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Evaluation of the *Sapindus saponaria L* extract as an acid medium corrosion inhibitor

Avaliação do extrato da *Sapindus saponaria L* como inibidor de corrosão do cobre em meio ácido

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ABSTRACT

Copper and its alloys have characteristics of electrical and thermal conductivity and good toughness. As copper has a positive value for standard reduction potential, it does not react with water, but with oxidizing acids. A useful method to protect metals and alloys is the addition of corrosion inhibiting substances in the solution, which has a high inhibition efficiency.However, many inhibitors are undesirable because of their toxicity to the environment and their high cost. Studies have been developed in order to investigate plant extracts as corrosion inhibitors. The *sapindus saponaria* L plant may have some technological interest in relation to corrosive processes.For this purpose, the techniques of potentiodynamic polarization of cyclic and linear scanning, chronoamperiometry, gravimetric by mass loss immersion, flame atomic absorption spectrometry and scanning electron microscopy were used. In cyclic voltammetry with the cathodic region extract, there is some interaction with the species in solution. From the polarization curves, linear voltammetry, the efficiency was 63.6%, where the extract behaved as a mixed type inhibitor. Determining the values of the corrosion rate in the absence and in the presence of the extract, the value of 59.8% of inhibitory efficiency in terms of mass loss immersion and 80.0% in terms of copper ions content in solution from flame atomic absorption were found.The micrographic images show that in the presence of the extract, on the copper surface there were no significant changes and the formation of corrosion products did not occur. It is concluded that the extract of *sapindus saponaria L* is a reasonable inhibitor of copper corrosion in HNO_3 1 mol/L.

Keywords: *Sapindus saponária L*, Copper, Corrosion, Acidic Medium

RESUMO

O cobre e suas ligas têm características de condutividade elétrica e térmica e boa tenacidade. Como o cobre tem um valor positivo para o potencial de redução padrão, ele não reage com a água, mas com os ácidos oxidantes. Um método útil para proteger metais e ligas é a adição de substâncias inibidoras de corrosão na solução, que possui uma alta eficiência de inibição. No entanto, muitos inibidores são indesejáveis devido à sua toxicidade para o meio ambiente e seu alto custo. Estudos foram desenvolvidos para investigar extratos de plantas como inibidores de corrosão. A planta *sapindus saponaria L* pode ter algum interesse tecnológico em relação a processos corrosivos. Para tanto, foram utilizadas as técnicas de polarização potenciodinâmica cíclica e linear, cronoamperiometria, gravimétrica por imersão em perda de massa, espectrometria de absorção atômica com chama e microscopia eletrônica de varredura. Na voltametria cíclica com o extrato da região catódica, há alguma interação com as espécies em solução. A partir das curvas de polarização, voltametria linear, a eficiência foi de 63,6%, onde o extrato se comportou como um inibidor do tipo misto. Determinando os valores da taxa de corrosão na ausência e na presença do extrato, foram encontrados o valor de 59,8% de eficiência inibitória em termos de imersão em perda de massa e 80,0% em termos de conteúdo de íons de cobre em solução da absorção atômica da chama. As imagens micrográficas mostram que, na presença do extrato, na superfície do cobre não houve alterações significativas e a formação de produtos corrosivos não ocorreu. Conclui-se que o extrato de *sapindus saponaria L* é um inibidor razoável da corrosão do cobre em $HNO_3$1 mol/L.

Palavras-chave: Sapindus saponaria L, Copper, Corrosion, Meio ácido

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1. INTRODUCTION

Copper is used in industries due to some favorable properties, such as high conductivity (electrical and thermal), mechanical malleability [1-4]. It is highly valued for its wide application in the oil, electronics and marine industries, as well as in the production of wires, sheets and pipes, power plants, heat exchangers, cooling tower, desalinators, besides being easy of handling and recycling. This is a very important aspect today [5-8].

Although copper is a relatively noble metal, it is susceptible to corrosion in acids and strongly alkaline solutions, especially in the presence of oxidants, such as nitric acid, because it attacks copper quickly, as hydrogen is not a product of the general reaction and the formation of solvated copper ions is thermodynamically favored, since the presence of oxygen also increases its corrosion rate in acidic solution considerably [1-8].

Therefore, the corrosion of copper and its inhibition in a wide variety of media has attracted the attention of many researchers. One of the most important methods of protecting metals against corrosion is the use of inhibitors [9-11].Corrosion inhibitors are substances or a mixture of substances that, when present in appropriate concentrations, in the corrosive environment, reduce or eliminate corrosion.The interactions between inhibitory molecules and a metallic surface are mainly physical and/or chemical adsorption [12, 13].

These compounds normally contain nitrogen, oxygen or sulfur in a conjugated system in which their molecules, through adsorption, adhere to the metal surface, forming a barrier against corrosive attack [14-17]. However, the toxic effects of synthetic inhibitors in their production or application have led to the search for new formulations of corrosion inhibitors that meet industrial objectives, but under strict and conscious criteria, in such a way that these products are not directed against society's desires and goals [18-21].

In view of this, there is currently a search for corrosion inhibitors that are cheap and non-toxic, for example, natural inhibitors, that is, those from plants, representing means of sustainable development and innovation [1].

From this point of view, the development of green inhibitors has a highly promising future as they are ecologically friendly and less harmful and low cost.Among them, plant extracts have different organic compounds such as (tannins, alkaloids, pigments, *saponins*, carbohydrates, proteins and amino acids), some of which have been reported to have corrosion inhibiting ability because they have triple bonds or conjugated with aromatic rings in their molecular structures, which are the main centers of adsorption [16, 22-24].

Sapindus saponaria L species have been researched as a source of *saponins* for cosmetic use, for their surfactant properties as well as for pharmacological use, since these compounds classified as triterpenoids, have ant ulcerative and antineoplastic activity. Popularly known as “soldier's soap”, “soap”, “monkey soap”, it is a species of regular distribution in the Brazilian states of the North, Northeast and Midwest regions. Its fruits are used by the population as soap, in the bath and in the fight against ulcers, skin wounds and inflammation [25, 26].

In order to study this effect, electrochemical techniques of linear and cyclic potentiodynamic polarization and chronoamperiometry were used to observe the behavior of the extract and the oxidation and reduction reactions of the metal in the absence and presence of the extract. Gravimetric techniques by mass loss immersion were used to calculate the inhibitory efficiency from the mass loss of copper. Flame atomic absorption spectrometry was used to calculate the inhibitory efficiency from the copper ions content in solution after the copper mass loss testsand scanning electron microscopy (SEM) associated with X-ray dispersive energy analysis spectroscopy (EDX) to assess copper morphology after acid attack in the absence and presence of the plant extract of *Sapindus saponaria L.*

2. MATERIALS AND METHODS

The extract was tested for the presence of compounds considered anti-corrosive using the following standard tests: Molisch test for carbohydrates, Shinoda test for flavonoids, fourth test for *saponins*, Salkowski for terpenes and sterols, $FeCl_3$ and Mayer reagents for the detection of tannins and alkaloids, respectively [26].

2.1 Preparationofelectrodes

Copper plates with a square shape of 1 cm^2(approximately) were used. The metal surface was sanded in the polishing machine (Arotec), using 400, 600 and 1200 sandpaper (SiC). After this process, the specimens were washed with alcohol to remove any residue from the sandpaper and the metal surface was dried with a hot air jet. Afterwards, their masses were measured on a precision analytical balance, model FA2404N. A thin platinum plate constituted the auxiliary electrode. The reference electrode was Ag/AgCl, KCl (sat).

2.2 Obtaining natural extract

Sapindus saponaria L leaves were collected near the city of Mossoró, in Brazil. After washing and drying the leaves, they were submerged in 70% ethyl alcohol for seven days. After this period, the mixture was filtered. The supernatant liquid was subjected to extraction by vaporization of the solvent, using a rotary evaporator, obtaining the ethanolic extract. Phytochemical analysis was performed at the Natural Products Laboratory of the State University of Ceará (UECE).

2.3 Test Descriptions

The immersion test was carried out at room temperature. A copper plate was immersed and exposed to the acid attack suspended by an inert wire. After the pre-established immersion time (0.5, 1, 4, 10, 15 and 24 h), the samples were removed from the acidic solutions, washed and then dried. The inert material was removed and the samples were immediately subjected to the measurement of their masses, making it possible to estimate the variation in mass as a function of immersion time. Corrosion rates were obtained by slope using Origin 8.0 software. Corrosion rates were expressed in $g.cm^{-2}h^{-1}$.

Subsequently, 5 mL aliquots of the solutions after the pre-established time immersion tests were performed for analysis by the Flame Atomic Absorption Spectrometry (FAAS) technique, in order to determine the total copper ions content in the solution. The technique was performed on a Spectr AA-55 (Varian) spectrometer. The content of total copper ions in the solution obtained by the technique was expressed in ppm or mg/L; this parameter was correlated with the volume used in the experiment, that is, 10 mL and with the exposed geometric area of the metal, to express the total content of copper ions in solution in mg/cm^2 for the immersion time in h. Calculations of inhibition efficiencies (E%) from the results of the mass loss and spectrometer tests were obtained by Equation 1:

$$E\% = \frac{T_s - T_c}{T_s} x100\% \qquad (1)$$

Where:

T_s = Corrosion rate of samples with no extract

T_c = Corrosion rate of the samples with extract

For the cyclical and linear potentiodynamic polarization, a potential scan rate of 1 $mV.s^{-1}$ was used; the potential was scanned from -1.0 V to +1 V.0 in order to observe the potential for corrosion in the absence and presence of the extract in the solution at room temperature (~ 25 ºC), using the potentiostat MQGP-01. From the values of the corrosion current, it was possible to estimate the inhibitory efficiency of the extract EI, starting from the Equation 2:

$$E\% = \frac{i_s - i_c}{i_s} x100\% \qquad (2)$$

Where:

i_s = sample current with no extract

i_c = sample current with extract

The combined use of SEM and EDX techniques was of great importance for the characterization of the material's surface.After 24 hof immersion test in the absence and presence of the inhibitor, the samples were properly conserved and sent for analysis.For this purpose, the scanning electron microscope (SEM), Philips, model XL-30, was used, with a camera attached for analysis by EDX, available at the Materials Characterization Laboratory of the Federal University of Ceará.

3. RESULTS AND DISCUSSION

By phytochemical analysis, the extract of the plant *Sapindus saponaria L* has the following compounds:catechetical tannins, flavonoids and *saponin*; and also identified the presence of steroid, triterpenoids (alpha and beta *amirine, lupeol*). These results are in accordance with that found by Rashed, 2013 [9], since this was the stratum of the stem and in this work the extract was from the leaf.

From the immersion tests, the mass variation (Figure 1) of the metal in acidic solution was obtained in the presence and absence of the ethanolic extract *Sapindus saponariaL*, as well as the concentration of copper ions (Figure 2) found in the electrolyte. The corrosion rate values were determined. From these values found, inhibition efficiencies were calculated according to Equation 1.

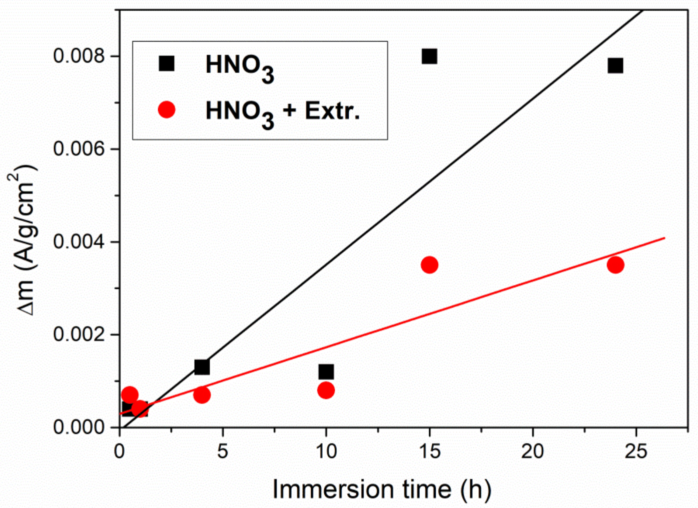

Figure 1: Mass variation of copper in 1M HNO_3 after immersion test in times of (0.5; 1; 4; 10; 15 and 24 h)

It is observed in the absence of the extract in the solution that the profile of the mass loss is accentuated when compared with the profile in the presence of the extract. Both profiles denote that the corrosive process on the copper surface occurs, however, it is minimized in the presence of the extract. Therefore, indicating that the extract has an inhibitory effect. A value of 60% inhibitory efficiency was found.

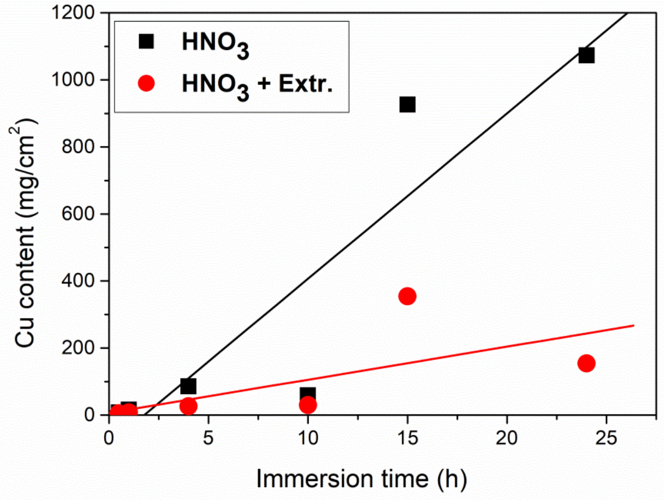

Figure 2: Variation in concentration of Cu^{2+} ions in HNO_3 1M solution after immersion test in times of (0.5; 1; 4; 10; 15 and 24 h)

The content of total copper ions in the immersion solution as a function of time is observed in

Figure 2. It was possible to calculate the corrosion rate and, from these values found, the inhibition efficiencies were calculated according to Equation 1. The value of 80% inhibitory efficiency was found.

Figure 3 shows the polarization curves, that is, the logarithmic scale of current density versus the potential of the copper electrode in the absence and presence of the extract.

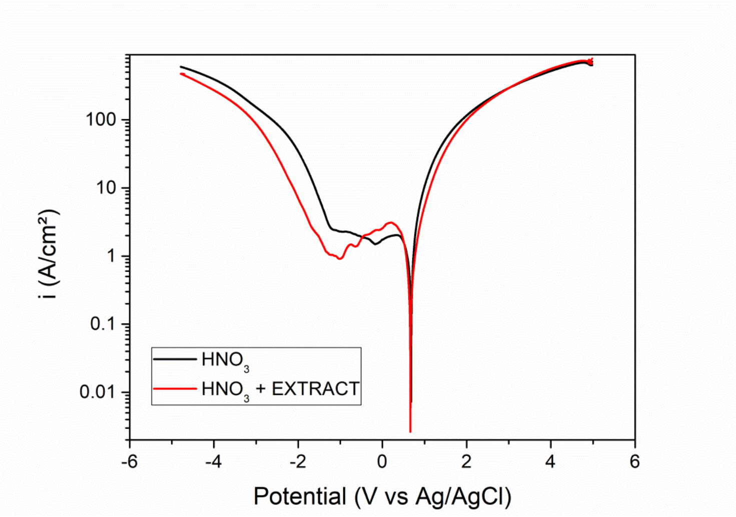

Figure 3: Potentiodynamic polarization curves of the copper electrode in 1M HNO_3 in the absence and in the presence of the extract in an acidic medium of 1 M HNO_3 on a copper surface (scan rate of 1 mV.s^{-1}).

It is observed that the current density values (Icorr), observed in the anodic and cathodic regions, have a lower value than that observed in relation to the solution without the extract, indicating that the extract is behaving as a mixed type inhibitor. It is also possible to observe that there is an overlap between the corrosion potentials (E_{corr}) of the polarization curves. The potential in the presence of the extract changes to more negative values in relation to the value of the potential in the absence of the extract. , suggesting the inhibition of the cathodic reaction.

The voltammogram in Figure 4 shows the behavior of the extract in a neutral medium. It indicates that in the potential in the range of approximately -0.8 V there is release of hydrogen, also causing the possible adsorption of the extract to the metal.

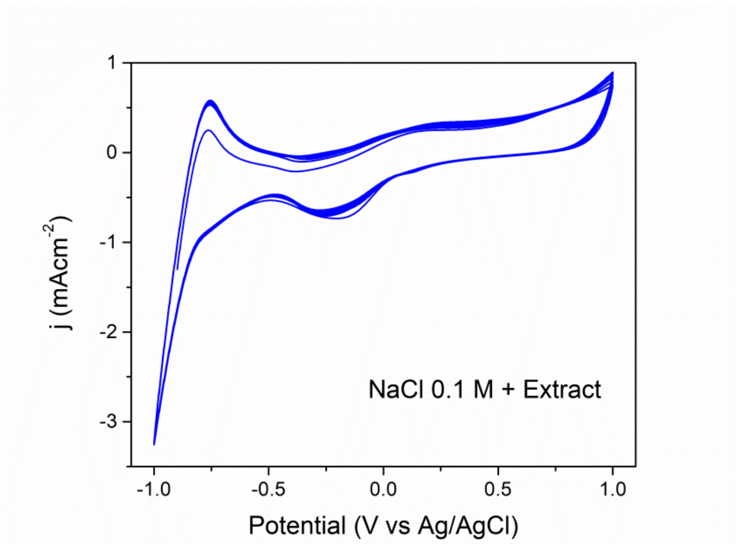

Figure 4: Cyclic voltammogram for the Sapindussapo-naria L extract in neutral 0.1 M NaCl medium on platinum surface (scan rate of 100 mV.s^{-1}).

Figure 4, it was observed that the potential in the range of -0.3 V represents the peak of reduction of a possible compound present without extract. The confirmation or extraction command of *Sa-pindussaponaria L*can act as a corrosion inhibitor, resulting from one or more compounds present in the extractor.

Figure 5 shows the metallographic images of the metal samples. It is possible to observe the blank copper surface before the test (Figure 5a) and the surface of the same sample, in the same location area after the chronoamperiometry test (Figure 5b). After 600 s of analysis time, deposition on copper metal was observed, that is, the formation of a superficial layer.

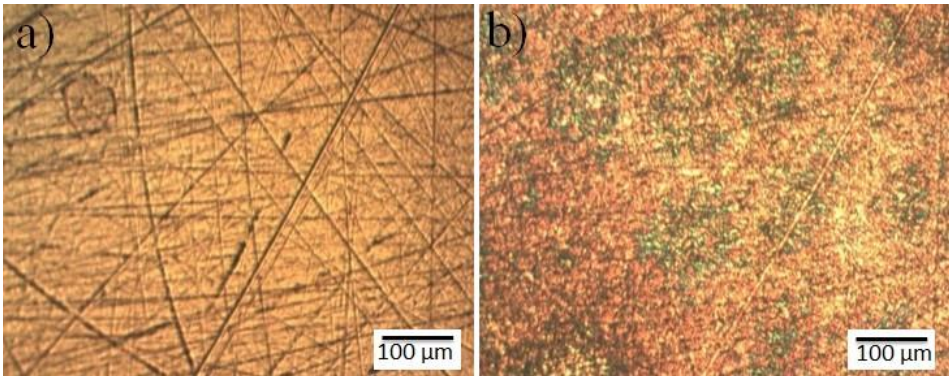

Figure 5: Metallographic image of the copper surface (a) before and (b) after the test.

Figure 6 shows the cyclic copper voltamogram in the absence and presence of the extract at room temperature in the potential range of -0.5 to +0.5 V. For this potential range, the reduction of nitrate ions (NO^{3-}) and the oxygen oxidation do not interfere during the analysis.

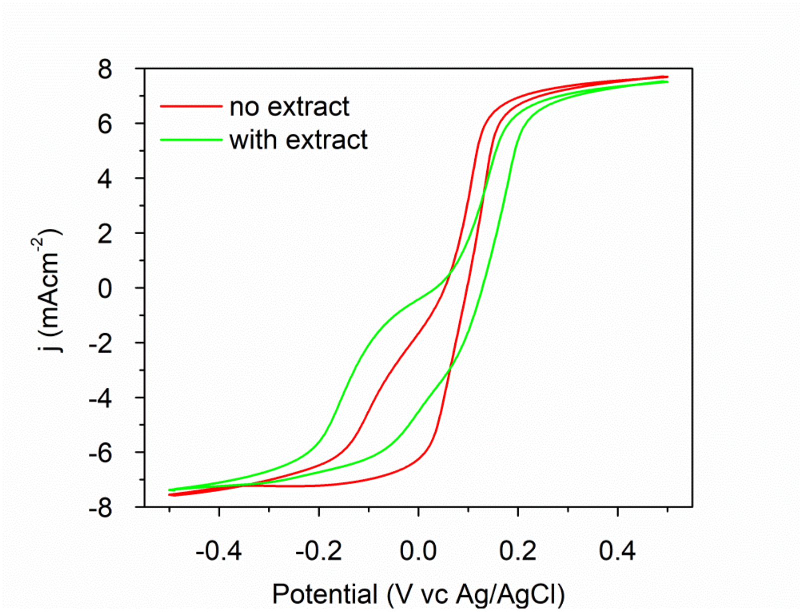

Figure 6: Cyclic voltamograms of copper in 1M HNO_3in (a) absence and (b) presence of the extract in an acidic HNO3 medium on a copper surface (scan rate of 100 mV.s^{-1}).

It was observed that in the absence of the extract, the anodic region presents a greater potential difference, tending to more positive potentials, while in the cathodic region this potential difference with the passage of cycles does not occur or does not undergo a great variation, indicating that there is a continuous flow of current.

In the voltammogram with the addition of the extract, the anodic region, when compared in the absence of the extract, has a difference in the potential of the cycles and does not vary with the cyclic sweep, indicating the dissolution of copper and the formation of copper ions. In the cathodic region, this difference between the potentials of the cycles is clearly visible, tending to more negative potentials. No peak is presented in relation to the reduction of copper ions, therefore, there may be some interaction with the species in solution, preventing this reaction, suggesting that an extract adsorption process may be taking place on the copper surface.

Figure 7 shows the micrographic images of the surface of the sanded copper (Figure7a), after the immersion test in HNO_3 1 mol/L for a period of 24 h without extract (Figure7b) and in the presence of the extract (Figure7c).

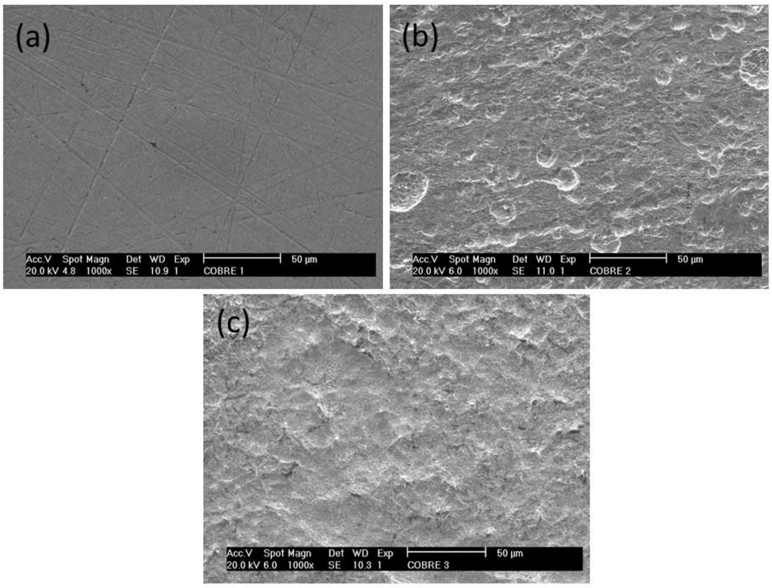

Figure 7: Micrographic images of the surface of the (a) sanded copper and after the immersion test (24 h) in (b) absence of extract and in the presence of the plant extract (c) *Sapindussaponaria L*.

From the microscopic analysis of the copper surface, after the 24 h immersion test, it was observed that the metal surface has undergone few changes in the absence of the inhibitor, showing uniform corrosion due to the corrosion resistance of the metal. However, the formation of insoluble products on the surface was observed, that is, the formation of hydroxides and/or oxides in Figure 8b. An interesting fact observed is that, with the addition of the plant extract (Figure 8c),there was no significant change in the form of corrosion on the copper surface, without formation of corrosive products. This indicates that the plant extract inhibits the corrosive process and the formation of corrosion products in the metal.

4. CONCLUSIONS

The results obtained showed that the ethanolic extract of the *Sapindus saponaria L* plant provided inhibitory efficiency in the corrosion of copper in an acidic HNO_3 medium 1 mol/L. For the tests carried out with the extract solution with 1 M HNO_3, the compound *saponins* was identified, obtained inhibition efficiency equal to 60%, in terms of mass variation, and 80% in terms of Cu ions in solution, for the concentration of 1000 ppm.In the linear scan, 70% efficiency was obtained for a concentration of 1000 ppm and this indicates that the extract behaves as a type of mixed inhibitor. The micrographic images revealed that the copper surface was modified, presenting a different behavior for the compound deposited on the metal surface in the absence as well as in the presence of the extract. The agreement between the values is reasonably acceptable.

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6. BIBLIOGRAPHY

[1] FATEH, A., ALIOFKHAZRAEI, M., REZVANIAN, A.R., “Review of corrosive environments for copper and its corrosion inhibitors”. Arabian Journal Of Chemistry, v. 13, pp.2-8, Jun 2017.

[2] COULIBALY, N.H., BROU, Y.S., AKPA, S., *et al*. “Corrosion inhibition of copper in 2M nitric acid solution by 2-(thiobenzyl)-5-nitro-1H-benzimidazole”. International Journal of Applied Pharmaceutical Sciences and Research, v. 4, pp. 54-63, Oct. 2018.

[3] FOUDA, A. S., SHALABI, K., IDRESS, A. A., Ceratoniasiliqua extract as a green corrosion inhibitor for copper and

brass in nitric acid solutions", Green chemistry letters and reviews, v. 8, pp.17-29, Oct. 2015.
[4] TASIĆ, Ž.Z., MIHAJLOVIĆ, M.B., RADOVANOVIĆ, M.B., *et al.* "New trends in corrosion protection of copper". Chemical Papers, v. 73, pp. 2103-2132. Apr. 2019
[5] PAREEK, S., JAIN, D., HUSSAIN, S., *et al.*, "A new insight into corrosion inhibition mechanism of copper in aerated 3.5 wt.% NaCl solution by eco-friendly Imidazopyrimidin Dye: experimental and theoretical approach",Chemical Engineering Journal, v. 358, pp. 725-742, Fev. 2019.
[6] QIANG, Y., ZHANG, S., GUO, L., *et al*. "Experimental and theoretical studies of four allyl imidazolium-based ionic liquids as green inhibitors for copper corrosion in sulfuric acid". Corrosion Science. v. 119, pp. 68-78. May. 2017.
[7] TOMI, I.H., AL-DARAJI, A.H., AZIZ, S.A. "Synthesis, characterization, and study the inhibitory effect of thiazole and thiadiazole derivatives toward the corrosion of copper in acidic media". Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry, v. 3; pp. 605-13. Apr. 2015
[8] KARTHIK, G., SUNDARAVADIVELU, M. "Amikacin disulfate: an aminoglycoside antibiotic drug as a corrosion inhibitor for copper in 1 M nitric acid medium. Journal of adhesion science andTechnology", v. 18pp. 1072-86.May. 2016.
[9] ELDESOKY, A. M.; HASSAN, HALA M.; FOUDA, A. S. "Studies on the corrosion inhibition of copper in nitric acid solution using some pharmaceutical compounds". International Journal of Electrochemical Science, v. 8, pp. 10376-10395, May. 2013.
[10] ASKARI, M., ALIOFKHAZRAEI, M., GHAFFARI, S. *et al.*"Film former corrosion inhibitors for oil and gas pipelines-A technical review". Journal of Natural Gas Science and Engineering., v. 58, pp. 92-114, Oct. 2018.
[11] KHALED, K. F, FADL-ALLAH, S. A., "Hammouti, B., Some benzotriazole derivatives as corrosion inhibitors for copper in acidic medium: Experimental and quantum chemical molecular dynamics approach", Materials Chemistry and Physics,v. 117, pp. 148-155. May.2009.
[12] JMIAI, A., IBRAHIMI, B. EL, *et al*, "The effect of the two biopolymers "sodium alginate and chitosan" on the inhibition of copper corrosion in 1 M hydrochloric acid", Materials Today: Proceedings, v. 22, pp. 12-15, Aug. 2020.
[13] AL-NAMI SY, F.A.E. "Corrosion Inhibition Effect and Adsorption Activities of methanolic myrrh extract for Cu in 2 M HNO3". International Journal of Electrochemical Science. v. 15, pp. 1187-205, Sept. 2020.
[14] THANAPACKIAM, P., RAMESHKUMAR, S., SUBRAMANIAN, *et al*, "Electrochemical evaluation of inhibition efficiency of ciprofloxacin on the corrosion of copper in acid media", Materials Chemistry and Physics, v. 174, pp. 129-137, Mar. 2016.
[15] IBRAHIMIL, EL, B., JMIAI, A., BAZZI, L., *et al.*"Amino acids and their derivatives as corrosion inhibitors for metals and alloys". Arabian Journal of Chemistry, v.13, pp.740-771, Jan.2020.
[16] GECE, G., BILGIC, S. "A theoretical study on the inhibition efficiencies of some amino acids as corrosion inhibitors of nickel". Corrosion Science, v. 10, pp. 3435-43, Oct. 2010.
[17] KHALED, K.F., AMIN, M.A., AL-MOBARAK, N.A. 'On the corrosion inhibition and adsorption behaviour of some benzotriazole derivatives during copper corrosion in nitric acid solutions: a combined experimental and theoretical study. Journal of applied electrochemistry', v. 40, pp. 601-13. Mar. 2010.
[18] GAO, L., PENG, S., HUANG, X, "A combined experimental and theoretical study of papain as a biological eco-friendly inhibitor for copper corrosion in H2SO4 medium", Applied Surface Science, v. 511, pp. 145446, Jan. 2020
[19] LEE, W.J. "Inhibiting effects of imidazole on copper corrosion in 1 M HNO3 solution". Materials Science and Engineering, v. 15, pp. 217-26. May. 2003.
[20] MOURYA, P., CHAUBEY, N., SINGH, V.K., *et al.*"Eco-friendly inhibitors for copper corrosion in nitric acid: experimental and theoretical evaluation". Metallurgical and Materials Transactions, v. 47, pp. 47-57, Feb. 2016.
[21] XU, W., HAN, E.H., WANG, Z. Effect of tannic acid on corrosion behavior of carbon steel in NaCl solution. Journal of Materials Science & Technology, v. 35, pp. 64-75. Jan. 2019.
[22] ZHANG, T. B., JIANG, W. F., WANG, H. L., "Inhibition and interfacial behaviour of novel amidine inhibitors against brass corrosion in 1 M HNO3 under flow conditions", Journal of Adhesion Science and Technology, v. 34, pp. 25-47, Jan. 2020.
[23] MOTAWEA, M.M., EL-HOSSIANY, A., FOUDA, A.S. "Corrosion control of copper in nitric acid solution using chenopodium extract". International Journal of Electrochemical Science, v.14, pp. 1372-87. Jan. 2019.
[24] SINGH, A, DAYU, X., ITUEN, E., *et al*, "Tobacco extracted from the discarded cigarettes as an inhibitor of copper and zinc corrosion in an ASTM standard D1141-98 (2013) artificial seawater solution". Journal of Materials Research and Technology, v. 9, pp. 5161-5173. May. 2020.
[25] SANTOS, C. M., *et al.* Enzymatic and Antagonist Activity of Endophytic Fungi from Sapindus saponaria L.(Sapindaceae). ActaBiológicaColombiana, v. 24, n. 2, p. 322-330, Aug. 2019.
[26] RASHED, K., LUO, M., "Phytochemical Content and Anti-HIV-1 Activity of Sapindus saponaria L.", v. 2, pp. 22-26, Jul. 2013.

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