Environmentally safe corrosion inhibition of aluminum by greenleafy vegetables extracts in 1M HCl

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Abstract: The corrosion inhibition of aluminum was investigated in HCl solution using *Petroselinum Crispum* (Parsley) extracts as environmentally safe corrosion inhibitors. The corrosion inhibitor efficiency was tested using weight loss measurement and the surface morphology was tested by scanning electron microscopy (SEM). The corrosion rate was calculated in the absence and the presence of the GLV extracts the inhibition efficiency increased with the increase in GLV extracts concentration and decrease with temperature. The corrosion inhibition process was investigated. The activation energy and the heat of adsorption were calculated all data reveal that the adsorption of extract on the aluminum surface is a physical adsorption and obeys Langmuir's isotherm.
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1. Introduction

Aluminum and its alloys are today the most used metals in electrical transmission lines and network distribution, its electrical conductivity and processability make it the material of choice in a wide variety of applications, the corrosion of aluminum and its alloys limits their use as ideal structural materials for the lightweight engineering applications [1,2] The corrosion resistance of aluminum depends on the formation of thin protective film on the surface [3-5]However, halide ions, spatially chloride ions (Cl^-), show a strong attack to this passive film, it penetrate and accumulate at the defect sit on the passive layer at the metal surfaceinitiating the corrosion at different forms, as pits grow, they often develop into intergranular corrosion the corrosion products can lead to a layered appearance, known as exfoliation corrosion [6-8] Therefore it is important to find a way to protect metals against electrochemical corrosion, the use of corrosion inhibitors is usually the best way to achieve this goal [9-11]some surface pretreatments such as chromate have been used in commercial application in order to improve corrosion resistance of metals [12].Chromate containing materials are extremely environmentally hazardous and their uses are highly restricted worldwide [13]. Therefore it is important to find other environment-friendly materials that can provide a good protection of aluminum.

Natural products as plant extracts which contain natural chemical compound have been used as corrosion inhibitors in many corrosion systems [14], which can be extracted by simple procedures with low cost provide both environmental and economic benefits.

The aim of this work is to investigate the corrosion inhibition of aluminum in 1M HClby GLV extract *Petroselinum Crispum* (Parsley) using weight loss, and scanning electron microscopy (SEM) The corrosion rate and corrosion inhibition efficiency were calculated using different concentration of the inhibitor at different temperature.

2. Experimental

2.1. Specimen preparation

The working electrode was made of pure aluminum with exposed area of 1 $cm^2$to contact with the corrosive medium. The electrochemical cell was a three-electrode all-glass cell, with a platinum counter electrode and saturated calomel reference electrode. Before each experiment, the working electrodes were ground with 800 and 1200 grit grinding papers and washed with distilled water and acetone.

2.2. Inhibitors

GLV were dried in an electric furnace for 10-20 min then ground to powder. GLV dried powder (5g) were mixed with 500 ml of 1M 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 (0.1- 0.5 g/l) were prepared from the stock solutions by dilution with 1M HCl solution.

2.3. Fourier transform infrared spectroscopy (FT-IR)

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

2.4. 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 The weight loss was calculated in different concentrations of the inhibitor (0.1- 0.5 g/l) and two temperature (298K,333K).

2.5. SEM

Surface morphology of aluminum surface was examined after the each experiments using scan electron microscopy (SEM) available at KSU.

3. Results and discussion

3.1. FTIR results of GLV extracts

The important IR absorption bands of *Petroselinum Crispum* (Parsley) are given in Fig. 1 and their respective FT – IR peaks are given in Table 1. The results showed that *Petroselinum Crispum*(Parsley) contain functional groups with O, N atoms and aromatic ring, which commonly appear in corrosion inhibitors

3.2. Weight loss measurement

3.2.1. Corrosion rates

Using the weight loss measurements of aluminum in 1M HCl in the absence and presence of different concentrations of *Petroselinum Crispum* (Parsley) extract at 298K, the corrosion rate and inhibition efficiency were calculated and the results are shown in Table 2.

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

$$\eta_w\% = \frac{\mathrm{CR0} - \mathrm{CR}}{\mathrm{CR0}} \times 100 \qquad (1)$$

$$C_R = W/_{At} \qquad (2)$$

$C_R$is the corrosion rate (mg cm^{-2} 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)

The results on Table 2. indicate decrease in the corrosion rate of aluminum in the presence of *Petroselinum Crispum* (Parsley) extract, it is clear that the corrosion rate decrease with the increase in the concentration of *Petroselinum Crispum* (Parsley) extract, and the inhibition efficiency increase with the presence of parsley extract 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 parsley extract on aluminum surface [16]

3.2.2. Activation energy and heat of adsorption

Table 3.Summarized the effect of increase in solution temperature on the corrosion rate C_R of aluminum in the absence and presenceof different concentration of *Petroselinum Crispum* (Parsley) extract and the degree of surface coverage ($\theta = \frac{\eta w\,\%}{100}$). Using Arrhenius equation [17] the apparent activation energy E_a of the corrosion reaction was calculated as follows:

$$\mathrm{Log} = \frac{CR2}{\mathrm{CR1}} = \frac{Ea}{2.303R}\left(\frac{1}{T1} - \frac{1}{\mathrm{T2}}\right) \qquad (3)$$

C_{R1} andC_{R2} are the corrosion rates at temperature T_1 and T_2, respectively.

Q_{ads} (heat of adsorption) was calculated from the trend of surface coverage

θ with temperature as follows [18]:

$$Q_{ads} = 2.303\left(\log\frac{\theta 2}{1-\theta 2} - \log\frac{\theta 1}{1-\theta 1}\right) \times \left(\frac{T1T2}{T2-T1}\right) \qquad (4)$$

θ_1 and θ_2 are the degrees of surface coverage at temperatures T_1 and T_2 the value of θ_1,θ_2,$E_a$and $Q_{ads}$are shown in Table 3.

The results in Table 3.Shows a higher values of E_a in the presence of different concentrations of *Petroselinum Crispum* (Parsley) extract which suggest a physical adsorption of (Parsley) extract molecules on the aluminum surface, causing the increase in the activation energy [19].with the increase of(Parsley) extract concentrations the value of E_a increases which indicate that the presence (Parsley) extract increase the energy barrier for the corrosion reaction and with the increase of (Parsley) extract concentrations the energy barrier increase [20].

The adsorption process is exothermicin nature as we can see from the negative value of Q_{ads} and the negative values of Q_{ads} indicate decrease in the degree of surface coverage with the increase in temperature that due to the process of physical adsorption is usually rapid and reversible but the process in chemisorption are relatively slow and not reversible due to the chemical reactions occurs at the metal surface [21-23].

3.3. Adsorption Isotherms

The adsorption of molecules of plant extract onto the metal surface can be explained by several adsorption isotherms applying the experimental data on those isotherms will determine the corrosion inhibition mechanism. The expiration for several adsorption isotherms can be written as eq.5 [24-26]

$$f(\theta,X)\exp(-\alpha\theta) = K_{ads}C \qquad (5)$$

$f(\theta, X)$ is the configuration factor, it depend in the physical model and the proposed isotherm

X is the size ratio which represents the relative size of the adsorbed molecule to the solvent molecule
A is the molecular interaction
C is the inhibitor concentration
K_{ads} is the adsorption equilibrium constant.
We used different adsorption isotherms including Langmuri, Frumkin, Temkin and Freundlich to test the data obtained from weight loss measurements, the best fit was obtained with the Langmuriadsorption isotherms. According to Langmuri isotherm θ is related to the inhibitor concentration C_{inh} via [27]

$$\frac{Cinh}{\theta} = \frac{1}{Kads} + C_{inh} \quad (6)$$

Fig.2 shows the plot of $C_{inh}/\ \theta$ verses C_{inh} a linear relationship is 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 [28].

$$\Delta G^{\circ}_{ads} = -\ RT \ln (K_{ads}) \quad (7)$$

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

The isotherm parameters were calculated and listed in Table 4. The value of regression coefficient R^2 almost equal to unity confirmed that the adsorption of *Petroselinum Crispum* (Parsley) extract on the metal surface follows Langmuir adsorption isotherm. The slop of the straight liens are almost unity which suggest adsorption isotherm of the inhibitor molecules was of monolayer on the metal surface and there is no interaction between the adsorbed inhibitor molecules[29] the high value of the adsorption equilibrium constant K_{ads} indicate the high adsorption ability of *Petroselinum Crispum* (Parsley) on the metal surface. The negative value of ΔG°_{ads} means a spontaneous adsorption of the *Petroselinum Crispum* extract on the meatal surface and a strong interaction between inhibitor molecules and metal surface.[30] the corrosion inhibition was due to the electrostatic interactions between the charged molecules and the charged metal surface as we can see from the value of ΔG°_{ads} which is less than 20KJ/mol and this indicate a physical adsorption.

3.4. The morphology of the Surface

Using the scanning electron microscope (SEM) the morphology of the aluminum surface were taken Fig.3a shows the SEM image of polished aluminum surface, the surface is smooth with no corrosion product Fig.3b shows the SEM image for aluminum in 1M HCl the image revel that the surface is severely corroded due to the aggressive attack by HCl. In the presence of the inhibitor used in this study (*Petroselinum Crispum* extract) less corrosion attack was observed as we can see from Fig.3c. the improvement in the metal surface can be explained by the adsorption of the inhibitor (Parsley) extract on the metal surface a good protective film adsorbed on the metal surface which reduce the corrosion rate. The adsorption of the organic compounds present in Parsley extract on aluminum surface induce the inhibition of aluminum in aggressive media as most of the organic compounds have at least one polar atoms that act as the reaction center for the adsorption process.

Table 1: FT-IR Peaks of GLV Extracts *Petroselinum Crispum* (Parsley)

Inhibitors GLV	Peaks from FT-IR spectra	Possible functional groups
Petroselinum Crispum(Parsley)	403.20	C–C (aliphatic)
	617.89	–C=C stretch
	1068.10	P–O–C stretch
	1247.46	$O–SO_2–O$
	1411.10	$X–SO_2–X$
	1614.22	C=N stretch
	2927.20	C–H (aromatic)
	3339.39	N–H stretch

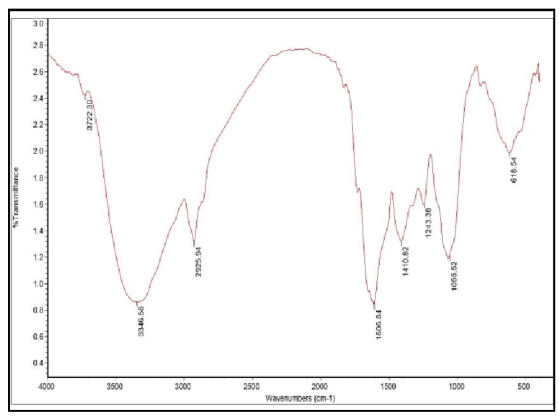

Fig. 1. FTIR Spectra of *GLV* Extract *Petroselinum Crispum* (Parsley)

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

Petroselinum Crispum (Parsley) extracts conc.(g/L)	C_R (mg/cm^{2}h)×10^{-5}	η_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

Table 3. the values of corrosion rate (CR), degrees of surface coverage (), activation energy (Ea) and heat of adsorption (Q_{ads}) for aluminum in HCl at the absence and the presence of different concentrations of Parsley extract at298 and 333K.

Extract con.(g/L)	C_{R1}(mg/cm^{2}h)×10^{-5} 298 K	C_R (mg/cm^{2}h)×10^{-5} 333K	θ_1 298 K	θ_2 333K	Ea kJ/mol	Q_{ads} kJ/mol
Blank	5.33	9.1	-	-	16.11	-
0.1	4.42	8.1	0598	0.491	17.2	- 15.9
0.2	3.21	7.2	0.633	0.553	23.1	- 11.32
0.3	3.01	9.9	0.719	0.616	23.8	- 13.12
0.4	1.51	4.2	0.881	0.734	28.49	- 17.71
0.5	1.01	3.1	0.961	0.892	30.21	- 19.13

Table 4. R^2 and slope

R^2	slope	K_{ads}(L/g)	ΔG°_{ads}(kJ/mol)
0.997	0.986	14.92	- 22.51

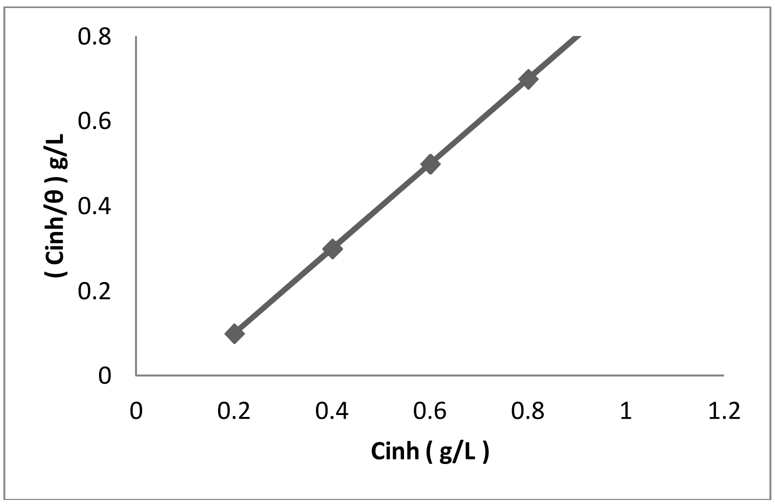

Fig. 2. Curve Fitting of weight loss data for aluminum electrode in HCl containing parsley extract to langmuri adsorption isotherm at 298 K.

Fig.3. SEM image of aluminum electrode (a) polished, (b) immersed in 1M HCl and (c) immersed in 1M HCl containing 0.3 M Inhibitor.

4. Conclusion

1- Parsley extract is a good inhibitor for the corrosion of aluminum in HCl solution, the inhibition efficiency depends on the concentration of the inhibition and the temperature.

2- The inhibition efficiency of Parsley extracts increases with increasing the concentration of the inhibitor, and decreases with the increase of temperature.

3- Langmuri adsorption isotherm is the best fit to explain the efficiency of Parsley extracts to inhibit the corrosion of aluminum in HCl solution.

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5/1/2016