International Journal of ChemTech Research
CODEN (USA): IJCRGG ISSN: 0974-4290
Vol.7, No.01, pp 37-43, 2014-2015

Citrus sinensis L. leaf extract as an efficient green corrosion inhibitor for mild steel in aqueous medium

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Abstract: Objective: To study the morphology, biochemistry and corrosion inhibition of *Citrus sinensis* L. leaf extract. Methods: Morphological studies on *Citrus sinensis* L. leaf extract were carried out by using weight loss method, pH, UV–Vis, and FT-IR. To prepare the extract, the shade-dried leaf of *Citrus sinensis* L. were soaked in ethanol. For antibacterial studies weight loss method was followed by using various biocides. Results: Detailed phytochemical, and corrosion inhibition studies on a medicinal fern *Citrus sinensis* L. showed its inhibition efficiency. The presence or absence of the *Citrus sinensis* L. leaf extract was the key factor for corrosion inhibition of this species. FT-IR and UV showed the presence of various kinds of terpenoids, alkaloids, tannins, saponins and flavonoids in it. Conclusions: The present study shows that *Citrus sinensis* L. leaf extract have several bioactive compounds, can be used as corrosion inhibitor and such rare morphovariant should be conserved in nature. The next step is to isolate the pure compounds and to screen the bioactivity.
Keywords: *Citrus sinensis*; Weight loss method; UV–Vis; FT-IR.

1. Introduction

Many pharmaceutical innovations are developed from a starting point of knowledge derived from the biological activities of natural organisms. In the case of the random screening of natural product, Aylward et al. [1] argued that the sheer scale of the resource, in the order of 10 to 100 million species, and the continuing evolution of new screens and new disease targets imply that biodiversity will never be fully explored for its pharmaceutical potential. The protection of metal against corrosion is a major industrial problem. The use of inhibitor is one of the best options of protecting metals against corrosion. Several inhibitors in use is either synthesized from cheap raw materials or chosen from compounds having hetero atoms in their aromatic or long chain carbon system. These organic compounds can adsorb on the metal surface, block the active sites and thereby reduce the corrosion rate considerably [2]. Most of the synthetic organic compound shows good anti-corrosive activity, which are highly toxic to cause severe hazards to both human beings and the environment during its applications [3]. The safety and environmental issues of corrosion inhibitors arisen in industries have always been a global concern. The recent trend is to save human being and environment by using eco-friendly inhibitors. Some investigator [4,5] studied the plant extracts and the derived organic species become more important as an environmentally benign, readily available, renewable and acceptable source for a wide range of inhibitors. Several efforts have been made using corrosion preventive practices and the use of green corrosion inhibitors [6]. The plant extract are rich sources of molecules which have appreciably high inhibition efficiency and hence termed as “Green Inhibitors” [7]. These inhibitors are biodegradable and do not contain heavy metals or other toxic compounds [8]. The successful use of naturally occurring substances to inhibit the corrosion of metals in acid and alkaline environment have been presented by some research groups running through references [9-14]. In our present study, we have chosen eco-friendly bio-inhibitor, a green approach to prevent environmental pollution by harmful organic chemicals. The influence of *Citrus sinensis* extract in aqueous medium on carbon using mass loss measurements have been studied. The characterization of alcoholic crystals of inhibitor and the corrosion product on carbon steel in the presence of inhibitor is also reported by UV and IR studies.

2. Experimental

2.1. Preparation of extract

The leaves of *Citrus sinensis* were taken and shade dried and ground well into powder. From this 50 g of sample was refluxed using soxlet in 500 ml of ethanol, the extract and solvent was separated using distillation process. The pure extract was made up to 100 ml using double distilled water.

2.2. Preparation of specimens

steel specimens (0.0267% S, 0.06% P, 0.4% Mn, 0.1% C and the rest iron) of dimensions 1.0 x 4.0 x 0.2 cm were polished to a mirror finish and degreased with trichloroethylene.

2.3. Weight loss method

Carbon steel specimens in triplicate were immersed in 100 ml of the solutions containing various concentrations of the inhibitor for one day. The weight of the specimens before and after immersion were determined using Shimadzu balance, model AY 62. The corrosion products were cleansed with Clarke's solution [15]. The inhibition efficiency (IE) was then calculated using the equation;

$$IE = 100\,[1 - (W_2/W_1)]\,\% \qquad (1)$$

where W_1 is the corrosion rate in the absence of the inhibitor, W_2 is the corrosion rate in the presence of the inhibitor.

2.4. Surface examination

The carbon steel specimens were immersed in various test solutions for a period of one day, taken out and dried. The nature of the film formed on the surface of metal specimens was analyzed by Perkin-Elmer 1600 FTIR spectroscopy and fluorescence spectra was recorded with Hitachi F-4500 fluorescence spectrophotometer.

3. Results and discussion

3.1. Analysis of results from weight loss method

Table 1 shows the values of corrosion rates and inhibition efficiencies obtained from mass loss measurements of different concentrations of *Citrus sinensis* extract (CSE). 3 ml of the CSE offered 92.1% corrosion inhibition efficiency to carbon steel immersed in 100 ml solution. When the concentration of CSE was increased, the inhibition efficiency was decreased. This is due to the fact that when higher concentrations of *Citrus sinensis* are added the protective film (Fe^{2+}– *Citrus sinensis* complex) formed on the metal surface goes into the solution and thus destroying the protective film. It may be considered that the protective film formed may go into transpassive state, where the film is broken [16].

Table 2 shows the values of corrosion rates and inhibition efficiencies obtained from mass loss measurements using *Citrus sinensis* extract (CSE) and of different concentrations of biocides (*Ocimum sanctum*). When the concentration of biocides was increased, the inhibition efficiency was also increased.

Table 3 shows the values of corrosion rates and inhibition efficiencies obtained from mass loss measurements of using *Citrus sinensis* extract (CSE) and of different pH value. When the pH was increased, the inhibition efficiency was decreased.

Table 1. Corrosion rates (CR) of carbon steel immersed in the presence and absence of inhibitors and the inhibition efficiencies (IE) obtained by weight loss method. Inhibitor: CSE; Period: 1 day.

***Citrus sinensis* (ml)**	**Corrosion rate (ppm)**	**Inhibition efficiency (%)**
0	38	-
1	11	71.05
2	6	84.21
3	3	92.11
4	12	68.42

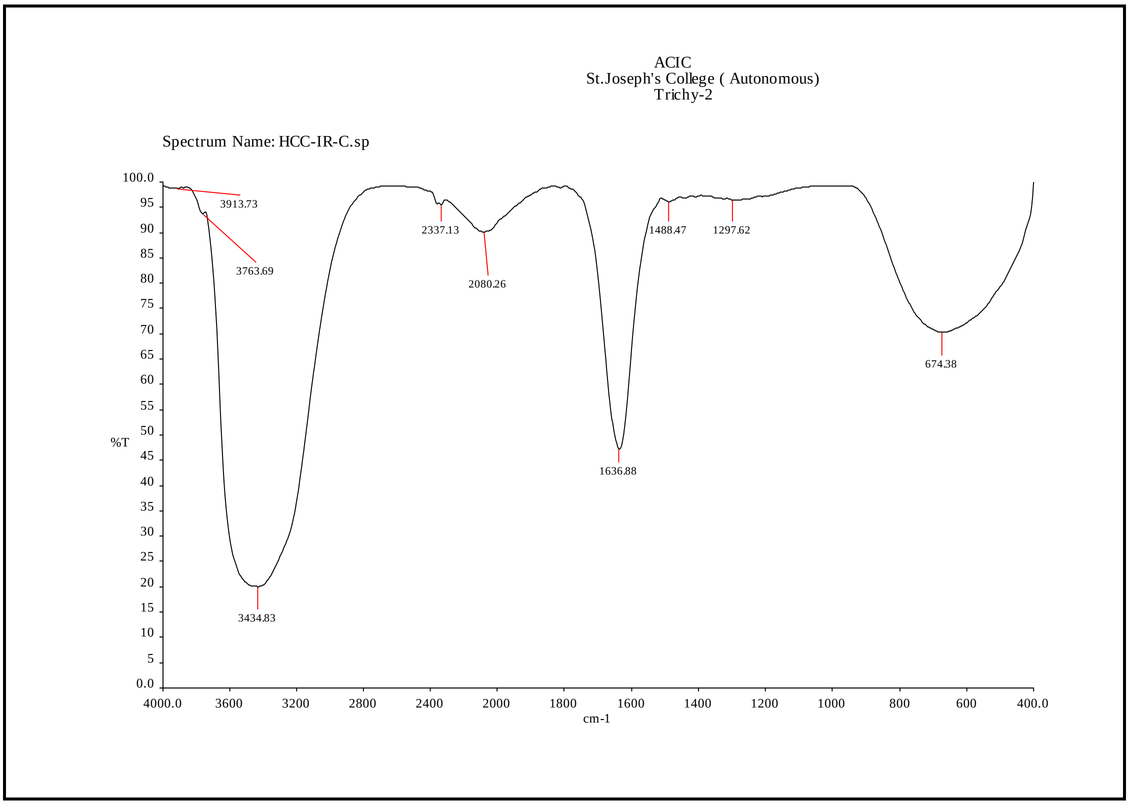
Table 2. Corrosion rates (CR) of carbon steel immersed in the presence of biocides. Inhibitor: CSE; Period: 1 day.

S. No.	*Citrus sinensis* (ml)	Mn^{2+} (ppm)	Biocides (*Ocimum sanctum*) (ml)	Corrosion rate (ppm)	Inhibition efficiency (%)
1	3	20	-	3	92.11
2	3	20	1	8	78.95
3	3	20	2	1	97.37
4	3	20	3	4	89.47
5	3	20	4	6	84.21
6	3	20	5	2	94.74

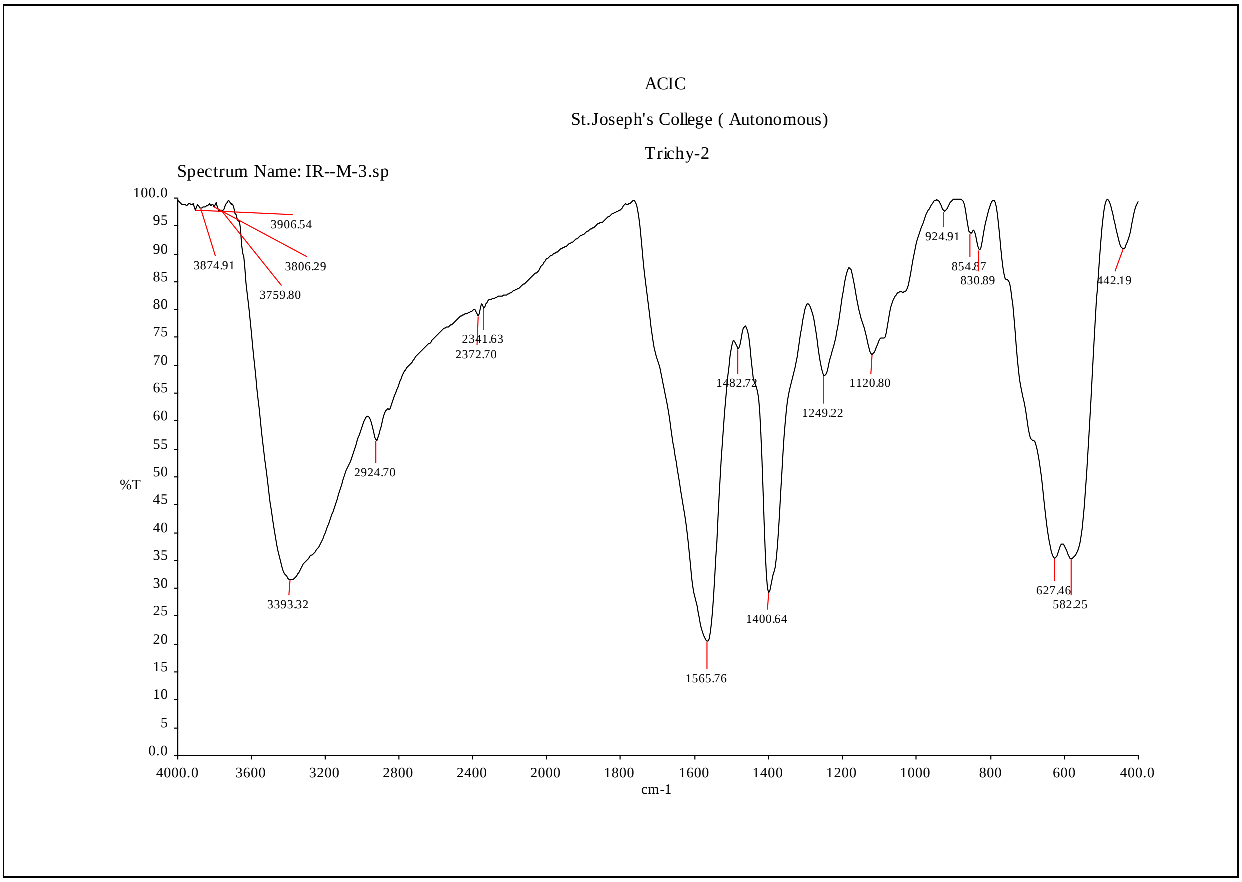
Table 3. Corrosion rates (CR) of carbon steel immersed with different pH. Inhibitor: CSE; Period: 1 day pH

pH	*Citrus sinensis* (ml)	Mn^{2+} (ppm)	Corrosion rate (ppm)	Inhibition efficiency (%)
1	3	20	22.8	40
3	3	20	21.5	43.52
5	3	20	15.21	59.9
7	3	20	1.38	96.3
9	3	20	5.52	85.47

3.2. Fourier transfer infrared spectra (FTIR)



(a)



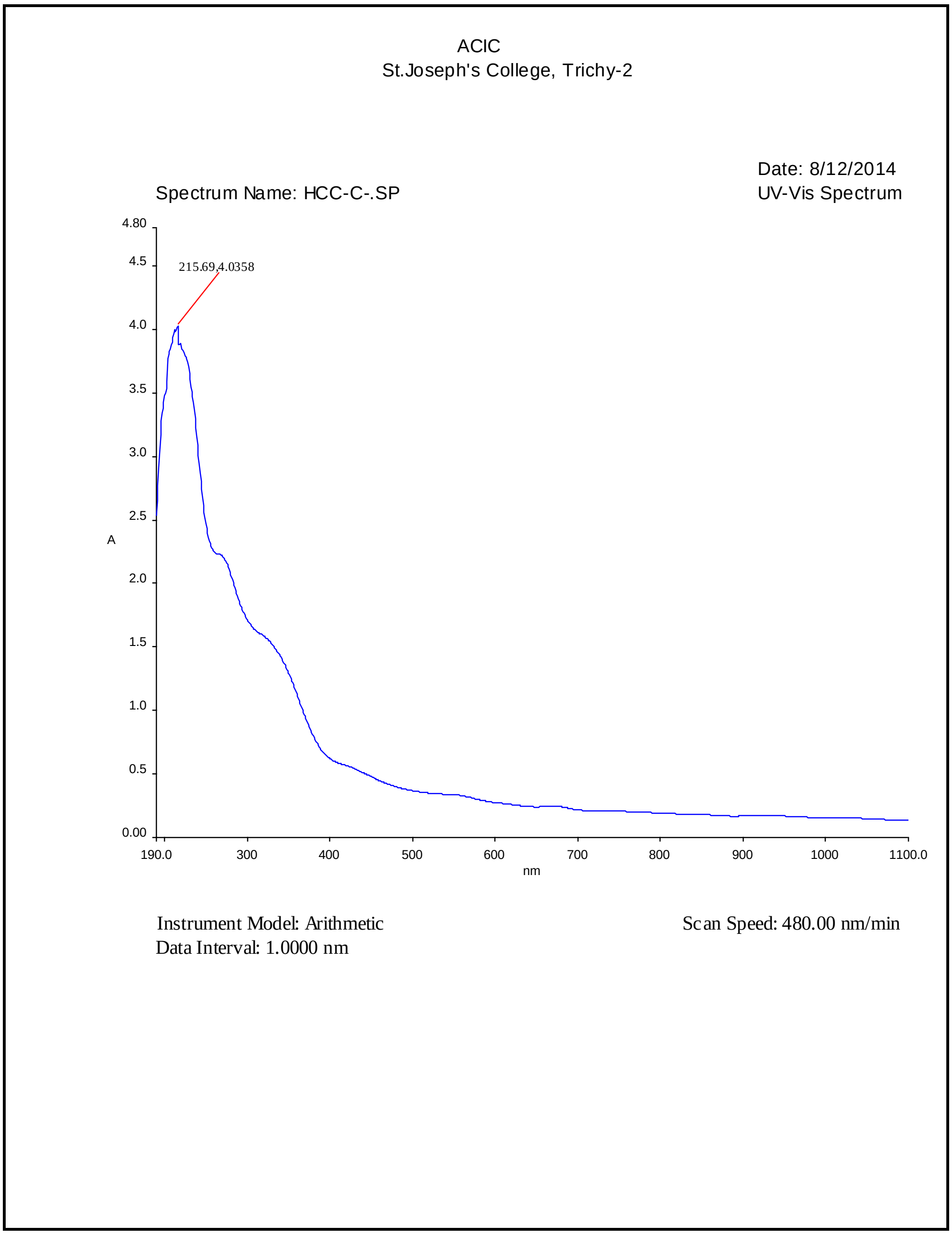
(b)

Figure 1. FTIR spectra of (a) pure CSE (b) film formed on the metal surface after immersion in aqueous solution + CSE (3 ml)

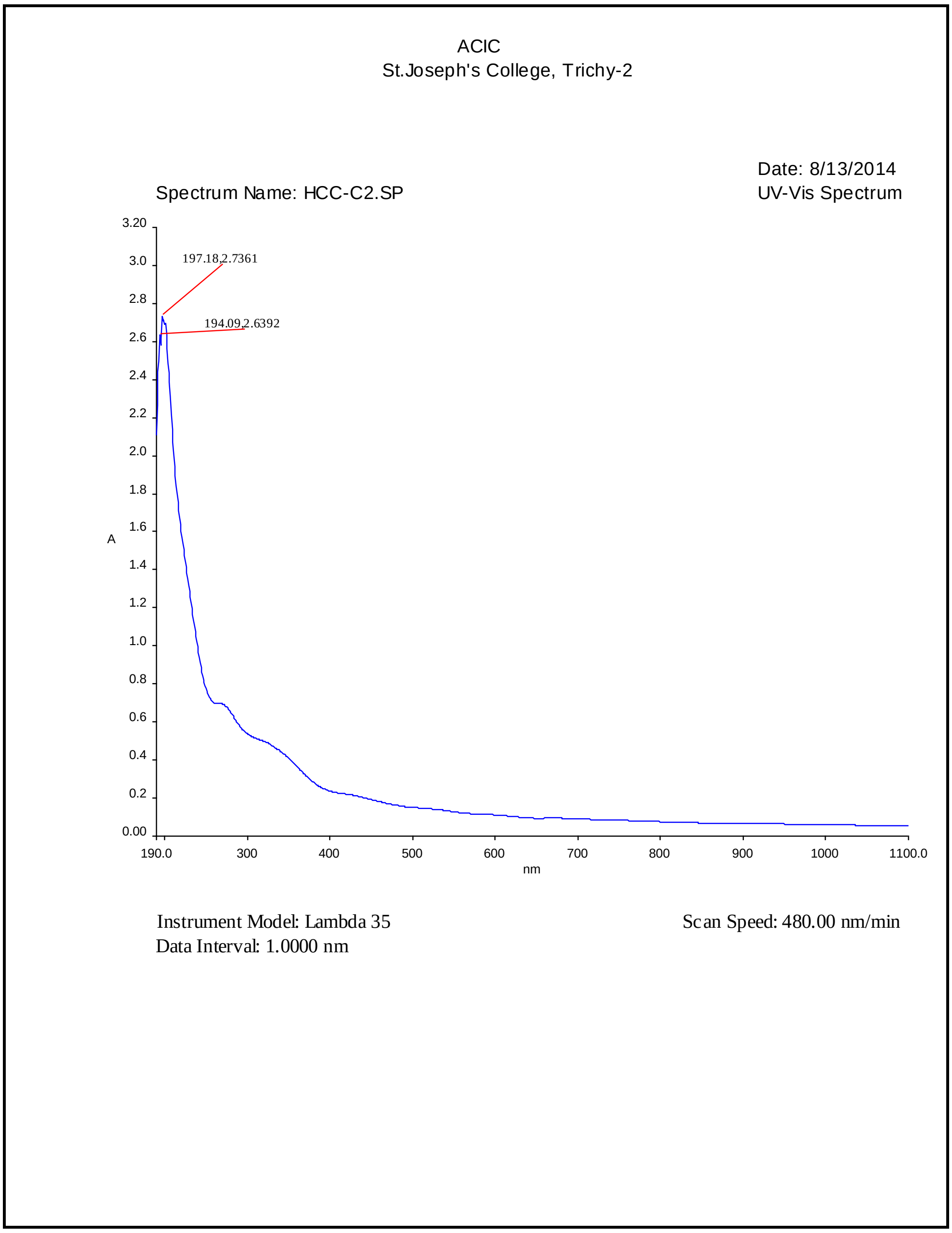
Citrus sinensis extract FTIR spectrum is shown in Figure 1(a), –C=C stretching frequency appeared at 2080.26 cm^{-1}. The aliphatic –CH stretching frequency appeared at 3434.83 cm^{-1}. The ring oxygen stretching frequency at 1297.62 cm^{-1}, $–OCH_3$ stretching frequency appeared at 1636.88 cm^{-1} (Figure 1(b)) [19,20]. The FTIR spectrum of the protective film formed on the surface of the metal after immersion in the aqueous solution containing 3 ml of *Citrus sinensis* is shown in Figure 1(b). It is found that the –C=C stretch has shifted from 1400.64 cm^{-1} to 2341.63 cm^{-1}. The aromatic $–CH_2$ stretching frequency appeared at 2341.63 cm^{-1} to 3393.32 cm^{-1}. The ring oxygen stretching frequency at 924.91 cm^{-1} to 1120.80 cm^{-1}. It is inferred that the oxygen atoms of ring oxygen and $–OCH_3$ group have coordinated with Fe^{2+} resulting in the formation of Fe^{2+}–CSE complex formed on the anodic sites of the metal surface.

3.3. Fluorescence spectra

The UV–Vis adsorption spectrum of aqueous solution of *Citrus sinensis* is shown in Figure 2(a) and (b). Peak appears at 228 nm, 268 nm. When the Fe^{2+} is added to the aqueous solution of *Citrus sinensis*, peaks appear at 225 nm and 265 nm.


ACIC
St.Joseph's College, Trichy-2
Date: 8/12/2014
Spectrum Name: HCC-C-.SP
UV-Vis Spectrum
4.80
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.00
A
215.69,4.0358
190.0
300
400
500
600
700
800
900
1000
1100.0
nm
Instrument Model: Arithmetic
Data Interval: 1.0000 nm
Scan Speed: 480.00 nm/min

(a)



(b)

Figure 2. UV-spectra (a) aqueous solution of CSE (b) aqueous solution of CSE Fe^{2+} + 3 ml *Citrus sinensis* extract.

Conclusions

1. Inhibition efficiency is high at 3 ml of *Citrus sinensis*, so it is found to best system.
2. Corrosion rate decreases with increase in biocide concentration.
3. An aqueous extract of (*Citrus sinensis*) has excellent is inhibition efficiency in controlling corrosion of carbon steel in aqueous solution.
4. The protective film consists of Fe^{2+}– *Citrus sinensis* complex.

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