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Eco-friendly *Allium cepa L.* seeds extracts as corrosion inhibitor for mild steel in 1 M HCl solutions

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Abstract

Ethanolic extracts of *Allium cepa L.* seeds were investigated as green corrosion inhibitors for mild steel in 1 M HCl solution. Corrosion behavior was evaluated using weight loss measurements and electrochemical methods. Electrochemical techniques reveal that extracts exhibit excellent inhibition efficiency and act as mixed type inhibitor at the studied temperature (308 K). The inhibition efficiency was reached average values of 94.5% and 88% for mild steel in 1 M HCl solution containing (1 g/L) oilextracted by ethanol from the seeds of *Allium cepa L.*obtained from two regions in Morocco, Doukkala (EED), and Amposta (EET) respectively. Adsorption studies showed that the process follows Langmuir adsorption isotherm.

I. Introduction

In recent years, research into the use of low-cost and eco-friendly compounds as corrosion inhibitors for mild steel were intensified. Natural products as corrosion inhibitors for various metals have been widely studied by several authors [1-5]. Many researchers have studied the use of plant based inhibitor and the results show that this new type of inhibitors is proven effectively to reduce the corrosion rate on the metal [6-12]. The use of natural polymeric structures, derived from extracts of leaves or seeds, as green corrosion inhibitors is receiving strong preference. The metal corrosion inhibition activity of plant extracts can be attributed to the presence of heterocyclic compounds like alkaloids, flavonoids, and other compounds such as tannins, cellulose and polycyclic compounds. These compounds form a thin on the metal surface, thus preventing corrosion.

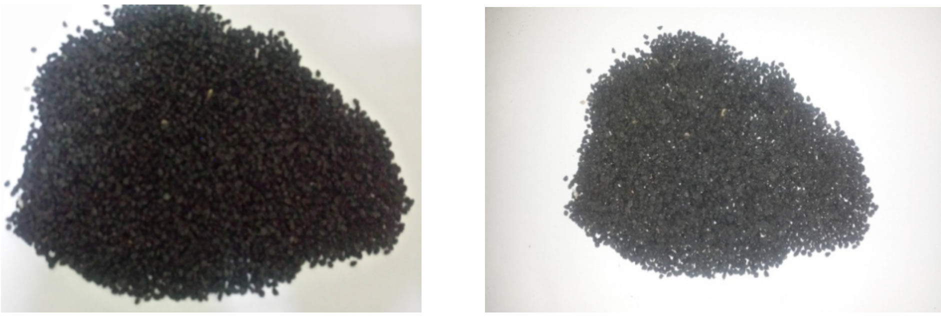
The red onion is an herbaceous species, perennial by its single bulb, grown as an annual or biennial plant. Today, onion is known to have very strong antioxidant properties [13]. It is very rich in a wide variety of cancer protective agents. It is particularly rich in quercetin [14], a protective antioxidant very effective in the prevention of cancers of the digestive tract [15]. Onion is particularly indicated for the bloated or oedematous plethoric patient, dyspeptic, diabetic [16-17], prostatic. It exerts anti-inflammatory, antiallergic activity [18], and helps to prevent certain cancers. Its antiseptic and anti-catarrhal activity [19] makes it useful in the case of colds. Its platelet anti-aggregation activity appears to be insufficient in vivo. It is also neuroprotective [20] and inhibits osteoclastic activity. The onion is due to its properties which prevent the proliferation of cancer cells but also because it destroys the harmful bacteria that can trigger cancer of the stomach [21]. The red onion seeds Amposta crushed are used in medicine Traditional Moroccan to treat asthma attacks [22]. Nevertheless, the data are insufficient with regard to the extraction and use of vegetable oil from the seeds of the red onion which is still unvalued, in particular in the field of the inhibition of corrosive activity [23], It is with this objective that we extracted the oil from the seeds of red onions of two varieties of Morocco Amposta and that of Doukkala [24].

In the present study, the inhibitive effect of the ethanolic extracts of *Allium cepa L.* seeds on corrosion of mild steel in hydrochloric acid solution was investigated using weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) methods.

II. Materials and Methods

II.1. Materials

Hydrochloric acid and ethanol reagents were purchased from (E. Merck). All other chemicals and solvents were of the highest analytical grade and used as supplied. Seeds of two varieties of red onion were harvested from two regions in Morocco, one from Doukkala (EED) and the other one from Tetouan Amposta (EET) in July 2013 as shown in Fig. 1 and Fig. 2.



(a) (b)

Figure 1: Allium cepa L. seeds from, a: Doukkala (EED), b: Amposta (EET)

Figure 2: Places show the two regions in Morocco from where the red onion seeds were obtained

The above map of the northern part of Morocco (Fig. 2), shows the place of Doukkala located to the south-west of Casablanca, the place from which the red onion seeds (EED) were harvested as well as the place of Amposta located in the south-east from Tetouan, from which the other seeds (EET) were obtained.

The seeds of red onion were separated from their envelopes, freed from all impurities, dried outside under the sun for 20 days. After that, the seeds were placed in the oven at 55 °C for 4 hours in order to remove the residual moisture and then they were finely ground and conditioned at laboratory temperature in aluminum foil before doing the extraction process.

II.2. Preparation of ethanolic extracts

100 g of the seeds powder was introduced into a one-liter round-bottomed flask, then 300 mL of ethanol was added. The mixture was refluxed for 20 min and then stirred with magnetic stirrer for 36 hours at room temperature. The mixture was filtered and the filtrate was evaporated under vacuum in order to remove the solvent. The percentage yields of oil obtained from Doukkala (EED) and from Amposta (EET) were equal to 18.5%, and 15.8%, respectively.

II.3. Preparation of corrosive medium

The concentration of the corrosive solution used in this work was 1M HCl. This solution was prepared from the concentrated 37% HCl reagent by dilution using distilled water. The exact molarity of HCl solution was obtained using standard NaOH solution.

II.4. Preparation of Mild Steel Coupons and inhibitors

Mild steel sheet was obtained commercially. The used mild steel coupons have percent composition (% wt.) of 0.09% P, 0.38% Si, 0.01% Al, 0.05% Mn, 0.21% C, 0.05% S and 99.21% Fe. The coupons were abraded using emery paper (400 - 1200 grid); and then rinsed with distilled water, degreased with acetone and dried with warm air before use. The concentrations of 0.125, 0.25, 0.5 and 1 g/L of EED and EET oils in 1 M HCl were prepared by vigorous stirring at room temperature. The volume of the solution for each run was 100 ml of 1 M HCl with inhibitor. The blank test solution was also 100 mL of 1 M HCl, but without inhibitor. All tests were performed in aerated medium at constant temperature of 308 K and under atmospheric pressure by the three methods: gravimetric, polarization and EIS.

II.5. Weight loss, polarization and EIS measurements

Weight loss measurements were carried out in a double walled glass cell equipped with a thermostat-cooling condenser at 308 K (± 1 K). The dimensions of coupons were 1.5 cm x 1.5 cm x 0.05 cm. They were immersed in 1M HCl in the absence and presence of various inhibitor concentrations for 6 hours. The specimens were washed with double-distilled water, dried and then weighed before and after each run. The corrosion rate was presented as mg cm^{-2} h^{-1}. Electrochemical measurements were obtained in a three-electrode configuration, in this system mild steel was the working electrode (WE) in the form of disc cut with 1 cm^2 surface area and was embedded in polytetrafluoro ethylene, a saturated calomel electrode (SCE) was the reference electrode and the disc platinum electrode wasthe auxiliary electrode. The electrochemical analyzer was PGZ100 potentiostat which piloted by Voltamaster soft-ware. The polarization curves are obtained from −800 to −200 mV with the 0.5 mV s^{-1} scan rate. The electrodes reached the stable open circuit potentials after 30 minutes; therefore the exposure time was 30 minutes for each electrochemical measurement. The electrochemical impedance spectroscopy (EIS) measurements were carried out at open circuit potential values for each electrode between 100 kHz and 10 MHz frequency region and sine wave voltage was 10 mV (peak to peak). All experiments were repeated three times to ensure the reproducibility of results.

III. Results and discussion

III.1. Weight loss technique

The corrosion behavior of mild steel in 1 M HCl in the absence and presence of the EET and EED oils was studied at 308 K by the weight loss measurements and the results were tabulated in Table 1. The corrosion rate (v) was calculated using the following equation:

$$v = \frac{w}{st} \quad \textbf{(1)}$$

Where, W is the average weight loss, S is the total area, and t is the immersion time. The inhibition efficiency (E_w) was calculated using following equation:

$$Ew\ \% = \frac{v_0 - v}{v_0} X\ 100 \quad \textbf{(2)}$$

Where, v_0 and v are the corrosion rate without and with inhibitor, respectively.

Table 1: The corrosion rate (v) and inhibition efficiency (E%) data for mild steel in 1 M HCl solutions without and with various concentrations of EET and EED oils at 308 K.

Inhibitor	**Inhibitor Concentration (g/L)**	**v ($mg.cm^{-2}h^{-1}$)**	**E (%)**
Blank (1 M HCl)	-	0.695	-
EET	1	0.027	**96**
	0.5	0.104	85
	0.25	0.143	79
	0.125	0.198	71
EED	1	0.068	**90**
	0.5	0.139	80
	0.25	0.173	75
	0.125	0.253	63

The results of Table1 show that, the corrosion rate decreases as the concentration of ETE and EDE inhibitors increases. The corrosion rate decreases gradually from 0.695 ($mg.cm^{2-}.h^{1-}$) in 1 M HCl solution in the absence of inhibitor to reach a minimum value of 0.027 ($mg.cm^{2-}.h^{1-}$) and 0.068 ($mg.cm^{2-}.h^{1-}$) in the presence of (1g/L) of EET and EED, respectively. On the other hand, the inhibition efficiency (E%) increases with increase in the concentration of both inhibitors. The (E%) increases gradually from 71% and 63% for the concentration of (0.125 g/L) to reach a maximum value of 96% and 90% for the concentration of (1 g/L) of EET and EED, respectively.

The oil obtained from the ethanolic extracts of *Allium cepa L.* seeds of EET and EED are an excellent green nontoxic inhibitors for mild steel in 1 M HCl solutions. Noor et col. [25] reported that the addition of 5.00 mL of aqueous extract of Allium cepa L. seeds acts as good inhibitor for the corrosion of steel in 0.75 M H_3PO_4. They obtained 86.18 % as inhibition efficiency. Moreover, S-Alkenyl Cysteine Sulfoxide was identified from the red onion seeds and its antioxidant activity was evaluated [26]. Noor et col. [28] suggested that $^-NH_3$ and the lone pair of electrons on S atom play an important role for cysteine adsorption on steel surface.

III.2. Electrochemical impedance spectroscopy

The results represented in Table 2 were extracted from Nyquist plots, (EIS) method, that shown in Figures 3 and 4. Table 2 shows that the inhibition efficiency (E%) in 1 M HCl solution increases with the increase in the concentration of both EED and EET inhibitors. The results of (EIS) are in good agreement with the previous gravimetric measurements. Both of them show that EET inhibitor is slightly more effective than EED. The maximum (E%) values for EET and EED are (96% and 90%), respectively using gravimetric method, while the maximum values are (93 and 86%) for EET and EED, respectively using EIS method as shown in Tables 1 and 2.

Table 2: Impedance parameters and inhibition efficiency values for mild steel immersed for half an hour in 1 M HCl solutions without and with different concentrations of EET and EED oils at 308 K.

Inhibitor	**Inhibitor Concentration(g/L)**	**R_{ct} ($\Omega.cm^2$)**	**f_{max} (Hz)**	**C_{dl} ($\mu F/cm^2$)**	**E (%)**
Blank (1 M HCl)	-	20.23	79.36	9.91E-5	-
EED	1.000	147.50	15.82	68.16	**86**
	0.500	117.70	20	67.59	**82**
	0.250	72.07	25	69.77	71
	0.125	57.71	25	87.71	65
EET	1.000	310.00	15.82	32.46	**93**
	0.500	107.80	20	73.85	81
	0.250	70.99	25	89.72	71
	0.125	55.20	31.64	91.17	63

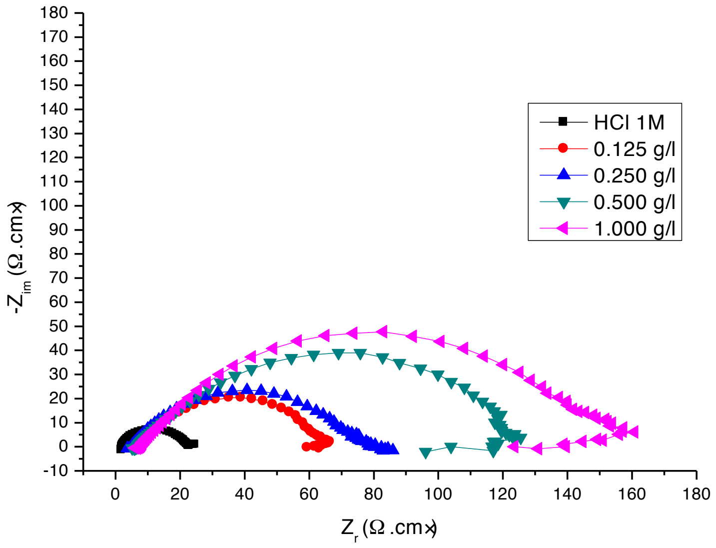


Figure 3 : Nyquist plots for mild steel in 1 M HCl solutions in the absence and presence of various concentrations of EED oil at 308 K.

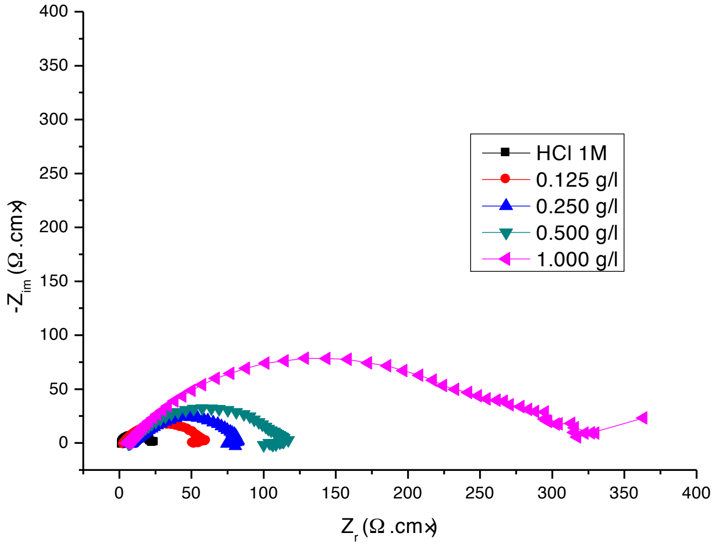


Figure 4: Nyquist plots for mild steel in 1 M HCl solutions in the absence and presence of various concentrations of EET oil at 308 K.

III.3. Potentiodynamic polarization study

Tafel plots show a linear relationship between electrode potential (E) and the logarithm of current (log i), if the electrode is sufficiently polarized to a large potential values, in both anodic and cathodic directions. These regions are very well known and called Tafel regions. By passingthe potentiallineson both sides of the anodic and cathodic Tafel regions linearly and extrapolating them to corrosion potential (E_{corr}), the points of intersectionsgive the corresponding corrosion current density (i_{corr}) values. The plot of E versus log i in the anodic and cathodic Tafel regions gives the corresponding Tafel slopes (βa and βc). The percentage inhibition efficiency (E_p%) values were calculated using the following equation (3):

$E_p\% = (i_{corr(0)} - i_{corr(inh)} / i_{corr(0)})*100$ **(3)**

where $i_{corr(0)}$ and $i_{corr(inh)}$ represent corrosion current density values without and with inhibitor, respectively.

Polarization curves for mild steel in 1 M HCl solution at 308 K in the absence and presence of EED and EET oils are shown in Figures 5 and 6. All the calculated electrochemical corrosion parameters such as corrosion current density (i_{corr}), corrosion potential (E_{corr}), anodic and cathodic Tafel slopes (βa and βc, respectively) are presented in Table 3.

Table 3: Polarization parameters and inhibition efficiency for mild steel in 1M HCl solutions in the absence and presence of various concentrations of EED and EET oils at 308 K.

Inhibitor	Concentration Inhibitor (g/L)	$-E_{Corr}$ (mV)	β_C (mV/dec)	β_a (mV/dec)	I_{Corr} (mA/cm^2)	E (%)
Blank (HCl)	-	460.3	-267.4	219.1	2.9796	-
EED	1.000	-506.1	-143.3	93.9	0.2468	**91**
	0.500	-494.3	-128.5	110.3	0.3492	88
	0.250	-503.6	-224.6	148.5	0.5503	81
	0.125	-483.7	-291.1	258.0	1.9631	34
EET	1.000	-498.6	-110.4	102.5	0.0548	**98**
	0.500	-509.8	-170.7	110.5	0.2740	91
	0.250	479.4	-201.3	145.0	0.9654	68
	0.125	-485.5	-310.9	216.4	1.2844	57

From the polarization curves (Tafel plots), Figures 5 and 6, the corrosion current density (i_{corr}), corrosion potential (E_{corr}), and anodic (βa) and cathodic (βc) Tafel slopes were determined and tabulated in Table 3. The values of βa and βc indicate that both EET and EED behave as mixed type inhibitors. This method shows also that EET inhibitor ($E\%_{(max)}$= 98%) is more efficient than EED ($E\%_{(max)}$ = 91%). These results are also in good agreement with the previous gravimetric and EIS methods.

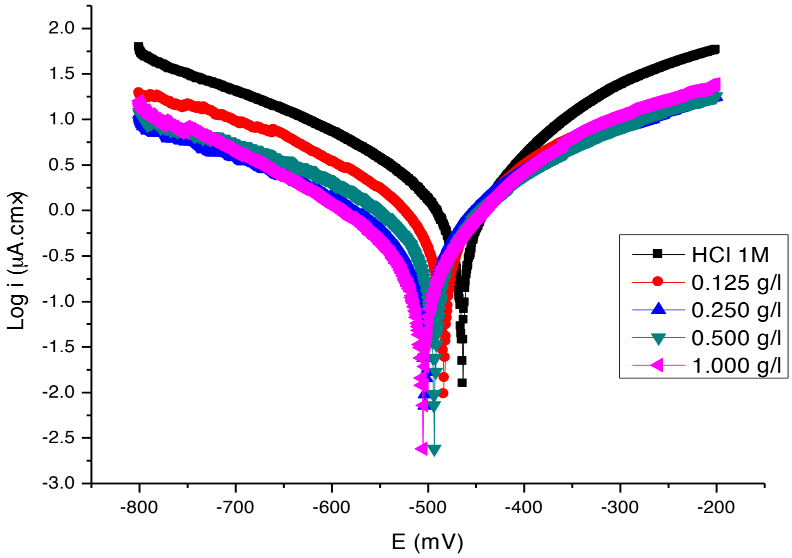


Figure 5: Potentiodynamic polarization curves for mild steel in 1 M HCl solutions in the absence and presence of various concentrations of EED oil at 308 K.

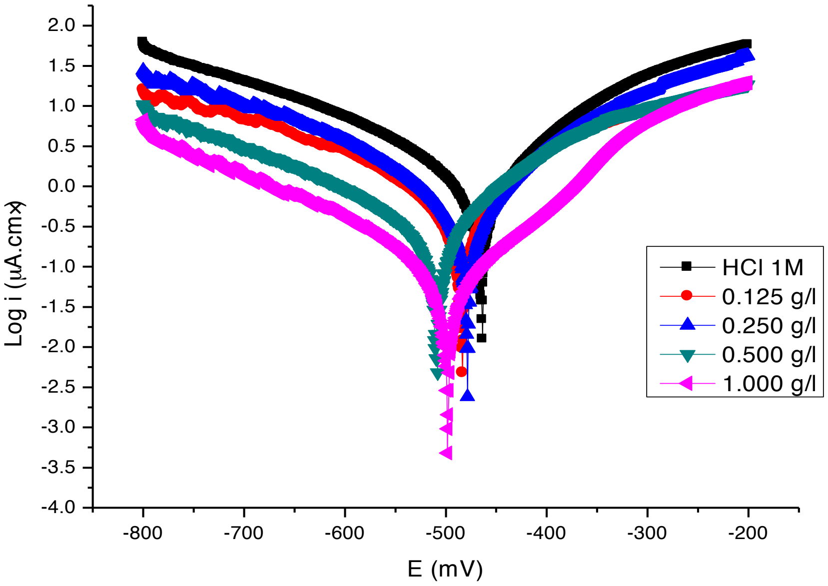


Figure 6: Potentiodynamic polarization curve for mild steel in 1 M HCl solutions in the absence and presence of various concentrations of EET oil at 308 K.

Conclusions

From the results obtained in this study, the following can be concluded:

1- The ethanolic extracts of *Allium cepa L.* seeds were found to an excellent eco-friendly corrosion inhibitors for mild steel in 1 M HCl solution.
2- The Inhibition efficiency increases with the increase in the concentration of EET and EED inhibitors.
3- The Inhibition efficiency for mild steel in 1 M HCl in the presence of the inhibitor was so high, and reached an average value of (96% ± 3%) and (89%± 3%) at a concentration of (1 g/L) of EET and EED inhibitors, respectively.
4- Both EET and EED inhibitors behave as a mixed type inhibitor.
5- EET inhibitor is more efficient as a corrosion inhibitor for mild steel in 1 M HCl than EED.

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