

Corrosion Inhibition of Aluminum in Acidic Solution by Aqueous Extract of *Ajowan* Plant as Green Inhibitor

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Abstract

The inhibition of aluminum corrosion in 0.5 M hydrochloric acid by *Ajowan* plant was studied using chemical (weight loss) and electrochemical (impedance and polarization) methods. The *Ajowan* plant extract was found to be good inhibitor for aluminum corrosion in 0.5 M hydrochloric acid in the studied concentration range of inhibitor. Corrosion inhibition could be explained by considering an interaction between metal surface and the inhibitor molecules. Electrochemical measurements showed that *Ajowan* inhibitor affects both cathodic and anodic Tafel slopes in HCl medium and act as mixed type inhibitor. The adsorption of *Ajowan* extract on the aluminum surface from HCl follows Langmuir adsorption model.

Key words: Aluminum, corrosion inhibition, acidic solution, ajowan plant extract.

1. Introduction

Corrosion is a fundamental process playing an important role in economics and safety, particularly for metals. Corrosion of metals is a serious environmental problem that has been given adequate attention in the oil industrial processes such as acid cleaning and etching, metal surfaces are often made to come in contact with acidic medium, indicating that the use of inhibitors is necessary. Although there are numerous options for controlling the corrosion of metals, the use of inhibitors is one of the best methods of protecting metals against corrosion. An inhibitor can be chosen from compounds that have hetero atoms in their aromatic ring system or synthesized from or cheap materials (Trabanelli, 1991; Quraishi et al., 2001).

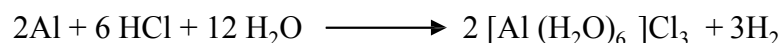
Corrosion affects most of industrial sector and may cost billions of dollars each year for preventing and replacement of maintenance (Roberge, (2008)). Thus, modern world today made an investigation to overcome this problem by doing enrichment study of corrosion inhibitors.

Hydrochloric acid is widely used in industries, the most important fields of

application being acid pickling, industrial acid cleaning, acid descaling and oil well acidizing. It is also used for removal of oxide from metallic parts before applying coating. The use of acid solution during industrial applications leads to the corrosive attack on metal. Therefore, inhibitors are commonly used to minimize metal dissolution and acid consumption (Abboud et al., 2007).

Aluminum is selected for variety of engineering applications it has an amazing economic and industrial importance due to its low cost, lightweight, high thermal and electrical conductivity, heat and light reflectivity and hygienic and non toxic qualities (Sethi et al., 2008) but it suffers from a serious corrosion problem causing considerable revenue loss throughout the world (Chowdhary et al., 2004).

Aluminum and its alloys are very important in many industrial as well as household applications due to their corrosion passivity in neutral media and atmospheric conditions due to formation of passive oxide layer on them (Ashassi-Sorkhabi et al., 2005). Although it is very reactive in emf series but becomes passive on exposure to water and atmosphere but it dissolves in hydrochloric acid liberating H₂ gas.



When aluminum is exposed in high concentrations of acids or bases or in neutral solution containing pitting agents such as chloride ions, these solutions dissolve the passive film. The dissolution leads to the formation of pitting corrosion. It is well known that a compact, strongly adherent and continuous film is developed on aluminum upon exposure to the atmosphere or aqueous solutions. This film is responsible for the corrosion resistance of aluminum in most environments (Young, 1961 and Pourbaix, 1963). Nevertheless, in some cases, aluminum may be exposed to high concentrations of acids or bases. These solutions dissolve the passive film. In addition, aluminum may be used in neutral solutions containing pitting agents such as chloride ions. These solutions cause pitting corrosion. Under these circumstances and due to the corrosiveness of acids, corrosion inhibitors should be used to reduce the rate of dissolution of metals to forms salts.

The principle of corrosion inhibition is based on the absorption and desorption of water by an organic corrosion inhibitor on the surfaces of the metal. The ability of the organic compound to exchange the adsorbed water molecules on the metal surfaces determine the efficiency of that compound to acts as corrosion inhibitor as shown in Figure 1.

Consequently, several authors conducted a lot of work to find effective inhibitors for aluminum corrosion in deferent media. Compounds containing nitrogen, sulphur and oxygen have been reported as inhibitors, called organic inhibitors (El-Etre, 2006 and Bothi Raja et al., 2008).

The organic inhibitors establish their inhibition via the adsorption of their molecules on the metal surface forming a protective layer (Khamis, 1990; Garrigues et al., 1996; Hefter et al., 1997; Muller et al., 1998). On the other hand, the inorganic inhibitors which are mainly oxidizing agents such as chromates act as anodic inhibitors and their

metallic atoms are enclosed in the film improving its corrosion resistance (Mahnoud, 1995; Bazzi et al., 1998). Most of investigated compounds are toxic and cause severe environmental hazards. Recently, good results were obtained when lanthanide salts, which have a low toxicity, were employed as aluminum corrosion inhibitors (Macdonald, 1993; Bethencourt et al., 1998). Unfortunately, these compounds are very expensive.

There are varieties of synthetic corrosion inhibitors available but our present focus on the naturally occurring inhibitors which are eco-friendly, economic and having no toxic effects without affecting the natural properties of metal, named green inhibitors.

The recent research by the electrochemists and corrosion engineers tried to find naturally organic substances or biodegradable organic materials to be used as inhibitors.

There are several criteria that affect the adsorption of the green inhibitor on the surfaces of the metal. These are the electronic structure of inhibiting molecules, steric factor, aromaticity, and electron density at donor site of the inhibitor, the presence of other functional group, the structure of the inhibitor, molecular area and molecular weight of the inhibitor molecule (El-Etre, 2006; Chauhan and Gunasekaran, 2007).

Investigation of natural substances as corrosion inhibitors has attracted considerable attention because they have been shown to be cheap, ecologically friendly and possess no threat to the environment. Plant extracts including their leaves, barks, seeds, fruits and roots comprise of mixtures of organic compounds and their corrosion inhibitive properties have been widely examined. The inhibitive properties of natural honey (El-Etre, 1998), *Anacardium occidentale* (Loto et al., 2000), *Rosmarinus officinalis* (Kliskic et al., 2000), *Mimosa* tannin (Martinez and Stern, 2001), *Vernonia amygdalina* (Ramesh et al., 2001), *Andrographis panizulata* (Avwiri and Igbo, 2003), *Magnifera indica* (Loto et al., 2003), *Carica papaya* (Ebenso et al., 2004), *Zenthoxylum alatum* (Gunasekeran and Chauhan, 2004), *Telfaria occidentalis* extract (Oguzie, 2005), *Allium sativum* (Okafor et al., 2005), *Datura metel* (Sethuraman and Raja, 2005), *Occimum basilicum* (Oguzie et al., 2006), *Prunus cerasus* (Ashassi-Sorkhabi and Seifzadeh, 2006), oil from *Mentha pulegium* (Bouyanzer et al., 2006), *Azadirachta indica* (Ebenso et al., 2004; Oguzie, 2006), have been reported. Also reported are the inhibitive effects of natural *Artemisia* oil (Bouyanzer and Hammouti, 2004) on steel and *Jojoba* oil (Chetouani et al., 2004) on aluminum in acidic medium. El-Etre has also reported on the effect of *Khillah* extract (El-Etre, 2006) and *Opuntia* extract (El-Etre, 2003) as eco-friendly corrosion inhibitors for steel and aluminum, respectively. *Guar gum* (Abdallah, 2004), *Quinine* (Awad, 2006), *Sansevieria trifasciata* extract (Oguzie, 2007) and *Hibiscus sabdariffa* (Oguzie, 2008) have been shown to be effective corrosion inhibitors for metals in aggressive acid environments. Results show that all the natural substances act as effective corrosion inhibitors in the different test media.

The present work is another trial to found a cheap and environmentally safe

inhibitor for aluminum corrosion in the acidic solution, where the aqueous extract of *Ajowan* plant seeds is tested.

2. Experimental

2.1. Materials

The chemical composition of the aluminum sample is listed in Table 1.

2.2. Inhibitor

Ajowan fruits (Figs 2a & 2b) are an important commercial product for the food/flavouring industry, and they accumulate up to 5 % essential oil in compartments referred to as canals or vittae (Bhargava and Haksar, 1959). Reports on the antimicrobial and antioxidant properties of thymol have been reviewed in a previous article (Gersbach et al., 2001), and similar properties have been attributed to extracts of ajowan seeds (Mehta et al., 1994; Srivastava et al., 1999).

The composition of the essential oil has been analyzed extensively. Up to 55 % is the aromatic monoterpene thymol, and there are significant amounts of the thymol precursors p-cymene and γ -terpinene (Balbaa et al., 1973; Ashraf and Bhatti, 1975; Nagalakshmi et al., 2000). The aromatic ring structure of the monoterpene thymol, with its aromatic protons and their particular spectral characteristics. In ajowan, the main component of the fruit is lipid in the form of reserve oil (triglyceride). This is present in greater abundance than monoterpenes, but the triglyceride and essential oil are located in separate, well-defined compartments, the seed endosperm and vittae, respectively.

2.3. Solutions

Appropriate concentration of aggressive solution used (0.5 M HCl) was prepared by dilution of analytical grade (37%) with bi-distilled water. The concentration range of aqueous extract of inhibitor used was 2–50%v/v.

2.4. Chemical measurements

2.4.1. Mass-Loss method

For mass-loss measurements, aluminum specimen was immersed in 50 ml uninhibited and inhibited solutions and allow to stand for several interval at $30 \pm 0.2^\circ$ C in water thermostat. Therefore, the mass losses given by:

$$\Delta m = (m_1 - m_2) \quad (1)$$

where m_1 and m_2 are the weights of specimen before and after exposure to the corrosive solution, respectively. The percentage inhibition efficiency (IE%) and the degree of surface coverage (Θ) of the investigated inhibitor was calculated from the following equations:

$$IE\% = [1 - (\Delta m_{inh} / \Delta m_{free})] \times 100 \quad (2)$$

$$\Theta = [1 - (\Delta m_{inh} / \Delta m_{free})] \quad (3)$$

Where Δm_{free} and Δm_{inh} are the weight losses per unit area in the absence and presence of inhibitor, respectively.

2.5. Electrochemical measurements

Electrochemical experiments were performed by use of a three electrodes cell designed specifically for EIS and PDP measurements (Fig.(3)). The reference electrode was a saturated silver/silver chloride electrode ($\text{Ag}(\text{AgCl}_{(s)}, \text{KCl}_{(aq.)})$) and the counter electrode a platinum wire. The 1.695 cm^2 working electrode of aluminum was used. The working electrode used in chemical and electrochemical measurements were polished with emery papers in the range (60-1200) grit rinsed with bi-distilled water and with acetone and dried with a stream of air. The working electrode was immersed in the test solution during 20 min. until a steady state open circuit potential (E_{ocp}) was obtained.

2.5.1. Impedance method

Electrochemical impedance spectroscopy measurements were carried out over a frequency range of 0.5 kHz to 10000 Hz, with a signal amplitude perturbation of 10 mV. Nyquist plots were obtained from the results of these experiments. Values of the charge transfer resistance (R_{ct}) were obtained from these plots by determining the difference in the values of impedance at low and high frequencies, as suggested by (Tsuru et al, 1978). Values of the double layer capacitance (C_{dl}) were calculated from the relation:

$$C_{\text{dl}} = 1 / 2\pi f_{\text{max}} R_{\text{ct}} \quad (6)$$

where, f_{max} is frequency at which the imaginary part ($Z_{\text{imag.}}$) of the impedance is a maximum. The inhibition efficiency (IE%) and surface coverage (Θ) of the investigated inhibitor was calculated from the following equations:

$$\text{IE}\% = [(R_{\text{ct}} - R_{\text{ct}}^{\circ}) / R_{\text{ct}}] \times 100 \quad (7)$$

$$\Theta = [(R_{\text{ct}} - R_{\text{ct}}^{\circ}) / R_{\text{ct}}] \quad (8)$$

where R_{ct}° and R_{ct} are the charge transfer resistance values in the absence and presence of the inhibitor, respectively.

2.5.2. Polarization method

The polarization curves were recorded by polarization from -780 mV to -700 mV under potentiodynamic conditions corresponding to 0.5 mV/s (sweep rate) and under air atmosphere. All measurements were carried out with aluminum electrode in 0.5 M HCl in the absence and presence of different concentrations (1%v/v – 100%v/v) of the investigated inhibitor at 30 °C. All experiments were carried out at 30 ± 0.2 °C. The inhibition efficiency and surface coverage (Θ) were calculated from the following equations:

$$\text{IE}\% = [(1 - I_{\text{corr.}(inh.)} / I_{\text{corr.}(free)})] \times 100 \quad (9)$$

$$\Theta = [1 - I_{\text{corr.}(inh.)} / I_{\text{corr.}(free)}] \quad (10)$$

where $I_{\text{corr.}(free)}$ and $I_{\text{corr.}(inh.)}$ are the corrosion current densities in the absence and presence of inhibitor, respectively.

3. Results and Discussion

3.1. Weight loss studies

The loss in weight of aluminum in 0.5 M HCl in the absence and in presence of different concentrations of *Ajowan* extract for 90 minutes at 30° C was determined. The corrosion rate and IE were calculated and represented in Table 2. Inspection of the data in Table 2 reveals that *Ajowan* inhibit the corrosion of aluminum in hydrochloric acid media. The inhibition efficiency (IE) increases with the increase of concentration of *Ajowan* extract inhibitor reaching a maximum (80.98%) at a higher concentration (50 %v/v). This suggests that the increase in the inhibitor concentration increases the number of molecules adsorbed over the aluminum surface, blocks the active sites in which direct acid attack proceed and protects the metal from corrosion.

Ajowan is an aromatic compound containing Thymol with hydroxyl groups arranged around the aromatic ring. The adsorption of *Ajowan* on aluminum surface would take place through this functional group. This simultaneous adsorption of the group forces *Ajowan* molecule to be horizontally oriented at the metal surface. The area of the surface covered by one molecule is the maximum in case of horizontal orientation of the adsorbed molecules. This situation results in high protection efficiency even in case of low inhibitor concentrations. As the inhibitor concentration is increased, the part of the metal surface covered by inhibitor molecule increases leading to an increase in IE.

A parameter (θ), which represent the part of the metal surface covered by the inhibitor molecules was calculated for different inhibitor concentrations and represented in Table 2. Inspection of Table 2 reveals the (θ) increases as the inhibitor concentration (C) is increased. This suggests that increase in the inhibitor concentration increases the number of molecules adsorbed over the aluminum surface, blocks the active sites in which direct acid attack proceed and protects the metal from corrosion.

3.2. Electrochemical studies

3.2.1. Impedance method

The Nyquist plots of the impedance behavior of aluminum in 0.5 M HCl in the presence of various concentrations of *Ajowan* extract is shown in Figure 4. These plots indicate that the dissolution process occurs under activation control. The impedance diagrams obtained are not perfect semicircles and this difference has been attributed to frequency dispersion (Mansfeld et al., 1981; Mansfeld et al., 1982). These semicircles are of a capacitive type whose size increases with increasing *Ajowan* extract concentration. The charge transfer resistance (R_{ct}) and the interfacial double layer (C_{dl}) values derived from these curves are listed in Table 3. The inhibition efficiency (IE) of the corrosion of aluminum is calculated by charge transfer resistance using equation (8) and also recorded in Table 3.

It is found that as *Ajowan* extract concentration increases, the R_{ct} values increase, but the C_{dl} values tend to decrease with increase in the inhibitor concentration. The decrease in the C_{dl} values is due to the adsorption of *Ajowan* molecules on the metal surface.

The impedance spectra for different Nyquist plots were analyzed by fitting the experimental data to a simple equivalent circuit model as: $R(QR(LR)(LR))$ (Figs. 5a) at low concentrations (0.0-10%v/v) and as: $R(QR(LR))$ (Fig. 5b) at high concentrations (20-50%v/v) of *Ajowan* extract.

3.2.2. Polarization method

The potentiodynamic polarization behavior of aluminum in 0.5 M HCl with the addition of various concentrations of *Ajowan* extract are shown in Figure 6. The electrochemical parameters such as corrosion potential ($E_{corr.}$), corrosion current density ($I_{corr.}$), anodic and cathodic Tafel slopes (b_a and b_c) and the inhibition efficiencies (IE) derived from these curves are given in Table 4. From the table it is found that the addition of *Ajowan* extract decreases the dissolution rate of aluminium in acid media (0.5 M HCl) and the corrosion current density values ($I_{corr.}$) decreased but slightly affect the values of corrosion potential ($E_{corr.}$) and the shift in the values of $E_{corr.}$ is not significant indicating that *Ajowan* seeds extract could act as pickling inhibitor (Lyberatos and Kobotiatitis, 1991). The data clearly show that, the addition of the *Ajowan* inhibitor increases both of the anodic and cathodic over potentials (but mainly the cathodic), it can be concluded that the *Ajowan* inhibitor exert through mixed mode inhibition nearly cathodic.

The results of electrochemical studies agreed well with those of weight loss studies (Table 5) with the slight deviation in the values. Variation in the immersion period of aluminum in corrosion medium is the reason for the observed deviation (Tamil Selvi, S. et al., 2003).

The plot of IE% from three methods with logC gives S- shape curves as in figure (7).

4. Adsorption isotherm and Mechanism of corrosion inhibition

To understand the mechanism of corrosion inhibition, the adsorption behavior of the organic adsorbates on the metal surface must be known. The surface coverage (θ) { $\theta = IE/100$ } values were evaluated using weight loss values.

Plotting ($C_{inh.}/\theta$) against C gives a straight line with unit slope value (Fig.1) indicating that adsorption of *Ajowan* inhibitor from HCl solution on aluminum surface follows Langmuir adsorption isotherm (Fig. 8). From this result it could be concluded that there is no interaction between the molecules adsorbed at the metal surface.

As far as the inhibition process is concerned, it is generally assumed that the adsorption of the inhibitor at the metal-solution interface is the first step in the mechanism of action of inhibitor in aggressive media. Four types of adsorption may take place involving organic (inhibitor) molecules at the metal - solution interface.

- i- Electrostatic between charged molecules and the charged metal.
- ii- Interaction of unshared electron pairs in the molecule with the metal.
- iii- Interaction of π - electrons with the metal and
- iv- a combination of the above (Paul Schweinsberg et al., 1988).

Therefore, the inhibitive effect can be explained on the basis of a mechanism

suggesting adsorption of the plant (*Ajowan*) extract-complex on the surface of the native metal (aluminum) which in turns acts as a film forming species decreasing the active area available for acid (HCl) attack.

4. Conclusion

Following conclusions can be drawn from the present study.

- 1- The extract of *Ajowan* seeds inhibits the corrosion of aluminum in 0.5 M HCl acid.
- 2- The adsorption of *Ajowan* extract on the aluminum surface from HCl follows Langmuir adsorption isotherm.
- 3- *Ajowan* inhibitor affects both cathodic and anodic Tafel slopes in HCl medium and act through mixed mode nearly cathodic. .
- 4- Thymol in *Ajowan* constituent present may be responsible for the corrosion inhibitive effect.
- 5- The inhibition mechanism depends on the formation of a stable plant extract-complex on the metal surface.

5. References

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