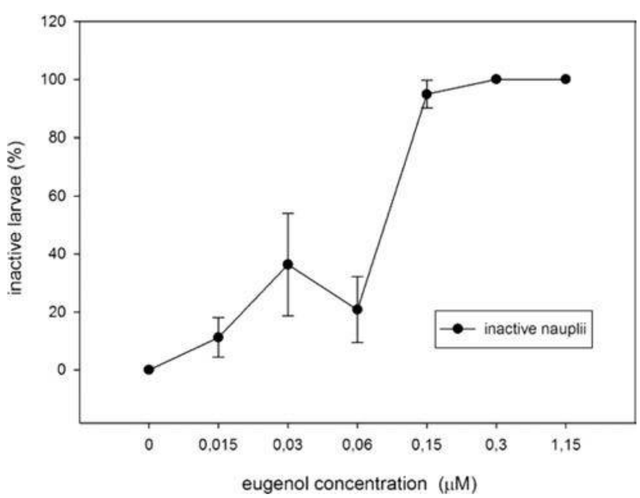
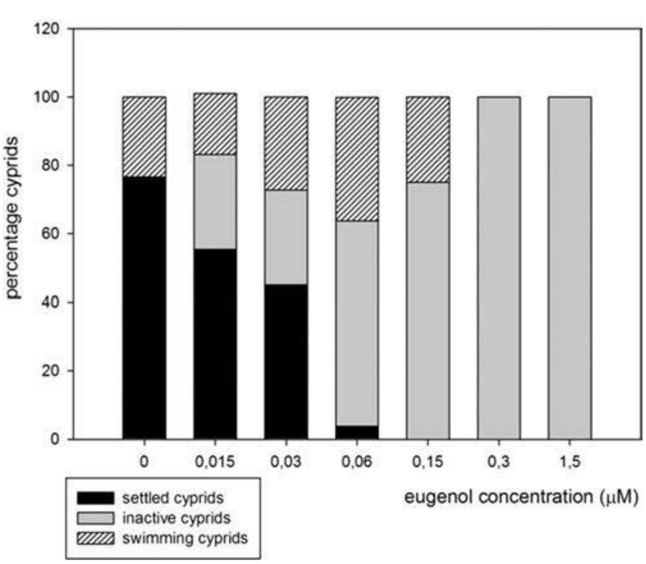


Figure 3 Effect of eugenol solutions on *B. amphitrite* cyprids



As the International Maritime Organization (IMO) (2007) prohibits the use of organotins in antifouling paints, alternative biocides were developed. In this context, several compounds have been presented. The most frequently used booster biocides worldwide are Irgarol 1051, diuron, Sea-Nine 211, chlorothalonil, dichlofluanid and zinc pyrithione, and some of these compounds have also been found to accumulate in coastal waters at levels that are harmful for marine organisms (Omae, 2003; Konstantinou and Albanis, 2004; Bellas, 2006; Thomas and Brooks, 2010). Therefore, the use of non-toxic natural compounds such as eugenol is a promising way to reduce the copper content in antifouling paints.

Field tests

In a previous paper (Bhattarai *et al.*, 2007), the use of eugenol for antifouling control was proposed. However, authors have conducted field trials using a vinyl varnish containing 10 per cent of eugenol. Even though their results were promising, further research is needed to develop an antifouling paint, i.e. development and improvement of the formulation.

After 12 months of immersion in Mar del Plata harbour, paints containing 16 per cent copper (PCI) and copper + eugenol were the most effective because they showed significant differences on fouling cover percentage for both PCII (1.6 per cent copper) and acrylic panels ($p < 0.05$). On the other hand, no differences on cover percentage between copper + eugenol and PCI paints were registered ($p > 0.05$) (Figure 4). Although both paints showed similar performances, it is important to note that the use of copper + eugenol as antifouling pigment allowed a higher reduction in copper content in the order of ten times in comparison with cuprous oxide-based paints. Based on the present findings, it could be inferred that eugenol is also responsible for antifouling action. In contrast, PCII paint was unable to significantly reduce biofouling settlement because the concentration of copper was not sufficient.

To switch to biocide-free, non-copper, biodegradable coatings will demand time due to the process requires ormulation development, ecotoxicological risk assessment, industrial-scale production and market inclusion (Rittschof, 2000, 2009; Hellio *et al.*, 2002). The ban on harmful substances in antifouling paints requires the development of new strategies. In the past years, a variety of approaches have been undertaken to replace toxics containing in antifouling paints. One of the alternatives is focused on reducing copper content by the incorporation of additives which should keep good performance, low cost and low toxicity to the environment.

In previous studies, good performances with antifouling paints based on low copper content pigments were obtained. The use of cuprous thiocyanate, core-shell pigments and cupric tannate reduced high copper content

Figure 4 Painted and control panels after 12 months exposure

(a) (b) (c) (d)

Notes: (a) acrylic; (b) PCII; (c) PCI; (d) Cu+eugenol

in relation to traditional antifouling paints (Vetere *et al.*, 1997; Pérez *et al.*, 2003, 2006). Although in such cases, the reduction of copper content was very important, the industrial process to prepare these antifouling pigments implies an economic investment. In contrast, our efforts are focused to obtain new antifouling paint formulations involving the use of cheap raw materials available in the market, such as cuprous oxide and eugenol.

Conclusions

Eugenol is a potent inhibitor of nauplii and cypris larvae of *Balanus amphitrite* by a nontoxic mechanism. It is important to remark that the effectiveness of paints formulated with copper + eugenol was similar to paints containing 16 per cent copper. However, copper + eugenol-based paint contains 90 per cent lesser copper than traditional copper-based formulations.

These facts suggest that eugenol is a suitable additive to reduce the amount of copper in antifouling paints.

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