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Coconut Husk Fiber Proanthocyanidins: Ecofriendly Corrosion Inhibitor, Ecotoxicity and Biocide Activity

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Abstract— **Coconut (Cocos nucifera) husk fiber present high content of polymeric phenolic compounds (proanthocyanidins). These compounds are natural antioxidant, so it could possibly present anticorrosive effect. Then, the main objective of this study was evaluate the activity of coconut husk fiber proanthocyanidins as corrosion inhibitor for carbon steel AISI 1020 in neutral medium, its ecotoxicity and its biocide effect for microorganisms involved in biocorrosion. The experiments achieve inhibition efficiency for corrosion process greater than 90%. The coconut proanthocyanidins concentration did not interfere in lettuce seeds germination, with a germination perceptual higher than 90% in all concentrations tested. No biocide effect was observed for microorganisms studied under the concentrations tested (0.1-1 g/L). The results suggest coconut condensed tannin as a promising anticorrosive agent, although further tests are necessary to evaluate its effect on biofilm, and the efficiency of the anticorrosive effect.**

Index Terms— **Biocorrosion, Green corrosion inhibitor, Polymeric phenolic compounds, Seed germination toxicity test.**

I. INTRODUCTION

Cocos nucifera is a palm tree cultivated in tropical coconut producing countries. In Brazil, more than 3,000 tons of coconut are produced per year [1]. Unfortunately, coconut consumption leads to the generation of large volumes of solid waste, mainly due to its husk fiber, which corresponds to approximately 80% of the fruit. However, all coconut husk fiber could be converted into raw material of geotextiles products, carpets, gardening, craftwork and energy source, as charcoal [2]. Beyond these applications, the coconut husk fiber could have its chemical composition exploited, including for its proanthocyanidins content [3]. Proanthocyanidins are polymeric phenolic compounds also called condensed tannins and described by their antimicrobial [4], antioxidant [5] and anticorrosive activities [6].

Corrosive processes, with and without microorganisms influence, cause serious damages to the entire industry. Therefore, it is necessary alternatives to control and prevent corrosion processes [7]. Among these alternatives are the biocides and corrosion inhibitors application, and researches on natural products, does like proanthocyanidins, as green corrosion inhibitors or biocides have gained evidence [8].

However, these natural compounds must also have their environmental toxicity evaluated to avoid damage or negative interference to the environment. The ecotoxicity could be verified through the application of different test-organisms does like vegetable seeds (*Lactuca sativa* L., *Allium* sp. and *Eruca sativa*), fish, crustaceans, cnidarian and earthworm species [9].

For this, the main objective of this study was evaluate the activity of 1 g/L coconut husk fiber proanthocyanidins as corrosion inhibitor for carbon steel AISI 1020 in neutral medium, its ecotoxicity for lettuce (*Lactuca sativa*) seed germination test, and its biocide effect for microorganisms involved in biocorrosion: *Pseudomonas aeruginosa*, *Shewanella sp.* and Sulphate Reducing Bacteria (SRB).

II. EXPERIMENTAL PROCEDURES

A. Plant Material

Cocos nucifera L. (*Palmae*) var. typica A, commonly known as 'Olho-de-Cravo' were collected, in Sergipe, Brazil. The samples were authenticated by Dr Benedito Calheiros Dias (Centro de Pesquisas do Cacau, Bahia, Brazil) and deposited with voucher code of CPC 2190.

B. Coconut Proanthocyanidins Aqueous Extract

The coconut husk fiber proanthocyanidins aqueous extract was obtained by decoction in distilled water. Afterwards, the extract was filtered, lyophilized, storaged at -20(±2)ºC. Before the experiments, the lyophilized was resuspended in distilled water and sterilized by membrane filtration (0,22 μm pore). The coconut husk fiber proanthocyanidins was previously characterized and its content was mostly condensed tannins (catechin and epicatechin) [10]. The proanthocyanidins content was determined as described in [11]

C. Working Fluid

The experiments were conducted in a solution simulating water from a cooling system, composed by 500 ppm of chloride (829 mg/L of NaCl), 150 ppm of sulphate (222 mg/L of Na_2SO_4), 150 ppm of calcium carbonate ($CaCO_3$), adjusted for neutral pH (7±0.2) with 0.5 M HCl solution.

D. Microorganisms

The strains of *Pseudomonas aeruginosa*, *Shewanella sp.*, and Sulphate Reducing Bacteria (SRB) consortium were obtained from a sample of water from the cooling system of an oil refinery with corrosion history. Then, the microorganisms were deposited in the microbial bank of the Biocorrosion and Biodegradation Laboratory of the National Institute of Technology in Rio de Janeiro/Brazil.

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E. Corrosion Inhibitor Activity

The anticorrosive activity test was carried out in 100 mL glass cells, maintained at controlled temperature (25±2ºC) and slow shaking. Prior to each test, square carbon steel AISI 1020 working electrodes were mechanically polished using SiC papers of 80, 120, 220, 320, 400, 500, and 600 grit, washed with distilled water, cleaned with alcohol and dried with hot air. These tests were conducted in a three-electrode electrochemical cell connected to an AUTOLAB PGSTAT302N Potentiostat/Galvanostat. The working electrode with 1 cm^2 of exposed area, a platinum counter electrode, and a reference KCl-saturated calomel electrode (SCE) were immersed in the solution for 24 hours for Tafel data acquisition.

The inhibition efficiency (IE) perceptual was calculated by using Tafel data (1), where J^0_{corr} and J'_{corr} are the corrosion current density values without and with 1g/L of coconut husk fiber proanthocyanidins, respectively.

$$IE(\%) = \frac{J^0_{corr} - J'_{corr}}{J^0_{corr}} \times 100 \quad (1)$$

F. Ecotoxicity Test

The toxicity of coconut husk fiber proanthocyanidins was determined by lettuce (*Lactuca sativa* L.) seeds germination test [9]. The toxicity was evaluated in 4 different concentrations between 0.125 and 1 g/L. The germination seeds perceptual was determined by using (2), where %GS is the percentage of germinated seeds, GT is the total germinated seeds in the proanthocyanidins test, and GC is the total germinated seeds in control.

$$\%GS = \left(\frac{GT}{GC}\right) \times 100 \quad (2)$$

G. Biocide Activity

The biocide activity was determined by the Minimum Inhibitory Concentration (MIC) obtained by microdilution, for *P. aeruginosa* and *Shewanella sp.*, and macrodilution, for SRB consortium described by Clinical and Laboratory Standards Institute [12]. Beyond the turbidity observation, a growth test was performed to confirm the MIC. The maximum concentration of coconut husk fiber proanthocyanidins tested was 1 g/L.

III. Results and Discussion

A. Corrosion Inhibitor Activity

The corrosion inhibition of coconut husk fiber proanthocyanidins on AISI 1020 carbon steel in neutral solution containing 500 ppm of chloride, 150 ppm of sulphate and 150 calcium carbonate has been evaluated by Tafel measurements as shown in Table I. The corrosion potential (E_{corr}), corrosion current density (J_{corr}) and corrosion rate were obtained from linear polarisation resistance curve.

Based on the action mechanism the corrosion inhibitors can be classified as anodic, cathodic or mixed-type [13]. Previous studies suggest that if the inhibitor cause variation of at least 85 mV, it could be classified as anodic or cathodic corrosion inhibitor. However, if this variation is shorter than 85 mV it possibly is a mixed-type inhibitor [14].

The difference of corrosion potential (E_{corr}) between the test and the control (Table I) is 26 mV. So, it suggests that coconut husk fiber proanthocyanidins is a mixed-type corrosion inhibitor. Usually, this kind of corrosion inhibitor form a film on metal surface able to block surface-active sites avoiding or reducing corrosion reactions [13][14]. After 24 hours, it was observed the formation of a black film on metal surface. The same protective film was described in similar studies [15][16].

The addition of 1 g/L of coconut husk fiber proanthocyanidins reduced the corrosion speed since it was able to reduce the corrosion current density and corrosion rate more than 10 times (Table I). By using (1) the inhibition efficiency was calculated, and show more than 90% of efficiency after 24 hours of immersion.

The most common is the evaluation of anticorrosive activity in acid mediums. However, the industrial application of corrosion inhibitor involves different pH ranges and these compounds must maintain their efficiency throughout these variations. The proanthocyanidins are described as efficient corrosion inhibitors in acid environments [15]-[17]. Nevertheless, its activity in neutral medium was not described before.

Table I – Galvanostatic (Tafel) parameters of corrosion inhibitor activity tests after 24 hours of immersion

Inhibitor (g/L)	Tafel data			
	E_{corr} (mV, SCE)	J_{corr} (Acm^{-2})	Corrosion Rate (mpy)	Inhibition (%)
0	-732	6.215E-06	2.845	-
1	-758	5.275E-07	0.242	91.51

B. Ecotoxicity Test

Toxicity tests using vegetables seeds are practical resources of low cost and reasonable sensitivity for qualitative indication of the presence of toxic substances [19]. In this study, no significant toxic effect was observed on lettuce seeds, with a germination perceptual higher than 90% in all concentrations tested (Table II) [9].

Table II – Perceptual of germinated seeds in contact with different concentrations of coconut husk fiber Proanthocyanidins

Proanthocyanidins concentration (mg/L)	Germinated seeds (%)
0.125	93
0.5	93
0.75	100
1	100

These results suggest that even though the proanthocyanidins may present some biocidal effect, up to the concentration of 1 g/L, it does not present toxicity to lettuce seeds.

C. Biocide Activity

Coconut husk fiber proanthocyanidins have already had its antimicrobial activity studied [10]. However, the biocide efficiency varied with the microbial species and the proanthocyanidins concentration, which varied between 1 and 2.5 g/L [19]-[22]. The MIC of coconut husk fiber for *P. aeruginosa*, *Shewanella sp.* and SRB consortium (Table III) was greater than the highest concentration tested (1 g/L).

Table III – Minimum Inhibitory Concentration (MIC) of Coconut Husk Fiber Proanthocyanidins

Microorganism	MIC
Pseudomonas aeruginosa	> 1 g/L
Shewanella sp.	> 1 g/L
SRB consortium	> 1 g/L

Proanthocyanidins also have activity on the formation of biofilms and mature biofilms [19][20]. And, if this biofilm is formed on metal surfaces, the complexation of metal ions and proanthocyanidins have cytotoxic properties, collaborating with the anticorrosive properties [22][23].

IV. Conclusions

Currently, the concept of sustainable development is much more widespread and it induces us to the conscious use of the natural resources, maximum of use and less waste generation. So, the extraction of a potential corrosion inhibitor from a solid waste that is a huge problem in tropical countries is an interesting alternative in this way. This study showed that a concentration of 1g/L of coconut husk fiber proanthocyanidins is a potential corrosion inhibitor with more than 90% of efficiency after 24 hours of immersion, while similar surveys have reached this efficiency with a maximum of 6 hours of immersion. In addition, this study present that proanthocyanidins are also efficient corrosion inhibitors in neutral mediums. Besides its corrosion inhibitor activity, the germination test with lettuce seeds suggest that its application has no toxicity to the environment. However, for the maximum concentration tested (1 g/L) the coconut husk fiber proanthocyanidins do not present biocide activity for *P. aeruginos*, *Shewanella* sp. and SRB consortium.

More studies are necessary to comprehend the stability of protector film formed on metal surface, the influence of proanthocyanidins and metal ions complexes in microbial community and the effect of coconut husk fiber proanthocyanidins on biofilm formation and mature biofilm.

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