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Inhibitive Properties of Leaf Sheath Extract of Cocos Nucifera as Green Inhibitor for Mild Steel in HCl Medium

R. RAJALAKSHMI[1,*] and A.S. SAFINA[2]

[1]Department of Chemistry, Avinashilingam University for Women, Mettupalayam Road, Coimbatore-641 043, India
[2]Department of Chemistry, V.L.B. Janakiammal College of Engineering & Technology, Coimbatore-641 042, India

*Corresponding author: E-mail: rajivardhan@gmail.com; raji_adu@yahoo.com; safinashariff@gmail.com

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Inhibitive properties of leaf sheath extract of cocos nucifera for the corrosion of mild steel were studied using conventional weight loss and electrochemical measurements of monitoring corrosion. The results revealed that leaf sheath extract of cocos nucifera inhibited the corrosion of mild steel. The inhibitor was found to function by being adsorbed on the surface of mild steel. The adsorption of the inhibitor followed the Langmuir and Temkin type adsorption isotherm. Optical images of the corrosion product (without inhibitor) and the corrosion product (with the inhibitor) confirmed that the inhibitor is an adsorption inhibitor. Physical adsorption mechanism at low temperature and chemical adsorption mechanism at high temperature had been proposed from the values of thermodynamic parameters obtained. Electrochemical studies reveal that the plant extracts act as mixed type inhibitors. Optical electron microscope and FTIR were carried out to confirm the investigated inhibitor was adsorbed on mild steel surface. The leaf sheath extract of cocos nucifera in HCl medium proved to be zero cost inhibitor, eco-friendly, non-toxic and highly economical.

Key Words: Corrosion, Inhibition, Mild steel, Leaf sheath extract.

INTRODUCTION

Corrosion is the damage of material resulting from exposure and interaction with the environment. It is a major problem that must be confronted for safety, environment and economic reasons. Use of inhibitors is one of the most practical methods for protection against corrosion especially in acid solutions to prevent unexpected metal dissolution and acid consumption[1]. Different organic and non-organic compounds have been studied as inhibitors to protect metals from corrosion attack.

Usually, organic compounds that exert a significant influence on the extent of adsorption on the metal surface and therefore can be used as effective corrosion inhibitors. The efficiency of these organic corrosion inhibitors is related to the presence of polar functions with S, O or N atoms in the molecule, heterocyclic compounds and π electrons[2-7]. The polar function is usually regarded as the reaction center for the establishment of the adsorption process[8].

The known hazardous effects of most synthetic organic inhibitors and restrictive environmental regulations have now made researchers to focus on the need to develop cheap, non-toxic and environmentally benign natural products as corrosion 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 and are biodegradable in nature. The use of these natural products such as extracted compounds from leaves or seeds as corrosion inhibitors have been reported to be good inhibitors by several authors[9-21].

This study aims to gain some insight into the corrosion of mild steel in HCl in the presence of leaf sheath extract of cocos nucifera as a corrosion inhibitor. The inhibitor effect of this agricultural waste of coconut (leaf sheath)-cocos nucifera leaf sheath (CNLS) on the corrosion of mild steel in 1 M HCl was investigated by weight loss method. The effect of temperature on corrosion and inhibition processes are thoroughly assessed and discussed. Thermodynamic parameters governing adsorption process were also calculated. To understand the mode of action of inhibitors on mild steel surface, potentiodynamic polarization studies and electrochemical impedance studies were also carried out.

EXPERIMENTAL

Specimen preparation: Mild steel specimen of composition, C: 0.132, Mn: 0.23, Si: 0.021, P: 0.034, S: 0.031, Cr: 0.031, Mo: 0.016, Ni: 0.015 and remaining Fe were chosen for the present study. The specimens of dimension 5 cm × 1 cm were polished mechanically, degreased, cleaned successively in deionized water, dried, stored in a dessicator and used for all studies. Mild steel specimen of 1 cm^2 area was used for electrochemical studies.

Extraction of cocos nucifera leaf sheath: The plant materials were collected from the near by residential area. 25 g of leaf sheath was weighed and dried for 24 h. The extract was prepared by refluxing the leaf sheath powder in 500 mL of hydrochloric acid for 3 h, kept overnight and filtered to get 5 % extract.

Weight loss measurement: The mechanically polished and preweighed mild steel specimens of uniform size were suspended in 100 mL test solutions with and without the addition of different concentrations of inhibitor for various periods of immersion at room temperature and at different temperatures. Then the specimens were washed, dried and weighed. From the weight loss data, the inhibition efficiency (IE) was calculated as follows

$$IE = \frac{W_0 - W}{W_0} \times 100$$

where, W_0: weight loss of steel in uninhibited solutions; W: weight loss of steel in inhibited solutions.

Shelf life of cocos nucifera leaf sheath: The weight loss method was used to evaluate the performance of the cocos nucifera leaf sheath under study. It was determined for a period of 10 weeks. A part of the extract was kept at room temperature and the other portion was maintained in refrigerated condition. The same procedure as described for weight loss measurement was followed for an immersion period of 3 h.

Electrochemical measurements: A three electrode cell assembly containing mild steel coupons, embedded in specimen holder as the working electrode, a large area platinum mesh as counter electrode and a saturated calomel electrode as reference electrode were used. All electrochemical experiments were conducted at room temperature using 100 mL of electrolyte (1 M HCl) in stationary condition. The potentiodynamic polarization studies were carried out over a potential range of -0.1 V to -1 V with respect to reference electrode with a scan rate of 2 mV s^{-1}. The above procedures were repeated for each concentration of cocos nucifera leaf sheath. Electrochemical impedance spectroscopy (EIS) measurements were carried out using ac signals of amplitude 10 mV peak to peak in the frequency range of 20-0.1 Hz. Solatron electrochemical analyzer model (1284 Z) interfaced with an IBM computer and Z plot and Corrware softwares were used for data acquisition and analysis.

Surface analysis: The mild steel specimens were immersed in maximum concentration of test solutions for a period of 3 h. The specimens were taken out, dried and analyzed using optical electron microscope (Carl Zeiss) to examine the surface of mild steel in the absence and presence of the inhibitor.

FT-IR technique: In order to observe the presence of plant constituents adsorbed on the metal surface FT-IR technique was followed. The metal specimens were immersed in the test solution for 24 h at a concentration of 0.3 of the inhibitor and then dried using acetone. The surface of the dried specimens was scratched with a knife and the resultant powder was used. In case of FT-IR studies of the extract, the leaf sheath was dried in a water bath so that the acid got evaporated and the powder thus obtained was used for FT-IR analysis.

Phytochemical constituents present in cocos nucifera leaf sheath: The major chemical constituents of these fibers are found to be[22] cellulose (39-46 %) and lignin (13-25 %).

RESULTS AND DISCUSSION

Weight loss measurements

Effect of concentration: Table-1 shows the percentage of inhibition efficiency obtained with different concentrations of the cocos nucifera leaf sheath extract in HCl medium by weight loss method. The inhibition efficiency was found to

TABLE-1
VARIATION OF INHIBITION EFFICIENCY (IE) OF COCOS NUCIFERA LEAF SHEATH WITH CONCENTRATION AND TIME OF IMMERSIONIN HCl

Conc.(%)	Immersion time(h)											
	1/2		1		3		6		12		24	
	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)
Blank	524	–	73	–	583	–	839	–	240	–	728	–
0.05	275	47.4	25	65.8	212	63.5	144	82.7	107	55.1	158	78.2
1.00	238	54.4	23	67.5	175	69.9	101	87.8	75	68.6	79	89.0
0.15	214	59.0	23	68.1	144	75.2	90	89.2	65	72.5	59	91.8
0.20	192	63.2	20	71.6	140	75.9	70	91.6	62	74.0	52	92.8
0.25	179	65.7	19	72.8	127	78.2	65	92.2	49	79.3	50	93.0
0.30	173	66.8	19	73.2	99	82.9	60	92.8	43	82.0	36	94.9
0.35	184	64.7	14	79.5	91	84.2	57	93.1	33	85.9	44	93.9
0.40	188	64.0	15	78.8	93	83.9	60	92.8	35	85.3	44	93.9
0.45	191	63.5	15	78.4	95	83.6	63	92.4	35	85.3	49	93.2

increase with increase in the concentration of the extract with maximum inhibition efficiency of 94.9 % at 0.3 % concentration. There is a gradual increase in inhibition efficiency from 0.05-0.3 % of inhibitor concentration, but above that there is not much change in efficiency. Maximum inhibition efficiency 93 % was observed at 0.3 % concentration of cocos nucifera leaf sheath. From the values of IE % it is evident that the corrosion inhibition may be due to adsorption of the plant constituents on the metal surface. The adsorption of the phytoconstituents on the metal surface makes a barrier for mass and charge transfers thus protecting the metal surface from corrosion. The degree of protection increases with the increasing surface fraction occupied by the adsorbed molecules.

Effect of immersion time: The variation of weight loss with exposure time for the mild steel specimen immersed in 1 M HCl with and without the addition of varied concentration of leaf sheath extract are presented in the Table-1. From the experimental results it can be concluded that the inhibitor molecule are being adsorbed on the mild steel surface effectively up to 6 h (92 %) and after that there is slight decrease in inhibition efficiency up to 12 h (85 %) and then there is increase in inhibition efficiency upto 24 h (93 %). The increase of inhibition efficiency with respect to time of immersion indicates the stability of adsorbed layer on the metal surface.

Effect of temperature: To study the effect of temperature on the corrosion inhibition properties, mild steel specimens were exposed to 1 M HCl containing various concentration of cocos nucifera leaf sheath in the temperature range of 305, 315, 325, 335 and 345 K. The calculated corrosion rate and inhibition efficiencies are shown in Figs. 1 and 2. Inhibition efficiency increased with increase in temperature up to 335 K, with higher concentrations of the inhibitor. Maximum inhibition efficiency at 335 K was found to be 85 % at highest concentration of cocos nucifera leaf sheath extract. Further increase in temperature showed a decrease in efficiency. This may be due to the fact that constituents of inhibitor are adsorbed physically on the surface of the mild steel. The increase of the temperature might cause desorption of the inhibitor constituents from the surface of the metal, due to the decrease in the strength of adsorption process at higher temperatures[23].

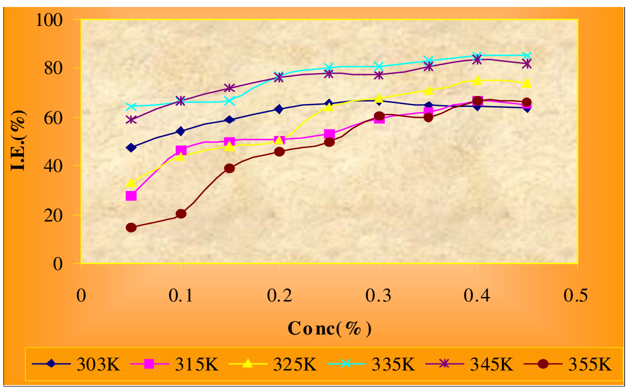


Fig. 1. Effect of concentration on IE of cocos nucifera leaf sheath at various temperature

Adsorption behaviour: The adsorption characteristics of cocos nucifera leaf sheath extract on the surface of mild steel were investigated by fitting curves for different adsorption

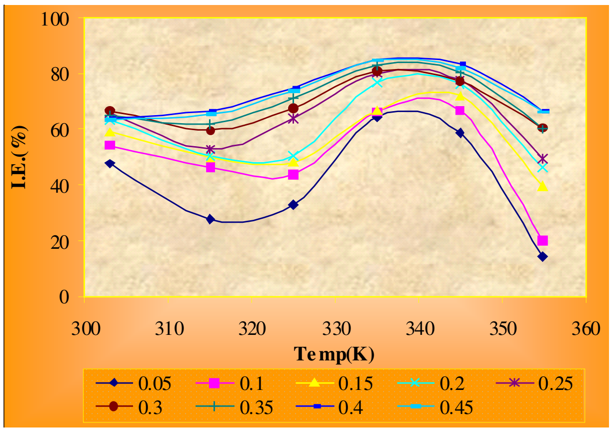


Fig. 2. Effect of temperature of inhibition efficiency of cocos nucifera leaf sheath

models. The isotherms that best described the adsorption behaviour of cocos nucifera leaf sheath extract on the surface of mild steel were Langmuir and Temkin adsorption isotherms. Langmuir adsorption isotherm can be expressed according to eqn.

$$\log\left[\frac{\theta}{1-\theta}\right] = \log K + \log C$$

where θ is the surface coverage, C is the concentration and K is the equilibrium constant of adsorption process. The plot of (θ/1-θ) *versus* log C is shown in Fig. 3. The application of Langmuir adsorption isotherm to the adsorption of this inhibitor indicates that there is no interaction between the adsorbate and the adsorbent[24]. According to Temkin adsorption isotherm, the degree of surface coverage (θ) is related to the concentration of inhibitor (C) in the bulk electrolyte. The plots of θ *versus* log C were linear, implying that the assumptions of Temkin isotherm are valid. The correlation values are almost 1 showing that the data obey both Langmuir and Temkin isotherms.

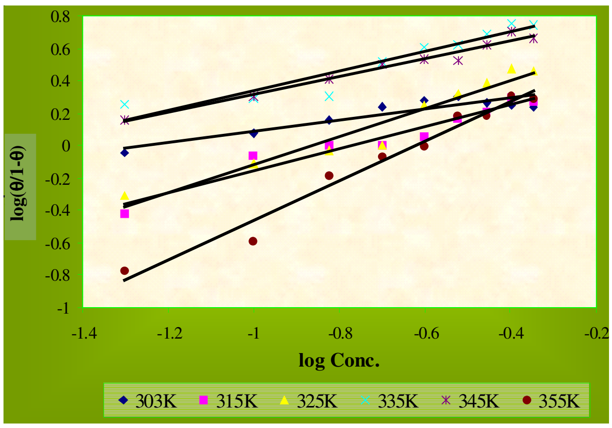


Fig. 3. Langmuir absorption isotherm for cocos nucifera leaf sheath

Activation and thermodynamic parameters: The activation energy at different concentration of the inhibitor in HCl was calculated by plotting log C.R *versus* 1/T. The dependence of logarithm of the corrosion rate on the reciprocal values of the absolute temperature gives a straight line. The values of the slope of these straight lines permit the calculation of activation energy E_a by the application of following equation,

$$C.R = A.e^{(-E_a/RT)}$$

The estimated values of E_a for mild steel in leaf sheath extract in 1 M HCl are listed in Table-3. From the table it is clear that higher value of the activation energy of the process with inhibitors when compared to that in their absence is attributed to its physisorption and suggests that the adsorbed organic compounds creates a physical barrier to charge and mass transfer for given conditions at low temperature and chemisorption at higher temperatures.

Free energies of adsorption (ΔG) of leaf sheath extract on the surface of mild steel were calculated using the equation[25].

$$\log C = \log\left(\frac{\theta}{1-\theta}\right) - \log B$$

where log B = -1.74 – (–ΔG/2.303RT), C = inhibitor concentration.

Calculated values of (ΔG) are recorded in Table-2. These values are negative and less than -40 kJ mol^{-1}, indicating that adsorption of cocos nucifera leaf sheath extract on the surface of mild steel is spontaneous and occurred according to the mechanism of physical adsorption.

The negative values of ΔG ensure the spontaneity of the adsorption process and stability of the adsorbed layer on the mild steel surface[26]. Further more it is found that ΔG slightly increases with temperature upto 345 K. The values of ΔG increases with increase in temperature indicates that cocos nucifera leaf sheath extract is adsorbed physically at low temperature while chemisorption is favoured at higher temperatures. The negative values of ΔH also show that the adsorption of inhibitor is an exothermic process[27]. Generally an exothermic process signifies either physical or chemisorption while endothermic process is attributable unequivocally to chemisorption[28]. The adsorption of inhibitor molecule is accompanied by positive values of ΔS. Positive values of ΔS shows a decrease in the system disorder[29].

Polarization measurement

Potentiodynamic polarization results: Typical potentiodynamic polarization curves for mild steel in 1 M HCl in the absence and in the presence of different cocos nucifera leaf sheath concentrations are shown in Fig. 4. The figure show that addition of cocos nucifera leaf sheath shifts anodic and cathodic parts of the polarization curves to more noble values indicating that the extract could be classified as mixed-type inhibitor. The corrosion current density was calculated from the intersection of cathodic and anodic Tafel lines and the values of the electrochemical parameters for different cocos nucifera leaf sheath concentrations are given in Table-3. The displayed data show that increasing cocos nucifera leaf sheath concentration decreases the corrosion current density (I_{corr}) but slightly affect the values of corrosion potential (E_{corr}) indicating

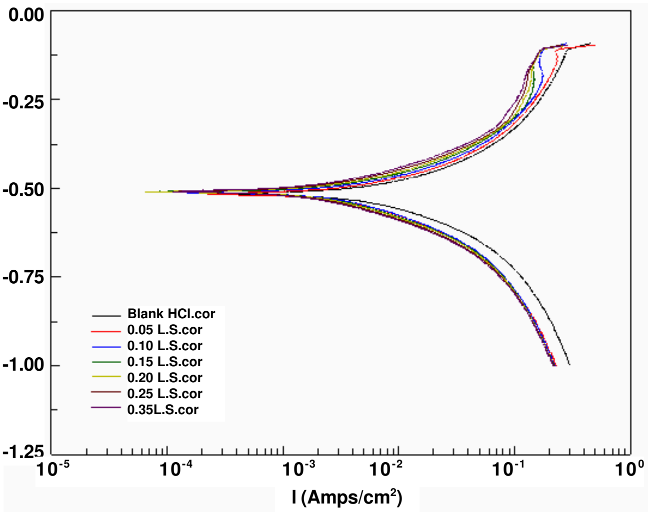


Fig. 4. Polarization curves of mild steel in the presence of cocos nucifera leaf sheath in acid medium

TABLE-2
KINETIC AND THERMODYNAMIC PARAMETER OF MS IN PRESENCE OF CNLS IN 1 M HCl

Conc. (%)	Activation energy (E_a) (KJ/mol)	Free energy of adsorption (-ΔG) (KJ/mol)						Heat of adsorption (ΔH) (KJ/mol)	Entropy change (ΔS) (KJ/mol)
		305 K	315 K	325 K	335 K	345 K	355 K		
Blank	69.70	–	–	–	–	–	–	–	–
0.05	69.78	17.38	15.81	16.99	21.13	21.10	15.40	-20.45	11.99
1.00	71.53	16.34	16.13	16.35	19.42	20.07	14.56	-15.38	10.18
0.15	68.99	15.79	15.45	15.73	18.38	19.66	16.14	-15.68	10.06
0.20	67.05	15.51	14.74	15.20	18.93	19.41	16.10	-19.95	11.31
0.25	67.14	15.22	14.42	16.12	18.91	19.00	15.88	-20.26	11.39
0.30	66.10	14.88	14.65	16.09	18.51	18.41	16.62	-17.15	10.37
0.35	65.30	14.26	14.50	16.07	18.48	18.61	16.13	-22.83	12.08
0.40	61.54	13.85	14.69	16.25	18.54	18.75	16.58	-26.04	13.08
0.45	61.96	13.50	14.24	15.81	18.15	18.13	16.15	-24.99	12.61

TABLE-3
CORROSION PARAMETERS OF MS IN THE PRESENCE OF CNLS IN HCl

Conc. of LSE (%)	$-E_{corr} \times (10^{-3})$ (V)	$I_{corr} \times (10^{-4})$ (Amp/cm^2)	b_a (mV/dec)	b_c (mV/dec)	IE (%)	R_p (Ohm/cm^2)	IE (%)
Blank	513	184.45	254.64	183.16	–	2.55	–
0.05	515	55.741	175.07	131.75	69.7	5.89	56.6
0.10	511	49.165	165.67	127.63	73.3	6.41	60.1
0.15	509	39.035	152.7	120.54	78.8	7.58	66.3
0.20	509	34.979	146.98	119.23	81.0	8.16	68.6
0.25	508	24.003	129.9	110.35	86.9	9.48	73.0
0.35	506	21.059	120.48	98.713	88.5	10.81	76.3

that it could act as pickling inhibitor[30]. The percentage inhibition efficiency was calculated using the relation:

$$IE = \frac{I_{corr\,(Blank)} - I_{corr\,(Inhibitor)}}{I_{corr\,(Blank)}} \times 100$$

$I_{corr\,(Inhibitor)}$: Corrosion current in the presence of inhibitor. $I_{corr\,(Blank)}$: Corrosion current in the absence of inhibitor.

The higher inhibition efficiency (88.5 %) obtained at higher concentrations suggests that the cocos nucifera leaf sheath could serve as effective corrosion inhibitor. In all concentrations b_a is greater than bc suggesting that though the inhibition is under mixed control, the effect of the inhibitor on the anodic polarization is more pronounced than on the cathodic polarization.

Electrochemical impedance studies: The Nyquist plots for mild steel in acid media are not perfect semicircles, which is attributed to non-homogeneity of the surface and roughness of the metal[31]. From the plots, it could be seen that impedance response of mild steel is increased by the addition of inhibitor[32]. The C_{dl} and R_{ct} values calculated from the Nyquist plots are listed in Table-4. The R_{ct} values increased with the increase of the concentration of inhibitor, which shows protection of mild steel surface by the inhibitor while the values of C_{dl} decreased with the increase in the concentration of inhibitor, which is due to the increase in the thickness of protective layer at higher concentrations[33,3]. Maximum inhibition efficiency calculated using R_{ct} value was found to be 86 % at 0.3 % concentration.

TABLE-4
IMPEDANCE PARAMETERS OF MS IN THE PRESENCE OF CNLS IN HCl

Conc. of LSE (%)	R_{ct} (Ω cm^2)	IE (%)	C_{dl} ×10^{-5} (µF)	θ
Blank	9.2	–	60.1	–
0.05	32.4	71.4	25.6	0.57
0.10	44.8	79.3	35.0	0.41
0.15	48.6	80.9	34.1	0.43
0.20	58.3	84.1	33.3	0.44
0.25	64.7	85.6	30.8	0.48
0.35	66.6	86.0	28.7	0.52

Comparison of electrochemical techniques with the conventional weight loss method: In the current investigation on inhibitive properties of cocos nucifera leaf sheath extract on mild steel acid corrosion by various techniques conducted infer that IE obtained by weight loss method are different from IE obtained using electrochemical techniques (Fig. 5). The difference observed can be attributed to the fact that weight loss methods give average corrosion rates where as electrochemical methods give instantaneous corrosion rates. This difference may also expected to arise because of the difference in the time required to form an adsorbed layer of the plant extract which can bring down corrosion[34].

Shelf life of the extract: Natural inhibitors are estimated by their stability, consistent performance and biodegradability. To test the consistent performance of the extracts under study, weight loss experiments were conducted for a period of 3 months. The extract was stored at room temperature and in refrigerator. The results are presented in the Table-5.

The data in table revealed that the inhibition efficiency slowly decreased during storage. This may be due to some

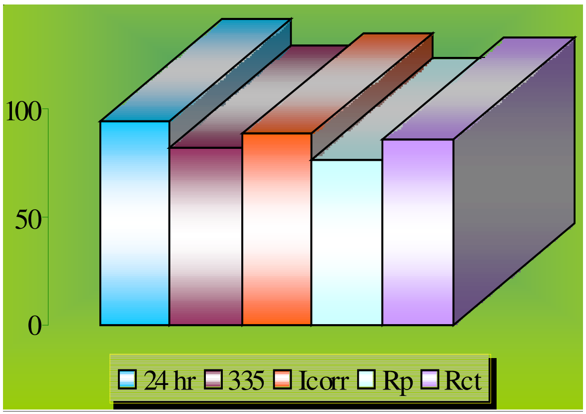


Fig. 5. Performance evaluation of cocos nucifera leaf sheath extract on mild steel corrosion using various techniques

TABLE-5
SHELF LIFE OF CNLS

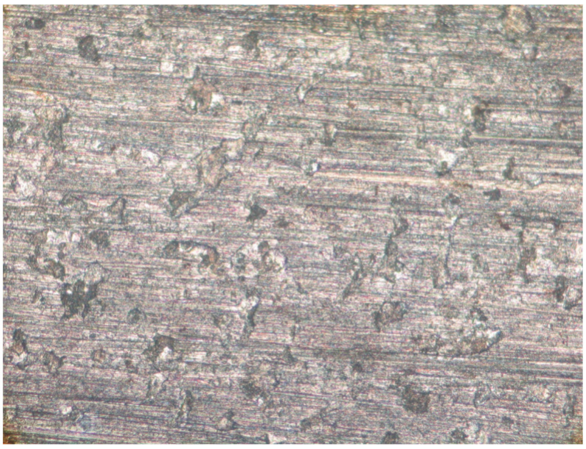
Period of study (weeks)	IE (%)	
	RT	RC
1	98.0	94.7
2	96.7	92.3
3	94.3	89.6
4	92.6	87.9
5	88.5	86.4
6	87.8	81.9
7	86.8	77.8
8	80.8	76.9
9	77.7	74.3
10	76.3	73.1

chemical reactions between the constituents. Due to the reactions the active groups responsible for the adsorption on the MS surface may not be available for adsorption. Therefore the total surface covered decreased showing decline of inhibition efficiency. 75 % of inhibition efficiency after 3 months is appreciable. This confirms that they can be stored at room temperature itself.

Optical electron microscope: Optical electron microscope was used to evaluate the change in the surface morphology caused by the contact with the acid solutions and to monitor the effect of addition of the inhibitor.

Samples pickled without inhibitor (Fig. 6a) show an overall attack upto 80 % of mild steel surface which was reduced to about 10-20 % by the addition of inhibitor (Fig. 6b).

(a)



(b)

Fig. 6. Photomicrograph of mild steel in presence of HCl (a) and in presence of cocos nucifera leaf sheath (b)

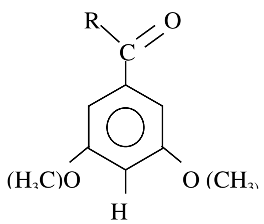
FT-IR technique: Cellulose and lignin are the main phytochemical constituents of the acid extract of cocos nucifera leaf sheath.

The FT-IR spectrum taken using the extract shows the characteristic -OH absorption peaks at 3400-3200 cm^{-1} (broad) and at 1610 cm^{-1}. The band at 1035 cm^{-1} represents the primary alcoholic group.

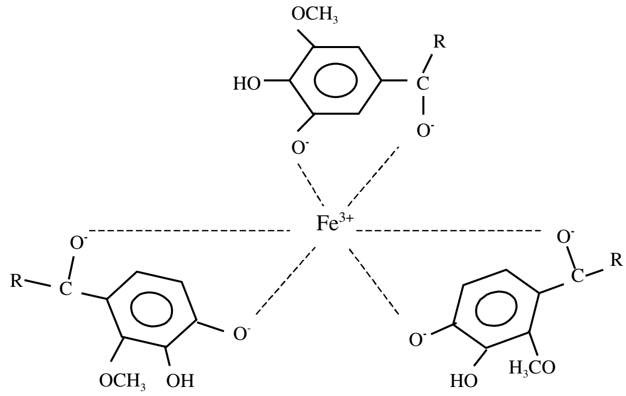
In FT-IR spectra taken using the adsorbed material of the extract on mild steel surface the broad band at 3400-3200 cm^{-1} is completely absent showing that the constituents of the extract are adsorbed on the metal surface through the -OH groups. It was found that the primary alcoholic band at 1035 cm^{-1} was shifted to 1041 cm^{-1} indicating that there is an interaction between the inhibitor and mild steel surface[35].

Mechanism of inhibition: From the literature survey it was found that the major phytochemical constituents present in L.S.E. are cellulose and lignin.

These phytochemical constituents have active adsorption centres. Greater the number of active centres stronger is the adsorption on mild steel surface. These constituents are being adsorbed on the mild steel surface and it forms a protective layer on mild steel. This layer prevents the metal dissolution and hydrogen evolution, thus retards corrosion. Numerous OH groups around the molecules present in the phytochemical constituent make them more ready to form strong links with hydrogen. In addition they can form complexes with metallic cations as Cu, Ca, Al, Fe, which are rarely soluble in aqueous environment. Probable iron-lignate complexes have been suggested[36]. These complexes can cause blocking of micro anodes and/or micro cathodes that are generated on the metal surfaces when in contact with electrolytes and so can retard the subsequent dissolution of the metal.



Molecular structure of lignin monomers



Part of the suggested structure for the ferric-lignate chelate where R represents the rest of the lignin molecule

Three lignate ions reacted with each ferric ion to form a stable octahedral coordination compound. As lignin molecules are generally polymers of the basic flavanoid structure, each molecule could react with a number of ferric ions to form a network structure[37]. In the present investigation, it may be concluded that there was a formation of ferric-lignate complex on MS surface and that will form a protective blanketing layer on MS surface and prevent corrosion.

Thus, the extract of leaf sheath is found to be promising inhibitor to retard the corrosion of MS in acid medium.

Conclusion

The results obtained during this investigation have been summarized as follows: Acid extract of cocos nucifera leaf sheath is found to be an effective inhibitor for mild steel in acidic medium giving up to 94.9 % efficiency. The extract under study resists corrosion at higher temperature, the optimum temperature being 335 K in the presence of cocos nucifera leaf sheath extract. Adsorption of inhibitor molecules on the mild steel surface is found to obey the Langmuir adsorption isotherm and Temkin isotherm. Increase in activation energy of corrosion process in presence of cocos nucifera leaf sheath indicates physical adsorption. The values of Tafel slopes b_a and b_c obtained from Tafel intercept method would confirm the inhibition of corrosion of mild steel is under mixed controls. Increase in R_p and R_{ct} values and decrease in I_{corr} and C_{dl} values confirm that the cocos nucifera leaf sheath extracts are adsorbed on the mild steel surface and inhibition process is followed by monolayer adsorption. Results obtained for the durability test infer the strong inhibitive action of the inhibitor kept at room temperature as well as in the refrigerator for 3 months. Examination of the surface of the metal in the presence of the inhibitor confirmed the deposition of inhibitor on the metal surface. cocos nucifera leaf sheath in HCl medium efficiently inhibits the corrosion and prove to be zero cost and non-toxic inhibitor to the environment.

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