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Comparative Study of Corrosion Inhibition of *Commiphora caudata* and *Digera muricata* for Mild Steel in 1 M HCl Solution

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Commiphora caudata and *Digera muricata* extracts as corrosion inhibitors for mild steel in 1 M HCl were studied by weight loss and surface analysis techniques. It showed that both plant extracts inhibited the mild steel corrosion. Inhibition efficiency increased with increasing inhibitor concentration and temperature which suggested that the chemical mechanism. The inhibitors adsorbed onto the mild steel surface followed Langmuir adsorption isotherm. The surface morphology of mild steel showed that the addition of the extract reduces the mild steel corrosion.

Keywords: ***Commiphora caudata*, *Digera muricata*, Mild steel, Langmuir.**

INTRODUCTION

Mild steel has been widely used for structural and industrial applications. Acid solutions are widely used in the industries for acid pickling, industrial acid cleaning, acid descaling and oil well acidizing [1]. Mild steel gets rusted when it comes in contact with any acid. Corrosion inhibitors are used to prevent the corrosion of mild steel in acid. The chemical inhibitors and natural inhibitors are reduced the corrosion [2,3]. Specifically natural inhibitors are mostly preferred due to they are cheap, easily available, non-toxic and renewable [4]. The inhibitors have centre for π-electrons and contains hetero atoms such as sulphur, nitrogen, oxygen and phosphorous which allows the adsorption of compounds on the mild steel surface [5,6]. Several plant extracts like *Euphorbia hirta* [7] *Lawsonia inermis* [8], *Morinda tinctoria* [9], ankado [10], *Curcuma longa* [11], *etc.* have been reported to act as good corrosion inhibitors for mild steel in acid medium. The present study is aimed at investigating the corrosion inhibition and adsorption properties of *Digera muricata* and *Commiphora caudata* extract for the corrosion of mild steel in 1 M HCl medium.

EXPERIMENTAL

Leaves of *Digera muricata* and *Commiphora caudata* were collected, washed, shade dried and grind to fine powdered. 50 g of this powder was added to 1000 mL of 1 M HCl. This mixture was refluxed for 3 h at 80 °C and kept overnight and then it was filtered.

Mild steel sheets cut into rectangular coupons of size 5 cm × 1 cm provided with holes on top of the strip. These mild steel pieces were mechanically polished with fine emery sheets and degreased with acetone, washed with distilled water, dried and stored in desiccators.

Weight loss measurements: Metal samples were weighed using and triplicate immersed in 100 mL of 1 M HCl with different concentrations of plant extract (0.1, 0.2, 0.3, 0.45, 0.5, 0.65, 0.7, 0.8 and 0.9 %, v/v) and without plant extract (Blank).

The experiment was carried out at different immersion periods (0.5, 2, 4, 6, 8 and 24 h) at 303 K. Corrosion inhibition studies were also carried out at different temperatures (303, 313, 323, 333 and 343 K).

From this study, the weight loss, inhibition efficiency (IE), surface coverage (θ) and corrosion rate were determined. The inhibition efficiency was calculated using the following formula [12]

$$\text{Inhibition efficiency (\%)} = \frac{\text{Wu - WI}}{\text{Wu}} \quad (1)$$

where, Wu = weight loss in the absence of inhibitor; WI = weight loss in the presence of inhibitor.

Determination of corrosion rate: In this present study, the corrosion rate (CR) is expressed in American units, mpy (mils per year) [13].

$$\text{Corrosion rate (mmpy)} = \frac{87.6 \times \text{Weight loss (mg)}}{\text{Density (g/cc)} \times \text{Area (cm}^2) \times \text{Time (h)}} \quad (2)$$

where, mpy = mils per year, W = weight loss in mg, D = density in g/cm^2 (7.9 g/cm^2 for mild steel), A = area in square inch and T = immersion time (h).

Determination of activation energy (E_a): The Arrhenius plot obtained for the plot of log CR *vs.* 1/T with slope equal to E_a/2.303 R. Thus the E_a values can be calculated from the slope of the Arrhenius plot by using the equation [14]

$$E_a = - 2.303 \text{ RT} \times \text{slope} \quad (3)$$

where, E_a is the activation energy, T is the absolute temperature and R is the universal gas constant.

RESULTS AND DISCUSSION

Preliminary phytochemical screening of 1 M HCl extract of *Commiphora caudata* and *Digera muricata*: The results obtained from phytochemical screening of extract are displayed in Table-1

TABLE-1
PHYTOCHEMICAL SCREENING OF EXTRACT OF *Commiphora caudata* AND *Digera muricata*

Phytochemical	*Commiphora caudate*	*Digera muricata*
Tannins	+	-
Alkaloids	-	+
Terpenoids	+	+
Glycosides	+	-
Flavanoids	+	-
Saponins	+	+++
Carbohydrates	-	+
Phenols	-	+
Protein	+	+

Weight loss measurements

Effect of concentration of inhibitor and time of immersion: The inhibition efficiency increased by increasing acid extract of *Digera muricata* and *Commiphora caudata* concentration and time. The maximum inhibition efficiency of 94.58 and 95.13 % were noticed at a concentration 0.7 % of the *Commiphora caudata* and *Digera muricata* inhibitor at 6 h in 1 M HCl (Table-2). Since more adsorption takes place on the metal surface, the inhibitor efficiency increases with an increase in immersion time. It was found that the optimum inhibition efficiency is reached in 6 h and further increase in time did not cause any appreciable change in the performance of the inhibitor [15]. The inhibition efficiency was found to decrease with the immersion time was increased from 6 h to 24 h. This may be because, prolonged immersion may result in desorption of the inhibitor molecules from the mild steel surface [16].

Effect of temperature: Analysis of the Fig. 1 indicates that, as the temperature increases from 303 to 343 K, the inhibition efficiency also increased [17-20]. The increase in inhibition efficiency was from 73.63 to 90.17 % for 0.7 % concentration of *Commiphora caudata* in 1 M HCl and increase from 85.7

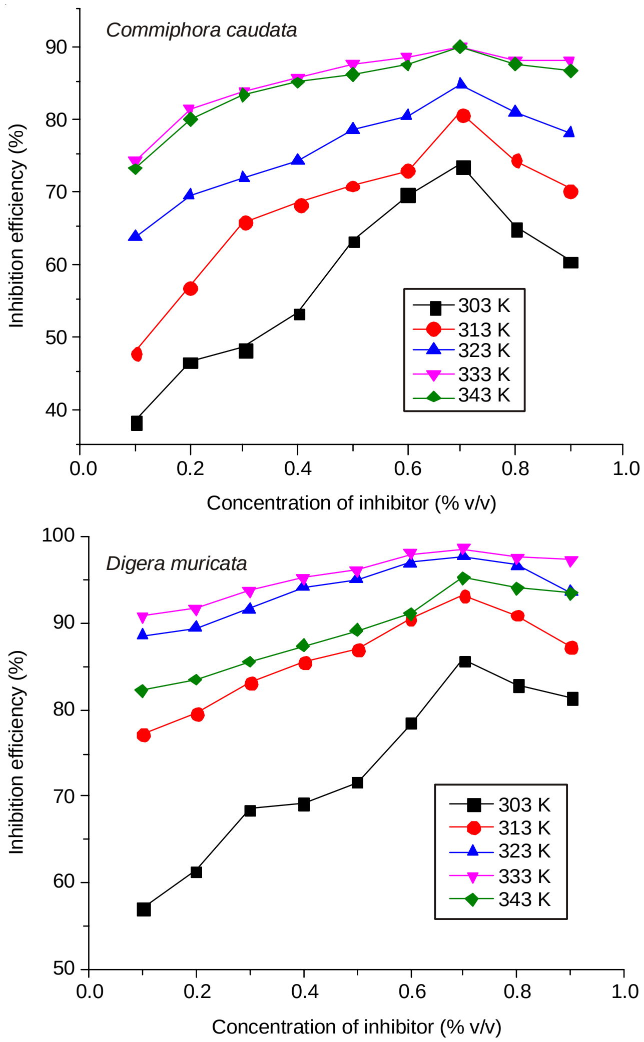


Fig. 1. Variation of inhibition efficiency of *Commiphora caudata* and *Digera muricata* extract, at different concentrations, on mild steel in 1 M HCl at different temperatures

TABLE-2
INFLUENCE OF CONCENTRATION OF *Commiphora caudata* AND *Digera muricata* EXTRACT ON THE CORROSION OF MS IN 1 M HClAT DIFFERENT TIME INTERVAL

Inhibitor conc. (% v/v)	Inhibition efficiency (%) of *Commiphora caudata*						Inhibition efficiency (%) of *Digera muricata*					
	0.5 h	2 h	4 h	6 h	8 h	24 h	0.5 h	2 h	4 h	6 h	8 h	24 h
0.1	38.33	70.38	78.82	87.77	78.3	76.6	57.14	61.03	83.69	84.37	64.73	55.60
0.2	46.67	73.81	79.93	90.36	83.2	78.2	61.43	62.91	87.12	87.66	66.42	59.82
0.3	48.33	78.46	83.24	90.78	84.7	79.6	68.57	70.42	87.55	88.56	74.53	66.49
0.4	53.33	81.15	84.35	91.81	87.1	81.6	69.29	71.83	88.41	89.01	82.09	69.20
0.5	63.33	85.00	86.92	92.77	88.4	84.3	71.71	76.41	90.34	90.94	86.69	74.52
0.6	69.67	86.54	88.60	93.01	90.2	85.3	78.57	84.51	92.27	93.58	90.11	80.26
0.7	73.63	88.85	93.55	94.58	92.4	87.5	85.71	91.60	93.13	95.13	91.55	82.29
0.8	65.00	88.08	90.79	93.99	89.6	86.4	82.86	88.73	90.99	91.39	83.58	79.63
0.9	60.50	88.04	88.58	93.37	88.9	84.9	81.43	83.10	91.42	90.60	76.22	75.50

to 98.1 % for 0.7 % concentration of *Digera muricata* in 1 M HCl at 333 K. Further rise in temperature results in slight depletion of inhibitor efficiency [21]. From the data, it can be inferred that the protective layer formed on mild steel surface, due to adsorption of plant extract, was stable up to 333 K and after that there may be desorption of plant extract at 343 K [22]. Considering the magnitude of rise in temperature and the marginal drop in inhibition efficiency %. It is concluded that the extract worked out as a temperature resistant inhibitor in 1 M HCl.

Thermodynamic consideration

Activation energy (E_a): The inhibitive properties of the inhibitor and the temperature dependence on the corrosion rate, the apparent activation energy (E_a) for the corrosion process in the absence and presence of inhibitor were evaluated from Arrhenius equation. From the Tables 3 and 4, it is evident that the addition of extract leading to an abrupt decrease in the apparent activation energy (E_a) to a value less than that of the uninhibited solution followed by the monotonous decrease with an increase in inhibitor concentration indicates that the inhibitory action of on mild steel in1 M HCl occurs *via* chemical adsorption [23-25].

Change in free energy of adsorption: The value of ΔG are obtained from the following equation [26]:

$$\Delta G_{ads} = -RT \text{ In } (55.5 \text{ K}) \quad (4)$$

where K is given by

$$K = \theta/C\ (1-\theta)$$

where θ = surface coverage on the metal surface, C = concentration of inhibitor in mol/L; K = equilibrium constant.

The slope (ΔS_{ads}) and intercept (ΔH_{ads}) obtained from the plot - ΔG_{ads} *vs.* T was depicted in Fig. 2 for extract of *Commiphora caudata* and *Digera muricata* leaves in 1 M HCl.

Tables 3 an 4 show that the calculated values of activation energy (E_a), free energy of adsorption (ΔG_{ads}), the enthalpy of adsorption (ΔH) and the entropy of adsorption (ΔS) for mild steel in 1 M HCl with and without extract. The negative value of free energy of adsorption (ΔG_{ads}) ensure the spontaneity of the adsorption process and the stability of the adsorbed layer on the mild steel surface as well as a strong interaction between the inhibitor molecules and the metal surface.

Generally, values of ΔG_{ads} up to -20 kJ mol^{-1}, the types of adsorption was regarded as physisorption [1], the inhibition acted due to the electrostatic interactions between the charged molecules and the charged metal, while the values around -40 kJ mol^{-1} or smaller were associated with chemisorption as a result of sharing or transfer of electrons from organic molecules to the metal surface to form a coordinate type of bond (chemisorption) [27]. Here, the calculated ΔG_{ads} values are indicating that the adsorption mechanism of *Commiphora caudata* and *Digera muricata* on mild steel in 1 M HCl solution at the studied temperatures is both electrostatic-adsorption (ionic) and chemisorption (molecular) [28]. The positive values of enthalpy indicate the endothermic reaction suggesting that a high temperature favours the complexation process [19] and the same is in good agreement with the increasing stability with temperature. This also supports the assumption of chemical adsorption. The negative values of ΔS indicates that the activated complex in the rate determining step represents

TABLE-3
THERMODYNAMIC DATA FOR MILD STEEL IN 1 M HCl IN THE PRESENCE AND ABSENCE OF ACID EXTRACT OF *Commiphora caudata* AT 303 K TO 343 K

Concentration (%)	E_a (kJ/mol)	- (ΔG) (kJ/mol)					-(ΔS) (kJ/mol)	(ΔH) (kJ/mol)
		303 K	313 K	323 K	333 K	343 K		
Blank	65.39							
0.1	44.89	14.70	16.19	18.46	20.40	20.23	0.153	31.34
0.2	41.19	13.81	15.35	17.30	19.65	19.37	0.154	32.67
0.3	39.34	12.96	15.25	16.53	18.95	18.88	0.155	33.66
0.4	39.00	12.74	14.81	16.10	18.53	18.42	0.151	32.62
0.5	41.22	13.22	14.55	16.08	18.45	18.04	0.135	27.68
0.6	42.63	13.48	14.33	15.96	18.20	17.87	0.127	24.94
0.7	42.93	13.58	15.10	16.35	18.22	18.13	0.122	23.20
0.8	40.79	12.22	13.78	15.23	17.27	17.10	0.133	27.72
0.9	38.55	11.43	12.96	14.47	16.94	16.58	0.143	31.63

TABLE-4
THERMODYNAMIC DATA FOR MILD STEEL IN 1 M HCl IN THE PRESENCE AND ABSENCE OF ACID EXTRACT OF *Digera muricata* AT 303 K TO 343 K

Concentration (%)	E_a (kJ/mol)	- (ΔG) (kJ/mol)					-(ΔS) (kJ/mol)	(ΔH) (kJ/mol)
		298 K	313 K	323 K	333 K	343 K		
Blank	60.41							
0.1	36.57	16.62	19.60	22.44	23.80	21.71	0.1440	25.67
0.2	37.13	15.32	18.18	20.83	22.24	20.03	0.1349	24.24
0.3	37.48	15.09	17.73	20.44	21.96	19.35	0.1275	22.26
0.4	34.46	14.45	17.45	20.68	21.90	18.99	0.1353	25.00
0.5	31.92	14.19	17.20	20.58	22.00	18.87	0.1416	27.18
0.6	30.15	14.66	17.67	21.44	23.43	18.94	0.1431	27.00
0.7	25.98	15.51	18.24	21.97	24.13	20.37	0.1561	30.39
0.8	29.16	14.63	17.04	20.44	22.15	19.36	0.1458	28.37
0.9	28.07	14.08	15.71	18.28	21.37	18.77	0.1504	30.92

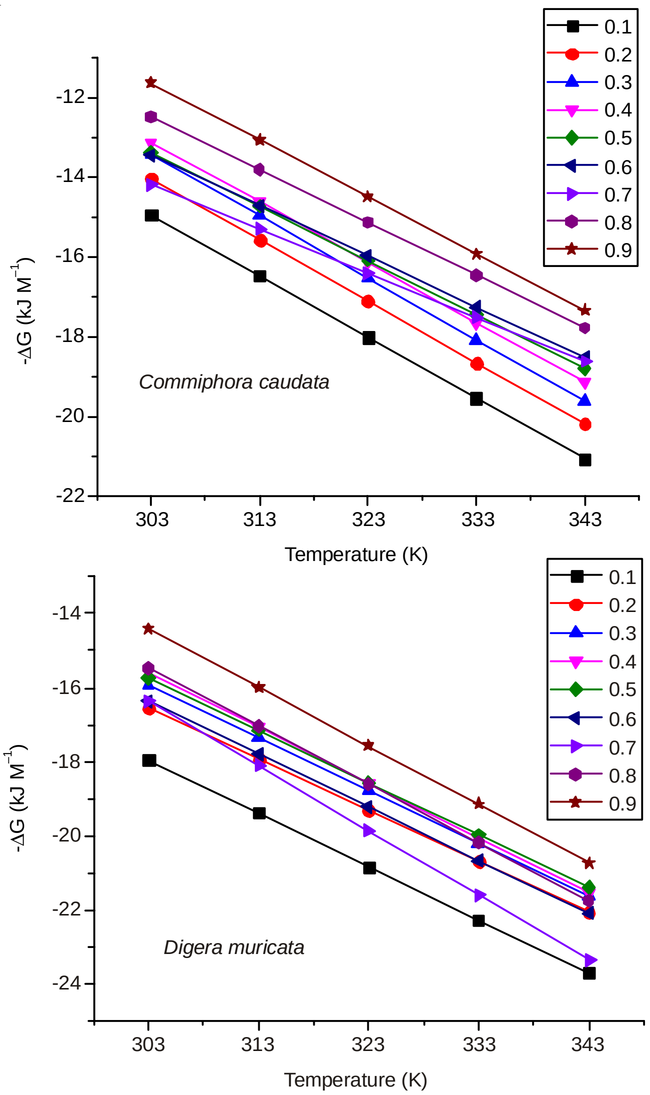


Fig. 2. ΔG_{ads} as a function of temperature in the presence of *Commiphora caudata* and *Digera muricata* extract in 1 M HCl

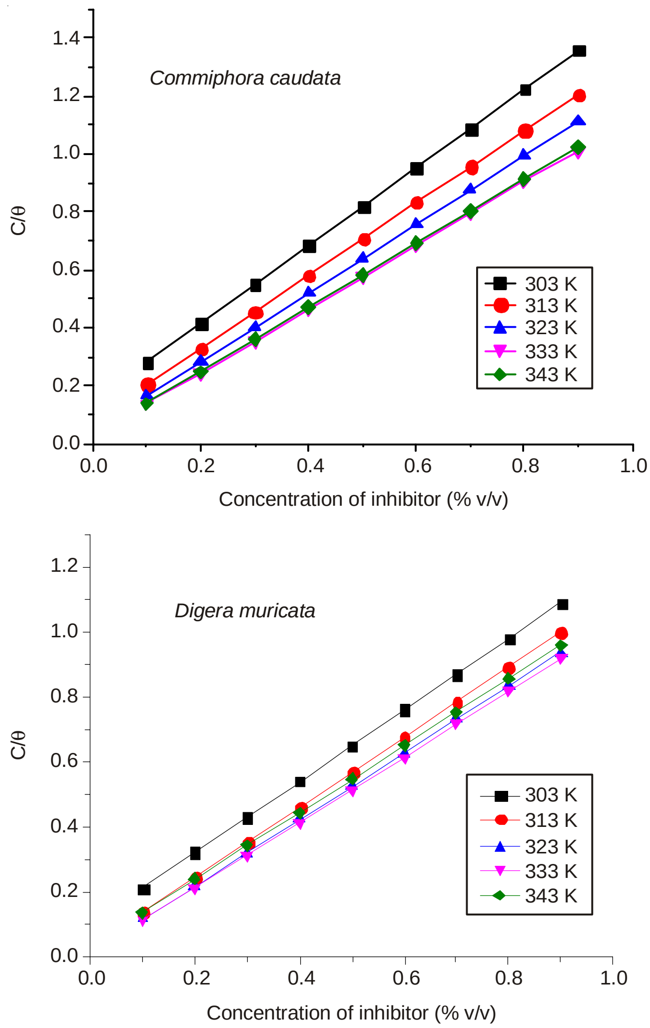


Fig. 3. Langmuir adsorption isotherm plot for the different concentrations of *Commiphora caudata* and *Digera muricata* extract on the mild steel in 1 M HCl at 303 and 333 K

an association rather than a dissociation step, meaning that a decrease in disordering takes place on going from reactants to the activated complex [29,30]. It is obviously that the ΔS shifts to more negative values with increasing inhibition efficiency, this can be explained that the inhibitor species may involved in the activated complex of the corrosion reaction leading to more ordered system [31].

Adsorption consideration: The adsorption isotherm study describes the adsorptive behaviour of inhibitor in order to know the adsorption mechanism of inhibitor to the metal surface. The most frequently used adsorption isotherms are Langmuir, Temkin, Frumkin and Freundlich isotherms. The Langmuir adsorption isotherm was found to provide the best description of the adsorption behaviour (Fig. 3) with the regression coefficient almost unity (0.998). This suggests that the Langmuir adsorption isotherm provides the best description for the adsorption of *Commiphora caudata* and *Digera muricata* on mild steel surface [32].

Langmuir adsorption isotherm could be represented as:

$$\frac{C}{\theta} = \frac{1}{K} + C$$

Morphology examination of mild steel with *Digera muricata* extract: The polished mild steel specimens were immersed in the acid solution 1 M HCl in the acids containing inhibitor *Commiphora caudata* and *Digera muricata* extract for 6 h and then the specimens were taken out, dried and observed under scanning electron microscope. The micrograph are shown in the Fig. 4 depicts that the polished specimen and when it was kept in the blank solution of 1 M HCl associated with polishing scratches. Fig. 5 shows specimen which was kept in optimum concentration of inhibitor solution in 1 M HCl depends upon the concentration of the inhibitor solution suggesting that the presence of adsorbed layer of the inhibitor on mild steel surface which impedes corrosion rate of metal appreciably. This is attributed to the involvement of the compounds in the interaction with the active sites of metal surface. This results in enhanced surface coverage of the metal so that there is a decrease in the contact between metal and the aggressive medium [33].

Conclusions

- The plant extract of *Commiphora caudata* and *Digera muricata* under study behave as an effective inhibitors for mild steel in 1 M HCl by weight loss method and surface analysis.

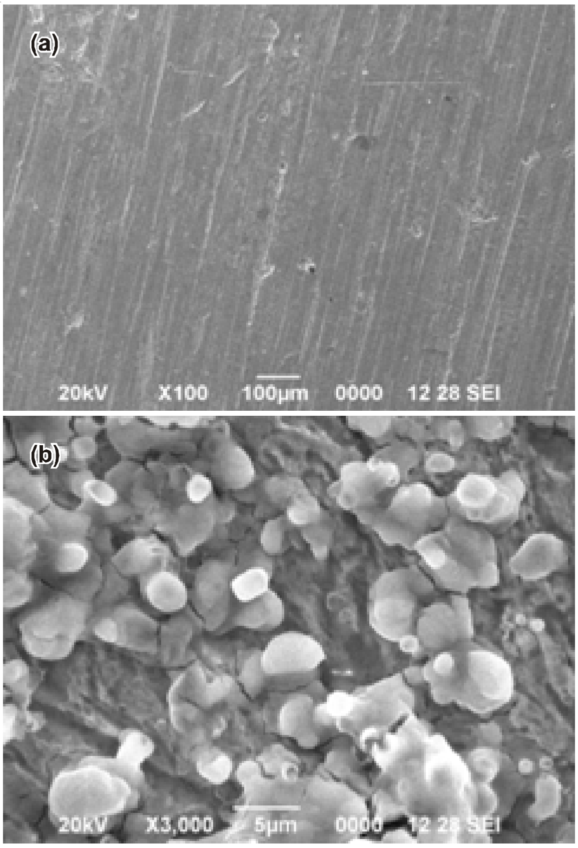
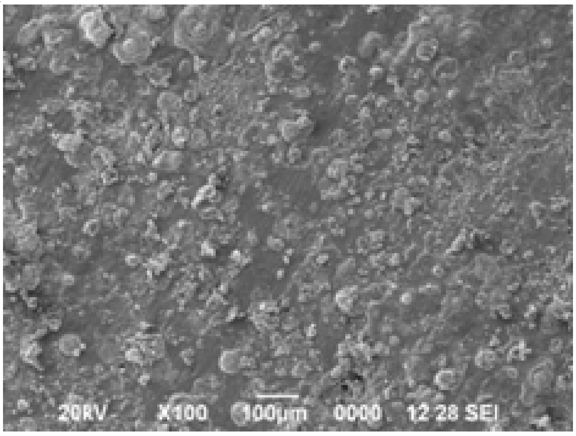
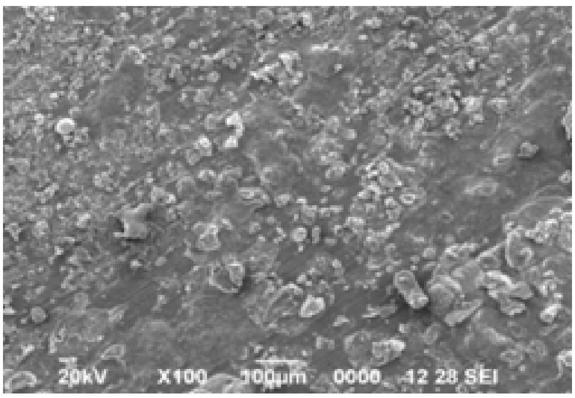


Fig. 4. SEM photograph of (a) polished mild steel and (b) mild steel immersed in 1 M HCl



Commiphora caudata



Digera muricata

Fig. 5. SEM photograph of mild steel immersed in 1 M HCl containing 0.7 % of *Commiphora caudata* and *Digera muricata* extract

• In 1 M HCl, the inhibition efficiencies of the extracts were found to follow the order:

Commiphora caudata < *Digera muricata*

• The inhibition efficiencies (IE) of plant extracts are found to increase with increase of concentration and exposure time.

• The inhibition efficiencies increase with increase in temperature. Hence it was found to be highly temperature resistance. The temperature resistant inhibitors could play an important role in cooling water system. The inhibitors are found to obey Langmuir adsorption isotherm.

• Activation energies decrease in the presence of the extract, probably implying that chemical adsorption of the plant phytochemical constituents may be responsible for the observed inhibition action.

• The adsorption of inhibitors on mild steel was both *via* chemisorption and physisorption.

• The negative values of free energy of adsorption of inhibitor indicate the spontaneity of adsorption.

• The results obtained from weight loss and SEM analysis are found to agree very well with each other.

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