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Evaluation of *Ginkgo* leaf extract as an eco-friendly corrosion inhibitor of X70 steel in HCl solution

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ABSTRACT

The corrosion inhibition of X70 steel in 1 M HCl by *Ginkgo* leaf extract (GLE) was investigated by conducting electrochemical measurements. The inhibition efficiency exceeded 90% in the presence of 200 mg/L GLE at all of the tested temperatures. The excellent inhibition capacity, which was attributed to the formation of inhibitor–adsorption films on the surface of the X70 steel, was confirmed by field emission scanning electron microscopy and atomic force microscopy. The adsorption of GLE on steel surface followed the Langmuir adsorption model. Potential of zero charge measurement and quantum chemical calculation were adopted to elucidate the inhibition mechanism.

1. Introduction

Although using organic corrosion inhibitors is the most efficient and economical approach among all anticorrosive methods, such materials cannot be used for large-scale corrosion inhibition because of the growing ecological awareness about their high hazardous environmental implications [1]. As such, non- or low-toxic alternatives must be developed to replace traditional hazardous inhibitors. Given their biodegradability and wide availability, plant extracts are natural products that have drawn considerable attention as environmentally friendly inhibitors for steel corrosion [2,3]. To date, numerous plant extracts have been employed as efficient inhibitors for steel corrosion in acid solution; these extracts include *Zenthoxylum alatum* [4], lupine [5], henna [6], *Justicia gendarussa* [7], *Uncaria gambir* [8], *Oxandra asbeckii* [9], *Punica granatum* [10], *Artemisia pallens* [11], *Osmanthus fragran* [12], bamboo [13,14], *Salvia officinalis* [15], *Tagetes erecta* [16], *Geissospermum* [17], *Musa paradisiac* [18], *Nigella sativa* [19], orange peel [20], and *Thymus vulgaris* [21]. These studies attributed the inhibitive ability of plant extracts to the complex constituents, including tannins, alkaloids, flavonoids, and nitrogen bases. These organic compounds are rich in heteroatoms (i.e., N, S, O), electronegative groups, and conjugated double bonds, all of which are present in good corrosion inhibitors as major adsorption centers.

In recent years, *Ginkgo* has attracted some attention in the field of corrosion. Deng et al. investigated the inhibition effect of GLE on cold roll steel in HCl and H_2SO_4, and they demonstrated that GLE is more effective in 1 M HCl than in 0.5 M H_2SO_4 [22]. Lin et al. explored the use of the fruit extract of *Gingko* as a corrosion inhibitor of J55 steel in 3.5 wt% NaCl solution saturated with CO_2 [23]. To our knowledge, no work has focused on the inhibition behavior of X70 steel in HCl medium with GLE. Thus, this work aimed to investigate GLE as a corrosion inhibitor of X70 steel in 1 M HCl by using electrochemical methods (potentiodynamic polarization measurement and electrochemical impedance spectroscopy). Microscopic surface observations (field emission scanning electron microscopy (FE-SEM) and atomic force microscopy (AFM)), potential of zero charge (PZC) measurement, and density functional theory (DFT) calculations were combined to discuss the roles of the inhibitive ability and mechanism of GLE in X70 steel corrosion.

2. Experimental method

2.1. Preparation of GLE

GLE was synthesized in a similar procedure reported by Deng et al. [22]. Fresh *Ginkgo* leaves were collected in Chongqing University, cleaned with distilled water, dried for 50 h at 333 K, and then ground to powder. Exactly 20 g of powder was refluxed in 80% alcohol at 353 K for 3 h. Thereafter, the refluxed solution was filtered, degreased with petroleum ether, and extracted with a separating funnel. Then, the solution was concentrated in a rotary evaporator, and then dried in a vacuum dry oven at 333 K for 24 h. Finally, a dark brown solid residue (approximately 2 g) was collected and stored in a desiccator.

The solid plant extract was characterized through Fourier transform

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infrared (FTIR) spectroscopy. The spectra were obtained by using a Thermo Scientific FTIR spectrophotometer (Nicolet iS50) in the range of 4000–400 cm^{-1} through KBr disk technique.

2.2. Electrode and solutions preparation

The testing specimens were cut from a X70 steel sheet and contained 0.16 wt% C, 1.7 wt% Mn, 0.45 wt% Si, 0.01 wt% S, 0.02 wt% P, 0.06 wt % V, 0.05 wt% Nb, 0.35 wt% Mo, 0.06 wt% Ti, and the remainder in Fe. The steel specimens were sealed in epoxy, leaving a 1 cm^2 area exposed to the aggressive solution for electrochemical tests. The steel coupons used for FE-SEM and AFM had dimensions of 0.50 cm × 0.50 cm × 0.30 cm and 1.00 cm × 1.00 cm × 0.10 cm, respectively. Prior to each measurement, the steel electrode was abraded with emery papers with 400–3000 grit, washed ultrasonically with distilled water and anhydrous alcohol, and dried under cold wind.

The aggressive solution was prepared by using 1 M HCl solution without and with various concentrations (25, 50, 100, and 200 mg/L) of GLE. The 1 M HCl solution, which was treated as the blank for comparison, was diluted from AR grade 37% HCl. Besides, 1% alcohol was added to dissolve GLE absolutely. A freshly prepared solution was used for each experiment.

2.3. Electrochemical tests

The electrochemical measurements were performed with a CHI 760E electrochemical station equipped with a traditional three-electrode system. The X70 steel specimen was used as a working electrode (WE), a 4 cm^2 platinum sheet was utilized as the counter electrode (CE), and a saturated calomel electrode served as the reference electrode (RE). In this study, all of the potentials were are in reference to the RE. The tests were conducted in a temperature-controlled water bath at a wide range of temperature (298, 308, and 318 K).

First, the WE was immersed in the test solution for 1200 s to obtain a stable open circuit potential (E_{OCP}). The corresponding OCP–time curves are depicted in Fig. 1. Then, electrochemical impedance spectroscopy (EIS) was performed on the E_{OCP}. The disturbance signal was a 10 mV peak-to-peak sinusoidal wave in the frequency range of 100000–0.01 Hz. The EIS data were fitted and analyzed carefully by using Zsimpwin. The inhibition efficiency (η) obtained by the EIS test was calculated as follows:

$$\eta(\%) = \frac{R_{ct} - R_{ct,0}}{R_{ct}} \times 100 \quad (1)$$

where R_{ct} and $R_{ct,0}$ are the charge transfer resistances of the WE with and without studied organics, respectively. Finally, the potentiodynamic polarization curves were recorded at a scan rate of 1 mV s^{-1}. The obtained values of η were deduced as follows:

$$\eta(\%) = \frac{i_{corr,0} - i_{corr}}{i_{corr,0}} \times 100 \quad (2)$$

where $i_{corr,0}$ and i_{corr} denote the current densities of the unprotected and protected WE, respectively. To determine the PZC of X70 steel, the impedance of the steel electrode was measured at various potentials in 1 M HCl solution containing 200 mg/L GLE at 298 K. Each measurement was performed thrice under the same experimental conditions to ensure a satisfactory reproducibility.

2.4. Surface investigation

After 0.5 or 4 h immersion in 1 M HCl solution with and without 200 mg/L GLE at different temperatures, the X70 steel samples were descaled with a soft brush, thoroughly rinsed with deionized water, and dried under cold air. The morphologies of the 4 h immersion samples were observed through FE-SEM (JEOL-JSM-7800F, JEOL Ltd., Japan) under high vacuum. The morphologies of the 0.5 h immersion samples with same procedure were examined through AFM (MFP-3D-BIO, Asylum Research, America) under tapping mode.

2.5. Calculation details

Quantum chemical calculation was conducted by using Gaussian 03W software to explore the relationship between the inhibition ability of GLE and the electron structure of its main constituents, which are shown in Fig. 2 [24]. Organic molecules such as isorhamnetin (IH), sciadopitysin (SD), 6-hydroxykynurenic acid (HKA), and 4-O-methylpyridoxine (MP) were in neutral form and were fully optimized by using B3LYP method at the DFT level with a 6–311 + + G(d, p) basis set in the gas phase. Then, several parameters, including the energy of the highest occupied molecular orbital (E_{HOMO}), that of the lowest unoccupied molecular orbital (E_{LUMO}), and the dipole moment (μ), were obtained. Other parameters, such as the energy gap (ΔE), electronegativity (χ), global hardness (γ), ionization potential (I), and electron affinity (A), were calculated as follows [25]:

$$\Delta E = E_{LUMO} - E_{HOMO} \quad (3)$$

$$I = -E_{HOMO} \quad (4)$$

$$A = -E_{HOMO} \quad (5)$$

$$\chi = (I + A)/2 \quad (6)$$

$$\gamma = (I - A)/2 \quad (7)$$

The fraction of electrons transferred from the inhibitor molecules to the metal atoms (ΔN) can be calculated by [26]

$$\Delta N = \frac{\chi_{Fe} - \chi_{Inh}}{(\gamma_{Fe} + \gamma_{Inh})} \quad (8)$$

where γ_{Fe} and γ_{Inh} are the global hardness of Fe and the inhibitor molecule; χ_{Fe} and χ_{Inh} are the electronegativity of Fe and the inhibitor molecule, respectively. In accordance with the literature, theoretical χ_{Fe} and γ_{Fe} values of 7 and 0 eV/mol were used for the bulk Fe atom [26,27]. The optimized molecular structures, HOMO, LUMO, and ESP

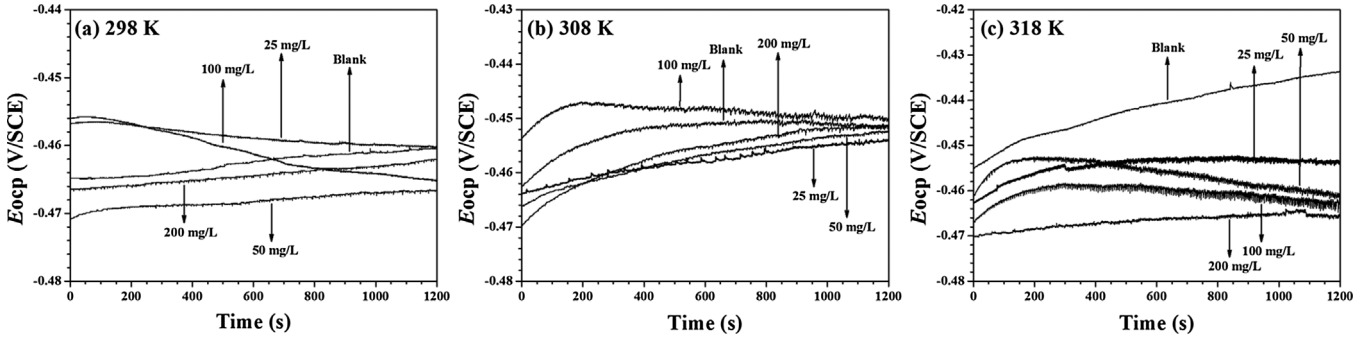

Fig. 1. OCP–time curves for X70 steel in 1 M HCl solution without and with different concentrations of GLE at different temperatures.