



## A Novel Eco-Friendly Corrosion Inhibitor for Mild Steel Protection in Two Different Aggressive Artificial Corrosive Medium

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### ABSTRACT

In this study, the effect of new corrosion inhibitor namely *Pithecollobium Dulce* (PCD) extract on the protection of mild steel (MS) in 3.5% sodium chloride (NaCl) and 1 M hydrochloric acid (HCl) solutions were investigated using weight loss measurements and electrochemical techniques. Weight loss method proved that a significant decrease in the corrosion rate of MS was observed in the presence of inhibitor. Electrochemical measurements showed that the inhibition efficiencies increased with increasing inhibitor concentration. The UV-Vis spectroscopy, Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy (SEM) analysis were carried out to characterize the surface film.

**Keywords:** *Pithecollobium dulce* extract; Mild steel; Electrochemical studies; SEM, FTIR and UV-Vis spectroscopy

### INTRODUCTION

Metals are the pre-eminent important materials used in structural and decorative applications. The corrosion, deterioration or destruction of metals is an unavoidable but controllable process. The corrosion of metals has a significant impact on the development of a country, which can be compared to any natural disasters. It was also suggested that about 25-30% of the annual corrosion costs could be saved by means of optimum corrosion management practices. Hence, the corrosion inhibition of steels in acid medium becomes an intensive field of research [1]. Since the first report for the use of an organic inhibitor against corrosion of steel in acid medium [2], numerous number inhibitors were reported as potential candidates for inhibition of steel corrosion [3-10]. Among them, chromium-based inhibitors were found to be very useful. Drawbacks of using chromium inhibitors included severe health issues and non eco-friendliness. Therefore, organic inhibitors were studied more in the past decade as a replacement of chromium inhibitors [10-13]. Especially, inhibitors derived from natural sources, such as plant extracts were more attractive for this purpose. The advantages for using plant based inhibitors include eco-friendliness and economy. Recently many of the plant derivatives were used as green corrosion inhibitor for the control of chemical corrosion in steels, such as *Areca catechu*, *Syzygium cumini*, *Tragia plukenetii*, *Azadirachta indica*, *Calotropis gigantea*, *Gossypium hirsutum*, *Artemisia pallens*, garlic peel extract, Papaya seeds and etc., [10-16]. 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. In view of the abundance, eco-friendliness, and economy, in the present study, the ethanolic extract of PCD was evaluated as a potential steel corrosion inhibitor in hydrochloric acid medium. Corrosion protection behavior of the inhibitor on MS has been studied by weight-loss method and electrochemical

measurements. The surface morphology and formation of passive film on MS was characterized by UV-Vis, FTIR and SEM.

## EXPERIMENTAL SECTION

### 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.

### 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.

### Preparation of *Pithecellobium dulce* Leaves Extract

Dried *pithecellobium dulce* (PCD) leaves (100 g) were powdered and soaked in 500 ml ethanol for 24 h. The mixture is passed through the soxlet apparatus was then filtered and the filtrate was refluxed for 6 h 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.

### Weight Loss Measurements

Weight loss measurements were conducted under total immersion using 250 mL capacity beakers containing 200 mL test solutions (1 M HCl and 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:

$$\text{Corrosion rate, (CR)} = \frac{534w}{DA t}$$

Where W is the weight loss (g), D is the density of the specimen (97.85 g/cm<sup>3</sup>), A is the surface area of specimen (cm<sup>2</sup>) and t is the immersion time (days). The efficiency of the inhibitor was computed using the following equation [17-19],

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

Where, W<sub>0</sub> and W<sub>1</sub> are weight loss without inhibitor and with inhibitor.

### Electrochemical Studies

Electrochemical corrosion measurements were carried out by CH1660B electrochemical workstation with the conventional three electrode cylindrical glass cell using HCl and 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).

### 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 4000–400 cm<sup>-1</sup> with the resolution of 4 cm<sup>-1</sup>. UV-Vis spectrum was recorded using “TECHCOMP” UV-visible spectrometer model 8500.

## RESULTS AND DISCUSSION

## 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 programmes. Tables 1 and 2 shows the corrosion rate and inhibition efficiency of MS by weight-loss measurements at different concentrations of the inhibitor in 1M HCl and 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 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, while the decrease in inhibition efficiency with temperature rise is suggestive of electrostatic interaction (physical adsorption) of the phyto-constituents of the extract on mild steel surface forming a protective layer and shielding the metal from corrosion [20-23]. 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.

**Table 1: Inhibition efficiency, corrosion rate and surface area for mild steel in 1 M HCl in the presence and absence of various concentrations of PCD inhibitors obtained from weight-loss method**

Inhibitor concentration (ppm)	7 days				14 days				21 days				28 days			
	wt loss	IE%	CR(mm/pt) 10 <sup>-4</sup>	Surface area Θ	wt loss	IE%	CR(mm/pt) 10 <sup>-4</sup>	Surface area Θ	wt loss	IE%	CR(mm/pt) 10 <sup>-4</sup>	Surface area Θ	wt loss	IE%	CR(mm/pt) 10 <sup>-4</sup>	Surface area Θ
Blank	1.3422		22.25		2.2866		18.88		2.55		14.05		2.819		11.64	
200	1.3062	2.97	21.59	0.03	1.882	17.49	15.54	0.175	2.401	5.839	13.23	0.05839	2.695	4.395	11.13	0.0439
400	1.2642	6.09	20.89	0.061	1.7978	21.37	14.84	0.214	2.393	6.5786	13.18	0.06578	2.517	10.684	10.39	0.1068
600	1.2241	9.06	20.23	0.091	1.7621	22.93	14.55	0.229	2.378	6.756	13.09	0.06756	2.472	12.28	10.21	0.1228
800	1.1921	11.52	19.7	0.115	1.6842	26.34	13.91	0.263	2.36	7.47	13.02	0.0747	2.452	12.99	10.13	0.1299
1000	1.1631	13.6	19.22	0.136	1.6472	27.96	13.6	0.28	2.333	8.521	12.85	0.08521	2.445	13.24	10.1	0.1324

**Table 2: Inhibition efficiency, corrosion rate and surface area for mild steel in 3.5% NaCl in the presence and absence of various concentrations of PCD inhibitors obtained from weight-loss method**

Inhibitor concentration (ppm)	7 days				14 days				21 days				28 days			
	wt loss	IE%	CR(mm/pt) 10 <sup>-4</sup>	Surface area Θ	wt loss	IE%	CR(mm/pt) 10 <sup>-4</sup>	Surface area Θ	0.0164	IE%	CR(mm/pt) 10 <sup>-4</sup>	Surface area Θ	wt loss	IE%	CR(mm/pt) 10 <sup>-4</sup>	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

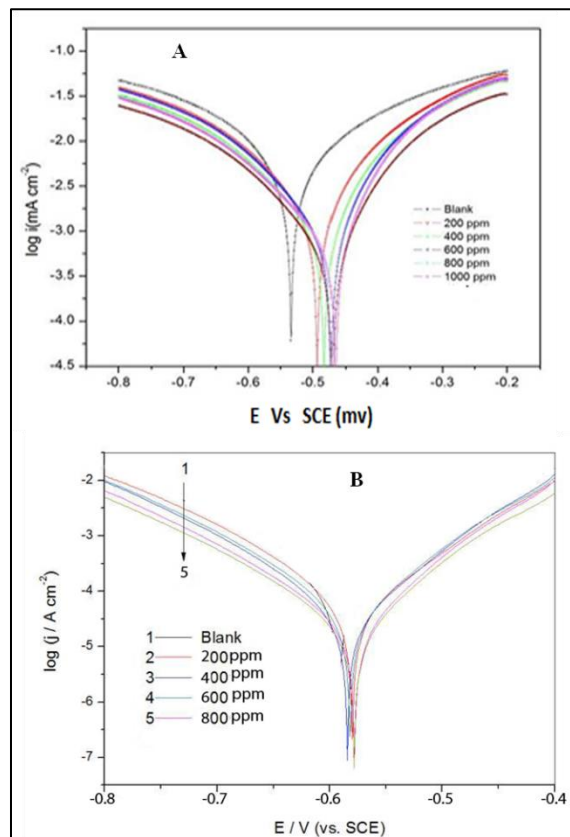
## Potentiodynamic Polarization Studies

Polarization curves of mild steel in 1 M HCl and 3.5% NaCl solutions in the absence and presence of inhibitor at different concentrations are shown in Figure 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 3. 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,  $i_{\text{corr}}$  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  $E_{\text{corr}}$  values increased and  $I_{\text{corr}}$  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 [24-27].



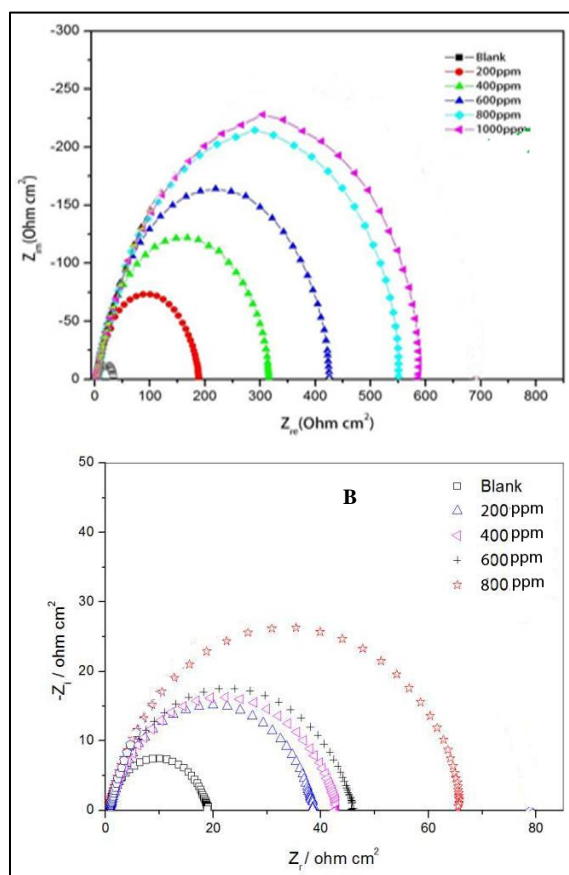
**Figure 1: Tafel plot for mild steel in (A) 1 M HCl and (B) 3.5% M NaCl solutions in the absence and presence of various concentration of the PCD inhibitor**

### Electrochemical Impedance Spectroscopy Studies

The corrosion behavior of MS in HCl and NaCl solutions were investigated by electrochemical impedance spectroscopy at room temperature. Nyquist plots of mild steel in the absence and presence of various concentrations of inhibitor are given in Figure 2 (Figure 2A for 1M HCl and Figure 2B for 3.5% NaCl solutions). Both the Nyquist plots 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.

**Table 3: Tafel parameters and inhibition efficiency for corrosion of mild steel in 1 M HCl and 3.5% NaCl solutions containing different concentrations of inhibitor DPL extracts**

PCD Concentrations (ppm)	$E_{corr}$ (mV)	$I_{corr}$ mA cm <sup>-2</sup>	Tafel Constants		Inhibition Efficiency (%)
			$ba$ (mV dec <sup>-1</sup> )	$bc$ (mV dec <sup>-1</sup> )	
<b>HCl Medium</b>					
Blank	-559	4	96	107	-
200	-492	0.791	82	106	80.53
400	-486	0.519	83	107	87.22
600	-480	0.375	81	105	90.67
800	-476	0.245	84	108	93.97
1000	-472	0.227	86	109	94.41
<b>NaCl Medium</b>					
0	-592	1.28	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



**Figure 2: Nyquist diagram for mild steel in (A) 1 M HCl and (B) 3.5% M NaCl solutions in the absence and presence of various concentration of the PCD inhibitor**

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 4. From the data in Table 4, 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 [28-32].

The inhibition efficiency obtained by weight loss measurements is lower than that from electrochemical experiments; this difference is attributed to weight loss experiments giving average corrosion rates, whereas the electrochemical experiments give instantaneous corrosion rates. Therefore, the discrepancy in inhibition efficiency obtained by the two methods is understandable. However, the trend of inhibition efficiency with increasing of inhibitor concentration is similar no matter whether electrochemical or weight loss method is selected: the inhibition efficiency increased as inhibitor concentration increased.

**Table 4: Nyquist plots and inhibition efficiency on mild steel in artificial seawater containing 1 M HCl and 3.5% NaCl solutions containing different concentrations of PCD inhibitor**

PCD Concentration (ppm)	$R_s$ ( $\Omega cm^2$ )	$R_{ct}$ ( $\Omega cm^2$ )	$C_{dl}$ ( $\mu F cm^{-2}$ )	Inhibition Efficiency (%)
<b>HCl medium</b>				
0	1.736	39	284	-
200	1.793	190	115	79
400	1.602	315	78	88
600	1.636	430	57	91
800	1.937	560	44	93
1000	1.842	595	24	94
<b>NaCl medium</b>				
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

### UV-Vis and FTIR Spectroscopy Studies

In order to confirm the possibility of the formation of PCD-Fe complex, UV-Visible absorption spectra obtained from 1 M HCl solution containing 800 ppm of PCD extract before and after 7 days of mild steel immersion is shown in Figure 3. The electronic absorption spectra of PCD extract before the steel immersion (Figure 3A) display three bands (one band in the UV region and two bands in the visible region). The absorption band in the lower wavelength (290 nm) can be assigned to the  $\pi-\pi^*$  transition of the benzenoid rings and the absorption bands at longer wavelengths (410 and 675 nm) are as a result of the presence of aromatic systems with quinoid units. From the spectroscopic analysis, it can be concluded that the PCD extract is highly conjugated. After 7 days of steel immersion (Figure 3B), the band at 290 nm is shifted to the longer wavelengths and the remaining peaks are disappeared which showing a possibility of interaction between PCD and mild steel (physisorption). These experimental findings give strong evidence for the possibility of the formation of a complex between  $Fe^{2+}$  cation and PCD in HCl [33,34].

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. Figure 4a shows the IR spectrum of the ethanol extract of PCD extract. The absorption at  $3401\text{ cm}^{-1}$  (associated hydroxyl) was overlapped by the strong stretching mode of N-H. A peak at  $1610\text{ cm}^{-1}$  indicated N,C-N stretching of imidazoline ring. The peak at  $1290\text{ cm}^{-1}$  can be assigned to stretching mode of C-N group. The bands at  $1474\text{ cm}^{-1}$  are attributed to C-C in ring (for aromatic). The absorption band at  $1527\text{ cm}^{-1}$  is assigned to the N-O Asymmetric stretch and  $1070\text{ cm}^{-1}$  is assigned to C-O stretch. A peak observed at  $2930$  and  $2860\text{ cm}^{-1}$  in the spectrum of pure PCD extract powder indicates C-H stretching of methyl group. A peak at  $1630$  and  $1468\text{ cm}^{-1}$  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. Figure 4b 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  $830\text{ cm}^{-1}$  are due to the presence of goethite ( $\alpha\text{-FeOOH}$ ) and magnetite ( $Fe_3O_4$ )

and the peaks around 1017 and 436  $\text{cm}^{-1}$  designating the presence of lepidocrocite. These results suggested that the inhibitor molecule is strongly adsorbed over the surface of mild steel [35].

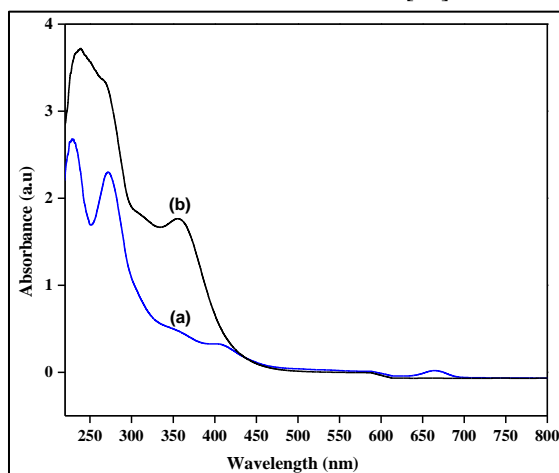


Figure 3: UV-visible spectra of the solution containing 1 M HCl with 800 ppm PCD inhibitor (a) before and (b) after 3 days of mild steel immersion

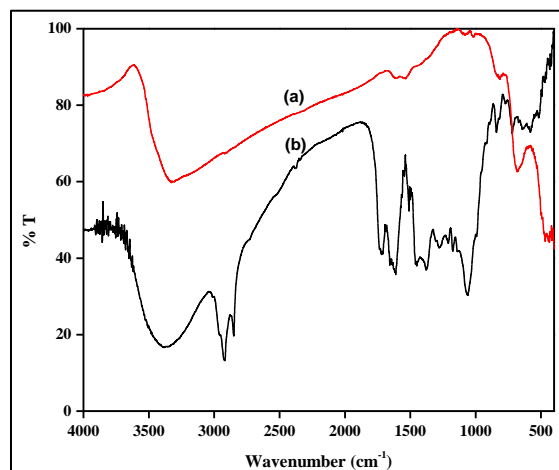


Figure 4: FTIR spectra of (a) surface product formed on the metal after the corrosion test in the presence of PCD inhibitor and (b) Pure PCD Extract powder

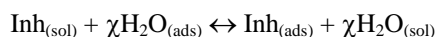
### Surface Morphology and Compositional Analysis

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 1 M HCl and 3.5% NaCl solutions are shown in Figure 5. Figure 5A shows bare MS surface before immersion in the corrosive medium showed that a uniform surface finishing is produced by the mechanical polishing. Figures 5B and 5C shows the surface of the mild steel specimen after immersion in 1 M HCl and 3.5% NaCl solution for 1 h in the absence of inhibitor. Figures 5D and 5E 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 [36].

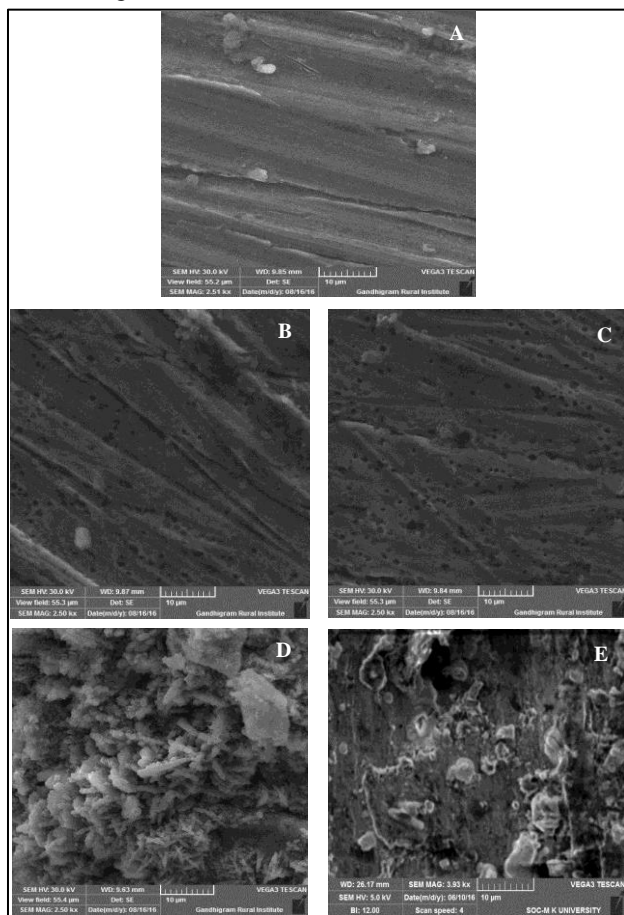
### Corrosion Protection Inhibition Mechanism

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 [Inh(sol)] and water molecules adsorbed at the metal surface [H<sub>2</sub>O(ads)] as follows:



Where,  $\chi$  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.



**Figure 5: SEM images of (A) Bare MS, (B) and (C) in the absence of inhibitor and (D) and (E) presence of inhibitor of MS in 1M HCl, and 3.5% NaCl solution**

## CONCLUSION

- *Pithecollobium Dulce* extract was found to be an inhibitor for mild steel corrosion in HCl and NaCl. Inhibition efficiency of the extract increased with an increase in concentration of the inhibitor.
- Polarization studies revealed that  $E_{\text{corr}}$  shifted in the noble directions and the corrosion current decreased with increasing the concentration indicated the inhibition.
- EIS measurements show that charge transfer resistance ( $R_{\text{ct}}$ ) increases and double layer capacitance ( $C_{\text{dl}}$ ) decreases in the presence of inhibitors indicating the adsorption of the inhibitors over the surface of steel.
- UV-Vis and 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 extract under specified conditions. The new environmentally friendly inhibitor could find possible applications in metal surface anodizing and surface coating in industries.

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