Utilization of watermelon rind extract as a green corrosion inhibitor for mild steel in acidic media

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ABSTRACT

Electrochemical techniques were used to investigate the efficacy of watermelon rind extract (WMRE) as corrosion inhibitor for mild steel in HCl and H_2SO_4 solutions. The inhibition efficiency increased as the concentration of the extract increases. Potentiodynamic polarization results indicate that WMRE act as a mixed-type inhibitor. The values of effective capacitance obtained by utilizing the impedance parameters in both acidic media are in the range of double layer capacitance. Corrosion inhibition effect of WMRE can be attributed to the adsorption of constituents of WMRE onto the mild steel surface which can be approximated by Temkin adsorption isotherm model.

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1. Introduction

Mild steels are frequently used for a wide range of applications in construction industry due to their very good mechanical properties and low cost compared with many metallic materials. The poor corrosion resistance of mild steel in acid [1–3] is a major constraint in its applications. The use of inhibitors in controlling its corrosion processes has proven to be efficient and most practicable [4,5]. However, most of the compounds that constitute these inhibitors are toxic to human and its environments. The toxicity of these organic and inorganic inhibitors has paved way to explore the use of non-toxic natural products inhibitors [6–9] that are environmentally friendly. The use of extracts of some plants to inhibit the corrosion of steel in acid media has been reported in the literature [10–27].

Watermelon is vine-like flowering plant which belongs to the family of *Cucurbitaceae* with varieties of seeded and seedless species. It is widely grown due to its large edible fruits that contain a hard green rind and a watering reddish, yellowish or pink pulp. It is an essential agricultural product utilized in the production of many food products such as fruit cocktails, juices and nectars [28,29]. The most useful part of the watermelon in the food industry is its pulp. Watermelon, *Citrullus lanatus* has been reported by Johnson et al. [30] to contain valuable amount of anti-nutrients namely saponin, alkaloids, hydrogen cyanide, tannins, phytate, phenol, oxalate and flavonoids in fresh and dried watermelon peel (WMP), watermelon pulp (WMPu) and watermelon rind (WMR). In addition, WMR being an agricultural waste product has been reported to be a natural source of citrulline, a non-essential amino acid [31]. The chemical structure of citrulline (major component of WMRE) is shown in Fig. 1. These compounds contain heteroatoms (N, O) and aromatic ring which are regarded as centers of adsorption hence the extracts obtained from watermelon waste products could function as a potential corrosion inhibitor. There are few reports on the use of watermelon parts as corrosion inhibitor for metals in some corrosive environments. For instance watermelon peel extract (WMPE) and watermelon leaf have been used for corrosion protection of zinc in natural sea water [32]. However, there is no report to the best of our knowledge on the use of watermelon rind as corrosion inhibitor for any metal in any corrosive environment. Therefore our main objective in the present work is to utilize extract of WMR as a corrosion inhibitor for mild steel in acidic media (HCl and H_2SO_4) using electrochemical impedance spectroscopy (EIS), potentiodynamic polarization (PDP) and linear polarization (LPR) methods.

2. Experimental

2.1. Materials preparation

1 M HCl and 0.5 M H_2SO_4 solutions as corrosive media were prepared with A-R grade 37% HCl (Sigma–Aldrich) and 98% H_2SO_4

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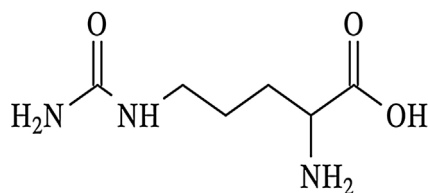E-mail address: adewalen@kfupm.edu.sa (N.A. Odewunmi).

Fig. 1. Chemical structure of citrulline.

(Baker), respectively, and double distilled water. Extract of the WMR was prepared by weighing 5 g of dried grounded WMR in 1 L of 1 M HCl and 0.5 M H_2SO_4 and boiled for 10 min. The solutions were cooled and later filtered with sintered glass Buchner funnel No. 36060 to obtain 5 g/L stock solution. Different concentrations of the extract (0.1–2.0 g/L) were prepared from the stock solution by dilution with the respective corrodents (1 M HCl and 0.5 M H_2SO_4).

The chemical composition (weight %) of the mild steel sample used in the experiment is: C, 0.15; Mn, 1.26; V, 0.017; Si, 0.035; S, 0.008; Cr, 0.036; Ni, 0.03; Al, 0.083; Cu, 0.038 and Fe (balance). The mild steel was cut into coupons of 3 cm × 3 cm × 0.25 cm dimension, abraded with silicon carbide abrasive papers of different grades (# 120–800), and rinsed with distilled water. The residues of polished particles were removed by sonication in ethanol bath for 10 min. The cleaned mild steel specimens were kept in the desiccator prior to use for corrosion test using electrochemical measurements.

2.2. Electrochemical measurements

The electrochemical measurements were performed in a single compartment electrochemical cell designed for mounting varieties of flat samples for electrochemical test at 25 °C with three electrodes system. Gamry potentiostat/galvanostat/ZRA (Reference 3000) embedded with Gamry framework system composed of ESA410. Gamry software applications include EIS300 for the electrochemical impedance spectroscopy (EIS) measurements, DC105 for the potentiodynamic polarization (PDP) and linear polarization (LPR) measurements and Echem Analyst 6.0 for data fittings. The exposed area of the working electrode (mild steel) to the corrosive acidic medium was 0.7855 cm^2; graphite rod and the saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively.

Tafel curves were obtained from the potentiodynamic polarization measurements between the potential range of +250 mV and −250 mV against the open circuit potential (E_{corr}) at scan rate of 1 mV s^{-1}. A scan rate of 0.125 mV s^{-1} was used to generate a linear polarization resistance (LPR) at +20 mV and −20 mV against the E_{corr}. EIS measurements were done at frequencies of 100 kHz to 100 mHz with an alternative (ac) amplitude of 5 mV r.m.s. (7.07 mV peak-to-peak) signal from the E_{corr}. The open circuit potential (E_{corr}) was allowed to attain a stable state which was achieved after 1800 s before the electrochemical measurements were carried out both in the absence and presence of the inhibitor (WMRE).

3. Morphological studies

A JSM-5800 LV scanning electron microscope (SEM) was used to examine the surface morphology of the mild steel specimen with and without WMRE in the acidic media (1 M HCl and 0.5 M H_2SO_4) after 24 h exposure. Prior to the exposure in different test solutions, the mild steel coupons of dimensions 3 cm × 3 cm × 0.25 cm were ground with silicon carbide abraded papers of different grades (# 120–800) followed by polishing with a cloth using 1 μm diamond

paste to near mirror surface finish. The same procedure for removing the residue of polishing by sonication in ethanol bath was employed. The cleaned mild steel specimens were immersed in both 1 M HCl and 0.5 M H_2SO_4 without and with 2.0 g/L WMRE. The coupons were retrieved after 24 h, rinsed with distilled water, dried and submitted for SEM examination.

4. Results and discussion

4.1. Open circuit potential

The variation of open circuit potential (E_{ocp}) with time for mild steel in 1 M HCl and 0.5 M H_2SO_4 without and with addition of different concentrations of WMRE is shown in Fig. 2. It could be observed from the figure that a stable OCP values were attained after 1800 s immersion both in the absence and presence of the inhibitor. It is also observed that on introduction of WMRE into the corrosive medium, the potentials shift to noble values than those observed in the blank acid solution. The positive shift of corrosion potential was found to be concentration dependent. This suggests a possible influence of the extracts on both anodic and cathodic polarization.

4.2. Electrochemical impedance spectroscopy (EIS) measurements

EIS measurements were taken to characterize the kinetics of the electrochemical processes and the capacitive behavior of WMRE on mild steel. Figs. 3 and 4 show the Nyquist and Bode (modulus and phase angle) plots of WMRE in 1 M HCl and 0.5 M H_2SO_4 without and with different concentrations of WMRE respectively. The Nyquist plots in both media exhibited a semi-circle (one shoulder) and a single relaxation process (one time constant) over the range of the studied frequencies as shown by the Bode phase angle plots. The number of distinguishable maxima or related shoulder is an indication of number of relaxation (time constant) taking place in electrochemical system as reported by Beverskog et al. [33]. Also, Figs. 3c and 4c revealed a phase angle maxima smaller than 90°. It is observed from the plots (Figs. 3a and 4a) that the semi circles are not perfect but depressed with the centers under the real axis. Some reasons advanced to explain this behavior include the surface roughness, frequency dispersion of time constants as a result of local inhomogeneity in the dielectric material, relaxation and porosity in mass transport effects [34]. To account for these effects, a constant phase element (CPE) must be introduced to the equivalent circuit to estimate the EIS experimental results [35,36]. Fig. 5 shows the equivalent circuit used to accurately fit the experimental data obtained from EIS measurements for mild steel in (a) 1 M HCl and (b) 0.5 M H_2SO_4 in the absence and presence of WMRE. The circuit comprised of the CPE in parallel with the charge transfer resistance (R_{ct}) and solution resistance (R_s) in HCl medium and additional inductive elements (L and R_L) in H_2SO_4 medium.

In HCl solution, there is no change in the corrosion mechanism in spite of the addition of different concentrations of WMRE as the shape of the impedance plots largely remain the same as shown in Fig. 3, however, the diameter of the semi-circle (Fig. 3a) and the real impedance value (Fig. 3a and b) increased as the extract concentration increases from 0.1 g/L up to 1.5 g/L and a lower diameter as the concentration was raised to 2.0 g/L. The solution resistance (R_s) and the R_{ct} are assigned as the high and low frequencies intercept on the real impedance axis, respectively. However, for mild steel corrosion in 0.5 M H_2SO_4 the impedance is characterized by a large capacitance loop at high-medium frequency region and an induction loop at the low frequency (LF) in the presence of WMRE (Fig. 4a). The high frequency capacitive loop could be attributed to double layer capacitance in parallel with the R_{ct} but the phenomenon of the LF inductive loop