Electrochemical evaluation of the corrosion inhibition effect of essential oil extracts on mild steel in acidic environments

Roland T. Loto1*, Tiwa Olukeye1 and Eugene Okorie1

1Department of Mechanical Engineering, Covenant University, Ogun state, Nigeria
Corresponding Author; tolu.loto@gmail.com

Abstract

The corrosion inhibition property of the combined admixture of neem leaf and basil oil extracts (NB) on mild steel in in 1M H2SO4 and HCl solution was studied with weight loss measurement, potentiodynamic polarization and optical microscopy analysis. Results show NB performed effectively at all concentration studied in HCl solution with average inhibition efficiency above 94% and 91% (weight loss and polarization test) whereas the compound performed poorly in H2SO4 solution at all concentrations (excluding highest concentration, 2.5%) with average inhibition efficiency of 17% and 31%. At 2.5% concentration in H2SO4, the inhibition efficiency is 98.34% and 85.36%. NB exhibited mixed type inhibition property from the polarization plots. This observation was further confirmed from optical characterization of the steel surfaces where the morphology of the inhibited steel was relatively smooth while the non-inhibited morphology was badly corroded with visible corrosion pits.

Keywords: corrosion; steel; inhibitor; adsorption

1. Introduction

The low price of mild steels (MS) in the international market and their unique mechanical and physical properties are the major factor is responsible for their versatility and application in most industries worldwide [1, 2]. They are the material of construction for cold worked fasteners and bolts to high density machine parts, structures and component which includes shafts, nuts, sprockets, spindles, screws, pins, pipes, rods and gear assemblies etc. MS has extensive application in petrochemical refineries, chemical processing plants, construction industries, energy generation industries, automobile industries, mining and extraction etc. The significantly weak resistance of MS to electrochemical deterioration hugely impacts their operational service life and versatility; hence limiting their usefulness to specific industrial conditions. The absence of chromium in the metallurgical structure of these steels is responsible for the inability of the steel to passivate making them completely vulnerable to the action corrosive anions in aggressive environments. Corrosion damage in concerned industries accounts for huge maintenance and repair costs due to the redox electrochemical interactions and reactions between MS parts and environments of applications. This leads to industrial downtimes, avoidable accidents, costly shut downs replacement of metallic parts of equipment [3]. Organic chemical compounds known as corrosion inhibitors have been used extensively to mitigate MS corrosion. This has help increased the extent of versatility of MS [4-7]. Inhibitors are economically useful petrochemical, extraction, processing and transportation, mineral extraction and processing, heavy industrial manufacturing, automobile radiators, boilers and water treatment facilities etc. to drastically reduce general and localized corrosion damage, and unscheduled downtimes [8]. The corrosion inhibitors largely used in industry are toxic and create complications for the environment [9, 10]. Application of cost effective green chemical compounds for corrosion inhibition is a much better alternative. Use of non-toxic green chemical compounds for corrosion control of mild steel in industrial environments contaminated with Cl− and SO42− anions serves as a sustainable alternative to toxic chemical inhibiting compounds. However, corrosion inhibitors are specific in action and proper documentation of their effective...
inhibition properties with respect to the specific nature of industrial environments is hugely important. The data presented in this article evaluates the corrosion inhibition performance of the combined admixture neem leaf and basil oil extracts on mild steel in HCl and H2SO4 solution.

2. Material and methods
Mild steel (MS) with diameter of 0.65cm was cut into 14 test samples. 7 MS samples were embedded in resin mounts, smoothened with emery papers (80, 120, 240, 320, 400, 600, 800, 1000, 1200, 1500, 2000 and 2500 grits), and thereafter cleansed with distilled H2O and propanone for potentiodynamic polarization test. The other 7 MS specimens were initially weighed and individually submerged in 200 mL of dilute acid electrolyte for weight loss measurement. Neem leaf and basil oil extracts (NB) sourced from NOW Foods, USA are the compounds studied for their synergistic inhibiting properties. They were admixed in ratio 1:1 and formulated in volumetric concentrations of 0%, 1%, 1.5%, 2% and 2.5% in 200 mL of 1M HCl and H2SO4 solutions prepared from standard grade of the acids (98% H2SO4 and 37% HCl). Potentiodynamic polarization test was done with Digi-Ivy 2300 potentiostat at 30°C ambient temperature. Resin embedded MS electrodes with exposed area of 1.33 cm², Pt counter electrode and silver chloride reference electrode (Ag/AgCl) were placed in 50 mL of the NB/HCl and NB/H2SO4 solution, and linked to the potentiostat/computer. The test was measured between potentials of -0.75V to 0 V at a scan rate of 0.0015 V/s. The corrosion current density \( i_{corr} \) and corrosion potential \( E_q \) were calculated from the Tafel plots of potential versus log current. The corrosion rate \( \gamma \) was determined from equation 1.

\[
R = \frac{0.00327 \times I_{corr} \times E_q}{D}
\]

(1)

where \( I_{corr} \) is the current density in \( \mu A/cm^2 \), \( D \) is the density in \( g/cm^3 \), \( E_q \) is the specimen equivalent weight in grams. 0.00327 is a constant for corrosion rate calculation in mm/y. The percentage inhibition efficiency \( \eta \) was calculated from corrosion rate values using the equation below;

\[
\eta = 1 - \frac{R_2}{R_1} \times 100
\]

(2)

where \( R_1 \) and \( R_2 \) are the corrosion rates with and without NB inhibitor. Polarization resistance \( R_p, \Omega \) was calculated from equation (3) below;

\[
R_p = 2.303 \times \frac{BaBc}{Ba + Bc} \times \frac{1}{I_{ct}}
\]

(3)

where \( Ba \) is the anodic Tafel slope and \( Bc \) is the cathodic Tafel slope, both are measured as (V vs Ag/AgCl/dec).

Weight loss was determined from the difference between the initial weight of the steel (which was constant for 216 h) and the final weight of the steel measured every 24 h. The corrosion rate \( R \) data from the weight loss value was determined according to the equation below;

\[
R = \frac{87.6W}{DAT}
\]

(4)

\( W \) is the weight loss in grams, \( D \) is the density in \( g/cm^2 \), \( A \) is the area in \( cm^2 \), and \( T \) is the time of exposure in hours. The data of inhibition efficiency \( \eta_2 \) calculated from the equation below;

\[
\eta_2 = \frac{W_i - W_2}{W_i} \times 100
\]

(5)

\( W_i \) and \( W_2 \) are the weight-loss of the control and inhibited MS in the acid media with respect to exposure time.

Omax trinocular metallurgical microscope was employed to visualize and capture images of the mounted steel before corrosion and after corrosion with and without NB inhibitor.

3. Results and discussion
The Fig. 1(a) and (b) shows the plot of MS corrosion rate versus exposure time at specific concentrations of NB in HCl and H2SO4 solution, while Fig. 2(a) and (b) shows the variation of NB inhibition efficiency in HCl and H2SO4 acid solution versus exposure time. Potentiodynamic polarization plots of MS corrosion in both acids are shown in Fig. 3(a) and (b). Table 1 shows the potentiodynamic polarization data. The corrosion rate of non-inhibited MS samples (0% NB concentration) were significantly higher than the corrosion rate results gotten from MS samples at specific NB concentrations. This difference is due to the electrochemical action of corrosive anions (SO42- and Cl-) on the surface of MS leading to surface oxidation of MS and release of Fe into the electrolyte. NB in the acid media protonates and adheres unto MS surface thus hindering the diffusion and electrolytic transport of the corrosive species. NB inhibitor performed effectively in HCl solution at all concentrations studied with inhibition efficiency above 94%. Its performance in H2SO4 was very poor at 1%, 1.5% and 2% NB concentration. However, at 2.5% the inhibition efficiency was unexpectedly over 90%. There is no proven explanation for this but the observation confirms the specific action of corrosion inhibitors with respect to inhibitor concentration and nature of corrosive environment. Polarization test gave comparable results. The slope of MS at 0% NB in HCl solution is significantly higher than the slopes obtained at higher NB concentrations. Due to active redox reaction processes. The decrease in the oxidation and H2 evolution reactions is due to the inhibiting action of NB. However, cathodic Tafel slope values show the H2 evolution and O2 reduction reaction processes is under activation control indicating that NB inhibiting action has limited influence on reduction reactions. The significant difference in anodic Tafel slope value between MS at 0% NB and MS at 1% to 2.5% NB concentration shows surface coverage of MS surface dominates the reaction process. However, changes in NB concentration do not influence the mechanism of NB inhibitor reaction mechanism. The anodic-cathodic Tafel slope of MS in Fig. 3(b) at 0% NB is significantly lower than the counterpart in Fig. 3(b) and much similar to the slopes at 1% to 2.5% NB concentration due to the poor inhibiting action of NB in H2SO4 solution. The variation in corrosion potential shows NB is a mixed type inhibitor in HCl and H2SO4 solution. Fig. 4 to Fig. 6(c) shows the shows the macro optical images (mag. x10) of MS before corrosion test and after corrosion in 1M H2SO4 and HCl solution at 0%, 1% and 2.5% NB concentration. The optical images before corrosion [Fig. 4] presents the sample as received after sample preparation. Fig. 5(a), (b) and Fig. 6(a) shows the optical images of MS from H2SO4 solution at 0% and 1% NB concentrations, and 0% NB in HCl solution. The severe surface and structural deterioration is due to the electrochemical action of SO42- and Cl- anions in the acid solution. In agreement with the result from weight loss and potentiodynamic polarization test, it’s quite visible that NB inhibitor performed poorly at 1% NB in H2SO4 solution [Fig. 5(b)]. The images show severe morphological and structural deterioration compared to Fig. 5(c) where the optical image of MS showed effective NB inhibition. Fig. 6(b) and (c) show effective inhibition of MS in HCl solution compared to the morphological deterioration in H2SO4. Color variation of the inhibited and corroded confirmed surface coverage by NB dominated the inhibition mechanism.

Table 1: Potentiodynamic polarization data for MS corrosion in 1M HCl and H2SO4 solution at 0% to 2.5% NB concentration

| Sample | NB Conc. (%) | MS Corrosion Rate (mm/y) | NB Inhibition Efficiency (%) | Corrosion Current (A) | Corrosion Current Density (A/cm²) | Corrosion Potential (V) | Polarization Resistance (Ω) | Cathodic Tafel Slope (V/dec) | Anodic Tafel Slope (V/dec) |
|--------|--------------|--------------------------|-----------------------------|----------------------|----------------------------------|------------------------|-----------------------------|-----------------------------|-----------------------------|
| A      | 0            | 19.1                     | 0                           | 1.89E-03             | 1.67E-03                        | -0.469                 | 13.58                       | -6.675                      | 0.495                       |
| B      | 1            | 1.23                     | 93.58                       | 1.21E-04             | 1.07E-04                        | -0.467                 | 211.6                       | -6.377                      | 16.8                        |
| C      | 2            | 1.10                     | 94.24                       | 1.09E-04             | 9.63E-05                       | -0.466                 | 236.1                       | -6.719                      | 15.16                       |
| D      | 3            | 1.63                     | 91.48                       | 1.61E-04             | 1.43E-04                       | -0.463                 | 159.4                       | -7.358                      | 15.86                       |
| E      | 4            | 1.33                     | 93.05                       | 1.32E-04             | 1.16E-04                       | -0.454                 | 195.4                       | -6.137                      | 16.1                        |
| Sample | NB Conc. (%) | MS Corrosion Rate (mm/y) | NB Inhibition Efficiency (%) | Corrosion Current (A) | Corrosion Current Density (A/cm²) | Corrosion Potential (V) | Polarization Resistance (Ω) | Cathodic Tafel Slope (V/dec) | Anodic Tafel Slope (V/dec) |
|--------|-------------|--------------------------|------------------------------|----------------------|----------------------------------|-------------------------|-----------------------------|-----------------------------|---------------------------|
| A      | 0           | 11.98                    | 0                            | 1.19E-03             | 1.05E-03                        | -0.475                  | 21.65                       | -7.175                      | 1.521                     |
| B      | 1           | 8.95                     | 25.29                        | 8.87E-04             | 7.84E-04                        | -0.394                  | 57.8                        | -4.709                      | 16.571                    |
| C      | 2           | 8.1                      | 32.36                        | 8.03E-04             | 7.10E-04                        | -0.422                  | 65.4                        | -9.269                      | 18.43                     |
| D      | 3           | 7.62                     | 36.36                        | 7.55E-04             | 6.68E-04                        | -0.440                  | 76.5                        | -8.58                       | 20.09                     |
| E      | 4           | 1.72                     | 85.66                        | 1.70E-04             | 1.51E-04                        | -0.434                  | 150.9                       | -6.941                      | 17.97                     |

(a) Figure 1: Plot of MS corrosion rate versus exposure time at 0% to 2.5% NB concentration from 1M HCl solution and (b) from 1M H₂SO₄ solution
Figure 2: Plot of NB inhibition efficiency versus exposure time at 0% to 2.5% NB concentration (a) from 1M HCl solution and (b) from 1M H2SO4 solution.

Figure 3: Potentiodynamic polarization plot of MS corrosion at 0% to 2.5% NB concentration (a) from 1M HCl solution and (b) from 1M H2SO4 solution.
Figure 4: Optical image of MS before corrosion test

Figure 5: Optical image of MS after corrosion from H_2SO_4 solution (a) at 0% NB, (b) at 1% NB and (c) at 2.5% NB concentration

Figure 6. Optical image of MS after corrosion from HCl solution (a) at 0% NB, (b) at 1% NB and (c) at 2.5% NB concentration
4. **Conclusion**

The synergistic effect of neem leaf and basil oil extracts effectively decreased the electrochemical deterioration of mild steel in dilute HCl and H_2SO_4 solution. The combined inhibitor formulations inhibited the corrosion of mild steel more effectively in HCl solution than in H_2SO_4 solution. The performance of the inhibitor in H_2SO_4 solution was very poor with the exception of the highest inhibitor concentration. The inhibitor displayed mixed inhibiting properties despite dominant anodic inhibition through surface coverage. The weight loss and potentiodynamic polarization results were corroborated with the optical images which confirmed effective inhibition in HCl solution and severe surface and structural deterioration in H_2SO_4 solution.

**Acknowledgement**

The authors appreciate Covenant University Ota, Ogun State, Nigeria for the funding of the research.

**References**

1. Loto, R. T., Leramo, R., & Oyebade, B. (2018). Synergistic combination effect of salvia officinalis and lavandula officinalis on the corrosion inhibition of low-carbon steel in the presence of SO_4^{2−} and Cl^{−} containing aqueous environment. Journal of Failure Analysis and Prevention, 18(6), 1429–1438.
2. Loto, R. T., & Olowoyo, O. (2018). Corrosion inhibition properties of the combined admixture of essential oil extracts on mild steel in the presence of SO_4^{2−} anions. South African Journal of Chemical Engineering, 26, 35-41.
3. Loto, R. T. (2018). Surface coverage and corrosion inhibition effect of rosmarinus officinalis and zinc oxide on the electrochemical performance of low carbon steel in dilute acid solutions. Results in Physics, 8, 172–179.
4. Loto, R. T., & Tobilola, O. (2018). Corrosion inhibition properties of the synergistic effect of 4-hydroxy-3-methoxybenzaldehyde and hexadecyltrimethylammoniumbromide on mild steel in dilute acid solutions. Journal of King Saud University – Engineering Sciences, 30, 384–390.
5. El-Etre, A. Y. (1998). Natural honey as corrosion inhibitor for metals and alloys. i. copper in neutral aqueous solution, Corrosion Science, 40(11), 1845-1850.
6. Parikh, K. S., & Joshi, K. J. (2004). Natural compounds onion, garlic and bitter gourd as corrosion inhibitors for mild steel in hydrochloric acid. Transactions of the SAEST, 39(1-2) 29.
7. Loto, R. T., Loto, C. A., Ayozie, B. U., & Sanni, T. (2018). Anti-corrosion Properties of Rosemary Oil and Vanillin on Low Carbon Steel in Dilute Acid Solutions, TMS 2018 147th Annual Meeting & Exhibition Supplemental Proceedings, The Minerals, Metals & Materials Series. https://doi.org/10.1007/978-3-319-72526-0_84.
8. Loto, R. T. (2017) Anti-corrosion performance of the synergistic properties of benzenecarbonitrile and 5-bromovanillin on 1018 carbon steel in HCl environment. Scientific Reports, 7(17555. Doi:10.1038/s41598-017-17867-0.
9. Hughes, A. E., Gorman, J. D., & Paterson, P.J.K. (1996). The characterization of Ce-Mo-based conversion coatings on Al-alloys: Part I. Corrosion Science, 38(11), 1977-1990.
10. Schem, M., Schmidt, T., Gerwann, J., Zheludkevich, M. L., et al., CeO_2-filled sol–gel coatings for corrosion protection of AA2024-T3 aluminium alloy. Corrosion Science, 51(10), 2304-2315.