

Corrosion Inhibition Efficiency of *Azadirachta Indica* on AISI 316L Austenitic Stainless Steel in Hydrochloric Acid Solution

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Abstract

A study on the corrosion inhibition efficiency of *Azadirachta Indica* on AISI 316L austenitic stainless steel in 1 M hydrochloric acid solution was conducted with both potentiodynamic polarization and weight loss methods, respectively. The corrosion rate, inhibition efficiency, weight loss of the steel and other potentiodynamic parameters were evaluated in varied concentrations in the range of 0 to 7 g/cm³ of the inhibitor for a duration of 360 hours respectively. The results obtained indicated that maximum positive inhibitive corrosion activity was achieved at an optimum concentration of 5 g/cm³ beyond which negative inhibitive corrosion activity sets in. Both the potentiodynamic polarization and weight loss test results were in concurrence with the effectiveness of the use of *Azadirachta Indica* as a green corrosion inhibitor.

Keywords: *Azadirachta Indica*, Austenitic stainless steel, Inhibition, HCl, Potentiodynamic polarization

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1. Introduction

Corrosion leads to the deterioration of materials due to interactions with their surroundings and causes significant economic loss annually. One of the primary factors contributing to the corrosion of stainless steel is the existence of acids and chlorides, which is a major concern in engineering sectors (Sanni *et al.*, 2018). Stainless steel possesses a strong resistance to corrosion which creates a protective layer of chromium-rich oxide in the presence of oxygen at lower temperatures forming a barrier against its environment. However, this coating can be compromised when exposed to chloride compounds like NaCl and HCl (Eugene *et al.*, 2016; Aimad *et al.*, 2021). Corrosion pits form in two stages: initial metastable growth followed by stable growth (Madu *et al.*, 2019). Corrosion inhibitors are used to slow down the deterioration of this layer in various media. These inhibitors can decrease the rate of anodic oxidation, cathodic reduction, or both. The inhibitors create a protective film on the metal surface. It has been postulated that the inhibitors adhere to the metal surface either through physical (electrostatic) adsorption or chemical adsorption.

Corrosion inhibitors, which can be synthetic or natural chemicals, reduce the rate of corrosion of

steel when present, even in small quantities, in a corrosive environment. Generally speaking, the ability of materials to prevent metal corrosion depends on the presence of heteroatoms (O, N, S, etc.), their structure, their electrons, the direction and nature of the donor electrons of the π orbital (Pruthviraj, *et al.*, 2021; Adama and Onyechu, 2022). Furthermore, as the guidelines for the use of inhibitors become stricter in the ecological context, the development of biodegradable and environmentally friendly inhibitors constitutes an important issue. This group of corrosion inhibitors has many advantages in that they are generally chemical-free, inexpensive, environmentally friendly, effective, and produced by stable sources. Certain plant extracts have been shown to have beneficial properties for inhibiting corrosion. The anti-corrosion properties are due to certain phytochemicals present in this plant.

Most of the acid inhibitors that are widely recognized are organic compounds that contain nitrogen, sulphur and oxygen atoms. In acidic environment, heterocyclic corrosion inhibitors and their derivatives that also contain nitrogen, sulphur and oxygen are the most effective inhibitors. Their effectiveness as inhibitors is because they create a protective layer of organic on the surface of a metal.

The selection of a corrosion inhibitor is influenced by various factors, such as cost, quantity and the impact it has on the environment (Eugene *et al.*, 2016).

Extensive work has been done studying the inhibiting and/or stimulating phenomena of organic compounds on ferrous as well as nonferrous metals. Organic inhibitors have a critical concentration value, below which inhibition ceases and stimulation begins. Incorrect choice or the use of organic inhibitors in acid solutions can lead to corrosion stimulation and/or hydrogen penetration into the metal. In general, stimulation of corrosion is not related to the type or structure of the organic molecule. This adverse action depends on the type of acid. For example, (4-dimethylamino-phenylantipyrilcarbinol and its derivatives) at a 10^{-4} concentration inhibited attack of steel in hydrochloric acid solutions, but stimulated attack in sulphuric acid solutions. Studies have reported that the impact of inhibition is primarily influenced by various physical and chemical properties of the organic inhibitor including its functional groups, steric effects, electronic density of donor atoms and orbital characteristics of electrons donations. The ability of organic compounds to inhibit the dissolution of metallic species is typically linked to adsorption interactions between the inhibitors and the metal surface. The planarity (p) and presence of lone pairs on N, O and S atoms are crucial structural attributes that govern the adsorption of these molecules onto the surface of the metal. Recent studies have shown that organic compounds containing polar functional groups are quite efficient in minimizing the effect of corrosion of metals in addition to heterocyclic compounds containing polar groups and π -electrons. Examples of heterocyclic compounds are N-heterocyclic compounds such as triazole, tetrazole, pyridine, etc. used in investigating their inhibition efficiency in acidic media on steel species. Conversely, the surface state and excess charge of the metal have also been reported to affect the adsorption behaviour of inhibitor molecules onto the metal surface. Generally, the tendency to form a stronger coordination bond, consequently resulting in high inhibition efficiency, increases in the order of $O < N$

$< S < P$. The molecular structure and size of the organic compound influence their inhibitive action. The structures with benzene rings are particularly effective inhibitors. Efficiency decreases with increasing chain length.

Previous studies have investigated corrosion inhibition capabilities of plant extracts on stainless steels in halide containing media. Nnanna *et al.* (2011), did a Comparative study of corrosion inhibition of aluminium alloy of type AA3003 in acidic and alkaline media by *Euphorbia Hirta* extract. Rajendran *et al.* (2012), carried out a research on the inhibitive effect of extract of flowers of *Cassia Auriculata* in 2 M HCl on the corrosion of aluminium and mild steel. Alcoholic extract of *Andrographis Paniculata* as corrosion inhibitor on stainless steel in natural sea water environment was investigated by Rani & Selvaraj (2012), Ajanaku *et al.*, (2015) reported on the adsorption properties of *Azadirachta indica* extract on corrosion of aluminium in 1.85 M hydrochloric acid., Madu *et al.* (2019), undertook a study of the corrosion inhibition efficiency of *terminalia catappa* leaves extracts on stainless steel in hydrochloric acid, but this study seeks to investigate the corrosion inhibition efficiency of *Azadirachta Indica* (AZI) on AISI 316L austenitic stainless steel in hydrochloric acid solution.

2. Materials and methods

2.1 Materials

Commercial AISI 316L austenitic stainless steel with elemental chemical composition by weight as shown in Table 1, obtained from a local vendor was used for this study. The steel was sectioned into electrodes measuring 20 mm × 20 mm × 10 mm. Thereafter, the steel coupons were abraded with different grits of silicon carbide papers (100 to 800 grits). The steel coupons were then polished with diamond paste to achieve a mirror-like finish. Next the steel coupons were washed with double distilled water and thoroughly rinsed with acetone to remove any impurities, then they were dried to remove any trace of moisture and stored in desiccators for potentiodynamic polarization and weight loss tests according to ASTM G59-97.

Table 1: Elemental composition of AISI 316L steel used in this study

Element	Cr (%wt.)	Ni (%wt.)	Mn (%wt.)	S (%wt.)	Mo (%wt.)	C (%wt.)	Si (%wt.)	N (%wt.)	P (%wt.)	Fe (%wt.)
AISI 316L	18.000	14.000	2.000	0.030	2.500	0.030	1.000	0.10	0.045	Bal.

2.2 Method

2.2.1. Preparation of inhibitor

Fresh, matured and healthy AZI leaves were obtained, washed and dried before being ground into powdered form, and soaked in acetone for 4 days after which the solutions were triple-filtered. The filtrate was subsequently subjected to evaporation process in order to remove any trace of the solvent, and stored at 20 °C in an airtight bottle. The AZI leaf extract obtained was used in preparing various concentrations of the extract by dissolving different masses of the extract into hydrochloric acid solutions. In order to replicate the results, the experiment was conducted several times at ambient conditions, by separately immersing pre-weighed samples in 1 M HCl acid solution contained in 250 cm³ beakers at varying concentrations of the AZI extract for a duration of 360 hours (15 days). After each immersion time, the test coupons were thoroughly washed with distilled water and rinsed with acetone. After drying in air, the test coupons were reweighed to determine the weight loss.

2.2.2 Potentiodynamic polarization tests.

The Potentiodynamic polarization tests were performed according to ASTM G59-97. A graphite rod was used as the auxiliary electrode and a silver chloride electrode (Ag/AgCl) as the reference electrode. AISI 316L austenitic stainless steel electrodes embedded in resin with an unconcealed surface area of 1 cm² were prepared. Potential applied against current was plotted. Corrosion current density (j_{corr}) and Corrosion potential (E_{corr}) values were obtained using the Tafel extrapolation method. In the anodic and cathodic curves, the linear slope part gives Tafel anodic and cathodic constants (β_a and β_c) respectively. The polarization resistance R_p was calculated from Equation (1) and results were recorded in Table 2.

$$R_p = \frac{B}{j_{corr}} \quad (1)$$

where B is known as Stern-Geary Coefficient and is given by Equation (2)

$$B = \frac{\beta_a \beta_c}{2.303(\beta_a + \beta_c)} \quad (2)$$

The corrosion rate (CR) (Equation 3), the inhibition efficiency (\mathcal{E}) (Equation 4) and degree of surface coverage (Θ) (Equation 5), were calculated from the mathematical relationships

according to ASTM G102-89 (2015). Plots of degree of surface coverage (Θ) against corrosion current density, inhibition efficiency (\mathcal{E}) and corrosion rate (mm/year) against inhibitor concentration were obtained from the recorded readings.

$$CR = \frac{3.27 \times 10^{-3} \times j_{corr} \times W_{eq.}}{\rho} \quad (3)$$

where j_{corr} is in $\mu\text{A}/\text{cm}^2$, $W_{eq.}$ is the equivalent weight of the steel sample in g, ρ is the density in g/cm^3 and 3.27×10^{-3} is a constant for calculation of corrosion rate in mm/yr. The inhibition efficiency was obtained from corrosion current density in Equation (4):

$$\mathcal{E} = \frac{j_{corr_1} - j_{corr_2}}{j_{corr_1}} \times 100 \quad (4)$$

where j_{corr_1} and j_{corr_2} are the corrosion densities with and without inhibitor, respectively. The degree of surface coverage (Θ) was calculated from Equation (5).

$$\Theta = 1 - \frac{j_{corr_2}}{j_{corr_1}} \quad (5)$$

2.2.3 Weight loss method

The weight loss method was utilized for corrosion measurements according to Afabor (2022). Corrosion rate CR was determined by Equation (6) following ASTM G102-89.

$$CR = 87.6 \times \frac{\Delta W}{\rho A T} \quad (6)$$

where: ΔW = weight loss in mg, ρ = steel sample density in g/cm^3 , A = total exposed surface area of steel sample in cm^2 , T = time of exposure of the steel sample in hours, 87.6 is a constant used for corrosion rate calculation in mm/yr. Plot of inhibitor concentration versus weight loss was obtained.

3. Results and discussion

Potentiodynamic polarisation and weight loss methods were used to study the corrosion inhibition of stainless steel in 1 M HCl solution with and without AZI inhibitor. The potentiodynamic polarisation plot of the activity of the corrosion behaviour of AZI in 1 M HCl solution are shown in Fig. 1. The experimental results from the potentiodynamic polarisation tests are presented in

Table 2. Plot of inhibitor concentration against inhibition efficiency, inhibitor concentration against inhibition efficiency and corrosion current density against surface coverage are presented in Fig. 2, 3 and 4, respectively. From Fig. 2, it was revealed that the effectiveness of the inhibitor is observed to appreciate with higher concentration, attaining optimum efficiency of 85.30% at a concentration of 7 g/cm³ beyond which the action of the concentration declined to negative after a duration of 360 hours. From Fig. 3, it is observed that there was a significant reduction in corrosion rate, attaining the lowest corrosion rate at the optimum concentration of 7 g/cm³ after which there was slight increase in corrosion rate. Also, the plot of corrosion current density versus surface coverage in Fig. 4, displayed an inverse relationship exist between them, indicating that as more of the inhibitor are adsorbed to the surface of the steel, the lesser the number of active sites for corrosion activity. Experimental data from Table 1 and Fig. 1, 2, and 3 clearly indicate that increasing the concentration of the AZI inhibitor shifted the corrosion potentials to more passive region, which

shows better corrosion resistance of the steel in hydrochloric acid. The difference in corrosion rate of 316L austenitic steel in HCl acid is essentially attributable to the degree of adsorption of AZI inhibitor on the steel surface. It was observed that corrosion rate and corrosion current density reduced appreciably with higher inhibitor concentration. This assertion is supported by the report of Manoj *et al.* (2021)

The results obtained from weight loss test are displayed in Fig. 3 and a bar plot of inhibitor concentration versus weight loss is presented in Fig. 5 for 316L austenitic stainless in AZI inhibited solution of 1 M HCl acid. The weight loss value was found to decrease with higher concentrations of inhibitor up to an optimum concentration value of 5 g/cm³ before maintaining a uniform weight loss values for inhibitor concentration greater than that of the optimum. This is in agreement with the findings of Sribharathy *et al.* (2018). Experimental data from Table 3 further validates that inhibitor concentration of 5 g/cm³ exhibited the maximum inhibition efficiency and minimum corrosion rate values.

Table 2: Electrochemical Parameters obtained for 316L stainless steel in 1 M HCl with and without AZI inhibitor

Inhibitor Concentration (g/cm ³)	Corrosion Potential E _{corr} (mV)	Corrosion Current Density j _{corr} (μA/cm ²)	Anodic Tafel Constant β _a (mV/dec.)	Cathodic Tafel Constant β _c (mV/dec.)	Polarization Resistance R _p (Ω/cm ²)	Corrosion Rate CR (mm/yr.)	Inhibition Efficiency ε (%)	Surface Coverage θ
0.00	-344.7	69.4	123	156	430.3	0.81942	-	-
1.00	-234.8	27.3	132	110	954.3	0.32234	60.66	0.6066
2.00	-216.5	22.0	135	106	1170.9	0.25976	68.23	0.6823
3.00	-218.1	18.7	121	104	1298.7	0.22079	73.05	0.7305
4.00	-206.4	17.2	129	96	1389.5	0.20308	75.22	0.7522
5.00	-199.0	10.9	130	100	2251.6	0.12870	84.29	0.8429
6.00	-213.6	10.2	122	95	2273.7	0.12043	85.30	0.8530
7.00	-213.9	13.6	110	98	1654.7	0.16058	80.40	0.8040

Table 3: Weight loss corrosion measurements at 360 hours for AZI in 1 M HCl acid solution

S/N	Inhibitor Concentration (g/cm ³)	Weight loss (mg)	Corrosion Rate CR (mm/yr.)	Inhibition Efficiency ε (%)
1	0.0	1.924	0.02926	0
2	1.0	0.721	0.01097	62.53
3	2.0	0.583	0.00887	69.70
4	3.0	0.522	0.00794	72.87

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5	4.0	0.468	0.00712	75.68
6	5.0	0.263	0.00400	86.33
7	6.0	0.264	0.00402	86.28
8	7.0	0.264	0.00402	86.28

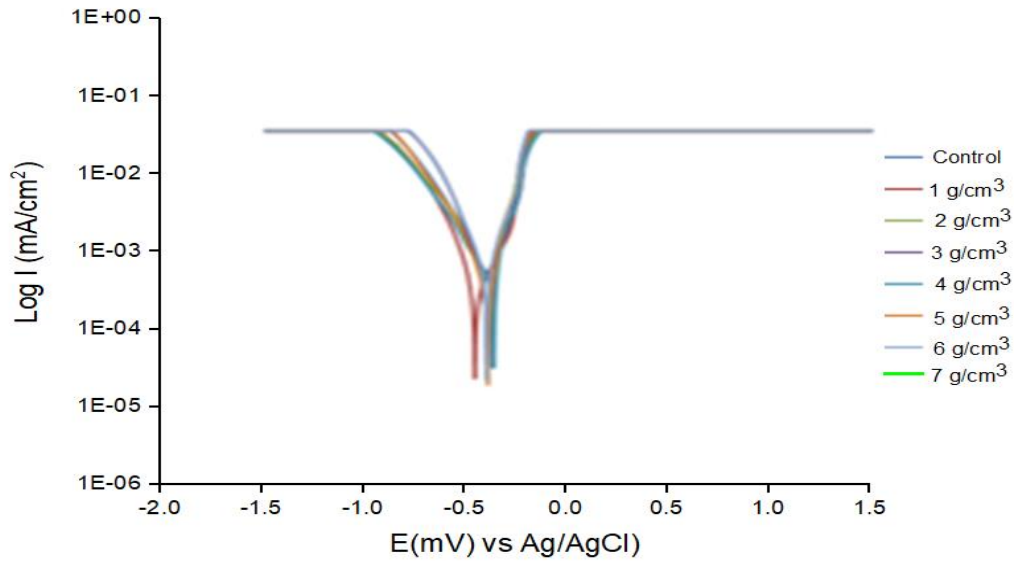


Fig. 1: Potentiodynamic polarization plots for AZI in 1 M HCl

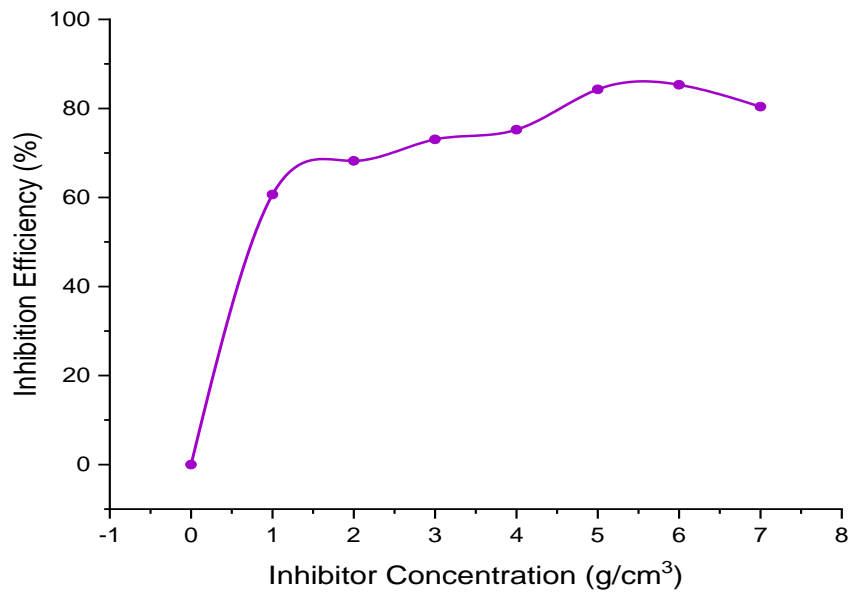


Fig. 2: Inhibitor concentration versus inhibition efficiency

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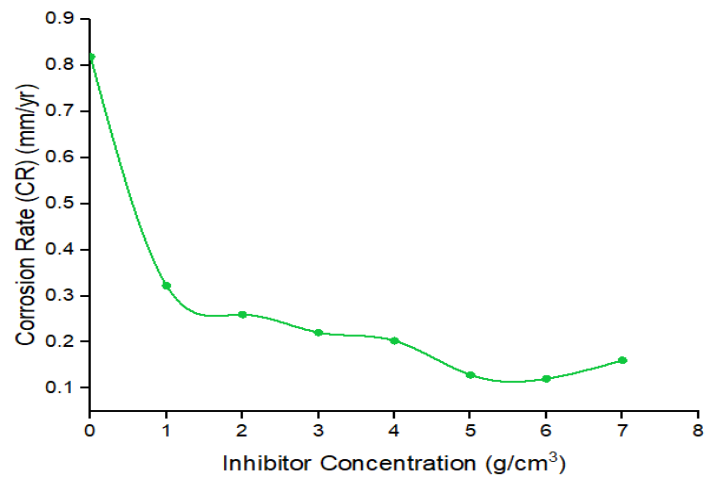


Fig. 3: Inhibitor concentration versus corrosion rate

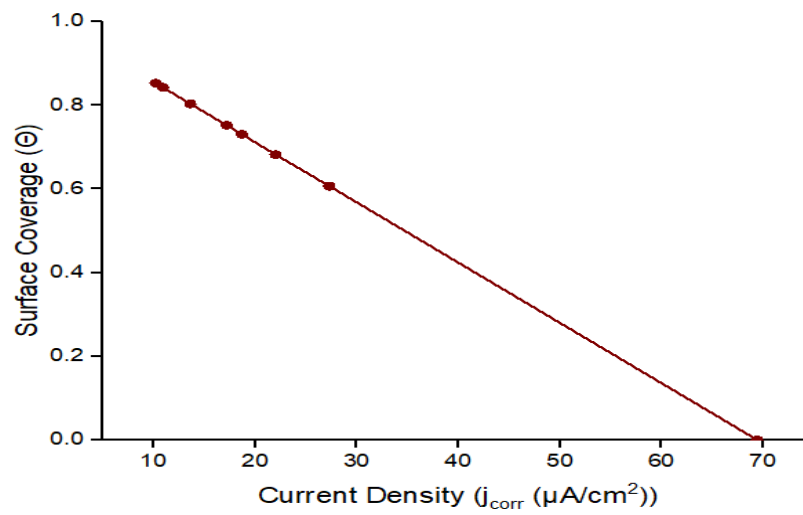


Fig. 4: Corrosion current density versus surface coverage

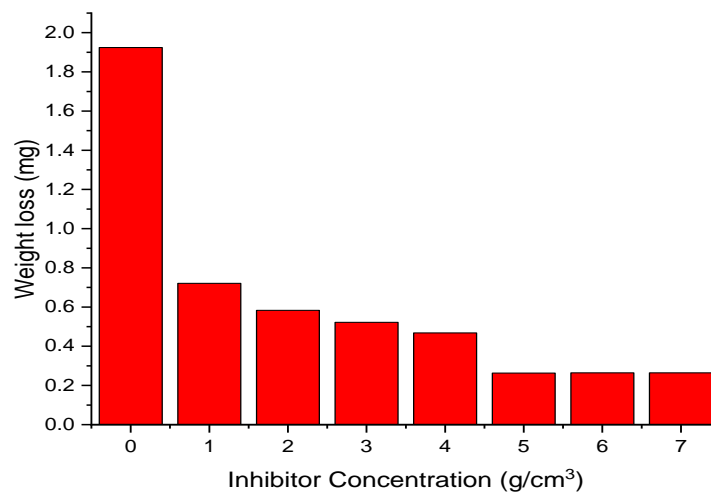


Fig. 5: Inhibitor concentration versus weight loss

4. Conclusion

The corrosion behaviour of 316L austenitic stainless steel in 1 M HCl acid solution inhibited with *Azadirachta Indica* shows that it is an effective green corrosion inhibitor in the stated medium. Results obtained from this study indicate that *Azadirachta Indica* which is an organic inhibitor has a critical concentration value (5 g/cm³), above which inhibition ceases and stimulation begins.

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