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Tara tannin a natural product with antifouling coating application

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ABSTRACT

The international trade by marine transportation has increased continuously since the 70s. The undesirable accumulation of a wide variety of marine organisms (biofouling) on ship hulls can lead to significant increased costs, principally by increased fuel consumption. On the other hand, there is a great concern about the biocides commonly used in commercial antifouling (AF) protective systems due to the high concentration encountered in coastal areas and the potential damage they could cause to marine organisms. As a consequence, the development of alternative AF coatings with new natural products as biocides inhibit is a key factor. In this approach, tara tannin (TT) is being proposed as a promising solution. It is important to note that TT is obtained from the pods of the tree avoiding its cutting down. The aim of this research was, primarily, to explore the possible application of a natural and abundant product, such as the TT, in the preparation of AF coatings. So, a TT derivative was obtained and characterized to be employed as the bioactive compound in AF coatings. Previous to the immersion in natural environments, the dissolution of TT from AF coating in artificial sea water (ASW) was studied. TT was incorporated into the coating as zinc "tannate". One of the tested coatings proved to be efficient in AF protection in natural sea water (NSW) at Mar del Plata (38°08′17″S–57°31′18″W) harbor during eight months. The addition of 2% by weight of zinc oxide to the coating extended its service life until the year.

1. Introduction

AF coatings prevent the undesirable accumulation of a wide variety of marine organisms, known as biofouling, on hard substrates. Algae, barnacles, mussels, polychaetes, ascidians, bryozoans, etc. are the most commonly found organisms. One of the main consequences of fouling is the increased fuel consumption to maintain the cruising speed as a consequence of the increased friction of the vessel hull with water. It is estimated that the increased friction could be as high as 70% for ships without AF protection [1]. Apart from extra fuel consumption, other concomitant problems could appear; the most frequent are: metallic corrosion [2,3]; reduction in the efficiency of heat exchange in atomic power plants [4]; blockage of pipes and filtration systems in different industries [5]; cages deterioration in fish farming [6]; scale formation in water cooling systems of off-shore sea platforms as well as the weight increased of these structures [7], etc.

Taking into account the importance of the shipping industry and the international trade, economical losses caused by fouling, according to projections for 2020, could originate a leakage of U$S 150 billion per year all around the world [8].

Nowadays, the most used protective systems are based in a self-polishing copolymer with Cu_2O or ZnO and organic biocides such as Irgarol 1051, Diuron, Seanine, etc. Conventional soluble matrix AF coatings with the same biocides but with another type of binder (rosin or some of its derivatives) are also commercialized [9,10]. As the rosin dissolution rate could be high, it is usually blended with co-binders or plasticizers to obtain suitable solubility and good mechanical properties. These coatings do not ensure protection for more than 12–18 months, because of the constant erosion that they undergo during their service life [10,11].

There is a great concern about the biocides commonly used in commercial AF protective systems due to the high concentration encountered in coastal areas and the potential damage they could cause to marine organisms [12–14].

The replacement of these biocides by more environment friendly ones is a matter of great interest. In this sense the use of natural products which inhibit the settlement of fouling organism is a key factor in AF coating technology [13,14]. From this point of view, tannins have been proposed as a promising solution [15–18].

Tannins are polyphenols produced by different plants as part of their defense system against pathogenic agents [19,20]. As it was demonstrated that they possess a narcotic effect on nauplii of *Balanus amphitrite*, they became of interest in the field of AF coatings [15]. Because their higher solubility in water, tannins extracts, are not used directly in coatings. Recent research has shown that "quebracho" tannin coagulated with metallic cations, such as

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aluminium, copper and zinc, to form the corresponding "tannates", was less soluble than the original tannin [16–18]. AF efficiency of aluminium and zinc "tannates" did not extend beyond six months but copper "tannate" performed satisfactorily during 12 months in NSW immersion tests but copper contaminates severely the environment [16–18].

A different kind of tannin extract, TT, obtained from the fruits pods of tara tree (*Caesalpinia spinosa*) was used in this research. *C. spinosa* is a small thorny tree whose distribution covers several arid areas of South America with high amount of tannin (40–60 wt%) in their fruit pods whose average yield ranged between 20 and 40 kg per tree per year [21,22]. TT has different industrial applications such as leather tanning. It is also employed in the food industry to clarify wines, substitute malt and give body to beer [20]. The TT is mainly of the hydrolyzable type and consists of basic units of gallic acid linked by ester unions to quinic acid [21,23,24]. Peruvian exportations of tara powder is about 10000 tons/year at 400 US$ per ton [24].

The aim of this research was, primarily, to assess the possible application of a natural and abundant product, as it is TT, in the preparation of AF coatings. Therefore preliminary screening was carried out in laboratory and, then, in natural sea water environment in static conditions [25]. A TT derivative has been obtained by coagulating it with zinc cation which due to its size and charge decreases TT solubility. The derivative was characterized in relation to its bioactivity with *Artemia* larvae. AF coatings with a soluble matrix and the "tannate" as biocide were formulated. The tannin leaching rate of these coatings in ASW was determined by spectrophotometry using the Folin–Denis reagent (FDr). Their biocidal activity was assessed in NSW and qualified according to a given scale.

At the present status of this research, it must be considered that the paints developed in this investigation could be useful for pleasure boats which are more frequently repainted. For larger vessels further experiments must be carried out.

2. Materials and methods

2.1. Precipitation curves

The variables for precipitating TT with zinc cation were optimized from the corresponding precipitation curve. In order to obtain this curve, 1.000 g of TT was dispersed in distilled water for 10 min and, then, treated with 0.50, 1.25, 2.50 and 5.00 ml, respectively, of 0.65 M zinc nitrate. Distilled water was added to match a final volume of 25.0 ml. After the addition of zinc nitrate, the suspensions were stirred for 5 min and the pH adjusted to 4.0 using 0.5 M NaOH. The suspensions were stirred during 1 h more, the pH was adjusted again, and the systems were allowed to settle down for 24 h to accomplish complete flocculation. Finally, an additional pH adjustment was carried out under stirring and, then, the solids were separated by centrifugation and dried at 50 ± 5 °C until constant weight.

2.2. Preparation of zinc "tannate"

The chemical structure of the TT used to synthesize zinc "tannate" (TZn) is showed in Fig. 1 [24,26,27]. Zinc "tannate" (TZn) was prepared taking into account the suitable ratio of reactants according to the results obtained from the analysis of the precipitation curve.

In this sense, 150.0 g of TT was dispersed in 3.0 l of distilled water and 750 ml of 1 M zinc nitrate was added under constant stirring to precipitate TZn. Immediately, pH was adjusted to 4.0 using a 0.5 M NaOH and the suspension was stirred during 1 h. The suspension was kept overnight without stirring and pH was adjusted once more before separating the solids from the supernatants. The solids were washed with distilled water by decantation, centrifuged, dried at room temperature with the aid of an air current and, finally, in a stove at 50 ± 5 °C.

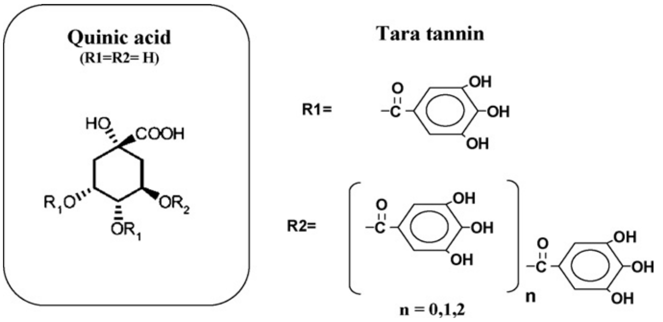


Fig. 1. Basic chemical structure of tara tannin.

2.3. Characterization

The amount of water in TZn was determined by indirect gravimetry, heating the solid at 105 ± 5 °C. Zinc was determined as zinc oxide by a gravimetric procedure heating the solids at 900 °C. The amount of tannin was calculated as the difference between the mass of dried TZn and the zinc oxide content. The density of the pigment, needed for coating formulation, was determined according to a standardized procedure (ASTM D 1475). The Fourier spectrum of TT and the TZn were obtained using the potassium bromide disc technique and a Perkin-Elmer Spectrum One FTIR Spectrometer.

The solubility of the TZn in ASW (ASTM D 1141) was determined as described in a previously published paper [20]. The concentration of tannin in the saturated solution as total polyphenols (TP) was obtained spectrophotometrically at 750 nm using FDr. This wavelength corresponds to the maximum of the so-called molybdenum blue compound obtained due to the reducing ability of tannin [28–31].

2.4. Bioassay

Toxicity tests with *Artemia* nauplii have the advantage of their rapidity, low cost as well as a good predictive potential as alternative to other crustacean test species like barnacles (*B. amphitrite*) [32,33]. The concentration which kills 50% of the *Artemia* nauplii population within 24 h (LC_{50}) was determined using a short term toxicity test [34].

Artemia persimilis eggs, commercially available, were hatched in artificial sea water (ASTM D1141-98), at 22 ± 2 °C during 24 h, under gentle aeration with an aquarium pump [33]. After 48 h a homogenous population of instar II–III nauplii were obtained and used for the test. A saturated solution of zinc "tannate" was diluted adequately with ASW to prepare different solutions containing 2.5, 12.5, 35.0, 50.0, 125 ppm of TP respectively. Ten nauplii were placed in a vessel with 10 ml of the respective diluted TZn solution together a control with ASW. Copper sulphate was used as positive control being the concentrations of the testing solutions 1.0, 10.0, 50.0, 100 and 200 ppm, respectively. Three replicates were set up for each concentration, including the controls. After an incubation period of 24 h, dead larvae were counted and LC_{50} values were calculated by Probit analysis [35].

2.5. Formulation and preparation of coatings

Two binders were formulated to carry out this research (Table 1). Coating 1 contained WW rosin as film forming material.

Table 1
Composition of coatings as % of solids by volume.

Components	Coating 1	Coating 2
TZn	34.6	27.0
Chalk	8.8	18.1
WW rosin	32.8	45.1
SAC	17.2	–
Chlorinated parafin	6.6	–
Oleic acid		9.8

Table 2
A scale for settlement degree assessment.

Settlement degree	Efficiency (%)
0, no settlement	100
1, little	80
2, limited	60
3, common	40
4, abundant	20
5, completely covered	0

Styrene-acrylate copolymer (SAC) was added as co-binder and the ratio rosin/SAC was 1.9/1, by volume (Table 1). The plasticizer was chlorinated paraffin with 42% of chloride. This plasticizer is commonly recommended for the styrene-acrylate copolymer and it is also compatible with the rosin resin [36,37]. The ratio SAC/plasticizer was 2.6/1, by volume. Rosin was dissolved in xylene employing the high speed disperser; SAC was also dispersed in xylene with the plasticizer.

TZn was dispersed in a fraction of the solvent (xylene/white spirit 4/1) in a ball mill jar (3.3 l) during 24 h. Then, the vehicle, pine oil (0.5% by weight of total coating formula) and chalk were incorporated into the jar and the dispersion was continued for other 24 h. After this, 2% by weight of castor oil gel was dispersed into the coating. Castor oil gel (15% by weight) was previously activated with xylene, using a shear stress at 40–45 °C, until a stable colloidal structure was obtained. Finally, castor oil gel was added in a load of 2% by weight of the total coating.

The binder for coating 2 differed from that for coating 1 because no SAC was used and oleic acid was employed as plasticizer. Two coatings were formulated with this binder, coatings 2a and 2b have almost the same composition but coating 2b contained 2% by weight of zinc oxide, with respect to the total coating formulation, to decrease the acidity imparted by rosin. Rosin with zinc ions forms resinates which are less soluble in seawater, thus reducing the dissolution rate of the binder [38]. Control coatings were also elaborated with the same formula of 2a and 2b but the TT derivative was replaced in volume by TiO_2.

2.6. Determination of leached polyphenols and zinc ions in ASW

Coatings were applied on 8 cm × 8 cm sandblasted acrylic panels. Three or four coats were applied and allowed to dry 24 h between each application. The total dry film thickness was $120 \pm 5\,\mu$m. Not more than 48 h elapsed for the painted panels to be submerged in plastic container containing 150 ml of ASW. The leached “tannate” was determined on a 2 ml aliquot using the FDr. The original level of the liquid in the containers was restored periodically with distilled water and the pH was adjusted to 8.2. The concentration of zinc cation was determined by atomic absorption spectroscopy.

In order to assess film quality, microscopic examination of exposed coatings to ASW during three months was carried out by scanning electron microscopy (SEM) employing a PHILLIPS SEM 505 coupled with an EDAX OX PRIME 10 (energy-dispersed form).

2.7. Essays in NSW

Sandblasted acrylic panels (8 cm × 12 cm) were coated as described being the total dry film thickness of $180 \pm 5\,\mu$m. Not more than 48 h elapsed before the painted panels were immersed in a natural sea environment (NSE) at Mar del Plata harbor in Argentina (38°08′17″S–57°31′18″W) [39].

Panels were immersed 50–60 cm deep and fouling settlement degree was evaluated monthly according to the scale presented in Table 2 [40]. The behavior of an AF coating is considered satisfactory if its qualification is 1 or lower. For settlement degree 0 (no settlement) only bacteria and diatoms could be found on the panel under study; for settlement degree 1 (little settlement), barnacles and serpulids are excluded. Other organisms such as ascidians, bryozoans, algae and polychaetes are frequent in Mar del Plata harbor and could be attached onto the panels [4,39,41]. The distances smaller than 1 cm from the edge of the panels were not considered. Uncoated panels were used as control and immersed in the same conditions as the painted ones.

3. Results and discussion

3.1. Preparation and characterization of zinc “tannate”

The analysis of the precipitation curve revealed that the flocculation of tannin could be achieved with zinc cation (Fig. 2). Practically, the curve presented two different regions characterized by their slopes. The amount of precipitated tannin, for a given amount of zinc, increased faster at the beginning of the experiment. So, it was decided to carry out this precipitation employing 0.940–1.000 g of $Zn(NO_3)_2$ per g of tannin at pH = 4. The chemical composition of TZn was 69.00% of tannin, 18.50% of zinc, being the rest (12.50%) water. The density of TZn was 2.18 g/cm^3.

The spectra of Fig. 3 showed a broad absorption band at 750 nm due to the reaction of the FDr with TT and TZn solutions. This band was used to quantify the concentration of TP in the saturated solution of TT and its derivative in ASW. These concentrations were found to be equal to 8546 and 524 ppm respectively.

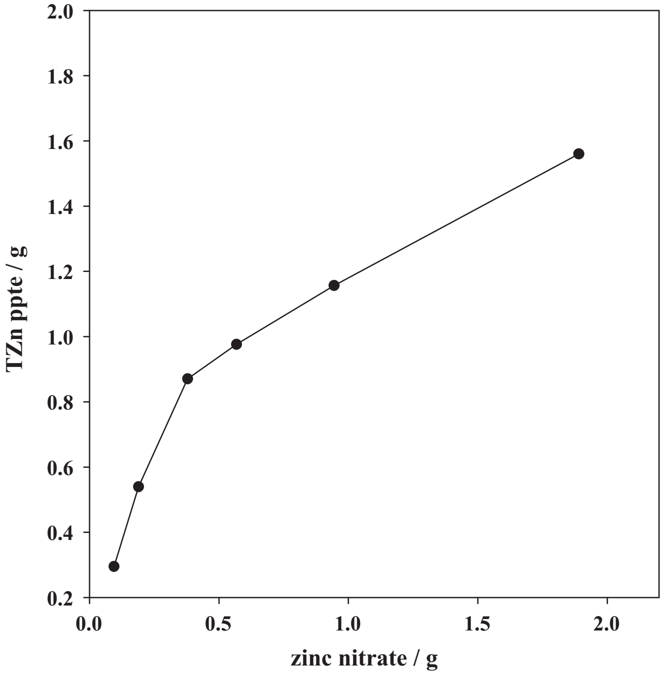


Fig. 2. Amount of tara tannin (TT) derivative precipitated as a function of the amount of zinc nitrate.

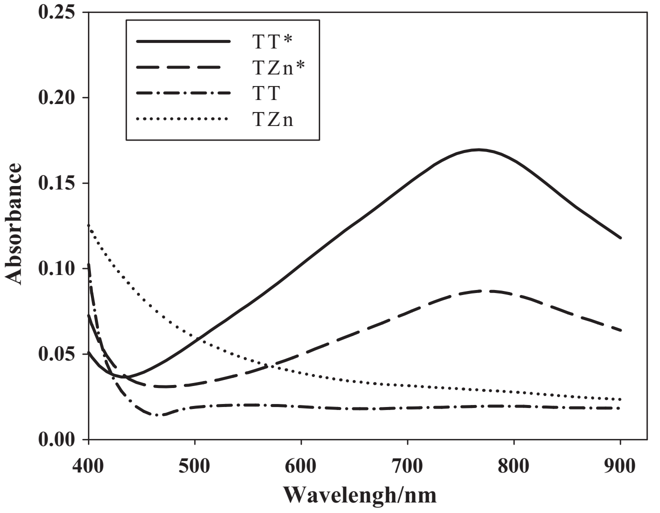


Fig. 3. UV–vis spectra of the aqueous solutions of tara tannin (TT) and its derivative (TZn) with (*) and without the Folin–Denis reagent.

FTIR spectra showed that both TT and TZn had a broad intense band around 3400–3600 cm^{-1} which corresponds to the stretching of the OH group (Fig. 4). The greatest band broadening observed in the TT spectrum was attributed to a larger number of hydrogen bonds [42]. In change, the narrow band in TZn spectrum showed a decrease in this type of interaction. In this last spectrum it was also observed a sharp decrease of the peak at 1715 cm^{-1} which corresponds to the stretching of the carbonyl group of ester linkages. Concomitantly, it was detected the widening of the peak at 1620 cm^{-1} which could be assigned to the ionized carboxyl groups produced during the hydrolysis of ester unions [35]. The ionized carboxyl groups interact with the metal ions to coagulate and precipitate the corresponding "tannate". Carbonyl stretching frequencies are affected by electrical effects due to the release of electrons from the carbon–oxygen double bond [43]. The TT spectrum shows two peaks to 1540 and 1450 cm^{-1} due to the stretching of C═C bond of the aromatic ring which, in the case of TZn, were displaced to lower wavenumbers (1490 and 1430 cm^{-1}, respectively). In both cases the sharp peak at 1230 cm^{-1} corresponds to the C–O bond of phenols and the peak next to 1090 cm^{-1} corresponds to the vibration of C–O bond [43,44].

3.2. Bioassays

After an incubation period of 24 h, LC_{50} was found to be 42 ± 10 mg/l for TZn and 7 ± 2.0 mg/l for copper sulphate (positive control), respectively. These results showed that TZn is active against *A. persimili* larvae; however its toxicity is much lower than that of copper sulphate.

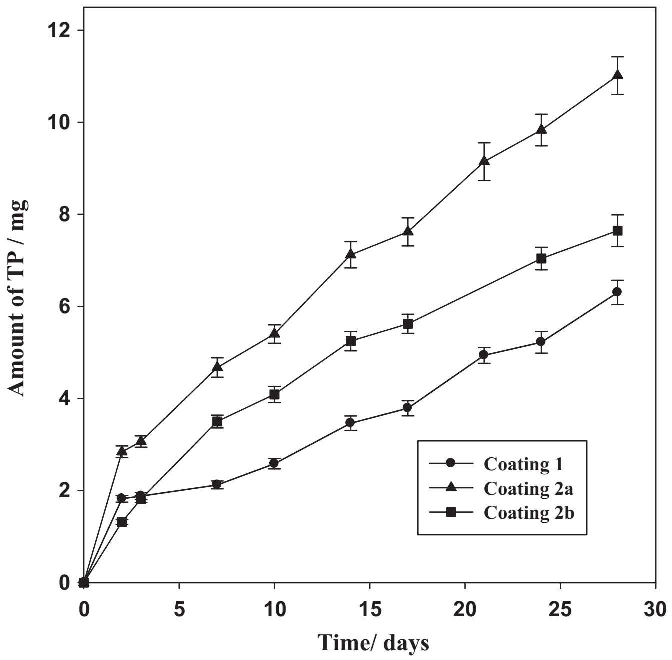


Fig. 5. Amount of tannin leached from the antifouling coatings.

3.3. Determination of leached polyphenols as a function of time

Results of the leaching experiments are shown in Figs. 5–8. In these systems, the reproducibility is acceptable and the variation coefficient between measurements is ~4%. Coating 1, formulated with rosin and SAC binders leached lesser amounts of tannin than coating 2a and 2b without SAC (Fig. 5). The PT leached from coating 2b was intermediate between coatings 1 and 2a (Fig. 5). The highest leaching rate was detected for coating 2a (Fig. 6). As it will be shown latter, the results from NSW essays indicate that the amount of biocide leached from coating 1 was not enough to maintain good AF efficiency over time and coating 2a deteriorated in a shorter time. During the first week of testing, there was a sharp drop in the leaching rate of coatings 1 and 2a (Fig. 6). At the end of the trial, coating 2b showed a leaching rate of tannin close to a half of that exhibited by the coating 1 and 2a. According to biological tests in NSW the leaching rate of paint 2b (2.5 μg cm^{-2} dia^{-1} of PT) seemed

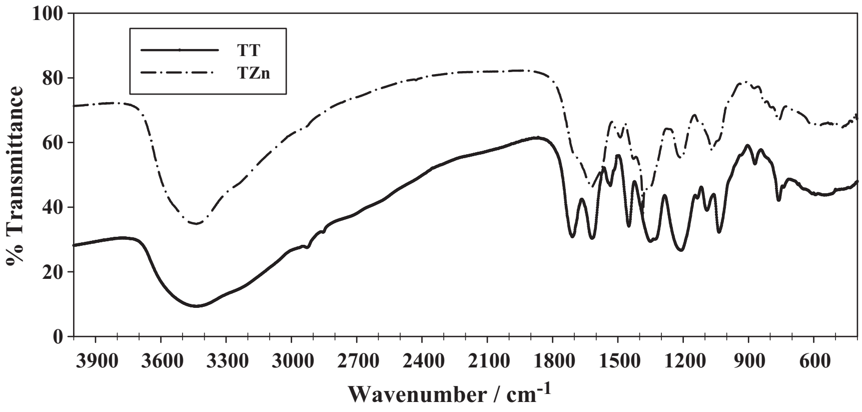


Fig. 4. IR spectrum of tara tannin (TT) and its derivative (TZn).

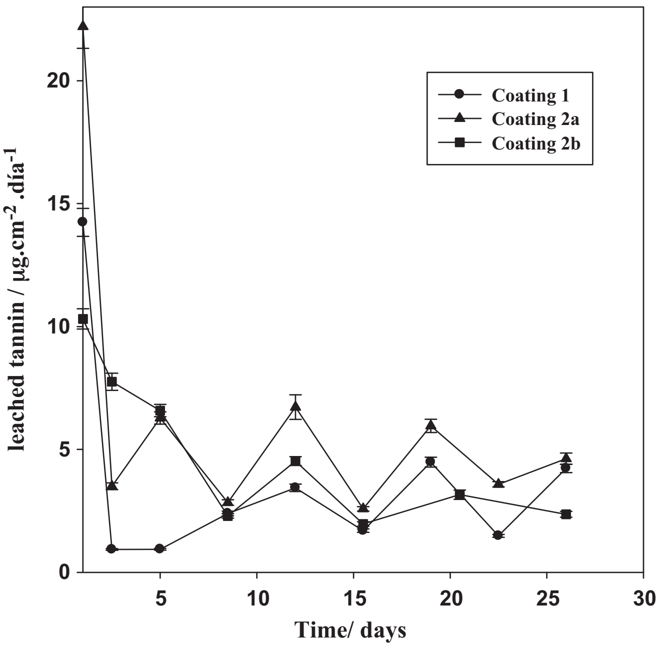


Fig. 6. Tannin leaching rate from the antifouling coatings.

to be adequate to an acceptable achieve antifouling activity for this type of pigment.

At the beginning of the assay, coatings 1 and 2b leached an amount of zinc three times lower than paint 2a, this difference decreased to the end of the experiment (Fig. 7). The level of zinc leached from the coating ranged between 1 and 2 μg cm^{-2} day^{-1} at the end of the assay (Fig. 8). This fact is of great importance because lower amounts of metals would be released to the environment during coating service life. According to bibliographic data, zinc leaching rate from biocide-free commercial AF paints is approximately 4–8 times higher than the value determined in this research [12,45].

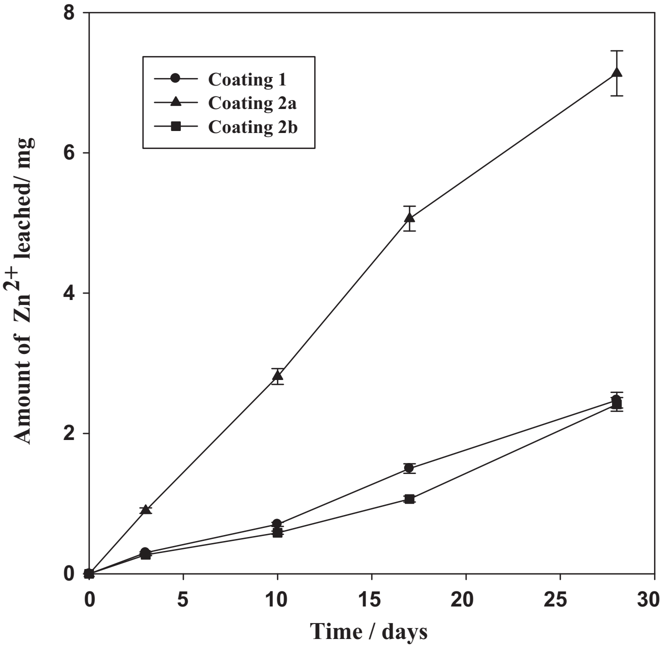


Fig. 7. Amount of zinc ions leached from the coating films.

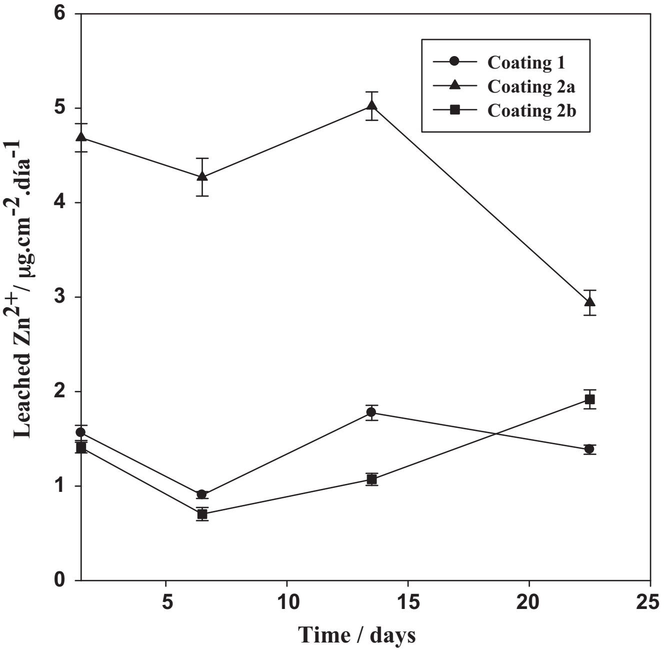


Fig. 8. Zinc ions leaching rate from the antifouling coatings.

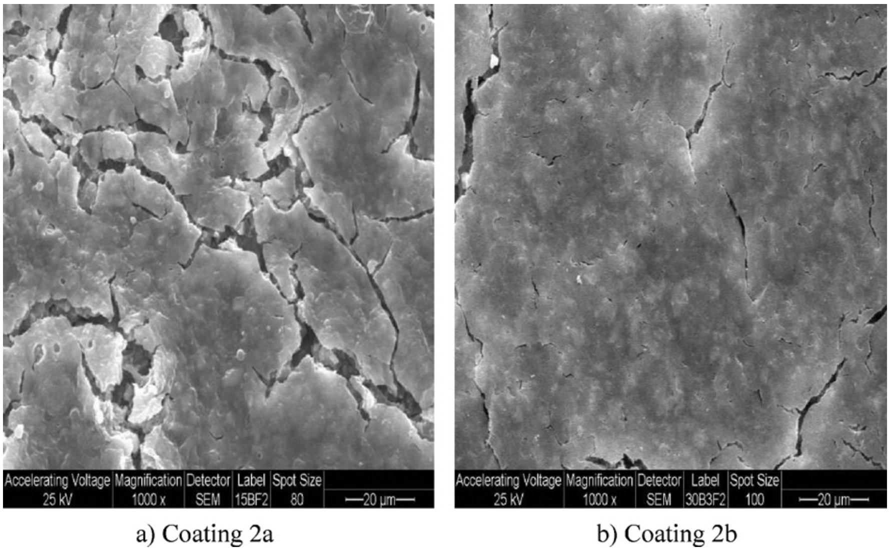
In addition, results obtained from surface observation by SEM (Fig. 9) showed that the coating 2a, after three months of immersion in ASW, presented higher deterioration than the coating 2b. These results demonstrated that the addition of low amounts of ZnO modified the surface characteristics of the coating. It should be also noted that the cracked surface was originated by the high vacuum employed during SEM exploration. Regarding zinc leaching rates presented in Fig. 8, it could be said, there were not abrupt changes as those reported for polyphenols (Fig. 6), keeping almost constant values. This could be attributed to the fact that zinc ion tends to precipitate in ASW. Then, zinc hydroxide partially dissolves by the formation of chlorinated complexes as shown below:

$$\mathrm{T_2Zn + M^{2+} \leftrightarrow T_2M + Zn^{2+} (M = Ca; Mg)}$$
$$\mathrm{Zn^{2+} + 2HO^- \rightarrow Zn(OH)_2 \downarrow}$$
$$\mathrm{Zn(OH)_2 + 4Cl^- \leftrightarrow {ZnCl_4}^{2-} + 2HO^-}$$

In the proceeding representation the reaction among polyphenols, with multiple phenolic hydroxyl groups, and Mg^{2+} and Ca^{2+} to form metal complexes was represented [46]. These complexes are formed especially with higher charge and smaller ionic radius ions such as Mg^{2+} and Ca^{2+} in relation to Na$^+$.

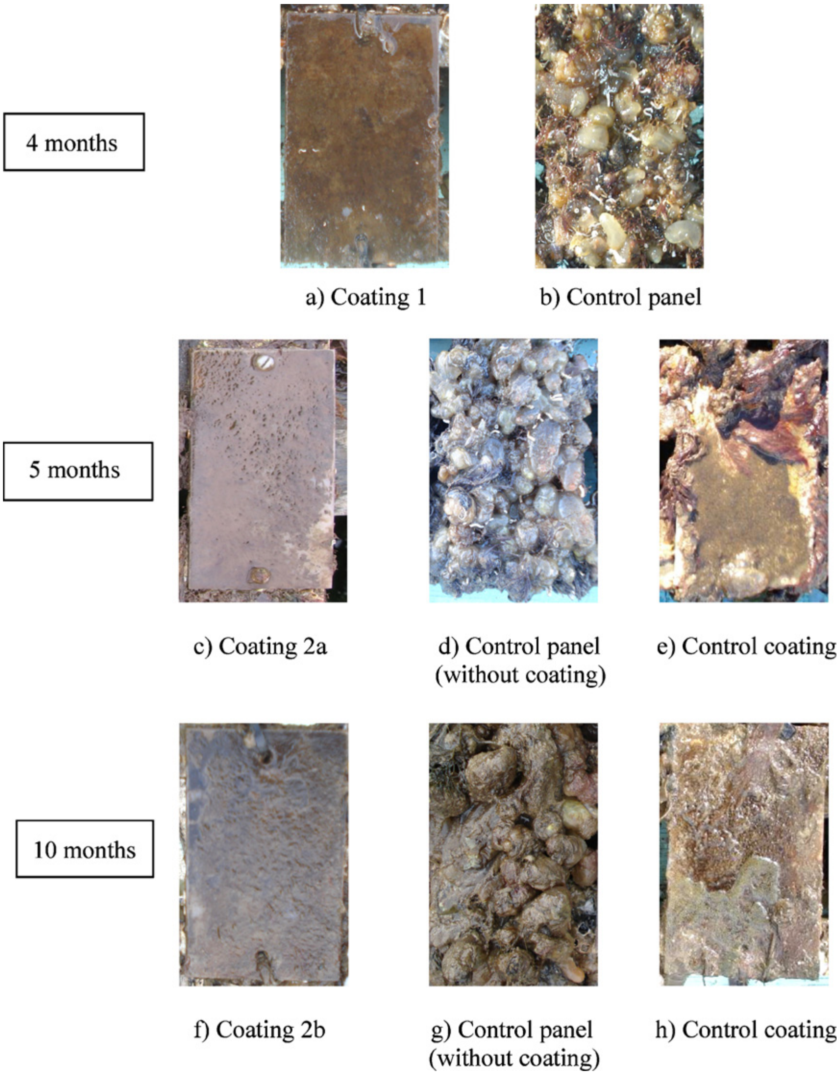
3.4. Essays in NSW

All painted panels performed better than the control (Fig. 10). After four months, coating 1 showed an efficiency of 80%, settlement degree 1–2 (Fig. 10a); while the settlement degree of the control was 5 (Fig. 10b) which relate to 0% efficiency. In both cases serpulids were found to be attached onto the panels. After ten months of exposure, the settlement degree corresponding to coating 1 was 3–4. Coating 2a (rosin ww/oleic acid) showed an efficiency of 100% at fifth month with an incipient erosion of the film (Fig. 10c), the control panels' settlement degree was 5 (Fig. 10d). The control panels with the same formulation that coatings 2a but replacing TZn by TiO$_2$ showed a high settlement degree (4–5) after five months although the underlying coating remained intact. Algae, ascidians and serpulids were attached on the coated panels (Fig. 10e). After eight month panels with coating 2a had lost 80% of the coating but without signs of macrofouling on the



a) Coating 2a b) Coating 2b

Fig. 9. SEM micrograph of panels immersed three months in ASW (observed cracks respond to high vacuum conditions).



a) Coating 1 b) Control panel

c) Coating 2a d) Control panel (without coating) e) Control coating

f) Coating 2b g) Control panel (without coating) h) Control coating

Fig. 10. Photographs of panels immersed in sea water environment.

panels. Panels with coating 2b (Fig. 10f) showed an AF efficiency of 90% (settlement degree, 0–1), after ten months of immersion, with incipient erosion. As it was said previously, control panels presented (Fig. 10g) a high settlement degree (5) and were completely covered with ascidians, algae, serpulids, barnacles and bryozoans. At the same time control panels with the same formulation than that of coatings 2b, with 2% by weight of ZnO, but replacing TZn by TiO_2 were completely fouled (Fig. 10h). The addition of ZnO to coating 2b extended its service life until the year of exposure, with a settlement degree of 1, as it could be expected for this type of paint [10,11]. Then, panels lost 90% of coating increasing the settlement degree. Photographs of exposed panels could be seen in Fig. 10a–h.

4. Conclusions

The total amount of polyphenols leached by coatings formulated with rosin–oleic acid binder was higher than that from the coating containing rosin and SAC. As a consequence, coatings formulated with rosin–oleic acid binder were more efficient in NSW environments. The addition of zinc oxide increased the service life of the coatings formulated with rosin and oleic acid, diminishing, at the same time, the TP leaching rate and the coating damage by erosion.

The AF performance of "tara" tannin derivative was better than that of "quebracho" tannin. In additions, the use of the fruit pods of the TT avoids the cutting down of the trees as it occurs in the case of "quebracho" trees.

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