NATURAL CORROSION INHIBITOR AND ADSORPTION KINETICS OF MILD STEEL IN HYDROCHLORIC ACID MEDIUM

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Abstract: One of the most important metal corrosion inhibitors is the extract of natural plants. They are readily available, non-toxic, environmentally friendly, biodegradable, highly efficient and renewable. This study focuses on the corrosion inhibition effects of the *Caralluma indica* stem extract in 1M HCl solutions using weight loss techniques and followed by isotherms adsorption. The results obtained show that the extracts from 1M HCl solutions acted as good corrosion inhibitors. The inhibition efficiency was increased with the increase in the concentration of extract. The extract *Caralluma indica* has inhibitory effectiveness. Phytochemical components with functional groups in extracts of plants adsorbed on the metal surface are responsible for the effective performance of the inhibitor. Data from weight loss experiments and adsorption isotherms (Temkin and Freundlich) have shown that plant extract represents corrosion of steel in acidic media and confirms the adsorption mechanism. The result shows that the *Caralluma indica* stem extract acts as a corrosion inhibitor and can promote surface protection by blocking the active areas on the metal.

Keywords: Anticorrosion, Hydrochloric acid, *Caralluma indica* stem, Phytochemicals
Citation:

INTRODUCTION

The industry is highly dependent on the use of metals and alloys. One of the most difficult and difficult tasks for the industry is to protect metals from corrosion. Corrosion is an omnipresent problem which remains of great relevance in a variety of industrial applications and products. It leads to the dismantling and possible failure of components and systems in the processing and manufacturing industry as well as to the lifespan of many components. Corrosion control of metals and alloys is an expensive process, and the industry spends huge quantities to control this problem. Corrosion costs in industrialized countries such as the United States and the European Union are estimated to represent around 3 – 5% of their gross national product (Bhaskaran et al., 2005; EEMC, 1978a, 1978b).

Corrosion damage can be avoided by various methods such as upgrading materials, mixing production fluids, process control and chemical inhibition (Düdükcü et al., 2004; Galal et al., 2005). Among these methods, the use of corrosion inhibitors (Raja and Sethuraman, 2008; De Souza and Spinelli, 2009) is preferable to prevent the destruction or degradation of metallic surfaces in corrosive media. The use of corrosion inhibitors is the most economical and practical method of reducing caustic attack on metals. Corrosion inhibitors are synthetic or natural chemicals when added in small quantities to an environment. Reduce the rate of environmental attack on metals. We know that a number of synthetic compounds (Bentiss et al., 2002; Abd El-Maksoud, 2004) are applicable as good corrosion inhibitors for metals. However, the popularity and use of synthetic compounds as corrosion inhibitors is decreasing due to strict environmental regulations and the toxic effects of synthetic compounds on human and animal life (Kilmartin et al., 2002; Nishimura and Maeda, 2004). Hence the need, develop a new class of green corrosion inhibitors with low toxicity, eco-friendliness and good efficiency.

Over the centuries, plants have been used by people for their basic needs such as the production of food, accommodation, clothing, fertilizer, flavors and perfumes, medicines and in particular food, accommodation, clothing, fertilizers, Flavorings and perfumes used as corrosion inhibitors. The use of natural substances as corrosion inhibitors dates back to 1930 ', pickling baths were used as extracts from *Chelidonium majus* plants [Celandin] and other plants for the first time in H_2SO_4. Subsequently, interest in the use of natural substances as corrosion inhibitors increased significantly, and scientists around the world have reported several extracts of plants (Sanyal, 1981; Benabdellah, et al., 2006) and phytochemical lines (Oguzie, . 2007) as a promising green anticorrosiva. Although a number of plants and their phytochemical lead have been reported as anticorrosive, the vast majority of plants have not yet been properly examined for their anticorrosive activity

Recently, many eco-friendly corrosion inhibitors have been developed. For example, *Zygophyllum album* L Leave (Derfouf et al., 2017), *Anacyclus pyrethrum* L. stem (Selles et al., 2012) and *Mentha Pulegium* leaf extract (Khadraoui et al., 2015) were successfully reported for their anticorrosion properties. The observed results showed that all the above said plants have excellent anticorrosion effect and most importantly eco-friendly. In the present study, *Caralluma indica* stem, *Phoenix pusilla* leaves and *Sansevieria roxburghiana* leaves extract was investigated for its effectiveness as a natural inhibitor to prevent corrosion of mild steel in 1M HCl using the weight loss method and Adsorption Isotherm followed by Langmuir and Temkin model.

MATERIALS AND METHODS

Collection and Preparation of alcoholic extract

The *Caralluma indica* stem was collected in Sengipatti, Thanjavur and Tamil Nadu. The collected parts of the plant were dried in the shade and a fine powder was produced with a mixed grinder. 10 grams of *Caralluma indica* stem powder were used for extraction. The extraction was carried out by cold extraction using the maceration method in ethanol solvents for 24 hours using the intermittent shaking method to obtain an extract. The extract was filtered using the Whatman filter No. 1 and the filtrate was used for phytochemical analysis and anti-corrosive activity.

Qualitative Preliminary phytochemical analysis

A preliminary phytochemical test was carried out by using standard procedure (Sofowara 1993; Trease and Evans, 1989; Harborne 1973 and 1984).

ANTICORROSIVE STUDY

Effect of *Caralluma indica* stem extract in different concentrations on mild steel

The mass loss studies were carried out at temperature 37°C in 100 ml of blank 1M HCl and test solutions of various concentrations of *Caralluma indica* stem extract (5, 10, 30, 50, 70 and 100 ppm) for 72 hours. At the end of the reaction the specimens were taken out, washed with water, dried with air drier and weighed. Blank has taken as without sample. Corrosion rates (decrease in weight in gram per cm^2 per hour) were calculated using the following expression.

$$\text{Corrosion Rate (CR)} \ (g.cm^{-2}\ h^{-1}) = \frac{W_1 - W_2}{A \times T}$$

Where, W_1 = initial weight of rod, W_2 = weight of rod after treatment, $W_1 - W_2$ = weight loss (g), A = surface area, T = time in hours

The surface coverage (ϴ) as a result of adsorption of inhibitor and inhibition efficiency (%) were calculated from corrosion rate values by using the following equation

$$\textbf{Surface coverage}\ (\Theta) = \frac{CR_B - CR_I}{CR_B}$$

Inhibition efficiency %

$$= \frac{CR_B - CR_I}{CR_B} \times 100$$

Where, CR_B = Corrosion Rate Blank and CR_I = Corrosion Rate Iinhibitor.

Adsorption Isotherm followed by Langmuir and Temkin model

The inhibition effect can be explained by adsorption of *Caralluma indica* stem extract at the mild-steel surface. The *Caralluma indica* stem extract replaces the water molecules at the metal interface according to the Langmuir and Temkin model (Hosseini et al., 2003; Rudresh and Mayanna, 1977).

Atomic Absorption Spectroscopy (AAS)

The effect of inhibitor on mild steel specimen was observed using atomic absorption spectroscopy. *Caralluma indica* stem extract was tested for its efficiency against 1 M HCl by incubating mild steel in the absence and presence of inhibitor (5, 10, 30, 50, 70 and 100 ppm) for 3 h at 303 ± 1.00 K (Fadare et al., 2016). After immersion time, the corrodent solutions were observed for the concentration of dissolved ions in each solution to calculate the IE % using the following formula:

$$\textbf{IE \% = B-A/B × 100}$$

where, A and B represents the amount of dissolved ions in the uninhibited and inhibited (with different concentration of inhibitor) corrodent solutions

RESULTS AND DISCUSSION

Preliminary Phytochemical Screening of the plant Extract

In this study to investigate the phytochemical analysis of alcoholic extracts from the stem of *Caralluma indica*. The qualitative phytochemical analysis of the alcoholic extracts of *Caralluma indica* stem shown that the presence of tannin, saponin, flavonoids, steroids, terpenoids, triterpenoids, alkaloids, anthroquinone, polyphenol and glycoside.

Weight Loss Method

Among the many experimental methods available to determine the percentage of inhibition efficiency and the corrosion rate, the weight loss method is the simplest and most commonly used. In this study, the experiments were carried out by varying the concentrations of the inhibitor. This study is also carried out at different temperatures and the immersion time is fixed at 72 hours. The weight loss calculated in grams is the difference between the weight of the metal coupon before and after immersion in an inhibitory solution. The corrosion rate of mild steel in a 1M hydrochloric acid solution was examined using the blank solution weight loss method and with various concentration of *Caralluma indica* stem.

Effect of Concentration of *Caralluma indica* stem extract on corrosion inhibition

The inhibition efficiency and the corrosion rate values for all the studied inhibitors and the blank system were determined and given in Table 1. The corrosion rate decreases and the inhibition efficiency increases with the increase in the concentration of *Caralluma indica* stem extract for all inhibitors and the concentration range is 5 to 100ppm for 72 h immersion of the metal in inhibitore solution at room temperature (Figure 1). The inhibition efficiency increases because of the inhibitor molecules present in the *Caralluma indica* stem extract getting adsorbed on the metal surface. The maximum inhibition efficiency and the lower corrosion rate are found at high concentration (100ppm) for inhibitors (81.57%) while minimum inhibition efficiency at low concentration (5ppm) for inhibitors (23.68%).

Table 1: Effect of *Caralluma indica* stem extract in corrosion rates, inhibition efficiency and surface coverage at various concentrations

Concentrations (ppm)	Weight loss ($gm.cm^{-2}$)	Corrosion rate ($g.cm^{-2}/h$) × 10^{-4}	Surface coverage (Θ)	Inhibition efficiency (%)
Control	1.14	3.29	-	-
5	0.87	2.51	0.23	23.68
10	0.64	1.85	0.43	43.85
30	0.48	1.38	0.57	57.89
50	0.38	1.09	0.66	66.66
70	0.26	0.75	0.77	77.19
100	0.21	0.60	0.81	81.57

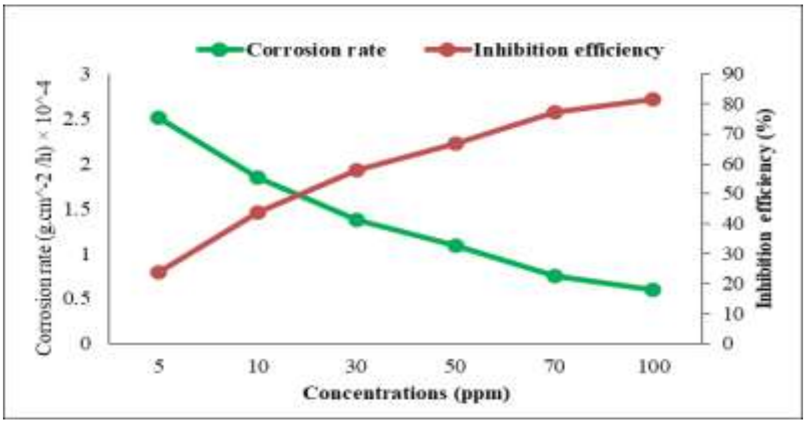

Figure 1: Effect of *Caralluma indica* stem extract in anti-corrosion activity

Inhibition Adsorption Isotherm model

The inhibition effect can be explained by adsorption of *Caralluma indica* stem extract at the mild-steel surface. The *Caralluma indica* stem extract replaces the water molecules at the metal interface according to the Langmuir and Temkin model figure 3 and 4.

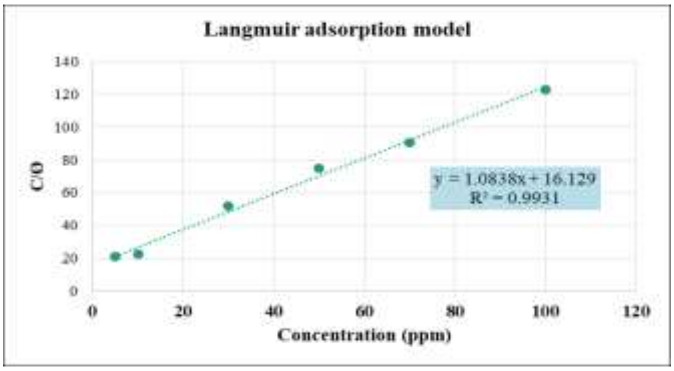

Figure 3: Langmuir Adsorption Isotherm plot for mild steel in 1M HCl with different inhibitory concentration of *Caralluma indica* stem extract

The Langmuir adsorption model was applied. Plotting the experimental data C/θ versus C resulted in a fitted straight line as shown in Figure 3. Concentrations (ppm) is the inhibition concentration of *Caralluma indica* stem extract and θ is the surface coverage. It is clear that the adsorption follows Langmuir adsorption isotherm, as indicated by the correlation coefficient (R) = 0.996 and the slope = 1.083 as expected from Langmuir model followed by Ali and Mahrousb (2017)

$$c/\theta = c + 1/K_{ads}$$

Thus, the adsorption of *Caralluma indica* stem extract as corrosion inhibitor was harmonious with Langmuir adsorption isotherm. The strength and stability of the adsorbed layer formed by *Caralluma indica* stem extract was evaluated from inverse of the plot intercept. The K_{ads} was found to be equal to 0.062 ppm^{-1}.

Temkin model was achieved by plotting log(θ/C) versus θ, Figure 4. The obtained straight line has adjustable correlation coefficient R = 0.962. Thus, Temkin model is less acceptable than Langmuir model because of less R value (Faiz et al., 2020).

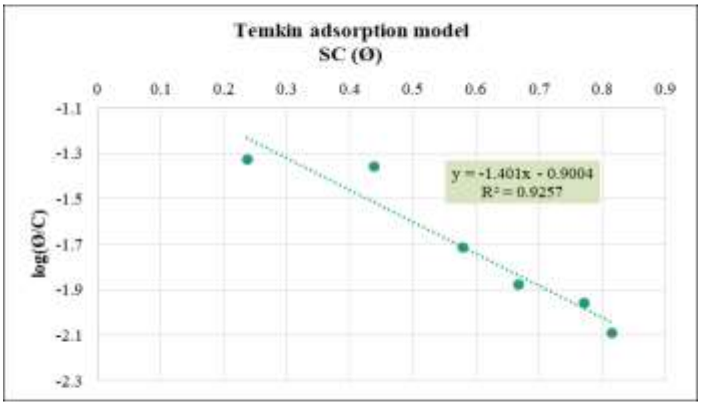

Figure 4: Temkin Adsorption Isotherm plot for mild steel in 1M HCl with different inhibitory concentration of *Caralluma indica* stem extract

Atomic Absorption Spectroscopy

The analysis of dissolved ions in corrodent solution without inhibitor with that of corrodent solution with different concentrations of inhibitor (5, 10, 30, 50, 70, 70 and 100 ppm) were examined through AAS. The results (Table 2) were in correlation with mass loss measurement which exhibited corrosion inhibition in concentration dependent manner. Maximum level of inhibition against 1 M HCl corrosion was 79.83 % with 100 ppm at 303 ±1.00 K. A study on acid inhibitor preventing ferrous (iron) pigment corrosion. The inhibition efficiency of the plant extract based on concentration apparently happens by the adsorption of active constituents of *Caralluma indica* onto the surface of metal forming protective film thereby prohibiting oxidation and reducing the ferrous (iron) ion diffusion in the corrodent solution.

Table 2: AAS study of dissolved ferrous (iron) ions in corrodent solution against 1 M HCl control and different concentrations of *Caralluma indica* stem extract inhibitor

Concentrations (ppm)	Amount of ferrous (iron) corrodant (mg/l)	Inhibition efficiency (%)
Control	27.18	-
5	21.72	20.08
10	18.46	32.08
30	13.73	49.48
50	9.38	65.48
70	7.05	74.06
100	5.48	79.83

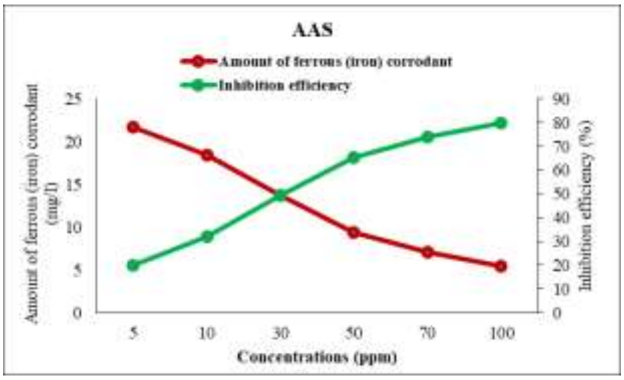

Figure 5: AAS study of dissolved ferrous (iron) ions in corrodent solution against 1 M HCl control and different concentrations of *Caralluma indica* stem extract inhibitor

The present study, the efficacy of *Caralluma indica* stem extract as an environmentally friendly inhibitor was demonstrated by investigating the mass loss behavior of mild steel in solutions of 1 M HCL. This indicates a high sensitivity of *Caralluma indica* stem extract toward inhibition of mild steel in acidic medium. It was also observed that adsorption follows Langmuir and Temkin isotherm model.

Conclusion

The extract of *Caralluma indica* stem extract have shown promising corrosion inhibition properties for mild steel in 1M HCl media. The inhibition efficiency was found to be directly propotional to the extract concentrations. Adsorption of inhibitor on the surface of the mild steel obeyed both Langmuir and Temkin adsorption isotherms. Further investigations to assess the corrosion morphology and to isolate and confirm the active phytochemicals responsible for the inhibition of mild steel corrosion in acidic media are required.

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