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Research Article

Corrosion behaviour of Sauropus Androgynus Leaves (SAL) on mild steel in natural sea water

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ABSTRACT

The Inhibitive nature of *Sauropus androgynus* leaves extract on mild steel in Natural Sea Water has been investigated using various concentrations of inhibitor as well as temperature by mass loss measurements. The observed result reveals that the percentage of inhibition efficiency increased with increase of inhibitor concentration and temperature. Thermodynamic parameters (E_a, Q_{ads}, ΔG_{ads}, ΔH_{ads}, ΔE and ΔS) suggests that the adsorption of SAL extract is endothermic, spontaneous and chemisorptions process. It follows the Langmuir adsorption isotherm. The corrosion product may also be confirmed by the spectral studies such as UV, FT-IR, EDX and SEM.

Keywords: Mild Steel, Mass Loss, SAL, Natural Sea Water, Spectral Studies.

1. INTRODUCTION

The protection of various metals against corrosion is a major industrial problem in the world wide. Most of the scientist is attempted for their research work in this corrosion field. The heavy loss of metal whenever it contact with acid and other environment can be minimized to a great extent by the use of corrosion inhibitors. Mild steel is widely used for mechanical and structural engineering purpose, boiler, plates, steam engine parts and automobile etc. For this reason, the corrosion behaviour of these metals has attracted more awareness of several investigators. Iron and steel is the most corrosion vulnerable metal. Thus, much attention is given for its protection from the hostile environments. The heavy loss of metals is a result of its contact with the pollution environment can be minimized to a great extent by the use of corrosion inhibitors, inorganic compounds like chromates, phosphates, molybdates etc. and a variety of organic compounds containing heteroatom like nitrogen, sulphur oxygen and olefins are being investigated as corrosion inhibitor. Pure synthetic chemicals are costly, but some of them are easily biodegradable and their disposal creates pollution problems. Plant extracts are environmentally friendly, bio-degradable, non-toxic, plenty and potentially low cost. Recently, a few investigators studied the plant extracts and the derived organic species become more important as an environmentally benign, readily available, renewable and acceptable source for a wide range of inhibitors. Several efforts have been made using corrosion preventive practices and the use of green corrosion inhibitors. The plant extract are rich sources of molecules which have appreciably high inhibition efficiency and hence termed as “Green Inhibitors”. These inhibitors are biodegradable and do not contain heavy metals or other toxic compounds. Recent studies using plants containing heteroatom such as oxygen, nitrogen and sulphur like Tamarind tea leaves, Beet root[1-2], Saponin[3], Terminalia bellerica[4], Oxandra asbeckii[5],Argemone mexicana[6], Betanin[7], Henna[8], Wheat[9], Ginger[10],Marraya koeningii[11], Garlic extract[12], Ananas sativum[13] have been found effective corrosion inhibitors for mild steel[14-23].. In continuous of our research work, the present investigation is the corrosion resistant behaviour of *Sauropus androgynus leaves* on mild steel in Natural Sea Water have been investigated with various periods of contact and temperature using the mass loss measurements. Also the corrosion product on the metal surface is analyzed by UV, FT-IR, SEM and EDX spectral studies [24-35]

2. MATERIALS AND METHODS

2.1 Specimen preparation

Mild steel specimen were mechanically pressed cut to form different coupons, each of dimension exactly 20cm^2 (5x2x2cm), polished with emery wheel of 80 and 120, and degreased with trichloroethylene, then washed with distilled water cleaned, dried and then stored in desiccators for the use of our present study.

2.2 Preparation of *Sauropus androgynus Leaves (*SAL) Extract:

About 3 Kg of *Sauropus androgynus* leaves was collected from in and around Western Ghats and then dried under shadow for 5 to 10 days. Then it is grained well and finely powdered, exactly 150g of this fine powder was taken in a 500ml round bottom flask and a required quantity of ethyl alcohol was added to cover the fine powder completely, and left it for 48 hrs. Then the resulting paste was refluxed for about 48 hrs, the extract was collected and the excess of alcohol was removed by the distillation process. The obtained paste was boiled with little amount of activated charcoal to remove impurities, the pure plant extract was collected and stored.

2.3 Properties of *Sauropus androgynus* leaf:

Sauropus androgynus belongs to *Euphorbiaceous* family and it is an annual herbaceous climbing plant with a long history of traditional medicinal uses in many countries, especially in tropical and subtropical regions. The common Name is Mathurakeerai. *Sauropus androgynus* is rich in Vitamin C and polyphenols, such as tannin.

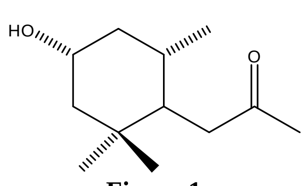

Figure 1

Chemical structure of the main active compounds present in *Sauroupus Androgynus* leaves extract

2.4 Mass loss measurement

In the mass loss measurements on mild steel in triplicate were completely immersed in 50ml of the test solution in the presence and absence of the inhibitor. The metal specimens were withdrawn from the test solutions after 24 to 360 hrs at room temperature and also measured 313K to 333K. The Mass loss was taken as the difference in weight of the specimens before and after immersion using LP 120 digital balance with sensitivity of ±1 mg. The tests were performed in triplicate to guarantee the reliability of the results and the mean value of the mass loss is reported.

From the mass loss measurements, the corrosion rate was calculated using the following relationship.

$$\text{Corrosion Rate}\left(\text{mmpy}\right) = \frac{87.6 \times W}{DAT} \text{ ------------- (1)}$$

Where, mmpy = millimeter per year, W = Mass loss (mg), D = Density (gm/cm^3),

A = Area of specimen (cm^2), T = time in hours.

The inhibition efficiency (%IE) and degree of surface coverage (θ) were calculated using the following equations.

$$\%\ IE = \frac{W_1 - W_2}{W_1} \times 100 \text{ --------------------- (2)}$$

$$\theta = \frac{W_1 - W_2}{W_1} \text{ --------------------- (3)}$$

Where W_1 and W_2 are the corrosion rates in the absence and presence of the inhibitor respectively.

3. RESULT AND DISCUSSION

3.1 Mass loss measurements

The dissolution behavior of mild steel in Natural sea water environment containing in the absence and presence of SAL extract with various exposure times (120to 480 hrs) are shown in Table-1**.** The observed values are clearly indicates that in the presence of MEL extract the value of corrosion rate decreased from 0.3115to 0.1487 mmpy (120 hrs) and 0.1766 to 0.0802 mmpy (480 hrs) with increase of inhibitor concentration from 0 to 500 ppm. The maximum of 65.67 % of inhibition efficiency is achieved even after 120 hrs exposure time. This achievement is mainly due to the presence of active phytochemical constituents present in the inhibitor molecule which is adsorbed on the metal surface and shield completely to prevent further dissolution from the aggressive media of chloride ion (Cl^-). The observation of maximum surface coverage clearly suggests that the hetero atoms (such as nitrogen and oxygen) present in the inhibitor molecules can able to bind with the metal ions from the surface, very strongly and protect the metal ions from corrosive environment [36]

3.2 Temperature Studies

The corrosion resistant behavior of SAL extract on mild steel in Natural Sea Water at 313 to 333K is shown in Table-2.

3.3 Effect of Temperature:

3.3.1. Activation energy

The values of Corrosion rate obtained from the mass loss measurements are substituted in equation and the values of activation energy (E_a) are presented in Table-3. The observed values are ranged from 1.8443 to 27.5611 kJ/mol for Mild steel in Natural Sea Water containing various concentration of inhibitor. The average value of E_a obtained from the blank (55.4210) is greater than that in the presence of inhibitor and suggest that there is a strong chemical adsorption bond between the SAL inhibitor molecules and the Mild steel surface[37-39].

3.3.2 Heat of adsorption:

The value of heat of adsorption (Q_{ads}) on Mild steel in Natural Sea Water containing various concentration of SAL extract is calculated using Equation and the values of Q_{ads} are ranged from 67.4467 to 4.3934 kJ/mol (Table-3). These positive values are reflected that the adsorption of SAL extract on Mild steel follows endothermic process.

3.3 Adsorption studies:

The adsorption isotherm is a process, which are used to investigate the mode of adsorption and it characteristic of inhibitor on the metal surface. In our present study the Langmuir adsorption isotherm is investigated. The straight line in Fig-2 clear that the inhibitor follows Langmuir adsorption isotherm.

3.4 Free energy of adsorption:

The standard free energy of adsorption (ΔG_{ads}) can be calculated using the Equation and the observed negative values are (Table-4) ensure that the spontaneity of the adsorption process and the stability of the adsorbed layer is enhanced.

3.5. Thermodynamic parameters

The another form of transition state equation which is derived from Arrhenius equation is shown below (4)

$$CR=RT/Nh \exp(\Delta S/R) \exp(-\Delta H/RT) \text{ ----- } (4)$$

Where h is the Planck's constant, N the Avogadro's number, ΔS the entropy of activation, and ΔH the enthalpy of activation. A plot of log (CR/T) Vs 1000/T gives a straight line (Fig. 3) with a slope of (−ΔH/R) and an intercept of [log(R/Nh)) + (ΔS/R)], from which the values of ΔS and ΔH were calculated and listed in Table-5. The positive value of enthalpy of activation clear that the endothermic nature of dissolution process is very difficult. The increase of ΔS is generally interpreted with disorder which may take place on going from reactants to the activated complex**.**

3.6 MORPHOLOGY STUDIES

3.6.1 UV spectrum:

Figure- 4 & 5 shows that the UV visible spectrum of ethanolic extract of SAL and the corrosion product on the surface of mild steel in the presence of SAL extract in natural sea water. In this spectrum, the two absorption bands around 302, 430 and 670nm were noticed (Fig 4) but in the presence of inhibitor additional one band was appeared (340nm). When compare both these spectra, the changes of absorption band may confirmed the strong co-ordination bond between the active group present in the inhibitor molecules and the metal surface[40-41].

3.6.2 FT-IR studies of SAL extract on Mild steel surface in Natural Sea Water:

The figures- 6 and 7 reflect that the FTIR spectrum of the ethanolic extract of inhibitor and the corrosion product on Mild steel in the presence of SAL extract in Natural Sea Water. On comparing both of the spectra the prominent peak such as, the -O-H stretching frequency for alcohol is shifted from 3392.17 to 3463.53 cm^{-1}, the C-O stretching in ester is shifted from 1115.62 to 1107.9 cm^{-1} 1633.41 corresponds to C-H stretching frequency is shifted to 1619.91cm^{-1}. These results also confirm that the FTIR spectra support the fact that the corrosion inhibition of SAL extract on mild steel in Natural Sea Water may be the adsorption of active molecule in the inhibitor and the surface of metal[42].

3.7 EDX Analysis

EDX spectroscopy was used to determine the elements present on the mild steel surface before and after exposure to the inhibitor solution. Figure 8 & 9 represents the EDX spectra for the corrosion product on metal surface in the absence and presence of optimum concentrations of SAL extract with Natural sea water environment. In the absence of inhibitor molecules, the spectrum may confirms the existence of iron, silicon, carbon, stannum which are the part of composition of mild steel. However, in the presence of the optimum concentrations of the inhibitors, oxygen atom is found to be present on the metal surface. It clearly indicates that the hetero atom present in the inhibitor molecules may involve the adsorption process with metal atom and hence it may protect the metal surface against the corrosion[43].

3.8 SEM Analysis

The surface morphology of steel surface was studied by scanning electron microscopy (SEM). The Figure-10 (a) and (b) shows the SEM micrographs of mild steel surface immersed in Natural seawater respectively. The SEM photographs showed that the surface of metal has number of pits and it is localized, but in presence of inhibitor plug type SEM image is observed which minimize on the metal surface. It indicates the formation of passive layer on the metal surface[44-45].

4. Conclusion

Using *Sauropus androgynus* leaves (SAL) extract on mild steel in natural sea water. Corrosion of mild steel in natural sea water is increased with increase of exposure period from 120 to 480 hours. Using SAL extract on mild steel, the corrosion rate markedly reduced with increase of concentrations from 0 to 500ppm. The maximum inhibition efficiency is achieved 65.67%. even after 120 hrs exposure time. This is due to strong bindings between the inhibitor molecule and ions from the metal surface. In temperature studies, the percentage inhibition efficiency increased with rise of temperature from 313 to 333K is due to the adsorption of active inhibitor molecules on the metal surface is higher than desorption process. The maximum 87% inhibition efficiency is attained. It follows chemisorptions. The activation energy (E_a), heat of adsorption (Q_{ads}), Standard free energy adsorption (ΔG_{ads}), enthalphy (ΔH), entropy (ΔS), suggests that, strong chemical bond, endothermic, spontaneous process respectively. The SAL inhibitor obeys Langmuir adsorption isotherm. The film formation may confirm UV, FT-IR, XRD, SEM, EDX, spectral studies.

5. ACKNOWLEDGEMENTS

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Table 1
The corrosion parameters of mild steel in Natural Sea Water containing different concentration of SAL extract after 120 to 480 hours exposure time

Con. of Inhibitor (ppm)	120 hrs		240 hrs		360 hrs		480 hrs	
	C.R	% I.E	C.R	% I.E	C.R	% I.E	C.R	% I.E
0	0.3115	--	0.2231	--	0.1618	-	0.1766	--
10	0.1441	53.70	0.1929	13.54	0.1487	17.9	0.1197	32.23
50	l0.1487	52.24	0.1673	25.00	0.1244	25.3	0.1011	42.76
100	0.1069	65.67	0.1627	27.08	0.1146	36.7	0.1034	41.44
500	0.1255	59.70	0.1348	39.58	0.1084	50.6	0.0976	44.73
1000	0.1487	52.24	0.0966	59.37	0.0976	63.9	0.0802	54.60

Table 2
The corrosion parameters of mild steel in Natural Sea Water containing different concentration of SAL extract at 313 to 333 K

Con. of inhibitor (ppm)	313 K		323 K		333 K	
	C.R	% I.E	C.R	% I.E	C.R	% I.E
0	15.0649	--	40.7312	--	54.1222	--
10	12.8331	14.81	35.7095	12.32	13.3910	75.25
50	11.1592	25.92	34.5936	15.06	12.8331	76.28
100	8.3694	44.44	23.9923	41.09	9.4853	82.47
500	4.4636	70.37	12.8331	68.49	6.6955	87.62
1000	5.0216	66.66	15.6229	61.64	10.6995	80.41

Table 3
Calculated values of Activation energy (E_a) and heat of adsorption (Q_{ads}) of SAL extract on Mild steel in Natural Sea Water environment.

S.No	Conc. of inhibitor(ppm)	% of I.E		E_a ($KJmol^{-1}$)	Q_{ads} ($KJmol^{-1}$)
		40^o	60^o		
1.	0	--	--	55.13	--
2.	10	14.81	75.25	1.84	67.46
3.	50	25.92	76.28	6.05	40.56
4.	100	44.44	82.47	5.42	18.06
5.	250	70.37	87.62	17.57	3.803
6.	500	66.66	80.41	32.78	4.008

Table 4
Langmuir adsorption parameters for the adsorption of SAL inhibitor on Mild steel in Natural Sea Water

Adsorption isotherms	Temperature (Kelvin)	Slope	K	R^2	ΔG_{ads} kJ/mol
Langmuir	313	0.5740	1.2537	0.9706	-11.042
	323	0.5126	1.4532	0.8652	-11.791
	333	0.97093	0.1523	0.9998	-5.9105

Table 5
Thermodynamic parameters of mild steel in natural sea water obtained from weight loss measurements.

S.No	Concentration of SAL (ppm)	ΔH (kJ mol−1)	ΔS (J k−1 mol−1)
1	0	23.0407	-22.7357
2	10	10.2719	-85.7547
3	50	1.8808	-80.9916
4	100	1.8166	-79.6260
5	250	6.8000	-78.4176
6	500	11.8848	-61.649

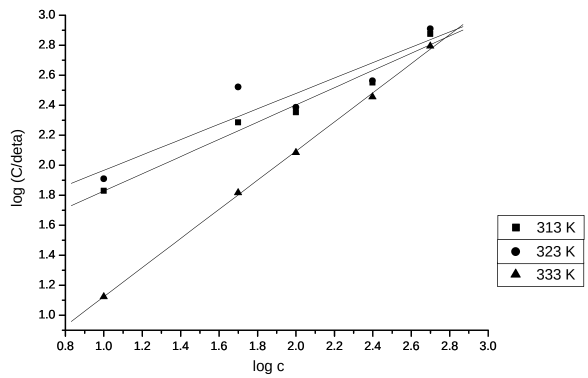

Figure 2
Langmuir isotherm for the adsorption of SAL inhibitor on Mild steel in Natural Sea Water Environment.

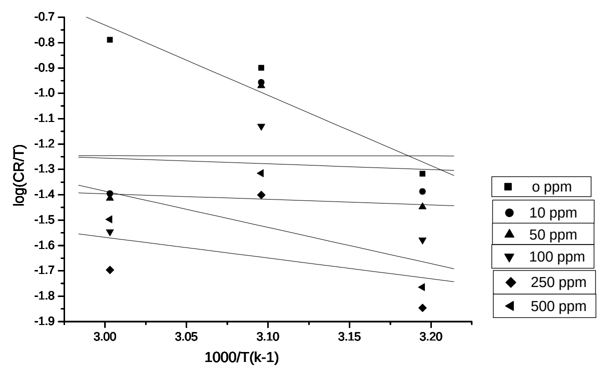

Figure 3
The relation between log (CR/T) and 1/T for different concentrations of SAL extract.

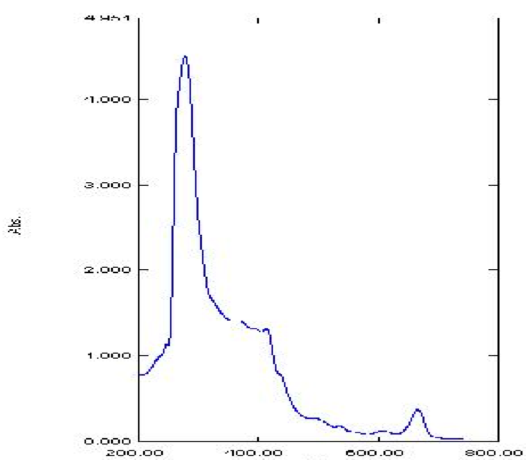

Figure 4
UV spectrum of ethanolic extract of SAL

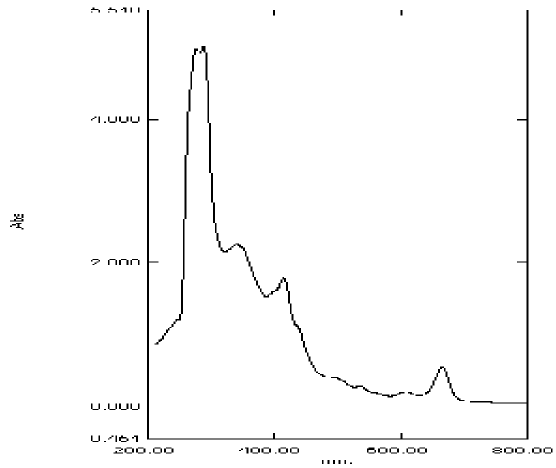

Figure 5
Corrosion product on mild steel in Natural Sea Water in the presence of SAL extract.

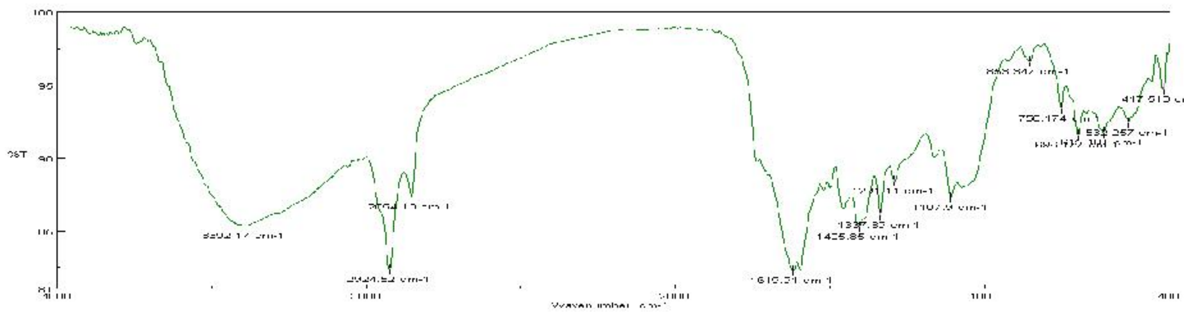

Figure 6
FT-IR spectrum of ethanolic extract of *Sauropus Androgynus* leaves (SAL)

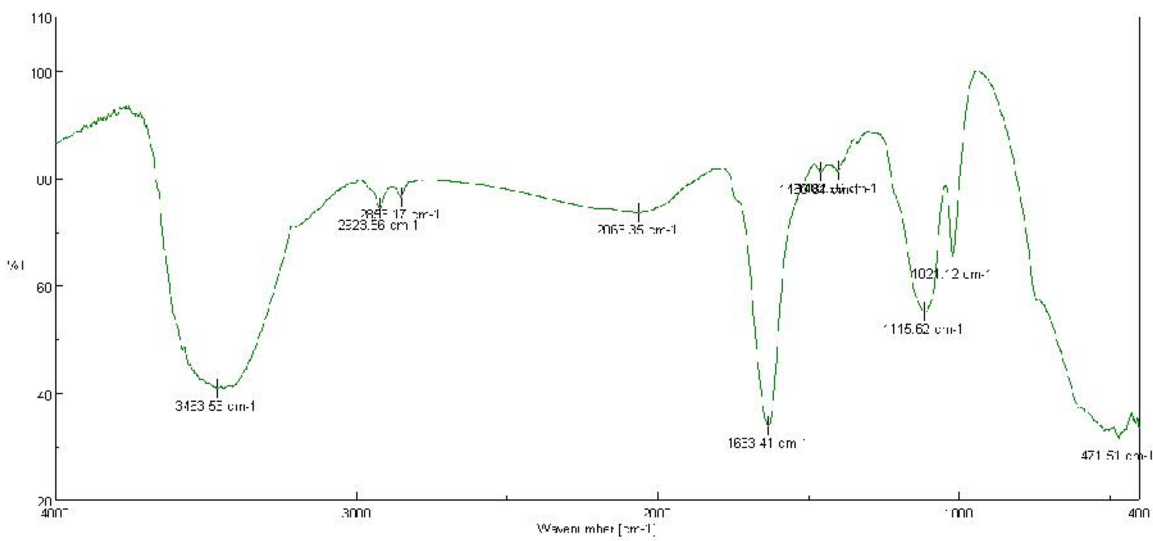

Figure 7
FT-IR spectrum for the corrosion product on Mild steel in the presence of SAL extract with Natural Sea Water

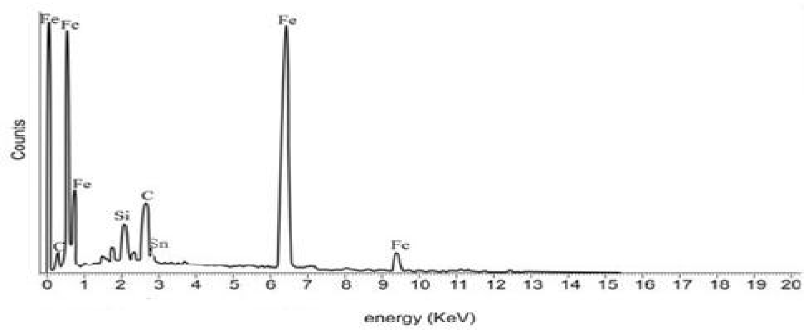

Figure 8
EDX spectrum of the corrosion product on mild steel surface in Natural seawater.

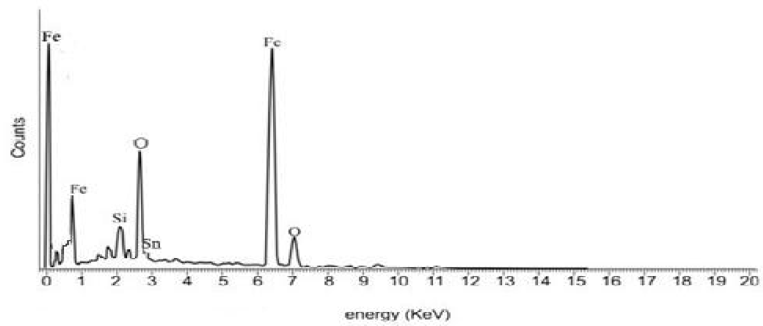

Figure 9
EDX spectrum of the corrosion product on mild steel surface with the presence of SAL extract in Natural seawater.

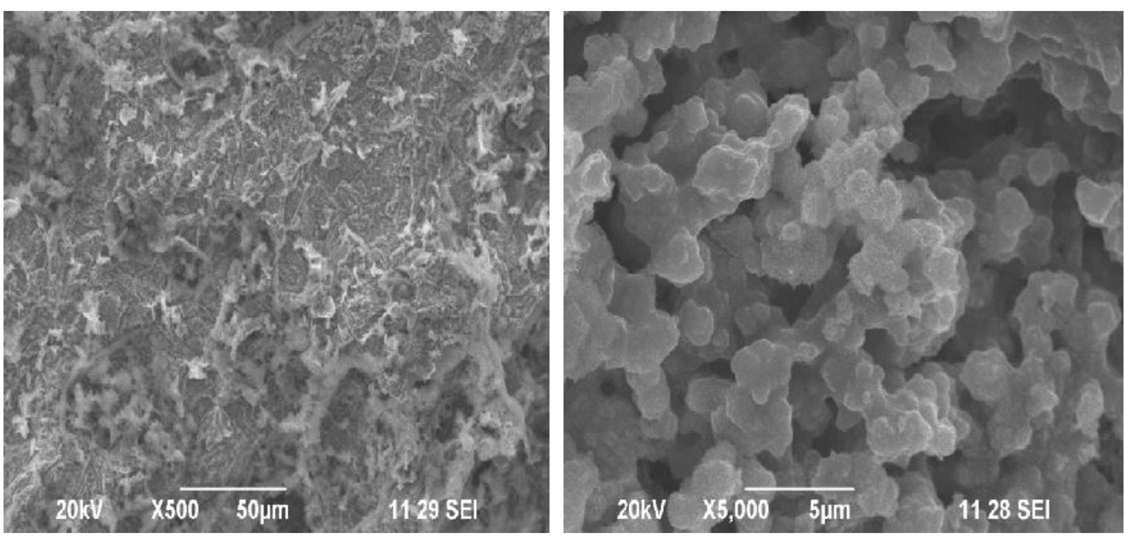

Figure 10
SEM images of the mild steel surfaces: (a) immersed in Natural seawater; (b) immersed in natural sea water with SAL extract

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