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Green Approach to Corrosion Inhibition of aluminium and copper by *Ziziphus mauritiana* Fruit Extract in Hydrochloric Acid Solution

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Abstract: The corrosion behaviour of Aluminium and copper exposed to HCl solution and their inhibition in HCl containing 0.0644 – 1.288 g/L *Ziziphus mauritiana* Fruit Extract used as inhibitor was studied at room temperature using weight loss method. From weight loss data it was observed that the Inhibition efficiency increases with increase in concentration of the inhibitor reaching a maximum of 76.8% at room temperature for aluminium and 88.58% at room temperature for copper at 1.288 g/L concentration of EE*Zm*F. Corrosion rate was also found to decrease in the presence of inhibitor compared to the free acid solution. The inhibitor, *Ziziphus mauritiana* was found to obey Langmuir adsorption isotherm for both the metals. *Ziziphus mauritiana* is a better corrosion inhibitor for copper than aluminium. Surface analysis (FT-IR) was also carried out to establish the mechanism of corrosion inhibitor on aluminium and copper corrosion in hydrochloric acid medium.

Keywords: Aluminium,Copper, *Ziziphus mauritiana.* F ethanolic extract, Langmuir adsorption isotherm, FT-IR.

Introduction

Many metals and alloys which used in different human activities are susceptible to different mechanisms of corrosion due to their exposure to different corrosive media. Among these, aluminium and copper are very important. Aluminium is the second most used metal after iron; it is used in a large number of applications by itself and is used in a wide range of alloys. Because of the low atomic mass and the negative value of the standard electrode potential, aluminium potentially attracts as an anode material for power sources with high energy densities. Aluminum and its alloys lend themselves too many engineering applications because of their combinations of lightness with strength, their thermal and electrical conductivities, heat and light reflectivity and their hygienic and non-toxic qualities. Copper has been one of the preferred materials in industry due to its high electrical and thermal conductivities, mechanical workability, and its relatively noble properties. It is widely used in many applications in electronic industries and communications as a conductor in electrical power lines, and pipelines for domestic and industrial water utilities, including sea water, heat conductors, heat exchangers, etc. In efforts to mitigate aluminium and copper corrosion, the main tactic is to separate the metal from corrosive environments. This can be achieved using corrosion inhibitors. An inhibitor is a substance that retards the rate of corrosion of metals when added in minute quantity [1]. Every year, billions of dollars are spent on capital replacement and control methods for corrosion infrastructure [2]. Therefore, environmental protection legislation raised to prevent using the environmentally unacceptable materials[3]. Recently, the use of chemical inhibitors has been limited due to environmental regulations; plant extract are viewed as an incredibly rich source of naturally synthesized chemical compounds that can be extracted by simple procedures with low cost. A lot of natural products were previously used as corrosion inhibitors for different metals in various environments(4-9) and their optimum concentrations were reported. As far as the inhibition process is concerned, it is generally assumed that the adsorption of the inhibitors at the metal/aggressive solution interface is the first step in the inhibition mechanism.

As a continuation of our current interest on eco-friendly corrosion inhibitors, we report for the first time the inhibitive action of fruit extracts of *Ziziphus mauritiana* on the acid corrosion of aluminium and copper using the weight loss method at room temperature.

The *Ziziphus mauritiana* (ber) is one of the most common fruit trees of India and is cultivated practically all over the country. Ber fruits can be within the reach of the poor people and hence known as poor man's fruit. The phytochemical components of *Ziziphus mauritiana* fruit are fructose, glucose and galactose organic acids, citric, malonic and malic identified and other organic components such as tannins, phenolic compounds and flavonoids phenolic compounds identified are vanillic acid, ferulic acid and *p*-hydroxybenzoic acid, gallic acid[10-14].

Experimental

Preparation of specimens

Sheet of aluminium and copper obtained locally and of 0.16cm thickness was mechanically cut in to coupons of 3x2.4 cm^2 size, having a hole of uniform diameter of 0.12mm to facilitate suspension of the coupon in the test solution. The coupons were mechanically cleaned followed by polishing with emery sheet of fine quality to expose shining polished surface. To remove any oil and organic impurities coupons were degreased with acetone and finally with de-ionised water, dried and stored in a desiccator. Accurate weight of the samples was taken using electronic balance.

Inhibitor Material

Plant material (fruits of *Ziziphus mauritiana*) in natural condition was air dried (shade dried) for 20-25 days in shade. Then grained & powered. 35 g of finely powered dried material was taken in 1litre round bottom flask & sufficient quantity of ethyl alcohol (350ml.) was added to cover the powder completely. The RBF was covered with stopper & left for 8-10 days. On the completion of soaking period, the ethanolic solution is refluxed for 24 hrs. To concentrate the inhibiting chemicals. Thereafter, it is distilled & then filtered to remove any suspended impurities. The stock solution of the extract was stored in a clean corked bottle for further use. Or the extract of pods of *Ziziphus mauritiana* was obtained by refluxing it in Soxhlet in ethanol.

Preparation of Test Solutions

The solution of 0.5N HCl was prepared using doubly distilled water. 50 ml. of the aggressive solution (0.5N HCl) was measured in six separate 100ml. beakers labelled as S-0, S-1, S-2, S-3, S-4, S-5, & S-6. EE*Zm*F was added in the order of increasing concentration so as to have 0.0644, 0.1288, 0.322, 0.644, 1.030 & 1.288g/L in S-1, S-2, S-3, S-4, S-5& S-6 beakers respectively. No extract was added to the first beaker (S-0). All chemicals used were of AR grade.

Weight loss method

Experiments were conducted for the immersion times 6hour, 12hour, 18hour, 24hour, 48hour,and 72hours. Pre-weighted aluminium and copper specimens were suspended for different immersion periods in 0.5HCl with and without the inhibitor in different concentrations ranging from 0.0644 to 1.288 g/L. After the specified time the coupons were removed from test solution, thoroughly washed with double distilled water, dried well and then weighted. The percentage of inhibitor efficiency (IE%) for various concentrations of inhibitor were calculated as

$$\%IE = [(\Delta M_u - \Delta M_i) / \Delta M_u] \times 100 \qquad (1)$$

Where ΔM_u is mass loss without inhibitor and ΔM_i is mass loss with inhibitor.

Surface analysis

Fourier-Transfrom Infrared (FTIR) Spectroscopy

The formation of the adsorbed protective film over the surface of copper coupon was further established by carrying out FT-IR spectroscopic investigations. FT-IR was conducted on 8400 Shimadzu, Japan FT-IR spectrometer in the IR range from 4000 to 400 cm^{-1}. The FT-IR spectrum of the protective film was recorded by carefully removing the film, mixing it with KBr & making the pellet.

Results and Discussion

Weight loss data

The results concerned with the effect of period of immersion at various concentrations of the inhibitors on aluminium and copper metals in 0.5N HCl are shown in Table 1. It was found that extract inhibits the corrosion of aluminium and copper in 0.5N HCl solution at all the concentrations used in this study viz. 0.0644g/L to 1.288g/L. It was observed that inhibition efficiency increases with increasing concentration of inhibitor and maximum efficiency was observed at1.288g/L for both the metals.

The effect of immersion time on inhibition efficiency is shown in Fig.1 (a) for copper & (b) for aluminium. It has been observed that increase in immersion time for copper metal is affecting the inhibition efficiency and it increasing as we increase the immersion period from 6-72h. But for aluminium metal that increase in immersion from 24-72 h did not cause any significant change in inhibition efficiency, suggesting that inhibitor is effective in acid solution over this immersion range for aluminium. The inhibitor shows efficiencies in the range from 75% to a maximum 88.52% for copper and 43.75% to a maximum 76.8% for aluminium. The effect of concentration of EE*Zm*F on inhibition efficiency is shown in Fig.2 (a) for aluminium & (b) for copper. It was observed that inhibition efficiency increases with increasing concentration of inhibitor and maximum efficiency was observed at1.288g/L for both the metals. This excellent inhibition efficiency of *Ziziphus mauritiana* fruit extract may be attributed to the formation of a barrier film due to adsorption of inhibitor molecules on metal surface involving interactions between pi electrons of inhibitor molecules and vacant d-orbitals of both the metal surface atoms [6]. EE*Zm*F acts as inhibitor for both copper and aluminium metal corrosion in acidic medium.

The effect of immersion time on Corrosion rate is shown in Fig.3 (a) for aluminium & (b) for copper. It has been observed that Corrosion rates values are seen to decrease with increase in concentration. This actually shows that addition of EE*Zm*F to the acid solution retard the corrosion rate of both metals and that the extent of retardation is concentration dependent.

Kinetic /thermodynamic Treatment of Weight Loss Results

Assuming that the corrosion rate of aluminium copper & against the concentration of the EE*Zm*F obeys the kinetic relationship as shown:

$$\log \rho_{corr} = \log k + B \log C \qquad (2)$$

Where k is the rate constant and equals to ρ_{corr} at inhibitor concentration of unity; B is the reaction constant which, in the present case, is a measure for the inhibition effectives and C is the concentration of EE*Zm*F in g/L.

Fig.4 clearly illustrates a linear relationship between log ρ_{corr} vs. log C at 30 ± 1^{o}C for 0.5 M HCl, which confirm that the kinetic parameters (k and B) can be calculated by using the above equation. Table 2 shows the values of k and B. The slopes of the lines were observed negative, depicting the rate of corrosion process is inversely proportional to EE*Zm*F concentration, i.e. EE*Zm*F becomes more effective with increasing its concentration.

Adsorption isotherm

The efficacy of an organic compound as a successful inhibitor is mainly dependent on its ability to get adsorbed on the metal surface, which consists of the replacement of water molecules at the corroding interface. The adsorption of the inhibitor is influenced by the nature and the charge of the metal, the chemical nature of the inhibitor, distribution of the charge in the molecule, and the type of electrolyte [15, 16]. Basic information dealing with the interaction between the inhibitor molecule and metal surface can be provided by adsorption isotherm. The degree of surface coverage values for different concentrations of *Ziziphus mauritiana* extracts from the weight loss measurements obtained from (θ = % I/100), assuming a direct relationship between surface coverage and inhibition efficiency has been adapted to determine the adsorption characteristics of *Ziziphus mauritiana* fruit extracts in 0.5NHCl solution. To ascertain the nature of adsorption, the surface coverage values for *Ziziphus mauritiana* fruit extracts for both the metals were fitted into different adsorption isotherm models and correlation coefficients (R^2) were used to determine best fit which was obtained with the Langmuir adsorption isotherm. Fig.5 show Langmuir adsorption isotherm. It could be seen from table no. 3 that correlation coefficients (r^2) were in the range $0.999 \geq r^2 \geq 0.810$ for both the metals. The linear plots obtained suggest that the experimental data fit the Langmuir adsorption isotherm which is given by

$$(C/\theta) = C + 1/K_{ad} \qquad (3)$$

Where, C is the concentration of the inhibitor (EE*Zm*F), θ is the fractional surface coverage, and K_{ad} is the adsorption equilibrium constant.

Table 1. Corrosion Parameters for aluminium & copper in 0.5N HCl in Absence and Presence of Various Concentrations of Ethanolic Extract of *Ziziphus mauritiana* from Weight Loss Measurements at 30°C for various immersion period.

Time (h)	EE*Zm*F Concentration (g/L)	Corrosion parameters									
		Aluminium					Copper				
		Weight loss (mg)	Corrosion rate (ρcorr) (mmy^{-1})	Inhibition Efficiency (IE %)	Fractional Surface coverage (θ) x 10^{-2}	Adsorption Equilibrium Constant (K_{ad})	Weight loss (mg)	Corrosion rate (ρcorr) (mmy^{-1})	Inhibition Efficiency (IE %)	Fractional Surface coverage (θ) x 10^{-2}	Adsorption Equilibrium Constant (K_{ad})
6	S0	16	5.3645				8	0.8110			
	S1 0.0644	15	5.0292	6.25	6.25	1.0352	7	0.70962	12.5	12.5	2.2183
	S2 0.1288	14	4.6939	12.5	12.5	1.1091	6	0.6082	25	25	2.5880
	S3 0.322	13	4.3586	18.75	18.75	0.7167	5	0.5069	37.5	37.5	1.8633
	S4 0.644	12	4.0234	25	25	0.5175	4	0.4055	50	50	1.5528
	S5 1.030	10	3.3528	37.5	37.5	0.5823	3	0.3041	62.5	62.5	1.6175
	S6 1.288	**9**	**3.0175**	**43.75**	**43.75**	**0.6039**	**2**	**0.2027**	**75**	**75**	**2.3292**
12	S0	36	6.0350				18	0.9123			
	S1 0.0644	33	5.5321	8.33	8.33	1.4116	14	0.7096	22.22	22.22	4.4366
	S2 0.1288	31	5.1968	13.89	13.89	1.2522	12	0.6082	33.33	33.33	3.8819
	S3 0.322	29	4.8616	19.44	19.44	0.7496	10	0.5069	44.44	44.44	2.4845
	S4 0.644	27	4.5263	25	25	0.5176	8	0.4055	55.56	55.56	1.9410
	S5 1.030	22	3.6881	38.89	38.89	0.6176	6	0.3041	66.67	66.67	1.9410
	S6 1.288	**18**	**3.0175**	**50**	**50**	**0.7764**	**4**	**0.2027**	**77.78**	**77.78**	**2.7174**
18	S0	45	5.0292				30	1.0137			
	S1 0.0644	41	4.5822	8.89	8.89	1.5149	22	0.7434	26.67	26.67	5.6465
	S2 0.1288	38	4.2469	15.56	15.56	1.4302	18	0.6082	40	40	5.1759
	S3 0.322	36	4.0234	20	20	0.7763	15	0.5069	50	50	3.1056
	S4 0.644	31	3.4646	31.11	31.11	0.7013	12	0.4055	60	60	2.3292
	S5 1.030	26	2.9058	42.22	42.22	0.7092	9	0.3041	70	70	2.2645
	S6 1.288	**20**	**2.2352**	**55.56**	**55.56**	**0.9704**	**6**	**0.2027**	**80**	**80**	**3.1056**
24	S0	63	5.2807				5	1.2671			
	S1 0.0644	56	4.6939	11.11	11.11	1.9409	35	0.8870	30	30	6.6548
	S2 0.1288	52	4.3586	17.46	17.46	1.6423	29	0.7349	42	42	5.6222
	S3 0.322	49	4.1072	22.22	22.22	0.8873	23	0.5829	54	54	3.6457
	S4 0.644	42	3.5204	33.33	33.33	0.7764	19	0.4815	62	62	2.5335
	S5 1.030	32	2.6822	49.21	49.21	0.9402	14	0.3548	72	72	2.4956
	S6 1.288	**26**	**2.1793**	**58.73**	**58.73**	**1.1048**	**9**	**0.2281**	**82**	**82**	**3.5369**
48	S0	103	4.3167				215	2.7244			
	S1 0.0644	86	3.6043	16.50	16.50	3.0695	119	1.5079	44.65	44.65	12.526
	S2 0.1288	74	3.1013	28.15	28.15	3.0426	109	1.3812	49.30	49.30	7.5503
	S3 0.322	55	2.3050	46.60	46.60	2.7103	53	0.6716	75.35	75.35	9.4926
	S4 0.644	40	1.6764	61.16	61.16	2.4456	49	0.6209	77.21	77.21	5.2605
	S5 1.030	35	1.4668	66.02	66.02	1.8855	45	0.5702	79.07	79.07	3.6663

	S6 1.288	**28**	**1.1735**	**72.81**	**72.81**	**2.0796**	**30**	**0.3801**	**86.05**	**86.05**	**4.7878**
	S0	125	3.4925				305	2.5765			
	S1 0.0644	100	2.7940	20	20	3.8819	165	1.3938	45.90	45.90	13.175
	S2 0.1288	80	2.2352	36	36	4.3672	14	1.1826	54.10	54.10	9.1504
72	S3 0.322	58	1.6205	53.6	53.6	3.5874	75	0.6335	75.41	75.41	9.5238
	S4 0.644	45	1.2573	64	64	2.7605	50	0.4224	83.61	83.61	7.9192
	S5 1.030	38	1.0617	69.6	69.6	2.2219	40	0.3379	86.88	86.88	6.4295
	S6 1.288	**29**	**0.8103**	**76.8**	**76.8**	**2.5701**	**35**	**0.2957**	**88.52**	**88.52**	**5.9893**

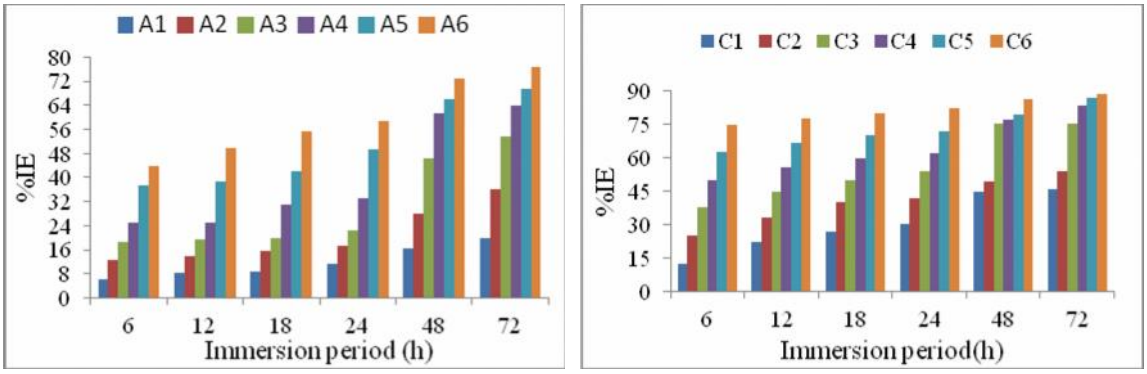

Fig.1 Shown the effect of immersion time on inhibition efficiency (a) for aluminium & (b) for copper.

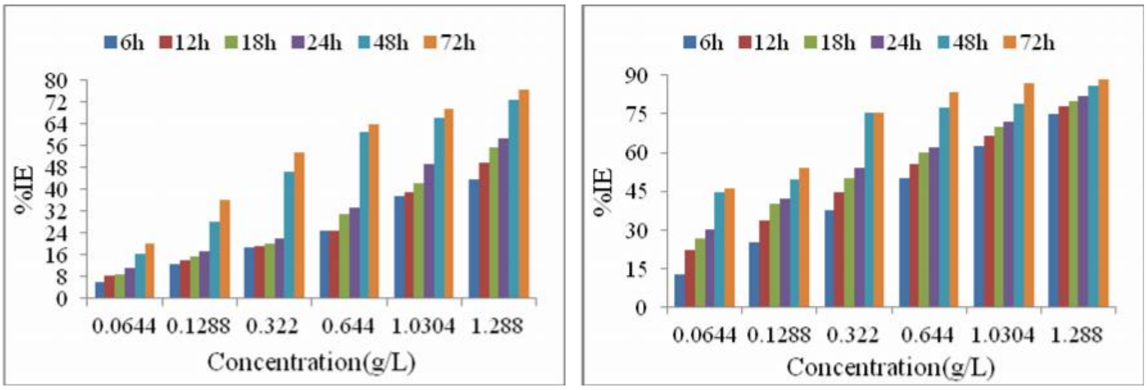

Fig.2 Shown the effect of concentration of EEZ*m*F on inhibition efficiency (a) for aluminium & (b) for copper.

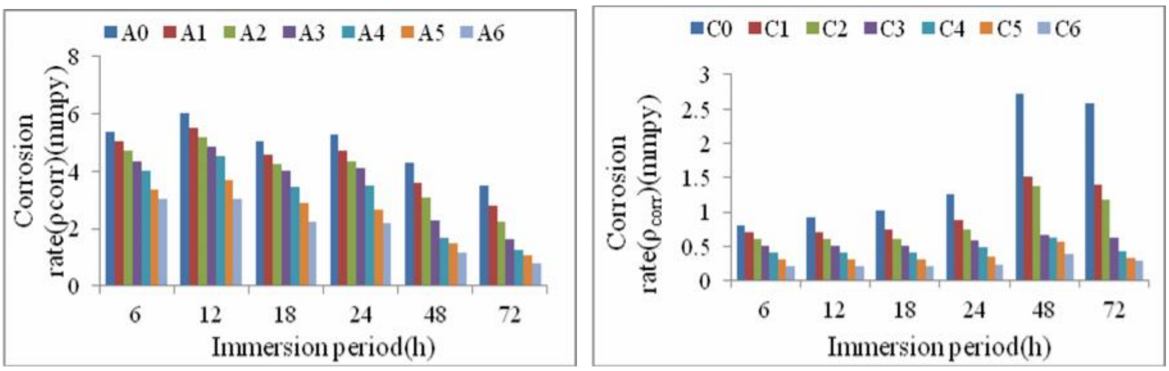

Fig.3 Shown the effect of immersion time on corrosion rate (a) for aluminium & (b) for copper.

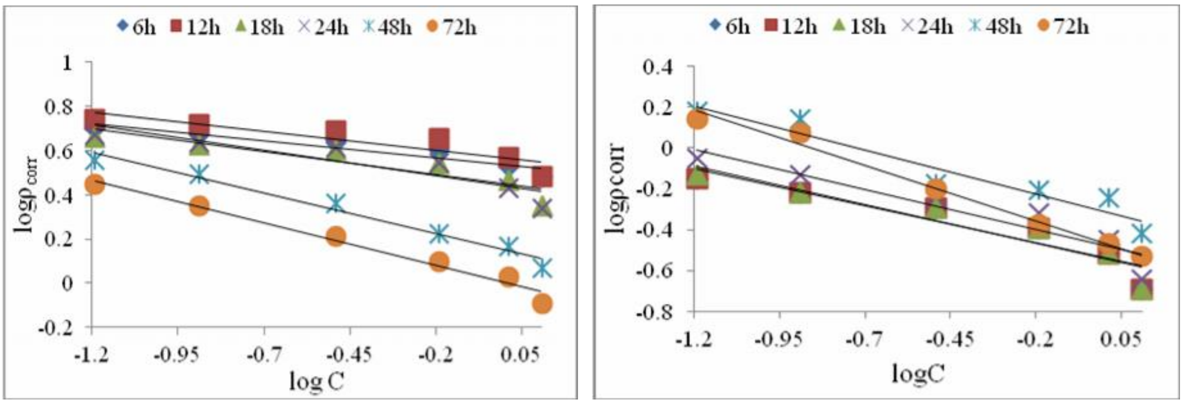

Fig.4: log ρ_{corr} vs. log C (a) for aluminium & (b) for copper.

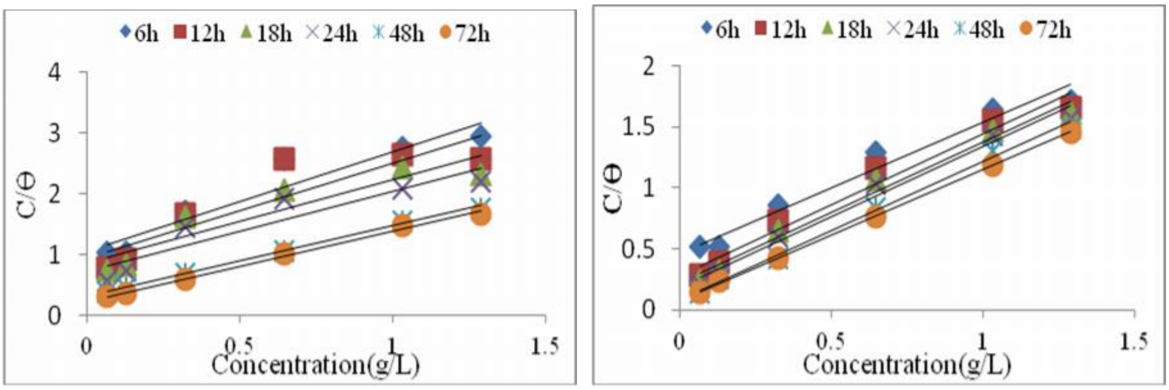

Fig.5 plot of C_{inh}/θ versus C_{inh} (a) for aluminium & (b) for copper.

Table 2 Kinetic parameters for aluminium and copper metal

Time (h)	Aluminium		Copper	
	B	k	B	k
6	-0.156	1.706	-0.365	0.584
12	-0.172	1.758	-0.365	0.584
18	-0.204	1.570	-0.376	0.583
24	-0.229	1.550	-0.395	0.621
48	-0.364	1.163	-0.434	0.732
72	-0.385	1.003	-0.544	0.628

Table 3 the correlation coefficient and slopes from Langmuir adsorption isotherm at different immersion time periods

Immersion Period (h)	Aluminium		Copper	
	Correlation coefficient (R^2)	(adsorption coefficient)	Correlation coefficient (R^2)	(adsorption coefficient)
6	0.904	0.9515	0.965	2.1141
12	0.810	1.0482	0.972	3.4246
18	0.849	1.1547	0.980	4.4643
24	0.858	1.3441	0.982	5.0761
48	0.997	3.1645	0.995	10.869
72	0.996	4.2194	0.999	11.764

FT-IR analysis

The FT-IR spectrum of the protective film was recorded by carefully removing the film, mixing it with KBr & making the pellet. Fig 6,7 and 8 show the FT-IR spectrum *of Ziziphus mauritiana* extract, film formed on aluminium and copper metal respectively. The broad peaks between 3200cm-1 to 3500cm^{-1}assigned to the presence of a superficial absorbed water, stretching mode of an OH and /or NH. The peaks at 2929 & 2858 corresponds to stretching vibration of aliphatic and aromatic C-H .The peaks at 1670, 1654, 1560, 1527,1122 & 1091cm^{-1} corresponds to stretching vibration of R2C=N; C=O; Aromatic substituted C=N, C=C (Aromatic ring) , stretching vibration of ether linkage (C-O) and stretching vibration of C-O. Shifting in the stretching frequency of C-O shows that there is shifting of electron cloud density from O atoms to co-ordinate with metal surface to form metal plant extract complex [17].

Mechanism of Inhibition

The existing data show that most organic inhibitors adsorb on the metal surface by displacing water molecules on the surface and forming a compact barrier. Availability of nonbonded (lone pair) and p-electrons in inhibitor molecules facilitate electron transfer from the inhibitor to the metal. A coordinate covalent bond involving transfer of electrons from inhibitor to the metal surface may be formed. Most organic inhibitors contain at least one polar group with an atom of oxygen nitrogen or sulphur or in some cases selenium and phosphorus.

The plant extractof *Zizyphus mauritiana* contain the phytochemical constituents such as fructose, glucose and galactose organic acids, citric, malonic and malic identified and other organic components such as tannins, phenolic compounds and flavonoids phenolic compounds identified are vanillic acid, ferulic acid and *p*-hydroxybenzoic acid, gallic acid. The above said phytochemical constituents present in *Zizyphus mauritiana*, having many active centers such as oxygen and nitrogen, are adsorbed on the metal surface and the effectiveness of these inhibitors on the corrosion of aluminium and copper may be due to the electron densities on the active centres. The adsorption takes place through the active centers. The possible synergistic interactions between adsorbed species could also contribute to the high IE of the extract. In the current investigation the fruit extract of *Zizyphus mauritiana* was found to perform as a good inhibitor for aluminium and copper corrosion.

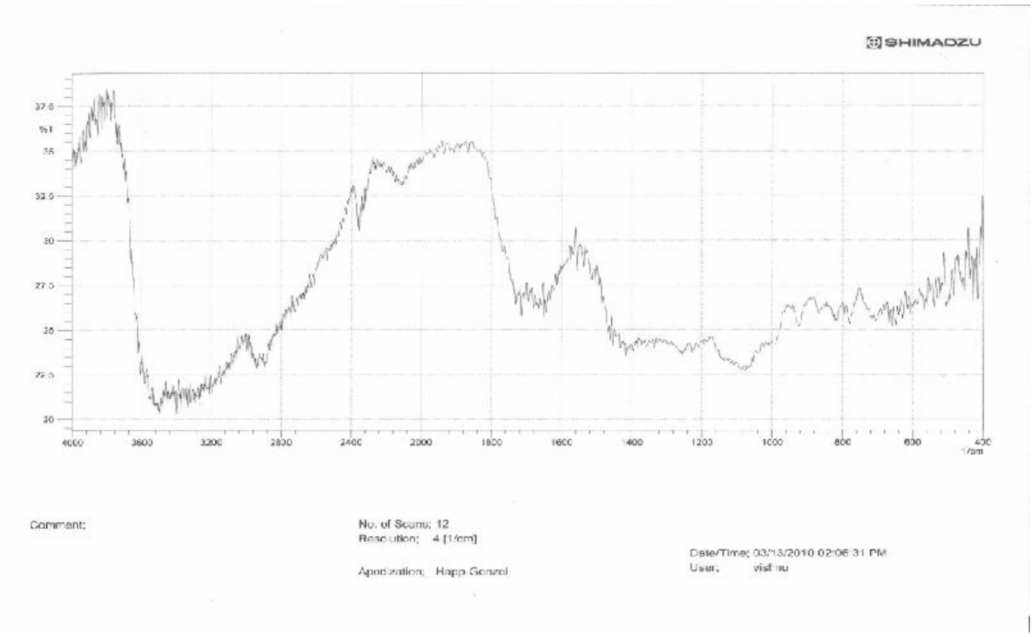

Fig:6 FTIR spectra of EE*Zm*F

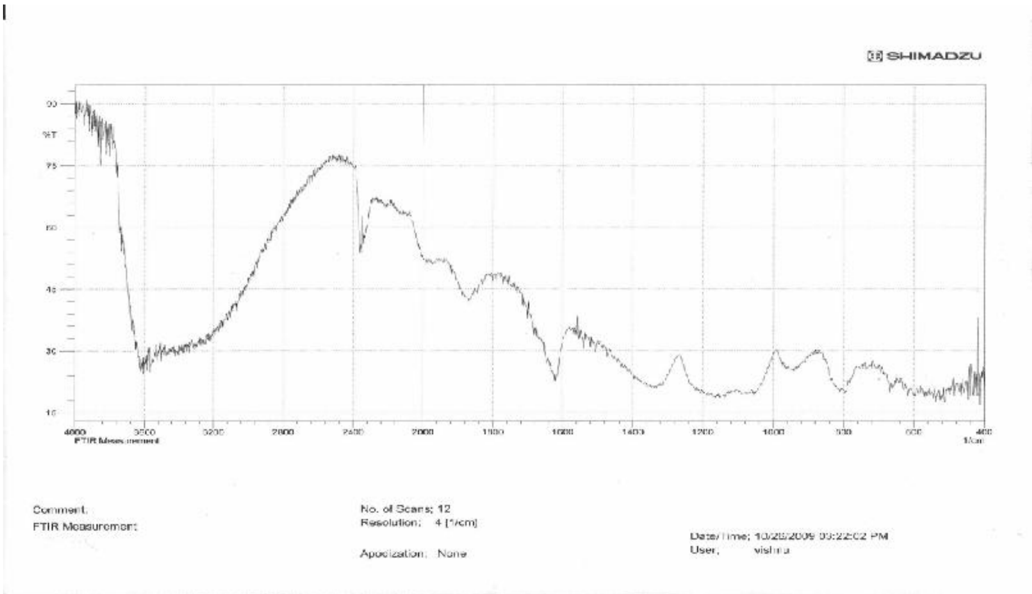

Fig: 7 FTIR spectra of adsorbed film of EE*Zm*F on Al metal surface in 0.5 N HCl containing 1.288g/L EE*Zm*F

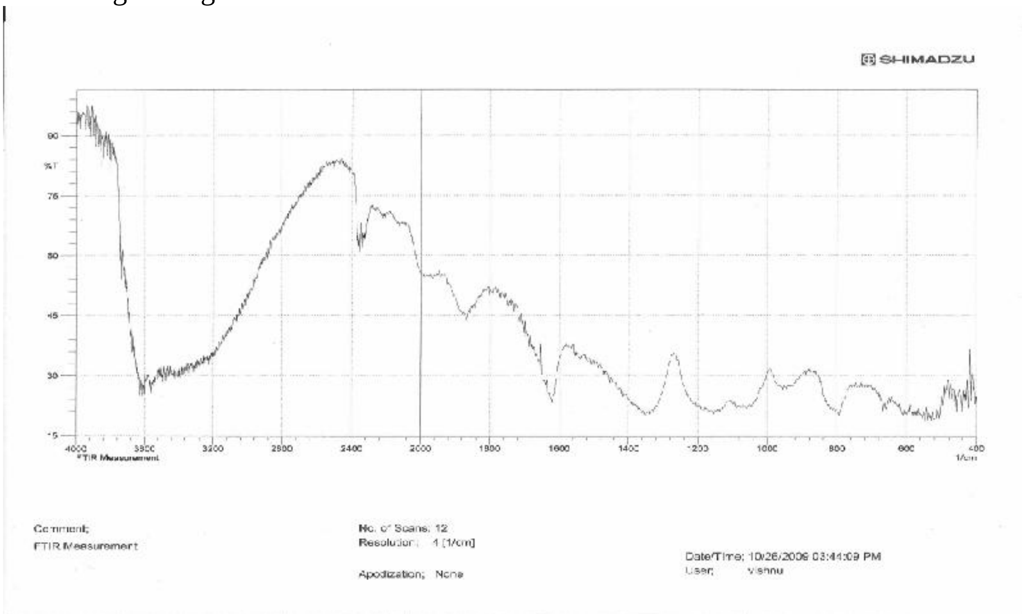

Fig: 8 FTIR spectra of adsorbed film of EE*Zm*F on Cu metal surface in 0.5 N HCl containing 1.288g/L EE*Zm*F.

Conclusion

1. The natural extract *Zizyphus mauritiana* was found to be effective inhibitor in the acidic medium giving up to 76.5% and 88.52% efficiency for aluminium and copper metal respectively. The optimum concentration of extract is 1.288g/L at 303 K.
2. *Ziziphus mauritiana* acts as inhibitor for both aluminium and copper corrosion in acidic medium being a better inhibitor for copper than for aluminium.
3. Adsorption model-Langmuir adsorption isotherm fit well as evident from the correlation coefficient values (R @ 1 in all cases). This proves the applicability of all the models to the process.
4. The surface analysis study by FT-IR spectroscopy confirms the corrosion inhibition by the inhibitor *Zizyphus mauritiana*.
5. The FTIR spectrum showed that the inhibition is due to the formation of the film on the metal/acid solution interface through adsorption of *Zizyphus mauritiana* (ber) fruit extract molecules.

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