

Corrosion resistance of mild steel (hull plate) in sea water in the presence of a coating of an oil extract of plant materials

R. Dorothy,^{1*} T. Sasilatha¹ and S. Rajendran² 

¹Department of EEE, AMET University, Kanathur, East Coast Road, Chennai, India

²Corrosion Research Centre, Department of Chemistry, St. Antony's College of Arts and Sciences for Women Thamaraipady, Dindigul – 624005, Tamil Nadu, India

*E-mail: contactrdorothy@gmail.com, susairajendran@gmail.com

Abstract

Mild steel can be used as hull plates in ship industry. Mild steel has to be in contact with sea water which contains aggressive sodium chloride ions to the extent of 3.5%. This leads to severe corrosion problems. To mitigate this corrosion problem an oil coating containing extracts of natural products has been used. The corrosion protection nature of this oil coating has been evaluated by weight loss method which reveals that the oil coating offers 99% inhibition efficiency to mild steel immersed in natural sea water. The polarization study reveals that the coating acts as a barrier film controlling the anodic reaction predominantly. The corrosion potential is shifted from -0.875 V SCE to -0.611 V SCE. The linear polarization value increases from $1630 \text{ Ohm}\cdot\text{cm}^2$ to $9238 \text{ Ohm}\cdot\text{cm}^2$ ($IE=82.35\%$). The corrosion current decreases from $1.918 \times 10^{-5} \text{ A/cm}^2$ to $0.3538 \times 10^{-5} \text{ A/cm}^2$ ($IE=81.55\%$). These factors confirm that the oil coating controls the corrosion of hull plates in sea water. The AC impedance spectra confirm that the protective coating is very stable as revealed by the fact that in the presence of coating on mild steel, its charge transfer resistance increases, impedance increases, whereas corrosion current decreases to a great extent. Vickers hardness study confirms that in the presence of sea water, the hardness of mild steel decreases whereas in the presence of coating the hardness of mild steel increases. SEM images of various metal surfaces reveal that in the presence of sea water alone, pits are noticed on mild steel whereas in the presence of oil coating the surface appears to be smooth, when immersed in sea water. When mild steel is immersed in sea water, the contact angle decreases when compared with polished metal. But for oil coated mild steel the contact angle increases, hydrophobicity increases and hence corrosion protection increases. It is suggested that this oil coating containing extracts of plant material may be coated on hull plates made of mild steel to protect them from severe corrosion due to the aggressive ions present in sea water.

Keywords: ship corrosion, hull plates, mild steel, oil containing extracts of natural products, green inhibitors.

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Introduction

In ship industry, the corrosion caused by sea water on the hull plates made of mild steel is a major issue. Hence several studies have been reported on the measures taken to control corrosion of metals and alloys in sea water. Shen *et al.* have made a study of pitting corrosion inhibition effect on aluminum alloy in seawater by biomineralized film. The electrochemical results showed that the radius of the impedance arc of the alloy immersed in seawater with bacteria increased gradually with time. The bacteria promoted the formation of the $\text{CaMg}(\text{CO}_3)_2$ film, which blocked seawater from the alloy and consequently, inhibited pitting corrosion [1]. Xu *et al.* have investigated steel rebar corrosion in artificial reef concrete with sulphaaluminate cement. It has been observed that a 2% dosage of corrosion inhibitor can significantly decrease the steel rebar corrosion in a new artificial reef concrete (NARC) to a similar corrosion degree of ordinary artificial reef concrete (ARC) [2]. Colloidal ZrO_2 nanoparticles have been used for corrosion protection of AA2024 in synthetic sea water by Elbasuney *et al.* Inhibition efficiency of 93.6% was achieved. It was noted that ZrO_2 could act as cathodic inhibitor by suppressing the dealloying of the intermetallic particles [3]. In marine conditions, especially in the Arctic, the problems of reliability and safety of marine corrosion protection systems are relevant. Reliability can be enhanced by corrosion inhibitors. Phosphating compound with anode inhibitors have been used by Plaskeeva and Trusov [4]. Duduna *et al.* have compared various adsorption isotherm models for allium cepa as corrosion inhibitor on austenitic stainless steel in sea water. The sorption data of the allium cepa extract obeyed Langmuir, Freundlich, Temkin, El-Awady and Adejo Ekwonchi isotherm of which Langmuir Isotherm gave the best model fit [5]. Corrosion studies of zinc coated steel parts in sea water have been made by Karthikeyan and Jeeva. The corrosion inhibition of zinc coated steel sheets immersed in 3.5% NaCl with sulfisoxazole (SSZ) has been reported by weight loss, potentiodynamic polarization, electrochemical impedance spectroscopy, hydrogen permeation studies and quantum mechanical studies. Polarization studies confirmed that the inhibition mode follows a mixed type. The adsorption of the compounds onto the zinc coated steel surface obeyed Langmuir adsorption isotherm [6]. Managing corrosion in desalination plants has been discussed by Schorr *et al.* To protect the desalination plant (DP) materials, industrial paints, polymeric coatings and rubber linings compatible with the DP fluids are applied. Cathodic protection with sacrificial anodic metals or impressed direct electrical current and corrosion inhibitors are supplied [7]. Influence of inhibitors on reinforced bar corrosion of coral aggregate seawater concrete has been investigated by Da *et al.* The effect of inhibitors on corrosion behavior of reinforced bar in coral aggregate seawater concrete (CASC) in artificial sea water was studied by means of linear polarization resistance method (LPR) and electrochemical impedance spectroscopy (EIS). Two inhibitors, calcium nitrite rust inhibitor (CN) and amino-alcohol rust inhibitor (AA) are used. The effect of inhibitors on corrosion behavior of reinforced bar in coral aggregate seawater concrete (CASC) in artificial sea water was studied by means of linear polarization resistance method (LPR) and electrochemical impedance spectroscopy (EIS)

[8]. Ahmad *et al.* have reported synthesis, identification, theoretical and experimental studies for carbon steel corrosion inhibition in sea water for new urea and thiourea derivatives linkage to 5-Nitro Isatin Moiety. Isatin derivative has been chosen as the best inhibitor by polarization study [9]. Evaluation of leaf and bark extracts of *Acacia tortilis* as corrosion inhibitors for mild steel in seawater has been reported by Ali *et al.* Polarisation study reveals that the extracts act as mixed type inhibitors. AC impedance spectra confirm the formation of a protective layer on the metal surface. The adsorption of the inhibitors on the steel surface follow Langmuir adsorption isotherm model [10].

The present study is undertaken to investigate the corrosion resistance of mild steel, which is used in the manufacture of hull plates, immersed in sea water, in the absence and presence of an oil coating containing plant extracts. The corrosion inhibition efficiency has been evaluated by weight loss method. The mechanistic aspects of corrosion inhibition have been studied by polarization study and AC impedance spectra. The protective film has been analyzed by FTIR spectroscopy. The surface morphology has been investigated by SEM. The hardness of the metal surface has been measured. The contact angle of various surfaces has been found out to know the hydrophobic nature of the various surfaces.

Experimental

Composition of mild steel

The composition of mild steel is given in Table 1. This mild steel is used in the construction of hull plates.

Table 1. Composition of mild steel.

Element	Average, %	Abs. Std. Dev.	Ref. Std. Dev.	1	2
C	0.101	0.0014	1.4	0.102	0.1
Si	0.055	0.0021	3.89	0.053	0.056
Mn	1.629	0.0057	0.35	1.633	1.625
P	0.0087	0.0003	3.25	0.0085	0.0089
S	0.0028	0.0003	10.1	0.0026	0.003
Cr	0.036	0.0014	3.93	0.037	0.035
Mo	0.0086	0.00007	0.83	0.0086	0.0085
Ni	0.033	0.0007	2.18	0.033	0.32
Cu	0.0063	0.00007	1.13	0.0062	0.0063
Al	0.044	0.0014	3.21	0.043	0.045
As	0.0011	0	0	0.0011	0.011
B	0.0027	0.0005	18.68	<0.00010	<0.00010

Element	Average, %	Abs. Std. Dev.	Ref. Std. Dev.	1	2
Bi	<0.00010	0.00002	84.85	<0.0025	0.003
Ce	0.0032	0.0013	42.65	0.0041	0.0022
Co	0.011	0	0	0.011	0.011
Mg	0.0003	0	0	0.0003	0.0003
Nb	0.03	0.0007	2.4	0.029	0.03
Pb	0.0081	0.0013	15.71	0.0072	0.009
Sb	0.004	0.0004	8.95	0.0037	0.0042
Sn	0.0034	0	0	0.0034	0.0034
Ta	0.03	0.0071	23.57	0.025	0.035
La	0.0071	0	0	0.0071	0.0071
Ti	0.0035	0	0	0.0035	0.0035
V	0.138	0.0014	1.02	0.137	0.139
W	0.071	0.0078	11.03	0.076	0.065
Zn	0.0024	0	0	0.0024	0.0024
Zr	0.0051	0.0002	0.2	0.0052	0.0049
Se	<0.0005	0.0001	4.42	<0.0005	<0.0005
N	0.0093	0.00007	0.76	0.0092	0.0093
Ca	0.0014	0.0001	10.1	0.0013	0.0015
Te	0.0026	0.0025	97.91	<0.0010	0.0044
Fe	97.74	0	0	97.74	97.74

Sea water

The corrosion resistance of mild steel in sea water was investigated, before oil coating and after oil coating. The composition of sea water used in this study is given in Table 2. Sea water was collected in Bay of Bengal, located at Kanampadi, East Coast Road, Chennai, India (near AMET University, Kanampadi, East Coast Road, Chennai, India).

Table 2. Composition of sea water used in this study (all the values, except pH, are in ppm).

S. No.	Physical Examination	Acceptable Limit	Permissible limit	Sample Value
1	Colour	–	–	Unobjectionable
2	Odour	Unobjectionable	Unobjectionable	
3	Turbidity NT Units	1	5	0.2

S. No.	Physical Examination	Acceptable Limit	Permissible limit	Sample Value
4	Total Dissolved Solids mg/l	500	2000	29400
5	Electrical Conductivity micro mho/cm	—	—	42000
6	pH	6.5–8.5	6.5–8.5	7.46
7	pH Alkalinity as CaCO ₃	—	0	0
8	Total Alkalinity as CaCO ₃	200	600	140
9	Total Hardness as CaCO ₃	200	600	4000
10	Calcium as Ca	75	200	1200
11	Manganese as Mn	30	100	240
12	Iron as Fe	0.1	1	0
13	Magnesium as Mg	0.1	0.3	NT
14	Free Ammonia as NH ₃	0.5	0.5	0.48
15	Nitrite as NO ₂	0.5	0.5	0.104
16	Nitrate as NO ₃	45	45	25
17	Chloride as Cl	250	1000	15000
18	Fluoride as F	1	1.5	1.8
19	Sulphate as SO ₄	200	400	1170
20	Phosphate as PO ₄	0.5	0.5	1.47
21	Tids Test 4hrs as O ₂	—	—	NT

Preparation of inhibitor (Oil containing extracts of plant materials)

5 g Each of Cardamom (dismbiguation), Clove (dismbiguation), Nutmeg, India Sambrani (loban), Chrysopogon zizanioides, commonly known as vetiver and Camphor were boiled along with sandalwood oil for 15 minutes in an iron vessel. The suspended impurities were removed by filtration. The total volume of the oil extract of the above was 100 ml. This oil extract of the plant materials was used in the present study.

The main active ingredients of the above materials are given in Table 3, and their structures are shown in Figure 1.

Table 3. Ingredients of natural products.

S. No.	Natural products	Ingredients
1	Cardamom	α -terpineol, myrcene, 1,8-cineol
2	Clove	Eugenol
3	Nutmeg	Myristicin, tremyristicin, myristic acid
4	India Sambrani (loban)	Benzoin
5	Vetiver	α -vetivone, β -vetivone, khusimol
6	Camphor	(+)-Camphor, (–)-Camphor
7	sandalwood oil	α -santalol, β -santalol

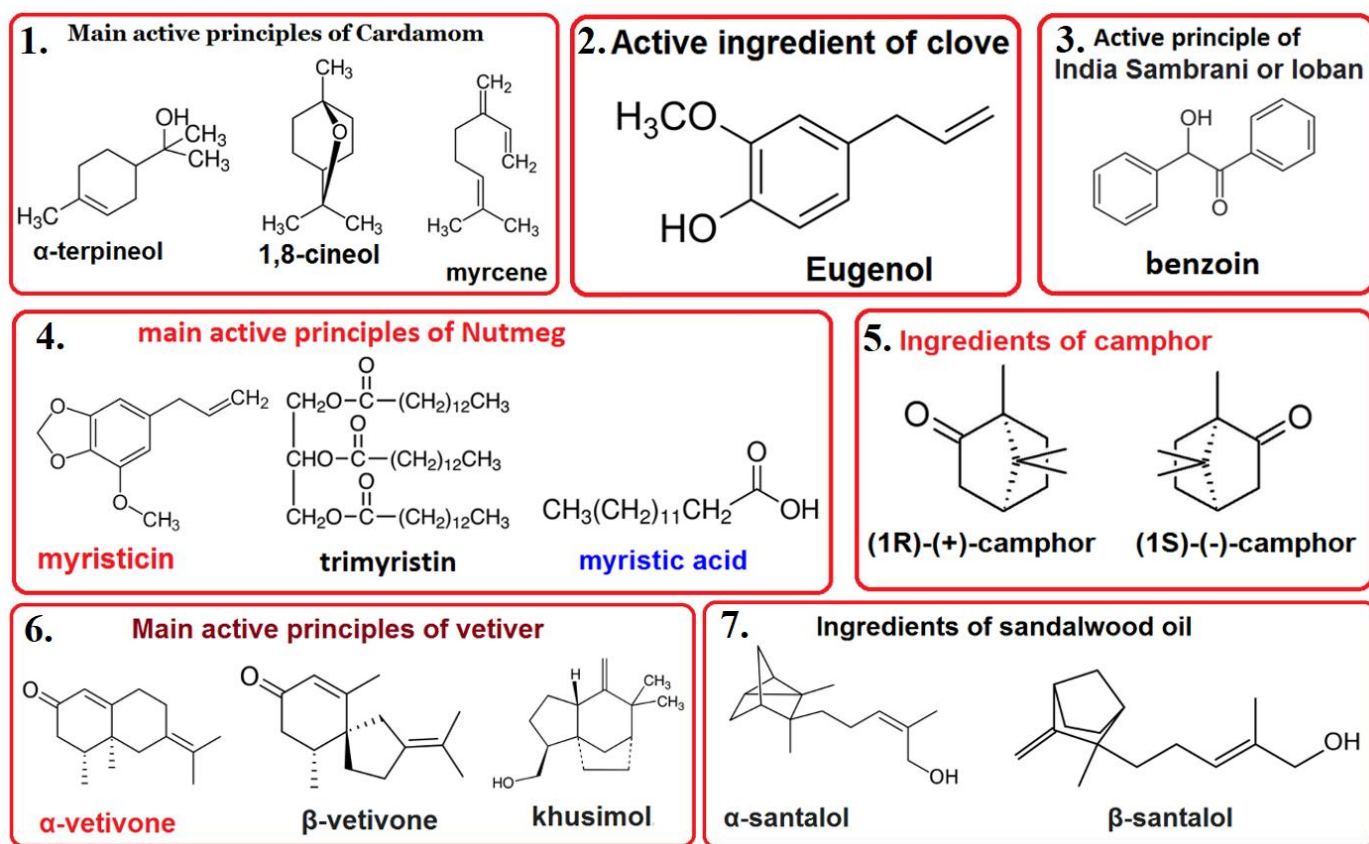


Figure 1. Ingredients of natural products: 1 – active principles of cardamom; 2 – active principles of clove; 3 – active principles of loban; 4 – active principles of nutmeg; 5 – active principles of camphor; 6 – active principles of vetiver; 7 – active principles of sandalwood oil.

Weight loss method

Weights of the three polished mild steel specimens were measured before and after immersion in various test solutions. The inhibition efficiencies were calculated from the relation:

$$IE = \frac{CR_1 - CR_2}{CR_1} \cdot 100\%,$$

where CR_1 is the corrosion rate in the absence of inhibitor and CR_2 is the corrosion rate in the presence of inhibitor (oil coating).

Electrochemical studies

In the present work the corrosion resistance of mild steel specimens immersed in various test solutions was measured by Polarization study and AC impedance spectra.

Polarization study

Polarization studies were carried out in a CHI Electrochemical work station model 660A. It was provided with automatic iR compensation facility. A three electrode cell assembly was used (Figure 2). The working electrode was mild steel. A SCE was the reference electrode. Platinum was the counter electrode. From polarization study, corrosion parameters such as corrosion potential (E_{corr}), corrosion current (I_{corr}), Tafel slopes anodic = b_a and cathodic = b_c and LPR (linear polarisation resistance) values were derived. The scan rate (V/S) was 0.01. Hold time at (E_{fcs}) was zero and quiet time (s) was 2.

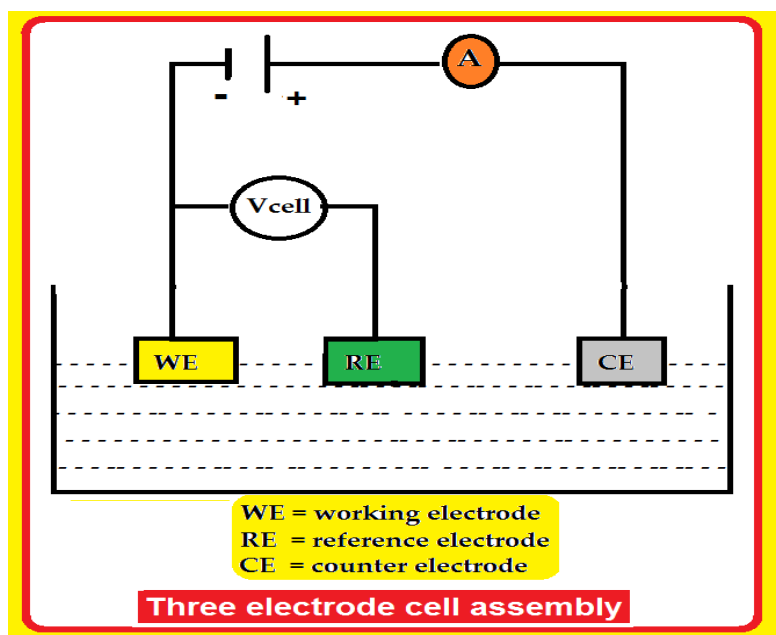


Figure 2. Three electrode cell assembly.

AC Impedance spectra

The same instrument and set-up used for polarization study was used to record AC impedance spectra also. The real part (Z') and imaginary part ($-Z''$) of the cell impedance were measured in Ohms at various frequencies. AC impedance spectra were recorded with initial $E(V)=0$, high frequency (1×10^5 Hz), low frequency (1 Hz), amplitude (0.005 V) and

quiet time (2 s). From Nyquist plot the values of charge transfer resistance (R_t) and the double layer capacitance (C_{dl}) were calculated.

Surface analysis by FTIR spectra

FTIR spectra were recorded using a Perkin-Elmer 1600 FTIR spectrophotometer with a resolving power of 4 cm^{-1} . In the FTIR spectral study, the following method was adopted. A few drops of the oil extract was placed on a glass plate and dried in the air. The film was carefully scratched with glass rod and mixed with KBr and made into a pellet. Its FTIR spectrum was recorded. In the next stage, the metal was immersed in the oil extract for one day. After one day, the metal was taken out and dried. The film formed on the metal surface was carefully scratched with glass rod and mixed with KBr and made into a pellet. Its FTIR spectrum was recorded. Mild steel was immersed in sea water alone for one day. Brown iron oxides were formed. Their FTIR spectrum was recorded.

Scanning Electron Microscopic studies (SEM)

The surface morphology of various metal surfaces was examined using JEOL MODEL 6390 computer controlled scanning electron microscope.

Contact angle measurement

Contact angle measurements of various surfaces were measured using Goniometer model G16.

Results and Discussion

Analysis of results of weight loss method

Corrosion resistance of mild (hull plate) in natural sea water, before and after oil coating has been evaluated by weight loss method. The results are given in Table 4 and Figure 3.

Table 4. Inhibition of corrosion of mild steel in seawater. Inhibitor system: Oil containing plant extract, Immersion period: 1 day.

System	Corrosion rate (mdd)	Inhibition efficiency, (%)	Surface coverage (θ)
Mild steel immersed in Sea water	16.23	0	0
Oil extract coated mild steel immersed in sea water	0.1623	99	0.99

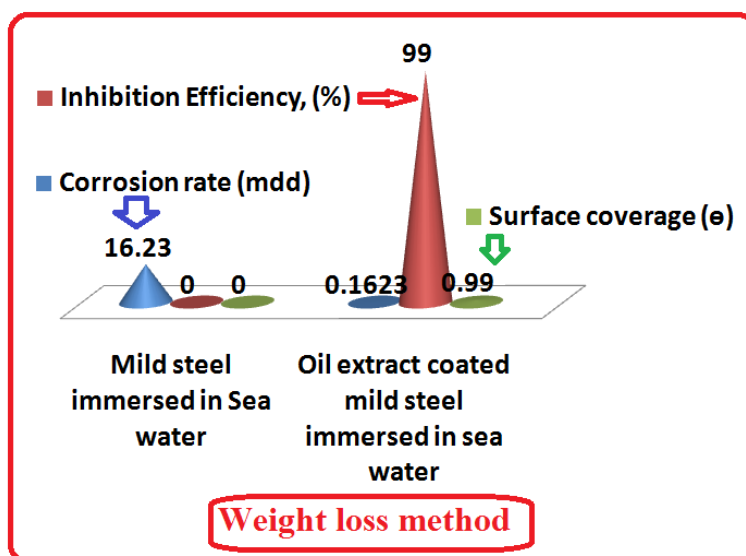


Figure 3. Summary of results of weight loss method.

It is observed from Table 4 that oil coating offers 99% corrosion protection to mild steel which is used as hull plates.

Implication

It implies that the hull plates may be coated with the oil containing the plant extract, to protect the metal from corrosion caused by sea water.

Electrochemical studies

The hull plates of the ship are always in contact with sea water, which contains aggressive ions such as chloride ions. So the hull plates undergo corrosion. To prevent this type of corrosion the hull plates were coated with an oil extract of natural products. The hull plate specimens were made of mild steel as discussed in experimental section. The preparation of the oil extract has also been explained in experimental section. The corrosion resistance of mild steel (hull plate) in sea water before and after coating has been evaluated by weight loss method and electrochemical studies such as polarization study and AC impedance spectra [11–30].

Analysis of polarisation curves

Polarisation study has been used to detect the formation of protective film on the metal surface. When a protective film is formed on the metal surface, the linear polarisation resistance (*LPR*) increases and the corrosion current (*I*) decreases (Figure 4).

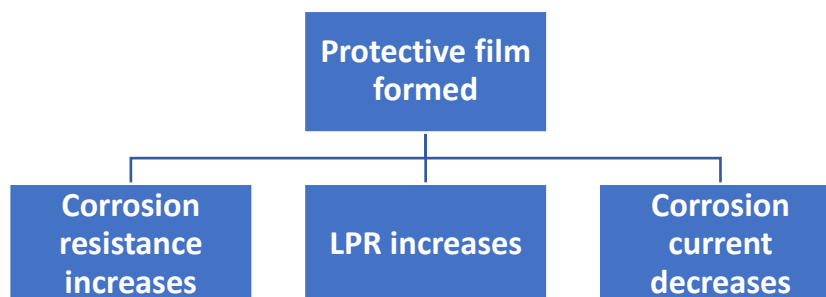


Figure 4. Correlation among corrosion parameters in polarization study.

Corrosion parameters derived from polarisation study, namely corrosion potential (E_{corr}), Tafel slopes (b_c , b_a), Linear Polarisation Resistance (LPR) values and Corrosion Current (I_{corr}) values are given in Table 5. The polarisation curves of mild steel (hull plate) immersed in sea water in the absence and presence of oil coating containing plant extract are shown in Figure 5.

Table 5. Corrosion parameters of mild steel (hull plate) immersed in sea water in the absence and presence of oil containing plant extracts, obtained by Polarization study.

System	E_{corr} , V _{SCE}	b_c , V/decade	b_a , V/decade	LPR , Ohm·cm ²	I_{corr} , A/cm ²
Mild steel immersed in sea water	−0.875	9.428	4.476	1630	1.918×10^{-5}
Oil coated mild steel immersed in sea water	−0.611	3.779	9.524	9238	0.3538×10^{-5}

It is observed from the Table 5 that when mild steel is immersed in sea water, the corrosion potential is -0.875 V vs. SCE; the LPR value is 1630 Ohm·cm². The corrosion current value is 1.918×10^{-5} A/cm². It is inferred from the Table 5, that in the presence of inhibitor (oil coated mild steel), the corrosion potential is shifted from -0.875 V to -0.611 V vs. SCE. This anodic shift indicates that the anodic reaction of metal dissolution ($\text{Fe} \rightarrow \text{Fe}^{2+} + 2e^-$) is controlled predominantly in the presence of the oil coating containing plant extracts. It is further noticed that the LPR value increases (Figure 6) from 1630 Ohm·cm² to 9238 Ohm·cm². Correspondingly the corrosion current value decreases from 1.918×10^{-5} A/cm² to 0.3538×10^{-5} A/cm². These observations confirm that a protective film is formed on the metal surface. This controls the corrosion of metal. If a protective film is formed on the metal surface, LPR value increases and corrosion current decreases.

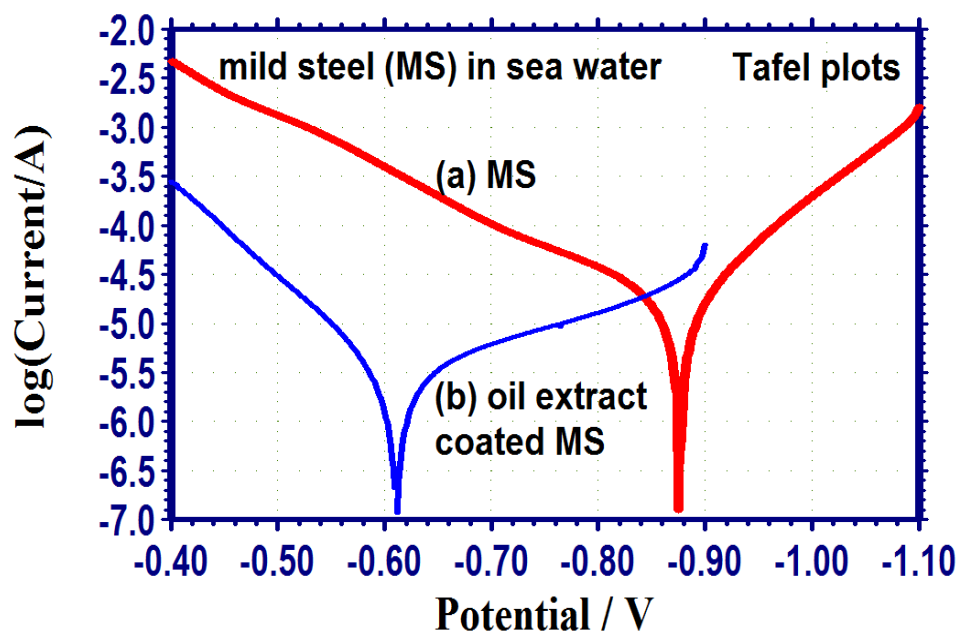


Figure 5. Polarisation curves of mild steel immersed in various test solutions: (a) MS in sea water, (b) oil extract coated MS in sea water.

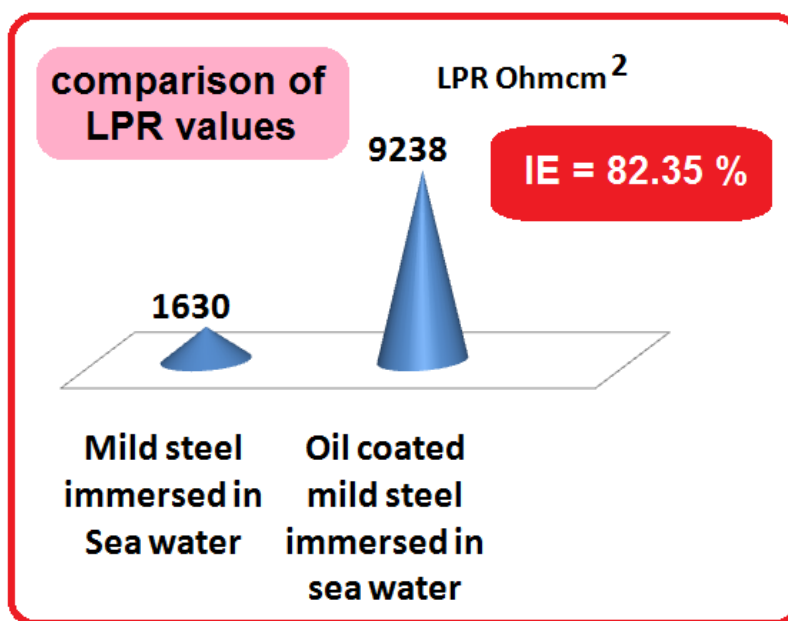


Figure 6. Comparison of *LPR* values.

Implication

Polarization study leads to the conclusion that oil coated mild steel immersed in sea water is more corrosion resistant than bare mild steel in sea water. It implies that the hull plates may be coated with the oil containing plant extracts.

AC impedance spectra

The protective film formed on the metal surface is confirmed by AC impedance spectra. If a protective film is formed on the metal surface, the charge transfer resistance (R_t) value increases; double layer capacitance value (C_{dl}) decreases and the impedance [$\log(Z/\text{Ohm})$] value increases (Figure 7). The AC impedance spectra of mild steel (hull plate) immersed in sea water in the absence and presence of oil coating containing plant extract are shown in Figures 8 and 9. The AC impedance spectra of mild steel (hull plate) immersed in sea water in the absence and presence of oil coating containing plant extract are shown in Figure 8 (Nyquist plot), Figure 9 (Bode plots). The corrosion parameters, namely R_t , C_{dl} , and impedance values are given in Table 6. It is observed from the Table 6 that, when mild steel is immersed in well water, the R_t value is $6.93 \text{ Ohm}\cdot\text{cm}^2$. The C_{dl} value is $7.359 \times 10^{-7} \text{ F/cm}^2$. The impedance value is 1.114 Z/Ohm . In the presence of inhibitor system, the R_t value increases (Figure 10) from $6.93 \text{ Ohm}\cdot\text{cm}^2$ to $403.3 \text{ Ohm}\cdot\text{cm}^2$. The C_{dl} value decreases from $7.359 \times 10^{-7} \text{ F/cm}^2$ to $0.1265 \times 10^{-7} \text{ F/cm}^2$. The impedance value increases from 1.114 to 2.65 Z/Ohm .

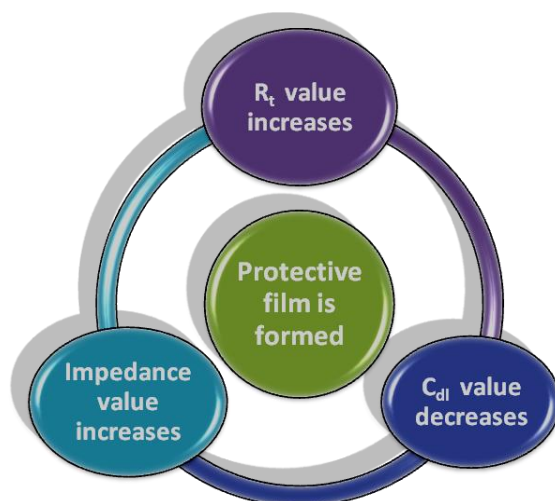


Figure 7. Relation among corrosion resistance and impedance parameters.

Table 6. Corrosion parameters of mild steel immersed in sea water obtained by AC impedance spectra.

System	R_t $\text{Ohm}\cdot\text{cm}^2$	C_{dl} F/cm^2	Impedance $\log(Z/\text{Ohm})$
Mild steel immersed in sea water	6.93	7.359×10^{-7}	1.114
Oil extract coated mild steel immersed in sea water	403.3	0.1265×10^{-7}	2.65

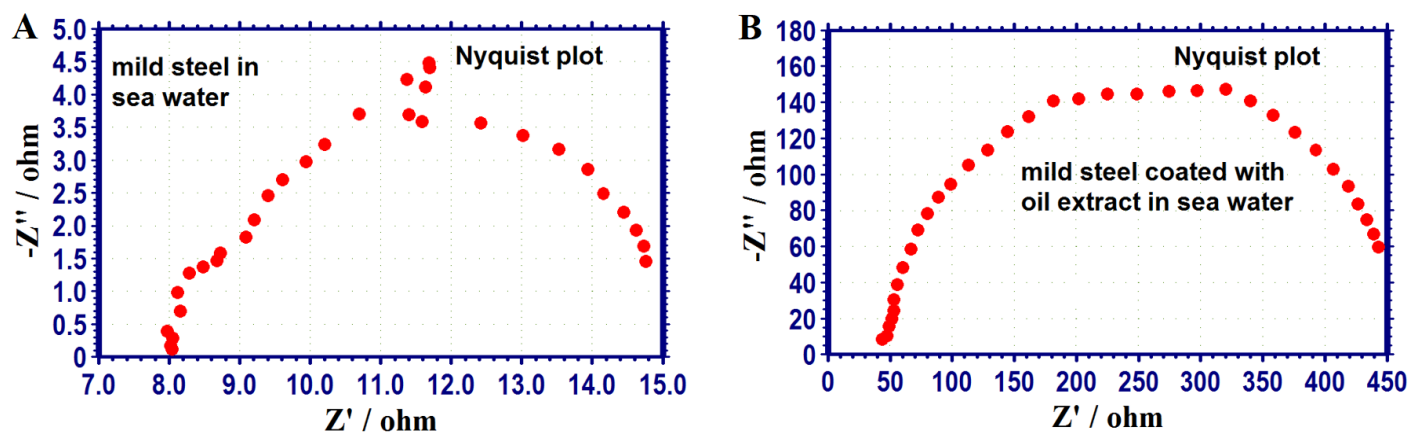


Figure 8. Nyquist plot of: A – mild steel immersed in sea water; B – oil extract coated mild steel immersed in sea water.

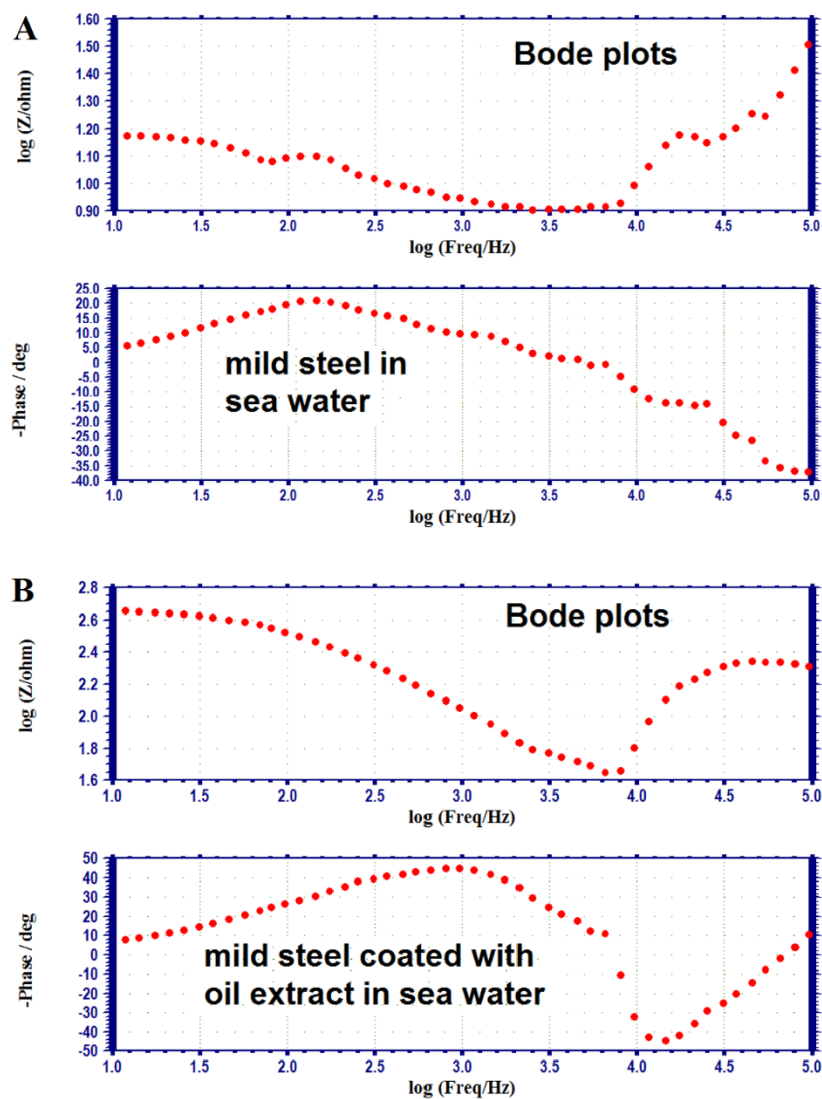


Figure 9. Bode plots of: A – mild steel immersed in sea water; B – oil extract coated mild steel immersed in sea water.

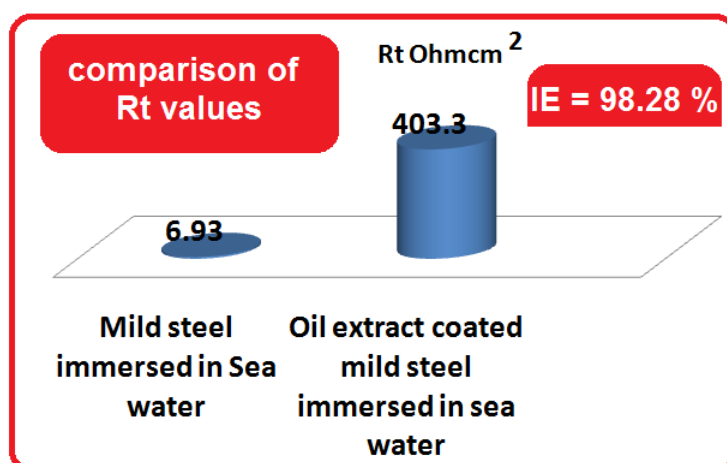


Figure 10. Comparison of R_t values.

Implication

AC impedance spectra lead to the conclusion that oil coated mild steel immersed in sea water is more corrosion resistant than bare mild steel in sea water. It implies that the hull plates, made of mild steel may be coated with the oil containing plant extracts to protect them from corrosion.

Analysis of Vickers hardness

The Vickers test is often easier to use than other hardness tests since the required calculations are independent of the size of the indenter, and the indenter can be used for all materials irrespective of hardness. The basic principle, as with all common measures of hardness, is to observe a material's ability to resist plastic deformation from a standard source. The Vickers test can be used for all metals and has one of the widest scales among hardness tests. The unit of hardness given by the test is known as the Vickers Pyramid Number (HV).

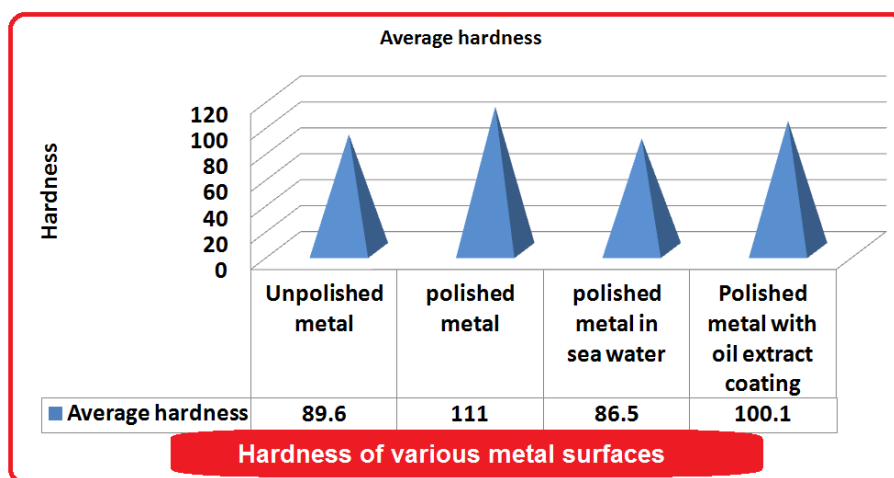
The hardness was measured for polished mild steel surface (system A), polished mild steel surface immersed in corrosive medium (sea water) (system B) and polished mild steel surface coated with oil containing plant extract, immersed in corrosive medium (sea water) (system C). The values are given in Tables 7 and 8. It is observed that for system A the hardness is high. For system B the hardness is low because the corroded surface contains iron oxide film which is porous and amorphous. The surface is very rough. Pits are noticed due to corrosion. For system C the surface is smooth, due to the formation of protective film. Usually the hardness is in between that of system A and B. That is, lower than that of polished metal but higher than that of corroded surface (Figure 11). This is due to the formation of a protective film formed on the metal during corrosion inhibition process. The protective film consists of the paint coated on mild steel. Thus the Vickers hardness is used in corrosion inhibition study. Weight loss method reveals that the paint coating offers an inhibition efficiency of 99% to carbon steel immersed in sea water.

Table 7. Hardness of various metal (mild steel-hull plate) surfaces.

S. No.	System	S. No.	L1	L2	HV	Average hardness
1	Unpolished metal	1	44.65	48.27	85.8	–
2	Unpolished metal	2	43.60	45.51	93.4	89.6
3	polished metal	1	40.41	41.54	110	–
4	polished metal	2	40.27	41.02	112	111
5	polished metal in sea water	1	45.17	47.22	86.2	–
6	polished metal in sea water	2	45.64	46.28	86.8	86.5
7	Polished metal with oil extract coating	1	42.36	43.25	101	–
8	Polished metal with oil extract coating	2	42.66	43.77	99.2	100.1

Table 8. Summary of Hardness of various metal (mild steel-hull plate) surfaces.

S. No.	System	Average hardness
1	Unpolished metal	89.6
2	polished metal	111
3	polished metal in sea water	86.5
4	Polished metal with oil extract coating	100.1

**Figure 11.** Harness of various metal surfaces.

It is noted from Figure 11 that the hardness of mild steel increases in the presence of oil coating. Hence such oil coating is recommended for hull plates to prevent them from corrosion caused by sea water.

Analysis of SEM images

The surface morphology of various metal surfaces has been picturised by SEM images and they are anchored in images (Figure 12). It is interesting to note that pits are noticed on mild steel when it is immersed in sea water. However, the pits have disappeared when oil coating is given, and the metal is sea water. Because of the hydrophobic nature of the oil coating water cannot enter onto the metal surface. Thus corrosion of hull plates can be prevented.

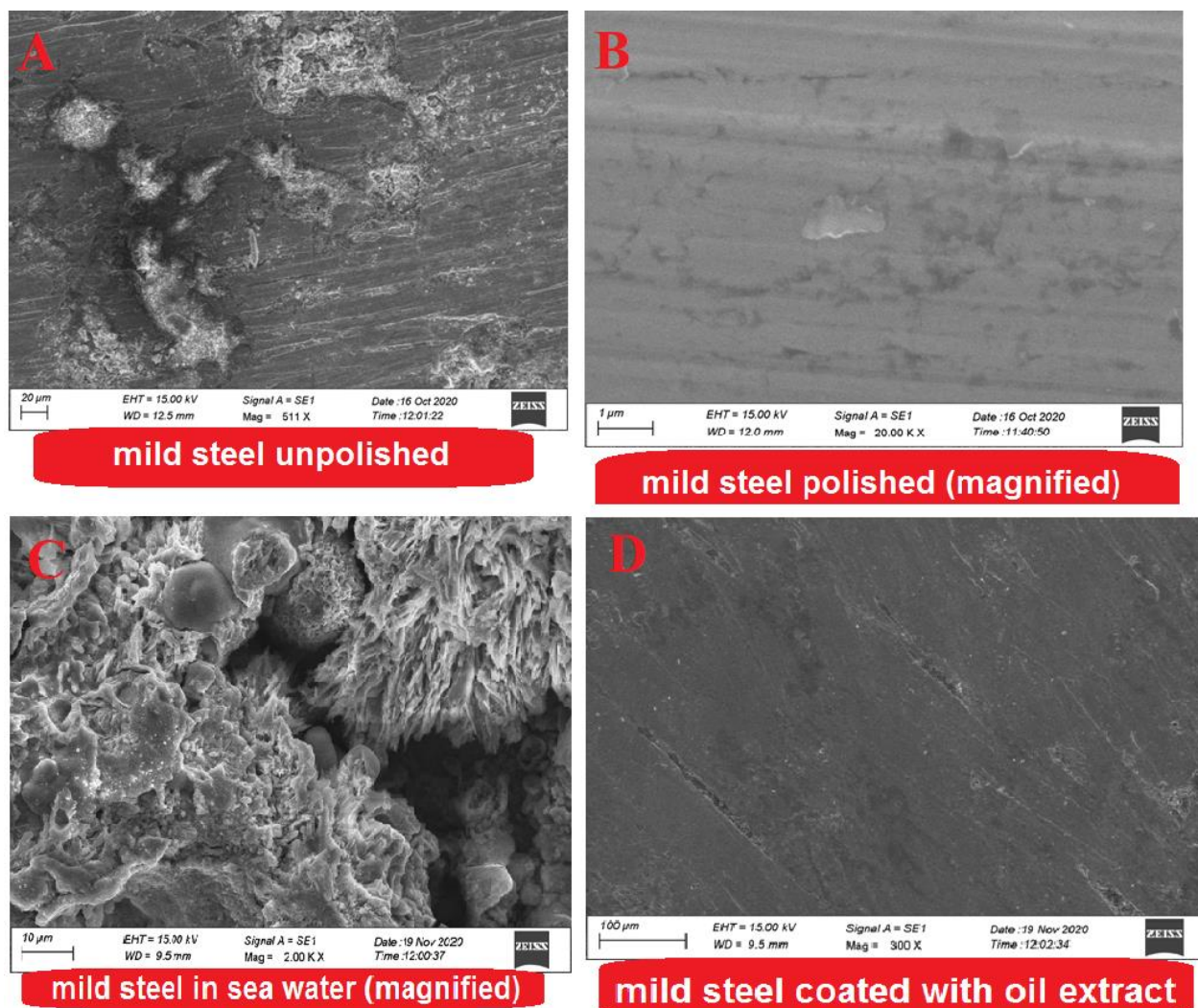


Figure 12. SEM image of: A – unpolished mild steel; B – unpolished mild steel; C – polished mild steel immersed in sea water; D – polished mild steel coated with oil extract and immersed in sea water.

Contact angle measurements

Contact angle measurements can be used to predict the hydrophobic nature of metal surfaces. When contact angle increases, hydrophobicity increases. This results in increase in corrosion inhibition efficiency (Figure 13).

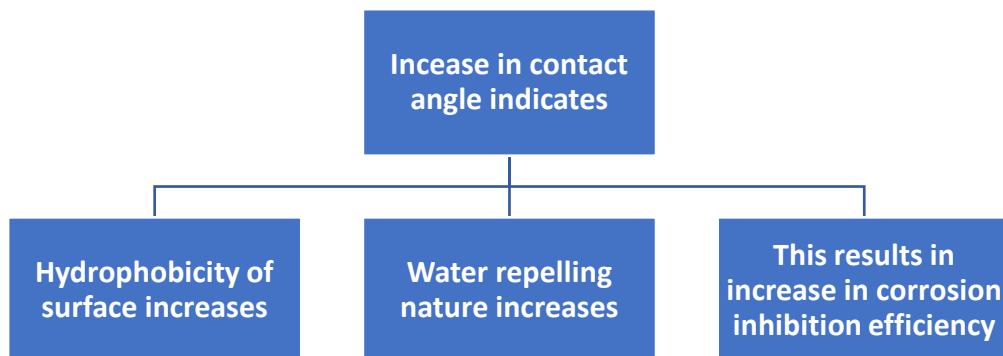


Figure 13. Contact angle and corrosion inhibition efficiency.

The contact angles of various metal surfaces are shown in Figure 14. For polished mild steel the contact angle is 108.5° . When mild steel is immersed in the corrosive medium the contact angle decreases to 23.6° . However, when oil coating is given the contact angle increases from 23.6° to 74.3° . This results in very high corrosion inhibition efficiency, namely, 99% as revealed by weight loss method.

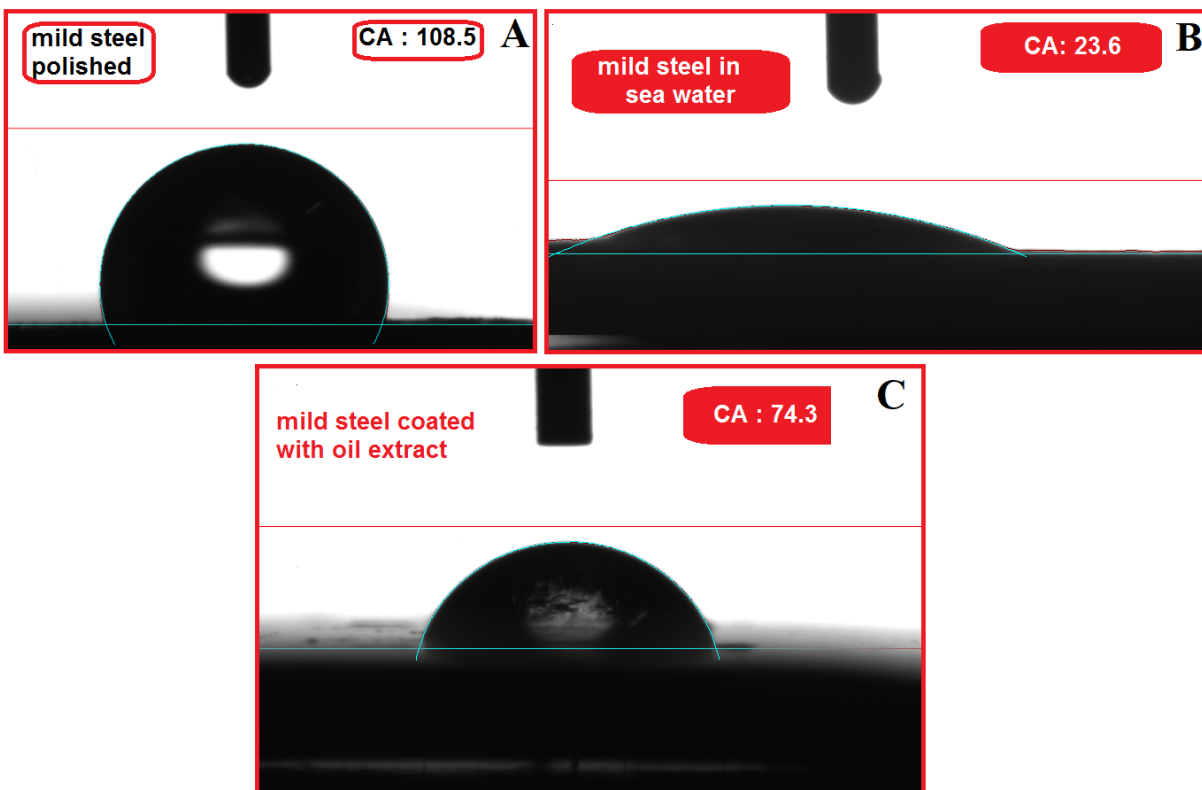


Figure 14. Contact angle of: A – polished mild steel surface; B – polished mild steel surface after immersion in sea water; C – polished oil coated mild steel surface after immersion in sea water.

Analysis of results of FTIR spectra

5 g of each Cardamom (disambiguation), Clove (disambiguation), Nutmeg, India Sambrani (loban), Chrysopogon zizanioides, commonly known as vetiver, and Camphor were boiled along with sandalwood oil for 15 minutes in an iron vessel. The suspended impurities were removed by filtration. The total volume of the oil extract of the above was 100 ml. This oil extract of the plant materials was used in the present study. The main active ingredients of the above materials are given in Table 3, and their structures are shown in Figure 1, in the experimental section.

FTIR spectra have been used to characterize the protective film formed on the metal surface. This protective film controls the corrosion of metal immersed in the corrosive medium, sea water in the present study.

An oil (sandalwood oil) extract of plant materials was coated on the metal surface. The oil extract was prepared by heating the shade dried plant materials such as, Cardamom, Clove, Nutmeg, vetiver and Camphor. The active principles of the oil extract contain the functional groups given in the Table 3.

In the FTIR spectral study, the following method was adopted. A few drops of the oil extract was placed on a glass plate and dried in the air. The film was carefully scratched with glass rod and mixed with KBr and made into a pellet. Its FTIR spectrum is shown in Figure 15. The stretching frequencies of various functional groups are shown in Table 9.

Table 9. FTIR stretching frequencies of functional groups.

S. No.	Functional group	Oil extract of natural products (glass plate), frequency, cm^{-1}	Protective film on metal surface, frequency, cm^{-1}
1	Cyclohexene	1650 C=C	1630.4
2	Cyclohexane	2925	2926
3	$-\text{CH}_3$ Aliphatic C–H	2925.58, 2854.49	2926, 2855
4	–OH	3437.11 3436	3437
5	–O– Ether aliphatic	1119.2	1116
6	Benzene, aromatic ring C=C	1746	1746
7	Aliphatic C=C	1630	1630.4
8	Aliphatic aromatic ether	1240, 1162, 1119, 1036	1164, 1116, 1024
9	C=O carboxyl group	1746	1744
10	C=O	1746	1744

In the next stage, the meal was immersed in the oil extract for one day. After one day, the meal was taken out and dried. The film formed on the metal surface was carefully scratched with glass rod and mixed with KBr and made into a pellet. Its FTIR spectrum is

shown in Figure 16. The stretching frequencies of various functional groups are shown in Table 9. There is shift in the position of the frequencies of the various functional groups. This suggests that the active principles present in the oil extract have combined with Fe^{2+} on the metal surface forming the protective film. Thus it is inferred that the protective film consists of Fe^{2+} – active principle complexes, formed on the metal surface.

The FTIR spectrum of the metal surface immersed in the corrosive medium namely sea water (SW) is shown in Figure 17. The peaks indicate the presence of various oxides of iron [31, 32]. Surprisingly the magnetic oxide of iron, Fe_3O_4 , is present as nanoparticles. This layer is very close to the iron surface; next comes the α - FeOOH layer and then FeOOH layer present on the upper layer of the cannon. Similar observation is made in the case of Delhi iron pillar also.

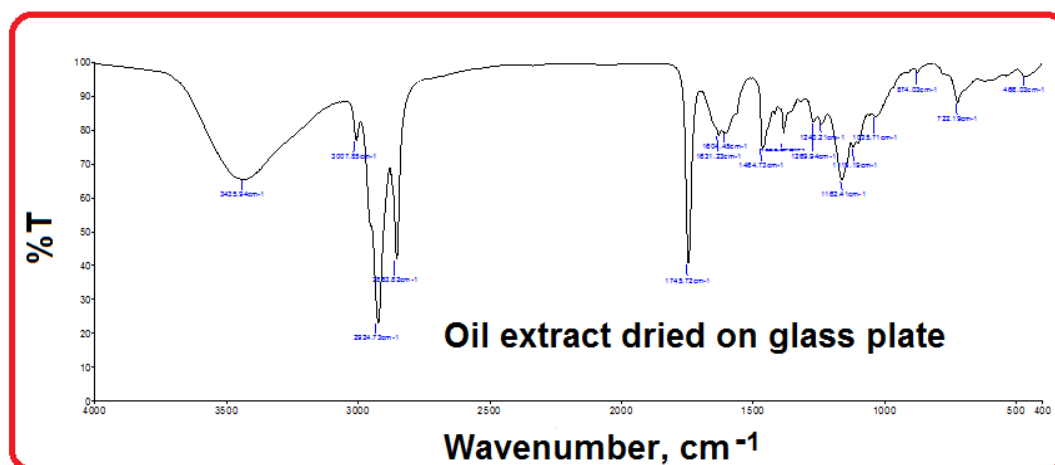


Figure 15. FTIR spectrum of oil extract dried on glass plate.

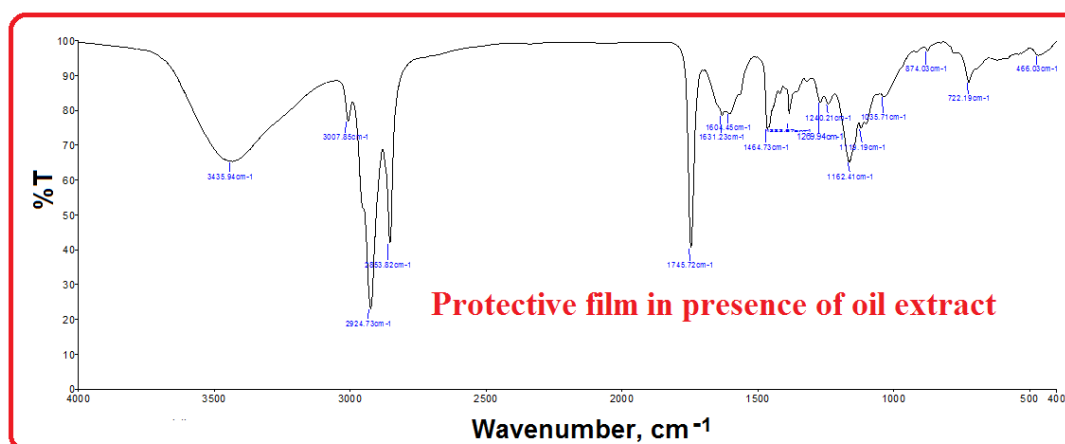


Figure 16. FTIR spectrum of protective film.

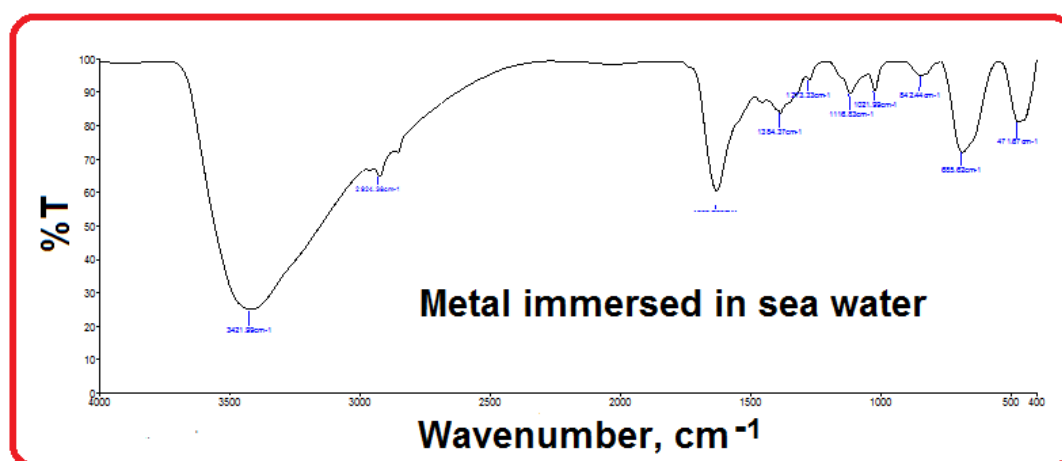


Figure 17. FTIR spectrum of mild steel immersed in sea water (oxides of iron).

The peak at 686 cm^{-1} is due to the iron–oxygen bond. The peaks due to magnetic iron oxide (Fe_3O_4) nanoparticles appear at $3422, 1633, 1022\text{ cm}^{-1}$ [31, 32].

Table 10. FTIR stretching frequencies of iron oxides.

S. No.	Iron oxide	Frequency, cm^{-1}
1	FeOOH	472, 1022
2	Fe_3O_4	2924, 1384, 1022
3	$\alpha\text{-Fe}_2\text{O}_3$	1633
4	Iron-oxygen bond	686
5	Magnetic iron oxide nanoparticles Fe_3O_4	3422, 1633, 1022

Conclusions

- Mild steel can be used as hull plates in ship industry. Mild steel has to be in contact with sea water which contains aggressive sodium chloride ions to the extent of 3.5%. This leads to severe corrosion problems.
- To mitigate this corrosion problem an oil coating containing extracts of natural products was used.
- The corrosion protection nature of this oil coating has been evaluated by weight loss method which reveals that the oil coating offers 99% inhibition efficiency to mild steel immersed in natural sea water.
- The polarization study reveals that the coating acts as a barrier film controlling the anodic reaction predominantly. The corrosion potential is shifted from -0.875 V SCE to -0.611 V SCE . The linear polarization value increases from $1630\text{ Ohm}\cdot\text{cm}^2$ to $9238\text{ Ohm}\cdot\text{cm}^2$. The corrosion current decreases from $1.918\times 10^{-5}\text{ A/cm}^2$ to

$0.3538 \times 10^{-5} \text{ A/cm}^2$. These factors confirm that the oil coating controls the corrosion of hull plates in sea water.

- The AC impedance spectra confirm that the protective coating is very stable as revealed by the fact that in the presence of coating on mild steel, its charge transfer resistance increases and impedance increases, whereas corrosion current decreases to a great extent.
- Vickers hardness study confirms that in the presence of sea water, the hardness of mild steel decreases whereas in the presence of coating the hardness of mild steel increases.
- SEM images of various metal surfaces reveal that in the presence of sea water alone, pits are noticed on mild steel whereas in the presence of oil coating the surface appears to be smooth, when immersed in sea water.
- When mild steel is immersed in sea water, the contact angle decreases when compared with polished metal. But for oil coated mild steel the contact angle increases, hydrophobicity increases and hence corrosion protection increases.
- It is suggested that this oil coating containing extracts of plant material may be coated on hull plates made of mild steel to protect them from severe corrosion due to the aggressive ions present in sea water.

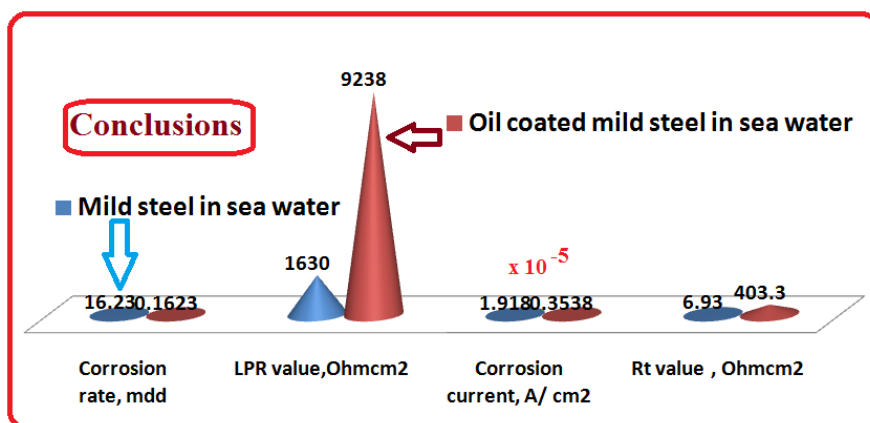


Figure 18. Conclusions 1.

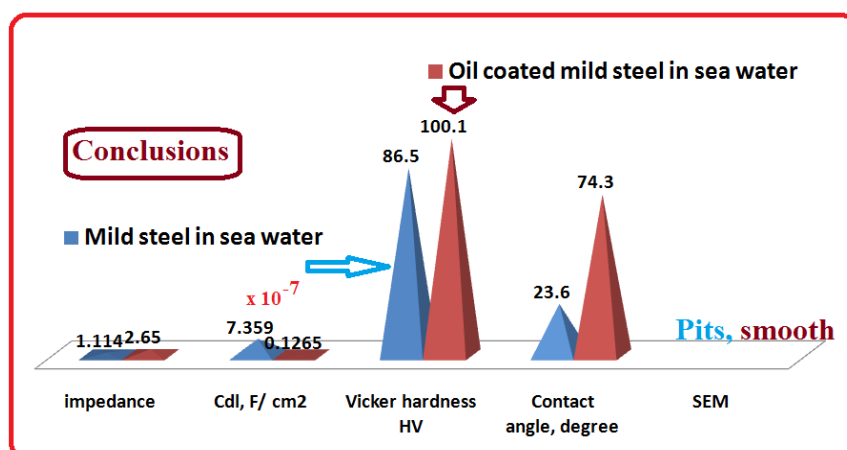


Figure 19. Conclusions 2.

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