Research Article

NATURAL PLANTS AS A SOURCE OF GREEN CORROSION INHIBITORS ON MILD STEEL IN HYDROCHLORIC ACID

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ABSTRACT
There is a growing trend to utilize plant extracts and pharmaceutical compounds as corrosion inhibitors. The inhibitive performance of extract of Leaves *Cissus quadrangularis* (CQ) on the corrosion of mild steel in 0.5 M HCl was studied using mass loss and electro chemical measurements. Results confirmed that the extract of *Cissus quadrangularis* Leaves (CQ) acts as an effective corrosion inhibitor in the acid environment. Potentiodynamic polarization and electrochemical impedance studies confirmed that the system follows mixed mode of inhibition.

Keywords: Mild steel*, Cissus quadrangularis* Leaves (CQ), corrosion inhibition, electrochemical measurements.

1. INTRODUCTION

Mild steel is widely used in many industrial applications. In most industrial processes, the acidic solutions are commonly used for the pickling, industrial acid cleaning, acid descaling, oil well acidifying, etc.[1–5]. Unfortunately, iron and its alloys could corrode during these acidic applications particularly with the use of hydrochloric acid and sulphuric acid, which results in terrible waste of both resources and money[6]. Corrosion prevention systems favor the use of environmental chemicals with low or zero environmental impacts. The decreasing of corrosion rate of metals provides saving of resources and economical benefits during the industrial applications as well as increasing the lifetime of equipments and also decreasing the dissolution of toxic metals from the components into the environment. As acidic media, hydrochloric acid (HCl) and sulphuric acid (H_2SO_4) are often used as industrial acid cleaners and pickling acids. Large numbers of organic compounds revealed that N, S and O containing organic compounds acted as promising inhibitors. However, most of these compounds are not only expensive, but also toxic to living beings. It is needless to point out the importance of cheap and safe inhibitors for corrosion of mild steel. So, considerable efforts are made to select corrosion inhibitors which are environmentally safe, readily available and of relatively low cost. Literature shows a growing trend in the use of natural products known as non-toxic compounds, called also green inhibitors, as corrosion inhibitors. Available literature has shown that naturally occurring plant leaves such as *Azadirachta indica* leaves, *Murraya koenigii* leaves, *Ervatamia coronaria* leaves, *Ananas comosus* leaves, *Purpurea* leaves, *Olive* leaves[6-9] have been reported to inhibit the corrosion of metals in acidic media. The present article is concerned with corrosion inhibition studies using *Cissus quadrangularis* leaves extract (CQ) on mild steel in acidic medium using Mass loss and electrochemical measurements.

2. MATERIALS AND METHODS
2.1. Materials
All chemicals were purchased from Merck, Mumbai, India, Hydrochloric acid, Methanol, mild steel

2.2. Preparation of HCl stock solution
The medium used in this present study of HCl solution. The HCl was used in the present study. The HCl was purchased commercially. It is very soluble in water and the aqueous solution is colourless. The solution prepared by 89 ml of HCl was in 1000 ml of double distilled water and then made up to 1000 ml standard flask. The thousand fold dilution of stock solution (1000 ppm).

2.3. Preparation of Plant Extract
The *Cissus quadrangularis* stem extract was collected and cut into small pieces and they dried in sunlight for 15 days. They were ground well into powder. From this, 20 g of the sample was refluxed with 200 ml methanol for 6 hours. The refluxed solution was filtered carefully and evaporated to remove the methanol content to get the dried inhibition sample. The inhibition concentration such as 50, 100, 150, 200, 250 and 300 ppm were prepared using 0.5 M HCl solution

Classification:
Tamil name **:** Perandi
Kingdom **:** Plantae
Division : Magnoliphyta
Class : Magnoliopsida
Order **:** Vitaceae
Genus : Cissus
Species **:** *quadrangularis*
1g of the sample was accurately weighed and dissolved in 1000 ml of double distilled water made in 1000 ml standard flask. The thousand fold dilution of stock solution (1000 ppm).

3. RESULTS AND DISCUSSION
3.1. Determination of corrosion rates and inhibition efficiency:
Two weighed specimen samples were suspended by means of glass hooks in 100 ml beakers containing 100 ml of HCl and distilled water. The variation of weight loss monitor at interval of 15 minutes, progressively for total of 60 minutes started from 30 minutes. After predetermined time the immersion of mild steel specimens were taken out from the beakers, scrubbed with cotton and a mild cleaning solution, washed with distilled water, treated with acetone to remove traces of moisture and grease and dried with an air drier. The mild steel specimens were then re-weighed. The corrosion inhibition efficiency (IE) was calculated using the following equation.

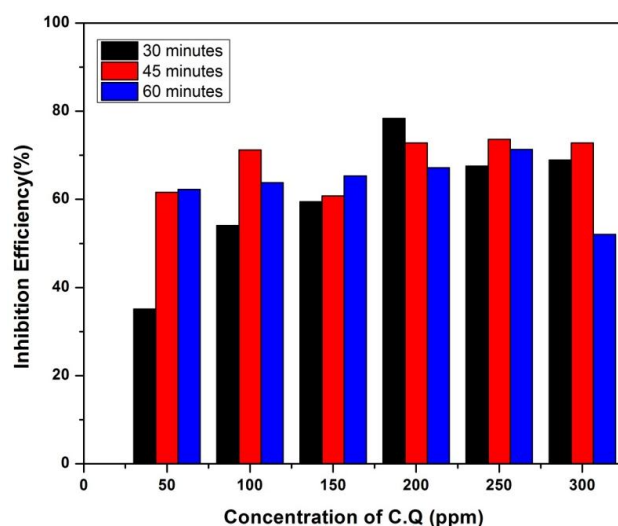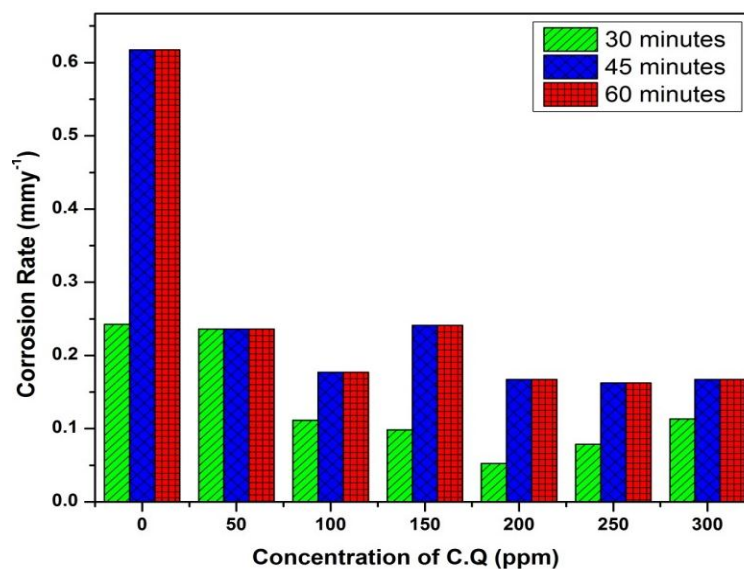$$I.E\ (\%) = \frac{Blank - Inhibitor}{Blank} \times 100$$

Accuracy in weighing up to 0.0001g and in surface area $0.1cm^2$, as recommended by Denver balance TP 214 model. The immersion period of 30, 45 and 60 minutes was fixed in view of the considerable magnitude of the corrosion inhibition efficiency in the absence and presence of inhibitor after this immersion period. The immersion period was maintained accurately up to 30 minutes in view of the lengthy immersion time of 60 minutes. Under the conditions of accuracy, the relative standard error in corrosion rate determinations is of the order of 2% or less for an immersion time of 1 hour.

3.2. Weight loss Measurements
The corrosion rate of mild steel in solutions containing 0.5 M HCl in the absence and presence of various concentrations of inhibitor obtained by the weight - loss method for 30 minutes, 45 minutes and 60 minutes system are given in the Table 1. The corrosion rate and inhibition efficiency are also shown as the function of inhibitor concentration.

Table 1: 0.5 M HCl in various concentration of C.Q   at time interval

S. No.	C.Q (ppm)	30 minutes		45 mines		60 mines	
		I.E	CR	I.E	CR	I.E	CR
1	0	0	0.2427	0	0.6175	0	0.86932
2	50	35.13	0.2361	61.6	0.2361	62.26	0.32804
3	100	54.05	0.1115	71.2	0.1771	63.77	0.31492
4	150	59.45	0.0984	60.8	0.2411	65.32	0.24931
5	200	62.37	0.0524	72.8	0.1673	67.16	0.28212
6	250	67.56	0.0787	73.6	0.1623	71.32	0.24931
7	300	68.91	0.1131	72.8	0.1673	52.07	0.41338

Fig. 1: Variation of Inhibition efficiency with in the absence (inserted) and presence of various concentrations of methanol extract of *Cissus Quadrangularis* the corrosion of mild steel in 0.5 M HCl

Fig. 2: Variation of Corrosion rate in the absence (inserted) and presence of various concentrations of methanol extract of Cissus Quadrangularis the corrosion of mild steel in 0.5 M HCl

The weight - loss method was done for mild steel in 0.5 M HCl with various concentrations of C.Q extract ranging from 50 ppm to 300 ppm and the corresponding values of inhibition efficiency and corrosion rate are given in Table 1. It is observe from the table that the corrosion rate decreased and thus inhibition efficiency increases with increasing concentration of C.Q extract (50 ppm-300 ppm). The maximum inhibition efficiency of about 71.32% was achieved at 200 ppm of C.Q extract. This behavior is due to the fact the adsorption and coverage of the inhibitor on the mild steel surface interaction with the inhibitor concentration[10]. This result indicated that C.Q extract could act as an excellent corrosion inhibitor. At concentration ≥ 250 ppm of C.Q, the protection efficiency decreases of may be due to the fact that these molecules aggregate to gather to form micelles. They are not uniformly adsorbed on the metal surface. Hence corrosion inhibition efficiency decreases.

3.3. Electrochemical impedance studies
Nyquist plots for mild steel immersed in control solution of 200 ppm of inhibitor solution of 0.5 M HCl in the absence and presence of formulations are shown in Fig.3. The impedance parameters, charge transfer resistance (Rct), Double layer capacitance (C_{dl}) from the Nyquist plot values are shown in Table.2. When mild steel immersed in 0.5 M HCl medium the Rct value is found to be 20 (Ω cm^2). The C_{dl} value is 132 (μF/cm^2). When 250 ppm of Cissus Quadrangularis are added to 0.5 M HCl medium the Rct value is formed to be 78 (Ω cm^2). The C_{dl} value is 15 (μF/cm^2). When 200 ppm of Cissus Quadrangularis solution are added to 0.5 M HCl medium the Rct value has increased from 20 to 78 (Ω cm^2) and the Cdl value decreased from 132 to 15 (μF/cm^2). The increase in Rct value and decreases in double layer capacitance values obtained from impedance studies justify the good performance of a compound as an inhibitor in 0.5 M HCl medium. This behaviour means that the fim obtained acts as a barrier to the corrosion process.

Table 2: Impedance spectra studies

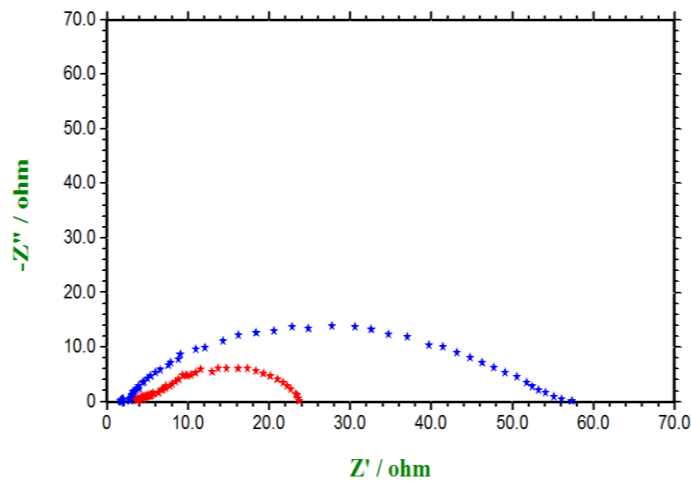| concentration	Rct (Ωcm^{-2})	C_{dl} (μfcm^{-2})	I.E(%)
0.5 M HCl	24	132	_
200 ppm of C.Q	56	15	72

Fig. 3: Impedance spectra curves of mild steel in various test solutions (a) 0.5 M HCl, (b) 200ppm of C.Q
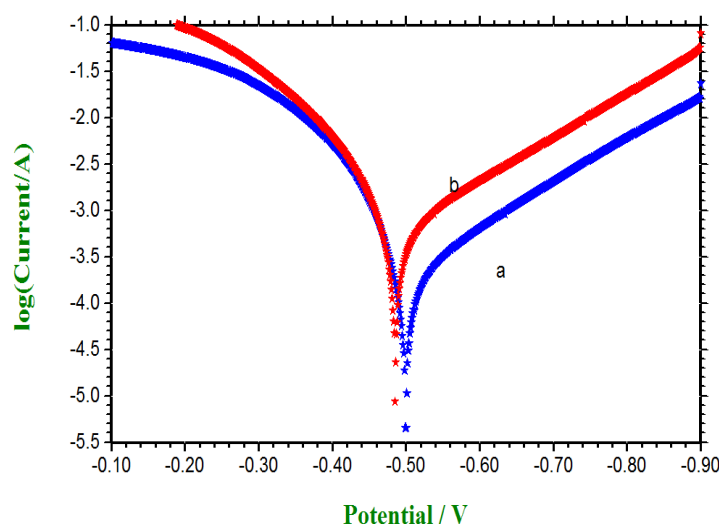
Fig .4: Tafel curves in 0.5 M HCl solution with and without addition of inhibitors

Table 3: Polarization studies of 0.5 M HCl solution with and without addition of inhibitors

Concentration (ppm)	E_{corr} (mv/sce)	I_{corr} ($\mu A_{/cm}^{-2}$)	Ba (mv/dec^{-1})	Bc (mv/dec^{-1})	I.E (%)
0.5 M HCl	-0.500	2.628×10^{-4}	179	99	--
200 ppm C.Q	-0.499	2.768×10^{-4}	207	141	72

The values of the electrochemical parameter obtained from the Tafel curves,namely corrosion potential (Ecorr) cthodic slope (β_c) anodic Tafel slope (β_a), corrent density (I_{corr}), inhibition efficiency η Tafel (%) for the presence and absence of inhibitor are given Tabel.3. It can be seen from the Fig. 4 that, in the presence of inhibitor, the curves are shifted lower current region, showing the inhibition tendency of the inhibitor In the present study, shift in E_{corr} values are in the range of 2-6 mV suggested that they are all acted as mixed inhibitor [10] Investigation of table 2 revealed that the values of βa change slightly in the presence of inhibitor where as more pronounced change occur in the values of βc Indicated that both anodic and cathodic are affected but the effect on the cathodic reaction is more prominent This C_q inhibitor acted as mixed type but predominantly cathodic inhibitor

4. CONCLUSIONS
The inhibition efficiency increases with increasing inhibitor concentrations to attain maximum value of 93.67 % for   inhibitor respectively. The formulation consisting of 0.5 M HCl medium, 300 ppm of C.Q plant extract offers 93.67 % inhibition efficiency. The synergistic effect was exists between 0.5 M HCl-C.Q plant extract systems. The inhibitors show better inhibition efficiency than individual.

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