Modified Cassava Starches as Potential Corrosion Inhibitors for Sustainable Development

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Activated (AS) and carboxymethylated ($CMS_{0.24}$) cassava starch derivatives were studied as corrosion inhibitors for carbon steel XC35 in a 200 mgL^{-1} NaCl solution. They were characterized by back titration and Fourier Transform Infrared Spectroscopy (FTIR). Electrochemical techniques were used to evaluate the inhibitive properties of starches at room temperature and the chemical composition of the protective films was determined by X-Ray Photoelectron Spectroscopy (XPS). Electrochemical measurements revealed that AS acts as mixed inhibitor, whereas $CMS_{0.24}$ mainly inhibits the anodic reaction. In both cases, the protection increased with the inhibitor concentration; nevertheless, after 24 hours of immersion, the $CMS_{0.24}$ loses its properties, while AS molecules still maintains them. XPS analyses show that the inhibitive films are composed of an iron oxide/hydroxide mixture in which starch molecules are incorporated. Results were explained taking into consideration the hydrophilicity and the strength of the ionic interaction of the starches with the metal surface.

Keywords: *carbon steel, green corrosion inhibitors, electrochemical measurements, cassava starch*

1. Introduction

There is currently considerable interest in developing "green" or low toxicity corrosion inhibitive formulations in response to legislation changes concerning environmental protection. Chemicals disposal, which is a common practice in corrosion and scaling treatments for "clean" water systems, such as cooling water circuits or potable water systems, is being more and more restricted and penalized. Therefore, there is a growing need to produce corrosion inhibitors that are not toxic for human beings and that have a low eutrophication level with an optimal biodegradability. Initial interest in "green inhibitors" began in the 1990s; since then, there has been an increasing research activity on the inhibitive properties of eco-friendly and harmless compounds. In this sense, some authors have reported the use of tannins, amino acids, vitamins, proteins, polymers, and phosphono compounds as corrosion and scaling inhibitors[1-3] to replace toxic metal cations, phosphates, and polymers having a low biodegradability level[1,4-19]. Unfortunately, these last compounds are still used because they are effective at relatively low cost.

Starch is a renewable, biodegradable, and readily available polymer at low cost, which may be obtained from rice, corn, wheat, and cassava, among other sources. Starches are widely employed in food, paper-making, textile,

and pharmaceutical industries. It is also used as additive in cements and drilling muds in oil wells[20]. Native starch may, however, exhibit some drawbacks that restrict its use, such as insolubility in cold water and sensitivity to shearing and low pH[21]. The physical and/or chemical modification of this polysaccharide may, therefore, enhance its applications range. The carboxymethylation of starch results in a modified starch (CMS) with carboxylate groups (CH_2COO^-), which disturb the ordered structure of native starch, reduce the gelatinization temperature, increase solubility in water, and lead to higher storage stability[22]. The synthesis of CMS has been previously studied[23], but recently, researchers have focused their investigations on the improvement of the products and synthesis paths to obtain appropriate degrees of substitution (DS)[23-28].

The aim of this work is to prepare and use cassava starch derivatives as "green" inhibitors for corrosion protection of carbon steel. Cassava starch was selected as precursor for the derivatives because cassava is a woody shrub that is extensively cultivated in tropical and subtropical regions[21], but it has not been as widely commercialized as, for example, corn starch. It must be noticed that up to our knowledge, only few works have been published dealing with the use of starches as protective material against corrosion[11,29,30]. Sugama et al.[11] employed a polyorganosiloxane-grafted potato starch and an unmodified potato starch as coating

to afford protection of aluminum. On the other hand, Abd El Halemm et al.[29] employed a soluble starch, among other compounds, to improve the pitting corrosion resistance of a carbon steel; nevertheless, these authors did not specify the starch they used and the type and amount of functional groups present in the starch. Other work that can be mentioned is the publication of Rosliza and Wan Nik[30] in 2009, who reported that cassava starch could improve the corrosion resistance of an aluminum alloy in seawater. It should be mentioned that in most of the works dealing with natural products as corrosion inhibitors, tests have been performed under acid conditions, and significantly less work has been published about the use of natural compounds in neutral-alkaline solutions[1,2,8,10,29]. More recently, we have reported that modified cassava starches exhibit corrosion inhibitive properties for carbon steel in a solution that simulates the chemical composition of tap water[31-33]. In this work, electrochemical measurements and X-ray Photoelectron Spectroscopy (XPS) analysis were coupled to investigate parameters such as type of modification, inhibitor concentration and time of immersion, with the aim of understanding the inhibition mechanism of these species.

2. Experimental

2.1. *Preparation and characterization of modified starches*

The biopolymers used as inhibitors were an activated cassava starch (AS) and a carboxymethylated cassava starch (CMS); their chemical structures are shown in Figure 1. They were prepared from native cassava starch, provided by Agroindustriales Mandioca S.A., following the procedure described in previous works[31-33]. The success of the modification process was determined by means of Fourier Transform Infrared Spectroscopy (FTIR), using a Nicolet Magna IR 760 spectrometer with a resolution of 4 cm^{-1}, to obtain the spectra from films casted onto AgBr discs. The CMS degree of substitution was determined by back titration, with the experimental procedure described in previous investigations[32,33].

2.2. *Corrosion experiments*

The corrosive medium was a 200 mgL^{-1} sodium chloride solution, maintained at 25°C in contact with air. This medium is a simplification of the composition of natural waters, which has been often employed[32,34-36] to study corrosion and inhibition due to its low conductivity, fairly high corrosivity, and because it is easily reproducible at a laboratory scale. Modified cassava starches (AS and CMS) were tested as inhibitors at different concentrations: 200, 400 and 600 mgL^{-1}. The pH of the solution containing the inhibitors was of 10.0 ± 0.5. For the blank solution, the pH was modified to 10.0 by adding sodium hydroxide. It should be pointed out that the addition of the starch molecules produces an increase in the solution viscosity[27], leading to a reduction of the relative oxygen solubility[37], which in this case is the corrosive agent. Even though the addition of the starch modifies the solution viscosity, the 200 mgL^{-1} sodium chloride solution was employed for comparison purposes because the maximum decrease of the relative oxygen solubility is of only about 7%[37] when CMS is added.

A rod of XC 35 carbon steel having a cross-sectional area of 0.79 cm^2 was used as working electrode. Its nominal composition in percentage by weight is 0.35C, 0.65Mn, 0.25Si, 0.035P, 0.035S, and Fe balance. The electrodes were covered by a heat-shrinkable sheath to leave only the tip of the carbon steel cylinder in contact with the solution. Before carrying the electrochemical tests, the steel samples were polished with SiC paper down to grade 1200. Afterwards, they were cleaned with ethanol, rinsed with distilled water, and dried with warm air.

Polarization curves and electrochemical impedance diagrams were recorded using a Gamry Potentiostat DC-105 model. These techniques were coupled with a rotating disk electrode to control mass transport phenomena. The electrode rotation rate was fixed at 1000 rpm. Experiments were performed in a standard Pyrex double wall cell. The counter-electrode was a platinum grid, and a saturated calomel electrode (SCE) was used as reference. Potentiodynamic polarization curves were obtained after 2 hours of immersion at the open circuit potential for all concentrations. Then, the working electrode was polarized continuously from the cathodic to the anodic range (–0.950-0.150 V/SCE). Potential sweep rate was fixed at 10 mV/min[38]. The polarization curves were corrected for the ohmic drop. Electrochemical impedance measurements were carried out under potentiostatic regulation in a frequency range of 100 kHz to 6 mHz with eight points per decade using a 8 mV peak-to-peak sinusoidal potential. Impedance diagrams were obtained at the corrosion potential for different inhibitor concentrations and immersion times. Electrochemical results were obtained from at least three experiments to ensure reproducibility.

2.3. *Surface analysis*

The surface chemical composition of the inhibitive layers was studied using X-ray photoelectron spectroscopy (XPS). The XPS measurements were carried out in a VG Escalab model 220i-XL. The samples to be analysed were obtained by cutting disks of about 3 mm of thickness from the metallic cylinder used as working electrode. They were pasted with a conductive adhesive to the steel rod to be immersed in the 200 mgL^{-1} NaCl solution containing the inhibitors. Then, the samples were maintained at
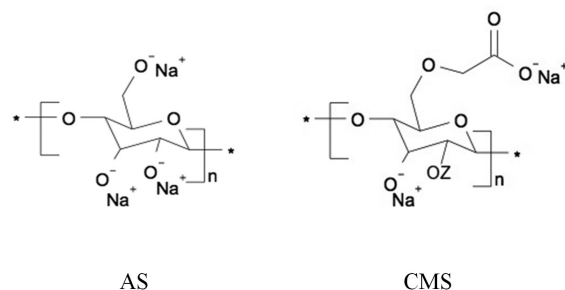

Figure 1. Chemical structures of activated (AS) and carboxymethylated starch (CMS), where Z indicates a Na$^+$ cation or a carboxymethyl group.

the corrosion potential for different immersion times at 1000 rpm. After the measurements, they were removed from the solution, dried in warm air, and the disks were placed in a vacuum chamber. Once the ultra-high vacuum regime (10^{-9} Torr) was reached, the specimens were irradiated with a non monochromatic MgKα X-ray source of 300 W. Measurements were carried out at a take-off angle θ = 90°. The experimental resolution of the binding energy was less than 0.5 eV. After background substraction, peak deconvolution was performed using the XPSPEAK4.1 software. Binding energies were corrected for possible charging effects by referencing to the C1s at 284.5 eV using the XPSGRAF102 software. The chemical state of iron was tested by examining the $Fe2p_{3/2}$ signal. The adsorption of the inhibitors on the steel surface was monitored by means of the characteristic C1s and O1s peaks.

3. Results

3.1. *Structural characterization of the starches*

The chemical changes of the starch were verified by FTIR. Figure 2 shows a comparison of the FTIR spectra for activated (AS) and carboxymethylated (CMS) starch. In both spectra, bands at 575, 765, and 862 cm^{-1} are observed and attributed to C-C stretching and C-H bending vibrations of the anhydroglucose unit (AGU). In the fingerprint region between 900 and 1500 cm^{-1}, the bands located at about 933, 1000, 1082, and 1157 cm^{-1} correspond to -C-O-C- bonds in the AGU[39]. The band at 1649 cm^{-1} originates from tightly bound water present in starch[40], and those observed at 2929 cm^{-1} and ~3350 cm^{-1} are due to the characteristic vibrations of C-H and –OH bonds. In the spectrum of the CMS, two new signals are clearly appreciated at 1605 cm^{-1} and 1417 cm^{-1}, which correspond to non-symmetric and symmetric stretching of carboxylate (-COO⁻) groups[27,28,41], demonstrating the successful reaction of monochloroacetic acid with the starch backbone. At this point, it should be mentioned that in the case of AS, only alkoxy groups (-CO⁻)
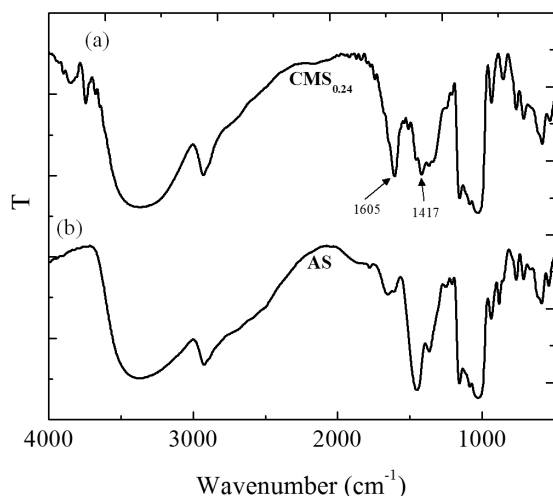
are available to interact with the steel surface, whereas in the CMS, both alkoxy and carboxylate (COO⁻) groups are capable to be adsorbed on the metal surface. This is in agreement with our previous results, where structural characterization of modified starches was carried out by Nuclear Magnetic Resonance[32].

3.2. *Effect of the concentration and modification process of starches on the corrosion inhibitive properties*

Figure 3 shows the variation of the corrosion potential, E_{corr}, of the carbon steel electrode as a function of the immersion time, in the presence of different concentrations of AS and $CMS_{0.24}$, respectively. It is observed that the corrosion potentials in the presence of inhibitors are close to that obtained for the blank solution, whatever the inhibitor concentration. In addition, regardless of the inhibitive species, these values remain constant at around –400 mV/SCE, after approximately one hour of immersion, indicating that the electrochemical system reaches the steady state.

Potentiodynamic polarization curves obtained after two hours of immersion in the solution containing AS or $CMS_{0.24}$ at different concentrations are presented in Figure 4. They are compared with the current-voltage curve obtained without inhibitor. In the presence of AS and $CMS_{0.24}$, it may be observed that the anodic and cathodic kinetics depend on inhibitor concentration. The anodic and the cathodic branches describe the iron dissolution and the oxygen
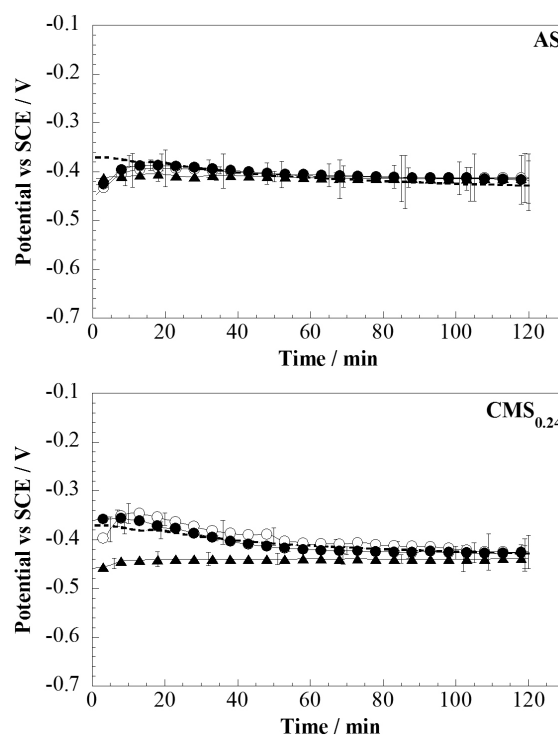
Figure 3. Corrosion potential of the carbon steel electrode as a function of immersion time in the 200 mgL⁻¹ NaCl solution (---) and in the presence of inhibitors: (▲) 200 mgL⁻¹, (●) 400 mgL⁻¹, (○) 600 mgL⁻¹.

Figure 2. FTIR spectra of (a) $CMS_{0.24}$ and (b) AS.

reduction reaction, respectively. Furthermore, the shape of the polarization curves suggests that both kinetics are under mixed control. When using AS, it is observed that in the anodic domain, the current densities are lower than for the blank solution for the whole overpotential range; for $CMS_{0.24}$ it happens only at potentials near E_{corr}. For the lowest $CMS_{0.24}$ concentration (200 mgL^{-1}), the anodic branch shows the active dissolution of the metal; in contrast, for AS, the anodic current density remains lower than that obtained for the blank solution. At higher inhibitor concentrations, the inhibitive effect is enhanced in the presence of both species, but the anodic current density is remarkably lower for 600 mgL^{-1} of activated starch. In the cathodic domain, the current density only decreases for the highest AS concentration, while for 200 and 400 mgL^{-1}, cathodic currents are similar to that
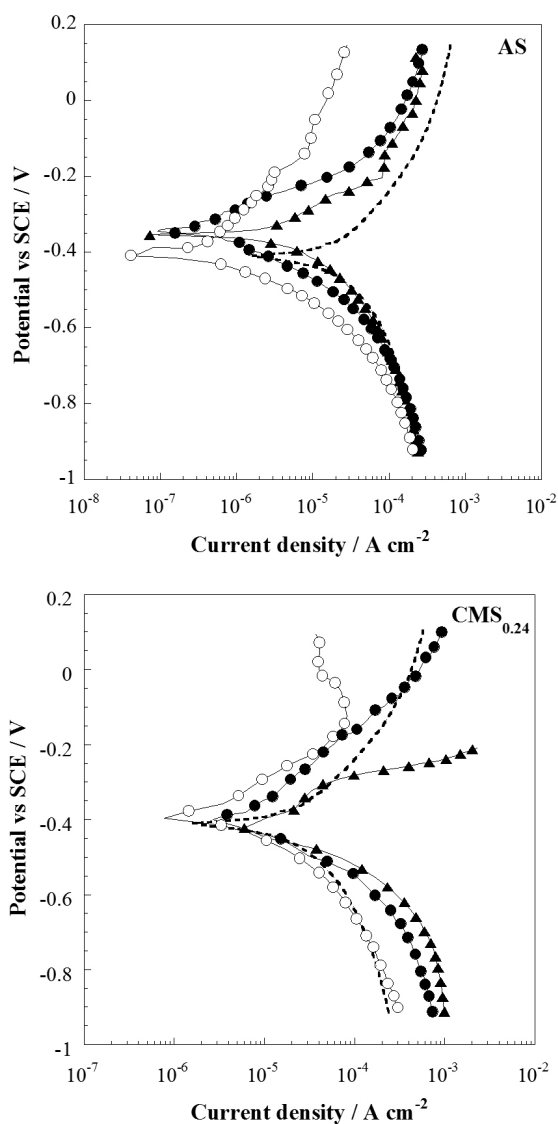
obtained for the blank solution. This was not observed for $CMS_{0.24}$ because of the higher current densities compared with the reference curve. The increase of the cathodic kinetic could be related to desorption of the macromolecules when the working electrode is negatively polarized; therefore, the oxygen reduction reaction is accelerated by the presence of bared areas on the metal surface. Results obtained from the polarization curves indicate that AS acts as mixed inhibitor, whereas $CMS_{0.24}$ acts as anodic one.

Figure 5 shows the electrochemical impedance diagrams obtained at the corrosion potential, after 2 hours of immersion in the solution containing AS or $CMS_{0.24}$, at different concentrations. Electrochemical parameters obtained from these diagrams are listed in Table 1. The polarization resistance values of the films formed on the electrode surfaces (Rp) were obtained by extrapolating the impedance diagrams on the real axis and, the CPE parameters, Q_{eff} and α, were determined using the graphic method proposed by Orazem et al.[42,43] in order to take into account the distribution of reactivity of the electrode surface.

It can be noted that when inhibitors are added to the corrosive solution, the impedance diagrams are larger than in the blank solution; this result accounts for the inhibitive effect of the starch molecules. The size of the impedance diagrams increases with the inhibitor concentration; however, in the presence of AS, the spectra are significantly larger than those obtained for $CMS_{0.24}$ at the highest concentration. In addition, the impedance spectra are composed by a single capacitive loop for all AS concentrations, but the flattened shape of the impedance spectra suggests the presence of at least two time constants for CMS, in agreement with the α parameter. The increase of Rp and the decrease of Q_{eff} values, particularly in the presence of AS, suggest differences in the adsorption mechanisms of these biopolymers.
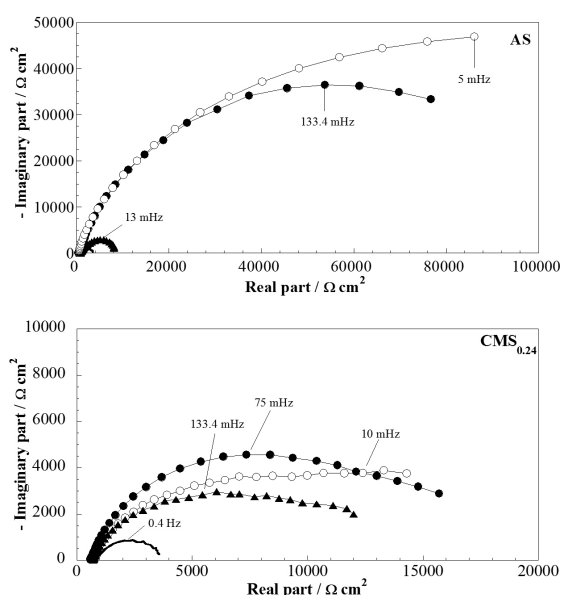

Figure 4. Polarization curves obtained for the carbon steel electrode after 2h of immersion at E_{corr} in the 200 mgL^{-1} NaCl solution (---) and in the presence of inhibitors: (▲) 200 mgL^{-1}, (●) 400 mgL^{-1}, (○) 600 mgL^{-1}.

Figure 5. Electrochemical impedance diagrams obtained after 2h of immersion at E_{corr} in the 200 mgL^{-1} NaCl solution (---) and in the presence of inhibitors: (▲) 200 mgL^{-1}, (●) 400 mgL^{-1}, (○) 600 mgL^{-1}.

Table 1. Characteristic parameters and inhibition efficiency obtained from the impedance diagrams presented in Figure 5.

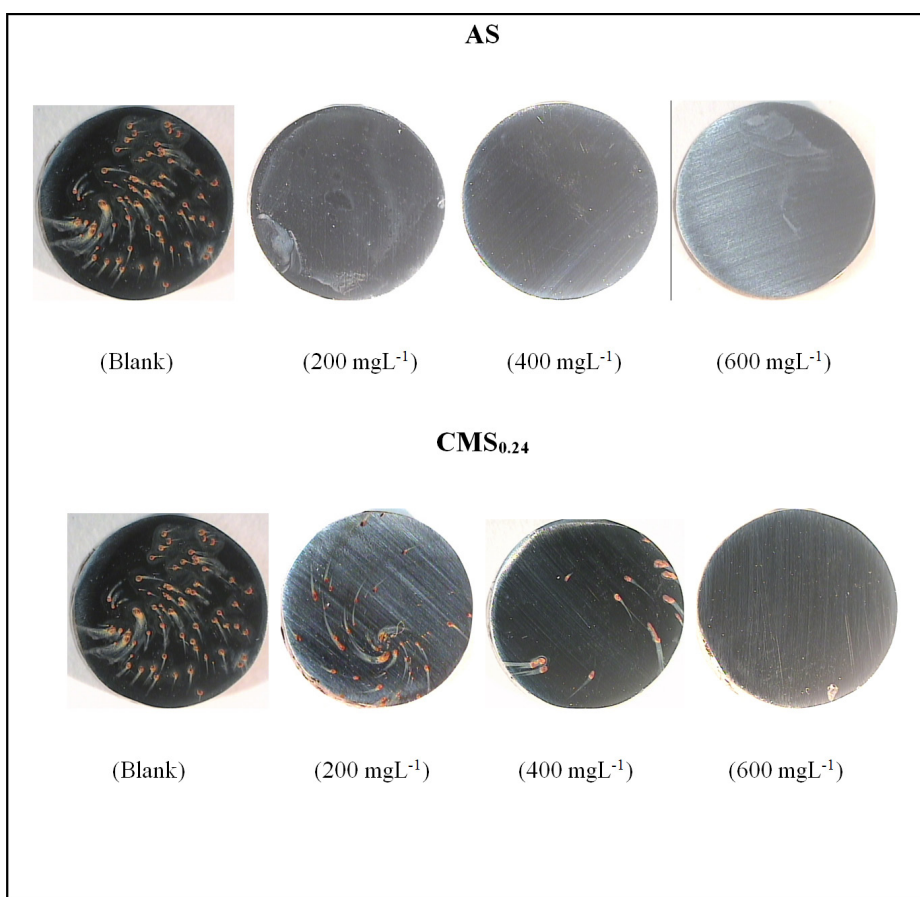|	Inhibitor concentration (mgL⁻¹)	R_P (Ω.cm²)	Q_{eff} (µF.cm⁻²)sα⁻¹	α	ε (%)
Blank		3900 ± 400	290	0.5	-
AS	200	8200 ± 800	215	0.6	59
	400	110000 ± 8000	73	0.8	97
	600	175000 ± 7000	68	0.8	98
CMS₀.₂₄	200	14000 ± 700	121	0.7	77
	400	17400 ± 800	177	0.7	82
	600	19100 ± 900	135	0.6	84

Figure 6. Pictures of the XC 35 carbon steel surfaces after 2h of immersion without inhibitor (a) and in the presence of inhibitors: (b) 200 mgL⁻¹, (c) 400 mgL⁻¹, (d) 600 mgL⁻¹.

Figure 6 shows pictures of the electrode surfaces taken after two hours of immersion in the corrosive medium. It can be observed that many corrosion product spots that follow the hydrodynamic of the system are developed from pits on the metal surface. The traces of rust tend to disappear when the inhibitors are added to the sodium chloride solution. It has to be highlighted that this effect is observed with just 200 mgL⁻¹ of AS; however, higher CMS concentrations are required in order to obtain a bright metallic surface. The images described are in accordance with the electrochemical results.

Table 1 shows the inhibition efficiency calculated according to Equation 1, where Rp and Rp' are the polarization resistance values with and without inhibitor, respectively.

$$\varepsilon = \frac{R_p - R'_p}{R_p} \times 100 \tag{1}$$

It may be observed that for AS, the efficiency values are as high as 98%, revealing the higher effectiveness of this compound in comparison with other natural products at similar concentrations[1-4,8-12]. In agreement with previous results, the inhibition efficiency obtained for AS at high concentrations is greater than with CMS₀.₂₄.

In order to determine the chemical composition of the inhibitive films, XPS analysis were carried out on the carbon steel surface after two hours of immersion in the solution containing 600 mgL⁻¹ of AS or $CMS_{0.24}$. At this concentration, the highest inhibition efficiency was achieved as shown previously. Figures 7 and 8 illustrate a comparison of the X-ray photoelectron spectra of $Fe2p_{3/2}$, O1s, and C1s obtained from the inhibitive films formed on the steel surface, and from AS and $CMS_{0.24}$ powders, respectively.

From Figure 7a (when AS was employed), the $Fe2p_{3/2}$ spectrum is essentially composed by a broad signal, whose deconvolution results in three peaks at 712.5, 710, and 707 eV. The peak located at 707 eV is attributed to metallic iron, while those at 710 eV and 712.5 eV may be assigned to iron oxide/hydroxide species[44-47]. Similar signals are also

apparent in the deconvoluted $2p_{1/2}$ envelope centered around 725 eV (not shown). The O1s peak is composed of three peaks at 530.3, 531.9, and 532.8 eV; the first two peaks correspond to the binding energy of the O^{2-} and OH^- ions, in agreement with the presence of the iron oxide/hydroxide layer as detected in the $Fe2p_{3/2}$ spectrum. The signals at 531.9 eV and 532.8 eV also corresponds to oxygen in the C-O, O-C-O, and C-O species, which are present in the inhibitor[48,49]. Their presence, especially in the latter ones, demonstrates that the activated starch molecules are adsorbed on the steel surface. This is in agreement with the signals in the C1s region, where peaks due to C-H and C-C bonds at 283.5 eV and 284.7 eV, and to O-C-O and C-O bonds at 287eV and 289.1 eV were obtained[50-51]. Indeed, these peaks are also observed in the XPS spectra of the
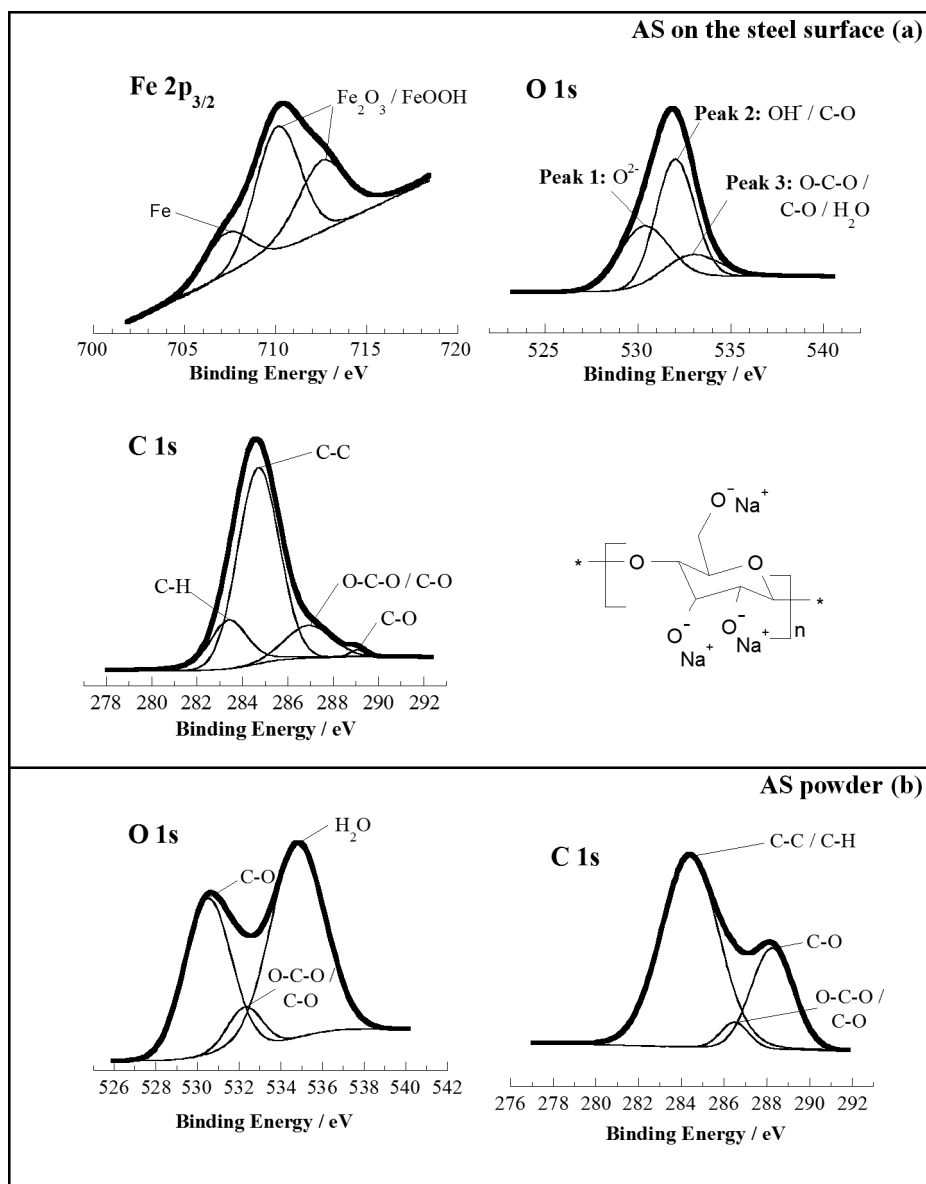

Figure 7. XPS spectra obtained for (a) the carbon steel surface after 2 h of immersion in the solution containing 600 mgL⁻¹ of AS and (b) AS powder.

activated starch powder shown in Figure 7b. It should be mentioned that the hydrophilic character of the starch leads to the presence of an important water signal in the O1s spectrum of the starch powder, which is also found in the O1s spectrum of the inhibitive layer, but with a lower intensity, as expected.

By analyzing Figure 8, some differences may be appreciated when the spectra of $Fe2p_{3/2}$, O1s, and C1s are compared with those shown in Figure 7. The metallic iron signal is not observed in the Fe2p spectrum of Figure 8, suggesting that the inhibitive layer formed in the presence of $CMS_{0.24}$ is thicker; the three signals observed are located in the region corresponding to iron oxide/hydroxide species. In addition, there appears a peak at 533 eV in the O1s spectrum, which corresponds to the binding energy of the carboxylate

groups ($O=C-O^-$) grafted to the starch molecules after the chemical modification[49]. In fact, the equivalent signal is observed both in the C1s spectra obtained on the steel surface and from the $CMS_{0.24}$ powder. As in the case of the AS, the presence of these signals reveals that $CMS_{0.24}$ molecules are incorporated to the iron/hydroxide layer formed on the metal surface.

3.3. *Influence of the immersion time on the inhibitive properties of the starches*

With the purpose of monitoring the inhibitive properties of the activated and carboxymethylated starch, impedance diagrams were recorded at the corrosion potential after 24 hours of immersion in the solution containing 600 mgL^{-1} of inhibitor (Figure 9). In the presence of AS, it may be
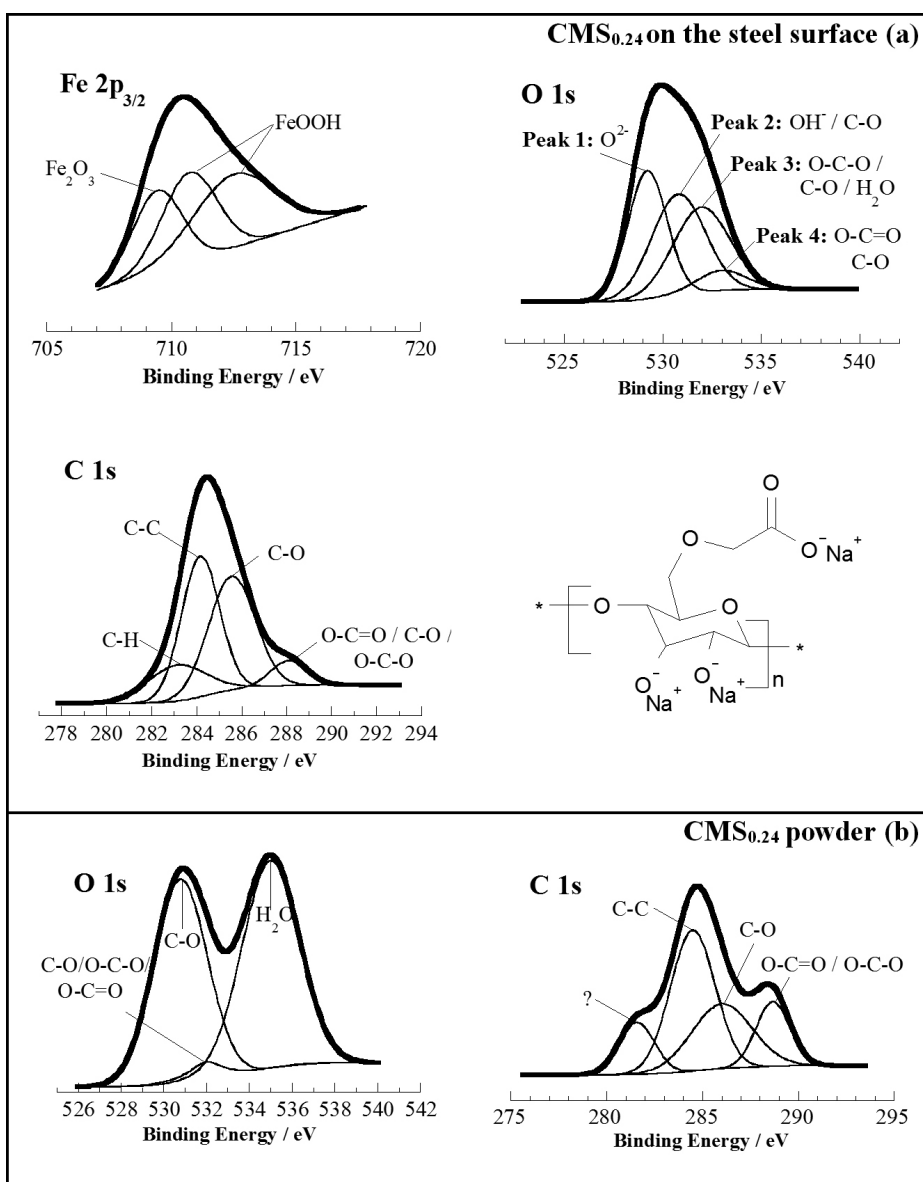

Figure 8. XPS spectra obtained for (a) the carbon steel surface after 2 h of immersion in the solution containing 600 mgL^{-1} of $CMS_{0.24}$ and (b) $CMS_{0.24}$ powder.
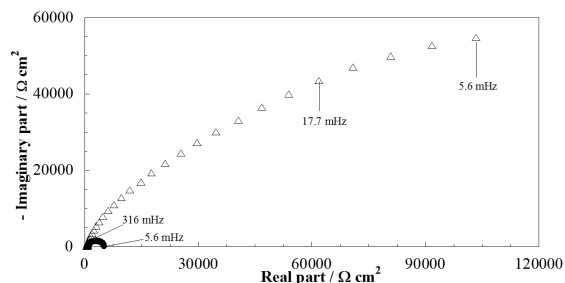
Figure 9. Electrochemical impedance diagrams obtained after 24 h of immersion at E_{corr} in the solution containing 600 mgL^{-1} of AS (Δ) and CMS$_{0.24}$ (●).
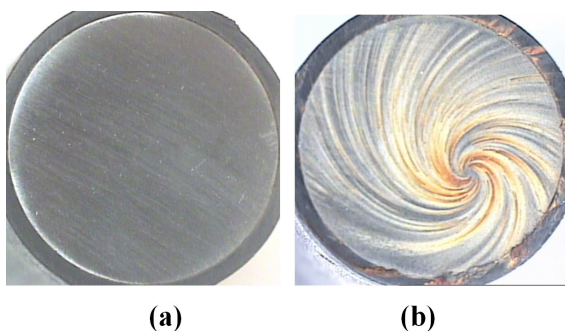

(a)   **(b)**

Figure 10. Pictures of the XC 35 carbon steel surfaces after 24 h of immersion in the solution containing 600 mgL^{-1} of (a) AS and (b) CMS$_{0.24}$.

noticed that the size of the impedance diagram remains relatively constant in comparison with that obtained after two hours of immersion. Conversely, when CMS$_{0.24}$ is employed, the size of the capacitive loop is significantly reduced with immersion time. These results agree with the images of the surface electrode shown in Figure 10. This result demonstrates that the CMS$_{0.24}$ loses its inhibitive properties after 24 hours of immersion, whereas AS molecules maintains them. This could be explained by the higher hydrophilic character of CMS$_{0.24}$, which leads to a weak chemical bond between carboxylate groups and metal surface.

In order to investigate the behavior shown by AS with the immersion time, XPS analysis were carried out on the electrode surfaces, after 24 hours of immersion in the solution containing 600 mg L^{-1} of this biopolymer (Figure 11). The spectra were similar to those of Figure 7, indicating that the AS macromolecules still remain adsorbed on the steel surface, with the only difference that the signal associated to the metal iron (707 eV) disappeared. This result could be related to a thickening of the inhibitive film when the immersion time increases, as evidenced by AFM images published in our previous work[32].

4. Discussion

The structural characterization of the bioinhibitors revealed that the modified cassava starches have active groups capable to interact with the metal surface: alkoxy (-CO$^-$) groups in the presence of AS, and both alkoxy and carboxylate (COO$^-$) groups when CMS$_{0.24}$ is employed.
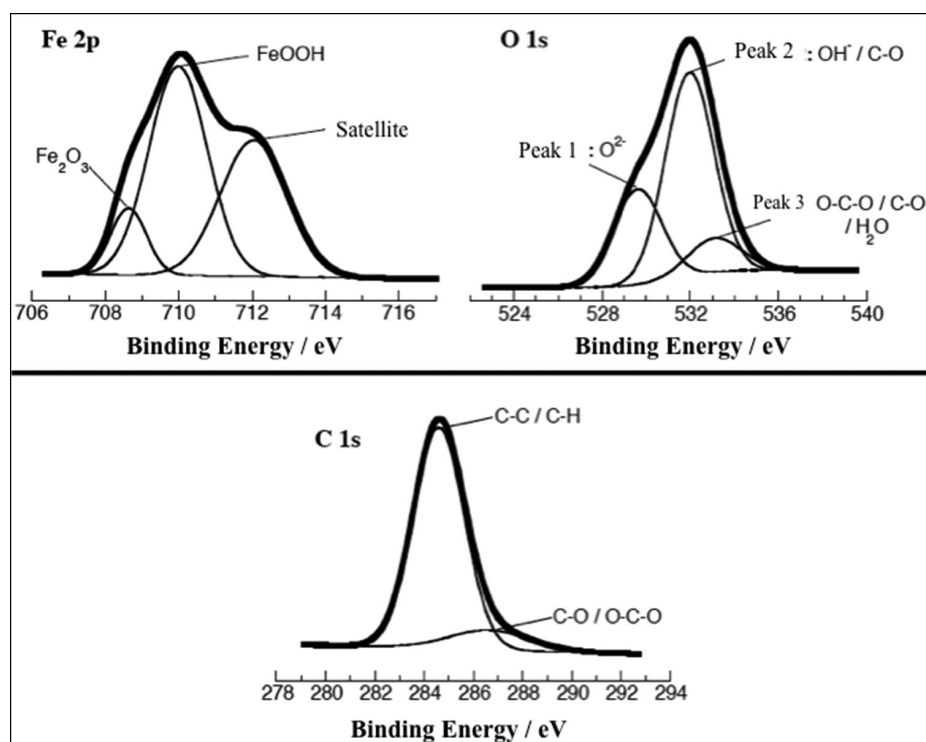

Figure 11. XPS spectra obtained for the carbon steel surface after 24 h of immersion in the solution containing 600 mgL^{-1} of AS.

From electrochemical measurements, it was demonstrated that both macromolecules act as corrosion inhibitors of carbon steel in 200 mgL^{-1} sodium chloride solution. It was found that the inhibitive properties increase with the concentration, independently of the modified starch used; nevertheless, impedance diagrams showed that the protective properties exhibited by AS are significantly larger and that they are kept high with the immersion time. XPS analyses demonstrated that the inhibitive film is composed by an iron oxide/hydroxide layer, in which starch molecules are incorporated. The signal at 533 eV in the O1s regions (Figure 7a and 8a) may be attributed to the formation of a chelate between starch molecules and the oxidized metal substrate[36,52,53]. When AS is employed, such chelate is formed between alkoxyde groups (-CO$^-$) and ferrous cations, while in the case of CMS$_{0.24}$, the chelate would be preferentially formed between carboxylate groups and the oxidized metal substrate, due its faster accessibility determined by the greater size of the monomeric unit (see Figure 1). If the relative areas of the signals located at 533 eV for both inhibitors are compared, it is found that a higher chelate fraction is achieved with AS. Thus, the inhibition mechanism is related to the formation of chelates between the active groups of the macromolecules and the ferrous cations, thereby sealing the pores and defects of the corrosion products layer deposited onto the metal surface, at the first stage of the electrochemical process. The higher inhibition performance achieved in the presence of AS can be explained by the stronger ionic interaction between AS and metal cations as was demonstrated by an electrostatic potential mapping of the AS and CMS monomeric units[32]. The relative weakness of the ionic interaction between CMS molecules and metal substrate may be also explained by resonance stabilization of the carboxylate anions[26]. Furthermore, CMS$_{0.24}$ is more hydrophilic than AS[22] and has a lower molecular weight. Both of these parameters would contribute to increase the solubility of CMS in water, establishing a competence between solution and adsorption of CMS molecules. This suggests that the reduction of the inhibitive properties of CMS$_{0.24}$ with the immersion time could be attributed to desorption of the carboxymethylated starch and/or a degradation of this natural polymer.

All previous results indicate that the inhibitive film formed on the metal surface in the presence of AS is more stable than the film formed with CMS$_{0.24}$. Moreover, with AS the inhibitive properties improve with the immersion time in contrast with the behavior shown by the CMS$_{0.24}$. These results are attributed to an increased adsorption of the AS molecules on the metal surface and a densification that may be related to a retrogradation process. In fact, it has been reported that starch molecules may retrograde in the presence of water[54]; i.e, that the amylose fraction of the starch may crystallize.

5. Conclusions

From electrochemical measurements it was clearly shown that modified cassava starches, such as AS and CMS$_{0.24}$, are able to inhibit carbon steel corrosion. Depending on the type of modification, they may act as mixed (AS) or anodic (CMS$_{0.24}$) inhibitors, whose protective properties increase with concentration. The impedance diagrams recorded at the corrosion potential indicated that AS is a better corrosion inhibitor because it promotes the formation of a more stable, compact, and protective film than CMS$_{0.24}$. These results were explained taking into account the stronger ionic interaction with the metal surface and lower hydrophilicity. XPS analysis showed that the protective films are composed by an iron oxide/hydroxide layer, in which the starch molecules are incorporated, that blocks the active sites by means of the formation of a chelate between the alkoxyde and/or carboxylate groups present in the starches, and the oxidized metallic surface. These results, together with the low cost, biodegradability, and high availability of activated cassava starch, make of this compound a potential commercial product as green corrosion inhibitors.

Acknowledgments

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