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CORROSION INHIBITORY ATTRIBUTES OF MIXTURE OF *Codiaeum variegatum* AND *Ficus benjamina* FOR MILD STEEL IN HYDROCHLORIC ACID MEDIUM

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ABSTRACT

The deterioration of metals/alloys in diverse media is a challenge that is receiving tremendous attention owing to its negative impact on the economy. The efficacy of a mixture of *Codiaeum variegatum* and *Ficus benjamina* as an environmental pleasant inhibitor for mild steel (M-S) in hydrochloric acid was studied using potentiodynamic polarization. Ethanolic extract of *Codiaeum variegatum* (CV) and *Ficus benjamina* (FB) were mixed in a ratio of 1:1 to obtain CV-FB. Open circuit potential values changed substantially when CV-FB was introduced, indicating that CV-FB influenced M-S deterioration in hydrochloric acid. Corrosion current density decreased from 1211 μAcm^{-2} (without CV-FB) to 342 μAcm^{-2} (in the presence of 800 ppm CV-FB) and the decrease was consistent with CV-FB dosage. Percentage inhibition efficiency improved with a surge in CV-FB dosage. The maximum inhibition efficiency obtained was 71.8 %. The adsorption of CV-FB on the surface of M-S conformed to Langmuir adsorption isotherm. The alteration in corrosion potential values upon introduction of CV-FB was < 85 mV, indicating that CV-FB exhibited mixed-type traits. A mixture of leaves extract of *Codiaeum variegatum* and *Ficus benjamina* could be employed as an environmental pleasant inhibitor for acid-induced deterioration of M-S.

Keywords: Corrosion inhibitor, Mild steel, *Codiaeum variegatum*, *Ficus benjamina*, Potentiodynamic polarization

INTRODUCTION

Acid solutions are employed for cleaning metals/alloys in industries including mild steel (M-S) (Haque *et al*., 2023; Odozi *et al*., 2021). The harsh nature of acids often results in the deterioration of the metal (i.e corrosion). Corrosion of metals is among the glitches facing different industries in different countries. Interaction of metal/alloys with dissolved CO_2, acids, H_2S, bases and salts is known to induce deterioration. Despite technical advances over the past years, deterioration of metals still impacts negatively on many areas (Barbouchi *et al*., 2023).

The application of M-S as a construction material in numerous industries is due to its relatively stumpy price, availability and remarkable attributes (Chugh *et al*., 2020; Mchihi *et al*., 2024). However, despite its wide application in various industries owing to interesting properties, M-S is susceptible to deterioration, principally in aggressive media such as HCl. As a result, it is necessary to develop mitigation techniques to protect mild steel from corrosion.

Researchers have invented several techniques for metallic corrosion mitigation. Among various available methods, one of the widely used techniques for mild steel corrosion mitigation in an acidic medium is the use of corrosion inhibitors. Several compounds have been utilized as corrosion inhibitors. Some of these compounds include pyrazoline derivatives (Lgaz *et al*., 2018), 2-{4-[(2E)-3-(4-fluorophenyl)prop-2-enoyl]phenoxy}acetic acid hydrate (Ajees *et al*., 2017), Schiff bases (Gupta *et al*., 2016; Jamil *et al*., 2018), sulphonamide derivatives (Murulana *et al*., 2016), chromone-3-acrylic acid derivatives (Kumar *et al*., 2017), coumarin derivatives (Zinad *et al*., 2020), 3-((5-(3,5-dinitrophenyl)-1,3,4-thiadiazol-2-yl)imino)indolin-2-one (Al-Azawi *et al*., 2018) and 1,4-dioctyl-6-methyl-1,4-dihydroquinoxaline-2,3-dione (Zouitini *et al*., 2019). The majority of these compounds exhibited good inhibition efficiency for the protection of the metal or alloy in the studied media. For instance, in the study conducted by Lgaz et al. (2018) on the efficacy of two pyrazoline derivatives as inhibitors for M-S deterioration in an acid medium, 91 and 95% inhibition efficiency were achieved in the study. Similarly, 4-((4-((4-hydroxy-3-methoxybenzylidene)amino)-5-thioxo-4,5-dihydro-1*H*-1,2,4-triazol-3-yl)methyl)-coumarin showed tremendous inhibition efficiency of 96% at a dosage of 0.5 mM (Zinad *et al*., 2020).

Due to the high toxicity and high cost associated with the use of synthesized organic and inorganic compounds for corrosion mitigation, the usage of extracts of plants is currently getting consideration. Several reports on the use of extracts for metallic corrosion mitigation revealed high inhibition efficiency (Al Otaibi and Hammud, 2021; Odozi *et al*., 2024; Haque *et al*., 2023; Mchihi *et al*., 2023; Mchihi *et al*., 2024c; Odozi *et al*., 2021). The inhibitory effect of extracts of different plant parts is attributed to the presence of diverse compounds in plants that contain hetero atoms that aid their adsorption on the metal surface, resulting in the establishment of a protective film. *Ficus benjamina* (popularly known as Benjamin tree) and *Codiaeum variegatum* (commonly known as garden croton) are known to contain diverse compounds in their leaves and other parts (Mahomoodally *et al*., 2019; Bijekar and Gayatri, 2014). The purpose of this work was to scrutinize the efficacy of a mixture of *Codiaeum variegatum* and *Ficus Benjamina* as eco-friendly corrosion inhibitor for M-Z in hydrochloric acid.

MATERIALS AND METHODS

Sample Collection

The two different leaves used for this study were collected at Fadeyi, Lagos and taken to the University of Lagos Herbarium where they were identified as *Codiaeum variegatum* and *Ficus benjamina* and assigned the numbers 100151 and 100152 respectively. Mild steel sheet was bought from an open market in Lagos, Nigeria.

Extraction Procedure

The procedure reported by Eziuka et al. (2023) was adopted for extraction with slight modification**.** *Codiaeum variegatum* (CV) leaves were washed with distilled water to remove dust particles, dried in the oven at 323 K for 24 h and pulverized into fine powder. 80 g of the pulverized sample was drenched in a volumetric flask comprising ethanol (250 mL). The resulting mixture was comprehensively agitated and then allowed to stand for 48 h. The mixture was then filtered, after which a rotary evaporator was employed to recover the solvent content of the filtrate. The same procedure was repeated for *Ficus benjamina* leaves (FB). CV an FB semi-solid mass obtained was mixed in the ratio of 1:1 to obtain CV-FB which was used to prepare different concentrations of inhibitor solution.

Electrochemical Test Procedure

The free dissolution potential of M-S was determined before other electrochemical analyses by determining the open circuit potential (OCP) for 30 mins. This was done to decrease charging current influence and ensure system stability. The dissolution process lasted until a steady OCP was realized. Thus, all the electrochemical experiments were done at OCP conditions. The electrochemical assessments were performed using a set-up comprising of 1 cm^2 exposed M-S (which functioned as the working electrode), Ag/AgCl as a reference electrode (hence, all reported potentials in this study are vs. Ag/AgCl) and platinum wire which was employed as a counter electrode. 1 M hydrochloric acid was employed as the electrolyte (i.e aggressive media). The potentiodynamic polarization inquiry was piloted at the potential range of ±250 mV versus OCP. 0.2 mV s^{-1} was the scanning rate. Measurements were carried out without CV-FB and in company of CV-FB. The percentage inhibition efficiency was computed using values of corrosion current density (Icorr) in accordance with equation 1.

$$\%IE = \frac{\text{Icorr in the absence of inhibitor} - \text{Icorr in the presence of inhibitor}}{\text{Icorr in the absence of inhibitor}} \text{ X } 100 \quad (1)$$

RESULTS AND DISCUSSION

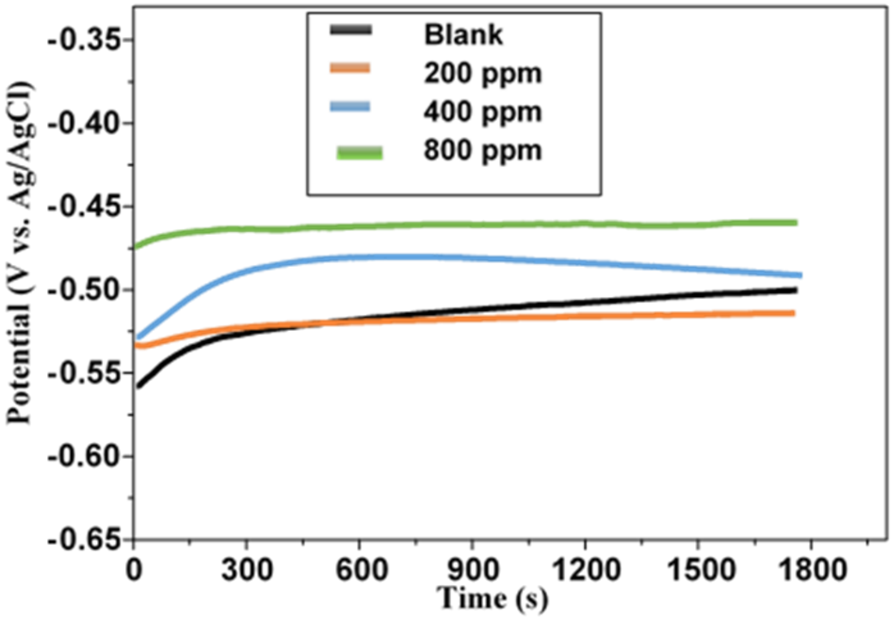

Figure 1: Open circuit potential versus time plots for mild steel in 1 M HCl in the presence and absence of CV-FB

Open Circuit Potential

The OCP versus time plot for M-S corrosion in 1 M hydrochloric acid without CV-FB and in the presence of different CV-FB dosages is presented in Fig. 1. It can be deduced from the plot that stable values of OCP were attained after 900 s for all CV-FB concentrations in 1 M HCl (Al Otaibi and Hammud, 2021). The OCP values shifted towards the positive direction upon the introduction of 400 and 800 ppm of the CV-FB. However, a slight shift of OCP in the negative direction was observed in the presence of 200 ppm of the CV-FB. The shift in OCP values upon the introduction of CV-FB suggests that CV-FB has a great influence on the corrosion of M-S in the aggressive medium (Mchihi *et al.,* 2024a).

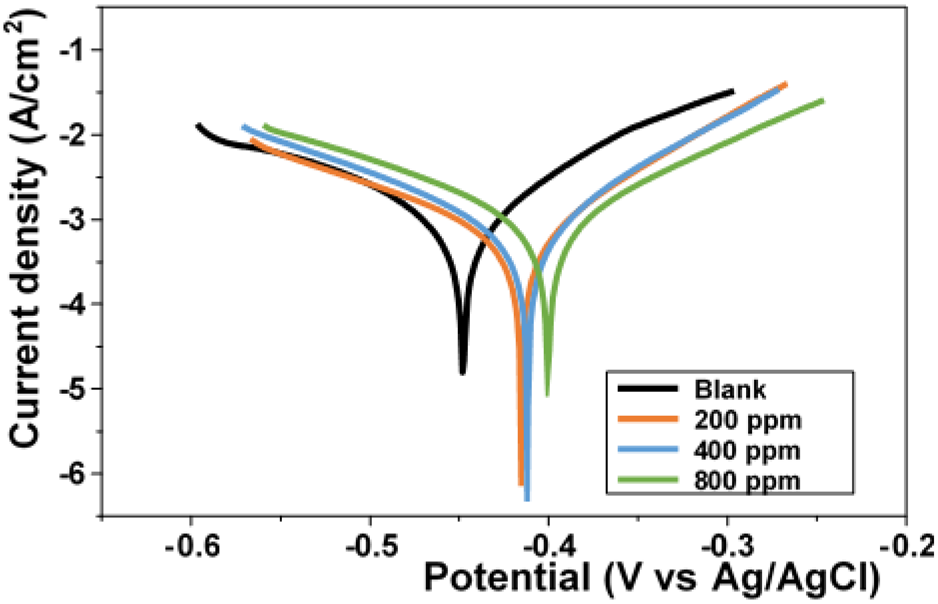

Figure 2: Potentiodynamic polarization plots for M-S in 1 M HCl in the presence and absence of CV-FB

Table 1: Parameters obtained from PDP measurements

System	E_{corr} (mV/SCE)	I_{corr} (μAcm^{-2})	βa ($mVdec^{-1}$)	βc ($mVdec^{-1}$)	θ	IE (%)
Blank	-419	1211	43	84		
200 ppm	-423	579	48	68	0.52	52.2
400 ppm	-420	471	62	54	0.61	61.1
800 ppm	-425	342	63	50	0.72	71.8

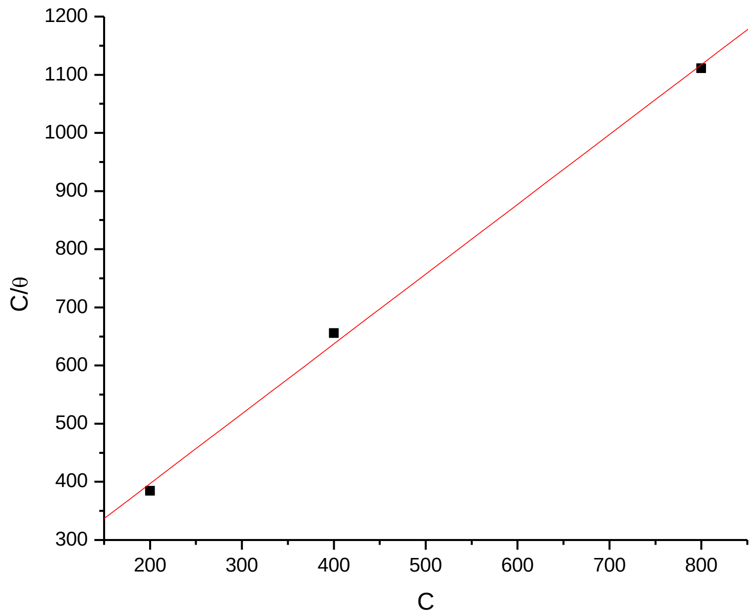

Figure 3: Langmuir plots for M-S in 1 M HCl in the presence and absence of CV-FB using PDP data

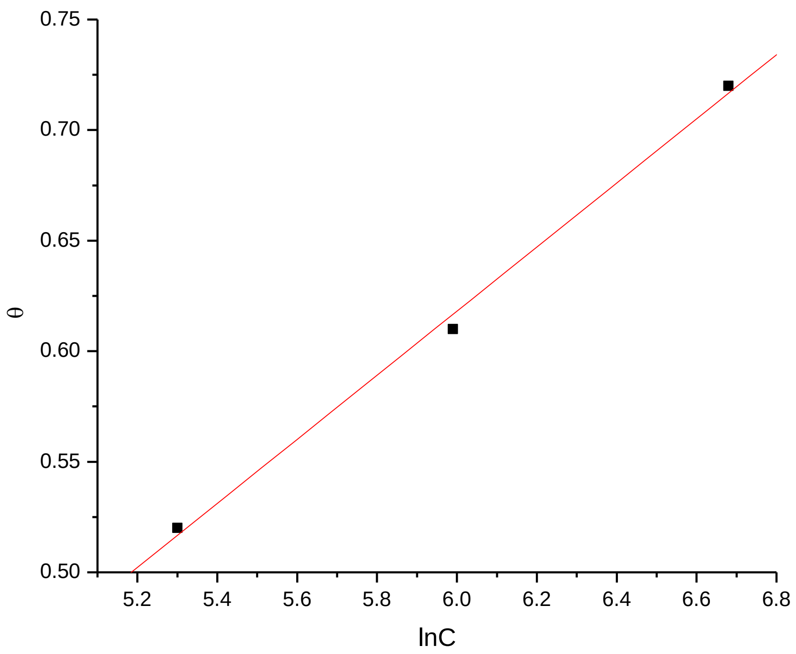

Figure 4: Temkin plots for M-S in 1 M HCl in the presence and absence of CV-FB using PDP data

Potentiodynamic Polarization

Figure 2 depicts polarization plots for M-S deterioration in 1 M hydrochloric acid without CV-FB and in the company of different dosages of CV-FB. The associated parameters such as I_{corr} and corrosion potential (E_{corr}) are presented in Table 1. A noticeable decrease in I_{corr} in the presence of CV-FB can be observed. This decrease in I_{corr} is consistent with an increase in the concentration of CV-FB. The observed shift in E_{corr} obtained in the company of CV-FB compared to Ecorr obtained in the absence of CV-FB is less than 85 mV which suggests that CV-FB exhibited mixed-type inclination (Mchihi *et al.,* 2024a). Inhibition efficiency obtained in potentiodynamic polarization increased with an increase in concentration of CV-FB (Al Otaibi and Hammud, 2021; Hamdouch *et al.*, 2023; Mchihi *et al.,* 2024b). The marked surge in inhibition efficiency with an upsurge in CV-FB dosage is likely to be due to a surge in CV-FB molecules, thus increasing the tendency of the establishment of shielding film on M-S (Al Otaibi and Hammud, 2021).

Adsorption Isotherm

The adsorption isotherm analysis is a vital analysis for understanding the interaction of corrosion inhibitors with the metal surface. In this study, Langmuir adsorption isotherm and Temkin adsorption isotherm were used in line with equations 2 and equation 3 respectively. Langmuir and Temkin's plots generated using data obtained from potentiodynamic polarization studies are presented in Figures 3 and 4. A high regression coefficient (R^2 = 0.99999) was obtained for the Langmuir adsorption isotherm (Table 2) suggesting that, the adsorption of CV-FB on M-S surface conformed to the Langmuir adsorption isotherm.

$$\frac{C}{\theta} = C + \frac{1}{Kads} \quad (2)$$

$$\theta = -\frac{1}{2a} lnC - \frac{1}{2a} lnK \quad (3)$$

Due to the presence of diverse compounds in different concentrations, the inhibition process is generally rationalized by the synergistic intermolecular influence of the several molecules contained in the plant extract (Haque *et al*., 2023). According to reports, the synergistic intermolecular effect facilitates easy adsorption on the M-S surface and shields aggressive hydrogen ions. The possibility of complex formation is more likely owing to the presence of one or more phytochemicals in natural extracts (Mchihi *et al*., 2024).

Table 2: R^2 values obtained from Isotherm studies

Isotherm		slope	Intercept (1/K)	R^2
Langmuir	PDP	1.20047	156.935	0.99999
Temkin	PDP	0.14493	-0.25145	0.99834

CONCLUSION

The efficacy of a mixture of *Codiaeum variegatum* and *Ficus Benjamina* as an eco-friendly corrosion inhibitor for mild steel in hydrochloric acid solution was studied using potentiodynamic polarization. Corrosion current densities decreased in the presence of inhibitor and the decrease depended on the concentration of the inhibitor. The percentage inhibition efficiency increased with an increase in concentration of the inhibitor. The highest inhibition efficiency obtained was 71.8 %. The adsorption of the inhibitor on mild steel surface obeyed Langmuir isotherm. The inhibitor acted as a mixed-type inhibitor. The mixture of *Codiaeum variegatum* and *Ficus benjamina* leaves extract could be utilized as an environmental friendly inhibitor for mild steel in a hydrochloric acid medium.

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