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Control of zinc corrosion in acidic media: Green fenugreek inhibitor

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Abstract: Fenugreek seeds extract was examined as a green corrosion inhibitor for Zn in 2.0 mol/L H_2SO_4 and 2.0 mol/L HCl solutions by mass loss and electrochemical measurements. Scanning electron microscope (SEM) images show that the surface damage is decreased in the presence of the inhibitor. X-rays photoelectron spectroscopy (XPS) analysis was performed to identify the corrosion product, ZnO, and to prove the inhibitor adsorption mechanism. The maximum inhibition efficiency values are 90.7% after 1 h and 66.6% after 0.5 h by 200 mL/L of fenugreek extract in H_2SO_4 and HCl solutions, respectively. Addition of I^- ion greatly improves the inhibition efficiency of fenugreek seeds extract for Zn corrosion in HCl due to the synergistic effect. Potentiodynamic polarization and EIS measurements prove the inhibition ability of fenugreek for Zn corrosion in HCl as indicated by the decreased corrosion current density and increased charge transfer resistance values in the presence of fenugreek.
Key words: zinc; corrosion mechanism; inhibitor; synergetic effect

1 Introduction

Due to environmental regulations, plant extracts have again become important as they are environmentally acceptable, readily available and renewable source for a wide range of needed inhibitors. Plant extracts are viewed as rich source of naturally synthesized chemical compounds that can be extracted by simple procedures with low cost. A lot of natural products were previously reported as green corrosion inhibitors for Zn in various environments such as aloe vera extract [1], citrullus vulgaris peel [2], mansoa alliacea plant extract [3], moringa oleifera extract [4], red onion skin acetone extract [5], and thiourea [6]. The corrosion rate was determined by mass loss measurements [1,2,4−6], polarization [3,4] and electrochemical impedance spectroscopy [4]. It was found that the inhibition efficiency increased with increasing concentration of the extract but decreased with increasing temperature [1,2,4,5]. The adsorption of the inhibitor molecules on Zn surface was in accordance with Langmuir [1,2,6] or Temkin [2,4] adsorption isotherms. Thermodynamic parameters such as heat of adsorption and free energy of adsorption suggested that the adsorption of inhibitor on the Zn metal surface is exothermic and followed by spontaneous process [1,2,4,6]. Potentiodynamic polarization curves indicated that the plant extract [3,4] behaves as mixed-type inhibitor and retards the anodic and cathodic corrosion reactions. The inhibition efficiency values were found to be 67.1% [1] and 68% [5] and 59.8% [6] in 2.0 mol/L HCl solution, 72.7% in natural sea water [2], 88.4% [4] and 92.0% in 3% NaCl solution [3].

The effect of aqueous extract of fenugreek leaves and seeds on the corrosion of mild steel in HCl and H_2SO_4 solutions was investigated [7]. Seeds inhibit mild steel corrosion more than leaves, and the inhibition efficiency is always greater in HCl (82.4% and 84.9%) than in H_2SO_4 (65.8% and 63.7%) solutions, respectively. In HCl solution, the adsorption of fenugreek inhibitor on mild steel surface obeys the Langmuir adsorption isotherm in HCl solution, while obeys the Temkin adsorption isotherm in H_2SO_4 solution. AGARWAL [8] reported the inhibitive action of the extracts of lemon peel and fenugreek leaves on the corrosion of mild steel in HCl solution. The adsorption of lemon peel and fenugreek leave extracts on the mild steel surface in HCl solution obeys the Langmuir adsorption isotherm model and the adsorption is physical and spontaneous. The maximum inhibition efficiency is 85.2 % by using 50 mL/L of the extract. On the other hand, synergism has

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been reported for zinc corrosion only in alkaline media [9−11].

In the present work, the inhibition ability of fenugreek extract for Zn corrosion in 2.0 mol/L H_2SO_4 and HCl solutions is investigated by mass loss and electrochemical methods. Several factors are studied such as immersion time, inhibitor concentration and temperature, to identify best conditions for the inhibition performance of fenugreek. The proper adsorption isotherm is identified and important thermodynamics parameters are calculated. Furthermore, a possible improvement of the fenugrueek inhibition performance in HCl medium is presented.

2 Experimental

2.1 Materials

Zn (BDH grade) was used in this study with the following chemical composition: 0.001% lead, 0.002% iron, 0.001% cadmium, 0.003% copper and rest is Zn.

Zn specimens used have a cylindrical form (length, 6.3 mm; radius, 6.0 mm). Pre-treatment of specimens prior to experiments was carried out by polishing with series of a proper polishing paper (grade 180, 600 and 1500), rinsing with purified water, degreasing in acetone in an ultrasonic bath immersion for 5 min, washing again with purified water and then drying at room temperature before use.

The acid solutions (2.0 mol/L H_2SO_4 and 2.0 mol/L HCl) were prepared by dilution of 95%−97% H_2SO_4 (Sigma Aldrich) and 37% HCl (Sigma Aldrich), respectively with double-distilled water. KI (99.5% Sigma Aldrich) was used as received.

2.2 Preparation of fenugreek extracts

Commercial seeds of fenugreek were obtained (about 10 g), ground and boiled in distilled water for 1 h. The extract was left over night, then filtered and completed to 250 mL by distilled water [7].

2.3 Mass loss measurements

The gravimetric measurements were carried out using a sensitive balance (precision ±0.1 mg). After immersion period, Zn specimens were removed from the test solution, washed with distilled water, dried at room temperature and then reweighed. Experiments were carried out three times to ensure reproducibility and the mean value of the mass loss is calculated.

The corrosion rates (C_R) were calculated using Eq. (1):

$$C_R = \frac{KW}{DAt} \tag{1}$$

where C_R is corrosion rate in mils per year (mpy), W is mass loss in g, A is the specimen surface area in cm^2, t is the immersion period in h, D is density of zinc in gm/cm^3 and K is a constant equal to 3.45×10^6.

From the corrosion rate, the surface coverage (θ) as a result of adsorption of the extract components, and inhibition efficiencies of the plant extracts η were determined using Eqs. (2) and (3), respectively.

$$\theta = \frac{C_{R0} - C_{Ri}}{C_{R0}} \tag{2}$$

$$\eta = \frac{C_{R0} - C_{Ri}}{C_{R0}} \times 100\% \tag{3}$$

where C_{R0} and C_{Ri} are the corrosion rates in the absence and presence of the plant extracts, respectively.

2.4 Electrochemical measurements

Electrochemical measurements were carried out using a Solartron SI 1287 and frequency response analyzer 1252A system in a conventional three electrode-one compartment cell with Zn as the working electrode, 3.0 mol/L Ag/AgCl as a reference electrode, and a large surface area sheet of platinum as an auxiliary electrode. Potentiodynamic polarization was carried out by scanning the potential from −0.25 to 0.25 V versus open-circuit corrosion potential (OCP) at a scan rate of 1 mV/s. Electrochemical impedance spectroscopy (EIS) was measured at OCP in the frequency range from 100 kHz to 10 mHz under excitation of a sinusoidal wave of 5 mV amplitude. Before Tafel polarization and EIS experiments, the OCP of the working electrode was measured as a function of time during 5 min, the time needed to achieve a quasi-stationary value for the OCP.

2.5 Surface and structural characterization

Scanning electron microscopy (SEM) analysis was done by Quanta FEQ 250 with accelerating voltage of 30 kV.

XPS analysis was done by Thermo scientific K-Alpha XPS. A monochromatic Al K_α X-ray source was used for all the samples, along with pressure in the analysis chamber of 1×10^{-8} Pa. The resolution of the instrument has been found to have a width of 0.35 eV using silver Fermi edge. All spectra were analyzed using Avantage data software version 3.10 (Thermo Scientific Instruments)

3 Results and discussion

3.1 Surface characterization

The surface morphology of Zn was studied by SEM after being immersed in two corrosive media, H_2SO_4 and HCl for 1 and 0.5 h, respectively, in the absence (Figs. 1(a) and (c)) and presence (Figs. 1(b) and (d)) of