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Albizia lebbeck seed extract as effective corrosion inhibitor for Mild steel in acid medium

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ABSTRACT

The inhibitive performance of alcoholic extract of *Albizia lebbeck* seed towards the corrosion of Mild steel in 1N Hydrochloric acid medium has been studied by mass loss measurement with various periods of contact and temperature. The present study revealed that the percentage of inhibition efficiency is enhanced with the increase of inhibitor concentration and decreased with the rise in immersion time. The temperature studies reflect that the adsorption of inhibitor on metal surface takes place *via* physisorption. The calculated values of Q_{ads} and ΔG_{ads} suggested that the adsorption may be an exothermic and spontaneous process. It was found that the adsorption of ALS inhibitor follows Langmuir adsorption isotherm. The protective film formed on the metal surface may be also confirmed by spectral studies.

Keywords: *Mild steel, corrosion, inhibition, Albizia lebbeck seed, mass loss, adsorption isotherm.*

1. INTRODUCTION

Mild steel is one of the most important metal widely used in different fields of industries, automobiles, engineering, submarine etc. However this metal is severely affected due to the environmental pollutant such as chlorate, sulphate, nitrate, phosphate etc [1]. In order to overcome this problem, the use of inhibitor is one of the best method to protect the metal against corrosion. Thus corrosion of mild steel and its inhibition in acid and other environments have more attention from numerous previous of investigators [2-6]. Most of the chemicals containing hetero atoms like oxygen, nitrogen and sulphur is used as corrosion inhibitors which are very toxic to all living organisms even in very small concentration thereby green corrosion inhibitors are used nowadays which is biodegradable, non toxic, eco- friendly and do not contain heavy metals [6-7]. Recently numerous investigators have been studied the corrosion of metals using various plant extract as green inhibitors such as *Musa acuminate* peel [8], orange juice [9], S*trychnos nuxvomica* [10], Mango Bark And Leaf Extract[11], *Acacia seyal* var. *seyal* [12], *Uncaria gambit* [13], *Solanum melongena* [14], *Punica granatum*[15], *Emblica officinalis*[16], *Andrographis paniculata* [17], *Citrullus vulgaris* Peel [18], *Anogessus leocarpus* [19]. In our present investigation consists of the inhibitive and adsorption properties of *Albizia lebbeck* seed extract on the corrosion of Mild steel in 1N Hydrochloric acid have been observed at various concentrations of inhibitor using mass loss measurements at different time duration and temperature. By utilizing the spectral studies vis UV, FT-IR, EDX, SEM the formation of protective film on the metal surface may also confirmed.

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2. EXPERIMENTAL SECTION

2.1. Specimen preparation. Mild steel specimen were mechanically pressed cut to form different coupons of the same size 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 desiccator for the present study.

2.2. Preparation of *Albizia lebbeck* seed (ALS) extract. Freshly available *Albizia* lebbeck seed (ALS) were dried well, grinded and soaked in alcohol solvent for about 48hrs, and then filtered followed by evaporation in order to remove the alcohol completely and the pure plant seed alcoholic extract was collected. From this extract the different concentration of 100,250,500,750,1000ppm stock solution was prepared and used throughout the present investigation. All reagents used for this present study were Analar grade and double distilled water for their preparation.

2.3. Mass Loss measurement. In mass loss measurement, Mild steel specimen is immersed exactly in 50ml of the test solution in the presence and absence of the inhibitor. The specimens were withdrawn from the test solutions after an hour at the temperature range of 303K to 333K and after 24 to 168hrs at room temperature. From this observed data, the corrosion rate (mmpy), percentage inhibition efficiency(%I.E) and surface coverage (θ) was calculated using the following formula

$$\text{Corrosion Rate}\left(\text{mmpy}\right) = \frac{87.6 \times \text{W}}{\text{DAT}} \qquad (1)$$

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

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

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

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

2.4. Surface characterization. The SEM analyses of mild steel coupons after abrading and immersion in 1N HCl in the absence and presence of optimum concentration (500 ppm) of ALS was performed on a instrument (Model Jeol - JSM 6390) at an accelerating voltage of 20 kV and magnification of 20K. The predominant elements present in the corrosion products was recorded by an EDX detector using a model Oxford Instrument Model - INCA Penta xFET. The change of frequency of the functional groups in the corrosion product was analysed by FT-IR spectrum using the model Jasco/Japan**.** The UV spectrum was analysed by the instrument Model Jasco V670.

3. RESULTS SECTION

The Corrosion parameters of Mild steel in 1N Hydrochloric acid containing various concentration of ALS extract with different exposure time were listed out in Table 1. It reveals that the loss of mass increased (132mg to 520mg) with increase of exposure time (24 hrs to 168 hrs) in the absence of inhibitor concentration. But in the presence of Albizia lebbeck seed extract, the corrosion rate was significantly reduced from 8.922 to 0.4731 mmpy for 24hrs and 5.0211 to 0.830 mmpy for 168 hrs respectively. The maximum of 94.69% inhibition efficiency was achieved at 1000 ppm of inhibitor concentration even after 72hrs exposure time. This was mainly due to the blocking effect of surface by film formation which reduces the corrosion rate by the attack of acid environment. This

achievement exhibited by the hetero atoms like nitrogen, oxygen and olefinic bonds present in the inhibitor. The observed surface coverage (θ) were almost greater than 94% (Figure1) was mainly due to the formation of insoluble stable complex between the ion in the metal surface and the hetero atom present in the phytoconstituent of ALS extract.

Table 1: Corrosion parameters of Mild steel in 1N Hydrochloric acid containing various concentration of ALS extract with different exposure time.

Time immersion (hrs)	Concentration of inhibitor (ppm)	Mass loss (mg)	Corrosion rate (mmpy)	Inhibition efficiency (%)
24	0	132	8.922	---
	100	29	1.9601	78.03
	250	16	1.0814	87.87
	500	10	0.6759	92.42
	750	7	0.4731	94.69
	1000	7	0.4731	94.69
48	0	202	6.8268	---
	100	62	2.0953	69.30
	250	48	1.6222	76.23
	500	39	1.3180	80.69
	750	32	1.0814	84.15
	1000	28	0.9462	86.14
72	0	272	6.1283	----
	100	78	1.7574	71.32
	250	65	1.4645	76.10
	500	52	1.1716	80.88
	750	49	1.1040	81.98
	1000	34	0.7660	87.50
96	0	312	5.2722	---
	100	101	1.7067	67.62
	250	78	1.3180	75.00
	500	59	0.9969	81.09
	750	52	0.8787	83.33
	1000	42	0.7097	86.53
120	0	389	5.2587	-----
	100	142	1.9196	63.49
	250	92	1.2437	76.35
	500	74	1.0003	80.98
	750	69	0.9327	82.26
	1000	55	0.7435	85.86
144	0	442	4.9793	---
	100	162	1.8250	63.35
	250	140	1.5771	68.32
	500	98	1.1040	77.83
	750	87	0.9800	80.32
	1000	72	0.8111	83.71
168	0	520	5.0211	----
	100	180	1.7380	65.39
	250	168	1.6222	67.69
	500	110	1.0621	78.84
	750	92	0.8883	82.31
	1000	86	0.8304	83.46

3.1.Effect of temperature. The Figure 2 reflects that the concentration of inhibitor versus the corrosion rate (mmpy) at various temperature ranges from 303K to 333K. The maximum of 80.62 % and 74.95% have been attained at 303K and 333K respectively. This was mainly due to the

desorption of the active molecules present in the inhibitor molecules on the metal surface more preferential than adsorption process at higher temperature.

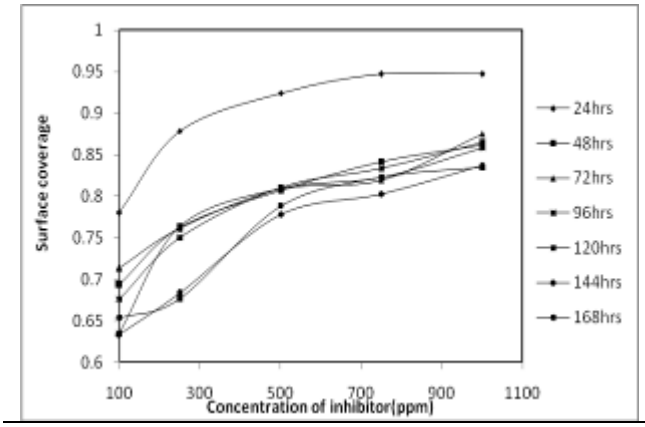

Figure 1: Variation of surface coverage with different concentration of ALS extract on Mild steel in 1N Hydrochloric acid

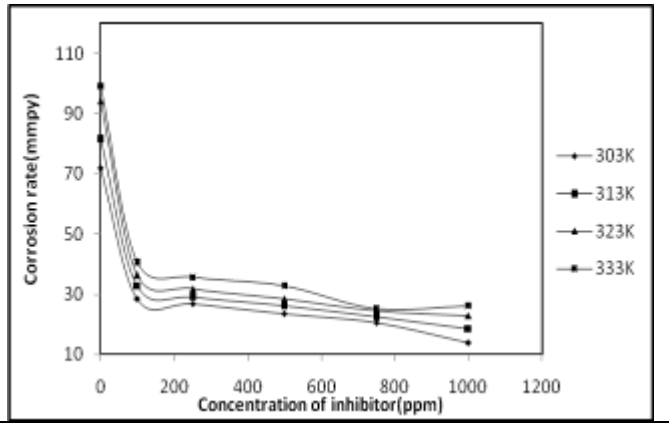

Figure 2: Variation of corrosion rate with concentration of ALS extract on Mild steel in 1N Hydrochloric acid

Table 2: Corrosion parameters of Mild steel in 1N Hydrochloric acid containing various concentration of ALS extract with different temperature

Temperature (K)	Concentration of inhibitor (ppm)	Mass loss (mg)	Corrosion rate (mmpy)	Inhibition efficiency (%)
303	0	129	71.8854	-----
	100	51	28.4198	60.46
	250	48	26.7481	62.79
	500	42	23.4045	67.44
	750	37	20.6185	71.32
	1000	25	13.9313	80.62
313	0	146	81.3587	----
	100	59	32.8778	59.58
	250	52	28.9776	64.38
	500	47	26.1908	67.81
	750	40	22.2900	72.60
	1000	33	18.3893	77.39
323	0	169	94.1755	-----
	100	65	36.2214	61.53
	250	57	31.7633	66.27
	500	51	28.4198	69.82
	750	44	24.5191	73.96
	1000	41	22.8473	75.73
333	0	178	99.1908	----
	100	73	40.6793	58.98
	250	64	35.6641	64.04
	500	59	32.8779	66.58
	750	45	25.0763	7472
	1000	41	26.1908	74.95

From the mass loss data with different temperature range of 303 K-333 K, the activation energy was evaluated. These observed values (E_a) were calculated using the following Arrhenius equation and its derived form and the observed results were presented in Table 3.

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

$$\log(CR_2/CR_1) = E_a/2.303\ R\ (1/T_1 - 1/T_2) \quad (5)$$

Where CR_1 and CR_2 are the corrosion rates of Mild steel at temperatures of T_1 and T_2 respectively. T_1-Initial temperature, T_2-Final temperature, E_a is the activation energy and R is the universal gas constant. It can be seen from the Table 3, the activation energy (E_a) of the corrosion of Mild steel in 1N HCl solution in the presence of ALS extract was higher than that in the free acid solution which may be interpreted as physical adsorption mechanism [20-21]. The heat of adsorption (Q_{ads}) on Mild steel in the presence of inhibitor was derived by the following equation (6)

$$Q_{ads} = 2.303\ R\ [\log (\theta_2/1-\theta_2) - \log (\theta_1/1-\theta_1)]\ x\ (T_2T_1/T_2-T_1) \qquad (6)$$

Where R is the gas constant, $\theta_1$and θ_2 is the degree of surface coverage at temperatures T_1 and T_2 respectively. The negative Q_{ads} values were indicated that the degree of surface coverage decreased with rise in temperature in the presence of ALS extract may supporting the physisorption mechanism and this process was exothermic one [22]

Table 3: Thermodynamic parameters such as Activation energy (E_a) and heat of adsorption (Q_{ads}) of ALS extract on Mild steel in 1N Hydrochloric acid.

S.No	Electrolyte (HCl+ALS) (ppm)	% of I.E		E_a ($KJmol^{-1}$)	Q_{ads} ($KJmol^{-1}$)
		303K	333K		
1.	Blank	---	---	09.004	-----
2.	100	60.46	58.98	10.030	-01.720
2.	250	62.79	64.04	08.045	-01.506
3.	500	67.44	66.58	09.505	-07.479
4.	750	71.32	7472	05.474	-04.831
5.	1000	80.62	74.95	17.655	-09.216

3.2.Adsorption studies. The surface coverage values (Table 2) were fitted with Langmuir adsorption isotherm which was given by the following expression

$$\log C/\theta = \log C - \log K \qquad (7)$$

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. This isotherm assumed that the adsorbed molecules occupied only on one site and there was no interaction with other molecules adsorbed. The linearity of Langmuir adsorption isotherm of ALS inhibitor represents the formation of monolayer on the mild steel surface [23].

The equilibrium constant of adsorption of ALS extract on the surface of metal is related to the free energy of adsorption (ΔG_{ads}) by the following Equation (8)

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

Where R is the gas constant, T is the temperature and K is the equilibrium constant of adsorption. The value of ΔG°_{ads} was found to be less than -20 kJ/mol which clearly indicates that the adsorption of ALS on the mild steel surface was a typical physisorption [24]. The negative values of ΔG_{ads} suggested that the adsorption of ALS extract on to metal surface was a spontaneous process and the adsorbed layer was more stable one.

3.3. Morphology examination of mild steel.

3.3.1. UV spectral analysis. Figure 4, 5 and 6 shows that the UV visible spectrum of the ALS extract, corrosion product on the surface of Mild steel in the absence and presence of ALS extract in 1N Hydrochloric acid. In the absence of inhibitor, the UV absorption maximum of around 289nm and in the presence of inhibitor two peaks appeared at around 280 and 375nm which is different from the 265nm(ALS extract alone). The change of adsorption band from the above spectrum

revealed a strong co-ordination between the active group present in the inhibitor molecules and the metal surface.

Table 4: Langmuir adsorption parameters for the adsorption of ALS extract on Mild steel in 1N Hydrochloric acid.

Adsorption Isotherms	Temperature (Kelvin)	Slope	K	R^2	ΔG_{ads} kJ/mol
Langmuir	303	0.8877	0.45777	0.9970	-08.150
	313	0.8926	0.44582	0.9990	-08.351
	323	0.9095	0.39402	0.9998	-08.286
	333	0.8921	0.44981	0.9990	-08.909

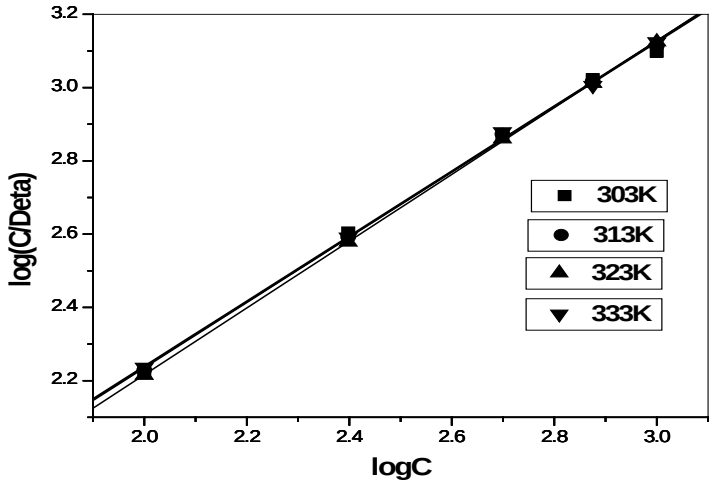

Figure 3: Langmuir adsorption isotherm of ALS extract on Mild steel in 1N Hydrochloric acid.

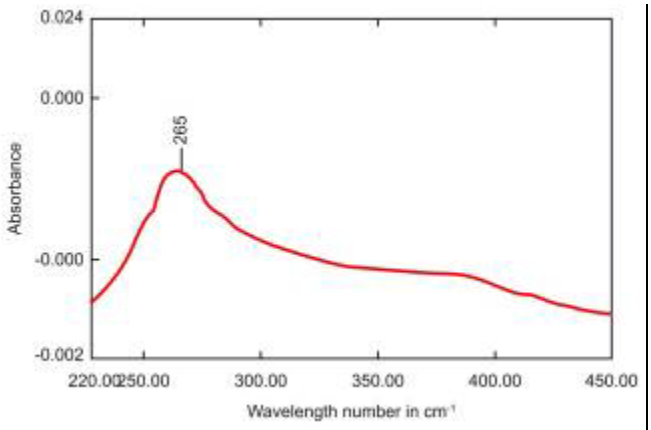

Figure 4: UV spectrum of the ALS extract

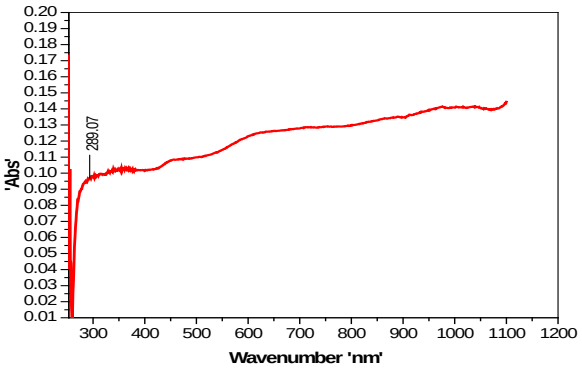

Figure 5: UV spectrum for corrosion product on Mild steel with 1N Hydrochloric acid

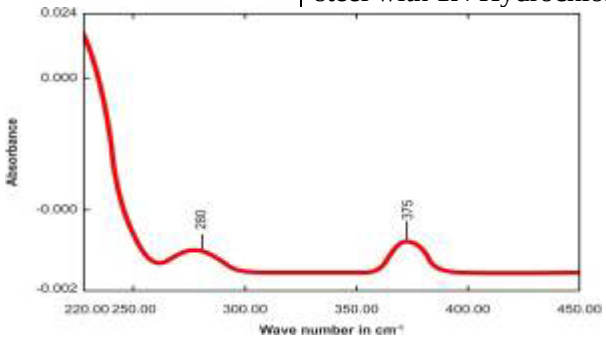

Figure 6: UV spectrum for corrosion product on Mild steel in the presence of ALS extract with 1N Hydrochloric acid

3.3.2.FT-IR Analysis. The Figure 7(a) & (b) reflects that the FT-IR spectrum of the ethanolic extract of ALS and the corrosion product on Mild steel respectively. The observed stretching frequency and the corresponding band assignment were given in Table 5.

Table 5: FT- IR spectrum of the corrosion product on Mild steel in the presence of ethanolic extract of ALS as an inhibitor in Acid environment.

Frequency(cm^1) Pure extract of ALS	Frequency(cm^{-1}) Extract adsorbed on mild steel	Band assignment
3317.64	3375.88	-OH in alcohol
1654.81	1627.81	C=C in alkene
1400.22	1450.28	C=C in aromatic ring
1122.49	1312.50	C-N in amine
----	750.26	C-Cl in chloroalkane

These shifting frequencies suggested that the formation of barrier film on the metal surface which may confirm the co-ordination between inhibitor molecule and metal surface.

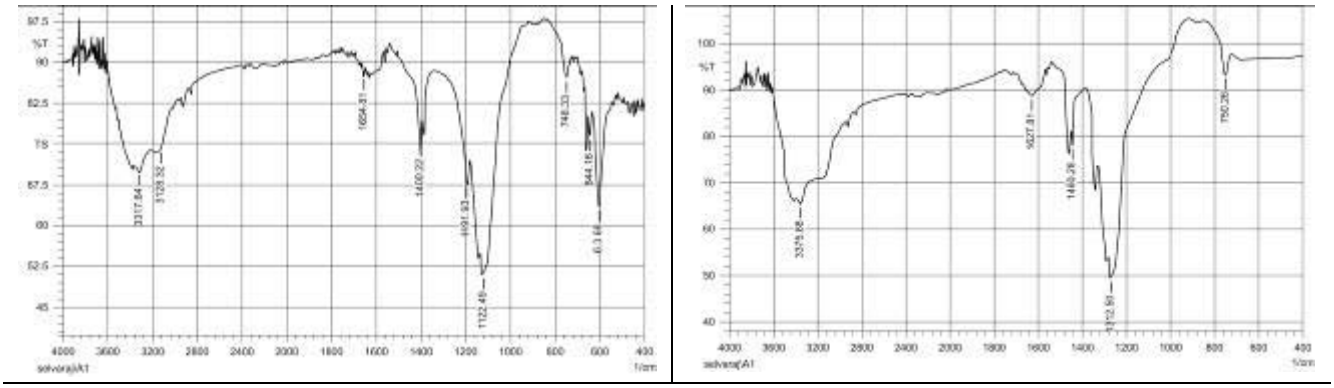

Figure 7: FT-IR spectrum of (a) the alcoholic extract of *Albizia lebbeck* seed and (b) the corrosion product on Mild steel in the presence of ALS extract with 1N Hydrochloric acid environment.

3.3.3.EDX Studies. EDX spectroscopy was used to determine the elements present on the mild steel surface before and after exposure to the inhibitor solution. Figures 8 and 9 represent the EDX spectra for the corrosion product on metal surface in the absence and presence of optimum concentrations of ALS extract with 1N Hydrochloric acid. In the absence of inhibitor molecules, the spectrum may confirm the existence of chlorine due to the formation of chlorides of mild steel. In addition to this the spectrum consists of iron, silicon, carbon which is the part of composition of mild steel. However, in the presence of the optimum concentrations of the inhibitors, nitrogen and oxygen atoms are found to be present on the metal surface. It clearly indicates that these hetero atoms present in the inhibitor molecules may also confirm the adsorption process with metal atom and hence it may protect the metal surface against corrosion.

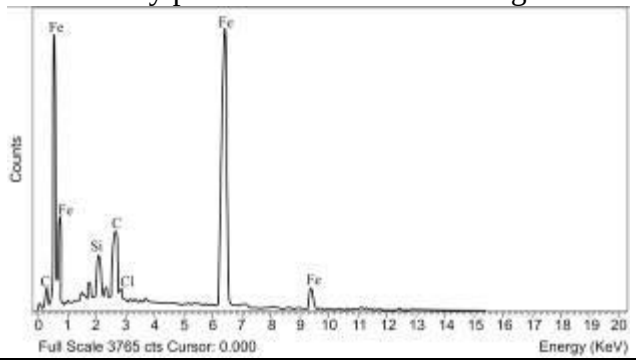

Figure 8: EDX spectrum of the corrosion product on mild steel surface in 1N HCl

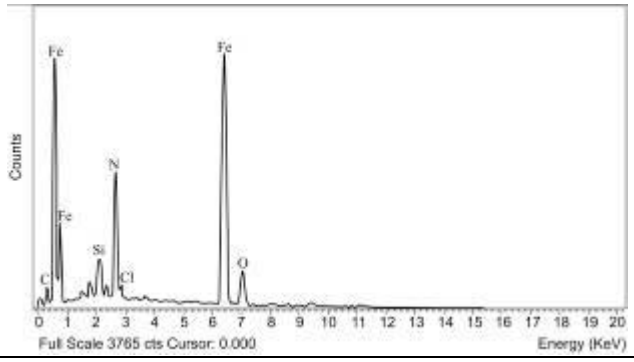

Figure 9: EDX spectrum of the corrosion product on mild steel surface with the presence of ALS extract in 1N HCl

3.3.4. Scanning electron microscopic studies (SEM). The Fig. 10 (a) [25] & (b) shows that the morphological view of mild steel in the absence and presence of ALS extract in 1N Hydrochloric acid. This SEM photographs reflected that the surface of the metal has a number of pits, porous and cracks, when exposed to 1N Hydrochloric acid (Fig.10a) [25]. In the presence of inhibitor, the magnification of SEM photograph (Fig.10b) revealed that the spongy mass is completely covered the entire surface of the metal may confirm the minimization of the damage of metal surface.

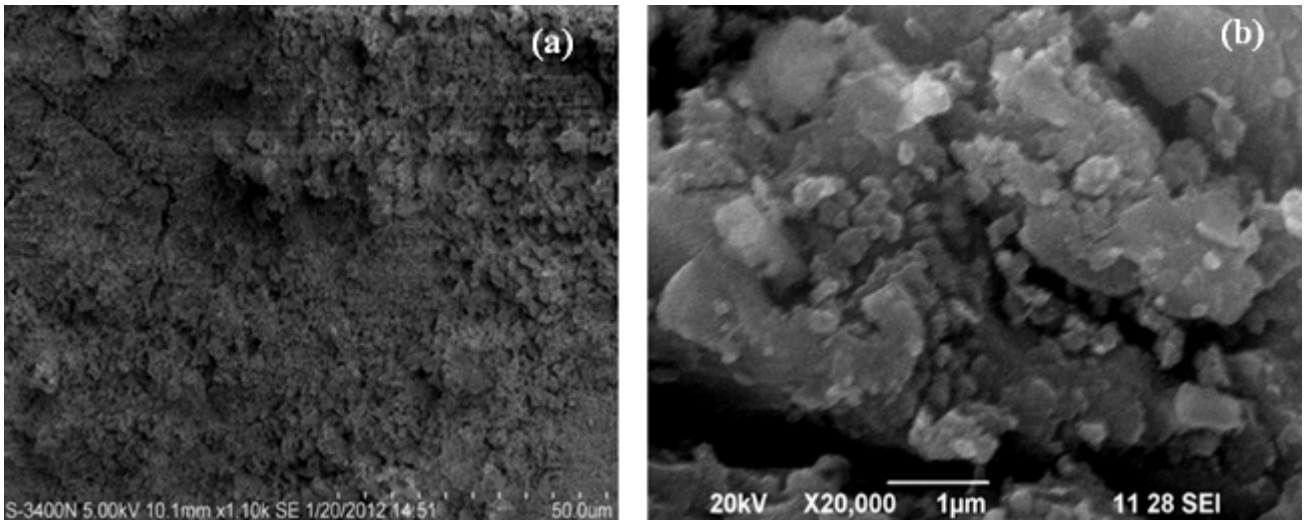

Figure10: Scanning electron micrograph of mild steel sample after 24hrs immersion in (a): 1N HCl solution (b): 500ppm of ALS inhibitor.

4. CONCLUSIONS

Albizia lebbeck seed has shown excellent inhibition performance for mild steel in 1N HCl solution. The inhibition efficiency increased with the increase of inhibitor concentration. The maximum inhibition efficiency was achieved 94.69%. However, the inhibition efficiency gradually decreased with the rise in temperature ie, 80.62% to 74.97% for 303K and 333K respectively. This is due to the destability of the formed protective film on metal surface. It follows physical adsorption mechanism. The inhibitor is found to obey Langmuir adsorption isotherm. The values of free energy (ΔG_{ads}) and heat of adsorption (Q_{ads}) are negative suggested that the process is spontaneous and exothermic respectively. The thin film formation on the metal surface may also be confirmed by SEM, EDX, FT-IR and UV spectral studies.

5. ACKNOWLEDGMENT

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