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Corrosion Inhibition Property of Mangala Dry Arecanut Seed Extract on Mild Steel Surface in Hydrochloric Acid Environment

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Abstract

The green approach is rapidly growing and replacement of toxic synthetic compounds by natural products is greatly increased for health and environmental concerns. Green chemicals from plant products are available in large amounts from various renewable sources. The material corrosion is an inescapable but controllable process. Generally, plant species contain P, S, N and O atoms in their extracts expected to show good corrosion inhibition property. Hence, in the current study, we selected Mangala dry arecanut seeds. The chemical and electrochemical behavior of mild steel in an acid environment (0.5M HCl) was studied in the presence of Mangala dry arecanut seed extract as a corrosion inhibitor by gravimetric (mass loss), Tafel, impedance and scanning electron microscopy studies. The increase in the concentration of seed extract increased the protection efficiency but it was decreased with the rise in time and temperature as observed by the mass loss technique. The Tafel diagram and surface characterization by scanning electron microscopy hinted the superior anticorrosion property of Mangala dry arecanut seed extract. The corrosion inhibition mechanism of Mangala dry arecanut seed extract was further explained by the thermodynamic principles.

Introduction

One of the most useful methods to protect the metal corrosion is by adding the corrosion inhibitors into the corrosive system. The corrosion inhibitors are chemical substance introduced into the acid or alkali system to decrease the mild steel corrosion rate [1]. When the corrosion inhibitors are introduced into the aggressive solution the compounds are adsorbed at the mild steel-HCl interface, which makes a barrier for the charge and mass transfer [2]. With the rise in the concentration of the inhibitor, the degree of protection rate against disintegration enhances due to enhanced surface fraction acquired by the adsorbed species [3]. Numerous organic, inorganic and polymeric species adsorb on the surface of the metal and hinders the dissolution of metal [4]. The process of adsorption affects both cathodic and anodic reactions. Low solubility, expensive and toxic nature of synthetic species with prominent structures in the aggressive system greatly hinders the development and industrial applications of synthetic compounds [5].

Mild steel corrosion in the hydrochloric acid system has been a subject of vital research because of its relevance in different applications in various industrial sections in an unstoppable mild steel weight loss [6]. Mild steel protection is a global subject and dissolution is one of the major harms faced by all chemical industries [7]. Mild steel corrosion is spontaneous destruction which results in irreparable damage to the mild steel surface [8]. HCl solution used in oil well acidizing, acid cleaning, descaling and industry acid pickling. HCl has an aggressive effect on metals [9]. Corrosion affects safety, human health and nation economy [10]. Protection of metal by organic compounds originates from the fact that the electron-rich elements from the organic compounds adsorb on the surface of the metal and generates an inhibiting film against corrosion in the aggressive media [11, 12]. Many factors affect inhibitor efficiencies such as substrate surface, corrosive environment, structure and charge of the inhibitor [13].

Because of strict environmental rules, research interest is focused towards the eco-friendly corrosion inhibitors [14, 15]. The natural species are cheap, safe and rich sources of electrons [16, 17]. In this study, we selected Mangala dry arecanut seeds (MDRS). Previous research articles confirmed that MDRS extract contains guvacine, isoguvacine, arecolidine, arecaidine, arecoline and guvacoline [18-20]. In this study, the role of MDRS extract as a corrosion inhibitor for mild steel in the acid medium was measured by mass loss, Tafel plot, impedance and scanning electron microscope techniques.

Materials and Methods

Mild steel strips with the chemical composition shown in Table 1 were employed for weight loss (gravimetric) and electrochemical (Tafel plot and alternating current impedance spectroscopy) techniques. The strips were thoroughly polished by the different grade of sandpapers.

Table 1 Mild steel chemical composition in percentage by weight.

Mn	C	P	S	Si	Fe
0.6	0.18	0.04	0.05	0.1	99.03

Preparation of inhibitor

Well-powdered 80 grams of arecanut seeds were placed in the Soxhlet extraction chamber. Green chemicals were extracted with 400 ml of double-distilled water for about five hours. The inhibitor was purified with the help of Whatman no. 1 filter paper. The range of the amount of inhibitor used was from 5 g/L to 30 g/L. The hydrochloric acid solution of 0.5 M HCl solution was prepared by diluting the analytical grade HCl solution. Volumetric titration method was used to standardize the hydrochloric acid solution.

Mass loss (gravimetric) technique

The mass loss technique was performed on mild steel sheets with 100 ml of 0.5 M HCl solution for different times at laboratory temperature (30℃). To study the relationship between temperature and corrosion rate, the experiment was performed at 35℃, 40℃, 45℃ and 50℃ for one-hour immersion period.

The percentage efficiency of the green compound was calculated from the equation below: Percentage efficiency of the green compound

$$= \frac{(W_1 - W_2)}{W_1} \times 100$$

Where W_1= weight loss in the absence of extract and W_2= weight loss in the presence of extract.

The corrosion rate was calculated using the equation below:

$$\text{Corrosion rate } = \frac{534W}{ATD}$$

Where, W= weight loss in milligram, A= area of the electrode in square inches, T= immersion time in hours and D = density of electrode in gram per cubic centimeter.

Electrochemical studies

While performing Tafel plot and impedance studies, mild steel strips were used as working electrode, calomel as reference and platinum was used as an auxiliary electrode. Tafel plots were obtained with a scan rate of 0.01 V/s. Following equation was used to calculate the protection efficiency of the inhibitor.

$$\text{Protection efficiency} = [\,1 - \frac{i'_{corr}}{i_{corr}}\,] \times 100$$

Where i'_{corr} and i_{corr} are corrosion current density for mild steel in protected and bare solutions, respectively.
Impedance study was performed in the frequency range 10^5 to 1 Hz.

Scanning electron microscopy studies

Corrosion probes in 0.5 M hydrochloric acid environment were achieved by submerging the mild steel specimen without and with the MDRS extract for two hours. Subsequently, the mild steel pieces were retrieved from the acid solution and the mild steel surface was deployed for the scanning electron microscopy analysis.

Statistical analysis

All Data was subjected to ANOVA to determine the significance of treatment effect and differences among treatments were evaluated using Duncan's multiple range test using software STATISTIX 8.1 (Analytical Software, Inc., Tallahassee, FL, USA).

Results and Discussion

Weight loss study

The influence of enhancing the MDRS extract concentration on the loss of weight of mild steel in the 0.5 M HCl solution is presented in Table 2 and Table 3. The weight loss of mild steel was reduced in the presence of MDRS extract, which shows that the presence of MDRS extract reduces the mild steel corrosion rate. The protecting vigor of an extract of MDRS could be interpreted by greater blocking adsorption over the mild steel due to different compounds present in the MDRS extract. The adsorbed film behaves as a barrier between the mild steel and 0.5 M HCl system, leading to a reduction in the mild steel dissolution rate [18]. Weight loss analysis is a practical method for the corrosion inhibition study. The mild steel weight loss values in the presence of MDRS extract were lower compared to the inhibitor-free solution (Table 2). This signifies that the MDRS extract has corrosion inhibition role for the mild steel in the acid medium by isolating the mild steel from the 0.5 M HCl solution. The decrease in mild steel corrosion with the introduction of MDRS extract is ascribed due to the surface coverage of mild steel, which increases as it adsorbs MDRS extract molecules [19].

Table 2 Effect of Mangala dry arecanut seed extract on corrosion rate and protection efficiency at different concentrations and time at 30℃.

Time (hours)	Concentration (g/l)	Corrosion rate ($\times 10^{-4}$ MPY)	Protection efficiency (%)
	Blank	10.09 a	-
	5	2.76 b	72.61 d
1	10	1.88 c (F)	81.30 c (A)
	20	1.36 d	86.52 b
	30	0.70 e	93.04 a
	Blank	12.06 a	-
	5	3.46 b	71.27 d
2	10	2.63 c (E)	78.18 c (B)
	20	1.86d	84.55 b
	30	0.87e	92.73 a
	Blank	14.62 a	-
	5	4.38 b	70.00 d
3	10	3.21 c (D)	78.00 c (C)
	20	2.50 d	82.90 b
	30	1.17 e	92.00 a
	Blank	16.45 a	-
	5	4.94 b	69.93 d
4	10	3.73 c (C)	77.33 c (C)
	20	2.85 d	82.67 b
	30	1.37 e	91.67 a
	Blank	17.55 a	-
	5	5.35 b	69.50 d
5	10	4.40 c (B)	74.90 c (D)
	20	3.33 d	81.00 b
	30	1.49 e	91.50 a
	Blank	24.13 a	-
	5	8.99 b	62.73 d
10	10	7.02 c (A)	70.90 c (E)
	20	5.74 d	76.18 b
	30	4.38 e	81.82 a

MYP = miles per year
Different small letters show significant differences between different concentrations of Mangala dry arecanut seed extract and different capital letters in brackets show significant differences among different times at $P<0.05$ according to Duncan's multiple range test.

Effect of temperature and immersion period are the most important factors considered before using the inhibitor in the chemical and pharmaceutical industry. From the weight loss results, it is clear that, with an increase in both time and temperature, the mild steel corrosion rate increased, which was due to the etching or desorption of MDRS extract molecules on the mild steel surface (Table 3). The

Table 3 Effect of Mangala dry arecanut seed extract on corrosion inhibition efficiency at different concentrations and temperatures.

Temperature	Concentration (g/l)	Inhibition efficiency (%)
30℃	5	72.61 d
	10	81.30 c
	20	86.52 b (A)
	30	93.04 a
35℃	5	69.78 d
	10	78.72 c
	20	85.53 b (B)
	30	91.49 a
40℃	5	67.35 d
	10	75.51 c
	20	79.59 b (C)
	30	89.79 a
45℃	5	67.30 d
	10	73.07 c (D)
	20	78.46 b
	30	86.53 a
50℃	5	63.70 d
	10	72.22 c (E)
	20	77.77 b
	30	83.33 a

Different small letters show significant differences between different concentrations of Mangala dry arecanut seed extract and different capital letters in brackets show significant differences among different temperatures at *P*<0.05 according to Duncan's multiple range test.

Table 4 Thermodynamic parameters at five different solution temperatures used to determine the effect of Mangala dry arecanut seed extract on the corrosion of mild steel.

Temperature (℃)	K_{ads} (L/g)	ΔG^o_{ads} (kJ/mol)
30℃	480.64 a	-32.96 d
35℃	429.59 b	-33.22 c
40℃	365.88 e	-33.34 c
45℃	391.98 d	-34.06 b
50℃	400.95 c	-34.65 a

Different small letters show significant differences at *P*<0.05 according to Duncan's multiple range test.

desorption of MDRS extract molecules causes the contact of more mild steel surface area to the acid system, hence resulting in higher mild steel corrosion rate. The increase in time and temperature sometimes also enhances the molecular decomposition, which auxiliary decreases the protection efficiency [20]. The Langmuir adsorption isotherm model is used in order to explain the mild steel corrosion inhibition (Fig. 1). A thermodynamic parameter such as the free energy of adsorption (ΔG^o_{ads}) and adsorption equilibrium constant (K_{ads}) at five different temperatures are shown in Table 4**.** The calculated ΔG^o_{ads} values are in between the -32 and -34 kJ/mol, clearly showing that the adsorption of MDRS extract on mild steel surface in 0.5 M HCl solution at all studied temperatures involves both physical and chemical adsorption (mixed adsorption). The higher K_{ads} values accompanying with the superior trend to adsorb on the surface of the mild steel in acid medium. This is a hint of the strength of adsorption forces existing in between the MDRS extract molecules and mild steel surface. The high K_{ads} values also indicate the forward adsorption process dominated the backward desorption process.

The maximum protection efficiency of MDRS extract on the mild steel surface in 0.5 M HCl system obtained in the present investigation was 93.04%. In a previous investigation, mature arecanut husk extract exhibits 93.48% protection property [21]. In addition to that, banana peel extract exhibits 89% corrosion protection property on mild steel surface in 1 M HCl solution system at 500 ppm [22]. The protection efficiency of plant extracts could be thoroughly explained on the different green chemicals present in the different plant extracts. The various green chemicals present

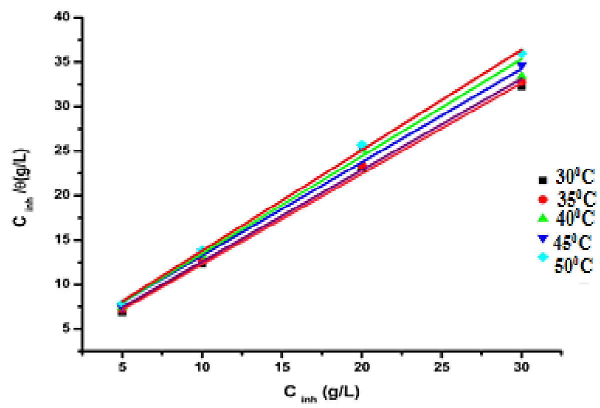

Fig. 1 Langmuir adsorption model at five different solution temperatures.

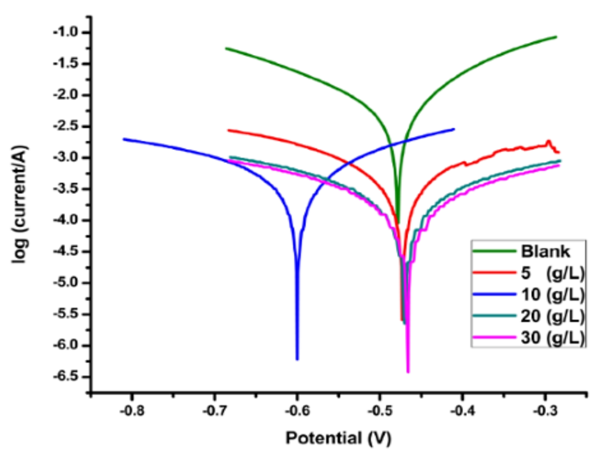

Fig. 2 Tafel plots without and with Mangala dry arecanut seed extract at different concentrations.

Table 5 Tafel parameters in the absence and presence of Mangala dry arecanut seed extract at different concentrations.

Concentration (g/l)	E_{corr} (mV)	$i_{corr}\times10^{-3}$ (A)	βc (V/dec)	βa (V/dec)	Protection efficiency (%)
Blank	-478 b	6.39 a	5.79 a	7.18 a	-
5	-473 bc	0.57 b	5.11 b	4.22 e	91.04 c
10	-600 a	0.53 c	4.30 d	5.43 b	91.64 c
20	-470 c	0.21 d	4.83 c	4.96 c	96.69 b
30	-466 d	0.18 e	4.85 c	4.87 d	97.24 a

E_{corr} = corrosion potential; i_{corr} = corrosion current density

in the plant species facilitate the process of adsorption and enhance surface coverage.

Polarization measurements

Fig. 2 shows the influence of adding MDRS extract on anodic and cathodic polarization curves of mild steel in the 0.5 M HCl medium. The Tafel parameters are shown in Table 5. The decrease in corrosion current density (i_{corr}) values shows that the presence of MDRS extract decreased the anodic and cathodic dissolution on mild steel surface in 0.5 M HCl solution. The Tafel slope (βa, and βc) values and corrosion potential (E_{corr}) values did not direct towards any particular positive and negative direction indicating a mixed inhibitory role of MDRS extract. The corrosion potential values exceeding 85mV are considered to be anodic or cathodic or mixed type corrosion inhibitor [23]. In the present investigation, the corrosion potential values are less than 85mV and anodic and cathodic Tafel slope values does not direct towards any direction. Hence, the MDRS extract is classified into mixed type corrosion inhibitor by reducing the mild steel corrosion current density values. This behavior demonstrates that MDRS extract species adsorbed on the mild steel surface. The formed adsorption layer reduces the dissolution process. The process of adsorption increases with the MDRS extract amount leading to the enhanced protection efficiency.

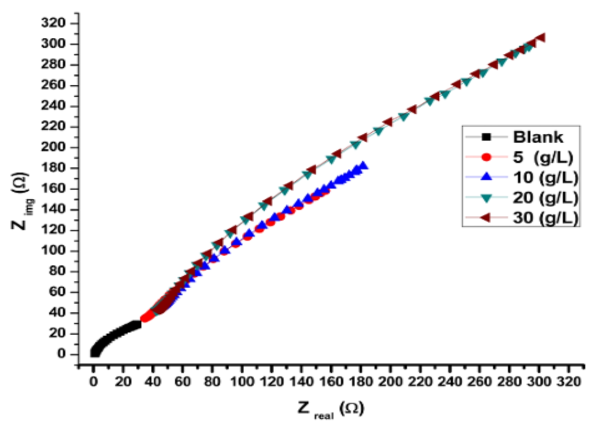

Fig. 3 Nyquist plots without and with Mangala dry arecanut seed extract at different concentrations.

Impedance studies

To support the weight loss and Tafel results, we also carried out AC impedance studies and obtained Nyquist plots are presented in Fig. 3. From this figure, it is clear that the enhanced diameter of depressed semi-circle obtained in 0.5 M HCl solution increased with MDRS extract. This clearly signifies the inhibitory role of MDRS extract on the mild steel corrosion in the studied system by the charge transfer process.

Scanning electron microscopy (SEM) studies

The surface of mild steel was examined by scanning electron microscopy after 2 h dipping in 0.5M HCl solution before and after the introduction of MDRS extract. The surface morphology is shown in Fig. 4 This suggested that, mild steel immersed in 0.5 M HCl solution has a greater roughness than the inhibited (by MDRS extract) mild steel surface. The smooth, mild steel surface is due to the compacted adsorption layer existed on the surface of the mild steel preventing the corrosion process. Similar results were found in pour previous report [24].

Conclusions

MDRS extract showed good inhibition of mild steel corrosion in the 0.5 M HCl medium. The protection efficiency was enhanced with increase in the dose of MDRS extract and decreased with rising time and temperature. Tafel plot revealed the mixed inhibition property of the MDRS extract on mild steel surface in 0.5 M HCl solution. The adsorption of MDRS extract on mild steel surface in the 0.5 M HCl solution was confirmed by impedance studies. The scanning electron microscopy study further proved the chemical and electrochemical results.

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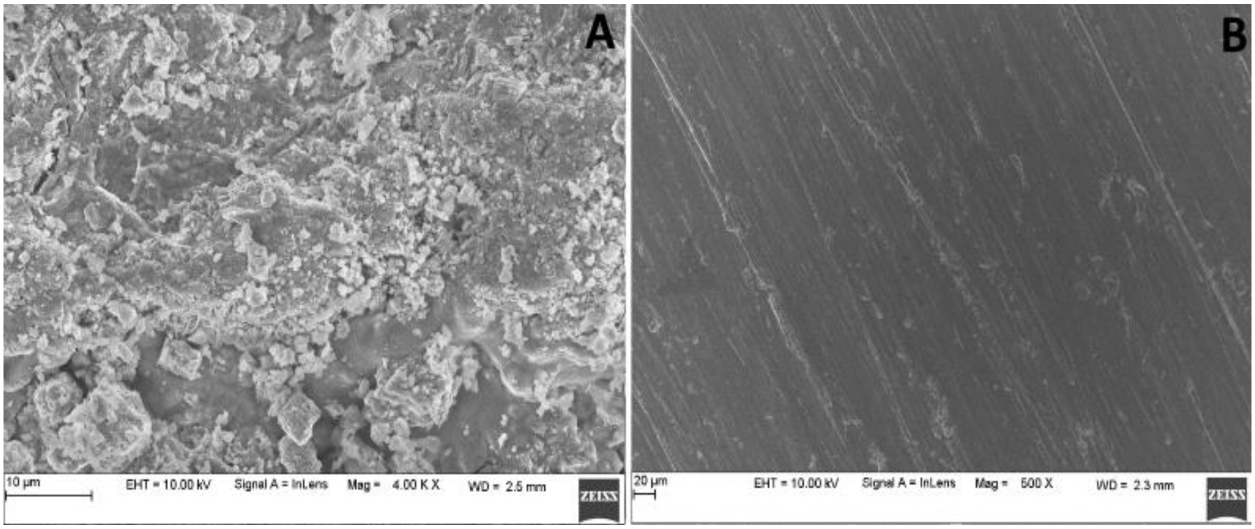

Fig. 4 Scanning electron microscopy images without (**A**) and with (**B**) Mangala dry arecanut seed extract.

Conflict of Interest

The authors have no conflict of interest.

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