



## **Corrosion Inhibition and Adsorption Properties of *Prosopis juliflora* Leaves Extract for the Corrosion of Mild Steel in 1M HCl Solution**

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### **Authors' contributions**

*This work was carried out in collaboration between all authors. All authors read and approved the final manuscript.*

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### **ABSTRACT**

Corrosion of materials such as mild steel causes big losses in the economy of many countries due to the huge amount of funds needed in order to minimize it. The aim of this paper is to investigate the effect of *Prosopis juliflora* leaves extract as an effective and eco-friendly source of corrosion inhibitor for the corrosion inhibition of mild steel in 1M HCl using weight-loss method. The inhibition efficiency in the present study increases with the increase of extract concentration, but decreased with increase in temperature. The adsorption of the *Prosopis juliflora* extract on mild steel in 1M HCl surface was found to obey Langmuir adsorption isotherm model with  $R^2$  values very close to unity. Negative values of free energy of adsorption and activation energy <80 KJ/mol implied spontaneous process with physical adsorption mechanism.

**Keywords:** Corrosion; inhibitor; Langmuir isotherm; *Prosopis juliflora*.

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## 1. INTRODUCTION

Corrosion is the disintegration of a material or its properties by reaction when interacting with its surrounding environment such as moisture, acids, bases, salts, aggressive metal polishes and many other liquid chemicals. Corrosion of materials such as mild steel causes big losses in the economy of many countries due to the huge amount of funds needed in order to be minimized. Mild steel and of course low-alloy steels are the most widely used materials in the marine environment, lightly stressed component (studs, bolts, gear, shaft e.t.c), and constructions purposes due to its excellent mechanical properties, low cost, and availability. Applications of mild steel are also for the fabrication of number reaction vessels, tanks, pipelines and underground structures [1]. However, mild steel is affected by different forms of corrosion in the surrounding environments such as pitting, intergranular, waterline, soil corrosion respectively. Corrosion inhibitors, prevents the corrosion and are coated over substrate forming a barrier to oxygen and moisture by complexing with metal ions or with forming of passivating film or nano coating on the metal or alloys surface [2,3]. Several inhibitors in use today were usually synthesized; hence, there is increasing concern about their toxic effect not only to the living organism but also causes environmental pollution in general. Chromates for example are used in the pretreatments of aluminum alloys and they are found to be both toxic and carcinogenic [4]. Therefore, the use of inhibitors derived from bio materials is one of the best options of protecting metals against corrosion which are also biodegradable and do not contain heavy metals or toxic compounds. Most of the well-known acid inhibitors are organic compounds containing nitrogen, sulfur, oxygen, phosphorous, alkaloids, proteins, carbohydrates, and aromatic ring or triple bonds [5]. The mechanism of inhibition follows a transition of metal/solution interface from a state of active dissolution to the passive state which is attributed to the adsorption of the inhibitor molecules on the metal surface, forming a protective film (metal complex) and hence, the reactive metal surface is shield from the aggressive environment [6]. Over the past years, extensive research and development have led to increased interest in the evaluation of natural products of plant origin as efficient organic corrosion inhibitor for metal and alloy in different environment. Many researchers have utilized wide range of extracts of plant materials to

control the corrosion of mild steel such as *Parkia Biglobosa* [7], bitter leaf root extract [8], *Aloe vera* [9], ethanolic extract from *Nauclea latifolia* [10], IT *Heinsia crinata* [11], *Dacryodis edulis extract* [12] etc.

*Prosopis juliflora* locally known as ‘Angaraji babul’ is one of the most economically and ecologically important tree species in arid and semi-arid zones of the world [13]. It’s a thorny shrub with thick rough grey-green bark that becomes scaly with age and thrives in most soils. *Prosopis juliflora* has been used as a folk remedy for catarrh, cold, diarrhea, dysentery, excrescences, flu, hoarseness, inflammation, measles, sore throat and in healing of wounds [14]. Phytochemical screening of the leaf had been reported in many literatures which indicated that the leaf contained various phytochemical compounds such as alkaloids (prosoflorine, juliprosine e.t.c), phenolic compounds, flavonoids, terpenes, steroids, saponin [15-17]. The aim of this paper is to investigate the effect of *Prosopis juliflora* leaves extract as an effective and eco-friendly source of corrosion inhibitor for the corrosion inhibition of mild steel in 1M HCl using weight-loss method at different experimental temperatures.

## 2. MATERIALS AND METHODS

### 2.1 Extraction of *Prosopis juliflora*

The leaves of *Prosopis juliflora* were collected from the compound of Jodhpur National University, Jodhpur; India and authenticated by Dr. N. L. Vyas (a botanist). The leaves were washed with deionized water and then air dried at room temperature. 15 g of dried leaf was taken and to that 10 mL of HCl was added, along with this, 300 mL of double-distilled water was also added [18]. The mixture was boiled for a period of 30 minutes and then kept aside for 48 hours. The resultant mixture was filtered and the filtered solution was then used for experiment. HCl stock solution was used as a blank solution. *Prosopis juliflora* extract was added to the acidic solution in concentrations ranging from 10-30 g/L.

### 2.2 Steel Coupons

Materials used for the study were mild steel sheets of composition: Mn (0.6), Pb (0.36), C (0.16), Si (0.03) and Fe (98.85). The sheets were cut into coupons, in dimensions of 3 x 4 x 0.2 cm. Each coupon was degreased by washing with ethanol, rinsed in acetone and air dried before

they were preserved in desiccator. All reagents used for the study were analytical grade and double distilled water was used for their preparation.

### 2.3 Weight Loss Experiment

A previously weighed metal (mild steel) coupon was completely immersed in the test solution using 250 mL open beaker. The beaker was then covered with aluminum foil and inserted into a water bath maintained at 303 K for 1 hour. The corrosion product was removed by washing each coupon (withdrawn from the test solution) first with distilled water and then in a solution containing 50% NaOH and 100 gL<sup>-1</sup> of zinc dust. The washed coupon was rinsed in acetone and dried in air before reweighing. The experiment was repeated at 313, 333, 353 and 373 K for 1 hour each respectively.

### 3. RESULTS AND DISCUSSION

The role of inhibitors is to form a barrier of one or several molecular layers against acid attack and this depends on phytochemical compounds which vary widely on the part of the plant and its

geographical location [19]. It was previously reported that *Prosopis juliflora* leaves extract contained many phytochemical compounds like tanins, saponins, alkaloids, and flavanoids [15,16]. Weight loss measurements were carried out at different temperatures ranging from 303-373 K. From the average weight loss (mean of triplicate analyses) results, the % inhibition of the inhibitor, the degree of surface coverage ( $\theta$ ) and the corrosion rate of mild steel (CR) were calculated using equation 1, 2, and 3 respectively

$$\%I.E = \frac{w_1-w_2}{w_1} \times 100\% \quad (1)$$

$$\theta = \frac{W_1-W_2}{W_2} \quad (2)$$

$$CR = \frac{W \times 87.6}{A \times D \times T} \quad (3)$$

Where W2 and W1 are the weight losses (g) for mild steel in the presence and absence of the inhibitor,  $\theta$  is the degree of surface coverage of the inhibitor, A is the area of the mild steel coupon (in cm<sup>2</sup>), T is the period of immersion (in hour) and W is the weight loss of mild steel after time T, D is the density of the mild steel (cm<sup>3</sup>). The results were shown in Table 1.

**Table 1. Corrosion parameters, arrhenius slope and activation energy for weight loss experiment**

Temp. (K)	Conc.(g/L)	Blank	10	15	20	25	30
303	% I.E	----	81.51	85.25	88.18	91.95	95.12
	$\theta$	----	0.8151	0.8525	0.8818	0.9195	0.9512
	CR (g/cm <sup>2</sup> h)	1.5153	0.2800	0.2238	0.1792	0.1220	0.0739
	Log CR	0.1805	-0.5560	-0.6506	-0.7470	-0.9137	-1.1300
	C/ $\theta$	-----	12.27	17.60	22.68	27.19	31.54
313	% I.E	----	71.08	75.01	78.61	83.48	86.36
	$\theta$	----	0.7108	0.7501	0.7861	0.8348	0.8636
	CR (g/cm <sup>2</sup> h)	2.2541	0.6518	0.5633	0.4812	0.3723	0.3075
	Log CR	0.3530	-0.1859	-0.2492	-0.3180	-0.4290	-0.5121
	C/ $\theta$	----	14.07	20.00	25.44	29.95	34.70
333	% I.E	----	60.08	63.40	70.86	75.70	77.44
	$\theta$	----	0.6080	0.6340	0.7086	0.7570	0.7744
	CR (g/cm <sup>2</sup> h)	3.1430	1.2543	1.1504	0.9160	0.7638	0.7090
	Log CR	0.4973	0.0984	0.0608	-0.0382	-0.1170	-0.1493
	C/ $\theta$	----	16.64	23.66	28.22	33.03	38.74
353	% I.E	----	67.39	70.53	75.50	78.76	80.20
	$\theta$	----	0.6739	0.7053	0.7550	0.7876	0.8020
	CR (g/cm <sup>2</sup> h)	4.3720	1.4253	1.2851	1.0710	0.9283	0.8653
	Log CR	0.6410	0.1539	0.1089	0.0300	-0.0323	-0.0628
	C/ $\theta$	----	14.84	21.27	26.49	31.74	37.41
373	% I.E	----	55.61	60.06	63.20	67.04	71.50
	$\theta$	----	0.5561	0.6010	0.6320	0.6704	0.7150
	CR (g/cm <sup>2</sup> h)	5.2073	2.3117	2.0820	1.9166	1.7161	1.4840
	Log CR	0.7166	0.3639	0.3185	0.2830	0.2345	0.1714
	C/ $\theta$	----	17.98	25.00	31.65	37.29	41.90
Arrhenius slope		-827.4	-1428	-1433	-1462	-1714	-1819
Ea (kJ/mol)		6.88	11.87	11.91	12.16	14.26	15.12

### 3.1 Effect of Inhibitor Concentration on Inhibition Efficiency

From the inhibition efficiencies obtained from the weight loss experiments for the different concentrations of inhibitor (10-30 g/L) using 1M HCl solution, it was observed that the inhibition efficiency increases with increase in inhibitor concentration at all the particular experimental temperatures, thus decreasing the corrosion rate as shown in Fig. 1. The increase in efficiency of the inhibitor with increase in concentration may be attributed to increase in number of molecules occupied by the inhibitor on the steel–acid solution interface [5]. This indicates that the inhibitors were adsorbed onto the mild steel surface and inhibits the corrosion process and reduce corrosion rate.

### 3.2 Effect of Temperature on Inhibition Efficiency

The inhibition efficiency of the extracts has been evaluated at different temperature and the results were shown in Fig. 1. It is evident that increase in temperature leads to the decrease in inhibition efficiency. Maximum inhibition efficiency was obtained at the lowest temperature (303 K). This might be attributed to the desorption of some inhibitor substituent as the temperature increases. It has been established that increase in temperature leads to gradual desorption of the outer layer of dimeric inhibitor film and at the same time the underlying layer effectively protect the metal surface from acid attack [20]. Furthermore, the complex effect of temperature on the inhibited acid-metal reaction result from the changes in the metal surface such as rapid etching, desorption of inhibitor itself and inhibitor undergoing decomposition/ or rearrangement which contribute to this observed effect/ behavior [21].

Further analysis was carried out with Arrhenius equation to assess the kinetic corrosion parameters for the temperature influence on mild steel in the absence and presence of various inhibitors concentration. The Arrhenius equation is given in equation 4 [22]

$$\text{Log CR} = \text{logA} - (\text{Ea}/2.303\text{RT}) \quad (4)$$

Where

CR= the rate of corrosion on mild steel  
 A= The Arrhenius constant  
 Ea= the activation energy

R= the universal constant  
 T= temperature

Log CR was plotted against the inverse of temperature (1/T) values for mild steel in 1M HCl in absence and presence of inhibitors. The activation energy was evaluated from the slope of the plots and the results obtained were presented in Table 1. Increased activation energy (Ea) in the inhibited solution compared to the uninhibited 1 M HCl solution suggests that the inhibitor adsorbed on the corroding mild steel surface and it can be seen that the activation energies obtained in the present were below the threshold values of 80 kJmol<sup>-1</sup> expected for chemical adsorption, hence the inhibitor action was through physisorption mechanism, while either unchanged or lower Ea in the presence of inhibitor suggest chemisorptions. However, It has been suggested that adsorption of an organic inhibitor can affect the corrosion rate by either decreasing the available reaction area (geometric blocking effect) or by modifying the activation energy of the anodic or cathodic reactions occurring in the inhibitor-free surface in the course of the inhibited corrosion process [23,24].

### 3.3 Adsorption Consideration

Adsorption isotherm study describes the mechanism of the interaction between inhibitor and the metal surface. The most usually used adsorption isotherms are Langmuir, Temkin, Freundlich, Frumkin and some other various isotherms, however Langmuir adsorption isotherm were tested and found most appropriate isotherm to explain the present experimental data. Langmuir adsorption isotherm is represented by following equations 5 [25].

$$C/\theta = 1/K_{\text{ads}} + C \quad (5)$$

Where  $\theta$  is the surface coverage, C is the concentration,  $K_{\text{ads}}$  is the equilibrium constant of adsorption process. Fig. 2 represent the plots of Langmuir adsorption model for the process. The adsorption data deduced from the isotherms are shown in Table 2. From the results obtained, the slopes and the correlation coefficient values for the Langmuir plots are very close to unity indicating the adsorption data very much fit the Langmuir adsorption isotherm model, likewise the equilibrium constant of adsorption(  $K_{\text{ads}}$ ) was related to free energy of adsorption  $\Delta G_{\text{ads}}$  as given in equation 6 [26].

$$\Delta G^\circ = -2.303RT \log (55.5K_{ads}) \quad (6)$$

Where 55.5 is the water concentration, R is the universal gas constant and T is the thermodynamic temperature. The values

of the free energies obtained were negatives and this implied that the adsorption of *Prosopis juliflora* on mild steel surface is spontaneous with mechanism of physical adsorption.

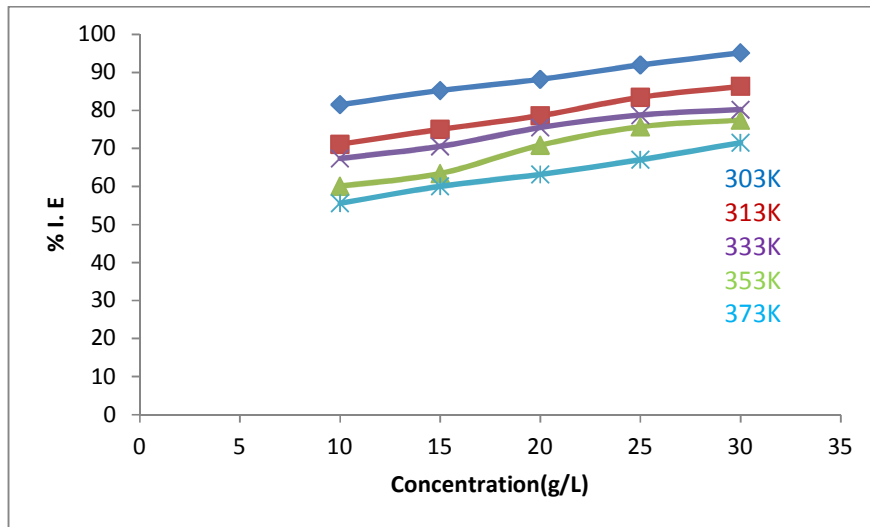


Fig. 1. Variation of %IE with various concentrations of *Prosopis juliflora* leaf extracts for the corrosion of mild steel in 1M HCl solutions

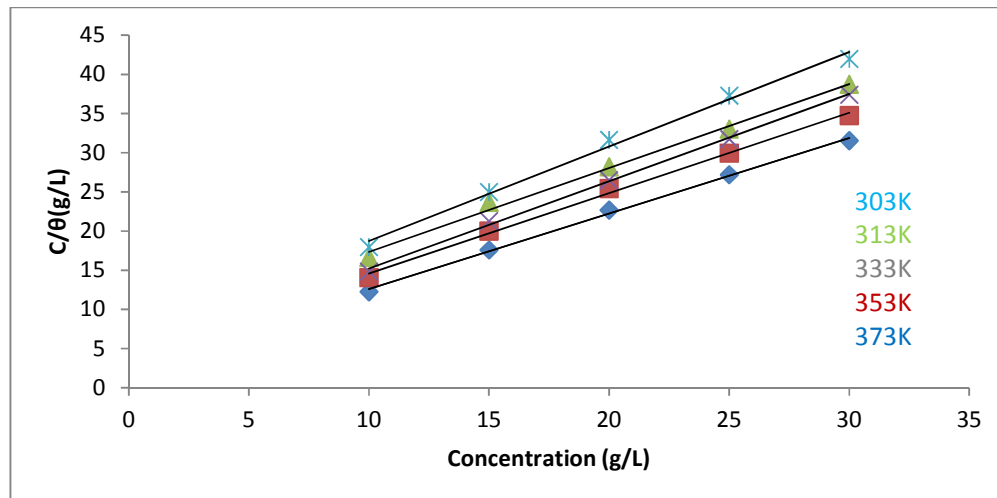


Fig. 2. Langmuir isotherm for the adsorption of *Prosopis juliflora* on 1M mild steel surface

Table 2. Some parameters from Langmuir isotherm model

Temp (K)	$\Delta G_{ads}$ (KJ/Mol)	Slope	$K_{ads}$ (g/L)	$R^2$
303	-7.35	0.9624	0.3329	0.998
313	-6.64	1.0250	0.2313	0.996
333	-5.88	1.0710	0.1508	0.994
353	-7.64	1.1124	0.2435	0.998
373	-6.57	1.2050	0.1498	0.998

### 3.4 Structure of Some Alkaloids Isolated from the Leaf of *Prosopis juliflora* [17]

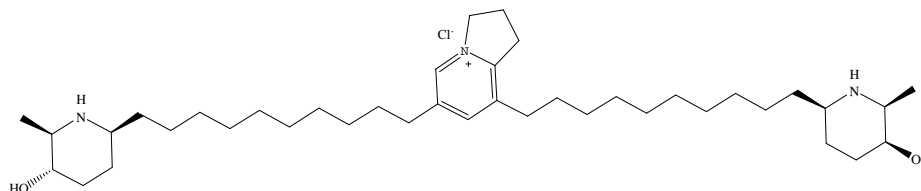


Fig. 1. Structure of prosoflorine

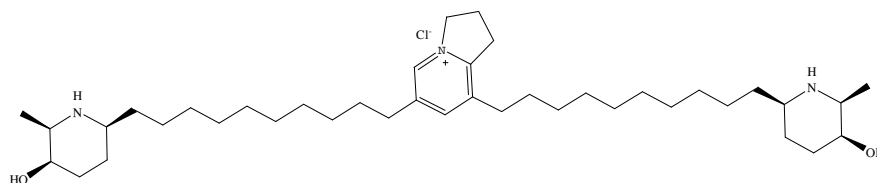


Fig. 2. Structure of Juliprosine

## 4. CONCLUSION

The corrosion inhibition potential of *Prosopis juliflora* extract on mild steel in 1M HCl was examined by weight loss method at different temperatures. The inhibition efficiency in the present study increases with the increase of extract concentration and maximum % efficiency was obtained for 30 g/L at 30°C, but the inhibition efficiency decreased with increase in temperature. The adsorption of the *Prosopis juliflora* extract on mild steel in 1M HCl surface was found to obey Langmuir adsorption isotherm from the fit of the experimental data at all the concentrations and temperatures studied. Additionally, progressive increase in activation energy as the concentration of the inhibitor increase and negatives free energy of adsorption values implied spontaneous process with physical adsorption mechanism. Conclusively, the leaf extract of this plant could be serve as effective and eco- friendly source of corrosion inhibitors for mild steel in acidic medium.

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## COMPETING INTERESTS

Authors have declared that no competing interests exist.

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