Arabian Journal of Chemistry (2011) **xxx**, xxx–xxx

King Saud University

Arabian Journal of Chemistry

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ORIGINAL ARTICLE

The effect of *Tinospora crispa* extracts as a natural mild steel corrosion inhibitor in 1 M HCl solution

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Received 2 April 2011; accepted 6 July 2011

KEYWORDS

Tinospora crispa;
Mild steel;
Polarization;
EIS;
Acid inhibition

Abstract The potential of *Tinospora crispa* extracts as a corrosion inhibitor of mild steel in 1 M HCl was determined using weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy methods (EIS). Maximum inhibition was attained at the concentration of 800 and 1000 ppm for TCDW (*T. crispa* water extract) and TCAW (*T. crispa* acetone–water extract). The inhibition efficiencies of *T. crispa* extracts obtained from the impedance and polarization measurements were in good agreement where the maximum inhibition is around 70–80%. Potentiodynamic polarization measurement studies revealed that *T. crispa* extracts behave predominantly as an anodic inhibitor. The adsorption of *T. crispa* extracts was found to follow Langmuir's adsorption model.

1. Introduction

The use of mild steel as construction material in industrial sectors has become a great challenge for corrosion engineers or scientists nowadays. In practice, most of the acidic industrial applications such as refining crude oil, acid pickling, industrial cleaning, acid descaling, oil–well acid in oil recovery and petrochemical processes use mild steel as their material. Hydrochloric acid is one of the most widely used agents in the industrial sector. Due to the aggressiveness of acid solution to mild steel, the use of inhibitor to prevent the metal dissolution process will be inevitable (Ostovari et al., 2009). Most synthetic inhibitors are highly toxic and thus lead to the investigations on the use of a naturally occurring corrosion inhibitor which at the same time is not harmful to both human and the environment.

Tinospora crispa (Menispermaceae) a climber plant found in tropical and subtropical India and parts of the Far East (such as Indonesia, Malaysia, Thailand and Vietnam), and in primary rainforest or mixed deciduous forest (Sulaiman et al., 2008; Dweck and Calvin, 2006). The plant has been recently showing an ethnopharmaceutical uses for the treatment of fever, diabetes, hypertension, cholera, rheumatism, hyperglycemia, wounds, intestinal worms, and skin infections. Besides that, *T. crispa* is also used to treat tooth and stomach aches, coughs, asthma and pleurisy (Najib et al., 1999; Zakaria et al., 2006; Kongkathip et al., 2002; Noor and Ashcroft, 1989, 1998). It was revealed that the chemical constituents

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Peer review under responsibility of King Saud University.
doi:10.1016/j.arabjc.2011.07.002

Production and hosting by Elsevier

isolated from various parts of *T. crispa* contained flavonoid and quaternary alkaloids including flavavone-O-glycosides (apigenin), berberine, picroretoside, palmatine (Umi Kalsom and Noor, 1995; Bisset and Nwaiwu, 1984), borapetol A and B, borapetoside A and B, tinocrisposide, N-formylanondine,N-formylnornuciferine, N-acetyl nornuciferine, γ-sitosterol, picroretine and tinotubride (Misak, 1995). Two new triperpenes, cycloeucalenol and cycloeucalenone from *T. crispa* were previously isolated (Kongkathip et al., 2002). Previous studies have also determined the proximate composition of its stem and leaves. The analysis approximately showed that *T. crispa* contains protein:leaves = 4.7%, stem + 1.2%; fat:leaves = 1.5%, stem = 0.43%; carbohydrate:leaves = 11.8%, stem = 19.4%; ash:leaves = 2.7%, stem = 1.1%; moisture:leaves = 79.3%, stem = 77.9%; fiber:leaves = 1.59%, stem = 0.65%; and energy:leaves = 1.59%, stem = 0.65% (Zulkhairi et al., 2008).

It was revealed that an organic compound containing heteroatoms such as O, N or S and multiple bonds showed good potential as a corrosion inhibitor (Hussin and Kassim, 2011). Previous studies have shown that the utilization of naturally occurring compounds in acidic solution can inhibit the corrosion of metals (Hussin and Kassim, 2011; de Souza and Spinelli, 2009; Ahamad et al., 2010; Satapathy et al., 2009). The presence of alkaloid and polyphenol compounds in *T. crispa* extracts will show a corrosion inhibition property. The corrosion behavior of *T. crispa* extracts on mild steel was determined via weight loss measurement, potentiodynamic polarization measurement and electrochemical impedance spectroscopy (EIS). Besides, the adsorption nature and surface morphology analysis using a scanning electron microscope (SEM) were also determined.

2. Material and methods

2.1. Preparation of *T. crispa* extract

T. crispa stems were collected around from Gurun, Kedah, Malaysia. *T. crispa* were washed under the running tap water and then were cut into small pieces, which were about 1 cm each piece. *T. crispa* stems in small pieces were then sun dried for seven days to remove water before being ground into fine powder and sieved with a 250 μm mesh. Initially, the dried powder was diluted with distilled water in the ratio of 1:10 (w/v). The solution was then placed in a water bath at 80 °C for 24 h and then filtered to obtain the supernatant. The collected supernatant was then freeze dried for at least 3 days. The dried extract obtained was ground into powder and labeled as TCDW, was kept at 4 °C for further use. The same extraction process goes to the next extracting solvent. The dried powder was diluted with 70% acetone solution (v/v) in the ratio of 1:10 (w/v). The collected supernatant was then concentrated at 45 °C under reduced pressure in a rotatory evaporator and dried in an oven at 50 °C. The dried extract obtained was ground into powder and labeled as TCAW, was kept at 4 °C for further use.

2.2. Specimen preparation

Mild steel specimen having the composition (wt%) of 0.08 C, 0.01 Si, 1.26 Mn, 0.02 P and remaining Fe was used. Coupons were cut into $3 \times 4 \times 0.1$ cm dimensions used for weight loss measurements, whereas specimens with $6 \times 4 \times 0.1$ cm dimensions were used as working electrode for polarization and EIS measurements. The exposed area was mechanically abraded with 400, 600 and 800 grades of SiC papers, degreased with isopropyl alcohol (IPA) and rinsed with distilled water before each electrochemical experiment.

2.3. Solutions preparation

About 1 M HCl solutions were prepared by the dilution of 37% HCl using distilled water. The concentration range of *T. crispa* extract employed was varied from 200 to 1000 ppm. This concentration range was chosen upon the maximum solubility of *T. crispa* extract. The powder extract was first dissolved in 1% (v/v) methanol before it was diluted with 1 M HCl solution.

2.4. Weight loss measurement

The rectangular mild steel specimens of dimension $6 \times 4 \times 0.1$ cm were immersed (complete immersion) in 100 mL of deaerated electrolyte in the absence and presence of different concentrations of *T. crispa* extracts at an ambient temperature (303 K). The weight loss of mild steel specimens was determined after 24 h of immersion. The percentage inhibition efficiency (IE%) was calculated using the following formula:

$$\mathrm{IE}\% = \frac{W_0 - W_i}{W_0} \times 100 \quad (1)$$

where W_0 and W_i are the weight loss values in the absence and in the presence of the inhibitor.

2.5. Potentiodynamic polarization measurement

Polarization measurements were conducted in a conventional three electrode Pyrex cell with an overall volume of 50 mL. The exposed geometrical surface area of the working electrode (WE) was fixed with an area of 0.785 cm^2 to the electrolyte, a graphite gauze was used as the auxiliary electrode (CE), and a saturated calomel electrode (SCE) as the reference electrode (RE). All the experiments were carried out using deaerated unstirred solutions at 303 K. The measurements were carried out using a PC controlled Volta Lab PGP 201 system with Voltamaster 4 software at a scan rate of 1 mV s^{-1}. The open circuit potential, E_{ocp} was measured for 30 min to allow the stabilization of the steady state potential. The potential range was calculated from the E_{ocp} values obtained (±250 mV). The inhibition efficiency (IE%) was calculated using the relation:

$$\mathrm{IE}\% = \frac{I_{corr} - I_{corr(i)}}{I_{corr}} \times 100 \quad (2)$$

where I_{corr} and $I_{corr(i)}$ are referred to as the corrosion current density without and with the addition of the inhibitor, respectively.

2.6. Electrochemical impedance spectroscopy (EIS)

The electrochemical impedance spectroscopy (EIS) was carried out using a Gamry Instrument Reference600 with the open circuit potential E_{ocp}, of every sample was immersed for 30 min over a frequency range of 100 kHz to 0.01 Hz with a

Please cite this article in press as: Hussin, M.H. et al., The effect of *Tinospora crispa* extracts as a natural mild steel corrosion inhibitor in 1 M HCl solution. Arabian Journal of Chemistry (2011), doi:10.1016/j.arabjc.2011.07.002