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Ziziphus Jujuba Leaves as Corrosion Inhibitor for Mild Steel in 0.5M H_2SO_4

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Abstract: *The inhibitive nature Ziziphus Jujuba leaves (ZJL) on the corrosion of Mild steel in 0.5M* H_2SO_4 *has been examined by weight loss method and polarization technique. The acid extract of ZJL brought out a maximum inhibition of 99.08%.The extract was temperature resistant in nature and the inhibition efficiency was found to be 92.82% at 353° C. The results obtained were fit into Langmuir and Temkin adsorption. Thermodynamic parameters were also calculated.*

Keywords: Inhibitor, Acid extract, *Ziziphus Jujuba,* Mild steel.

I. INTRODUCTION

Corrosion is an electrochemical reaction between a metal and its environment. This causes change in the properties of the metal which leads to impairment of the function of the metal. Corrosion inhibitors are substances generally used to reduce corrosion rates. Natural products from plant extracts are of great interest as green inhibitors [1]. Green inhibitors are excellent inhibitors due to their non-toxicity and biodegradability [2]. The plant extracts presumably possess biocompatibility due to their biological origin. The literature survey revealed large number of green inhibitors is used as potential inhibitors under a variety of corrosive environments for most of the metals [3]. The present study aim to show the efficacy of *Ziziphus Jujuba*leaves as inhibitor on mild steel corrosion in0.5M H_2SO_4

II. MATERIALS AND METHODS

The design of the present investigation contains the following steps.

2.1 Sample Selection

Mild steel which is used as an engineering material in structural and automobile applications suffers severe corrosion in aggressive environment. Hence the present study was carried out using mild steel. Rectangular sample of area 1×5 $cm^2$was cut from a large sheet of mild steel and a hole was drilled at the top, mechanically polished, degreased, washed with de ionized water then thoroughly dried and kept in desiccators for weight loss tests. The mild steel specimens used had the following percentage elemental composition.

Element	C	Mn	Si	P	S	Cr	Mo	Ni
% Composition	0.143	0.271	0.041	0.035	0.030	0.002	0.018	0.006

2.2 Test Medium

Acid solutions are widely for acid pickling and acid cleaning process in industries [4]. Among the commercially available acids hydrochloric acid and sulphuric acid are used in nearly all industries and is vital commodity in our national economy. Experiments were performed in 0.5 M H_2SO_4.

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2.3 Preparation of Inhibitors

The extracts was prepared by refluxing 25gms of Ziziphus *Jujuba* leaves (ZJL)in 500ml of H_2SO_4 for three hours and kept overnight for cooling. The cooled extract was filtered and made up to 500ml with 0.5M H_2SO_4 to get 5% extract of the inhibitor.

2.4 Techniques Employed

- Weight loss method
- Electrochemical measurements

Weight Loss Method

Pre weighed coupons were immersed in triplicate with the help of glass hook into a beaker containing 100 ml of acid with and without inhibitor for a particular period of time. The coupons are then washed, dried and reweighed. The average weight loss of the coupons was recorded. Varying the parameters such as concentration(0.1% - 0.7%),time of immersion(1/2 hr, 1 hr, 3 hrs, 6 hrs, 12 hrs,&24 hrs) and temperature (313 K – 353 K)the experiments were conducted.

Corrosion rate(C.R), percentage of inhibition(I.E) and surface coverage(θ)arewere calculated using the following equations

$$C.R\ (mpy) = \frac{534 \text{ X W}}{\text{D X A XT}}$$

$$I.E\ (\%) = \frac{\text{W0}-\text{W}}{\text{Wo}}\ \ \text{X}\ 100$$

$$\theta = W_0 - W / W_0$$

Electrochemical Methods

Polarization Techniques

Polarization studies were conducted at a scan rate of 2mV/sec starting from -0.1 to -1mV with respect to the corrosion potential in the presence and absence of the inhibitor. 1sq.cm. of polished mild steel surface was exposed and the electrochemical studies are carried out at 303 K.

Tafel Plot

In the ***Tafel*** plot technique, a controlled scan can be applied, extending in both the anodic and the cathodic directions of corrosion potentials for a few hundred milli volts. The linear region of the plot (applied potential Vs log current) is projected to intersect. This defines corrosion current (I_{corr}) and the corrosion potential (E_{corr}) and the slope of the linear region is the Tafel slopes (b_a and b_c).

The inhibitor efficiency was calculated using the following equation,

$$I.E\ (\%) = \frac{\text{Icorr(blank)}-\text{Icor(inhibited)}}{\text{Icorr(blank)}}\ \ \text{X}\ 100$$

From LPR technique

$$I.E\ (\%) = \frac{\text{Rp(inhibited)}-\text{Rp(blank)}}{\text{Rp(inhibited)}}\ \ \text{X}\ 100$$

Impedance Spectroscopy

In this method an AC signal of 5 – 10 mV of frequency 10 KHz to 10MHz is applied to the system. Impedance date can be presented in the form of Nyquist or Bode plot. From the data, the R_{ct} and C_{dl} are obtained.

The I.E can be calculated using the equation,

$$I.E\ (\%) = \frac{\text{Rct(inhibited)} - \text{Rct(blank)}}{\text{Rct(inhibited)}}\ \text{X}\ 100$$

III. RESULTS AND DISCUSSION

Results obtained for the investigations on *Ziphusjujuba* leaves (ZJL) as corrosion inhibitor for mild steel in0.5M H_2SO_4 are tabulated and discussed here.

3.1 Weight Loss Method

The results are illustrated in Table I and Fig.1. The data revealed that the corrosion rate of mild steel decreased with increasing concentration of the extract. From the experimental results, it can be concluded that the inhibition efficiency increased upto 6 hrs (99.08 %) and after that there is slight decrease in inhibition efficiency at 12 hrs and then stabilizes at 24 hrs. In the present investigation it is also observed that the inhibitor functions very well at higher concentration for all periods of immersion [5].The increase in IE with increase in concentration of the extract may be attributed to the increase in the number of molecules adsorbed over the MS surface.

TABLE 1: Effect of Concentration & Time on inhibition efficiency of ZJL extract in 0.5 M H_2SO_4

S. No	Conc (%)	1/2h		1h		3h		6h		12h		24h	
		CR	IE (%)	CR	IE (%)	CR	IE (%)	CR	IE (%)	CR	IE (%)	CR	IE (%)
	Blank	514.59		453.53		1032.05		844.90		1020.06		1073.87	
	0.1	313.98	38.98	165.71	63.46	178.79	82.67	144.26	82.92	175.52	82.79	108.47	89.89
	0.2	279.10	45.76	187.51	58.65	129.37	87.46	114.10	98.43	138.09	86.46	104.11	90.30
	0.3	279.10	45.76	161.35	64.42	119.19	88.45	101.75	98.6	120.64	88.17	96.66	90.99
	0.4	204.96	60.16	128.64	71.63	109.74	89.36	117.37	98.38	105.8	89.66	92.30	91.40
	0.5	139.55	72.88	100.30	77.88	101.02	90.21	94.48	98.7	99.93	90.20	91.21	91.50
	0.6	130.82	74.57	91.57	79.80	93.20	90.96	91.57	98.74	86.48	91.52	81.40	92.41
	0.7	113.38	77.96	100.30	77.88	87.21	91.54	74.13	99.98	61.41	93.97	70.86	93.40
	0.8	113.38	77.96	78.99	82.58	84.30	91.83	66.86	99.08	54.87	94.62	59.77	94.43

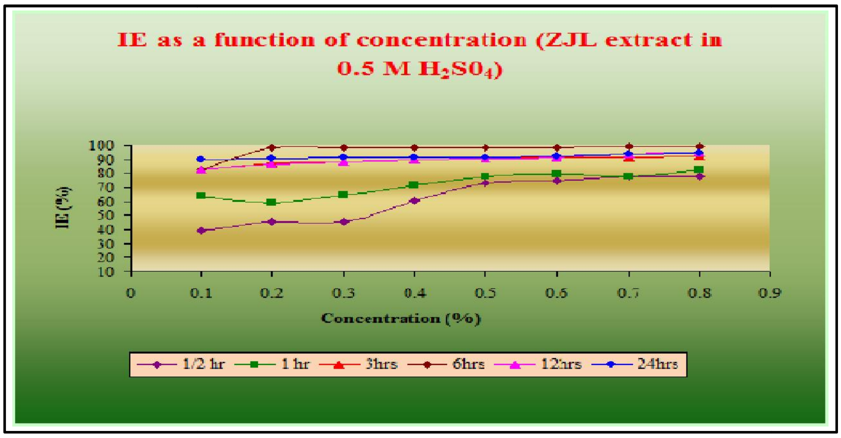

Fig.1 Inhibition efficiency as a function of concentration of ZJL

Temperature studies were also carried out in the absence and presence of varying concentration of the inhibitor at 303 K, 313 K, 323 K, 333 K, 343 K and 353 K. The results are presented inTable II and Fig.2The results infer that inhibition efficiency increased with temperature up to 323 K. Further increase in temperature showed a decrease in efficiency and it stabilised to 92.8% at 353 K. The decreased protection efficiency at higher temperature may be explained from the fact that increase of temperature affected the rate of adsorption/ desorption ratio and if the rates of the desorption was faster than the rate of adsorption, there might be decrease in inhibition efficiency with temperature

TABLE 2: Effect of Temperature on the IE of ZJL extract in 0.5 M H_2SO_4

Sl. no	**Conc**	**303K**		**313K**		**323K**		**333K**		**343K**		**353K**	
		CR	**IE (%)**	**CR**	**IE (%)**	**CR**	**IE (%)**	**CR**	**IE (%)**	**CR**	**IE (%)**	**CR**	**IE (%)**
1	Blank	514.59		1744.38		2773.56		5904.72		9393.48		17007.70	
2	0.1	313.98	38.98	566.92	67.5	409.92	85.22	1430.39	75.77	2040.92	78.27	4169.06	75.48
3	0.2	279.10	45.76	453.53	74.0	427.37	84.59	1203.62	79.61	1692.04	81.98	2921.83	82.82
4	0.3	279.10	45.76	401.20	77.0	375.04	86.47	1125.12	80.95	1578.66	83.19	2511.90	85.23
5	0.4	204.96	60.16	383.76	78.0	331.43	88.05	994.29	83.16	1378.06	85.32	2197.99	87.07
6	0.5	139.55	72.88	375.76	78.5	313.98	88.67	915.79	84.49	1247.23	86.72	2084.53	87.74
7	0.6	130.82	74.57	357.39	79.5	305.26	88.99	959.40	83.75	1238.50	86.81	1569.94	90.76
8	0.7	113.38	77.96	313.98	82.0	305.26	88.99	889.63	84.93	1116.40	88.11	1395.50	91.79
9	0.8	113.38	77.96	261.65	85.0	244.21	91.19	680.30	88.47	1055.34	88.76	1221.06	92.82

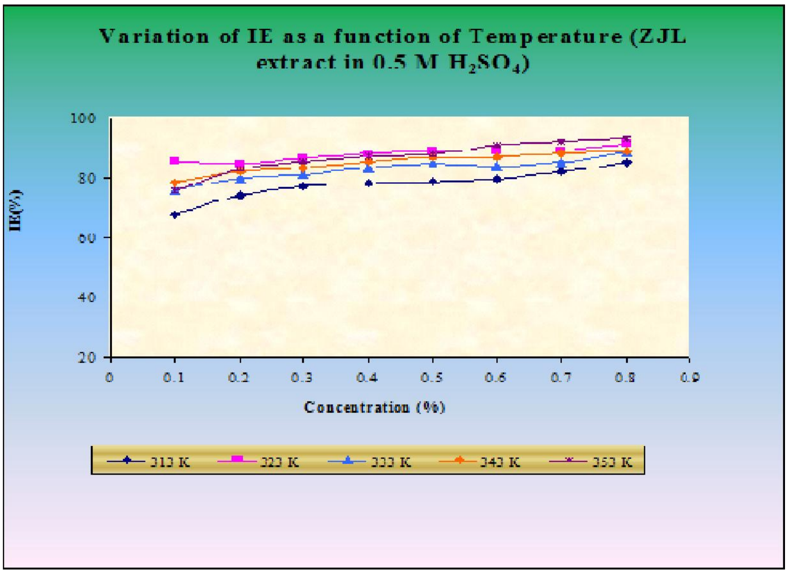

Fig.2 variation of IE as a function of temperature

Adsorption isotherm

The dependence of surface coverage on concentration is studied through the following adsorption isotherms[6].

Langmuir [log (θ /1 – θ) Vs log C]

Temkin (θ Vs log C)

The plots of C_{inh}/θ versus C_{inh} gave a straight line (Fig 3) and thus follow the Langmuir adsorption isotherm. This suggests that the inhibitor molecules are adsorbed over the metal surface forming a barrier, which prevents further contact of the metal with electrolyte.

A straight line was obtained when the surface coverage was plotted against log C for the inhibitor. This shows that the adsorption of the inhibitor at the mild steel acidic solution interface obeys Temkin adsorption isotherm (Fig 4).

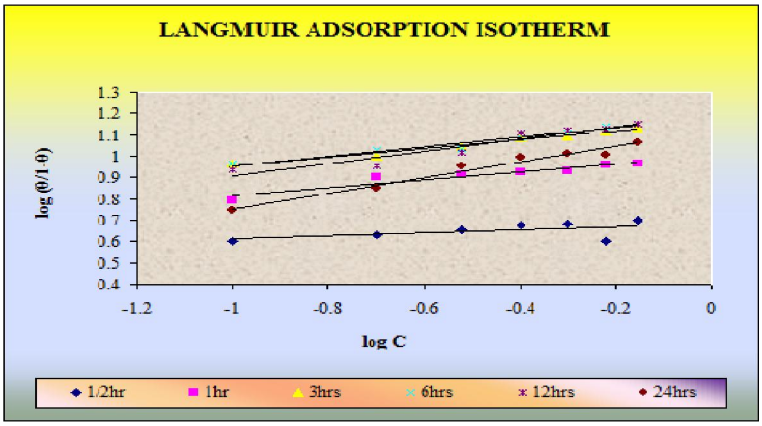

Fig 3.Langmuir adsorption isotherm

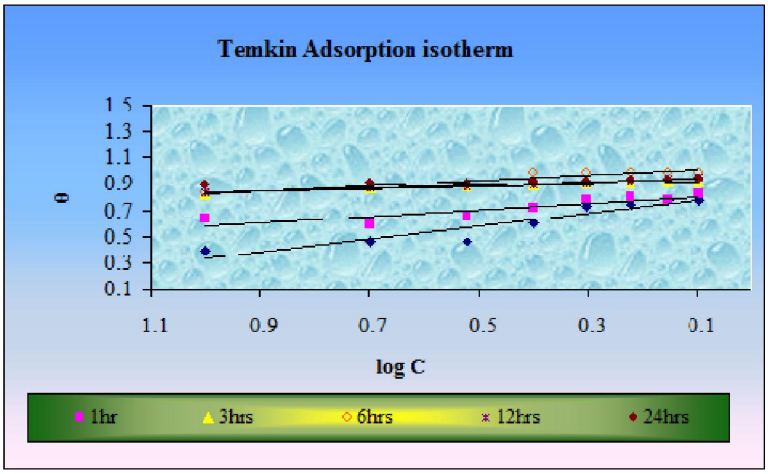

Fig.4 Temkin adsorption isotherm

Activation energy (E_a)

The activation energy at different concentration of the inhibitor at various temperatures was determined by plotting log CR Vs 1/T [7]. (Arrhenius plot). The estimated values of E_a for MS in ZJL in 0.5M H_2SO_4 are listed in the Table III and Fig 5.From Table III, it is can be seen that the energy of activation changes in the presence of the inhibitor.The results infer that the interaction between the metal surface and the inhibitor under study is strong enough to prevent corrosion.

TABLE III: Variation of thermodynamic and kinetic parameters with concentration and temperature (ZJL in 0.5 M H_2SO_4)

Sl. No	-Ea (KJ/mol)	ΔG at various temperature (KJ/mol)					ΔS KJ/mole	ΔH KJ/mole
		313K	323K	333K	343K	353K		
1	53068.7	12.33	15.46	14.25	15.08	15.06	-0.05	2.222
2	51037.4	13.15	15.33	14.86	15.74	16.37	-0.0411	-1.1597
3	46703.8	13.57	15.74	15.10	15.98	16.90	-0.034	-3.786
4	46794.9	13.72	16.12	15.51	16.44	17.85	-0.0338	-4.1526
5	45002.1	13.79	16.28	15.78	16.77	17.53	-0.0493	0.6909
6	43986.4	13.95	16.37	15.63	16.80	18.84	-0.0491	0.5623
7	40052.9	14.37	16.37	15.88	17.13	18.84	-0.0452	-0.9484
8	39390.3	14.94	17.03	16.73	17.32	19.27	0.8545	-4.52834

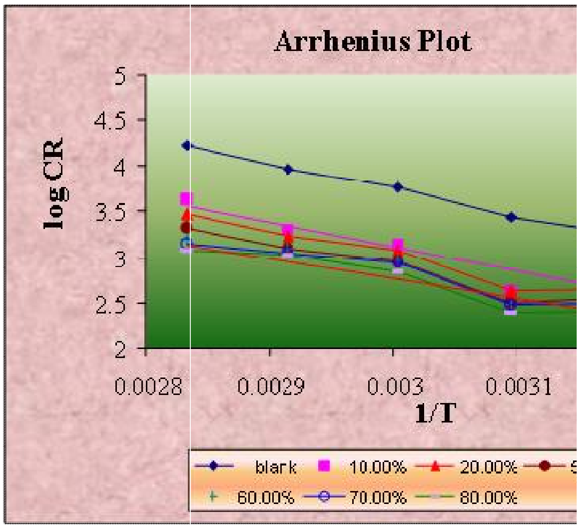

Fig 5. Arrhenius plot

Free energy of adsorption

The obtained value of ΔG (Table III) suggests a strong physical adsorption of the components of the extract on to the steel surface in 0.5M H_2SO_4 solutions and it is spontaneous[8].

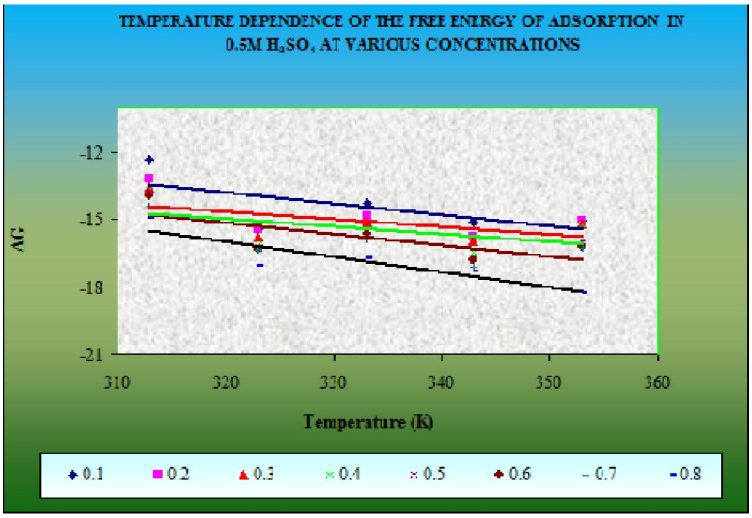

Fig 6. Free energy of adsorption

Enthalpy and Entropy of Adsorption

The intercept (ΔH) and slope (ΔS) obtained from the plot – ΔG vs. T (Fig 6) was listed in the Table III. This agrees with general suggestion that more negative values of ΔG and positive value of ΔS lead to increase in inhibitor efficiency. The negative values of ΔH obtained in this study indicate that the adsorption of ZJL extract molecules is an exothermic reaction. The values for the heat of adsorption for the inhibitor in 0.5M H_2SO_4 was found to be less than (40KJ/mol).

This indicates that the inhibitor was adsorbed physically. The positive values of entropy of adsorption ΔS suggest the adsorption to be a spontaneous process.

Electrochemical Measurement

Potentiodynamic Studies

Kinetic parameters of corrosion processes ($I_{corr,\ be}$ & b_c) estimated from the polarization curves obtained in the presence and absence of the inhibitor are recorded in Table A.the results indicated a considerable reduction in I_{corr} values in the presence of the inhibitor. This confirms the inhibitive nature of the extract and also the adsorption of the plant extract on metal surface. The values of IE are found to be increasing with with increase in concentration of inhibitor. A maximum of 91.83% of inhibition was obtained with 0.7% concentration. No significant change in E_{corr} values in the presence of inhibitor indicates the mixed nature of the inhibitor.

TABLE IV: Tafel Polarization measurements of mild steel in the presence of the ZJL extract in 0.5M H_2SO_4

Sl.No	**Conc. (%)**	**I_{corr} (Amp/cm^2)**	**b_a (mv/dec)**	**b_c (mv/dec)**	**E_{corr} (mv/sec)**	**IE %**
1	Blank	0.0005174	217.87	187.5	-544.23	
2	0.1	0.0006094	117.14	86.98	-511.82	88.22
3	0.2	0.0007771	142.77	96.01	-506.21	84.98
4	0.3	0.0006937	142.84	92.73	-505.31	86.59
5	0.4	0.0007775	148.69	94.31	-494.83	84.97
6	0.5	0.0007199	143.43	91.94	-493.05	86.08
7	0.6	0.0004295	154.24	82.29	-499.16	91.69
8	0.7	0.0004222	153.41	80.03	-495.45	91.83
9	0.8	0.0004568	152.22	81.71	-495.67	91.17

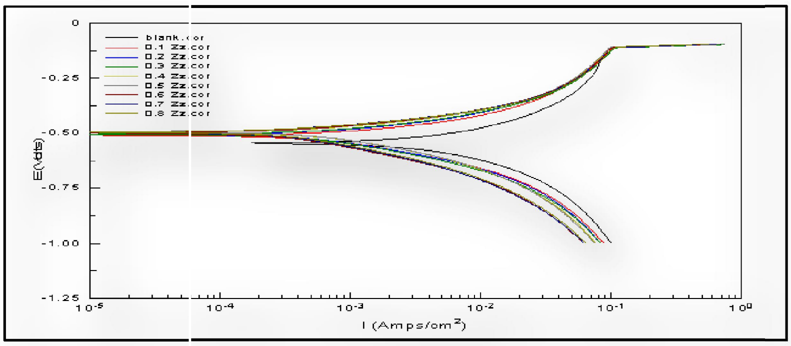

Fig 7. Potentiodynamic polarization curves of ZJL Extract 0.5M H_2SO_4

Impedance

The impedance parameters and the Nyquist plot of mild steel in 0.5M H_2SO_4 in the presence of various concentrations of the inhibitor is shown in Table V and Fig 8.It can be seen that the impedance spectra are not perfect semicircle[9]. It is due to adsorption of inhibitor as well as the the pits on the electrode surface. Table V shows R_{ct} values increased withincreased concentration of ZJL. The high R_{ct} values of inhibited electrodes can be explained by the building up of protective layers and the effective barrier behaviour of adsorbed layers. The C_{dl} values tend to decrease with increase in concentration of ZJL. The decrease in C_{dl} values can result from a decrease in local dielectric constant or an increase in thickness of the electrical double layer.

TABLE V: R_{ct}, R_p, C_{dl}, &IE of MS in presence of ZJL extract

Sl.no	Conc	R_{ct}(Ωcm^2)	IE	R_P	IE	C_{dl}	θ

	(%)		(%)	Ω/cm^2	(%)	(f/cm^2)	
1	Blank	11.77		8.644		0.00014015	
2	0.1	60.44	80.51	25.706	66.37	0.00012001	0.1437
3	0.2	54.61	78.43	31.363	72.43	0.00020107	-0.4346
4	0.3	62.25	81.08	33.162	73.93	0.0001875	-0.3378
5	0.4	51.18	76.98	32.807	73.66	0.00015198	-0.0844
6	0.5	50.44	76.65	34.510	74.95	0.00013815	0.01427
7	0.6	88.01	86.61	49.388	82.49	0.00006892	0.50820
8	0.7	130.19	90.95	51.562	83.23	0.00006936	0.5049
9	0.8	108.1	89.10	48.057	82.01	0.00008188	0.4157

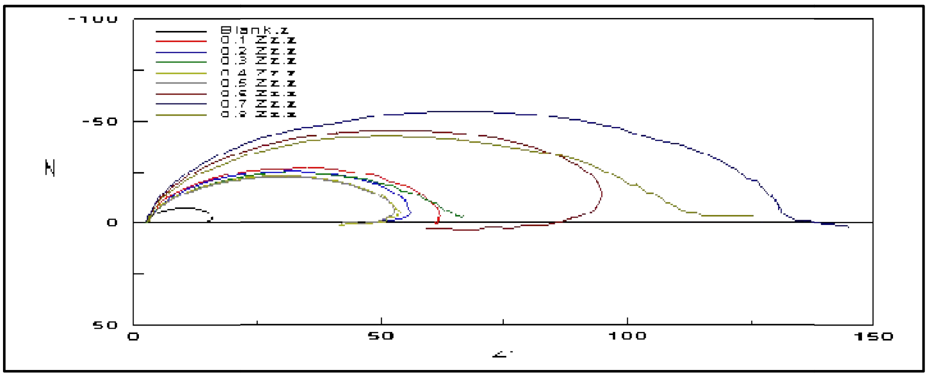

Fig. 8 Impedance curves of Mild steel in the presence of ZJL extract 0.5M H_2SO_4

Comparison of weight loss and electrochemical methods

The difference in inhibition efficiency by different techniques can be attributed to the fact that weight loss method gives average corrosion rates, while electrochemical measurements give instantaneous corrosion rates. The difference may be expected to arise because of the difference in time required to form an adsorbed layer, which brings down corrosion. Fig 9 depicts the performance of ZJL extract by weight loss and electrochemical measurements.

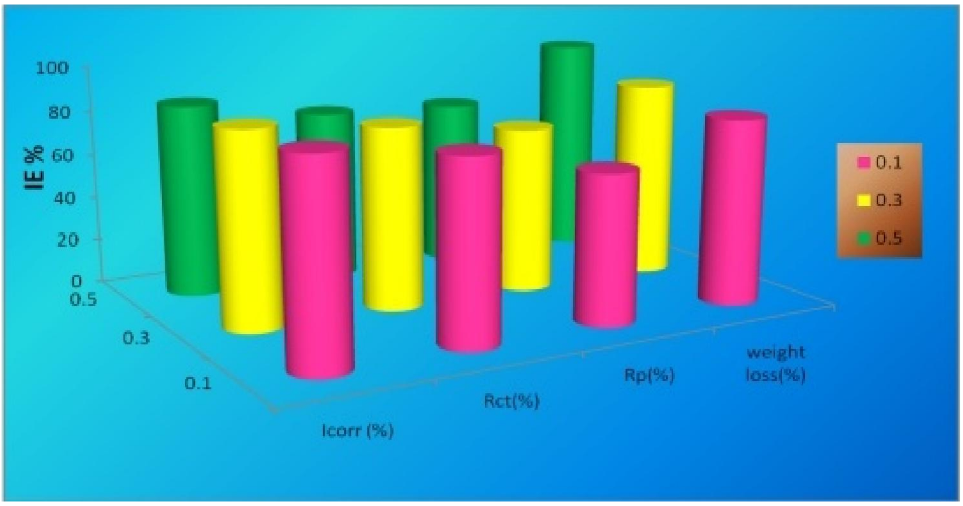

Fig 9 Performance evaluation of ZJL extract by various methods

Shelf – life of leaves extract of ZJL

The performance of the extract of ZJL was studied every one week for duration of two and half months by storing them at room temperature and the refrigerator. Every week the efficiency of the extracts was studied using weight loss method. The results are presented in table VI.No fungal growth was noticed in the extract at both storage conditions. There was no unfavourable odour or release of toxic gases during storage. The data in table revealed that the inhibition efficiency slowly decreased during storage. This may be due to the some chemical reactions between the constituents. Due to the reactions the active groups responsible for the adsorption on the MS surface covered decreased showing decline of inhibition efficiency. The extract showed almost same efficiency at room temperature which confirms that it can be stored at room temperature itself. The performance of the extract may be maintained by adding suitable stabilizing agents. The extract was found to have reasonable 'shelf life'.

TABLE VI: *Comparison of durability test for ZJL*

Weeks	IE%	
	Room temperature	**Refrigerated condition**
1st week	91.94	91.38
2nd week	90.14	89.14
3rd week	88.02	87.37

IV. CONCLUSION

The acid extract of ZJL could bring out a maximum inhibition of 99.08% in H_2SO_4 acid and 92.82% at 353 K. Thermodynamic parameters calculated could reveal chemisorption process and spontaneity of adsorption. The inhibitor used in the current study followed Langmuir and Temkin adsorption isotherm. Results from the polarization techniques such as tafel and impedance spectroscopy could be comparable with the classical weight loss methods. The eco-friendly inhibitor under study behaved as mixed type inhibitor [10]. Thus,Ziziphus*jujuba* leaves extract has proved to be zero cost, eco-friendly and highly economical inhibitor.

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