Application of an Aqueous Extract of Cotton Seed as a Corrosion Inhibitor for Mild Steel in HCl Media

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The present work aims to study the aqueous cotton seeds extract as a natural inhibitor of the corrosion of mild steel in 1 mol L⁻¹ HCl using gravimetric tests, potentiodynamic polarization curves, electrochemical impedance measurements and surface morphological analysis by scanning electron microscopy (SEM). The aqueous cotton seed extract acted as a good corrosion inhibitor reaching an inhibition efficiency of 95.7% after 24 h of immersion for 800 mg L⁻¹ inhibitor concentration. For the gravimetric tests varying the temperature, a decrease of the activation energy (Ea) was observed, suggesting a chemical adsorption on the surface of the metal. 400 mg L⁻¹ of the high molecular weight fraction isolated from the total extract showed inhibition efficiency equal to 800 mg L⁻¹ of the total extract, 97.3% and 94.2% from electrochemical impedance and polarization curves data, respectively, suggesting that the macromolecules present a fundamental participation in the inhibitive process.

Keywords: Mild steel, corrosion inhibitor, cotton seed, natural products.

1. Introduction

Corrosive processes are directly or indirectly linked to our daily lives. According to Leitão and Gentil, corrosion means the physicochemical deterioration of a material in a given medium and depending on the wear of the material, various forms of corrosion are considered.

Corrosion is a problem present in many places, such as industries, buildings, viaducts, as well as ancient and modern works of art. In this scenario, new studies are developing more sustainable methods, such as inhibitors, to control the effects of corrosion causing less damage to the environment.

The application of corrosion inhibitors is one of the most useful and effective methods found in the literature. However, some synthetic compounds can result in environmental damage, increasing the risk to human health. New biodegradable, inexpensive, and environmentally friendly products have been used for corrosion control.

Adding small amounts of these natural extracts in solution may decrease the corrosion rate of the metal. Natural inhibitors, for the most part, are considered adsorption inhibitors because they create a barrier between metal and electrolyte by blocking active sites and reducing metal dissolution and/or reduction reaction.

Plant extracts contain many organic compounds, having heteroatoms such as O, P, S and N and π electrons. These compounds can adsorb on the metal surface by the hetero atoms or π electrons forming protective films. In most cases, where natural extracts were applied as corrosion inhibitors, the inhibition efficiency obtained was associated with the presence of these organic molecules, including proteins and phenolic compounds.

In this sense, oil-bearing seeds could be an excellent source of compounds with anti-corrosion properties. Brazil has a diversity of oilseeds such as cotton, castor beans, soybean and oil palm, a variety of plants and natural products. Cotton seeds (Gossypium hirsutum L.) contain carbohydrates (45.06% w/w), lipids (21.29% w/w), proteins (23.28% w/w), water (6.92% w/w) and mineral residue known as ashes (3.44% w/w).

There is no work in the literature employing the aqueous extract of cotton seed as a natural corrosion inhibitor. As cotton seed presents high protein content, it may perform an important role in inhibiting steel acidic corrosion. In our previous works it was showed that the macromolecules as proteins and/or polysaccharides can be important in the inhibitive action towards the mild steel corrosion in acidic medium. We have studied the inhibitory action of some aqueous oilseed extracts like castor beans and soybean meal extracts towards the mild steel corrosion in acidic media. 800 mg L⁻¹ aqueous castor beans and soybean meal extracts showed inhibition efficiency of 94.4 and 88.8%, respectively, from weight loss data after 2 h immersion. The idea would be the use of the cotton cake, a residue obtained from the oil and biodiesel cotton production, as a new corrosion inhibitor.

Based on that fact, the objective of this work is to investigate the inhibitory action of the aqueous cotton seeds extract (ACSE) and its high molecular weight fractions (HMWF) in the mild steel corrosion in 1 mol L⁻¹ HCl by gravimetric tests, potentiodynamic polarization curves, electrochemical
impedance measurements and surface analysis by scanning electron microscopy (SEM).

2. Experimental

2.1 Materials and corrosive medium

The chemical composition of the mild steel was (% w): C: 0.18, P: 0.05, S: 0.05, Mn: 0.30 and the remaining percentage of Fe.

For gravimetric tests specimens of approximately 14 cm² were submitted by the following treatment: the mild steel coupons were previously abraded with 100 mesh water grit paper, sand blasted, washed with doubly distilled water, degreased with acetone and dried with hot air.

For electrochemical tests, the mild steel coupons were manually abraded with 100, 320, 600, 1000, 1200, 1500 and 2000 mesh water grit papers, washed with double distilled water, degreased with ethyl alcohol and dried with hot air.

All tests were performed using 1 mol L⁻¹ hydrochloric acid solution as electrolyte which was prepared using 37% hydrochloric acid from Merck Co. (Darmstadt, Germany) and double distilled water.

2.2 Obtaining the extract

2.2.1 Aqueous Cotton Seeds Extract (ACSE)

The cotton seeds were supplied by Embrapa Algodão (Campina Grande, Paraíba, Brazil), ground and passed in the sieve. 30.0 g of cotton seeds were placed in 300 mL of double distilled boiling water for 1 hour infusion. Simple filtration was performed with cotton pad where the filtrate was placed in a freezer at −4 °C. Finally, the frozen filtrate was lyophilized (Liotop; model L101) at an average temperature of −52 °C, generating a dry powder as final product.

2.2.2 High molecular weight fraction (HMWF)

The high molecular weight fraction (HMWF) was isolated from the aqueous cotton seeds extract by diafiltration. Aqueous cotton seeds extract (ACSE) was poured in an ultrafiltration 3 kDa cut-off membrane (Millipore) and submitted to centrifugation at 3500 rpm for 60 minutes. The filtrate retained was frozen and lyophilized (HMWF). The liquid that passed through the 3 kDa membrane, which corresponds to the low molecular weight fraction (LMWF) was also collected, frozen and lyophilized.

2.3 Gravimetric tests

The gravimetric measurements have been detailed in our previous works. Initially, the weight loss measurements were performed with different immersion times (2, 4 and 24 h) and varying the concentrations of the extract in 100, 200, 400 and 800 mg L⁻¹. The temperature variation tests were performed at 25, 35, 45, 55 °C for 2 h of immersion in the absence and presence of 400 mg L⁻¹ of the aqueous cotton seeds extract. The weight loss measurements were obtained according to ASTM G31-7. The gravimetric tests were repeated in triplicate with precision of 0.1 mg. The inhibition efficiency (IE%) was obtained using Equation 1:

\[
IE(\%) = \frac{W_{corr,0} - W_{corr}}{W_{corr,0}} \times 100
\]  

Where, \( W_{corr,0} \) is the corrosion rate (g cm⁻² h⁻¹) in the absence of the inhibitor and \( W_{corr} \) is the corrosion rate in the presence of the inhibitor.

The apparent activation energy of the system (\( E_a \)), kinetic parameter that relates to \( W_{corr} \), was obtained using Equation 2:

\[
\log W_{corr} = \frac{-E_a}{2303RT} + \log A
\]  

Where, \( W_{corr} \) is the corrosion rate (g cm⁻² h⁻¹), \( E_a \) is the apparent activation energy (kJ mol⁻¹), \( A \) is the pre-exponential factor, \( T \) is the absolute temperature (K) and \( R \) is the constant of ideal gases (8.314 J K⁻¹ mol⁻¹).

The activation entropy and entropy were calculated through an alternative Arrhenius equation (Equation 3):

\[
W_{corr} = \frac{RT}{Nh} \exp \left( \frac{-\Delta S^*}{R} \right) \exp \left( \frac{-\Delta H^*}{RT} \right)
\]  

Where, \( h \) is the Planck constant (6.63 x 10⁻³⁴ J s), \( N \) is the Avogadro number (6.02 x 10²³), \( \Delta S^* \) and \( \Delta H^* \) are the activation entropy and enthalpy, respectively.

2.4 Electrochemical methods

The electrochemical cell was composed of three electrodes: the reference electrode (saturated calomel electrode), the counter electrode (platinum wire with large area) and the working electrode (mild steel coupon with an area exposed to the corrosive medium equal to 0.785 cm²).

All the electrochemical tests were performed at concentrations of 10, 50, 100, 200, 400, 800 mg L⁻¹ for the aqueous cotton seeds extract and at 400 mg L⁻¹ for HMWF obtained from ACSE.

The electrochemical experiments were performed using an Autolab PGSTAT 128 N potentiostat/galvanostat, controlled by GPES 4.9 electrochemical software from Metrohm Autolab (The Netherlands).

In order to perform electrochemical impedance measurements, the open circuit potential (OCP) was first recorded as a function of time for 4000 seconds. The impedance was performed with polarized working electrode at the OCP, in a frequency range from 10 kHz to 10 mHz, with 10 points per decade and amplitude of 10 mV. The inhibition efficiency (IE%) obtained by electrochemical impedance was calculated according to Equation 4:

\[
IE(\%) = \frac{R_p - R_{p,0}}{R_p} \times 100
\]  

Where, \( R_p \) and \( R_{p,0} \) are the polarization resistances obtained in the presence and absence of the inhibitor, respectively.

Potentiodynamic anodic and cathodic polarization curves were performed using a scan rate of 1 mV s⁻¹ from −300 mV to +300 mV relative to the stable open-circuit corrosion potential. Corrosion current density (\( j_{corr} \)), corrosion potential (\( E_{corr} \)), anodic (\( j_a \)) and cathodic (\( j_c \)) Tafel constants were obtained by the Tafel extrapolation method.

The inhibition efficiency (IE%) was calculated from potentiodynamic polarization curves, according to Equation 5:

\[
IE(\%) = \frac{R_p - R_{p,0}}{R_p} \times 100
\]  

Where, \( R_p \) and \( R_{p,0} \) are the polarization resistances obtained in the presence and absence of the inhibitor, respectively.
IE(%) = \frac{j_{corr,0} - j_{corr}}{j_{corr,0}} \times 100 \tag{5}

Where, \( j_{corr,0} \) and \( j_{corr} \) are the corrosion current densities (mA cm\(^{-2}\)) in the absence and presence of the inhibitor, respectively.

2.5 Surface analysis by Scanning Electron Microscopy (SEM)

Mild steel coupons used for the surface analysis were mechanically abraded with 100, 320, 600, 1200, 1500 and 2000 mesh water grit papers and immersed in 1 mol L\(^{-1}\) HCl in the absence and presence of 400 mg L\(^{-1}\) of the inhibitor (extracts and HMWF) at room temperature for 2 h.

The analysis was performed in a scanning electron microscope (FEI QUANTA 200) with an acceleration voltage of 20 kV. The images were obtained with 2000 times of magnification.

3. Results and Discussion

3.1 Gravimetric Tests

Table 1 presents the average corrosion rates (\( W_{corr} \)), their standard deviations (SD) and the corrosion efficiencies (IE) for different immersion times in the absence and presence of ACSE.

The results presented in Table 1 indicated that the addition of the aqueous cotton seed extract reduced the corrosion rates of the mild steel in acid medium and this reduction increased with the extract concentration and immersion time. For the ACSE concentration of 200 mg L\(^{-1}\), for example, IE ranged from 76% at 2 hours of immersion to 94% at 24 hours. Therefore, the addition of ACSE, even at low concentrations, indicates the adsorption of the extract components on the mild steel, occupying the active sites, creating a protective layer on the metallic surface.

Table 2 shows the effect of temperature on the inhibitory efficiency of the aqueous cotton seed extract.

The data of Table 2 presented an increase in corrosion rates with temperature, which occurs for blank assays and those containing ACSE. Nevertheless, \( IE \) values increases with temperature, indicating an adsorption process of chemical nature, where organic molecules from the extract adsorb on the steel surface involving charge sharing or transfer from the inhibitor molecules present in the ACSE to the mild steel surface, having \( IE \) percentages varying from 82% to 89% in the temperature range of 25 °C to 55 °C, respectively. The increase in \( IE \) suggests that the temperature increase provides the water desorption from the metallic surface, leading to more active sites for inhibitory molecules to adsorb on the metallic surface.

From the results of Table 2, the Arrhenius plot was obtained (Figure 1A) and the apparent activation energy (\( E_a \)) of the corrosive process was acquired based on the Arrhenius equation (Equation 2). Plotting log \( W_{corr} \) vs. \( 1/T \) (K\(^{-1}\)) the \( E_a \) value was calculated for both uninhibited and inhibited systems.

An alternative form of the Arrhenius equation (Equation 3) was used to calculate the activation entropy and enthalpy related to the mild steel corrosion process in the absence and presence of the extract. Similarly, the plot of \( \ln(W_{corr}/T) (g \text{ cm}^{-2} \text{ h}^{-1} \text{ K}^{-1}) \) vs. \( 1/T \) (K\(^{-1}\)) provides a line which

![Figure 1](image-url). Arrhenius plots of: (A) (log\( W_{corr} \) vs. \( 1/T \)); (B) (log(\( W_{corr} / T \)) vs. \( 1/T \)) for the mild steel corrosion in the absence and presence of ACSE.
slope is $-\Delta H^*/R$ and linear coefficient of $\ln(R/Nh) + \Delta S^*/R$. Those parameters allow us to obtain $\Delta H^*$ and $\Delta S^*$ values (Figure 2B). All the thermodynamic activation functions of the corrosion process are presented in Table 3.

Table 3. Thermodynamic activation functions of the corrosion processin the absence and presence of ACSE.

<table>
<thead>
<tr>
<th></th>
<th>$E_a$ (kJ mol$^{-1}$)</th>
<th>$\Delta H^*$ (kJ mol$^{-1}$)</th>
<th>$\Delta S^*$ (J mol$^{-1}$ K$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>39.0</td>
<td>36.4</td>
<td>-172</td>
</tr>
<tr>
<td>ACSE</td>
<td>26.2</td>
<td>23.6</td>
<td>-166</td>
</tr>
</tbody>
</table>

In the presence of the extract, the $E_a$ and $\Delta H^*$ values were 26.2 kJ mol$^{-1}$ and 23.6 kJ mol$^{-1}$, respectively, where as for the blank assay these parameters were 39.0 kJ mol$^{-1}$ and 36.4 kJ mol$^{-1}$, corroborating with the assumption of a chemisorption process where molecules from the extract share or donate electrons to the metal surface. Both activation enthalpies were positive, indicating that the mild steel dissolution process was endothermic. Besides that, it is noticed for both uninhibited and inhibited systems that $E_a$ values are greater than $\Delta H^*$ which suggests that the corrosion process involves a gaseous reaction; in this case, the reduction of hydrogen ions to hydrogen gas in the cathodic process. The difference $E_a - \Delta H^*$ is equal to RT (2.6 kJ mol$^{-1}$), suggesting that the metal dissolution is a unimolecular reaction$^{33}$. Activation entropies were negative both in the absence ($\Delta S^* = -172$ J mol$^{-1}$ K$^{-1}$) and presence of the inhibitor ($\Delta S^* = -166$ J mol$^{-1}$ K$^{-1}$), indicating that the activated complex in the determinant step is related more to an association process than a dissociation one$^{31-35}$.

### 3.2 Electrochemical assays

The high molecular fraction (HMWF) was also investigated by electrochemical measurements. This study was performed to elucidate the compounds class responsible for the inhibitory action of the ACSE towards the mild steel corrosion in 1 mol L$^{-1}$ HCl.

#### 3.2.1 Open circuit potential (OCP)

Open circuit potentials (OCP) were recorded for mild steel in the presence and absence of inhibitor during 4000 s. Figure 2 shows that the potential decreases quickly in the first minutes of immersion due to the dissolution process of the air formed oxide film and the attack on the mild steel surface$^{36}$.

The steady open circuit potential is acquired quite soon for the blank assay where as with the addition of inhibitor a longer period is required to stabilize, around 2000 s for 10 mg L$^{-1}$ of ACSE, and around 4000 s for higher ACSE concentration, with increase of OCP for positive values. The stabilized OCP for the blank was -503 mV while in the presence of the inhibitors dislocates the OCP towards positive values which stabilized at -490 and -493 mV for 800 mg L$^{-1}$ of ACSE and 400 mg L$^{-1}$ of HMWF, respectively. The HMWF presented the same OCP behavior seen with the ACSE. All curves show a slight anodic shift with respect to the blank with a maximum displacement of 24 mV for OCP, demonstrating that the extracts act as a mixed-type inhibitor at open potential circuit with a bit anodic character.

#### 3.2.2 Electrochemical Impedance Spectroscopy (EIS)

Figure 3 shows the Nyquist diagrams for mild steel in 1 mol L$^{-1}$ HCl solution in the absence (Figure 3A) and presence of ACSE at different concentrations as well as at 400 mg L$^{-1}$ of its HMWF (Figure 3B).

In the absence of the ACSE, only one capacitive loop was observed in all frequency range which could be attributed to the charge transfer and double layer capacitance. This loop is depressed and is often attributed to dispersion effects, which have been ascribed to surface roughness and in homogeneities during corrosion$^{31-35}$. The addition of ACSE as well as its HMWF did not change the result, indicating that the corrosion mechanism remained the same for all the studied cases.

Nyquist plots were analyzed based on an equivalent circuit shown in Figure 4, where $R_s$ is the solution resistance, $R_p$ is the polarization resistance and $CPE$ is the constant phase element. The constant phase element (CPE) was introduced into the circuit in place of the pure capacitor of the double electric layer.

The impedance of the CPE is expressed by the following Equation 6$^{31,37}$:

$$Z_{CPE} = \frac{1}{Y_o (j \omega)^n}$$  \hspace{1cm} (6)

Where, $Y_o$ is the magnitude of CPE and $n$ represents the deviation from the ideal behavior falling between -1 and 1, $\omega_{max} = 2\pi f_{max}$ and $j^2 = -1$.

The double layer capacitance ($Cdl$) was then acquired through the CPE magnitude, according to the Equation 7$^{31}$:

$$C_{dl} = Y_o (\omega_{max})^{n-1} \hspace{1cm} (7)$$

Where, $Y_o$ is the magnitude of CPE, $n$ is the deviation from ideal behavior, $\omega_{max} = 2\pi f_{max}$, and $f$ the frequency where the imaginary component of the impedance is maximal.

Table 4 displays the parameters achieved from the electrochemical impedance analyses at different ACSE concentrations and at 400 mg L$^{-1}$ of HMWF.

The data exposed on Table 4 and the electrochemical impedance diagrams presented in Figure 3B point out that extracts addition in the corrosive solution leads to a decrease in the double layer capacitance and an increase...
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in the polarization resistance, demonstrating that the adsorption process from the molecules of the extracts is occurring which corroborates the gravimetric results. The extract concentration increase provides an increase in the capacitive loop diameter and, consequently, higher values of $R_p$ are obtained, which increases the inhibition efficiency, reaching a maximum value of 97.3% at 800 mg L$^{-1}$ of ACSE. It is also stated that extremely low concentrations of ACSE provided a high IE result as 88.5% for 10 mg L$^{-1}$, and that the presence of 400 mg L$^{-1}$ of the HMWF showed a similar loop seen for 800 mg L$^{-1}$ of ACSE; resulting in the same IE (97.3%). These results suggest once again that the macromolecules can be the main responsible for the inhibitory effect.

The diagrams of Bode (Figure 5) show a single time constant for all curves with a little frequency shift towards lower frequencies in the presence of the inhibitor, where the maximum phase angle for the blank assay is close to 39° and this value increases significantly in the presence of 10 mg L$^{-1}$ of CSE (~ 61°), however above 50 mg L$^{-1}$ the phase angle keeps quite constant, achieving a value close to 65° at 800 mg L$^{-1}$. Higher phase angles were obtained for the samples containing the ACSE and its HMWF, suggesting that a protective film was formed in these conditions.

### 3.2.3 Adsorption isotherms

The interaction between the inhibitor and the metal surface can be described by adsorption isotherms. These isotherms require the degree of surface coverage ($\theta$) for different inhibitor concentrations, which were calculated using the values $IE$ shown in Table 4, according to the Equation 8.

$$\theta = \frac{IE}{100}$$

In order to evaluate the adsorption process of the inhibitory molecules contained in ACSE on the mild steel surface, the adsorption isotherms of Langmuir, Temkin, Flory-Huggins and El-Awady were evaluated and the data obtained are presented in Table 5 and Figure 6. Figure 6 and Table 5 show that the Langmuir isotherm showed a better linear correlation, with a linear correlation coefficient of 0.9999 and an angular coefficient of 1.0264, suggesting the formation of a protective monolayer on the metal surface with a fixed number of adsorption sites and each site holds an adsorbate with no interaction between the adsorbate molecules. Although the excellent linear correlation shown in Table 5, the obtained angular coefficient deviated from one unit, allowing to suggest the interaction between adsorbed molecules of the inhibitor or the relation between active site for each adsorbed molecule is not of one unit.

### 3.2.4 Potentiodynamic polarization curves

Figure 7 shows the polarization curves for mild steel in 1 mol L$^{-1}$ HCl solution, in the absence and presence of ACSE with concentrations of 10, 50, 100, 200, 400, 800 mg L$^{-1}$ and at 400 mg L$^{-1}$ of its HMWF. Table 5 presents the kinetic parameters acquired from the Tafel extrapolation method.

Figure 7 and Table 6 point out the decrease of the anodic and cathodic current densities with the presence of the ACSE and its HMWF if compared to the system without the inhibitor, being this decrease more expressive to the cathodic branch. Overall, the same behavior previously seen from weight loss measurements and electrochemical impedance
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Table 4. Electrochemical parameters acquired from the EIS diagrams in the absence and presence of ACSE and its HMWF.

<table>
<thead>
<tr>
<th>[Inhibitor] (mg L⁻¹)</th>
<th>$f_{max}$ (Hz)</th>
<th>$n$</th>
<th>$Y_e$ (µMho cm⁻²)</th>
<th>$C_d$ (µF cm⁻²)</th>
<th>$R_p$ (Ω cm²)</th>
<th>$IE$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>71.6</td>
<td>0.895</td>
<td>250</td>
<td>131</td>
<td>16.2</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>22.3</td>
<td>0.852</td>
<td>103</td>
<td>49.5</td>
<td>141</td>
<td>88.5</td>
</tr>
<tr>
<td>50</td>
<td>17.6</td>
<td>0.827</td>
<td>79.0</td>
<td>35.0</td>
<td>300</td>
<td>94.6</td>
</tr>
<tr>
<td>100</td>
<td>8.75</td>
<td>0.821</td>
<td>84.6</td>
<td>41.3</td>
<td>442</td>
<td>96.3</td>
</tr>
<tr>
<td>200</td>
<td>8.75</td>
<td>0.829</td>
<td>80.5</td>
<td>40.6</td>
<td>482</td>
<td>96.6</td>
</tr>
<tr>
<td>400</td>
<td>6.93</td>
<td>0.824</td>
<td>81.3</td>
<td>41.8</td>
<td>521</td>
<td>96.9</td>
</tr>
<tr>
<td>800</td>
<td>5.48</td>
<td>0.824</td>
<td>74.6</td>
<td>40.0</td>
<td>603</td>
<td>97.3</td>
</tr>
<tr>
<td>HMWF</td>
<td>6.93</td>
<td>0.836</td>
<td>71.6</td>
<td>38.6</td>
<td>603</td>
<td>97.3</td>
</tr>
</tbody>
</table>

Table 5. Data of straight lines obtained by linear adjustment.

<table>
<thead>
<tr>
<th>Isoterms</th>
<th>Line Equation</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>$\frac{C}{\theta} = \frac{1}{K} + C$</td>
<td>$y = 1.0264x + 1.4645$</td>
</tr>
<tr>
<td>Temkin</td>
<td>$\theta = \left(\frac{-2.303}{2a}\right) \log K + \left(\frac{-2.303}{2a}\right) \log C$</td>
<td>$y = 0.0449x + 0.8576$</td>
</tr>
<tr>
<td>Flory-Huggins</td>
<td>$\log \left( \frac{\theta}{C} \right) = \log K + x \log (1 - \theta)$</td>
<td>$y = 2.7585x + 1.6563$</td>
</tr>
<tr>
<td>El-Awady</td>
<td>$\log \left( \frac{\theta}{1 - \theta} \right) = \log K + y \log C$</td>
<td>$y = 0.3475x - 0.6174$</td>
</tr>
</tbody>
</table>

* $C$ is the ACSE concentration; $K$ is the adsorption constant, $a$ is the lateral interaction parameter between the adsorbed molecules, $x$ is the number of water molecules substituted by a single inhibitor molecule and $y$ is the number of inhibitor molecules adsorbed in a given active site.

is maintained, where ACSE and its HMWF reached an $IE$ of 94.2% at 800 and 400 mg L⁻¹, respectively, suggesting that probably the macromolecules present an important role in the inhibitory action of the ACSE towards the mild steel corrosion.

The presence of ACSE and its HMWF displaced the $OCP$ to more positive values with a maximum displacement of +24 mV while the $E_{corr}$ shifted to more negative values, with a maximum displacement of −26 mV in the presence of 400 mg L⁻¹ ACSE, demonstrating that the extract acts as a mixed-type inhibitor with a cathodic character when polarized. The anodic Tafel constant did not significantly change with the extracts addition, suggesting that both ACSE and its HMWF do not change the mechanism of the anodic reaction. However, the cathodic Tafel constant increased (in module) from the addition of 50 mg L⁻¹ of ACSE and its HMWF which can be explained by a change of the cathodic reaction mechanism. These results suggest that the ACSE and its HMWF act like most organic compounds, where the screening effect is added to the activation effect.

Both ACSE and its HMWF are mixed type where the screening effect is added to the activation effect. They act by...
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A mixed type mechanism since the apparent activation energy decreased with their addition. Although normalized $R_p$ results are equal to the blank result with the correction of the electroactive area, i.e., normalizing these two quantities by $(1 - \theta)$, being $\theta$ determined by electrochemical impedance diagrams (Table 4). Table 7 shows that the $C_{dl}$ values do not keep constant with the area normalization. According to the Fernandes et al., in the presence of their inhibitor the $C_{dl}$ was mainly related to the electroactive area $(1 - \theta)$. However, if the normalization is performed for each extract concentration the $C_{dl}$ values did not keep constant how it should be. Certainly, their inhibitor is a mixed type where the screening effect is added to the activation effect.

The behavior seen with the HMWF where the $IE$ was equal to its total extract (ACSE) was also seen in our previous works with gorse, coffee husk and grains, biomass of *Spirulina Maxima* microalgae and barley agro-industrial residues aqueous extracts. All these studies reinforce the hypothesis that macromolecules (proteins or polysaccharides) are probably responsible for the inhibitive action which would explain the deviation of a unit in the angular coefficient of Langmuir equation, allowing to suggest that the relation between active site for each adsorbed molecule is not of one unit.

According to S. Banerjee et al., polymers maybe a better choice, as they have long chain molecules and show effect, acting only by surface screening their both normalized $R_p$ and $C_{dl}$ values should be equal to the blank results with the correction of the electroactive area, i.e., normalizing these two quantities by $(1 - \theta)$, being $\theta$ determined by electrochemical impedance diagrams (Table 4). Table 7 shows that the $C_{dl}$ values do not keep constant with the area normalization. According to the Fernandes et al., in the presence of their inhibitor the $C_{dl}$ was mainly related to the electroactive area $(1 - \theta)$. However, if the normalization is performed for each extract concentration the $C_{dl}$ values did not keep constant how it should be. Certainly, their inhibitor is a mixed type where the screening effect is added to the activation effect.

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**Figure 6.** Adsorption isotherms of (A) Langmuir, (B) Temkin, (C) Flory-Huggins and (D) El-Awady for ACSE on the mild steel surface in 1 mol L$^{-1}$ HCl solution.

**Figure 7.** Polarization curves of mild steel in 1 mol L$^{-1}$ HCl in the absence and presence of different concentrations ACSE and at 400 mg L$^{-1}$ of its HMWF.
high inhibition efficiency at very low concentration in most aggressive media. For a chemically modified natural polysaccharide the authors found 96.6% of IE at 100 ppm using EIS data. In the work of Haruna et al. the inhibitory action of gelatin on carbon steel in an acid medium was studied. This protein proved to be a good inhibitor with an efficiency of 88.1% for 2.5 w/v using EIS data.

In our work, the aqueous cotton seed extract acted as a good corrosion inhibitor reaching an inhibition efficiency of 95.7% after 24 h of immersion for 800 mg L\(^{-1}\) inhibitor concentration. From Rp data, it was seen that 400 mg L\(^{-1}\) of the high molecular weight fraction isolated from ACSE showed inhibition efficiency equal to 97.3%, where as ACSE presented 96.9%, suggesting that the macromolecules present a fundamental participation in the inhibitive process. The literature results with gelatin and polysaccharides corroborates our hypothesis.

### 3.3 Surface analysis

Figure 8 presents the SEM micrographs for the mild steel. Figure 8a shows the abraded surface of the mild steel, without acidic exposition. The surface immersed in the acid medium without the inhibitor was strongly corroded leaving it rough; however, the surface immersed in the acid medium in the presence of the ACSE showed a smoother surface, indicating therefore that the surface was protected by the extract, which corroborates all the previously discussed results. These analyses show that the aqueous cotton seed extract acted as a good corrosion inhibitor of mild steel, as indicated by the gravimetric and electrochemical tests.
4. Conclusions

Cotton seed extract was found to be an effective natural corrosion inhibitor for mild steel in 1 mol L⁻¹ hydrochloric acid aqueous medium, as well as its high molecular weight fraction. The inhibitory action may be related to the presence of proteins and polysaccharides present in cotton seeds.

The results obtained by the gravimetric analyses showed an increase of the inhibition efficiency with the increase of the extract concentration and the immersion time. The results with temperature varying showed that the inhibitor adsorption is of chemical nature. The inhibitor adsorption followed the Langmuir isotherm model, which admits the formation of a monolayer of the inhibitor molecules on the metal surface.

The electrochemical results indicated that the inhibitory molecules in both ACSE and its HMWF adsorb in the metal surface acting as a mixed type inhibitor like the majority of organic compounds, where the screening effect is added to the activation effect.

The surface analysis corroborated the gravimetric and electrochemical tests and showed that mild steel surface is much less corroded when in the presence of aqueous cotton seed extract.

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6. Referências


