Corrosion Science 87 (2014) 15–26

Contents lists available at ScienceDirect

Corrosion Science

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

Inhibition effect of bamboo leaves' extract on steel and zinc in citric acid solution

Xianghong Li [a,*], Shuduan Deng [b], Xiaoguang Xie [c], Hui Fu [a]

[a] Faculty of Science, Southwest Forestry University, Kunming 650224, PR China
[b] Faculty of Materials Engineering, Southwest Forestry University, Kunming 650224, PR China
[c] School of Chemical Science and Technology, Yunnan University, Kunming 650091, Yunnan, PR China

ARTICLE INFO

Article history:
Received 11 October 2013
Accepted 26 May 2014
Available online 21 June 2014

Keywords:
A. Steel
A. Zinc
B. Polarization
B. EIS
B. Modeling studies
C. Acid inhibition

ABSTRACT

The inhibition effect of *Phyllostachys nigra Munro* leaves' extract (PMLE) on cold rolled steel (CRS) and zinc in 0.2 M citric acid ($H_3C_6H_5O_7$) solution was studied by weight loss, potentiodynamic polarization curves and electrochemical impedance spectroscopy (EIS) methods. Quantum chemical calculation of DFT including the solvent effect was applied to investigate the adsorption mode through light on chemical molecular structure. The results show that PMLE is a good inhibitor for both steel and zinc in 0.2 M $H_3C_6H_5O_7$ solution, and inhibition efficiency follows the order: zinc > steel. The adsorption of PMLE on both metal surface obeys Langmuir adsorption isotherm.

1. Introduction

The use of inhibitors is one of the most practical methods for protection metals against corrosion, especially in acid media [1]. In the 21st Century, the research in the field of "green" or "eco-friendly" corrosion inhibitors has been addressed toward the goal of using cheap, effective compounds at low or "zero" environmental impact. Plant extract is low-cost and eco-friendly, and can be obtained through simple extraction process as well as biodegradable. The main advantage of using plant extract as the corrosion inhibitor is due to both economic and environmental benefits.

Up to now, some plant extracts have been studied as effective corrosion inhibitors of steel in inorganic acids (HCl, H_2SO_4, H_3PO_4), such as henna [2,3], *Nypa fruticans* Wurmb [4], *Zenthoxylum alatum* [5], *Mentha pulegium* [6], olive [7], *Phyllanthus amarus* [8], Damsissa [9], *Occimum viridis* [10,11], *Murraya koenigii* [12], lupine [13], *Ananas comosus* [14], *Lasianthera africana* [15], *Strychnos nux-vomica* [16], *Justicia gendarussa* [17], *Oxandra asbeckii* [18], *Ferula assa-foetida* [19], coffee [20], fruit peel [21], Halfabar [22], *Kopsia Singapurenis* [23], *Jasminum nudiflorum* [24], *ginkgo* [25], *Artemisia pallens* [26], *Salvia officinalis* [27], *Osmanthus fragran* [28], *Uncaria gambir* [29], *garlic peel* [30], *Neolamarckia cadamba* [31], *Zenthoxylum alatum* [32], *Acalypha indica* L. [33], *Acer truncatum* [34] and *Acer buergerianum* [35]. Besides steel, the plant leaves' extracts such as *Hibiscus subdariffa* [36] and *Aloe vera* [37] as effective corrosion inhibitors of zinc in HCl have also been reported.

Comparing with the corrosion inhibition in inorganic medium, there are lower attentions in organic medium. As a frequently used organic acid, citric acid ($H_3C_6H_5O_7$) is a medium–strong acid. The use of citric acid in cleaning of scales is non-toxic, small risk and less over-pickling. Citric acid still shows strong corrosiveness on steel and zinc, so there is a great need to add inhibitor to protect steel and zinc in citric acid solution. Entering into the 21st century, the plant leaves' extract of *Piper Nigrum* L. [38] as an effective corrosion inhibitor for steel in citric acid has also been reported. Obviously, confronting with the vast varieties of plant, the data regarding the use of plant leaves' extract as the corrosion inhibitor for steel in citric acid is rather scarce. What is more, to the best of our knowledge, the literature available to date about plant extract as a corrosion inhibitor for zinc in citric acid solution is almost scant.

In our laboratory, much work has been conducted to study the inhibition by bamboo leaves' extract (BLE) on the corrosion of metals in different media. The main reason for the choice of BLE is that bamboo leaves are abundant resources (about 1200 species and 70 genera of bamboo in the world) with fast renewal and continual, and BLE is virtually nonpoisonous [39,40]. Recently, the bamboo leaves' extracts have been reported as the good inhibitors for steel in HCl and H_2SO_4 solutions [41], and aluminum in HCl and H_3PO_4 solutions [42]. In continuation of our previous study, the present

* Corresponding author. Tel.: +86 871 63863375; fax: +86 871 63863150.
E-mail address: xianghong-li@163.com (X. Li).

http://dx.doi.org/10.1016/j.corsci.2014.05.013
0010-938X/

work first reports the inhibition effect of *Phyllostachys nigra Munro* leaves' extract (PMLE) on the corrosion of cold rolled steel (CRS) and zinc in 0.2 M citric acid ($H_3C_6H_5O_7$) solution. Fourier transform infrared spectroscopy (FTIR) and ultraviolet spectroscopy (UV) were employed to characterize PMLE. The contents of total flavonoids and rutin in PMLE were determined by $NaNO_2$–$Al_2(SO_4)_3$–NaOH coloration and high performance liquid chromatography (HPLC), respectively. Weight loss, polarization curves and electrochemical impedance spectroscopy (EIS) methods were used to evaluate corrosion rate and inhibition efficiency. Meanwhile, the difference in inhibition performance between PMLE and rutin is discussed to gain some insight into the contribution of major components to the corrosion inhibition. Quantum chemical calculation of density function theory (DFT) is applied to elucidate the adsorption center of flavones backbone structure (FBS). Meanwhile, the difference in inhibition performance between PMLE and rutin is discussed to gain some insight into the contribution of major components to the corrosion inhibition, and then discuss the inhibitive mechanism. It is expected to provide useful information on the inhibition effect of bamboo leaves' extract for steel and zinc in citric acid ($H_3C_6H_5O_7$) solution.

2. Experimental

2.1. Materials

Cold rolled steel (CRS) coupons are obtained from Pangang Group Panzhihua Steel & Vanadium Co., Ltd., and have the following composition (wt.%): C 0.07%, Mn 0.3%, P 0.022%, S 0.010%, Si 0.01%, Al 0.030% and Fe balance. Zinc sheets were of analytical pure ($\geqslant$99.9%), and supplied by Shanghai Chemical Reagent Company of China. The aggressive solutions of 0.2 M $H_3C_6H_5O_7$ were prepared by dilution of AR grade $H_3C_6H_5O_7$ with distilled water. Rutin of pure standard was obtained from Shanghai Chemical Reagent Company of China.

Fresh *Phyllostachys nigra Munro* leaves were picked in campus of Southwest Forestry University, and then cleaned with running water to eliminate ash of mud, dried for about 2 d in an oven at 60 °C, and ground to powder. 15 g sample of the powder was refluxed in 450 ml 40% (percent by volume) C_2H_5OH at 75 °C for 2 h. The refluxed solution was filtered, and the filter liquor was evaporated to 100 ml of dark brown residue, and then degreased with petroleum ether (boiling bracket: 60–90 °C) using separating funnel. Thereafter, the solution was evaporated to about 50 ml dark brown residues using rotary evaporator, dried in vacuum drying oven at 60 °C until complete dryness (about 2 d). Then the dark brown solid residue (about 1.6 g) of *Phyllostachys nigra Munro* leaves' extract (PMLE) was obtained and preserved in a desicator.

2.2. FTIR and UV of PMLE

The solid plant extract of PMLE was characterized by Fourier transform infrared (FTIR) spectroscopy. FTIR spectra were recorded in an AVATAR-FTIR-360 spectrophotometer (Thermo Nicolet Company, USA), which extended from 4000 to 400 cm^{-1}, using the KBr disk technique.

On the other hand, the solutions of PMLE were analyzed by UV spectral measurements using UV-2401PC spectrophotometer (Shimadzu Company, Japan). The absorption spectra of these solutions were determined with distilled water as reference.

2.3. Determining the content of total flavonoids

The content of total flavonoids is determined by $NaNO_2$–$Al_2(SO_4)_3$–NaOH coloration system with rutin as standard sample. Accurately weighed 0.0250 g rutin or PMLE, dissolved in 100 ml volumetric flask using 60% ethanol, and the standard solution of 250 mg l^{-1} rutin or PMLE was obtained. Test solution (different quantity of standard solution or PMLE solution) accurately quantified to 50 ml measuring flask was added 5% $NaNO_2$ to 2.0 ml, shook up, laid 6 min, then added 10% $Al_2(SO_4)_3$ 2.0 ml, shook up, laid 6 min, added 10% NaOH 20 ml, finally fixed the solution to 50 ml with distilled water, laid 15 min, determined the absorbency at 510 nm with corresponding reagents as blank solution. The content of total flavonoids in PMLE (solid extract) is determined three times.

2.4. High performance liquid chromatography (HPLC)

The chromatographic separation was performed on a Waters1525-HPLC (Waters, USA) equipped with Waters 2996 photo-diode array detector (PDAD) plus Waters717 autosampler. The column is Waters C18 (5 μm, 4.6 mm × 250 mm). The measurement was controlled by Waters Empower Chromatography Data Software. The mobile phase is $V(CH_3OH):V(H_2O) = 50:50$. The flow rate is 1 ml min^{-1}, and the detected wavelength is 258 nm.

2.5. Weight loss measurements

Weight loss tests were conducted under total immersion in 250 ml of non-deaerated $H_3C_6H_5O_7$ solutions without and with inhibitor. The experimental temperature was controlled at 20 °C by a water thermostat (±0.1 °C). CRS sheets of 2.5 cm × 2.0 cm × 0.06 cm and zinc sheets of 2.5 cm × 2.0 cm × 0.025 cm were abraded by a series of emery paper (grade 320-500-800) and then washed with distilled water and acetone. After weighing by digital balance (±0.1 mg), the specimens were totally suspended in a beaker containing test solution using glass hooks and rods. After 24 h, the specimens were taken out, washed with bristle brush under running water to remove the corrosion product, dried with a hot air stream, and re-weighed accurately. Then the tests were repeated at different temperatures. In order to get good reproducibility, experiments were carried out in duplicate. In the present study, the relative phase difference (RPD) values between two parallel experiments are found to be lower than 5%, indicating good reproducibility. The corrosion rate (v) and inhibition efficiency (η_w) were calculated [24].

2.6. Electrochemical measurements

Electrochemical experiments were carried out in the conventional three-electrode cell with a platinum counter electrode (CE), a saturated calomel electrode (SCE) coupled to a fine Luggin capillary as the reference electrode (RE) and a working electrode (WE). The WE was in the form of square CRS embedded in polyvinyl chloride (PVC) holder using epoxy resin so that the flat surface was the only exposed surface in the electrode. The test surface area of WE was 1.0 cm × 1.0 cm, and prepared as described above (Section 2.5). The electrolyte is 250 ml 0.2 M citric acid without and with different concentrations of PMLE. For the electrochemical experiments, the surface area of platinum counter electrode (CE) is larger than that of WE, and the CE is countered to the total exposed surface of WE. Thus, the electrical field distribution could be uniform.

All electrochemical measurements were taken using a PARSTAT 2273 advanced electrochemical system (Princeton Applied Research). In order to minimize ohmic contribution, the tip of Luggin capillary was kept close to WE. Experiments were carried out in duplicate to ensure reproducibility of results.

Before electrochemical measurements, the electrode was immersed in test solution at open circuit potential (OCP) for 6 h at 20 °C to be sufficient to attain a stable state. The potential of