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THERMODYNAMIC STUDY OF GREEN CORROSION INHIBITOR ON MILD STEEL WITH AQUEOUS EXTRACT OF *ZIZIPHUS JUJUBA* STEM IN 1M HCL SOLUTION

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The Corrosion inhibition of mild steel in 1 M HCl solution with aqueous extract of *Ziziphus Jujuba stem* is studied by weight loss method at 303-333K temperatures. It is found that inhibition efficiency rise with increase in concentration of extract and decreased with rise in temperature. Maximum 78.05% inhibition efficiency was observed at 303 K and 8% (v/v) concentration of *Ziziphus Jujuba stem*. Value observed for Activation energy, Gibbs free energy and variation in I.E. with temp. Suggest physisorption. Adsorption of extract at mild steel surface follows Langmuir adsorption isotherm. Negative values of Gibbs energy reveals the spontaneity of inhibition process in extracts at studied temperatures.

KEYWORDS : *Ziziphus Jujuba* stem, Corrosion, Langmuir adsorption isotherm, Mild steel, Weight loss method

INTRODUCTION

Mild steel has widespread use in industries such as chemical processing, petroleum, constriction, pipelines, mining, marine applications and refining. Although it is one of the common metal alloys used in various industries but it suffers a major problem which is corrosion. Corrosion is the degradation of metal and their alloys by an electrochemical reaction with environment. Corrosion of metals and alloys is a well studied industrial problem hence found a fertile research field in green chemistry also. The introduction of corrosion inhibitors is the best way to prevent metallic corrosion and save the great economic loss of country[1].

Generally many chemical compounds is used as corrosion inhibitors but most of these are toxic and expensive. Green inhibitors are generally extracts of various parts of plants. Plant extracts are low cost and environmental safe. So the main advantage of using plant extracts as corrosion inhibitors are economic and environment safe. They have great corrosion inhibitor property. So they are widely used as corrosion inhibitors for metals and alloys in acidic, basic and neutral media.

Literature survey reveals various plant extracts that have been used as corrosion inhibitors for protection of different metals and their alloys. Extract of fenugreek seeds and roots [2], essential oils of *Menthaspicata, Lavandulamultifida, Pulicariamauritanica* [3,4] *Azadirachtaindica* [5,6], extract of *Ananascomosus L.*[7], *Embilicaofficinalis* [8], *Garcinacola and Cola nitida* [9], *Neriumolender leaves, Calotropisprocera* etc. have been studied. In the continuity of above corrosion inhibition studies to find out better corrosion inhibitor, the present work has been carried out which reveals the adsorption behaviour and corrosion prevention properties of aqueous extract of stem & fruits of *Ziziphus Jujuba* for mild steel in 1 M HCl solution.

MATERIALS AND METHODS

Preparation of Ziziphus jujuba stem

The stem of *Ziziphus Jujuba* plant were taken, washed and air dried for 6-7 days, crushed and grind mechanically. 20 g of stem powder was heated in 200 mL distilled water for one hour using air condenser at 70°C – 80°C. This extract was left overnight and then filtered and make up to 500 mL with distilled water for the experiment.

Selection of steel specimens

Rectangular mild steel (grade 220) specimens of 5 cm length and 1cm width and 0.03cm thickness were taken and abraded with a series of emery papers, degreased with acetone, washed with distilled water, dried and constant weight was recorded by electronic balance.

Solution Preparation

1M HCl solution was prepared by 37% HCl (Merck Ltd.) using distilled water. The employed concentration range of aqueous extract of *Ziziphus Jujuba stem* and *Ziziphus Jujuba fruits* was 1% to 8% (v/v).

Gravimetric Measurements

Gravimetric method is widely used method because of its reliability and simplicity in corrosion inhibition experiments. For each experiment 100 mL test solution was taken in 250 mL beaker and Rectangular specimen was immersed in it with plastic thread for onehour.

The experiments were carried out at different temperatures from 303 K to 333K in thermostatic water bath. After one hour specimens were removed, washed with distilled water, acetone dried and abraded with series of emery papers and then weighted accurately with electronic balance. It was noted that the surfaces of specimens became rougher in test solutions without the inhibitor than the surfaces of specimens which were immersed in test solutions containing different concentrations of inhibitor.

RESULT AND DISCUSSION

Corrosion rates

Corrosion rates were calculated by following equation [10,11**]**

$$\text{C R (g cm}^{-2}\text{min}^{-1}) = (W_1\text{-}W_2/At) \qquad \text{...(1)}$$

where CR is corrosion rate, W_1 is weight of mild steel specimen without inhibitor and W_2 is weight of mild steel specimen with inhibitor, A is area of MS specimen and t is immersion time. **Tables 1** shows that corrosion rates of mild steel decrease with rise in concentration of *Ziziphus Jujuba* stem inhibitor at all studied temperatures. This could be subjected to the adsorption of the phyto-constituents of inhibitor molecules with increase in concentration of inhibitor. The corrosion rate obeys Arrhenius type reaction, as it increases with rise in temperature [12].

Table 1. Mild steel corrosion rates in 1 M HCl solution in absence and presence of different concentrations of *Ziziphus jujuba* STEM at different temperatures

C_{inh}in (v/v)%	CR × 10^{-3} (g cm^{-2} min^{-1}) 30°C	40°C	50°C	60°C
0	0.82	1.41	2.11	2.78
1	0.59	1.21	1.87	2.65
2	0.42	1.03	1.64	2.49
3	0.37	0.91	1.47	2.37
5	0.27	0.78	1.31	2.21
8	0.18	0.66	1.22	2.15

Inhibition efficiency

From the obtained corrosion rates, inhibition efficiencies were calculated by using following equation (2).

$$\text{IE\%} = \frac{CR_{blank} - CR_{inh}}{CR_{blank}} \times 100 \qquad \text{...(2)}$$

where CR_{blank} is the corrosion rate in absence of inhibitor and CR_{inh} is corrosion rate in presence of inhibitor. *Ziziphus jujuba* stem data are given in Table 1 show that %IE increase with in extract concentration and indication that increase in number of components of extract adsorbed on mild steel surface, which block the active sites of metal from acid attack and protect the metallic corrosion [13]. Further the decrease in % I.E. with rise in temperature suggests electrostatic interaction (physical adsorption) of the extract molecules on mild steel surface. This further indicates desorption of adsorbed inhibitor species at higher temperatures and metal dissolution takes place. [14] 78.05% inhibition efficiency is observed at 8% (v/v) concentration of inhibitor *Ziziphus jujube*stam.

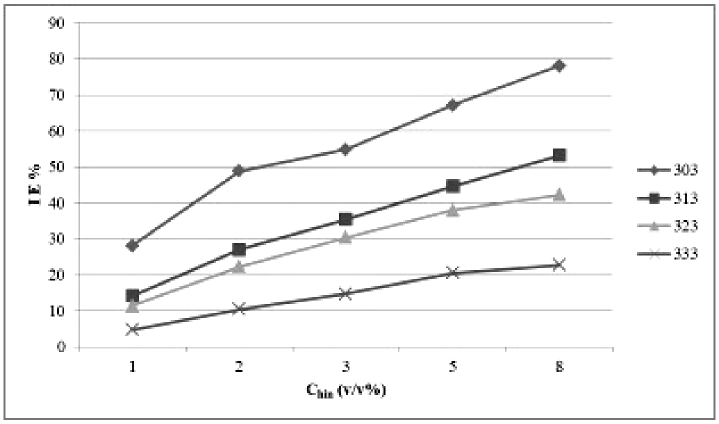

Fig. 1. Variation in IE % for mild steel corrosion in 1M HCl at different concentrations of *Ziziphus jujuba* stemat different temperatures

Table 2. Inhibition efficiencies of *Ziziphus jujuba* stem at different concentrations and temperatures in 1 MHCl solution

C_{inh} in (v/v)%	I E (%)			
	30°C	40°C	50°C	60°C
1	28.04	14.18	11.37	4.68
2	48.78	26.95	22.27	10.43
3	54.88	35.46	30.33	14.75
5	67.07	44.68	37.91	20.50
8	78.05	53.19	42.18	22.66

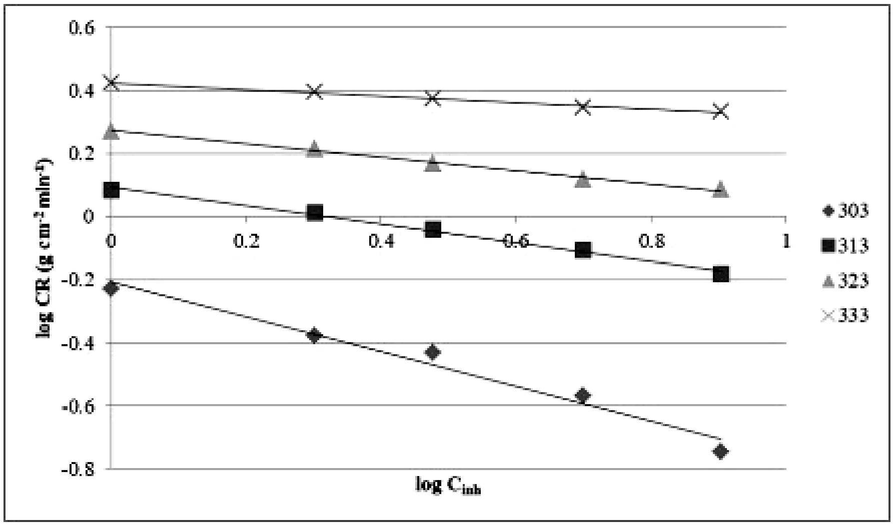

Figure 2. Variation in log CR with log C_{inh} for mild steel corrosion in 1M HCl in presence of different concentration of Ziziphus jujuba stem at various studied temperatures

Kinetic Parameters

Assuming that corrosion rates of steel specimens against concentration of inhibitor obeys kinetic relationship as equation (3)

$$\log CR = \log K + B \log C_{inh} \qquad ...(3)$$

where K is rate constant and equal to CR when inhibitor concentration is unity. B is reaction constant which is measure of inhibitor effectiveness and C_{inh} is the concentration v/v% (mL/100mL) of *Ziziphus jujuba* stem. Figure 2 plots between log CR and log C_{inh} values at various studied temperatures. B and K were calculated by slope and intercept of straight lines obtained in **Figure 1** .The obtained results are summarized in **Table 2** which can be discussed as follows [24]. Negative values of B indicate that corrosion rate is inversely proportional to concentration of inhibitor. In other words the corrosion rates decrease with rise in concentration of inhibitor species. The high negative values of B reflects good inhibitive property of inhibitor High negative value of B can be observed as steep slope in graph (**Figure 2**).Value of B is high at lower temperatures, indicates that inhibitive species is more effective at comparatively lower temperatures. The rise in K values with increase in temperature, indicating the rise in corrosion rates with temperatures.

Temperature (°C)	**Kinetic Parameters**	
	B	**K ×10^{-3} (g cm^{-2} min^{-1})**
30°C	–0.552	0.6209
40°C	–0.291	1.2359
50°C	–0.212	1.8707
60°C	–0.105	2.6546

Table 3. Kinetic parameters for mild steel corrosion in 1 M HCl solution with *Ziziphus jujuba* stem

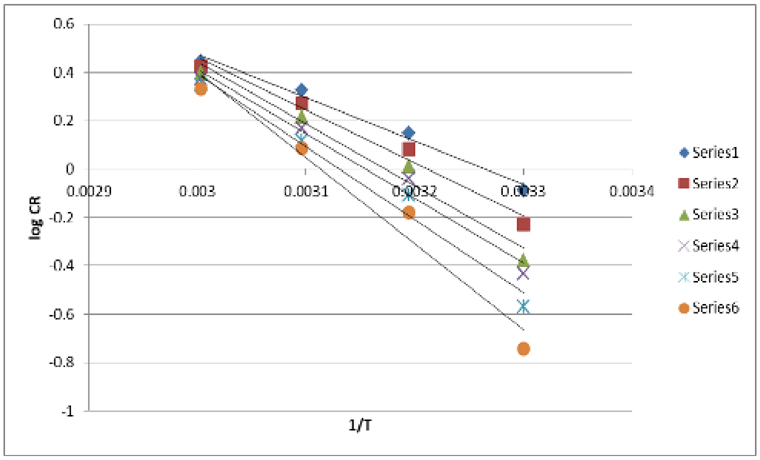

Figure 3. Arrhenius plots for mild steel corrosion in 1M HCl in absence and presence of various concentration of *Ziziphus jujuba* stem

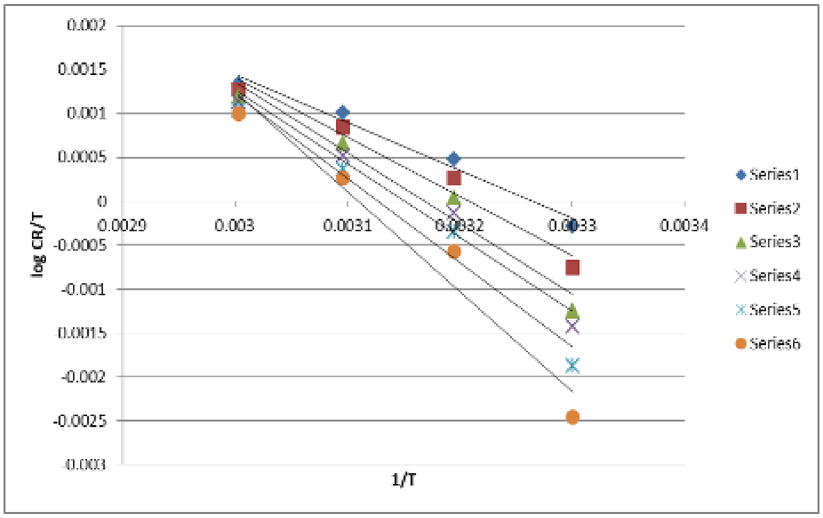

Figure 4. Transition-state plots for mild steel corrosion in 1M HCl in absence and presence of various concentrations of *Ziziphus jujuba*stem

Thermodynamic and activation parameters

Thermodynamic and activation parameters like apparent activation energy E_{act}, enthalpy of activation Δ H*entropy of activation **Δ**S* can be calculated for steel dissolution process. Activation energies E_{act} were calculated by applying Arrhenius equation (4)

$$\log CR = \log A - \frac{Eact}{2.303RT} \quad (4)$$

where A is Arrhenius pre-exponential factor, E_{act} is activation energy, R is universal gas constant, T is absolute temperature. The slope of log CR vs 1/Tin **Figure 3** gives the values of activation energies at studied concentrations. **Table 4** contains the calculated data of activation energies. The values of activation energies in presence of inhibitor were found higher than in uninhibited solution. This indicates the formation of higher energy barrier in corrosion reaction by inhibitor molecules. The increase in E_{act} for corrosion process in inhibitor solution further interpreted as physical adsorption of inhibitor species on mild steel surface [15,16,17**]** Besides this according to Damaskin [18**]**, the value of activation energy lesser than 80kJ/ mol and even smaller than 5kJ /mol represent physical adsorption. This assertion supports the experimental results obtained in the present study. The values of enthalpy of activation ΔH* and entropy of activation **Δ**S*can be calculated by following transition state equation (5).

$$\log(CR/T) = [\log(R/Nh) + [\Delta S^*/2.303R - [\Delta H^*/2.303RT)] \quad ...(5)$$

where h is plank's constant, N is Avogadro number R is the gas constant A plot of log(CR/T) vs 1/T gave a straight line with slope of (-ΔH*/2.303R) and intercept of [(log R/Nh) +(ΔS*/2.303 R)] from which the values of ΔH* and **Δ**S* can be calculated (**Figure 4**). These values are tabulated in Table 4. Values of ΔH*were found positive. Positive values indicate endothermic nature of steel dissolution process. [19] Endothermic process further indicates that mild steel dissolution reduces at lower temperatures and increases with in temperatures. Negative values of ΔS* are indicative of formation of activated complex in rate determining step, which further indicate association rather than dissociation step, meaning the decrease in disorder takes place on going from reactants to activated complex. [20,21] It is also observed from data in Table 4 that E_{act} and ΔH* vary in the same manner. Values of both E_{act} and ΔH* with in concentration of inhibitor, suggesting that energy barrier rise within inhibitor concentration. This means that corrosion reaction will further be pushed to surface sites that are characterized by progressively higher values of E_{act} as the concentration of inhibitor becomes higher [22, 23**].** The values of activation energy were found higher than corresponding values of enthalpy of activation, indicate the involvement of a gaseous reaction, simply hydrogen evolution in corrosion process, associated with a decrease in total reaction volume.

Table 4. Activation and thermodynamic parameters for mild steel corrosion in 1 M HCl solution with *Ziziphus jujuba*

C_{inh}in (v/v)%	E_{act}(kJ/mol)	ΔH^*(kJ/mol)	ΔS^*(J/mol/K)
0	34.22	31.64	-221.9
1	41.63	39.17	-182.12
2	48.92	46.64	-171.58
3	50.95	48.81	-138.46
5	57.52	55.54	-43.23
8	67.93	66.02	-43.23

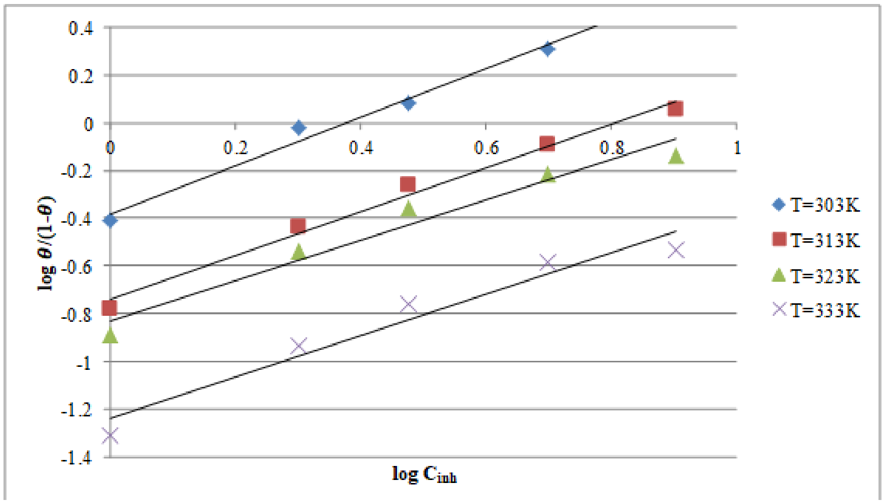

Figure 5. Langmuir adsorption isotherms of *Ziziphus jujuba* stem on mild steel surface in 1M HCl at different studied temperatures

Adsorption isotherm and Gibbs energy

The nature of adsorption can be explained by the process at metal/electrolyte interface. Further to understand the nature of adsorption, obtained surface coverage θ were fitted in different adsorption isotherms. Langmuir adsorption isotherm was the best fit. The mathematical expressions for Langmuir adsorption isotherm can be expressed by the following equation [24-28].

$$\frac{c}{\theta} = \frac{1}{K_{ads}} + C_{inh} \qquad (6)$$

Rearranging the above equation (6) we get

$$\frac{\theta}{1-\theta} = K_{ads} C_{inh} \qquad ...(7)$$

$$\log\left(\frac{\theta}{1-\theta}\right) = K_{ads} + C_{inh} \qquad ...(8)$$

where K_{ads} is the equilibrium constant of adsorption, θ is the surface coverage, (1-θ) is the uncovered surface, C_{inh} is the concentration of inhibitor. Values of K_{ads} were calculated from the intercept of Langmuir adsorption isotherm drawn according to the equation (8) between log (θ /1- θ) and log C_{inh} (**Figure 5**). The value of K_{ads} obtained from Langmuir adsorption isotherm is related to Gibbs energy according to the following equation (9).

$$K_{ads} = 1/CH_2O \exp^{(-\Delta G/RT)} \qquad ... (9)$$

It can be written as :

$$\Delta G_{ads} = -2.303\, RT \log(K_{ads}.CH_2O) \qquad ...(10)$$

where CH_2O is the concentration of water in (mL / L) at metal/solution interface, R is universal gas constant and T is absolute temperature. The values of ΔG_{ads} were tabulated in

Table 5. Obtained values of Gibbs energy were plotted against temperature in accordance with the following basic equation [29].

$$\Delta G_{ads} = \Delta H_{ads} - T\Delta S_{ads} \qquad ...(11)$$

Intercept of graph between ΔG_{ads} vs T in **Figure 6** gives value of ΔH_{ads} and by putting the value of intercept in equation (11) values of ΔS_{ads} were obtained. These obtained adsorption parameters Gibbs free energy of adsorption (ΔG_{ads}), enthalpy of adsorption (ΔH_{ads}) and entropy of adsorption (ΔS_{ads}) are in **Table 4**. ΔG_{ads} values have been found negative at all studied temperatures indicating spontaneous adsorption process of inhibitor molecules on metal surface [30-33]. Generally values of ΔG_{ads} upto -20 KJ/mol are consistent with electrostatic interactions (physical adsorption) between charged molecules and charged metal surface and values upto -40 KJ/mol or higher involve charge sharing or transfer from inhibitor molecules to metal surface to form coordinate type of bond (chemical adsorption) [34-38]. The obtained values of ΔG_{ads} were found less than -20kJ/mol indicated physical adsorption of inhibitor molecules. It has been observed that adsorption of negatively charged species is facilitated due to the positively charged metal. But positively charged species can also be adsorbed and protect the positively charged metal surface acting with a negatively charged intermediate such as acid anions, adsorbed on metal surface.

Values of ΔH_{ads} have been found negative indicating the exothermic adsorption process [39], which further indicates lower %IE at higher temperatures, due to desorption of inhibitor molecules. The exothermic process is attributed to either physical or chemical adsorption or mixture of both [40]. In exothermic process, values of ΔH_{ads} predict physisorption or chemisorptions in exothermic process. For physisorption values of ΔH_{ads} is lower than 40kJ/mol while for chemisorption it reaches to 100kJ/mol [41,42]. Values of ΔH_{ads} in Table 9 and 10 indicate physisorption. Negative values of ΔS_{ads} indicate decrease of entropy of adsorption process. This behaviour can be explained as that before the adsorption of inhibitor molecules onto mild steel surface, they might freely move in bulk solution (inhibitor molecules were chaotic), but with the process of adsorption, inhibitor molecules became orderly and adsorbed onto the steel surface as a result decrease in entropy is observed. A more interesting behaviour is observed from Table 4 that negative ΔH_{ads} value is accompanied with negative ΔS_{ads} value. This further agrees that when the adsorption is an exothermic process, it must be accompanied by a decrease in the entropy change and vies versa.The obtained positive values of ΔS_{ads} are the algebraic sum of the adsorption of organic molecules and the desorption of water molecules [43]. Therefore the positive values of entropy of adsorption may result due to substitution process, which can be attributed to the solvent entropy and more positive water desorption entropy [44].

Table 5. Adsorption parameters for mild steel corrosion in 1 M HCl solution with *Ziziphus jujuba* stem

Temperature(^{o}C)	ΔG_{ads}(kJ/mol)	ΔH_{ads}(kJ/mol)	ΔS_{ads}(J/mol/K)
30^{o}C	-8.5325	-45.43	-121.774
40^{o}C	-7.0761		-122.536
50^{o}C	-6.7765		-119.67
60^{o}C	-4.5762		-122.684

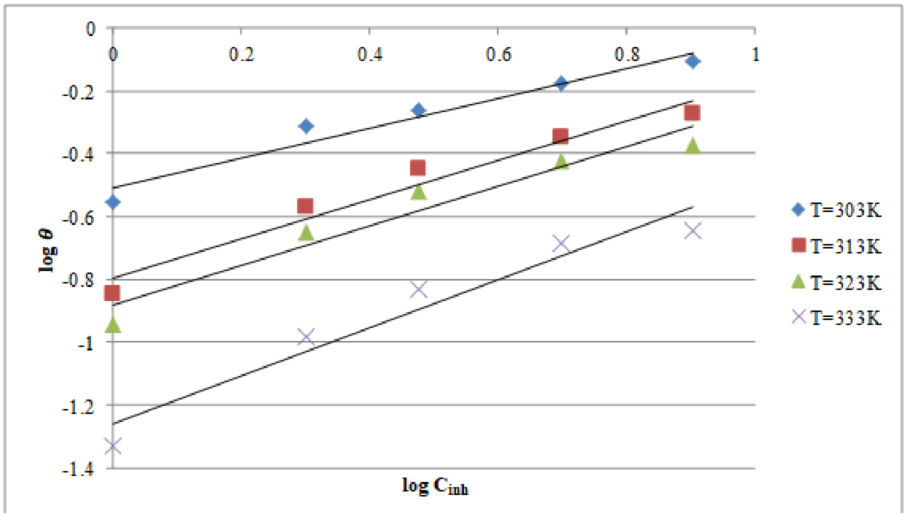

Figure 6. Freundlich adsorption isotherms of *Ziziphus jujuba* stem on mild steel surface in 1M HCl at different studied temperatures

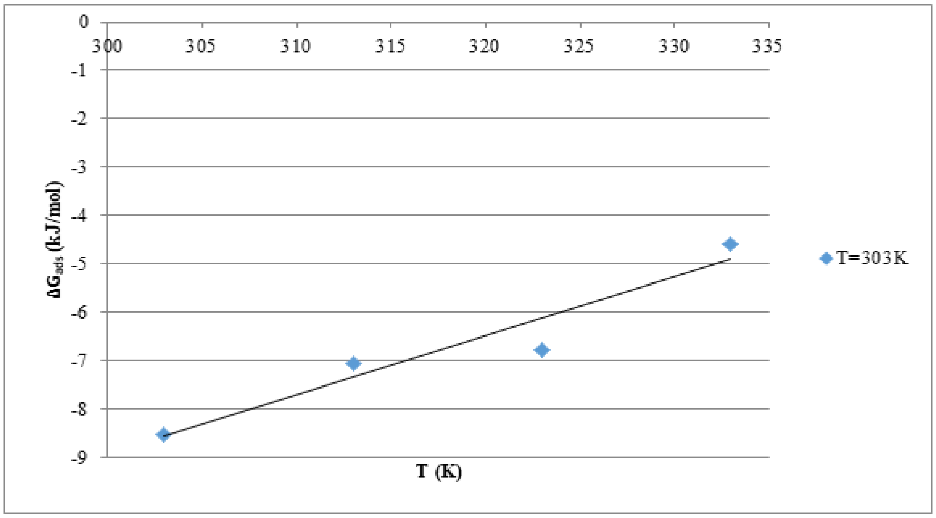

Figure 7. The Variation of ΔG_{ads}(kJ/mol) with T (K) for mild steel corrosion in 1M HCl solution with *Ziziphus jujuba*stem

CONCLUSION

Result showed that ZIZIPHUS JUJUBA STEM is good corrosion inhibitors for mild steel in 1M HCl solution. Corrosion rates with in temperature and decrease with in inhibitor concentration. Inhibition efficiencies at lower temperature suggests the physisorption process of inhibitor on mild steel surface. Apparent activation energy with in inhibitor concentration also suggests physisorption. Enthalpy of adsorption show exothermic and physical adsorption process of inhibitor. Nagative values of Gibbs free energies shows spontaneity of corrosion inhibition process of mild steel in 1 M HCl in Ziziphus jujuba stem.

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