Available online at www.joac.info

ISSN: 2278-1862

Journal of Applicable Chemistry

2018, 7 (1): 239-249

(International Peer Reviewed Journal)

Eco Friendly Green Inhibitor for Corrosion of Mild Steel in 1N Hydrochloric Acid Medium - A Comparative Study

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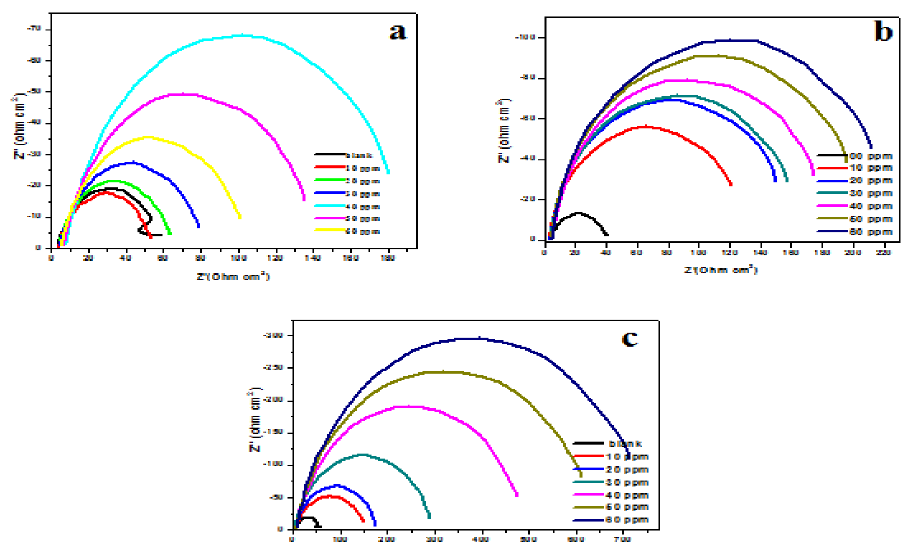
Accepted on 22nd January 2018, Published online on 27th January 2018

ABSTRACT

The mass loss, electrochemical polarization and impedance studies were carried out to investigate the comparative corrosion protection efficiency of plants extract of Artocarpus genus (AG), Terminalia tomentosa (TT) and Pergularia daemia (PD), on mild steel in 1N HCl medium. Polarization methods indicated that the plants extracts behave as mixed type inhibitor. The EIS measurement revealed that the charge transfer resistance process mainly controls the corrosion of mild steel. The adsorption character of plant extract on mild steel surface obey Temkin isotherm. The values obtained in all methods are in good agreement with each other and the inhibition efficiency follows in the order of TT>AG>PD.

Graphical Abstract:



Nyquist plots for mild steel in 1N HCl acid solution without and with presence of different concentration of (a) TT, (b) PD and (c) AG extract of leaves.

Keywords: Mild steel; EIS; SEM; Polarization; Acid Corrosion.

INTRODUCTION

Corrosion, which is an inevitable problem, faced by almost (different metals and alloys) all industry in the world wide. Many studies have been carried out to find suitable compounds to use as corrosion inhibitors; most of these compounds are synthetic chemicals which may be hazardous and very expensive to environments and living organism [1-5]. The plant extract or green inhibitors are used as corrosion preventive practice method. It is most important to select very cheap, nontoxic, naturally available and safety handled compounds to be used as corrosion inhibitors [6-12]. The role of an inhibitor is to form a barrier of one or several molecular layer against corrosion attack and also found useful application in the formulation of anti-corrosive properties [13-18].The object of the work is to direct attention to the inhibitive properties of some natural compounds extracted from some commonly used plants such as Artocarpus genus (AG), Terminalia tomentosa (TT) and Pergularia daemia (PD) for mild steel in aqueous media.

MATERIALS AND METHODS

Preparation of mild steel specimen: Mild steel strips of C- 0.030 %, Mn- 0.169 %, Si- 0.015 %, P- 0.031 %, S - 0.029 %, Cr- 0.029 %, Ni- 0.030 %, Mb- 0.016 %, Cu- 0.017 % and the remainder Fe, were mechanically cut into dimension of 4 cm x 2 cm x 0.1cm and were used for weight loss studies.

Inhibitor: The leaves of the medicinal plants AG, PD, TT was dried and ground well into powder. 10g of the powder from each was refluxed in 150 mL distilled water and kept overnight. The aqueous solution was filtered from the suspending impurities and making into500 mL. The extract was used as corrosion inhibitor in the present study.

Mass loss method: The polished mild steel specimens with uniform size tied with threads and were immersed in 200 mL test solution in the absence and presence of inhibitor for 24 h. The mild steel specimens were washed, dried and the weight loss was calculated. The inhibition efficiency (%) was calculated using equation (1)

$$\text{IE }\% = \frac{W_0 - W_i}{W_0} \text{ x } 100 (1)$$

Where, W_0 and W_i are the weight loss in the absence and presence of the inhibitor.

Potentiodynamic polarization methods: Potentiodynamic polarization measurements were carried out (CHI660E electrochemical analyser)using conventional three electrode cell assembly with mild steel ($1cm^2$) area was used as working electrode, a rectangular Pt electrode as the counter electrode and a saturated calomel electrode as standard reference electrode . The measurements were carried out in the frequency range 10^{-6} -10^{-2}Hz at the open circuit potential (OCP).

$$\text{IE }\% = \frac{I_{Corr} - I_{*Corr}}{I_{Corr}} \text{ x } 100 \quad (2)$$

Where I_{corr} and I_{*corr} are corrosion current in the absence and presence of inhibitors.

Electrochemical impedance method: Experiments were carried out in a conventional three electrode cell assembly as that used for polarization studies. A plot of Z' versus Z" was made.

$$C_{dl} = \frac{1}{2\pi} f_{max} R_{ct} (3)$$

R_{ct} is charge transfer resistance, and C_{dl} is double layer capacitance.

$$\text{IE}\% = \frac{R_{ct} - R^0_{ct}}{R_{ct}} \text{ x } 100 \qquad (4)$$

R_{ct} and R^0_{ct} are the charge transfer resistance values in the inhibited and uninhibited solution.

RESULTS AND DISCUSSION

Mass loss methods: This method is simple and practically used, but it requires a long time for immersion. The mass reductions occur because the metal is destructed and soluble in to its oxidized condition and are caused by the presence of chemical reaction between metal and the environment [19-21]. The corrosion parameters obtained in the weight loss methods are listed in table1. As can be seen from the Table that the corrosion rate of mild steel decreases with an increase in concentration of the inhibitors. The stability and the inhibition efficiency of the plant extract (TT, AG and PD) on mild steel with respect to time was calculated and are presented in Table 2.The thermostat experiments were performed at various temperatures range (303-323K) with and without different concentrations of the inhibitor during the immersion period of 2 h and are presented in table 3.These observations clearly suggested that the corrosion of mild steel was prevented through adsorption process by plant extract

Table 1. Percentage of inhibition efficiency (IE %) and corrosion rate (CR) at different concentration of inhibitor in 1N HCl medium

Name of plant	Conc. of the extract (ppm)	Corrosion rate (mmpy)	Inhibition efficiency (%)
TT **Leaves**	Blank	1.8969	-
	10	0.4434	73.98
	20	0.1844	90.27
	30	0.1315	93.06
	40	0.0589	96.89
	50	0.0814	95.70
	60	0.0854	95.49
PD **Leaves**	10	0.0611	72.50
	20	0.0480	77.98
	30	0.0475	78.85
	40	0.0337	80.96
	50	0.0314	83.14
	60	0.0326	84.40
AG Leaves	10	0.0611	74.96
	20	0.0480	80.32
	30	0.0475	80.53
	40	0.0337	86.18
	50	0.0396	84.01
	60	0.0401	83.22

Table 2. Inhibition efficiency as a function of various immersion times

Name of plant	Conc.of the extract (ppm)	Inhibition efficiency (%)					
		1h	3h	5h	7h	9h	12h
TT **Leaves**	Blank	-	-	-	-	-	-
	10	65.23	71.53	56.36	44..39	54.32	65.56
	20	74.56	79.25	68.24	66.76	60.12	68.72
	30	79.44	85.99	77.76	75.96	72.49	72.95
	40	86.79	88.16	83.15	80.37	81.30	84.10
	50	90.55	91.44	88.03	86.12	92.55	91.78
	60	93.98	96.78	96.89	90.44	97.86	98.65
PD **leaves**	Blank	-	-	-	-	-	-
	10	85.14	82.08	79.13	73.06	78.38	90.12
	20	88.92	87.13	82.22	77.72	86.88	94.78
	30	94.71	91.22	85.63	79.15	87.22	95.92
	40	96.47	92.34	90.34	84.09	90.78	96.91

	50	96.99	96.98	93.22	89.45	94.67	97.22
	60	97.90	97.59	94.55	95.33	98.43	98.32
AG **leaves**	Blank	-	-	-	-	-	-
	10	62.01	58.90	66.14	74.21	83.89	78.90
	20	75.95	64.16	75.33	76.78	87.28	82.13
	30	78.84	75.56	77.60	82.59	87.99	89.98
	40	80.21	81.89	82.69	90.17	93.89	95.16
	50	89.32	86.78	84.90	97.23	94.03	96.34
	60	94.09	93.90	93.66	98.12	96.55	97.99

Table 3. The percentage inhibition efficiency of TT, PD and AG plants leaves at various temperature

Name of plant	Conc.of the extract (ppm)	IE (%)		
		303K	313K	323K
TT **leaves**	Blank	-	-	-
	10	44.10	46.22	60.17
	20	57.66	58.61	74.88
	30	62.50	62.88	82.22
	40	71.23	77.35	86.10
	50	85.67	80.45	88.39
	60	96.01	89.77	94.90
PD **Leaves**	Blank	-	-	-
	10	57.01	64.50	62.15
	20	62.50	71.19	67.04
	30	79.14	77.79	72.76
	40	84.64	81.35	80.64
	50	91.76	86.96	82.43
	60	97.22	91.54	90.22
AG **leaves**	Blank	-	-	-
	10	44.39	65.50	51.67
	20	66.65	68.33	59.59
	30	70.10	72.74	66.29
	40	77.07	78.98	75.65
	50	81.48	84.12	79.39
	60	82.22	89.22	81.02

FTIR measurement: FTIR spectra of TT, PD and AG leaves extract was shown in Fig. 1. For TT leaves, the broad peak obtained at 3317.18 cm^{-1} can be assigned to O-H stretching vibration. Absorption peak obtained at 2850.74 cm^{-1} maybe due to N-H stretching vibration. Strong peak at 1683.33 cm^{-1}may correspond to C=O bending vibration. For PD leaves extracts, the peak at 3292.42 cm^{-1} can be assigned to O-H stretching vibration. The absorption Peak obtained at 1647.57 cm^{-1}were C-H bending or C=O stretching vibration of aromatic ring. Similar kinds of functional groups were found for AG leaves extract.

Potentiodynamic polarization studies: The polarization parameters for different concentration of the plant extracts are listed in table 4 and the Tafel curves are shown in Figure 2. One could be seen from the Table that the values of anodic and cathodic Tafel slopes (ba and bc) are slightly changed, which indicates the plants extracts act as mixed type of inhibition. The decreased in corrosion current density values clearly suggest that the higher inhibition efficiency of green inhibitor in the acid medium.

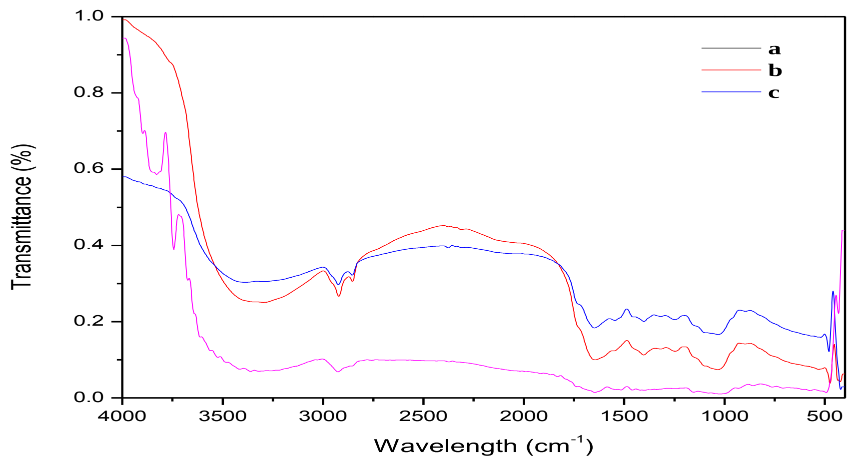


Figure 1. FTIR Spectra of (a) TT, (b) PD and (c) AG Plants leaves extracts

Table 4. Electrochemical parameters from polarization measurement and calculated values of inhibition efficiency

Name of plant	Conc. (ppm)	E_{corr}/ (mV/ SCE)	I_{corr}/ (mA/cm^2)	b_c (mV/dec.)	b_a (mV/dec.)	IE (%)
TT **leaves**	Blank	-0.474	3.369	108	101	*
	10	-0.476	2.719	103	098	92.09
	20	-0.478	2.175	097	095	93.57
	30	-0.482	1.834	095	093	94.53
	40	-0.505	1.556	098	094	95.23
	50	-0.498	1.334	102	095	95.25
	60	-0.486	1.184	094	094	96.25
PD **leaves**	Blank	-0.472	4.101	110	105	*
	10	-0.466	2.37	096	096	47.08
	20	-0.472	1.986	097	097	54.83
	30	-0.481	1.791	099	101	57.90
	40	-0.486	1.648	098	104	61.20
	50	-0.493	1.519	099	104	63.90
	60	-0.494	1.444	098	105	65.76
AG **Leaves**	Blank	-0.474	3.369	108	115	*
	10	-0.473	2.213	147	093	34.31
	20	-0.497	1.872	126	095	44.45
	30	-0.502	1.228	119	090	63.55
	40	-0.510	7.644	112	094	77.31
	50	-0.515	5.820	110	098	82.72
	60	-0.521	4.902	108	102	85.44

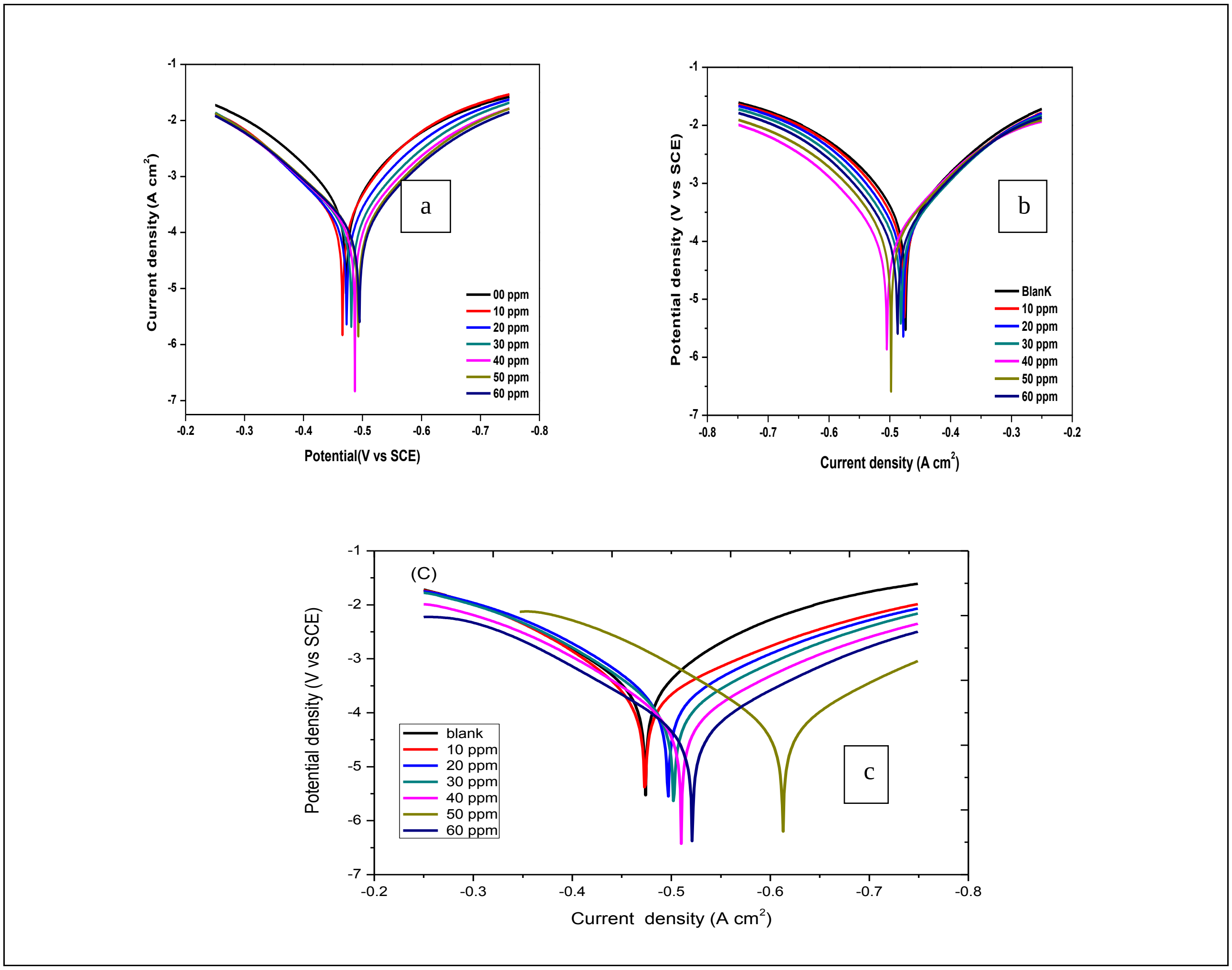


Figure 2. Potentiodynamic polarization (Tafel) curves for mild steel in 1N HCl solution in the absence and presence of different concentration of (a) TT, (b) PD and (c) AG extracts of leaves

Electrochemical impedances methods: Electrochemical impedance spectra (Nyquist plot)for mild steel in 1N HCl with different concentration of the inhibitors is presented in Figure 3 and Impedance parameters derived from these investigations are given in Table 5. As noticed from Figure 3, the obtained Nyquist graphs are almost in a single semi-circular, indicating that the R_{ct} values mostly controls the mild steel corrosion [33-35]. It is observed that in the presence of inhibitor, R_{ct} values increases and C_{dl} values decreases. This indicates the formation of a protective film on the metal surface.

Table 5. Impedance parameter for mild steel in 1 N HCl acid solution in the absence and presence of varied concentration of inhibitor

Name of plant	Concentraion of solution (ppm)	R_{ct} (ohm cm^2)	C_{dl} ($\mu F/cm^2$)	IE (%)
TT **leaves**	Blank	41.76	8.612	*
	10	43.21	8.397	03.35
	20	49.56	8.174	15.85
	30	61.66	8.192	32.21
	40	78.87	7.974	47.05
	50	108.01	7.695	61.33

	60	145.90	7.185	71.37
PD **leaves**	Blank	31.07	7.366	*
	10	113.01	2.377	72.50
	20	141.10	1.739	77.98
	30	146.90	1.525	78.84
	40	163.22	1.443	80.96
	50	199.52	1.292	84.40
	60	184.36	1.342	83.14
AG **leaves**	Blank	43.76	8.312	*
	10	115.40	3.667	62.07
	20	150.11	2.424	70.84
	30	249.89	2.220	82.48
	40	407.30	2.111	89.25
	50	521.88	1.930	91.61
	60	616.70	1.818	92.90

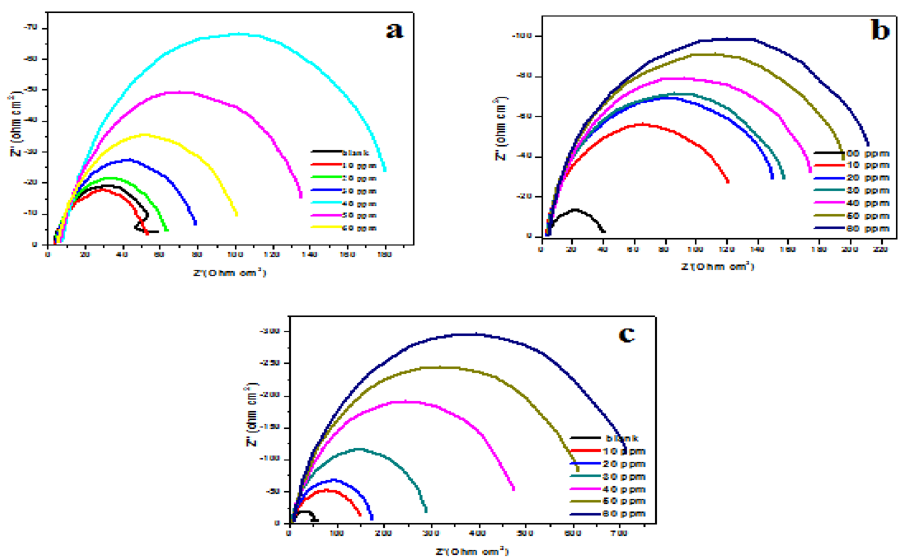


Figure 3. Nyquist plots for mild steel in 1N HCl acid solution without and with presence of different concentration of (a) TT, (b) PD and (c) AG extract of leaves.

Phytochemical Screening test: Phytochemical screening of the aerial parts of plant's powder (aqueous) extract was tested in order to find the presence of various chemical constituent included Alkaloids, Carbohydrates, Proteins, Saponins, Triterpenoid and the results are listed in Table 4.

Table 4. Phytochemical screening test of extract of TT, PD and AG leaves

Phytochemical test	TT leaves	PD leaves	AG leaves
Alkaloids	+	+	+
Carbohydrates	+	+	_
Proteins	+	+	+
Saponins	-	-	+
Thiols	+	-	_
Tannins	-	-	+

Flavanoids	-	+	+
Phenol	-	+	+
Glycosides	-	+	+

(+).. Presence (-)... Absence

Surface examination studies: Surface analysis using SEM proved a significant improvement on the surface morphology of mild steel specimen in the presence of plants extract and SEM images of uninhibited and inhibited mild steel in1N HCl are shown in fig.4. It is seen from the Figure 4a. The rough surface was notified for mild steel immersed in 1N HCl solution and smooth surface was observed for the entire inhibited mild steel surface (4b -4d). The smooth surface on the inhibited mild steel may due to the formation of protective film which are strongly adsorbed on the surface [36].

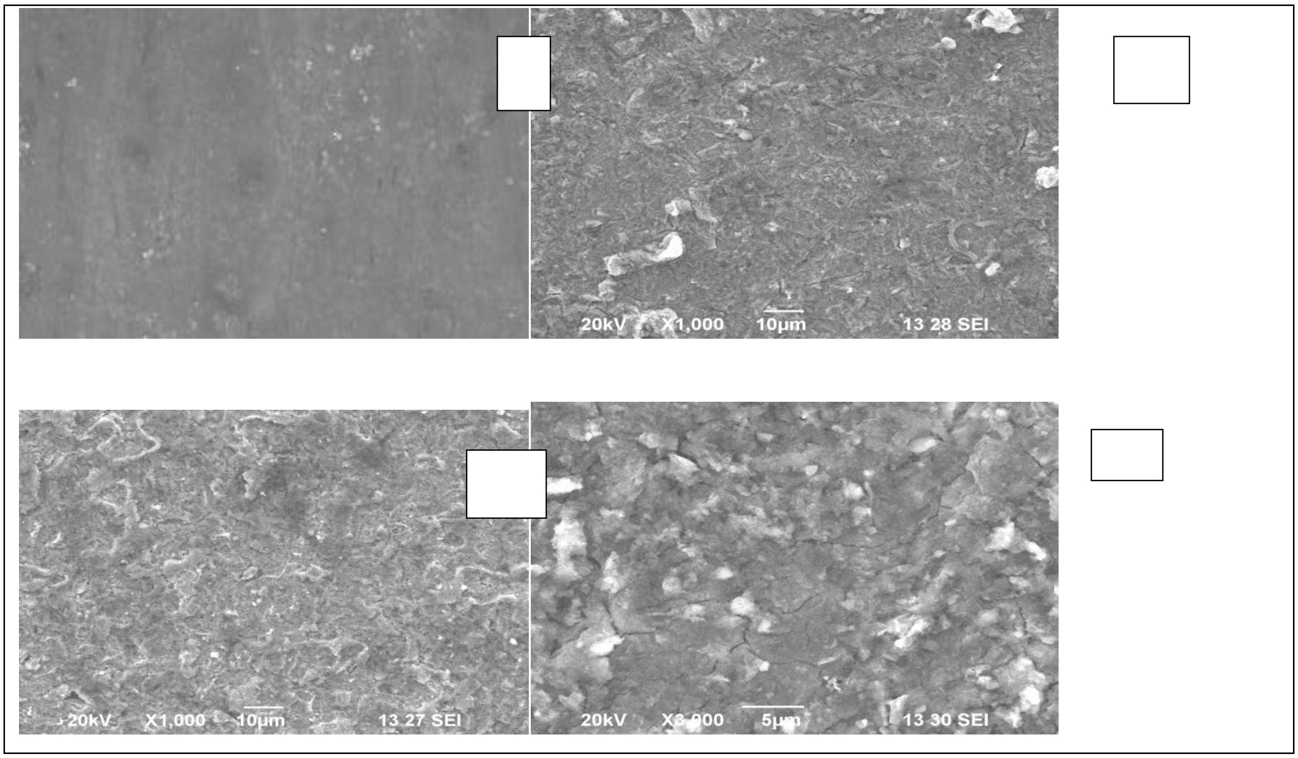


Figure 4. SEM image of the surface of mild steel after immersion for 24 hours in 1N HCl solution (a) blank and in the presence of optimum concentration of the plant extracts from (b) TT (c) PD and (d) AG Leaves.

Adsorption isotherms: Understood the mechanism of corrosion inhibition adsorption behaviour of plant extract absorbent on the metal surface and it character most are known. The most used isotherm is Bockris – Swinkless, Frumkin, Deboer, Langmuir, Flory – Huggins and Temkin. In our present study the Temkin adsorption isotherm is investigated. The straight line in figure 6 clearly indicates that the inhibitor obeys Temkin adsorption isotherm.

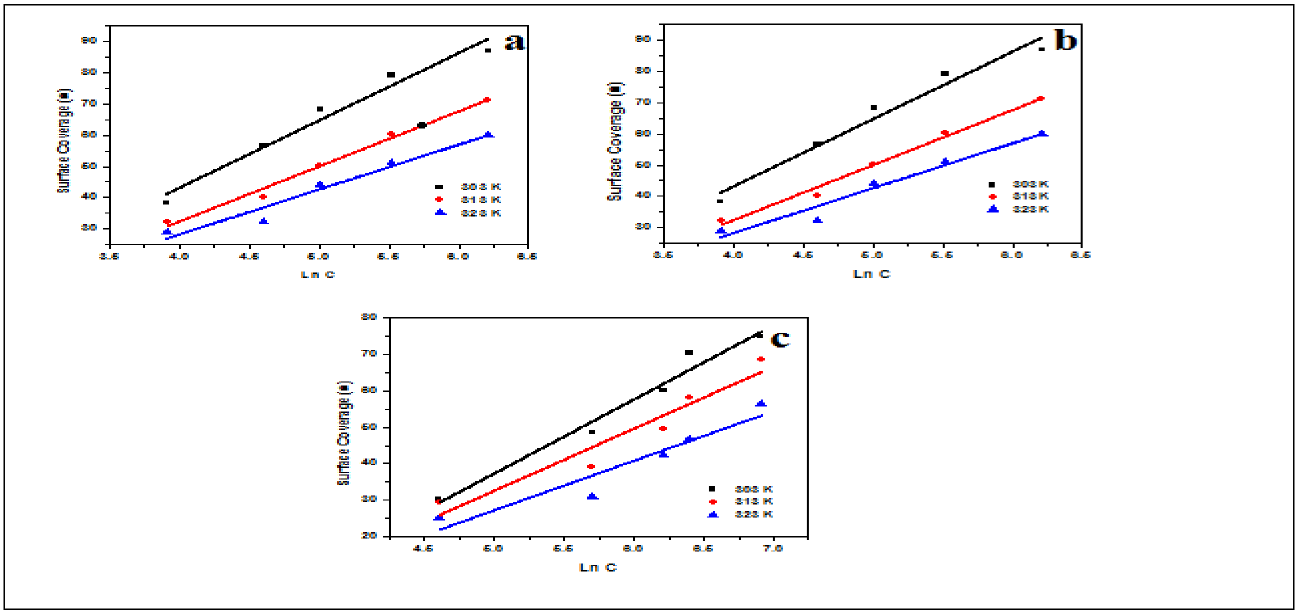


Figure 6. Temkin adsorption isotherm plot for mild steel in 1N HCl containing different concentration (a) TT (b) PD and (c) AG leaves.

APPLICATIONS

The plant leaves extract exhibit excellent corrosion resistance to the mild steel in HCl medium. The TT, PD and AG inhibitor that has little or no impact on the environment i.e. the inhibitor is eco-friendly, safe and some extent good corrosion resistance with temperature. Therefore, this inhibitor can be used for the corrosion protection of mild steel in acid medium for various industries.

CONCLUSIONS

The results obtained showed that TT, PD and AG leaves extract is a good corrosion inhibitor for mild steel under acidic condition. It was also found that inhibitor worked as a mixed type inhibitor retarding both anodic and cathodic reactions. Surface images of the mild steel surface clearly showed that the leaves extract inhibited corrosion of mild steel by getting adsorbed on the metal surface. The adsorption fits well to the Temkin adsorption isotherm. The results suggest that medicinal plants leaves are good corrosion inhibitor for mild steel in HCl and they can be used to replace toxic and non-bio gradable inhibitors.

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