



Evaluation of the anticorrosion performance of malt bagasse as corrosion inhibitor for AISI 1020 carbon steel in acidic solution

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ABSTRACT

The malt bagasse is a solid residue, highly produced in the brewing industry. The presence of high levels of antioxidants in its composition makes this residue an attractive possibility as a corrosion inhibitor, besides being a sustainable and low cost alternative to the inorganic procedures currently used to prevent corrosion. In this sense, this work evaluated the efficiency of the malt bagasse powder as a corrosion inhibitor on the surface of AISI 1020 carbon steel, in different concentrations, in acidic medium 0.5 mol.L^{-1} HCl. The resistance to corrosion was tested by electrochemical techniques, such as electrochemical impedance spectroscopy (EIS) and anodic and cathodic polarization curves. The efficiency of the corrosion inhibitor was evaluated by weight loss tests. Fourier transform infrared spectroscopy (FTIR) and optical microscope surface image analysis were respectively used as chemical and morphological characterization techniques, respectively. From the EIS results, it can be said that the powder has its efficiency increased once the concentration is higher. On the other hand, the polarization curves shows the malt bagasse powder as an inhibitor presents both anodic and cathodic behavior. The weight loss results confirmed the electrochemical results, showing 92.5% efficiency for the 1.77 g.L-1 concentration. The adsorption isotherm on the steel surface follows Languimir's Isotherm. The FTIR analysis indicates the presence of heteroatoms such as C, N, O, incorporated in functional groups that could be responsible for the inhibitory properties found in the powder. The images obtained from the optical microscope, showed that the corrosion process, in the presence of the inhibitor in the electrolyte, is retarded. Therefore, the results indicate that the malt bagasse powder has the potential to be a corrosion inhibitor for steel in acidic medium, adding value in the beer production chain. Keywords: Malt bagasse, natural inhibitor, corrosion, acidic medium, EIS.

1. INTRODUCTION

The beer is one of the oldest alcoholic beverages in the world. Beer, by definition, is the beverage obtained by the alcoholic fermentation of the brewer wort, prepared with malted barley, water, hop and yeast action [1, 2].

In order to produce a high quality beer, much care is needed, ranging from hygiene conditions to the choosing of the ingredients, which should be of good origin and high quality [3]. Among the ingredients used for the brewing process, should be highlighted, the malted barley as a source of carbohydrates, proteins, minerals, etc., the hop, which is responsible for the bitter and characteristic beer flavor and a high quality water [4].

The brewing process can be divided into six stages: malt milling; mashing; wort filtration; boiling; fermentation and maturation [5].

Malt is a result of the malting process of grains, such as barley and wheat. This process happens by moistening the barley grains in a controlled environment, causing the germination of the cereal. The

dormancy of the grains is broken with the use of temperature and humidity conditions, inducing the activation of enzymes contained in them, such as amylolytic enzymes [6].

Malt has several characteristics that justify its use in the production of beer: it is rich in starch, contains enzymes, has a shell that gives protection to the grain during malting and gives the product characteristic aroma and taste [6]. Few beers are made using only one type of malt, knowing the characteristics of each type of malt that is used in the manufacture of beer is important for a better quality production [7, 8].

Chocolate malt contains cocoa, which is a good source of minerals, including flavonoids, phosphorus and magnesium, and milk, which includes carbohydrates, proteins, fats, vitamins and minerals [9]. The Munich Malts have a predominant presence of furans, pyrroles and aldehydes. Pilsner 2 row Ger has polyphenols derived from hydrobenzoic acids: gallic acid, protocatechuic acid, siringic acid and hydroxycinnamic acids: ferulic acid, p-cumic acid, caffeic acid [10].

In the manufacturing process, there are several important steps. The step that most stands out and directly influences the final product is the choice of the type of fermentation. There are two types of fermentation, low fermentation and high fermentation. The first occurs at lower temperatures, the Lager type, and the second occurs at higher temperatures, the Ale type. Ale-type beers are generally clear, with a strong hop flavor, slightly acidic, and the alcoholic percentage varying between 4 % to 8 %. In Ale-Type beer, Porter, Weissbier, Stout, Altbier, Kolsch, English Pale Ale (Bitter) and India Pale Ale (IPA) [11]. The malt milling has direct influence upon the speed of the physicochemical transformations, yield, clarification, and the quality of the final product. The aim is to reduce the malt grain uniformilly, which will cause the breakage of the shell. With exposure and total disintegration of the internal portion of the grain, the endosperm, a better enzymatic performance will be promoted [12].

The mashing, or the enzymatic treatment of the must, is the mixture of the milled malt with the brewing water in the mash tub, malt cooker or in the first pan, if processed on a small scale. In this stage, a very rigorous control of time and temperature is implemented, aiming to favor the biochemical reactions needed in the process [13]. The filtration aims to separate the solid part, called malt bagasse; and the liquid part, the real interest of the manufacturing process, the brewer must [14].

The malt bagasse is a residue, result of the initial part of the brewing process, generated from the filtration of the must, before the boiling stage. The shells of the malted barley [15] mainly constitute the bagasse. This residue is considered a protein concentrate in the international food classification, since it presents approximately 70 % fibers, 20 % protein, 1.2 % of phenolic mono and di acid, and it is also a source of complex B vitamins, thus possessing a high nutritional value [16]. This material constitutes most of the solid waste of the brewing process, about 85% of the total, being produced in large amounts per year, at little to no cost to be acquired [17]. Several studies have shown that this byproduct can be utilized in human food and animal feed, energy production, products of industrial interest, and the development of biotechnological processes [18].

Whenever possible, waste should be the raw material for a new process. The reuse of malt bagasse as a corrosion inhibitor is a sustainable alternative for the use of solid waste generated in the brewing industry, adding value to the beer production chain, which involves social, economic and environmental issues. As a natural, biodegradable, non-toxic, widely available product from renewable sources, this residue is an attractive possibility for corrosion prevention studies. Conversely, the commonly used corrosion inhibitors are synthetic chemicals, characterized by high manufacturing costs, toxicity and are configured as harmful to human health [19].Therefore, the study of natural corrosion inhibitors is prominent, mainly due to the sustainable profile, the low cost and the ease of obtaining of the raw material [20].

Malt bagasse has the same antioxidant compounds that are found in other residues already established as corrosion inhibitors, such as: garlic peel [20], palm oil cake [21], cocoa bark [22], Hunteria umbellata seed husk extracts [23], Turmeric and ginger [24], fruit peels (orange, passion fruit, mango and cashew) [25], Guinea pepper leaves (Piper guinensis) [26]. In this way, this residue can be tested as a corrosion inhibitor, replacing synthetic inhibitors, which are toxic to human health and the environment.

Considering the interest in preserving carbon steel structures and to obtain an inhibitor of lower toxicity, this study aims to evaluate the behavior of a natural corrosion inhibitor obtained from malt bagasse as a possible replacement for synthetic inhibitors on the corrosion protection of carbon steel AISI 1020 in acidic medium.

2. EXPERIMENTAL

2.1 Steel sample preparation

The steel used in the evaluation of corrosion resistance was the carbon steel AISI 1020. It is a widely utilized steel with a carbon content inferior to 2 %, being considered a high added value material, used in many industrial sectors, due to its great applicability and advantageous mechanical properties for engineering applications [27]. Its chemical composition (%) is mainly made of: 0.17 C; 0.30 Mn; 0.04 P; 0.05 S and Fe for balance [28]. The 1020 carbon steel samples were used in dimensions of 20 x 20 x 8 mm. The surface of each specimen was progressively treated with sandpaper of grades 80, 120, 320, 400, 600 e 1200. To remove impurities and corrosion products from the material surface, the samples were subjected to the treatment presented in in a flowchart, Figure 1.



Figure 1: Surface treatment performed on AISI 1020 carbon steel samples.

2.2 Inhibitor preparation

The malt bagasse of the type beer English Pale Ale (Bitter) as acquired at the Center of Studies on Craft Beer - NECA, located at the State University of Santa Cruz. To obtain the malt bagasse powder, the material was treated as shown in Figure 2.



Figure 2: Process of obtaining malt bagasse powder.

The 170 mesh granulometry size was selected and labeled as malt bagasse powder. The inhibitor was preserved under conditions of ambient pressure and temperature, free from humidity.

2.3 Electrochemical tests

The electrochemical tests were performed in triplicate with a Metrohm Autolab model PGSTAT302N potentiostat / galvanostat, with impedance module, controlled by NOVA 1.11 software. For data processing, was used the Microcal[®] Origin[®] 8.0 software. An electrochemical cell with three electrodes was utilized: a Ag | AgCl | KClsat reference electrode, a rhodium-coated titanium wire counter electrode and a working electrode (AISI 1020 carbon steel) with an exposed area of 1 cm². The electrolyte used was 0.5 mol.L⁻¹ HCl aqueous solution with and without different malt bagasse powder concentrations: 0.77 g.L⁻¹, 1.11 g.L⁻¹, 1.44 g.L⁻¹ and 1.77 g.L⁻¹. These concentrations of inhibitor and electrolyte were used by the research group in natural inhibitor studies and were maintained for means of comparison [20-22, 29].

The electrochemical tests were performed, at room temperature 25° C, following this sequence: initially the open circuit potential – OCP for 90 minutes; electrochemical impedance spectroscopy - EIS; and finally, the Potentiodynamic polarization curves.

The EIS tests were carried out in the frequency range from 100 kHz to 10 mHz with 10 points per decade and a 10 mV perturbation amplitude rms. For quantitative analysis, the EIS data were processed with Z-View software. Anodic -30 mV vs OCP to + 250 mV vs OCP and cathodic + 30 mV vs OCP to - 250 mV vs OCP curves were obtained with separate working electrodes, both with scanning rate of 0.5 mV.s⁻¹.

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2.4 Gravimetric tests

The gravimetric tests were carried through in triplicate and followed the procedure established in the technical standard ASTM G1[30], at room temperature 25°C. The carbon steel samples, previously sanded and cleaned, were weighted in an analytical scale (Marte, model AY220) with 0.1 mg of precision, and then immersed in a 0.5 mol.L⁻¹ HCl solution with and without the inhibitor concentrations previously mentioned. The samples remained immersed for 120 min. After this time, the samples were removed from immersion, brushed with a soft brush, washed with distilled water, alcohol, acetone, and finally dried, being posteriorly weighted to verify the weight loss. The performed tests were made in a non-agitated, aerated solution.

The inhibition efficiency (η_{WL}) was calculated from Equation 1, where C_{Ro} and C_{Ri} are the carbon steel corrosion rates in the absence and presence of inhibitor, respectively [21].

$$\eta_{WL} = \left(1 - \frac{c_{Ri}}{c_{Ro}}\right) x 100 \tag{1}$$

CR values were calculated from Equation 2, where ΔW is the average weight lost in grams, A is the total exposed area, and t is the immersion time in hours [21].

$$C_R = \frac{\Delta W}{A.t} \tag{2}$$

The corrosion current density (i_{corr}) was calculated from Equation 3, where 96500 is the Faraday constant (C) and Eq_{metal} is the gram equivalent for carbon steel, which was assumed to be 27.93 g, corresponding to pure iron [29].

$$i_{corr} = C_R \frac{96500}{Eq_{metal}} \tag{3}$$

Through these tests, data on the metallic surface coverage degree were obtained. Subsequently, with the aid of electronic spreadsheets, a linear regression of the data was calculated, whose independent and dependent variables were established according to the different models of adsorption isotherms tested: Langmuir, Freundlich, Temkin, Flory-Huggins and Frumkin.

2.5. Fourier Transform Infrared Spectroscopy (FTIR)

The chemical characterization analysis of the malt bagasse powder were executed by Fourier Transform Infrared Spectroscopy (FTIR) using the Attenuated Total Reflectance (ATR) Thermo Scientific Nicolet, model IS10. The spectrum was obtained in the average wavelength range from 4000 to 400 cm⁻¹, with a resolution of 4 cm⁻¹.

2.6. Morphological analysis

The surface morphology of the samples in the presence and in the absence of the inhibitor was analyzed by the optical microscope Labored CZM6, after for 120 min of immersion in a $0.5 \text{ mol}.\text{L}^{-1}$ HCl solution with and without the 5 inhibitor concentrations previously mentioned.

3. RESULTS AND DISCUSSION

3.1 FTIR

Figure 3 shows the FTIR spectra acquired from malt bagasse powder. The absorption band at 3283.16 cm⁻¹ may be related to the presence of N-H and O-H groups in the inhibitor's composition. Carboxylic acids, phenols and amines may be present in the inhibitor studied. These functional groups form complexes compounds with the hydrogen (H^+) present on the metal surface, which cause blockage of anodes that are generated on the metal surface in contact with the electrolyte, thus slowing the oxidation-reduction reactions on the surface of the metallic sample [23, 31, 32].

The band obtained at 2882.30 cm⁻¹ is observed in the spectrum, which may correspond to the stretching vibration -CH [33]. The band at 1643 cm⁻¹ may be attributed to the double bond of -C=O, which comes from the group carbonyl present in fatty acids as well as, possibly, flavonoids and tannins [34, 35].

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The band at 1519.79 cm⁻¹ is characterized by the vibrations of the double -C=C bonds present in aromatic rings, which come from phenolic groups (tocopherols, flavonoids and tannins), which adsorbs on metallic surfaces [36, 37]. At 1238.71 cm⁻¹ and in the strong band at 1020.79 cm⁻¹ there is a presence corresponding to -CN or -CO [20, 34].



Figure 3: FTIR spectrum of the malt bagasse powder.

Therefore, the results indicate the presence of functional groups O-H, N-H, C = O, C-N, C-O, S=O and aromatic structure rings in the malt bagasse powder, which are usually attributed to the antioxidant properties of corrosion inhibitors. These properties are generally the result of the adsorption ability of these compounds, which can form a film that acts as a barrier between metal and electrolyte [29].

3.2 Weight loss techniques

The results of the gravimetric tests, after immersion for 120 minutes of AISI 1020 carbon steel in 0.5 mol.L⁻¹ HCl solution in the absence and presence of different concentrations malt bagasse powder are shown in Table 1.

Table 1: Corrosion rate, corrosion current density, inhibitory efficiency and degree of coverage (θ) of the metallic surface obtained by the gravimetric analysis of AISI 1020 carbon steel after 120 min of immersion in 0.5 mol.L⁻¹ HCl solution, in the absence (blank) and in the presence of inhibitors for different concentrations.

CONCENTRATION (g.L ⁻¹)	C_{R} (g.h ⁻¹ .cm ⁻²)	i _{corr} (A.cm ⁻²)	η_{WL}	Θ
Blank	2.8x10 ⁻³	9.6x10 ⁻³		
0.77	8.3x10 ⁻⁴	2.9x10 ⁻³	70.0%	0.700
1.11	4.0x10 ⁻⁴	1.4×10^{-3}	85.3%	0.853
1.44	4.1x10 ⁻⁴	1.4x10 ⁻³	85.4%	0.854
1.77	2.1x10 ⁻⁴	7.2×10^{-4}	92.5%	0.925

The results presented in Table 1 demonstrate that the efficiency of malt bagasse powder's inhibition against AISI 1020 carbon steel corrosion, increased up to 92.5 % when 1.77 g.L^{-1} was added to the solution.



In addition, all concentrations in the presence of inhibitor showed inhibitory efficiency higher than or equal to 70 %, which is indicated, according to the classical literature, as an acceptable value for an efficient inhibitor [38].

Table 1, shows that the addition of malt bagasse powder to the electrolyte lowers the corrosion rate, such as the corrosion current density, and increases the efficiency against the corrosion process. According to the literature, this process occurs due to the adsorption of molecules with inhibitory properties on the surface of the metal, which hinders the electron transfer between the metallic surface and the electrolyte [21]. This adsorption and efficiency is related to the chemical structure and to physicochemical properties of the compounds, electronic structure, size and length of the molecule, the type of chemical bond and its strength, capability of interbonding and solubility in the electrolyte [39].

The presented results, follows the tendency found in the literature to natural inhibitors. Quraishi et al. (2010) investigated the inhibition of carbon steel corrosion in hydrochloric acid solutions by the aqueous extract of curry leaves (Murraya koenigii). The results obtained showed that the curry leaf extract can act as an effective inhibitor of carbon steel corrosion in hydrochloric acid, since the obtained inhibition efficiency (EI%) was 97 % for a concentration of 600 mg.L⁻¹ inhibitor [40]. Rocha et al. (2014) observed a 95 % and 97 % efficiency using Orange and mango peels respectively, in acidic medium [40]. Meanwhile, Santos et al. (2017), observed an 83 % efficiency corresponding to the best concentration using castor bark powder, also in acidic medium [29].

3.3 Adsorption Isotherms

Knowing the inhibitor concentration values (C) and the results of the metallic surface coverage degree (θ), obtained from the gravimetric analyses, the data were adjusted in different adsorption isotherm models. The isotherms tested were: Langmuir; Freundlich; Temkin; Flory-Huggins; and Frumkin.

Table 2 presents the results of the adjustments and the coefficient of linear correlation (R^2) to each isotherm.

ADSORPTION ISOTHERMS	R²	LINE'S EQUATION
Langmuir (C/ θ versus C): C/ θ = 1/K + C	0.9840	0.4204 + 0.848x
Freundlich (log θ versus log C): $\theta = K_f \cdot C^{\frac{1}{n}}$	0.8917	- 0.1078 + 0.312x
Temkin (θ versus log C): $\theta = \left(\frac{2.303}{a}\right)\log K + \left(\frac{2.303}{a}\right)\log C$	0.9011	0.7844 + 0.577x
Flory-Huggins (log(θ /C) versus log (1- θ)): log $\left(\frac{\theta}{c}\right) = \log K + x \log(1 - \theta)$	0.8208	0.1654 + 0.399x
Frumkin (log ($\theta/(1-\theta)$.C) versus θ): log($\theta/(1-\theta)$.C) = log K + g θ	0.8566	- 0.5967 + 1.5127x

Table 2: Adsorption parameters, where: K is the adsorption constant, K_f is the Freundlich constant, *n* is the indication whether the process is favorable or not, *a* and *g* are the parameters of lateral interaction among the adsorbed molecules, *x* represents the number of molecules of adsorbed water replaced by the inhibitor molecules [42, 43].

Observing the data presented by Table 2, it is noticed that the obtained results, adjusts better to the Langmuir Isotherm, which is shown in Figure 4. This isotherm model assumes that the adsorbed molecules exhibits an ideal behavior and considers that each site is responsible for the adsorption of only one molecule [44, 45]. In most of the researches reported in the literature about green inhibitors in acidic medium, is verified a better adjustment to this adsorption isotherm [29, 43, 45-47].



Figure 4: Langmuir's line for the AISI 1020 carbon steel, in the presence of different concentrations of the malt solid waste in 0.5 mol.L⁻¹ HCl.

From the Langmuir's equation, the linear coefficient 1/K can be found. Therefore, the adsorption equilibrium constant equals to 2.379 L.g⁻¹. Knowing the value of this constant is possible to calculate the Gibbs adsorption free energy (ΔG°_{ads}), according to equation 04 [42].

$$\Delta G^{\circ}_{ads} = -RT \ln(C_{H2O}.K)$$
⁽⁴⁾

In this equation: T is the absolute temperature (in this study T=298K), R is the universal constant of gases (8.3147 J.mol⁻¹.K⁻¹), C_{H20} is the concentration of water, and its value is 55.5 mol.L⁻¹(1000 g.L⁻¹) [42].

In this sense, Gibbs adsorption free energy is -19.263 kJ.mol⁻¹. The negative sign indicates that the process of adsorption of organic molecules on the carbon steel surface occurs spontaneously. In addition, Gibbs adsorption free energy (ΔG^{o}_{ads}) indicates the type of adsorption, since it is close to -20 kJ.mol⁻¹, is a physisorption. Then, the inhibitor molecules contained in the malt bagasse powder, were physically adsorbed on the carbon steel surface. The physisorption phenomenon involves relatively weak adsorption forces [29, 43, 44].

3.4 Electrochemical Techniques

3.4.1 Potenciodynamic Polarization Curves

Figure 5 shows the potentiodynamic polarization curves obtained after EIS measurements and 110 min of immersion in 0.5 mol. L^{-1} HCl solution, in the absence and presence of different inhibitor concentrations, in order to verify if the powder has a anodic, cathodic or both inhibitory effect.

Observing the polarization curves, it is noticed that the corrosion potential for malt bagasse powder shifts to higher values when compared to the powder-free sample in the anodic curves Figure 5a and cathodic curves Figure 5b, revealing the presence of the adsorbed inhibitor on the metal surface that retards electrolyte / substrate interfacial reactions. The corrosion current densities are lower for samples in the presence of the inhibitor rather than for the ones in the absence of it, in both anodic and cathodic curves. The analysis of the curves indicates an active dissolution in the anodic branch. The decrease in the anodic dissolution speed is noticed with the trend of stabilization of the current density, however the anodic current density continues to increase gradually, characterizing a region of pseudo passivation.

The analysis of Figure 5 shows that in the presence of inhibitors there is an inhibitory effect in both cathodic and anodic reactions. In this sense, it is said that the malt bagasse powder function as both anodic and cathodic inhibitor. Afia et al. (2014) through the observation of the anodic and cathodic polarization

curves, found the same behavior using garlic extract as corrosion inhibitor in acidic media The shift in the potentials to more positive, smaller values of anodic and cathodic current densities indicates a delay in the corrosive process [52]. Hussin et al. (2016) also observed this behavior in acid medium for lignin oil extracted from palm leaves [43].



Figure 5: Anodic (a) and cathodic (b) polarization curves obtained for carbon steel after 110 min of immersion in 0.5 $mol.L^{-1}$ HCl solution in the absence and in the presence of different amounts of malt bagasse powder.

Through Figure 5, the Ecorr and icorr values were determined using the Tafel extrapolation method and the results are depicted in Table 3.

CONCENTRATION	E _{corr}	İ _{corr}	
(g.L⁻¹)	(V)	(A.cm ⁻²)	η _{w∟}
Blank	-0.46	8.34x10 ⁻⁵	-
0.44	-0.41	4.35x10 ⁻⁶	94.7%
0.77	-0.37	4.02x10 ⁻⁶	95.2%
1.11	-0.36	3.66 x10 ⁻⁶	95.6%
1.44	-0.31	2.13 x10 ⁻⁶	97.4%

Table 3: Corrosion potential, corrosion current density and inhibitory efficiency obtained in the analysis of the Polarization curves.

Table 3 shows that the addition of malt bagasse powder to the electrolyte decreased the corrosion current density and increased the potential and efficiency against the corrosion process, reaching an efficiency of 97.4% for the highest concentration of inhibitor. All concentrations in the presence of inhibitor showed an inhibitory efficiency greater than or equal to 70%, which is indicated in the classic literature as an acceptable value for an efficient inhibitor [38].

3.4.2 Electrochemical Impedance Spectroscopy (EIS)

The resistance to corrosion of the AISI 1020 carbon steel in 0.5 mol. L^{-1} HCl in the absence and in the presence of the malt bagasse powder in increasing concentrations, was evaluated by the electrochemical impedance spectroscopy (EIS).

The EIS diagrams, acquired after 90 min of immersion in the electrolyte, are shown in Figure 6. Analyzing the Nyquist diagrams the Figure 6a, is possible to observe the occurrence of a flattened capacitive arc, which diameter is always larger in the presence of the inhibitor, when compared to the diagram that represents the test in the absence of the malt bagasse powder. In this sense, it can be said that there is a reduction in corrosive activity in the presence of the natural inhibitor. The maintenance of the appearance of the diagrams, when added the inhibitor to the solution, suggests that the compound only retards the corrosive process, without modifying its mechanism [21]. Ferreira et al. (2016) studied the brown onion skin extract as a corrosion inhibitor in acidic media and it was observed on the EIS results that increasing the inhibitors concentration, the impedance is also increased. With these techniques, the author determined that 0.30 g.L⁻¹ is the best concentration to be used in the studied conditions [48]. Barreto et al. (2018) in similar study, for the cocoa bark ethanol extract determined that the 1.11 g.L⁻¹ was the best concentration to be used, noticing the increase of the impedance [22]. Santos et al. (2020) studied the palm kernel cake powder (Elaeis guineensis Jacq.) as corrosion inhibitor in acidic media 0.5 mol.L⁻¹ HCl. The highest IE of 87 % was obtained for the highest corrosion inhibitor concentration used (1.77 g.L⁻¹) [21].

Confirming the results showed by the Nyquist diagrams, the Bode diagram on the phase angle Figure 6b, showed that in the presence of any of the concentrations of the inhibitor, the phase angle, in a broad range of frequency, increase its value. That indicates a more effective adsorption of the inhibitory compounds on the substrate surface, which slows the corrosive process [49]. The Figure 6c shows that the addition of the inhibitor to the aggressive environment causes an increase on the AISI 1020 Carbon Steel's impedance module, indicating an effective corrosion inhibition.

The highest value of real impedance, phase angle and Impedance Module were obtained when the 1.77g.L⁻¹ concentration of the malt bagasse powder was added to the electrolyte. Thus in this concentration, there is a slower corrosion process.





Figure 6: EIS diagrams obtained with 10 mV perturbation amplitude for AISI 1020 carbon steel in 0.5 mol. L^{-1} HCl in the absence and in the presence of different amounts of malt bagasse powder: (a) Nyquist, (b) Bode Phase and (c) Impedance Module.

The electrochemical impedance data obtained in Figure 6 was analyzed with the equivalent circuit shown in Figure 7 using the Z-View software, where R_s represents the resistance of the solution, R_{ct} is the resistance to the charge transfer and CPE_{dl} represents the capacitance of the electric double layer, considering the introduction of the phase constant element.



Figure 7: Equivalent electrical circuit

In search of a more precise adjustment, the phase constant element was inserted instead of a pure double layer electric capacitor, thus compensating for deviations from the ideal behavior. This equivalent circuit model, shown in Figure 7, is widely used in studies of natural inhibitors in the literature [21, 22, 29, 44-46]. The impedance data adjustment for the 1.77 g.L⁻¹ concentration of green inhibitor on the Z-View software simulation interface can be seen in Figure 8.



Figure 8: Z-View software interface for the adjustment of electrochemical impedance data (in the presence of 1.77 g.L^{-1} of inhibitor) to the equivalent electrical circuit.

CPE impedance (Z_{CPE}) can be expressed according to equation 05 [37]

$$Z_{CPE} = \frac{1}{Y_0(j\omega)^n}$$
(5)

In which: Y_0 is the CPE value, ω is the angular frequency, j is an imaginary number (being j^2 equivalent to -1) e n is the dispersion factor, whose value is in between 0 and 1, which can be used as an indicative of the homogeneity or roughness of the surface. When this factor is equal to 1, it is said that the surface is homogeneous, thus being related to a pure capacitor, revealing the behavior of an ideal electrode [43, 45].

In possession of the resistance to the charge transference (R_{ct}) value, expressed in the equivalent circuit, it is possible to calculate the efficiency of the corrosion inhibitors (η_{wL}), as is presented in the equation 06 [51]:

$$\eta_{\rm WL} = \frac{R_{\rm ct} - R_{\rm ct,0}}{R_{\rm ct}} \times 100 \tag{6}$$

In which: $R_{ct,0}$ represents the resistance to the charge transference in the absence of the natural inhibitor, R_{ct} is the resistance to the charge transference in the presence of the natural inhibitor.

The parameters obtained from the equivalent circuit are presented in Table 4.

CONCENTRATION (g.L ⁻¹)	$R_s (\Omega.cm^2)$	$\mathbf{R}_{\mathrm{ct}}(\Omega.\mathrm{cm}^2)$	CPE_{dl} $(\mu Fcm^{-2}s^{(\alpha-1)})$	n	χ²	INHIBITORY EFFICIENCY (%)
Blank	10.78	219	2.11 x 10 ⁻⁴	0.84	2.97 x 10 ⁻³	-
0.44	9.95	1227	6.90 x 10 ⁻⁵	0.82	2.05 x 10 ⁻³	82.15
0.77	9.23	1395	5.95 x 10 ⁻⁵	0.83	1.85 x 10 ⁻³	84.30

Table 4: Obtained parameters from the system's equivalent circuit.

1.11	10.23	1596	7.26 x 10 ⁻⁵	0.81	1.50 x 10 ⁻³	86.28
1.44	9.67	2078	6.60 x 10 ⁻⁵	0.83	2.17 x 10 ⁻³	89.46

The consonance among the adjusted data from the equivalent circuit and the experimental data was expressed by the χ^2 (chi-squared).

The χ^2 values obtained are in the 1.50 x 10⁻³ to 2.97 x 10⁻³ range, being inferior to 1.00 x 10⁻², demonstrating that the experimental data and the proposed equivalent circuit validate each other [37, 41]. The dispersion factor values vary in the 0.81 to 0.84 range, being close to 0.9. That indicates a high proximity to an ideal capacitor homogeneous surface (*n*=1) [29].

 R_s is the ohmic resistance of the electrolyte [47]. The values of R_s in the presence of the inhibitor were slightly lower than the values of R_s in the blank. This may possibly have occurred due to some small change in the conductivity of the electrolyte, caused by the organic compounds present in the malt bagasse powder.

When comparing the CPE_{dl} values in the inhibitor's presence to the value in the absence of it blank, a decrease is noticed, suggesting a superficial coverage increase, caused by the adsorption of the inhibitory molecules. This indicates that a smaller area of the surface was exposed to the aggressive environment. It is also noticeable from the data exposed on Table 4, that with the increase of the malt waste concentration, the Rct values increase as well. The growth of the resistance to the charge transference is related to the lower occurrence of ionic exchange between the steel surface and the electrolyte, therefore, it is said that the inhibitory molecules form a layer, that function as a barrier, protecting the metallic surface [44, 46, 50].

Increasing R_{ct} values results in increased inhibitory efficiency. The highest value of efficiency was found for the highest inhibitor concentration (1.77 g.L⁻¹). Even at the lower concentration, the efficiency is greater than 70 %, which is contemplated by the classical literature [38] to be the minimum efficiency value for an inhibitor to be considered efficient as a protection against corrosion. Thus, malt residue may represent an effective corrosion inhibitor for AISI 1020 carbon steel in 0.5 mol.L⁻¹ HCl solution.

3.4.3 Evaluation of immersion time in the corrosion inhibition

This technique was employed to evaluate the influence of immersion time in the efficiency of malt bagasse powder. The experiments were performed using 1.77 g.L^{-1} malt bagasse powder which presented the best impedance in the previous experiments. Impedance was analyzed for different periods 2 h, 6 h, 12 h, 24 h, 48 h and 72 h of immersion in electrolyte with inhibitor. The EIS diagrams are presented in Figure 9.



Figure 9: EIS diagrams obtained for AISI 1020 carbon steel in 0.5 mol.L^{-1} HCl in the presence malt bagasse powder for different immersion periods: (a) Nyquist, (b) Bode Phase.

In the Figure 9a it is observed that there is an increase in impedance up to 24 hours of immersion when, from that time, corrosion resistance decreases, probably due to the interaction of adsorbed molecules by physisorption, as determined by the adsorption isotherm. Since the interaction forces are weak, after long immersion periods, the corrosion inhibition efficiency is reduced [29, 43]. For the Bode phase angle diagram Fig. 9b, the phase angle is higher for all conditions compared to the condition without the inhibitor, indicating the existence of a barrier layer.

Similarly performed for electrochemical impedance (in the absence and in the presence of different inhibitor concentrations), impedance data at different immersion times were also analyzed using the equivalent electrical circuit approach. The values of χ^2 (less than 1.00 x 10⁻²) indicated a good fit of the data to the equivalent circuit used, therefore, through the values of R_{ct}, the inhibition efficiencies were calculated at the different immersion times, as it can be seen in Figure 10.



Fgure 10: Inhibitory efficiency at different electrolyte immersion periods.

From Figure 10, it is possible to observe that in 24 hours of immersion there is the highest value of inhibitory efficiency (95.12%). After this period, the efficiency decreases. In other words, after 24 hours of immersion, the inhibitory effect of the malt residue is reduced. This loss of efficiency is due to the deterioration of the protective layer formed on the surface of the steel, which may be related to the loss of inhibitory properties of the physically adsorbed organic molecules, which present weak bond force, causing a weak interaction between the molecules and the surface, indicating a desorbed ption process [21]. Thus, malt residue cannot be applied in very long immersion periods [29, 51].

3.5 Morphological analysis

With an optical microscope, using a 5x magnification, the images were obtained for AISI 1020 carbon steel, after the gravimetric tests, in $0.5 \text{ mol}.\text{L}^{-1}$ HCl solution in the absence and in the presence of 1.77 g.L⁻¹ of malt bagasse powder. The images are shown in Figure 11.



(a)



Figure 11: Images for AISI 1020 carbon steel surface (500 μ m): (a) before immersion, (b) after immersion for 2 hours in 0.5 mol.L⁻¹ HCl in the absence of inhibitor, (c) after immersion of 2 hours in 0.5 mol.L⁻¹ HCl in the presence of 1.77 g L⁻¹ inhibitor.

Figure 11a shows the carbon steel image before immersion in aggressive environment. This image has a surface free of corrosion products, but contains scratches due to sanding. However, the substrate surface after 2 h of immersion in the acid medium the Figure 11b revealed a surface completely covered for corrosion product. For the sample in presence of inhibitor the Figure 11c, the surface was less attacked than the one without inhibitor. It is observed that the corrosion process was not uniform, indicating that there are defects due to the formation of a protective film, that is a result from the adsorption of the antioxidant molecules present in malt bagasse powder that are not adsorbed homogeneously on the carbon steel surface. Scratch lines are still visible and there is a significant reduction in the formation of corrosion products, indicating inhibitory property of malt bagasse powder.

4. CONCLUSIONS

The FTIR spectrum shows the presence of compounds that are usually found in corrosion inhibitors such as oxygen and nitrogen atoms in different functional groups O-H, N-H, C = O, C-N, C-O, C = C as well as aromatic rings. These compounds may be adsorbed in the substrate surface, which could explain their inhibitory properties.

The electrochemical impedance results in acidic media showed that with increasing inhibitor concentration, higher values of inhibitory efficiency were obtained, with a maximum value of 89.38 % for 1.77 g.L^{-1} of powder. Electrochemical measurements indicate that the value of the impedance module increases with the addition of the inhibitor in the electrolyte. Potentiodynamic polarization curves indicated that the powder acts as both anodic and cathodic type of inhibitor. The curves also showed that the presence



of inhibitors decreases the corrosion current density values. In addition, the inhibition process occurs due to the physic adsorption of the powder on the steel surface, which adjusts best to the Langmuir adsorption isotherm.

In the gravimetric tests, the inhibitory efficiency was 92.5 % for the malt bagasse powder at 1.77 g.L⁻¹, corroborating with the electrochemical results.

The results showed that malt bagasse powder is a potential corrosion inhibitor of AISI 1020 carbon steel in 0.5 mol.L⁻¹ HCl, with its inhibition efficiency higher than 70 % regardless of the concentration studied in this work.

Malt bagasse can be used as a corrosion inhibitor in the studied condition, adding value in the beer production chain.

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