

***Asteriscus Imbricatus* Extracts: Antifungal Activity and Anticorrosion Inhibition**

B. Senhaji¹, D. Ben Hmamou¹, R. Salghi^{1,*}, A. Zarrouk², B. Chebli¹, H. Zarrok³, I. Warad⁴, B. Hammouti², S. S. Al-Deyab⁴

¹ Ecole Nationale des Sciences Appliquées, Equipe Génie de l'Environnement et de Biotechnologie, Université Ibn Zohr, B.P 1136, 80000 Agadir, Morocco.

² LCAE-URAC18, Faculté des Sciences, Université Mohammed Premier, B.P. 4808, 60046 Oujda, Morocco

³ Laboratoire des procédés de séparation, Faculté des Sciences, Kénitra, Morocco

⁴ Department of Chemistry, College of Science, King Saud University, B.O. 2455, Riaydh 11451, Saudi Arabia

*E-mail: r_salghi@yahoo.fr

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The antifungal activity of different extracts of *Asteriscus Imbricatus* against *botrytis cinerea* isolated from tomato show that the percentage of the inhibition was almost 100% for the four extracts of organic solvents at 500 ppm. At 250 ppm the percentage of inhibition was almost 70% for the ether extract and for the chloroform extract, 60 % and 50% for the ethyl acetate extract and for methanol extract, respectively. While the aqueous extract of *Asteriscus Imbricatus* exhibited moderate antifungal activity. The corrosion inhibition by an *Asteriscus Imbricatus* extract (AIE) on C38 steel in hydrochloric acid (HCl) solution has been investigated by electrochemical methods and weight loss. Potentiodynamic polarization studies clearly reveal that the presence of AIE does not change the mechanism of the hydrogen evolution reaction and they act essentially as cathodic and anodic inhibitor. Inhibition efficiency of AIE reached 96.33% at 0.6 g/l. The adsorption of AIE on C38 steel surface obeys the Langmuir isotherm.

Keywords: Antifungal activity *Asteriscus Imbricatus*, *botrytis cinerea*, Corrosion inhibition, Steel.

1. INTRODUCTION

Medicinal and aromatics plants play a significant role in the economy of Morocco. As part of a contribution to the development of natural Moroccan heritage, many researches are currently testing the efficacy of medicinal plant extracts against human's diseases or plant diseases or for industrial purpose [1].

Steel is widely used in most industries because of its low cost and availability for the manufacture of reaction vessels such as cooling tower reservoirs, pipelines, etc...[2]. Large numbers of organic compounds were studied and are being studied to investigate their corrosion inhibition potential. All these studies reveal that organic compounds especially those with N, S and O showed significant inhibition efficiency [3–17]. But, unfortunately most of these compounds are not only expensive but also toxic to living beings.

Recently, several researcher focalize their works to use of natural products named green inhibitor, as corrosion inhibitors [18-28]. Among these compounds was tested in our laboratory, we cite extract compounds such as; Chamomile extract [29], Argan extract [30-33], Verbena extract [34], *Marrubium Vulgare L.* extract [35], These compounds tested have been reported to be excellent inhibitors for metals and alloys in acidic solutions. Also, excellent activities against plant fungal pathogens was investigate in our laboratory [36-37].

In this sense we tested in vitro antifungal activity of different extracts of *Asteriscus Imbricatus* against *botrytis cinerea* isolated from tomato and the effect of concentration on the inhibition efficiency of C38 steel corrosion in molar hydrochloric solution has been also studied.

2. EXPERIMENTAL METHODS

2.1. Collection and preparation of plant

The aerial part of *Asteriscus imbricatus* was collected randomly in the Cape Ghir, 60 km north of the city of Agadir (Morocco). Plant samples were cleaned and air dried in the shade then the leaves were grounded to a fine powder using a electric laboratory grinding mill and stored in the dark at 4 °C until use [38].

2.2. Pathogen culture

The fungi were isolated from infected leaves of tomato and identified in laboratory of School of Applied Sciences of Agadir in Morocco. The fungi were isolated as follows: circles are taken from infected areas in tomato leaves and rinsed with tap water three times then we placed these circles in petri plates containing PDA medium .The plates are incubated at 298 K in an incubator. A week later, the fungi were transferred to new plates and the transplanting is repeated several times to get a sufficient amount of fungi [37].

2.3. Preparation of extracts

2.3.1. Extraction using organic solvents

We conducted a hot extraction using Soxhlet apparatus: a inside the extractor, we used a cellulose cartridge we filled with plant material powder. This cartridge is attached to a solvent reservoir and is surmounted by a refrigerant. Solvents we used are in order of increasing polarity: petroleum ether, the chloroform, ethyl acetate and methanol [39].

2.3.2. Aqueous extraction

The aqueous extraction was performed using 20 g of the powdered herb to 50 ml of distilled water. After three hours of maceration, magnetic stirring was used. The mixture was filtered through filter paper. The remaining cake is recovered and the operation is repeated five times to make five exhaustions. Extracts obtained were stored at 4°C and protected from light until use [40].

2.4. Antifungal tests

For the organic extraction we have prepared a solution of 3000 ppm from which we made a series of dilutions 2000, 1000, 500, 250, 125, 100 and 50 ppm. For the aqueous extraction we have prepared a series of dilutions ranging from 25000 ppm to 1000 ppm starting from a solution of 80000 ppm. Prepared solutions were dispensed into 8.5 cm diameter petri plates. Pathogen grown on PDA without plant powders was used as control. Three plates for each concentration were prepared and inoculated aseptically with 0.7 cm diameter disks of the test fungus taken from the actively growing edge of one week old culture and incubated at 25 °C for seven days.

2.5. Materials

The steel used in this study is a carbon steel (Euronorm: C35E carbon steel and US specification: SAE 1035) with a chemical composition (in wt%) of 0.370 % C, 0.230 % Si, 0.680 % Mn, 0.016 % S, 0.077 % Cr, 0.011 % Ti, 0.059 % Ni, 0.009 % Co, 0.160 % Cu and the remainder iron (Fe). The C38 steel samples were pre-treated prior to the experiments by grinding with emery paper SiC (120, 600 and 1200); rinsed with distilled water, degreased in acetone in an ultrasonic bath immersion for 5 min, washed again with bidistilled water and then dried at room temperature before use. The acid solutions (1.0 M HCl) were prepared by dilution of an analytical reagent grade 37% HCl with double-distilled water. The concentration range of *Asteriscus Imbricatus* extract (AIE) employed was 0.1 g/l to 0.6 g/l.

2.6. Measurements

2.6.1. Weight loss measurements

The gravimetric measurements were carried out at a definite time interval of 6 h at room temperature using an analytical balance (precision ± 0.1 mg). The C38 steel specimens used have a rectangular form (length = 1.6 cm, width = 1.6 cm, thickness = 0.07 cm). Gravimetric experiments were carried out in a double glass cell equipped with a thermostated cooling condenser containing 80 mL of non-de-aerated test solution. After immersion period, the C38 steel specimens were withdrawn, carefully rinsed with bidistilled water, ultrasonic cleaning in acetone, dried at room temperature and then weighted. Triplicate experiments were performed in each case and the mean value of the weight loss was calculated.

2.6.2. Electrochemical measurements

Electrochemical experiments were conducted using impedance equipment (Tacussel-Radiometer PGZ 100) and controlled with Tacussel corrosion analysis software model Voltmaster 4. A conventional three-electrode cylindrical Pyrex glass cell was used. The temperature is thermostatically controlled. The working electrode was C38 steel with the surface area of 1 cm². A saturated calomel electrode (SCE) was used as a reference. All potentials were given with reference to this electrode. The counter electrode was a platinum plate of surface area of 1 cm². A saturated calomel electrode (SCE) was used as the reference; a platinum electrode was used as the counter-electrode. All potentials are reported vs. SCE. All electrochemical tests have been performed in aerated solutions at 298 K.

For polarization curves, the working electrode was immersed in a test solution during 30 min until a steady state open circuit potential (E_{ocp}) was obtained. The polarization curve was recorded by polarization from -800 to -200 mV/SCE with a scan rate of 1 mV s⁻¹. AC impedance measurements were carried-out in the frequency range of 100 kHz to 10 mHz, with 10 points per decade, at the rest potential, after 30 min of acid immersion, by applying 10 mV ac voltage peak-to-peak. Nyquist plots were made from these experiments. The best semicircle can be fit through the data points in the Nyquist plot using a non-linear least square fit so as to give the intersections with the x -axis.

2.7. Scanning electron microscopy (SEM)

Immersion corrosion analysis of C38 steel samples in the acidic solutions with and without the optimal concentration of the inhibitor was performed using SEM. Immediately after the corrosion tests, the samples were subjected to SEM studies to know the surface morphology using SEM Jeol JSM-5800 scanning electron microscope.

3. RESULTS AND DISCUSSION

3.1. Evaluation of antifungal activity of plant extracts

Figs. 1 & 2 showed the antifungal effect of the organic solvents and aqueous extracts of *Asteriscus Imbricatus* on the rate of growth inhibition of *botrytis cinerea*.

The percentage inhibition of mycelia growth of the fungus was calculated using the following formula [41]:

$$PI = \frac{(A-B)}{A} \times 100 \quad (1)$$

where, A and B are the average diameter of fungal growth on control medium with and without extract test, respectively.

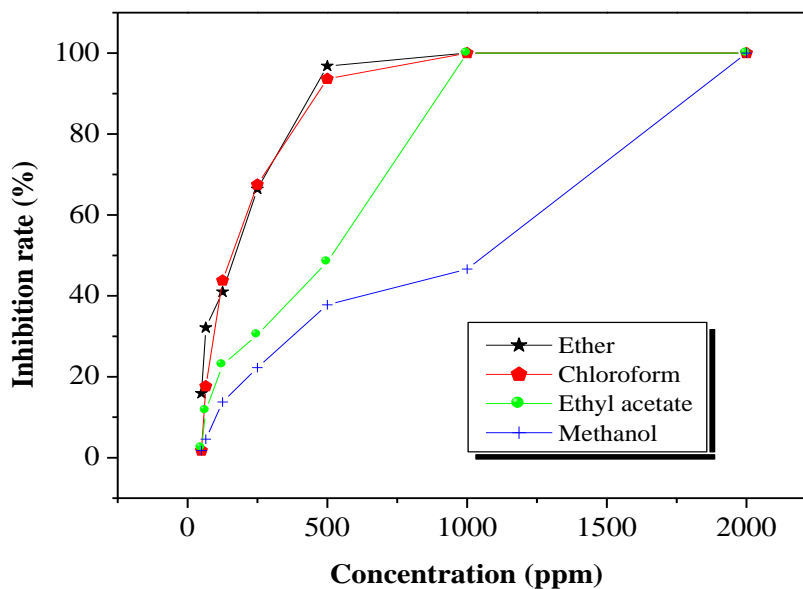


Figure 1. Antifungal effect of the organic solvents extracts of *Asteriscus Imbricatus* on the rate of growth inhibition of *botrytis cinerea*.

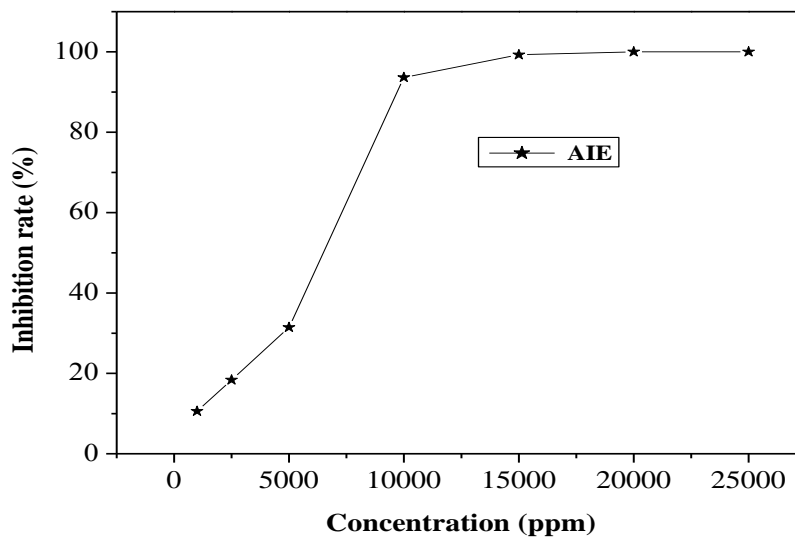


Figure 2. Antifungal effect of the aqueous extracts of *Asteriscus Imbricatus* on the rate of growth inhibition of *botrytis cinerea*

The different extract reduced the colony growth of the fungus. However the inhibitory effect varied between the extracts of organic solvents and the aqueous solution (Fig. 3). The percentage of the inhibition was almost 100% for extracts of the four the organic solvents at the concentration of 500 ppm. Ether and chloroform extracts at 250 ppm showed 66.43 % and 67.49% of the inhibition of the mycelium growth respectively (Fig. 1). While, ethyl acetate and methanol extracts exhibited moderate

activity since the inhibition percentages were 60 % and 50% respectively. For the aqueous extracts the inhibition percentage was 99.29% and 53% at 15000 ppm and 10000 ppm, respectively (Fig. 2).

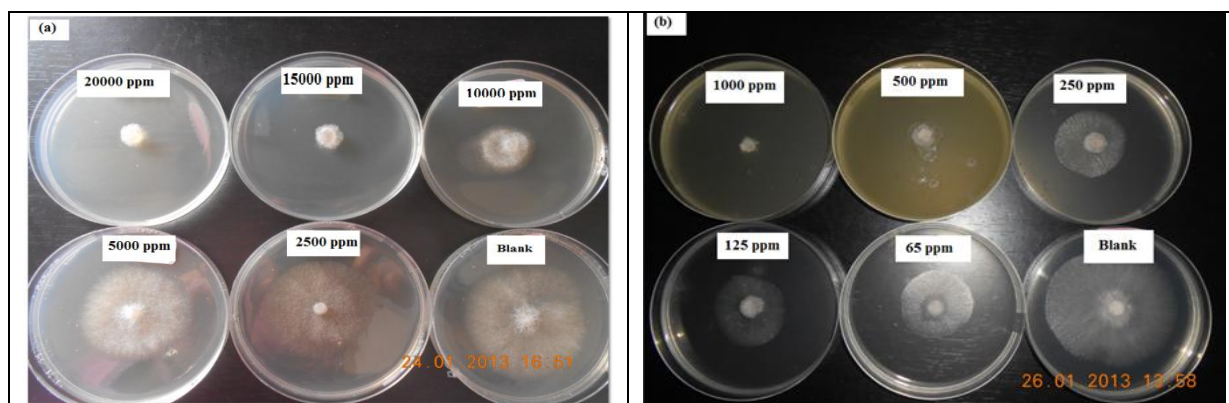


Figure 3. Mycelium growth of the fungus four days after incubation using aqueous extracts (a) and ether extracts (b).

Due to antifungal activity of extracts of this plant and due to their miscibility with water extracts of this plant can be easily used with the irrigation water to reduce the damages caused by *botrytis cinerea* in in tomato the plants. The results of this study show the correlation between traditional healing practices and research of antifungal activity in vitro using medicinal plants as a potential source of natural pesticides.

3.2. Electrochemical experiment

3.2.1. Polarization curves

Fig. 4 shows polarization curves of the working electrode in 1.0 M HCl in the presence and absence of AIE. From Fig. 4 we can get the corrosion current density (I_{corr}) extrapolating the Tafel lines to the corrosion potential [42]. The corrosion inhibition efficiency, η_{Tafel} %, was calculated by the equation:

$$\eta_{Tafel} \% = \frac{I_{corr}^{\circ} - I_{corr}^i}{I_{corr}^{\circ}} \times 100 \tag{2}$$

where, I_{corr}° and I_{corr}^i are the corrosion current density in absence and presence of inhibitor, respectively.

The corrosion parameters including corrosion current densities (I_{corr}), corrosion potential (E_{corr}), cathodic Tafel slope (bc) and inhibition efficiency (η_{Tafel} %) are listed in Table 1.

The obtained results show that the inhibition efficiency increased, while the corrosion current density decreased when the concentration of the inhibitor is increased. This could be explained on the

basis of adsorption of AIE on the C38 steel surface and the adsorption process enhanced with increasing inhibitor concentration.

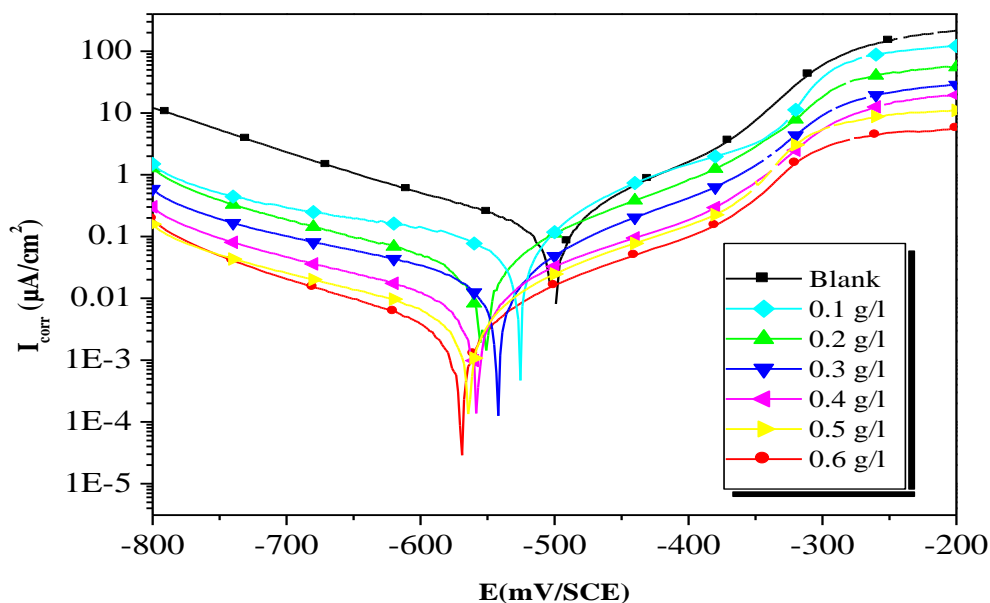


Figure 4. Potentiodynamic polarisation curves of C38 steel in 1M HCl in the presence of different concentrations of AIE.

Table 1. Electrochemical parameters of C38 steel at various concentrations of AIE in 1.0 M of HCl and corresponding inhibition efficiency.

Inhibitor	Conc. (g/L)	E_{corr} (mV/SCE)	I_{corr} ($\mu\text{A}/\text{cm}^2$)	$-b_c$ (mV/dec)	η_{Tafel} (%)
Blank	1.0	-510	124.00	149	-
AIE	0.6	570	04.55	120	96.33
	0.5	-565	16.43	154	86.75
	0.4	-563	24.32	139	80.32
	0.3	-544	36.58	163	70.50
	0.2	-556	49.15	157	60.36
	0.1	-526	64.18	208	48.24

In acidic solutions, the anodic reaction of corrosion is the passage of metal ions from the metal surface into the solution, and the cathodic reaction is the discharge of hydrogen ions to produce hydrogen gas or to reduce oxygen [43-45]. In every curve, it is observed that the current densities of the anodic and cathodic branch are displaced towards lower values. This displacement is more evident with the increase in concentration of the corrosion inhibitor when compared to the blank material. From Table 1, the corrosion current density decreased with the increase of the inhibitor concentration.

These results indicated that the presence of AIE inhibited both iron oxidation and hydrogen evolution, consequently AIE can be classified as mixed corrosion inhibitor [46-47].

3.2.2. Electrochemical impedance spectroscopy (EIS)

Fig. 5 shows the Nyquist plots for C38 steel in 1 M HCl solution in the absence and presence of different concentrations of the AIE at 298K. The percent inhibition efficiency is calculated by charge transfer resistance obtained from Nyquist plots, according to the equation:

$$IE_{R_t} \% = \frac{R_t - R_t^0}{R_t} \times 100 \tag{3}$$

where R_t^0 and R_t are the charge transfer resistance values without and with inhibitor, respectively.

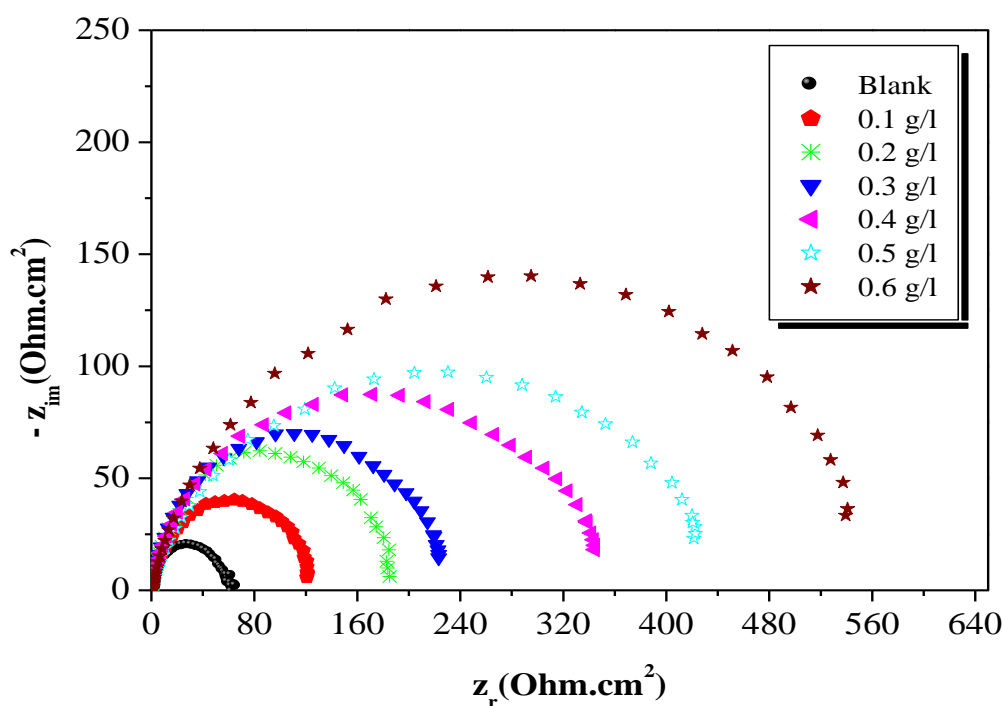


Figure 5. Nyquist diagrams for C38 steel electrode with and without AIE at E_{corr} after 30 min of immersion.

The electrochemical impedance parameters derived from these investigations are mentioned in Table 2.

The equivalent circuit model employed for this system is presented in Fig. 6. The resistance R_s is the resistance of the solution; R_t reflects the charge transfer resistance and C_{dl} is the double-layer capacitance.

Table 2. Electrochemical Impedance parameters for corrosion of C38 steel in acid medium at various contents of AIE.

	Conc. (g/L)	R_t ($\Omega\cdot\text{cm}^2$)	n	Q ($\text{s}^n/\Omega\cdot\text{cm}^2$)	C_{dl} ($\mu\text{F}/\text{cm}^2$)	IE_{Rt} (%)
Blank	1.0	51	0.89	0.00019103	107.88	-
AIE	0.6	560	0.89	0.000103370	72.68	90.81
	0.5	440	0.89	0.000083761	55.70	88.31
	0.4	360	0.87	0.000087014	51.86	85.71
	0.3	220	0.86	0.000083682	43.76	76.62
	0.2	155	0.85	0.000082541	38.24	66.82
	0.1	102	0.84	0.000081324	32.64	49.58

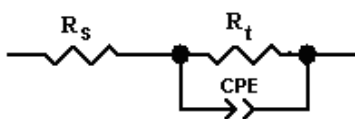


Figure 6. The equivalent circuit of the impedance spectra obtained for AIE.

Fig. 7 gives an example of fitting curve, where we see clearly that the fitted data match the experimental.

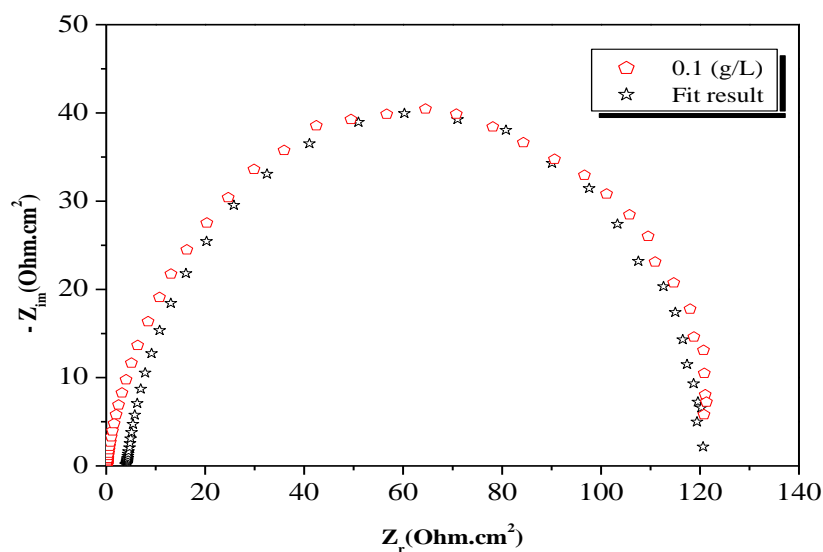


Figure 7. Curves fitting of EIS data of C38 steel in 1 M HCl with 0.1 g/l of AIE to Nyquist plots at E_{corr}

The dispersion of the capacitive semicircle is explained also by surface heterogeneity due to surface roughness, impurities or dislocations [48-49], distribution of activity centres, inhibitors adsorption and formation of porous layers [22-23]. The impedance of the constant phase element (CPE) is [41-42] :

$$Z_{CPE} = Q^{-1} (j\omega)^{-n} \tag{2}$$

where Q is a proportionality coefficient and n an exponent related to the phase shift. For whole numbers of n = 1, 0, -1, CPE is reduced to the classical lumped elements capacitor (C), resistance (R) and inductance (L), respectively. The value of n = 0.5 corresponds to Warburg impedance (W). Values of n can serve as a measure of the surface heterogeneity [48,49]. Note that the capacitances were calculated from Q and R_t using the equation [50-51] :

$$Q = \frac{(C R_t)^n}{R_t} \tag{4}$$

These results are in reasonably good agreement with the values of inhibitor efficiency obtained from polarization technique. It is apparent from Fig. 5 that, the Nyquist plots of C38 steel in uninhibited and inhibited solutions show a semicircular shape. Although the appearance of Nyquist plots remained the same, their diameter increased after the addition of inhibitors to the corrosive solution [52]. This increase was more and more pronounced with increasing concentration of the AIE.

3.2.3. Gravimetric study

Table 3 . Effect of AIE concentration on corrosion data of C38 steel in 1M HCl at 298K.

Inhibitor	Conc. (g/L)	W _{corr} (mg. cm ⁻²)	E _w (%)
Blank	1.0	1.2614	-
AIE	0.6	0.0966	92.34
	0.5	0.1678	86.69
	0.4	0.2430	80.73
	0.3	0.3475	72.45
	0.2	0.5062	59.86
	0.1	0.6110	51.56

Values of corrosion rate and inhibition efficiencies are given in Table 3. The inhibition efficiencies E_w(%) corrosion was calculated from the following equation:

$$E_w(\%) = \left(1 - \frac{W_{cor}}{W_{cor}^o}\right).100 \tag{4}$$

where W_{corr}^0 and W_{corr} are the corrosion rates of C38 steel due to the dissolution in 1 M HCl in the absence and the presence of definite concentrations of the inhibitor, respectively.

According to this table, it is clear that for this *Asteriscus Imbricatus* extract the C38 steel corrosion rate values decrease when the concentration increases. The inhibiting action is more pronounced with 0.6 g/l (92.34%) which is the maximal concentration of *Asteriscus Imbricatus* extract (AIE). The results of electrochemical studies (impedance and polarization measurements) and weight loss measurements were in good agreement with slight deviations.

3.3. Adsorption isotherm

Additional information about the properties of the tested compounds may be provided from the kind of adsorption isotherm. Several adsorption isotherms were tested and the Langmuir adsorption isotherm was found to provide best description of the adsorption behaviour of the investigated inhibitor. The Langmuir isotherm is given by the equation [53]:

$$\frac{C}{\theta} = \frac{1}{K} + C \quad (5)$$

Where C is the inhibitor concentration, θ the fraction of the surface covered determined by percent inhibition efficiency /100, k the equilibrium constant.

Plot C/θ versus C yield a straight line (Fig. 8) with regression coefficient, R^2 , almost equal to 1. This suggests that AIE in present study obeyed the Langmuir isotherm and there is negligible interaction between the adsorbed molecules.

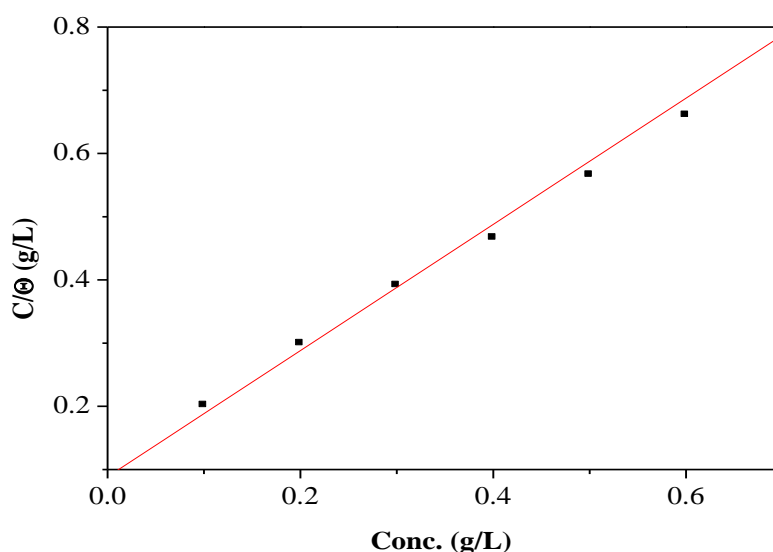


Figure 8. Adsorption isotherm according to Langmuir's model derived from electrochemical impedance spectroscopy

3.4. SEM analysis

Fig. 9 shows the C38 steel surface before corrosion and after immersion in 1.0 M HCl with and without the addition of the AIE at 0.6 g/l after 06 h at 298 K. From Fig. 9a, it can be seen that the fresh C38 steel surface was uniform. However, it can be observed that the C38 steel surface was strongly damaged due to some cracks and pits as a result of the attack of corrosive solution in the absence of inhibitor (Fig. 9b). In presence of AIE inhibitor, the data (Fig. 9c) gave the formation of thick films on C38 steel surface. It is revealed that there is a good protective film adsorbed on the specimen's surface which is responsible for the inhibition of corrosion.

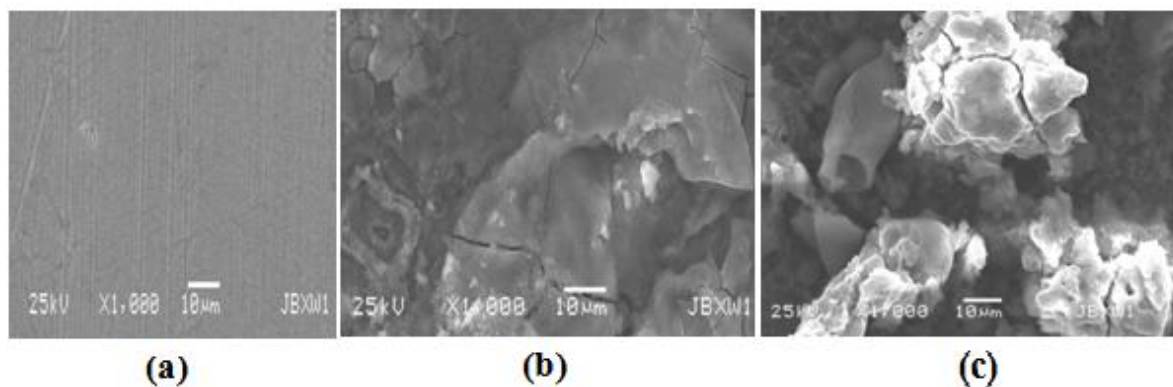


Figure 9. SEM (x2000) of C38 steel (a) before immersion (b) after 6 hours of immersion in 1.0 M HCl (C) after 6 hours of immersion in 1.0 M HCl + 0.6 g/l of AIE.

4. CONCLUSIONS

It can be concluded that:

- As a mixed-type inhibitor AIE inhibits the reduction of H^+ ions by merely blocking the reaction sites of C38 steel surface.
- Inhibition efficiency increases with the increase in the concentration of AIE.
- A good agreement is obtained between the polarization data, electrochemical impedance spectroscopy measurements and gravimetric methods.
- The adsorption of AIE on the C38 steel surface obeys to the Langmuir isotherm model.
- Antifungal activity of extracts of AIE can be easily used with the irrigation water to reduce the damages caused by *botrytis cinerea* in tomato the plants.
- The correlation between traditional healing practices and research of antifungal activity in vitro using medicinal plants as a potential source of natural pesticides.
- The SEM images confirm the protection of C38 steel corrosion in 1.0 M HCl by AIE.

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References

1. F. Fadel, B. Chebli, S. Tahrouch, A. Benddou, A. Hatimi, *Bull. Soc. Pharm. Bordeaux*. 150 (2011) 19.
2. S. Ramesh, S. Rajeswari, S. Maruthamuthu, *Mater. Lett.* 57 (2003) 4547.
3. H. Zarrok, H. Oudda, A. Zarrouk, R. Salghi, B. Hammouti, M. Bouachrine, *Der Pharm. Chem.* 3 (2011) 576.
4. M. Mihit, K. Laarej, H. Abou El Makarim, L. Bazzi, R. Salghi, B. Hammouti, *Arab. J. Chem.* 3 (2010) 55.
5. H. Zarrok, A. Zarrouk, B. Hammouti, R. Salghi, C. Jama, F. Bentiss, *Corrosion Science*. 64 (2012) 243.
6. K. Barouni, L. Bazzi, R. Salghi M. Mihit, B. Hammouti, A. Albourine, S. El Issami, *Mater. Lett.* 62(2008) 3325.
7. S. El Issami, L. Bazzi, M. Mihit, B. Hammouti, S. Kertit, E. Ait Addi, R. Salghi, *Pig. Res. Tech.* 36 (2007) 161.
8. M. Mihit, R. Salghi, S. El Issami, L. Bazzi, B. Hammouti, El. Ait Addi, S. Kertit, *Pig. Res. Tech.* 35(2006) 151.
9. M. Mihit, S. El Issami, M. Bouklah, L. Bazzi, B. Hammouti, E. Ait Addi, R. Salghi, S. Kertit, *Appl. Surf. Sci.* 252(2006) 2389.
10. S. El Issami, L. Bazzi, M. Mihit, M. Hilali, R. Salghi, El. Ait Addi, *J. Phys. IV*. 123 (2005) 307.
11. S. El Issami, L. Bazzi, M. Hilali, R. Salghi and S. Kertit, *Ann. Chim. Sci. Mat.* 27 (2002) 63.
12. R. Salghi, L. Bazzi, B. Hammouti, S. Kertit, *Bull. Electrochem.* 16 (2000) 272.
13. B. Hammouti, R. Salghi, S. Kertit, *J. Electrochem. Soc. India*. 47 (1998) 31.
14. H. Zarrok, A. Zarrouk, R. Salghi, Y. Ramli, B. Hammouti, M. Assouag, E. M. Essassi, H. Oudda and M. Taleb, *J. Chem. Pharm. Res.* 4(12) (2012) 5048.
15. Zarrouk, B. Hammouti, H. Zarrok, R. Salghi, M. Bouachrine, F. Bentiss, S. S. Al-Deyab, *Res Chem Intermed.* 38 (2012) 2327
16. H. Bendaha, A. Zarrouk, A. Aouniti, B. Hammouti, S. El Kadiri, R. Salghi, R. Touzani, *Phys. Chem. News.* 64 (2012) 95
17. A. Zarrouk, H. Zarrok, R. Salghi, N. Bouroumane, B. Hammouti, S. S. Al-Deyab, R. Touzani, *Int. J. Electrochem. Sci.* 7 (2012) 10215.
18. N. Lahhit, A. Bouyanzer, J.M. Desjobert, B. Hammouti, R. Salghi, J. Costa, C. Jama, F. Bentiss, L. Majidi, *Port. Electrochim Acta.* 29 (2011) 127.
19. L. Bammou, M. Mihit, R. Salghi, L. Bazzi, A. Bouyanzer, B. Hammouti, *Int. J. Electrochem. Sci.* 6(2011) 1454
20. M. Larif, A. Elmidaoui, A. Zarrouk, H. Zarrok, R. Salghi, B. Hammouti, H. Oudda, F. Bentiss, *Res Chem Intermed.* (2012) DOI 10.1007/s11164-012-0788-2.
21. D. Ben Hmamou, R. Salghi, A. Zarrouk, B. Hammouti, S.S. Al-Deyab, Lh. Bazzi, H. Zarrok, A. Chakir, L. Bammou, *Int. J. Electrochem. Sci.* 7 (2012) 2361.
22. D. Ben Hmamou, R. Salghi, A. Zarrouk, O. Benali, F. Fadel, H. Zarrok, and B. Hammouti, *International Journal of Industrial Chemistry.* 3 (2012) 25.
23. D. Ben Hmamou, R. Salghi, A. Zarrouk, H. Zarrouk, M. Errami, B. Hammouti, L. Afia, Lh. Bazzi, L. Bazzi, *Res Chem Intermed.* (2012) DOI 10.1007/s11164-012-0609-7.
24. D. Ben Hmamou, R. Salghi, A. Zarrouk, B. Hammouti, S. S. Al-Deyab, Lh. Bazzi, H. Zarrok, A. Chakir, L. Bammou, *Int. J. Electrochem. Sci.* 7 (2012) 2361.
25. L. Afia, R. Salghi, L. Bammou, El. Bazzi, B. Hammouti, L. Bazzi, A. Bouyanzer, *J. Saudia Chemistry Science.* (2011) DOI.org/10.1016/j.jscs.2011.05.008.
26. L. Afia, R. Salghi, El. Bazzi, L. Bazzi, M. Errami, O. Jbara, S. S. Al-Deyab, B. Hammouti, *Int. J. Electrochem. Sci.* 6 (2011) 5918.

27. N. Lahhit, A. Bouyanzer, J. M. Desjobert, B. Hammouti, R. Salghi, J. Costa, C. Jama, F. Bentiss and L. Majidi, *Port. Electrochim. Acta.* 29 (2011) 127.
28. L. Bammou, B. Chebli, R. Salghi, L. Bazzi, B. Hammouti, M. Mihit and H. El Idrissi, *Green. Chem. Lett. Rev.* 3 (2010) 173.
29. D. Ben Hmamou, R. Salghi, A. Zarrouk, M. Messali, H. Zarrok, M. Errami, B. Hammouti, Lh. Bazzi, A. Chakir, *Der Pharma Chemica.* 4(4) (2012) 1496.
30. D. Ben Hmamou, R. Salghi, L. Bazzi, B. Hammouti, S.S. Al-Deyab, L. Bammou, L. Bazzi, A. Bouyanzer, *Int J Electrochem. Sci.* 7 (2012) 1303.
31. L. Afia, R. Salghi, L. Bazzi, M. Errami, O. Jbara, S.S. Al-Deyab, B. Hammouti, *Int J Electrochem. Sci.* 6 (2011) 5918.
32. L. Afia, R. Salghi, L. Bammou, E. Bazzi, B. Hammouti, L. Bazzi, *Acta Metall. Sin.* 25 (2012) 10.
33. L. Afia, R. Salghi, E. Bazzi, A. Zarrouk, B. Hammouti, M. Bouri, H. Zarrouk, L. Bazzi, L. Bammou. *Res Chem Intermed.* (2012) DOI:10.1007/s11164-012-0496-y
34. D. Ben Hmamou, R. Salghi, A. Zarrouk, S. S. Al-Deyab, H. Zarrok, B. Hammouti, E. Errami, *Int. J. Electrochem. Sci.* 7 (2012) 6234.
35. D. Ben Hmamou, R. Salghi, A. Zarrouk, H. Zarrok, O. Benali, M. Errami, B. Hammouti, *Res Chem Intermed.* (2012) DOI 10.1007/s11164-012-0840-2
36. B. Chebli, M. Hmamouchi, M. Achouri, L.M. Hassani, *Journal of Essential Research.* 16(5) (2004) 507.
37. B. Chebli, M. Achouri, L.M. Idrissi Hassani, M. Hmamouchi, *J. Ethnopharmacology*, 89 (2003)165.
38. L. Talibi, H. Askarne, E. H. Boubaker, F. Boudyach, B Msanda, A. Saadi, A. Ait Ben Aoumar, *Crop Protection.* 35 (2012) 41.
39. N. Doho, K. Yamni, A. Badoc, *Bull. Soc. Pharm. Bordeaux.* 143 (2004) 31.
40. O. Senhaji, M. Faid, M. ELYachioui, M, *Medical mycology.* 15 (2005) 220.
41. K.D. Kra, H.A. Diallo, Y. J. Kouadio, *Journal of Applied Biosciences.* 24(2009)1488.
42. F.Z. Bouanis, F. Bentiss, M. Traisnel, C. Jama, *Electrochim. Acta.* 54 (2009) 2371.
43. M.S. Morad, A.M.K. El-Dean, *Corros. Sci.* 48 (2006) 3398.
44. K. Tebbji, B. Hammouti, H. Oudda, A. Ramdani, M. Benkadour, *Appl. Surf. Sci.* 252 (2005) 1378.
45. A. Yurt, A. Balaban, S. Ustun Kandemir, G. Bereket, B. Erk, *Mater. Chem. Phys.* 85 (2004) 420.
46. L. j. M. Vračar, D. M. Dražić. *Corros. Sci.* 44 (2002) 1669.
47. X. H. Li, S. D. Deng. *Corros. Sci.* 509 (2008) 420.
48. Z. B. Stoynov , B. M. Grafov, B. Savova-Stoynova, V. V. Elkin, *Electrochemical Impedance* (in Russian), Nauka, Moscow, 1991.
49. F. B. Growcock, R. J. Jasinski, *J. Electrochem. Soc.* 136(1989) 2310.
50. X. Wu, H. Ma, S. Chen, Z. Xu, A. Sui, *J. Electrochem. Soc.* 146 (1999) 1847.
51. H. Ma, S. Chen, B. Yin, S. Zhao, X. Liu, *Corros. Sci.* 45 (2003) 867.
52. M. Behpour, S. M. Ghoreishi, N. Soltani, M. Salavati-Niasari, *Corros. Sci.* 51 (2009) 1073.
53. F. Mansfeld, M.W. Kending, S. Tsai, *Corrosion.* 37 (1982) 301.