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# Assessment of Negro pepper (*Xylopia aethiopica)* fruit extracts as corrosion inhibitors for Mild steel

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## Abstract
The adverse effects of corrosion on the environment and economy of the chemical industry resulting from the inability of metals to support designed load requirements cannot be overemphasized. Despite the effectiveness of synthetic corrosion inhibitors, they are nonetheless associated with problems of toxicity, disposal and enormous costs. This study therefore aimed at investigating the efficacy of Negro pepper (*Xylopia aethiopica*) fruit extracts as corrosion inhibitors for mild steel. Hexane, water and ethanol extracts of the fruit were applied at room temperature on mild steel immersed in 5 M sulphuric acid solution. The efficiency and mechanism of corrosion inhibition was studied using gravimetric techniques, Fourier Transformed Infra-Red spectroscopy, Scanning Electron Microscopy and phytochemical analyses of the extracts. Langmuir and Freundlich adsorption isotherms were also tested on the weight loss data. It was observed that increase in concentration of the extracts resulted in increased inhibition efficiency; the range was: water extract (30.38-93.00%), hexane extract (38.90-97.18%) and ethanol extract (41.32-98.32%). Corrosion rate however, decreased with increase in concentration of the extracts. The corrosion inhibition process using each of the extracts was better described by Langmuir isotherm ($R^2$ = 0.9742, 0.9695, 0.9782 for ethanol, hexane and water, respectively) than Freundlich isotherm.

## 1. Introduction
The need for controlling the corrosion of metals in the environment cannot be over emphasized. Corrosion control is an important activity that has technical, economic, environmental and aesthetical relevance. An important method of protecting metals is the use of corrosion inhibitors that hinder the corrosion reaction and thus reduces the corrosion rate [1]. Synthetic organic inhibitors such as 5-methyl-2H imidazol-4-carboxaldehyde and 1H-Indole-3-carboxaldehyde has been used and studied. Inorganic complexes and their derivatives such as pyridoxal-(4-methyl semicarbazone) and its zinc (II) complex have also been studied [2]. However, due to their toxicity and cost, attention is now focused on the development of new classes of environment-friendly and inexpensive alternatives. Plants extracts are more eco-friendly, biodegradable and easily available. In fact, some of the plants investigated are weeds such as *Phyllantus amarus* [3]. The corrosion inhibition efficiency of aqueous extracts of other plants (or plant parts) such *Hemidesmus indicus* leaves [4], *Phyllanthus fraternus* leaves [5], *Reutera lutea* [6], *Opuntia ficus* [7], *Pistacia atlantica* extract [8], *Anacyclus pyrethrum* [9] and Punica plant [10] on mild steel and other metals in various highly corrosive acidic media have also been investigated. Studies have also been conducted on alcoholic extracts of *Phoenix dactylifera* [11], and leaves, bark and roots of

*Nauclea latifolia* [12], *Lawsonia inermis* leaves [13], *Androphagus paniculata* and *Vernonia amygdalina* [14]. Others are oil of *Thymus pallidus* plant from Morocco [15], Retamaretam extract [16], acid extract of *Ephedra alata* [17], extracts of Pomegranate [18], extract of *Dodonaea viscosa* and *Larrea tridentate* leaves [19, 20], *Ziziphus mauritiana* fruit extract [21], extract of *Carica papaya* [22], *Stevia rebaudiana* leaves extracts [23], *Polycarpaeacory Mbosa* and *Desmodium triflorum* leaves extracts [24], and roasted coffee seed extract [25].

Peppers are known for their burning sensations; they are therefore suspected to possess anti-corrosion properties on metals in different corrosive environments. Extracts of black pepper, for example, have been studied for their corrosion inhibitory potential on mild steel in sulphuric acid [26, 27] and hydrochloric acid [28, 29]. The extract was also tried on aluminium in hydrochloric acid [30]. The efficiency of piperine isolate of black pepper has also been investigated on steel in various acidic media [28, 29]. Similarly, a study has been conducted on the potential application of red pepper seed oil for inhibition of corrosion [31].

*Xylopia aethiopica* commonly called Negro pepper is known to be non-toxic, environment friendly and less expensive. Its essential oil was found to contain alkaloids, carbohydrates, cyanogenic glycosides, flavonoids saponins, tannins and sterols [32]. The aim of this study is to investigate the inhibition effect (weight loss, inhibition efficiency, corrosion rate and surface coverage) of ethanol, water and hexane extracts of Negro pepper fruits on mild steel in sulphuric acid solution.

## 2. Material and Methods

### *2.1 Mild steel preparation*

The mild steel coupons used in this study were obtained from Mechanical Engineering Workshop of Ladoke Akintola University of Technology, Ogbomoso, Nigeria. Each sheet of 0.2 mm thickness was cut into coupons of dimension 4.0 x 5.0 cm for gravimetric measurements. A hole of uniform diameter was made to facilitate suspension of the coupons in the test solutions. Prior to each measurement, the coupon samples were polished using series of emery papers of variables grades, starting from the coarsest and proceeding in steps to the finest grade, degreased with absolute ethanol, dipped into acetone, air dried and stored in desiccator before use.

### *2.2 Preparation of plant extract and test solution*

The Negro pepper (*Xylopia aethiopica*) fruits used in this study were purchased at Wazobia market in Ogbomoso, Nigeria. It was identified at the Department of Pure and Applied Biology, Ladoke Akintola University of Technology, Ogbomoso (voucher number LHO539). It was oven-dried at 50°C and ground into powdery form. 100 g of the powder was extracted with hexane and ethanol in a soxhlet extractor while water extract is made by cold extraction and thereafter concentrated by using water bathe. A stock inhibitor/corrodent mixture (10 g/L) for each extract was prepared by mixing 10 g of each of the plant extracts separately with 1 L of 5 M $H_2SO_4$ solution. The resultant homogeneous mixtures were kept for 24 hours, filtered and stored [4]. Different working concentrations (0.5 g/L, 1.0 g/L, 2.0 g/L, 4.0 g/L and 6.0 g/L) of the media were prepared from the stock.

### *2.3 Surface Morphology*

Scanning Electron Microscopy (SEM) was used to assess the change in the surface morphology caused by the interaction of mild steel coupons with the test solutions and to monitor the effect of adding the inhibitors. It was deployed to examine surface profile of the mild steel after corrosion in the presence of the inhibitor at a magnification of x10000. The superficial effects on the surface of mild steel samples after contact with 10.0 g/L test solution at room temperature of 30°C for 24 hours were examined by FEI Nova NanoSEM instrument.

*2.4 Fourier Transform Infrared Spectroscopy*

The Infrared spectrum of the inhibitor and that of the corrosion product in the presence and absence of the inhibitors were recorded in the range of 4,000 $cm^{-1}$ to 450 $cm^{-1}$ using KBr disk as reference with the aid of Buck M530 IR spectrophotometer. The coupon was dipped in 250 mL of 10 g/L of $H_2SO_4$-inhibitor concoction for 5 days to form an adsorbed layer after which it was retrieved, dried and the surface was scraped with a sharp razor blade. The IR spectra of the scraps were taken and compared with the spectrum of the plant extracts [33].

*2.5 Weight loss measurements*

Gravimetric (weight loss) experiments were conducted as described by [34] and [2] at room temperature (± 28°C). With the aid of glass rods and hooks, the steel coupons were suspended in seven beakers labelled Blank ($H_2SO_4$ only), 0.5 g/L, 1.0 g/L, 2.0 g/L, 4.0 g/L, 6.0 g/L and 10.0 g/L containing corresponding concentration of the test solutions. The steel coupons were weighed prior to immersion and their masses recorded. The coupons were then removed after 2 h, washed thoroughly in 20% NaOH solution containing 10 g of zinc dust until clean, dried in acetone, re-weighed and re-immersed. To obtain the Weight loss, the mass obtained after the experiment was subtracted from the mass before the experiment with the aid of Shimadzu Analytical balance ATX124. The coupons were also weighed after 4, 6, 8 and 10 hours of immersion.

*2.6 Evaluation of Corrosion Parameters*

After obtaining the weight loss data, the corrosion rate, inhibitor efficiency and surface coverage were then calculated in the absence and presence of the extracts.

Corrosion rate is evaluated by Equation (1) as stated below:

$$\text{Corrosion Rate} = \frac{W}{A \times t} \quad (1)$$

where t = immersion time in hours, W = Weight loss in grams and A = Area of sample in square cm ($cm^2$)

$$\text{Surface Coverage } (\Theta) = \frac{W_c - W}{W_c} \quad (2)$$

Where:

$W_c$ = Weight loss of metal sample in the control solution (solution without inhibitor) and

W = Weight loss of metal sample in solution with acid-inhibitor mixture.

The inhibition efficiency (IE %) based on mass data can be obtained from the relationship in Equation (3):

$$(\text{I.E.\%}) = \frac{CR_{blank} - CR_{inh}}{CR_{blank}} \times 100 \quad (3)$$

Where:

$CR_{blank}$ = Corrosion rate of sample in $H_2SO_4$ medium and

$CR_{inh}$ = Corrosion rate of metal sample in the presence of the inhibitor and the acid.

*2.7 Phytochemical Analysis of Negro pepper extract*

Negro pepper fruit was analysed quantitatively for alkaloids, saponins, tannins, phenols and flavonoids using the methods described in [35-39].

## 3. Results and Discussion

### *3.1 Surface Morphology study*

SEM was used to examine the surface morphology of the mild steel after corrosion in the presence of the inhibitor at a magnification of (x10,000). The superficial effects on the surface of mild steel samples after contact with 10.0 g/L test solution in the presence of ethanol, water and hexane extracts of Negro pepper at room temperature of 30$^{O}$C for 24 hours was examined by FEI Nova Nano SEM instrument. Figure 1(a-e) shows the surface morphology of mild steel before and after treatment with test solutions.

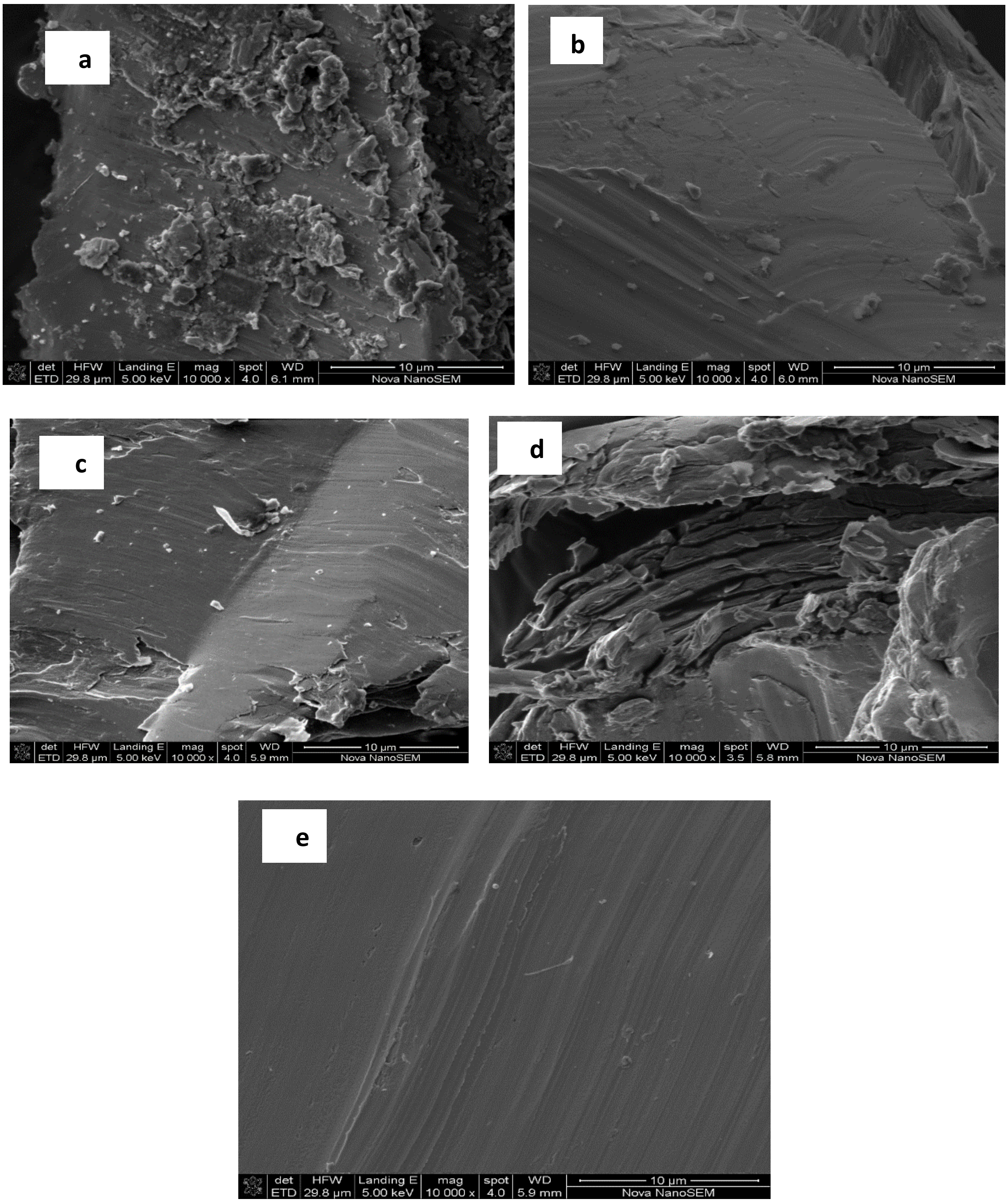



**Figure 1:** Photomicrograph of Mild steel in the absence and presence extracts test solution at room temperature (a) Mild steel in corrodent (b) Polished mild steel (c) Mild steel in 10 g/L Aqueous extract (d) Mild steel in 10 g/L Hexane extract (e) Mild steel in 10 g/L Ethanol extract of Negro pepper at magnification of (x10,000).

The presence of pits or roughness of surface of mild steel indicates corrosion. The photomicrograph reveals that the inhibited metal surface is smoother than the uninhibited surface, a good protective film present on the metal surface. This confirms the highest inhibition efficiency of the inhibitor [40].

### *3.2 Fourier Transformed Infra-red Analysis*

On the quest to study the interaction of Negro pepper extracts on mild steel, Buck M530 IR spectrophotometer was used. The IR spectrum of the extracts of Negro pepper fruit was studied in relation to the spectrum produced as a result of the protective film formed on the surface of the steel after immersion in the solution containing 10 g/L ethanolic extract for five (5) days.

Table 1 shows the absorption band for ethanol, hexane and water extracts of Negro pepper before and after treatment with mild steel. On the spectrum, there is an aromatic out-of-plane C-H shift from 871 $cm^{-1}$ from the extract to 883 $cm^{-1}$ on the treated mild steel; carboxylic C-O shift from 1153 $cm^{-1}$ to 1276 $cm^{-1}$. In addition, there is a C-H shift from 2961 $cm^{-1}$ to 2805 $cm^{-1}$ in the aldehyde ring. An aromatic shift was also observed from 3104 $cm^{-1}$ to 3010 $cm^{-1}$ and 3241 $cm^{-1}$ to 3240 $cm^{-1}$ which is hydrogen bonded. Free alcoholic O-H group was also observed as a shift from 3506 $cm^{-1}$ to 3572 $cm^{-1}$. However, C-O stretching from akyl aryl ether ring at 1237 $cm^{-1}$ was missing suggesting that the bond was used for adsorption of the inhibitor onto the surface of the mild steel. In other word, the missing adsorption band indicates that there is interaction between the ethanol extract of Negro pepper and the surface of mild steel.

**Table 1:** Summary of the interaction of Negro pepper (*Xylopia aethiopica*) fruit extracts on mild steel using FT-IR

| Sample | Absorption range ($cm^{-1}$) | | Inference |
|---|---|---|---|
| | Before Treatment | After Treatment | |
| Ethanol extract | 871 | 883 | Aromatic out-of-plane C-H shift |
| | 1153 | 1276 | a carboxylic acid C-O shift |
| | 2961 | 2805 | Aldehyde C-H shift |
| | 3104 | 3010 | Phenolic carboxylic O-H shift |
| | 3241 | 3240 | H-bonded alcoholic O-H shift |
| | 3506 | 3572 | Free alcoholic O-H group shift |
| Water extract | 746 | 651 | a C-X chloride shift |
| | 814 | 748 | Out-of-plane Aromatic C-Hshift |
| | 1135 | 1009 | Alcoholic C-O shift |
| | 1557 | 1555 | Primary amine N- H (bend) shift |
| | 2611 | 2727 | C-H Aldehyde shift |
| | 3064 | 3002 | C-H (stretch) Alkenes shift |
| Hexane extract | 1213 | 1009 | a C-N Amine shift |
| | 3367 | 2612 | a carboxylic acid O-H shift |

On the spectra of mild steel treated with aqueous extract, there is a C-X chloride shift from 746 $cm^{-1}$ to 651 $cm^{-1}$. There is also an out of plane aromatic C-H shift from 814 $cm^{-1}$ to 748 $cm^{-1}$, alcoholic C-O shift from 1135 $cm^{-1}$ to 1009 $cm^{-1}$, a primary amine N-H shift from 1557 $cm^{-1}$ to 1555 $cm^{-1}$. In addition, a shift from 2611 $cm^{-1}$ to 2727 $cm^{-1}$ indicating the presence of C-H aldehyde and an alkenes C-H shift from 3064 $cm^{-1}$ to 3002 $cm^{-1}$ was observed. The interaction of hexane extract of Negro pepper on mild steel was studied. Report shows that there was a C-N amine shift from 1213 $cm^{-1}$ to 1009 $cm^{-1}$ and an Alcoholic O-H shift from 3367 $cm^{-1}$ to 2612 $cm^{-1}$ indicating the presence of carboxylic acid and alcoholic or phenolic group. The shift in frequencies indicates that there is interaction between the mild steel and the inhibitor [41].

*3.3 Results of Gravimetric analysis of Mild steel treated with Negro pepper extracts*

The variation in weight loss of the coupon with the contact time for all the concentrations of the plant extracts are presented in Figure 2(a-c). The surface area of the specimen used is 40.36 $cm^2$. It was observed that weight loss increased with increase in time and decreased with extract concentration in all cases studied.

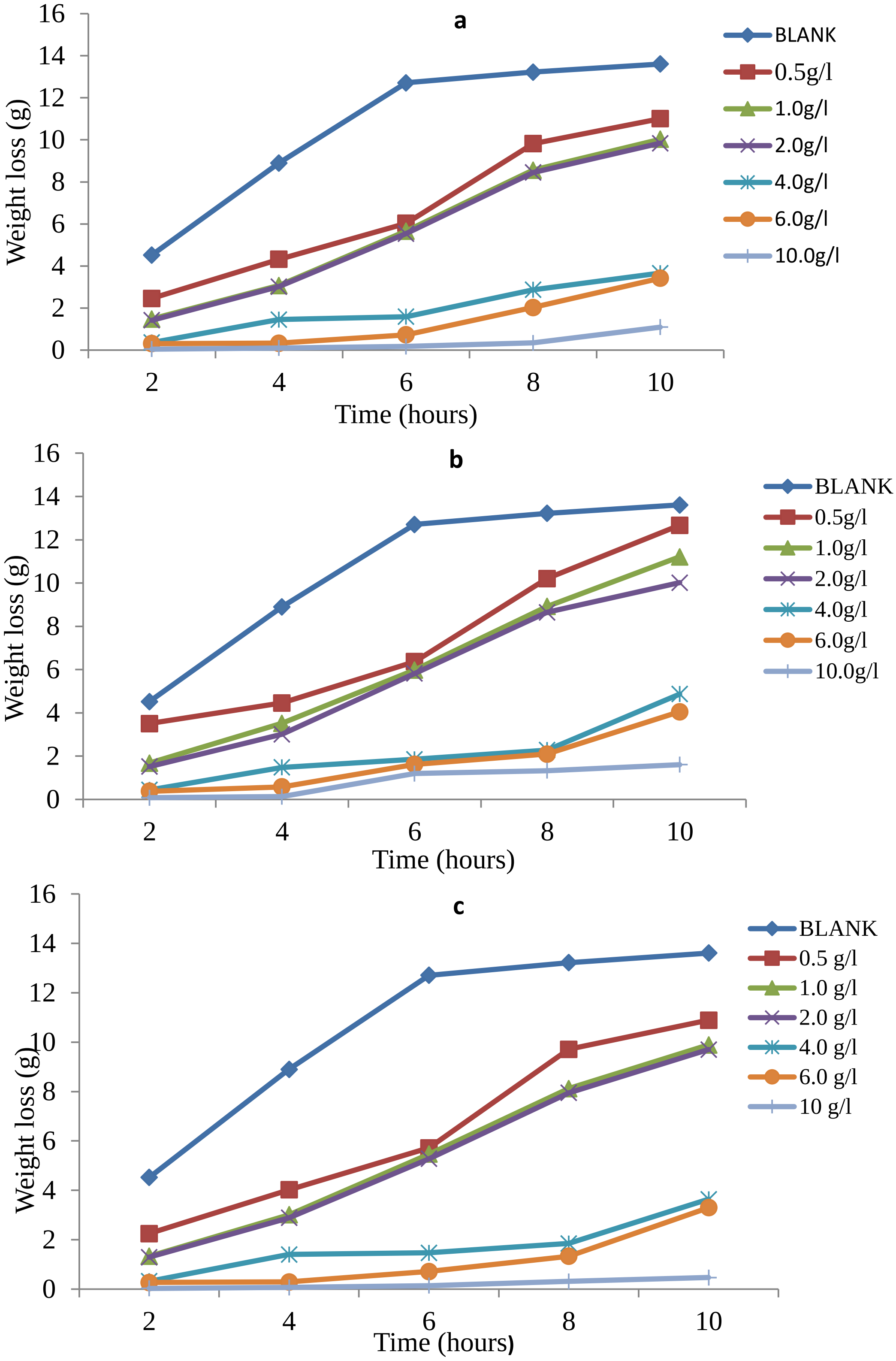
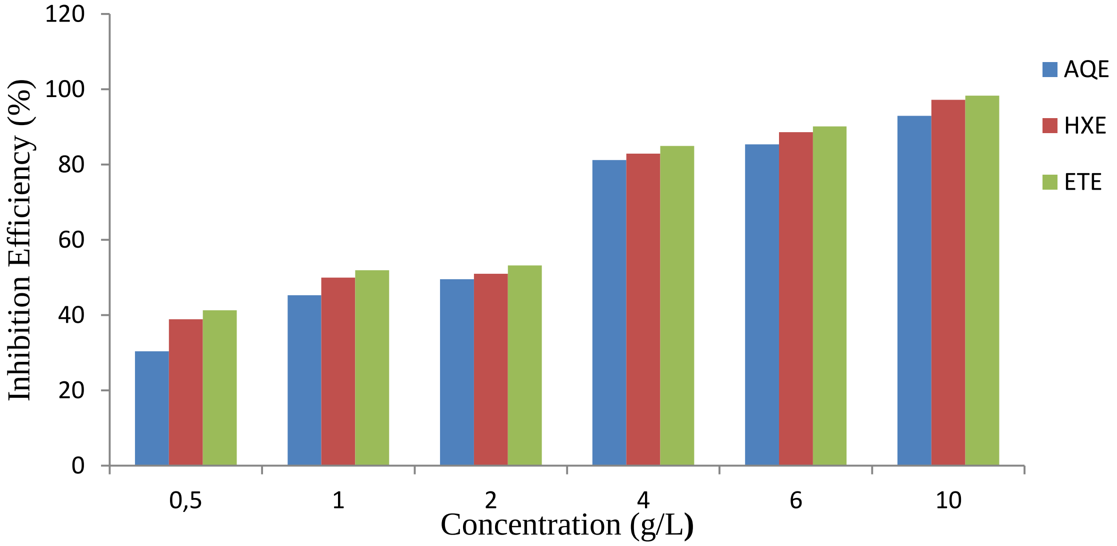



**Figure 2:** Variation of weight loss with time for mild steel coupons in 5 M sulphuric acid solution containing different concentrations of (a) Hexane (b) Water and (c) Ethanol extracts of Negro pepper.

It was observed that corrosion rates decreases as the inhibitors concentration increases with water extract of Negro pepper having the highest and ethanolic extract with the least values as shown in Table 2. Similar trend was observed with plant extracts [42-45]. This could be attributed to the replacement of $SO_4^{2-}$ ions from the corrodent with $H^-$ released from the mild steel. Consequently, inhibition efficiency of the extracts increased with increase in extract concentration. A comparison of the average inhibition efficiency of the three (3) extracts reveals that ethanol extract of Negro pepper has the highest inhibition efficiency followed by hexane extract. Water extract of Negro pepper has the least inhibition efficiency as shown in Figure 3. The degree of surface coverage (ϴ) for the three extracts is presented in Table 3. It was observed that surface coverage values increased with increase in extract concentration. This could be as a result of high spread force of the concentrated molecules of the extracts which forms a thicker covering on surfaces.

**Table 2**: Rate of corrosion of mild steel in different concentrations of the extracts

| | Corrosion Rate (mg $cm^{-2}hr^{-1}$) | | | | | | |
|---|---|---|---|---|---|---|---|
| Extracts | **Blank** | **0.1 g/L** | **1.0 g/L** | **2.0 g/L** | **4.0 g/L** | **6.0 g/L** | **10.0 g/L** |
| **Hexane** | 4.7656 | 2.7966 | 2.2418 | 2.1946 | 0.7594 | 0.4732 | 0.1138 |
| **Water** | 4.7656 | 3.2086 | 2.4544 | 2.2626 | 0.8286 | 0.6290 | 0.2998 |
| **Ethanol** | 4.7656 | 2.6688 | 2.1478 | 2.0866 | 0.6690 | 0.4076 | 0.0702 |




HXE = Hexane extract AQE = Aqueous extract ETE = Ethanol extract

**Figure 3**: Variation of inhibition efficiency of the Negro pepper extracts in sulphuric acid solution on mild steel

### *3.4 Adsorption behavior of Negro pepper extracts*

An adsorption isotherm offers explanation for the relation between the metal exposed surface to the coverage of an interface with adsorbed species. The degree of surface coverage (θ) for varying inhibitor concentration at room temperature was used to elucidate the adsorption isotherm in order to establish the adsorption processes involved [46]. For the purpose of this study, only Langmuir and Freundlich isotherm models were considered. Table 4 summarizes the adsorption parameters for ethanol, hexane and water extract of Negro pepper fruits on the surface of mild steel. The isotherm with the regression value ($R^2$) closer to unity is taken as the better fit isotherm for the adsorption process. A large adsorption coefficient signifies a greater adsorption capacity [47]. The adsorption characteristic of ethanol, hexane and water extracts of Negro pepper conforms to Langmuir adsorption isotherm ($R^2$ = 0.9742, 0.9695, 0.9782 respectively) better than Freundlich isotherm.

**Table 3:** Surface coverage (Ɵ) for mild steel coupons containing different concentration of hexane, water and ethanol extract of Negro pepper

| | | Surface Coverage (Ɵ) | | | | | |
|---|---|---|---|---|---|---|---|
| **Extracts** | **Time (hrs)** | **0.5 g/L** | **1.0 g/L** | **2.0 g/L** | **4.0 g/L** | **6.0 g/L** | **10.0 g/L** |
| Hexane | 2 | 0.46 | 0.67 | 0.69 | 0.92 | 0.93 | 0.99 |
| | 4 | 0.52 | 0.66 | 0.66 | 0.84 | 0.96 | 0.99 |
| | 6 | 0.53 | 0.56 | 0.56 | 0.88 | 0.94 | 0.99 |
| | 8 | 0.26 | 0.35 | 0.36 | 0.78 | 0.85 | 0.97 |
| | 10 | 0.19 | 0.26 | 0.28 | 0.73 | 0.75 | 0.92 |
| Water | 2 | 0.22 | 0.63 | 0.66 | 0.90 | 0.92 | 0.98 |
| | 4 | 0.50 | 0.60 | 0.66 | 0.83 | 0.94 | 0.99 |
| | 6 | 0.50 | 0.53 | 0.54 | 0.85 | 0.87 | 0.91 |
| | 8 | 0.23 | 0.33 | 0.35 | 0.83 | 0.84 | 0.90 |
| | 10 | 0.07 | 0.18 | 0.26 | 0.64 | 0.71 | 0.88 |
| Ethanol | 2 | 0.50 | 0.71 | 0.72 | 0.93 | 0.94 | 0.99 |
| | 4 | 0.55 | 0.66 | 0.68 | 0.84 | 0.97 | 0.99 |
| | 6 | 0.55 | 0.57 | 0.59 | 0.88 | 0.94 | 0.99 |
| | 8 | 0.27 | 0.39 | 0.40 | 0.86 | 0.90 | 0.98 |
| | 10 | 0.20 | 0.27 | 0.29 | 0.73 | 0.76 | 0.97 |

**Table 4**: Adsorption parameters for Ethanol, Hexane and Water extract of Negro pepper fruits on the surface of mild steel.

| Isotherms | Extracts | Regression Values ($R^2$) | Adsorption Coefficient |
|---|---|---|---|
| Langmuir | Ethanol | 0.9742 | 0.6765 |
| | Hexane | 0.9695 | 0.6166 |
| | Water | 0.9782 | 0.4501 |
| Freundlich | Ethanol | 0.9447 | 2.1159 |
| | Hexane | 0.9387 | 2.2167 |
| | Water | 0.7234 | 2.7893 |

### *3.5 Phytochemical Analysis of Negro Pepper*

Based on the mass spectra of reference compounds in the National Institute of Standards and Technology (NIST 14) database [48], *Xylopia aethiopica* fruit extract had been studied to contain various phytochemical constituents using GC-MS detector. In this study, the ethanol extract of Negro pepper fruits was analysed quantitatively to contain 75.17 ± 1.90 mg/g Alkaloids, 163.82 ± 2.25 mg/g Saponins, 55.56 ± 0.28 mg/g Tannins, 7.62 ± 0.07 mg/g Flavonoids and 43.93 ± 0.18 mg/g Phenols. Aqueous extract of the fruit was observed to contain 11.02 ± 0.03 mg/g, 26.81 ± 0.18 mg/g, 49.30 ± 0.13 mg/g, 12.16 ± 1.56 mg/g, and 106.40 ± 0.56 mg/g for Flavonoids, Phenols, Tannins, Alkaloids and Saponins respectively. In addition, Hexane extract of the pepper was examined to contain 45.11 ± 0.13 mg/g, 127.42 ± 0.41 mg/g, 98.29 ± 0.05 mg/g, 16.43 ± 0.38 mg/g and 114.90 ± 0.81 mg/g for Flavonoids, Phenols, Tannins, Alkaloids and Saponins respectively. The results are summarized in Table 5. It can be inferred from these results that various phytochemicals in ethanol, hexane and water extracts of Negro pepper fruit may be responsible for the inhibition process. The greater the amount of phytochemicals, the more they act to prevent corrosion. [49] reported that saponin, flavonoids and alkaoids constituents of *Taraxacum officinale* leaves inhibit stainless steel corrosion in hydrochloric acid medium.

**Table 5**: Result of quantitative phytochemical analysis of Negro pepper (*Xylopia aethiopica*) extracts

| Extracts | Flavonoids (mg/g) | Phenols (mg/g) | Tannins (mg/g) | Alkaloids (mg/g) | Saponins (mg/g) |
|---|---|---|---|---|---|
| Ethanol | 7.62 ± 0.07 | 43.93 ± 0.18 | 55.56 ± 0.28 | 75.17 ± 1.90 | 163.82 ± 2.25 |
| Water | 11.02 ± 0.03 | 26.81 ± 0.18 | 49.30 ± 0.13 | 12.16 ± 1.56 | 106.40 ± 0.56 |
| Hexane | 45.11 ± 0.13 | 127.42 ± 0.41 | 98.29 ± 0.05 | 16.43 ± 0.38 | 114.90 ± 0.81 |

Values are Mean ± SD (standard deviation) of 3 replicates.

## Conclusion

The hexane, water and ethanolic extracts of Negro pepper (*Xylopia aethiopica*) fruit inhibited the corrosion of mild steel in sulphuric acid solution with ethanolic extract of the pepper having the highest inhibition efficiency followed by the hexane extract. Water extract has the least inhibition efficiency. The inhibition efficiencies of the three extracts applied increased with increase in their concentration. The adsorption characteristic of ethanol, hexane and water extracts of Negro pepper conforms to Langmuir adsorption isotherm. Functional groups of compounds present in extracts of Negro pepper studied, greatly influenced the inhibitory action of the compounds. It is suspected that the presence of these phytochemicals is responsible for corrosion inhibition in mild steel.

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