

Insight into the Anti-Corrosion Performance of *Spinacia Oleracea* Extracts as a Sustainable Corrosion Inhibitor for Copper in 1M Solution of Nitric Acid

O. Sanni, S.A. Iwarere, M.O. Daramola*

Sustainable Energy & Environment Research Group (SEERG), Department of Chemical Engineering, Faculty of Engineering, Built Environment & Information Technology, University of Pretoria, Hatfield, 0028, Pretoria, South Africa.

*Corresponding author: michael.daramola@up.ac.za

Abstract. Green corrosion inhibitors play a significant role in lowering the rate at which metal corrodes as well as the environmental effect of hazardous substances. Using electrochemical and gravimetric methods, *Spinacia Oleracea* extract was employed in this work as an environmentally friendly green inhibitor to minimize Cu dissolution in 1 M HNO₃. Activated parameters were identified and addressed, with varying inhibitor doses. The extract exhibits a corrosion inhibition efficacy of 98.9% at 500 ppm. Furthermore, its corrosion inhibition performance continuously stays above 90% even at higher temperatures. According to the Langmuir adsorption isotherms, the experimental results show that the adsorption process protects Cu from corrosion. Scanning electron microscopy was used to analyze the surface and show that a protective extract coating had precipitated on the Cu surface. Fourier transform infrared spectroscopy was used to examine the extract's interaction with copper. The application not only broadens the resource utilization of plant extracts but also brings an effective and innovative corrosion inhibitor to the field of environmentally friendly chemistry.

Keywords: Green corrosion inhibitor, corrosion inhibition, HNO₃, Unused Spinach leaf extract, Copper

1. Introduction

Copper is one of the most vital material used in industries, because of its high mechanical strength, electrical and thermal conductivities, resistance to corrosion, weldability, and other qualities, as a conductor in electrical power line, pipelines for industrial and domestic water services, including heat conductors, heat exchangers, etc., it finds extensive usage in the communications and electronic sectors [1-2]. Copper can dissolve in a variety of environments when it reacts with ambient oxygen, producing complex oxides and a range of corrosion byproducts. Acid pickling is a common and effective industry technique for getting rid of these corrosion products. Unfortunately, the copper substrate is inevitably damaged even if this cleaning procedure successfully eliminates all corrosion products [3]. This has detrimental effects on the metal's characteristics and may result in large financial losses; it may also present safety risks [4]. It can compromise the geometric integrity of metal components by lowering the mechanical qualities of metallic materials, such as strength, ductility, and toughness. It can also worsen the physical performance of metals, increase wear between components, and impair their electrical and optical properties.

Using corroded equipment can also result in disastrous events like explosions and fires. According to literature, the annual economic loss resulting from metal corrosion can reach up to 4% of GDP [5]. As a result, numerous researchers have focused on copper corrosion and its prevention in a range of media [6-8]. Consequently, a number of corrosion prevention and control techniques have been documented, such as material selection, cathodic and anodic protection, protective coatings, and corrosion inhibitors [9]. Using corrosion inhibitor is one of the most economical and practical ways to manage corrosion among the protection techniques [10]. High efficiency, ease of use, and affordability are just a few benefits of corrosion inhibitors. Moreover, they can be employed without requiring modifications to the apparatus and procedure. Since HNO₃ is frequently used to remove deposits and oxide layers from copper's surface [11], its corrosion protection in aqueous HNO₃ solution has been a significant consideration in the field of metal protection. In order to limit the loss to the copper substrate and accomplish the goal of safeguarding the copper substrate, it is often necessary to add a corrosion inhibitor to the pickling solution in order to mitigate copper corrosion in the aggressive solution.

Researchers have utilized different corrosion inhibitors to prevent metals and alloys corrosion. These inhibitors are either make up of organic or inorganic substances. In contrast to organic chemicals, particularly azole compounds [12], which shown notable decreases in copper corrosion, inorganic compounds had a low inhibitory efficacy. According to Kertit et al. [13], 1-phenyl-5-mercapto-1,2,3,4-tetrazole has a major impact on the 70Cu30Zn and 60Cu40Zn corrosion in HNO_3 . However, the level of environmental toxicity of these compounds limits their usage, and research has focused on waste recovery and corrosion inhibitors that are acceptable to the environment. To solve two pressing problems: reducing food waste and long-term protection of critical metal infrastructure, researchers are looking into innovative ways to reuse waste materials. Typically, molecules with heteroatoms like nitrogen, oxygen, and sulphur make up organic corrosion inhibitors [14]. These special qualities can successfully guarantee that corrosion inhibitor molecules are adsorbed onto the metal surface.

Copper can be effectively protected by azole chemicals, bio-macromolecules, ionic liquids, amino acids, food flavours, drugs, and plant extracts, among other organic corrosion inhibitors. Most of the corrosion inhibitors reported is harmful to both human health and the environment. The investigation of novel environmentally friendly corrosion inhibitors has been a research topic against the backdrop of the current emphasis on green environmental protection. Notably, plant extracts constitute of a significant source of eco-friendly corrosion inhibitors in this field. Plant extracts are easily and affordably made from various plant parts. It is a novel type of green corrosion inhibitor because of its affordability, renewability, non-toxicity, and environmental friendliness. Plant extracts adsorb on metal surfaces to prevent corrosion. In general, organic materials that contain heteroatoms or π electrons in plant extracts have the ability to adhere to the surface of metal, hence preventing corrosion. The most frequent active centre interacting with the copper surface, given the chemical makeup of plants, is oxygen. Recent research has shown that plant extracts can effectively prevent corrosion in acidic environments.

Pourmohseni et al. [18] conducted a thorough investigation into the anti-corrosion properties of several medicinal plants, such as ribes rubrum, yarrow, mauroorum, wormwood, and marjoram on mild steel submerged in one molar hydrochloric acid. According to the authors, out of all the extracts they examined, the marjoram plant extract had the highest inhibitory efficacy (up to 92%). Chidiebere et al. [16] used gravimetric, potentiodynamic polarization, and electrochemical impedance spectroscopy techniques to investigate the anti-corrosion performance of aqueous punica granatum (PNG) extracts on mild steel in 0.5 M H_2SO_4 and 1 M HCl solution. In contrast to 1 M HCl, which peaked at 400 mg/L (92%) and then declined, the test findings demonstrated that inhibitory efficiency in 0.5 M H_2SO_4 climbed continuously with increasing concentration, reaching an optimal value of 95% at 600 mg/L PNG. The effectiveness of Luffa cylindrica leaf extract (LCLE) in preventing corrosion on mild steel in a 0.5 M HCl media was investigated by Ogunleye et al. [17], the reported inhibition efficiency ranges from 70.24 to 88%. After 12 hours of corrosion testing at temperatures up to 60 °C, the maximum IE (87.98%) was achieved with an LCLE concentration of 1.0 g/L.

The ability of Glebionis Coronaria extract (GCE) to suppress corrosion on carbon steel in 0.5 M H_2SO_4 and 1 M HCl media was examined by Kellal et al. [18]. With GCE 2 g/L at 293 K, EIS and PDP measurement was conducted in acidic solutions with GCE. The results showed efficiency of 79% and 86.6% for the sulphuric and hydrochloric solutions, respectively, the GCE performs as a mixed type inhibitor via adsorption towards the steel surface in accordance with the Langmuir isotherm. As the temperature rose in both media, the IE% increased as well, reaching 84.4% and 92.2% in the sulphuric and hydrochloric media. Ji et al. [19] investigated how extract from the leaves of the Asteraceae family plant Parthenium hysterophorus inhibited corrosion of mild steel in HCl solutions. The use of water extract from the Parthenium hysterophorus plant as an inhibitor results in a notable reduction in the rate of corrosion. At 1100 mg L^{-1} , the extract's maximal potential was achieved with 84% efficiency. Even though plant wastes are just as powerful as conventional inhibitors, using them is a sustainable way to manage agricultural waste. In light of these findings, there are advantages to using plant extracts as corrosion inhibitors for copper in terms of environmental preservation and waste reduction.

The lush green vegetable spinach (*Spinacia Oleracea*) has Persian origins. Natural pigments including pyrrole, carbonyl, and formyl rings, as well as unsaturated double bonds and hydrophobic hydrocarbon chains, are found in spinach leaf extract. These pigments include chlorophyll, carotene, and lutein. Spinach leaves also include proteins, flavonoids, terpenoids, glycosides, quinine, and carbohydrates [20-21], all of which are frequently present in corrosion inhibitors. It is linked to quinoa and beets and is a member of the amaranth family. One vegetable that is incredibly nutrient-rich is spinach. In addition to having high levels of carotenoids, vitamin C, vitamin K, folic acid, iron, and calcium, it also has potassium, magnesium, and the vitamins B6, B9, and E. Spinach may lower blood pressure, prevent

cancer, improve eye health, and lessen oxidative stress [22-23]. Examining its capacity to shield copper from corrosion in an acidic environment seemed intriguing in light of this. Therefore, this research novelty lies in examining the corrosion inhibition behaviour of *Spinacia Oleracea* (SLE), which has never been studied in 1 M HNO₃ for copper corrosion before as far as we know. Gravimetric and potentiodynamic polarization measures were used to assess the inhibitory potency of SLE. After these evaluations, a thorough thermodynamic investigation was conducted, which included a thorough examination of numerous kinetic parameters.

2. Experimental details

2.1. Material and solution preparation

After being mechanically polished with various grade of emery papers, the copper samples were cleaned with distilled water and air dry at room temperature. The experiment's corrosive media is a 1 M HNO₃ solution. Here, analytical reagent grade 65% HNO₃ was diluted with double distilled water to create 1 M HNO₃. To perform the gravimetric and electrochemical experiments in this study, a cylindrical working electrode made of 99.9% pure copper was used. The concentrations of the corrosion inhibitor were established at 100, 200, 300, 400, and 500ppm respectively, based on the preliminary experiment. The experiment was carried out in triplicate for reproducibility.

2.2. Preparation of *Spinacia Oleracea* extract

The experiment's corrosion-inhibiting unused spinach leaves were gathered from Pretoria, South Africa. The procedure used to gather the plant from nature, wash, dry, extract, and make the inhibitor solution was identical to the ones reported in the literature [24]. Under laboratory circumstances, the maceration technique was used to carry out the extraction process. To get rid of the dust and water-soluble contaminants, the gathered leaves were cleaned with distilled water. After being cleaned, the spinach leaf was dried before being processed into a powder. In summary, a glass flask containing 100 g of dry spinach leaves was filled with 2 L of methanol, and the extraction procedure was carried out for 72 hours. A rotary evaporator was used to remove the solvent after the extraction procedure at low temperature below 40 °C to prevent component deterioration. Before being used, the dried leaves were kept at +4 °C in a refrigerator.

Due to its variable solubility in the chosen solvent, ease of solvent removal from the extract, low toxicity, and ease of obtaining at a reasonable cost, methanol was chosen for the extraction process. Furthermore, when compared to other solvent such as ethylacetate, acetone, ethanol and dichloromethane hexane, methanol exhibits greater extraction efficiency and the capacity to extract a greater number of functional secondary metabolites [25]. The extraction method can be readily repeated since it does not use physicochemical process such as additional pressure, temperature, mixing, synthesis steps, and catalyst, and it eliminates highly dependent variable factors. The dried leaf stored was dissolved in a 1 M HNO₃ solutions to create a variety of SLE.

2.3. Gravimetric studies

Copper coupon, measuring 2 x 2 x 0.2 cm each, were used in the weight loss tests. The weight loss and corrosion rates calculation was in accordance with ASTM G1 and ASTM G 31–72 [26-27]. The corrosive solution had a volume of roughly 500 millilitres. Prior to being submerged in the corrosive media, the copper coupons were weighed using analytical scale (accuracy ±0.1 mg), the coupon was abraded, dried, and weighed before being suspended in the 1 M HNO₃ solutions with and without varying quantities of the SLE under investigation. At an interval of 24 hours exposure period, the electrode was taken out, cleaned, dried, and weighed. In each case, three measurements were taken, and the average weight loss was reported.

2.4. Electrochemical studies

The Cu sample which serves as the working electrode (WE) was mounted in glass rods with 1 cm² exposed area. The gap between the copper electrode and glass rod was filled with epoxy resin. The electrode, which came in the shape of a disc, was placed in a Teflon holder and embedded in epoxy resin. A copper wire was inserted into the metal sample's base to create electrical contact. The saturated silver electrode served as the reference electrode, and the platinum rod served as an auxiliary electrode. Using silicon carbide sandpapers ranging from 400 to 2000 grit to remove the oxide layers from the surface before being repeatedly cleaned with distilled water before being dried.

Tafel polarization curve was produced by automatically varying the electrode potentials from (-250 to +250 mV) in a standard electrochemical cell with a 250 ml capacity in relation to open circuit potential at a 1.0 mV s⁻¹ scan rate.

Before the measurements, the electrode was submerged in these solutions for one hour, to reach a quasi-stationary value for the open circuit potential. Every experiment was conducted using a thermostat to maintain a constant temperature in a freshly prepared solution.

2.5. Surface examinations

The chemical bonds of the inhibitor were identified by FTIR spectroscopy in the frequency range of 400–4000 cm^{-1} . Copper coupons in a 1 M HNO_3 solution were examined using SEM with and without inhibitor. SEM analysis has been performed in the current study using a metal strip that is used for weight loss analysis. The metal strip has first been submerged for a predetermined amount of time in the electrolytic and inhibitor-containing solution.

3. Results and discussion

3.1. Characterization of spinach extract

Figure 1 displays the spinach leaf extract's FTIR spectrum. The O–H bond is represented by the large peak seen at 3384 cm^{-1} . The C–H bond is responsible for the peak at 2927 cm^{-1} . The C = O bond is responsible for the peak at 1612 cm^{-1} . The peak at 1400 cm^{-1} is caused by the $-\text{CH}_3$ bond. The C–N bond is responsible for the peak at 1230 cm^{-1} . The C–H bond on the aliphatic or aromatic is what causes the absorption peak at 1000 cm^{-1} . In line with earlier findings [23–25], the functional groups of the extract show that it is abundant in phytochemical components, including amino acids, tannins, alkaloids, flavonoids, phenols, and carbohydrates.

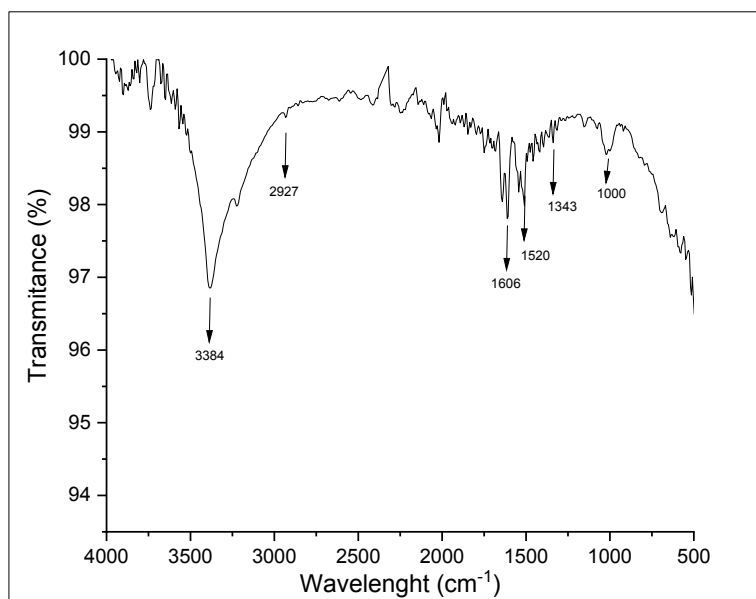


Fig. 1. The FTIR spectrum of spinach leaf extract.

3.2. Gravimetric result

3.2.1. Corrosion inhibition performance by SLE

The SLE's ability to prevent copper alloys from corroding after 504 hours at 30 °C in a 1 M HNO_3 solution is demonstrated in Figure 2. The figure's results clearly show that the inhibitor successfully prevented copper from

dissolving in the acidic solution. Copper in inhibited HNO_3 solution corrode at a maximum rate of 0.1242 mm/year (500 ppm), whereas the blank sample corrode at a maximum rate of 8.07662 mm/year (0 ppm). The Figure makes it evident that copper is better protected at high inhibitor concentrations than at lower inhibitor concentrations. These findings suggest that the inhibitor effectively prevents acid corrosion in the metal under study. After proving that SLE can successfully delay the metal corrosion under study in HNO_3 solutions, the effects of immersion duration and concentration on this inhibitor's functionality were examined.

Figure 2 illustrates how the dosage of SLE affects the corrosion rate and inhibition efficiency of copper submerged in a 1M HNO_3 solution at 30 °C. Figure 2(a) shows that the rate of corrosion decreases as concentration rises, reaching its lowest value at 500 ppm concentration. This finding implies that the ideal inhibitor concentration of copper is 500 ppm. A thorough examination of figure 2(b) reveals that the 400 and 500 ppm concentrations' inhibitive efficacy differs by a negligible amount. For example, after 504 hours, the rates of inhibition for copper at 100, 200, 300, 400 and 500 ppm SLE are 66.61%, 68.85%, 71.81%, 91.42%, and 94.92%, respectively. This suggests that the desired protection of the metallic components can be obtained with the low SLE. It should be noted that the corrosion rate for the metal under study using the SLE concentrations is within an acceptable range.

Figure 3 illustrates how, under the examined experimental conditions, the corrosion rate (a) and the inhibition efficiency (b) of 500 ppm varies with immersion time for the metal under study. The length of immersion has an inverse relationship with the corrosion rate of the metal under study. The accumulation of corrosion product on the sample surface, which offered some protection to the sample surface, may be the observed cause of the drop in the rate of corrosion with immersion duration [28-29]. However, the observed rise in copper corrosion rate in the unprotected solution with exposure time points to the native oxide layers breaking down at longer immersion times [29]. The efficiency of SLE as an inhibitor for the examined metal is further demonstrated by the significant decrease in the alloy rate of corrosion under study in the inhibited system compared to the blank. The thickness, stability, and hardness of an adsorption inhibitor layer are critical factors in preventing the entry of corrosive ions [30]. One could claim that sufficient SLE molecules were adsorbed on the sample surface at extended immersion time. The corrosion rate was discovered to have decreased as a result of the adsorbed inhibitor films' significant obstruction of the corrosive ions' entry into the medium.

The literature on corrosion makes a similar case [28, 31-33]. As immersion time increases, SLE's inhibitory efficiency trend against Cu-resist corrosion continuously declines. Other authors have noted a similar decrease in inhibitory efficiency with immersion time on steel in acid solution [34-35]. An increase in the inhibitor adsorbed molecules on the metal surface is thought to be the cause of the rise in inhibition efficacy with increasing inhibitor concentration [35]. The observed decline in inhibitory efficacy with exposure time can be attributed to a number of variables. First, the observed phenomena may be due to partial desorption of bound inhibitor molecules at extended immersion times. The second option is that the cathodic metal nodules and anodic iron matrix in contact with the extremely conductive acid solution may have experienced rapid galvanic corrosion, which could have been prevented by using 500 ppm of SLE.

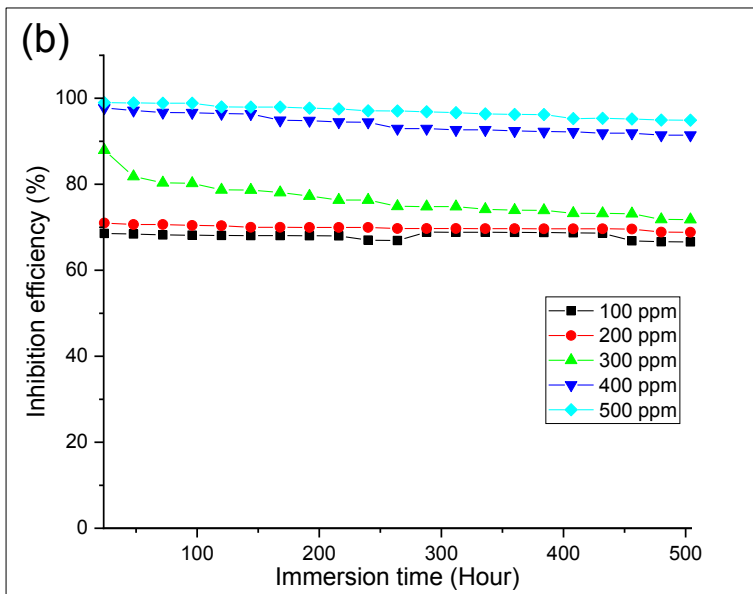
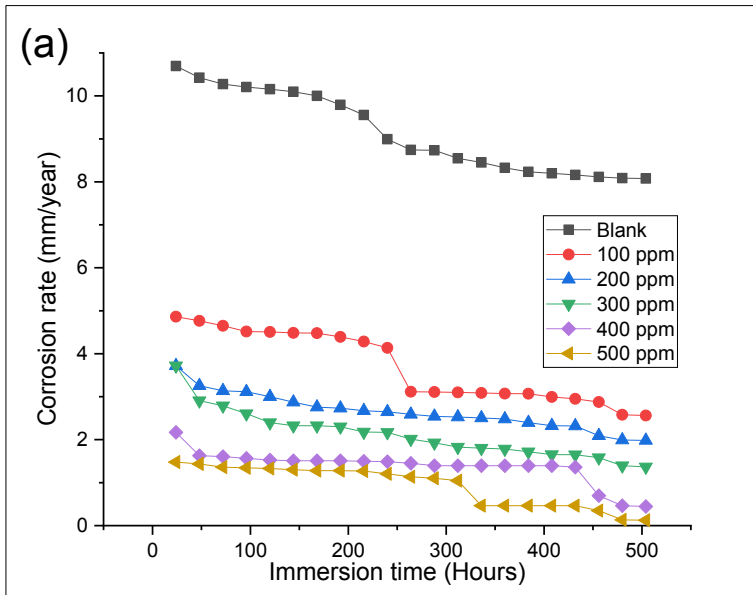


Fig. 2. Variation of (a) corrosion rate and (b) inhibition efficiency with spinach leaf extract for copper immersed in 1M HNO₃ solution for 504 hour at 30°C.

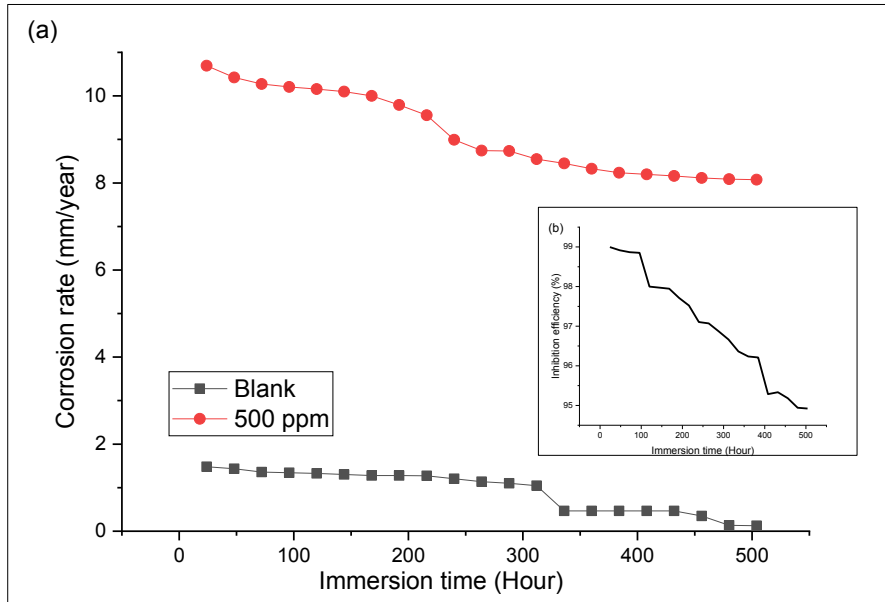


Fig. 3. Variation of (a) corrosion rate and (b) inhibition efficiency with immersion time for copper specimen exposed to 1M HNO₃ solution without and containing 500 ppm spinach leaf extract at 30°C.

3.3. Linear polarization resistance

A useful method for assessing the electrochemical resistance reactions of metal at the metal-electrolyte interface is linear polarization resistance (LPR). The potentials are scanned between low anodic and cathodic overpotential vs E_{ocp}, in contrast to the potentiodynamic polarization approach, that does not considerably polarize the surface of the metal or disrupt the solution/metal contact. With equation 1, the R_p was determined from the slope of plots showing the flowing current through the system as a function of applied potential:

$$R_p = \frac{SdE}{dI} \tag{1}$$

Where *I* is the current flowing through the electrochemical systems, *E* is the electrode potential, and *S* is the Cu surface area exposed to the electrolytes.

Table 1 displays the results of calculated R_p of Cu in 1 M HNO₃ solution with or without varying amounts of SLE. The following equation was used to determine the percentage corrosion inhibition efficiency (η%):

$$\eta\% = \left(\frac{R_p^0 - R_p}{R_p^0} \right) 100 \tag{2}$$

R_p and R_p^0 represent the steel electrode's polarization resistance in uncontrolled and inhibited 1.0 M HNO_3 solutions, respectively, in this equation.

The corresponding $\eta\%$ values were calculated and shown in Table 1. As a result, Table 1's data shows that SLE compound is creating physical barriers that protects the copper's surface and slows down the metal's rate of corrosion. Furthermore, variations in extract concentration boost the isolate's capacity for Cu protection up to 400 ppm. High inhibitor concentration may cause more extracts molecule to adsorb to the surface of the metal [36], improving corrosion resistance. Nevertheless, the R_p and inhibition efficiency values increased once more when the concentration was raised to 500 ppm, which is in line with the gravimetric test outcomes and the explanation given in the preceding section.

Table 1. Electrochemical data for copper derived from LPR measurement in 1 M HNO_3 solutions in the presence and absence of various spinach leaf extract at 30°C.

C (ppm)	R_p ($\Omega \text{ cm}^2$)	$\eta\%$
Blank	18.26	-
100	63.85	71.88
200	88.09	79.55
300	107.20	83.18
400	196.22	90.31
500	216.70	91.67

3.4. Potentiodynamic polarization curves

The cathodic curves' shift indicates that cathode reactions are the primary cause of corrosion acceleration, in accordance with corrosion theory [37]. HNO_3 is hence a potent copper oxidizer that can attack copper quickly. Furthermore, there is no sharp slope in the anodic range of the Tafel polarisation curves, indicating that no passive film form on the surface of copper. As a result, Cu may dissolve in 1 M HNO_3 solution. It is known from the Pourbaix diagram for the copper-water system [38] that in nitric acid solutions, copper corrodes to Cu^{2+} and that no oxide film forms to shield the surface of Cu from corroding. The following is a description of the electrochemical processes for copper in nitric acid solution:

Anodic reaction:

Soluble Cu (II) species diffusion from the outer Helmholtz plane to the bulk solution regulates copper dissolution.



Cathodic reactions:



The nitrate ion is reduced when copper corrodes in nitric acid. The copper surface may also experience a reduction in dissolved oxygen in aerated nitric acid solutions. At $30 \pm 1^\circ\text{C}$, the cathodic and anodic polarization curves for copper corrosion were examined both with and without different doses of the inhibitors under investigation. It demonstrates that the corrosion current density (i_{corr}) significantly dropped in comparison to the blank sample as the compound concentration increased, and the efficiency increased considerably with the inhibitor concentration. An increase in inhibitor concentration is found to decrease both the anodic and cathodic current densities in every instance. Figure 5 illustrates the Tafel polarization behaviour of Cu in HNO_3 both without and with varying SLE concentrations. Corrosion variables derived such as E_{corr} (corrosion potential), i_{corr} (corrosion current density), β_a and β_c (anodic and cathodic Tafel slopes), and CR (corrosion rate) are shown in Table 2.

From the extrapolation of the linear portion of the anodic current-potential curve to their corrosion potential, the current density was determined. Copper has an E_{corr} of -0.355 V in the corrosive solution, as shown in Figure 4. The reduction and oxidation current density drop and the electrode acquire greater negative potential values when the SLE is combined with the corrosive media. As a result, the extract mostly affects the cathodic hydrogen evolution reaction, making it a mixed-type corrosion inhibitor. E_{corr} becomes somewhat less negative potentials when the content of leaf extract is increased. But when 500 ppm of extract was present, there was a noticeable shift in potential towards less negative value.

The performance of the inhibitory activity increases as the inhibitor intensity increases, but i_{corr} and CR considerably decrease (Figure 4 and Table 2). This suggests that adding SLE to the corrosive medium stops metal dissolution. By creating an adsorbed thin inhibitor coating between the metal and the corrosive media, inhibition can be achieved. As the extract concentration in the corrosive media rises, so does the protective capacity. The $\eta\%$ achieves its highest value of 91.8% at 400 ppm. In comparison to 500 ppm, the protective ability seems to slightly increase with greater doses. Furthermore, the cathodic current-potential curves for the inhibitor and its absence are nearly parallel, indicating that the SLE slows down the hydrogen evolution reaction without changing its mechanism. By preventing the H^+ reduction in the cathodic zone, the surface film lowers the reaction rate.

In this instance, corrosion only develops on exposed portions of the metal exposed or pores in the surface coating. At 500 ppm extract, the best surface coverage was obtained. This improves the barrier between the metal's surface and the corrosive media by sealing the holes in the surface coating. The results of the polarization measurements are consistent with those obtained by LPR and gravimetric tests. Additionally, Table (2) shows that the cathodic and anodic Tafel slopes were roughly constant, indicating that these chemicals' inhibitory activity was achieved by merely restricting the accessible surface area. Stated differently, the inhibitors had no effect on the reaction process but reduced the surface area accessible for oxygen reduction and anodic dissolution.

Table 2. Electrochemical parameter for copper derived from potentiodynamic polarization measurement obtained in 1 M HNO_3 solutions in the presence and absence of various spinach leaf extract at $30^\circ C$.

Inhibition Concentration (ppm)	E_{corr} (V)	i_{corr} (Acm^{-2})	β_a (V/dec)	β_c (V/dec)	Corrosion rate (mm/year)
Blank	-0.355	0.0069	0.042	0.161	6.178
100	-0.399	0.0004	0.079	0.158	5.009
200	-0.423	0.0003	0.091	0.177	2.087
300	-0.518	7.037E-5	0.075	0.254	1.050
400	-0.558	2.781E-5	0.050	0.184	0.372
500	-0.622	1.432E-6	0.071	0.035	0.002

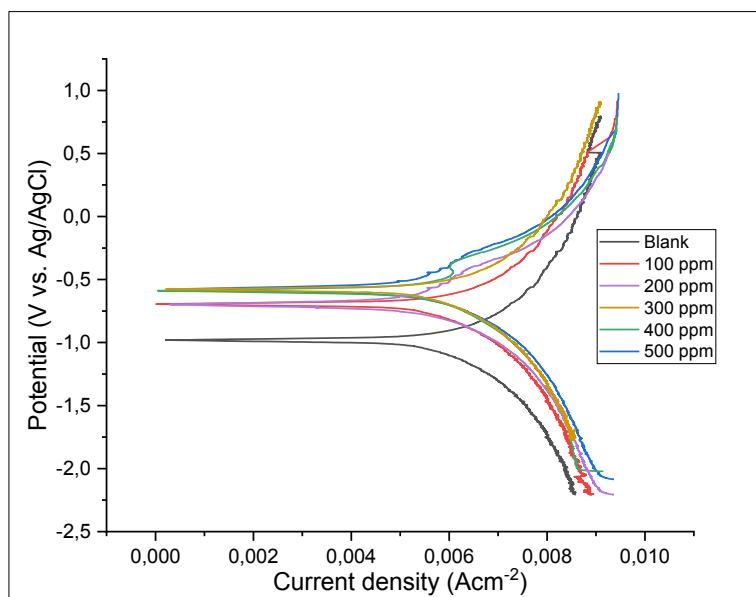


Fig. 4. Polarization curves of copper in 1 M HNO₃ solution with and without spinach leaf extract after 1 hour immersion time.

3.5. Surface characterization studies

Figure 5 displays the copper SEM images exposed to 1 M HNO₃ and 1 M HNO₃ + 500 ppm SLE following the weight loss tests. As shown in Figure 5a and b, excessive metal dissolution caused the copper surface to deteriorate considerably. It was anticipated that the Cu would sustain uneven damage and undergo pitting corrosion in this media. When 500 ppm SLE was added to the corrosive electrolyte solution, the copper surface developed a protective homogeneous coating and holes and cracks was minimal as shown in Figure 5b. By adding 500 ppm of extract to the inhibited HNO₃ solution, a greater coverage, and almost evenly distributed protective film has been produced. The gravimetric and electrochemical results, which demonstrate the spinach leaf extract's strong protective ability, are supported by the morphological examinations.

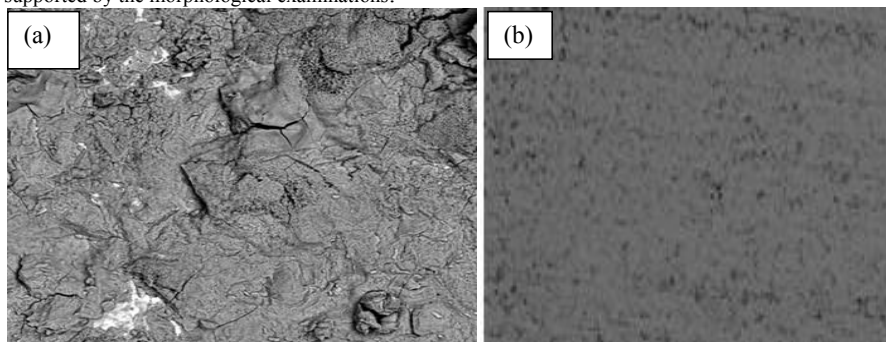


Fig. 5. SEM image of copper exposed to (a) 1 M HNO₃ and (b) 1 HNO₃+500 ppm leaf extract

3.7. Adsorption isotherms and thermodynamic consideration

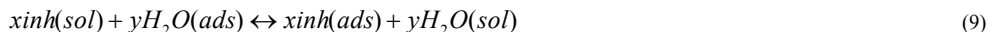
The capability of organic compounds to control corrosion is directly correlated with their ability to adsorb to metal surfaces and form a protective film. The chemical or physical interaction between organic molecule and the surface of the metal causes adsorption, and this depends on the characteristics of the metal surface, the molecules' chemical structure and kind and quantity of adsorption active centres they contain, the charge of the molecules and the surface, and the medium's temperature. Important details regarding the interactions and associated thermodynamic values are provided by adsorption isotherms. The corrosion inhibition efficiency is expected to have a linear connection with the surface coverage (θ) in order to establish the optimal isotherm; this value is obtained from $\eta\%$ using Equation (7):

$$\theta = \frac{\eta\%}{100} \tag{7}$$

For this purpose, many experiments were carried out, and as shown in Figure 6, the Langmuir adsorption isotherm provides the best fit. The linear regression coefficient, which was high (0.97938) and close to 1, supports this idea. Then, we hypothesise that SLE molecules form a uniform single protective layer by adhering to the metal surface [39]. The Equation (8) defines the Langmuir adsorption isotherm:

$$\frac{C_{inhibitor}}{\theta} = \frac{1}{K_{adsorbition}} + C_{inhibitor} \tag{8}$$

Where K_{ads} denotes the equilibrium constant for the adsorption-desorption process and C is given in ppm. Based on Figure 6 and Equation (8), $K_{ads} = 19.71$ indicating that the SLE molecule have high degree of consistency and a significant ability to adsorb on the metal surface. The isolate molecules' great adsorption capacity on the metal surface is indicated by K_{ads} . It is possible to conclude that the SLE molecules adsorption on the copper surface is preferable to desorption since the K_{ads} value is connected to the equilibrium constant for the subsequent process [40].



The following equation could be used to calculate the ΔG^0_{ads} (standard free energy of adsorption), which gives details about the adsorption energy of organic molecule on the metal surface:

$$\Delta G^0_{ads} = -RT \ln(C_{H_2O} K_{ads}) \tag{10}$$

The water concentration that is present in the medium is represented by CH_2O in this equation [41]. Using Equation (10) to obtain the ΔG^0_{ads} , the result is $-24.4 \text{ kJ mol}^{-1}$. As anticipated, the extract particle self-adsorb on the copper layer, as indicated by the negative value of ΔG^0_{ads} . The ΔG^0_{ads} value of the extract is closer to -20 kJ mol^{-1} than it is to -40 kJ mol^{-1} . As a result, both chemical and physical interaction influences the SLE adsorption, with the former being more important than the latter. Chemical interactions may also take place following the first physical interaction between the surface and the extract molecules.

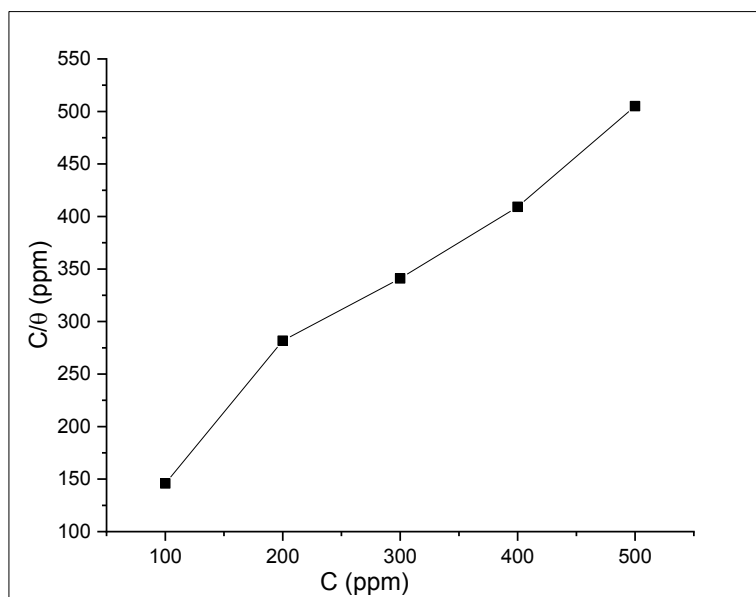


Fig. 6. Langmuir adsorption plots of copper in 1 M HNO₃ solutions with the addition of various spinach leaf extract concentrations.

4. Conclusions

In this investigation, a spinach leaf extract (SLE) was examined as inhibitor to protect copper corrosion in a 1 M HNO₃ solution. Gravimetric and electrochemical methods were employed to examine the extracts' capacity for protection. The copper surfaces were analyzed using SEM measurements following exposure to the corrosive media. According to the findings, the SLE molecules attach to the surface of the metal, disperse evenly, and create a protective layer that prevents copper corrosion. The alloy's surface was strongly inhibited from corrosive attacks when the SLE concentration increased to 500 ppm. Interestingly, the inhibitory efficiency can reach approximately 98.9% at 500 ppm. The SLE can be considered an effective inhibitor that operates on both cathodic and anodic processes (mixed-type inhibitor) based on the PDP curves. Through chemical and physical interactions, the SLE molecule adhered to the copper surface, following the Langmuir adsorption process. The morphological study evaluations show that the SLE film was successfully adsorbed onto the copper surface and acted as a protective barrier. **According to the present results, experiments at higher temperatures are recommended in order to support the corrosion inhibition of spinach leaf extracts' efficiency at high temperature.**

References

1. Z. Benzarti, N. Arrousse, R. Serra, S. Cruz, A. Bastos, J. Tedim, R. Salgueiro, A. Cavaleiro, S. Carvalho. Copper corrosion mechanisms, influencing factors, and mitigation strategies for water circuits of heat exchangers: Critical review and current advances. *Corros. Rev.* **45**, 429 (2025).
2. V. Naveenprabhu, K. Veeramanikandan, B.S. Poorani, K. Gokulamadhavan, K. Suba. A critical overview on corrosion characteristics of copper fin. In *AIP Conference Proceedings*, AIP Publishing LLC. **3221**, 020025 (2024).
3. M. Elbatouti, H.A. Fetouh. Extraction of eco-friendly and biodegradable surfactant for inhibition of copper corrosion during acid pickling. *Adsorp. Sci. Technol.* **37**, 649 (2019).

4. D. M. Bastidas, M. Criado, S. Fajardo, V. M. La Iglesia, E. Cano, J. M. Bastidas. Copper deterioration: causes, diagnosis and risk minimisation. *Int. Mater. Rev.* **55**, 99 (2010).
5. H. Kania. Corrosion and anticorrosion of alloys/metals: the important global issue. *Coatings*. **13**, 216 (2023)
6. A.M. Eldesoky, H.M. Hassan, A.S. Fouda. Studies on the corrosion inhibition of copper in nitric acid solution using some pharmaceutical compounds. *Int. J. Electrochem. Sci.* **8**, 10376 (2013).
7. G.O. Tansuğ, T.U. Tüken, E.S. Giray, G. Fındıkkıran, G. Sığircik, O.N. Demirkol, M.E. Erbil. A new corrosion inhibitor for copper protection. *Corros. Sci.* **84**, 21 (2014).
8. A. Fateh, M. Aliofkhaezrai, A.R. Rezvanian. Review of corrosive environments for copper and its corrosion inhibitors. *Arab. J. Chem.* **13**, 481 (2020).
9. Y. H. Liu, J.B. Xu, J.T. Zhang, J. M. Hu. Electrodeposited silica film interlayer for active corrosion protection. *Corros. Sci.* **120**, 61 (2017).
10. O. Sanni, S. A. Iwarere, M. O. Daramola. Investigation of eggshell agro-industrial waste as a potential corrosion inhibitor for mild steel in oil and gas industry. *Sustainability*. **15**, 6155 (2023).
11. A. K. Singh, S. K. Shukla, M. Singh, M. A. Quraishi. Inhibitive effect of ceftazidime on corrosion of mild steel in hydrochloric acid solution. *Mater. Chem. Phys.* **129**, 68 (2011).
12. V. Lakshminarayanan, R. Kannan, S. R. Rajagopalan. Cyclic voltammetric behavior of certain copper-azole systems using carbon paste electrodes. *J. Electroanal. Chem. and JEAC.* **364**, 79 (1994).
13. M. Mihit, M. Belkhaouda, L. Bazzi, R. Salghi, S. El Issami, E. A. Addi. Behaviour of brasses corrosion in nitric acid with and without PMT. *Port. Electrochim. Acta.* **25**, 471 (2017).
14. D. K. Verma, Y. Dewangan, A. K. Dewangan, A. Asatkar. Heteroatom-based compounds as sustainable corrosion inhibitors: an overview. *JBTC.* **7**, 15 (2021).
15. M. Pourmohseni, A. Rashidi, M. Karimkhani. Preparation of corrosion inhibitor from natural plant for mild steel immersed in an acidic environment: experimental and theoretical study. *Sci Rep* **14**, 7937 (2024).
16. M. A. Chidiebere, C. E. Ogukwe, K. L. Oguzie, C. N. Eneh, E. E. Oguzie. Corrosion inhibition and adsorption behavior of Punica granatum extract on mild steel in acidic environments: Experimental and theoretical studies. *Ind. Eng. Chem. Res.* **51**, 668 (2012).
17. O. O. Ogunleye, A. O. Arinkoola, O. A. Eletta, O. O. Agbede, Y. A. Osho, A. F. Morakinyo, J. O. Hamed. Green corrosion inhibition and adsorption characteristics of Luffa cylindrica leaf extract on mild steel in hydrochloric acid environment. *Heliyon.* **6**, 1 (2020).
18. R. Kellal, D. B. Left, M. Azzi, M. Zertoubi. Insight on the corrosion inhibition performance of Glebionis coronaria plant extract in various acidic mediums. *J. Appl. Electrochem.* **53**, 811 (2023).
19. G. Ji, S. K. Shukla, P. Dwivedi, S. Sundaram, E. E. Ebenso, R. Prakash. Parthenium hysterophorus plant extract as an efficient green corrosion inhibitor for mild steel in acidic environment. *International Journal of Electrochemical Science.* **7**, 9933 (2012).
20. Olagoke O. Phytochemical analysis and antibacterial activities of spinach leaf. *Am. J. Phytomed Clin. Ther.* **6**, 8 (2018).
21. I. M. Ibrahim, N. V. Oluchukwu, A. Salisu, O. M. Nkemakonam. Nutritional and phytochemical analysis of spinach leaf aqueous extract: A comprehensive study on proximate composition, minerals, vitamins, and antioxidant activity. *Eurasian j. sci. technol.* **5**, 302 (2025).
22. B. Ramaiyan, J. Kour, G. A. Nayik, N. Anand, M. S. Alam. Spinach (*Spinacia oleracea* L.). In *Antioxidants in vegetables and nuts-Properties and health benefits*. Singapore: Springer Singapore 159 (2020).
23. R. M. Gutierrez, E. G. Velazquez, S. P. Carrera. Spinacia oleracea Linn considered as one of the most perfect foods: A pharmacological and phytochemical review. *Mini Reviews in Medicinal Chemistry.* **19**, 1666 (2019).
24. F. Kaya, R. Solmaz, I. H. Geçibesler. Investigation of adsorption, corrosion inhibition, synergistic inhibition effect and stability studies of Rheum ribes leaf extract on mild steel in 1 M HCl solution. *J. Taiwan Inst. Chem. Eng.* **143**, 104712 (2023).
25. D. H. Truong, D. H. Nguyen, N. T. Ta, A. V. Bui, T. H. Do, H. C. Nguyen. Evaluation of the use of different solvents for phytochemical constituents, antioxidants, and in vitro anti-inflammatory activities of *Severinia buxifolia*. *J. Food Qual.* **2019**, 8178294 (2019).
26. ASTM International. Standard practice for preparing, cleaning, and evaluating corrosion test specimens, ASTM G1-03, (2003).
27. ASTM G31-72. Standard Practice for Laboratory Immersion Corrosion Testing of Metals. New York: American (2004).
28. I. B. Obot, M. M. Solomon, I. B. Onyeachu, S. A. Umoren, A. Meroufel, A. Alenazi, A. A. Sorour. Development of a green corrosion inhibitor for use in acid cleaning of MSF desalination plant. *Desalination.* **495**, 114675 (2020).

29. M. K. Pavithra, T. V. Venkatesha, K. Vathsala, K. O. Nayana. Synergistic effect of halide ions on improving corrosion inhibition behaviour of benzisothiazole-3-piperazine hydrochloride on mild steel in 0.5 M H₂SO₄ medium. *Corros. Sci.* **52**, 3811 (2010).
30. S. A. Umoren, M. M. Solomon. Application of polymer composites and nanocomposites as corrosion inhibitors. *Corrosion inhibitors, principles, mechanisms, and applications.* 27 (2017).
31. J. Zhou, X. Niu, Y. Cui, Z. Wang, J. Wang, R. Wang. Study on the film forming mechanism, corrosion inhibition effect and synergistic action of two different inhibitors on copper surface chemical mechanical polishing for GLSI. *Appl. Surf. Sci.* **505**, 144507 (2020).
32. Y. Qiang, S. Zhang, L. Wang. Understanding the adsorption and anticorrosive mechanism of DNA inhibitor for copper in sulfuric acid. *Appl. Surf. Sci.* **492**, 228 (2019).
33. O. Sanni, S. A. Iwarere, M. O. Daramola. Evaluation of corrosion inhibition of essential oil-based inhibitors on aluminum alloys. *ACS omega.* **7**, 40740 (2022).
34. M. Yadav, R. R. Sinha, S. Kumar, T. K. Sarkar. Corrosion inhibition effect of spiropyrimidinethiones on mild steel in 15% HCl solution: insight from electrochemical and quantum studies. *RSC advances.* **5**, 70832 (2015).
35. A. A. Al-Amiry, L. M. Shaker, A. H. Kadhum, M. S. Takriff. Exploration of furan derivative for application as corrosion inhibitor for mild steel in hydrochloric acid solution: Effect of immersion time and temperature on efficiency. *Materials Today: Proceedings.* **42**, 2968 (2021).
36. A. Miralrio, A. Espinoza Vázquez. Plant extracts as green corrosion inhibitors for different metal surfaces and corrosive media: a review. *Processes.* **8**, 942 (2020).
37. D. A. Jones. *Principles and prevention of corrosion.* (1996).
38. M. Pourbaix. *Atlas of electrochemical equilibria in aqueous solutions.* NACE. (1966).
39. A. Oulabbas, S. Abderrahmane, A. Salcı, T. H. Geçibesler, R. Solmaz. Adsorption and corrosion inhibition of *cactus cladode* extract and effect of KI addition on mild steel in 0.5M H₂SO₄. *Chemistry Select.* **7**, e202200212 (2022).
40. C. M. Goulart, A. Esteves-Souza, C. A. Martinez-Huitile, C. J. F. Rodrigues, M. A. M. Maciel, A. Echevarria. Experimental and theoretical evaluation of semicarbazones and thiosemicarbazones as organic corrosion inhibitors. *Corros Sci.* **67**, 281 (2013).
41. N. A. Odewunmi, S. A. Umoren, Z. M. Gasem, S. A. Ganiyu, Q. Muhammad. L-Citrulline: an active corrosion inhibitor component of watermelon rind extract for mild steel in HCl medium. *J Taiwan Inst Chem En.* **51**, 177 (2015).