



Corrosion Prevention of St37 Steel in Mediterranean Seawater Thanks to a Green Plant Extract: Gravimetric and Electrochemical Studies

Hana Lahbib^{1,3,4,*}, Pierangela Cristiani², Husnu Gerengi³, Stefano Trasatti⁴, Yasser Ben Amor^{5,6}

¹ Research Laboratory of Environmental Sciences & Technologies, Higher Institute of Environmental Sciences and Technology, Carthage University, BP.1003 Hammam-Lif, 2050 Ben Arouse, Tunisia

² RSE e Ricerca sul Sistema Energetico S.p.A, Sustainable Development and Energy Sources Dept., 20133 Milan, Italy

³ Corrosion Research Laboratory, Faculty of Engineering, Mechanical Engineering, Duzce University, Duzce, Turkey

⁴ Department of Chemistry, Università degli Studi di Milano, Via Golgi 19, 20133 Milan, Italy

⁵ Higher Institute of Environmental Sciences and Technology, Carthage University, BP.1003 Hammam-Lif, 2050 Ben Arouse, Tunisia

⁶ Water Researches and Technologies Center Borj-Cedria Technopark, Waste water and Environment Laboratory, Tourist Route of Soliman Nabeul, BP.273 - 8020 Soliman

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Abstract

Metal corrosion is undoubtedly one of the most challenging problems facing by industry. The introduction of corrosion inhibitors is a sensible approach to protecting metal surfaces. An efficient and environmentally friendly method to mitigate corrosion is the use of corrosion inhibitors derived from natural products. In the present work, the inhibition efficiency of cardoon (*Cynara cardunculus*) leaf extracts (CC) on the corrosion of St37 steel in natural Mediterranean seawater was investigated. The corrosion inhibition percentage (IE%) of 30 ppm of (CC) extract, determined as a reference amount at temperatures of 298 and 328 K respectively, depending on the time (1, 7, 14, 21 and 28 days), was studied by weight loss and potentiodynamic polarisation (PDP) methods. The morphological changes on the metal surface were also analyzed by SEM and EDS. It was observed that the percentage of corrosion protection of 30 ppm CC decreased from about 85% to 68% with increasing temperature. The time-dependent study also shows that even after one month at 298 K, it protects about 74% of the ST37 metal against corrosion in natural Mediterranean seawater.

Keywords: Corrosion inhibition, *Cynara Cardunculus* (Cardoon), St37 steel.

1. Introduction

Steel corrosion problems have received significant attention in the industry such as metallurgy, water distribution, and oil, energy and petroleum production [1]–[3]. This phenomenon remains a major focus due to its natural disaster-like consequences [4]. Most often, industrial sector operations are located in the marine environment [5] and use low carbon steel in their facilities which are very susceptible to corrosion.

In the industrial world, the consumption of metals is unavoidable, that's why the protection of metals through corrosion inhibitors are more and more necessary to stop or to delay their damage in an aggressive solution[6].

For corrosion protection, different solutions are available. Nevertheless, the synthetic inhibitors have good inhibition performance [7], but they are difficult to obtain, expensive and have negative effects on the environment. For these reasons, researchers are interested to develop green inhibitors that are environmentally benign, readily available, and biodegradable [2] [8]–[10]. The effectiveness of plant extracts in preventing corrosion and shielding carbon and low-alloy steel in saline solutions (NaCl) has been the subject of numerous investigations over the past few decades [11]. The natural green inhibitors, which are taken from medicinal plants, have the ability to effectively control corrosion by interacting with the surface of metals through the functional groups present in their molecular structure [12]. Among the

*Corresponding author: lahbib_hana@outlook.fr

researches performed, M. Rana et al [13], proved that different jus plants, *Catharanthus roseus*, *Areca catechu*, and *Laurus nobilisin* could be employed as eco-friendly inhibitors for controlling the corrosion of mild steel inside 0.5 M NaCl solution in open air through an average temperature of 28 ± 1 °C. According to Langmuir and Temkin adsorption isotherms, these extracts are adsorbed on the mild steel surface, which reduces the steel's corrosion rate as a function of extract concentration up to 2000 ppm. In addition, Y. Fernine et al [14], examined the effectiveness of different concentrations of *Ocimum basilicum* seed extract (OBSE) with a 3% wt NaCl solution to prevent the corrosion of 2024-T3 aluminium alloy. The corrosion inhibition efficiency rose to 95.5% at a concentration of 1 g/L with an increase in OBSE concentration, according to the data. In addition, surface studies prove a reduction in surface roughness based on the Langmuir isotherm model, which describes the extract molecules' adsorption onto the surface.

This study attempts to confirm that cardoon leaf extract can effectively inhibit corrosion of St37 steel as a function of two different variables: firstly, as a function of immersion time at a stable temperature of 298 K and, secondly, as a function of temperature for a stable immersion period of one week in a natural seawater environment. The investigation was performed by Potentiodynamic polarization (PDP) as well as the weight reducing method. These measurements were complemented by the surface analysis using the SEM-EDS analysis.

2. Material and methods

2.1. Metal sample

The chemical composition of the metal used is detailed in our recent publications [3]. For the weight loss measurements, St37 steel sample coupons with dimensions of $1 \times 1 \times 1$ cm were used. For the electrochemical analysis, circular samples were used. The samples were surrounded by inert resin to give an active surface area of 0.785 cm^2 . Before each experiment, the samples were mechanically polished using a range of abrasive papers (400-2000), degreased in an ultrasonic bath using acetone for 3 minutes, then rinsed with distilled water and dried at room temperature.

2.2. Medium

Each experiment was evaluated in natural seawater both with and without 30 ppm of cardoon leaf extract, which is the optimum corrosion inhibition concentration previously demonstrated by Hana et. al [3].

2.3. Jus leaf extraction of the cardoon plant

The cardoon plant used as a green inhibitor was collected from the Nabeul region of northern Tunisia (Fig. 1). The choice of this plant was justified by its availability and its high content of antioxidant substances [15]. The extraction method used in this study was maceration. The experimental protocol chosen was comparable to the technique described by Hana et al [3], Wahiba et al [16] and Etteyeb and Novoa [17]. The initial concentration in water was 8.36 g/L. For each test, the concentration of only 30 ppm is the focus of this investigation.



Figure 1. Photo of Cardoon plant

2.4. Weight loss measurement

The present test was conducted using the standard analysis method (ASTM, G31-72). Measurements were recorded at various temperature (298-328 K) and immersion times (1h, 24h, 48, 1 week, 2 week and 28 days). In the beginning, St37 steel samples were weighed using an electronic balance. Following that, the weighed samples were submerged in 100 milliliters of seawater pure and containing 30 ppm of the plant extract. After different immersion times, the specimens were removed, dried in an oven for 10 min and reweighed. to ensure repeatability, three experiments were carried out, then, the following formula was used to determine the corresponding corrosion rate (CR). [18]:

$$C_R = \frac{\Delta m}{A t} \quad (1)$$

Where Δm : the weight loss (g), t : the immersion time (h) and S : the surface area of the sample (cm^2).

The inhibition efficiency of the aqueous extract was calculated from the obtained weight loss values [19]:

$$IE_{wl}(\%) = \frac{C_{R(blank)} - C_{R(inh)}}{C_{R(blank)}} \times 100 \quad (2)$$

Where C_R (blank) and C_R (inh) are the rate of corrosion without and with inhibitor.

2.5. Electrochemical investigations

The electrochemical tests were carried out using a conventional three-electrode cell, consisting of the Ag/AgCl reference electrode, the platinum plate auxiliary electrode and the St37 steel working electrode. These measurements were carried out using a potentiostat/galvanostat (Gamry-ZRA 600) controlled by Gamry Instruments software. To ensure repeatability, each measurement was repeated in triplicate. At the beginning of each electrochemical experiment, the open-circuit potential (OCP) test was performed for 60 min to obtain the stability of the electrode in solution. The Tafel curves were recorded by changing the electrode potential from -250 to 250 mV vs. OCP at a scanning rate of 1 mV s⁻¹.

The inhibitive efficiency of CC.L extract was determined by Tafel investigations applying the following formula [20]:

$$IE_p(\%) = \left(1 - \frac{i_{corr}}{i_{corr}^0}\right) \times 100 \quad (3)$$

Where, i_{corr} and i_{corr}^0 represent the current density in the inhibited solution and in the uninhibited medium, respectively.

Using the Stern-Geary correlation, the polarization resistance R_p (Ω cm²) was calculated [21][12]:

$$R_p = \frac{\beta_a \beta_c}{2.30 i_{corr} (\beta_a + \beta_c)} \quad (4)$$

In this equation, β_a and β_c symbolize the anodic and the cathodic Tafel slopes, respectively. IE_{Rp} (%), was computed using Eq (5) based on the resistance polarization data.

$$IE_{Rp}(\%) = \left(1 - \frac{R_{corr}^0}{R_{corr}^{inh}}\right) \times 100 \quad (5)$$

Where R_{corr}^0 and R_{corr}^{inh} are the polarization resistance values obtained in the inhibited solution and in the uninhibited medium, respectively.

2.6. Surface characterization

The morphology of St37 steel surface working electrode was characterized by SEM, EDS technique. the analysis was recorded on the metallic surface at 298 and 328 K during 1 week of immersion time in the Blank and inhibited solution.

SEM-EDS spectra were obtained with an energy dispersive X-ray detector using a Quanta 250 field emission gun (FEG) type in order to analyze the elemental composition.

3. Results and discussion

3.1. Weight loss measurement

St37 steel samples immersed in natural seawater without and with 30ppm of CC leaves extract were measured for weight loss in function of immersion time (1h-28 days) at 298K.

The variation of inhibition efficiency is indicated below in table 1. It has been shown that the (IE_{WL} (%)) value decreased from 92% to 79% when the immersion period increase. As a result, the plant jus function as a good metal protective against corrosion even with a long immersion time.

Table1. Parameters of WL for low carbon steel St37 immersed in the blank (SW) and inhibited solution during various immersion time at 298K.

Days	Blank SW		SW+30ppm CC		
	WL(*10 ⁻³)	C _R (*10 ⁻³)	WL (*10 ⁻³)	C _R (*10 ⁻³)	%IE
1	0,34	0,0025	0,026	0,00019	92.4
7	4.1	0.031	0.61	0.0046	85.1
14	6.2	0,047	1.62	0,0061	87
21	12.4	0,031	2.16	0,0054	82.5
28	19.7	0,037	4.09	0,0077	79.19

Table 2: Parameters of St37 steel weight loss immersed in blank and inhibited solution during 1 week of immersing time at different temperature.

	Blank SW		SW+30ppm CC		
	W (*10 ⁻³)	C _R (*10 ⁻³)	W (*10 ⁻³)	C _R (*10 ⁻³)	%IE
298	4.1	0.031	0.61	0.0046	85.1
308	8.7	0.059	1.58	0.012	79.6
318	12.8	0.097	3.16	0.024	75.2
328	18.2	0.124	5.29	0.040	67.7

Moreover, Weigh loss measurement of St37 steel were performed during 1 week of immersing time in blank

solution (SW) without and with 30ppm of CC leaves extract at different temperature (298 - 328 K). Table

2 illustrate the evolution of inhibition efficiency (IE %). It has been shown that the IE % decreased from 85% to 67% when the temperature rang increase. The final observation shown that plant extract components working well like a protective agent against corrosion even at high temperature.

3.2. Tafel extrapolation

The efficiency of the optimal concentration of plant extract against corrosion was controlled by the polarization test as a function of time.

Figures 2 (a and b) shows the Tafel plots of the polarization curves of the St37 steel immersed in Natural seawater pure and inhibited with the jus plant extract at 298 K in various immersion time.

The Tafel polarization parameters was presented at different immersion time in Table 3. The shown result demonstrate that the value of current density I_{corr} reduces from 1h (91%) to 1day (74%) and then seems like stable in function of immersion time (1day-1 month (February 28 days)). The present result can be explained by the adsorption of a thick layer on the electrode surface. From 1 day to 28 days, the metal surface was protected thanks to the green plant and the IE% varying from 73 to 91%. It has been proven that cardoon leaf extract maintains its activity and is considered an effective agent for protecting the surface of St37 steel against deterioration, even after a long period of immersion.

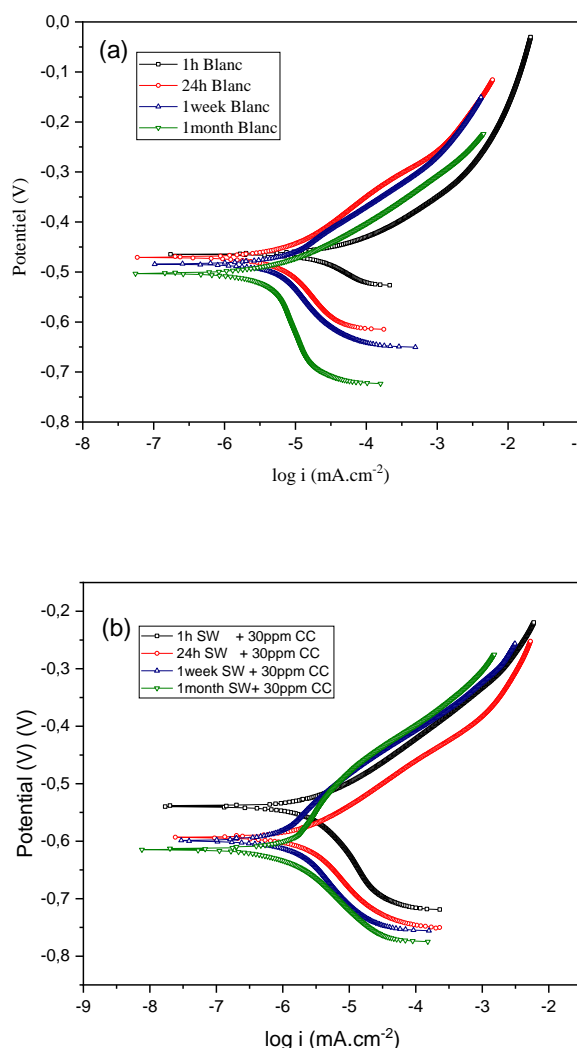


Figure 2: Typical Tafel curves of steel immersed inside the blank solution in the absence (a) and presence of (b) 30ppm CC leaves extract in function of different immersion time at 298K

Table 3. Evaluation of Tafel polarization parameters for St37 steel in the absence and presence of the inhibitor in function of immersion time at 298K.

	Blank (SW)			SW+30ppm CC			
	I_{corr}	β_a	β_c	I_{corr}	β_a	β_c	%IE
1h	45.938	89.147	192.526	3.693	56.693	117.919	91.96
1day	4.403	74.138	109.763	1.136	51.535	66.323	74.20
1 week	3.733	50.871	93.892	0.734	87.739	67.199	80.33
1month	2.564	49.675	123.432	0.670	70.308	64.112	73.87

4. Surface characterization

To observe the changes produced during the corrosion inhibition process, SEM micrographs were taken of

St37 steel surfaces exposed to the corrosive and the inhibited solution. Figure 3 shows SEM images taken on St37 steel before the experiment (Figure 3 a), after

1 week of immersion time, respectively on the corrosive and inhibited solution, at 298 K (Figure 3 b, d), and at 328K (Figure 3 c, e). Comparing the SEM images results significant damage to the surface of the working electrode during 1 week of immersion time in 298 K (Figure (3 b) which is accentuated at 328 K (Figure (3 d)). In addition, a film was clearly observed on the electrode surface, following immersion of the metal in the inhibited solution. This film covered the surface at both 289 K and 328 K after one week's immersion (Figure 3 c, 3e).

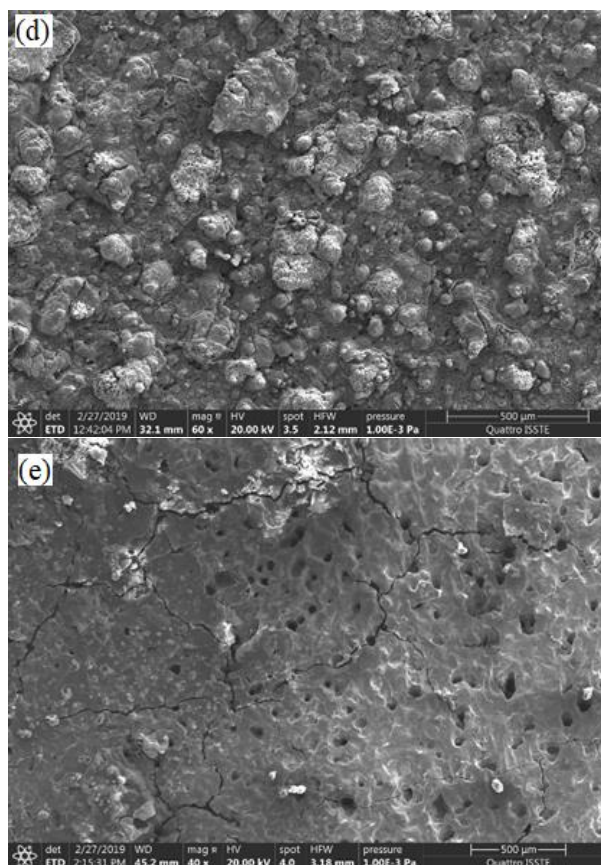
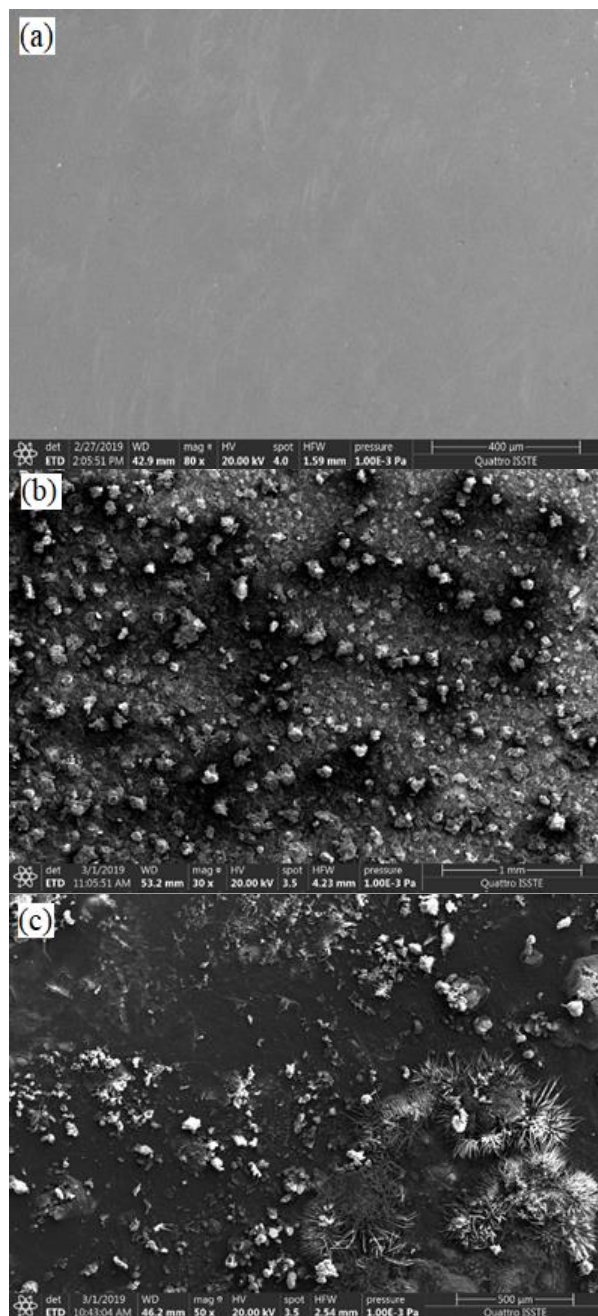


Figure 3: SEM view of St37 steel: (a) in a polished state; following 1 week's exposure to the (b, d) blank solution (SW); (c, e) inhibited solution, at 298 K and 328 K respectively.

EDS analyses (Table 4) performed on the uninhibited specimens contain significant concentrations of Fe, O, and Cl. These are probably caused by the formation of Fe_3O_4 and $FeCl_3$, according to Ebdelly et al [16] and Hana et al [3]. In addition, other elements including C and Mn depend on the composition of the St37 steel sample. The percentage of Fe, C and Mn atomic quantities in aggressive solutions was reduced compared to that of bare St37 steel (Table 4).

Moreover, the analysis of the surface of st37 immersed in the inhibited solution by 30ppm of the plant extract was tested, a protective layer that is well deposited on the electrode surface at 298K and even at 328K is depicted in the SEM result (figures 3 (c and e)). Therefore, thanks to the inhibited solution with only 30 ppm of the plant extract, the surface of St37 was well protected against corrosion after one week of immersion, even at high temperatures, compared to the results obtained with the non-inhibited solution. The results confirm that the plant extract's efficacy is not significantly affected by temperature, this means that the plant extract remains an effective corrosion inhibitor even at elevated temperatures. Consequently,

SEM-EDS analysis confirmed both the electrochemical and gravimetric results.

Table 4: EDS analysis

Element		Fe	C	O	Mn	Mg	Si	Cr	Na	Cl
Bare St37 steel		96.82	1.26	-	1.08	-	0.30	0.55	-	-
298 K	Blank (SW)	40.18	0.47	36.28	0.57	0.36	0.41	0.52	10.71	11.35
	SW+30ppm CC	69.18	4.7	12.26	0.95	0.84	0.61	0.54	11.15	9.29
328 K	Blank (SW)	20.43	0.42	59.71	0.24	0.43	0.49	0.39	18.30	20.14
	SW+30ppm CC	50.34	3.9	19.47	0.82	0.68	0.57	0.48	20.58	19.32

5. Conclusion

The present study investigated the capacity of cardoon (*Cynara cardunculus*) leave extracts to act as an effective barrier for St37 steel in seawater at high temperatures and for long periods of immersion. The main results obtained can be summarized as follows: The CC extract proved to be an effective inhibitor against corrosion of St37 steel in weight loss tests when exposed to different immersion times (1 day to 28 days) and temperatures between 298 K and 328 K. The PDP results show that the corrosion inhibition percentage (IE%) decreases over a month from 91% to 74% at 298K. This is still an acceptable level of effectiveness for a considerable period of time.

The SEM-EDS study reveals that there is an additional layer of protection on the studied electrode surface, suggesting that the inhibitor molecules have effectively attached to the surface of the St37 steel samples.

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