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Studies on the anticorrosive & antifouling properties of the *Gracilaria edulis* extract incorporated epoxy paint in the Gulf of Mannar Coast, Mandapam, India

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ABSTRACT

The anticorrosive and antifouling properties of the *Gracilaria edulis* extract (1%, w/v) incorporated epoxy paint have been evaluated in the Gulf of Mannar Coast, Mandapam, India for an year. The antibacterial activity of *G. edulis* extract was determined by disc diffusion method and minimum inhibitory concentration against 5 bacterial isolates by Broth Macro dilution method using Mueller Hinton broth. The anticorrosive property of the *G. edulis* extract was studied by Salt spray test and electrochemical impedance measurements. The extract was characterized by FTIR, NMR and atomic absorption spectrometer. Laboratory tests reveal the antibacterial and anticorrosive properties of the extract. *G. edulis* extract incorporated epoxy based paint exhibited both anticorrosive and antifouling properties in natural seawater for 6 months.

1. Introduction

Marine fouling is the result of the growth of several organisms such as, barnacles, mussels, algae and others, on the surface of submerged objects [1]. Since the beginning of the history of navigation, many materials have been used in order to minimize the fouling problem. However, the development of antifouling paints began only in the mid of 1800s [2]. Currently, TBT and other tin-based antifouling agents are banned by the International Maritime Organization [3] and instead of the TBT free formulations, the tin is replaced by metals like, copper [4–6], zinc [7] and titanium [8]. Copper has excellent antifouling properties against barnacles and algae, even though some species are resistant to this metal [9]. Indeed even the so called biocide free antifouling marine paints are toxic to marine organisms as has been demonstrated recently [10,11]. Therefore there is an urgent quest for new environment friendly antifoulants [12].

Many marine macroalgae, as well as benthic marine invertebrates, are relatively free of epibiosis due to the production of biogenic compounds that possess antibacterial, antialgal, antifugal, antiprotozoan and anti-macrofouling properties. These agents are usually seaweed secondary metabolites [13] and they can be used for developing new antifouling agents [14–17]. The phylogenetic pattern in antifouling activity among the macroalgae clearly shows that the red macroalgae has the highest proportion (55%) of active species (moderate or strong fouling inhibition), followed by brown macroalgae (14%). These results [18,19] suggest that research efforts should be focussed on the more prolific red macroalgae in the quest for new natural product antifoulants from seaweeds. Antifouling marine natural products have been recognized as a promising alternative to the commercial antifoulants [20,21].

The antibacterial activity of *Gracilaria edulis* extract against gram negative and gram positive bacteria has been well established by several researchers [22,23]. The relation between the inhibition of microorganisms, i.e. employing microbial assays as antfouling tests and inhibiton of fouling in the field (natural seawater) has long been controversial and thus the extrapolation of such results must be performed with caution [24]. Field study evaluation of anticorrosive & antifouling properties of paint formulations with bioactive compounds derived from marine natural product has not found a place in the literature. Considering the well established antibacterial potentials of the *G. edulis* in the laboratory assay tests, in the present study an attempt has been made to elucidate the anticorrosive and antifouling properties of the *G. edulis* extract incorporated epoxy based paint in the Gulf of Mannar Coast, Mandapam, India, which is the first of its kind.

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2. Materials and methods

2.1. Collection of seaweeds

The seaweeds *G. edulis* was collected from the East coast of Mandapam, Tamil Nadu, India and taxonomically identified at the Centre for Advanced Studies in Marine Biology, Annamalai University.

2.2. Preparation of seaweed extracts

The collected *G. edulis* sample was cleaned and the necrotic parts were removed, washed with tap water to remove any associated debris and shade dried at room temperature (28 ± 2 °C) for 7 days or until they are brittle easily by hand. The clean seaweeds were frozen and lyophilized. The dry material was stored at −20 °C.

After complete drying the seaweed materials were ground to a fine powder using electrical blender and the powdered seaweeds were extracted successively using isoamyl alcohol in Soxhlet extractor until the extract was clear. The extract was evaporated to dryness under reduced pressure using rotary vacuum evaporator and the crude extract was deep frozen (−20 °C) and stored until further use.

2.3. Determination of antibacterial activity of G. edulis

2.3.1. Disc diffusion method

The bacterial isolates like *Enterobacter aerogenes*, *Klebsiella pneumonia*, *Pseudomonas aeruginosa*, *Salmonella typhii*, *Staphylococcus aureus*, were obtained from the Microbiology Laboratory of Marine Algal Research Station, CSIR-CSMCRI Unit, Mandapam. The antibacterial activity of *G. edulis* extracts was determined by Disc diffusion method proposed by Bauer et al. [25]. The inoculums were prepared from 24 h old cultures in nutrient broth. Nutrient agar plates were prepared and the inocula were seeded by spread plate technique. Whatman No.1 filter paper disc of 6 mm diameter were sterilized, saturated with extracts and air dried before placing on the seeded agar plate. Controls soaked in the same solvent (isoamyl alcohol) and dried were also run simultaneously. After 24 h of incubation at 37 °C the inhibition zone from the edge of the disc to the inner margin of the surrounding bacterial growth was measured in mm by using graduated scale and recorded.

2.3.2. Minimum inhibitory concentration (MIC)

MIC of the *G. edulis* extract against the bacterial isolates, *E. aerogenes*, *K. pneumonia*, *P. aeruginosa*, *S. typhii*, *S. aureus*, was tested in Mueller Hinton broth by Broth Macro dilution method. The seaweed extract was dissolved in 5% dimethylsulfoxide (DMSO) to obtain 128 mg/ml stock solution. 5 ml of stock solution was incorporated into 0.5 ml of Mueller Hinton broth for bacteria to get a concentration of 80, 40, 20, 10, 5, 2.5 and 1.25 mg/ml of G. edulis extract and 50 μl of standardized suspension of the test organism was transferred on to each tube. The control tube contained only organisms and devoid of G. edulis extract. The culture tubes were incubated at 37 °C for 24 h. The lowest concentration which did not show any growth of tested organism after macroscopic evaluation was determined as MIC.

2.4. Formulation of coatings

The coating formulation I was developed with the following composition, epoxy equivalent of 425–450 grade was used as binder, polyamide as hardener and pigment such as zinc phosphate, iron oxide, talc and mica were used for the development of primer to a thickness of 80 ± 5 μm. The primer was formulated with a pigment volume concentration (PVC) of 35%. The middle coat comprises of epoxy equivalent of 425–450 grade as binder, polyamide as hardener and pigment such as micacious iron oxide, talc and silica, to a thickness of 65 ± 5 μm with a pigment volume concentration (PVC) of 35%. The top coat comprises of epoxy equivalent of 425–450 grade as binder, polyamide as hardener and pigment such as, TiO_2 (Anatase), talc and mica as extender pigments and Cu_2O as antifoulant, to a thickness of 45 ± 5 μm with a pigment volume concentration (PVC) of 20%.

The coating formulation II was developed with the addition of booster biocide – 1% (w/v) of *G. edulis* extract in the top coat of the coating formulation I. The above coating formulations I & II, were prepared in a laboratory scale using attritor ball mill for 25 min with mixed solvents such as, xylene, butyl cello solvent and methyl isobutyl ketone (MIBK) of equal volume ratio, to achieve an efficient dispersion.

2.5. Coupon preparation and application of coatings

Commercially available metal sheets of mild steel (C: 0.16%, S: 0.4%, Mn: 0.7%, S: 0.04%, P: 0.04% and Fe: balance) of 2 mm thickness supplied by M/s. Lawrence Metal Industries, Chennai were used in this study. Sheets of mild steel were cut into required number of coupons of sizes, 150 mm × 100 mm for salt spray & natural sea water immersion studies and 25 mm × 75 mm for electrochemical impedance study. The coupons were pickled [26] & sandblasted [27], and three coats of the paint formulations I & II, were applied by brush and allowed to dry for 24 h between each application, with a final dry film thickness of 190 ± 5 μm. All the coated coupons were allowed to get cured at room temperature for 7 days and preserved in desiccators with proper packing for conducting lab and field studies.

2.6. Evaluation of the anticorrosive property of the coating systems – I & II by Salt spray test ASTM B-117

Sufficient numbers of coated coupons of paint formulations I & II, were exposed in the standard salt spray chamber for evaluation of their anticorrosive property, as per ASTM B117 [28]. The coated coupons were suspended between 15 and 30° from the vertical and preferably parallel to the principal direction of horizontal flow of the fog through the chamber, with necessary interspaces, ensuring avoidance of direct impingement. 5% NaCl solution was used for fog creation by employing clean compressed air for atomization. The chamber temperature was maintained at 35 °C with pH ranging between 6.5 and 7.2. Periodic visual observations on the coated coupons were made with a time interval of 24 h, either until the failure of the coating systems or up to 1000 h, whichever is earlier.

2.7. Characterization of G. edulis extract by FTIR, NMR and AAS

The FTIR spectrum of the *G. edulis* extract was recorded in NICOLET- 380 model Fourier transform infrared Spectrophotometer in the mid IR region of 400–4000 cm^{-1}. NMR spectrum of *G. edulis* extract was recorded using Bruker–Advance 400, FT-NMR (400 MHz). The heavy metals present in *G. edulis* extract were determined by using Atomic Absorption Spectrometer, Model Spectra AA 220.

2.8. Electrochemical impedance studies

The coated coupons of paint formulations I & II were subjected to Electrochemical impedance spectra (EIS) studies using PAR model 6310 EG & G instruments A.C. impedance analyzer (Naderi R, 2004) over the frequency range of 10 kHz to 100 MHz using AC signal

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