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The impact of some factors on the inhibitory action of Radish seeds aqueous extract for mild steel corrosion in 1 M H_2SO_4 solution

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The impact of some factors (such as inhibitor concentration, solution temperature, I^- ions addition, surface finishing and immersion time) on the inhibitory action of radish seeds aqueous extract (RSAE) for mild steel corrosion in 1 M H_2SO_4 solution was investigated by using electrochemical measurements. The inhibition efficiency of RSAE increases with the increase of its concentration but decreases drastically at relatively high temperatures (50 °C). The addition of I^- ions synergistically increased the inhibition efficiency of RSAE and this synergistic effect depends on the concentration of both inhibitor and I^- ions. It was found that the inhibition efficiency of RSAE increases with a surface roughness of up to 400 grits after which it decreases with additional increases in surface roughness. The data revealed that the inhibition efficiency of RSAE increases with increasing immersion time in the tested solution which may be attributed to a slow rate of adsorption process. The inhibitory action of RSAE is suggested to be due the synergistic effect of its constituents.

1. Introduction

Corrosion is defined as the destruction of a material due to a reaction with its environment [1]. Corrosion commonly occurs on a metal surface in the presence of oxygen and moisture, involving two electrochemical reactions. Oxidation takes place at an anodic site and reduction occurs at a cathodic site. In an acidic medium, hydrogen evolution reaction predominates. One of the most widely used industrial materials, mild steel, suffers serious acid corrosion. Corrosion protection, such as the use of corrosion inhibitors, is often required for the use of mild steel in acidic media. Inhibitors often work by adsorbing themselves on the metallic surface, protecting the metallic surface by forming an invisible, thin, or sometimes a visible bulk precipitate [2]. Generally numerous organic compounds containing hetero atoms such as, O, N and S have been documented as being very effective corrosion inhibitors for mild steel in various acid solutions [3–9]. Because of the fact that most of the chemical compounds that prevent the corrosion of metals and alloys are toxic, and thus pose threat both for human health and environment, their usage is limited. For this reason, various researchers have turned to the use of eco-friendly inhibitors, such as extract of common plants that contain a variety of organic compounds, for example, acids, amino acids, alkaloids, pigments, proteins and tannins, as a green alternative for toxic and hazardous compounds [10].

Recently, natural products, for example, Artemisia oil [11], *Nypa fruticans* (Wurmb leaves) extract [12], Lawsonia extract [13], *Telfaria occidentalis* extract [14], *Prunus cerasus* juice [15], Pennyroyal oil (*Mentha oulegium*) [16], *Occimum viridis* extract [17], Fenugreek leaf and seed extracts [18], camel urine [19], henna extract [20], and *Citrus aurantiifolia* leaves extract [21] all have been reported to be effective in reducing the corrosion rate of steel in acidic media.

The radish (*Raphanus sativus*) belongs to family Brassicaceae that was domesticated in Europe in pre-Roman times. Radishes are grown and consumed throughout the world, and have numerous varieties, varying in size, color, and duration of required cultivation time. There are some radishes grown for their seeds; others, such as oilseed radishes, are grown, as the name implies, for oil production [22]. There is a wide variety of medical uses for radish. Antibacterial, antioxidants, antiseptic, choleretic, stomachic, laxative, expectorant, digestive antiviral, and aperients are examples of medical uses of radishes [23]. Proximate analysis revealed that radish seeds are high in vitamin C (ascorbic acid), vitamin B3 (niacin or nicotinic acid), vitamin B6 (pyridoxal-phosphate), vitamin B9 (folic acid), vitamin A, vitamin B1 (thiamin), riboflavin, vitamin B5 (pantothenic acid), magnesium, phosphorus, calcium, and iron [24]. In addition, glucosinolates can be found in the root, seeds, leaf and stem of the plant, while the youngest tissues contain the highest amount [25]. Glucoraphanin is the major glucosinolate found in radish seeds [25,26]. Glucoraphanin is hydrolyzed by an

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endogenous plant myrosinase to form either the potent anticarcinogen sulforaphane or sulforaphane nitrile [27].

In view of the above, the present study aims to investigate the inhibitory action of the radish seeds aqueous extract (RSAE) on mild steel corrosion in 1 M of H_2SO_4 solution under the impact of such factors, as inhibitor concentration, solution temperature, iodide (I^-) ion addition, surface roughness, and immersion time. Because of the short measurements time and mechanistic information that electrochemical methods provide, electrochemical impedance spectroscopy (EIS) and/or potentiodynamic polarization (PDP) methods were used to evaluate the present study.

2. Experimental methods

The mild steel used in the present investigation contained besides iron (the major component), the following 0.25% C, 0.48% Mn, 0.3% Si, 0.04% Ni, 0.06% Cr, 0.02% Mo, 0.021% S, and 0.019% P.

The radish seeds aqueous extract, RSAE, was prepared by heating 20 g of dried and ground seeds in 250 mL of deionized water for 1 h in a boiling water bath. The extract was left all night and then filtered and completed to 250 mL by deionized water and kept it in a dark refrigerator. The aggressive solution used was made of AR grade (BDH) H_2SO_4. Appropriate concentration (1 M) of H_2SO_4 was prepared using deionized water in the absence and presence of various concentrations of RSAE. The employed concentration range of RSAE was of 1–10% (v/v). The effect of I^- ions addition was evaluated by using AR grade (BDH) KI with concentrations of 5.0×10^{-5}, 1.0×10^{-4}, and 1.0×10^{-3} M.

EIS and PDP experiments were conducted through an ACM Gill AC instrument model 655 by using a conventional electrochemical cell with a platinum wire as counter electrode and a saturated calomel electrode (SCE) as reference electrode. The working electrode was in the form of a cylindrical rod from mild steel inserted into a Teflon tube just larger than the sample and was fixed with an adhesive. The cross-sectional area exposed to the solution was 0.785 cm^2. Prior the electrochemical measurements, the working electrode was abraded with successive emery papers ranging from 80 to 1000 grit, washed with de-ionized water and acetone, dried at room temperature and finally immersed and left for 10 min in the tested solution to maintain the open circuit potential. EIS measurements were carried out over the frequency range of 10 kHz to 0.5 Hz, with a signal amplitude perturbation of 30 mV. After each EIS run, the instrument turns on automatically to record the PDP curves with scan rate of 60 mV min^{-1} from −600 mV to −350 mV *vs.* SCE. All experiments were conducted in open air stagnant solutions at 30 °C unless otherwise stated.

3. Results and discussion

3.1. Effect of inhibitor concentration and solution temperature

3.1.1. EIS measurements

The impedance data of mild steel plotted after immersion time of 10 min in 1 M H_2SO_4 in the absence and presence of different concentrations of RSAE at two temperatures (30 and 50 °C) are presented as Nyquist plots in Fig. 1. The existence of a single semicircle shows the occurrence of a single charge transfer process during dissolution that is unaffected by the presence of inhibitor species [28]. The depressed nature of the semicircles is a characteristic of solid electrodes; such frequency dispersion has been attributed to micro roughness and other inhomogenities of the solid electrode [28,29]. For the purpose of impedance spectra analysis, the experimental data were fitted using the ZSimDemo 3.20 equivalent circuit program. In all cases studied, the best fit of the experimental data was achieved with the circuit shown in Fig. 2. This circuit has been proposed in previous studies on steel surface corrosion process in acidic solutions [30–32]. In Fig. 2, R_s, R_{ct}, and Q_{dl} represent the solution resistance, the charge transfer resistance and the double layer capacitance element, respectively. The R_{ct} value is a measure of electron transfer across the surface and is inversely proportional to the to the corrosion rate. The impedance of the double layer capacitance element is presented by constant phase element (CPE) instead of pure capacitance as follows [33]:

$$Z_{CPE} = (Q_{dl}(j\omega)^n)^{-1} \quad (1)$$

The exponent n has values between −1 and 1. A value of −1 is characteristic of an inductance, a value of 1 corresponds to a capacitor and a value of 0.5 can be assigned to diffusion phenomena. Inhibition efficiencies, Inh_R (%), from impedance data were calculated through the following expression:

$$Inh_R(\%) = \left(1 - \frac{R^o_{ct}}{R_{ct}}\right) \times 100 \quad (2)$$

where R^o_{ct} and R_{ct} represent the charge transfer resistance in absence and presence of inhibitor, respectively.

Table 1 lists the estimated values of electrochemical impedance parameters (R_{ct} and Q_{dl}) and Inh_R (%) for mild steel in 1 M H_2SO_4 in the absence and presence of different RSAE concentrations at 30

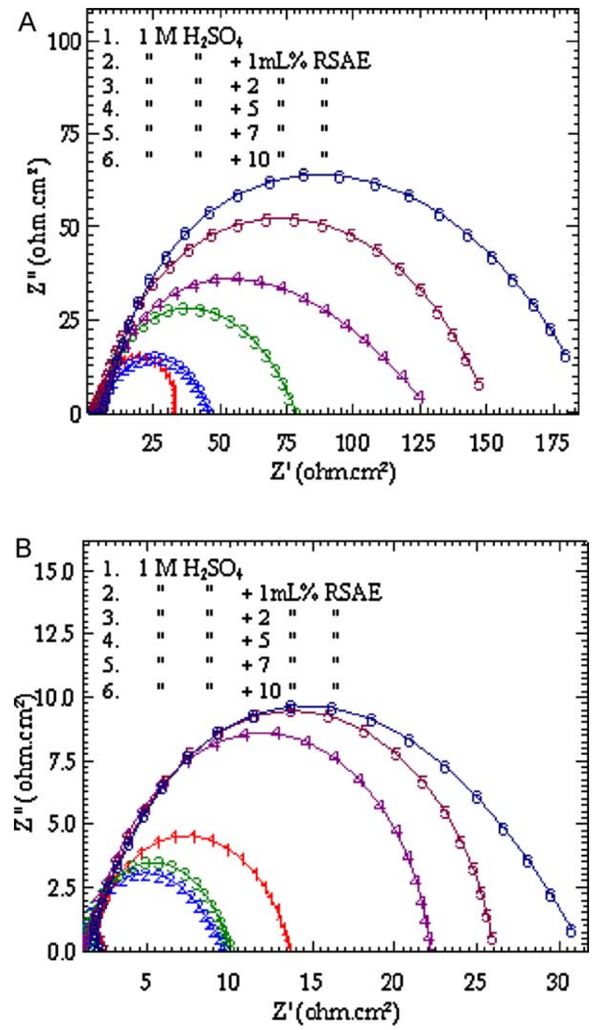

Fig. 1. Nyquist plots for mild steel in 1 M H_2SO_4 solution in the absence and presence of different concentrations of RSAE at: (A) 30 °C and (B) 50 °C.

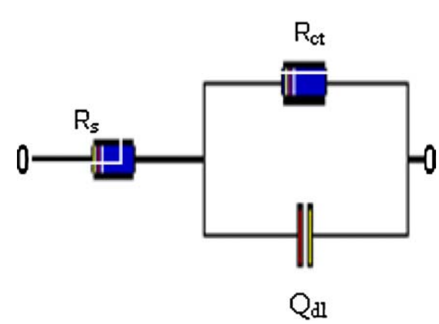

Fig. 2. Equivalent electrical circuit model.