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## Juniper oxycedrus extract as corrosion inhibitor for carbon steel in HCl medium

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### ABSTRACT

The inhibitive action of the Juniper Oxycedrus Extract (JOE) against corrosion of carbon steel in a 1.0 M HCl solution was investigated using electrochemical impedance spectroscopy, potentiodynamic polarization curves and weight loss measurements. The results indicate that the extracts functioned as a good inhibitor in acidic medium environments and inhibition efficiency increased with extracts concentration. Temperature studies revealed an increase in inhibition efficiency with rise in temperature and activation energies decreased in the presence of the extract. Polarization curves show that JOE behaves as a mixed-type inhibitor in hydrochloric acid. EIS shows that charge-transfer resistance increase and the capacitance of double layer decreases with the inhibitor concentration, confirming the adsorption process mechanism. The adsorption of Juniper Oxycedrus Extract on the surface of the carbon steel follows the Langmuir adsorption isotherm.

**Keywords:** Juniper Oxycedrus Extract, HCl, Carbon steel, EIS, Polarization, Weight loss.

### INTRODUCTION

Industrial processes such as pickling and acid cleaning often involve contact between a metal and aggressive solution, requiring the use of an inhibitor [1]. Most effective inhibitors are organic compounds containing electronegative functional groups and  $\pi$  electrons in triple or conjugated double bonds [2-16]. These compounds also have heteroatoms (such as N, O, and S) and aromatic rings in their structure, which are the major adsorption centers [17-29]. In view of this, several inhibitors have been synthesized and used successfully to inhibit corrosion of metals, including carbon steel. However, the major problem associated with most of these inhibitors is that they are not ecofriendly as they contain heavy metals and other toxic compounds [1]. "Green" corrosion inhibitors are biodegradable and do not contain toxic substances [30,31]. Most of the natural products are non-toxic, biodegradable and readily available in plenty. These advantages have incited us to draw a large part of program of our laboratory to examine natural substances as corrosion inhibitors such as: Fennel oil [32], prickly pear seed oil [33], Argan extract [34], Argan oil [35], Rosemary oil [36], Thymus oil [37], Pennyroyal Mint oil [38], Lavender oil [39], Jojoba oil [40] and Artemisia [41].

This paper reports the effect of Juniper Oxycedrus Extract (JOE) as corrosion inhibitor for carbon steel in 1 mol L<sup>-1</sup> hydrochloric acid, using anodic and cathodic polarization curves, electrochemical impedance measurements and weight loss measurements.

## MATERIALS AND METHODS

### Materials

The steel used in this study is carbon steel (Euronorm: C35E carbon steel and US specification: SAE 1035) with a chemical composition (in wt%) of 0.370 % C, 0.230 % Si, 0.680 % Mn, 0.016 % S, 0.077 % Cr, 0.011 % Ti, 0.059 % Ni, 0.009 % Co, 0.160 % Cu and the remainder iron (Fe). The carbon steel samples were pre-treated prior to the experiments by grinding with emery paper SiC (120, 600 and 1200); rinsed with distilled water, degreased in acetone in an ultrasonic bath immersion for 5 min, washed again with bidistilled water and then dried at room temperature before use. The acids solution (1.0 M HCl) was prepared by dilution of an analytical reagent grade 37% HCl with double-distilled water. The concentration range of JOE employed was 1 g/L to 6 g/L.

### Measurements

#### Weight loss measurements

Gravimetric measurements were carried out at definite time interval of 6 h at room temperature using an analytical balance (precision  $\pm 0.1$  mg). The carbon steel specimens used have a rectangular form (length = 2.0 cm, width = 1.0 cm, thickness = 0.3 cm). Gravimetric experiments were carried out in a double glass cell equipped with a thermostated cooling condenser containing 100 mL of non-de-aerated test solution. After immersion period, the steel specimens were withdrawn, carefully rinsed with bidistilled water, ultrasonic cleaning in acetone, dried at room temperature and then weighted. Triplicate experiments were performed in each case and the mean value of the weight loss was calculated. The corrosion rate ( $v$ ) was calculated by the following equation:

$$v = \frac{w}{St} \quad (1)$$

Where  $v$  was the corrosion rate in ( $\text{mg cm}^{-2} \text{ h}^{-1}$ ),  $w$  is the average weight loss of three parallel carbon steel sheets (mg),  $S$  was the total area of one carbon steel sheet ( $\text{cm}^2$ ), and  $t$  was immersion time (h).

With the calculated corrosion rate, the inhibition efficiency ( $\eta_{WL}$  %) was obtained as the following equation:

$$\eta_{WL} \% = \frac{v_0 - v}{v_0} \times 100 \quad (2)$$

Where  $v_0$  and  $v$  are the values of corrosion rate without and with different concentration of inhibitor, respectively.

#### Electrochemical measurements

Electrochemical experiments were conducted using impedance equipment (Tacussel-Radiometer PGZ 100) and controlled with Tacussel corrosion analysis software model Voltmaster 4. A conventional three-electrode cylindrical Pyrex glass cell was used. The temperature was thermostatically controlled. The working electrode was carbon steel with the surface area of  $0.32 \text{ cm}^2$ . A saturated calomel electrode (SCE) was used as a reference. All potentials were given with reference to this electrode. The counter electrode was a platinum plate of surface area of  $1 \text{ cm}^2$ . A saturated calomel electrode (SCE) was used as the reference; a platinum electrode was used as the counter-electrode. All potentials are reported vs. SCE. All electrochemical tests have been performed in aerated solutions at 298 K.

For polarization curves, the working electrode was immersed in a test solution during 30 min until a steady state open circuit potential ( $E_{ocp}$ ) was obtained. The polarization curve was recorded from -800 to -100 mV/SCE with a scan rate of  $1 \text{ mV s}^{-1}$ . AC impedance measurements were carried-out in the frequency range of 100 kHz to 10 mHz, with 10 points per decade, at the rest potential, after 30 min of acid immersion, by applying 10 mV ac voltage peak-to-peak. Nyquist plots were made from these experiments. The best semicircle was fit through the data points in the Nyquist plot using a non-linear least square fit so as to give the intersections with the x-axis.

## RESULTS AND DISCUSSION

### Effect of concentration

#### Polarisation curves

The effect of *Juniper Oxycedrus Extract* (JOE) concentration on the anodic and cathodic polarization behavior of carbon steel in 1.0 M HCl solution has been studied by polarization measurements and the recorded Tafel plots are

shown in Fig. 1. The potential of potentiodynamic polarization curves was started from cathodic potential of -800 mV to anodic potential of -100 mV vs. OCP at a sweep rate of 1.0 mV s<sup>-1</sup>. Inhibition efficiency ( $\eta_p$ %) is defined as:

$$\eta_p \% = \frac{I_{corr} - I_{corr(inh)}}{I_{corr}} \times 100 \quad (3)$$

where  $I_{corr}$  and  $I_{corr(inh)}$  represent corrosion current density values without and with inhibitor, respectively. The respective kinetic parameters derived from the above plots are given in Table 1. It is illustrated from the data of Table 1 that both anodic metal dissolution of iron and cathodic hydrogen evolution reaction were inhibited after the addition of JOE to 1.0 M HCl solution. The inhibition of these reactions was more pronounced on increasing JOE concentration. In presence of JOE, the corrosion potential of carbon steel shifted 2-10 mV anodically compared to the blank and also small change in cathodic Tafel slopes were noticed. An inhibitor can be classified as cathodic or anodic type if the displacement in corrosion potential is more than 85 mV with respect to corrosion potential of the blank [42]. This indicates that JOE acts as mixed-type inhibitor. The cathodic current-potential curves (Fig. 1) gave rise to parallel lines indicating that the addition of JOE to the 1.0 M HCl solution did not modify the hydrogen evolution mechanism and the reduction of H<sup>+</sup> ions at the carbon steel surface taken place mainly through a charge transfer mechanism. The JOE molecules were first adsorbed on the carbon steel surface and blocked the reaction sites of the carbon steel surface. In this way, the surface area available for H<sup>+</sup> ions was decreased while the actual reaction mechanism remains unaffected [43]. A higher coverage of the JOE on the surface was obtained in solutions with the higher concentrations.

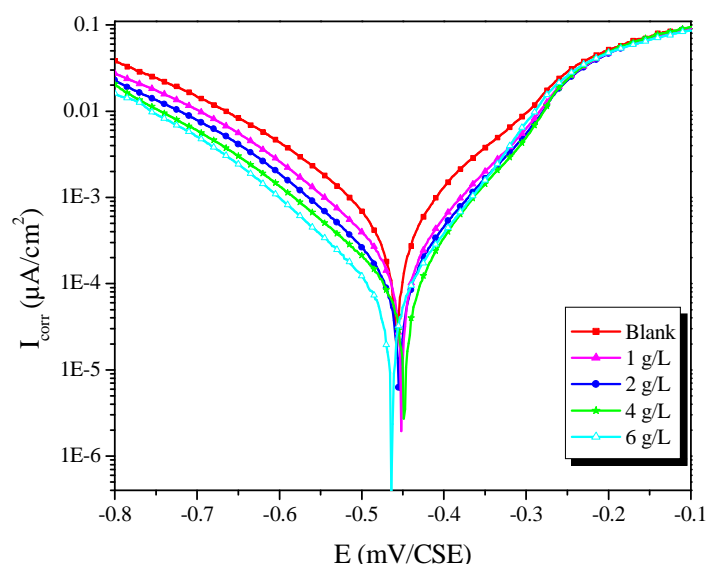


Figure 1. Polarization curves for carbon steel in 1.0 M HCl at various concentrations of JOE at 298K.

Table 1. Electrochemical parameters for carbon steel in 1.0 M HCl at various concentrations of JOE at 298K.

Conc (g/L)	$I_{corr}$ ( $\mu\text{A}/\text{cm}^2$ )	$E_{corr}$ (mV/SCE)	$-\beta_c$ (mV/dec)	$\eta_p$ (%)
Blank	594	-457	-199	
1	232	-453	-175	60.9
2	168	-455	-184	71.7
4	108	-447	-175	81.8
6	54	-449	-155	90.9

#### Electrochemical impedance spectroscopy

The corrosion behavior of steel, in acidic solution in the absence and presence of JOE, was also investigated by EIS method at 298 K after 30 min of immersion. The inhibition efficiency can be calculated by the following formula:

$$\eta_i = \left( \frac{R_{ct(inh)} - R_{ct(uninh)}}{R_{ct(inh)}} \right) \times 100 \quad (4)$$

where  $R_{ct(inh)}$  and  $R_{ct(uninh)}$  are the charge-transfer resistance values with and without inhibitor, respectively.

The electrochemical impedance diagrams for carbon steel in 1.0 M HCl solution in the absence and presence of various concentrations of *Juniper Oxycedrus Extract* (JOE) are shown in Fig. 2. Table 2 summarizes impedance data from the EIS experiments carried out both in the absence and presence of increasing extract concentrations. The electrochemical impedance diagrams show only one depressed capacitive loop, which is attributed to the one time constant, in the absence and presence of the *Juniper Oxycedrus Extract*, which indicates two significant effects: the charge-transfer resistance significantly increases, and the  $f_{max}$  decreases, in the presence of the extract, decreasing the capacitance value, which may be caused by reduction in the local dielectric constant and/or by an increase in the thickness of the electrical double-layer. These results show that the presence of the extracts modifies the electric double-layer structure suggesting that the inhibitor molecules act by adsorption at the metal/solution interface. The thickness of this protective layer ( $\delta$ ) is related to  $C_{dl}$  in accordance with Helmholtz model, given by the following equation

$$C_{dl} = \frac{\epsilon \epsilon_0 A}{\delta} \quad (5)$$

where  $\epsilon$  is the dielectric constant of the medium,  $\epsilon_0$  the vacuum permittivity,  $A$  the electrode area [44]. Deviations from a perfect circular shape indicate frequency dispersion of interfacial impedance. This anomalous phenomenon is attributed in the literature to the non homogeneity of the electrode surface arising from the surface roughness or interfacial phenomena [38,45-47]. The charge-transfer resistance ( $R_{ct}$ ) values were calculated from the difference in impedances at lower and higher frequencies. The double-layer capacitance ( $C_{dl}$ ) was calculated from the following equation:

$$C_{dl} = \frac{1}{2\pi f_{max} R_{ct}} \quad (6)$$

where  $f_{max}$  is the frequency at which the imaginary component of the impedance is maximal. A  $C_{dl}$  value of 115  $\Omega$   $cm^{-2}$  was found for the carbon steel electrode at 1.0 HCl. From Table 2, it is clear that the  $R_{ct}$  values increased and that the  $C_{dl}$  values decreased with increasing inhibitor concentration. This result indicates a decrease in the active surface area caused by the adsorption of the inhibitor on the carbon steel surface, and it suggests that the corrosion process became hindered; this hypothesis is corroborated by the anodic and cathodic polarization curves and the corrosion potential results.

**Table 2. Impedance parameters for corrosion of steel in 1.0 M HCl without and with different concentrations of JOE at 298 K.**

Conc (g/L)	$R_{ct}$ (Ohm $cm^2$ )	$C_{dl}$ ( $\mu F$ $cm^2$ )	$\eta_i$ (%)
blank	15.09	115	-- ---
1	48.97	92	69.4
2	65.84	78	77.2
4	80.27	69	81.3
6	140.11	61	89.3

### Weight loss tests

The non-electrochemical technique of weight loss was done in order to determine the corrosion rate and percentage of inhibition. This physical measurement will provides direct answer on how the corrosive environments affect the test samples and also show to us the average corrosion rate during the experiment. Table 3 shows the inhibition efficiency of carbon steel with and without the addition of different concentrations of *Juniper Oxycedrus Extract* determined after 6 h at room temperature. It has been observed that 6 g/L of *Juniper Oxycedrus Extract* serves as an optimum concentration that exhibit higher efficiency of corrosion inhibition. An increase of inhibitor concentration beyond 6 g/L resulted in a diminished corrosion protection. This may be due to the withdrawal of adsorbate (inhibitor) back into the bulk solution when the concentration of inhibitor closed to or beyond the critical concentration [48]. The above effect leads to the weakening of metal-inhibitor interactions, resulting in the replacement of inhibitor by water or chloride ions ( $Cl^-$ ) with decrease in inhibition efficiency [49]. Interestingly, the color of working electrode consisting *Juniper Oxycedrus Extract* were changed to a dark blue complex which indicated the formation of a stable magnetite on the carbon steel. The magnetite was strongly adhered to the metal and consequently results an impermeable layer to stop further corrosion [50,51].

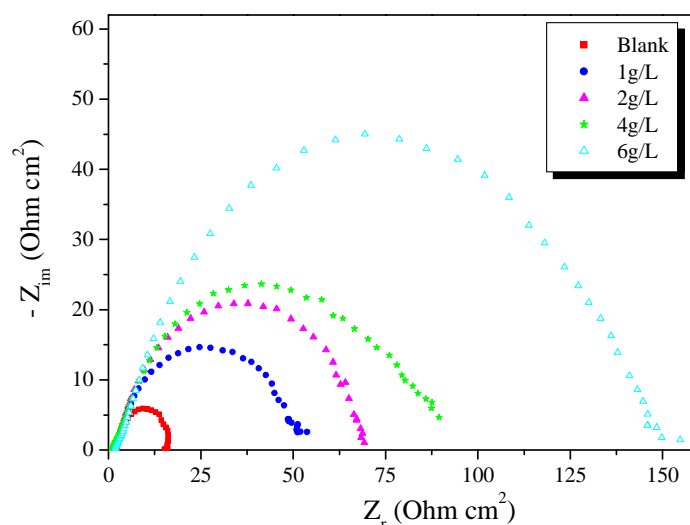


Figure 2. Nyquist plots of carbon steel in 1.0 M HCl without and with different concentrations of JOE at 298 K.

Table 3. Effect of inhibitor concentration on inhibitor efficiency of JOE by weight loss in 1.0 M HCl.

Conc (g/L)	$v$ ( $\text{mg cm}^{-2}\text{h}^{-1}$ )	$\eta_{\text{WL}}$ (%)	$\theta$
Blank	1.84	-----	-----
1	0.75	59.2	0.592
2	0.56	69.6	0.696
4	0.32	82.6	0.826
6	0.24	87.0	0.870

### Effect of temperature

Two main types of interaction often describe adsorption of organic inhibitors on a corroding metal surface viz: chemical adsorption and physical adsorption. It has been suggested [52,53] that physisorbed molecules are attached to the metal at local cathodes and essentially retard metal dissolution by stifling the cathodic reaction whereas chemisorbed molecules protect anodic areas and reduce the inherent reactivity of the metal at the sites where they are attached. The more efficient inhibitors appear to protect anodic areas preferentially by chemisorption. Initial deduction of the adsorption mechanisms in this study involved the assessment of the effects of varying system temperature between 298 and 328K on corrosion and inhibition processes. Fig. 3 and Fig. 4, show the Tafel plots of carbon steel in 1.0 M HCl in absence and presence of 6 g/L JOE in temperature range 298-328K. The variation of inhibition efficiency with temperature is given in Table 4. In the absence and in the presence of the JOE, the  $I_{\text{corr}}$  values increased with increasing temperature, indicating that the *Juniper Oxycedrus Extract* affected the carbon steel electrochemical dissolution.

Table 4. Electrochemical parameters for corrosion of steel in 1.0 M HCl at different temperatures in the absence and presence of 6 g/L JOE.

Conc (g/L)	Temp (K)	$E_{\text{cor}}$ (mV/SCE)	$I_{\text{cor}}$ ( $\mu\text{A}/\text{cm}^2$ )	$\eta_{\text{p}}$ (%)
Blank	298	-457	594	----
	308	-458	900	----
	318	-500	3360	----
	328	-487	6820	----
JOE	298	-449	54	90.9
	308	-479	81	91.0
	318	-490	294	91.2
	328	-492	529	92.2

The apparent activation energies ( $E_a$ ) for the corrosion process in absence and presence of inhibitor were evaluated from Arrhenius equation:

$$I_{corr} = k \exp\left(-\frac{E_a}{RT}\right) \quad (7)$$

where  $E_a$  is the apparent activation corrosion energy,  $R$  is the universal gas constant and  $k$  is the Arrhenius pre-exponential constant.

From the Arrhenius plots, the apparent activation energy ( $E_a$ ) of the corrosion process can be calculated. Some conclusions on the mechanism of the inhibitor action can be obtained by comparing  $E_a$ , both in the presence and absence of the corrosion inhibitor. Values of  $E_a$  for mild steel in 1.0 M HCl with the absence and presence various concentrations of JOE were determined from the slopes of  $\ln(I_{corr})$  vs.  $1/T$  plots (Fig. 5) and shown in Table 5.

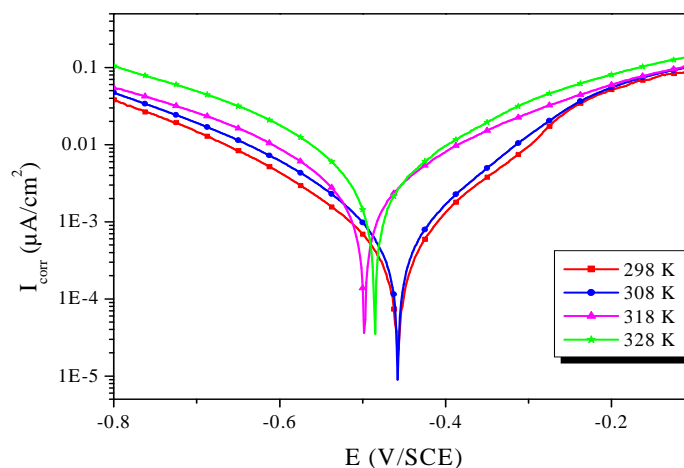


Figure 3. Potentiodynamic polarisation curves of carbon steel in 1.0 M HCl at different temperatures.

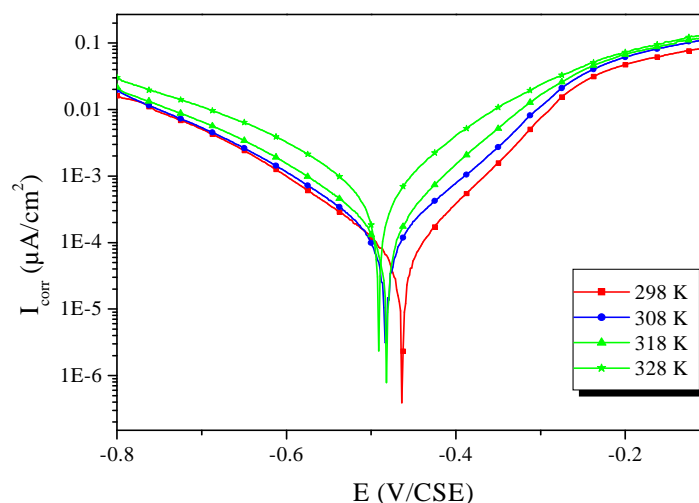


Figure 4. Potentiodynamic polarisation curves of carbon steel in 1.0 M HCl in the presence of 6 g/L of JOE inhibitor at different temperatures.

The  $E_a$  determined from the slope of the Arrhenius plots corresponds to  $69.97 \text{ kJ mol}^{-1}$  in the absence and  $65.93 \text{ kJ mol}^{-1}$  in the presence of JOE. The lower  $E_a$  value obtained in the presence of caffeic acid when compared to that in its absence indicates chemisorptions of the corrosion inhibitor. According to Radovici, cited by Popova *et al.* [54], lower  $E_a$  values in solutions containing inhibitor indicate a specific type of adsorption of the inhibitors, while Szauer and Brandt [55] associate this behavior with the chemisorption of the inhibitor to the metal surface and Machu, cited in reference [54], to the action of powerful corrosion inhibitors. Taking into consideration these references and the  $E_a$  value calculated from Arrhenius plots, the action of JOE as a corrosion inhibitor for carbon steel in acid solution

can be attributed to a strong adsorption bond which is of a chemisorptive nature, involving charge sharing or charge transfer from the molecule of JOE to the carbon steel surface to form a coordinate-type bond.

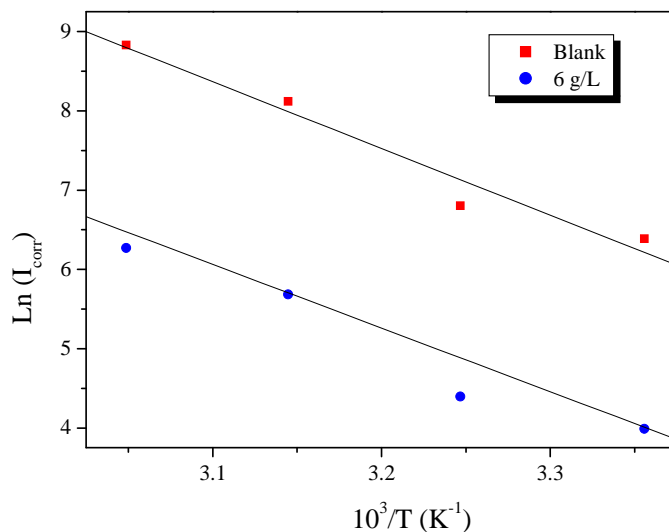


Figure 5. Arrhenius plots of carbon steel in 1.0 M HCl with and without 6 g/L JOE.

Table 5. The values of activation parameters for steel in 1.0 M HCl in the absence and presence of 6 g/L of JOE.

	$E_a$ (kJ mol <sup>-1</sup> )	$\Delta H_a$ (kJ mol <sup>-1</sup> )	$\Delta S_a$ (J mol <sup>-1</sup> K <sup>-1</sup> )
Blank	69.97	67.37	32.95
6 g/L	65.93	63.33	-0.32

An alternative formulation of Arrhenius equation is [56]:

$$I_{corr} = \frac{RT}{Nh} \exp\left(\frac{\Delta S_a}{R}\right) \exp\left(-\frac{\Delta H_a}{RT}\right) \quad (8)$$

where  $I_{corr}$  is the corrosion rate,  $A$  is the pre-exponential factor,  $h$  is Planck's constant,  $N$  is the Avogadro number,  $R$  is the universal gas constant,  $\Delta H_a$  is the enthalpy of activation and  $\Delta S_a$  is the entropy of activation.

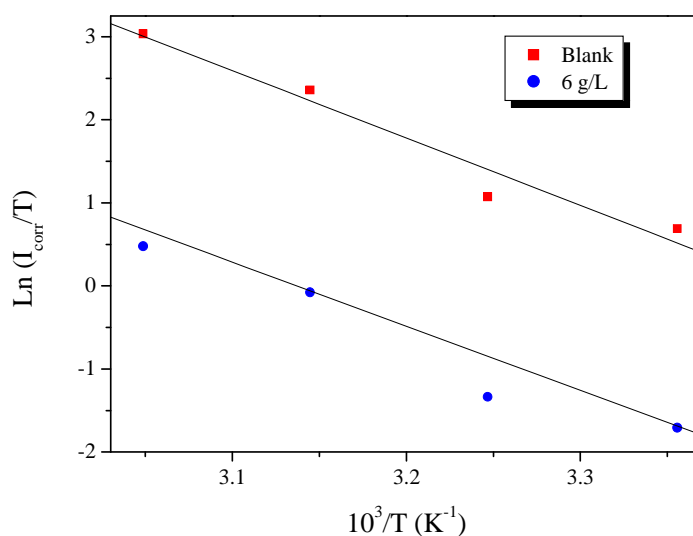


Figure 6. Variation of  $\text{Ln}(I_{corr}/T)$  versus  $10^3/T$  for blank and 1.0 M HCl + 6 g/L of JOE.

Fig. 6 shows a plot of  $\ln(I_{\text{corr}}/T)$  against  $1/T$ . Straight lines are obtained with a slope of  $(-\Delta H_a/R)$  and an intercept of  $(\ln(R/Nh) + (\Delta S_a/R))$  from which the values of  $\Delta H_a$  and  $\Delta S_a$  are calculated and listed in Table 5. The positive signs of  $\Delta H_a$  reflect the endothermic nature of the mild steel dissolution process. The analysis of the results of Table 5 shows that the activation energy  $E_a$  and activation heat  $\Delta H_a$  against the JOE vary in the same manner.

The value of  $\Delta S_a$  for carbon steel is positive (32.95 J/mol K) whereas for JOE is positive (-0.32 J/mol.K). The entropy of activation for carbon steel is positive value as the transition state of the rate determining recombination step represent less orderly arrangement relative to the initial state.

### Adsorption isotherm

The values of surface coverage to different concentrations of inhibitors, obtained from weight loss measurements at 298K, have been used to explain the best isotherm to determine the adsorption process. Adsorption isotherms are very important in determining the mechanism of organo-electrochemical reactions [57]. The most frequently used isotherms are Langmuir, Temkin, Frumkin, Parsons, Hill de Boer, Flory-Huggins and Dahar-Flory-Huggins and Bockris-Swinkel [58-64]. All these isotherms are of the general form:

$$\int(\theta, x) \exp(2a\theta) = KC_{\text{inh}} \quad (9)$$

where  $\int(\theta, x)$  is the configurational factor which depends upon the physical model and the assumptions underlying the derivation of the isotherm. "θ" is the surface coverage degree, "C" is the inhibitor concentration in the bulk of solution "a" is the lateral interaction term describing the molecular interactions in the adsorption layer and the heterogeneity of the surface. "K" is the adsorption-desorption equilibrium constant. The surface coverage  $\theta$  for different concentrations of JOE in 1.0 M HCl at 298K for 6 h of immersion time has been evaluated from weight loss. The data were tested graphically, see Fig. 7, by fitting to Langmuir isotherm which given by equation 10.

$$\frac{C_{\text{inh}}}{\theta} = \frac{1}{K_{\text{ads}}} + C_{\text{inh}} \quad (10)$$

where  $C_{\text{inh}}$  is the equilibrium inhibitor concentration,  $K_{\text{ads}}$  adsorptive equilibrium constant,  $\theta$  representing the degree of adsorption ( $\eta_{\text{WL}}\%/100$ ).

By far the best fit was obtained with the Langmuir isotherm (the strong correlation ( $R^2 = 0.999$ )). The plots of  $C_{\text{inh}}/\theta$  vs.  $C_{\text{inh}}$  yield a straight line (Fig. 7). This confirms that this inhibitor (*Juniper Oxycedrus Extract*) obeys Langmuir adsorption isotherm at 1.0 M HCl medium. It indicates that the adsorbing *Juniper Oxycedrus Extract* species occupies typical adsorption site at the metal/solution interface. It is very important to note that discussion of the adsorption isotherm behaviour using natural product extracts as inhibitors in terms of thermodynamic parameters (such as the standard free energy of adsorption value ( $\Delta G_{\text{ads}}$ )) is not possible because the molecular mass of the extract components is not known. For example, there are a several phenolic compounds in the aqueous extract. Valek and Martinez [65], in their study on acid corrosion with *Azadirachta indica* leaf extract, noted the same limitation.

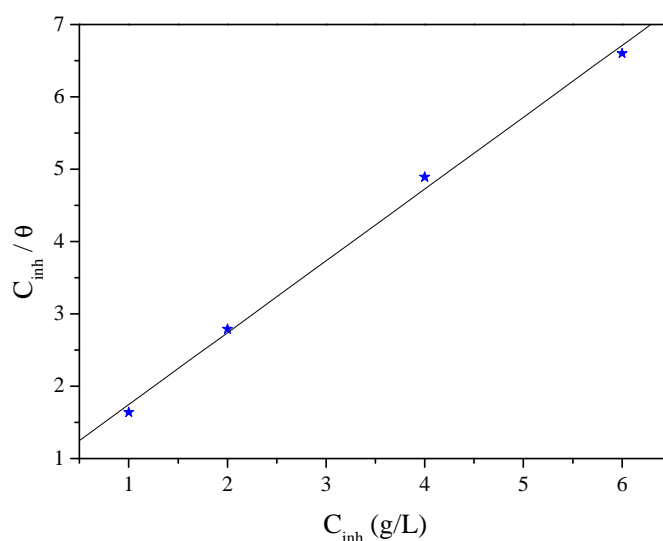


Figure 7. Langmuir isotherm adsorption of JOE on the carbon steel electrode in 1.0 M HCl.



## CONCLUSION

The conclusions drawn from the study are:

- The alkaloids extract of *Juniper Oxycedrus Extract* behaved as a potent inhibitor to carbon steel in 1.0 M HCl. The protection efficiency of the inhibitor was found to increase with increase in concentration of the inhibitor showing a maximum efficiency of 90.9 % at 6 g/L.
- The extract under study resists corrosion effectively even at higher temperature, further increase in temperature results an increase in IE%.
- The results obtained from the polarization studies reveal that the extract behaved as a mixed type of inhibitor.
- The adsorption behavior of the extract is consistent with Langmuir adsorption model.

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