Journal of the Taiwan Institute of Chemical Engineers 000 (2015) 1–10

Contents lists available at ScienceDirect

Journal of the Taiwan Institute of Chemical Engineers

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

Highly efficient *Ligularia fischeri* green extract for the protection against corrosion of mild steel in acidic medium: Electrochemical and spectroscopic investigations

Mayakrishnan Prabakaran[a], Seung-Hyun Kim[a], Kathirvel Kalaiselvi[b], 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 5 June 2015
Revised 25 August 2015
Accepted 29 August 2015
Available online xxx

Keywords:
Ligularia fischeri
Polarization
Adsorption isotherm
Electrochemical impedance spectroscopy
Atomic force microscopy

ABSTRACT

A methanol extract of *Ligularia fischeri* was studied for its inhibitive effect on the corrosion of mild steel in a 1 M hydrochloric acid medium, using the metrics of weight loss, potentiodynamic polarization, and electrochemical impedance spectroscopy (EIS). The corrosion rate of mild steel and *Ligularia fischeri's* inhibition efficiencies were calculated. The inhibition efficiency [η (%)] was observed to increase with increasing concentrations of *Ligularia fischeri*. A maximum inhibition efficiency of 92% was achieved using 500 ppm of the inhibitor. The weight loss experiments were performed at different temperatures to understand the thermodynamic mechanism of inhibition. A mixed inhibition mechanism was proposed for the effects of *Ligularia fischeri* extract, as revealed by the potentiodynamic polarization technique. A solution analysis by atomic absorption spectroscopy (AAS) for mild steel showed decreased dissolution of iron in the presence of *Ligularia fischeri*. The adsorption mechanism and surface morphology of the mild steel, both with and without the inhibitor, were studied using UV–visible, Fourier transform infrared (FT-IR), Raman, wide-angle X-ray diffraction (WAXD), scanning electron microscopy/energy-dispersive X-ray spectroscopy (SEM-EDS), and atomic force microscopy (AFM).

1. Introduction

Mild steel, containing less than 0.15% carbon [1], is widely used structurally in automobiles, pipes, and industrial applications [2]. Unfortunately, mild steel suffers from severe corrosion in aggressive media such as acids, used in pickling processes and descaling operations [3]. Hydrochloric (HCl) and sulfuric acids are frequently used for the pickling of mild steel [4,5]. However, a recent trend shows the growing use of plant extracts as corrosion inhibitors. This has been demonstrated to be among the most practical and economical methods for protection against unexpected metal dissolution in aggressive aqueous media [6]. Several organic compounds containing nitrogen, oxygen, sulfur, phosphorus, and multiple bonds or aromatic rings in their structure have been reported as efficient corrosion inhibitors [7]. The corrosion inhibition property of organic compounds having highly electron-dense heteroatoms such as N, S, and O is well established. Unfortunately, most of the synthetic organic inhibitors are toxic in nature. Plant extracts are preferred as corrosion inhibitors over synthesized organic compounds for their low cost, easy availability, non-toxic properties, renewability, and eco-friendliness. Various plant parts, such as the seed, leaves, flowers, and fruits, have been used as anticorrosion factors [8,9]. Many plant extracts have been closely studied as corrosion inhibitors, including *Zanthoxylum alatum* [2], *Justicia gendarussa* [6], *Chlorophytum borivilianum* [7], *Clematis gouriana* [8], *Argemone mexicana* [10], *Acalypha torta, Lawsonia inermis, Oxandra asbecki, Argemone mexicana, Berberis, Isertia coccinea, Palicourea guianensis* [11–16], *Schinopsis lorentzii* [17], *Lycium shawii, Teucrium oliverianum, Ochradenus baccatus, Anvillea garcinii, Cassia italica, Artemisia, Carthamus tinctorius* and *Tripleurospermum auriculatum* [18].

A number of biological activities, including protective effects against chronic alcohol use and hepatotoxicity, cancer prevention, the generation of antioxidant enzymes, and antimutagenic and antigenotoxic activities have been reported to arise from *Ligularia fischeri* extract. The plant is regarded as an important source of dietary antioxidants, especially considering its high radical scavenging activity [19]. Several biological constituents, including terpenoids, flavonoids, and phenolic acids, have been identified in different parts of the plant.

Four new compounds (1β-hydroxy-6α-isobutyryloxy-9-noreremophil-7(11),8(10)-dien-8(12)-olide, 1β-acetoxy-6α-isobutyryloxy-

* Corresponding author. Tel.: +82 2 4503730; fax: +82 2 4467856.
E-mail address: imcim@konkuk.ac.kr (I.-M. Chung).

http://dx.doi.org/10.1016/j.jtice.2015.08.023
1876-1070/

9-noreremophil-7(11),8(10)-dien-8(12)-olide, ligularate, and 9-oxoplatyphyllide) were discovered by Zhang et al. in *Ligularia fischeri* plant extract. These compounds contain more heteroatoms and phenyl rings, which may lead to the extract's performance as a good anticorrosion inhibitor [20].

In particular, several derivatives of caffeoylquinic acids have been isolated from the extract, suggested to represent the major phenolic constituents in the leaves. Our present investigation focused on the extraction and use of the inhibitive role of these constituents. The study was performed to investigate the corrosion-inhibitive effect of *Ligularia fischeri* extract on mild steel in 1 M HCl solution, using weight-loss measurements with various concentrations and different temperatures. The mechanism of corrosion inhibition was evaluated by potentiodynamic polarization studies and AC-impedance analysis. The nature of adsorption and the morphology of the steel surface were determined by FT-IR, UV–visible, Raman, WAXD, AAS, SEM-EDS, and AFM.

2. Experimental

2.1. Materials and methods

Cultivated *Ligularia fischeri* var. *spiciformis* Nakai was collected in Seoul, Republic of Korea in November 2013. Mild steel consists 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 a balance of iron. HCl, methanol, and analytical reagent (AR)-grade acetone were used to prepare the test solutions, using triple-distilled water. The corrosion inhibition from *Ligularia fischeri* plant extract on mild steel in 1 M HCl was investigated. Several techniques, such as weight loss, potentiodynamic polarization, AC impendence, FT-IR, UV–visible, Raman, and AAS, were performed to establish the mechanism.

2.2. Inhibitor preparation

The *Ligularia fischeri* plant was washed carefully with tap water to remove adhered mud particles, rinsed in double-distilled water, and then dried in an air oven for 5 days at 323 ± 1 K. The plant material was ground to a fine powder. Approximately 150 g of the resultant fine powder was placed in a 2.5 L round-bottom flask. To this, 2 L of methanol solvent was added, and then heated until the mixture boiled. The mixture was permitted to cool for 24 h and then filtered. The filtrate was subjected to an evaporation process to remove excess solvent. A green inhibitor was obtained in its pure form at the end of the evaporation process. The obtained extract was used to prepare solutions of different concentrations by dissolving 0.01 mg of the extract in various acidic solvents.

2.3. Techniques used

2.3.1. Weight-loss analysis

Prior to the experiment, mild steel specimens 3 × 1 × 0.5 cm in size were polished using 1/0, 2/0, 3/0, and 4/0-grit emery sheets, and then washed with acetone. Subsequently, the initial weights of the polished plates were measured. Blank solutions of 1 M HCl containing various concentrations of the inhibitor extract were placed in 100 mL beakers; the metal specimens were suspended in the solutions using glass hooks. The specimens were immersed completely in the solution, without touching the walls of the beaker. After a period of 3 h, the specimens were cleaned according to ASTM G-81 and their weights were recorded using analytical balance. From the initial and final weight of each specimen, the weight loss was calculated. From the weight loss data, the inhibition efficiency [η (%)], corrosion rate [C_r (millimeters per year, mmpy)], and surface coverage (θ) were calculated using the following formulas:

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

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

where W_0 and W_i are the weight loss of the mild steel in the absence and presence of the inhibitor, respectively, and

$$C_r = 87.6\,W/Atd \quad (3)$$

where W is weight loss in milligrams, A is the area of the mild steel specimen in square centimeters, t is the immersion time in hours, and d is the density of the mild steel.

2.3.2. Temperature studies

The same weight-loss analysis was performed at different temperatures of 303, 313, 323, and 333 K using a thermo state to study the inhibition efficiency of the extract. This provided details on the nature of the adsorption and activation energies. The activation energy (E_a) of the inhibitor was calculated by a graphical method, plotting log (C_r) *versus* 1000/T (K^{-1}) for the temperatures of 303, 313, 323, and 333 K in 1 M HCl, both with and without the inhibitor at all extract concentrations. E_a was calculated using the formula:

$$E_a = -2.303 \times 8.314 \times \text{Slope}\,(J) \quad (4)$$

$$K = \theta/[C(1-\theta)] \quad (5)$$

where θ is the surface coverage of the inhibitor, C is the concentration of the inhibitor in mM/100 mL, K is the equilibrium constant, and T is the temperature.

2.3.3. Electrochemical studies

Electrochemical measurements were performed on Ivium Compact Stat instrument using in a glass cell with a 100 mL capacity. Platinum and saturated calomel were used as the counter and reference electrodes, respectively. A mild steel rod of size 0.6 mM was placed in the test solution (uninhibited or inhibited) for 10–15 min before the electrochemical measurements were made. Electrochemical impedance spectroscopy (EIS) and Tafel polarization were conducted in an electrochemical measurement unit. The EIS measurement was made at the corrosion potential over a frequency range of 100 kHz to 10 mHz with a signal amplitude of 10 mV. The Tafel polarization was made after EIS within the potential range of –200 to +200 mV with respect to the open-circuit potential, at a scan rate of 1 mV/s [11]. The electrochemical resistance (R_{ct}) and double-layer capacitance (C_{dl}) were calculated from the Nyquist plot (Z_{real} *versus* $Z_{imaginary}$). The corrosion potential (E_{corr}), corrosion current (I_{corr}), and Tafel slope for the cathodic and anodic reaction (b_c and b_a, respectively) were obtained from the plot of potential, E *versus* log (I).

The corrosion inhibition efficiency (η) by potentiodynamic polarization was calculated from the value of I_{corr} by using the formula [21–23]

$$\eta(\%) = \frac{(I'_{corr} - I_{corr})}{(I'_{corr})} \times 100 \quad (6)$$

where I'_{corr} and I_{corr} are the corrosion currents in the absence and presence of the inhibitor, respectively. The inhibition efficiency by AC impedance was calculated using the equation [24]

$$\eta(\%) = \frac{(R_{ct} - R'_{ct})}{(R_{ct})} \times 100 \quad (7)$$

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

Please cite this article as: M. Prabakaran et al., Highly efficient *Ligularia* fischeri green extract for the protection against corrosion of mild steel in acidic medium: Electrochemical and spectroscopic investigations, Journal of the Taiwan Institute of Chemical Engineers (2015), http://dx.doi.org/10.1016/j.jtice.2015.08.023