

Full Length Research Paper

Inhibition of mild steel corrosion using *Juniperus* plants as green inhibitor

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The corrosion inhibition of mild steel in H_2SO_4 solution in the presence of *Juniperus* plant at a temperature range of 30 to 60°C was studied using chemical (HE and WL) and electrochemical (PDP and EIS) methods. The *Juniperus* plant acts as an inhibitor in the acid environment. The inhibition efficiency increases with increase in inhibitor concentration but decreases with an increase in temperature. The inhibitive effect of the *Juniperus* plant could be attributed to the presence of some compound in the plant which is adsorbed on the surface of the mild steel. The *Juniperus* plant was found to conform to the Frumkin adsorption isotherm and Temkin adsorption isotherm at all the concentration levels and temperature studied. The phenomenon of physical adsorption is proposed from the activation parameters obtained. Thermodynamic parameters revealed that the adsorption process is spontaneous.

Key words: Corrosion-inhibition, frumkin adsorption isotherm and temkin adsorption isotherm, physical adsorption, *Juniperus* plant.

INTRODUCTION

Corrosion and corrosion inhibition of iron and iron alloys; and steel, in particular, have received enormous attention in different media (Fouda et al., 2006; (Tamilselvi and Rajeswari, 2003) with and without various types of inhibitors. The corrosion inhibition of C-steel becomes of such interest because it is widely used as a constructional material in many industries and this is due to its excellent mechanical properties and low cost (Keera, 2003).

Some investigations have in recent times been made into the corrosion inhibiting properties of natural products of plant origin, and have been found to generally exhibit good inhibition efficiencies (Okafor and Ebenso, 2007). The significance of this area of research is primarily due to the fact that natural products are environmentally friendly and ecologically acceptable. The yield of these

natural products as well as the corrosion inhibition abilities of the plant extracts vary widely depending on the part of the plant and its location. Of importance also, is the specificity of corrosion inhibiting compounds. One compound effective in a certain medium with a given metal may be ineffective for the same metal in another medium (Okafor et al., 2005).

Nevertheless, the known hazardous effects of most synthetic organic inhibitors and the need to develop cheap, non-toxic and environmentally benign processes have now made researchers to focus on the use of natural products. These natural organic compounds are either synthesized or extracted from aromatic herbs, spices and medicinal plants. The use of natural products as corrosion inhibitors have been widely reported by several authors. (Saleh et al., 1982) reported that *Opuntia*



Figure 1. Juniperu plant.

extract, Aloe Vera leaves, orange and mango peels give adequate protection to steel in 5 and 10% HCl at 25 and 40°C. Srivatsava and Srivatsava (1981) found that tobacco, black pepper, castor oil seeds, acacia gum and lignin can be good inhibitors for steel in acid medium.

In fact, the first patented corrosion inhibitors used were either natural product such as flour, yeast etc., or byproducts of food industries for restraining iron corrosion in acid media (Cabrera et al., 1977) found that molasses treated in alkali solution inhibit the corrosion of steel in HCl used in acid cleaning (Cabrera et al., 1977). (Srivatsava and Sanyal 1973) studied the performance of caffeine and nicotine in the inhibition of steel corrosion in neutral media. (Khamis and Al-Andis, 2002) has proved the use of herbs (such as coriander, hibiscus, anis, black cumin and garden cress) as new type of green inhibitors for acidic corrosion of steel. (Parikh and Joshi, 2004) studied the anticorrosion activity of onion, garlic and bitter gourd for mild steel in HCl media. Ethanolic extract of *Ricinus communis* leaves was studied for the corrosion inhibition of mild steel in acid media by Anauda et al. (2005) have studied the inhibitory mechanism of low carbon steel corrosion of Mimosa tannin in H_2SO_4 media. Oguzie (2004) investigated the efficiency of *Telfaria occidentalis* extract as corrosion inhibitor in both HCl and H_2SO_4 media. The extracts of Chamomile, Halfabar, Black cumin and kidney bean were analyzed for their inhibitive action of corrosion of steel in acid media by Abdel-Gaber et al. (2006).

Natural chemical compounds are widely researched topics worldwide because of their potential activity against cerebrovascular diseases. Chemicals from *Juniperus phoenicea* berries are reported by Nasri et al. (2011), that Lipids (11%) from seeds are mainly unsaturated (86%). Minerals like Na (63.8 mg per 100 g DW) or K (373.9 mg per 100 g DW) are also quantified. Total reduced sugars are ca 192.6 mg g⁻¹ DW. Polyphenols and flavonoids from berries are

highly present with an average of 1764 ± 174.3 mg gallic acid per 100 g DW and 890 ± 47.6 mg rutin per 100 g DW, respectively. Mean free radical scavenging activities, determined by 1,1-diphenyl-2-picrylhydrazyl (DPPH) and 2,2'-azino-bis-3-ethylbenzthiazoline-6-sulphonic acid (ABTS), are 1337 ± 126.2 mM TEAC per 100 g DW and 1105.7 ± 95.9 mM TEAC per 100 g DW, respectively. All findings improve the possible presence of biologically active fractions in phytocomplex that could be used as such and/or extracted for the formulation of supplements and/or ingredients for pharmaceutical industries (Nasri et al., 2011).

The main aim of this research work is to study the chemical behaviors of mild steel in 2.0 M H_2SO_4 solutions at different temperatures using chemical and electrochemical techniques, and also, the effect of adding *Juniperus* plants as corrosion inhibitor for mild steel.

MATERIALS AND METHODS

Aggressive solution

H_2SO_4 (BDH) and bi-distilled water were used for preparing the aggressive solution (2.0 M) for all experiments in the absence and presence of various concentrations of *Juniperus* plant. The concentration of the inhibitor compounds ranged from 5% to 30% in 2M H_2SO_4 (Figure 1).

Preparation of plant extracts

Juniperus plants were collected in powder forms from Perfume shops. Stock solution of aqueous extract of the *Juniperus* plant were prepared by weighing four gram of the plant and mixed in a blender with 1000 ml deionized water for 15 min, heating until 90°C before boiling. The mixture is cooled for 24 h. The aqueous extract was separated by filtration and the solution kept in a flask at low temperatures in a refrigerator (for weight loss and gasometric measurements, respectively). From the stock solution (4g/l), plant extracts test solutions were prepared at concentrations of 5, 15, 20 and 30 %.

Specimen

The metal used for the study was mild steel electrode, the chemical composition was (wt%) P (0.035), Si (0.03), Mn (0.5), Cr (0.9), C (0.38) and Fe (97.64), it was a rod with a length of 4.0 cm and a diameter of 1.0 cm. The specimen surface was polished with different grade of emery papers (60, 120, 220, 400, 600, 800 and 1200), washed with bi-distilled water, degreased with acetone and dried with a stream of air and weighed.

Chemical measurement

Hydrogen gas evolution (Gasometric) method

The gasometric assembly used for the measurement of hydrogen gas evolution from the reaction was as originally described (Onuchukwu and Adamu 1990; Orubite and Oforika 2004). The gasometric assembly measures the volume of gas evolution from the reaction system. A reaction vessel was connected to a burette through a delivery tube. The corrodent was introduced into a tow-necked flask, and the initial volume of air in the burette was recorded. Thereafter, mild steel sample was dropped into the corrodent (2.0M H₂SO₄), and the flask quickly closed. The volume of hydrogen gas evolved from the corrosion reaction was monitored by the volume change in the level of the paraffin oil.

The change in volume was recorded every 5 min for 60 min. The same experiment was repeated in the presence of the additives. Hydrogen gas evolution measurements were carried out at 303, 313, 323 and 333°K. From the volume of hydrogen gas (H₂) evolved per minute, the degree of surface coverage (θ), and inhibition efficiency (I,%) was calculated from the equations:

$$\theta = 1 - \frac{R_{inh}}{R_{free}} \quad (1)$$

$$I(\%) = \left(1 - \frac{R_{inh}}{R_{free}} \right) \times 100 \quad (2)$$

where R_{inh} and R_{free} correspond to the corrosion rates in the presence and absence of inhibitor, respectively, as determined from the H₂ evolution curves.

Weight loss (gravimetric) method

On completion of each test, mild steel sample is separated from the test solution, washed with bi-distilled water and acetone, dried with stream of air and then re-weighed. From the weight loss data, the corrosion rates (CR) were calculated from

$$CR = \frac{WL}{At} \quad (3)$$

Where WL is weight loss in g, A is the specimen surface area (of 20 cm²) and t , the immersion period in hours. From the weight loss data obtained, the inhibition efficiencies (%I) for the corrosion of mild steel in 2.0M H₂SO₄ containing different concentration of inhibitor were calculated using:

$$\%I = \left(\frac{CR_{blank} - CR_{inh}}{CR_{blank}} \right) \times 100 \quad (4)$$

Where CR_{blank} and CR_{inh} are the corrosion rate in the absence and presence of the inhibitor, respectively.

Electrochemical measurements

Electrochemical testing of inhibitors has the major benefit of short measurement time and providing vital information about the mechanism of inhibition. The electrochemical cell is a conventional three-electrode Pyrex glass cell. The mild steel specimen was embedded in Teflon holder using epoxy resin with an exposed area of 0.785 cm². A platinum wire was used as an auxiliary electrode. The reference electrode was a Saturated Calomel Electrode (SCE) coupled to a Luggin capillary whose tip was located between the working electrode and the auxiliary electrode.

Electrochemical measurements were run using a potentiostat/galvanostat (ACM Gill AC instrument model 655) and a personal computer was used. ACM Gill software was used for Electrochemical Impedance Spectroscopy (EIS) and Potentiodynamic polarization (PDP) analysis. Prior to each experiment, the working electrode was polished successively with different grade of emery papers, then the polished metal surface was rinsed with de-ionized water, ethanol and finally dipped in the tested solution. After 10 min of electrode immersion to attain open circuit potential, the electrochemical measurement was done as follows:

Firstly, the EIS measurements were carried out using AC signals of amplitude 10 mV peak-to-peaks at the open circuit potential in the frequency range of 10 KHz to 0.5Hz. The charge transfer Resistance (R_{ct}) values have been calculated from the difference in the impedance at low and high frequencies. The capacitances of the double layer (Cdl) values are estimated from the frequency (f) at which the imaginary component of the impedance ($-Z''$) is maximum and obtained from the equation:

$$f(-Z''_{max}) = \left(\frac{1}{2\pi C_{dl} R_{ct}} \right) \quad (5)$$

The percentage inhibition efficiency, IE (%), values from EIS measurements were calculated from R_{ct} data as:

$$IE_R = \left(1 - \frac{R_{ct}^0}{R_{ct}} \right) \times 100 \quad (6)$$

where R_{ct} and R_{ct}^0 are the charge transfer resistance with and without certain concentration of *Juniperus* plants, respectively.

Secondly, for each experiment, after impedance spectrum was obtained, the potentiodynamic current potential curves was recorded immediately by changing the electrode potential automatically from -750 to -100 with scan rate of 1 mV s⁻¹. Tafel lines extrapolation method was used for detecting i_{corr} and E_{corr} values for the studied systems. Because of the presence of a degree of nonlinearity in the part of the obtained polarization curves, the corresponding anodic and cathodic Tafel slopes (ba and bc) were calculated as a slope of the points after corrosion potential (i) by ± 50 mV using a computer least square analysis. The IE (%) values from PDP measurements were calculated as follows:

$$IE_i \% = \left(1 - \frac{i_{corr}}{i_{corr}^0} \right) \times 100 \quad (7)$$

where i_{corr} and i_{corr}^0 are the corrosion current densities with and

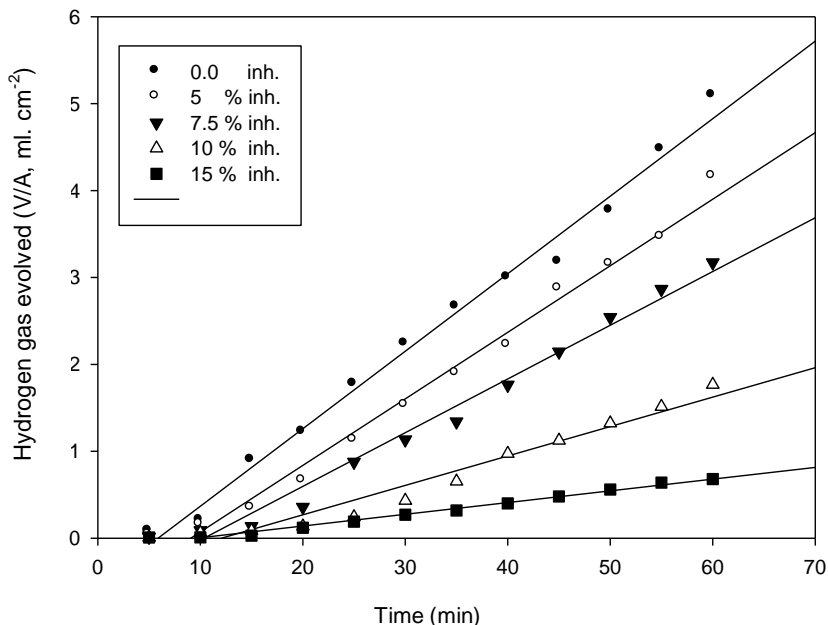


Figure 2. Volume of hydrogen / time curves for mild steel corrosion in 2.0 M H₂SO₄ in the absence and presence of different concentration of aqueous extract of *Juniperus* plant at 30°C.

Table 1. Corrosion rate (cm³.minute⁻¹) for the corrosion of mild steel in H₂SO₄ containing various concentration of *Juniperus*.

Concentration %	CRx10 ⁻⁵ (303)	CRx10 ⁻⁴ (313)	CRx10 ⁻⁴ (323)	CRx10 ⁻⁴ (333)
Blank	8.39	1.35	2.94	3.89
5	6.92	1.15	2.60	3.56
15	5.15	0.866	2.02	2.77
20	3.53	0.615	1.42	1.97
30	1.44	0.285	0.715	1.04

without certain concentration of *Juniperus* plants, respectively.

All the electrochemical measurements were performed in stagnant, aerated solutions adjusted at 30°C.

RESULTS AND DISCUSSION

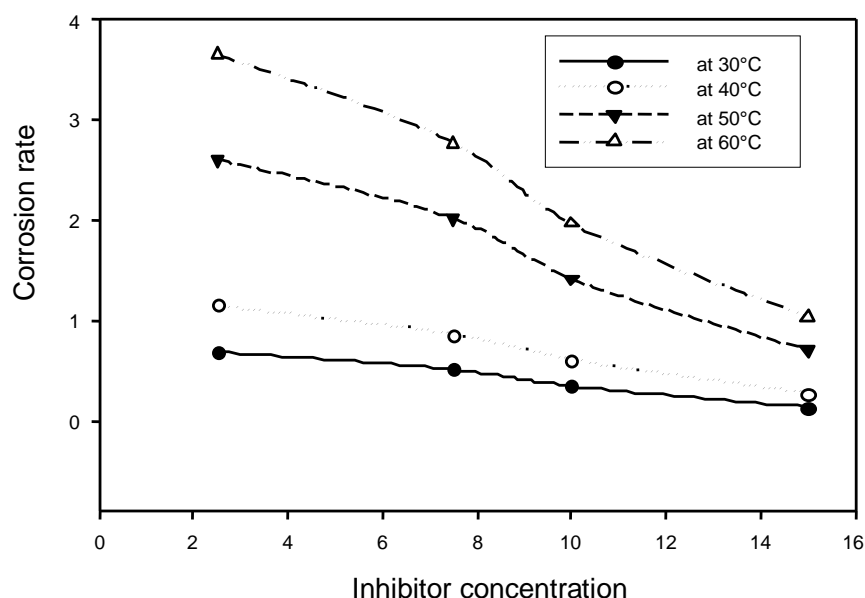
Corrosion rates and inhibition efficiency

Figure 2 shows the volume-time curves for dissolution of mild steel in 2.0M H₂SO₄ at 30°C in absence and presence of *Juniperus* plant over the concentration of range (5 to 30 %). The linear increase of hydrogen evolution with time indicates that the reaction is zero or greater than one. The data in Tables 1 and 2 shows that the dissolution rate decreases with increase in *Juniperus* plant concentration and hence the percentage inhibition efficiency increases.

Figure 3 shows the plot of corrosion rate against inhibitor concentration for mild steel corrosion in 2M H₂SO₄ in presence of different concentration of aqueous extract of *Juniperus* at different temperatures from weight loss measurements. The figure reveals that the rate of corrosion of mild steel in 2M H₂SO₄ decreases with increase in inhibitor concentrations at the various temperatures studied. The increase in inhibition efficiency with increase in concentration of the compound studied can be explained on the basis of increased adsorption of the compound on the metal surface. The plot of inhibition efficiency against concentration for *Juniperus* at different temperatures from (a) Gasometric and (b) Weight loss measurements is shown in Figure 4. Inspection of the figure revealed that inhibition efficiency increases with increase in the concentration of the inhibitor *Juniperus* and decreases with increase in temperature.

Table 2. Values of inhibition efficiency (%) of *Juniperus* for the corrosion of mild steel in H₂SO₄.

Concentration %	Gasometric				Weight loss			
	303	313	323	333	303	313	323	333
Blank	-	-	-	-	-	-	-	-
5	14.23	11.41	9.48	6.92	17.65	14.81	11.56	8.48
15	35.51	33.69	29.62	26.82	38.52	35.85	31.29	28.79
20	56.28	51.54	49.48	47.31	57.62	54.71	51.70	49.36
30	81.34	77.76	74.58	71.82	82.83	78.89	75.68	73.26

**Figure 3.** Plot of corrosion rate against inhibitor concentration for mild steel corrosion in 2 M H₂SO₄ in presence of different concentration of aqueous extract of juniperus at different temperature.

Decrease in inhibition efficiency with increase in temperature may be attributed to increase in the solubility of the protective films and of any reaction products precipitated on the surface of the metal that may otherwise inhibit the reaction. Ergun et al. (2008) has attributed the inhibition efficiency decrease with rise in temperature to be due to an enhanced effect of temperature on the dissolution process of steel in acidic media and/or the partial desorption of the inhibitor from the metal surface. A similar trend has been reported in Umoren et al. (2007). 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 (Niu et al., 2005).

Considering the dependence of inhibition efficiency on the concentration as represented in FigureS 3 and 4, it seems to be possible that the inhibitor acts by adsorbing and blocking the available active centre for steel

dissolution. In other words, the inhibitor decreases the active centre for steel dissolution. The adsorption process is made possible due to the presence of heteroatom such as O which is regarded as active adsorption centre. *Juniperus* molecule contains α -pinene, camphene, β -pinene, sabinene, myrcene, α -phellandrene, α -terpinene, γ -terpinene, 1,4-cineole, β -phellandrene, p-cymene, terpinen-4-ol, bornyl acetate, cayophyllene, limonene, camphor, linalool, linalyl acetate, borneol and nerol. The compound could be absorbed by the interaction between the lone pair of electrons of the oxygen atom or the electron rich π systems of the aromatic rings and the mild steel surface. This process as earlier reported by Umoren and Ebenso (2007) may be facilitated by the presence of vacant d-orbital of iron, making the steel as observed in d-group metals or transition element.

In addition to the molecular form, *Juniperus* can be present in protonated species in an acidic solution. The formation of positively charged protonated species

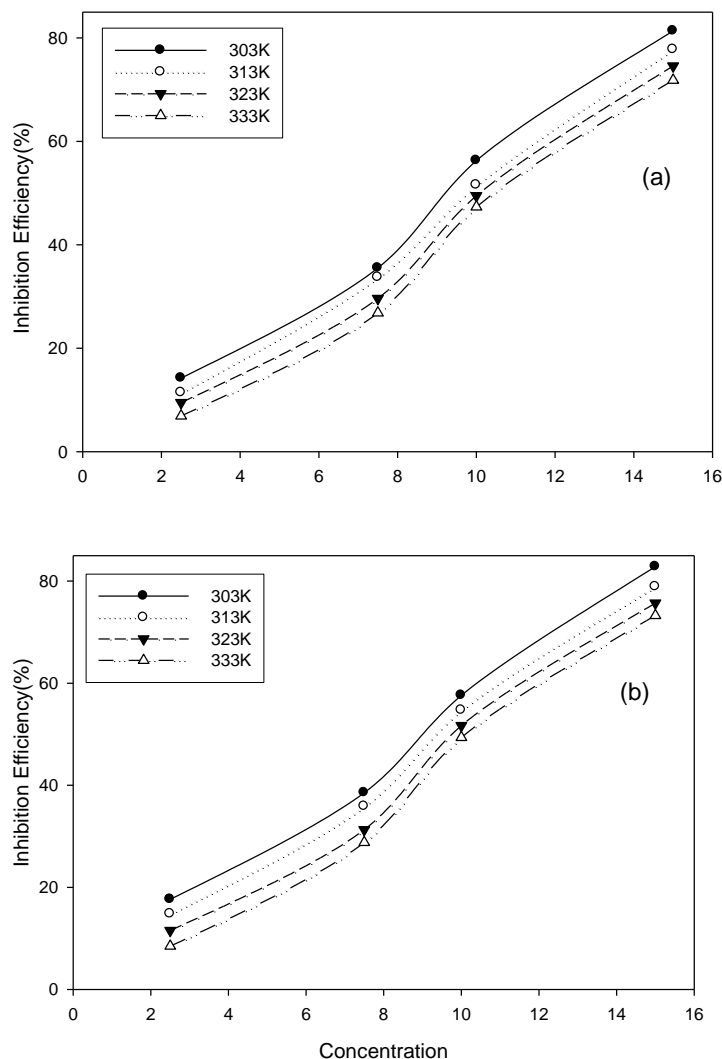


Figure 4. Plot of inhibition efficiency against inhibitor concentration for mild steel corrosion in 2 M H_2SO_4 in presence of different concentration of aqueous extract of juniperus (a) HE and (b) WL measurements at different temperature.

facilitates adsorption of the compound on the metal surface through electrostatic interaction between the organic molecules and the metal surface Feng et al. (1999).

EIS measurements

Figure 5 shows the Nyquist plots recorded for mild steel in 2.0 M H_2SO_4 , in the absence and presence of increasing concentrations of *Juniperus*. In general, as impedance diagrams for solutions examined have almost a semicircular appearance, it indicates that the corrosion of mild steel is mainly controlled by a charge transfer process (Metiko et al., 1998; Larabi and Harek (2004; Bentiss et al., 2005).

The equivalent circuit model of the previous systems is shown in Figure 6, which consists of parallel combination of resistor, R_{ct} and a capacitor, C_{dl} , both are in series to resistor, R_{sol} . Equivalent circuit was successfully applied for some corrosion and corrosion inhibition systems (Zhao et al., 2005; Dehri and Ozcan, 2006; Khaled, 2006). All the obtained EIS parameters (R_{ct} and C_{dl}) and the $IE_{R_{ct}}$ for mild steel corrosion in 2 M H_2SO_4 in absence and presence of different concentrations of *Juniperus* were recorded in Table 3. The results in this table can be illustrated as follows:

In general, R_{ct} value increases and C_{dl} value decreases as the concentration of extracts increases in 2.0 M H_2SO_4 which indicates the adsorption of the inhibitor on the metal surface. This was a result of increasing surface

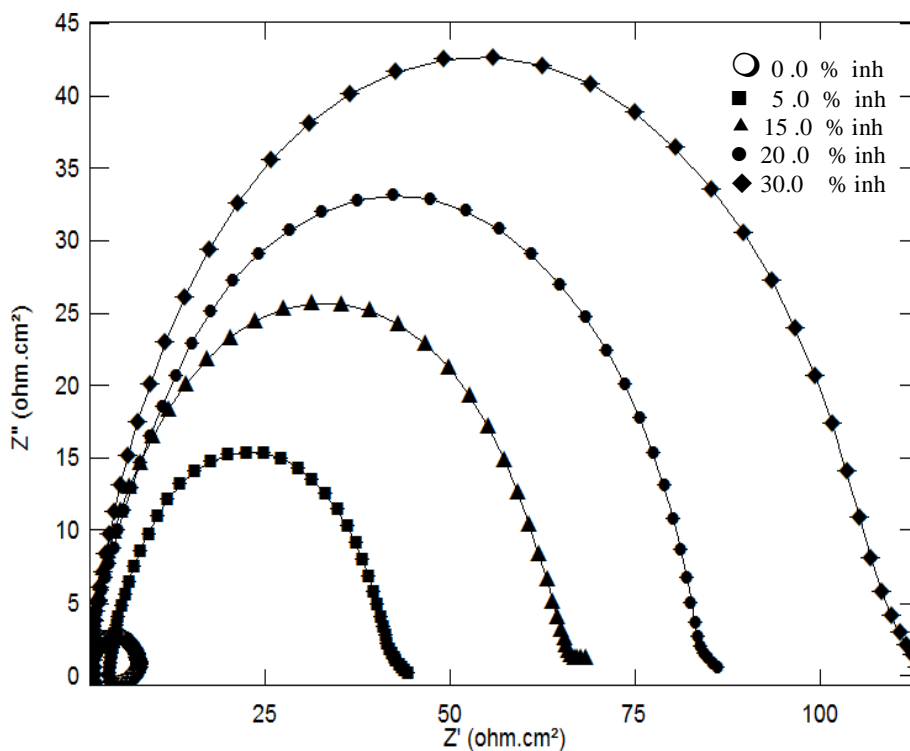


Figure 5. Nyquist plots for mild steel in 2.0 M H₂SO₄ in absence and presence of different concentration of aqueous extract of *Juniperus* plant at 30°C.

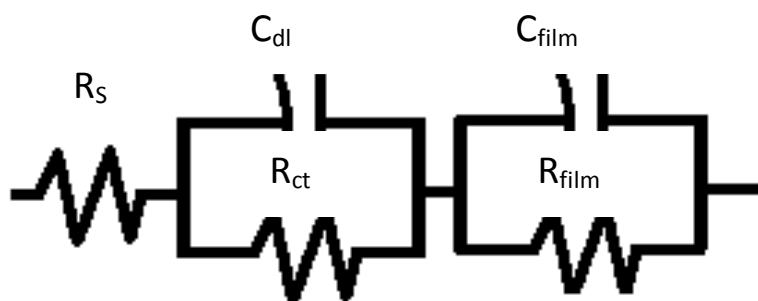


Figure 6. EIS equivalent circuit of Al in 2.0 M H₂SO₄ with and without different concentrations of *Juniperus*.

Table 3. Corrosion parameters obtained from Electrochemical measurements for mild steel in 2.0 M H₂SO₄ with and without different concentrations of *Juniperus*.

$C_{inh.}\%$	Impedance		PDP					
	R_{ct} (ohm cm ²)	C_{dl} ($\mu\text{F cm}^{-2}$)	$IE_{R_{ct}}$ %	$-E_{corr.}$ (mV)	b_a (mV)	b_c (mV)	$I_{corr.}$ ($\mu\text{A cm}^{-2}$)	$IE_{I_{corr.}}$ (%)
0.0	2.133	137.7	-	465.76	50.74	61.28	1.589	-
5	3.688	108.9	20.65	503.10	68.47	63.93	1.301	18.12
15	9.018	103.6	76.35	516.90	76.68	79.03	0.400	74.76
20	11.46	92.47	81.39	492.31	84.59	86.90	0.301	81.05
30	14.27	82.75	85.05	498.68	69.34	57.98	0.491	84.90

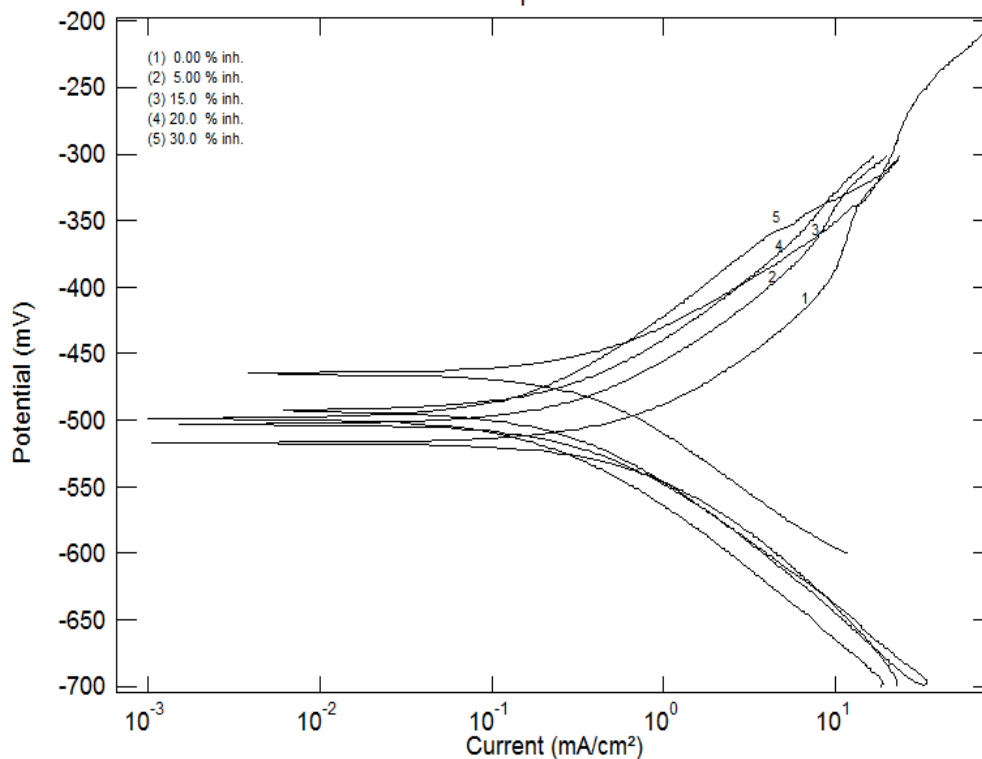


Figure 7. PDP curves for mild steel in 2.0 M H₂SO₄ in absence and presence of different concentration of aqueous extract of *Juniperus* plant at 30°C.

coverage by the inhibitor, which led to an increase in IE%.

PDP measurements

Figure 7 show the effect of *Juniperus* on the anodic and cathodic polarization curves for mild steel in 2.0 M of H₂SO₄. It was observed that steel in 2.0 M of H₂SO₄ extracts increased, both of the anodic and cathodic over potentials but its influence on the cathodic side is much less obvious (that is, act predominately as anodic inhibitors). All polarization parameters, that is, corrosion potential (E_{corr}), Tafel slopes (b_c and b_a), corrosion current density (i_{corr}) and the corresponding IE_{corr} (%) values for mild steel corrosion in 2.0 M of H₂SO₄ in the absence and presence of different concentrations of extracts were estimated and listed in Table 3 and the following observations could be drawn.

The anodic (b_a) and cathodic (b_c) Tafel slopes do not change significantly in inhibited solution as compared to uninhibited solution. These observations suggest that *Juniperus* adsorb on the metal surface by blocking the active sites of steel surface, without affecting the mechanism of corrosion.

This type of behaviour has been observed for mild steel

in acid solutions containing *Ammi majus* L. fruit extracts (Arab et al., 2005):

- (1) The values of E_{corr} change somewhat to less negative values with increasing extracts concentration in 2.0 M H₂SO₄.
- (2) The IE_{corr} values are in good agreement with that obtained from EIS measurements.

Effect of temperature

The results obtained from temperature studies of the corrosion of mild steel in 2M H₂SO₄ in the absence and presence of *Juniperus* in the temperature range 30-60°C revealed that increasing temperature increases corrosion rate and decreases inhibition efficiency at all the concentrations studied. According to Dehri and Ozcan (2006), the relationship between the temperature dependence of percent inhibition efficiency (IE %) of an inhibitor and the activation energy found in its presence was given as follows:

- (a) Inhibitors whose IE% decrease with temperature increases, while the value of activation energy (E_a) found is greater than that in the uninhibited solution;
- (b) Inhibitors whose IE% does not change with

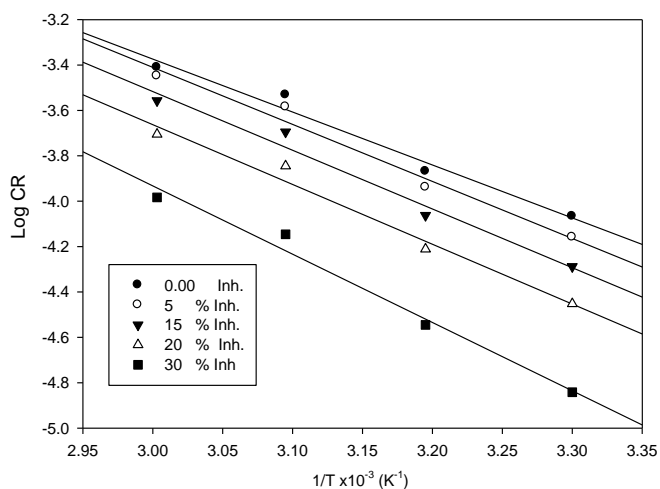


Figure 8. Arrhenius plot for mild steel corrosion in 2.0 M H₂SO₄ in the absence and presence of different concentration of aqueous extract of *Juniperus* plant.

Table 4. Kinetic/thermodynamic parameters for mild steel corrosion in 2M H₂SO₄.

System/concentration	E_a (kJ.mol ⁻¹)	$-\Delta H^\circ$ (kJ.mol ⁻¹)	$-\Delta S^\circ$ (J/mol.K ⁻¹)
Blank	0.069	0.0065	104.28
5	0.079	0.00998	105.55
15	0.081	0.01955	108.84
20	0.081	0.01079	106.53
30	0.098	0.01796	109.66

temperature variation, the activation energy (E_a) does not change with the presence or absence of inhibitors;

(c) Inhibitors whose IE% increases with temperature increase, the value of activation energy (E_a) found is less than that in the inhibited solution. In an acidic solution the corrosion rate is related to temperature by the Arrhenius Equation:

$$\log CR = -E_a / 2.303 RT + \log A \quad (8)$$

where CR is the corrosion rate, E_a is the apparent activation energy, R is the molar gas constant, T is the absolute temperature and A is the frequency factor. Figure 8 shows the plot of log CR versus 1/T. Linear plots were obtained for both *Juniperus*. The values of E_a were computed from the slope of the straight lines and are listed in Table 4. It is clear from the table that E_a values in the presence of the additives are higher than that in the absence. The higher activation energies imply a slow reaction and that the reaction is very sensitive to temperature. Similar results have been reported in

(Umoren and Ebenso 2008). The increase in the activation energy in the presence of *Juniperus* signifies physical adsorption (Awad 2006). This conclusion is denoted by the decrease in inhibition efficiency with increasing temperature. Enthalpy and entropy of activation ΔH° and ΔS° were obtained by applying the transition state equation:

$$CR = (RT/Nh) \exp(\Delta S^\circ/R) \exp(-\Delta H^\circ/RT) \quad (9)$$

Where h is the Planck's constant, N is the Avogadro's number, T is the absolute temperature, and R is the universal gas constant. Plots of Log (CR/T) as a function of 1/T were made as seen in (Figure 9). Straight lines were obtained with a slope of $(-\Delta H^\circ/R)$ and an intercept of $(\ln R/Nh + \Delta S^\circ/R)$ from which the values of ΔH° and ΔS° were calculated, and listed in Table 3. While an endothermic adsorption process ($\Delta H^\circ > 0$) is attributed unequivocally to chemisorptions, an exothermic adsorption process ($\Delta H^\circ < 0$) may involve either physisorption or chemisorptions or a mixture of both process (Umoren et al., 2008). The negative values of

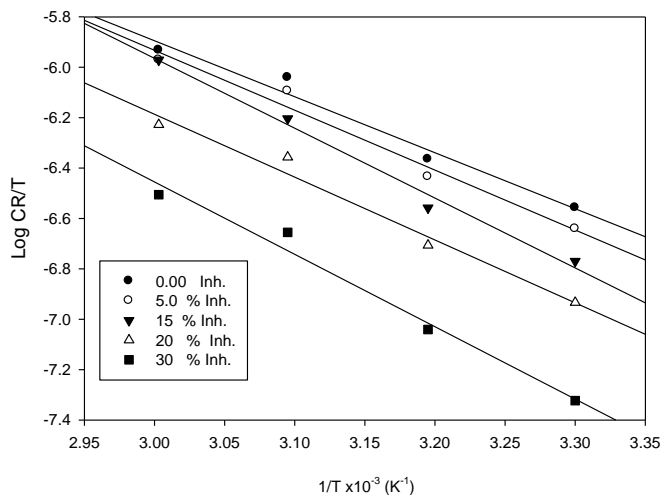


Figure 9. Transition state plot for mild steel corrosion in 2.0 M H_2SO_4 in the absence and presence of different concentration of aqueous extract of *Juniperus* plant.

ΔH° show that the adsorption is exothermal with an ordered phenomenon ascribed by the negative values of ΔS° . This order may more probably be explained by the possibility of the formation of iron complex on the metal surface (Bousseksou et al., 2007; Herrag et al., 2008).

Adsorption isotherm

The nature of inhibitor interaction on the corroding surface during corrosion inhibition of metals has been deduced in terms of adsorption characteristics of the inhibitor. The decrease in the corrosion rate by the addition of aqueous extract of *Juniperus* plant is attributed to either adsorption of the plant components on the metal surface or, the formation of a barrier film separating the metal surface from the corrosive medium (Arab et al., 2008), and this is usually confirmed from the fit of the experimental data to various adsorption isotherms. The adsorption process is influenced by the nature and surface charge of the metal, by the type of aggressive electrolyte and by the chemical structure of the inhibitors (Refaey et al., 2004). The information on the interaction between the inhibitor and mild steel surface can be provided by the adsorption isotherm. Attempts were made to fit to various isotherms including Frumkin Langmuir, Temkin, Freundlich, Flory-Huggins, and it was found that the adsorption of *Juniperus* plant follows Frumkin adsorption isotherm. Frumkin adsorption isotherm can be written in the form (Lj Vracar and Drazic, 2002):

$$\theta/(1-\theta) = K_{ads} c e^{a\theta} \quad (10)$$

where θ is the coverage degree, c is the concentration of

the inhibitor in the electrolyte, K_{ads} is the equilibrium constant of the adsorption process, and a is an interaction parameter, taking into account the attraction ($a > 0$) or repulsion ($a < 0$) between the adsorbed species. For $a = 0$ (no interaction) this isotherm becomes equivalent to the Langmuir isotherm (Christov and Popova, 2004). In order to determine the parameters K_{ads} and a , the Frumkin isotherm was linearized in the form:

$$\ln(\theta/(1-\theta)C) = 2 a \theta + \ln K_{ads} \quad (11)$$

Plot of $\ln(\theta/(1-\theta)C)$ vs. θ (Frumkin adsorption plot) for the adsorption of *Juniperus plant* on the surface of mild steel in 2M H_2SO_4 , without and *Juniperus* is shown in Figure 10. The obtained plot for Frumkin adsorption isotherm is linear with a correlation coefficient higher than 0.98.

The result indicates that Frumkin adsorption isotherm is valid for concentrations of *Juniperus* plant. Frumkin adsorption isotherm considers lateral interactions between adsorbed inhibitor molecules as well as those among inhibitor and water molecules, indicating that the inhibitor is displacing water molecules from the metal surface. The value of the interaction parameter calculated from the slope in the plot representing Frumkin adsorption isotherm (Figure 10). The positive sign of the constant a , indicates highly attractive lateral interactions in the adsorbed layer (Lj Vracar and Drazic, 2002). With increasing corrosion inhibitor, concentration inhibitor molecules probably start to desorb due to interaction between the inhibiting molecules already adsorbed at the surface and those present in the solution. With increasing concentration of the inhibitor, the interactions become stronger, leading to secondary desorption.

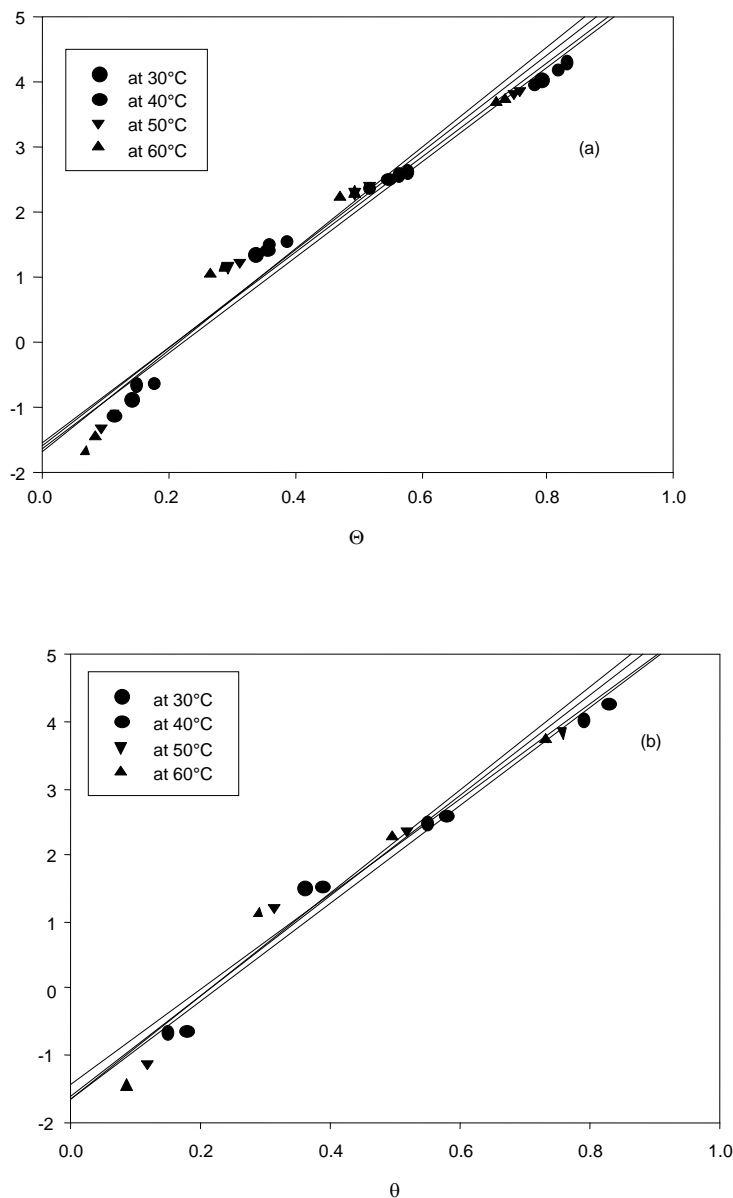


Figure 10. Frumkin adsorption isotherm plot for mild mild steel corrosion in 2 M H₂SO₄ in the presence of different concentrations of the aqueous extract of Juniperus (a) Gasometric and (b) Weight loss measurement.

Thermodynamic parameters are important to study the inhibitive mechanism. The standard free energy of adsorption ΔG_{ads}° related to the equilibrium constant of the adsorption process K_{ads} can be obtained from the following Equation (Zhang et al., 2010):

$$K_{ads} = 1/55.5 \exp (-\Delta G_{ads}^{\circ} / RT) \quad (11)$$

where 55.5 is the concentration of water in the solution in 1 mol·dm⁻³, R the universal gas constant and T the thermodynamic temperature. Calculated value for K_{ads} ,

ΔG_{ads}° , obtained from the adsorption isotherm is shown in Table 5a.

The negative value of ΔG_{ads}° indicates that the inhibitor is spontaneously adsorbed on the mild steel surface (Fouda et al., 2012). It is generally accepted that the values of ΔG_{ads}° in aqueous solution up to -20 kJmol^{-1} indicates physisorption. In this type of adsorption the inhibition acts are due to the electrostatic interaction between the charged molecules and the charged metal. While the values of ΔG_{ads}° around -40 kJmol^{-1} or lower, are seen as chemisorptions, which is due to the charge

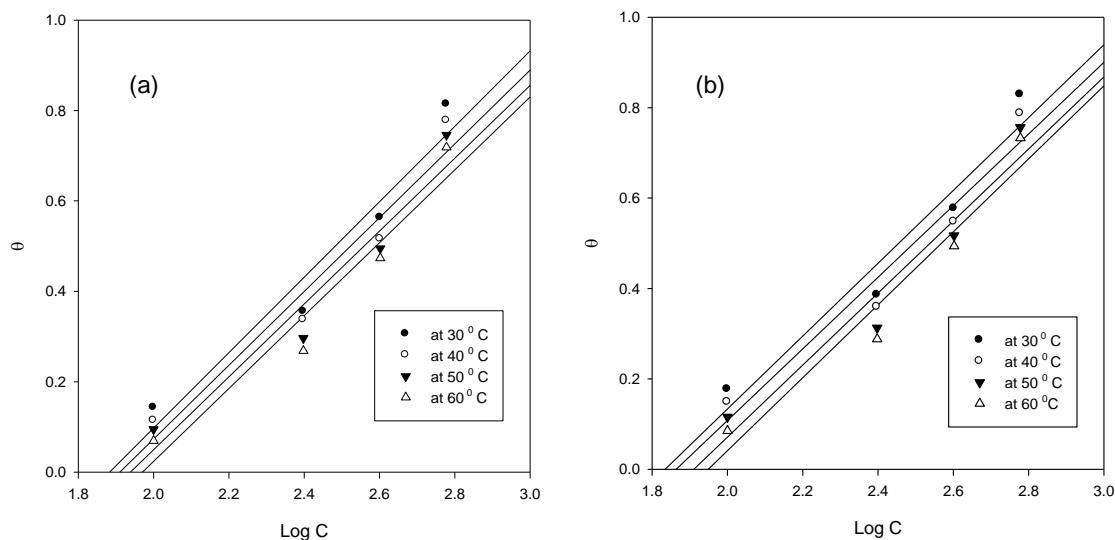


Figure 11. Temkin adsorption isotherm plot for mild steel corrosion in 2M H₂SO₄ in the presence of different concentrations of the aqueous extract of *Juniperus* (a) Gasometric and (b) Weight loss measurements.

Table 5a. Some parameters of the linear regression from Frumkin adsorption isotherm.

Parameter	Temperature (°C)	-ΔG (kJ.mol ⁻¹)	Frumkin isotherm		
			a	K	R ²
Gasometric	30	6.13	3.68	0.196	0.98
	40	6.44	3.66	0.214	0.97
	50	5.34	3.70	0.131	0.96
	60	4.63	3.85	0.096	0.95
Weight loss	30	5.96	3.67	0.192	0.98
	40	6.72	3.56	0.238	0.98
	50	6.48	3.74	0.201	0.97
	60	6.47	3.86	0.187	0.95

sharing between inhibitor molecules and the metal surface (Khaled and Al-Qahtani 2009). The obtained value of standard free energy of adsorption, ΔG_{ads}° in this study is lower than -20 kJ mol^{-1} and it indicates that the adsorption of *Juniperus* on mild steel surface represents the pure physisorption. Figure 11 shows the plot of surface coverage (θ) as a function of logarithm of inhibitor concentration ($\log C$) for mild steel in 2 M H₂SO₄ containing *Juniperus* at different temperatures. Linear plots were again obtained, which shows that Temkin adsorption isotherm is obeyed. The characteristics of Temkin isotherm are given by the equation:

$$\exp(-2a\theta) = KC \quad (12)$$

The adsorption parameters deduced from Temkin isotherm are presented in Table 5b. It is also seen that

the values of 'a' are positive in all cases, indicating highly attractive lateral interactions in the adsorbed layer (Tang et al., 2006), K values, as shown in Table 5b.

The decrease in inhibition efficiency with rise in temperature, as illustrated in Tables 1 and 2, suggests possible desorption of some of the adsorbed inhibitor from the metal surface at higher temperatures. Such behavior shows that the additives were physically adsorbed on the metal surface (Oguzie, 2004). This is further confirmed by the decrease in K values with rise in temperature, as seen in Table 5a, b. The proposed physisorption mechanism may be rationalized by considering the fact that the *Juniperus* could interact with the corroding steel surface via the protonated N atom, which can be adsorbed at cathodic sites and hinder the hydrogen evolution reaction, with possible contributions from the lone pair of the electrons on the oxygen atom.

Table 5b. Some parameters of the linear regression from Temkin adsorption isotherm.

Parameter	Temperature (°C)	-ΔG (kJ.mol ⁻¹)	Temkin isotherm		
			a	K	R ²
Gasometric	30	6.16	0.41	0.208	0.95
	40	6.39	0.40	0.210	0.95
	50	6.59	0.40	0.209	0.94
	60	6.72	0.40	0.204	0.94
Weight loss	30	6.27	0.42	0.218	0.94
	40	6.50	0.41	0.219	0.95
	50	6.64	0.40	0.214	0.94
	60	6.74	0.40	0.206	0.95

Conclusion

Juniperus plant acts as an inhibitor for corrosion of mild steel in 2M H₂SO₄ solution. The inhibition efficiency increases with increase in concentration of *Juniperus plant* but decreases with an increase in temperature. The *Juniperus plant* was found to obey Frumkin adsorption isotherm and Temkin adsorption isotherm from the fit of experimental data. The values of ΔG°_{ads} are negative which suggest that the inhibitors were strongly adsorbed on the mild steel surface. The values obtained, support the physical adsorption mechanism. Thermodynamic parameters revealed that the adsorption process is spontaneous.

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