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Potential of *Ziziphus jujuba* leaves extract as green corrosion inhibitor against carbon steel in 1N HCl solution

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ABSTRACT

The inhibitive action of the Ziziphus jujubaleaves (ZJL) extract against corrosion of carbon steel in 1N HCl was investigated using weight loss measurements, gasometric method, potentiodynamic polarization curves and electrochemical impedance spectroscopy methods. The results obtained from these methods indicate that the extracts perform as a good green corrosion inhibitor in acidic medium and inhibition efficiency increased with extracts concentration. The maximum inhibition efficiency of 82.2% was obtained at the best concentration of 800 ppm of ZJL extract. The effects of temperature and immersion time on carbon steel in 1N HCl were also studied. Polarization curves show that ZJL extract act as a mixed-type inhibitor in hydrochloric acid. EIS shows that the capacitance of double layer decreases and charge-transfer resistance increase with the optimum concentration of 800 ppm of ZJL extract, confirming the adsorption process mechanism. The adsorption of ZJL extract on the surface of the carbon steel follows the Langmuir adsorption isotherm. The mechanism of inhibition was confirmed by kinetic and thermodynamic parameters obtained from 303K to 363K temperatures using weight loss method. The metallurgical microscope results established the formation of a protective layer on the carbon steel surface.

Keywords: Ziziphus jujubaextract, Corrosion inhibitors, Carbon steel, Polarization, EIS.

INTRODUCTION

Carbon steel, stainless steel and mild steel are the most widely used structural and fabrication materials in industries and constructions because of its low cost, easy availability and ease of fabrication [1] but the poor corrosion resistance in acid is a major constraint in their applications [2] and cause economic consequences in terms of repair, replacement, product losses, safety, and environmental pollution. [3].Therefore, investigation of corrosion inhibitors for steel corrosion in acid solutions is important for its realistic applications [4].Many studies have been reported that almost all corrosion inhibitors are synthetic organic compounds containing hetero atoms such as nitrogen, sulphur, phosphorous, and oxygen show significant inhibition efficiency but most of these substances are not only expensive but also toxic non-biodegradable thus causing pollution problems [5].Thus, these deficiencies have incited the search for their substitution.The naturally occurring molecules exhibiting a strong affinity for metal surfaces under different environment because they are environmentally acceptable, non-toxic, cost effective, and have abundant availability [6].Recently, several natural plants such as, *Combretum bracteosum,Medicago Sativa, Justicia gendarussa, Jasminum nudiflorum, Vitex negundo, Prosopis cineraria, Emblica officinalis, Solanam Xanthocarpum, Kopsia singapurensis, Heinsia crinata, Dacryodis edulis, Murraya koenigii, Oxandra asbeckii, Sennaauriculata* [7-20] have been used as corrosion inhibitors commonly known as green corrosion inhibitors.

Ziziphus jujuba is a shrub belongs to family Rhamnaceae and it is known as “Elantai” in Tamil. It is distributed in many parts of the world but mainly populates in tropic and warm, temperate region. [21]. Phytochemically, it has high medicinal value due to the presence of cyclopeptide alkaloids, polysaccharides, flavonoids, terpenoids, tannins, saponins, pectin, triterpenoic acids and lipids [22]. It has a major part in treatment of various ailments like analgesic, antipyretic, anti-inflammatory, sedative, antioxidant, antibacterial, GIT protective, antispasmodic, antidiabetic and antifungal activities [23].The present research work is devoted to study the inhibition characteristics of *Ziziphus jujuba leaves (ZJL)* extract on the corrosion of carbon steel in 1N HCl medium, using weight loss, gasometric, Tafel polarization and AC impedance studies. From this, a suitable mechanism regarding the mode of inhibition was proposed. Surface morphology on the carbon steel with and without inhibitor was made to confirm the adsorptive layer on the surface of carbon steel.

MATERIALS AND METHODS

2.1 Material preparation

Rectangular carbon steel strips with specifiedcomposition (wt%: 0.18C, 0.30Mn, 0.15Si, 0.02S, 0.02P andrest Fe) and dimension (4.5cm × 2cm × 0.2cm) containing a small hole of about 2 mm diameter near the upper edge has been employed for weight loss and gasometric studies. The specimens used were polished mechanically followedby different grades of emery papers and then degreased with acetone. A cylindrical carbon steel specimens with an exposed area of 1 cm^2 (remaining area covered with Teflon holder) were used for electrochemical studies.HCl (AR) and double distilled water were used throughout the studies for preparing the aggressive solutions (1N HCl).

2.2 Preparation of *Ziziphus jujube* leaves(*ZJL*) extract

Ziziphus jujuba leaves were cleaned and dried in an air oven at 70°C for 2 hrs. The dried leaves were ground well and make it well into powder. 10 g of the leaf powder was refluxed in 100 mL of distilled water for 1 hr. Whatmann No.1 filter paper was used to filter the extract and the filtrates were heated on water bath until the moisture content gets evaporated completely [24]. Corrosion test solutions range from 200 ppm to 800 ppm were prepared by dissolving specified amount of dried *ZJL* extract in 1N HCl solution and used for corrosion study.

2.3 Weight loss studies

Weight loss measurements were carried out as described elsewhere [25]. Already weighed carbon steel specimens were immersed in 100 mL of uninhibited and inhibited solutions for 3 hours at 30°C. After the specified time, the carbon steel specimens were taken out from the acid solution and then washed immediately with double distilled water, dried, and re-weighed. Duplicate tests were also conducted for each experiment. Weight loss measurements were also performed at different immersion time from 3 to 24 hours at 30°C and at four different temperatures of 303, 323, 343 and 363 K for the best concentration (800 ppm) of *ZJL* extract. From the weight loss, the corrosion rate (mmpy) and inhibition efficiency percentage were calculated to evaluate the corrosion inhibition using the formulas as described somewhere else [26].

2.4 Determination of surface coverage

The degree of surface coverage (θ) was calculated from the weight loss measurement results using the following formula [27].

$$\text{Surface coverage } (\theta) = W_B - W_I / W_B$$

where W_B is the weight loss in the absence of the *ZJL* extract, W_I is the weight loss in the presence of the *ZJL* extract (200,400,600 and 800 ppm) in 1N HCl solution. From these data, a suitable isotherm were fitted graphically.

2.5 Gasometric studies

The design of the studies is described elsewhere[28].The carbon steel specimen was suspended from the hook of the glass stopper and was introduced into the sample cell containing 100 mL of 1N HCl solution. Volume of hydrogen gas liberated was measured for a period of three hours in the absence and presence of various concentrations of *ZJL* extract at 30°C and at constant atmospheric pressure. From the volume of hydrogen gas liberated, the inhibition efficiency was calculated using the formula:

$$\text{Inhibition Efficiency (\%)} = (V_0 - V_1 / V_1) \times 100$$

where V_0 is the volume of hydrogen evolved in the absence of *ZJL* extract and V_1 is the volume of hydrogen evolved in the presence of *ZJL* extract (200,400,600 and 800 ppm) in 1N HCl solution. This method gives accurate results compared to that of conventional weight loss method.

2.6 Electrochemicalpolarization studies

Electrochemical polarization measurements were carried out using Electrochemical analyzer(BioLogic-VSP, France) in a conventional three-electrode assembly containing a working electrode (cylindrical carbon steel specimen with an exposed area of $1cm^2$),counter electrode (platinum foil of surface area $2cm^2$),and a reference electrode (saturated calomel electrode).Both anodic and cathodic polarization curves were recorded in the absence and presence of optimum concentration (800 ppm) of the *ZJL* extract in the potential range of -200 mV to +200 mV with respect to OCP at a scan rate of 1 mV/s.From the polarization curves, corrosion potential and corrosion current were calculated. The inhibitor efficiency was calculated using the formula [29]:

Inhibition Efficiency (%) = I_{corr}- I^*_{corr}/ I_{corr}×100

where $I_{corr}$and I^*_{corr} are corrosion current in the absence and presence of *ZJL* extract in 1N HCl solution.

2.7 Electrochemical impedance studies

The corrosion inhibition efficiency of *ZJL* extract on carbon steel in 1N HCl solution in the absence and presence of best concentration (800 ppm) was investigated by using electrochemical analyzer(BioLogic-VSP, France). The impedance measurements were carried at the open circuit potential in the frequency range of 100kHz to 1mHz.A plot of Z' vs Z" were made. From the Nyquist plot, the charge transfer resistance (R_t) was calculated and the double layer capacitance (C_{dl}) was calculated using the following equation [30]:

$$C_{dl} = \frac{1}{2\pi f_{max} R_t}$$

where$R_t$ischarge transfer resistance andC_{dl} is double layer capacitance. The percentage of inhibition efficiency was calculated using the equation [31]:

Inhibition Efficiency (%)= $\frac{R^*t - R_t}{R^*t} \times 100$

where R_t* and R_t are the charge transfer resistance in the presence and absence of *ZJL* extract in 1N HCl solution.

2.8 Surface morphologicalstudies

The study was carried out by immersing the carbon steel specimens in 1N HCl in the absence and presence of the best concentration of *ZJL*extract for 3 hoursat 30°C.After 3 hours, the specimens were taken out, dried and kept in desiccators. The protective film formed on the surface of carbon steel was confirmed by metallurgical microscope with the magnification of 1000x.

RESULTS AND DISCUSSION

3.1 Weight loss studies

Weight loss of carbon steel in 1N HCl was determined at 303K in the absence and presence of *ZJL* extract concentrations ranging from 200 to 800 ppm. From the weight loss, percentage of inhibition efficiency (IE %) and corrosion rate are calculated and summarized in table 1. It is cleared from the table that the percentage of inhibition efficiency increases with concentration of *ZJL* extract. The decrease in corrosion rate with increase in concentration of *ZJL* is due to the fact that the surface coverage of metal increases by the adsorption of inhibitor molecules. A maximum inhibition efficiency of 82.2% is obtained at the concentration of 800 ppm of extract.

Table-1 Corrosion parameters obtained from weight loss measurements for carbon steel in 1N HCl containing different concentrations of ZJL extract

Conc. of*ZJL* extract (ppm)	Initial weight (g)	Final weight (g)	Weight Loss (g)	Corrosion Rate (mmpy)	Inhibition Efficiency (%)	Surface Coverage (θ)
Blank	3.7096	3.6601	0.0495	20.4581	----	----
200	3.7611	3.7462	0.0149	6.1582	70.0	0.700
400	3.6239	3.6101	0.0138	5.7035	72.2	0.722
600	3.8879	3.8759	0.0120	4.9593	75.8	0.758
800	3.6324	3.6236	0.0088	3.6370	82.2	0.822

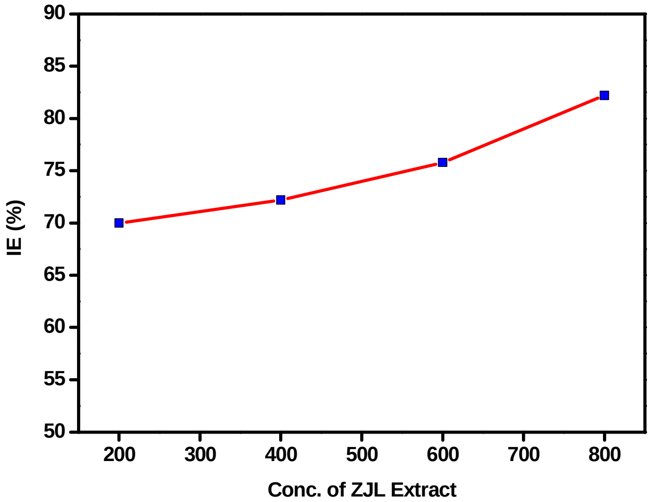


Fig. 1 Variation of inhibition efficiency with various concentrations of ZJL extract on carbon steel in 1N HCl solution

3.2 Effect of immersion time

The results obtained for the effect of immersion time on percentage inhibition efficiency of carbon steel in 1N HCl at 30°C in presence of the best concentration (800 ppm) of *ZJL* extract is shown in Table 2. The variation of inhibition efficiency against immersion time is shown in Fig.2. It shows that inhibition efficiency of the extract was decreased with increasing immersion time from 3 to 24 hours. Higher inhibition efficiency of 82.3% at 3 hour reflects the strong adsorption of constituents present in the *ZJL* extract on the carbon steel surface. But when the time is increased from 3 to 24 hour, the inhibition efficiency is slightly decreased to 80.0% which shows desorption process started slowly.

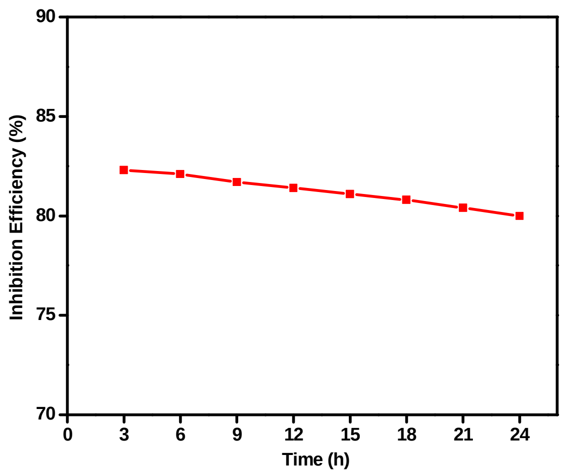


Fig. 2 Effect of immersion time on percentage inhibition efficiency of carbon steel in 1N HCl at 30°C in presence of an optimum concentration (800ppm) of ZJL extract

Table -2 Effect of immersion time on percentage inhibition efficiency of carbon steel in 1N HCl at 30°C in the presence of an optimum conc. (800ppm) of ZJL extract

System	Inhibition Efficiency (%)							
	Time (h)							
	3	6	9	12	15	18	21	24
800 ppm	82.3	82.1	81.7	81.4	81.1	80.8	80.4	80.0

3.3 Gasometric studies

The results obtained from gasometric studies were given inTable 3. From the table it was observed that the volume of hydrogen gas evolved is decreased from 7.4 to 1.3 mL with increase in the concentration of *ZJL* extract from 200 to 800 ppm. The maximum inhibition efficiency of 82.4% is obtained at the concentration of 800 ppm. It is revealed that *ZJL*extract had the tendency to inhibit carbon steel corrosion in acid medium.

Table 3 Inhibition efficiency obtainedfrom gasometric measurements for carbon steel in 1N HCl containing various concentrations of ZJL extract at 30˚C

Conc. of *ZJL*Extract (% in v/v)	Volume of Hydrogen Gas evolved (mL)	Inhibition Efficiency (%)
Blank	7.4	--
200	2.2	70.1
400	2.0	72.5
600	1.8	75.9
800	1.3	82.4

3.4 Electrochemical polarization studies

Fig. 3 shows the polarization curves for carbon steel in 1N HCl solution in the absence and presence of optimum concentration (800 ppm) of *ZJL* extract and their corresponding electrochemical polarization parameters are given in Table 4. It was obvious from the table that the corrosion potential (E_{corr}) was not shifted markedly in the presence of optimum concentration (800 ppm) of *ZJL* extract. The I_{corr} value for the best concentration of *ZJL* extract was decreased when compared to blank solution. Thisdecrease in I_{corr} is an indication of decrease in corrosion reaction, since corrosion current is proportional to themagnitude of corrosion reaction. The I_{corr}, b_a and bcvalues were changed upon the addition of *ZJL* extract,which means the extract molecules are adsorbed both on the anodic and cathodic sites. This results in the inhibition ofboth anodic metal dissolution and cathodichydrogen evolution reactions. Hence, it is inferred that the *ZJL* extract works through mixed mode of inhibition [32].

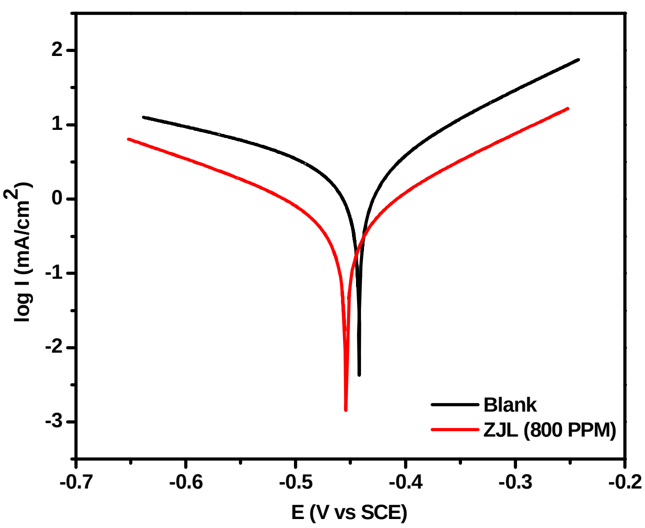


Fig. 3 Potentiodynamic polarization curves for carbon steel in 1N HCl solution in the absence and presence of an optimum conc. of ZJL extract

Table-4 Potentiodynamic polarization parameters for carbon steel in 1N HCl in the absence and presence of an optimum concentration of ZJL extract

Conc. of *ZJL* Extract (ppm)	E_{corr} (V vs SCE)	I_{corr} (mA/cm^2)	Tafel Slope (mV/decade)		Inhibition Efficiency (%)
			b_a	b_c	
Blank	-0.442	3.785	204.6	224.8	__
800 ppm	-0.454	0.666	145.0	201.0	82.30

3.5 AC- impedance studies

Fig.4 shows the impedance spectra for carbon steel in 1N HCl solution in the absence and presence of an optimum concentration (800 ppm) of *ZJL* extract and their corresponding impedance parameters such as double layer capacitance (C_{dl}**)**, charge transfer resistance (R_t) and inhibition efficiency are given in Table 5. It can be seen from theNyquist plot that a single semicircle has been observed is due to charge transfer takes place at electrode/solution interface. From the table it was observed that the decrease in C_{dl} value can be attributed to the decrease in local dielectricconstant and/or an increase in the thickness of electricaldouble layer and the increase in $R_t$value indicates that the extent of adsorption increases in presence of the best concentration (800 ppm) of *ZJL* extract and also the adsorbed extract forms a protectivefilm on the carbon steel surface which becomes a barrier to hinderthe mass and charge transfer processes [33]. These results are anincrease in the inhibition efficiency. The maximum R_t value of 113.89Ω cm^2 and the minimum C_{dl} value of 20.52µF/cm^2 was obtained at the best concentration of 800ppm of the *ZJL* extract, which gave the maximum inhibition efficiency of 81.8 %. This result has good concurrence with the results obtained from non-electrochemical methods.

Table-5 Impedance parameters for the corrosion of carbon steel in 1N HCl in the absence and presence of an optimum concentration of ZJL extract at 30^{0}C

Conc. of *ZJL* Extract (ppm)	R_t (Ω cm^2)	C_{dl} (µF/cm^2)	Inhibition Efficiency (%)
Blank	20.65	116.9	-
800 ppm	113.89	20.52	81.8

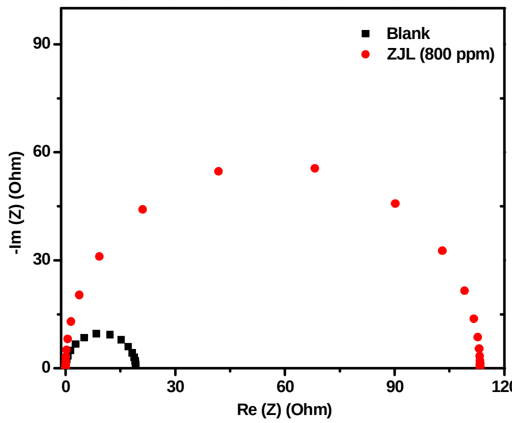


Fig. 4 Impedance diagrams for carbon steel in 1N HCl solution in the absence and presence of an optimum concentration of ZJL extract

3.6 Effect of Temperatures

Fig.5 shows the influence of different temperatures on the corrosion inhibition efficiency of best concentration (800ppm) of *ZJL* extract on carbon steel immersed in 1N HCl solution. The corrosion rate and inhibition efficiency were calculated for blank and best concentration of *ZJL* extract from weight loss measurements at different temperatures (30, 50, 70 and 90°C) are shown in the Table 6. From the table it is clear that the corrosion rate of carbon steel increased with temperature both in the absence and presence of *ZJL* extract and the inhibition efficiency was found to slightly decreases from 82.3% to 74.9%. This shows that the adsorption of the extract on the carbon steel may be due to physical adsorption. However, the inhibitor could be efficiently used at 30°C and maximum efficiency being 82.3%.

Table - 6 Corrosion of carbon steel in the absence and presence of an optimum concentration of ZJL extract in 1N HCl at different temperatures obtained by weight loss method

System	Temperature (°C)	Corrosion Rate (mmpy)	Inhibition Efficiency (%)
Blank	30	122.46	---
	50	152.92	---
	70	189.46	---
	90	241.60	---
800 ppm	30	21.66	82.3
	50	28.44	81.4
	70	40.54	78.6
	90	60.64	74.9

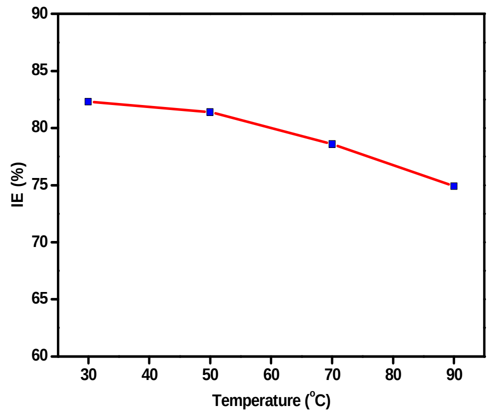


Fig. 5 Effect of temperature on the corrosion inhibition efficiency of carbon steel in 1N HCl in presence of an optimum concentration (800ppm) of ZJL extract

3.7 Mechanism of corrosion inhibition

To explain the mechanism of corrosion inhibition the activation parameters were calculated from Arrhenius-type plot according the following equation [34].

$$\ln r = A - Ea / RT$$

where r is the corrosion rate, A is the pre-exponential factor, E_a is the apparent activation energy, T is the absolute temperature and R is the universal gas constant.

Arrhenius plots for the corrosion of carbon steel in the absence and presence of the best concentration (800 ppm) of *ZJL* extract in 1N HCl medium are shown in Fig.6.It showing a straight line and revealing the effect of temperature. The calculated values of activation energy (E_a), enthalpy of adsorption (ΔH), free energy of adsorption (ΔG°) and entropy of adsorption (ΔS) for carbon steel in the absence and presence of the best concentration (800 ppm) of *ZJL* extract in 1N HCl solution are shown in Table 7. It shows that the higher value of Eain presence of the *ZJL* extract compared to that in the absence of the extract is due to physical adsorption [35] andthe adsorbed organic matter creates a physical barrier to charge and mass transfers, leading to reduction in corrosion rate.The free energy of adsorption was calculated using the following equation:

$$\Delta G^\circ_{ads} = -RT \ln (K\ 55.5)$$

where the value of 55.5 is the concentration of water in solution (mol L^{-1}). K is the degree of surface coverage on the metal surface, R is the universal gas constant and T is the absolute temperature.

The negative sign of free energy of adsorption indicates that the adsorption of *ZJL* extract on carbon steel surface is a spontaneous process. In this study, the ΔG° values are in the range of -10.46 kJ mol^{-1} at 363K.As the values of free energy of adsorption are less than -20 kJ mol^{-1}, where the mode of inhibition is due to physisorption [36].The positive values of ΔH both in the absence and presence of *ZJL* extract reflect the endothermic nature of the carbon steel corrosion process. It is also obvious that the activation energy supporting the proposed inhibition mechanism. Low and positive values of ΔS entropies imply that the process was slow and the activated complex is the rate determining step represents an association rather than a dissociation step, meaning that a decrease in disordering takes place on going from reactants to the activated complex. Similar observation has been reported in the literature[37].From the literature survey it was found that the majorterpenoid present in *ZJL* extract are betulonic acid, oleanonic acid, ursolic acid, ceanothic acid, cecropiacic acid, hydroxyoleanoic acid lacton etc.shown in Fig. 7.[38].These compounds adsorbed on the carbon steel surface made a barrier for charge and mass transfers leading to a decrease in the interaction of carbon steel with the corrosive environment. As a result, the corrosion rate of carbon steel decreased.

Table-7 Calculated values of activation energy (Ea), enthalpy of adsorption (ΔH), free energy of adsorption (ΔG°) and entropy of adsorption (ΔS) for carbon steel in the absence and presence of an optimum conc. of ZJL extract in 1N HCl solution

System	Temp. (K)	E_a (KJ mol^{-1})	ΔG° (KJmol^{-1})	ΔH (KJmol^{-1})	ΔS (KJmol^{-1})
Blank	303	---	---	---	---
	323	9.04	---	6.35	----
	343	9.87	---	7.02	---
	363	12.58	---	9.56	---
800 ppm	303	---	-8.73	---	---
	323	11.08	-9.31	8.39	0.055
	343	16.32	-9.89	13.47	0.068
	363	20.84	-10.46	17.82	0.078

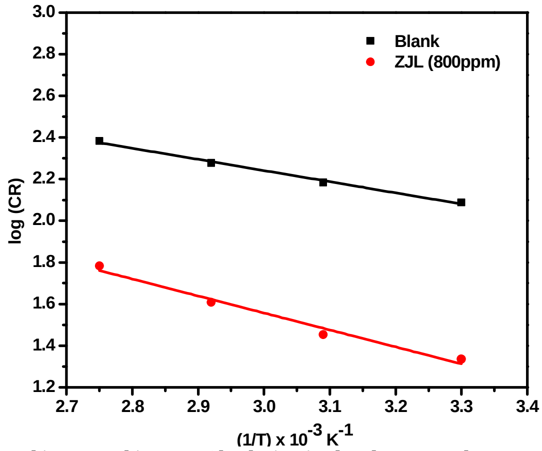
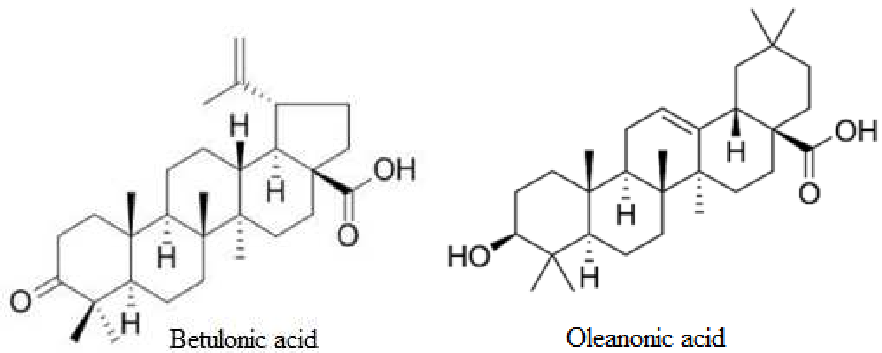


Fig. 6 Arrhenius plots for carbon steel immersed in 1N HCl solution in the absence and presence of an optimum concentration (800ppm) of ZJL extract



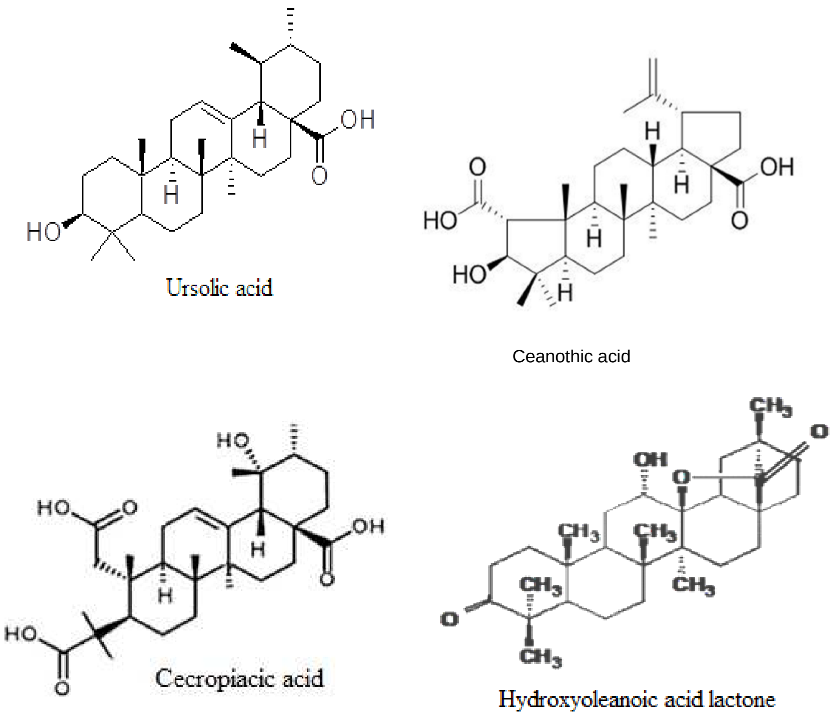


Fig.7 Structure of Triterpinoids

3.8 Adsorption isotherm

Adsorption isotherm provides information about the interaction between the *ZJL* extract and the carbon steel surface. The value of surface coverage (θ) has been obtained from weight loss measurements were fitted to different isotherms.A plot of C/θ versus C gives a straight line (Fig. 8) with a unit slope suggesting that the adsorption of *ZJL* extract on the surface of carbon steel in 1N HCl solution follows Langmuir adsorption isotherm.

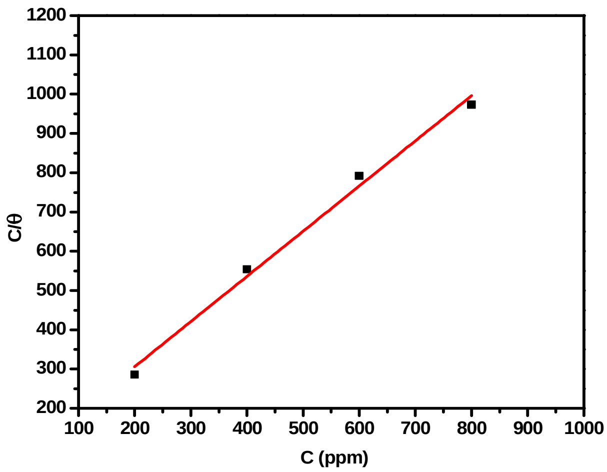
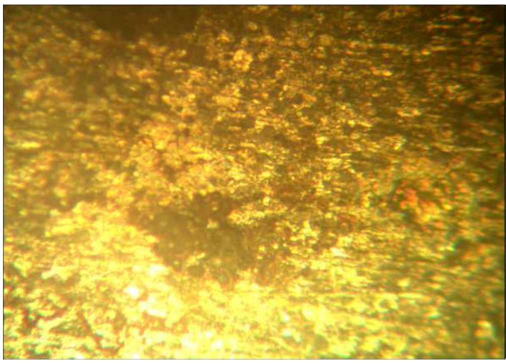


Fig. 8 Langmuir adsorption isotherm plot for the adsorption of various concentrations of ZJL extract on the surface of carbon steel in 1N HCl solution

3.9 Surface morphologicalstudies

The micrographs obtained for carbon steel immersed in 1N HCl solution in the absence and presence of 800 ppm of *ZJL* extract are shown in Fig.9 (a & b). A comparison has been done with the morphology, uninhibited carbon steel showed more pits and rough surface, while inhibited carbon steel showed smooth and less corroded surface. This may be due to adsorption of phytochemical constituents present in *ZJL* extract on carbon steel.



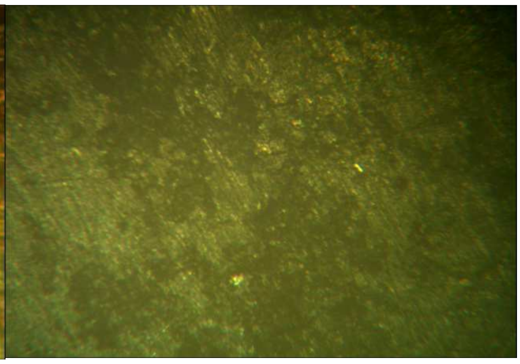


Fig.9(a) Metallurgical microscopeimage of carbon steel immersed in 1N HCl solution (blank)

Fig. 9(b) Metallurgical microscopeimage of carbon steel immersed in 1NHClsolution containing 800ppm of ZJL extract

CONCLUSION

The ziziphus jujuba leaves extract behaves as good corrosion inhibitor for carbon steel in 1N HCl solution and it shows maximum inhibition efficiency (82.2%) at the concentration of 800 ppm. It acts as mixed type inhibitor since its E_{corr} values are not shifted significantly with respect to the blank. The inhibition efficiency percentage obtained from weigh loss measurements are comparable with those obtained from electrochemical measurements. The adsorption of the extract follows Langmuir adsorption isotherm. The obtained thermodynamic parameters indicate that the adsorption of *ZJL* extract on carbon steel may be due to physisorption process.Surface morphological studies showed that the carbon steel in 1N HCl with the *ZJL* extract was found smother than without the *ZJL* extract.

REFERENCES

[1] K. F. Khaled, *Int. J. Electrochem. Sci.*,**2008**, 3, 462– 475.
[2] N.A. Odewunmi, S.A. Umoren and Z.M. Gasem, *J Ind Eng Chem.*, **2015**, 21,239-247.
[3] J. Buchweishaija, *Tanz. J. Sci.*, **2009**, 35,77-92.
[4] M. Bourayed, H. Rabaa, A. Srhiri, J.Y. Saillard, A. Ben Bachir and A. Le Beuze, *Corros. Sci.*, **1998**, 41, 501-517.
[5] Pandian Bothi Raja, Ahmad Kaleem Qureshi, Afidah Abdul Rahim, Hasnah Osman, and Khalijah Awang, *Corros. Sci.*, **2013**, 69, 292-301.
[6] Aprael S. Yaro, Anees A. Khadomand Rafal K. Wael, *Alexandria Engineering Journal*, **2013**, 52, 129-135.
[7] P.C. Okafor, I.E. Uwah, O.O. Ekerenam and U.J. Ekpe, *Pigm Resin Technol.*, **2009**, 38(4), 236-241.
[8] A.M. Al-Turkustani, S.T. Arab and L.S.S. Al-Qarni, *J. Saudi Chem. Soc.*, **2011**, 15(1), 73-82.
[9] A.K. Satapathy, G. Gunasekaran, S.C. Sahoo, K. Amit and P.V. Rodrigues, *Corros. Sci.*, **2009**, 51(12), 2848-2856.
[10] S. Ambrish, A. Ishtiaque, V.K. Singh and M.A. Quraishi, *J Solid State Electrochem.*, **2011**, 15(6), 1087-1097.
[11] K. Hema, B.R. Venkatraman and A. Subramania, *J. Environ. Nanotechnol.*, **2015**, 4(3), 42-50.
[12] M. K. Sharma, P. Arora, S. Kumar, S.P. Mathur and R. Ratnani, *Corros Eng Sci Technol.*, **2008**, 43, 213-218.
[13] R. Saratha and V.G. Vasudha, *Eur. J. Chem.*, **2010**, 7, 677-684.
[14] K. Hema, A. Sirajunisa, B.R. Venkatraman and A. Subramania, *Int. j. adv. res. chem. sci.*,**2015**, 2(9), 10-20.
[15] P.B. Raja, A.A. Rahim, H. Osman and K. Awang, *Acta Phys. Chim. Sin.*, **2010**, 26, 2171-2176.
[16] N.O. Eddy and A.O. Odiongenyi, *Pigm. Resin Technol.*,**2010**, 39, 288-295.
[17] E.E. Oguzie, C.K. Enenebeaku, C.O. Akalezi, S.C. Okoro, A.A. Ayuk and E. N. Ejike, *J. Colloid Interface Sci.*, **2010**, 349(1), 283-292.
[18] A. Sharmila, A.A. Prema and P.A. Sahayaraj, *Rasayan j. chem.*, **2010**, 3(1), 74-81.
[19] M. Lebrini, F. Robert, A. Lecante and C.Roos, *Corros. Sci.*, **2011**, 53(2), 687-695.
[20] K. Hema, B.R. Venkatraman and A. Subramania, *Chem. Sci. Trans*., **2015**, 4(4), 927-939.
[21] Waqar Ahmad Kaleem, Naveed Muhammad, Haroon Khan and Abdur Rauf, *Middle East J Sci Res.*, **2014**, 21(8), 1243-1263.
[22] Manoj Goyal, Badri Prakash Nagori and Dinakar Sasmal, *Spatula DD.*, **2012**, 2,107-116.
[23] A. Sirajunnisa, M.I. Fazal Mohamed, A. Subramania and B.R.Venkatraman, *European Journal of Applied Sciences and Technology*,**2014**, 1(1), 23-31.

[24] S.S. Shivakumar, K. N. Mohana and D.M. Gurudatt, *Chem. Sci. Trans.*, **2013**, 2(1), 163-175.
[25] G.E. Badr, *Corros. Sci.*, **2009**, 51(11), 2529-2536.
[26] A. Sirajunnisa, M.I. Fazal Mohamed and A. Subramania, *Der Chemica Sinica*, **2014**, 5(1), 148-156.
[27] A. Sirajunnisa, M.I. Fazal Mohamed, A. Subramania, *J. Chem. Pharm. Res.*, **2014**, 6(1), 580-588.
[28] V. Sureshkumar, B.R. Venkatraman and A. Subramania, *Res. J. Chem. Sci.*, **2012**, 2(10), 87-94.
[29] A. Subramania, N.T. Kalyana Sundaram, R. Sathiya Priya, K. Saminathan, V.S. Muralidharan, and T. Vasudevan, *J. Applied Electrochem.*, **2004**, 34(7), 693-696.
[30] A. Subramania, N.T. Kalyana Sundaram, R. Sathiya priya, V.S. Muralidharan and T. Vasudevan, *Bull Electrochem.*, **2004**, 20(2), 49-58.
[31] Ehteram A. Noor, *J. Appl. Electrochem.*, **2009**, 39, 1465-1475.
[32] F. Bentiss, M. Librini, H. Vezin, F. Chai, M. Traisnel and M. Lagrene, *Corros. Sci*., **2009**, 51, 2165-2173.
[33] M. Lebrini, M. Traisnel, M. Lagrenee, B. Mernari and F. Bentiss, *Corros. Sci.*, **2008**, 50(2), 473-479.
[34] A.S. Fouda, G.Y. Elewady, K. Shalabi and S. Habouba, *Int. j. innov. res. sci. eng. technol.*, **2014**, 3(4), 11210-11228.
[35] K. Lakshmi Prabha, Shameela Rajam and B.R. Venkatraman, *Der Chemica Sinica*, **2012**, 3(1), 114 –123.
[36] M. Shyamala and A. Arulanantham, *Nat. Env. & Poll. Tech.*, **2008**, 7(3), 415-422.
[37] J. Rosaline Vimala, A. Leema rose and S. Raja, *Int. J. ChemTech Res.*, **2011**, 3(4), 1791-1801.
[38] Sheng Guo, Jin-ao Duan, Yuping Tang, Yefei Qian, Jinlong Zhao and Dawei Qian, *Biochem. Systematics and Ecol.*,**2011**, 39, 880-882.