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The Study of Mallotusphilippensis Leaves Extract as Green Inhibitor of Mild Steel in 1N HCl Medium

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Abstract: *The plant extracts are eco-friendly, acting as a corrosion inhibitor for mild steel (MS) in 1N HCl acidic medium. In this study, Mallotusphilippensis leaves (MPL) extract was used which acted as corrosion inhibitor for MS. The inhibition efficiency was tested for MPL corrosion inhibitor by weight loss method, various immersion time and varying the temperature (313 K to 353 K) at different concentration. The FTIR results showedvarious functional group are being adsorbed on the metal surface. The surface analysis was* carried *out by using EDXand SEM techniques. The electrochemical techniques were conducted byPotentiodynamic polarization method and Electrochemical impedance spectroscopy at room temperature.*

Keywords: *Mallotusphilippensis leaves, Mild steel, Corrosion inhibitor, SEM-EDS, FTIR*

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I. Introduction

Most of the industries were using MS because of good mechanical properties and low cost. However, exposed on the acidic atmosphere the mild steel gets oxidized and thus causing extremely large resource waste and economic losses [1]. The green corrosion inhibitor usage was encouraged because of its biodegradability, low cost, non-toxic in nature. The natural products containing the secondary metabolites such as tannis, alkaloids, organic, amino acids present in plant extracts are subjected to a wide range of investigation. The hetro atoms such as O, N, S, and P are present in effective inhibitors. So, these compounds are easily adsorbed on the metal surface [2]. In various industriesHCl is used in pickling process of mild steel [3]. In present study, the inhibition efficiency of the leaves extract of Mallotusphilippensis on MS in 1N HCl solution has been investigated using the various techniques.

II. Materials And Method

2.1 Preparation of the specimens:

MS specimens containing C-0.025 %, Si-0.018 %, Mn-0.176 %, P-0.014 %, S-0.0076 %, Cr-0.020 %, Mo-0.0024 %, Ni-0.0093 %, Al-0.064 %, Co-0.0005 %, Nb-0.0005 %, Ti-0.005 %, V-0.0005 %, Pb-0.005 %, Sn-0.0003 %, Mg-0.0031 %, Bi-0.0010 %, Sb-0.0005 %, Z-0.019 %, Fe-99.62 % is used for present corrosion studies. The area of the specimens is about 5*2*.1 cm ($1cm^2$). The impurities are removed using emery sheet, washed with doubly distilled water and finally degreased with acetone.

2.2 Preparation of plant extracts:

The fresh leaves ofMallotusphilippensiswerewashed, dried in room temperature. The dried leaves were ground well. 25 g of powdered leaves were mixed with 500 mL of doubly distilled water and boiled for 3 hours. After that solution was refluxed overnight and then filtered. The filtrate is made up to 500 mL and used for further corrosion studies [4].

2.3Weight loss method:

Weight loss measurement proved that the MS specimens in 1N HCl solution were inhibited by using various concentration of leaves extract. Each sample is weighed by an electronic balance and then immersed in the acid solution. The duration of the immersion is 24 hours and the experiment is carried out at various immersion period (1, 3, 5, 7, 24 hours) at room temperature. Corrosion inhibition studies were also carried out at various temperature ranges of (313-353 K). After immersion, the surface of the metals were washed by doubly distilled water rinsed with acetone, the samples are weighed repeatedly to calculate Inhibition efficiency (%) and Corrosion rate (CR). The experiments were done in triplicate and the average value of the weight loss was noted. For all experiments, a recently prepared solution was used.
The surface coverage (θ), Inhibition efficiency (%) were determined by using this formula,

$$\theta = \frac{W_0 - W_i}{W_0} \qquad (1)$$

$$\text{IE (\%)} = \frac{W_0 - W_i}{W_0} \text{ X } 100 \qquad (2)$$

Where, W_0 and $W_i$are the weight loss in the absence and presence of the inhibitor
Corrosion rate of mild steel is calculated by using the formula,

$$\text{CR (mmpy)} = \frac{K \; X \; Weight \; loss}{D \; X \; A \; X \; t \; (in \; hours)} \qquad (3)$$

Where, K = $8.76x10^4$ (constant), D is density in gm/cm^3 (7.86), W is weight loss in grams and A is area in cm^2.

2.4 FTIR measurements:

FTIR spectra were recorded in a Bruker ALPHA 8400 S spectrophotometer. The film was sensibly removed, mixed thoroughly with KBr made into pellets and FTIR spectra were recorded.

2.5 Electrochemical studies:

The electrochemical technique was carried out using PAR 2273 advance electrochemical system. In this technique three electrode cell was used and MS acted as the working electrode. The working electrode was fabricated from MS rod of 5 mm dia and 15 mm length, which was secured in a Teflon tube and shined using various grades of sand paper. Silver and platinum electrodes were used as reference and platinum electrode. A stabilization period of 1 hour was allowed for potentiodynamic polarization and electrochemical impedance technique. Tafel runs were conducted in the potential range from -250 mV to 500 mV relative to the corrosion potential. A scan rate of 1 mVs^{-1} was used for the Tafel run. Corrosion current and other Tafel fit parameters were calculated from Tafel extrapolation method.
The inhibition efficiency was calculated using this formula,

$$\text{IE (\%)} = \frac{I_{corr \; (blank \;) - I_{corr \; (inhibitor \;)}}}{I_{corr \; (blank \;)}} \; X \; 100 \qquad (4)$$

Where, $I_{corr\ (blank)}$ as Corrosion current without inhibitor, $I_{corr\ (Inhibitor)}$ as Corrosion current with inhibitor
The EIS run was conducted from 1 KHz to 0.01 KHz. The impedance measurement was conducted at OCP. This technique was conducted at room temperature using 1N HCl and different concentration of plant extract.
The double layer capacitance (C_{dl}) were calculated using this formula,

$$C_{dl} = \frac{1}{2\pi} f_{max} \, R_{ct} \qquad (5)$$

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

$$\text{IE (\%)} = \frac{R_{ct} - R^0_{ct}}{R_{ct}} \; X \; 100 \qquad (6)$$

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

2.6 Phytochemical Screening:

Phytochemical screening was carried out on the freshly prepared aqueous MPL extract according to the common phytochemical method. The different chemical constituents tested includes Alkaloids, Phenolic compounds, Saponins, Tannins etc.

III. Result And Discussion

3.1 Weight loss method:

3.1.1 Effect of immersion time on corrosion rate and inhibition efficiency (%):

The inhibition efficiency and corrosion rate variation was tabulated in table 1. The corrosion rate was decreased with increasing the concentration of MPL extract for all immersion periods. The optimal inhibition efficiency was observed at 25 mL of the inhibitor in 1N HCl medium. The inhibition efficiency was increased with increasing the immersion time. So high adsorption has taken place on the metal surface. Table 1 clearly proved that maximum inhibition efficiency was reached at 5 hour in 1N HCl medium [3].

Table.1 Inhibition efficiency of MPL extract in various immersion time

Conc. of MPL extract (mL)	Inhibition efficiency (%)				
	1h	3h	5h	7h	24h
5	82.42	80.56	94.75	84.87	87.57
10	84.70	82.64	95.04	85.67	87.84
15	86.75	85.75	95.80	85.98	90.31
20	86.60	87.39	95.83	86.34	90.41
25	87.44	87.73	97.85	87.85	91.46

3.1.2 The effect of temperature:

The effect of temperature on inhibition reaction of inhibited acid was highly complex in metal surface, because multiple changes may occur on the metal surface, likewiserupture, rapid etching, desorption of the inhibitor and the rearrangement or decomposition of the inhibitor. To analyse the stability of the MPL inhibitor at higher temperature, experiments were performed at various temperature in the range of 313 K to 353 K in 1N HCl medium. The attained inhibition efficiency and corrosion ratedatas are listed in table 2. From table 2 it was clear that the inhibition efficiency was increasing from the temperature 313 K to 333 K, because the metal was undergoing dissolution and the inhibitor was chemically adsorbed on the metal surface. But there would be desorption occurred by increasing the temperature from 343 K to 353 K. This was proved that the inhibition effect of inhibitor decreased as the temperature was increasing, because of physical adsorption of the plant extract on the metal surface [5].

Table.2 Inhibition efficiency and corrosion rate of MPL extracts at various temperatures

Conc. of MPL extract (mL)	313K		323K		333K		343K		353K	
	CR (mmpy)	IE (%)	CR (mmpy)	IE (%)	CR (mmpy)	IE (%)	CR (mmpy)	IE (%)	CR (mmpy)	IE (%)
Blank	105.87	*	1430.74	*	2580.07	*	4076.29	*	5498.68	*
5	78.01	26.31	256.33	82.08	319.02	87.63	522.42	87.18	1127.04	79.50
10	72.44	31.57	199.21	86.07	208.96	91.90	277.23	93.25	801.04	85.43
15	64.08	39.47	183.89	87.14	158.81	93.84	234.04	94.25	501.52	90.87
20	50.15	52.63	164.38	88.51	123.98	95.19	189.46	94.51	397.04	92.77
25	40.40	61.84	161.60	88.70	75.22	97.08	186.67	95.42	370.57	93.26

3.2 FTIR analysis:

FT-IR spectrum was used to analyse various functional groups present in the plant species. Some of the functional groups present in the MPL extract was shown in the figure1. The peak at 3500 $cm^{-1}$and 3700 cm^{-1} were due to the presence of O-H stretching frequency. The frequency at 3265.49 cm^{-1} was due to N-H (or) O-H bending bond. The peak in the frequency range 2922.16 cm^{-1} and 2852.72 cm^{-1} could be assigned due to the presence of C-H stretching frequency. The absorption band which was observed in the region 1739.79 cm^{-1} and at 1610.56 cm^{-1}were due to aldehyde or ketonic C=O stretching vibration. The peak at 1041.56 cm^{-1} was due to C-O str. Frequency which was found to be highly intense. Some of the peaks below 1000 cm^{-1} were due to aliphatic C-H group. The presence of all these groups showed that the plant extract acted as a good inhibitor by means of the adsorbed or protective layer formed on the metal surface [5].

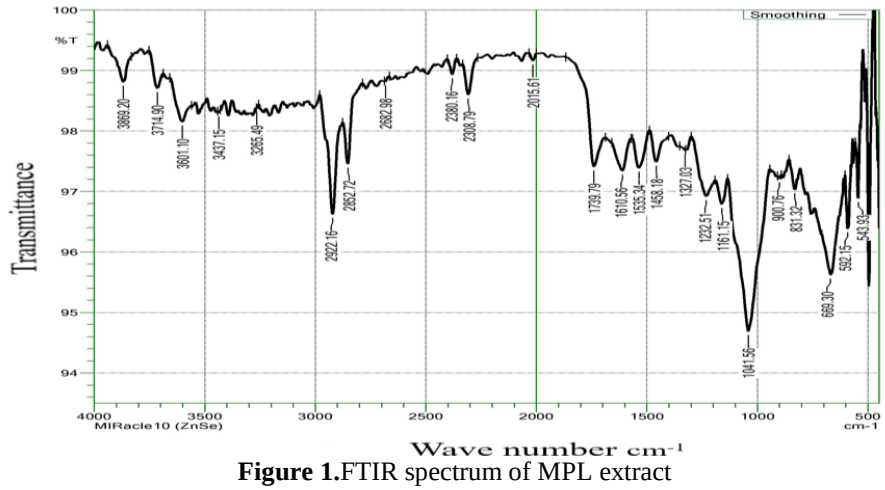


Figure 1.FTIR spectrum of MPL extract

3.3 Potentiodynamic polarization method:

The Tafel parameters for MS with and without inhibitor concentration of MPL extract in 1N HCl are presented in table 3 and its polarization curves are shown in Fig 2. From Fig 2 it was shown that the addition of MPL extracts does not affect the values of corrosion potential (E_{corr}) but anodic dissolution of MS and cathodic reduction reaction was noticed. It was indicating that plant extract acted as a mixed type of inhibitor. From the table 3 that the corrosion current density (I_{corr}) decreased with increasing MPL extract concentration. The maximum inhibition was detected at 20mL of concentration.It proved that more inhibitor molecules were

adsorbed on the metal surface. The maximum inhibition efficiency of 91.07% was observed for MPL extract in 20mL [6].

Table 3 The various parameters of potentiodynamic polarization for mild steel in various concentrations of MPL extract with 1N HCl.

Conc. of MPL extract (mL)	E_{corr} (mV)vs (SCE)	I_{corr} (mA/cm^2)	CR (mmpy)	b_c (mV/dec)	b_a (mV/dec)	IE (%)
Blank	-485	2.891	1.320	194	133	*
5	-476	0.4444	0.2029	185	95	84.62
10	-474	0.3584	0.1636	155	91	87.60
15	-479	0.2642	0.1206	159	97	90.86
20	-457	0.2579	0.1178	187	95	**91.07**
25	-478	0.2849	0.1301	172	87	90.14

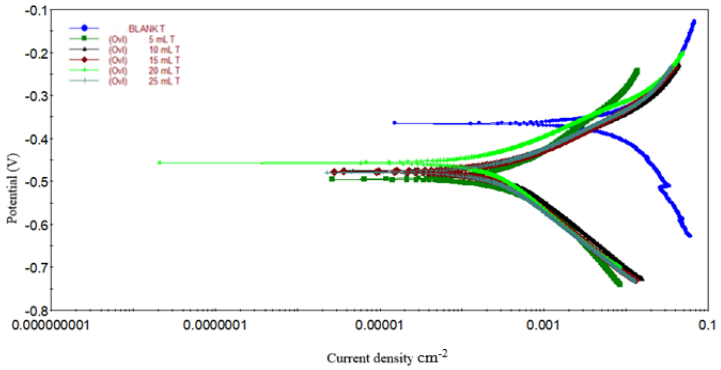


Figure 2. Tafel slope of mild steel in the blank and various concentration of MPL extract

3.4 Electrochemical impendence spectroscopy:

The corrosion behaviour of MPL extract on MS in 1N HCl was investigated by the electrochemical impedance spectroscopy technique.Nyquist plots of MS with and without inhibitor acid solution containing different concentrations of MPL extract are plotted in Fig 3. The concentration of the inhibitor was increased and consequently the inhibition efficiency also increased. The semicircle of impedance spectrum proved the single charge transfer mechanism during dissolution of MS which was controlled in inhibitor compared to blank solution.

The impedance data forMS in 1N HCl with and without inhibitor are given in table 4. The higher R_{ct} value obtained for most inhibitor concentration proposed that the protective layer was formed on the metal surface. The dielectric constant or increase in the thickness of the double layer was the reason for decrease in the C_{dl} value. It was suggested that MS corrosion was inhibited using inhibitor molecule by adsorption at the metal interface. The electronegative heteroatoms present in the organic constituents of the extract and metal surface was electropositive, so the chemical constituents are adsorbed on the metal surface. The electrochemical parameters clearly proved that the corrosion control depends on the concentration of the inhibitor [7].

Table. 4 Measurement of impedance with blank and various concentrations of plant extract in1N HCl.

Conc. of MPL extract (mL)	C_{dl} (µFcm^{-2})	R_{ct} Ωcm^2	IE (%)
Blank	$5.643x10^{-5}$	6.008	*
5	$4.698x10^{-5}$	18.06	66.73
10	$4.434x10^{-5}$	19.67	69.45
15	$4.227x10^{-5}$	21.58	72.15
20	$4.071x10^{-5}$	47.23	**87.27**
25	$3.585x10^{-5}$	37.45	83.95

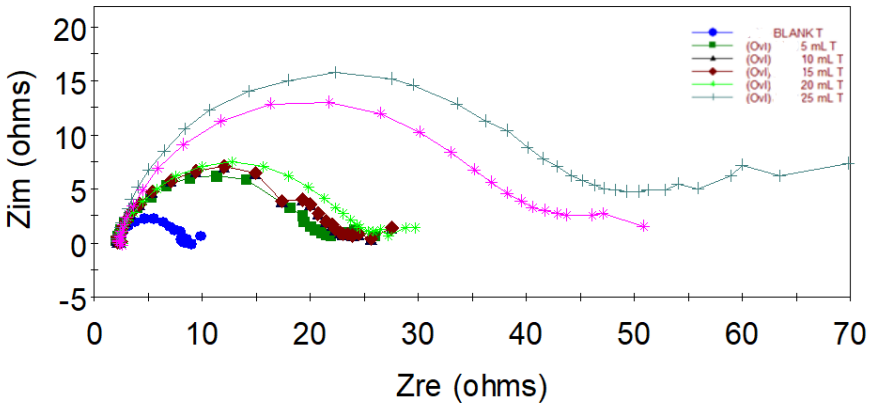


Figure3. Nyquist plot of MS in the presence and absence of AML inhibitor

Bode plots

Fig 4 was shown in Bode plots of MS with and without inhibitor containing different concentration of MPL extract. It is apparent that the MS specimen with MPL extract showed increase in maximum phase angle value, which signified an inhibition property on the surface of MS. The diffusion process controlled the metal dissolution rate, due to the linear portion observed in the low frequency region at the surface of MS [8].

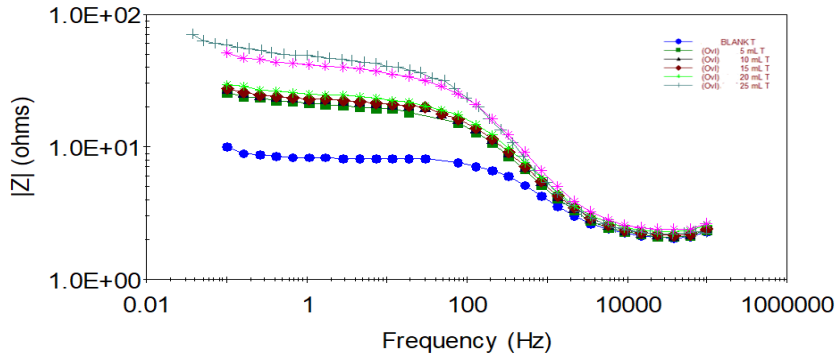


Figure 4. Bode plots of mild steel immersed in 1N HCl in absence and presence of different concentrations of MPL extract

3.5 Surface analysis:

3.5.1 SEM analysis:

SEM morphology of MS surface after immersion for 24 hours with and without MPL extract are shown in Figure 5. Figure (5a) shows the SEM morphology of MS without inhibitor in 1N HCl was highly damaged. It's defined as MS surface was highly corroded in the absence of inhibitor. Figure (5b) shows there is less damage on the MS surface in the presence of MPL extract. The above statement clearly proved the adsorption behaviour of inhibitor on MS surface [9].

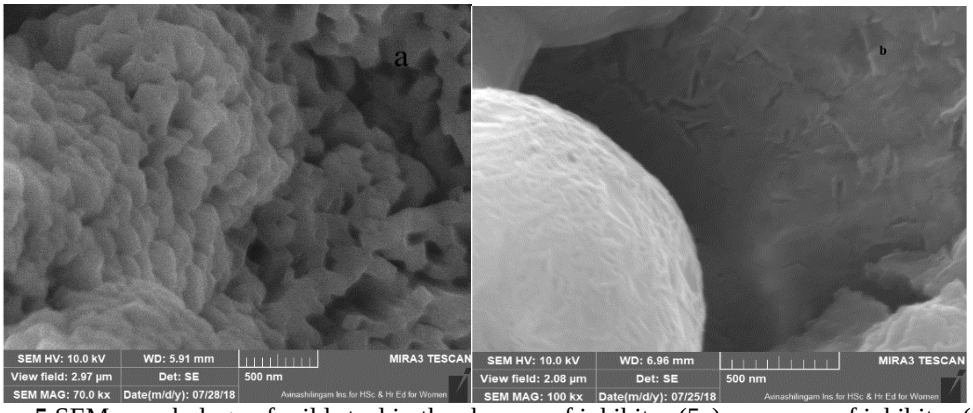
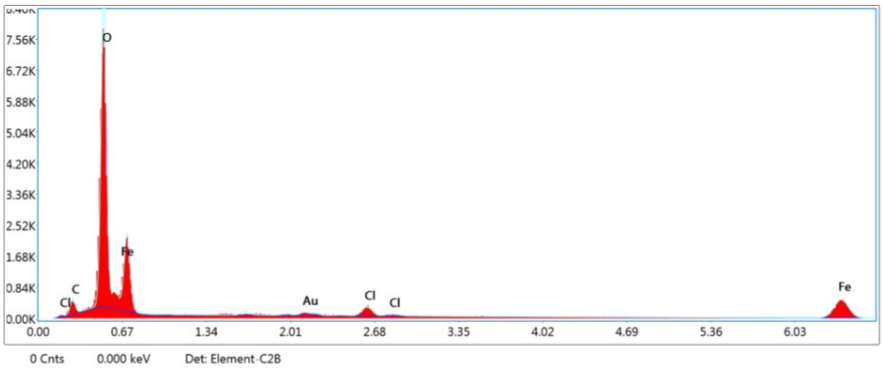


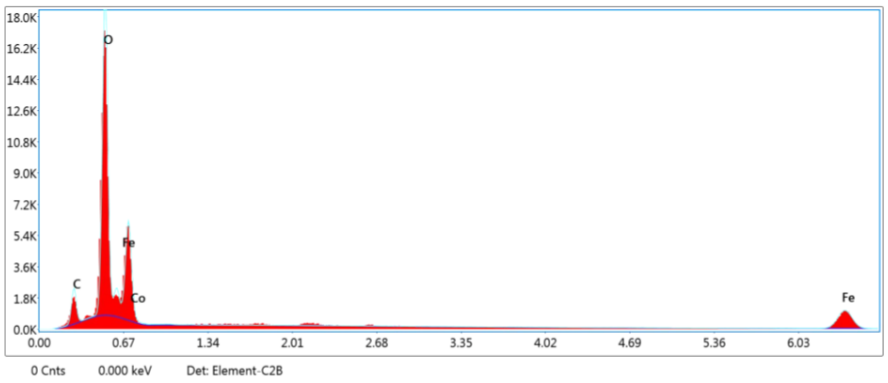
Figure5.SEM morphology of mild steel in the absence of inhibitor (5a), presence of inhibitor (5b)

3.5.2 EDX Analysis:

Fig 6 and Table 6 shows the EDX Spectra for the corrosion product on MS surface with and without Inhibitor concentration of MPL extract in 1N HCl medium. The spectrum without inhibitor showed that the metal oxide was formed on MS surface. However, the Co atom was formed in metal surface in presence of MPL extract may involved in the complex formation with metal ion, during the adsorption process and controlled the dissolution of the metal [9].



6(a)



6(b)

Figure 6. (6a) mild steel in the absence, (6b) mild steel in the presence inhibitor

Table. 6 Element composition (Atomic %) of mild steel sample in the presence and absence of inhibitor in 1N HCl solution after 24 h of immersion

Inhibitors/elements	C	O	Fe	Cl	Co
Mild steel in 1N HCl	9.25	71.55	15.60	3.60	-
Mild Steel in MPL extract	15.24	66.70	18.01	-	0.04

3.6 Adsorption isotherm:

The adsorption isotherm is defined as, the interaction between addition of inhibitor molecule that is adsorbed on the metal surface.

The surface coverage (θ) values for various concentration of the MPL extract (inhibitor) in the acid medium have been interpreted from the weight loss data.

The Langmuir adsorption is expressed from,

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C$$

Where, C is the inhibitor concentration, θ is the surface coverage andK_{ads} is the adsorption equilibrium constant. The MPL extract obeyed the Langmuir adsorption isotherm by getting a straight line for a plot of C/θ vs C. the plot at the different temperature studied which gives a straight line due to the adsorption of MPL extract on the MS[10].

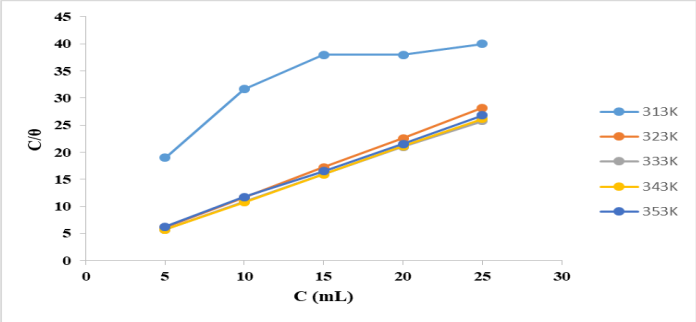


Figure 7. Langmuir adsorption isotherm of different temperatures of MPL extract

3.7 Phytochemical analysis:

Phytochemical screening was tested by the aqueous extract to the ordinary phytochemical method derived by Harborne [11]. The MPL extract acted as a good corrosion inhibitor because of the presence of some chemical constituent such as Alkaloids, Carbohydrate, Triterpenoids, Phenolic compounds, Flavanoids, Glycosides and Diterpenes.

Table. 6 Phytochemical screening of MPL extract

Phytochemical Test	MPL extract
Alkaloids	+
Carbohydrates	+
Triterpenoids	+
Phenolic compounds	+
Flavanoids	+
Glycosides	+
Diterpenes	+

(+) Presence (-) Absence

IV. Conclusion

From the above said investigations it was concluded that the MPL extract acted as a good corrosion inhibitor of MS in 1N HCl medium. The inhibition efficiency values increased with increase in the concentration of MPL extract. The adsorption of MPL extract on the mild steel surface obeyed the Langmuir adsorption isotherm. The electrochemical impedance results obtained from Nyquist plot and the mild steel corrosion is controlled by the charge transfer process. The PDP results obtained from Tafel plot, the results reveals that the inhibitor is a mixed type of inhibitor. High performance of the inhibition on the surface of MS has been confirmed by SEM morphology by the protective film formation. FTIR results confirmed the presence of organic moieties in the plant extract.

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