

## Inhibition Effect of *Cajanus cajan* Leaves Extract on the Corrosion of Mild Steel in 1 M HCl Solution

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### Abstract

In the present work, the corrosion inhibition property of *Cajanus cajan* leaves extract (CCLE) was investigated as green inhibitor for the corrosion of the surface of mild steel in 1M HCl by weight loss and SEM analysis. The adsorption of the extracts onto mild steel surface followed Langmuir adsorption isotherm. The mechanism of physical adsorption has been proposed based on the trend of inhibition efficiency with temperature. Morphological study of the mild steel surface was undertaken by scanning electron microscope (SEM).

**Keywords:** Adsorption, Mild steel, Inhibitor, Hydrochloric acid.

### Introduction

In various industries mild steel is widely used as a construction material due to its low cost and excellent mechanical properties, but its low corrosion resistance, restrains its utility. Hydrochloric acid solutions are commonly used for pickling, acid de-scaling, industrial acid cleaning, and in oil well acidifying processes [1]. The use of inhibitors to control the corrosive attack of acid environment was found to have widespread applications in many industries because of the corrosive and destructive nature of acid solutions (HCl, H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub> etc.) [2]. Organic and inorganic inhibitors are widely used as corrosion inhibitor in the various industries. But, nowadays, the use of such heavy metal ion based inorganic inhibitors is becoming restricted due to their harmful characteristics. Organic inhibitors may also be toxic and harmful. In this regard, the use of inexpensive green and biodegradable corrosion inhibitors, derived from different plant sources may be the most possible alternate [3]. Plant products have the advantage of being environmental friendly, renewable, biodegradable in nature, economical and easily accessible. Recently plant extracts, have been reported to be environmentally benign, excellent, and economical source of corrosion inhibitors [4]. Among the corrosion inhibitors, plant extracts possess the abundant phytochemical components of significant potential as cheap, inoffensive and renewable source of a wide range of organic molecules. The extracts of *Artemisia pallens* [5], *Coconut coir* [6], *Bamboo leaves* [7], *Mentha rotundifolia* [8], *Camellia sinensis* [9], *Musa paradisiac* [10], *Calotropis Gigantia* [11], *Alstonia angustifolia var. latifolia* [12] and *black pepper* [13] have been reported as good mild steel corrosion inhibitors in acidic media (HCl, H<sub>2</sub>SO<sub>4</sub>). The objective of the present work was to evaluate the corrosion parameters of CCLE for mild steel in 1 M HCl solution by means of gravimetric analysis, and surface analysis technique (SEM).

### Experimental

#### *Mild steel specimens*

Mild steel specimens of size 5cm x 2cm x 0.1 cm was used for weight loss measurements. The specimens were abraded using different grades of emery papers, washed with double distilled water, degreased with acetone, dried and stored in desiccator before immersing in the corrosive medium.

For the corrosion study the electrolytic solution (1 M HCl) was prepared by dilution of analytical grade HCl (Merck) of predetermined normality with purified water obtained from Elix essential 10 millipore water purifier.

#### *Preparation of inhibitor*

Fresh inhibitors were collected and washed with tap water followed by double distilled water than shade dried for few days. This dried inhibitors powdered into small pieces and 100g of the powdered was extracted in boiled double distilled water for few hours. The extracted solution then filtered which is used to study the corrosion inhibition property on mild steel. This solution was used to prepare the required concentrations of inhibitor solution.

#### *Weight loss measurements*

Most studies show that weight loss measurement is the most prominent method for the corrosion studies mainly because of its reliability, accurateness, simplicity and preciseness. The mild steel test coupons were weighed and suspended in 100 ml electrolytic solution for 6 h in the absence and presence of various concentration of inhibitors at temperatures ranging from 298K-328K. After immersion time the mild steel specimens were picked out, cleaned with millipore water, and dried in hot air oven for 5 minutes. The corrosion rate ( $\rho$ ) in mg cm<sup>-2</sup> h<sup>-1</sup> of CCLE calculated from the following equation [15]:

$$\rho = \frac{\Delta W}{At}$$

Where  $\Delta W$  is the weight loss in mg,  $A$  is the total area of metal specimen in  $\text{cm}^2$ , and  $t$  is the immersion time (6 h). Inhibition efficiency (%I) of CCLE was calculated from the following equation [15]:

$$\%I = \left( \frac{\rho^1 - \rho^2}{\rho^1} \right) \times 100$$

Where  $\rho^1$  and  $\rho^2$  are the corrosion rates of the test specimens in the absence and presence of inhibitor, respectively.

### Surface analysis

Mild steel specimens were treated with 1M HCl in the absence and presence of all studied corrosion inhibitors at various temperatures. Their surface morphology and changes in surface composition were analysed by using Scanning electron microscope. Scanning electron microscope ZEISS EVO SEM 18 model used for SEM analysis.

## Result and discussion

### Weight loss measurements

With the help of weight loss measurement, various corrosion parameters like corrosion rate, inhibition efficiency and surface coverage for mild steel in 1 M HCl solution. These parameters were determined in the absence and presence of different concentrations of the inhibitor at temperatures ranging from (298–328 K) and corresponding values are listed in Table 1. Examination of the data in Table 1, exposes that inhibition efficiency increases with increasing the inhibitors concentration.

Table 1 also reveals that the inhibition efficiency of CCLE decreases with an increase in temperature. Such behaviour can be understood on the basis that the inhibitor molecules exert their action by adsorbing themselves on the metal surface and an increase in temperature resulted in higher dissolution rate of mild steel as well as desorption of some adsorbed inhibitor molecules leading to a decrease in the inhibition efficiency [18].

**Table 1** The weight loss measurement parameters obtained for mild steel in 1M HCl containing different concentrations of inhibitor at studied temperatures.

Temperature (K)	Concentration (g/L)	Corrosion Rate $\rho$ ( $\text{mg cm}^{-2} \text{h}^{-1}$ )	Inhibition efficiency (% IE)	$\theta$
298	0.0	1.020	-	-
	0.2	0.150	85.26	0.852
	0.4	0.137	86.49	0.864
	0.6	0.123	87.86	0.878
	0.8	0.100	90.86	0.908
308	0.0	1.955	-	-
	0.2	0.242	79.04	0.790
	0.4	0.220	80.92	0.809
	0.6	0.151	86.93	0.869
	0.8	0.135	88.36	0.883
318	0.0	3.809	-	-
	0.2	0.612	83.88	0.838
	0.4	0.539	85.85	0.858
	0.6	0.498	86.92	0.869
	0.8	0.479	87.42	0.874
328	0.0	5.372	-	-
	0.2	1.002	81.34	0.813
	0.4	0.860	83.99	0.839
	0.6	0.762	85.00	0.850
	0.8	0.7025	86.92	0.869

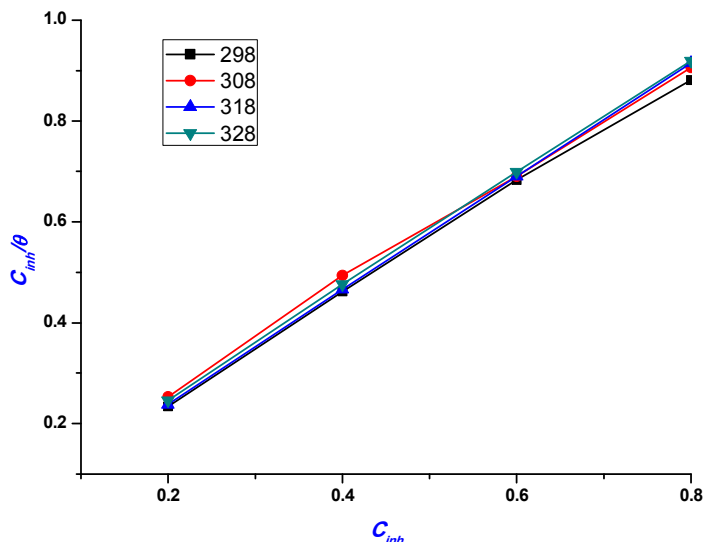
### Adsorption isotherm

To determine the adsorption behaviour of inhibitors on mild steel in 1 M HCl solution and to calculate the corresponding thermodynamic parameters of adsorption among several adsorption isotherms, the Langmuir adsorption isotherm is found to be best suited. According to isotherm, the degree of surface coverage ( $\theta$ ) calculated from the gravimetric analysis, is related to the concentration of the inhibitors ( $C$ ) following the relation given in equation [19]

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C$$

Where  $C$  is the inhibitors concentration,  $K_{ads}$  is the equilibrium constant of adsorption.  $K_{ads}$  values show the

binding ability of the inhibitor to the metal surface. Larger the  $K_{ads}$  value higher the binding ability of inhibitor on mild steel surface. Fig. 1 shows the adsorption plot for mild steel in acidic solution in the presence of utilized corrosion inhibitor at studied temperatures. Corresponding  $K_{ads}$  values of inhibitors in 1 M HCl solution given in Table 2. From Table 2 is clear that  $K_{ads}$  decreases as temperature increased.



**Fig. 1** Langmuir adsorption plot for mild steel in 1 M HCl in the presence of CCLE at different temperatures.

**Table 2** Thermodynamic parameters for the adsorption of inhibitor on mild steel in acidic solution at studied temperatures.

T(K)	Slope	R <sup>2</sup>	K <sub>ads</sub> (L g <sup>-1</sup> )	ΔG <sub>ads</sub> (kJ mol <sup>-1</sup> )
298	1.026	0.998	40.81	-19.14
308	1.062	0.997	21.27	-18.11
318	1.122	0.999	74.07	-22.00
328	1.181	0.999	40.81	-21.06

#### Effect of temperatures

To evaluate the effect of temperature on the inhibition efficiency of CCLE, the weight loss measurements were performed on mild steel coupons in the temperature ranging from 298 to 328 K in absence and presence of CCLE. From Table 1, it is clear that inhibition efficiency decreases from 98.86 to 86.92 % with increasing temperature from 298-328K this decrease in inhibition is due to desorption of inhibitor molecules from mild steel surface. Thus, at higher temperature, more desorption of inhibitor molecules takes place and larger surface area of metal come in contact with acid, resulting in an increase in corrosion rate. An alternative formulation of Arrhenius equation is:

$$\log \rho = \log A - \left( \frac{Ea}{2.303RT} \right)$$

Where  $\rho$  is the corrosion rate, R is the gas constant, Ea is the apparent activation energy of mild steel dissolution, A is the constant and T is the absolute temperature. Value apparent activation energy listed in Table 3. The entropy of activation ( $\Delta S^*$ ) and the enthalpy of activation ( $\Delta H^*$ ) for the mild steel corrosion in 1M HCl solution were obtained by applying the transition-state equation:

$$\log \left( \frac{\rho}{T} \right) = \left[ \log \left( \frac{R}{Nh} \right) + \left( \frac{\Delta S^*}{2.303} \right) \right] - \frac{\Delta H^*}{2.303RT}$$

Where  $\Delta S^*$  is the entropy of activation,  $\Delta H^*$  is the enthalpy of activation, h is the plank constant, N is the Avogadro's number, T is the absolute temperature and R is the universal gas constant. Values of enthalpy of activation ( $\Delta H^*$ ) and entropy of activation ( $\Delta S^*$ ) were calculated from straight lines of transition state plots and listed in Table 3.

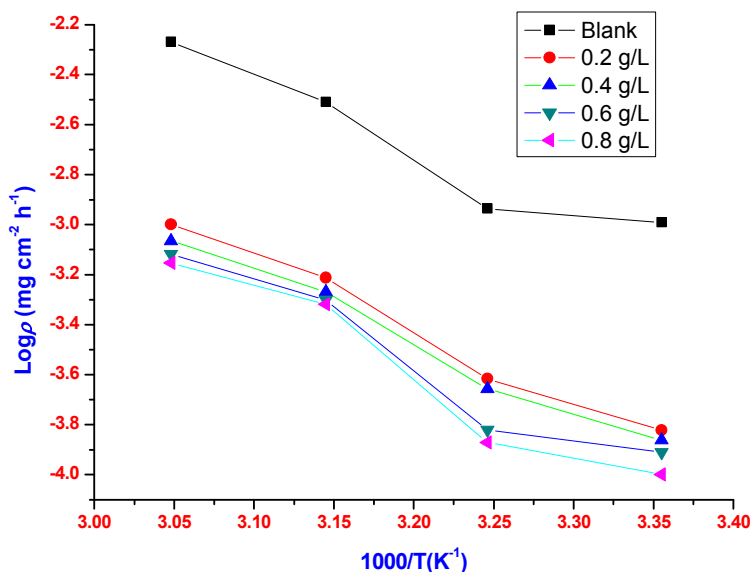


Fig. 2 Arrhenius plot for mild steel corrosion rates in 1M HCl in the absence and presence of different concentrations of CCLE at different temperatures.

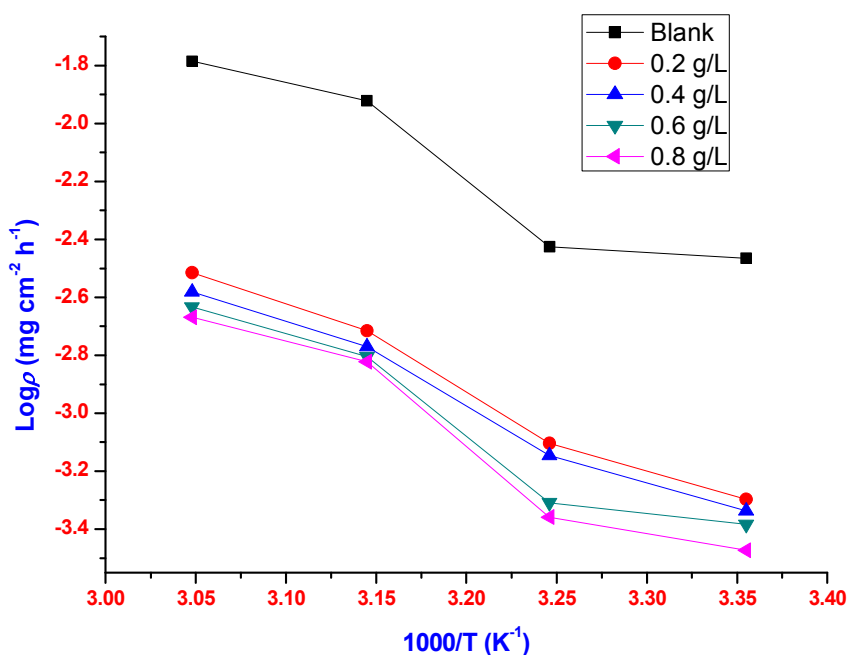


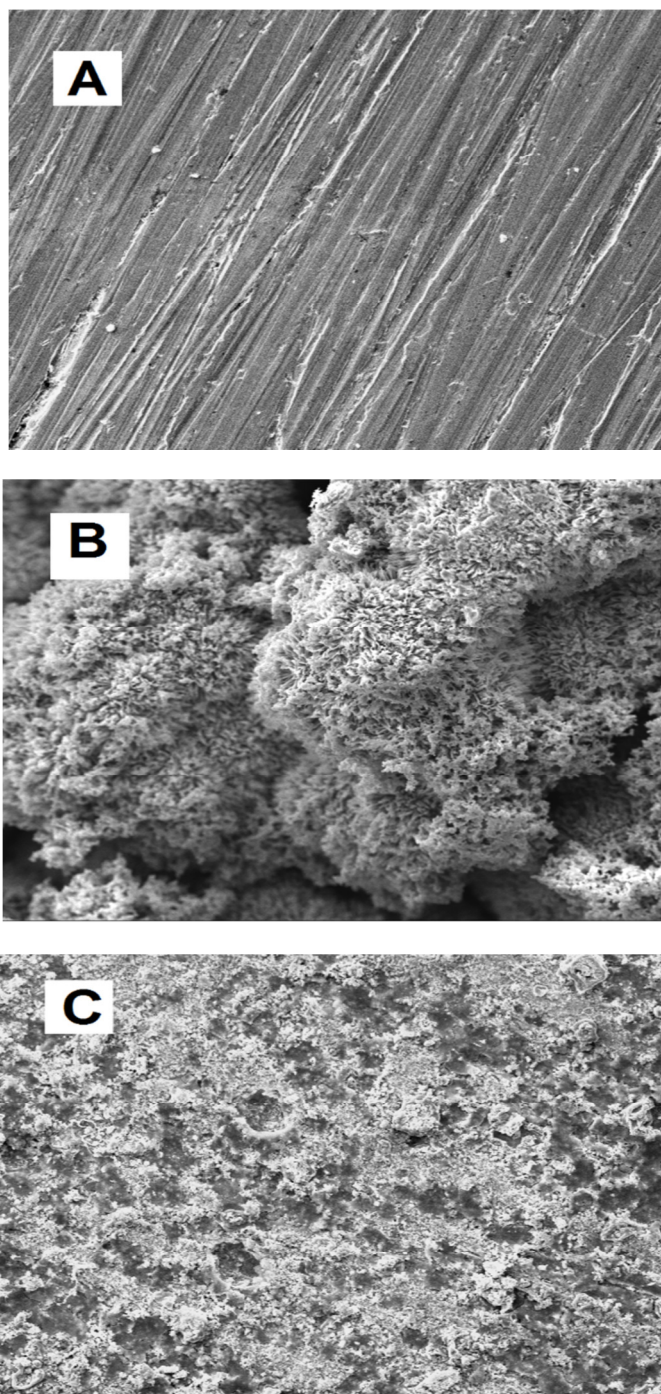
Fig. 3 Transition state plot for mild steel corrosion rates in 1M HCl in the absence and presence of difference concentrations of CCLE at temperature ranging from 298 to 328 K.

**Table 3** Activation parameters  $E_a$ ,  $\Delta H^*$  and  $\Delta S^*$  of the dissolution of mild steel in 1M HCl in the absence and presence of different concentration of CCLE.

Conc. (g l <sup>-1</sup> )	A (mg cm <sup>-2</sup> h <sup>-1</sup> )	$E_a$ (kJ mol <sup>-1</sup> )	$\Delta H^*$ (kJ mol <sup>-1</sup> )	$\Delta S^*$ (kJ mol <sup>-1</sup> )
0.0	$2.46 \times 10^5$	48.28	47.46	-10.44
0.2	$3.73 \times 10^5$	53.78	51.19	-10.75
0.4	$1.66 \times 10^5$	52.00	51.39	-10.81
0.6	$3.08 \times 10^5$	54.03	51.46	-10.94
0.8	$1.15 \times 10^6$	57.63	55.12	-09.64

### **SEM Analysis**

Figure 4 (a-c) shows the SEM microphotographs of metal surface before and after exposing to acidic solution in the absence and presence of CCLE. The mild steel immersed in 1 M HCl solution displays rough surface due to formation of the corrosion product. Figure 1 (c) shows the morphology of mild steel surface that resulted after immersing in optimum concentration of inhibitor in 1 M HCl. The microphotographs reveals the smooth and less damage on steel surfaces. These results shows that the inhibitor molecules can protect metal surface efficiently in acidic solution, which may be due to strong adsorption of the inhibitor molecules on mild steel surface to protect from the corrosion. The changes in the mild steel surface morphology in the acidic solutions can be attributed due to formation of the corrosion products like  $Fe_3O_4$ ,  $FeOOH$ ,  $FeCl_2 \cdot nH_2O$  and  $FeO \cdot nH_2O$  on the metal surface [20]



**Fig. 4** SEM image of mild steel (a) mild steel specimen (b) mild steel immersed in 1 M HCl and mild steel immersed in 1 M HCl in the presence of CCLE.

## Conclusion

Weight loss measurement reveals that inhibition efficiency of *Cajanus cajan* leaves extract increases with increasing inhibitor concentration, but decreases with increasing temperature (298–328 K). The optimum inhibition efficiency of 91.07 % was found at 0.8 g l<sup>-1</sup> *Cajanus cajan* leaves extract. The adsorption of inhibitors on the mild steel surface obeys the Langmuir adsorption isotherm. The surface analysis by SEM revealed that a passive film is formed on the mild steel surface upon immersion in the 1 M HCL in the presence of the inhibitors. The results of weight loss measurements and SEM analysis, shows that CCLE act as a good corrosion inhibitors on mild steel in 1 M HCl solution.

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