Madras Journal Series Pvt Ltd
Advanced Materials & Applications
Adv. Mater. App. 5 (2020) 1-10
ISSN: 2582-5070

Comparitive study of inhibition effect of various leaves extracts over mild steel in the aggressive media

A. P. Srikanth* and M. J. Judithaa

[1]Department of Chemistry, Government Arts College (Autonomous), Coimbatore-641018, Tamilnadu, India.

***Corresponding author:** apsrikanth8@gmail.com

Received 29 January 2020, Received in final form 07 February 2020, Accepted 07 February 2020

Abstract

The inhibition property of majidea zanquebarica leaves and filicium decipiens leaves on mild steel in 1N HCl medium are studied using various methods such as weight loss measurement, time variation, synergistic effect, effect of temperature and electrochemical methods. The surface analysis can be carried over using various techniques such as scanning electron microscopic studies, FTIR analysis and UV spectrophotometric techniques. The electrical and non-electrical methods are in good agreement with each other reveals that there is increase in inhibition efficiency with increase in concentration of majidea zanquebarica leaves and filicium decipiens leaves extracts. The percentage of inhibition efficiency is also studied on the basis of adsorption of plant extracts on mild steel specimen which obeys Langmuir adsorption isotherm. The conformational results obtained in the Tafel slope proved that the plant extracts act as a mixed type of inhibitors. All these results proved that the protective film of majidea zanquebarica leaves and filicium decipiens leaves extracts are formed over the MS plate which is examined by surface morphology gives assurance that both the leaves act as good corrosion inhibitors.

Keywords: *Inhibition efficiency, corrosion, majidea zanquebarica, synergistic effect, Langmuir adsorption isotherm, filicium decipiens.*

1. Introduction

In most of the industries, equipments are made up of mild steel which may losses its strength due to the corrosion process caused by the synergism of aqueous solution with the mild steel at the time of pickling process and water content which may contain chlorides, sulphates, nitrates. Corrosion cannot be eradicated but can be controlled by using some anticorrosive agents which can also be called as corrosion inhibitors. Inhibitors get adsorbed on the metal surface and block the active sites against dissolution of the metal or liberation of hydrogen, thereby controls the corrosion rate. The anticorrosive activity is present in both natural and synthetic compounds. The compounds which are synthesised using chemicals are mostly toxic in nature. This may affect the health of the human beings in spontaneous or non spontaneous manner. These compounds are used as organic inhibitors because of the presence of electron donating π bonds. Inspite of the presence of these π bonds, the toxic nature of these products are taken into consideration which may cause hazardous effect in the environment [1-10]. This hazardous effect of synthetic inhibitors triggered the researchers to use the naturally occurring compounds as corrosion suppressants which are found to be less expensive, non-toxic, environmental as well as eco-friendly in nature [11-12]. Nowadays plant extracts play a vital role in the corrosion field due to its availability and biodegradability. The plant extracts are the major sources of phytochemical constituents which can be easily prepared using simple procedures

2. Materials and methods

2.1. Preparation of plant extracts

The fresh leaves of Majidea zanquebarica and Filicium decipiens were collected,washed and dried in room temperature for 10 days. The dried leaves were ground well and used for the preparation of the plant extract. 25 g of each sample is taken in a round bottomed flask, refluxed in a condenser for 3 h using 500 ml of doubly distilled water. It was kept overnight and filtered. The filtrate was the stock solution, using this stock solution various concentrations of the plant extracts test solutions were prepared.

2.2. Preparation of Mild steel specimen

The mild steel coupons were prepared in the measurement of (5x2x0.2) cm where the area is found to be $1cm^2$. These coupons were used for the weight loss measurements,temperature studies and surface morphology. For the polarization and Electrochemical studies the mild steel is prepared as a cylindrical rod ingrained in Teflon with the disclosed area of about $1cm^2$. The mild steel specimens and cylindrical rod were cleaned using emery sheet, degreased with acetone, dried and used.

2.3. Characterization

The first and foremost analysis in the corrosion study was the weight loss method. In this technique the mild steel specimens were cleaned and weighed accurately. The mild steel stripes were immersed in blank as well as various concentrations of the two plant extracts such as Majidea zanquebarica leaves (MZL) and Filicium decipiens leaves (FDL) in 1N HCl medium in varying immersion time. Mass loss measurement could also be carried out by immersing mild steel stripes in various concentrations of the two leaves by maintaining different temperatures of about 313K to 353K in 2hrs time duration using thermostat controlled water bath[13]. Weight loss obtained from all these three experiments were used to analyse the corrosion rate as well inhibition efficiency using the following relation

$$\mathrm{IE}\,(\%) = \frac{W_0 - W_i}{W_0} \mathrm{X}\,100 \qquad (1)$$

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

Electrochemical measurements were carried out using PAR 2273 advanced electrochemical system. This system is made up of using three electrode system having platinum electrode, saturated calomel electrode and the working electrode. The working electrode was prepared as a rod of exposed area of about 1 cm diameter and the rest of the portions are covered using teflon coating. The rod was cleaned using emery sheet and degreased with acetone before immersing it in each concentration of the plant extracts. The potential range for tafel polarization was found to be -250 mv to 500 mv with respect to open circuit potential. The graph obtained due to cathodic and anodic segments were extrapolated in order to get the corrosion potential $E_{(corr)}$ and corrosion current density $I_{(corr)}$ values respectively. From the $I_{(corr)}$ value the IE(%) was calculated using the following relation

$$IE(\%) = \frac{I_{(Corr)Blank)} - I_{(Corr)(inh)}}{I_{(Corr)(Blank)}} \times 100 \qquad (2)$$

Where $I_{corr(inh)}$ and $I_{corr(Blank)}$ are corrosion current in the presence and absence of inhibitor. Using the same electrode and electrochemical system the electrochemical impedance spectroscopy was analysed in the frequency range of 1 kHZ to 0.01 HZ. From the semicircles obtained in the Nyquist plot the charge transfer resistance was calculated using the following relation

$$IE(\%) = \frac{\mathrm{Rct(inh)} - \mathrm{Rct(Blank)}}{\mathrm{Rct(Blank)}} \times 100 \qquad (3)$$

Where $R_{ct(in)}$ and $R_{ct(B)}$ are inhibited and uninhibited values of charge transfer resistance[14].

Using powdered form of MZL and FDL,the KBr pellets were prepared. The FTIR spectra were recorded using Bruker Alpha spectrophotometer using the range of about 4000 to 400 cm^{-1}. The mild steel stripes were submerged in 1N HCl which was uninhibited and inhibited with the addition of both the leaves extract for about 24hrs. After that they were cleaned using doubly distilled water and dried. Then the specimens were subjected to analyse the surface morphology using Field emission scanning electron microscopy [14]. The leaves extracts and the products obtained as a result of the deterioration process were exposed to UV-Visible spectrophotometric analysis in the wavelength range of 200-750nm using Agilent technologies Cary 8454/UV –Visible spectrophotometer.

3. Results and discussions

3.1. Weight loss method

Weight loss measurement of both MZL and FDL extracts were carried out by submerging mild steel stripes in 1N HCl containing various concentrations of the two leaves extracts. It was observed that the inhibition efficiency increased with increase in the concentration of the leaves extract. From the results obtained it was obvious that both the MZL and FDL extracts posses the inhibiting character against the destruction of the mild steel specimens.[15] It was clearly tabulated that the inhibition efficiency for MZL and FDL were 94.43% and 96.36% in the optimum concentration. Comparitively FDL acted as a better corrosion inhibitor than MZL .

3.2. Immersion time

It was evident from the immersion time experiment that as the duration of submerging of the mild steel stripes increased; there would be increase in the inhibition efficiency and decrease in

Table 1 Mass loss measurement of MS using MZL & FDL extracts in corrosive medium

Inhibitor	Concentration (ml)	CR (mmpy)	IE (%)
Majidea Zanquebarica	Blank	346.88	*
	5	131.94	61.96
	10	82.66	76.17
	15	49.68	85.68
	20	39.53	88.60
	25	19.32	94.43
Filicium Decipiens	Blank	382.88	*
	5	80.59	78.95
	10	53.86	85.93
	15	46.44	87.87
	20	21.71	94.32
	25	13.93	96.36

Table 2 Inhibition Efficiency of MZL and FDL extracts in various immersion time

Inhibitor	Concentration (ml)	% of inhibition efficiency						
		1h	3h	5h	7h	9h	12h	24h
Majidea Zanquebarica	5	55.32	66.86	74.06	80.42	86.72	88.18	92.79
	10	62.26	71.84	83.24	82.08	90.48	90.39	95.74
	15	63.19	83.70	86.13	87.07	92.21	92.21	96.34
	20	64.23	86.58	91.62	90.08	93.00	94.14	97.4
	25	71.18	89.58	93.75	93.84	95.26	95.58	97.6
Filicium Decipiens	5	57.81	63.61	67.24	71.67	75.47	79.10	91.87
	10	60.71	66.17	70.87	75.60	78.48	81.34	92.71
	15	70.20	70.15	75.44	78.10	81.68	87.87	96.62
	20	67.52	72.08	78.06	83.11	84.04	89.13	97.37
	25	74.21	77.21	82.86	86.83	88.16	91.29	97.40

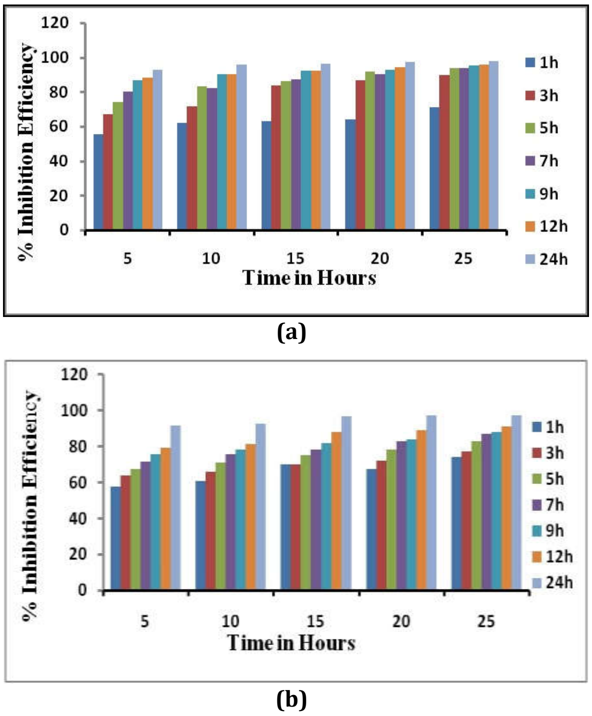


Fig. 1 *Variation of immersion time for (a) MZL and (b) FDL extract in acid medium*

the rate of corrosion while increasing the concentration of the MDL and FDL extracts at room temperature. This was the proof showed in the Table 2, as the destruction of metal stripes were controlled by the formation of protective layer on the metal surface due to the secondary metabolites present in the leaves of both the plants which could be adsorbed and blocked the active sites of the metals.

3.3. Effect of Temperature

The study of corrosion reaction of metal in the presence of inhibitor by varying the temperature is a tedious process because in the presence of the acid, deterioration on the metal surface were caused like dissolution of the metal and inhibitor may desorbed or decomposed [16-20]. This study revealed that the effect of temperature played an important role in the corrosion process. It was proved that the inhibitor controls the dissolution of the metal till the optimum temperature was reached. The analysis was carried out by maintaining various temperatures from 313K to 353k in the absence and presence of the inhibitor in 1N HCl medium at 2 h time duration.

Comparatively, the inhibition efficiency increased for MZL as the concentration of the inhibitor increases till the temperature reached 333K thereby occur the chemisorption. After that from the temperature 343K to 353K the inhibitor was desorbed where the physisorption had taken place. For FDL the corrosion rate increased by increasing the temperature from 313 K to 353 K due to the electrostatic interaction between the metal and the inhibitor where the plant extract was physically adsorbed on the metal surface. The results were shown in Table 3. The highest inhibition efficiency for MZL was found to be 94.92% at 333 K in the concentration of 25 mL of the plant extract whereas the maximum IE% for FDL was observed as 84.87% at 313 K in the concentration of 25 mL of the inhibitor.

3.4. Adsorption isotherm

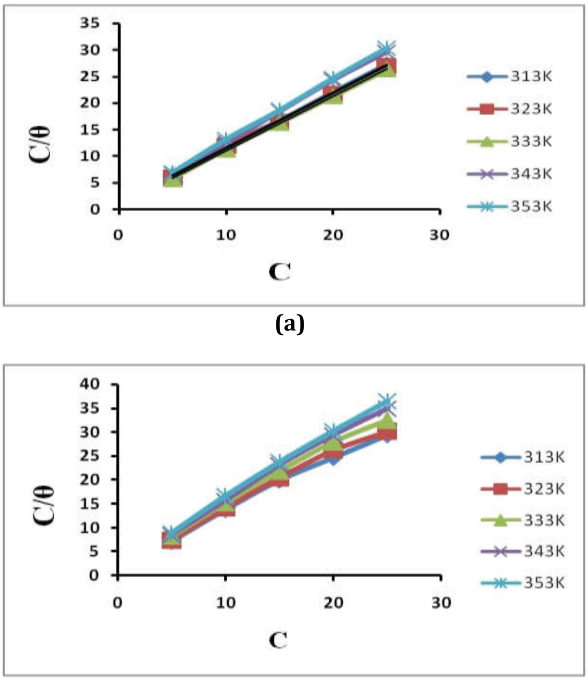
The inhibition mechanism can be explained using the Adsorption isotherm. Using the weight loss measurements the surface covered on the metal stripes could be evaluated for various concentrations of the plant extracts which was used to understand about the interaction between the inhibitor molecules and metal. By applying the values in various adsorption isotherms such as Langmuir, freundlich and temkin it was finalised that the results were best fit to the Langmuir adsorption isotherm which was proved using the following relation,

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \qquad (4)$$

Where C_{inh} the concentration of the inhibitor, Kads is is the adsorptive equilibrium constant and θ is the surface coverage. By plotting a graph between C vs C/θ a straight line was obtained from which K_{ads} could be found out from the intercept value. The K_{ads} values were related to the adsorption free energy values by the following relation

$$\Delta G_{ads} = -2.303RT \log (55.5K_{ads}) \qquad (5)$$

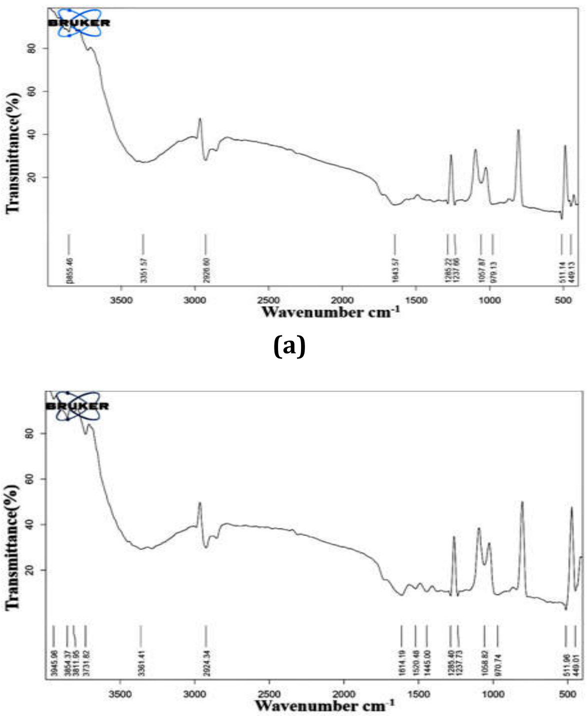
It was clearly stated in the Table 4 that the G_{ads} values were found to be negative thereby proved that the inhibitor was adsorbed on the metal surface spontaneously[21]. In this investigation it was observed that the K_{ads} values for MZL was increased till 333K which proved that the chemisorpion occurred indicates the sharing or transfer of electron from the inhibitor molecules to the metal surface and in the case of FDL the K_{ads} values decreased from 313K to 353K showed that physical adsorption has occurred pointed out the electrostatic interaction between the charged inhibitor molecules and the metal [22].



(a)

(b)

Fig. 2 *Langmuir adsorption isotherm of (a) MZL extract and (b) FDL extract*



(a)

(b)

Fig. 3 *FTIR spectrum of (a) MZL Extract and (b) FDL Extract*

Table 3 Effect of temperature on MS using MZL & FDL extracts of various concentrations (*Concentrated)

Inhibitor	Concent.* (ml)	313K		323K		333K		343K		353K	
		CR	IE(%)	CR	IE(%)	CR	IE(%)	CR	IE(%)	CR	IE(%)
Majidea Zanquebarica	Blank	463.21	*	485.50	*	576.06	*	2219.95	*	3464.71	*
	5	98.21	78.79	82.89	82.92	72.44	87.42	548.20	75.30	948.02	72.63
	10	82.19	82.25	80.10	83.50	66.17	88.51	442.32	80.07	835.88	75.87
	15	47.36	89.77	46.66	90.67	45.28	92.14	417.94	81.17	679.15	80.39
	20	43.18	90.67	38.31	92.10	34.32	93.95	400.52	81.95	658.25	81.00
	25	38.31	91.72	34.82	92.82	29.25	94.92	348.28	84.31	609.49	82.40
Filicium Decipiens	Blank	248.67	*	1044.15	*	1112.41	*	1139.58	*	3200.71	*
	5	74.56	70.02	338.53	67.57	436.05	60.80	469.48	58.80	1387.56	56.64
	10	68.96	72.26	305.10	70.78	381.02	65.74	413.76	63.69	1279.59	60.02
	15	61.99	75.07	278.62	73.31	348.28	68.69	399.83	64.91	1180.68	63.11
	20	47.36	80.95	247.28	76.31	316.24	71.57	363.61	68.09	1087.34	66.02
	25	37.61	84.87	177.62	82.98	252.85	76.95	323.21	71.64	1012.11	68.37

Table 4 Measurement of various parameters of temperature studies of MS dipped in plant extracts

Inhibitor	Temperature (K)	Slope	R^2	K_{ads}	ΔG_{ads}
Majidea Zanquebarica	313	1.034	0.999	0.5441	-8.8697
	323	1.030	0.998	0.6450	-9.6100
	333	1.024	0.999	0.8930	-10.574
	343	1.158	0.999	0.3481	-8.4458
	353	1.168	0.999	0.3038	-8.2925
Filicium Decipiens	313	1.110	0.993	0.2730	-7.0700
	323	1.150	0.991	0.2396	-6.9501
	333	1.225	0.999	0.1815	-6.3964
	343	1.329	0.996	0.1584	-6.2003
	353	1.381	0.997	0.1418	-6.0560

Table 5 *Parameters of Electrochemical impedance spectroscopy for MS in the presence and absence of MZL & FDL extracts*

Inhibitor	Concentration (ml)	C_{dl} (μFcm^{-2})	R_{ct} Ωcm^2	IE%
Majidea Zanquebarica	Blank	$4.235x10^{-4}$	1.673	*
	5	$8.766 x10^{-5}$	10.46	84.04
	10	$6.128 x10^{-5}$	19.03	91.20
	15	$5.262 x10^{-5}$	29.74	94.37
	20	$4.288 x10^{-5}$	34.83	95.20
	25	$3.791 x10^{-5}$	32.02	94.77
Filicium Decipiens	Blank	$5.5391x10^{-5}$	5.371	*
	5	$6.851x10^{-5}$	6.167	12.91
	10	$7.373 x10^{-5}$	7.295	26.37
	15	$4.840 x10^{-5}$	10.4	48.35
	20	$4.202 x10^{-5}$	13.44	60.04
	25	$3.799 x10^{-5}$	14.72	63.51

Table 6 *Potentiodynamic polarization parameters for MS in 1N HCl medium with various concentrations of MZL & FDL extracts*

Inhibitor	Concentration (ml)	E_{corr} (mV)vs(SCE)	I_{corr} (mA/cm^2)	bc (mV/dec)	ba (mV/dec)	IE%
Majidea Zanquebarica	Blank	-0.483.30	3.157	233.67	146.70	*
	5	-0.477.42	0.3055	170.82	83.76	90.32
	10	-0.477.42	0.3088	170.41	85.65	90.21
	15	-0.484.25	0.3163	158.40	89.69	89.98
	20	-0.502.67	0.1083	81.72	76.87	96.56
	25	-0.525.31	0.3654	159.24	162.43	88.45
Filicium Decipiens	Blank	-461.41	2.971	283.26	138.06	*
	5	-476.09	1.830	98.97	101.33	38.40
	10	-525.32	1.1160	376.33	679.49	62.44
	15	-500.24	0.3851	201.47	155.29	87.04
	20	-479.46	0.2433	159.86	82.78	91.81
	25	-484.16	0.2312	149.41	92.80	92.22

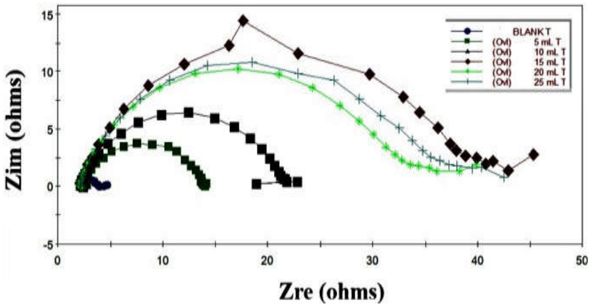
3.5. FTIR Spectroscopy

The FTIR spectrum of MZL and FDL extracts showed that the absoption bands at 3351 cm^{-1} and 3361 cm^{-1} were due to the presence of hydroxyl group. There was a shift of the band to 1641 cm^{-1} in MZL and the bands in the frequency range of 1520-1614cm^{-1} in FDL confirmed the existence of C=O stretching frequency [23]. The peak at 2926 cm^{-1} in MZL and band at 2924 cm^{-1} in FDL proved the presence of C-H stretching vibration. Both the plant extracts showed the absorption bands at 1057 and 1058 cm^{-1} and these were due to the presence of C-O stretching frequency. From the Fig. 3 (*a* and b) it was obvious that the peaks below 1000 cm^{-1} were correspond to the aliphatic C-H group.

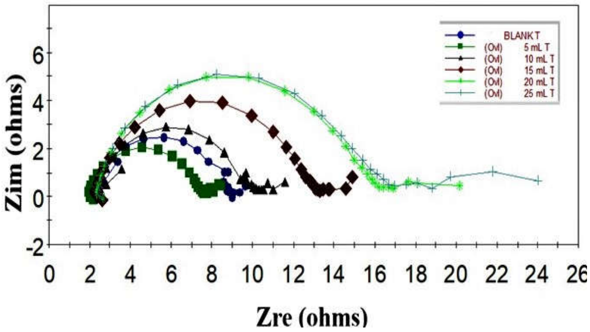
3.6. Electrochemical studies

3.6.1. Electrochemical Impedance spectroscopy

The inhibiting action of the two plant extracts over mild steel specimens in 1N HCl medium was carried out systematically by electrochemical measurements. From the differentiation of values of impedance in higher and lower frequencies the charge transfer resistance were noted that there were increase in the values as the concentration of the two inhibitors was raised. From the Table 5 it was clearly stated that, the lowering of C_{dl} values indicated the formation of protective layer on the MS surface by the phytochemical constituents present in the MZL & FDL extracts thereby increased the thickness of the electrical double layer and decreased coarseness of the metal surface [24]. It was observed from the Nyquist plot that the the diameter of the semicircle increased while increasing the concentration of the inhibitors. The increase in diameter get reflected in the R_{ct} values which in turn increased the inhibition efficiency. These were the inference for the adsorption of the plant extracts on the active sites of the metal surface. The inhibition efficiency for MZL was found to be 95.20% in the optimal concentration of 20ml of extract and for FDL it was about 63.51% in the concentration of 25ml of plant extract.

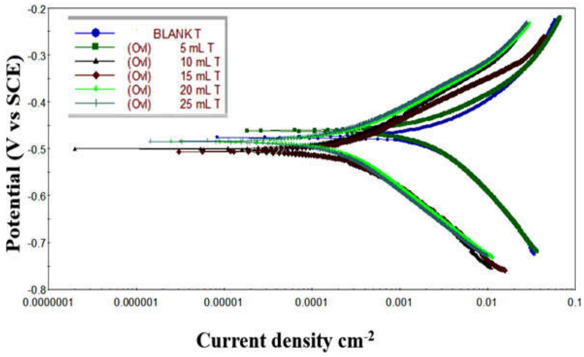


(a)

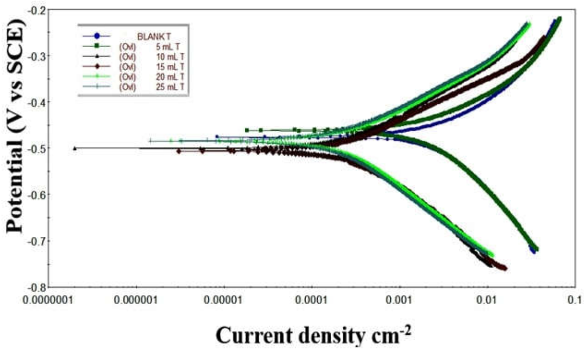


(b)

Fig. 4 *Nyquist plot for Mild steel immersed in various concentrations of (a) MZL extract and blank solution and FDL extract and blank solution*



(a)



(b)

Fig. 5 *Potentiodynamic polarization curves for mild steel in the presence and absence of (a) MZL extract and (b) FDL extract*

3.6.2. Potentiodynamic polarization study

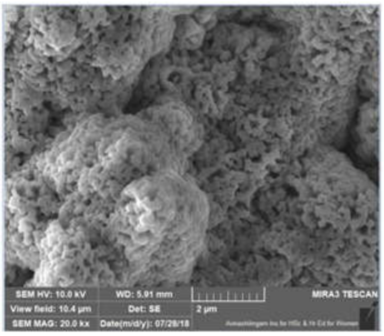
The potentiodynamic study could be carried out by measuring various parameters such as corrosion current density (I_{corr}), corrosion potential (E_{corr}), anodic tafel slope (ba) , cathodic tafel slope (bc) and inhibition efficiency. The depression in the I_{corr} values in the Table 6 proved that the addition of inhibitors to the aggressive medium increased the cathodic and anodic potentials. The oxidation reaction on the anode side and H_2 evolution on the cathode compartment are minimised due to the adsorption of inhibitors on the surface of the mild steel specimen. As a result the cathodic and anodic reactions are controlled which proved that MZL and FDL extracts were acted as mixed type of inhibitors. The highest inhibition efficiency at optimum concentration of 20ml of MZL extract was about 96.56% and for FDL the maximum inhibition efficiency at optimum concentration of 25ml extract was observed to be 92.22%.

3.7. Surface morphology

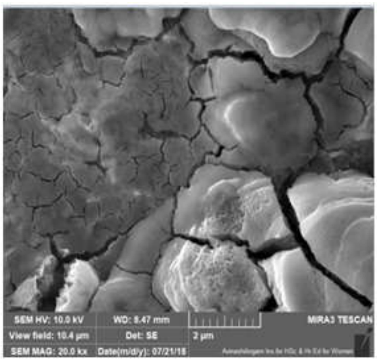
The surface analysis was carried out inorder to identify the inhibition behaviour of the plant extracts using scanning electron microscopy and UV-Visible spectroscopy. For SEM analysis the mild steel stripes were dipped in blank and optimum concentration of the inhibitors for 24 hrs washed, dried and examined using Field emission scanning electron microscopy. In UV-Visible spectroscopy for the pure inhibitor and the mild steel dipped in inhibitor in acid medium were examined using Agilent technologies Cary 8454/UV-Visible spectrophotometer.

3.7.1. SEM and EDX Analysis

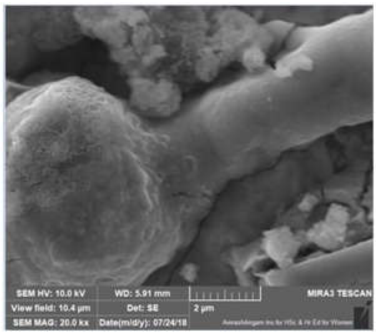
The images of mild steel dipped in the absence and presence of the inhibitor in aggressive medium for 24hrs were shown in the Fig. 4 (a-c).



(a)



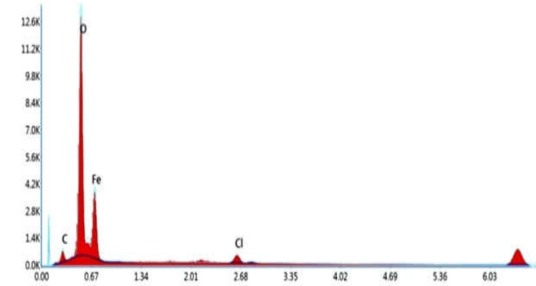
(b)



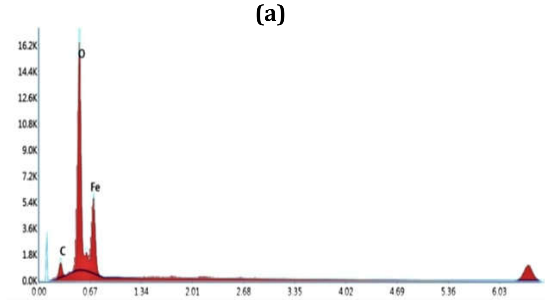
(c)

Fig. 6 *SEM images of (a) MS immersed in Blank, (b) MZL and (c) FDl extracts*

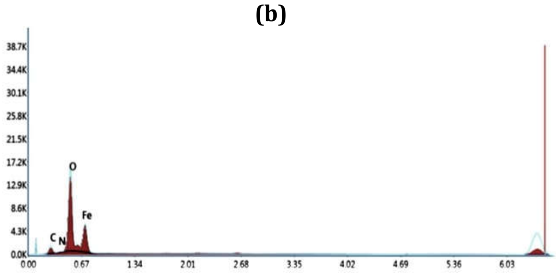
The MS stripe existed in the corrosive medium was highly damaged due to the corrosive nature of the acid. Comparitively the corrosion rate of the MS stripe immersed in the MZL & FDL inhibitor in 1N HCl medium was decreased because the constituents of the inhibitors get interacted with the MS specimens thereby blocked the active sites of the metal and acted as a barrier which protects the metal stripes from the corrosion.



(a)



(b)



(c)

Fig. 7 *EDX spectrum of mild steel dipped in (a) blank solution, (b) MZL and FDL extracts in 1N HCl medium.*

Table 7 *Atomic percentage of various elements for MS dipped in Blank, MZL and FDL in acid medium*

Inhibitor	Inhibitors/elements	C	O	Fe	Cl	N
Majidea Zanquebarica	Mild steel in 1N HCl	9.25	71.55	15.60	3.60	-
	Mild Steel in MZL extract	11.13	69.19	19.68	-	-
Filicium Decipiens	Mild steel in 1N HCl	9.25	71.55	15.60	3.60	-
	Mild Steel in FDL extract	13.50	66.16	19.94	-	0.41

Table 8 *Synergism parameters for MS in MZL and FDL extracts of various concentrations.*

Inhibitor	Concentration (ml)	IE% without Halide ion	KCl		KBr		KI	
			IE%	S_θ	IE%	S_θ	IE%	S_θ
Majidea Zanquebarica	5	49.80	60.23	1.11	65.06	1.19	70.18	1.34
	10	59.43	70.18	1.18	73.16	1.24	76.37	1.33
	15	68.94	76.56	1.07	78.67	1.13	80.12	1.13
	20	71.87	79.40	1.06	83.95	1.31	85.80	1.38
	25	74.34	83.10	1.12	90.76	1.97	93.61	2.57
Filicium Decipiens	5	75.95	81.40	1.14	84.41	1.28	85.77	1.34
	10	80.93	87.47	1.32	90.34	1.62	91.90	1.82
	15	84.87	88.89	1.10	91.88	1.44	92.98	1.56
	20	90.32	95.99	1.89	97.19	2.56	97.73	2.97
	25	93.36	97.58	2.03	98.01	2.37	98.43	2.71

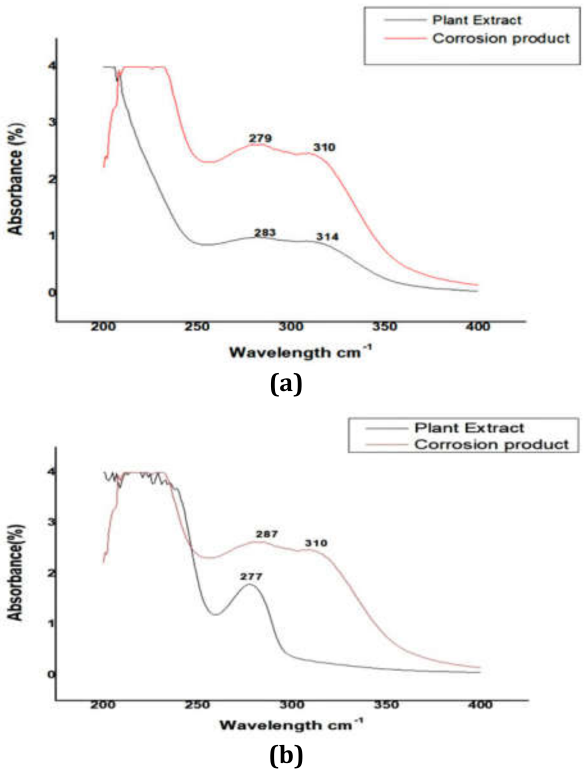


Fig. 8 *UV-Visible spectrum of (a) MZL & MS immersed in inhibitor in acid medium and (b) FDL & MS immersed in inhibitor in acid medium*

The chemical composition over the mild steel sample was analyzed using EDX analysis. The EDX spectra for the MS specimens dipped in 25ml concentration of the two extracts were shown in the Fig. 5 (a-c). It was noted from the Table 7 that the atomic percentage of the mild steel stripe in acid was about 15.60 but for the mild steel stripes immersed in the optimum concentration of MZL and FDL extracts in 1N HCl medium were increased to 19.68 and 19.94. This proved that the corrosion rate was slightly decreased due to the addition of the inhibitors. Comparatively the FDL extract showed higher value than MZL extract. So FDL showed better inhibiting behaviour than MZL extract.

3.7.2. UV-Visible Spectroscopy

The UV spectrums were recorded for the two plant extracts and the mild steel stripes submerged in the optimum concentration of MZL and FDL extracts in 1N acid medium for 24 h. From the Fig. 6 (*a* and b), it was proved that absorbance peaks were observed around 280 nm-315 nm which were due to n→ π* and π → π* transitions. The absorption spectra confirmed that the metal-complexes were formed between the metal and the phytochemical constituents present in the inhibitors.

3.8. Synergistic effect:

The synergism parameters for MZL and FDL could be calculated by means of weight loss measurements. From the Table 8 it was observed that the inhibition efficiency of the halide ions such as KCl, KBr and KI in addition with plant extracts were greater than the inhibition efficiency of the halide ions and the inhibitors separately. The synergism parameter S_θ was calculated by the following equation .

$$S_\theta = \frac{1-\theta_{1+2}}{1-\theta'_{1+2}}$$

Where, θ_1 is surface coverage by halide ion, θ_2 is surface coverage by inhibitor and θ'_{1+2} is surface coverage by the combination of halide ion and inhibitor. Based on the values obtained for S_θ three conditions may be possible.

1. If $S_\theta = 0$ there is no interaction between the inhibitor compounds
2. If $S_\theta > 1$ it enhances the synergistic effect.
3. If $S_\theta < 1$ there exists the Antagonistic effect.

The synergism parameter S_θ would be shown in the Table 8 proved that the values were greater than unity where the synergistic behaviour was enhanced. By comparing MZL and FDL the S_θ values for FDL extract were slightly greater than the MZL extract. FDL extract acted as a better corrosion inhibitor than MZL extract.

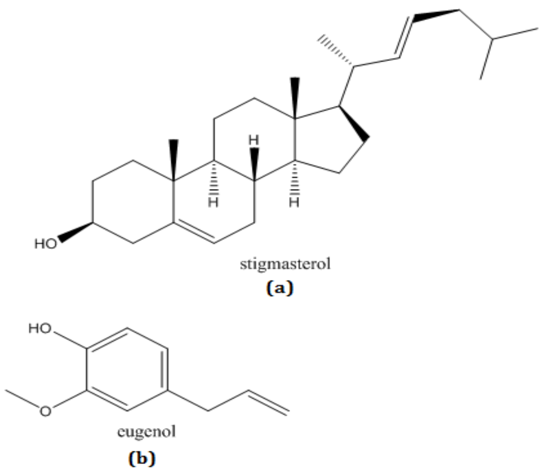


Fig. 9 *Molecular structure of (a) stigmasterol and (b) Eugenol*

3.9. Mechanism of inhibition

The chemical constituent present in Majidea zanquebarica is stigmasterol and the chemical constituent present in Filicium decipiens is Eugenol in which the molecular structures were shown in the fig9(a & 9(b)). Due to the presence of multiple bonds in both the structures were the witness for the presence of free electrons that take part in the bond formation with the mild steel which get adsorbed on the active sites of the metals and protected the metal against corrosion. This proved that the chemical constituent present in the plant extracts highlighted the inhibiting character thus MZL andFDL acted as a good corrosion inhibitors.

4. Conclusion

The Majidea Zanquebarica leaves and Filicium decipiens leaves protected the mild steel stripes by blocking the active sites of the metal thereby the two leaves acted as good corrosion inhibitor. From the weight loss measurements it was understood that the inhibition efficiency increased by increasing the concentration of the extracts. The electrochemical measurements proved that the rate of corrosion was decreased by increasing the charge transfer resistance. The control of cathodic and anodic reactions in the potentiodynamic polarization studies revealed that the two plant extracts acted as a mixed type of inhibitors. The MZL and FDL extracts obeyed the Langmuir adsorption isotherm and the negative values of free energy proved that the reactions were spontaneous. There was an electrostatic interaction between the plant inhibitors and the metal surface was proved in the temperature studies while raising the temperature as well as synergism was observed in both the inhibitors.

Acknowledgement

Authors are very thankful to the management and Dr. A. P. Srikanth, Assistant Professor in PG and Research Department of Chemistry, Government Arts college (Autonomous), Coimbatore, for his valuable guidelines and moral support. Authors are very grateful to the management, Principal and All the Faculty members (Science & Humanities) of PSG college of technology, Peelamedu and Avinashilingam Institute for Home science and Higher Education for Women, Coimbatore for their support.

References:

[1]. A. Bouyanzer, B. Hammouti, "Naturally occuring ginger as corrosion inhibitor for steel in molar hydrocloric acid at 353 K", Bull. Electrochem. 20 (2004) 63.

[2]. M. Dahmani, A. Et-Touhami, S. S. Al-Deyab, B. Hammouti, A. Bouyanzer, "Corrosion Inhibition of C38 Steel in 1 M HCl: A Comparative Study of Black Pepper Extract and Its Isolated Piperine", Int. J. Electrochem. Sci. 5 (2010) 1060.

[3]. L. Bammou, M. Mihit, R. Salghi, L. Bazzi, A. Bouyanzer, S. S. Al-Deyab, B. Hammouti, "Inhibition effect of natural artemisia oils towards tinplate corrosion in HCl solution: Chemical characterization and electrochemical study", Int. J. Electrochem. Sci. 6 (2011) 1454.

[4]. B. Zerga, M. Sfaira, Z. Rais, M. Ebn Touhami, M. Taleb, B. Hammouti, B. Imelouane, A. A Elbachiri, "Lavender oil as an ecofrindly inhibitor for mild steel in 1 M HCl", Materials and Technique 97 (2009) 297.

[5]. E. Chaieb, A. Bouyanzer, B. Hammouti, M. Berrabah, "Limonene as Green Inhibitor for Steel Corrosion in Hydrochloric Acid Solutions", Acta Phys. Chim. Sin. 25 (2009) 1254.
[6]. E. Elouariachi, J. Paolini, M. Bouklah, A. Elidrissi, A. Bouyanzer, B. Hammouti, J. M. Desjobert, J.Costa, "Adsorption properties of rosmarinus officinalis oil as green corrosion inhibitors on C38 steel in 0.5M H2SO4", Acta Mettall. Sin. 23 (2010) 1.
[7]. Z. Faska, A. Bellioua, M. Bouklah, L. Majidi, R. Fihi, A. Bouyanzer, B. Hammouti, "Effect of pulegone and pulegone oxide on the corrosion of steel in 1 M HCl", Monatsh. Chem. 139 (2008) 1417.
[8]. Chris O. Akalezi, Conrad K. Enenebaku, Emeka E. Oguzie, "Inhibition of acid corrosion of mild steel by biomass extract from the petersianthus macrocarpus plant", J. Mater. Environ. Sci. 4 (2013) 217.
[9]. M. Ramananda Singh, "A green approach: a corrosion inhibition of mild steel by Adhatoda vasica plant extract in 0.5 M H2SO4", J. Mater. Environ. Sci 4 (2013) 119.
[10]. O. Benali, H. Benmehdi, O. Hasnaoui, C. Selles, R. Salghi, "Green corrosion inhibitor: inhibitive action of tannin extract of Chamaerops humilis plant for the corrosion of mild steel in 0.5 M H2SO4", J. Mater. Environ. Sci 4 (2013) 127.
[11]. A. M. Abdel-Gaber, B. A. Abd-El-Nabey, M. Saadawy, "The role of acid anion on the inhibition of the acidic corrosion of steel by lupine extract," Corros. Sci. 51 (2009) 1038.
[12]. P. B. Raja, M. G. Sethuraman, "Natural products as corrosion inhibitor for metals in corrosive media-A Review", Mater. Lett. 62 (2008) 113.
[13]. ASTM NACE / ASTMG31-12a, Standard Guide for Laboratory Immersion Corrosion Testing of Metals, ASTM International, West Conshohocken, PA, 2012, www.astm.org
[14]. R. S. Nathiya, Vairamuthu Raj, "Evaluation of Dryopteris cochleata leaf extracts as green inhibitor for corrosion of aluminium in 1 M H_2SO_4", Egypt. J. Petrol. 26 (2017) 313.
[15]. Kanchan Agarwal, "Fenugreek leaves and lemon peel as green corrosion inhibitor for mild steel in 1M HCl medium", J. Mater. Sci. Surf. Eng. 1 (2014) 44.
[16]. P. Udhayakala, "Quantum chemical studies on the inhibition potentials of thiophene derivatives for the corrosion inhibitors of carbon steel", J. Chem. Pharm. Res 6 (2011) 5649
[17]. P. Singh, M. A. Quaraishi, "Study of amine as vapour phase corrosion inhibitors for mild steel under different aggressive atmospheric conditions at high temperature", Ind. J. Life Sci. 7 (2012) 12270.
[18]. Ghulamullah khan, Kazi, Md, Salim Newaz, Wan Jefrey Basirun, Hapipah Binti Mohd Ali, Fadhil Lafta Faraj, Ghulam Mustafa Khan.,"Application of Natural Product Extracts as Green Corrosion Inhibitors for Metals and Alloys in Acid Pickling Processes- A review", Int. J .Electrochem. Sci. 10 (2015) 6120.
[19]. Sudhish kumar shukla, Mumtaz ahmad quraishi "Effect of pharmaceutically active compound Omeprazole, on the corrosion of mild steel in hydrochloric acid solution", Corros. Sci. 52 (2010) 314
[20]. R. B. Rastogi, M. M. Singh, K. Singh, M. Yadav, "Organotin dithiobiurets as corrosion inhibitors for mild steel-dimethyl sulfoxide containing HCl", Afr. J. Pure App. Chem. 5 (2011) 19
[21]. A. K. Singh, M. A. Quraishi, "Effect of fruit extracts of some environmentally benign green corrosion inhibitors on corrosion of mild steel in hydrochloric acid solution", J. Mat. Environ. Sci. 1(2010) 163.
[22]. Evrim baran, Ahmet Cakir, Birgul yazici, "Inhibitory effect of Gentiana olivieri extracts on the corrosion of mild steel in 0.5 M HCl: Electrochemical and phytochemical evaluation", Arab. J. Chem. 12 (2019) 4303.
[23]. S. Gomathi, V. Kumaravelan, D. Dhivya priya, "Inhibition of mild steel corrosion in hydrochloric acid and phosphoric acid medium using Plectranthus Amboinicus (l) plant extract", Inter. J. Adv. Res. 3 (2015) 1307.
[24]. S. Aejitha, P. K. Kasthuri, P. Geethamani, "Comparison of the corrosion inhibition efficiencies of mild steel in different acidic mediums using commiphora caudata plant extract", Int. J. Adv. Tech. Engg. Sci. 3 (2015) 25.

