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Azwain (Trachyspermum copticum) seed extract as an efficient corrosion Inhibitor for Aluminium in NaOH solution

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Abstract

The present work investigates corrosion behaviour of the aluminium in 0.5 M NaOH solution in the presence of Azwain (Trachyspermum copticum) seed extract by weight loss and electrochemical techniques. Experimental results revealed that inhibition efficiency increases with increasing inhibitor concentration and reached at maximum 94% at 500 ppm inhibitor concentration. Adsorption of inhibitor molecules on the surface of aluminium followed Langmuir adsorption isotherm model. Tafel polarization analyses indicated that studied compound is mixed type inhibitor. The data obtained from polarization method and weight loss methods were in good agreement. The Azwain (Trachyspermum copticum) seed extract is environmental friendly, biodegradable, nontoxic, cheap and easily available source of material which is used as corrosion inhibitor for aluminium metal in 0.5 M NaOH.

Keywords: Corrosion, plant extract, aluminium, polarization, NaOH solution.

Introduction

Aluminium is the second most used metal after iron; it is used in a large number of applications by itself and is used in a wide range of alloys. Because of the low atomic mass and the negative value of the standard electrode potential, aluminium potentially attracts as an anode material for power sources with high energy densities[1]. The corrosion behavior of pure aluminium and its alloys in aqueous alkaline solutions have been extensively studied in the development of the aluminium anode for the aluminium/air battery[2-5]. Corrosion of aluminium cause many problems viz., (i) it passivate the cathode active material, (ii) its solid products increase the electrical resistance, (iii) its soluble products contaminate the electrolyte and increase the self-discharge rate, and (iv) the dissolved Al^{3+} ions migrate to the counter anode and reductively deposit. Despite the fact that aluminium/air battery is an eco-friendly system and the energy density of this system is excellent. It is not greatly used in practice due to severe hydrogen evolution problems resulting from corrosion of the aluminium electrode. Thus, commercial application of Al and its alloys requires control of the hydrogen gas evolution must necessarily be achieved without compromising the eco-friendly nature of the system.

In efforts to mitigate aluminium corrosion, the main tactic is to separate the metal from corrosive environments. This can be achieved using corrosion inhibitors. Recently, the use of chemical inhibitors has been limited due to environmental regulations; Plant extracts have again become important because they are the environmentally and renewable source for a wide range of needed inhibitors. Plant extracts are viewed as an incredibly rich source of naturally synthesized chemical compounds that can be extracted by simple procedures with low cost. A lot of natural products were previously used as corrosion inhibitors for different metals in various environments[6-16] and their optimum concentrations were reported. The obtained data showed that plant extracts could serve as effective corrosion inhibitors. It is well established that corrosion inhibition occurs via adsorption of their molecules on the corroding metal surface and efficiency of inhibition depends on the mechanical, structural and chemical characteristics of the adsorption layers formed under particular conditions.

As a contribution to the current interest on environmentally friendly, green, corrosion inhibitors, and the present study investigates the inhibiting effect of seed extracts of Azwain (Trachyspermum copticum) on the aluminium corrosion in 0.5 M NaOH solution using the weight loss and electrochemical techniques.

Material and Methods

Aluminium (Al-1060) strips were used for weight loss as well as electrochemical studies. The aluminium specimens were machined into test electrodes of dimension 8 cm × 1 cm and embedded in PVC holder by epoxy resin (araldite) leaving one surface of an area of 1 cm^2 for electrochemical measurements. The exposed surface was abraded with silicon carbide abrasive paper from 400 to 1200, degreased with acetone, rinsed in distilled water and dried in the air. The corrosive medium was 0.5 M NaOH solution prepared from analytical-reagent-grade NaOH (Merck) and bidistilled water. Stock solution of Azwain (Trachyspermum copticum) seed extract was extracted by reflux of 100 g of the dry materials in 500 mL bidistilled water for 5 h. The refluxed solution was filtered to remove any contamination. The concentration of the stock solution was calculated in terms of ppm.

Electrochemical experiments were carried out in a conventional three-electrode glass cell of capacity 100 mL, using a gamry potentiostat/ galvanostat pci 4 electrochemical workstation. a saturated calomel electrode (sce) equipped with a luggin capillary and a platinum foil of 1 cm × 1 cm were used as reference and counter electrode, respectively. all the potentials reported are with reference to SCE. Before measurement, the working electrode was immersed in test solution for approximately 30 min until a steady open-circuit potential (OCP) was reached. EIS measurement was carried out in the 100 kHz - 10 mHz frequency range at OCP.

The sinusoidal potential perturbation was 10 mV in amplitude and the cell temperature was maintained at 308 ± 1 K using a thermostatic water-bath. The electrochemical experiments data were collected and analyzed by electrochemical software Echem Analyst ver. 5.5. The polarization curves were carried out from cathodic potential of -0.25 V to anodic potential of +0.25 V with respect to the open circuit potential at a sweep rate of 1 MV s^{-1}. The linear Tafel segments of the anodic and cathodic curves were extrapolated to corrosion potential (E_{corr}) to obtain the corrosion current densities (I_{corr}). In each measurement, a fresh working electrode was used. Several runs were performed for each measurement to obtain reproducible data.

The aluminium specimens of 2.5 cm × 2 cm × 0.05 cm sizes were used for weight loss measurements and were abraded with a series of silicon carbide abrasive paper (grade 600-800-1000-1200) and degreased with acetone, rinsed in distilled water, and dried in the air, and weighed accurately. Aluminium specimens were immersed in 100 mL of 0.5 M NaOH with and without addition of different concentrations of Azwain (Trachyspermum copticum) seed extract. The temperature of the corrosive system was controlled by an air thermostat. After 1 h immersion, the aluminium specimens were carefully washed in double-distilled water, dried and then weighed.

The weight loss data were gained from the average value of three parallel samples in 0.5 M NaOH with Azwain (Trachyspermum copticum) seed extract at different concentrations.

Results and Discussion

Electrochemical measurements, Polarization measurements: Polarization curves of Al in 0.5 M NaOH solution without and with different concentrations of Azwain (Trachyspermum copticum) seed extract are shown in Figure 1. It could be observed that both the cathodic and anodic reactions were suppressed with the addition of Azwain (Trachyspermum copticum) seed extract, which suggested that the inhibitor exerted an efficient inhibitory effect both on anodic dissolution of metal and on cathodic hydrogen reduction reaction. Electrochemical parameters such as E_{corr}, I_{corr}, and anodic and cathodic Tafel slopes (β_a, β_c) obtained from the polarization measurements are listed in Table 1. The inhibition efficiency (η%) was calculated by following equation [17]:

$$\eta\% = \frac{I_{corr} - I_{corr(i)}}{I_{corr}} \times 100 \quad \text{.........................(1)}$$

I_{corr} and $I_{corr(i)}$ signify the corrosion current density in the absence and presence of inhibitors, respectively.

It is evident from table 1 that values of β_c had small changes with increasing extract concentration, which indicated that the Azwain (Trachyspermum copticum) seed extract was adsorbed on the metal surface and the addition of the inhibitor hindered the alkali attack on the aluminium electrode. Therefore, the inhibitor molecules did not change the hydrogen evolution reaction mechanism. In anodic domain, the value of β_a decreases with the presence of Azwain (Trachyspermum copticum) seed extract.

The shift in the anodic Tafel slope β_a might be attributed to the modification of anodic dissolution process due to the inhibitor modules adsorption on the active sites. Compared to the free NaOH solution, the cathodic and anodic curves of the working electrode in the alkaline solution containing the Azwain (Trachyspermum copticum) seed extract shifted obviously to the direction of current reduction, as it could be seen from these polarization results; the inhibition efficiency (η%) increased with extract concentration reaching a maximum value of 90% at 500 ppm. In literature [18], it is reported that only when the open circuit potential (OCP) displacement is at least 85 mV in relation to the one measured for the blank solution, can a compound be recognized as an anodic or cathodic inhibitor. Therefore, Azwain (Trachyspermum copticum) seed extract might act as a mixed-type inhibitor.

Electrochemical impedance spectroscopy (EIS) measurements: Equivalent circuit used is shown in Figure 2. Nyquist plots of aluminium in 0.5 M NaOH solution in the absence and presence of different concentrations of Azwain (Trachyspermum copticum) seed extract are given in Figure 3, where it can be observed that the diameter of the semicircle increases with increasing Azwain (Trachyspermum copticum) seed extract concentration. This increase in capacitive semicircles suggests that the inhibition action of these inhibitors is due to their adsorption on the metal surface without altering the corrosion mechanism.

Table-1
Electrochemical polarization parameters and the corresponding inhibition efficiencies for Al in 0.5 M NaOH solution in the absence and presence of different concentrations of Azwain (Trachyspermum copticum) seed extract

Inhibitor	E_{corr}	I_{corr}	β_a	β_c	η
(ppm)	(V/SCE)	(mA cm^{-2})	(V dec^{-1})	(V dec^{-1})	(%)
0.5 M NaOH	–1.54	59.8	8.746	0.56	-
300	–1.51	7.7	1.334	0.23	87
400	–1.51	6.8	1.001	0.14	89
500	–1.50	5.8	1.000	0.21	90

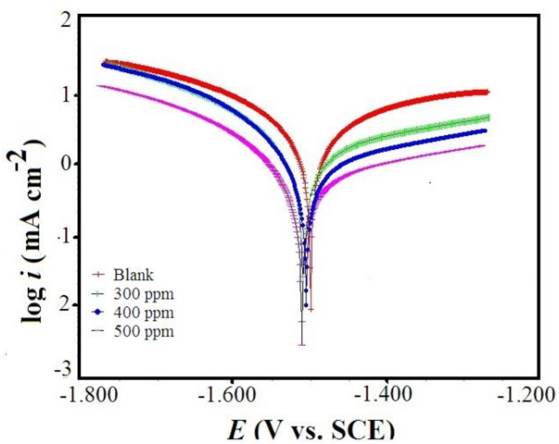

Figure-1
Polarization curves for Al in 1 M NaOH in Presence of different concentrations of Azwain (Trachyspermum copticum) seed extract

Further, the figure manifested two depressed capacitive semicircles, typical of Randles element, at higher and lower frequencies regions, separated by an inductive loop at intermediate frequencies. Inductive loops can be explained by the occurrence of adsorbed intermediate on the surface. Therefore, adsorbed intermediate species such as Al^{+}_{ads} and $Al^{3+}_{(ads)}$ might be involved in Al dissolution process [19]. The capacitive semicircle at higher frequencies is attributed to the redox Al–Al^{+} reaction since it was assumed to be the rate determining step in the charge transfer process [20].

Therefore, the resistance value obtained from intercepts of the first capacitive semicircle with real axis corresponds to the Al–Al^{+} charge transfer resistance. On the other hand, the second capacitive semicircle could be attributed to the fast complementary redox Al^{+}–Al^{3+} reaction. The curve manifested that addition of extract to alkaline NaOH solution leads to increase the size of the capacitive semicircles, indication for increasing the resistances and decreasing corrosion rate.

Weight loss measurements and adsorption isotherm : The values of Inhibition efficiency (η%) obtained from weight loss measurements for different concentrations of Azwain (Trachyspermum copticum) seed extract in 0.5 M NaOH are given in figure 4. The inhibition efficiencies, (η%) were calculated by the following equation:

$$\eta\% = \frac{W_0 - W}{W_0} \times 100 \quad \text{..................(2)}$$

W_0 and W are the corrosion rates in the absence and presence of the extract, respectively. The obtained results suggested that the inhibition efficiency increases with increasing concentration of extract.

As the concentration reached 500 ppm, the inhibition efficiency of extract obtained a high value of 94%, which represented excellent inhibitive property. Adsorption of Azwain (Trachyspermum copticum) seed extract can be explained on the basis that adsorption of the inhibitor was mainly via hetero atoms (viz., N) present in different constituents of extract in addition to the availability of π electrons in the aromatic system[21].

The phytoconstituents of Azwain (Trachyspermum copticum) seed extract includes Camphene, carvacrol, p-cymene, dipentene, myrcene, a- and b- pinesnes, phenol, a- and b-plellandrenes, g- terpinene, thymine, thymol, linoleic, oleic, palmitic petroselinic acid, resin acids are isolated from fruits and seeds[22, 23].

Conclusion

Azwain (Trachyspermum copticum) seed extract was found to inhibit the corrosion of aluminium in 0.5 M NaOH solution and inhibition efficiency increases with increasing extract concentration. At the highest extract concentration of 500 ppm, the inhibition efficiency is increased markedly and reached 94%. Potentiodynamic polarization curves proved that the Azwain (Trachyspermum copticum) seed extract was a mixed-type inhibitor. EIS plots indicated that the charge transfer resistances increase with increasing concentration of the extract. The Azwain (Trachyspermum copticum) seed extract inhibits corrosion of aluminium in alkali media by adsorption mechanism.

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Table-2
Electrochemical impedance parameters for mild steel in 1 M HCl in absence and presence of different concentrations of Azwain (Trachyspermum copticum) seed extract

Solution	Inhibitor	R_{ct}	Y_0	n	C_{dl}	η
	(ppm)	(Ω cm^2)	($10^{-6}\Omega^{-1}s^n cm^{-2}$)		(μF cm^{-2})	(%)
0.5 M NaOH	0	9.4 ± 0.04	65.8	0.827	44.60	-
	300	29.9 ± 0.3	40.6	0.923	24.75	68.54
	400	47.2 ± 0.9	82.5	0.897	19.43	79.73
	500	63.5 ± 1.2	32.9	0.854	15.15	85.10

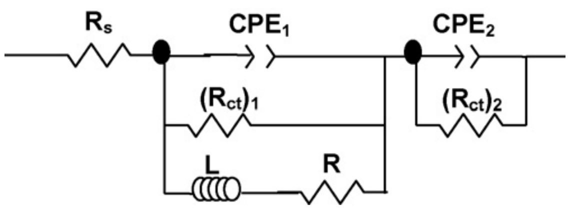

Figure -2
Equivalent circuit used

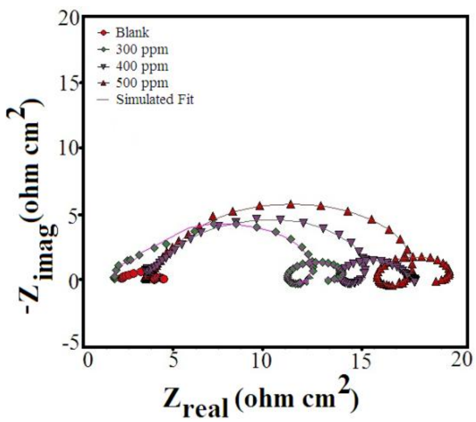

Figure – 3
Nyquist plots for aluminium in 1 M NaOH with various concentrations of Azwain (Trachyspermum copticum) seed extract

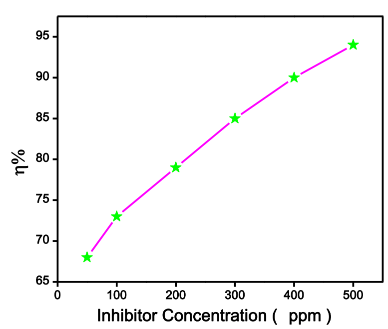

Figure -4
Inhibition efficiency vs. inhibitor concentration

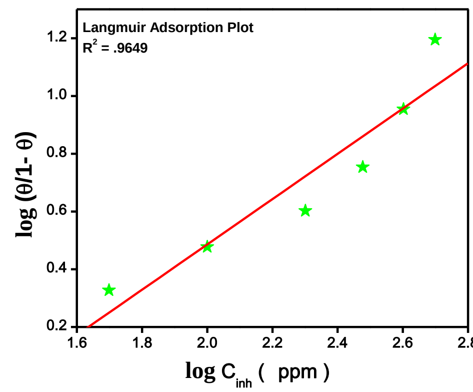

Figure-5
Langmuir adsorption isotherm plot

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