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Polarisation and Electrochemical impedance spectroscopy Studies on Date Palm Seed Extract as Green Corrosion Inhibitors for Carbon Steel in 0.5 M HCl Solution

[1]Naba Jasim Mohammed, *[2]Norinsan Kamil Othman

ABSTRACT--*This study investigated the function of the date plm seed (Phoenix Dactylifera) as a green corrosion inhibitor for carbon steel in 0.5 M HCl solution. The polarisation and Electrochemical Impedance Spectroscopy (EIS) methods were used to investigate inhibition efficiency, including the current density and resistance of the corrosion towards the carbon steel. As a result, Tafel polarisation displayed maximum inhibition efficiency at 900 ppm. The inhibition efficiency of 89.05% was observed from IES at 900 ppm, which subsequently decreased to 77.89% and 81% at the concentration levels of 1100 ppm and 1400 ppm respectively. In conclusion, date palm seed extract is an effective inhibitor t 25^{0}C and 900 ppm concentration level, and it could also be used to protect carbon steel from corrosion in an acidic medium*

Keywords-- *Date palm seeds; Green corrosion inhibitor; Electrochemical measurements; Carbon steel; HCl.*

I. INTRODUCTION

Hydrochloric acid (HCl) solution, including other acids, is generally used to remove rust and the scale of industrial methods, while HCl is commonly used in the processes of metal pickling. Inhibitors are the methods used specifically in acid solutions to prevent corrosions, metal dissolution, and acid consumption (Lahhit et al., 2011). However, the issue of HCl or any acid in this process lies in the use of acid treatment which accelerates the corrosion rate in gas and oil. Importantly, acid is essential in the inhibition of the corrosion rate for gas and oil wells in acid treatments (Mobin and Rizvi, 2016). Corrosion inhibitors are commonly used in acidic medium. Furthermore, although the main organic compound inhibitors consist of heteroatoms, including O, N and S. which could be absorbed into the metal surface, the use of corrosion inhibitors continues until today. Plant extracts are rich in natural source, leading to their good function as corrosion inhibitors. These extracts are also environment-friendly, renewable, inexpensive, easily available, so the seed and plant extracts could be applied as green corrosion inhibitor. In recent times, numerous reports have been made regarding the use of different plants as green corrosion inhibitors for the acidic medium with good inhibition efficiency (IE%). To illustrate, Punica Plant extract displayed 84.5% inhibition efficiency at 300 ppm concentration level (Fouda, Etaiw, & Elnggar, 2014), Psidium Guajava

[1] *Department of Applied Physics, Faculty of Science and Technology, University Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia.*
[2] **Materials Science Program, Department of Applied Physics, Faculty of Science and Technology, University Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia, insan@ukm.edu.my*

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Leaf extract displayed 82% inhibition efficiency at 1200mgL^{-1} (Victoria, Prasad, & Manivannan, 2015), Rice Husk extract exhibited an inhibition efficiency of 86% (Alaneme et al., 2015), Ginkgo leaves extract displayed an inhibition efficiency of 78% at 1200 mg/L (Deng and Li, 2012), Capsicum frutescens Biomass extract displayed an inhibition efficiency of 85.5% at 1000 mg/L (Emeka E Oguzie et al., 2013), and Radish seeds aqueous extract displayed 54.2% inhibition efficiency at 10%v/v (Noor, 2018). Meanwhile, the extract of Murraya koenigii leaves displayed 97.5% inhibition efficiency at 600 mg/l (Quraishi et al., 2010), Chenopodium Ambrosioides extract in sulfuric acidic solution exhibited 89% inhibition efficiency at 4 g/l (Bammou et al. 2018), and Butea monosperma extract in 0.5M H_2SO_4 displayed 98% inhibition efficiency at 500 ppm concentration level (Saxena, Prasad, & Haldhar, 2017). On the other hand, pendula leaves extract in 1 M HCl exhibited 93% inhibition efficiency at 0.4 g/l (Hcl et al., 2016). In a study by Alvarez et al. (2017), the Rollinia occidentalis extract used for carbon steel in an HCl solution displayed 79.7% inhibition efficiency. Notably, several reports were made in studies regarding the function of date palm waste extract as corrosion inhibitor. These could be seen from the research by Buchweishaija (2008) on Palm leaflet and Palm fiber for the same functions and an investigation by Gerengi (2012), where the juice of date palm was used in 3.5% of NaCl solution for aluminum alloy. However, few reports were made regarding the application of the waste of date palm extract as a corrosion inhibitor in 0.5 M HCl medium for carbon steel. Date palm (Phoenix dactylifera) is a resource which is naturally made, produces healthy fruit, possesses good medicinal value, and functions as a part of staple diet in most parts of Middle East and North Africa. Furthermore, the date palm is highly beneficial to consumers as it could be eaten fresh or died, and the seeds could be grown into plants. It was also proven from this study that the seeds valuable as green corrosion inhibitor. Following that, an evaluation was conducted on the corrosion inhibition efficiency of the DPS extract for carbon steel in 0.5 M HCl solution by using potentiodynamic polarisation and electrochemical impedance spectroscopy (EIS) measurements at 25 ^{o}C.

II. MATERIALS AND METHODS

2.1 Date palm seeds (DPS) extraction

Date palm seeds were collected from Baghdad city, Iraq, which was followed by manual separation of the seeds. After a cleansing process was done to remove the peels, the seeds were dried in the oven at 40 ^{o}C within a day. The dried seeds were ground using a mechanical grinder to produce powder, each with a size of 0.252 mm. This was followed by soaking 10 g powder of DPS in 1000 mL of 0.5 M HCl for 24 hours until a solution was formed. The solution was then filtered and evaporated to remove the solvent by using a rotary evaporator (Othman, Yahya, & Ismail, 2018). After the removal of solvent, the water was dried in an oven, and the volume of distilled water was adjusted to 1000 ml for the preparation of 2000 ppm of stock solution.

2.2 Solution preparation

The preparation of 0.5 M HCl was performed through the dilution of 37% of HCl from the analytical reagent grade using distilled water. For the preparation of the 2000ppm stock solution of DPS were used distilled water. (Fattah-alhosseini & Noori, 2016). The concentration levels involved in DPS amounted to 500 ppm, 800 ppm, 900

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ppm, 1100 ppm, and 1400 ppm, which were then tested as the corrosion inhibitors using electrochemical measurements.

2.3 Preparation of carbon steel:

Experiments were done using carbon steel, which consisted of a wt% composition of C 0.2%, P 0.04%, Si 0.003%, Mn 0.6%, Cr 0.008%, Cu 0.024%, Ni 0.0214%, Ti 0.017%, Al 0.035%, and Fe balance. ASTM standard of G1-03 was used to clean up the carbon steel (Musa et al., 2012). Furthermore, grinding-polishing Machine-Top-Tech-P2554-mecapol was used to rub the samples against Silicon Carbide papers, with grades ranging from 400 to 1200. To obtain the mirror brightness, cotton with buffing soap was used, followed washing process through distilled water and a drying process using a hairdryer (Lowmunkhong, Ungthararak, & Sutthivaiyakit, 2010).

2.4 Electrochemical measurement

This measurement was made using Gamry potentiostat-Galvanostat-ZAR Reference-3000, which was directed to the software. This potentiostat was connected to three electrode cells. Saturated calomel electrode (SCE) was used as a reference for the electrode, while Graphite acted as the counter electrode. The material used for the working electrode was the carbon steel, with a surface area of $1cm^2$. Based on the setup for cell shown in Figure 1 the working electrode should be placed near the reference electrode without any contact occurring between them. Following that, EIS experiments were conducted to gain an understanding of the kinetics and characteristics of electrochemical processes for carbon steel in 0.5 M HCl solution. The measurements of EIS were carried out at a frequency range from 100000 Hz to 0.1 Hz, which was superimposed on the resting potential. Moreover, computer programmes automatically controlled the measurements made on the rest potentials after 0.5 hours at 25ºC temperature level. potentiodynamic polarisation curves were created by changing the electrode potential from −250 to +250 mV against the open circuit potential (E_{corr}) at a scan rate of 1 mVs−1.

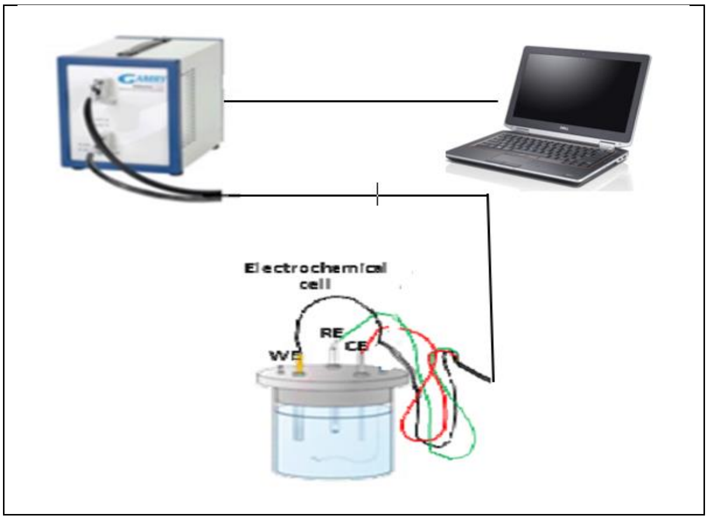

Figure 1: Electrochemical setup cell.

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III. RESULTS AND DISCUSSION

3.1 Potentiodynamic polarisation

Polarisation measurements are suitable for monitoring the mechanisms and progress of the anodic and cathodic reactions. potentiodynamic polarisation tests were conducted to determine the effects of the cathodic ($2H^+ + 2e \longrightarrow H_2$) and anodic ($Fe \longrightarrow Fe^{2+} + 2e$) reactions of the corrosion process. Furthermore, potentiodynamic polarisation curves for carbon steel in 0.5 M HCl with and without the presence of DPS extract are shown in Figure 2. The plots displayed the reactions of cathodic and anodic in a blank solution and the adjunct DPS extract, which was based on the law of Tafel. densities of corrosion (I_{corr}) was found from the linear of Tafel sections of the cathodic and anodic curves. Table 1 displays the parameters, (I_{corr}) as the corrosion current densities, (E_{corr}) as the potential for corrosion, the Tafel slope for anodic (β_a) and for cathodic (β_c), which was obtained from the curves polarisation It is indicated from the results in Table 1 that the current density of corrosion decreased in the presence of DPS extract compared to the blank solution. Furthermore, it was also found that no significant shift was made by the inhibitor on the (E_{corr}). A compound is usually classified as a cathodic or an anodic type inhibitor when the shift in (E_{corr}) was more significant than 85 mV (Zhang et al., 2011). As a result, the largest shift of (E_{corr}) amounted to 7 mv, indicating the classification of the inhibitor as a mixed type. A similar result was found in other studies of green corrosion inhibitor in acidic medium (Fragoza-mar et al., 2012). Specifically, although the inhibitor did not influence the cathodic hydrogen evolution mechanism, it decreased the H^+ ions on the carbon steel surface through a charge transfer mechanism. The absorption of the atoms of inhibitor occurred through by hindering the locales of responses on the carbon steel surface. Although this phenomenon resulted in a decrease in the existing surface area for hydrogen evolution, the mechanism reaction for hydrogen was not affected (E E Oguzie et al., 2012). The IE% of the inhibitors could be measured based on the value of polarisation resistance through the following Eq 1 (Hegazy et al. 2013):

$$EI = 1 - \left(\frac{Icor}{I^{\circ}cor}\right) \times 100\% \qquad (1)$$

Accordingly, (I_{corr}) and (I^0_{corr}) represent the corrosion current density with and without the presence of inhibitor. Table (1) illustrates that as 500 ppm was not sufficient as a corrosion inhibitor, the absorption of inhibitor amounted to zero. The increase in IE from 31% to 76.80% at 900 ppm, including the attraction of the total DPS extract particles towards the surface of carbon steel and a hindrance to the process of dissolution, took place. Furthermore, the IE% decreased to 49% at 1100 ppm and 75.70% at 1400 ppm. Figure 3 shows the relation between different concentration of DPS extract and IE%. It is indicated from table (2) that (I_{corr}) decreased in inhibitor solution compared with blank solution. In conclusion, the DPS extract is a good corrosion inhibitor at 900 ppm concentration level in 0.5 M HCl to reach the maximum inhibition efficiency of 76.80%.

Table 1: Potentiodynamic polarisation parameters for carbon steel in 0.5 M HCl with and without the presence of DPS extract.

Inhibitor concentrations (ppm)	I_{corr}(µA)	E_{corr}(mV)	B_a(V/dec)	B_c(V/dec)	IE%
Blank	84.3	-464	79.9	126.7	0
500ppm	124	-465	69.1	148.6	0
800ppm	58.5	-470	60.4	119.8	31%
900mm	19.6	-469	64.9	123.7	76.80%
1100ppm	43	-467	68.8	143.7	49%
1400ppm	20.5	-471	61.3	104.9	75.70%

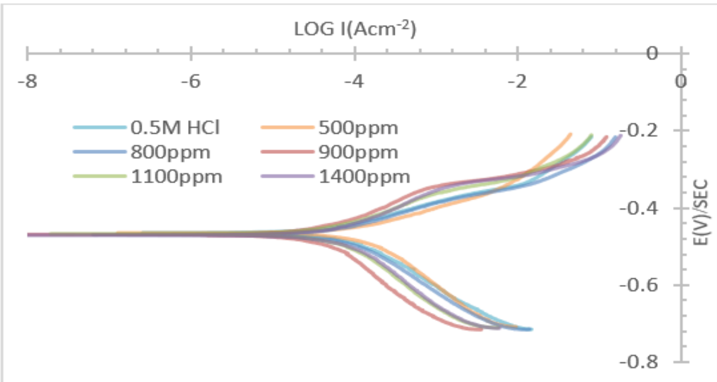

Figure 2: Potentiodynamic polarisation curves in 0.5 M HCl for carbon steel with various concentration of DSP extract

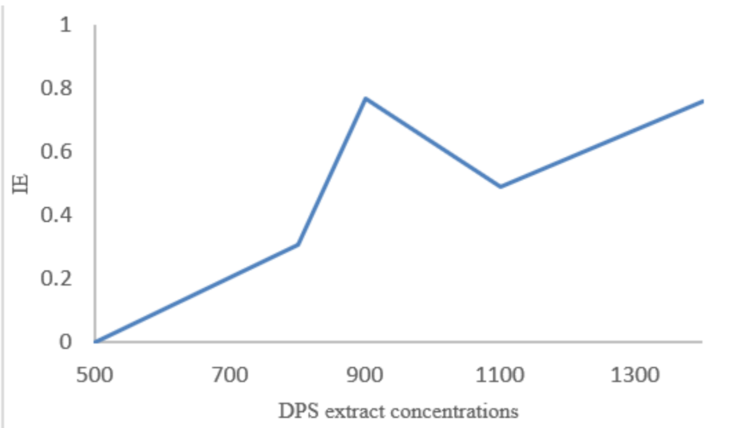

Figure 3: Corrosion inhibition efficiency with the concentrations of DPS extract through potentiodynamic polarization

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3.2 Electrochemical impedance spectroscopy (EIS)

To identify the kinetic characteristics and the electrochemical procedures of carbon steel in 0.5 M HCl, including how they were modified by DPS extract, EIS studies were conducted. Figure 4 (a) and (b) illustrate Nyquist and Bode plots with and without the incorporation of different concentrations of DPS extract for carbon steel corrosion in 0.5 M HCl. The Nyquist plots indicated single semicircles for all systems over the frequency range, which corresponded to one time constant in the Bode plots. The interception of the low frequency with the real axis was ascribed to the charge transfer resistance (R_{ct}), and the high frequency in the real axis in Nyquist plot was earmarked for the solution resistance (R_s). Furthermore, the absorption of DPS extract particles on the surface of carbon steel with different inhibition efficiency and the natural ability of DPS extract represented the simplification of the inhibitor's impacts compared to the blank solutions, which indicated the inhibition of corrosion procedure. However, the maximum sizes of the semicircles amounted to 900 ppm. The EIS was analyzed by equivalent circuit and the model for carbon steel in 0.5 M HCl is illustrated in Figure 6. Moreover, the circuit consisted of the solution resistance (R_s), the charge transfer resistance (R_{ct}), and constant phase element (∅). The electrochemical parameters obtained from the Nyquist plot for carbon steel corrosion in 0.5 M HCl with and without different concentrations of DPS extract are recorded in Table (2). It was found that the DPS extract increased the magnitude of Rct, in which the values were related to the increase in the diameter of the Nyquist semicircle. The inhibition efficiency was measured through the comparison between charge transfer resistance (R_{ct})and (R^o_{ct}) with and without DPS extract based on Eq 2 (Noor 2018):

$$EI\% = \left(\frac{R_{ct} - R^{\circ}_{ct}}{R_{ct}}\right) \times 100\% \qquad (2)$$

It was illustrated in Table (2) that the maximum inhibition efficiency amounted to 89.05% at 900 ppm concentration level, which was then reduced to 81% at 1400 ppm concentration for carbon steel in 0.5 M HCl. Meanwhile, in the presence of inhibitor took place the increase in R_{ct}, which led to higher IE%. This pattern indicated a good formation of a protective layer on the surface of carbon steel, which suggested that all particles of DPS extract were absorbed into the carbon steel surface. Although the inhibition efficiency at 500 ppm amounted to 66.30% in EIS, the inhibition efficiency amounted to 0% in potentiodynamic polarisation results. Therefore, 500 ppm was not an adequate concentration level for carbon steel protection. The difference between EIS and potentiodynamic polarisation was due to the Tafel plots, which evaluated the polarisation of the cathodic surface to an overpotential Meanwhile, EIS evaluated the response circulated from cathodic to anodic through the polarisation curve.

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Table 2: EIS parameters for carbon steel in 0.5 M HCl with and without the presence of DPS extrac

Inhibitor concentrations(ppm)	$R_s(\Omega(cm^2))$	$R_{ct}(\Omega cm^2))$	IE%
blank	66.43	622.3	0
500ppm	1.186	197.6	66.30%
800ppm	1.291	228	70.80%
900ppm	607	625.9	89.05%
1100ppm	299.6	790.1	77.89%
1400ppm	349.8	821	81%

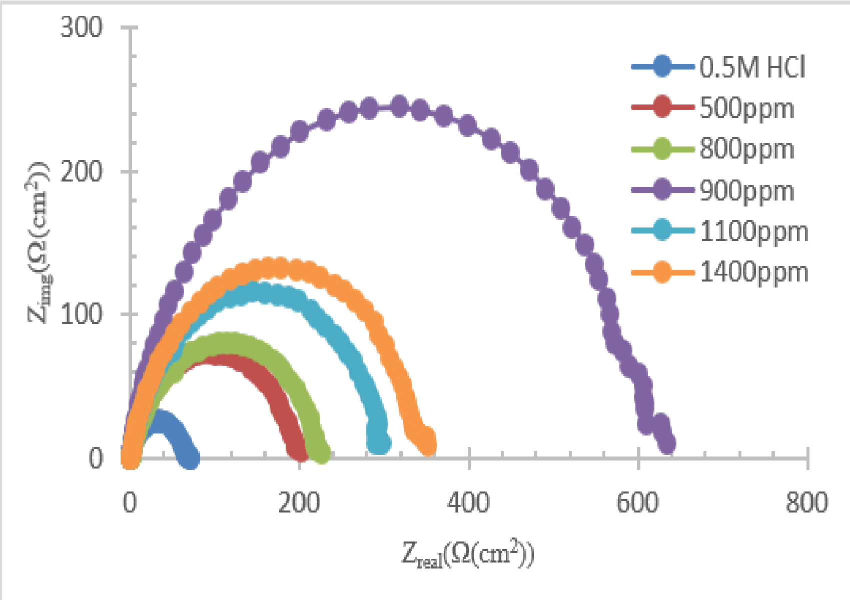

Figure 4: (a). EIS curves in 0.5 M HCl for carbon steel with various concentrations of DPS extract.

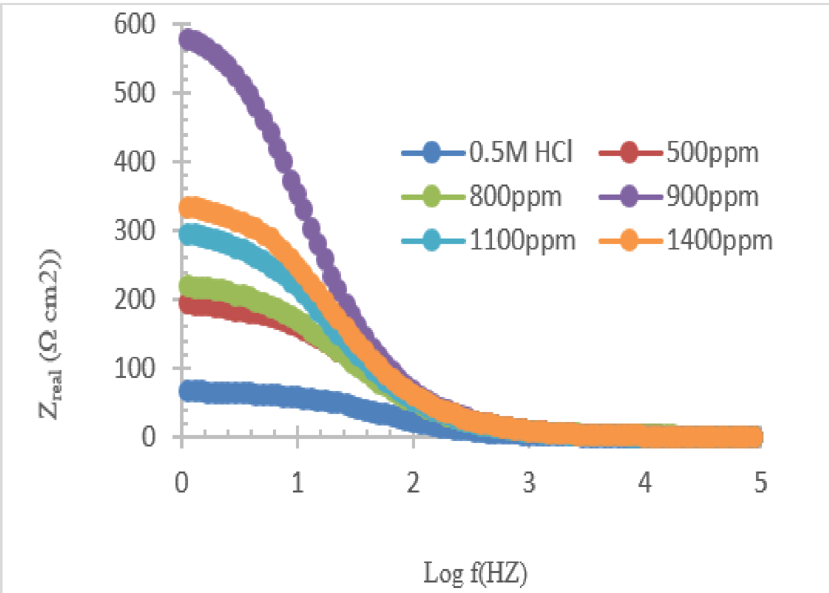

Figure 4: (b). Bode plot curves in 0.5 M HCl for carbon steel with various concentrations of DPS extract

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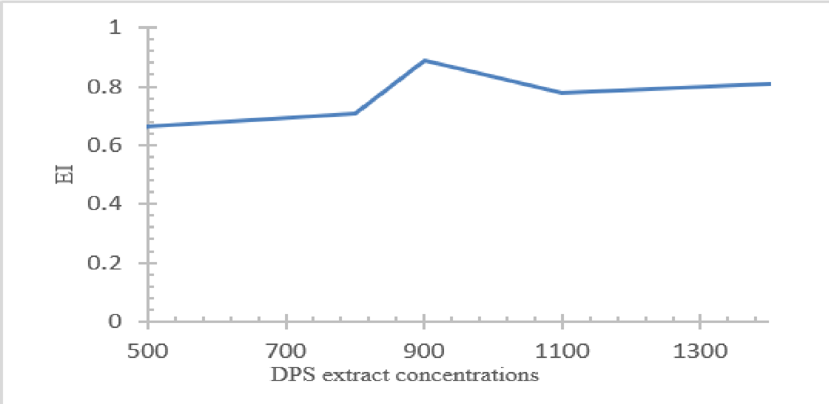

Figure 5: Corrosion inhibition efficiency with the concentrations of DPS extract through EIS

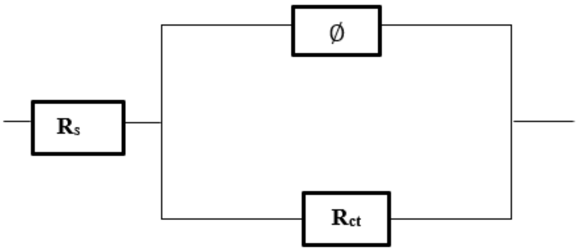

Figure 6: The equivalent circuit used to match the Nyquist data.

IV. CONCLUSION

It can be concluded from electrochemical impedance spectroscopy (EIS) and potentiodynamic polarisation studies that:

- Potentiodynamic polarisation studies indicated that IE% of carbon steel in 0.5 M HCl solution may increase up to 76.80% at 900 ppm.
- DPS extract inhibited the corrosion procedure of carbon steel by stopping the cathodic and anodic reactions.
- As the steel was not completely covered by 500 ppm concentration level, the absorbed inhibitor absorbed amounted to 0%. However, this concentration level was inadequate to protect the c-steel.
- The decrease in βc after the addition the inhibitor indicated that the particles of DPS extract are capable of reducing the dissolution of the anode and eliminating the reaction of the hydrogen evolution on the cathodic surface.
- It was strongly indicated that if the shift of E_{corr} values after the addition of inhibitor exceeded 85.0 mV, the inhibitor could be classified as the anodic or cathodic type.
- It was proven through the EIS technique that the absorption process or the DPS extract led to the formation of a thin layer, which functioned as a wall protecting the carbon steel from the process of dissolution.

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- It was shown from the EIS result that the IE% of carbon steel in 0.5 M HCl solution at 25 ^{o}C may increase up to 89.05%.
- A good match between Potentiodynamic polarization and EIS results was observed. In this case, the improvement in these two elements could be seen from 900 ppm concentration level, which was the most ideal concentration for corrosion inhibitor.

REFERENCES

1. Alaneme, K K, Y S Daramola, S J Olusegun, and A S Afolabi. 2015. "Corrosion Inhibition and Adsorption Characteristics of Rice Husk Extracts on Mild Steel Immersed in 1M H 2 SO 4 and HCl Solutions." 10: 3553–67.
2. Alvarez, Patricia E et al. 2017. "Rollinia Occidentalis Extract as Green Corrosion Inhibitor for Carbon Steel in HCl Solution." Journal of Industrial and Engineering Chemistry (February 2018). http://dx.doi.org/10.1016/j.jiec.2017.09.012.
3. Bammou, L et al. 2018. "Journal of the Association of Arab Universities for Basic Corrosion Inhibition of Steel in Sulfuric Acidic Solution by the Chenopodium Ambrosioides Extracts Corrosion Inhibition of Steel in Sulfuric Acidic Solution by the Chenopodium Ambrosioides Extracts." *Journal of the Association of Arab Universities for Basic and Applied Sciences* 16: 83–90. http://dx.doi.org/10.1016/j.jaubas.2013.11.001.
4. Buchweishaija, J. 2008. "Phytochemicals As Green Corrosion Inhibitors In Various Corrosive Media : A Review."
5. Deng, Shuduan, and Xianghong Li. 2012. "Inhibition by Ginkgo Leaves Extract of the Corrosion of Steel in HCl and H 2 SO 4 Solutions." 55: 407–15.
6. Fattah-alhosseini, Arash, and Mahdis Noori. 2016. "Corrosion Inhibition of SAE 1018 Carbon Steel in H 2 S and HCl Solutions by Lemon Verbena Leaves Extract." *Measurement*. http://dx.doi.org/10.1016/j.measurement.2016.09.029.
7. Fouda, A S, Safaa H Etaiw, and W Elnggar. 2014. "Punica Plant Extract as Green Corrosion Inhibitor for C-Steel in Hydrochloric Acid Solutions." 9: 4866–83.
8. Fragoza-mar, Lubanski, Octavio Olivares-xometl, Marco A Domínguez-aguilar, and Eugenio A Flores. 2012. "Corrosion Inhibitor Activity of 1 , 3-Diketone Malonates for Mild Steel in Aqueous Hydrochloric Acid Solution Corrosion Inhibitor Activity of 1 , 3-Diketone Malonates for Mild Steel in Aqueous Hydrochloric Acid Solution." *Corrosion Science* 61(May): 171–84. http://dx.doi.org/10.1016/j.corsci.2012.04.031.
9. Gerengi, Husnu. 2012. "Anticorrosive Properties of Date Palm (Phoenix Dactylifera L .) Fruit Juice on 7075 Type Aluminum Alloy in 3 . 5 % NaCl Solution."
10. Hcl, M, M Jokar, T Shahrabi Farahani, and B Ramezanzadeh. 2016. "Leaves Extract (MAPLE) as a Green Corrosion Inhibitor for Steel In." 0: 1–17.
11. Hegazy, M A, A M Badawi, S S Abd El, and W M Kamel. 2013. "Corrosion Inhibition of Carbon Steel Using Novel N - (2- (2-Mercaptoacetoxy) Ethyl) - N , N -Dimethyl Dodecan-1-Aminium Bromide during Acid Pickling." *Corrosion Science* 69: 110–22. http://dx.doi.org/10.1016/j.corsci.2012.11.031.
12. Lahhit, N et al. 2011. "Fennel (Foeniculum Vulgare) Essential Oil as Green Corrosion Inhibitor of Carbon

Steel in Hydrochloric Acid Solution." *Portugaliae Electrochimica Acta* 29(2): 127–38.

13. Lowmunkhong, Pongsak, Dusit Ungthararak, and Pakawadee Sutthivaiyakit. 2010. "Tryptamine as a Corrosion Inhibitor of Mild Steel in Hydrochloric Acid Solution." *Corrosion Science* 52(1): 30–36.
14. Mobin, Mohammad, and Marziya Rizvi. 2016. "Polysaccharide from Plantago as a Green Corrosion Inhibitor for Carbon Steel in 1M HCl Solution Polysaccharide from Plantago as a Green Corrosion Inhibitor for Carbon Steel in 1 M HCl Solution." (October 2017).
15. Musa, Ahmed Y et al. 2012. "Inhibition of Aluminum Corrosion by Phthalazinone and Synergistic Effect of Halide Ion in 1 . 0 M HCl." *CAP* 12(1): 325–30. http://dx.doi.org/10.1016/j.cap.2011.07.001.
16. Noor, Ehteram A. 2018. "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 The Impact of Some Factors on the Inhibitory Action of Radish Seeds Aqueous Extract for Mild Steel Corrosion in 1 M H 2 SO 4 Solution." *Materials Chemistry and Physics* 131(1–2): 160–69. http://dx.doi.org/10.1016/j.matchemphys.2011.08.001.
17. Oguzie, E E et al. 2012. "Broad Spectrum Corrosion Inhibition : Corrosion and Microbial (SRB) Growth Inhibiting Effects of Piper Guineense Extract." : 3592–3601.
18. Oguzie, Emeka E et al. 2013. "Natural Products for Materials Protection: Corrosion and Microbial Growth Inhibition Using Capsicum Frutescens Biomass Extracts."
19. Othman, N Kamil, S Yahya, and M Che Ismail. 2018. "Graphical Abstract." *Journal of Industrial and Engineering Chemistry*. https://doi.org/10.1016/j.jiec.2018.10.030.
20. Quraishi, M A et al. 2010. "Green Approach to Corrosion Inhibition of Mild Steel in Hydrochloric Acid and Sulphuric Acid Solutions by the Extract of Murraya Koenigii Leaves." *Materials Chemistry and Physics* 122(1): 114–22. http://dx.doi.org/10.1016/j.matchemphys.2010.02.066.
21. Saxena, Akhil, Dwarika Prasad, and Rajesh Haldhar. 2017. "Use of Butea Monosperma Extract as Green Corrosion Inhibitor for Mild Steel in 0 . 5 M H 2 SO 4." (August).
22. Victoria, S Noyel, Rohith Prasad, and R Manivannan. 2015. "Psidium Guajava Leaf Extract as Green Corrosion Inhibitor for Mild Steel in Phosphoric Acid." 10: 2220–38.
23. Zhang, J, X L Gong, H H Yu, and M Du. 2011. "The Inhibition Mechanism of Imidazoline Phosphate Inhibitor for Q235 Steel in Hydrochloric Acid Medium OH." 53: 3324–30.