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A comprehensive study on crude methanolic extract of *Artemisia pallens* (Asteraceae) and its active component as effective corrosion inhibitors of mild steel in acid solution

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ABSTRACT

Corrosion inhibition effects of crude methanolic extract of *Artemisia pallens* on mild steel in 1 mol l^{-1} HCl were studied by weight loss and electrochemical technique. Arbutin, an active principle from *A. pallens* and the crude methanolic extract exhibited inhibition efficiency of 93% and 98% in 400 mg l^{-1} concentration at 30 °C respectively. The results indicated that arbutin in acidic medium acted as good anticorrosive agent synergistically with its hydrolyzed products hydroquinone and D-glucose. Adsorption of both the inhibitors on mild steel surface conformed to the Langmuir isotherm with standard adsorption free energy of −33.07 kJ mol^{-1} for arbutin.

1. Introduction

Acid solutions are widely used in industry, the most important fields of application being acid pickling, industrial acid cleaning, acid descaling and oil well acidizing. Organic inhibitors are used in these processes to control the metal corrosion as well as dissolution, because of the general aggressiveness of acid solutions towards metals. Inorganic compounds like chromates, phosphates, molybdates, etc. and a variety of organic compounds containing heteroatom like nitrogen, sulphur and oxygen are investigated as corrosion inhibitors [1–10]. However, the environmental impact of these inhibitors has been considered in the recent decades due to their toxic effect on aquatic and possibly animal life [11]. In the past two decades, the research in the field of green corrosion inhibitors has been addressed toward the goal of using cheap, effective molecules at low or zero environmental impact. Currently, researches are being focusing on producing and testing eco-friendly corrosion inhibitors [12], such as fenugreek, henna, olive, jojoba, black pepper, *Occimum viridis*, *Andrographis paniculata*, *Phyllanthus amarus*, onion, garlic, *Eugenia jambolans*, *Pongamia glabra*, opuntia and eugenol, *Zenthoxylum alatum*, *Nypa fruticans* Wurmb, *Oxandra asbeckii*, *Ferula assa-foetida* and *Dorema ammoniacum*, *Lavandula angustifolia*, *Justicia gendarussa*, *Gissipium hirsutum*, *Lupinous albus*, *Aloe vera*, etc. [13–36].

Artemisia pallens wall ex DC is an aromatic herb, 60 cm in height. It contains major compound arbutin, a phenolic glycoside, germacranolides [37], davanone [38], pallensin and 4-epipallensin [39]. We have recently reported preliminary results of the methanolic extract of *A. pallens* as antibacterial and anticorrosive agent [40]. This manuscript deals with the results of comprehensive study on the crude methanolic extract and one of its active constituents as effective corrosion inhibitors of mild steel in 1 mol l^{-1} HCl solution.

2. Materials and methods

2.1. Extraction and isolation

The plant was dried in the shade for 7 days, ground to half dust (0.25 kg) and soaked in 1.5 l of aqueous methanol [1:1, MeOH: H_2O (v/v)] for 48 h at room temperature with occasional shaking. The extract was filtered and the residue was soaked with the same volume of fresh solvent. The entire procedure repeated twice to get maximum extract of the constituents. A rotary evaporator at 40 °C was used to evaporate the methanol. However, water was evaporated using high vacuum lyophiliser. The crude brownish colour solid mass (10 g) was collected. A 5 g of the crude methanolic

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extract was suspended in 50 ml of water, partitioned sequentially with ethyl acetate (3 × 100 ml) and *n*-butanol (3 × 100 ml). The solvents were evaporated to afford residues of ethyl acetate (1.4 g), *n*-butanol (2.5 g) and water extract (1.0 g). The *n*-butanol soluble fraction was subjected to silica gel (60–120 mesh) column chromatography and eluted with $CHCl_3$ with the increasing proportion of methanol. Seven fractions were obtained. Fractions 2, 3, 4 were combined and again and the solvent was removed to give a solid (1.8 g), which was further subjected to silica gel (60–120 mesh) column chromatography. Petroleum ether: ethyl acetate [8.5:1.5 (v/v)] eluent afforded arbutin (1.5 g, 30%), which was recrystallised from ethyl acetate.

2.2. Structure elucidation of arbutin (4-hydroxyphenyl-β-D-glucopyranoside)

The *n*-butanol soluble fraction was subjected to repeated silica gel (60–120 mesh) column chromatography to get a white solid of arbutin in pure form. The ^{1}H NMR spectra of the isolated compound showed signals at δ 6.85 (d, J = 8.8 Hz, 2H) and δ 6.65 (d, J = 8.8 Hz, 2H) indicating the presence of a para di-substituted benzene ring. Moreover in the ^{1}H NMR spectrum, the signal at δ 4.62 (d, J = 7.4 Hz, 1H) indicates the presence of an α anomeric proton. The ^{13}C NMR spectra of the compound showed the presence of an aromatic ring with signals at δ 116.43 (2C), 118.54 (2C), 151.23 and 153.06. It also indicated the presence of a typical hexose moiety with the signals at δ 61.70, 70.17, 77.50, 77.81 and 102.61. The mass spectrum (ESI) of the compound showed $[M+Na]^+$ at 295, which indicated the molecular weight of the compound is 272. The compound was thus characterized as arbutin (Fig. 1). The spectral data of isolated arbutin are identical with that of the authentic specimen [41].

2.3. Preparation of test coupons and other materials

Mild steel coupons containing 0.195 wt.% (C), 0.59 wt.% (Mn), 0.23 wt.% (Cr), 0.016 wt.% (Ni), 0.126 wt.% (Mo), 0.02 wt.% (Cu), 0.02 wt.% (P) and the remaining iron were used for weight loss, electrochemical, FTIR, Raman and XPS studies. The surface preparation of the mild steel coupons was carried out with emery papers by increasing grades (100, 400, 600 and 1200 grit size), then degreased with acetone and dried at room temperature before use. The aggressive solutions (1 mol l^{-1} HCl) were prepared by dilution of analytical grade 37% with double distilled water. The concentration ranges of the crude methanolic extract, arbutin, HQ (hydroquinone) and mixture of HQ and D-glucose were 50–400 mg l^{-1}. All reagents used for the study were of analytical grade.

2.4. Gravimetric measurements

Inhibition efficiency was determined by hanging the steel coupon measuring 2.0 × 2.0 × 0.05 cm^3 into the acid solution (100 cm^3) (in open air) containing various concentrations of the crude methanolic extract at 30, 40, 50 and 70 °C and arbutin, HQ and mixture of HQ and D-glucose at 30 °C for 24 h. At the end of the experiments the coupons were essentially washed in ethanol under ultrasound and then weighed. The temperature was controlled by an aqueous thermostat with constant temperature ± 0.5 °C.

The weight loss data were obtained from average value of three experiments of mild steel for different concentrations of the crude methanolic extract, arbutin, HQ and mixture of HQ and D-glucose in 1 mol l^{-1} HCl, 24 h of immersion period. The percentage inhibition efficiency (η%) was determined using the following equation:

$$\eta(\%) = \left(\frac{w_o - w_{inh}}{w_o}\right) \times 100 \quad (1)$$

where w_0 and w_{inh} represent weight loss in absence and presence of inhibitor, respectively. The weight loss experiments were carried out to calculate the mean corrosion rate (w) as expressed in mg cm^{-2} H^{-1}.

Following experiment was done to determine the effect of acidic medium on arbutin:

After the weight loss experiment of the mild steel immersed in 1 mol l^{-1} HCl with 50–400 mg l^{-1} arbutin, the solution was neutralized with sodium bicarbonate to pH 7. Thin layer chromatography (TLC) analysis of neutral solution containing arbutin and HQ was performed using the solvent system chloroform: methanol [98: 2 (v/v)].

2.5. Electrochemical measurements

The EIS measurements were performed using a 330C Gamry Potentiostat (supplied by M/S Gamry Instruments of USA). The electrochemical experiments were performed at fixed temperature of 30 ± 1 °C using a glass cell equipped with constant temperature water re-circulating Teflon tubes dipped into the test solution. Saturated Calomel Electrode (SCE) and graphite rods were used respectively as reference and auxiliary electrode. The exposed surface area of working electrode in the solution was 2 cm^2. To determine the polarization resistance for the mild steel plates in 1 mol l^{-1} HCl without and with different concentrations of the crude methanolic extract, Electrochemical impedance spectroscopy (EIS) studies were performed by imposing sinusoidal voltage of 10 mV amplitude at open circuit potential of the working electrodes. The frequency was varied between 100 kHz and 1 mHz. The data were analyzed using constant phase elements (CPE).

2.6. Surface analysis

The mild steel coupons of the size 1 × 1 × 0.25 cm^3 were exposed in 1 mol l^{-1} HCl containing 400 mg l^{-1} either crude methanolic extract or arbutin for 4 h at 30 °C and washed with water. After washing, specimens were dried in a critical point drying apparatus. The specimens were examined for structural and spectroscopic features of the adsorbed compound using X-ray photoelectron spectroscopy and Raman spectroscopy. For FTIR studies (KBr pellet method), the surface of the dried specimen was scratched with a knife and the resultant powder was used.

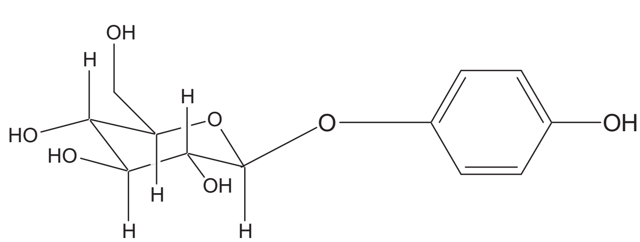

Fig. 1. Molecular structure of arbutin.

3. Results

The recent work on plant extracts as corrosion inhibitors has major limitations due to the lack of phytochemical investigations. Whereas the present work involved the phytochemical investigation of the crude methanolic extract of *A. pallens*, which led to the isolation of arbutin [40] as major component. Arbutin is known to undergo hydrolysis in HCl to yield D-glucose and HQ [42]. Thus, one might think that the anticorrosive efficiency of arbutin could