Electrochemical analysis of the corrosion inhibition properties of 4-hydroxy-3-methoxybenzaldehyde on low carbon steel in dilute acid media

Roland T. Loto1,2*

Abstract: The electrochemical behaviour of low carbon steel in 1 M H2SO4 and HCl acid was studied in the presence of 4-hydroxy-3-methoxybenzaldehyde (HMD) as the inhibiting organic compound through weight loss and potentiodynamic polarization technique. Results show HMD has strong corrosion inhibition effects on the steel in the acid solution. HMD performed excellently at all concentrations studied with optimal inhibition efficiency of 96.6 and 92.5% from weight loss analysis and 88.81 and 91.35% for potentiodynamic polarization tests in H2SO4 and HCl. The compound showed mixed inhibition properties in both solutions. Data from statistical analysis through ANOVA shows the overwhelming influence of inhibitor concentration in H2SO4 and exposure time in HCl on the inhibition efficiency of the organic compound. Adsorption of the compound obeyed the Langmuir isotherm. Thermodynamic calculations showed strong physiochemical interactions and spontaneous adsorption mechanism.

Subjects: Applied & Industrial Chemistry; Chemistry; Environmental Chemistry; Materials Chemistry; Materials Science; Metals & Alloys; Physical Chemistry

Keywords: adsorption; corrosion; carbon steel; inhibitor; hydrochloric; sulphuric

ABOUT THE AUTHOR
Roland T. Loto is a proven scholar and research scientist in the field of metallic corrosion reactions phenomena, corrosion measurement, control and prevention covering a very broad spectrum of technical areas and activities. He has a significant number of research publications including reviews in top international journals, conference proceedings and has consistently served as reviewer in respectable journals due to his intensive knowledge and technical expertise. He has undertaking a number renowned engineering research in collaboration with research institutes and educational institutions. His in-depth knowledge and experience in research experimentation is basically aimed at proffering solutions to the current depreciating effect of metallic degradation and failure in service in various engineering applications.

PUBLIC INTEREST STATEMENT
The economic impact and problems resulting from corrosion has drawn strong attention from scientists and engineers worldwide. Corrosion of mild steel in industrial environments is a major concern in chemical processing plants, oil and gas industry, manufacturing, automobile industry, marine operations, boiler plants and power generation plants due to the considerable cost involved in the replacement of metallic parts in their various applications. The consequence often leads to plant shutdowns, breakdown of industrial equipment, reduced efficiency, industrial downtime, high maintenance cost due to replacement of damaged part, wastage of valuable resources and expensive overdesign. A great number of studies have being devoted to the subject of corrosion inhibitors. Corrosion inhibition is of great practical importance, being extensively employed in curtailing wastage of engineering materials and minimizing costs of corrosion control.
1. Introduction

Acid solutions are commonly used in chemical industries for production of detergents, synthetic resins, dyestuffs, pharmaceuticals, petroleum catalysts, insecticides and antifreeze etc. as well as in various processes such as paper sizing, water treatment, oil well acidicizing, aluminium reduction and removal of scales from metallic surfaces, most especially carbon steels (Greenwood & Earnshaw, 1997). Carbon steel is a major material of construction, extensively used in chemical and allied industries for handling alkalis, acids and salt solutions due to its easy availability, low cost and uncomplicated fabrication (Melchers & Jeffrey, 2004, 2005; Saha, Kurmaih, & Hakerman, 1955; Singh, Ebensu, & Quraishi, 2012). As a result it corrodes when exposed to various industrial environments and service conditions. The addition of inhibitors protects the metal against corrosion effectively. Inhibitors are one of the most practical methods for protection against corrosion, especially in acidic media (Xianghong & Guannan, 2005). The use of corrosion inhibitors has considerably increased in recent years due to increase in awareness of corrosion worldwide. They play an important role in controlling corrosion of metals (Quraishi & Sardar, 2001). The applicability of organic compounds as corrosion inhibitors for metals in acidic media has been recognized for a long time (Ajmal, Mideen, & Quraishi, 1994; Bethencourt, Botana, Calvino, & Marcos, 1998; El Achouri et al., 2001; El-Etre, 1998; El-Rehim, Ibrahim, & Khaled, 1999; El-Sayed, 1997). Existing data show that most organic inhibitors act by adsorption on the metal surface. Phthalocyanine blue dye was evaluated for its corrosion inhibition and adsorption properties on carbon steel in dilute sulfuric acid through potentiodynamic polarization, electrochemical impedance spectroscopy and weight loss analysis at very low concentration. Results showed that it is an excellent inhibitor with anodic type inhibition and strong passivation characteristics (Valle-Quitana, Dominguez-Patiño, & Gonzalez-Rodriguez, 2014). Ochoa, Moran, and Pèbère (2004) studied the synergistic effect of phosphonocarboxylic acid salts and fatty amines on carbon steel in NaCl solution through electrochemical impedance measurements and X-ray photoelectron spectroscopy. Result showed that the combined admixture effectively inhibited the corrosion of the steel through adsorption. Oguzie, Unaegbu, Okolue, and Onuchukwu (2004) concluded from gravimetric analysis that indigo dye adsorbed onto mild steel according to Frumkins and Flory–Huggins isotherm model in dilute sulphuric acid through chemisorption mechanism inhibiting its corrosion. His work on the inhibitive effect of congo red dye on the mild steel corrosion in sulphuric acid solution showed that the compound adsorbed onto the steel through physiochemical mechanism in accordance with Flory–Huggins isotherm model only (Oguzie, 2004). Rosliza, Nor’aïni and Wan Nik (2010) studied the effect of vanillin on the corrosion inhibition of aluminum alloy in marine environment. The parameters from the electrochemical techniques applied confirmed excellent inhibition properties. Adsorption of the compound was found to obey the Langmuir adsorption isotherm. The effect of vanillin on the corrosion behavior of AA6061 Al alloy in NaCl solution was studied by Shahidi, Mansouri, Bohrami, and Hosseini (2015) through electrochemical techniques. Results showed that the organic compound adsorbed strongly onto the steel at very low concentrations with mixed type inhibition efficiency characteristics. Apricot juice showed good corrosion inhibition and physisorption adsorption properties on mild steel in dilute H3PO4 acid solution from the work of Aproel, Anees, and Rafal (2013) through weight loss analysis and statistical studies. The electrochemical behaviour of mild steel in HCl and H2SO4 acid media in the presence of N-(2-thiophenyl)-N/-phenyl thiourea showed the compound to be an efficient anodic inhibitor with greater inhibition efficiency in HCl than in H2SO4 media. Adsorption was observed to obey Temkins’ adsorption isotherm (Shetty, Shetty, & Nayak, 2006). The adsorption occurs through heteroatoms such as nitrogen, oxygen, phosphorus and sulphur, triple bonds or aromatic rings. These compounds adsorbed on the metallic surface blocking the active corrosion sites. The adsorption behavior of organic molecules on the surface of metals depends on the molecular structure of the compounds, surface charge density and zero charge potential of metals (Ai, Guo, Qu, Chen, & Zheng, 2006). 4-hydroxy-3-methoxybenzaldehyde has been previously studied for its corrosion inhibiting properties on aluminium in HCl and seawater however literature on its inhibiting properties on mild steel is rare (El-Etre, 2001; Rosliza et al., 2010). This research aims to investigate the inhibiting influence of 4-hydroxy-3-methoxybenzaldehyde on low carbon steel corrosion in 1 M H2SO4 and HCl acid solution through weight loss analysis, potentiodynamic polarization test and optical microscopy.
2. Experimental procedure

2.1. Material
The low carbon steel utilized for this research was sourced from the open market and analyzed at the Advanced Materials and Tribo-corrosion Research Laboratory, Department of Chemical and Metallurgical Engineering, Tshwane University of Technology, Pretoria, South Africa. The steel has the percentage nominal composition of 0.401C, 0.169Si, 0.440Mn, 0.005P, 0.012S, 0.080Cu, 0.008Ni, 0.025Al and 98.86Fe.

2.2. Inhibitor
4-hydroxy-3-methoxybenzaldehyde (HMD) solid white powdery granules obtained from Merck KGaA, EMD Millipore Corporation, Billerica, USA was the inhibiting compound employed. The structural formula of HMD is shown in Figure 1. The molecular formula is $C_{8}H_{8}O_{3}$, while the molar mass is 152.15 g mol$^{-1}$.

HMD was prepared and studied in molar concentrations of 0.008, 0.016, 0.025, 0.033, 0.041 and 0.049 respectively.

2.3. Test media
1 M of $H_{2}SO_{4}$ and 1 M HCl acid solution of 200 ml each prepared from deionized water with 1.5% recrystallized sodium chloride of analar grade were used as the corrosion test media.

2.4. Preparation of test specimens
The low carbon steel rods with cylindrical diameter of 14 mm were mechanical cut into specific number of test samples with average dimensions in length of 10 mm. A 3 mm hole was drilled at the steel center for suspension and observation during the experimentation. The steel samples were thereafter carefully cleansed with deionized water and dried with acetone in preparation for weight loss analysis. Metallographic preparation for potentiodynamic polarization tests involved mounting of the steel samples in resin and grinding of their exposed surface with silicon carbide abrasive papers of 80, 120, 220, 800 and 1,000 grits before polishing with 6–1 μm diamond paste. The samples were thereafter rinsed with distilled water and dried with acetone.

2.5. Weight-loss measurement
Weighted steel samples were individually immersed in 200 ml of the acid media at predetermined concentrations of the HMD for 504 h at ambient temperature. The steel samples were weighed every 72 h after been washed with deionized water and dried with acetone for accurate readings. Graphical illustrations of corrosion rate (mm/y) (calculated) vs. exposure time (h) (Figures 2(a) and 3(a)) for the two acid media and those of percentage inhibition efficiency (IE) (calculated) vs. exposure time (h) (Figures 2(b) and 3(b)) were made from tabulated results (Tables 1 and 2).

The corrosion rate ($R$) was calculated from Equation (1):

$$R = \frac{87.6W}{DAT}$$
where $W$ is the weight loss in milligrams, $D$ is the density in g/cm$^2$, $A$ is the area in cm$^2$, and $T$ is the time of exposure in hours. The $IE$ was determined from Equation (2):

$$IE = \left( \frac{R_1 - R_2}{R_1} \right) \times 100$$  \hspace{1cm} (2)

$R_1$ and $R_2$ are the corrosion rates with and without predetermined concentrations of HMD. The $IE$ was determined every 72 h through the study. The surface coverage is determined from Equation (3):

$$\theta = \left[ 1 - \frac{W_2}{W_1} \right]$$  \hspace{1cm} (3)

where $\theta$ is the substance amount of adsorbate adsorbed per gram (or kg) of the adsorbent. $W_1$ and $W_2$ are the weight loss of the low carbon steel in the inhibited and uninhibited acid solutions.

2.6. Potentiodynamic polarization analysis

Potentiodynamic polarization analyses were performed using cylindrical steel samples embedded in resin mounts with exposed surface of 154 mm$^2$. The analyses were performed at ambient temperature of 25°C with Digi-Ivy potentiostat. A platinum rod was used as the counter electrode and silver chloride electrode (Ag/AgCl) with pH of 6.5 was used as the reference electrode. The potentials were cursorily examined from $-1.5$ V to $+1.5$ V vs. OCP at a scan rate of 0.002 V/s. The corrosion current...
(i_{corr})$, corrosion current density ($i_{corr}$) and corrosion potential ($E_{corr}$) were determined from the Tafel plots of potential vs. log $i_{corr}$. The corrosion rate ($R$) was calculated from Equation (4):

$$R = \frac{0.00327 \times i_{corr} \times E_q}{D}$$

(4)

Figure 3. Graph of (a) corrosion rate vs. exposure time (b) inhibition efficiency vs. exposure time in 1 M HCl at 0–0.049 M HMD.

Table 1. Data obtained from weight loss measurements for low carbon steel in 1 M H₂SO₄ at specific concentrations of HMD after 504 h

| Sample | Corrosion rate (mm/y) | Surface coverage (θ) | Weight loss (mg) | Inhibition efficiency (%) | Inhibitor concentration (%) | Inhibitor concentration (M) |
|--------|-----------------------|-----------------------|-----------------|--------------------------|----------------------------|--------------------------|
| A      | 11.9                  | 0                     | 4.036           | 0                        | 0                          | 0                        |
| B      | 1.0                   | 0.912                 | 0.355           | 91.2                     | 0.0125                     | 0.008                    |
| C      | 1.2                   | 0.899                 | 0.407           | 89.9                     | 0.025                      | 0.016                    |
| D      | 1.4                   | 0.886                 | 0.461           | 88.6                     | 0.0375                     | 0.025                    |
| E      | 1.0                   | 0.917                 | 0.336           | 91.7                     | 0.05                       | 0.033                    |
| F      | 0.4                   | 0.966                 | 0.137           | 96.6                     | 0.0625                     | 0.041                    |
| G      | 1.4                   | 0.881                 | 0.481           | 88.1                     | 0.075                      | 0.049                    |
where \( i_{\text{corr}} \) is the current density in A/cm\(^2\), \( D \) is the density in g/cm\(^3\), \( E_q \) is the specimen equivalent weight in grams. The percentage inhibition efficiency (\( IE \)) was determined from Equation (5):

\[
IE = 1 - \left( \frac{R_2}{R_1} \right) \times 100
\]

Equation (5)

\( R_1 \) and \( R_2 \) are the corrosion current densities in absence and presence of HMD respectively.

2.7. **Optical microscopy characterization**

The surface morphology and topography of the inhibited and uninhibited steel samples were investigated after weight-loss analysis in 1 M H\(_2\)SO\(_4\) and 1 M HCl solutions using OMAX Trinocular metallurgical microscope for which optical micrograph were obtained.

2.8. **Statistical analysis**

Two-factor single level statistical analysis with ANOVA (F-test) was applied to evaluate the statistical importance of HMD concentrations and time of exposure on inhibition efficiency values of HMD in H\(_2\)SO\(_4\) and HCl acid solutions. The F-test was used to study the quantitative value of variation within each of the samples relative to the amount of variation between the samples.

The sum of squares among columns (exposure time) was obtained with Equation (6):

\[
SS_c = \frac{\sum T^2_c}{nr} - \frac{T^2}{N}
\]

Equation (6)

Sum of squares among rows (HMD concentration) was obtained with Equation (7):

\[
SS_r = \frac{\sum T^2_r}{nc} - \frac{T^2}{N}
\]

Equation (7)

While the total sum of squares was obtained from Equation (8):

\[
SS_{\text{total}} = \sum x^2 - \frac{T^2}{N}
\]

Equation (8)
3. Results and discussion

3.1. Weight-loss measurements

Weight-loss of the low carbon steel during the exposure period with and without specific concentrations of HMD in 1 M H₂SO₄ and HCl test solutions at ambient temperature was studied. The data for weight-loss (W), corrosion rate (R) and percentage inhibition efficiency (IE) in both acids are shown in Tables 1 and 2. Figures 2(a), (b) and 3(a), (b) shows the graphical plot of corrosion rate and percentage inhibition efficiency vs. exposure time in H₂SO₄ and HCl acid solutions respectively. The remarkable difference between the inhibited and uninhibited low carbon steel samples in the acid solutions as shown the figures earlier mentioned due to the presence of HMD and its electrochemical influence on the oxygen reduction, hydrogen evolution and oxidation corrosion processes which results in the effective protection of the exposed steel surface. In Figure 2(a) there is a progressive decrease in corrosion rate at the early onset of the exposure hours from 0.008 to 0.0033 M HMD and 0.049 M HMD concentration till 288 h exposure, after which the corrosion rate remains fairly constant, till the end of the exposure period. Figure 3(a) shows a slightly different phenomenon in HCl acid compared to H₂SO₄ where the corrosion rates were instantaneously very low in value due to the strong electrochemical action of HMD. This suggests that HMD inhibits corrosion more rapidly in HCl compared to H₂SO₄ acid, but the resultant effects are generally the same. The same phenomenon is observed in Figures 2(b) and 3(b) where there was a gradual increase in the inhibition efficiency of HMD in Figure 2(b) before remaining generally constant as compared to Figure 3(b).

HMD being an organic compound, its inhibition mode is through adsorption to the steel surface, due to its influence on the electrochemical reactions mechanism within the acid test solutions (Hackerman, Snively, & Payne, 1966) as shown in the surface coverage values in Tables 1 and 2. The HMD molecules adhere themselves onto the steel surface through adsorption inhibiting the electrolytic transport and diffusion of the corrosive species responsible for the deterioration of the steel. Visual observation of the steel samples in the test solutions suggests that cathodic inhibition plays a significant role in the inhibition characteristics of HMD. Cathodic inhibitors act by either slowing the cathodic reaction itself or selectively precipitating on cathodic areas to limit the diffusion of reducing species to the surface (Agarwal & Landolt, 1998; Corrosion Inhibitors, n.d.). Organic inhibitors are known to generally have heteroatoms such as O, N, and S which have higher basicity and electron density and thus act as corrosion inhibitor. These heteroatoms are the vital sites for the adsorption mechanism on the steel surface (Felicia, Santhanalakshmi, Wilson, John, & Susai, 2004). The inhibition efficiency of HMD as shown in the figures mentioned above is generally not proportional to its concentration and corrosion rate, but quantitatively commensurate to the amount of adsorbed HMD on the steel surface. Corrosion reactions are prevented from occurring over the active sites of the metal surface influenced by HMD molecules. Comparison of the uninhibited low carbon steels (0 M HMD) in H₂SO₄ and HCl solution with the inhibited solutions (0.008–0.049 M HMD) in Tables 1 and 2 evidently confirms that HMD at all concentrations effectively reduced the corrosion rates of the steel, thus protecting it.

3.2. Polarization studies

The influence HMD inhibitor concentration on the polarization diagrams of the low carbon steel in 1 M H₂SO₄ and HCl solutions was studied. Figure 4 shows the polarization plots of the relationship of the log of current density I (Acm⁻²) vs. the applied potential E (V) on the low carbon steel for HMD in 1 M H₂SO₄, while Figure 5 illustrates the plot of IE vs. HMD inhibitor concentration for potentiodynamic polarization test in the acid. Tables 3 and 4 show the potentiodynamic data obtained from the acid test solutions. As shown in Table 3 the inhibition efficiency of HMD is independent of its concentration value in the test solution. Increase in HMD concentration does not result in any change in inhibition efficiency. The inhibition efficiency data in Table 3 are generally similar form the lowest to the highest HMD concentration (0.008–0.049 M), an indication of HMD potency to counteract the corrosive effect of the acid test solution at all concentrations. The data for the parameters on the table shows that HMD inhibited the electrochemical process responsible for corrosion.
Figure 4. Potentiodynamic polarization plot for the low carbon steel in 1 M H$_2$SO$_4$ acid at specific HMD concentrations (0.008–0.049 M).

Figure 5. Plot of $IE$ vs. HMD inhibitor concentration for potentiodynamic polarization test in 1 M H$_2$SO$_4$.

Table 3. Potentiodynamic polarization test data for the low carbon steel in 1 M H$_2$SO$_4$ at specific HMD concentrations

| Sample | Inhibitor conc. (M) | Corr. rate (mm/y) | Inhibition efficiency (%) | Corr. current (A) | Corr. current density (A/cm$^2$) | Corr. potential (V) | Polarization resistance, $R_p$ (Ω) | $B_c$ | $B_a$ |
|--------|---------------------|-------------------|--------------------------|-------------------|-------------------------------|-------------------|-----------------------------------|------|------|
| A      | 0                   | 11.98             | 0                        | 1.59E-03          | 1.03E-03                     | −0.328            | 3.90                              | −0.715 | 0.014 |
| B      | 0.008               | 1.45              | 87.90                    | 1.93E-04          | 1.25E-04                     | −0.330            | 21.10                             | −0.767 | 0.057 |
| C      | 0.016               | 1.35              | 88.73                    | 1.79E-04          | 1.16E-04                     | −0.347            | 57.80                             | −0.747 | 0.111 |
| D      | 0.025               | 1.43              | 88.06                    | 1.89E-04          | 1.23E-04                     | −0.347            | 46.00                             | −0.773 | 0.070 |
| E      | 0.033               | 1.34              | 88.81                    | 1.77E-04          | 1.15E-04                     | −0.340            | 50.50                             | −0.763 | 0.075 |
| F      | 0.041               | 1.62              | 86.48                    | 2.14E-04          | 1.39E-04                     | −0.352            | 73.60                             | −0.683 | 0.127 |
| G      | 0.049               | 1.63              | 86.39                    | 2.16E-04          | 1.40E-04                     | −0.339            | 60.60                             | −0.637 | 0.113 |
Figure 6 shows the polarization plots of the relationship of the log of current density $I$ ($\text{A/cm}^2$) vs. the applied potential $E$ (mV) on the low carbon steel for HMD in 1 M HCl, while Figure 7 shows the plot of $IE$ vs. HMD inhibitor concentration for potentiodynamic polarization test in the acid. The potentiodynamic data obtained in HCl solution are shown in Table 4 where the inhibition efficiency are generally similar at all concentrations of HMD with slight increase at 0.025–0.033 M HMD concentration. The corrosion rate values in HCl are significantly lesser than in H$_2$SO$_4$ due to the more aggressive nature of SO$_2^{2-}$ ions in H$_2$SO$_4$ solution. HMD exhibited similar potency in HCl as in H$_2$SO$_4$ in inhibiting corrosion of the carbon steel samples under study.

Comparative observation of the polarization plot in Figure 4 and the corrosion potential in Table 3 shows that the corrosion potential shifts towards more negative potentials with increase in HMD concentration. The addition of HMD causes a remarkable decrease in the corrosion rate, i.e. shifts both the anodic and cathodic curves to lower current densities. This may be ascribed to adsorption of inhibitor over the corroded surface (Mu, Li, Qu, & Zhou, 2006). This phenomenon is attributed to anodic inhibition. Anodic inhibition involves surface coverage through film formation as a result of the interaction of HMD molecules with the steel surface. This does not negate cathodic inhibition which involves increase in surface impedance and inhibition of hydrogen evolution and oxygen reduction reactions. The major shift in corrosion potential is 24 mV indicating mixed type inhibition in H$_2$SO$_4$ acid. The polarization plot in Figure 6 and the corrosion potential in Table 4 shows that the shift in corrosion potential in both directions i.e. 22 mV in the positive direction and 41 mV in the negative direction. The values show that HMD inhibition in HCl is characteristically mixed type but to a slight degree cathodic (Şahin, Bilgiç, & Yılmaz, 2002). Thus in HCl steel passivation through adsorption is as a result of the deposition of HMD cations on the surface due to interaction between the inhibitor and the oxidized metal surface which effectively seals the surface against further reaction; however the cathodic process predominates over the anodic.
The corrosion inhibition behaviour of HMD in HCl and H₂SO₄ acid media with respect to concentration contrasts the results obtained from the work of Rosliza et al. (2010) and El-Etre (2001) where the same organic compound was used on aluminium in seawater and HCl acid media. The inhibition efficiency of the compound was observed to increase with increase in concentration (Inhibitor Efficiency, n.d.). The synergistic effect of HMD with protocatechualdehyde was studied by Emregül and Hayvalı (2004). Result show that the inhibition efficiency of the combined admixture increased with increase in concentration. These observations were confirmed from the results obtained from the use of non-ionic surfactants obtained from HMD in the combined mixture of saltwater and bentonite clay by Negm et al. (2015), however the compounds mentioned by the different authors displayed similar inhibition type (mixed type inhibition) with HMD and obeyed the Langmuir adsorption isotherm.

The $I_{corr}$ in Tables 3 and 4 associated with corrosion significantly decreased with increase in HMD concentration. In the presence of HMD, the insignificant change of $B_c$ in both acid solutions and the observable change of $B_a$ between the inhibited and uninhibited steel samples confirms that the corrosion mechanism of the cathodic process remains unchanged while the anodic dissolution of the steel was arrested, hence the difference in value of the anodic current. The results suggest that HMD acts by simple blocking of the available surface area [32], i.e. HMD decreases the surface area for corrosion through anodic inhibition. Furthermore, the inhibition efficiencies obtained from weight loss and polarization curves are in reasonably good agreement.

### 3.3. Inhibition mechanism

The inhibition performance of HMD is proportional to the extent to which it adsorbs over the metal surface. Adsorption depends on the molecular structure of the inhibitor, the surface charge of the metal, and on the type of corrosive media. Mixed type inhibitors have been known to protect metals in three possible ways: electrostatic adsorption, chemisorption and film formation. Electrostatic adsorption is the result of attraction between HMD and the metal surface. The metal surface is positively charged due to ionization (protonation) in the acid solutions which leads to electrostatic attraction of excess $\text{Cl}^-$ and $\text{SO}_4^{2-}$ anions in the acid media. This causes net negative charge on the metal surface resulting in the adsorption of protonated HMD ions and hence reducing the dissolution of Fe to Fe$^{2+}$ (Martinez, 2002; Unuabonah, Olu-Owolabi, Adebowale, & Ofomaja, 2007). The data on inhibition efficiency and surface coverage in Tables 3 and 4 suggest chemisorption mechanism due to chemical interactions which is responsible for HMD adhesion to the low carbon steel this is confirmed from thermodynamic calculations which will be discussed later. The physicochemical property of HMD is related to its functional groups (aldehyde, hydroxyl, and ether) and their chemical reactivity. Ethers are slightly polar i.e. they have a dipole moment. The C-O-C bond angle within their functional group is about 110°, and the C-O dipoles do not cancel out. However, the presence of two lone pairs of electrons on the oxygen atoms makes hydrogen bonding with water molecules possible.
Ethers are hydrolysed to alcohols in the presence of dilute acid thus increasing their solubility in the test solution. The hydroxyl functional group contains one oxygen atom connected by a covalent bonding to one hydrogen atom. It is the functional group of alcohols. This group has two reactive covalent bonds, the C–O bond and the O–H bond. The electronegativity of oxygen is substantially greater than that of carbon and hydrogen. Consequently, the covalent bonds of this functional group are polarized so that oxygen is electron rich and both carbon and hydrogen are electrophilic (Alcohol Nomenclature, n.d.).

The aldehyde functional group belongs to a class of organic compounds, in which the carbon atom shares a double bond with an oxygen atom, a single bond with a hydrogen atom, and a single bond with other atoms or group of atoms. The double bond between carbon and oxygen is known as the carbonyl group. The reactivity of these compounds arises largely through the polarity of the carbonyl group and the acidity of any \( \alpha \)-hydrogen that are present in their structure (Aldehyde Chemical Compound, n.d.). Aldehydes are polar molecules, thus they react with the nucleophile atoms of the corrosive species (\( \text{Cl}^- \) and \( \text{SO}_4^{2-} \)) with a deficiency of electrons to form a new covalent bond. The reaction of carbonyl group begins with an attack of a nucleophile (abbreviated as \( \text{Nu}^- \)) at the carbon atom of a carbonyl group, followed by combination of the now-negatively charged oxygen with a positive hydrogen ion.

\[
\text{R} - \text{C} = \text{O} + \text{Nu}^- \rightarrow \text{R} - \text{C} = \text{OH} + \text{H}^+ + \text{Nu} 
\]

Under the acidic conditions the positive hydrogen ion adds to the carbonyl oxygen first and then the nucleophile attacks the carbonyl carbon resulting in the loss of water. The newly formed \(-\text{OH}\) group leaves together with hydrogen from an adjoining atom. The result is formation of a double bond between the carbon and the nucleophile giving a C=S bond.

\[
\text{R} - \text{C} = \text{OH} \rightarrow \text{R} - \text{C} = \text{S} + \text{H}_2\text{O} 
\]

The interaction of the pi-orbitals of HMD functional groups with d-orbitals of the valence atoms of the metal is responsible for the adsorption bond strength and the nature of the protective film.

### 3.4. Adsorption isotherm

Further analysis of the corrosion inhibition mechanism of HMD obtained from its adsorption characteristics and behaviour on the metal surface. Effective corrosion inhibition due to the nature of the chemical bond between HMD molecules and the valence metal ions must be stronger than the interaction between HMD and water molecules. The adsorption of HMD at the metal/solution interface is due to the formation of electrostatic or covalent bonding between it and the ionized molecules of the metal surface atoms. Langmuir isotherms amongst others best explain the data obtained for HMD adsorption in 1 M \( \text{H}_2\text{SO}_4 \) and HCl solutions.

Adsorption isotherms are of the general form shown in Equation (11).

\[
f(\theta, x) \exp(-2a\theta) = KC
\]

where \( f(\theta, x) \) is the configurational factor subject to the physical model and assumption responsible for the derivation of the isotherm, \( \theta \) is the surface coverage, \( C \) is the inhibitor concentration, “\( a \)” is the molecular interaction parameter and \( K \) is the equilibrium constant of adsorption process.
The conventional form of the Langmuir isotherm is,

\[
\frac{\theta}{1 - \theta} = K_{\text{ads}} C
\]

and rearranging gives

\[
\theta = \frac{K_{\text{ads}} C}{1 + K_{\text{ads}} C}
\]

where \( \theta \) is the value of surface coverage on the steel alloy, \( C \) is HMD concentration in the acid solution and \( K_{\text{ads}} \) is the equilibrium constant of the adsorption process. The plots of \( \frac{C}{\theta} \) vs. the inhibitor concentration \( C \) were linear (Figures 8 and 9) indicating Langmuir adsorption.

The slight divergence of the slopes from unity in Figures 8 and 9 is due to the molecular interaction among the HMD molecules on the metal surface and changes in the values of the Gibbs free energy relative to the surface coverage.

Langmuir isotherm states the following proposition:

(a) The molecular interaction between HMD molecules on the metal surface is constant.
(b) The Gibbs free energy is independent of the value of surface coverage.
(c) The effect of lateral interaction between HMD molecules on the Gibbs free energy is negligible (Feng, Siow, Teo, & Hsieh, 1999).

Langmuir isotherm forecasts agreement between the fitted values but the derived values are less than unity for the slopes thereby indicating slight deviation from the absolute conditions stated in the isotherm.

3.5. Thermodynamics of the corrosion process

The values of Gibbs free energy (\( \Delta G_{\text{ads}} \)) for the adsorption process can be evaluated from the equilibrium constant of adsorption using the equation as shown in Tables 5 and 6.

\[
\Delta G_{\text{ads}} = -2.303RT \log [55.5K_{\text{ads}}]
\]

where 55.5 is the molar concentration of water in the solution, \( R \) is the universal gas constant, \( T \) is the absolute temperature and \( K_{\text{ads}} \) is the equilibrium constant of adsorption.

![Figure 8. Plot of \( \frac{\zeta}{\theta} \) vs. HMD concentration (C) in 1 M H\(_2\)SO\(_4\).](image)
The values of Free energy of Adsorption ($\Delta G_{\text{ads}}$) shown in Tables 5 and 6 provides further evidence of minimal divergence from absolute conditions of the Langmuir isotherm model as observed from the differential values of the Free energy of Adsorption ($\Delta G_{\text{ads}}$) with respect to the surface coverage ($\theta$) values.

The differential values of $\Delta G_{\text{ads}}$ in Tables 5 and 6 are due to the non-homogeneous nature of the steel. The topographic sites on the low carbon steel surface are not homogeneous thus the energy of adsorption is not equivalent. The energy of adsorption is subject to the topographic characteristics of metal and flaws (e.g. dislocations, vacancies, voids, inclusion and micro-distortions of crystal lattice) on the metal surface. The negative sign on $\Delta G_{\text{ads}}$ values depicts the spontaneous nature adsorption of HMD on the metal surface. The calculated values of $\Delta G_{\text{ads}}$ varies between $-34.80 \text{ kJ mol}^{-1}$ and $-29.52 \text{ kJ mol}^{-1}$ in $\text{H}_2\text{SO}_4$ solutions while in HCl it varies between $-33.95 \text{ kJ mol}^{-1}$ and $-29.77 \text{ kJ mol}^{-1}$. Values of $\Delta G_{\text{ads}}$ of about $-20 \text{ kJ/mol}$ or below relates to weak intermolecular interaction and values of $-40 \text{ kJ mol}^{-1}$ and above involves electrostatic attractions between the charged molecules and the charged metal i.e. the formation of covalent bond (Hosseini, Mertens, & Arshadi, 2009; Obot, Obi-Egbedi, & Umoren, 2009). The $\Delta G_{\text{ads}}$ data obtained shows that the adsorption mechanism of HMD on the low carbon steel varies from physiochemical (the combined action of electrostatic attraction and chemical reaction mechanism forming an insoluble protective film on the metal surface) to chemisorption interaction.

### 3.6. Optical microscopy characterization

The micrographs of the low carbon steel samples before and after the weight loss measurements are shown from Figures 10 to 12. The micrograph of the steel samples before the corrosion test as obtained commercially metallographic preparation of their surfaces at magnifications of $\times4$, $\times10$, $\times40$ and $\times100$ are presented in Figure 10(a)–(d). Figure 11(a)–(d) shows the micrograph of the steel specimens after the corrosion test without HMD. Its surface morphology significantly contrasts the micrographs in Figure 10. Degradation and surface deterioration of the sample is clearly visible due to corrosion from anions of sulphates and chloride within the acid solution. The anions react with the metal surface through the redox electrochemical process leading to the dissolution of the metal which passes into the solution as Fe$^{2+}$ cations. This observation was noticed during the exposure hours whereby there was a gradual buildup of sediments of iron compounds and significant discoloration of the acid solution. The morphology in Figure 11 shows that the steel is unacceptable for applications in corrosive environments as rapid deterioration occurs. The micrographs of the low carbon steel samples after immersion in the acid solution in the presence of HMD inhibiting compound are shown in Figure 12(a)–(d). In agreement with the results from weight loss and potentiodynamic polarization, the micrograph displays the topography of the steel shielded from corrosion due to the adsorption of HMD compound unto the steel surface.
Figure 10. Micrographic images of low carbon steel before exposure to acid solution (a) mag. ×4, (b) mag. ×10, (c) mag. ×100 and (d) mag. ×100.

Table 5. Data obtained for the values of Gibbs free energy, surface coverage and equilibrium constant of adsorption at varying concentrations of HMD in 1 M H2SO4

| Samples | Surface coverage (θ) | Inhibitor concentration (M) | Equilibrium constant of adsorption (K) | Gibbs free energy (ΔG) (kJ/mol) |
|---------|----------------------|-----------------------------|---------------------------------------|---------------------------------|
| A       | 0                    | 0                           | 0                                     | 0                               |
| B       | 0.912                | 8.22E-06                    | 1,261,462                             | −34.80                          |
| C       | 0.899                | 1.64E-05                    | 541,714                               | −32.70                          |
| D       | 0.886                | 2.46E-05                    | 315,333                               | −31.36                          |
| E       | 0.917                | 3.29E-05                    | 336,197                               | −31.52                          |
| F       | 0.966                | 4.11E-05                    | 691,656                               | −33.31                          |
| G       | 0.881                | 4.93E-05                    | 150,190                               | −29.52                          |

Table 6. Data obtained for the values of Gibbs free energy, surface coverage and equilibrium constant of adsorption at varying concentrations of HMD in 1 M HCl

| Sample | Surface coverage (θ) | Inhibitor concentration (M) | Equilibrium constant of adsorption (K) | Gibbs free energy (ΔG) (kJ/mol) |
|--------|----------------------|-----------------------------|---------------------------------------|---------------------------------|
| A      | 0                    | 0                           | 0                                     | 0                               |
| B      | 0.880                | 8.22E-06                    | 896,301.8                             | −33.95                          |
| C      | 0.918                | 1.64E-05                    | 683,716.9                             | −33.28                          |
| D      | 0.925                | 2.46E-05                    | 497,255.6                             | −32.49                          |
| E      | 0.891                | 3.29E-05                    | 249,618.7                             | −30.78                          |
| F      | 0.921                | 4.11E-05                    | 284,079.9                             | −31.10                          |
| G      | 0.891                | 4.93E-05                    | 165,734.7                             | −29.77                          |
Figure 11. Micrographic images of low carbon steel after exposure to acid solution without HMD compound (a) mag. ×4, (b) mag. ×10, (c) mag. ×40, (d) mag. ×100.

Figure 12. Micrographic images of low carbon steel after exposure to acid solution with HMD compound (a) mag. ×4, (b) mag. ×10, (c) mag. ×40, (d) mag. ×100.
3.7. Statistical analysis
Statistical analysis was employed through ANOVA at a confidence level of 95% i.e. a significance level of $\alpha = 0.05$. Data from ANOVA showed that the experimental sources of variation (HMD concentration and time of exposure) were statistically significant to the inhibition efficiency values with $F$-values of 18.52 and −11.40 in solutions, and −11.01 and 7.83 in HCl solution. These values are greater than the significance factor (significance $F$ in Tables 7 and 8) at $\alpha = 0.05$, thus they are significant at that level of probability. The statistical influence of the HMD concentration is 170.84% while the exposure time is −126.18% in H$_2$SO$_4$ depicting the overwhelming influence of HMD concentration on the values of inhibition efficiency from the experiments in comparison to the exposure time which is very negligible. In HCl only the exposure time (214.16%) is influential on the inhibition performance of HMD. The data from ANOVA tests are shown in Tables 7 and 8.

### Table 7. Analysis of variance (ANOVA) for inhibition efficiency of HMD inhibitor in 1 M H$_2$SO$_4$ (at 95% confidence level)

| Source of variation | Sum of squares | Degree of freedom | Mean square | Mean square ratio ($F$) | Min. MSR at 95% confidence level | $F$ (%) | Significance $F$ |
|---------------------|---------------|-------------------|-------------|------------------------|---------------------------------|---------|-----------------|
| Inhibitor concentration | 52,215.76 | 5 | 10,443.15 | 18.52 | 2.53 | 170.84 |
| Exposure time | −38,567.65 | 6 | −6,427.94 | −11.40 | 2.42 | −126.18 |
| Residual | 16,916.90 | 30 | 563.90 | | | |
| Total | 30,565.02 | 69 | | | | |

### Table 8. Analysis of variance (ANOVA) for inhibition efficiency of HMD inhibitor in 1 M HCl (at 95% confidence level)

| Source of variation | Sum of squares | Degree of freedom | Mean square | Mean square ratio ($F$) | Min. MSR at 95% confidence level | $F$ (%) | Significance $F$ |
|---------------------|---------------|-------------------|-------------|------------------------|---------------------------------|---------|-----------------|
| Inhibitor concentration | 59,035.40 | 5 | 11,807.08 | −11.01 | 2.53 | −250.96 |
| Exposure time | −50,379.03 | 6 | −8,396.51 | 7.83 | 2.42 | 214.16 |
| Residual | −32,180.66 | 30 | −1,072.69 | | | |
| Total | −23,524.29 | 69 | | | | |

4. Conclusion
4-hydroxy-3-methoxybenzaldehyde (HMD) showed excellent corrosion inhibition at all concentrations studied due to the effective inhibiting action of the compound. The corrosion rates of the carbon steel samples were significantly reduced from the onset of exposure in HCl solution and at 216 h in H$_2$SO$_4$ solution. Molecular adsorption of HMD onto the steel surface was determined to obey the Langmuir adsorption isotherm model through chemisorption mechanism from thermodynamic calculations. Statistical derivations showed that inhibitor concentration only is relevant to the inhibition performance of HMD in H$_2$SO$_4$ and the exposure time only in HCl acid.
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Author details

Roland T. Loto1,2
E-mail: tolu.loto@gmail.com

1 Department of Mechanical Engineering, Covenant University, Ota, Ogun State, Nigeria
2 Department of Chemical, Metallurgical & Materials Engineering, Tshwane University of Technology, Pretoria, South Africa.

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