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Pithecollobium dulce Extract: A Novel Eco-Friendly Corrosion Inhibitor for Mild Steel Protection in Artificial Corrosive Medium

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ABSTRACT

The effect of corrosion inhibition on mild steel in 3.5% sodium chloride (NaCl) solution was investigated using eco-friendly new corrosion inhibitor namely *Pithecollobium dulce* extract (PCD). A significant decrease in the corrosion rate of MS was observed in the presence of inhibitor. Electrochemical corrosion studies showed that the inhibition efficiencies increased with increasing inhibitor concentration. Inhibitive effect was afforded by adsorption of the extract components which was found to accord with Langmuir adsorption isotherm. The UV-Vis spectroscopy, Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy (SEM) analysis were carried out to characterize the surface film.

1. Introduction

Mild steel is a common constructional material for many industrial units because of its excellent mechanical properties. They are used widely in industries as reaction vessels, pipelines for petroleum industries, machinery, storage tanks, and chemical batteries. It is a well-known fact that sodium chloride (NaCl) was used in many industrial operations. Because of their aggressiveness, inhibitors are used to eliminate the undesirable destructive effect and prevent the dissolution of metal [1-4].

Many organic compounds containing nitrogen, oxygen, and/or sulfur atoms have been used to inhibit the corrosion of mild steel. The inhibiting actions of organic compounds are usually attributed to their interactions with the metal surface through adsorption. The adsorption of these compounds onto the metal surface depends on the nature and surface charge of the metal, the chemical composition of electrolytes, and the molecular structure and electronic characteristics of the inhibitor molecules [5-9].

Most of the organic compounds have high inhibitive performance; their high cost and toxicity are the main drawbacks in the use of these compounds as corrosion inhibitors. In recent times most corrosion inhibitors studies have been focused on the development of “environmental friendly” compounds in response to legislation changes concerning environmental protection. This term includes formulations that are not toxic to humans, have low environmental impact, optimal biodegradability, and maintain their efficiency and cost-effectiveness. Thus, since the 1990s, many investigations have been related to the evaluation of natural compounds as corrosion inhibitors; in this sense, some amino acids, vitamins, plant extracts, and soluble natural polymers have been tested [10-15].

Although there have been many research reports on the natural products as corrosion inhibitor for MS in aggressive solutions, but no published information to our knowledge is available on extract of *Pithecollobium dulce* as corrosion inhibitor for mild steel. The present research was aimed to investigate the corrosion inhibition effect of coconut *pithecollobium dulce* extract on mild steel in highly aggressive medium. Corrosion protection behavior of the inhibitor on MS has been studied by weight-loss method and electrochemical measurements, i.e. potentiodynamic polarization and electrochemical impedance

spectroscopy. The formation of passive film formed over the surface of MS was characterized by FTIR and SEM.

2. Experimental Methods

2.1 Chemical and Reagents

All the chemical and reagents used in the present investigation are analytical grade (AR) used as received. Deionized water was used throughout the experiments.

2.2 Specimen Preparation

According to ASTM method as reported already Mild Steel strips having the composition (wt%) of C (0.18), Si (0.09), Mn (0.87) P (0.044), S (0.057), Cr (0.14), Ni (0.09) Co (0.02), Cu (0.06) and remaining Fe were rest used. The specimens were polished mechanically with silicon carbide papers from 120 to 1200 grit and then the specimens were thoroughly washed with deionized water followed by degreased in acetone and used for corrosion studies.

2.3 Preparation of *Pithecollobium dulce* Leaves Extract

Dried *pithecollobium dulce* (PCD) leaves (100 g) were powdered and soaked in 500 mL ethanol for 24 hrs. The mixture is passed through the soxlet apparatus was then filtered and the filtrate was refluxed for 6 hrs at 60 °C. The resulting liquid was collected into the vacuum evaporation setup and the ethanol was removed by evaporation then the powdered PCD extract was collected and stored in dark room.

2.4 Weight Loss Measurements

Weight loss measurements were done under total immersion using 250 mL capacity beakers containing 200 mL 3.5% NaCl at room temperature. The mild steel coupons were weighed and suspended in the beaker with the help of rod and hook. The coupons were retrieved at 7 days interval progressively for 28 days, washed thoroughly in deionized water, cleaned, dried in acetone and re-weighed. The weight loss was taken as the difference in the weight of the mild steel coupons before and after immersion in different test solutions. The experiments were done by triplicate and the average weight loss was used to determine corrosion rate (CR) and inhibition efficiency as follows:

$$\text{Corrosion rate, (CR)} = 534W/DA$$

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where W is the weight loss (g), D is the density of the specimen (97.85 g/cm^3), A is the surface area of specimen (cm^2) and t is the immersion time (days). The efficiency of the inhibitor was computed using the following equation [14, 15],

$$\text{Inhibition efficiency \% (IE)} = \frac{W_0 - W_1}{W_0} \times 100$$

where W_0 and W_1 are weight loss without inhibitor and with inhibitor.

2.5 Electrochemical Studies

Electrochemical corrosion measurements were carried out by CH1660B electrochemical workstation with the conventional three

electrode cylindrical glass cell using NaCl as electrolytes. Cell assembly consisted of mild steel as working electrode (WE), a high-purity platinum foil as the counter electrode (CE), and a saturated calomel electrode (SCE), via a luggin capillary probe as the reference electrode (RE).

2.6 Instrumentation

The surface morphology of the specimen was observed with a scanning electron microscopy HITACHI SU6600 instrument with an accelerating voltage of 1.5 kV. FT-IR spectra were recorded using BRUKER (TENSOR 27) in the region $4000\text{--}400 \text{ cm}^{-1}$ with the resolution of 4 cm^{-1} . UV-vis spectrum was recorded using "TECHCOMP" UV-visible spectrometer model 8500.

Table 1 Inhibition efficiency, corrosion rate and surface area for mild steel in 3.5% NaCl in the presence and absence of various concentrations of inhibitors obtained from weight-loss method

Inhibitor concentration (ppm)	7 days				14 days				21 days				28 days			
	wt loss	IE%	CR (mm/py) 10^{-4}	Surface area Θ	wt loss	IE%	CR (mm/py) 10^{-4}	Surface area Θ	wt loss	IE%	CR (mm/py) 10^{-4}	Surface area Θ	wt loss	IE%	CR (mm/py) 10^{-4}	Surface area Θ
Blank	0.0126	-	20.82		0.053	-	20.89		0.016	-	9.03		0.059	-	24.55	
200	0.0115	8.73	19	0.087	0.0243	3.95	20.07	0.04	0.016	4.268	8.65	0.0426	0.054	9.42	12.21	0.0942
400	0.0108	14.28	17.85	0.143	0.023	9.09	18.99	0.091	0.014	16.463	7.54	0.1646	0.053	10.6	21.93	0.106
600	0.0099	21.42	16.36	0.214	0.0222	12.25	18.33	0.123	0.013	20.121	7.21	0.2012	0.052	11.78	21.64	0.1178
800	0.0091	27.77	15.04	0.278	0.0213	16.99	17.59	0.17	0.013	21.951	7.05	0.2195	0.052	12.96	21.35	0.1296

3. Results and Discussion

3.1 Weight Loss Method

The gravimetric method (weight loss) is probably the most widely used method of corrosion inhibition assessment. The simplicity and reliability of the measurement offered by the weight loss method is such that the technique forms the baseline method of measurement in much corrosion monitoring programs. Table 1 showed the corrosion rate and inhibition efficiency of MS by weight-loss method at different concentrations of the inhibitor in 3.5% NaCl at room temperature. The results showed that the corrosion rate of MS decreased whereas the inhibition efficiency increased with increasing inhibitor concentration. It has been pointed out that the increase in inhibition efficiency (IE) with increase in extract concentration is an indication of an increase in the number of components of the extract adsorbed over the mild steel surface blocking the active sites, in which direct corrosive ions attacks proceed and protect the metal from corrosion [16–18]. The maximum IE% of each inhibitor was achieved at 800 ppm and a further increase in concentration showed only a marginal change in the performance of the inhibitor. Hence, the optimum levels of concentration of the inhibitors were found to be 800 ppm.

3.2 Potentiodynamic Polarization Studies

Polarization curves of mild steel in 3.5% NaCl in the absence and presence of inhibitor at different concentrations are shown in Fig. 1. From the figure it was seen that the anodic and cathodic curves were shifted towards positive (Nobel) direction compared to the bare metal. Moreover, the nature of the curve remains almost same even after the addition of the inhibitors and also on increasing the concentration of the inhibitors indicating that the inhibitor molecules retard the corrosion process without changing the mechanism of corrosion process in the medium of investigation.

The electrochemical parameters such as corrosion potential (E_{corr}), corrosion current density (i_{corr}) and Tafel slopes are obtained from the polarization curves and the corresponding inhibition efficiency (IE) values at different inhibitor concentrations are reported in Table 2. The percentage inhibition efficiency at different inhibitor concentrations was calculated from the equation,

$$\% \text{ Inhibition Efficiency (\%IE)} = \frac{I_{\text{corr}} - I_{\text{corr(inh)}}}{I_{\text{corr}}} \times 100$$

where i_{corr} and $i_{\text{corr(inh)}}$ are the corrosion current densities in the presence and absence of inhibitor, respectively. It was observed from the table that the E_{corr} values increased and I_{corr} values decreased significantly for mild steel in the presence of inhibitors indicated that the inhibitors control both the anodic and cathodic reactions. It also can be seen from the table that increase in inhibitor concentration leads to an increase in inhibition efficiency and a decrease in corrosion rate. This result suggests that the

plenty of adsorbed inhibitor molecules moved onto the metal surface, then, the contact area between metal surface and aggressive solution became smaller and smaller leading to the decrease in active sites [19–24].

Table 2 Tafel parameters and inhibition efficiency for corrosion of mild steel in 3.5% NaCl containing different concentrations of inhibitor PCD extract

PCD Conc. (ppm)	E_{corr} (mV)	I_{corr} mA cm^{-2}	Tafel Constants		Inhibition Efficiency (%)
			b_a (mV dec $^{-1}$)	b_c (mV dec $^{-1}$)	
0	-592	1.280	96	107	---
200	-580	0.518	88	106	59
400	-584	0.456	84	101	64
600	-582	0.386	81	93	70
800	-576	0.304	80	88	76

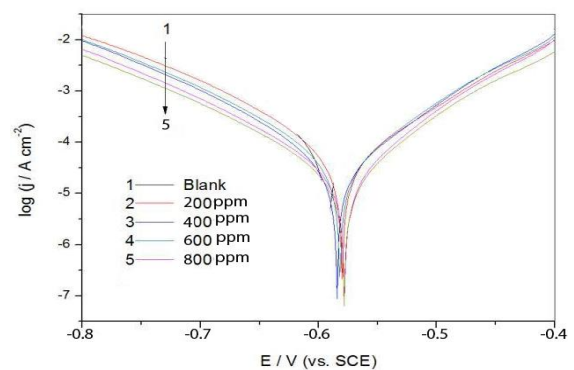


Fig. 1 Tafel plot for mild steel in 3.5% M NaCl solution in the absence and presence of various concentrations of the PCD inhibitor

3.3 Electrochemical Impedance Spectroscopy Studies

Nyquist plots of mild steel in the absence and presence of various concentrations of inhibitor in 3.5% NaCl are given in Fig. 2. The Nyquist plot showed a single semicircle capacitive loop in the high frequency range and an inductive loop in the low frequency range. Moreover, diameter of the semicircle increases with increasing inhibitor concentrations and the impedance spectra did not present perfect semicircles. The depressed semicircle was often attributed to the inhomogeneity of the steel surface. The capacitive loop was attributable to charge transfer of the corrosion process and the inductive loop originated from the adsorption/relaxation of intermediates and the adsorption-desorption process of inhibitive molecules on the metal surface.

The percentage inhibition efficiency (IE%) is calculated from the charge transfer resistance values using the following equation.

$$\% \text{ Inhibition Efficiency (\%IE)} = \frac{R_{ct} - R_{ct(inh)}}{R_{ct}} \times 100$$

where $R_{ct(inh)}$ and R_{ct} are the charge transfer resistance values with and without inhibitors respectively. The calculated impedance parameters are given in Table 3. From the data in Table 3, it is clear that the value of R_{ct} increases on increasing the concentration of the inhibitor, indicating that the corrosion rate decreases in the presence of the inhibitor. It is also clear that the value of C_{dl} decreases on the addition of inhibitors, indicating a decrease in the local dielectric constant and/or an increase in the thickness of the electrical double layer, suggesting the inhibitor molecules function by the formation of the protective layer at the metal surface [19–24].

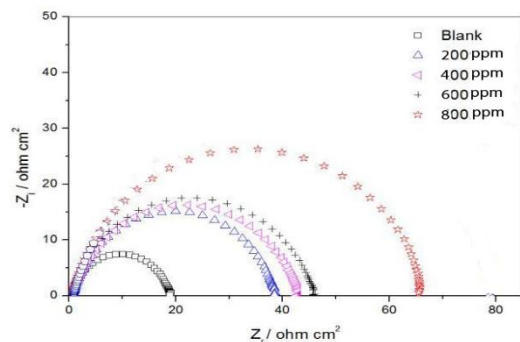


Fig. 2 Nyquist diagram for mild steel in 3.5% M NaCl solution in the absence and presence of various concentrations of the PCD inhibitor

Table 3 Impedance measurements and inhibition efficiency on mild steel in artificial seawater containing 3.5% NaCl containing different concentrations of inhibitor PCD extract

PCD Conc. (ppm)	R_s (Ωcm^2)	R_{ct} (Ωcm^2)	C_{dl} (μFcm^{-2})	Inhibition Efficiency (%)
0	0.79	18	392	--
200	0.89	43	232	58
400	0.83	47	180	62
600	0.72	67	160	73
800	0.86	78	148	77

3.4 FTIR Spectroscopy Studies

It is well established that FT-IR spectrophotometer is a powerful tool that can be used to identify the type of bonding particularly functional group(s) present in organic compounds. Fig. 3a shows the IR spectrum of the ethanol extract of PCD extract. The absorption at 3401 cm^{-1} (associated hydroxyl) was overlapped by the strong stretching mode of N-H. A peak at 1610 cm^{-1} indicated N-C-N stretching of imidazole ring. The peak at 1290 cm^{-1} can be assigned to stretching mode of C-N group. The bands at 1474 cm^{-1} are attributed to C-C in ring (for aromatic). The absorption band at 1527 cm^{-1} is assigned to the N-O Asymmetric stretch and 1070 cm^{-1} is assigned to C-O stretch. A peak observed at 2930 and 2860 cm^{-1} in the spectrum of pure PCD extract powder indicates C-H stretching of methyl group. A peak at 1630 and 1468 cm^{-1} in the spectrum is attributed to C=O stretching of carbonyl group. This shows that this plant extracts contains mixtures of compounds, that is, alkaloids, flavonoids, organic acids, and so on. Fig. 3b showed the surface product formed on the metal after the corrosion test in the presence of PCD inhibitor. This spectra showed most of the peaks of the PCD extract are disappeared and the some new peaks are formed. The peaks around 671 and 830 cm^{-1} are due to the presence of goethite ($\alpha\text{-FeOOH}$) and magnetite (Fe_3O_4) and the peaks around 1017 and 436 cm^{-1} designating the presence of lepidocrocite. These results suggested that the inhibitor molecule is strongly adsorbed over the surface of mild steel [25].

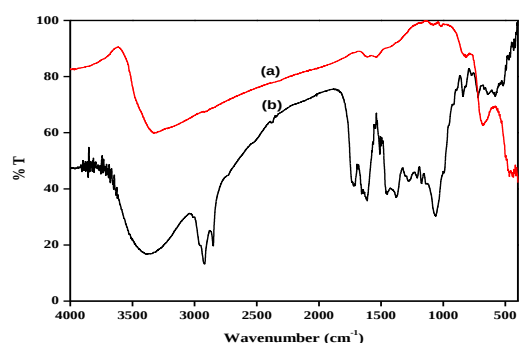


Fig. 3 FTIR spectra of (a) surface product formed on the metal after the corrosion test in the presence of PCD inhibitor and (b) Pure PCD extract powder

3.5 Surface Morphology and Compositional Analysis

SEM is one of the most powerful tools for observing the surface morphology as it provides a useful information about the substrate microstructure. The surface morphology of the mild steel specimens in the presence and absence of inhibitor immersed in 3.5% NaCl solutions are shown in Fig. 4. Fig. 4a shows bare MS surface before immersion in the corrosive medium showed that a uniform surface finishing is produced by the mechanical polishing. Fig. 4b shows the surface of the mild steel specimen after immersion in 3.5% NaCl solution for 1 h in the absence of inhibitor. Fig. 4c shows the surface of the mild steel specimen after immersion in the corrosive solution for the same period of time in the presence of inhibitor. SEM micrographs revealed that the surface morphology was strongly damaged in the absence of the inhibitor, but in the presence of inhibitor damage was considerably diminished [26].

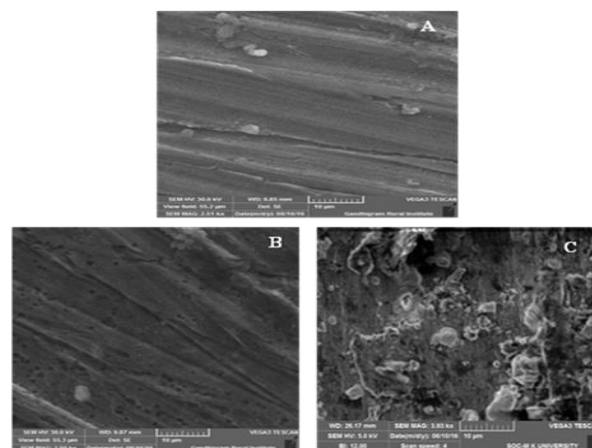
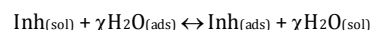


Fig. 4 SEM images of (a) Bare MS, (b) in the absence of inhibitor and (c) presence of PCD inhibitor of MS in 3.5% NaCl solution

3.6 Corrosion Inhibition Mechanism

From the experimental and theoretical results obtained, we note that a plausible mechanism of corrosion inhibition of mild steel in corrosion medium by PCD extract may be deduced on the basis of adsorption. Inhibitors are known to decrease metal dissolution via adsorption on the metal/corrosion products interface to form a protective film which separates the metal surface from the corrosive medium. The adsorption route is usually regarded as a substitution process between the organic inhibitor in the aqueous solution [$\text{Inh}(\text{sol})$] and water molecules adsorbed at the metal surface [$\text{H}_2\text{O}(\text{ads})$] as follows,



where χ represents the number of water molecules replaced by one molecule of adsorbed inhibitor. The adsorption bond strength is dependent on the composition of the metal and corrosion products, extract components, concentration as well as temperature. In depth consideration of some of these variables will normally yield useful information regarding the adsorption mechanism. Although, the complex nature of the corrosion inhibition process is not in doubt, this complexity is increased by several orders of magnitude when one considers plant extracts with their complicated chemical compositions. This makes it difficult to assign the inhibitive effect to adsorption of any particular constituent, since some of these constituents including tannins, alkaloids, flavonoids, and organic pigments are known to exhibit inhibiting action [10–22].

4. Conclusion

Pithecollobium dulce extract was found to be an effective inhibitor for mild steel corrosion in NaCl. Inhibition efficiency of the extract increased with an increase in concentration of the inhibitor. Polarization studies revealed that E_{corr} shifted in the noble directions and the corrosion current decreased with increasing the concentration indicated the inhibition. EIS measurements show that charge transfer resistance (R_{ct}) increases and double layer capacitance (C_{dl}) decreases in the presence of inhibitors indicating the adsorption of the inhibitors over the surface of steel. FTIR spectrophotometric studies clearly revealed that the formation of Fe-inhibitor complex may be responsible for the observed inhibition. Present study provides new information on the inhibiting characteristics of PCD under specified conditions.

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