Theoretical and experimental studies on the corrosion inhibition potentials of 3-nitrobenzoic acid for mild steel in 0.1 M H$_2$SO$_4$

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Theoretical and experimental studies on the corrosion inhibition potentials of 3-nitrobenzoic acid for mild steel in 0.1 M H₂SO₄

Paul O. Ameh¹ and Nnabuk O. Eddy²*

Abstract: The inhibition of the corrosion of mild steel in 0.1 M H₂SO₄ by 3-nitrobenzoic acid was studied using weight loss, electrochemical impedance spectroscopy (EIS), linear polarization resistant, potentiodynamic polarization, scanning electron microscopy, Fourier transformed infra-red spectroscopy and quantum chemical techniques. The results obtained indicated that 3-nitrobenzoic acid inhibited the corrosion of mild steel in solution of H₂SO₄. Maximum inhibition efficiency obtained from weight loss, potentiodynamic, linear polarization and EIS methods were 87.15, 90.51, 95.42 and 99.40% at inhibitor’s concentration of 0.01 M respectfully. The activation energies (which ranged from 26.02 to 59.02 J/mol) supported the mechanism of charge transfer from charged inhibitor to charged metal surface, which favours the mechanism of physical adsorption. The adsorption of the inhibitor was found to be exothermic and spontaneous. Although the adsorption characteristics of the inhibitor fitted the Langmuir adsorption model, the deviation of slope values from unity was explained by the existent of positive interaction parameters (attractive behaviour of the inhibitor’s molecules) according to the Frumkin model. 3-nitrobenzoic acid is dominantly a cathodic-type inhibitor and prevented the corrosion of mild steel by blocking the metal’s surface. Calculated values of the frontier molecular orbital energies and other semi-empirical parameters were in good agreement with...
those obtained for known and efficient corrosion inhibitors while Fukui function analysis indicated that the inhibitor is adsorbed unto the metal surface through the delocalization of electrons in the nitro oxygen bond, i.e. O(11)-N(10)-O(12).

Subjects: Computer Science; Engineering & Technology; Environment & Agriculture; Physical Sciences

Keywords: corrosion inhibitor; 3-nitrobenzoic acid; experiment and theoretical studies

1. Introduction
Metals are valuable components of almost all industrial installations and the cost of their installation is very expensive, indicating that they should have considerably long life span. However, their life span is often shortened by corrosion. Corrosion is an electrochemical process that returns metals to their natural states through interactions with some aggressive media (Karthikaisel & Subhashini, 2014).

Some of the options that are available for preventing metals against corrosion are painting, anodic/cathodic protection, electroplating and the use of corrosion inhibitors (Shukla & Ebenso, 2011). The use of corrosion inhibitors is widely acceptable as one of the most efficient method of corrosion protection. It has also been found that the inhibition efficiencies of most corrosion inhibitors are strongly dependent on some molecular and electronic parameters of the inhibitors (Eddy, Momoh-Yahaya, & Oguzie, 2015). Due to environmental requirement, trend in the choice of corrosion inhibitors, in recent times, has been directed towards the use of inhibitors that are less toxic, less expensive, biodegradable and environmental friendly (Kamal & Sethuraman, 2012; Umoren, Ogbobe, Okafor, & Ebenso, 2007; Yaro, Khadom, & Wael, 2014).

In view of the need to investigate and discover more green corrosion inhibitors, the present study is aimed at investigating the corrosion inhibition properties of 3-nitrobenzoic acid for mild steel in 0.1 M H2SO4. 3-nitrobenzoic acid is a derivative of benzoic acid, a carboxylic acid that occurs naturally in many plants and it serves as an intermediate in the biosynthesis of many secondary metabolites salts. Benzoic acid and some of its derivatives are used as food preservatives and it is an important precursor for the industrial synthesis of many other organic substances. The chemical structure of 3-nitrobenzoic acid is shown in Figure 1.

Although literature on the use of 3-nitrobenzoic acid as corrosion inhibitor is relatively scanty, Dinnappa and Mayanna (1981) have reported the corrosion inhibition properties of benzoic acid, toluic acid, p-nitrobenzoic acid, phthalic acid and tetephthalic acid. They found that these compounds are effective inhibitors for the corrosion of copper in HClO4 solution. The inhibition efficiencies of these compounds were also found to depend on temperature and concentration. Sibel (2002), also found that benzoic acid is an effective inhibitor for the corrosion of iron and aluminium in chloride solution. The studied inhibitor was reportedly found to be sensitive to temperature and functioned through the mechanism of physical adsorption. Some benzoic acids derivatives and related compounds have also been tested and found to be good corrosion inhibitors for mild steel and other metals. As far back as 1995, corrosion inhibition properties of hexamethyleneimine nitrobenzoate (Dorfman, 1995), carboxylate and sulphated carboxylates (Podobaev & Lorionov, 1995) were investigated and they were reported to be corrosion inhibitors. Quraishi and Jamal (2002) also found that some volatile

![Figure 1. Chemical structure of 3-nitrobenzoic acid.](image-url)
nitrobenzoic acid compounds are good corrosion inhibitors for steel. In spite of all these studies, literature is unavailable on the corrosion inhibition efficiency of 3-nitrobenzoic acid as a corrosion inhibitor for mild steel in H\textsubscript{2}SO\textsubscript{4}. It has long been established that corrosion inhibition efficiencies of inhibitors depends on numerous properties including electronic/molecular properties of the inhibitor, substituent’s constant, type of aggressive medium and metals, among others. In this work, gravimetric method, linear polarization resistant (LPR), potentiodynamic polarization (PDP) and electrochemical impedance spectroscopy (EIS) methods shall be used for the investigation of the inhibition efficiency of 3-nitrobenzoic acid. Scanning electron microscopy (SEM) shall be used to study the surface morphology of the metal before and after inhibition while Fourier transformed infra red spectrophotometer (FTIR) shall be used to study the functional group associated with the adsorption of the inhibitor on the surface of the metal. Finally, quantum chemical approaches shall be used to examine the local and global selectivity behaviour of the molecule towards corrosion inhibition.

2. Materials and methods

The mild steel sheet used in the study had the following chemical composition, Mn (0.60%), P (0.36%), C (0.15%), Si (0.03%) and Fe (98.86%). The metal was degreased by washing with absolute ethanol, rinsed in acetone and allowed to dry in the air. Gravimetric experiments were carried out at 303, 313, 323 and 333 K.

Containing various concentrations of 3-nitrobenzoic acid contained (solution of 0.1 M H\textsubscript{2}SO\textsubscript{4} without 3-benzoic acid was maintained as the blank).

2.1. Gravimetric method

In the gravimetric experiment, mild steel coupon was immersed in a 250 ml beakers, containing 200 ml of the test solution, (0.002–0.01 M of the inhibitor in 0.1 M H\textsubscript{2}SO\textsubscript{4}, respectively). The beaker was covered with aluminium foil and allowed to stand for 168 h. After 24 h of immersion, each coupon was withdrawn from the solution and washed with distilled water containing 50% of zinc dust. The washed coupon was re-weighed and re-immersed into the test solution. Weight loss measurements were taken after every 24 h of immersion for 7 days. The experiment was repeated for each of the test solutions and at different temperatures until corresponding values of weight loss were obtained after 168 h. From the results of weight loss measurements, the inhibition efficiency of 3-nitrobenzoic acid, its degree of surface coverage and the corrosion rate of mild steel were calculated using Equations (1)–(3), respectively (Ostovari, Hoseinieh, Peikari, Shadizadeh, & Hashemi, 2009),

\[
\% I = \frac{w_1 - w_2}{w_1} \times 100
\]  

(1)

\[
\theta = \left[1 - \frac{w_1}{w_2}\right]
\]  

(2)

\[
CR = \frac{w_1 - w_2}{At}
\]  

(3)

where \(w_1\) and \(w_2\) are the weight losses of mild steel (in grams) in the absence and presence of the inhibitor, respectively. \(\theta\) is the degree of surface coverage of the inhibitor, CR is the corrosion rate of mild steel, A is the surface area of the mild steel coupon in cm\(^2\) and t is the period of immersion in hours.

2.2. Electrochemical impedance spectroscopy

The electrochemical experiment was performed using a VERSASTAT 400 complete DC voltammetry for corrosion system, with V3 studio software. Test coupons with 1 cm\(^2\) exposed areas were used as working electrode and a graphite rod served as a counter electrode. The reference electrode was the saturated calomel electrode. All experiments were undertaken in stagnant aerated solutions and at a temperature of 30 ± 1°C. The working electrode was immersed in a test solution for one hour until a stable open-circuit potential was attained. From the electrochemical measurements, the real part
was plotted on the X-axis and the imaginary part on the Y-axis of a chart to develop a Nyquist Plot. The charge transfer resistance values \( (R_{ct}) \) were calculated from the difference in impedance at lower and higher frequencies (Dehri, Kardas, Solmaz, & Ozcan, 2008). The frequency at which the imaginary component of the impedance at maximum \( f(\text{Z}''\text{img}) \) was found and the double-layer capacitance \( (C_{dl}) \) values was calculated using Equation (4) (Vračar & Dražić, 2002).

\[
f \left( Z_{\text{img}} \right) = \frac{1}{2\pi C_{dl} R_{ct}}
\]

(4)

The inhibition efficiency was calculated from the charge transfer resistance values using the following equation (Khadom, Yaro, Kadum, & Musa, 2009).

\[
\% I = \frac{R_{ct(\text{Inh})} - R_{ct}}{R_{ct(\text{Inh})}} \times 100
\]

(5)

where \( R_{ct(\text{Inh})} \) and \( R_{ct} \) are values of the charge transfer in the presence and absence of the inhibitor.

2.3. Potentiodynamic polarization
The potentiodynamic current-potential curves were recorded by changing the electrode potential \( (E_{corr}) \) automatically with a scan rate 0.33 mV/s from a low potential of −800 to −300 mV (SCE). Before each run, the working electrode was immersed in the test solution for 30 min to reach steady state. The corrosion rate of the inhibitor was calculated through corrosion current density \( i_{\text{corr}} \), which was obtained by extrapolating the linear Tafel segments of the anodic and cathodic curves. The inhibition efficiency \( (I\%) \) was calculated using Equation (6) (Okafor & Zheng, 2009).

\[
\% I = \frac{i_{\text{corr}0} - i_{\text{corr}}}{i_{\text{corr}0}} \times 100
\]

(6)

where \( i_{\text{corr}0} \) and \( i_{\text{corr}} \) are the uninhibited and inhibited corrosion current densities, respectively.

2.4. Linear polarization resistance
LPR measurements were carried out within the potential range, ±20 mV with respect to the open-circuit potential, and the current response was measured at a scan rate of 0.5 mV/s. The over potential and current data was plotted on a linear scale to get LPR plots, and the slope of the plots in the vicinity of the corrosion potential gave the polarization resistance \( (R_p) \). From the measured values of \( R_p \), the inhibition efficiency \( (I\%) \) was calculated using Equation (7):

\[
\% I = \frac{R_{p(\text{Inh})} - R_{p}}{R_{p(\text{Inh})}} \times 100
\]

(7)

where \( R_p \) and \( R_{p(\text{Inh})} \) are the uninhibited and inhibited polarization resistance, respectively.

2.5. SEM studies
A SEM model JSM-5600 LV, was used to analyse the morphology of the mild steel surfaces, withdrawn from 0.1 M H\textsubscript{2}SO\textsubscript{4} in the presence and absence of the inhibitor. The sample was mounted on a metal stub and sputtered with gold in order to make the sample conductive, and the images were taken at an accelerating voltage of 10 kV using different magnifications.

2.6. FTIR analysis
FTIR analysis of the 3-nitrobenzoic acid and those of the corrosion products (in the absence and presence of the inhibitor) were carried out using Scimadzu FTIR-8400S Fourier transform infra-red spectrophotometer. The sample was prepared in KBr and the analysis was carried out by scanning the sample through a wave number range of 400–4,000 cm\textsuperscript{-1}.
2.7. Quantum chemical calculations
Full geometric optimization of 3-nitrobenzoic acid was achieved using molecular mechanics, ab initio and DFT levels of theory in the HyperChem release 8.0 software. Semi-empirical parameters were calculated using optimized structure of 3-nitrobenzoic acid as an input to the MOPAC software, while Mulliken charges were calculated using HyperChem release 8.0 software. All quantum chemical calculations were carried out on gas phase.

3. Results and discussions

3.1. Gravimetric results
Plots presenting the variation of weight loss of mild steel (in 0.1 M H$_2$SO$_4$) with time in the absence and presence of 3-nitrobenzoic acid at 303, 313, 323 and 333 K are shown in Figure 2. The plots revealed that weight loss of mild steel in solutions of H$_2$SO$_4$ increases with increase in the period of contact and with increasing temperature. These observations suggest that the rate of corrosion of mild steel in solutions of H$_2$SO$_4$ increases with increase in the period of contact and with increase in temperature. It is interesting to note that weight losses of mild steel in the blank solutions were higher than those obtained for systems containing the inhibitors. Therefore, 3-nitrobenzoic acid inhibited the corrosion of mild steel in solutions of H$_2$SO$_4$. Also, since the rate of corrosion decreased with increase in the concentrations of the inhibitor temperature, it is evident that the inhibition efficiency of 3-nitrobenzoic acid increases with increase in concentration but decreases with increasing temperature. These trends, characterize 3-nitrobenzoic acid as an adsorption inhibitor, which functions through the mechanism of physical adsorption. Adsorption inhibitors are characterized with increase in inhibition efficiency with increasing concentration and the mechanism of physical adsorption is obeyed when the inhibition efficiency decreases with increasing temperature (Khadom et al., 2009). Table 1 presents values of inhibition efficiency of 3-nitrobenzoic acid and corrosion rate of mild steel at various concentrations of the inhibitor at various temperatures. From the results obtained, the inhibition efficiency of 3-nitrobenzoic acid and the corrosion rate of mild steel exhibited characteristics that are similar to the information obtained from the plots. Thus while the inhibition efficiency increases with concentration and decreases with temperature, the corrosion rate decreases with concentration but decreased with increasing temperature.
3.2. Polarization study

Under polarization study, LPR and PDP measurements were carried out. Table 2 present polarization parameters for the corrosion of mild steel in solutions of H₂SO₄ containing various concentrations of 3-nitrobenzoic acid. Results obtained from LPR method revealed that the measured resistant for the blank was the least and that it increases with increasing temperature. This gave inhibition efficiency ranging from 70.02 (at concentration of 0.001 M) to 95.42% (at inhibitor’s concentration of 0.01 M).

On the other hand, in addition to the PDP data presented in Table 2, plots of the applied potential (E) versus log(current) for the various test solutions were developed and are presented in Figure 3. From the results obtained, the corrosion current is seen to decrease with increasing concentration of the inhibitor and the corrosion potentials are more negative as the concentration of the inhibitor is increased. The observed trend reveals that the presence of 3-nitrobenzoic acid shifted the corrosion potential to more negative value, indicating that 3-nitrobenzene functions as a cathodic inhibitor.

| C (M) | LPR | PDP |
|------|-----|-----|
|      | %I  | βa (mV/dec) | βc (mV/dec) | Ecorr (mV) | Icorr (μA) | I %   |
| Blank | 20.40 | – | 139.4 | 146.1 | –863 | 210.36 | – |
| 0.001 | 68.05 | 70.02 | 121.1 | 128.3 | –944 | 36.97 | 82.42 |
| 0.010 | 156.54 | 86.96 | 118.3 | 120.2 | –991 | 25.23 | 88.00 |
| 0.015 | 445.20 | 95.42 | 109.1 | 111.1 | –920 | 19.95 | 90.51 |

Table 2. Polarization data for the corrosion of mild steel in 0.1 M H₂SO₄ in the absence and presence of 3-nitrobenzoic acid at 303 K

![Figure 3. Potentiodynamic polarization curves for the mild steel in 0.1 M H₂SO₄ in the absence and presence of different concentrations of 3-nitrobenzoic acid.](image-url)
majorly. It should be stated that when a cathodic reaction is affected, the corrosion potential is shifted to more negative value as observed in this case. The cathodic inhibitors form a barrier of insoluble precipitates over the metal, covering it and restricts the contact between the metal and the corrosive environment (even when it was completely immersed), thus retarding the rate of corrosion reaction. Also, the displacement in corrosion potentials was also found to be less than 80 mV, therefore, the mechanism of inhibition of the corrosion of mild steel in solution of H$_2$SO$_4$ favours physical adsorption (Fouda, Mostafa, & El-Abbasy, 2010).

Calculated values of anodic and cathodic Tafel constants ($\beta_a$ and $\beta_c$) vary slightly with concentration which suggests that 3-nitrobenzoic acid blocks the actives sites for cathodic and anodic reaction, thereby protecting the metal against corrosion. Also, the cathodic Tafel slope value was higher than the anodic slope values, which explain the observed shift in the corrosion potential to the cathodic side more than to the anodic arm.

Generally, there are three basic modes, through which corrosion of metals can be inhibited. These include geometric blocking through the adsorption of the inhibitor, active sites blocking by the adsorbed inhibitor and electro-catalytic effect of the inhibitor or its reaction products. From the polarization results, it can be inferred that 3-nitrobenzoic acid acted via geometric blocking effect.

### 3.3. Electrochemical impedance spectroscopy

The Nyquist plots for the corrosion of mild steel in 0.1 M H$_2$SO$_4$ in the absence and presence of 3-nitrobenzoic acid are presented in Figure 4 while data obtained from EIS measurements are presented in Table 3. The plots clearly reveal that the semi-circle loop for the blank has the least diameter and tend to increase as the concentration of the inhibitor increases. This implies that 3-nitrobenzoic acid inhibited the corrosion of mild steel in solution of H$_2$SO$_4$. It is also evident from the results presented in Table 3 that the charge transfer resistance ($R_{ct}$) increases with increase in the concentration of the inhibitor, suggesting the formation of an insulating/protective film by the inhibitor at the metal/solution interface. On the other hand, the observed decrease in the value of the $C_{dl}$ with increasing concentration (resulting in the decrease of the double layer thickness and a decrease in the dielectric constant) can be attributed to the adsorption of the 3-nitrobenzoic acid onto the metal/electrolyte interface.
3.4. Effect of temperature

The Arrhenius equation was used to investigate the relationship between the rate of corrosion of mild steel and the activation energy, in the presence of various concentrations of 3-nitrobenzoic acid. The equation can be written as follows (Hasan & Sadek, 2014).

\[
CR = A \exp \left( \frac{-E_a}{RT} \right)
\]  

(8)

where CR is the corrosion rate of mild steel, A is the pre-exponential or Arrhenius constant, R is the universal gas constant, T is the temperature and \( E_a \) is the activation energy. Simplification of Equation (8) yields Equation (9).

\[
\ln (CR) = \ln (A) - \frac{E_a}{RT}
\]

(9)

Application of Equation (9) to the present data gave straight lines (Figure 5) when values of ln(CR) were plotted against 1/T. Excellent degrees of linearity were obtained and the activation energies deduced from the plots are presented in Table 4. The activation energies which ranged from 11.68 to 24.65 J/mol are within the range of values that favours the mechanism of physical adsorption. Interestingly, the activation energy for the blank was least and values of \( E_a \) increased with increase in the concentration of the inhibitor. Therefore, the corrosion of mild steel in solution of H\(_2\)SO\(_4\) is retarded by 3-nitrobenzoic acid. The Arrhenius constant was found to increase with increase in concentration of the inhibitor. Although the physical meaning of the Arrhenius constant has not been fully understood, it is generally believed to be connected to the degree of orderliness of the molecules during adsorption.

3.5. Thermodynamic/adsorption considerations

The mechanism of inhibition of the corrosion of mild steel by 3-nitrobenzoic acid is found to be physical adsorption indicating that the extent of adsorption decreases with increase in temperature. A critical insight into the nature and feasibility of adsorption can be gotten through thermodynamic/adsorption parameters. Therefore the standard enthalpy and entropy changes of adsorption...
of 3-nitrobenzoic acid were estimated through the Transition state plots. The Transition state equation, relates the corrosion rate with these parameters according to Equation (10) (Hamdy & El-Gendy, 2013).

\[
CR = \frac{RT}{N\hbar} \exp\left(\frac{\Delta S_{ads}^0}{R}\right) \exp\left(-\frac{\Delta H_{ads}^0}{RT}\right)
\]

where \( N \) is the Avogadro’s number, \( h \) is the plank constant, \( \Delta S_{ads}^0 \) is the standard entropy change of adsorption while \( \Delta H_{ads}^0 \) is the enthalpy change of adsorption. From the logarithm and rearrangement of Equation (10), Equation (11) was obtained:

\[
\ln\left(\frac{CR}{T}\right) = \ln\left(\frac{R}{Nh}\right) + \frac{\Delta S_{ads}^0}{R} - \frac{\Delta H_{ads}^0}{RT}
\]

Equation (11) is a linear model, indicating that a plot of \( \ln\left(\frac{CR}{T}\right) \) versus \( 1/T \) should give a straight line with slope and intercept equal to \( \frac{\Delta H_{ads}^0}{R} \) and \( \ln\left(\frac{R}{Nh}\right) + \frac{\Delta S_{ads}^0}{R} \), respectively. The Transition state equation for the corrosion of mild steel in solution of \( H_2SO_4 \) in the absence and presence of various concentrations of 3-nitrobenzoic acid is shown in Figure 6. Adsorption parameters deduced from the slope of the plots are presented in Table 4. From the results obtained, the change in entropy and enthalpy of adsorption are negative. Therefore the adsorption of 3-nitrobenzoic acid on mild steel surface is exothermic and occurs with orderliness.

The adsorption characteristics of 3-nitrobenzoic acid was investigated by fitting data for the degree of adsorption into the Langmuir, Temkin, Flory-Huggins, El Awardy et al., Frumkin, Freundlich and other adsorption isotherms. The tests revealed that the adsorption of 3-nitrobenzoic acid is best

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**Table 4. Arrhenius and Transition state parameters for the adsorption of 3-nitrobenzoic acid on mild steel surface**

| C (M) | Arrhenius parameters | Transition state parameters |
|-------|----------------------|-----------------------------|
|       | \( A \) | \( E_a \) (J/mol) | \( R^2 \) | \( \Delta S_{ads}^0 \) (J/mol) | \( \Delta H_{ads}^0 \) (J/mol) | \( R^2 \) |
| Blank | 0.0164 | 11.20 | 0.9703 | -174.96 | -8.58 | 0.9489 |
| 0.002 | 0.0413 | 11.68 | 0.9902 | -167.27 | -11.47 | 0.9860 |
| 0.004 | 0.0149 | 12.31 | 0.9258 | -167.42 | -9.07 | 0.8815 |
| 0.006 | 0.0167 | 14.09 | 0.8990 | -166.49 | -9.69 | 0.8485 |
| 0.008 | 0.5928 | 23.26 | 0.8991 | -167.64 | -12.57 | 0.9702 |
| 0.010 | 1.7402 | 25.45 | 0.9975 | -145.00 | -20.69 | 0.9970 |

---

**Figure 6. Transition state plot for the corrosion of mild steel in 0.1 M \( H_2SO_4 \) containing various concentrations of 3-nitrobenzoic acid.**
described by the Langmuir and Frumkin adsorption models. The assumptions establishing the Langmuir adsorption model can be summarized according to Equation (12) (Bammou et al., 2014).

\[
\log\left( \frac{C}{\theta} \right) = \log C + \log \left( \frac{1}{b_{\text{ads}}} \right)
\]  

(12)

where \( C \) is the concentration of the inhibitor in the bulk electrolyte, \( \theta \) is the degree of surface coverage of the inhibitor and \( b_{\text{ads}} \) is the equilibrium constant of adsorption. Figure 7 shows the Langmuir isotherm for the adsorption of 3-nitrobenzoic acid on mild steel surface. Adsorption parameters deduced from the isotherm are presented in Table 5. Although values of \( R^2 \) (calculated from the Langmuir plots) were very close to unity, the slope values were less than unity which means that the adsorption of 3-nitrobenzoic acid on mild steel surface deviates from the ideal Langmuir model. Hence there are some interactions between the adsorbed species. In order to account for the existence of interaction between the inhibitor’s molecules, the Frumkin model was considered. In the presence of molecular interaction, the Langmuir isotherm is reduced to the Frumkin isotherm, which can be expressed according to Equation (13) (Founda, Tawfik, Abdallahi, & Ahmd, 2013).

\[
\frac{\theta}{1 - \theta} e^{-2a\theta} = b_{\text{ads}} C
\]

(13)

where “\( a \)” is the molecular interaction parameter, which can be positive, negative or zero when there is attraction, repulsion and no interaction between the adsorbed molecules, respectively. Other parameters are as defined earlier. From the logarithm of Equation (13), Equation (14) is obtained.

| Table 5. Langmuir and Frumkin parameters for the adsorption of 3-nitrobenzoic acid on the surface of mild steel |
|---|---|---|---|---|---|---|
| Isotherm | \( T \) (K) | Slope | \( \log b_{\text{ads}} \) | “\( a \)” | \( \Delta G^0_{\text{ads}} \) (\( \text{kJ mol}^{-1} \)) | \( R^2 \) |
| Langmuir | 303 | 0.7982 | 0.3396 | - | -12.09 | 0.9982 |
| | 313 | 0.8097 | 0.2648 | - | -11.65 | 0.9927 |
| | 323 | 0.7939 | 0.2654 | - | -11.66 | 0.9999 |
| | 333 | 0.7611 | 0.2763 | - | -11.72 | 0.9988 |
| Frumkin | 303 | 1.8343 | 2.4358 | 0.92 | -24.25 | 0.9858 |
| | 313 | 1.6126 | 1.7404 | 0.81 | -20.88 | 0.9708 |
| | 323 | 1.5374 | 1.4600 | 0.77 | -19.82 | 0.9961 |
| | 333 | 1.5105 | 1.2417 | 0.76 | -19.04 | 0.9967 |
Equation (14) reveals that provided Frumkin model is obeyed, a plot of 
\[
\log\left(\frac{\theta}{1-\theta}\right) \times \frac{1}{C} = \log b_{ads} + 2a\theta
\]
should be linear with slope and intercept equal to \(2\theta\) and \(\log b_{ads}\) respectively. Frumkin isotherm for the adsorption of 3-nitrobenzoic acid on the surface of mild steel is shown in Figure 8 while adsorption parameters obtained from the plots are also recorded in Table 5. From the results obtained, it is evident that the adsorption of the inhibitor on the surface of mild steel fitted the Frumkin model excellently (\(R^2\) values ranged from 0.9708 to 0.9967). The interaction parameters at various concentrations of the inhibitor were found to be positive and decrease with increase in temperature. Therefore the attractive behaviour of the adsorbed molecules of 3-nitrobenzoic acid vary with temperature.

Values of the equilibrium constant of adsorption calculated from the intercepts of the Langmuir and Frumkin isotherms were use for the calculation of the standard free energy changes of adsorption (\(\Delta G^0_{ads}\)) through according to Equation (15) (Anejjar et al., 2014).

\[
b_{ads} = \frac{1}{55.5} \left(\frac{\Delta G^0_{ads}}{RT}\right)
\]

For the Langmuir model, the \(\Delta G^0_{ads}\) was found to range from -11.65 to 12.09 kJ/mol and from -19.04 to -25.25 kJ/mol for the Frumkin model. Classically, free energy values less negative than -40 kJ/mol is consistent with the mechanism of physical adsorption while free energy values more negative than -40 kJ/mol are consistent with the mechanism of chemical adsorption. Therefore the adsorption of 3-nitrobenzoic acid is spontaneous and occurred through physisorption mechanism.

### 3.6. Scanning electron microscopy
The SEM micrograph of mild steel in the presence and absence of the inhibitor (3-nitrobenzoic acid) are presented in Figure 9. The micrograph reveals that the surface of the metal whose corrosion was inhibited is smoother than the surface of the metal without inhibition. This confirms that 3-nitrobenzoic acid protected the metal through the formation of a protective layer on its surface.

### 3.7. FTIR study
The various functional groups/assignments deduced from the FTIR spectra of 3-nitrobenzoic acid and that of the corrosion product of mild steel (in the presence of 3-nitrobenzoic acid as an inhibitor) are presented in Table 6. A critical examination of the results presented in Table 6 reveals three major changes. These are:
(1) A shift in the wave number of absorption, from the higher wave number to a lower wave number (i.e. hypsochromic shift). In this case, the intensity of the absorption band was found to decrease.

(2) Disappearance of some absorption bands of 3-nitrobenzoic acid after inhibition.

(3) Formation of new absorption band.

The extent of frequency shift can be directly correlated with the level of specific molecular interactions, such as hydrogen bonding and dipole–dipole interactions. From the results obtained, hypsochromic shifts were observed for C–O stretch, C=O stretch, N–H stretch and OH stretch. Therefore, there is interaction between the inhibitor and the surface of mild steel. Those functional groups that are missing might have been used for the formation of new bonds or for absorption of the inhibitor unto the metal surface. The missing functional groups included C–H stretch, NO$_2$ symmetric stretch, aromatic C–H stretch and C–O stretch while the new bonds formed were C=O stretch at 1,698 cm$^{-1}$ and N≡C stretch at 2,100 cm$^{-1}$. Therefore, the adsorption of 3-nitrobenzoic acid on the surface of mild steel must have been through the delocalized nitro and the carbonyl group.
3.8. Quantum chemical study

3.8.1. Global selectivity
Calculated values of semi-empirical parameters of 3-nitrobenzoic acid for various Hamiltonians are presented in Table 7. The parameters include the frontier molecular orbital energies, the binding energy ($E_{\text{binding}}$), the core repulsion energy ($E_{\text{CCR}}$), the dipole moment ($\mu$), the electronic energy ($E_{\text{electronic}}$) and the total energy of the molecule ($E_{\text{TE}}$). These parameters are within the range of values reported for some efficient and excellent corrosion inhibitors (Eddy, 2010; Eddy & Ita, 2011a, 2011b; Fang & Li, 2002; Khaled, 2006). It is interesting to note that corrosion inhibition efficiency of a compound has strong relationship with the molecular and electronic parameters of a molecule. Significant differences were not found between a given parameter at various Hamiltonians indicating that the calculated electronic energies can be used for further modelling irrespective of the Hamiltonians.

3.8.2. Local selectivity
The local selectivity of the inhibitor was analysed using the Fukui function. Fukui or frontier function is a function that describes the electron density in a frontier orbital, as a result of a small change in the total number of electrons. The most standard definition of Fukui function is that it is the first derivative of the electronic density $\rho(r)$ with respect to the number of electrons, $N$ at a constant external potential ($v$) (Fuentealba, Pérez, & Contreras, 2000).
Fukui functions are related in part to the Frontier orbital theory (also known as The Fukui Theory of Reactivity and Selection) and describes how nucleophiles attack the HOMO while at the same time placing their surplus electrons into the LUMO. This implies that there are two basic forms of Fukui function associated with the HOMO and the LUMO, respectively. However, condensed Fukui function is applicable to an atom in a molecule. From the finite difference approximation, the changes in Fukui function occurs when a system with N atom moves to loose or donate electron and becomes N + 1 or N − 1 system. Therefore, we have,

\[ f^+ \]

associated with the LUMO and

\[ f^- \]

associated with the HOMO. These are expressed by Equations (17) and (18), respectively.

\[ f(r) = \left( \frac{\partial \rho(r)}{\partial N} \right)_V f(r) \]

(16)

Fukui functions are related in part to the Frontier orbital theory (also known as The Fukui Theory of Reactivity and Selection) and describes how nucleophiles attack the HOMO while at the same time placing their surplus electrons into the LUMO. This implies that there are two basic forms of Fukui function associated with the HOMO and the LUMO, respectively. However, condensed Fukui function is applicable to an atom in a molecule. From the finite difference approximation, the changes in Fukui function occurs when a system with N atom moves to loose or donate electron and becomes N + 1 or N − 1 system. Therefore, we have, \( f^+_x \) associated with the LUMO and \( f^-_x \) associated with the HOMO. These are expressed by Equations (17) and (18), respectively.

\[ f^+_x = \left( \frac{\delta \rho(r)}{\delta N} \right)^+_x = q_{(N+1)} - q_{(N)} \]

(17)

\[ f^-_x = \left( \frac{\delta \rho(r)}{\delta N} \right)^-_x = q_{(N)} - q_{(N-1)} \]

(18)

where \( \rho, q_{(N+1)}, q_{(N)} \) and \( q_{(N-1)} \) are the density of electron and the Milliken charges of the atom when it behaves as anion, neutral and as a cation. Table 8 presents values of the condensed Fukui functions for 3-nitrobenzoic acid (calculated from Equations (17) and (18)) at Ab initio and DFT levels of theory. From the results obtained, it is evident that the site for nucleophilic attack on the 3-nitrobenzoic acid is the nitro nitrogen atom (N10) while the site for electrophilic attack is in the carboxyl functional group. Results of Huckel charge calculation for the atoms in the molecule also revealed that the nitro nitrogen (N10) has the highest charge and will therefore be the site for nucleophilic attack. This finding is also supported by the HOMO and LUMO molecular orbital diagram of the inhibitor presented in Figure 10. In the orbital diagrams, red stands for positive and blue negative. The orbital were developed at cut-off points of −11.866 and −5.331 eV for the HOMO and LUMO, respectively.

3.9. Mechanism of inhibition

It has been found that the mechanism of inhibition of mild steel corrosion by 3-nitrobenzoic acid is physical adsorption. Ordinary, one will expect the carbonyl group to be the site for nucleophilic attack because in addition to the presence of two oxygen atom, one of the oxygen atom (O9) has a lone pair of electron but it can be argue that the nitro group has a delocalized system which makes it to be more reactive than the carbonyl group. In spite of this, one cannot completely rule out the participation of the carbonyl group in the bonding especially when we refer to the FTIR of the corrosion product after inhibition. Hence, since the mechanism of physical adsorption (which supports the formation of multimolecular layer) is established for the adsorption of 3-nitrobenzoic acid on mild steel surface, it can be stated that the adsorption of the inhibitor unto the metal surface occurred dominantly through the nitro group and partly through the carbonyl group.

| Hamiltonian | \( E_{\text{HOMO}} \) (eV) | \( E_{\text{LUMO}} \) (eV) | \( E_{\text{binding}} \) (eV) | \( E_{\text{electronic}} \) (eV) | \( E_{\text{CCR}} \) (eV) | \( \mu \) (Debye) | \( E_{\text{TE}} \) (eV) |
|-------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| INDO        | −12.44          | 1.11            | −5346.13        | −293716.58      | 210194.70       | 4.025           | −83521.87       |
| PM3         | −11.11          | −1.68           | −1853.21        | −238756.53      | 187115.60       | 4.146           | −51640.92       |
| AMI         | −11.146         | −1.68           | −1833.93        | −245551.58      | 189074.61       | 4.060           | −56476.97       |
| RMI         | −10.91          | −1.53           | −1183.16        | −244816.68      | 188990.41       | 3.736           | −55826.20       |
| MNDO        | −10.90          | −1.71           | −1825.19        | −245963.55      | 189320.54       | 3.947           | −56643.01       |
| CNDO        | −13.15          | 0.79            | −5637.45        | −297254.60      | 210194.70       | 4.261           | −87059.69       |

Table 7. Calculated semi-empirical parameters of 3-nitrobenzoic acid for various Hamiltonians
4. Conclusion
The present study revealed that 3-nitrobenzoic acid is an excellent inhibitor for the corrosion of mild steel in solution of tetraoxosulphate (VI) acid. The inhibitor has efficient average and instantaneous inhibition efficiency. The mechanism of the inhibition is by physical adsorption which agrees favourably with the Langmuir and Frumkin adsorption models. Findings from quantum chemical investigation indicated that the adsorption of the inhibitor, hence its excellent inhibition properties are due to the presence of delocalized nitro group in the inhibitor.

Table 8. Fukui functions for 3-nitrobenzoic acid calculated using Ab initio and DFT

| Atom No. | $f^+_{A}$ | $f^-_{A}$ | $f^+_{D}$ | $f^-_{D}$ | Huckel charge |
|----------|-----------|-----------|-----------|-----------|---------------|
| 1 C      | 0.0274    | -0.0617   | -0.1938   | -0.1315   | 0.5671        |
| 2 C      | -0.0406   | -0.0521   | 0.3326    | -0.2759   | -0.0075       |
| 3 C      | -0.0212   | -0.0013   | 0.2080    | -0.2017   | 0.0329        |
| 4 C      | -0.1335   | -0.5221   | -0.1062   | 0.1307    | 0.0863        |
| 5 C      | -0.0147   | -0.0342   | -0.2568   | 0.0641    | 0.0286        |
| 6 C      | -0.0162   | -0.0696   | 0.0168    | -0.2186   | -0.0300       |
| 7 C      | -0.0265   | -0.0674   | -0.1763   | -0.0045   | 0.0301        |
| 8 O      | 0.0842    | -0.1082   | 0.1488    | -0.2118   | -0.6696       |
| 9 O      | -0.1038   | -0.0330   | 2.2834    | -2.3159   | -0.1463       |
| 10 N     | -0.0464   | 0.0447    | -0.0526   | 0.2781    | 1.2699        |
| 11 O     | -0.3272   | -0.0698   | 1.5145    | -1.6966   | -0.7331       |
| 12 O     | -0.1255   | -0.0299   | 0.1807    | -0.0120   | -0.7333       |

Figure 10. Homo and LUMO diagrams of 3-nitrobenzoic acid calculated from extended Huckel theory.

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Author details
Paul O. Ameh1
E-mail: nocaseoche@yahoo.com
Nnabuk O. Eddy2
E-mail: nabukeddy@yahoo.com
1 Department of Chemistry, Nigeria Police Academy, Wudil, Kano, Nigeria.
2 Department of Chemistry, Federal University Lokoja, Lokoja, Kogi State, Nigeria.

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References
Anejjar, A., Salghi, R., Zarrour, A., Benali, O., Zarrak, H., Hammoudi, B., & Ebenso, E. E. (2014). Inhibition of carbon steel corrosion in 1M HCl medium by potassium...
thiocyanate. Journal of the Association of Arab Universities for Basic and Applied Sciences, 15, 21–27. 
http://dx.doi.org/10.1016/j.jaubas.2013.06.004
Bammou, L., Belhkhouda, M., Salgh, R., Benali, O., Zarrouk, A., Zarrak, H., & Hammouti, B. (2014). Corrosion inhibition of steel in sulfuric acidic solution by the Chenopodium ambrosioides extracts. Journal of the Association of Arab Universities for Basic and Applied Sciences, 16, 83–90. 
http://dx.doi.org/10.1016/j.jaubas.2013.11.001
Dehri, I., Kados, G., Solmaz, R., & Ozcan, M. (2008). Adsorption properties of barbiturates as green corrosion inhibitors on mild steel in phosphoric acid. Colloid and Surface A: Physicochemical and Engineering Aspects, 325, 57–63.
Dinnappa, R. K., & Mayanna, S. M. (1981). Benzoic acid and substituted benzoic acids as interfacial corrosion inhibitors for copper in HClO4. Journal of Applied Electrochemistry, 11, 111–116. 
http://dx.doi.org/10.1007/BF00615329
Dorfman, A. M. (1995). On the adsorption of hexamethylenimine nitrobenzoate, a corrosion inhibitor by iron. Protection of metals, 33, 321–326.
Eddy, N. O. (2010). Theoretical study on some amino acids and their potential activity as corrosion inhibitors for mild steel in HCl. Molecular Simulation, 36, 354–363. 
http://dx.doi.org/10.1080/089270209038343270
Eddy, N. O., & Ita, B. I. (2011a). Experimental and theoretical studies on the inhibition potentials of some derivatives of cyclopenta-1,3-diene. International Journal of Quantum Chemistry, 121, 3456–3473.
Eddy, N. O., & Ita, B. I. (2011b). Theoretical and experimental studies on the inhibition potentials of aromatic oxaldehydes for the corrosion of mild steel in 0.1 M HCl. Journal of Molecular Modeling, 17, 633–647.
Eddy, N. O., Momoh-Yahaya, H., & Ozogie, E. E. (2015). Theoretical and experimental studies on the corrosion inhibition potentials of some purines for aluminium in 0.1 M HCl. Journal of Advanced Research, 6, 203–217. 
http://dx.doi.org/10.1016/j.jare.2014.01.004
Fang, J., & Li, J. (2002). Quantum chemistry study on the relationship between molecular structure and corrosion inhibition efficiency of amides. Journal of Molecular Structure. THEOCHEM, 593, 179–185. 
http://dx.doi.org/10.1016/S0303-9440(02)00316-0
Fouda, A. S., Mostafa, H. A., & El-Abbasy, H. M. (2010). Antibacterial drugs as inhibitors for the corrosion of stainless steel type 30A in HCl solution. Journal of Applied Electrochemistry, 40, 163–173. 
http://dx.doi.org/10.1007/s10800-009-9992-3
Fouda, A. S., Tawﬁk, H., Abdallah, N. M., & Ahmd, A. M. (2011). Corrosion inhibition of nickel in HCl solution by some indole derivatives. International Journal of Electrochemical Science, 8, 3390–3405.
Fuentedido, P., Pérez, P., & Contreras, R. (2009). On the condensed Fukui function. The Journal of Chemical Physics, 113, 2544–2551. 
http://dx.doi.org/10.1063/1.3150879
Hardy, A., & El-Gendy, N. S. (2013). Thermodynamic, adsorption and electrochemical studies for corrosion inhibition of carbon steel by henna extract in acid medium. Egyptian Journal of Petroleum, 22, 17–25. 
http://dx.doi.org/10.1016/j.ejpe.2012.06.002
Hasan, B. O., & Sodek, S. A. (2014). The effect of temperature and hydrodynamics on carbon steel corrosion and its inhibition in oxygenated acid–salt solution. Journal of Industrial and Engineering Chemistry, 20, 297–307. 
http://dx.doi.org/10.1016/j.jiec.2013.03.034
Karral, C., & Sethuraman, M. G. (2012). Spirulina platensis—A novel green inhibitor for acid corrosion of mild steel. Arabian Journal of Chemistry, 5, 155–161. 
http://dx.doi.org/10.1016/j.arabjc.2010.08.006
Kartheiksel, R., & Subhashini, S. (2014). Study of adsorption properties and inhibition of mild steel corrosion in hydrochloric acid media by water soluble composite poly (vinyl alcohol–o-methoxy online). Journal of Association of Arab Universities for Basic and Applied Sciences, 16, 74–82.
Khodam, A. A., Yaro, A. S., Kadum, A. A. H., & Musa, A. Y. (2009). The effect of temperature and acid concentration on corrosion of low carbon steel in hydrochloric acid medium. American Journal of Applied Science, 6, 1403–1409.
Khaled, K. F. (2006). Experimental and theoretical study for corrosion inhibition of mild steel in hydrochloric acid solution by some new hydrazine carboxthio adipic acid derivatives. Applied Surface Science, 252, 4120–4128. 
http://dx.doi.org/10.1016/j.apsusc.2005.06.016
Okafor, P. C., & Zheng, Y. (2009). Synergistic inhibition behavior of methylbenzyl quaternary imidazole derivative and iodide ions on mild steel in H2SO4 solutions. Corrosion Science, 51, 850–859. 
http://dx.doi.org/10.1016/j.corsci.2009.01.027
Ostovari, A., Hoseinieh, S. M., Peikari, M., Shodizadeh, S. R., & Hashemri, S. J. (2009). Corrosion inhibition of mild steel in 1 M HCl solution by henna extract: A comparative study of the inhibition by henna and its constituents (Lawson, Gallic acid, α-d-Glucose and Tannic acid). Corrosion Science, 51, 1935–1949. 
http://dx.doi.org/10.1016/j.corsci.2009.05.024
Podobaev, N. I., & Larionov, E. A. (1995). Carboxylates and sulfated carboxylated carboxylates as inhibitors for steel corrosion in neutral media. Protection of metals, 31, 185–188.
Quraishi, M. A., & Jamal, D. (2002). Development and testing of all organic volatile corrosion inhibitors. Corrosion, 58, 387–391. 
http://dx.doi.org/10.5006/1.3277627
Shukla, S. K., & Ebenso, E. E. (2011). Corrosion inhibition, adsorption behavior and thermodynamic properties of streptomycin for mild steel in hydrochloric acid medium. International Journal of Electrochemical Science, 6, 3277–3291.
Sibel, Z. (2001). The effect of benzoic acid in chloride solutions on the corrosion of iron and aluminum. Turkish Journal of Chemistry, 26, 403–408.
Urmen, S. A., Ogbobe, O., Okafor, P. C., & Ebenso, E. E. (2007). Polyethylene glycol and polyvinyl alcohol as corrosion inhibitors for aluminum in acidic medium. Journal of Applied Polymer Science, 105, 3363–3370. 
http://dx.doi.org/10.1002/japp.2007014628
Vračar, L. M., & Dražić, D. M. (2002). Adsorption and corrosion inhibitive properties of some organic molecules on iron electrode in sulfuric acid. Corrosion Science, 44, 1669–1680. 
http://dx.doi.org/10.1016/S0010-938X(01)00166-4
Yaro, A. S., Khodam, A. A., & Wael, R. K. (2014). Apricot juice as green corrosion inhibitor of mild steel in phosphoric acid. Alexandria Engineering Journal, 52, 129–135.
