International Journal of Computer Science Engineering & Technology

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COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH (CSIR)– NEW DELHI INDIA .
ISSN :2455-9091

PLECTRANTHUS AMBOINICUS LEAVES EXTRACTS – A GREEN CORROSION INHIBITOR FOR MILD STEEL IN SEA WATER MEDIUM

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ABSTRACT: The anti-corrosion behavior of Plectranthus Amboinicus leaves extracts in Sea water solution on mild steel werestudied using gravimetric method (weight loss method), electrochemical method (potentiodynamicpolarisation) and scanning electron microscope(SEM) techniques. The extracts were shown to have good inhibition efficiencies for the gravimetricand electrochemical methods. Synergistic effect exists between the Plectranthus Amboinicus - Zn^{2+} system in controlling the corrosion of mild steel immersed in sea water in the absence and presence of Zn^{2+}. The formulation consisting of 250 ppm Plectranthus Amboinicus, 50 ppm of Zn^{2+} have 97% inhibition efficiency. A more stable and compact protective film formed on the metal surface. Polarization study reveals that the Plectranthus Amboinicus- Zn^{2+}system function as cathodic inhibitor. The FT-IR and SEM analysis reveal that the protective film is formed on the metal surface.

Keywords: [Plectranthus Amboinicus,corrosion inhibition,mild steel, Polarization, FT-IR and SEM.]

1. INTRODUCTION

Corrosion of materials is a natural phenomenon that is a cause of concern as it has incurred atotal damage of billions of dollars to many industries. Many ways of overcoming the corrosionproblem such as inhibitors, anodic protections, cathodic protections and coatings are developed.Among all the methods, corrosion inhibitors are popular due to the ease in application and the advantage of in situ application without disruption of the process. Corrosion inhibitors are substanceswhich when added in small concentrations to the corrosive environment will reduce the rate ofcorrosion [1]. There has been extensive research done to develop inhibitors that are cost effective and environmentally friendly. Most

of the inhibitors developed from natural sources such as plants arefound to have the presence of heterocyclic compounds, nitrogen, sulfur and oxygen atoms and thesecontribute greatly to inhibit ion of corrosion via various mechanisms [4-5]. Examples of plants that hadbeen studied as inhibitors includes Neolamarckiacadamba, Mangrove tannins, Xylopiaferruginea,apricot juice, Zenthoxylumalatum, Medicagosative and AquilariaCrassna [6-12]. Plectranthusamboinicus, once identified as Coleus amboinicus, is a tender fleshy perennial plant in the family Lamiaceae with an oregano-like flavor and odor. It is widely cultivated and naturalised elsewhere in the Old and New World tropics. It is used as a decorative plant in many houses in south India. GCMS analysis revealed the presence

of 11 chemical compounds constituting 97.6% of the total extract composition. The principle constituents include linalool (50.3%), nerol acetate (11.6%), geranyl acetate (11.7 %) and carvacrol (14.3%) [13].

2. EXPERIMENTAL
2.1. Preparation of Specimen
Mild steel specimen [0.0267 % S, 0.06 % P, 0.4% Mn, 0.1 % C and the rest iron] of dimensions 1.0 cm × 4.0 cm × 0.2 cm were polished to a mirror finish and degreased with trichloroethylene.

2.2. Weight-Loss Method
Mild steel specimens in triplicate were immersed in 100 mL of the solutions containing various concentrations of the inhibitor in the presence and absence of Zn^{2+} for one day. The weight of the specimens before and after immersion was determined using a Shimadzu balance, model AY62. The corrosion products were cleaned with Clarke's solution [16]. The inhibition efficiency (IE) was then calculated using the equation:

$$IE = 100\ [1- (W_2/W_1)]\ \%$$

where W_1 is the weight loss value in the absence of inhibitor and W_2 is the weight loss value in the presence of inhibitor.

2.3. Polarization Study
Polarization studies were carried out with a CHI-electrochemical workstation with impedance model 660A. A three-electrode cell assembly was used. The working electrode was mild steel. A saturated calomel electrode (SCE) was used as the reference electrode and a rectangular platinum foil was used as the counter electrode.

2.4. Surface Examination Study
The mild steel specimens were immersed in various test solutions for a period of one day. After one day, the specimens were taken out and dried. The nature of the film formed on the surface of the metal specimen was analysed by various surface analysis techniques.

2.4.1. Fourier Transform Infrared Spectra (FT-IR)
The FTIR spectra were recorded in a Perkin-Elmer-1600 spectrophotometer. The film formed on the metal surface was carefully removed and mixed thoroughly with KBr making the pellet.

2.4.2. Scanning electron microscopy and EDAX
The surface morphology of the formed layers on the mild steel surface after its immersion in control solutions containing sea water in the absence and in the presence of the inhibitor were carried out. After one day, the specimens were taken out, washed with distilled water and dried. The SEM photographs of the surfaces of the specimens were investigated using a VEGA3-TESCAN model scanning electron microscope.

3. RESULTS AND DISCUSSION
3.1. Weight-Loss Method
Table.1. Corrosion rates (CR) of mild steel immersed in sea water containing in the presence and absence of inhibitor system by weight loss method.
Inhibitor system : PA-Zn^{2+} Immersion period : One day

PA ppm	0 ppm of Zn^{2+}		25 ppm of Zn^{2+}		50 ppm of Zn^{2+}	
	IE%	CR(mm/y)	IE%	CR(mm/y)	IE%	CR(mm/y)
0		0.1618	9	0.1472	14	0.1391
50	5	0.1537	17	0.1343	42	0.0938
100	8	0.1489	26	0.1197	69	0.0502
150	13	0.1408	38	0.1003	82	0.0291
200	19	0.1311	45	0.0890	91	0.0146
250	24	0.1230	58	0.0680	97	0.0049

Table 1-Influence of immersion period on the inhibition efficiency (IE) of PA-Zn^{2+} system

System	Immersion Period (Days)			
	1	3	5	7
Sea water CR (mm/yr)	0.1618	0.1672	0.1759	0.1817
Sea water + PA (250 ppm) + Zn^{2+} (50 ppm) CR (mm/yr)	0.0049	0.0134	0.0281	0.0436
IE (%)	97	92	84	76

Table 2- gives values of the corrosion inhibition efficiencies and the corresponding corrosion rates of Plectranthus Amboinicus (PA)- Zn^{2+} in controlling corrosion of mild steel in seawater for a period of one day.

The PA alone has high rate of corrosion. The inhibition efficiency of PA is improved by adding various concentrations of Zn^{2+}. However, increasing the concentration of PA as well as Zn^{2+}, the maximum inhibition is achieved and the corrosion rate is decreased. It is found that 250 ppm of PA and 50 ppm of Zn^{2+} has 97% inhibition efficiency. The inhibition efficiency increases with the increase of concentration of inhibitors. This behaviour could be attributed to the increase of the surface area covered by the adsorbed molecules of Plectranthus Amboinicus with the increase of its concentration. It is generally

Assumed that the adsorption of the inhibitor at the metal/solution interface is the first step in the mechanism of inhibition in aggressive media.
From Table 2 gives the IE decreases with the increase in the duration of immersion.For example, the IE was found to be 97% for one day and decrease the IE to 76% on seventh day.This may due to the fact that as the period of immersion increases,the protective film formed on the metal surfacenamely,Fe^{2+}-PA complex is broken by the aggressive chloride ions present in the sea water and hence the IE decreases.

3.1.1. Synergism Parameter (S_I)

PA (ppm)	Zn^{2+}(ppm)	I_1	I_2	$I'_{(1+2)}$	S_I	I.E (%)
50	25	0.09	0.09	0.17	1.9426	17
100	25	0.08	0.09	0.26	1.9121	26
150	25	0.13	0.09	0.38	2.071	38
200	25	0.19	0.09	0.45	2.289	45
250	25	0.24	0.09	0.58	2.8013	58

Table 3-Synergism parameters for PA-Zn^{2+}(25 ppm) system in mild steel immersed in sea water for a period of one day

PA (ppm)	Zn^{2+}(ppm)	I_1	I_2	$I'_{(1+2)}$	S_I	I.E (%)
50	50	0.17	0.14	0.42	1.2307	42
100	50	0.26	0.14	0.69	2.0530	69
150	50	0.38	0.14	0.82	2.9622	82
200	50	0.45	0.14	0.91	5.2556	91
250	50	0.58	0.14	0.97	12.04	97

Table 4-Synergism parameters for PA-Zn^{2+}(50 ppm) system in mild steel immersed in sea water for a period of one day

The values of synergism parameters are shown in Table 4. Synergism Parameter (S_I) has been calculated to know the synergistic effect existing between two inhibitors [19, 20]. The values of $S_I > 1$ suggest a synergistic effect. $S_I$approaches 1 when no interaction exists between the inhibitor compounds. In

case of $S_I < 1$, the negative interaction of inhibitors prevails (i.e., corrosion rate increases). Synergism parameter is calculated using the relation.

$$S_I = (1-I_{1+2})/(1-I'_{1+2})$$

where I_1 is the surface coverage of inhibitor (PA), $I_2$is the surface coverage of inhibitor

(Zn^{2+}) and $I'_{1+2}$is the combined surface coverage of inhibitors (PA) and (Zn^{2+}).

3.2. Potentiodynamic Polarization Study

Polarization study has been used to detect the formation of protective film on the metal surface [21,22]. The polarization curves of mild steel immersed in various test solutions are shown in Fig 1. It shows that there is a clear reduction of both anodic and cathodic currents in the presence of PA-Zn^{2+}compared with those for the blank solution. Hence, it is clear that the cathodic reaction (oxygen reduction) and the anodic reaction (iron dissolution) were inhibited. The electrochemical parameters such as corrosion potential (E_{corr}), corrosion current density (I_{corr}) andTafel slopes (b_c-cathodic and b_a-anodic) are given in Table 5.

System	E_{corr} (mV vs SCE)	b_c (mV/dec)	b_a (mV/dec)	I_{corr} (A/cm^2)
Sea water	−702	125.5	162.3	8.213×10^{-5}
Sea water + 250 ppm PA + 50 ppm Zn^{2+}	−465	156.7	183.0	1.251×10^{-5}

Table 5- Analysis of potentiodynamic polarization study

When mild steel is immersed in seawater, the corrosion potential is -702 mV Vs SCE. The formulation consisting of 250 ppm PA + 50 ppm Zn^{2+} shifts the corrosion potential to - 465 mV Vs SCE. It shows that the corrosion potential is shifted to more negative side. This indicates that the cathodic reaction is controlled predominantly.

Figure1-Polarization curves of mild steel immersed in various test solutions (a) Sea water(b) Sea water + 250 ppm PA + 50 ppm Zn^{2+}

The corrosion current density value for seawater is8.213×10^{-5} A/cm^2. For the formulation of 250 ppm PA and 50 ppm Zn^{2+}, the corrosion current density value has decreased to 1.251×10^{-5} A/cm^2. The fact that the decrease in corrosion current density indicates adsorption of the inhibitor on the metal surface to block the active sites and inhibit corrosion and reduce the corrosion rate with the formation of a protective film on the metal surface.
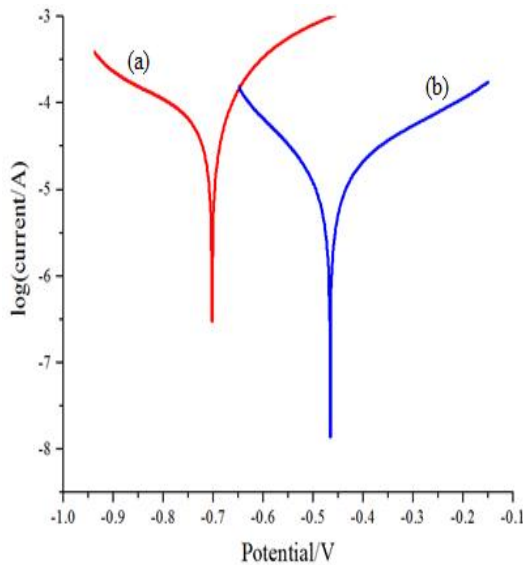
3.3. Scanning electron microscopy (SEM)

The scanning electron micrographs of mild steel are shown in Fig 4. The SEM micrograph of polished mild steel surface (control) is shown in Fig 4a. This shows the smoothness of the metal surface. This implies the absence of any corrosion product formed on the metal surface. The SEM micrograph of mild steel immersed in seawater is shown in Fig 4b. This shows the roughness of the metal surface by the corrosive environment and the porous layer of corrosion product is present. Pits are observed on the metal surface. Fig 4c shows that the presence of 250 ppm of PA and 50 ppm of Zn^{2+}in seawater gives the formation of thick films on the mild steel surface. This may be interpreted as due to the adsorption of the inhibitor on the metal surfaceincorporating into the passive film in order to block the active site present on the mild steel surface [27-28].
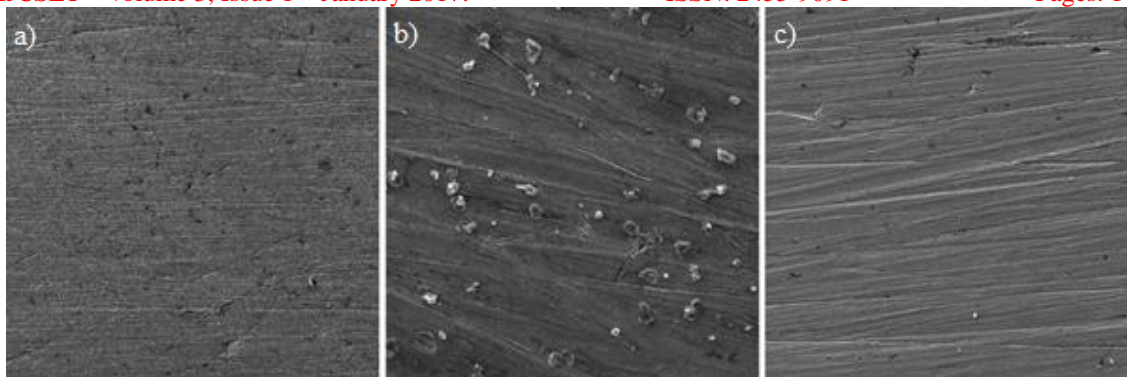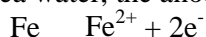
Figure 4- SEM images of mild steel surface (a) Polished metal (b) Sea water (c) Sea water+ 50 ppm of Zn^{2+} + 250 ppm PA

3.4. Mechanism of corrosion inhibition

In order to explain the above results, the following mechanism of corrosion inhibition is proposed: When mild steel is immersed in sea water, the anodic reaction is,

$$Fe \longrightarrow Fe^{2+} + 2e^-$$

The corresponding cathodic reaction is reduction of oxygen to hydroxyl ions,

$$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$$
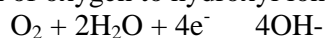
When the formulation consists of 250 ppm of PA and 50 ppm Zn^{2+} in seawater, there is formation of PA – Zn^{2+} complex in solution. When mild steel is immersed in this environment, the PA – Zn^{2+} complex diffuses from the bulk of the solution to the metal surface. The PA – Zn^{2+} complex is converted into PA Fe^{2+} complex on the anodic sites of the metal surface, the stability of Fe^{2+} – PA complex is higher than the corresponding Zinc complex.

$$Zn^{2+} - PA + Fe^{2+} \longrightarrow Fe^{2+} - PA + Zn^{2+}$$

The released Zn^{2+} combines with OH- to form $Zn(OH)_2$ on the cathodic sites of the metal surface.

$$Zn^{2+} + 2OH^- \longrightarrow Zn(OH)_2$$

The protective nature of the film is due to the presence of metal inhibitor complex and Zinc hydroxide. Formation of the metal inhibitor complex fills the pores of the otherwise porous film and makes it a protective film.

Thus, the protective film consists of Fe^{2+} – PA complex and $Zn(OH)_2$.

4. CONCLUSION

Synergistic effect exists between the Plectranthus Amboinicus - Zn^{2+} system in controlling the corrosion of mild steel immersed in sea water in the absence and presence of Zn^{2+}. The formulation consisting of 250 ppm Plectranthus Amboinicus, 50 ppm of Zn^{2+} have 97% inhibition efficiency, a more stable and compact protective film formed on the metal surface. Polarization study reveals that the Plectranthus Amboinicus - Zn^{2+} system function as cathodic inhibitor. The FT-IR and SEM analysis reveal that the protective film is formed on the metal surface.

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