

Study of a new ecological corrosion inhibitor for concrete reinforcement

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Abstract

The degradation of the concrete can be caused by corrosion of reinforcement elements due to the presence of aggressive ions, moisture, oxygen and carbonation. The objective of this work is to assess the effect of some Physical and chemical parameters of the pomegranate bark extract on the behaviour of the metal frames used in the constructions in civil engineering.

The process of corrosion and inhibitions, has been studied in a solution medium that simulate the carbonated concrete, by the gravimetric method and the electrochemical techniques including the polarization and the impedance tests

Keywords: Corrosion, reinforced concrete, inhibition, steel, carbonation.

Introduction

The corrosion of reinforcements elements of concrete structures exposed to the atmosphere is mainly due to the carbonation of the concrete, the effect of chlorides in the marine environment or exposed to deicing salts. Corrosion phenomena can be relatively rapid in the case of excessive porosity of the material or inadequate coating and lead to the deterioration of relatively young work[1]. The alkaline environment of concrete leads to the formation of a stable film of iron oxides at the steel / concrete interface that protects steel against corrosion. For structures exposed to air, under normal electrical conditions, the potential measurements of the reinforcements (relative to the Cu / CuSO₄ copper electrode) generally give values varying between -0.2V and 0.1V, reflecting the Passivation of steel. The carbonation of the concrete causes a decrease in pH to a value close to 9 [2, 3]. In such a medium, the reinforcement is no longer passivated and corrosion can generate in the presence of moisture and oxygen. The generalized corrosion leads to a progressive reduction in the section of the reinforcements. The corrosion products have a volume 2 to 7 times greater than that of steel. For reinforced concrete, the formation of corrosion products creates local tensile stresses in the concrete. As a result, cracks form on the surface of the concrete at right angles to the corroded reinforcement. Another consequence

of this corrosion is the loss of concrete steel adhesion. In fact, the corrosion products formed at the interface are friable and behave like a lubricating layer, in addition to the loss of confinement of the reinforcements due to the opening of the cracks[4, 5]. Many environmental phenomena are significantly influence the durability of reinforced concrete structures [6–8]. Carbonation is one of the main deterioration factors of reinforced concrete structures exposed to the atmosphere, and even more for structures exposed to high concentrations of carbon dioxide such as road tunnels, urban structures, underground car parks, Its diffusion through the porous structure of the concrete is conditioned by the hygroscopic state of the pores of the material [9].The application of corrosion inhibitors is one of the oldest techniques[10] added in a small concentration to an environment, causing a significant decrease in the corrosion rate of a metal located in this environment [11]. In order to reduce the corrosion of reinforcements in reinforced concrete structures. There are two types of inhibitors that are added to the fresh concrete during mixing and the inhibitors applied to the hardened concrete (organic amino-alcohol and mineral-type fluorophosphate). Inhibitors can also be classified into three categories according to the reaction at which they are involved at the anodic, cathodic and mixed levels[12]. The first molecules studied as inhibitors added to fresh concrete are chromates, phosphates, hypophosphates, nitrites and fluorides. Sodium nitrite and calcium nitrite have been studied extensively[13]. The use of sodium nitrite has resulted in a reduction of the compressive strength and possible alkali-reaction due to the sodium cation, leaving room for calcium nitrite which does not modify the mechanical properties of the concrete and which is compatible with the silica fumes [14]. The use of organic compounds to inhibit the corrosion of carbon steels is becoming increasingly widespread[15]. They possess at least one active center capable to exchanging electrons with the metal, such as nitrogen, oxygen, phosphorus or sulfur. The usual functional groups which allow them to be attached to the metal or alloy are generally amines ($-NH_2$), hydroxyls ($-OH$), thiols ($-SH$) or carboxyls ($-COOH$)[16]. Cruz et al. [17]have shown that the effectiveness of an organic inhibitor is related to its adsorption properties, which depend on the nature and surface state of the metal, as well as the corrosive environment. Ormellese et al. [18] concluded that amines have very dispersed results depending on their volatility. The amino acids have an inhibitory effect, but not sufficient for industrial applications. The carboxylates have a very marked inhibiting effect. In this study we will examine the possibility of using pomegranate extracts in the inhibition of corrosion of reinforced concrete.

Materials and Methods

Choice of material

In order to achieve gravimetric and electrochemical measurements, the tests are carried out on a steel (Fe E500) with the composition shown in the Table.1 and previously set in a

circular form. The electrode surface has been mechanically polished using SiC papers with the grades 400; 600; 800; 1000; 1200 1500; 2000, successively, then rinsed with distilled water, degreased with acetone and dried before all tests[19].

The Elements	C	Mn	Si	S	P	Cr	Ni	Cu	Mo	N
Chemical Elements in wt%	0.24	1.20	0.34	0.055	0.055	0.30	0.30	0.50	0.050	0.012

Table I. The chemical characteristics of the steel (FeE500).

Preparation of Media

The carbonation of the concrete is generally simulated to an aqueous solution of carbonate[20, 21].The solutions chosen to simulate this environment is given in Table 2.

	Solu 1	Solu 2	Solu 3	Solu 4
The quantity of the extract in (10 ³ ppm)	-----	1	3	5
NaHCO ₃	0,050 mol/l	0,050 mol/l	0,050 mol/l	0,050 mol/l
Na ₂ CO ₃	0,025 mol/l	0,025 mol/l	0,025 mol/l	0,025 mol/l
KHCO ₃	0,250 mol/l	0,250 mol/l	0,250 mol/l	0,250 mol/l
K ₂ CO ₃	0.125 mol/l	0.125 mol/l	0.125 mol/l	0.125 mol/l
PH	9	9	9	9

Table II. chemical compositions of the Middle Carbonate synthetic.

Preparation of the inhibitor

The extraction of the pomegranate bark was carried out by a liquid solid extraction operation using water as a solvent, the bark was dried and ground to increase their specific surface area in order to increase the yield of the extraction, the extraction protocol is shown in Fig.1

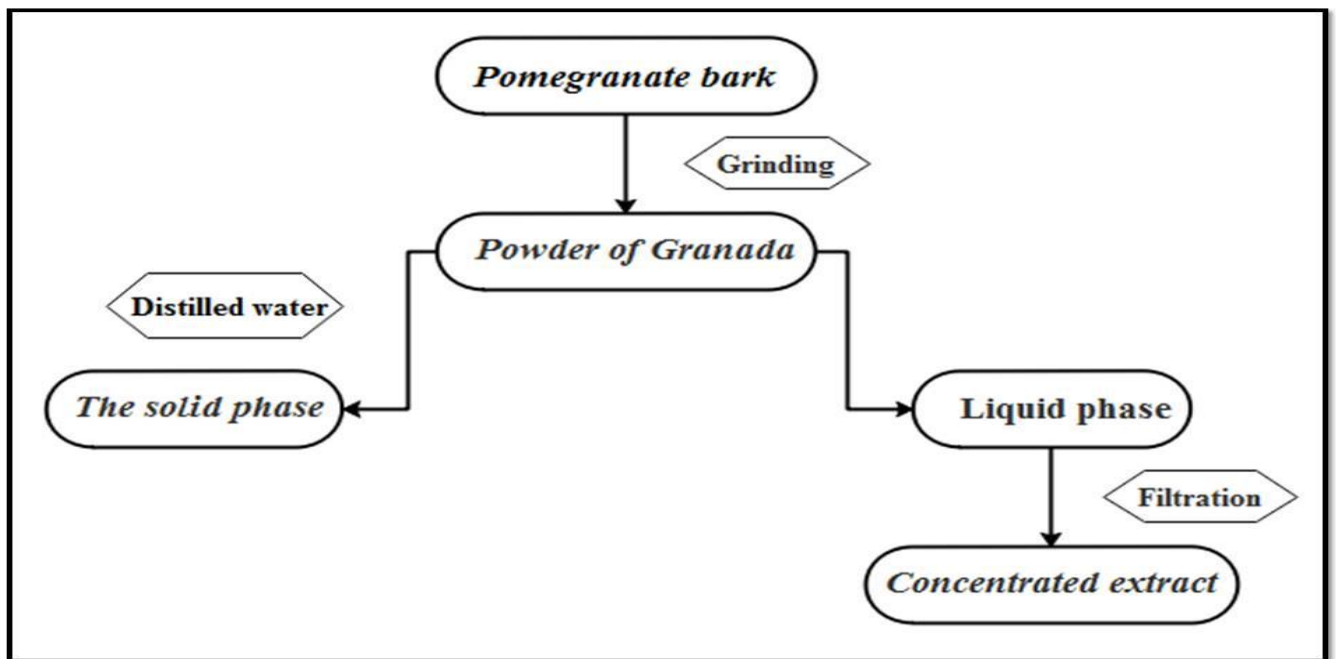


Figure 1. Protocol for the extraction of the pomegranate bark

Gravimetric Study

The gravimetric methods allow to estimate the rate of corrosion of the steel immersed in the electrolyte solution. The rate of corrosion is determined after 20 h of immersion at temperature 25°C, it is calculated by the formula1

$$V = \Delta M / S \cdot t \text{ (mg/h.cm}^2\text{)} \quad (1)$$

$$\Delta M = M_1 - M_2 \quad (2)$$

ΔM represents the difference between the initial weight M_1 and the final weight M_2 after a time t equal to 20 h. S is the surface of the metal exposed to the solution of study. This value of the corrosion speed is the average of three tests carried out in the same conditions for each concentration. The value of the inhibitory efficacy is given by the Formula 3:

$$\mu (\%) = ((V - V_{\text{inhi}}) / V) * 100 \quad (3)$$

Where, V and V_{inhi} represent respectively the speeds of corrosion without and in the presence of inhibitor.

Electrochemical study

The Electrochemical tests have been carried out using a cell to three conventional electrodes, the working electrode consists of a cylindrical steel rod Fe E500 of Section ($7 \cdot 10^{-2} \text{ cm}^2$) Covered With epoxy resin [22].

Results and discussion

Infrared spectroscopy

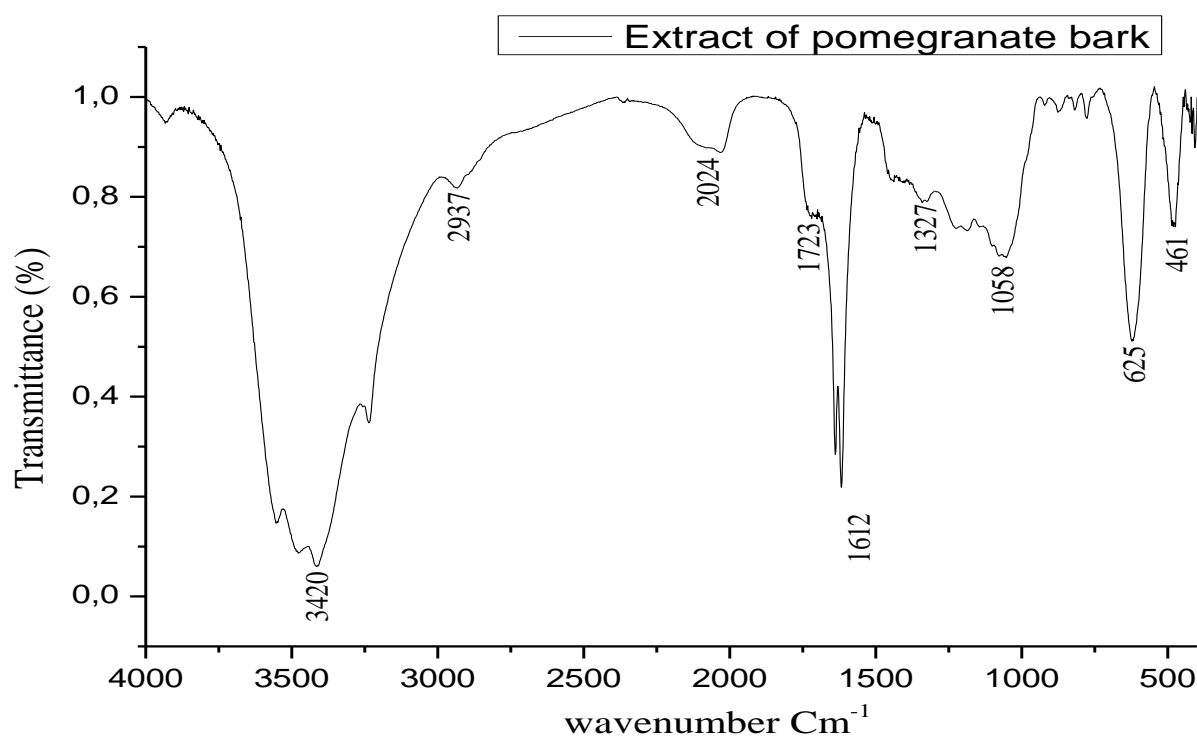


Figure 2. spectrum IR -Tf of the extract of the pomegranate bark

The obtained extract was characterized by infrared spectroscopy; the results are shown in Figure 2. Several studies have shown the existence of flavones, tannins and carboxylic acids of cyclitol in the extract of the pomegranate barks [23–25]. The spectrum shows the existence of main bands of adsorption at 3420, 1723 cm^{-1} correspond to the OH group, the bands in 1612 cm^{-1} and 1327 cm^{-1} are due to the presence of $\text{C}=\text{C}$. The other bands of adsorption at 2937, 2024 cm^{-1} and 1058 cm^{-1} are assigned successively to the attendance of the grouping CH_2 , OH and C-O

Gravimetric Study

The corrosion speed of the metal in solution in the absence and presence of the extract are given in table 3. It finds that the corrosion speed decreases when the concentration of the extract increases. The inhibitory efficiency is proportional to the rate of corrosion as shown in the fig.3, the maximum inhibition is recorded at $5 \cdot 10^3$ ppm of the extract. These results we have encouraged to complete the study by the electrochemical measurements in order to confirm the effect of inhibition of corrosion.

The quantity of the extract in (10^3 ppm)	Speed of corrosion $\text{mg.cm}^{-2}/\text{h}$	The inhibitory efficacy (%)
0	$8,15 \cdot 10^{-5}$	-----
1	$5,50 \cdot 10^{-5}$	32,63
3	$3,10 \cdot 10^{-5}$	61,96
5	$8,95 \cdot 10^{-6}$	89,01

Table III.Results of the study a gravimetric without and with the addition of inhibitors

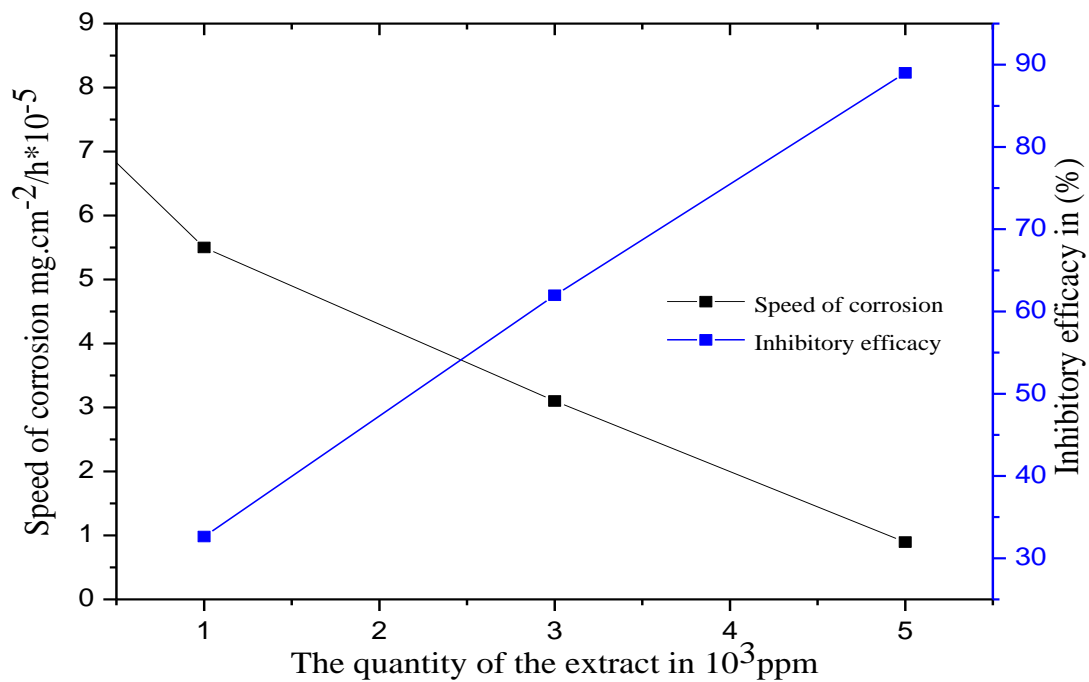


Figure 3. Evolution of the rate of corrosion and the inhibitory efficacy in function of the volume of the pomegranate bark extract

Electrochemical study

The curves of polarization

The inhibitory efficacy was determined by the exploitation of Tafel curves, from fig. 4 a clear displacement of the Tafel lines to the right are observed when the concentration of the inhibitor increases, the concentration lines $3 \cdot 10^3$ and $5 \cdot 10^3$ are almost superimposed, this may be explained by the saturation of the inhibitor medium. The corrosion parameters are given in Table IV.

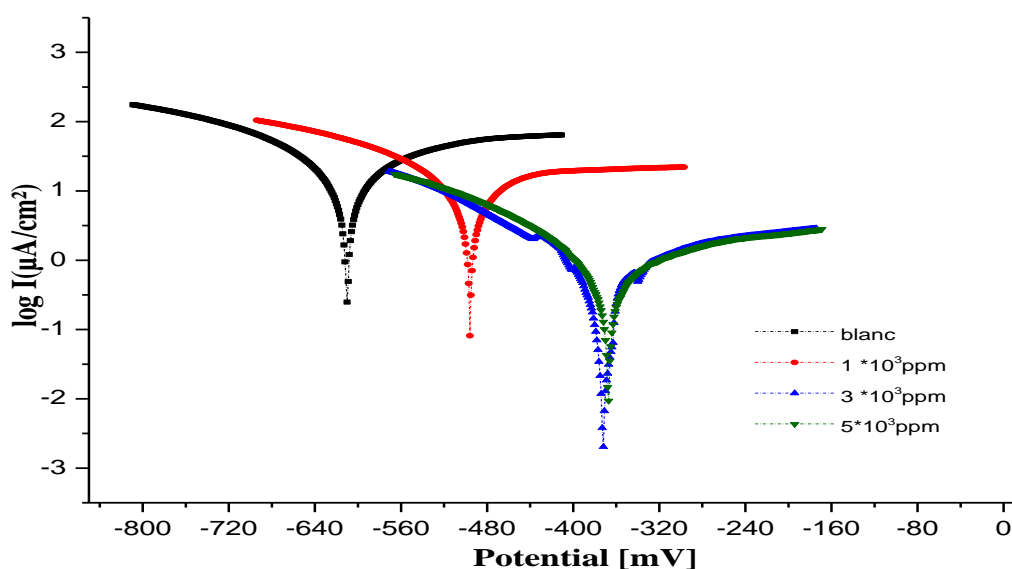


Figure4. Logarithmic representation of the density of the current as a function of the potential, iron in saline without and with the addition of the inhibitor (extract of the pomegranate bark).

	I_{corr}	E_{corr}	Ba	Bc
Without an Inhibitor	48,18 $\mu A/cm^2$	-610,8 mV	1586,4 mV	-351,5 mV
$1 \cdot 10^3$ Ppm	17,37 $\mu A/cm^2$	-496,6 mV	1845,4 mV	-228,5 mV
$3 \cdot 10^3$ Ppm	0,53 $\mu A/cm^2$	-372 mV	169,6 mV	-115,7 mV
$5 \cdot 10^3$ Ppm	1,75 $\mu A/cm^2$	-368,2 mV	120,17 mV	-191,6 mV

Table IV. Parameters of Tafel

Electrochemical impedances

The measures of the electrochemical impedances have been traced using an analyser frequency response, Type ORIGALYS 80. The amplitude of the sinusoidal disturbance is 60 mV with a range of frequencies ranging from 103Hz to 10Hz.

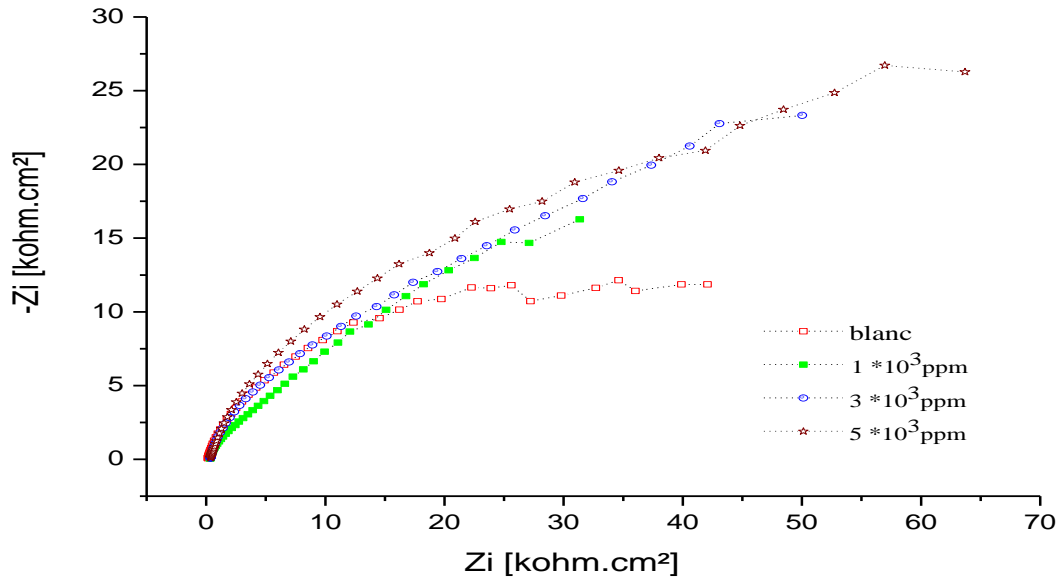


Figure 5: Represents the charts of impedance in the plan of Nyquist Z to different concentrations of inhibitor performed after 1 h of immersion at ambient temperature in the corrosion potential

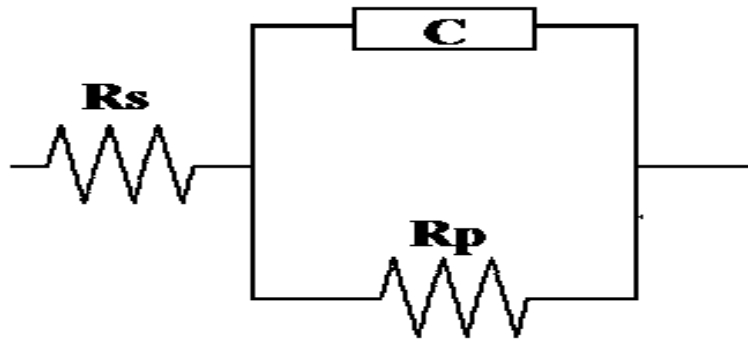
Table V present the impedometric parameters determines from the curves of the impedances[26] registered after 1h of (Fe E500) immersed in a carbonated environment in the absences and presence of the extract.

Extract in 10 ³ ppm	E _{corr} (mV)	Re/Ω.cm ²	Rp/Ω.cm ²	C/μFcm ⁻²
0	-610,8 mV	---	---	---
1	-496,6 mV	148.36	49.388	51.070
3	-372.0 mV	97.800	52.225	38.361
5	-368,2 mV	98.475	62.915	31.843

Table V. Impédancemétriques settings.

The curves forms exhibit the same behavior with a slight increase in the diameters of the curves obtained in presence of different concentration of the extract.[27]

The resistances of the polarization recorded for the four concentrations are increased as a function of the increase in the concentration of the extract in the medium. The highest polarization resistance is recorded for the concentration of $3 \times 10^3 \text{ ppm}$ thus making it possible to wait an inhibitory efficiency of 98%. Simplified circuit are chosen to modulate the comportment of the inhibitor in the carbonated medium this circuit comprises three elements.[28]



.Figure 6: The equivalent circuit model

Conclusion

In this study we examined the inhibitory efficacy of the bark pomegranate extract in a basic medium that simulates the pore solution of carbonated concrete, the main conclusions of this study are:

1–The Gravimetric study demonstrate that this extract can lower the speed of corrosion and therefore classify the extract as a corrosion inhibitor in the studied medium

2– the electrochemical tests have confirmed the inhibitory nature of the extract, the increase in the concentration of the extract Leads to increases of inhibitory efficacy, we can wait until the "More than 98% to $3 \times 10^3 \text{ ppm}$ ". This result has been confirmed by the impedance method And which has enabled to modeling the behavior by an electrical circuit equivalent

REFERENCES

- [1] J. M. Torrenti, "Caractérisation de la variabilité des performances des bétons–Application à la durabilité des structures," *AFGC, Paris*, 2009.
- [2] M.-T. Liang, W.-L. Jin, R.-J. Yang, and N.-M. Huang, "Predeterminate model of corrosion rate of steel in concrete," *Cement and concrete research*, vol. 35, pp. 1827-1833, 2005.
- [3] I.-S. Yoon, O. Çopuroğlu, and K.-B. Park, "Effect of global climatic change on carbonation progress of concrete," *Atmospheric environment*, vol. 41, pp. 7274-7285, 2007.
- [4] T. Vidal, "Requalification des structures dégradées par la corrosion," Thèse de doctorat de l'INSA de Toulouse, 2003.
- [5] A. Castel, "Couplage mécanique et corrosion dans les éléments de béton armé," 2000.
- [6] N. Ihekweba, B. Hope, and C. Hansson, "Carbonation and electrochemical chloride extraction from concrete," *Cement and concrete Research*, vol. 26, pp. 1095-1107, 1996.

- [7] P. Castro, E. Moreno, and J. Genescá, "Influence of marine micro-climates on carbonation of reinforced concrete buildings," *Cement and Concrete Research*, vol. 30, pp. 1565-1571, 2000.
- [8] H. Roper and D. Baweja, "Carbonation-Chloride Interactions and Their Influence Corrosion Rates of Steel in Concrete," *Special Publication*, vol. 126, pp. 295-316, 1991.
- [9] T. Chaussadent and R. Dron, "Influence of hydroxyis, carbonates and chlorides ions on the pitting corrosion of steel in concrete," *Materiales de construcción*, vol. 42, pp. 49-62, 1992.
- [10] U. Nurnberger, "Possibilities of corrosion protection of reinforcing steel in concrete," in *COST*, pp. 15-56.
- [11] N. E. Hammer, "NACE Glossary of Corrosion Terms," *Mat. Pro.*, vol. 4, p. 79, 1965.
- [12] O. S. B. Al-Amoudi, M. Maslehuddin, A. Lashari, and A. A. Almusallam, "Effectiveness of corrosion inhibitors in contaminated concrete," *Cement and Concrete Composites*, vol. 25, pp. 439-449, 2003.
- [13] A. Blankvoll, "Proceedings: International Conference on Repair of Concrete Structures: From Theory to Practice in a Marine Environment: Svolvær, Norway, 28-30 May 1997," in *International Conference on Repair of Concrete Structures, 1997, Svolvær, Norway*, 1997.
- [14] N. Berke and K. Sundberg, "Effects of calcium nitrite and microsilica admixtures on corrosion resistance of steel in concrete," *Special Publication*, vol. 122, pp. 265-280, 1990.
- [15] M. El Azhar, B. Mernari, M. Traisnel, F. Bentiss, and M. Lagrenee, "Corrosion inhibition of mild steel by the new class of inhibitors [2, 5-bis (n-pyridyl)-1, 3, 4-thiadiazoles] in acidic media," *Corrosion Science*, vol. 43, pp. 2229-2238, 2001.
- [16] C. K. Nmai, "Multi-functional organic corrosion inhibitor," *Cement and Concrete Composites*, vol. 26, pp. 199-207, 2004.
- [17] J. Cruz, R. Martinez, J. Genesca, and E. Garcia-Ochoa, "Experimental and theoretical study of 1-(2-ethylamino)-2-methylimidazoline as an inhibitor of carbon steel corrosion in acid media," *Journal of Electroanalytical Chemistry*, vol. 566, pp. 111-121, 2004.
- [18] M. Ormellese, L. Lazzari, S. Goidanich, G. Fumagalli, and A. Brenna, "A study of organic substances as inhibitors for chloride-induced corrosion in concrete," *Corrosion Science*, vol. 51, pp. 2959-2968, 2009.
- [19] O. Benali, L. Larabi, M. Traisnel, L. Gengembre, and Y. Harek, "Electrochemical, theoretical and XPS studies of 2-mercapto-1-methylimidazole adsorption on carbon steel in 1M HClO₄," *Applied surface science*, vol. 253, pp. 6130-6139, 2007.
- [20] L. Legrand, M. Abdelmoula, A. Géhin, A. Chaussé, and J.-M. Génin, "Electrochemical formation of a new Fe (II) • Fe (III) hydroxy-carbonate green rust: characterisation and morphology," *Electrochimica Acta*, vol. 46, pp. 1815-1822, 2001.
- [21] P. Refait, S. Drissi, J. Pytkiewicz, and J.-M. Génin, "The anionic species competition in iron aqueous corrosion: role of various green rust compounds," *Corrosion science*, vol. 39, pp. 1699-1710, 1997.
- [22] L. Sail, F. Ghomari, A. Khelidj, A. Bezzar, and O. Benali, "LA PERTE DE MASSE DANS L'INHIBITION DE," *Lebanese Science Journal*, vol. 14, p. 87, 2013.
- [23] Y. Abboud, O. Tanane, A. E. Bouari, R. Salghi, B. Hammouti, A. Chetouani, *et al.*, "Corrosion inhibition of carbon steel in hydrochloric acid solution using pomegranate leave extracts," *Corrosion Engineering, Science and Technology*, vol. 51, pp. 557-565, 2016.
- [24] M. Konwar and G. Baruah, "On the nature of vibrational bands in the FTIR spectra of medicinal plant leaves," *Archives of Applied Science Research*, vol. 3, pp. 214-221, 2011.
- [25] E. P. Lansky and R. A. Newman, "Punica granatum (pomegranate) and its potential for prevention and treatment of inflammation and cancer," *Journal of ethnopharmacology*, vol. 109, pp. 177-206, 2007.
- [26] M. Bautista, Y. Bultel, J. Diard, and S. Walkiewicz, "Etude par spectroscopie d'impédance électrochimique du comportement en fonctionnement d'une pemfc," in *Proceeding of the 14th Forum sur les Impédances Électrochimiques*, 2002, pp. 221-230.
- [27] C. Gabrielli, M. Ksouri, and R. Wiart, "Compensation de la chute ohmique par une methode analogique.: Application a la mesure des impedances electrochimiques et a la determination des courbes de polarisation," *Electrochimica Acta*, vol. 22, pp. 255-260, 1977.
- [28] C. Gabrielli and M. Keddam, "Progres recents dans la mesure des impedances electrochimiques en regime sinusoidal," *Electrochimica Acta*, vol. 19, pp. 355-362, 1974.