Journal of Industrial and Engineering Chemistry 37 (2016) 47–56

Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

journal homepage: www.elsevier.com/locate/jiec

# Evaluation of polyphenol composition and anti-corrosion properties of *Cryptostegia grandiflora* plant extract on mild steel in acidic medium

Mayakrishnan Prabakaran [a], Seung-Hyun Kim [a], Venkatesan Hemapriya [b], Ill-Min Chung [a,*]

[a] Department of Applied Bioscience, College of Life and Environmental Science, Konkuk University, Seoul 143 701, South Korea
[b] Department of Chemistry, PSGR Krishnammal College for Women, Coimbatore 641 004, Tamil Nadu, India

ARTICLE INFO

*Article history:*
Received 29 October 2015
Received in revised form 31 January 2016
Accepted 1 March 2016
Available online 7 March 2016

*Keywords:*
*Cryptostegia grandiflora*
Phenolic compounds
Corrosion
Electrochemical studies
Atomic force microscopy

ABSTRACT

The total phenolic and flavonoid compounds present in *Cryptostegia grandiflora* leaf extract were analyzed. The results confirmed that the extract contains the Myricetin 3582.22(μg/g) and Rutin 45.62(μg/g) as major components. *C. grandiflora* extract was evaluated for its anti-corrosion property on mild steel in 1 M $H_2SO_4$. A maximum inhibition efficiency of 87.54% was achieved by using 500 ppm of the inhibitor. Polarization studies indicate that the extract acts as a mixed inhibitor. The formation of productive layer on mild steel by inhibitor was confirmed by SEM-EDS and AFM. The extract is adsorbed on the mild steel according to Temkin adsorption isotherm.



## Introduction

Plant extracts are rich sources of phenolic and flavonoid compounds [1]. Plant extracts containing a mixture of various compounds such as hydroxycinnamic acid, flavonols, phenolic compounds, and hydroxyl benzoic acid are employed as natural corrosion inhibitors to keep the environment greener [2,3]. On a different note, mild steel and its alloys find numerous applications in various fields such as construction, automobile, engineering, oil, and petroleum industries owing to their excellent mechanical strength and low cost [4]. These industries currently make use of mineral acids such as hydrochloric acid and sulfuric acid for cleaning and descaling processes. A major problem with this approach is the fact that mild steel corrodes when exposed to an aggressive acid environment. Several methods have been adopted to reduce metallic corrosion. Among these, the most efficient one is the use of corrosion inhibitors. Inhibitors prevent corrosion either by forming a protective oxide film or by adsorption through N, O, S, and P heteroatoms and aromatic π electrons, thereby creating a barrier that prevents the access of corrosive agents to the metal surface. However, the environmental toxicity of conventional inhibitors limits their application [5,6].

Therefore, studies have increasingly explored the use of non-toxic, biodegradable, and eco-friendly inhibitors such as plant extracts [7,8]. In recent years, many studies have focused on the corrosion inhibition performance of plant extracts from an environmental viewpoint to avoid the destructive effect of synthetic corrosion inhibitors [9–11]. Extracts of *Ligularia fischeri* [12]; *Tragia plukenetii* [13]; *Phyllanthus amarus*, *Oxandra asbeckii*, *Phyllanthus amarus* [14]; *Zenthoxylum alatum* [15]; *Tripleurospermum auriculatum*, *Teucrium oliverianum* [16]; *Silybum marianum* [17]; *Egyptian licorice* [18]; and *Gingko biloba* [19] have been investigated as efficient metallic corrosion inhibitors.

This study focuses on the adsorption and corrosion inhibition performance of *Cryptostegia grandiflora* (*C. grandiflora*) leaf extract on mild steel in 1 M $H_2SO_4$ (sulfuric acid). *C. grandiflora* is a woody perennial vine, also called rubber vine that is native to southwest Madagascar and is widely distributed in India. It has the taxonomic rank Gentianales, and it belongs to the Apocynaceae family. Studies have reported various medicinal properties of *C. grandiflora*. A decoction of this plant species is consumed to treat nervous disorders [20]. It also shows various biological properties such as anti-cancer, anti-inflammatory, anti-oxidant, and anti-viral activities. However, no studies have investigated the corrosion inhibition properties of the methanolic extract of *C. grandiflora* [21–24].

The total phenolic contents (TPC) and total flavonoid contents (TFC) of the methanolic extract of *C. grandiflora* leaf have been examined, and its corrosion inhibition performance was investigated

* Corresponding author. Tel.: +82 02 450 3730; fax: +82 02 446 7856.
*E-mail address:* imcim@konkuk.ac.kr (I.-M. Chung).

http://dx.doi.org/10.1016/j.jiec.2016.03.006
1226-086X/

by weight loss and electrochemical impedance spectroscopy and polarization measurements. The surface morphology of mild steel was analyzed by scanning electron microscopy (SEM) equipped with energy dispersive X-ray spectroscopy (EDX) and by atomic force microscopy (AFM).

## Experimental

### *Materials preparation*

1 M $H_2SO_4$ for use as an aggressive corrosive media was prepared from analytical grade sulfuric acid (Sigma–Aldrich) and doubly distilled water. For weight loss measurements, mild steel specimens with chemical composition of 0.051% carbon, 0.012% sulfur, 0.002% silicon, 0.018% phosphorous, 0.019% chromium, 0.008% molybdenum, 0.031% nickel, 0.19% manganese, and balance Fe were used. The mild steel specimens were cut with dimensions of 3 cm × 1 cm × 0.05 cm, abraded with silicon carbide emery papers (1200–800), degreased with acetone in a sonication bath to remove impurities, and rinsed with doubly distilled water. Finally, the cleaned mild steel specimens were dried at room temperature (303 ± 1 K) and kept in a desiccator.

### *Preparation of plant extract*

The *C. grandiflora* plant was collected from Tamil Nadu, India. Fresh leaves of *C. grandiflora* were washed with running tap water and dried in atmospheric air. Dried powdered leaf samples were soaked in methanol at room temperature (303 ± 1 K). The methanol solvent was changed at intervals of 24 h. After 24 h, the extract solution was filtered, and the residue was suspended in 500 mL of double distilled water. The above-described procedure was repeated four times for exhaustive extraction. All the filtrate was collected and dried using a rotatory evaporator, and the stock solution was used to study the corrosion inhibition properties in acidic medium [14].

### *Determination of TPC and TFC*

The TPC and TFC samples were analyzed using a previously reported procedure [25,26]. In TPC analysis, distilled water (3.16 mL) was mixed with a methanol solution of the test compounds (40 μL). To the above mixture, 200 μL of Folin-Ciocalteu (FC) reagent was added. Then 600 μL of 20% sodium carbonate solution was added and mixed well. The resultant solutions were left at room temperature (303 ± 1 K) for 2 h. Then the absorption of the developed blue color was determined at 765 nm, using a Mecasys Optizen 2120UV plus UV-spectrophotometer (Mecasys, Korea). The concentration of the total phenolic content was determined as mg of gallic acid equivalent (GAE) by using an equation obtained from gallic acid calibration curve. In TFC analysis, 100 mg/mL extract (0.5 mL), 10% aluminum chloride (0.1 mL), 1 M potassium acetate (0.1 mL) and distilled water (4.3 mL) were mixed. After incubation at room temperature (303 ± 1 K) for 30 min, the absorbance was measured at 415 nm. Quercetion was used to plot the calibration curve.

### *Extraction of phenolic compounds for UHPLC analysis*

1 g of dried samples was extracted using a previously reported procedure [26]. The filtrate sample was subjected to UHPLC analysis in a Thermo Accela UHPLC (Thermo Scientific, Rochester, NY, USA) system. The sample was separated by using column HALO C18 (2.7 μm, 2.1 mm × 100 mm) and absorbance at 280 nm. Solvent A (0.1% glacial acetic acid in distilled water) and solvent B (0.1% glacial acetic acid in acetonitrile) are used as mobile phases. Before analyzing the plant extract sample, all standards were analyzed to dissolve in methanol in the UHPLC instrument. Various compounds such as ρ-coumaric acid, ferulic acid, m-coumaric acid, o-coumaric acid, chlorogenic acid, myricetin, quercetin, kaempferol, gallic acid, protocatechuic acid, syringic acid, gentisic acid, rutin, vanillin, resveratrol, naringenin, gormononetin, biochanin A, ρ-hydroxybenzoic acid, naringin, trans-cinnamic acid, catechin, and hesperetin were identified in the plant extract. The concentration was expressed in units of μg/g to identify the phenolic and flavonoid compounds.

### *Statistical analysis*

These experiments were three replicates for all measurements. The all data obtained from the analysis were statistically analyzed using SPSS Ver. 20 (SPSS Inc., Chicago, IL, USA) statistical software package.

### *Measurement techniques*

#### *Weight loss measurements*

Weight loss is the easiest way to determine the corrosion rate and inhibition efficiency. In the weight loss method, pre-treated and pre-weighed mild steel specimens were immersed in 100 mL of test solution with and without different concentrations of *C. grandiflora* extract (100, 200, 300, 400, and 500 ppm) at 303 ± 1 K. After 3 h, the specimens were taken out and washed according to ASTM G-31 and reweighed. From the weight loss data, the inhibition efficiency, corrosion rate, and surface coverage data were calculated.

$$\eta(\%) = \frac{W_0 - W_i}{W_0} \times 100 \quad (1)$$

$$\theta = \frac{\eta(\%)}{100} \quad (2)$$

where $W_0$ and $W_i$ are the weight loss of the mild steel with and without inhibitor, respectively, and

$$C_r = 87.6\frac{W}{Atd} \quad (3)$$

where $W$ is the weight loss (mg); $A$, the specimen area ($cm^2$) exposed to 1 M $H_2SO_4$; $d$, the density of mild steel in $g/cm^3$; and $t$, the exposure time in hours (h).

#### *Electrochemical method*

Electrochemical measurements were conducted in a conventional three-electrode cell assemblage with mild steel specimen (1 $cm^2$) as the working electrode, platinum electrode as the counter electrode, and saturated calomel electrode as the reference electrode by using the CHI 760C electrochemical analyzer. Electrochemical impedance spectroscopy (EIS) was conducted with an open circuit potential (OCP) in the frequency range of 100 kHz to 10 MHz at an amplitude of 10 mV. Electrochemical parameters such as $R_{ct}$ and $C_{dl}$ values were obtained, and the inhibition efficiency was estimated from the charge transfer resistance ($R_{ct}$) obtained from the real ($Z'$) versus imaginary ($Z''$) plot.

$$\eta(\%) = \frac{R_{ct} - R'_{ct}}{R_{ct}} \times 100 \quad (4)$$

where $R_{ct}$ and $R'_{ct}$ are the charge transfer resistances in the presence and absence of inhibitor, respectively.

A potentiodynamic polarization (Tafel) study was started from the cathodic to anodic potential direction with an open circuit potential at a scan rate of 1 mV/s. Electrochemical parameters such as the corrosion potential ($E_{corr}$), corrosion current ($I_{corr}$), and