IJESRT
INTERNATIONAL JOURNAL OF ENGINEERING SCIENCES & RESEARCH TECHNOLOGY

INHIBITIVE EFFECT OF WRIGHTIA TINCTORIA LEAVES AS GREEN INHIBITOR FOR MILD STEEL IN ACID MEDIUM

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ABSTRACT
The inhibition efficacy of Wrightia tinctoria leaves (WTL) extract on mild steel in 1.0N hydrochloric acid with various exposure time (24 to 360hrs) and temperature (313 to 333K) are investigated by mass loss measurements. The value of inhibition efficiency is increased with increase of inhibitor concentration and gradually decreased with rise in temperature is suggestive of physisorption. The adsorption of WTL onto the mild steel surface is found to follow the Langmuir adsorption isotherm. Both kinetic (activation energy and change in heat of absorption) as well as thermodynamics parameters (adsorption of enthalpy, entropy and Gibbs free energy) are calculated and discussed in details. The characterization of alcoholic extract of inhibitor and corrosion products formed on the metal surface is analyzed by UV, FT-IR and SEM spectral studies.

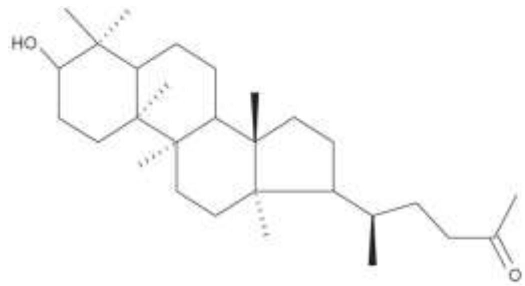
KEYWORDS: Mild Steel, Mass Loss, Green inhibitor, Adsorption, Spectral Studies.

INTRODUCTION
Corrosion is the deterioration of metal by chemical attack or reaction with its environment. It is a constant and continuous problem, often difficult to eliminate completely. Mild steel articles are prone to severe degradation in acid medium. As a corrosion prevention and protection method, application of inhibitor is very popular. A number of heterocyclic compounds with N, S, and O as hetero atoms are proved to be effective corrosion inhibitors and the screening of synthetic heterocyclic compounds is still being continued. Though many synthetic compounds showed good anticorrosive activity but most of them are highly toxic to both human beings and green environment. The safety and environmental issues of corrosion inhibitors arisen in industries have always been a global concern. The toxicity may manifest either during the synthesis of the compound or during its applications. In recent years many alternative ecofriendly corrosion inhibitors have been developed. Plant extracts are environmentally friendly, bio-degradable, non-toxic, plenty and potentially low cost. Several efforts have been made using corrosion preventive practices and the use of green corrosion inhibitors. The plant extract are rich sources of molecules which have appreciably high inhibition efficiency and hence termed as "Green Inhibitors". A few studies using plants containing heteroatom such as oxygen, nitrogen and sulphur like Oxandra asbeckii[1],Argemone mexicana[2], Betanin[3], Henna[4], Wheat[5], Ginger[6], Marraya koeningii[7], Garlic extract[8], Ananas sativum[9] ocimum sanctum[10] holy basil[11], Citrullus Vulgaris[12] Albizia lebbeck[13] Sauropus androgynus[14] mimusops elengi[15] kingiodendron pinnatum[16] have been found effective corrosion inhibitors for mild steel. In our continuous research work, the present investigation is the Wrightia Tinctoria leaves extract used as corrosion inhibitor on mild steel in 1.0N HCl have been investigated with various periods of contact and temperature using the mass loss measurements.Also the corrosion product on the metal surface is analyzed by UV, FT-IR and SEM spectral studies

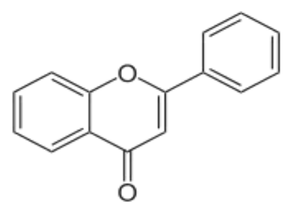
MATERIALS AND METHODS
2.1 Specimen preparation
Mild steel specimen were mechanically pressed cut to form different coupons, each of dimension exactly 20cm^2 (5x2x2cm), polished with emery wheel of 80 and 120, and degreased with trichloroethylene, then washed with distilled water cleaned, dried and then stored in desicator for the use of our present study.

2.2 Preparation of *Wrightia Tinctoria Leaves (*WTL) Extract:
About 3 Kg of *Wrightia Tinctoria* leaves was collected from in and around Western Ghats and then dried under shadow for 5 to 10 days. Then it is grained well and finely powdered, exactly 150g of this fine powder was taken in a 500ml round bottom flask and a required quantity of ethyl alcohol was added to cover the fine powder completely, and left it for 48 hrs. Then the resulting paste was refluxed for about 48 hrs, the extract was collected and the excess of alcohol was removed by the distillation process. The obtained paste was boiled with little amount of activated charcoal to remove impurities, the pure plant extract was collected and stored.

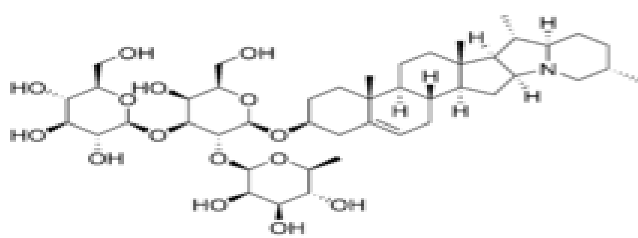
2.3 Properties of *Wrightia tinctoria leaf*:
Wrightia tinctoria belongs to *Appocynaceae family* and it is an annual herbaceous climbing plant with a long history of traditional medicinal uses in many countries, especially in tropical and subtropical regions. The common Names are *vepaalai*. The peel extract of this plant is used to regulate thyroid function and glucose metabolism. The main phytochemicals constituents present in this plant is wrightial, flavonoids, alkaloids, saponins, and triterpenes. A few structures are shown below.



Wrightial



Flavanoid



Saponin

Figure-1: Chemical structures of main active compounds present in WTL.

2.4 Mass loss measurement
In the mass loss measurements on mild steel in triplicate were completely immersed in 100ml of the test solution in the presence and absence of the inhibitor. The metal specimens were withdrawn from the test solutions after 24 to 360 hrs at room temperature and also measured 313K to 333K. The Mass loss was taken as the difference in weight of the specimens before and after immersion using LP 120 digital balance with sensitivity of ±1 mg. The tests were performed in triplicate to guarantee the reliability of the results and the mean value of the mass loss is reported.
From the mass loss measurements, the corrosion rate was calculated using the following relationship.

$$\text{Corrosion Rate}(\text{mmpy}) = \frac{87.6 \times W}{DAT} \quad \text{---------------------} (1)$$

Where, mmpy = millimeter per year, W = Mass loss (mg), D = Density (gm/cm^3),
A = Area of specimen (cm^2), T = time in hours.

The inhibition efficiency (%IE) and degree of surface coverage (θ) were calculated using the following equations.

$$\% IE = \frac{W_1 - W_2}{W_1} \times 100 \quad \text{--------------------- (2)}$$

$$\theta = \frac{W_1 - W_2}{W_1} \quad \text{--------------------- (3)}$$

Where W_1 and W_2 are the corrosion rates in the absence and presence of the inhibitor respectively.

2.5 Adsorption studies:

2.5. 1 Activation energy:

The activation energy (E_a) for the corrosion of metals in the presence and absence of inhibitors in 1.0N Hydrochloric acid, natural sea water environment was calculated using Arrhenius theory. Assumptions of Arrhenius theory is expressed by equation (4).

$$CR = A\exp(-E_a/RT) \quad \text{-------------- (4)}$$

$$\text{Log}(CR_2/CR_1) = E_a/2.303\,R\,(1/T_1 - 1/T_2) \quad \text{------------- (5)}$$

Where CR_1 and CR_2 are the corrosion rate at the temperature T_1 (313K) and T_2 (333K) respectively.

2.5.2 Heat of adsorption:

The heat of adsorption on the surface of various metals in the presence of plant extract in 1.0N Hydrochloric acid, Natural sea water environment is calculated by the following equation (6).

$$Q_{ads} = 2.303\,R\,[\log(\theta_2/1-\theta_2) - \log(\theta_1/1-\theta_1)] \times (T_2T_1/T_2-T_1) \quad \text{------ (6)}$$

Where R is the gas constant, θ_1 and θ_2 are the degree of surface coverage at temperatures T_1 and T_2 respectively.

2.5.3. Langmuir Adsorption Isotherm

The Langmuir adsorption isotherm can be expressed by the following Equation-4.10 is given below [38-40].

$$\text{Log}\,C/\theta = \log C - \log K \quad \text{-------- (7)}$$

Where θ is the degree of surface coverage, C is the concentration of the inhibitor solution and K is the equilibrium constant of adsorption of inhibitor on the metal surface.

2.5.4. Free energy of adsorption:

The equilibrium constant of adsorption of various plant extract on the surface of copper, Brass and Mild steel is related to the free energy of adsorption ΔG_{ads} by equation (8).

$$\Delta G_{ads} = -2.303\,RT\log(55.5\,K) \quad \text{---------------------------------- (8)}$$

Where R is the gas constant, T is the temperature, K is the equilibrium constant of adsorption

RESULT AND DISCUSSION

Mass loss measurements

The dissolution behavior of mild steel in 1.0 N Hydrochloric acid environment containing in the presence and absence of WTL extract with various exposure times (24hrs to 360 hrs) are shown in Table-1**.** The observed values are clearly indicates that the corrosion rate decreased from 0.1627to 0.0697 mmpy for 24 hrs and 0.1549 to 0.0495 mmpy for 360 hrs with increase of inhibitor concentration from 0 to 1000 ppm. The maximum of 83.33 % of inhibition efficiency is achieved even after 120 hrs exposure time. This achievement is mainly due to the presence of main active phytochemical constituents present in the inhibitor molecule which is adsorbed on the metal surface and shield completely to prevent further dissolution from the aggressive media of chloride ion (Cl^-).

Table-1: The corrosion parameters of mild steel in 1N Hydrochloric acid containing different concentration of WTL extract after 24to 360 hours exposure time

Conc (ppm)	Corrosion rate (mmpy)	Inhibition efficiency (%)

	24 hrs	72 hrs	120 hrs	240 hrs	360 hrs	24 Hrs	72 hrs	120 hrs	240 hrs	360 hrs
0	0.1627	0.1394	0.1394	0.1580	0.1549	-	-	-	-	-
10	0.1394	0.1007	0.0743	0.1348	0.1115	14.28	27.77	46.67	14.70	27.99
50	0.1162	0.0542	0.0604	0.1139	0.0991	28.56	61.11	56.67	27.94	35.99
100	0.1162	0.0542	0.0464	0.1022	0.0774	28.56	61.11	66.67	35.29	50.00
500	0.0929	0.0464	0.0325	0.0929	0.0635	42.85	66.67	76.67	41.17	59.00
1000	0.0697	0.0387	0.0232	0.0813	0.0495	57.14	72.22	83.33	48.53	68.00

3.2 Temperature Studies

The dissolution behavior Mild Steel containing various concentration of WTL extract in 1N Hydrochloric acid with temperature ranges from 313K to 333K is investigated by mass loss method and the values are listed out in Table-2. The observed values of corrosion rate decreased from 25.1082 to 3.9057 mmpy with increase of inhibitor concentrations. The percentage of inhibition efficiency gradually is increased from 62.32 to 84.44 % with increase of inhibitor concentration at 313 K. The corrosion resistant behavior of WTL extract on mild steel in 1N Hydrochloric acid at 313 to 333K is shown in Table-2.

Table-2: The corrosion parameters of mild steel in 1N Hydrochloric acid containing different concentration of WTL extract at 313 to 333 K

Conc. (ppm)	Corrosion rate (mmpy)			Inhibition efficiency (%)		
	313K	323K	333K	313K	323K	333K
0	25.1082	40.1732	50.2165	-	-	-
10	9.4853	21.7605	35.1515	62.32	45.83	30.00
50	7.8114	11.7171	26.7821	68.88	70.83	46.66
100	5.0216	8.9273	17.8547	80.00	77.77	64.44
500	4.4636	7.8114	15.6229	82.22	80.55	68.88
1000	3.9057	6.6955	10.6012	84.44	83.33	78.88

3.3 Effect of Temperature:

3.3.1. Activation energy:

The values of corrosion rate obtained from the mass loss measurement are substituted in equation-4 and the values of activation energy (E_a) are presented in Table-3. The observed values are ranged from 36.635 to 27.926 kJ/mol for Mild Steel in 1.0N Hydrochloric acid containing various concentration of inhibitor. The average value of E_a obtained from the blank (19.385) is lower than that in the presence of inhibitor and indicated that there is a strong chemical adsorption bond between the WTL inhibitor molecules and the Mild Steel surface.

Table -3: Calculated values of Activation energy (E_a) and heat of adsorption (Q_{ads}) Of WTL extract on Mild Steel in 1N Hydrochloric acid environment.

S.No	Conc. of Inhibitor (ppm)	I.E (%)		E_a ($KJmol^{-1}$)	Q_{ads} ($KJmol^{-1}$)
		30^0	60^0		
1	0	-	-	19.385	-
2	10	62.32	30.00	36.635	-37.769
3	50	68.88	46.66	34.459	-25.965
4	100	80.10	64.44	35.477	-22.139
5	500	82.22	68.88	35.037	-20.600
6	1000	84.44	78.88	27.926	-10.438

3.3.2. Heat of adsorption:

The value of heat of adsorption (Q_{ads}) on Mild Steel in 1.0N Hydrochloric acid containing various concentration of WTL extract is calculated using Equation -6 and the values of Q_{ads} are ranged from -37.769 to -10.438 kJ/mol (Table-3). These negative values are reflected that the adsorption of WTL extract on Mild Steel is follows exothermic process.

3.3.3 Adsorption studies:

The adsorption isotherm is a process, which are used to investigate the mode of adsorption and it characteristic of inhibitor on the metal surface. In our present study the Langmuir adsorption isotherm is investigated. The straight line observed in Fig- 2 suggest that the inhibitor follows Langmuir adsorption isotherm.

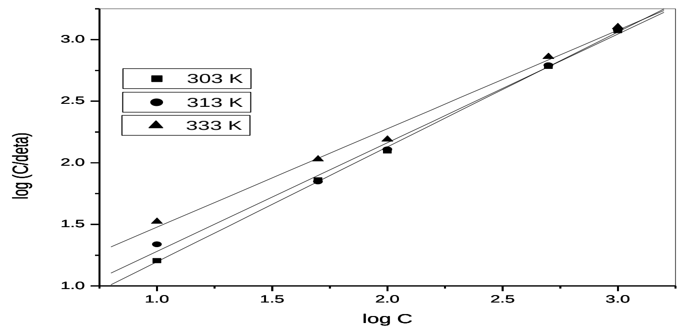


Figure-2: Langmuir isotherm for the adsorption of WTL inhibitor on Mild Steel in 1.0N hydrochloric acid environment.

3.3.4. Free energy of adsorption:

The standard free energy of adsorption ($\Delta G_{ads)}$ can be calculated using the Equation- 8 and the observed negative values (Table-4) ensure that the spontaneity of the adsorption process and the stability of the adsorbed layer is enhanced.

Table 4: Langmuir adsorption parameters for the adsorption of WTL inhibitor on Mild Steel in 1.0N Hydrochloric acid

Adsorption isotherms	Temperature (Kelvin)	Slope	K	R^2	ΔGads (KJ/mol)
Langmuir	303	0.9328	1.8341	0.9993	-11.6251
	313	0.8822	2.5037	0.9950	-12.8188
	333	0.7995	4.7631	0.9939	-15.4187

3.3.5. Thermodynamics parameters

The another form of transition state equation which is derived from Arrhenius equation -4 is shown below in equation- 9

$$CR=RT/Nh \exp (\Delta S/R) \exp (-\Delta H/RT) \text{ ----- } (9)$$

Where h is the Planck's constant, N the Avogadro's number, ΔS the entropy of activation, and ΔH the enthalpy of activation. A plot of log (CR/T) Vs 1000/T gives a straight line (Fig-3) with a slope of $(-\Delta H/R)$ and an intercept of $[\log(R/Nh)) + (\Delta S/R)]$, from which the values of ΔS and ΔH were calculated and listed in Table-5. The positive value of enthalpy of activation clear that the endothermic nature of dissolution process is very difficult. The ΔS is generally interpreted with disorder which may take place on going from reactants to the activated complex.

Table-5: Thermodynamic parameters of Mild Steel in 1N Hydrochloric acid Obtained from weight loss measurement

S.No	Conc. of inhibitor (ppm)	ΔH ($KJ\ mol^{-1}$)	ΔS ($J\ k^{-1}mol^{-1}$)
1	0	6.7728	9.4190
2	10	13.9561	11.4590
3	50	13.9003	11.3117
4	100	14.0034	11.2064
5	500	13.8233	11.1055
6	1000	10.5569	9.9901

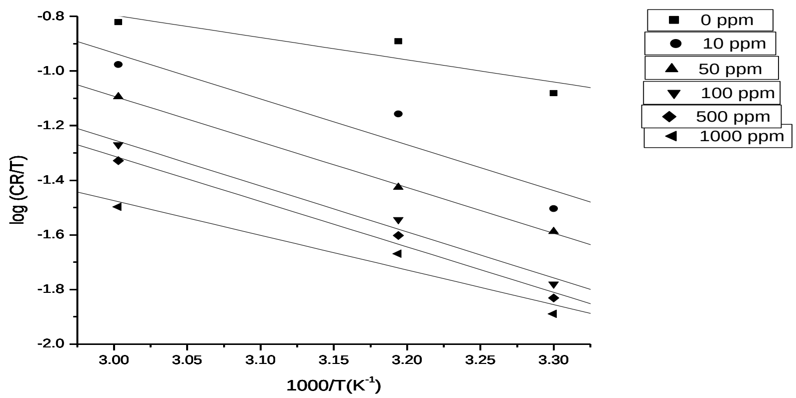


Figure-3: The relation between log (CR/T) and 1/T for different concentrations Of WTL extract

SPECTRAL STUDIES

4.1 UV analysis:

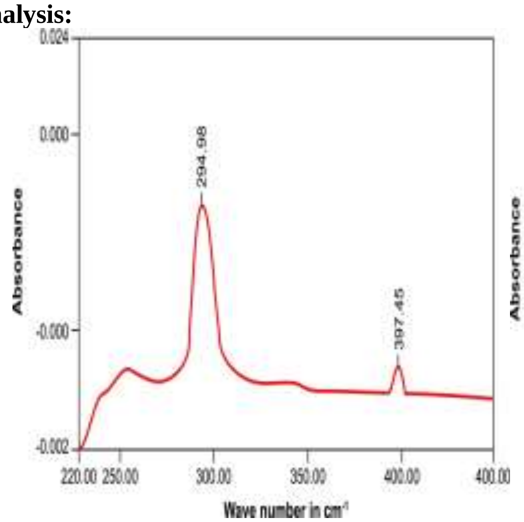


Fig-4

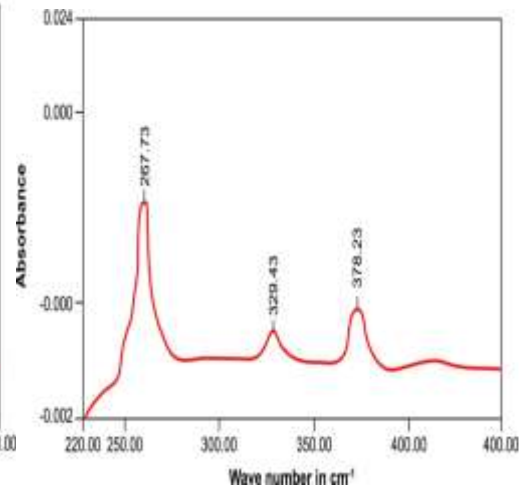


Fig-5

Figure-4 and 5: UV spectrum of corrosion product in the absence and presence Of WTL on the mild steel in 1.0N HCl.

Figure 4 and 5 shows that the UV visible spectrum of the corrosion product on the surface of mild steel in the presence and absence of WTL extract in 1.0N hydrochloric acid. In the absence of inhibitor, the UV absorption maximum of around two bands 294.98nm and 397.45nm were appeared. However in the presence of inhibitor three peaks were appeared at around 267.73, 329.43 & 378.23nm. The change of adsorption band from longer wavelength to shorter wavelength (i.e. hypochromic or blue shift) that a strong co-ordination bond between the active group present in the inhibitor molecules and the ions in the metal surface.

4.2. FT-IR Analysis

FT-IR studies of WTL extract on Mild Steel surface in 1.0N Hydrochloric acid:

The figures- 6 and 7 reflect that the FTIR spectrum of the ethanolic extract of inhibitor and the corrosion product on Mild Steel in the presence of WTL extract1.0N Hydrochloric acid . On comparing both of these spectra the prominent peak such as, the -O-H stretching frequency for alcohol is shifted from 3386.39 to 3413.39 cm^{-1}, the C-N stretching in amine is shifted from 1107 to 1123.23 $cm^{-1}$and the C-H stretching frequency is shifted from 1401.03cm^{-1} to 1388.78 cm^{-1}. These results also support the fact that the corrosion inhibition of WTL extract on Mild Steel in 1.0N Hydrochloric acid may be prevented further dissolution of the metal.

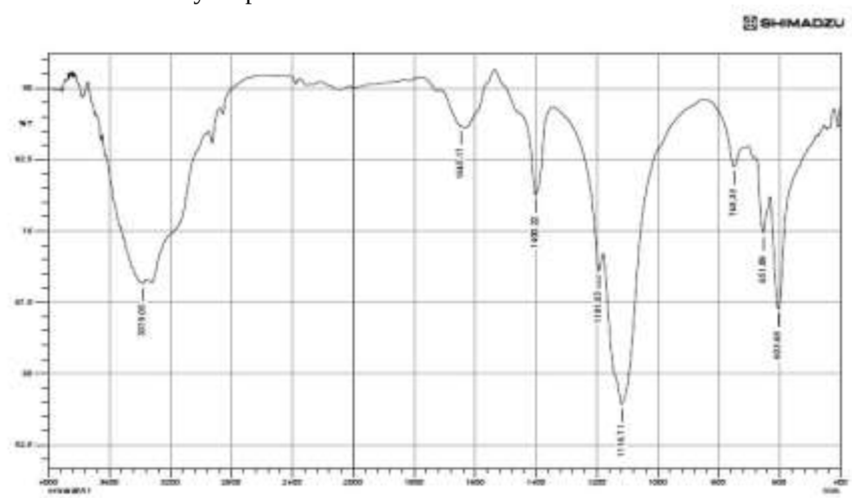


Figure-6: FT-IR spectrum of ethanolic extract of wrightia Tinctoria laeves (WTL)

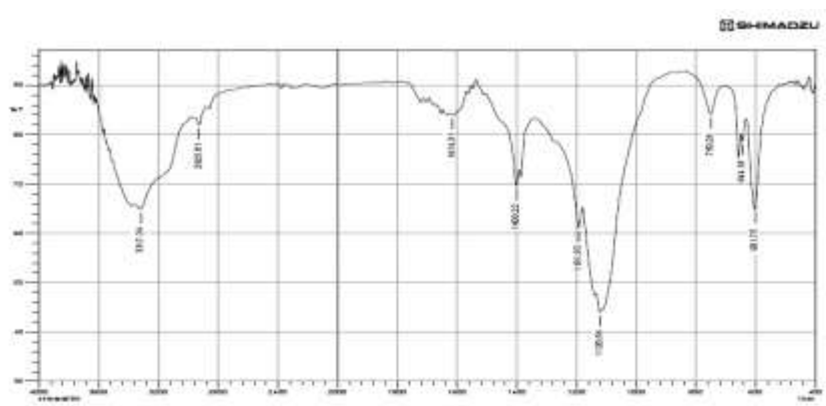
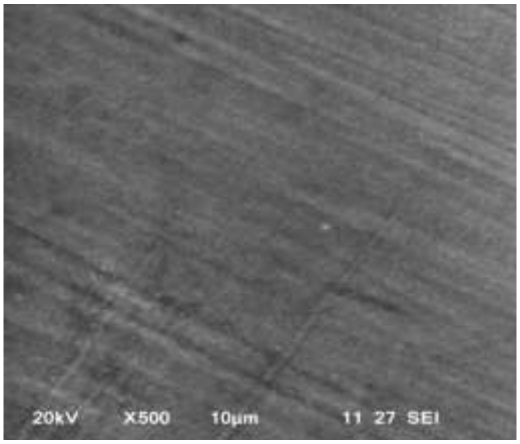


Figure-7: FT-IR spectrum for the corrosion product on Mild Steel in the presence of WTL extract with 1.0N Hydrochloric acid

SEM ANALYSIS

The surface morphology of Mild Steel surface was studied by scanning electron microscopy (SEM). The Figure- 8 and 9 shows that the SEM micrographs of copper surface before and after immersion in 1.0 N Hydrochloric acid respectively. The SEM photographs showed that the surface of metal has number of pits and cracks are visible in the surface, but in presence of inhibitor they are minimized significantly on the metal surface and clearly indicates that the formation of spongy mass covered on the entire metal surface leads to further dissolution of metal from acid environment.



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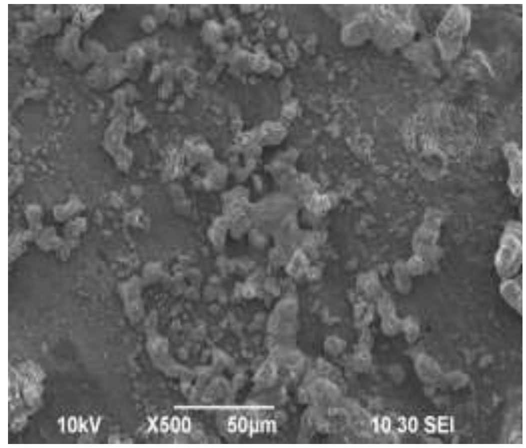

(9)

Fig-8: SEM image of polished mild steel surface Fig-9: SEM image of mild steel in 1.0N Hydrochloric acid having 100ppm of WTL inhibitor

CONCLUSION

Corrosion of mild steel in 1.0N Hydrochloric acid is increased with increase of exposure period. But using alcoholic extract of WTL on mild steel, the corrosion rate markedly reduced with increase of inhibitor concentrations from 0 to 1000ppm. The maximum inhibition efficiency is achieved 83.33%. The WTL is a suitable inhibitor in acid environment for mild steel. The maximum inhibition efficiency arrive due to strong bindings between the inhibitor molecule and ions from the metal surface by temperature studies, the percentage of inhibition efficiency gradually decreased with rise in temperature from 313 to 333K and the maximum inhibition efficiency is 84.44%.The process due to the adsorption of active inhibitor molecules on the metal surface is higher than desorption process. The activation energy (E_a), heat of adsorption (Q_{ads}), Standard free energy adsorption (ΔG_{ads}), enthalphy (ΔH), entropy (ΔS), suggests that, endothermic, physisorption spontaneous process respectively. The inhibitor obeys Langmuir adsorption isotherm. The film formation may confirm by SEM spectral studies and the characteristizations of corrosion products using UV and FT-IR Spectral studies.

ACKNOWLEDGEMENTS

The authors would like to thank the management of Sri Paramakalyani College, Alwarkurichi for providing the lab facilities for taking spectral studies in CSAR, PSN College of engineering and technology, Tirunelveli and SEM studies in Karunya University Coimbatore

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