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Effect of *Warionia saharae* extract on the behavior of reinforcement steel in simulated carbonated concrete pore solution

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- ✓ Reinforcement steel;
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- ✓ Inhibitor;
- ✓ Langmuir isotherm.

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1. Introduction

Abstract

The effect of the *Warionia saharae* extract on the behavior of reinforcement steel in simulated carbonated concrete pore solution in presence of different concentrations of chloride ions was studied using electrochemical measurements. The surface morphology of the electrode was observed by both optical and scanning electron microscopies. Results showed that the extract plant enhanced the protection of reinforcement steel in simulated carbonated concrete pore solution (CCPS). The evolution of the electrochemical parameters and inhibition efficiency depend on the chloride ions concentration. The optimal efficiency (\approx 53%) was obtained at 1g/L of the extract plant. Adsorption of the extract plant molecules corresponds to Langmuir adsorption isotherm in (CCPS).

Corrosion of reinforcement steel is a serious and significant problem for civil engineers. Because many existing concrete structures are under constant degradation from aggressive environments, they suffer from durability issues, particularly corrosion of the steel bars within such structures. Carbonation of the concrete, which decreases the pH of the pore solution, and the chloride ions originating from deicing salts or marine environment are the major parameters responsible of the initiation of this phenomenon in concrete. This problem can be mitigated by adopting various preventive measures such as the use of corrosion inhibitors. This protection technique is probably more attractive from the point of view of cost and ease of application. Environmental concerns require corrosion inhibitors to be nontoxic and eco-friendly. For this reason, harmful and toxic compounds used as corrosion inhibitors in civil engineering applications must be replaced [1,2].

These last years, the use of plant extracts as eco-friendly inhibitors became a desirable and easy application to perform. Considered as a rich source of organic molecules, the plant extracts were tested as green corrosion inhibitors in various corrosive environments and they gave very good inhibition results [3,4]. The research on plant extracts and their effect on metal corrosion have spread to the field of civil engineering. In concrete, these natural products were evaluated as corrosion inhibitors by several authors [5–11]. Investigations about their behavior in reinforced concrete remain insufficient and deserve a lot of attention. Therefore, in this study we decide to evaluate the effect of *Warionia saharae* extract on the behavior of reinforcement steel in simulated carbonated concrete pore solution in presence of chloride ions. Open circuit potential and electrochemical impedance spectroscopy measurements were used to determine the electrochemical parameters. The surface morphology of the electrode was observed by both optical and scanning electron microscopies.

2. Experimental

2.1. Plant extract

The leaves of *Warionia saharae* (collected from Chtouka Aït Baha region in Morocco) were air-dried in the laboratory at room temperature before their use. The extraction was realized by the soxhlet technique during six hours with methanol as solvent [12]. The extracted solution was filtered and the solvent was evaporated until getting solid phase which was afterwards kept at 4°C. To study de corrosion inhibition efficiency in simulated

carbonated concrete pore solution, without and with chloride ions, the methanolic extract of *Warionia saharae* was tested at different concentrations ranging from 0.25g/L to 1g/L.

2.2 Solutions

The testing solutions were chosen to simulate the carbonated concrete pore solution (CCPS) without and with chloride ions (Table 1). The value of pH was around 9. All chemical reagents used were of analytical grade and experimental water was demineralized water. pH measurements were performed using pH meter HANNA (HI 8519 pH/mV meter). Each measurement was repeated three times and an average value was calculated.

	K ₂ CO ₃	KHCO ₃	Na ₂ CO ₃	NaHCO ₃	NaCl
S_1 (mol.L ⁻¹)	0.125	0.25	0.025	0.05	-
$S_2 (mol.L^{-1})$	0.125	0.25	0.025	0.05	0.25
$S_3 (mol.L^{-1})$	0.125	0.25	0.025	0.05	0.5

Table 1: Chemical composition of the testing solutions.

2.3. Sample

The reinforcement steel which chemical composition is given in Table 2 was used as working electrode with a surface area of 0,158 cm². Surface sample was mechanically polished from 400 to 1500 grade of abrasive papers, rinsed abundantly with demineralized water and degreased with acetone before each electrochemical experiment.

Table 2: Chemical of	composition of reinfo	rcement steel.
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С	P	S	N_2	Mn	Cr	Ni	Си	Sn	Мо	V	Si	Fe
0,22	0,05	0,05	0,012	0,80	0,3	0,3	0,5	0,05	0,05	0,08	0,3	Base (wt %)

2.4. Electrochemical measurements

Electrochemical experiments were carried out with a potentiostat/galvanostat model voltalab 40 PGZ 301 (Radiometer Analytical) monitored by voltamaster 4 software. To study the behavior of the plant extract electrochemical measurements including Open circuit potential (OCP) and Electrochemical impedance spectroscopy (EIS) were performed in a three-electrode cell. The Reinforcement steel was used as working electrode, platinum as counter electrode and a saturated Ag/AgCl as reference electrode. The open circuit potential curves were recorded during four hours in the testing solutions without and with the extract plant. Electrochemical impedance spectroscopy measurements were carried out using AC signals of 10 mV of amplitude in the frequency range of 100 KHz to 10 mHz with data density of 10 points per decade. The electrode rotation rate was fixed at 1000 rpm. Each experiment was repeated three times to confirm the reproducibility of the results at $22\pm1^{\circ}$ C and aerated solution.

2.5. Surface analysis

The surface morphology of the reinforcement steel was examined by scanning electron microscope (SEM) (FEI Quanta 200, Type environmental (ESEM)). Images were taken using an accelerating voltage of 30 KV and a metallurgical microscope (OLYMPUS BX60F5).

3. Results and discussion

3.1. pH measurements

The influence of the methanolic extract of *Warionia saharae* on the pH of the simulated carbonated concrete pore solution was measured during four hours (Figure 1). The pH value of S_1 , remains constant during four hours and is slightly affected by the extract plant addition whatever its concentration.

3.2. Open circuit potential measurements

The evolution of the open circuit potential of reinforcement steel in the test solutions (S_1 , S_2 and S_3) without and with the extract is depicted in Figure 2. Immediately after immersion the corrosion potential was very negative in all the cases (around -400 mV). In S_1 without extract plant (Figure 2(a)), the potential increase rapidly to the anodic potential direction during the first hours and then progressively stabilizes at about (-260 mV) after four hours of immersion. This indicates the spontaneous growth of a protective oxide layer [13].



Figure 1: pH evolution of the S₁ solution with and without different extract plant concentrations.

The formation of this passive layer is probably due to the presence of carbonate/bicarbonate ions [14–16]. Without of the extract plant, the increase of chloride ions concentration shifts the potential toward more negative values. This sharp decline in potential with the increase of chloride concentration means the breakdown of passive film and the initiation of active corrosion [17]. The potential reached another steady state at about - 340 mV and -420 mV in presence of 0.25 (mol.L⁻¹) and 0.5 (mol.L⁻¹) of chloride ions respectively after four hours of immersion (Figure 2(b) and (c)). According to literature, this may result in a competitive adsorption between aggressive chloride ions and the inhibitive bicarbonate/carbonate ions [15,18]. However, if the adsorption of Cl⁻ predominates the passive film cannot form and an increase of the anodic dissolution of the metal occurs [14,15].



Figure 2: Evolution of corrosion potential value with immersion time of reinforcement steel in S_1 , S_2 and S_3 without and with different concentrations of the extract plant.

It is displayed in Figure 2(a) that the potential obtained in presence of the plant extract in S_1 attains steady values after two hours of immersion and became nobler for all extract plant concentrations. It reached values around -155 mV, which indicates an increase of about 100 mV after four hours. This can be explained by the contribution of the organic molecules of the extract plant in the development of more protective layer on reinforcement steel surface. The organic molecules adsorbed on the surface may lead to the formation of an adsorbed layer and induce changes in the composition and thickness of the passive film [19].

The presence of different concentrations of the extract plant in S_2 does not change the evolution of the potential toward nobler values with time (\approx -250 mV after four hours of immersion). But, it seems that this evolution is perturbed in presence of chloride ions. This finding is clearly confirmed in presence of higher concentration of Cl⁻ (Figure 2(c)), because the extract plant effect on the potential evolution disappears with immersion time. Thus, it is evident that the evolution of the open circuit potential in S_1 solution without and with extract plant depends on the chloride ions concentrations.

3.3. Electrochemical impedance spectroscopy

In this study, the impedance curves were plotted at open circuit potential after four hours of immersion in different solutions. Figure 3, depicts the EIS diagrams of reinforcement steel in S_1 with different chloride concentrations. Nyquist plots (Figure 3(a)), shows that the diameter of the capacitive loop decreased with increasing of the chloride concentration, which may indicate the breakdown of passivity and corrosion initiation [16,20]. Comparing with the Nyquist plots, it is suggested that Bode plots contained more information concerning with the time constant for the reinforcement steel in S_1 [21]. The phase angle decreased in presence of the higher chloride concentration and exhibited obvious variations in peak number and magnitude as shown in (Figure 3(b)). In S_1 without and with chloride ions (0.25 (mol.L⁻¹)), Bode plots are characterized by one time constant represented by a large peak. While, in presence of a high chloride concentration (S_3) two time constants appear. Indeed, the number of phase angle peaks is an indication of the number of time constants. In some cases, the time constant may overlap each other and become difficult to separate [22].



Figure 3: Electrochemical impedance spectroscopy curves (Nyquist plots (a); Bode plots (b)) of reinforcement steel in simulated carbonated concrete pore solution without and with different concentrations of chloride ions.

From Figure 4, it is observed that the presence of the extract plant at different concentrations influences the behavior of reinforcement steel in the three solutions. As a first remark, the shape of the diagrams is very similar for all the samples in S_1 and S_2 . This indicates there is no change in the corrosion mechanism in presence of inhibitor [23,24]. With increasing the extract plant concentration the capacitive loop increased in S_1 . It means that inhibition efficiency increases with to the concentration of the extract plant. But, in S_2 only the concentrations of the extract plant that are greater than 0.25 g/L increased the diameter of the capacitive loop (Figure 4 (c)). On the other hand, when the chloride ions concentration reached a very high value (0.5 (mol.L⁻¹)), the extract plant effect is reversed. Consequently, the diameter of the capacitive loop decreased.

Researchers propose different models of equivalent circuits in order to interpret the impedance data of reinforcement steel in simulated concrete pore solution [21,25–27].

Constant phase element (CPE) is used instead of a capacitance to take the non-ideal behavior of the interface metal/solutions [28]. The CPE is given by:

$$Z_{\text{CPE}} = \frac{1}{Q(j\omega)^{\alpha}}$$

(1)

Where α is related to the angle of rotation of a purely capacitive line on the complex plane plots and Q is a constant expressed in $(\Omega^{-1} \text{cm}^{-2} \text{ s}^{\alpha})$ or (F cm⁻² s (α^{-1})) [29–31]. In the present study, electrochemical parameters were graphically obtained: the solution resistance (*Rs*) and the resistance associated with the capacitive loop (*Rp*), physically related to the corrosion resistance, were directly measured from the impedance spectra [30].



Figure 4: Electrochemical impedance spectroscopy curves (Nyquist plots (a, c and e); Bode plots (b, d and f)) of reinforcement steel in S_1 , S_2 and S_3 without and with different concentrations of the extract plant.

The inhibition efficiency (*IE*) is calculated as follows: IE (%) = $[(R_P - R_P^0)/R_P] \ge 100$

(2)

Where R_P^0 and R_P are respectively the polarization resistance associated with the capacitive loop without and with plant extract plant.

The parameters α and Q were determined using the graphical methods presented by Orazem et al. and Musiani et al. [32,33]. The CPE parameter α was determined by the following formula according to Hirschorn et al. [34]:

$$\alpha = \left| \frac{d \log |Zi|}{d \log f} \right| \tag{3}$$

The CPE parameter Q was obtained by the following equation [32]:

$$Q_{eff} = \sin\left(\frac{\alpha\pi}{2}\right) \ \left(\frac{-1}{Zi \ (2\pi f)^{\alpha}}\right) \tag{4}$$

These calculated parameters for both uninhibited and inhibited solutions are summarized in Tables 3, 4 and 5. The effective capacitance C_{eff} (expressed in Farads), was calculated from the CPE parameters using the Hsu and Mansfeld formula [35]. Many authors used this formula for studies on passive films and corrosion inhibition [24,36,37].

$$C_{eff} = (Q \times R_P^{1-\alpha})^{1/\alpha}$$
(5)

Table 3: Values obtained from the EIS data for reinforcement steel in S_1 without and with different concentrations of the extract plant.

S ₁		Extract plant concentrations (g/L)					
Parameters	Blank	0.25	0.5	0.75	1		
Rs (Ω .cm ²)	5.6±0.8	3.80±0.03	3.81±0.07	3.86±0.01	3.73±0.02		
Rp (kΩ.cm ²)	124±10	207±8	223±3	233±4	260±12		
Q. 10^{-6} (F.cm ⁻² .s ^(a-1))	71±2	43.6±0.7	43±3	42.9±0.1	44.6±0.3		
α	0.93±0.00	0.94 ± 0.01	0.93±0.01	0.93 ± 0.00	0.93 ± 0.00		
$C_{eff}(\mu F.cm^{-2})$	83±3	50.8±0.3	50±4	51.1±0.3	53.8±0.5		
I.E %	-	40.4	44.5	47.1	52.5		

Table 4: Values obtained from the EIS data for reinforcement steel in S_2 without and with different concentrations of the extract plant.

S_2		Extract plant concentrations (g/L)						
Parameters	Blank	0.25	0.5	0.75	1			
Rs (Ω .cm ²)	2.55 ± 0.00	2.44 ± 0.08	2.76±0.03	2.79 ± 0.04	2.74 ± 0.07			
Rp (kΩ.cm ²)	66±4	63±1	79±10	87 ± 8	113±11			
Q. 10^{-6} (F.cm ⁻² .s ^(α-1))	99±2	63±1	61.5±0.6	57.6±0.8	54±5			
α	0.94 ± 0.00	0.92 ± 0.00	0.92 ± 0.00	0.92 ± 0.00	0.92 ± 0.01			
C_{eff} (μ F.cm ⁻²)	112±3	70±1	70±1	66±1	63±7			
I.E %	-	-	16.2	24.3	41.5			

Table 3 and 4 display the values obtained from the EIS diagrams of reinforcement steel in S_1 and S_2 respectively. Rs values are low in S_1 and S_2 solutions whatever the extract plant concentration due to the high alkalinity of the solutions. All the measurements, give values of α around 0.9, which agrees with the capacitive behaviors of CPEs [38,39]. In presence of different concentrations of the *Warionia saharae* extract, the polarization resistance (Rp) increases at except the concentration (0.25 g/L) in the case with chloride ions (0.25(mol.L⁻¹)) and attains optimal values of 260 (k Ω .cm²) in S₁ and 113 (k Ω .cm²) in S₂ at 1g/L of the extract plant. Thus, these results confirm the good effect of the extract plant in both solutions and its contribution to the

improvement of protective proprieties of the passive film. Consequently, the values of Q and C_{eff} decrease in presence of the extract plant and are around 42 (F.cm⁻². s^(α -1)) and 51 (μ F.cm⁻²) in S₁. While the values around 58 (F.cm⁻². s^(α -1)) and 67 (μ F.cm⁻²) are recorded in S₂. This indicates that the area of the adsorption film increases, the local dielectric constant decreases, or the thickness of the protective layer increases due to the adsorption of the extract plant molecules [27,40,41]. The values of the effective capacitance suggest that this capacitance could reasonably be attributed to the double layer with the passive film [42].

In presence of high concentration of chloride ions (Table 5), the behavior of reinforcement steel completely changes. With different concentrations of the extract plant the polarization resistance decreases. The decrease of the values of α show that the passive film became defective [21].

S ₃		Extract plant concentrations (g/L)					
Parameters	Blank	0.25	0.5	0.75	1		
Rs (Ω.cm ²)	2.26±0.00	1.94±0.06	1.96±0.00	1.91 ± 0.01	1.98 ± 0.01		
R_1 (k Ω .cm ²)	0.55 ± 0.05	-	-	-	-		
Q ₁ . 10 ⁻⁶ (F.cm ⁻² . s ^(α-1))	238±2	-	-	-	-		
α1	0.88 ± 0.00	-	-	-	-		
$C_{eff (1)} (\mu F. cm^{-2})$	180±2	-	-	-	-		
R_2 (k Ω .cm ²)	8±1	3.5±0.6	2.6±0.1	2.9±0.1	2.9±0.4		
Q ₂ . 10 ⁻⁶ (F.cm ⁻² . s $^{(\alpha-1)}$)	182±8	257±6	215±2	249±1	205±1		
α ₂	0.55±0.01	0.83±0.01	0.85±0.01	0.82 ± 0.00	0.85 ± 0.01		
$C_{eff (2)}$ (µF. cm ⁻²)	256±17	250±3	193±3	232.5±0.7	186±4		

Table 5: Values obtained from the EIS data for reinforcement steel in S_3 without and with different concentrations of the extract plant.

With (R_1, α_1, Q_1) and (R_2, α_2, Q_2) EIS parameters determined for phenomenons which occurs in high and low frequencies respectively.

Figure 5, shows the Inhibition efficiency recorded with different concentrations of the extract plant for reinforcement steel in simulated concrete pore solution without and with chloride ions. The efficiency attains \approx 53 % and \approx 42% at 1g/L of extract plant in S₁ and S₂ respectively.



Figure 5: Inhibition efficiency recorded with different concentrations of the extract plant for reinforcement steel in simulated concrete pore solution without and with chloride ions.

The results obtained from EIS measurements confirm that the polarization resistance will depend on the chloride ions concentration in the solution (Figure 6). Therefore, the inhibition efficiency will change also in function of

the concentration of these aggressive ions. The values of correlation coefficient which are close to (\approx 1) (Table 6) confirm this finding.



Figure 6: Evolution of polarization resistance (Rp) with chloride ions concentration without and with extract plant.

Table 6: Parameters of the evolution of polarization resistance (Rp) with chloride ions concentrations without and with extract plant.

Warionia saharae		Intercept ^(b)	Slope ^(a)	Correlation coefficient (R ²)	Equation
Blank	-	123.36	-229.95	1	
Extract plant	0.25	128.98	-253.07	0.9436	
concentrations (g/L)	0.5	221.03	-438.64	0.9955	y=a x + b
	0.75	229.96	-457.33	0.9926	
	1	251.45	-501.12	0.9927	

The optical and SEM micrographs of Figures 7 and 8 represent the surface of reinforcement steel immersed in S_3 without and with 1g/L of the extract plant for a period of 8 days. Inspection of these micrographs reveals that the electrode surface is covered with widespread and overlapped corrosion products, indicating severe corrosion induced by chloride ions.



Figure 7: Optical micrographs of the reinforcement steel surface morphology: (a (x100)) before immersion; (b (x100)) in S_3 after 8 days of immersion; (c (x100)) in S_3 with 1g/L of extract plant after 8 days of immersion, with different magnifications.

In S₃ without extract plant it is clear that the electrode surface is not completely covered by corrosion product (Figures 7 (b) and 8 (b')) compared to the case with extract plant (Figures 7 (c) and 8(c')). That may be due to the competitiveness between bicarbonate/carbonate ions which can ensure protection of the surface and chloride ions which cause a pitting corrosion. However, in presence of the extract plant it is evident that no inhibitive effect is obtained against corrosion in presence of the high chloride ions concentration. This confirms the result obtained with electrochemical measurements.



Figure 8: SEM micrographs of the reinforcement steel surface morphology: (a' (x1000)) before immersion; (b' (x100)) in S₃ after 8 days of immersion; (c' (x500)) in S₃ with 1g/L of extract plant after 8 days of immersion, with different magnifications.

3.4. Adsorption isotherm

Surface coverage values (θ) for the inhibitor were obtained from the EIS measurements for various concentrations of the extract plant at $22\pm1^{\circ}$ C.

(6)

(7) (8)

(9)

$$\theta = \left[(R_P - R_P^0) / R_P \right]$$

A correlation between surface coverage (θ) defined by Eq.6 and the concentration of inhibitor (C_{inh}) in solution can be represented by various isotherms including Langmuir, Temkin and Frumkin (Figure 9) [2,24,43,44]. These isotherms were obtained according to the following equations:

Langmuir:
$$\theta = K C_{inh} / (1 + K C_{inh})$$

Temkin: $e^{-2a\theta} = K C_{inh}$

Frumkin: $(\theta/(1-\theta)) e^{-2a\theta} = K C_{inh}$

Where θ is the degree of surface coverage, C_{inh} is the inhibitor concentration, *a* is the molecular interaction parameter and K is the equilibrium constant of the adsorption process.



Figure 9: Adsorption isotherms curve (Langmuir, Temkin and Frumkin) of the *Warionia saharae* extract in S_1 at 22±1°C.

The best fit was obtained with Langmuir isotherm (correlation $R^2 = 0.9842$). This confirms that the extract plant of *Warionia saharae* obeys to Langmuir isotherm in S₁ [24,45]. Langmuir assumes that there are a fixed number of sites on the surface. Each of these sites is capable of adsorbing a single atom or molecule. In addition, as it is assumed that no interactions between adsorbed species take place, the adsorption energy is constant [43].

Conclusion

The following conclusions were drawn from studying the effect of *Warionia saharae* extract on the behavior of reinforcement steel in simulated carbonated concrete pore solution:

- The extract plant enhanced the protection of reinforcement steel in simulated carbonated concrete pore solution;

- The corrosion potential, polarization resistance and inhibition efficiency depends on the concentrations of chloride ions concentration in solution;

- The optimal efficiencies recorded are (\approx 53%) and (\approx 42%) at 1g/L of extract plant in S₁ and S₂ respectively;

- The adsorption of the plant extract molecules in (CCPS) was consistent with Langmuir adsorption isotherm.

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