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Evaluation of the Inhibitory Gel *Aloe vera* against Corrosion of Reinforcement Concrete in NaCl Medium

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Abstract

Most reinforced concrete structures in seaside locations suffer from corrosion damage to the reinforcement, limiting their durability and necessitating costly repairs. To improve their performance and durability, we have investigated in this paper *Aloe vera* extracts as a green corrosion inhibitor for reinforcing steel in NaCl environments. Using electrochemical methods (zero-intensity chronopotentiometry, Tafel lines and electrochemical impedance spectroscopy), this experimental work investigated the effect of these *Aloe vera* (AV) extracts on corrosion inhibition of concrete reinforcing bar (HA, diameter 12mm) immersed in a 0.5M NaCl solution. The results show that *Aloe vera* extracts have an average corrosion-inhibiting efficacy of around 86% at an optimum concentration of 20%.

Keywords

Reinforced Concrete, Green Inhibitor, Corrosion, Reinforcement, Electrochemical Methods

1. Introduction

Corrosion induced by chloride ions from seawater or sea air is one of the main causes of deterioration in reinforced concrete structures. This problem, which

affects the whole world and Senegal in particular, represents a major technological and economic challenge, prompting owners to seek rapid, effective solutions to extend the service life of their structures, ensure user safety and optimize maintenance and repair costs. Several techniques for protecting steel against corrosion are now in use. Among these, the use of corrosion inhibitors offers a cost-effective and user-friendly alternative [1]. Thus, the need for more environmentally acceptable materials has led scientists to introduce new, more environmentally friendly alternative compounds as green inhibitors. Several categories of green inhibitors such as plant extracts, pharmaceutical drugs, ionic liquids, and synthetic inhibitors have become common sources. Plant extracts and oils are the essential source of the wide range of green corrosion inhibitors used in different acidic environments, due to their versatile physical, chemical and biological properties [2].

Numerous environmentally friendly inhibitors have been investigated over the last few decades [3] [4] [5] [6] [7]. Al-Turkustani *et al.* [7] examined alcoholic extracts from the Medicago Sativa plant as a corrosion inhibitor to control mild steel corrosion in H₂SO₄ 2M solution. They demonstrated the performance of the alcoholic extracts using electrochemical techniques. They also found that the extracts acted as mixed inhibitors and obeyed the Langmuir adsorption isotherm. According to the authors, chemical adsorption by charge transfer between the inhibitor molecules and the mild steel substrate emerged as the main corrosion inhibition mechanism. The inhibitory efficacy of aqueous extracts of Citrullus lanatus fruit was estimated at 91% by Dehghani *et al.* [4] using experimental and theoretical methods. They showed that the presence of C=C and O-H functional groups in the inhibitor's phytochemicals, such as citrulline, hesperetin, resveratrol and riboflavin, are largely responsible for the inhibitor's efficacy. Valeriana wallichii root straits have been shown to be highly effective at inhibiting mild steel in acidic environments, due to the presence of several phytochemicals, including naphthoic acid and an iridoid [5]. In recent years, *Aloe vera* leaf extract has been studied as a corrosion inhibitor due to its greater number of adsorption sites and its ecological character.

The corrosion-inhibiting properties of *Aloe vera* (AV) extract have been studied against the corrosion of mild steel [6], zinc, aluminium [7] [8] [9] and copper [10] in acid solutions. Studies by Al-Turkustani *et al.* [7] on aqueous aloe extract showed that the extract acts as a good corrosion inhibitor for aluminum in HCl solution. Abiola *et al.* [11] found that *Aloe vera* extract inhibited zinc corrosion in 2 M HCl solutions, with an inhibition efficiency of 67% at an extract concentration of 10% v/v. Mehdipour *et al.* [12] studied the inhibitory action of *Aloe vera* extract on a stainless steel substrate in a 1 M H₂SO₄ solution. The results of linear polarization and electrochemical impedance spectroscopy demonstrated the effectiveness of *Aloe vera* extract with increasing concentration. Singh *et al.* [13] studied the effect of *Aloe vera* gel on mild steel corrosion in a 1 M HCl medium. Tafel polarization studies revealed that *Aloe vera* gel extract acts as a mixed inhibitor. They showed that the inhibitor is absorbed by both physisorption and

chemisorption. The inhibitor showed an inhibition efficiency of over 90% and the lowest corrosion rate at an optimum concentration of 200 ppm.

However, the application of these green inhibitors, plant extracts in general and *Aloe vera* in particular, as corrosion inhibitors for high-adhesion (HA) concrete reinforcing bars remains little studied or almost non-existent.

In this study, the corrosion-inhibiting properties of *Aloe vera* are analyzed by electrochemical methods on a concrete reinforcing bar (HA) immersed in a saline solution (NaCl). The inhibitory efficacy of *Aloe vera* in NaCl solution is evaluated at levels of 10%, 20%, 30% and 40% relative to the volume of the solution.

To approximate the environmental conditions of reinforced concrete structures immersed in or in permanent contact with seawater, a solution (NaCl 0.5M) containing chloride ions was used as the aggressive medium.

2. Experimental Protocol

2.1. Extraction of the *Aloe vera* Gel Studied

The aloe-vera leaf has a bark covering its entire surface. Beneath the bark is a thin vascular layer in the form of a yellow gel. Inside is a white pulp [14]. The leaf structure is shown in **Figure 1**.

Aloe vera extract is used in this study as a corrosion inhibitor for concrete reinforcing steel. The *Aloe vera* gel extraction protocol is illustrated in **Figure 2**.

The *Aloe vera* leaves were sourced from a supermarket in France. They were then carefully cleaned and washed with demineralized water. Using a knife, the leaf bark was removed and the pulp was washed with demineralized water. The pulp is then ground using a blender, and the liquid filtered through a 0.80 mm sieve. Finally, the filtrate is poured into a plastic bottle lined with two layers of aluminum foil and stored in a refrigerator at 9°C.

Aloe vera gel contains over 70% saccharides and polysaccharides [15], particularly in the form of linear glucose and mannose chains known as polymannans due to the high presence of mannose. The chemical structures of some of the most important compounds in *Aloe vera* gel are shown in **Figure 3**.

Aloe vera is composed of several high molecular weight heterocyclic compounds [10] [17] containing numerous oxygen atoms in the functional groups and aromatic ring. In most inhibitors, π -electrons and heteroatoms (e.g., O, N) are responsible for adsorbing inhibitor molecules onto the metal surface and protecting against corrosion [18].



Figure 1. Cross-section of the *Aloe vera* (AV) leaf.

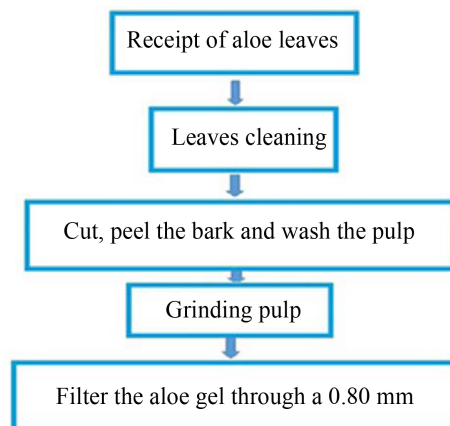


Figure 2. Gel extraction process used for our tests.

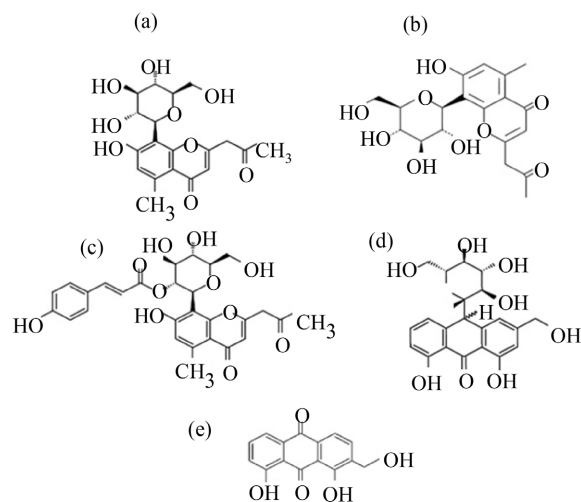


Figure 3. Chemical structure of the main components of Aloe Vera: (a) Aloines, (b) Aloesin, (c) Aloeresin, (d) Aloeresin, (e) Aloe Emodin (AEM) [16].

2.2. Sample and Corrosive Solution Preparation

For corrosion measurements, we used 12 mm diameter high adhesion (HA) re-bar. The surface exposed to the aggressive solution is equal to 1.13cm² and the rest is covered with epoxy insulation. The surface of the bar is polished with abrasive paper (80 grit), rinsed with distilled water and air-dried before each electrochemical test. A corrosive 0.5M NaCl solution was chosen to simulate sea water.

2.3. Electrochemical Methods

The experimental set-up used for electrochemical testing is illustrated in **Figure 4**, and comprises a Potentiostat/Galvanostat connected to an electrochemical cell and controlled by a computer running EC-Lab software. It displays the evolution of the various curves and automatically provides the electrochemical parameters.

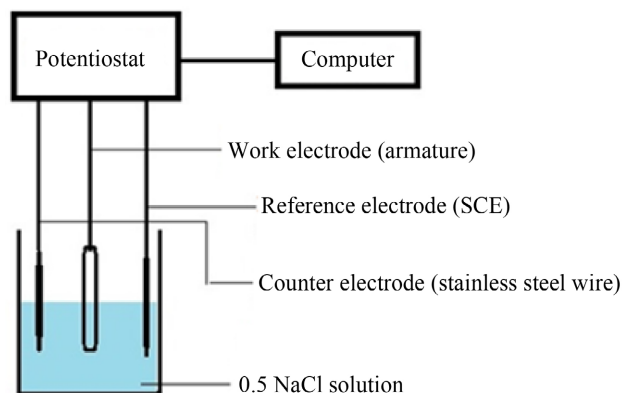


Figure 4. Experimental set-up used for electrochemical measurements.

The cell consists of a working electrode (WE, HA steel bar), a counter electrode (CE, stainless steel rod) and a saturated calomel reference electrode (RE, SCE).

Measurements begin by monitoring the open-circuit free corrosion potential (OCP) until a quasi-stationary regime is established after 6 hours. Tafel polarization measurements are then started, with a potential sweep around this OCP value. The sweep is performed in a potential range between -0.25 V and $+0.25$ V/OCP at a speed of 0.1 mV/s. The inhibitory efficiency is calculated from the polarization resistances according to the following formula [19]:

$$IE = \frac{i_{\text{cor}} - i_{\text{cor}}^{\circ}}{i_{\text{cor}}} \times 100$$

with i_{cor}° and i_{cor} are the current density in the absence and presence of inhibitor, respectively.

Impedance measurements were carried out at free-corrosion potential with an amplitude of 15 mV. Potential sweeps are performed at variable frequencies in the range 200 kHz - 10 mHz with 5 points/decade. All electrochemical curves are recorded using EC-Lab software, which is used to find the equivalent electrical circuit and its various components. Inhibitory efficacy was evaluated using equation [19]:

$$IE = \frac{R_{\text{ct}} - R_{\text{ct}}^{\circ}}{R_{\text{ct}}} \times 100$$

R_{ct}° and R_{ct} represent the charge transfer resistance in the absence and presence of inhibitor, respectively.

3. Results and Discussion

3.1. Monitoring Corrosion Potential

Figure 5 shows corrosion potential monitoring in the absence and presence of different inhibitor concentrations in a corrosive NaCl solution for 6 hours at 20°C . Examination of **Figure 5** shows that the addition of inhibitor shifts the corrosion potential towards anodic values.

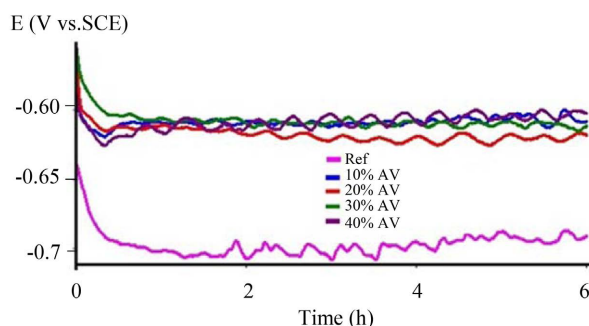


Figure 5. Monitoring the corrosion potential of rebar immersed in a NaCl solution containing different levels of *Aloe vera* plant extract for 6 h immersion.

In the absence of inhibitor in the corrosive solution, the corrosion potential monitoring curve shows two phases. The first is marked by a decrease in corrosion potential in the first few seconds, from -0.64 V/SCE to -0.72 V/SCE, before stabilizing after 1 h 45 mins. This decrease is attributed to metal dissolution. The second phase is characterized by numerous disturbances on the curve which can be attributed to corrosion of the sample with the formation of corrosion products.

In the presence of *Aloe vera* in the NaCl solution, there is a considerable reduction in the first phase (from 0 to around 25 min.), *i.e.* a decrease in metal dissolution. The disturbances seem to stabilize in the presence of aloe vera, indicating a probable protection of the framework by partial adsorption of *Aloe vera* molecules on the bar surface.

Nevertheless, we note that a non-stationary regime was established after 6 h. Tafel polarization and electrochemical impedance spectroscopy measurements are carried out after 6h of zero-current armature holding in the different solutions.

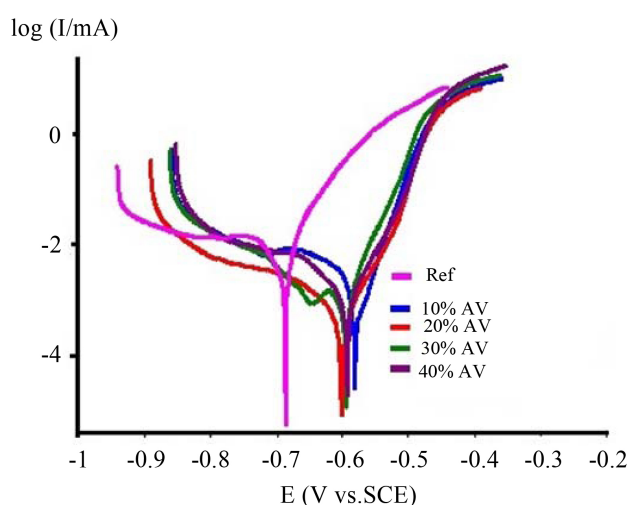
3.2. Tafel Polarization

Figure 6 illustrates the polarization curves of rebar exposed to 0.5 M NaCl solution and different contents (10% to 40%) of *Aloe vera* plant extract for 6 h. Tafel polarization parameters such as polarization resistance (R_p), free corrosion potential (E_{cor}), corrosion current density (i_{corr}), Tafel anodic slope (β_a) and Tafel cathodic slope (β_c) are presented in **Table 1**.

The polarization curves show that the presence of *Aloe vera* extract in the salt solution reduces the anodic and cathodic current intensities. The inhibitory effect of *Aloe vera* is most pronounced at the 20% level. This grade has the lowest cathodic and anodic branch intensities. In fact, in the presence of inhibiting molecules, a protective layer could form on the surface, blocking the active sites and modifying the surface state. This would lead to a shift of the anodic and/or cathodic branches towards lower current densities [20]. In addition, corrosion potentials shift towards less negative values (anodic side) compared to the control. These findings confirm the anodic character of aloe vera.

Table 1. Potentiodynamic polarization parameters of rebar (HA) in the absence and presence of the inhibitor studied.

Parameters	Contents	ref	10% Aloe vera	20% Aloe vera	30% Aloe vera	40% Aloe vera
R_p ($k\Omega\cdot cm^2$)		2.586	10.576	28.084	19.782	11.495
E_{cor} (mV)		-688.402	-584.677	-602.182	-600.678	-600.071
i_{cor} ($\mu A/cm^2$)		8.670	2.383	1.391	2.164	3.242
β_a (mV)		59.172	42.005	50.004	51.091	49.4
β_c (mV)		395.894	284.182	349.091	342.002	349.670
V_{cor} (mm/year)		0.102	0.027	0.016	0.025	0.036
EI (%)		-	72.485	83.896	75.102	62.302

**Figure 6.** Polarization curves of rebar immersed in a NaCl solution containing different levels of *Aloe vera* plant extract after 6 h immersion.

Cathodic polarization curves show a slight decrease in current densities in the presence of the inhibitor. However, negligible changes in Tafel slopes are observed in the presence of *Aloe vera* compared to the uninhibited solution. This shows that the reduction reaction at the steel surface is not altered by the addition of *Aloe vera*. The decrease in cathodic current density in the presence of *Aloe vera* extract could be linked to a blocking of cathodic sites without altering the oxygen reduction reaction.

In contrast to the evolution of cathodic branches, a decrease in anodic current densities is observed for solutions containing the inhibitor. This behavior is similar to that observed by Linter and Burstein [21]. It is clear from **Table 1** that the addition of *Aloe vera* extract to the NaCl solution resulted in a decrease in current density and corrosion rate compared to the solution without the inhibitor. Polarization resistance increased from 2.6 $k\Omega\cdot cm^2$ (control) to 28 $k\Omega\cdot cm^2$ for a 20% content, corresponding to the highest efficiency of 90.4%.

3.3. Electrochemical Impedance Spectroscopy (EIS)

The corresponding EIS spectra, illustrated in **Figure 7**, show a single capacitive loop, indicating that charge transfer is the dominant phenomenon controlling the corrosion process in the absence and presence of different levels of *Aloe vera* extract [12].

The diameter of the semicircles is greater in the presence of *Aloe vera* extract, indicating better resistance to charge transfer (R_{ct}) in the presence of *Aloe vera* extract. However, a higher charge transfer resistance was observed for 20% *aloe vera*. The equivalent electrical circuit adopted for simulating electrochemical impedance diagrams is shown in **Figure 8**, and comprises a solution resistor (R_s) connected in series with a constant phase element (CPE) connected in parallel with a charge transfer resistor (R_{ct}). Parameters extracted from EIS data in the presence and absence of *Aloe vera* are shown in **Table 2**.

The double-layer capacity is determined from the following equation [22]:

$$C_{dl} = \frac{(RQ)^{1/n}}{R}$$

Q is used to characterize the EPC according to the values of the coefficient n and to take into account the non-ideal behavior of the capacitance if its value is close to unity.

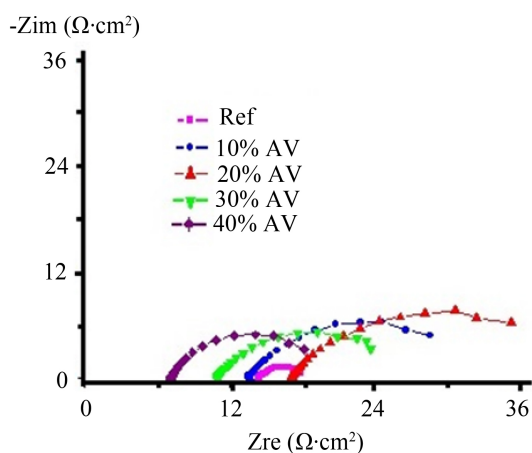


Figure 7. Nyquist plots of rebar exposed to 0.5M NaCl solution with and without inhibitor after 6 hours of immersion.

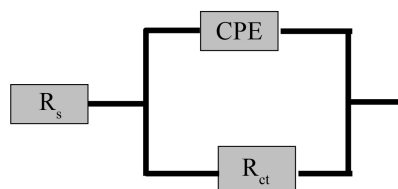


Figure 8. Equivalent electrical circuit used to model the impedance data shown.

Table 2. Impedance parameters for rebar in the absence and presence of the inhibitor studied.

Parameters	Contents	Ref	10% Aloe vera	20% Aloe vera	30% Aloe vera	40% Aloe vera
$C_{dl} \times 10^{-5} (F \cdot cm)^{-2}$		71.134	53.192	50.876	46.902	68.196
n		0.928	0.705	0.643	0.810	0.858
Rct ($\Omega \cdot cm^2$)		3.510	18.521	29.015	13.364	13.508
EI (%)		-	81.102	87.865	73.885	74.001

Values of the empirical coefficient n are close to 1 and range from 0.643 to 0.928. In these cases, EPC can be equated with pure capacitance, with deviation from unity reflecting surface inhomogeneities [23]. Charge transfer resistances are greater in the presence of *Aloe vera* extract than in the absence of aloe vera. This reflects a decrease in the kinetics of electrochemical reactions in the presence of aloe vera. Charge transfer resistances initially increased from 3.5 for control to 18.5 $\Omega \cdot cm^2$ for 10% aloe and then to 29.0 $\Omega \cdot cm^2$ for 20% aloe vera. In a second phase, charge transfer resistances decreased for 30% (13.4 $\Omega \cdot cm^2$) and 40% (12.5 $\Omega \cdot cm^2$). This variation indicates a maximum value of 29 $\Omega \cdot cm^2$ which corresponds to the optimum content of 20% for which the best inhibition efficiency of 80.7% is recorded. Finally, in parallel with the increase in charge transfer resistance in the presence of the inhibitor, we observe a decrease in double-layer capacity, reflecting adsorption of the inhibitor to the metal surface [13].

3.4. Surface Characterization Using a Zoom Device

Figure 9 shows photos of the samples after corrosion testing. An orange-colored layer formed on the surface of the reinforcement in the absence of *Aloe vera* (NaCl + 0% aloe vera). This could be attributed to corrosion products. On the other hand, in the presence of aloe vera, a layer of *Aloe vera* (AV) products was partially formed on the surface of the reinforcement. The image of the surface of the framework containing a 20% content reveals an almost uniform layer of *Aloe vera* products. These visual results are in agreement with the electrochemical results.

The absorption mechanism proposed by Mehdipour, shown in **Figure 10**, illustrates the corrosion and corrosion inhibition process of *Aloe vera* extracts. Considering that the surface of the framework in the NaCl solution is largely positively charged [24], an attractive force would be created between the Cl^- ions in the solution and the metal surface. The inhibitor being active anticorrosive would also be attracted to the electrode surface by electrostatic force between the positively charged surface and the O atoms or π electrons of the heterocyclic ring. This mechanism well explains the behavior of anodic slopes and the decrease in doubling capacity through the formation of inhibitory complexes, blocking anodic sites ($Fe \rightarrow Fe^{2+} + 2e^-$). It has been shown that physical adsorption could be the crucial step that could then accelerate the formation of the

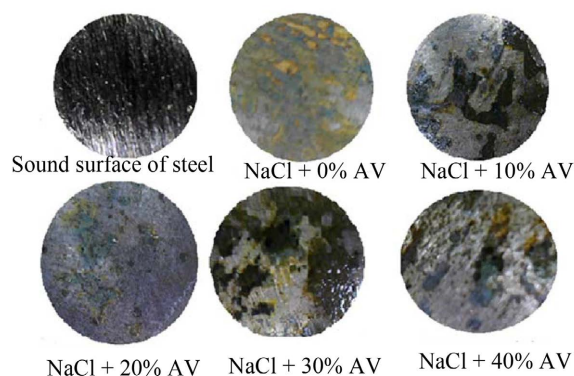


Figure 9. Photographs of samples after corrosion testing in the presence and absence of aloe vera.

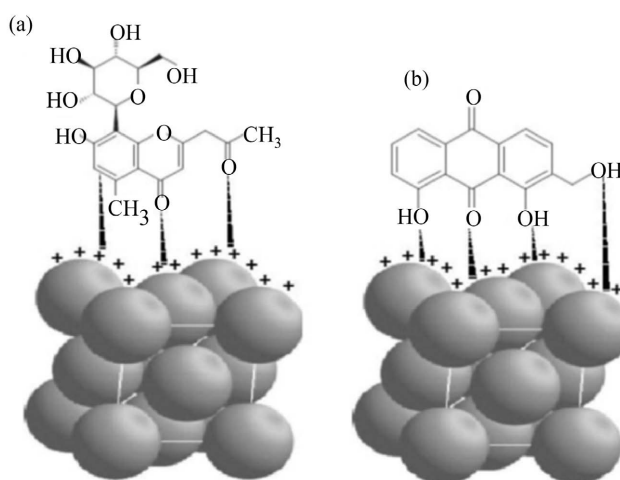


Figure 10. Schematic illustrations of interactions between inhibitors and steel surfaces: (a) Aloin and (b) Aloé-Emodin [13].

inhibitor complex on the metal surface [25]. The strong presence of oxygenated functional groups and heterocyclic groups with π electrons in *Aloe vera* molecules will contribute to the protective mechanism [13]. Studies have mentioned that aloe vera's anticorrosive properties may be due to *Aloe vera* components such as aloin and aloe-emodin [9].

4. Conclusions

The corrosion-inhibiting effect of *Aloe vera* was studied using electrochemical methods and image characterization on rebar (HA, diameter 12 mm) immersed in saline solution in the presence and absence of aloe vera.

Firstly, the results of polarization tests (Tafel method) showed that this inhibitor acts as an anodic inhibitor, with an efficiency of around 84% for an optimum concentration of 20%. The evolution of impedance diagrams in the Nyquist plane as a function of natural inhibitor concentrations confirms the formation of a protective layer, resulting in an increase in charge transfer resistance together with a decrease in double-layer capacitance.

The surface characterization study of the photographed steel revealed the presence of a layer of orange-colored corrosion products when the steel was immersed in the saline solution and in the absence of *Aloe vera*. In the presence of the inhibitor in the saline solution, a layer of *Aloe vera* products partially formed on the surface of the reinforcement. The image of the surface of the framework containing a 20% content reveals an almost uniform layer of *Aloe vera* products.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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