

Electrochemical investigations on the corrosion inhibition of aluminum by Green Leafy Vegetables in 1M HCl

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Abstract: The effects of *Lactuca sativa* (*Lactuca*) extracts on the corrosion of aluminum in 1M HCl were investigated as environmentally safe corrosion inhibitors using Potentiodynamic polarization and weight loss measurements. Surface morphology was tested by scanning electron microscopy (SEM). The results show that inhibition efficiencies increased with increase in extract concentrations. The adsorption of the inhibitor extract on aluminum surface is spontaneous and obeys Langmuir's isotherm. The results obtained from polarization measurements indicate that the *Lactuca sativa* (*Lactuca*) extracts act as mixed-type inhibitor with predominant anodic effectiveness.

[Sameerah I. Al-Saeedi, Ghadah M. AL-Senani, and Rasmiah Almufarij. **Electrochemical investigations on the corrosion inhibition of aluminum by Green Leafy Vegetables in 1M HCl.** *Life Sci J* 2016;13(12):100-105]. ISSN: 1097-8135 (Print) / ISSN: 2372-613X (Online). <http://www.lifesciencesite.com>. 14. doi:[10.7537/marslsj131216.14](https://doi.org/10.7537/marslsj131216.14).

Keywords: Hydrochloric acid, Corrosion inhibition, Green Leafy Vegetables, Adsorption

1. Introduction

Aluminum is one of the most widely used metals, in competition with steel, and increasingly utilized in the fields of architecture, transportation, and public works[1-5] Aluminum is used excessively in the modern world, and the uses of the metal are extremely diverse due to its many unusual combinations of properties as low cost, low density, good corrosion resistance, excellent electrical and thermal conductivities[6-8]. The corrosion resistance of aluminum and its alloys comes from the compact film on the metal surfaces upon exposure to the atmosphere or aqueous solutions, but the film will not protect the aluminum surface in corrosive media that contain high chloride concentrations[9,10]. A great number of investigations have been done to find effective inhibitors for aluminum corrosion in harsh environments[11,12] some researcher studied the use of chemical inhibitors and the effect of organic oxidants while others studied the use of organic compounds, the corrosion can be controlled by the selection of highly corrosion resistant materials with the considerations of toxicity, availability, cost and environmentally safe which mean the replacement of some toxic, expensive chemical inhibitors by inhibitors obtained from natural source. Recently, natural products as plant extracts which contain natural chemical compound have been used as corrosion inhibitors in many corrosion systems [13], which can be extracted by simple procedures with low cost provide both environmental and economic benefits.

The main aim of this work is to investigate the corrosion inhibition of aluminum in 1M HCl by the extracts of *Lactuca sativa* (*Lactuca*) using weight loss, Potentiodynamic polarization measurements and scanning electron microscopy (SEM).

2 Experimental

2.1 Materials and solution

Pure aluminum electrodes with exposed surface area of 1 cm² were exposed to electrolytes, the electrodes were ground with 800 and 1200 grit grinding papers and rinsed with distilled water and acetone. The electrochemical cell was a three-electrode all-glass cell, with a platinum counter electrode and saturated calomel reference electrode.

Fourier transforms infrared spectroscopy (FT-IR):

A KBr pellet was made from the dried extract and was characterized using FT-IR (Nicolet's auxiliary experiment module - AEM, Omnic software).

Preparation of plant extract:

GLV were dried in an electric furnace for 10 – 20 min at 50°C then ground to powder. *GLV* dried powder (5g) were mixed with 500 ml of 1 M HCl and refluxed at 50°C for 2 h. The extracts were cooled, and filtered through Whatman filter paper. The filtrate was then kept as the stock solution. Working solutions of different concentrations ranging from 20 to 60 % (v/v) were prepared from the stock solutions by dilution with 1 M HCl solution.

Test solutions

The test were performed in 1M HCl solution with the addition of various concentrations of *GLV* extract, for each run, freshly prepared solution was used.

During the experiments, the test solutions were opened to the air and experiments were performed under static conditions. The temperature of the test solution was controlled by immersing the cell in a water thermostat.

2.2 Weight loss measurements

Specimens of aluminum were used for weight loss measurements. The cleaned and dried specimens were completely immersed in 100 ml of 1M HCl solution with and without inhibitor for a period of 3-12 h the specimens were washed, dried and weighed using analytical balance. The weight loss was calculated in different concentrations of the inhibitor (0.1- 0.5 g/l) and temperature (298K).

2.3 Potentiodynamic polarization measurements

Electrochemical measurements were carried out using ACM instruments model 1783. The electrochemical cell consisted of a conventional three-electrode configuration with graphite as the counter electrode and a saturated calomel electrode (SCE) coupled with a Luggin-Haber capillary as the reference electrode. The tip of the Luggin capillary was placed very close to the surface of the working electrode in order to minimize the ohmic contribution.

The working electrode was prepared from aluminum with area exposed to solution of 1 cm^2 .

The working electrode was immersed in tests solutions in which the mixtures included 1 M HCl at 25°C with and without the inhibitor.

The polarization curves were obtained potentiodynamically with a scan rate of 0.2 mVs^{-1} in the potential range of $\pm 250\text{ mV}$ proportional to the potential of corrosion.

2.4 Scanning electron microscope (SEM):

Surface morphology of aluminum surface was examined after the required experiments using scan electron microscopy (SEM) model JSM-6380 LA with a high resolution of 3.0 nm and an accelerating voltage of 0.5 to 30 kV.

3. Result and dissection

3.1. FTIR results of GLV extracts

The important IR absorption bands of inhibitors are given in Fig. 1 and their respective FT-IR peaks are in Table 1. These results showed that the inhibitors containing functional groups with O and N atoms and other attached to aromatic ring, which commonly gather in corrosion inhibitors.

Table 1: FT-IR Peaks of GLV Extracts

Inhibitors GLV	Peaks from FT-IR spectra	Possible functional groups
Lactuca sativa (Lactuca)	414.78	C-C (aliphatic)
	603.00	-C=C stretch
	1055.94	P-O-C stretch
	1245.22	O-SO ₂ -O
	1407.43	X-SO ₂ -X
	1614.37	C=N stretch
	2922.57	C-H (aromatic)
	3345.47	NH ₂ stretch
	3738.73	N-C (aromatic)

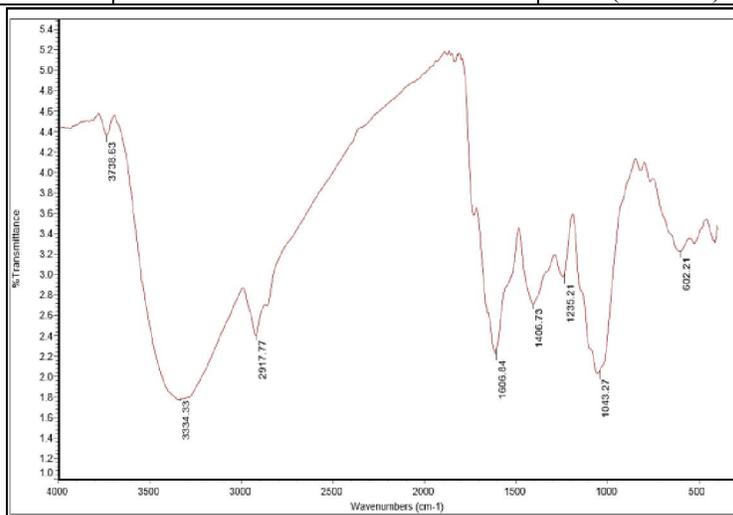


Fig. 1. FTIR Spectra of GLV Extract Lactuca sativa

3.2. Weight loss measurement

From the weight loss measurements of aluminum specimens in 1M HCl in the absence and presence of different concentrations Lactuca sativa extract at 298K, the corrosion rate and inhibition efficiency were calculated and the results are shown in Table 2.

The inhibition efficiency $\eta_w\%$ and the corrosion rate C_R are calculated using Eqs. (1) and (2), respectively [14-15].

$$\eta_w\% = \frac{C_{R0} - C_R}{C_{R0}} \times 100 \quad (1)$$

$$C_R = \frac{W}{At} \quad (2)$$

C_R is the corrosion rate ($\text{mg cm}^{-2} \text{h}^{-1}$) in the presence of inhibitor

C_{R0} in the absence of inhibitor

W is the weight loss (mg)

A is the exposed surface area (cm^2)

t is the exposure time (h)

Table 2. Corrosion rate (CR) and inhibition efficiency ($\eta_w\%$) values for the corrosion of aluminum in HCl in the absence and presence of different concentration of Lactuca sativa extracts at 298K.

Lactuca sativa extracts conc.(g/L)	C_R ($\text{mg/cm}^2\text{h}) \times 10^{-5}$	$\eta_w\%$
Blank	5.12	-
0.1	4.12	21
0.2	3.11	41
0.3	3.32	50
0.4	1.54	70
0.5	1.02	82

The results indicate a decrease in the corrosion rate of aluminum in the presence of Lactuca sativa (Lactuca) extract as shown in Table.2, and the corrosion rate decrease with the increase in the concentration of Lactuca sativa (Lactuca) extract, the inhibition efficiency increase with the presence of

Lactuca sativa (Lactuca) and the inhibition efficiency increases with the increase in the concentration of the corrosion inhibitor extract. The results indicate that the inhibitor extract decrease the corrosion rate of aluminum in HCl at all concentration used in this study and this result is most likely due to the adsorption of the organic compounds present in Lactuca sativa extract on aluminum surface [16-19].

3.2 Potentiodynamic polarization measurements

Fig.2 presents the potentiodynamic polarization curves of aluminum in 1M HCl with different concentrations of Lactuca sativa extracts at 298K. The electrochemical parameters i.e., corrosion potential (E_{corr}), corrosion current density (i_{corr}), anodic Tafel constant (β_a), cathodic Tafel constant (β_c), were calculated from tafel plots and shown in Table.3.

Potentiodynamic polarization curves indicate that the Lactuca sativa extracts caused a decrease in both anodic and cathodic current densities, which can be explained by the adsorption of the organic compounds present in the inhibitor extracts at the active sites of the aluminum surface. As Those aromatic rings or multiple bonds, found in organic compound acted as mixed type inhibitor [20,21],

Table 3 indicates that, in the presence of Lactuca sativa extracts, E_{corr} shifted anodically with respect to the blank. Which indicates that the Lactuca sativa extracts acts as a mixed-type inhibitor with predominant anodic effectiveness [22-24].

The inhibition efficiency ($\eta\%$) can be calculated from the electrochemical relation:

$$\eta_w\% = \frac{i - i_{\text{corr}}}{i} \times 100 \quad (3)$$

where i and i_{corr} are the corrosion current density values without and with inhibitor, respectively.

The results show that the inhibition efficiency increased and the corrosion current density decreased with the increased of inhibitor concentration.

Table 3. The values of corrosion potential (E_{corr}), corrosion current density (i_{corr}), anodic Tafel constant (β_a), cathodic Tafel constant (β_c), and inhibition efficiency ($\eta\%$) for aluminum in HCl in the absence and presence of different concentrations of Lactuca sativa extracts at 298K.

Concentration (g/L)	E_{corr} (mV)	β_a (mV)	β_c (mV)	I_{corr} (mA cm^{-2})	$\eta_w\%$
0	-866.13	241.11	121.07	12.33	-
0.1	-831.35	133.30	110.90	5.31	75.5
0.2	-829.60	101.75	114.30	3.18	80.8
0.3	-828.34	112.4	79.84	2.98	91.4
0.4	-816.97	111.12	89.23	0.85	94.7
0.5	-813.52	110.77	109.50	0.77	98.6

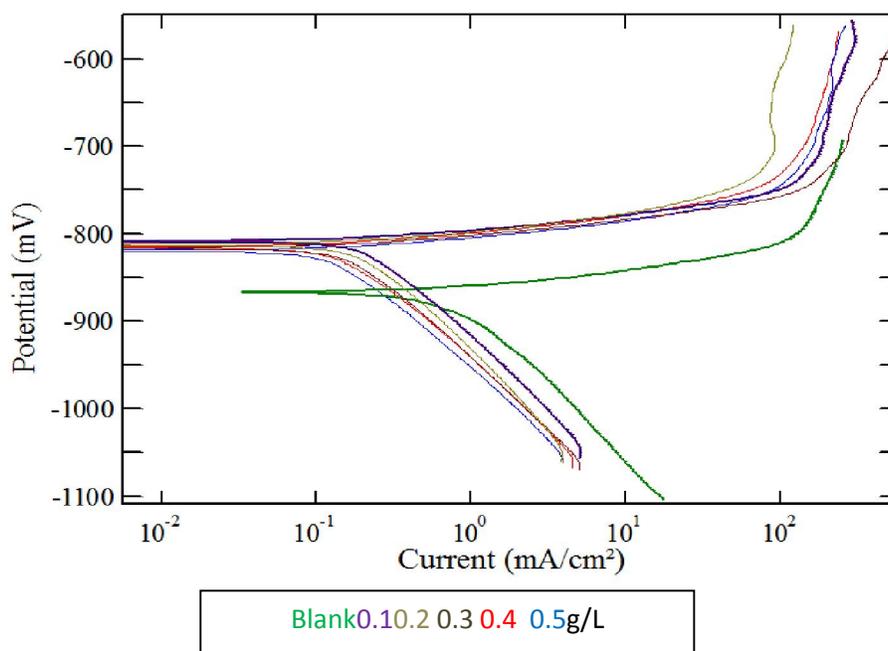


Figure 2. Potentiodynamic polarization curves of aluminum in 1M HCl in the absence and presence of different concentrations of *Lactuca sativa* extracts at 298K.

3.3 Application of adsorption isotherm

In our study different adsorption isotherms including Langmuir, Frumkin, Temkin and Freundlich used to test the data obtained from weight loss measurements, and potentiodynamic polarization measurements to determine the possible adsorption mode. The result indicate that the best fit was obtained with the Langmuir adsorption isotherms. According to Langmuir isotherm θ is related to the inhibitor concentration C_{inh} via [25].

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \quad (4)$$

Fig. 3 shows curve fitting of polarization and weight loss data a linear relationship was obtained and using the intercepts of the straight line K_{ads} can be calculated, then (ΔG°_{ads}) the standard energy of adsorption can be calculated [26].

$$\Delta G^{\circ}_{ads} = -RT \ln(K_{ads}) \quad (5)$$

Where R is the universal gas constant and T is the thermodynamic temperature.

The regression coefficient R^2 and lines slopes and calculated standard energy of adsorption are listed in Table 4. The results indicates that the value of regression coefficient R^2 almost equal to unity, the slop of the straight liens are almost unity, a high value of the adsorption equilibrium constant K_{ads} , and negative value of ΔG°_{ads} which can be explain as follow the value of regression coefficient R^2 almost equal to unity confirmed that the adsorption of *Lactuca sativa* extracts on the metal surface follows

Langmuir adsorption isotherm, a high value of the adsorption equilibrium constant K_{ads} indicate the high adsorption ability of *Lactuca sativa* extract on the metal surface. The negative value of ΔG°_{ads} means a spontaneous adsorption of *Lactuca sativa* extract on the metal surface and a strong interaction between inhibitor molecules and metal surface.[27-32].

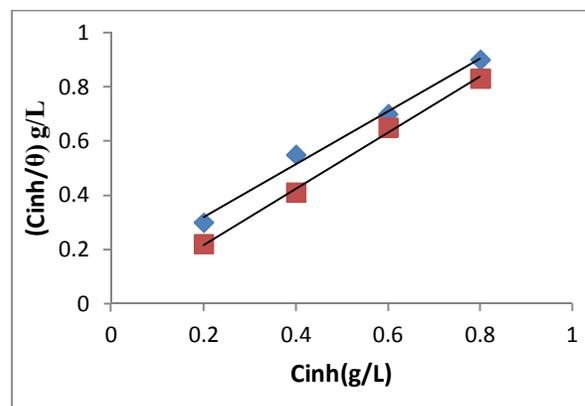


Fig. 3. Curve fitting of polarization and weight loss data obtained for aluminum electrode in 1M HCl containing *Lactuca sativa* extracts to Langmuir adsorption isotherm at 298 K.

Table 4. Adsorption isotherm parameters obtained from the corrosion data for aluminum in HCl containing *Lactuca sativa* extracts at 298K.

Method	R ²	slope	K _{ads} (L/g)	ΔG° _{ads} (kJ/mol)
Weight loss	0.997	0.986	14.92	- 22.51
Polarization	0.995	0.988	16.77	-21.99

3.4 The morphology investigation

The morphology of the aluminum surface in the absence and presence of 0.4 g/L *Lactuca sativa* extracts at 298K was investigated by SEM. Fig.4a shows the SEM image of polished aluminum surface, the surface is smooth with no corrosion product. The SEM image for aluminum in 1M HCl shows that the surface is severely corroded due to the aggressive attack by HCl as we can see from Fig.4b. In the

presence of the inhibitor used in this study less corrosion attack was observed as we can see from Fig.4c. The presence of inhibitor used in this study decrease the corrosion products on the metal surface which can be explained by the adsorption of the *Lactuca sativa* extracts as inhibitor on aluminum surface which protect the metal surface from corrosion by the adsorption of the organic compounds present in the inhibitor on aluminum surface.

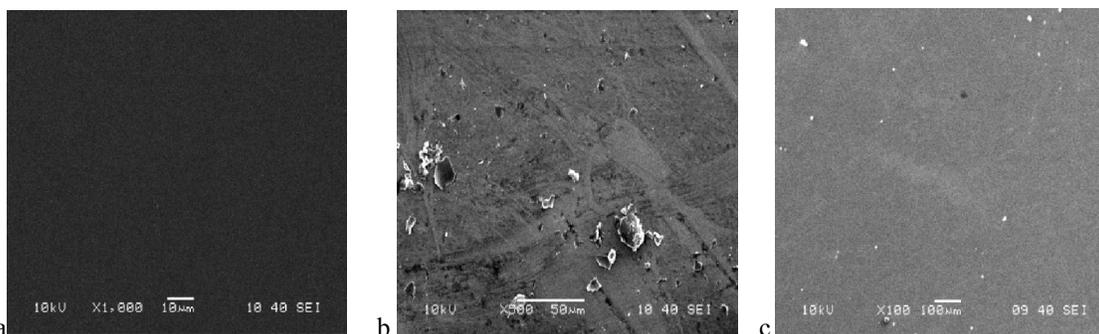


Fig 4: SEM image of aluminum electrode (a) polished, (b) in 1M HCl and (c) in 1M HCl with 0.4 M inhibitor.

4. Conclusion

1. *Lactuca sativa* extracts acts as a good inhibitor for the corrosion of aluminum in acidic media.
2. The inhibition efficiency of *Lactuca sativa* extracts increase with increasing the concentration of the extract.
3. The inhibition efficiencies obtained from potent iododynamic polarization and weight loss methods are in good agreement.
4. The adsorption of *Lactuca sativa* extracts on aluminum surface obeys Langmuir adsorption isotherm.
5. potentiodynamic polarization curves reveal that *Lactuca sativa* extracts is a mixed-type inhibitor with predominant anodic inhibitor.
6. The value of ΔG°_{ads} indicate that the adsorption of *Lactuca sativa* extracts was a spontaneous physisorption process.

Acknowledgment

The researchers would like to thank the Deanship of Scientific Research at Princess Nourahbint Abdulrahman University for providing the funding for this study under project number.72-35.

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