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Electrochemical Investigation Of The Corrosion Inhibition Of Mild Steel In 0.5 M HCl Using Napoleonae Imperialis Leaves Extract

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Abstract
The corrosion inhibitory behavior of Napoleonae imperialis leaves extract on mild steel in 0.5M HCl was investigated using electrochemical impedance spectrophotometer, potentiodynamic polarographer and electrochemical frequency modulation method. The inhibition efficiency of the leaves extract was investigated at different concentrations of the extract, at ambient temperature. Phytochemical analysis of the leaves extract revealed the presence of quercetin, saponins , quinine, alkaloids, flavone and tannins. Results obtained reveal that Napoleonae imperialis leaves extract is a good corrosion inhibitor and acts as a mixed type of inhibitor, affecting both anodic and cathodic reaction sites. The extract protects by forming passivation film coatings on the mild steel coupons through the mechanism of adsorption, resulting to decrease in the passive current density value. The corrosion inhibition efficiency increased with increasing extract concentrations. The highest inhibition efficiency was obtained at the highest concentration of the extract (2.5g/L). The corrosion inhibition ability of the extract is attributed to the presence of heteroatoms present in the leaves that got adsorbed on the mild steel coupons. Napoleonae imperialis leaves extract can be employed in the industries for protection of metals.

Keywords: *Corrosion, Inhibition, Napoleonae imperialis, mild steel, HCl, PDP, EIS, EFM.*

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I. Introduction

The application of acid solutions of different concentrations in removing scales and rusts formed on metal and alloy surfaces is a common practice in industries. Acidic and basic solutions are common corrosion agents that lead to deterioration of metal and alloy surfaces (Li *et al.,* 2019). Corrosion is a chemical or electrochemical attack that converts metal and alloy structures into a chemically stable form such as oxides, sulphides and hydroxides (Enyinnaya *et al*., 2021). Over the years, the use of corrosion inhibitors to fight against metal corrosion has been widely adopted (Ebenso *et al.,* 2009; Abiola *et al.,* 2010; Obi-Egbedi *et al.,* 2011). Nevertheless, some of the inhibitors (especially the synthetic ones) are harmful to both humans and the environment. Some are capable of changing the chemistry of any environment they are, especially the soil (Dariva and Galio, 2014).

Due to the above reasons, there has been a trending interest for naturally occurring inhibitors that are readily available, cost effective and more environmentally friendly (Loto *et al.,* 2006; Khadraoui *et al*., 2014). Plant materials are used as corrosion inhibitors because of the numerous phytochemicals contained in them such as alkaloids, saponins, flavonoids, quercetins, etc, which contain heteroatoms with lone pairs of electrons in their structures capable of being released when used as an inhibitor to form a protective coating on metals in acid or alkaline medium (Prabhu and Rao, 2019; Maduelosi and Timothy, 2019).

Napoleonae imperialis is known as *Soola- baato-gomen* in Ogoni language, Nigeria. Chahul *et al.,* (2019) reported the phytochemical screening of the leaves extract of *Napoleonal imperialis* to contain quercetin, saponins, quinine, alkaloids, flavone, tannins etc, which suggests their good inhibitory potentials. This study evaluated the corrosion inhibitory actions of *Napoleonae imperials* leaves extract on mild steel in 0.5 M HCl using electrochemical techniques.

II. Materials And Methods

Preparation of Coupons

The material used was mild Steel with 1 mm thickness. It was cut into 4 cm × 4 cm square and sand papered to make the surface smooth, after which the coupons were stored in a desiccator to prevent further oxidation on their surfaces. The initial and final weights of each coupon were taken before and after the corrosion work.

Collection and Preparation of Plant Extracts

The leaves of *Napoleonae imperialis* were collected from Laaboo Forest Nweol in Gokana local government area of Rivers State, Nigeria. They were washed and sun dried, after which it was ground to powder. 300g of it was soaked in 3000ml ethanol and stand for 7days for maximum equilibration and extraction. It was filtered and the ethanol was evaporated using rotary evaporator, leaving behind the extract in a paste like form. The phytochemical analysis of the extract was done using GC-MS spectrophotometer. Five different concentrations (g/L) of the extract: 0.5, 1.0, 1.5, 2.0, 2.5 g/L were prepared for the studies. The aggressive medium was 0.5M HCl.

Electrochemical Impedance Spectroscopic (EIS) Measurement

The electrochemical analysis was done in conventional three electrode cell with a Gamry Reference 3000 advanced electrochemical workstation. The reference electrode used was saturated calomel electrode (SCE). The counter electrode used was platinium electrode and the working electrode was metal (mild steel) with an exposed surface area of 1 cm^2. The electrolytes were the test solutions (0.5 M HCl) in the presence and absence of different concentrations of the *Napoleonae imperialis* extract. To get a steady state for accurate reading at open circuit potential (OCP), the metal electrode was immersed in the test solution for 3 hrs.

Measurements of Electrochemical Impedance Spectroscopy (EIS) were carried out over a broad range of frequency from 100 kHz to 10 mHz, with a 10 mV amplitude sinusoidal voltage. The Nyquist plots that provided charge transfer resistance values were gotten from the diameter of the semicircles and the corrosion inhibition efficiency ( ) was calculated using equation 1.

(1)

where R_{ct} is the charge transfer resistance without inhibitor and $R_{ct(inh)}$ is the charge transfer resistance with inhibitor.

Potentiodynamic Polarization (PDP) Measurement

The potentiodynamic polarization (PDP) measurements were done in the potential range of +250 to -250 mV in an open circuit potential (OCP) at 1 mVs^{-1} scan rate. To confirm validity of full potentiodynamic polarization scan, separate cathodic and anodic polarization experiments of all samples starting from the OCP with a new solution and a new specimen were conducted. Electrochemical parameters like corrosion potential (E_{corr}), corrosion current density (i_{corr}), cathodic and anodic Tafel slope (β_c *and* β_a) were deduced by the Tafel extrapolation technique. The corrosion inhibition efficiency ( ) was obtained using equation 2.

(2)

Where is the corrosion current density without inhibitor and i_{corr} is the corrosion current density with inhibitor.

Gamry Echem Analyst software was used to analyze data obtained from EIS and PDP curves. Each electrochemical measurement was done under the same experimental conditions to guarantee a satisfactory reproducibility.

III. Results

Table 1: Phytochemical Components and Composition of *Napoleonae imperialis* Leaves

Components	Composition (ppm)
Proanthocyanin	5.9951
Rutin	5.8959
Quinine	17.0082
Flavan-3-ol	22.5699
Ribalinidine	6.6096
Naringin	4.6357
Sapogenin	25.8884
Catechin	36.6653
Phenol	3.5333
Flavonones	3.4868
Steroids	9.8866
Kaempferol	1.5631
Phytate	0.8209
Oxalate	0.0000
Resveratrol .	9.2021
Favones	3.4902
Naringenin	1.0668

Table 2: Electrochemical Impedance Spectroscopy (EIS) Parameters of the *Ex*tract in 0.5 M HCl.

Inhibitor Conc. (g/L)	R_s (Ω)	R_{ct} (Ω)	n	C_{dl} (μFcm^{-2})	I_{EIS} (%)
Blank	0.799	97.6	0.849	56.79	-
0.5	0.831	456.9	0.852	23.87	78.6
1.0	0.858	670.3	0.859	21.63	85.4
1.5	0.894	883.2	0.866	18.25	88.9
2.0	0.926	1007.8	0.873	16.08	90.3
2.5	0.952	1290.1	0.880	15..5	92.4

Table 3: Potentiodynamic Polarization (PDP) Parameters of the Extract in 0.5M HCl

Inhibitor Conc. (g/L)	I_{corr} (*Acm^{-2}*)	-E_{corr} (V)	$_a$ (*mVdec^{-1}*)	$_c$ (*mVdec^{-1}*)	I_{PDP} (%)
Blank	1524.7	-0.590	137.8	97.4	-
0.5	316.8	-0.532	118.3	96.6	79.2
1.0	257.1	-0.507	114.7	90.5	83.1
1.5	209.5	-0.498	102.6	92.6	86.3
2.0	128.5	-0.486	96.4	91.8	91.6
2.5	101.2	-0.481	93.9	89.3	93.4

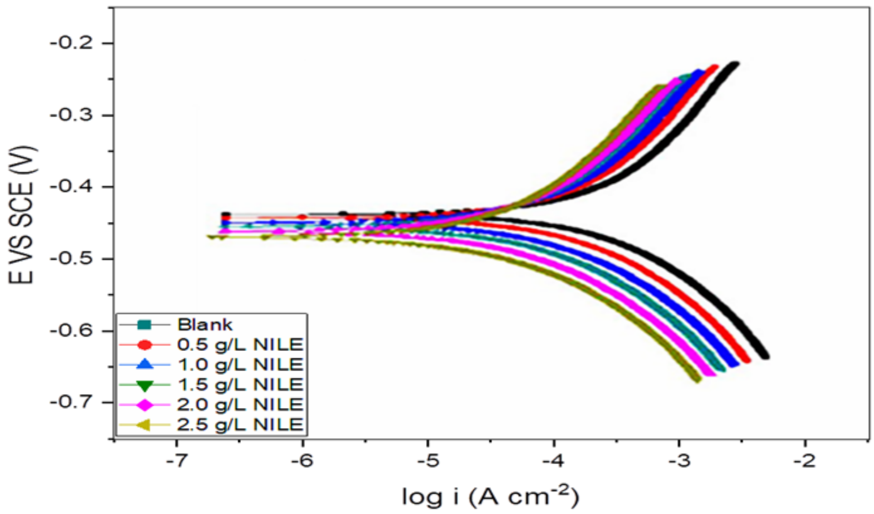


Figure 1. Graph of potentiodynamic polarization(PDP) of the extract

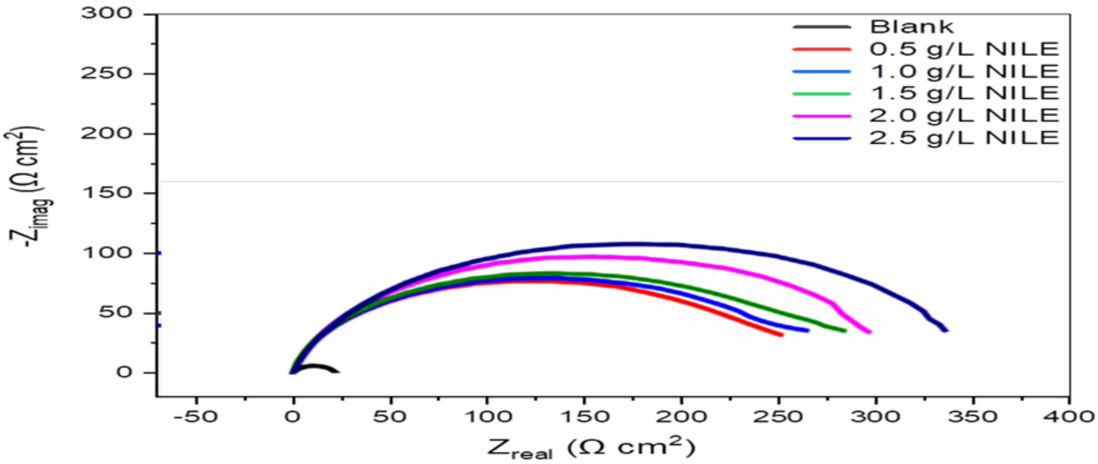


Figure 2. Effect of *Napoleonae imperialis* leaves extract on mild steel coupons in 0.5M HCl

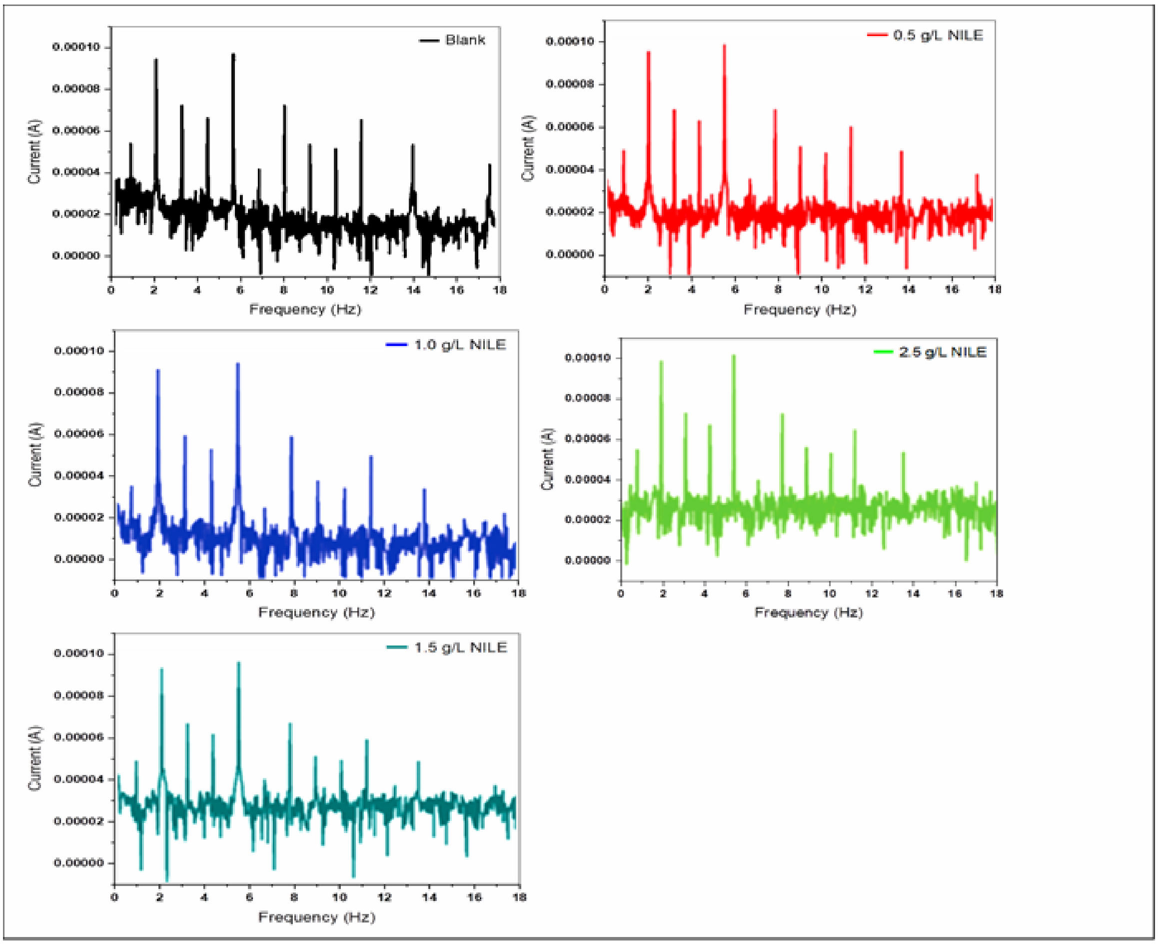


Figure 3. The spectra of electrochemical frequency modulation (EFM) of the different concentrations of the extract.

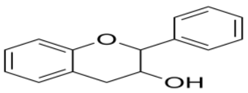
IV. Discussion

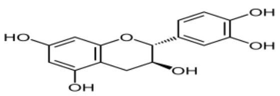
The phytochemical results presented in Table 1 show the presence of the following phytochemicals in the leaves of *Napoleonae imperialis*; Proanthocyanin, Rutin, Quinine, Flavan-3-ol, Ribalinidine, Naringin, Sapogenin, Catechin, Phenol, Flavonones, Steroids, Kaempferol, Phytate, Oxalate, Resveratrol, Favones and Naringenin.

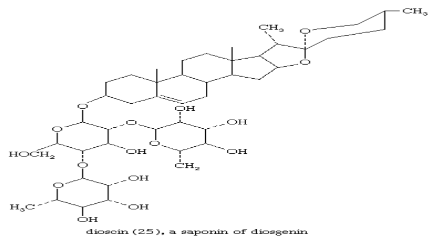
Figure 1 displays the graph of the potentiodynamic polarization of *Napoleonae imperialis* leaves extract on mild steel (Corrosion potential, E_{corr} (V/SCE) plotted against log i_{corr} (µA cm^{-2})). During the potentiodynamic polarization measurements, the potential of the working electrode was varied while observing the corrosion current (i_{corr}). The plots show the reactions at the anode and the cathode. The righthand side is the anodic branch while the lefthand side is the cathodic branch. The topmost branch shows the blank (without inhibitor). From the plots, it was observed that as the concentration of the plant extract increased, the anodic and cathodic branch decreased gradually to a lower current density, showing protection by the extract. The effect was more on the anodic branch, which indicates reduction in electron loss at the anode. The inhibition effect was felt on both the cathodic and anodic branch implying that the inhibitor is a mixed type as reported earlier by Saxena *et al.,* (2023) and Barineka *et al.,* (2024).

Figure 2 presents the results of the electrochemical impedance spectroscopic analysis of the extracts on mild steel in 0.5 M HCl solution. From the plots of the imaginary impedance ($-Z_{img}$) against the real impedance (Z_{real}); it is observed that there is a formation of a semicircle at the real impedance, beginning from zero (0) (the origin of the plots; region of high impedance to about 450 Ω (region of low impedance). The beginning of the semicircle measures the solution resistance while the end of the semicircle measures the charge transfer resistance as shown in Table 2. From the chart, the diameter of the semicircle increased as the concentration of the extract increased. This may be due to the adsorption of the active components present in the extract on the surface of the metal, thereby reducing the rate at which electrons move from the metal, hence increasing the impedance. The blank had the least diameter of the semicircle and this is attributed to the absence of inhibitor in it, which would have reduced the flow of electrons from the metal. Table 2 shows 92.4% maximum inhibition efficiency in the 2.5g/L extract concentration. Similar observation has been made (Lebrini *et al.,* 2010; Barineka *et al.,* 2024)

Table 3 presents the corrosion current (I_{corr}), corrosion potential (E_{corr}), cathodic slope β_c (mV dec^{-1}), anodic slope β_a (mV dec^{-1}), and **(%)** of the extract. From **the table, t**he anodic slope (β_a) values decreased more than the cathodic slope (β_c) values, suggesting that the inhibition is affecting the anodic branch more than the metal dissolution branch, and this helps to prevent corrosive attack on the metal. The presence of the *Napoleonae imperialis* leaves extract decreased the corrosion current (I_{corr}) from 1524.7 to 101.2 (µA cm^{-2}). This observation suggests that the presence of the extract in the acid test solution retarded the anodic reaction (loss of electrons) of the metal. The percentage inhibition efficiency obtained is directly proportional to the extract concentration. The decrease in corrosion current is also attributed to the phytochemicals present in the leaves, which contain heteroatoms that can easily donate their lone pair of electrons to the metal surface thereby preventing the oxidation of the metal. The extract also protects the metal by forming a protective coating through the mechanism of adsorption on the metal surface. This also that reduces the rate at which the metal losses electrons. Similar report was made earlier by Enyinnaya *et al.,* (2021).







1. Molecular structure of Flavon-3-ol. 2. Molecular structure of Catechin
3. Molecular structure of Saponin

Figure 3 shows the spectra of electrochemical frequency modulation of the leaves extract at different concentrations and the plot of current against frequency. Two prominent peaks are common at all the input frequencies in the entire spectra in figure 3 . There are several other peaks higher than the background noise shown on all the spectra. The presence of two prominent peaks indicates that the extract acts as a mixed type of inhibitor. Arias-Montoya *et al.,* (2017) made similar observation in their study.

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V. Conclusion

The results of the electrochemical studies of the corrosion inhibition of mild steel in 0.5M HCl using *Napoleonae imperialis* leaves extract confirm that the extract is a good corrosion inhibitor. The leaves contain good phytochemicals with lone pairs of electrons. The corrosion inhibition efficiency of the extract increases with increase in concentration. The highest inhibition efficiency was obtained at the highest concentration of the extract (2.5g/L). The inhibition is attributed to the presence of heteroatoms present in the leaves. EIS, PDP and EFM are good electrochemical tools for corrosion inhibition studies.

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