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Evaluation of Limonene-Based Compound as Volatile Inhibitor to Protect AISI 1020 Carbon Steel Against Corrosion

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Volatile corrosion inhibitors (VCIs) are used to protect metal objects temporarily, such as during storage and transport. Although widely used, in the last two decades traditional synthetic VCIs have been gradually replaced due to their high toxicity. A viable solution is the use of natural inhibitors. The objective of this study was to evaluate the efficiency of limonene-based natural VCI to protect AISI 1020 carbon steel against corrosion. The vaporization capacity of VCI was evaluated by the standardized sublimation test; the ability to form a protective barrier was analyzed by testing kraft paper as anticorrosive packaging; and the inhibition mechanisms against carbon steel corrosion were investigated by electrochemical methods of open circuit potential (OCP) measurement, potentiodynamic polarization (PP) and electrochemical impedance spectroscopy (EIS). According to the sublimation test, limonene-based VCI provided effective protection to the carbon steel at a concentration of 1.5 g/L. The kraft paper test confirmed the efficiency of the temporary use (4 days) of the natural VCI in packaging, without residue deposition. Furthermore, through electrochemical measurements, we found that limonene-based VCI provided an inhibition efficiency of 99% to AISI 1020 carbon steel in a 3.5% NaCl aqueous solution, thus identifying a potential alternative to toxic synthetic VCIs.

Keywords: *Corrosion, AISI 1020 Carbon Steel, Corrosion Inhibitor, Natural VCI.*

1. Introduction

Among the various methods of protection against corrosion, the use of inhibitors is one of the most widespread, due to their high protection efficiency compared to other methods[1]. Inhibitors are generally classified according to the mechanism of action as cathodic, anodic, or by adsorption. Adsorption (or mixed) inhibitors constitute around 80% of corrosion inhibitors and are generally organic compounds that have polar functional groups in their chemical structure. These compounds act to control corrosion through the adsorption of their molecules on the metal surface, forming a thin, adherent film that blocks the active sites and functions as a physical barrier (protective layer) that prevents contact between the metal and corrosive medium[2,3]. Numerous chemical compounds with inhibiting properties have been tested as reported in the relevant scientific literature, but few are used in practice. The reason is that in addition to the desirable inhibition properties, factors such as cost, toxicity, availability and impact on the environment are important[2].

Volatile corrosion inhibitors (VCIs) are commonly organic salts derived from amines, which have vapor pressure on the order of 10^{-3} to 10^{-2} Pa at room temperature. The action mechanism of VCIs is based on the transport of the inhibitor by sublimation and subsequent condensation and adsorption on the surface of the metal to be protected, resulting in the formation of a uniform and invisible anti-corrosion film. In closed environments, after a certain vapor concentration threshold in the medium has been attained, equilibrium is reached in the exchange between the inhibitor at the source and the inhibitor at the metal surface. In other words, the speeds of the vaporization and condensation mechanisms reach the same value, generating stability of the system[2,4,5]. Therefore, the efficiency of VCIs is associated with two main conditions: the ability to reach the metal surface to be protected and the transfer rate of the molecules, which must be faster than the start of corrosion reactions on the metal surface. These two conditions are related to the vapor pressure of the inhibitor, the distance between the source of the inhibitor and the metal surfaces, and their accessibility[2]. These inhibitors are already widely used in the electronics, petroleum, natural gas, civil construction and military sectors[6], since they protect against atmospheric corrosion of metal parts during transport and storage. This protection method is also very effective when there are gaps and small openings, where a limitation exists to the application of oils or other types of liquid protection[1].

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Although widely used in the past, in the last two decades traditional synthetic VCIs are being replaced because their high toxicity. In recent years, due to rising environmental awareness and increasingly stringent environmental regulations, a growing trend towards environmentally friendly approaches has existed, encouraging the use of substances and materials with low environmental impact[7]. In this regard, inhibitors based on natural products, also known as "green inhibitors", have emerged as potential alternatives to replace synthetic inhibitors, by their safety, biodegradability, ecological acceptance and renewability[4,8]. Some examples of compounds that can act as green inhibitors are amino acids, alkaloids, polyphenols and plant extracts, including byproducts of agro-industrial processes and crop residues[8-10].

Plants of the Rutaceae family produce citrus fruits such as oranges, lemons, grapefruits and limes. These plants have high levels of bioactive compounds, such as phenols, vitamins and essential oils, and their fruits are among the most cultivated globally. The global volume of citrus fruits processed annually is around 31.2 million tons, of which 50% to 60% is waste, mainly composed of water, mono- and disaccharides and essential oils[11-13]. In the case of citrus essential oils, R-(+)-limonene (monoterpene) is the most abundant component, reaching concentrations between 90% and 96%. Approximately 50 thousand tons of R-(+)-limonene is recovered per year as a byproduct of the global citrus industry. There are several applications for limonene in the chemical, pharmaceutical and food industries, for example as a solvent for resins and for synthesis of other chemical compounds (e.g., biodegradable polymers, paints and oil dispersing agents)[13,14].

Chaieb et al.[15], in 2009, studied the use of limonene (C10H16-1-methyl-4-(1-methylethenyl)-cyclohexene) as a corrosion inhibitor for carbon steel in an acidic environment, finding inhibition efficiency (IE) of 72% at a concentration of 0.22 g/L of limonene in the corrosive medium. In 2015, Boumhara et al.[16] studied the use of *Artemisia mesatlantica* essential oil as a corrosion inhibitor (3 g/L) of carbon steel in a 1 mol/L HCl solution, and through electrochemical measurements, identified IE of 92%. Also, in an acidic medium of 1 mol/L HCl, in 2018, Alibakhshi et al.[17] identified licorice leaf extract (*Glycyrrhiza glabra*) as a green corrosion inhibitor for carbon steel, achieving protection efficiency of 88%, based on polarization resistance data.

A good deal of research exist involving natural inhibitors. However, as far as we know, studies reporting the application of these inhibitors in their volatile form, such as VCIs, are still scarce, representing an important scientific gap that needs better investigation. Based on this scenario, in this study we evaluated the efficiency of a limonene-based compound as a natural corrosion inhibitor of the VCI type, with low environmental impact, non-toxicity[18] and economic feasibility, obtained from agro-industrial waste from the processing of citrus fruits.

2. Materials and Methods

2.1. Materials

The limonene-based natural volatile corrosion inhibitor, in the form of a diffuser gel and a liquid (inhibitor oil), and traditional synthetic VCI (commercial VCI) based on benzenesulfonates and naphthalenes, in the forms of diffuser powder and inhibitor oil (liquid), were supplied by local industry partner.

For the corrosion tests, samples of AISI 1020 carbon steel were used. The chemical composition of the steel was analyzed by X-ray fluorescence spectroscopy (MET7000, Oxford Instruments-UK), as shown in Table 1.

Before the corrosion tests, the surfaces of the steel samples were sanded with SiC abrasive sandpaper (3M) with grain sizes on the order of 240, 400 and 600. After sanding, the samples were cleaned by immersion in water, isopropyl alcohol and acetone for 1 minute in each solution, and finally air-dried and stored in a desiccator.

2.2. Methods

2.2.1. Vaporization inhibition capacity assays

The NACE standard test method TM0208-2018-SG[19] was used to evaluate the volatile inhibition capacity of the natural limonene-based VCI. In this test, cylindrical specimens (7 mm in diameter and 20 mm in length) made of AISI 1020 carbon steel were exposed to VCI in a hermetically sealed container. Then condensation of the VCI was forced onto the surface of the test sample. For this test, solid natural VCI was used, in the form of an emitting gel, for temporary protection against corrosion of AISI 1020 carbon steel. The corrosive medium used was saturated water vapor with 90% relative humidity. To evaluate the surface after the test, the corrosion classification criteria for carbon steel samples were used, following the NACE-2008 standard[19]. The limiting conditions for causing corrosion on the surface of bare AISI 1020 carbon steel were determined by using a reference test (without VCI).

2.2.2. Kraft paper test: barrier inhibition efficiency (packaging)

To carry out the experiment proposed by Cheng et al.[20], kraft paper samples measuring 12 cm × 10 cm were impregnated with 1.0 g of inhibitor oil, this mass being sufficient to completely cover the surface of the paper. AISI 1020 carbon steel test specimens (70 mm × 23 mm × 3 mm) were individually packaged in paper impregnated with natural limonene-based inhibitor, in triplicate. As references for comparison, the tests were also carried out with kraft paper without inhibitor and kraft paper impregnated with commercial inhibitor oil. All samples were placed inside a humidity chamber with temperature set at 35 °C and relative

Table 1. Chemical composition of the AISI 1020 carbon steel.

Element	Fe	C	Mn	Si	S	P
wt.%*	99.07	0.20	0.52	0.17	0.015	0.025

*σ=0.007%

humidity of 100%. The samples were kept in the chamber for 5 days, and photographic images were captured each day to monitor changes in both metal and paper samples. The estimation of the corroded areas was carried out using the ImageJ software, at the respective starting times of the corrosive process.

2.2.3. Electrochemical tests

For the electrochemical tests, it was used a conventional electrochemical cell with three electrodes, with the saturated calomel electrode ($Hg/Hg_2Cl_2/KCl_{sat}$) as the reference electrode, a spiral platinum wire as the counter electrode, and AISI 1020 carbon steel as the working electrode, with an exposed area of 0.28 cm^2. The electrolyte used was an aqueous solution of 3.5% NaCl at room temperature. The measurements were carried out using a potentiostat/galvanostat with impedance module (Princeton Applied Research, model VersaStat 4) and the VersaStudio software.

After immersing the AISI 1020 carbon steel samples for just 1 minute in the limonene-based natural inhibitor or commercial synthetic inhibitor, it was performed electrochemical measurements of open circuit potential (OCP), potentiodynamic polarization (PP) and electrochemical impedance spectroscopy (EIS). Measurements for steel without inhibitors were also carried out for comparison.

The OCP was monitored for 1 h and 24 h to evaluate the thermodynamic stability of the steel electrodes in the presence and absence of inhibitors.

The PP measurements were performed in the potential range of -1.5 V to 0.2 V, with a scanning speed of 1 mV/s. Through the polarization curves, the i_{corr} and E_{corr} parameters were obtained using the Tafel extrapolation method. From the i_{corr} data, the inhibition efficiency values (%IE) were calculated using the following equation:

$$\%IE = \frac{i_{corr(noinhib)} - i_{corr(inhib)}}{i_{corr(noinhib)}} \times 100 \quad (1)$$

where $i_{corr(noinhib)}$ is the steel corrosion rate without inhibitor and $i_{corr(inhib)}$ is the corrosion rate with inhibitor on the metal surface.

The EIS measurements were performed at open circuit potential after 1 h and 24 h of immersion in the 3.5% NaCl solution. The AC disturbance voltage was 10 mV in amplitude, and measurements were carried out in the frequency range from 10^5 Hz to 10^{-2} Hz, in duplicate for each system. The EIS data fitting was carried out using ZView 3.2b software.

3. Results and Discussion

3.1. Assessment of the adsorption efficiency of natural VCI: vaporization capacity

The vaporization capacity test was carried out following the NACE standard TM0208-2018-SG[19], to determine the minimum concentration of natural VCI and commercial VCI for the inhibition of electrochemical processes on the entire surface of the AISI 1020 carbon steel samples. According to this standard, the inhibitor is classified as grade 0 when no effect against corrosion is observed, grade 1 when a slight anticorrosive effect is observed, grade 2 when there is a medium effect against corrosion, and grade 3 when the effect against corrosion is good.

Therefore, the vaporization capacity test was started with an initial concentration of 0.5 g/L of natural or commercial inhibitor. As seen in Figure 1, for this concentration, the commercial inhibitor reached grade 3, i.e., good effect against corrosion, while the natural inhibitor did not provide any anticorrosive effect (grade 0). Therefore, we reduced the concentration of the commercial inhibitor and increased the concentration of the natural inhibitor, up to the limit of protection against corrosion. Figure 1 shows that the natural VCI reached system equilibrium from a concentration of 1.5 g/L (while the commercial VCI reached equilibrium at 0.4 g/L), providing effective protection (grade 3) of the entire surface of the AISI 1020 carbon steel. The fact that limonene has vapor pressure higher than most commercial VCIs (0.19 kPa at room temperature) favors high saturation in the environment and leads to greater consumption of the inhibitor[18].

3.2. Evaluation of the use of natural VCI in packaging to protect against corrosion

One of the first widespread uses of volatile corrosion inhibitors was through VCI-impregnated paper packaging, employed to wrap metal parts for transport and/or storage while protecting them against corrosion[21].

To simulate packaging with low environmental impact and a protective effect against corrosion of the packaged metal, we evaluated the feasibility and efficiency of using kraft paper impregnated with the limonene-based inhibitor (natural VCI) to protect AISI 1020 carbon steel samples against corrosion. Photographic records of the evolution of corrosion on metallic surfaces throughout the test period (5 days) are presented in Figure 2. The images in Figure 2 represent samples with average behavior among triplicate replicas. The results indicating the maximum inhibition periods for each system (kraft paper without inhibitor, kraft paper containing natural VCI and kraft paper containing commercial VCI), in addition to the estimated average values of the corroded areas and their respective percentages are presented in Table 2.

Visual analysis indicated excellent action of the limonene-based compound as a corrosion inhibitor for carbon steel. It is possible to observe in Figure 2 that the beginning of the corrosion process occurred on the second day for the kraft paper sample without inhibitor, on the fourth day for the kraft paper sample with natural inhibitor and on the fifth day for the kraft paper sample with commercial inhibitor. This pattern reveals that kraft paper alone, which is hydrophilic, does not protect against corrosion, but when the VCIs were impregnated on the surface of the paper, an effective hydrophobic barrier was formed, which prevented water molecules from penetrating through the paper and reaching the metal surface. Furthermore, with the adsorption of the inhibitor on the metal surface (vaporization and condensation), a protective film was formed, which reduced the corrosion rate. In this way, two barriers were protecting the metal sample, one on the paper surface and the other on the steel surface.

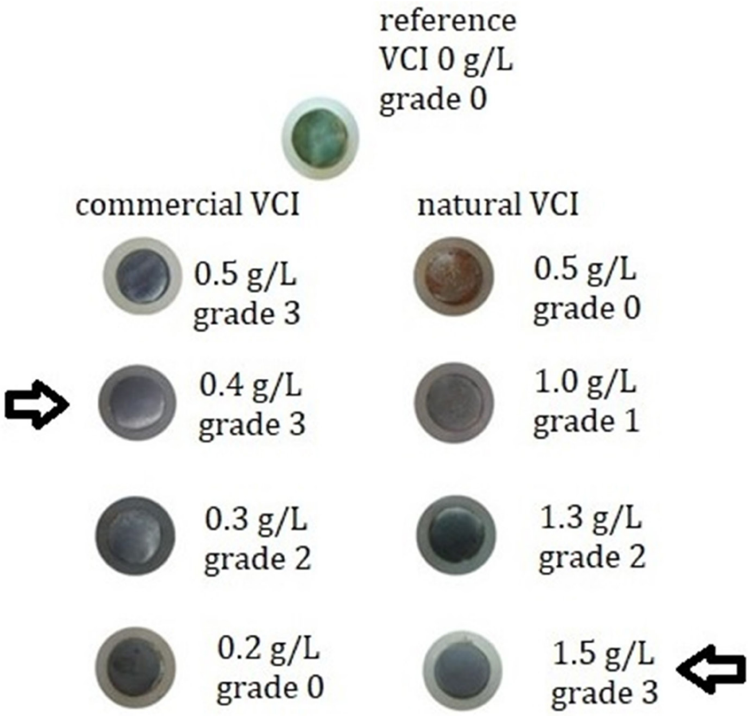

Figure 1. Photographs of AISI 1020 carbon steel samples and classification of vaporization capacity, according to the NACE TM0208-2018-SG standard, at different concentrations of volatile inhibitors.

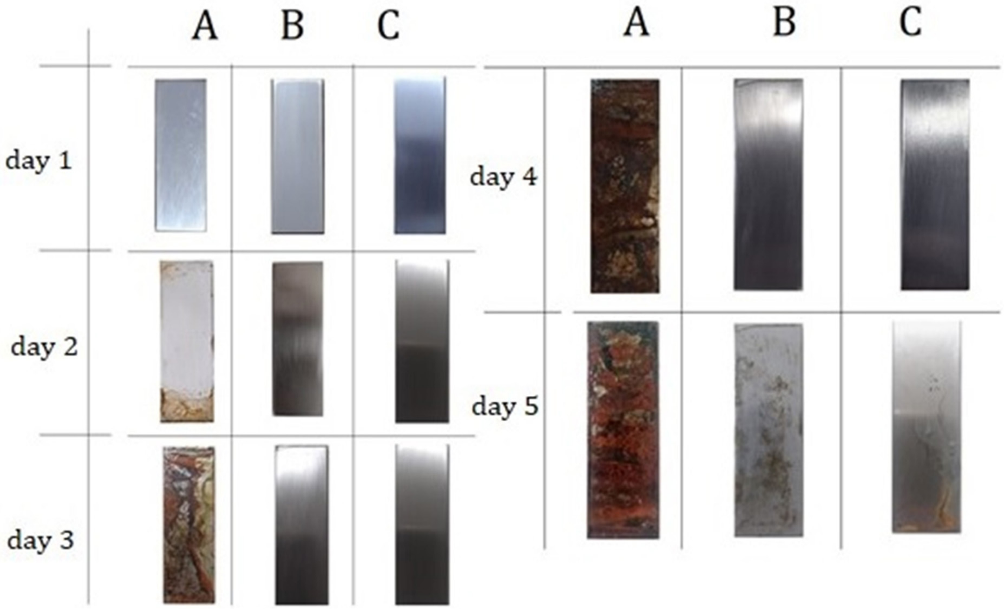

Figure 2. Photographs of the AISI 1020 carbon steel samples during the kraft paper test for 5 days in a humid chamber at 35 °C and 100% relative humidity: (A) sample in kraft paper without inhibitor; (B) sample in kraft paper impregnated with natural limonene-based VCI; and (C) sample in kraft paper impregnated with commercial synthetic VCI.

Again, from Figure 2 and Table 2, it can be seen that only on the fourth day did the protection barrier of the kraft paper system with natural VCI begin to lose its effectiveness, resulting in the start of the corrosion process and the formation of steel corrosion products ($Fe_2O_3 \cdot 3H_2O_{(s)}$ and Fe_3O_4), in 1.52% of the steel surface area. In turn, in

Table 2. Protection limit time and estimated average values of corroded areas after testing of kraft paper (packaging with or without VCI). Areas were calculated with the aid of the *Image J* software, at the respective starting times of the corrosion process for each system.

	Kraft paper without inhibitor	Kraft paper + natural VCI	Kraft paper + commercial VCI
Limit of protection	2 days	4 days	5 days
Corroded area (cm^2)	5.11	0.24	0.42
% corroded area	32.51	1.52	2.67

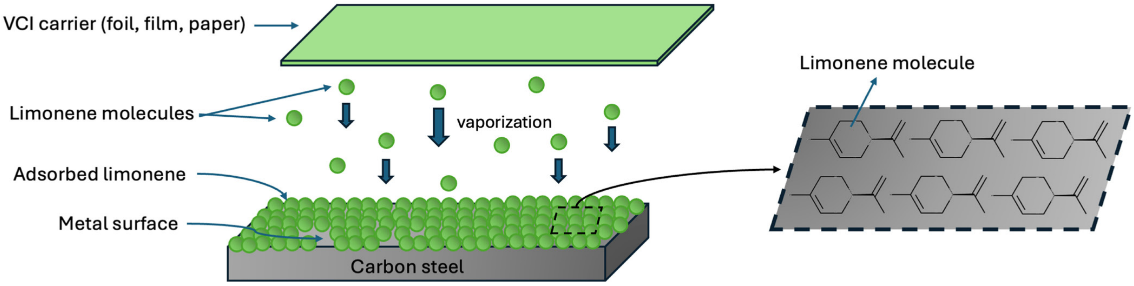

Figure 3. Schematic representation of the mechanism for protection against corrosion of carbon steel wrapped in kraft paper impregnated with limonene-based VCI.

the system with commercial synthetic VCI, the corrosion process started on the fifth day of testing, with a corroded area of 2.67%. Therefore, the limonene-based inhibitor with very low environmental impact acted effectively, virtually equivalent to the toxic commercial VCI (due to the presence of benzenesulfonate and naphthalene groups). The mechanism of protection against carbon steel corrosion by packaging impregnated with the limonene-based VCI is represented schematically in Figure 3.

It is important to highlight that only in samples containing commercial VCI was the presence of residues observed, namely whitish spots in certain regions of the sample surface, indicating that condensation was not homogeneous on the surface (see Figure 4A). This behavior was not observed for samples containing natural VCI, which maintained a residue-free surface, as shown in Figure 4B. This is one of the advantages of using the natural inhibitor based on limonene.

3.3. Analysis of protection against carbon steel corrosion by the limonene-based natural inhibitor using electrochemical techniques

To study the mechanism and use of the limonene-based inhibitor as a natural VCI in liquid form, it was analyzed the protection against corrosion of AISI 1020 carbon steel by the electrochemical techniques of open circuit potential (OCP), potentiodynamic polarization (PP) and electrochemical impedance spectroscopy (EIS).

The OCP measurements were performed to monitor the spontaneous dissolution process. The OCP data presented in Table 3 were obtained after immersing the metallic samples for 1 minute in the inhibitor oil (liquid VCIs require direct contact with the metallic surface), followed by 1 min of drying, and subsequent immersion in an aqueous 3.5% NaCl solution for 24 h.

Analysis of the open circuit potential data (Table 3) shows that the presence of natural VCI (limonene-based compound) on the steel surface caused a shift in the potential to a higher value (OCP = -549 mV) compared to steel without inhibitor (OCP = -665 mV), representing a 17.5% increase. This behavior indicates that the addition of the limonene-based inhibitor reduced the tendency for spontaneous oxidation reactions on the metal surface. Concerning the commercial VCI, the open circuit potential was -382 mV, representing an increase in OCP of 42.6% compared to bare steel, indicating a trend of more effective protection, as expected for a commercial inhibitor. Therefore, the limonene-based natural product improved the corrosion protection of carbon steel and had intermediate behavior compared to the commercial product. Similar results were reported in studies of natural inhibitors based on sage essential oil and beet extract[16,22].

The impedance spectra obtained for the steel samples in the presence or absence of inhibitors after 24 h of immersion in 3.5% NaCl solution are presented in the Nyquist (A) and Bode (B) diagrams in Figure 5. These diagrams enable analyzing the resistive and/or capacitive behavior of the electrochemical system under study, by obtaining the

Figure 4. Photographs of the surfaces of the AISI 1020 carbon steel samples after adsorption of the inhibitors: (a) commercial and (b) natural based on limonene.

impedance magnitudes and noting the presence of time constants characteristic of the corrosion and protection processes, as well as correlating this information with the corrosion resistance of the steel in an aggressive medium. Figure 5C shows the equivalent circuit used as a model to fit the EIS data and to obtain the values of the electrical circuit parameters from the EIS spectra, using the software Zview. R_S represents the resistance of the solution (electrolyte), R_{ct} corresponds to the charge transfer resistance and CPE_{DL} is the constant phase element associated with the double-layer capacitance at the metal/electrolyte interface. The CPE was used in the model instead of a pure capacitor due to the heterogeneities of the non-ideal systems, such as surface roughness. CPE is defined by two values, Q and α, where Q is the constant parameter of CPE (in $F.cm^{-2}.s^{\alpha-1}$) and α is the CPE exponent, which indicates the deviation degree of the system from ideal behavior. When α = 1, CPE represents a pure capacitance, while for α = 0, CPE represents a pure resistance. The electrical circuit parameters obtained through the data fittings are presented in Table 4.

Table 3. Open circuit potential (OCP) values obtained for AISI 1020 carbon steel samples in the presence of the limonene-based natural inhibitor, the commercial synthetic inhibitor and in the absence of inhibitors (reference) after 24 h of immersion in 3.5% NaCl solution.

System	OCP (mV)
Bare Steel	-665
Steel + Natural VCI	-549
Steel + Commercial VCI	-382

From the Nyquist spectra (Figure 5A), it is possible to clearly observe the performance of the natural and commercial VCI inhibitors, which have capacitive arcs with much larger diameters compared to bare steel (without inhibitor - reference). This behavior indicates the presence of a protective barrier at the metal/electrolyte interface, which increases the corrosion resistance of the steel. In the Bode spectra (Figure 5B), the maximum phase angles (~ -60° and ~ -70°) at high frequencies (10^3-10^5 Hz), for the natural and commercial VCI samples, respectively, also confirm the presence of a protective layer on the metal surface[23,24]. On the other hand, the maximum phase angle (~ -30°) at low frequencies (less than 10 Hz) presented by the reference sample (bare steel) is characteristic of the corrosion processes occurring at the working electrode[23,24]. Bare carbon steel is highly susceptible to corrosion in a saline environment, with an R_{ct} value of just 1.4 kΩ.cm² (Table 4). In the presence of the natural VCI inhibitor, the steel presented an R_{ct} value of 34.7 kΩ.cm², almost 25 times higher than the reference sample, indicating the protection against corrosion provided by the limonene-based inhibitor, which forms an adsorbed protective film on the metal surface[15]. The commercial synthetic VCI showed even greater protection of AISI 1020 carbon steel, with R_{ct} on the order of 1.4 MΩ.cm², indicating strong adhesion of the inhibitor layer to the metal surface and high protection efficiency, as expected for commercial inhibitors, which are widely used and proven to be efficient. In any case, it is worth highlighting that the natural inhibitor based on limonene (environmentally friendly) had an anticorrosive effect even in an environment that is extremely aggressive to carbon

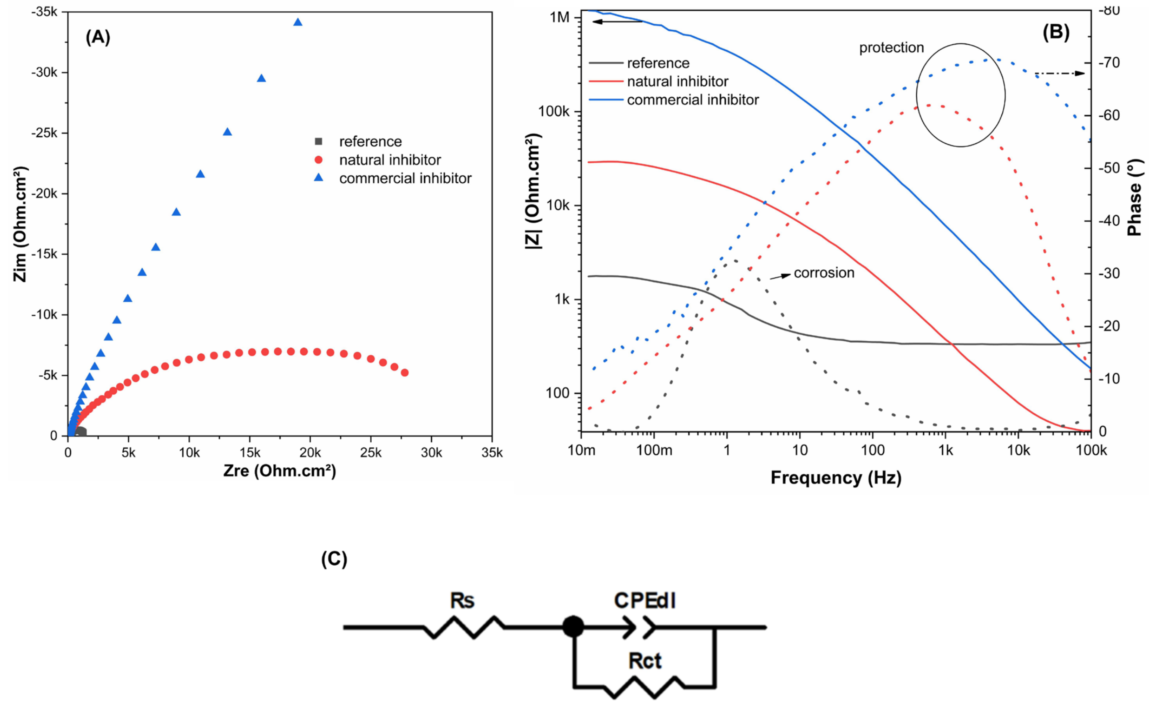

Figure 5. EIS spectra presented in Nyquist (A) and Bode (B) diagrams for AISI 1020 carbon steel samples with or without natural or synthetic VCI inhibitor on the metal surface, after 24 h of immersion in 3.5% NaCl solution. The electrical equivalent circuit used to fit the EIS data (C).

steel (NaCl 3.5%), making it an important alternative to the demonstrably toxic commercial inhibitor.

The polarization curves for AISI 1020 carbon steel samples with commercial VCI and natural VCI were obtained to verify the efficiency of the inhibitors in corrosion protection in accelerated tests. From the Tafel extrapolation of the polarization curves presented in Figure 6, the values of corrosion potential (E_{corr}) and corrosion current density (i_{corr}) were obtained, allowing calculation of the inhibition efficiency (IE%) using Equation 1. The electrochemical parameters obtained are presented in Table 5.

The polarization curves (Figure 6) together with the data presented in Table 5 reveal that in the presence of both corrosion inhibitors (natural and commercial), the carbon steel corrosion potential (E_{corr} = -964 mV) shifted to values less negative (nobler potentials), obtaining an E_{corr} of -576 mV for steel in the presence of natural VCI and E_{corr} of -355 mV for steel with commercial VCI. In Figure 6 it is also possible to observe that the anodic and cathodic current densities decreased in the presence of natural and commercial VCIs compared to bare steel (reference). This behavior indicates that the action mechanism of these inhibitors is mixed (inhibiting both cathodic and anodic reactions) due to the adsorption of their molecules and the formation of a protective film on the metal surface. The i_{corr} data (Table 5) also demonstrate the effective action of both inhibitors, since the corrosion current density (i_{corr}) values for steel in the presence of the inhibitors are approximately two orders of magnitude lower in comparison to steel without inhibitor (reference). Finally, the IE values obtained for the natural (99.0%) and commercial (99.8%) VCIs indicate that both have high inhibition efficiency, and that the limonene-based natural inhibitor has anticorrosive action comparable to the commercial synthetic inhibitor.

To improve the film stability of the limonene-based natural inhibitor on the surface of the steel samples, they were dried for 1 min or 24 h in air after immersion for 1 min in natural liquid VCI. After drying for 24 h, it was possible to observe by SEM images and EDS elemental analysis (see Figure S1 and Table S1), the presence of a film on the steel surface, and a decrease in the percentage of Fe element, together with an increase in the content of C and O elements, indicating the presence of an organic protective film on the surface of the steel (FeC) substrate.

The evaluation of the corrosion resistance of these systems was carried out using PP and EIS electrochemical techniques, in 3.5% NaCl solution. Figure 7 and Table 6 show the EIS spectra and the electrical circuit parameters obtained through the EIS data fittings, respectively, and Figure 8 shows the polarization curves for the steel samples after 1 min and 24 h of drying of the natural VCI on the metal surfaces. The equivalent circuit used to fit the EIS data was the same presented in Figure 5C.

Table 4. Electrical parameters obtained by fitting EIS data for AISI 1020 carbon steel samples with or without natural or synthetic VCI inhibitor on the metal surface after 24 h of immersion in 3.5% NaCl solution.

Sample	fixed R_S (kΩ.cm^2)	R_{ct} (kΩ.cm^2)	CPE_{DL}	
			Q_{DL} (F.cm^{-2}.s$^{\alpha-1}$)	α_{DL}
Reference	0.09	1.4	1.05×10^{-3}	0.72
Natural inhibitor	0.09	34.7	2.17×10^{-5}	0.53
Commercial inhibitor	0.09	1439.2	1.07×10^{-6}	0.54

*χ^2 (goodness of fit) was maintained in the order of 10^{-3} for all the fitted EIS spectra.

Table 5. Electrochemical parameters arising from the polarization curves of AISI 1020 carbon steel samples in the presence or absence of limonene-based natural VCI or commercial VCI on the metallic surface, after immersion in an aqueous solution of 3.5% NaCl.

System	E_{corr} (mV)	i_{corr} (A/cm^2)	IE (%)
Bare Steel	-964	6.76×10^{-6}	-
Steel + Natural VCI	-576	6.46×10^{-8}	99.0
Steel + Commercial VCI	-355	1.38×10^{-8}	99.8

Table 6. Electrical parameters obtained by fitting EIS data for AISI 1020 carbon steel samples with the limonene-based natural inhibitor after 1 min or 24 h of drying on the metal surface, followed by immersion in a 3.5% NaCl solution.

Sample	fixed R_S (kΩ.cm^2)	R_{ct} (kΩ.cm^2)	CPE_{DL}	
			Q_{DL} (F.cm^{-2}.s$^{\alpha-1}$)	α_{DL}
Reference	0.35	1.3	2.44×10^{-4}	0.82
Drying 1 min	0.35	2.1	1.04×10^{-4}	0.83
Drying 24 h	0.35	9.5	5.63×10^{-5}	0.82

* χ^2 (goodness of fit) was maintained in the order of 10^{-3} for all the fitted EIS spectra.

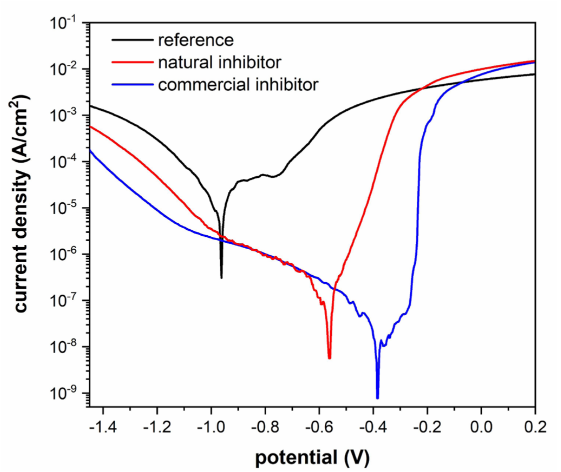

Figure 6. Polarization curves of AISI 1020 carbon steel samples in the presence or absence of limonene-based natural VCI or commercial VCI on the metal surface, after immersion in 3.5% NaCl aqueous solution.

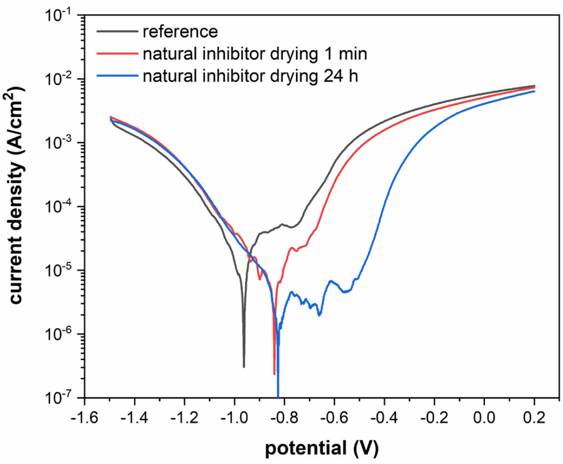

Figure 8. Polarization curves of AISI 1020 carbon steel samples without inhibitor (reference) and with limonene-based natural inhibitor after 1 min or 24 h of drying on the metal surface, followed by immersion in 3.5% NaCl solution.

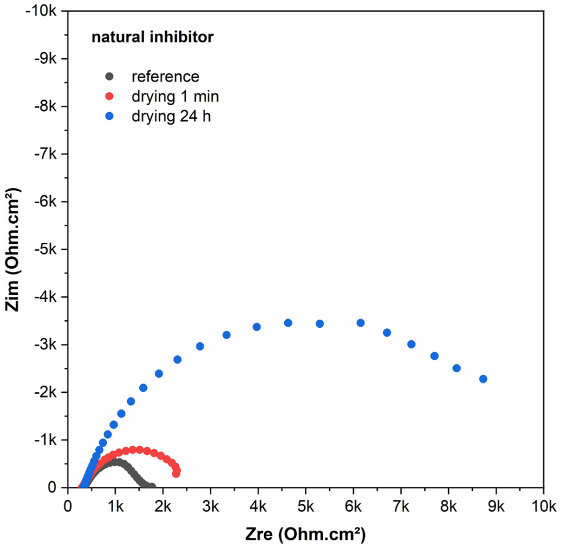

Figure 7. EIS spectra, represented in Nyquist diagrams, of AISI 1020 carbon steel samples with the limonene-based natural inhibitor after 1 min or 24 h of drying on the metal surface, followed by immersion in a 3.5% NaCl solution. Edc: OCP and Eac: 10 mV.

Figure 7 and Table 6 clearly show an increase in the corrosion resistance of steel when the limonene-based natural inhibitor was dried for 24 h on the metal surface, with the largest capacitive arc among the three systems studied. Drying the inhibitor for just 1 minute did not cause a significant increase in corrosion protection compared to bare steel (reference). These data revealed the importance of the 24-hour air drying process, which allowed the formation of a protective film that was more stable on the metal surface and, consequently had higher corrosion resistance compared to the other two systems studied. Additionally, drying for 24 h probably also contributed by delaying the diffusion/dissolution process of the limonene film on the surface, increasing the durability of the protection. While the system with inhibitor on the steel surface dried for 24 h presented R_{ct} of 9.5 kΩ.cm^2 (Table 6), the system with inhibitor dried for 1 min presented R_{ct} of only 2.1 kΩ.cm^2, revealing that drying for a longer time increased the charge transfer resistance by 350%. Despite this increase in charge transfer resistance, the R_{ct} values for both drying times remained in the order of magnitude of 10^3 Ω.cm^2. In the industrial context, this difference in charge transfer resistance can be considered insignificant when compared to the waiting time of 24 hours for drying. However, for a commercial application, keeping the protective barrier more stable guarantees greater durability and protection efficiency, which can represent greater protection security for parts when longer storage/transport times are required or when exposed to more aggressive environments (e.g., marine or industrial atmospheres).

The potentiodynamic polarization curves (Figure 8) indicate that for both drying times of the limonene-based natural inhibitor on the steel surface, there was a shift in the corrosion potential to nobler values (E_{corr} ≅ -837 mV) in comparison with bare steel (E_{corr} = -964 mV), indicating the presence of a protective film (barrier) formed by the adsorption of natural inhibitor molecules on the metal surface. Furthermore, analysis of the current densities (Figure 8) reveals a significant decrease in the anodic current densities for the system in which the natural inhibitor was dried for 24 hours on the steel surface. On the other hand, this effect was not observed for the system in which the natural inhibitor was dried for only 1 min. Thus, as also observed by the EIS analyses, this confirms that the drying of the natural limonene-based inhibitor for 24 hours on the steel surface allows the formation of a protective stable film, reducing the mobility of aggressive ions at the steel surface and delaying chemical oxidation reactions, which results in greater corrosion resistance.

4. Conclusion

The corrosion inhibition effect on carbon steel by the natural VCI inhibitor limonene-based was studied by electrochemical methods and by the kraft paper packaging method. The kraft paper test proved the effectiveness of using the limonene-based inhibitor for anti-corrosion packaging. In packaging with natural VCI, no signs of corrosion were found until the fourth day of exposure of the steel to a high-humidity environment, while with kraft paper packaging without inhibitor, the presence of corrosion products was identified on the second day of exposure. The electrochemical tests of PP and EIS in saline solution indicated a protective effect of limonene-based inhibitor when the AISI 1020 carbon steel was immersed for just 1 minute in the natural liquid inhibitor, followed by exposure to an aggressive environment. Impedance data showed that the R_{ct} of steel with natural limonene-based inhibitor was about 25 times higher than the R_{ct} of steel without inhibitor, while polarization measurements indicated inhibition efficiency of 99%, with a large increase in corrosion resistance of steel in the presence of this inhibitor. When the natural inhibitor was dried for 24 h on the steel surface before exposure to an aggressive medium, there was greater stability of the protective film compared to drying for just 1 minute, providing a 350% increase in the charge transfer resistance of the carbon steel. Finally, natural VCI (IE=99.0%) proved to be competitive with commercial VCI (IE=99.8%), both of which have high inhibition efficiencies. Furthermore, the limonene-based VCI studied is 100% natural, sustainable, and presents low environmental impact, so it has a strong potential for use in various industrial segments for temporary corrosion protection of metals.

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Supplementary material

The following online material is available for this article:

Figure S1 – SEM images of surfaces of steel (FeC) reference, FeC coated with limonene drying for 1 min and FeC coated with limonene drying for 24h.

Table S1 – Content (at.%) of chemical elements on the surfaces of steel FeC reference, FeC coated with limonene drying for 1 min and FeC coated with limonene drying for 24h by EDS analysis.