Anticorrosion properties of momilactone A isolated from rice hulls

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ABSTRACT

Momilactone A was isolated from rice hulls (*Oryza sativa* L.) using ethyl acetate as the solvent. Momilactone A has been investigated as a green inhibitor for the very first time. The result confirm highly efficient inhibition of the proposed isolated compound. As long as we know this is the first rice hull isolated compound to be reported for green inhibition properties. Mild steel is widely used in many industries. The corrosion inhibition of mild steel in 1 M HCl solution using momilactone A has been studied using electrochemical studies. Momilactone A maximum inhibition efficiency of 88% was achieved by using 1000 ppm.

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Introduction

Mild steel is extensively used in many industries due to its excellent mechanical properties, low cost, and easy availability compared to other materials. In acidic media, the high dissolution rate of steel causes rusting of the material in humid air, indicative of its poor corrosion resistance [1–3]. In modern technology, corrosion is the most devastating problem in many industries and hence, overcoming corrosion is of utmost importance for many scientists and engineers. The corrosion levels of steel are influenced by the presence of moisture, acid–base, dust particles, etc. on its surface. Researchers study the corrosion mechanism in addition to studying the corrosion behavior of mild steel in the environment. Acidic HCl solution is widely used as a pickling agent, and for the removal of undesirable scales and rust present in mild steel materials [4]. Corrosion is the process in which a refined metal or alloy reacts with the environment and is converted to a more stable form with loss of metal at the surface. Acid solutions are commonly used in many industries such as textiles, paper, sugar mill, chemical etc., and are utilized for the removal of fouling substances and unwanted corrosion products from the machine parts. Among all the mineral acids, HCl is the most economical [5–7]. In industries, acidic solutions are used for cleaning,

electrochemical etching, and descaling processes. They viciously damage the metal surfaces causing loss of material and an increase in corrosion rate. This is the major problem of using HCl solution in oil and gas exploration. Hence, corrosion inhibitors must be added to the acid to control the corrosion rate, which is the most popular of several methods used to reduce the corrosion rate [8–10]. It is one of the simplest methods, and has been proven effective in controlling corrosion, thereby protecting the metals. Corrosion inhibitors are small amounts of substances added to prevent further degradation of the metal by the environment. There are several aspects to be considered while choosing a corrosion inhibitor such as low cost, non-toxicity, easy availability, and environmental friendliness [11]. Most of the compounds that are established inhibitors are toxic to humans as well as the environment [12]. They reduce the corrosion rate by adsorption of ions or molecules over the metal surface, decreasing the electrical resistance of the metal surface, and decreasing the diffusion rate of reactants to the metal surface [13].

Rice (scientific name: *Oryza sativa* L.) is the principal cereal grain in many countries and it is a major source of food; therefore, several researchers conduct research on this plant seeking its application in various fields. There are two types of rice-one with white hulls, and the other with colored hulls; the white-hulled variety is more common and comprises 85% of the total rice. The germination of rice is of great agricultural importance and is influenced by the compounds present in the hull. The compound momilactone A isolated from rice hulls, is responsible for the

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germination and growth inhibition of rice. There is little information available regarding the influence of the compounds in rice hull on the rice yield. Rice hull is the most abundant agricultural by-product in rice growing areas, and the compound momilactone A can be isolated from rice hulls [14–16].

To the best of our knowledge, there is no report on the use of isolated momilactone A as a corrosion inhibitor of mild steel in corrosive environments. In this work, the corrosion inhibition of momilactone A on mild steel specimens in 1 M HCl solution was investigated via nuclear magnetic resonance (NMR), UV–vis, Fourier-transform infrared (FT-IR) spectroscopy, potentiodynamic measurements, electrochemical impedance spectroscopy (EIS), scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) studies.

Experimental

Plant material

The hulls of rice (*O. sativa* L.) were gathered from the experimental farm of Konkuk University located in the Chung-Ju city in Chung-Buk province, Seoul, Republic of South Korea. The rice was dried at the Department of Crop Science, Konkuk University.

Isolation of momilactone A

The isolation of momilactone A from rice hulls was accomplished following the methodology of Chung et al. [17]. In brief, the dried rice hulls (10 kg) were immersed in methanol (MeOH) at room temperature for 1 week and filtered through a Whatman filter paper (Grade 1). After the removal of methanol using a rotary evaporator, the remaining residue (150 g) was suspended in water and extracted successively with ethyl acetate (EtOAc) and hexanes. The organic ethyl acetate layer was separated and the solvent was removed under reduced pressure. The resulting extract (35 g) was then subjected to normal-phase column chromatography over silica gel, which yielded 40 fractions and 11 hexane fractions. Further elution with hexane and ethyl acetate (8:2) followed by elution with methylene chloride and methanol, yielded momilactone A (140 mg). The NMR spectrum of this compound recorded using a 500-MHz spectrometer, was identical to that of the momilactone A reported in literature; this confirms the structure of momilactone A. The isolated momilactone A was characterized using different spectroscopic techniques. A detailed account of the isolation methodology can be found in literature [17,18].

Proton nuclear magnetic resonance (^{1}H NMR)

Proton Nuclear Magnetic Resonance (^{1}H NMR) spectra were recorded at 500 MHz with a Bruker Avance III 500 MHz spectrometer using deuterated solvents: chloroform ($CDCl_3$), methanol (CD_3OD), and pyridine (C_5D_5N). The tetramethylsilane (TMS) peak was used as the reference peak in the NMR spectra. Coupling constants (J) were measured in Hertz (Hz), chemical shifts (δ) were measured downfield in ppm. The (s) denotes singlet, (d) denotes doublet and (t) denotes triplet.

UV–vis spectroscopy

A solution of momilactone A was analyzed by the UV–vis spectrophotometric method using a double beam Shimadzu UV-2600 spectrophotometer. To determine the absorption spectrum of the sample, distilled water was used as the reference.

Fourier-transform infrared spectroscopy (FT-IR)

FT-IR spectroscopy was used to identify the major functional groups in momilactone A. The spectra were recorded using a Thermo Scientific Nicolet iS5 FT-IR spectrometer. Sample preparation was done using KBr pellets and the data was collected over a wave number range from 4000 cm^{-1} to 400 cm^{-1}. The results confirm the presence of certain functional groups, and were compared to the standard FT-IR data.

Electrochemical studies

The electrochemical measurements were carried out in a conventional three-electrode cell connected to a potentiostat/galvanostat with a CHI 760C electrochemical workstation. A mild steel specimen, platinum, and a saturated calomel electrode were used as the working electrode, counter electrode, and reference electrode, respectively. Steel samples with an exposed area of 1 cm^2 were used for both impedance and potentiodynamic polarization studies. All the electrochemical experiments were carried out at room temperature using 1 M HCl (100 mL) with varying concentrations of the inhibitor, momilactone A. In potentiodynamic polarization measurements, the potentiodynamic polarization (Tafel) curves were obtained over the potential range from +250 mV to −250 mV against the open circuit potential (E_{corr}), with a scan rate of 1 mV s^{-1}. The scan rate affects the linearity of the polarization curves; hence, a scan rate of 1 mV s^{-1} was selected in this study so that linear and smooth polarization curves are obtained. The linear Tafel segments of anodic and cathodic curves were extrapolated to obtain a point of intersection, which corresponds to the equilibrium potential (E_{corr}) and corrosion density (I_{corr}) [19]. The theoretical Tafel line was plotted according to a previously described procedure [2]. Extrapolation analysis of the Tafel curves also enables the calculation of the slope of the straight lines that correspond to the anodic potential value (b_a) (from the theoretical curve) and the cathodic potential (b_c) value (from the experimental curve). The inhibition efficiency (η), calculated using the measured I_{corr} values is defined by the equation,

$$\eta \ (\%) = I^\circ_{corr} - I'_{corr}/I^\circ_{corr} \times 100 \tag{1}$$

where I°_{corr} and I'_{corr} are the corrosion currents in the absence and presence of the inhibitor, respectively.

Electrochemical impedance spectroscopy (EIS) was carried out at the open-circuit potential (OCP) in the frequency range from 10 mHz to 100 kHz at an amplitude of 10 mV. All the impedance data were analyzed using the ZSimpWin software. Prior to impedance measurements, the electrode was immersed in an acidic solution for half an hour. The inhibition efficiency of the inhibitor (η) is calculated using charge transfer resistance (R_{ct}) obtained from the impedance plot in the equation,

$$\eta \ (\%) = R_t^\circ - R_t^i/R_t^i \times 100 \tag{2}$$

where R_t° and R_t^i are the charge transfer resistance in the absence and presence of the inhibitor, respectively. The diameter of semicircle (one shoulder) and a single relaxation process (one time constant) over the studied frequency range is as shown by the Bode phase angle plots [20–22].

Surface analysis

The surface morphology of mild steel specimen was studied using scanning electron microscopy (SEM). A Philips XL 30 scanning electron microscope instrument was operated at 10 kV for higher magnification. The mild steel specimens with dimensions