

Electrochemical Corrosion Behaviour of *Vernonia amygdalina* on Mild Steel in Acid Environments

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Abstract: The corrosion inhibition characteristics of *Vernonia amygdalina* stem extract were studied using two electrochemical techniques of potentiodynamic polarization and electrochemical impedance spectroscopy. The study was carried out in a dual-acid environment to ascertain the effect of the two acids on the corrosion inhibition capacity. The results obtained showed that *Vernonia amygdalina* stem extract inhibited the corrosion of mild steel corrosion comparatively in both acid environments. The potentiodynamic polarization results showed the extract to be a mixed type inhibitor, and decreased the corrosion current density, while the electrochemical impedance spectroscopy showed that the extract acted by decreasing the dielectric constant and increasing the charge transfer resistance, attributable to adsorption of the molecules of *Vernonia amygdalina* stem extract to metal/acid interface.

Keywords: Adsorption; Corrosion inhibition; Electrochemical impedance spectroscopy; Pipeline steel; Potentiodynamic polarization; *Vernonia amygdalina*

1. Introduction

Corrosion of metallic and non-metallic materials has been an age long enigma. This problem was exuberated after the industrial revolution of 1760-1840, due to heavy reliance on iron and other metals for equipment and infrastructure. Iron and other metals are prone to worsening corrosion because of their electrochemical and thermodynamic properties.^[1-3] Corrosion is electrochemically and thermodynamically inevitable. In as much, the industrial revolution seemed an advantageous developmental stage in human earthly existence, enough attention was not earlier given corrosion mitigation. This led to heavy cost of corrosion and attendant economic and environmental consequence such petroleum spillage due to equipment failure. However, they are recent advances in corrosion mitigation. One the advances are in development of eco-friendly, cheap and renewable corrosion inhibitors to counter the negative consequences of earlier corrosion inhibitors.^[4-7]

As more acceptable corrosion inhibitors are daily developed, there is also additional need to understand the corrosive environment and its effect on corrosion inhibition performance. The common corrosive environments are acidic, basic and neutral or near neutral environments. There are different types of acids, among them are those associated to two common non-metallic elements, chlorine and sulphur. These are sulphuric acid and hydrochloric acid. These two acidic compounds are responsible for most acidic behaviour of our environment. Interestingly, many researchers have

reported corrosion inhibition by plant extracts in these environment,^[4-10] The major impediment against some phyto extract as corrosion inhibition has been the competition as food source thereby threatening food security.

Though, the corrosion inhibition capacity of *Vernonia amygdalina* extract (Bitter Leave - BL) in Hydrochloric acid and Sodium hydroxide using gravimetric method has been previously reported,^[10-11] this paper reports the corrosion inhibition characteristic of *Vernonia amygdalina* stem extract on the corrosion of mild steel in sulphuric acid and hydrochloric acids using electrochemical techniques. These two acids are more common in our environment. While the leaf of *Vernonia amygdalina* plant is mostly used as food and medicinal source,^[12] the stem is usually discarded as waste. The stem was therefore used to study its corrosion inhibition characteristics. These tend to create value of waste to wealth and reduce the challenge of municipal waste management.

2. Materials and Methods

2.1. Material preparation

2.1.1. Extract

Stems of *Vernonia amygdalina* were harvested from its farm in Trans Amadi area of Port Harcourt, Rivers state, Nigeria. The stems were at various stages of maturity. They were de-leaved, cut into small pieces and allowed to dry under the sun for three days. The dry

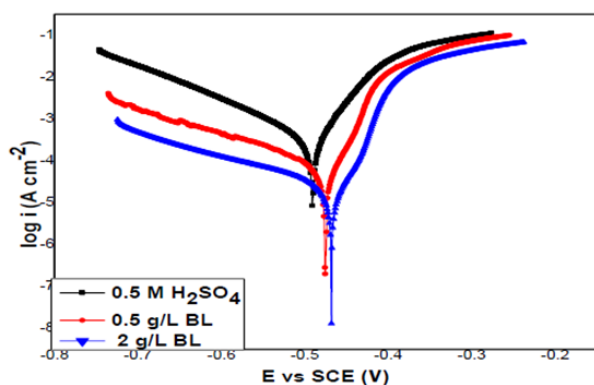


Fig. 1. Potentiodynamic polarization plot for the electrochemical corrosion of mild steel in 0.5 M H₂SO₄ with and without BL stem extract.

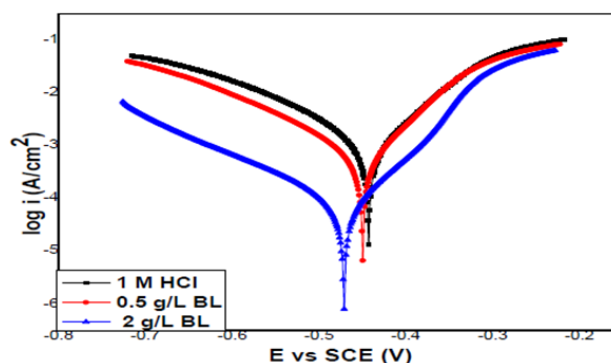


Fig. 2. Potentiodynamic polarization plot for the electrochemical corrosion of mild steel in 1.0 M HCl with and without BL stem extract.

stems were further broken down with sterile knife before been pulverized in a blender. About 500 g blended *Vernonia amygdalina* stem were packed in 1000 ml volumetric flask and 98 % ethanol was added to efficiently cover the extract. The set-up was allowed to stay for 48 hours. After which, it was filtered. The ethanol solvent was recovered using rotary evaporator. The extract was further dried using thermo-stated water bath at 30 °C. The extracts were then used to prepare diluents of extract in 0.5 M H₂SO₄ and 1.0 M HCl solutions.

2.1.2. Metal coupons

The metal coupons were obtained from Engineering workshop, University of Port Harcourt. They were mechanically cut into 1 × 1 cm² shape, polished with 200 – 2000 grade SiC paper, under distilled water. They were thereafter rinsed with absolute ethanol, acetone and dried in warm air. The ready coupons were stored in an active desiccator till; it was used as working electrode in the electrochemical set-up.

2.2. Solution Preparation

The corrosive medium was prepared as serial diluents of 0.0 to 2.0 g/L BL extract in 0.5 and 1.0 M, H₂SO₄ and HCl respectively.

2.3. Electrochemical experiments

The electrochemical determinations comprising of Potentiodynamic polarization and electrochemical impedance spectroscopy were performed using a three-electrode cell assembly connected to a VersaSTAT 400 complete DC Voltmeter and Corrosion system from Princeton Applied Research, with V3 studio software. A platinum foil of dimension 2 X 2 cm² and a saturated calomel electrode, served as the counter and reference electrodes respectively. While the already prepared Pipeline steel served as the third and working electrode. The working electrode was encapsulated with epoxy resin, in such a way that only one side with 1 cm² was exposed. All the experiments were conducted in an open, aerated and unperturbed cell. The experiments were carried at open circuit potential (OCP) after 30 minutes at a temperature of 303 ± 1 °K. The experiments were repeated in triplicate to ensure reproducibility.

2.4. Potentiodynamic polarization (PDP) determination

The potentiodynamic polarization (PDP) experiments were done at a cathodic potential of -250 mV to anodic potential of +250 mV vs. OCP at a scan rate of 0.333 mV s⁻¹. The PDP parameters were extrapolated, the corrosion current density (I_{corr}), equilibrium corrosion potential (E_{corr}) and other Tafel parameters. The Corrosion Inhibition efficiency (ηE) were evaluated using I_{corr} values by applying the equation:-

$$\eta E(\%) = \frac{I_{corr}^0 - I_{corr}^i}{I_{corr}^0} \times 100 \quad (1)$$

I_{corr}^0 and I_{corr}^i are corrosion current densities in the uninhibited and inhibited cells respectively.

2.5. Electrochemical impedance spectroscopy (EIS) determinations

The electrochemical impedance spectroscopy (EIS) experiments were conducted at open circuit potential over a frequency range of 100 kHz to 10 mHz using a signal of 5 mV amplitude. The corrosion inhibition efficiency was determined using the charge transfer resistance (R_{ct}) with the equation:

$$\eta E(\%) = \frac{R_{cti} - R_{ct}}{R_{cti}} \times 100 \quad (2)$$

R_{cti} and R_{ct} are the charge transfer resistance with and without BL extract respectively.

3. Results and Discussions

3.1. Potentiodynamic polarization (PDP) determination

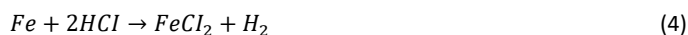
The potentiodynamic polarization studies of the effects of *Vernonia amygdalina* stem ethanoic extract (BL) on the corrosion of mild steel in 0.5 M H₂SO₄ and 1.0 M HCl environments are presented in Figs. 1 and 2 respectively. There was a comparable and remarkable effect of BL on both the anodic and cathodic arms of the electrochemical corrosion process. In both cells, the metals went into remarkable oxidation with consequent active dissolution without transition to a passive region within the studied potential range.

Table 1. Potentiodynamic polarization parameters for mild steel in 0.5 M H₂SO₄ with and without BL stem extract.

Inhibitor concentration. (g/L)	Blank 0.5 M H ₂ SO ₄	0.5 g/L BL 0.5 M H ₂ SO ₄	2.0 g/L 0.5 M H ₂ SO ₄
Inhib. Eff. (%)		48.4	90.6
<i>i</i> _{corr} (A/cm ²)	1359	701.4	128.3
<i>E</i> _{corr} (mV vs SCE)	-495.3	-472.4	-472.4

Table 2. Potentiodynamic polarization parameters for mild steel in 1.0 M HCl with and without BL stem extract

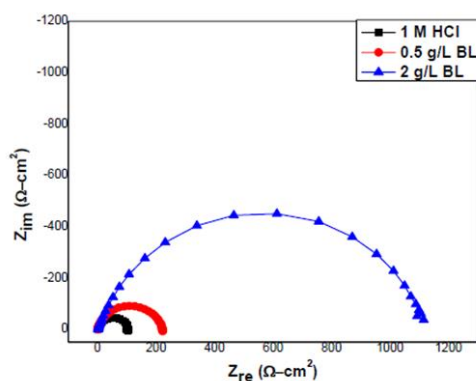
Inhibitor concentration. (g/L)	Blank 1.0 M HCl	0.5 g/L BL 1.0 M HCl	2.0 g/L BL 1.0 M HCl
Inhib. Eff. (%)		53.1	89.8
<i>i</i> _{corr} (A/cm ²)	185.0	86.7	18.8
<i>E</i> _{corr} (mV vs SCE)	-525.4	-518.4	-459.3



However, the introduction BL stem extract affected both the cathodic and anodic arm. This shows the BL stem extract functions as a mixed type corrosion inhibitor. These trends have been severally reported by researchers.^[13-15] The PDP electrochemical parameters are presented in Tables 1 and 2 respectively. Table 1 and 2 clearly indicates a decrease in the corrosion current density in both acids, indicating the corrosion inhibition character of BL stem extract.^[15-16] The results of the calculated (equation 1) corrosion inhibition efficiency of both acids indicates an increase in the inhibition efficiency as the concentration of BL extract increase.^[14-17] Another remarkable observation is the near values obtained in both acids. This is attributed to the basicity of both acids two for sulphuric acid and one for hydrochloric acid (equations 3 and 4). From equations 3 and 4, one mole of Sulphuric acid liberated one mole of hydrogen while two moles of hydrochloric acid liberated one mole of hydrogen. This translates to the fact that sulphuric acid is a stronger acid at same concentration of both. Interestingly, this difference in acidic strength is compensated by the difference in concentration of 0.5 M for H₂SO₄ and 1.0 M for HCl which resulted in the close values obtained for both. Therefore, H₂SO₄ is double the strength of HCl.

3.2. Electrochemical Impedance Spectroscopy (EIS)

The electrochemical corrosion characteristics of *Vernonia amygdalina* stem ethanoic extract (BL) on the acid-mild steel interface for the corrosion of mild steel in acid environment was studied with Hydrochloric acid with and without BL, and presented in the Nyquist plot Fig. 3. The Nyquist plots are depressed capacitive semicircles in the high frequency region corresponding to a single time constant. The depression at the center of the real axis is characteristic of solid electrodes that exhibit frequency depression. This behaviour has been previously reported by Oguzie et al., 2014, Khaled, 2009, Popova et al, 2003.^[18-20] Interestingly, the capacitive loops are similar both in the inhibited and uninhibited system suggesting that the presence of BL does not alter the corrosion mechanism. Basically, there are two resistances, solution resistance (*R*_s) and charge transfer resistance (*R*_{ct}). If the transfer function is represented by the solution resistance shorted by a capacitor C which is parallel to charge transfer resistance, equation 5.^[21] This is

**Fig. 3.** Electrochemical Impedance spectroscopic response for the corrosion of mild steel in 1.0 M HCl with and without BL.**Table 3.** Electrochemical Impedance spectroscopic parameters for the corrosion of mild steel in 1.0 M HCl with and without BL

System	<i>R</i> _s (Ω cm ²)	<i>R</i> _{ct} (Ω cm ²)	<i>N</i>	<i>C</i> _{dl} (F cm ⁻²)	IE(%)
1 M HCl	1.659	100.2	0.89	6.92E-05	
0.5g/L BL	2.113	208	0.88	7.62E-05	51.7
2g/L BL	2.782	1003	0.89	7.21E-05	90.2

applied mainly to homogenous systems with one time constant and the center of the semicircle lies on the abscissa, unable to explain the depression of the semi-circular capacitive loop. If a non-ideal frequency response occurs, the capacitor is exchanged with a constant phase element (CPE) with impedance *Z*_{CPE}, equation 6.^[18]

$$z(\omega) = R_s + \left(\frac{1}{R_{ct}} + j\omega C \right)^{-1} \quad (5)$$

$$Z_{CPE} = Q^{-1}(j\omega)^{-n} \quad (6)$$

Where Q and n represents constant phase element and exponent respectively while *j* = (-1)^{1/2} is an imaginary number, *ω* is the angular frequency in rad s⁻¹ (*ω* = 2π*f*), where *f* is frequency in Hertz. Interestingly, BL caused an increase in the charge transfer resistance from the uninhibited to the inhibited cell and consequent decrease in *C*_{dl} values. A physical observation reveals an increase in the diameter of the Nyquist semicircles translating to higher impedance in the inhibited cell by BL. This shows the obvious corrosion inhibition character of *Vernonia amygdalina* stem extract. While the decrease in the *C*_{dl} value indicates decrease in dielectric constant or increase double layer thickness caused by adsorption of inhibitor molecules at the metal/acid interface.

The corrosion electrochemical impedance spectroscopic parameters are presented in Table 3. The values of the corrosion inhibition efficiency calculated from equation 4, shows an increase as the concentration BL was increased. The trend has been severally reported.^[16-18]

The values of the corrosion inhibition efficiency calculated from potentiodynamic polarization and electrochemical impedance studies are in agreement, substantiating the good corrosion inhibition potentials of *Vernonia amygdalina* stem extract.

4. Conclusions

Studies on the electrochemical corrosion characteristics of *Vernonia amygdalina* stem ethanoic extract in acid environments showed that it is a good inhibitor of steel corrosion acid media. However, the basicity of the acid is an important factor in the inhibition performance. The extract exhibited mixed inhibition characteristics, while the mechanism of corrosion inhibition was attributed to adsorption of the molecules of *Vernonia amygdalina* stem extract on the metal/acid interface.

Conflicts of Interest

The authors declare no conflict of interest.

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