ELECTROCHEMICAL BEHAVIOR OF MILD STEEL IN HCL 1M MEDIUM WITH THE PRESENCE OF ROSE MYRTLE LEAVES EXTRACTION

Vo An Quan[1, *], Nguyen Tuan Anh[1], Tran Thi Ha[2], Le Xuan Que[1]

[1]*Institute for Tropical Technology, VAST, 18 Hoang Quoc Viet, Cau Giay, Ha Noi*

[2]*Insitute of Chemistry, Biology and Special document technique, 47, Pham Van Dong, Cau Giay, Ha Noi*

[*]Email: *vaquan@itt.vast.vn*

ABSTRACT

As the growing interest on green corrosion inhibitors, plant extracts have gradually showed the potential in replacing the traditional hazardous chemicals due to the eco-friendly and economy characteristics. Previous study reported that rose myrtle leaf-extract (*Rhodomyrtus tomentosa*, *Myrtaceae*) was as an efficient corrosion inhibitor for rust removal process of mild steel in H_2SO_4 acid medium. This study presents the corrosion inhibition assessments of rose myrtle leaf-extract on mild steel surface in HCl 1M solution. The potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) methods have been used to study the corrosion behaviors of mild steel. The corrosion rate, corrosion current and corrosion potential results indicate that only small amount of the leaf-extract (2 % vol.) was required for high inhibition efficiency (H_{in} = 83.9 %). By affecting on both anodic and cathodic branches of the Tafel plot, the corrosion inhibition mechanism is proposed by an adsorption forming different barriers on the steel surface.

Keywords: green inhibitor, Rhodomyrtus tomentosa, steel corrosion, EIS.

1. INTRODUCTION

Plenty of plant extracts have been reported to be acceptable corrosion inhibitors for metals in many types of corrosive medium [1, 2]. Basic components of extracts are sugars, steroids, aloin, gallic acid, ellagic acid, tannic acid, flavanoids, etc. The presence of tannins, cellulose, and polycyclic compounds has been reported to enhance a film formation over the metal surface, thus decreasing corrosion [3]. The downy rose myrtle (*Rhodomyrtus tomentosa,* Wight) is native to Asia, according to recent reports, the chemical constituents of *R. tomentensa* consist of hydrolysable tannins as major components, followed by flavones, triterpenes, steroids, meroterpenoid and acylphloroglucinols [4-7]. The tannins and polyphenolic compounds like quinic acid, gallic acid, caffeic acid, flavonoids and glycoside compounds, which possess vast of hydroxyl (-OH) and other functional groups which have potentially interaction with metal ions [8-13].

This work focuses on the application of leaves extracts of downy rose myrtle for corrosion protection of metals and the inhibition effect for steel in hydrochloric acid medium. In this study,

the inhibiting effects of plant leave water extracts for mild steel in 1M hydrochloric acid solution were investigated by using electrochemical techniques, such as the potentiodynamic polarization and electrochemical impedance spectroscopy (EIS).

2. MATERIALS AND METHODS

2.1. Materials

2.1.1. Metal sample preparation

The mild steel used for this study were CT3 grade with composition (wt%): C = 0.17, Si = 0.01, S = 0.02, P = 0.02, Mn = 0.46, Ni = 0.03, Cr = 0.01, Cu = 0.01 and the balance Fe. Steel electrodes were shaped into round plate with the working surface of 1 cm^2. They were polished with different grades (# 400, 600, 800 and 1000) silicon carbide paper, degreased in absolute ethanol, rinsed in acetone, dried and stored in a moisture-free desiccator prior to use.

2.1.2. Plant leaves extract preparation

The green leaves of *R. tomentosa* were collected from Xuan Mai, Vietnam in 2016, identified by Prof. Dr. Nguyen Nghia Thin, Vietnam National University. An amount of 1 kg of fresh leaves and young stem of *R. tomentosa* was extracted in boiled water and condensed to obtaining 1 L water extract. The solid content of the extract has been determined by water removal process under reduced pressure at 60-65 ^{o}C and concentrated at 70-80 ^{o}C, gave the result of 4.52 g solid residue/100 mL water extract. The extract has been then filtered to removing insoluble content to obtain aqueous extract (DS) used in the experiments.

From the preparation method, it could be said that the chemical constituent of DS samples is including most of the polar substances in the plant material.

2.1.3. Electrolytic solutions

The corrosive medium was HCl 1M. Deionized water was used for the preparation of all reagents. The electrolytic solutions have been prepared by adding to the acid medium an increasing concentrations of the DS sample ranging from 0; 0.1; 0.2; 0.5; 1; 2; 5; 10 %vol. For each experiment, 200 mL of electrolyte has been used. The applied concentration is equivalent to 0; 0.05; 0.09; 0.23; 0.45; 0.9; 2.26; 4.52 g/L of the solid residue of *R. tomentosa*.

2.2. Applied methods

2.2.1. Electrochemical measurements

Electrochemical measurements were carried on Biologic VSP-300 multichannel potentiostat (Bio-Logic Science Instruments, France). The experimental data are analyzed with the EC-Lab software. Measurement system is three electrodes glass cell. Working electrode is a plate mild steel of 1cm^2 effective surface. Platinum plate and a silver chloride electrode were used as a counter and reference electrodes, respectively.

Inhibition effects have been investigated by using linear polarization (LPR), potentiodynamic polarization and electrochemical impedance techniques. All measurements have been realized at room temperature (at 25 ^{o}C), after stabilization of the open circuit potential

E_{oc} (waiting time is 30 minutes). For LPR test, polarization resistances (R_p values) have been estimated in polarization range $\Delta E = E - E_{oc} = \pm 25$ mV with scan rate 0.1 mV/s. Whereas, the corrosion currents (I_{corr} values) measurement has been realized in polarization range $\Delta E = E - E_{oc} = \pm 200$ mV with scan rate 0.1 mV/s.

The corrosion inhibition efficiency ($H_R\%$) was calculated using R_p.

$$H_R\% = (R_p - R_p^a) / R_p \times 100 \ \%. \tag{1}$$

Electrochemical impedance spectroscopy (EIS) was determined on the steady-state current at a given potential, at frequencies between 100 kHz to 10 mHz. The impedance diagrams are given in the Nyquist representation. The inhibition efficiency got from the charge-transfer resistance is calculated by:

$$H_{im}\% = (R'_{ct} - R_{ct}) / R'_{ct} \times 100 \tag{2}$$

R_{ct} and R'_{ct} are the charge-transfer resistance values with and without inhibitor, respectively.

2.2.2. *FT–IR measurements*

For IR spectral studies, the transmission technique was used for obtaining the spectra of the solid content of water extraction. The used FTIR equipment is Nicolet iS10 Thermo Scientific (USA).
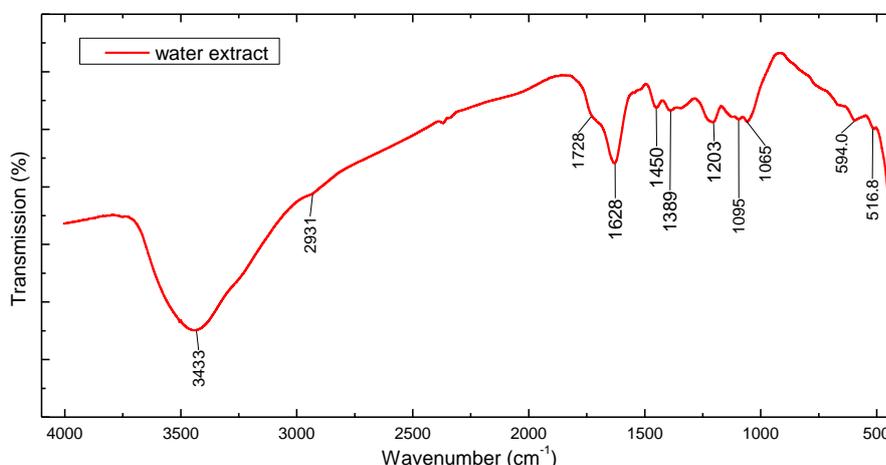
3. RESULTS AND DISCUSSION

3.1. FT-IR study

Figure 1. Infrared transmission spectrum of DS sample.

Obtained DS sample was characterized by FTIR (ν cm^{-1}): the OH phenolic group is at 3440 cm^{-1} (–OH stretching), the shape of the OH stretching band is broad and strong indicating the affect of hydrogen bonded structures and high degree of polymerization. The C-H stretching for aromatic compounds appears as weak shoulder at 2939 cm^{-1} while the symmetric stretching occurs at 1342 cm^{-1}. A distinctive peak for carbonyl stretching appears as weak shoulder at 1728 cm^{-1} for carbonyl stretching might indicates the presence of flavonols in the mixture or condensed compounds. The 1628 cm^{-1} for –C=C– bond in the aromatic rings could result as catechin monomer. The aromatic stretching –C=C– located at 1450 cm^{-1} while 1389 cm^{-1} of C–O

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stretching phenols & 1203 cm^{-1} (C–O stretching benzene nucleous), 1095 & 1065 cm^{-1} (C–O coupled with C–C stretch), 593 & 510 cm^{-1} (ring vibration). The FTIR spectrum of DS sample is most suite with IR spectrum of tannins, tannic acid that contain aromatic ring (Fig. 1) [14].

According to the FTIR spectrum, it could be stated that the main chemical constituent of DS sample is a mixture of condensed and hydrolysable tannins. These tannins contain various numbers of hydroxyl groups, as well as catechin monomer, galloyl units, diphenoyl groups bounded to sugar moiety.

3.2. Potentiodynamic polarization study

The linear polarization (LPR) results of steel in 1M HCl are shown in the Fig. 2. Based on the linear polarization diagram, corrosion potentials (E_{corr}) in the presence of DS is more positive than in acid medium but the different is relatively small, about 8 mV. The values of polarization resistance (R_p) are presented in Table 1.
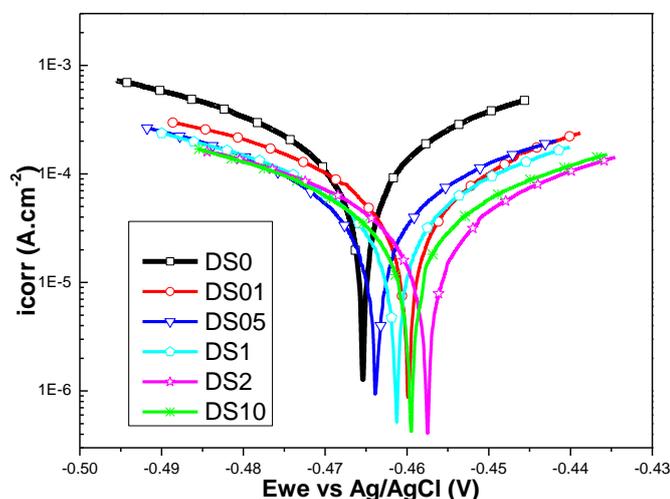

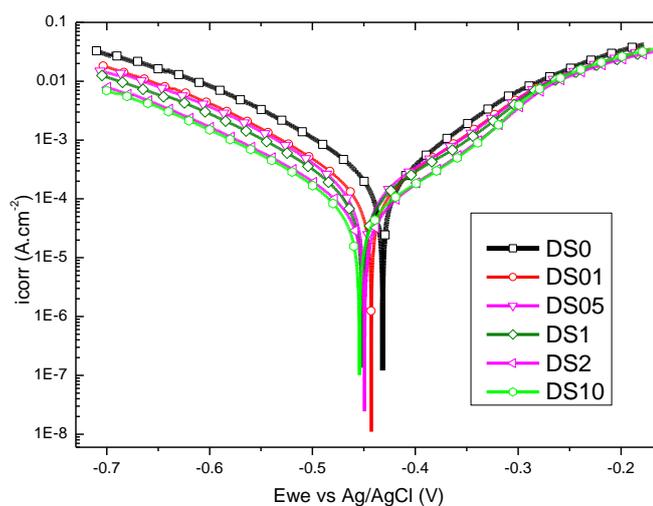*Figure 2.* Linear polarization of S05, RT1 and A05 samples.

Figure 3. Polarization curves of steel in HCl 1M with different concentration of DS.

Potentiodynamic polarization behavior of steel in 1M HCl in the presence and absence of inhibitors are shown in Fig. 3, in all of the experiment mediums, no passive expression found. The values of polarization resistance (R_p), corrosion current (I_{corr}), corrosion potential (E_{corr}), cathodic Tafel slope (β_c), anodic Tafel slope (β_a) and inhibition efficiency (E%) are collected in Table 1.

Table 1. Polarisation parameters for steel in HCl 1M at different contents of DS.

Samples	E_{corr} (mV)	I_{corr} (µA)	β_c (mV/dec)	β_a (mV/dec)	H_{icorr}(%)	R_P (Ω cm^2)	H_{RP}(%)
Acid	-435.273	385.996	124.6	112.4		41.9	
DS01	-442.812	143.656	108.5	96.8	62.78	95.1	55.94
DS05	-450.144	129.363	103.5	97.7	66.49	110	61.91
DS1	-451.639	101.151	103.8	94.6	73.79	124	66.21
DS2	-449.503	55.563	101.7	83.9	85.61	168	75.06
DS5	-455.181	62.963	100.9	85.5	83.69	147	71.50
DS10	-454.394	46.707	96.3	81.5	87.90	161	73.98

As can be seen in Fig. 3 and Table 1, the presence of the extract DS decreases both cathodic and anodic current density. The decrease is more clearly with the increase of the DS concentration. The corrosion potential is varied with the highest different about 20 mV in the presence of inhibitor. The presence of the DS only has small impact on the cathodic Tafel slope indicating that the mechanism of H^+ reduction is still activate control. In the anodic slop, the value of β_a is changing over the DS concentration. This result indicates that DS acts as a mix inhibitor by simple adsorbing into metal surface. The inhibitor molecules decrease the surface area of corrosion and only cause inactivation on part of the surface with respect to the corrosion medium.

The inhibition efficiency of DS reaches 85.6% at 0.9 g/L. Therefore, *R.tomentosa* extract is a good inhibitor and acts as a mix inhibitor.

3.3. Electrochemical impedance study

Electrochemical impedance spectroscopy (EIS) has been widely used to investigate corrosion inhibition processes in terms of the resistive as well as capacitive behaviors at metal/solution interface [15]. The corrosion inhibitor efficiency of DS has been assessed based on the electrochemical impedance results at the equivalence potential. The results have been collected and shown in the Table 2.

The Nyquist plots in Fig. 4 were characterized by the depressed semicircles at high to medium frequencies and an inductive loop at low frequencies of with the presence of inhibitor. This is often attributed to the surface roughness, inhomogeneity of the solid surface and adsorption of the inhibitor on the metal surface [16, 17]. It is also observed that the diameter of the impedance plot increased with increase in inhibitor concentration.
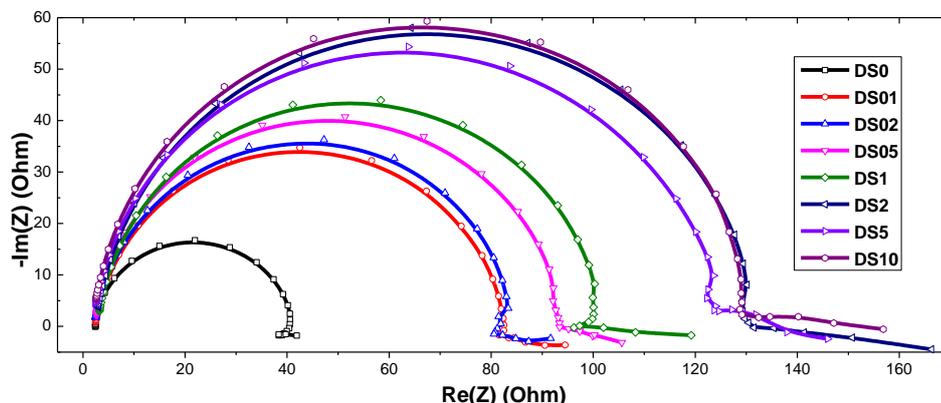
Figure 4. Nyquist plot of steel samples in HCl 1M with or without DS in different concentration.
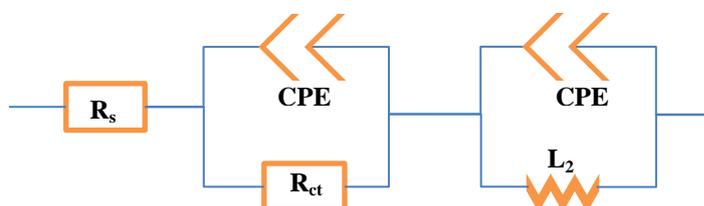

Figure 5. The proposed equivalent circuit model for qualitative parameters.

A proposed electrochemical circuit is presented in Fig. 5, with R_s is the solution resistance, R_{ct} is the charge transfer resistance, CPE is the constant phase element, L is inductor and presented for the dispersion phenomenon. The values of charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}) was determined from the fitting of Nyquist plots. The value of R_{ct} and calculated inhibition efficiency (H_{im}) has shown in Table 2.

Table 2. Double layer capacitance (C_{dl}) and charge transfer resistance (R_{ct}) values of DS samples and inhibition efficiency.

		Acid	DS01	DS05	DS1	DS2	DS5	DS10
Double layer capacitance (C_{dl})	**(mF)**	0.1822	0.1692	0.1333	0.1216	0.1167	0.1229	0.1036
Charge-transfer resistance (R_{ct})	**(Ωcm^2)**	38.47	80.59	91.6	98.85	129.3	121.9	128.6
Inhibition efficiency - H_{im}	**(%)**		52.26	58.00	61.08	70.25	68.44	70.09

Based on the Nyquist plot (Fig. 5), the charge transfer resistance (R_{ct}) of the steel in acid with or without DS has gradually increased with the DS concentration. The value of R_{ct} of DS2 was the highest with the inhibition efficiency reach 70.25 %. Though, the R_{ct} of the samples still shows the corrosion of steel substrate in the solution, but the corrosion rate is reduced in the presence of DS. The decrease in C_{dl} value from 0.182 mF in the acid to 0.1036 mF in DS10 means that a layer is formed on the surface while DS present. This adsorption layer takes place

on the metal surface in acidic solution, prevent the direct contact between the metal surface and the acid medium, forming micro electrodes and decreasing the effective surface which promotes the dissolution of metal.

The result is consistent with the E/t correlation before-mentioned (inhibition of anode process and advantage of cathode process).

4. CONCLUSIONS

The main findings of this research were:

The natural compounds in *R. tomentosa* (Rose myrtle) extract acts as a capable inhibitor for preventing corrosion on steel substrate in HCl 1M solution with the optimal inhibition efficiency reaches 85.6 % at 0.9 g/L from potentiodynamic polarization result.

Followed the obtained results on LPR and EIS measurements, the DS sample has shown capable corrosion inhibition efficiency at 2 vol% in HCl 1M which raised the charge transfer resistance (R_{ct}) value from 38.47 to 129.3 Ω and the polarization resistance (R_p) from 41.9 to 168 Ω.

With the presence of DS in corrosive medium, the anodic process has been inhibited (equivalent potential E_{corr} has moved to the positive area, which allows the cathodic process easily occurs). The DS shows the ability to decrease the corrosion rate of CT3 steel, though, the passive area does not form.

From the point of natural origin, the extract of *R. tomentosa* shows a possibility to for application as a green corrosion inhibitor of mild steel while conduct the metal surface treatment (pickling in acidic medium) in industrial.

REFERENCES

1. Raja P. B. and Sethuraman M. G. - *N*atural products as corrosion inhibitor for metals in corrosive media — A review, ScienceDirect, Materials Letters **62** (2008) p. 113-116.

2. Zaferani S. H., Sharifi M., Zaarei D., and Shishesaz M. R. - Application of eco-friendly products as corrosion inhibitors for metals in acid pickling processes – A review, Journal of Environmental Chemical Engineering, **1** (4) (2013) p. 652-657.

3. Mourya P., Banerjee S., and Singh M. M. - Corrosion inhibition of mild steel in acidic solution byTagetes erecta (Marigold flower) extract as a green inhibitor, Corrosion Science **85** (2014) 352–363.

4. Liu H. X., Zhang W. M., Xu Z. F., Chen Y. C., Tan H. B., and Qiu S. X. - Isolation, synthesis, and biological activity of tomentosenol A from the leaves of Rhodomyrtus tomentosa, RSC Adv. **6** (2016) 25882–25886.

5. Hamid H. A., Mutazah S. S. Z. R., and Yusoff M. M. - Rhodomyrtus tomentosa: a phytochemical and pharmacological review, Asian J Pharm Clin Res, **10** (1) (2017) p. 10-16.

6. Hiranrat A. - Chemical Constituents from Rhodomyrtus tomentosa (Aiton) Hassk. and Antibacterial Activity, 2010.

7. Tung N. H., Ding Y., Choi E. M., Kiem P. V., Minh C. V., and Kim Y. H. - New anthracene glycosides from rhodomyrtus tomentosa stimulate osteoblastic differentiation of mc3t3-e1 cells, Arch. Pharm. Re. **32** (4) (2009) 515-520.

8. Iglesias J., Saldaña E. G. D., and Jaén J. A. - On the Tannic Acid Interaction with Metallic Iron, Hyperfine Interactions **134** (2001) 109–114.

9. Obot I. B. and Madhankumar A. - Enhanced corrosion inhibition effect of tannic acid in the presence of gallic acid at mild steel/HCl acid solution interface, Journal of Industrial and Engineering Chemistry **25** (2015) 105-111.

10. Qian B., Hou B., and Zheng M. - The inhibition effect of tannic acid on mild steel corrosion in seawater wet/dry cyclic conditions, Corrosion Science **72** (2013) 1–9.

11. Khang P. V., Tuan V. A., Thao H. V., Quang N. V., and Uong Van Vy L. X. Q. - Some electrochemical characteristics of polyphenol extracted from Thai Nguyen green tea, in Proceedings of the 4th National Organic Chemistry Science and Technology Conference Ha Noi, 2007, p. 628-633.

12. Que L. X., Thu L. V., Dinh P. V., and Hoan H. V. - Study on the corrosion inhibition capacity on CT38 mild steel of water extraction of Thai Nguyen tea on H_2SO_4 1M, Vietnam Journal of Science and Technology **48** (3A) (2010) 63-67.

13. Hai L. T., Trang P. T. T., Cam D. N., and Tham T. V. - Study on extraction, chemical constituent identification of tannin from green tea leaves and its corrosion inhibition characteristic, Journal of Science and Technology, Da Nang University **1** (36) (2000).

14. Ricci A., Olejar K. J., Parpinello G. P., Kilmartin P. A., and Versari A. - Application of Fourier Transform Infrared (FTIR) Spectroscopy in the Characterization of Tannins, Applied Spectroscopy Reviews, Taylor & Francis, 2015.

15. Li P., Tan T. C., and Lee J. Y. - Impedance spectra of the anodic dissolution of mild steel in sulfuric acid, Corrosion Science **38** (11) (1996) 1935- 1955.

16. Singh A., Ahamad I., Singh V. K., and Quraishi M. A. - Inhibition effect of environmentally benign Karanj (Pongamia pinnata) seed extract on corrosion of mild steel in hydrochloric acid solution, Journal of Solid State Electrochemistry **15** (6) (2011) 1087-1097.

17. Amin M. A., El-Rehim S. S. A., El-Sherbini E.E.F., and Bayoumi R. S. - The inhibition of low carbon steel corrosion in hydrochloric acid solutions by succinic acid: Part I. Weight loss, polarization, EIS, PZC, EDX and SEM studies, Electrochimica Acta **52** (11) (2007) 3588-3600.