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# Inhibition, Adsorption and Thermodynamic Investigation of Iron Corrosion by Green Inhibitors in Acidic Medium

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***Abstract:***
*The corrosion inhibition potentials of alkaloid, saponin and flavonoid extracts of Ocimunbasilicumleaves were investigated by evaluating the corrosion behaviour of Iron immersed in 1.0 M $H_2SO_4$ solutions containing varied concentration of the extract (0.5 g/L, 1.0 g/L, 2.0 g/L, 3.5 g/L, 5.0 g/L, 7.5 g/L and 10.0 g/L) using chemical methods. Maximum temperature attained, reaction time, thermodynamic data and adsorption characterizations were utilized to evaluate the corrosion inhibition and adsorption properties of the extract. The results revealed that, the corrosion of Iron decreases with increase in concentration of alkaloid extract, saponin extract and flavonoid extract, also, increases with increase in $H_2SO_4$ concentration. The increase in addition of the green inhibitors to the corrosive medium, improve the values of inhibition efficiency of the extract in the order AEOBL > SEOBL > FEOBL. In all cases, Flavonoid extracts exhibits least effect on the corrosion of Zinc in comparison with alkaloids and saponins. Results obtained from adsorption studies indicated that, all the green inhibitors were adsorbed on the surface of the Iron and that the adsorption fit excellently with the assumptions of the Langmuir adsorption isotherm model. All data acquired revealed that Ocimunbasilicum leaves are efficient inhibitors of corrosion in acid medium due to the presence of heterocompounds: saponins, tannins, flavonoids, glycosides, carbohydrates, reducing sugars, terpenoids, steroids and alkaloids.*

***Keywords:*** *Weight loss, Langmuir isotherm, Gibbs free energy, inhibition efficiency, Ocimunbasilicum, crude extract.*

## 1. Introduction

Scientists are relentless in seeking better and more efficient ways of combating the corrosion of metals. Among other methods, adding inhibitors to the corrosion environment has been employed. The use of inhibitors has been well documented as an effective method of protecting metallic materials from corrosion (Jamal et al., 2002; Al-Otaibi et al., 2012).

Corrosion inhibitors are substances which when added in small concentrations to corrosive media decrease or prevent the reaction of the metal with the media. The efficiency of these inhibitors is sometimes improved by the addition of some other compounds which act in synergism e.g. tannins, flavonoids, alkaloids etc. Inhibitors are added to many systems, namely, cooling systems, refinery units, chemicals, oil and gas production units, boiler, and so forth. Most of the effective inhibitors contain hetero atoms such as O, N, and S with multiple bonds in their molecules through which they are adsorbed on the metal surface.

It has been observed that adsorption depends mainly on certain physicochemical properties of the inhibitor, such as functional groups, electron density at the donor atom, π-orbital character, and the electronic structure of the molecule (Gopal et al., 2012; Saedah 2014; Ugi et al., 2016). Many studies have been carried out using organic corrosion inhibitors e.g. Leaves of *Hibiscus sabdariffa* (Murthy and Vijayaragavan, 2014), Tea (Camellia Sinensis) extract (Lotto, 2011), natural gums (Peter et al., 2015), *Atropa belladonna* extract (Shalabi et al., 2014), Azadirachta indica (Sharma et al., 2015).

Though many synthetic compounds showed good anticorrosive activity, most of them are highly toxic to both human beings and environment. The use of chemical inhibitors has been limited because of the environmental threat recently, due to environmental regulations. These inhibitors may cause reversible (temporary) or irreversible (permanent) damage to organ system, namely, kidneys or liver, or disturbing a biochemical process or disturbing an enzyme system at some sites in the body. The toxicity may be manifested either during the synthesis of the compound or during its applications (Hui et al., 2013; Dada et al., 2012).

Use of inhibitors is one of the most practical methods for protection against corrosion especially in acid solutions to prevent unexpected metal dissolution and acid consumption (Eddy et al., 2015; Sharma et al., 2015). The use of chemical inhibitors has been limited because of the environmental threat, recently due to environmental regulations. Plant extracts have become important because they are environmentally acceptable, inexpensive, readily available and renewable sources of materials. Plant extracts including their leaves, roots, tuber, stems and bark have been widely examined (Jeeval et al., 2014).

*Ocimun basilicum* is shown to be antioxidant, antiviral and antimicrobial. It has some effects ranging from low blood pressure, prevention of blood clothing, etc. (Jamal et al., 2002; Jayasinghe et al., 2003). The interest in this plant for the adsorption characteristics and thermodynamic investigation of the mitigation of corrosion of Iron in acidic medium stems from the fact that it is a strong antioxidant and has not been exhaustively tried in the corrosion of metals especially Iron.

## 2. Experimentation

### *2.1. Dressing of Working Electrodes*

Iron sheet of 99.5% purity, used for this study which was procured commercially from System Metals Ltd, Calabar, Nigeria was mechanically press-cut into 4.0 x 0.1 x 2 cm coupons with a hole of 1mm drilled at the middle of the upper edge of the coupons. These coupons were mechanically polished to mirror finish with series of Emery paper of variable grades starting with the coarsest and proceeding in steps to the finest (600) grade. These coupons were degreased in absolute ethanol, rinsed in acetone, dried with hot air and stored in moisture-free desiccator prior usage.

### *2.2. Preparation of Inhibitors*

Dried leaves of *Ocimun basilicum* were blended to powder form; 75 g of powdered leaves was extracted through the use of a soxhlet extractor using 250 ml ethanol for 72 h. the crude extract was evaporated using a water bath to reduce significantly the volume of ethanol present. 5 g of the ethanol extract was partitioned between 200 ml of chloroform and 200 ml of 0.1 M HCl solution using a separating funnel. The float fraction from the separating funnel was further basified using 150 ml of ammonia and partitioned using 150 ml of chloroform. The float was taken as the alkaloid extract. Again, 5 g of the dried powdered sample was weighed into a beaker and extracted with 50 cm3 of 80% methanol at room temperature for one hour. The solution was filtered through filter paper. The filtrate was evaporated to dryness over water bath. The weight of the dried extract was taken and the amount of flavonoid present was calculated (Ikeuba et al., 2015). 4.0 g of flavonoids extract of *Ocimun basilicum* was digested in 250 mL of 5.0 M H2SO4 solution. The resultant solution was kept for 24 hours and filtered. In another experiment, 5g of extract in 30 ml of 20% methanol was heated for 4 hrs. in a water bath to reduce volume of ethanol to 15 mls. 20 mls diethyl ether was added to separate organic portion from the aqueous. The organic portion was discarded. This was followed by the addition of 15ml butanol to the methanolic fraction to obtain 30ml methanol/n-butanol fraction while both mixtures were evaporated to dryness to obtain a crystalline soapy extract which was used as the saponin extract. From the concentrates, inhibitor test solutions were prepared in the concentration range of 0.5 g/L, 1.0 g/L, 2.0 g/L, 3.5 g/L, 5.0 g/L, 7.5 g/L and 10.0 g/L. *Ocimun basilicum* is known to be predominantly composed of Rosmarimic acid, $C_{18}H_{16}O_8$ (3,4-dihydroxyphenyllactic acid) which is a phenolic acid (Figure 1). A caffeic acid ester of salvianic acid A and a naturally occurring polyphenolic compound (Jamal et al., 2002; Jayasinghe et al., 2003).

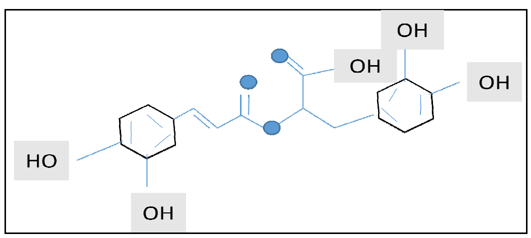


*Figure 1: 3,4-dihydroxyphenyllactic acid (Rosmarimic acid)*

### *2.3. Mass Loss Experiment*

In gravimetric measurements, Iron coupons were weighed before total immersion in a 250-ml beaker containing test solutions of different concentrations, being suspended by suitable hooks at 1 cm below the solution surface. The coupons were retrieved after 1 hour, scrubbed with brush under running bidistilled water, dried as before and weighed. The difference in weight of the coupons before and after immersion in different test solutions was taken as the weight loss. The corrosion rate for the metal was obtained from the slope of the trend line of the graph of weight loss against time. The inhibition efficiency of the inhibitor (*IE %*) of the inhibitors was calculated using equations 1.

$$IE\% = \frac{CR^0 - CR}{CR^0} \quad (1)$$

where CR and $CR^0$ are the corrosion rate in the presence and absence of inhibitors respectively.

### *2.4. Gasometric experiment*

One hundred ml of test solutions poured into a reaction vessel was used in the gasometric method. Upon introduction of the metal coupon, the vessel was quickly corked and the initial volumes of air in the burette, taken against that of the paraffin oil recorded. The decrease in volume of the paraffin oil in the burette due to hydrogen gas evolution was noted after every one minutes till the last volume of paraffin oil in the burette after 60 minutes. The rate for the hydrogen evolution was obtained from the slope of the trend line of the graph of volume of hydrogen evolved against time. The volume of hydrogen gas evolved was used to evaluate inhibition efficiency of the test inhibitors using equation 2

$$E_H\% = 1 - \frac{CR_H}{CR_H^0} \quad (2)$$

where $CR_H$ and $CR_H^0$ are corrosion rates got from total volume of gas evolved in the presence and absence of test inhibitors respectively.

## 3. Results

### *3.1. Mass Loss Results*

Iron sheet was found to corrode in 1 M $H_2SO_4$ solution. Results obtained clearly show that extracts of *Ocimun basilicum* leaves effectively retards corrosion rate of Iron sheet in 1 M $H_2SO_4$ solution, indicating inhibition of the corrosion reaction. The weight loss data reveal the dependence of inhibition efficiency of alkaloid, saponin and flavonoid extracts of *Ocimun basilicum* leaves and corrosion rate of Iron sheets on concentration (Figs. 2 – 3). In most of the cases, the oxygen atom present in the inhibitor molecules (3,4-dihydroxyphenyllactic acid (Rosmarimic acid) is easily protonated in acidic solution and converted into quaternary/oxonium ions (Ugi et al., 2016; Habib et al., 2015). These protonated species get adsorbed on the cathodic sites of the metal surface and decrease the hydrogen evolution hence retard metal dissolution (Pradeep and Mohana 2013; Okafor et al., 2012; Nnanna et al., 2010; Sudhish et al., 2011). The evaluated inhibition efficiency had the optimum inhibition efficiency obtained at 98.4 %, 92.4 % and 92.5 % for alkaloid, saponins and flavonoids extracts respectively at 303 K temperature with 10.0 g/L inhibitor concentration (Table 1).

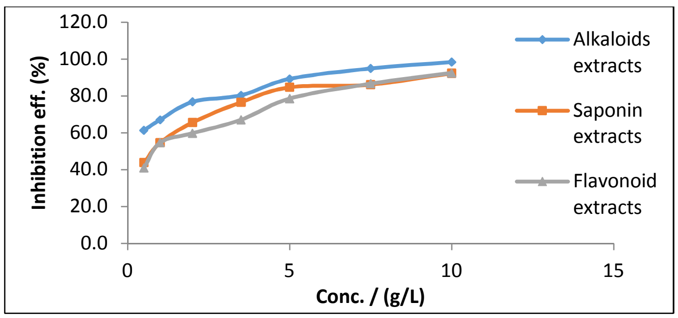


*Figure 2: Variation of inhibition efficiency with extracts concentration of Ocimun basilicum leaves on Iron in 1 M $H_2SO_4$*

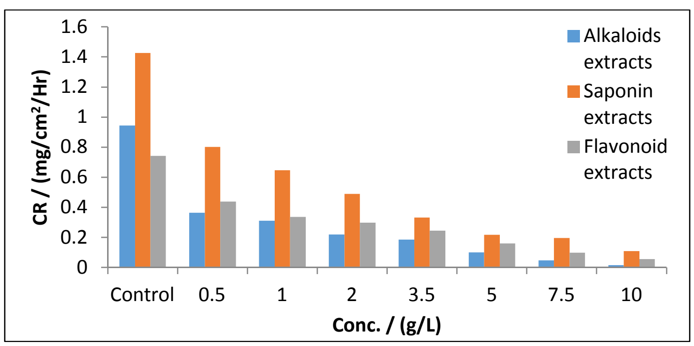


*Figure 3: Variation of corrosion rate with extracts concentration of Ocimun basilicum leaves on Iron in 1 M $H_2SO_4$*

| | Alkaloids extracts | | | Saponin extracts | | | Flavonoid extracts | | |
|---|---|---|---|---|---|---|---|---|---|
| **Conc.** | CR ($mg/cm^2/hr$) | θ | Inhibition Efficiency | CR ($mg/cm^2/hr$) | θ | Inhibition Efficiency | CR ($mg/cm^2/hr$) | θ | Inhibition Efficiency |
| **Control** | 0.9432 | - | - | 1.426 | - | - | 0.743 | - | - |
| **0.5 g/L** | 0.365 | 0.613 | 61.3 | 0.801 | 0.438 | 43.8 | 0.439 | 0.409 | 40.9 |
| **1.0 g/L** | 0.311 | 0.670 | 67.0 | 0.646 | 0.547 | 54.7 | 0.337 | 0.546 | 54.6 |
| **2.0 g/L** | 0.219 | 0.768 | 76.8 | 0.49 | 0.656 | 65.6 | 0.299 | 0.598 | 59.8 |
| **3.5 g/L** | 0.185 | 0.804 | 80.4 | 0.333 | 0.766 | 76.6 | 0.245 | 0.670 | 67.0 |
| **5.0 g/L** | 0.101 | 0.893 | 89.3 | 0.218 | 0.847 | 84.7 | 0.159 | 0.786 | 78.6 |
| **7.5 g/L** | 0.0479 | 0.949 | 94.9 | 0.197 | 0.862 | 86.2 | 0.099 | 0.867 | 86.7 |
| **10.0 g/L** | 0.0147 | 0.984 | 98.4 | 0.109 | 0.924 | 92.4 | 0.0557 | 0.925 | 92.5 |

*Table 1: Calculated values of corrosion rates, surface coverage and inhibition efficiency for extracts of Ocimun basilicum leave on Iron in 1 M $H_2SO_4$ at $30^oC$.*

### *3.2. Effect of Temperature*

The fact that inhibition efficiency decreased with increasing temperature (Tables 2 - 4) signifies that the inhibitors function effectively at lower temperatures (Atta et al., 2014; Al-Amiery et al., 2014; Dada et al., 2012). It also indicates that the time lag for the adsorption and desorption of the inhibitor molecules on Iron sheet surfaces become shorter at higher temperature. Corrosion rate increased linearly with increase in temperature but decreased with increasing extracts of *Ocimun basilicum* leaves concentration in the acid solution. It is clear from the Tables that increase in concentration of extracts molecules of *Ocimun basilicum* leaves for all tests performed at varying temperatures result in a decrease in corrosion reaction rate indicating geometric blocking effect of *Ocimun basilicum* leave extracts at active corrosion sites as also reported somewhere by Loto (2011); Allaoui et al., (2013). The volume of $H_2$ evolved was observed to reduce in the presence of test inhibitors as compared to the free acid solution. Further reduction in the volume of $H_2$ evolved was observed as concentration of test inhibitor molecules increased. Tables 2 - 4 revealed that the most remarkable reduction in the volume of $H_2$ evolved was observed with alkaloid extracts of *Ocimun basilicum* leaves molecules at 10.0 g/L with inhibition efficiency of the inhibitor at 97.5 %. The inhibition efficiency of the inhibitor obtained from the hydrogen gas evolution measurements also increased with increase in inhibitor molecules concentration. When the surface coverage of the adsorbed inhibitor species increases, lateral reactions between inhibitor molecules may arise, thereby influencing inhibition efficiency. Attractive lateral interactions usually give rise to stronger adsorption hence higher inhibition efficiency (Kamal et al., 2012; Eddy et al., 2015). The results obtained in the gasometric experiments are in agreement with the trend reported for mass loss.

| | **313K** | | | **323K** | | | **333K** | | |
|---|---|---|---|---|---|---|---|---|---|
| **Inhibitor Conc.** | CR ($mg/cm^2/min$) | θ | IE (%) | CR ($mg/cm^2/min$) | θ | IE (%) | CR ($mg/cm^2/min$) | θ | IE (%) |
| **Control** | 1.093 | - | - | 1.101 | - | - | 1.138 | - | - |
| **0.5 g/L** | 0.500 | 0.543 | 54.3 | 0.512 | 0.535 | 53.5 | 0.619 | 0.456 | 45.6 |
| **1.0 g/L** | 0.422 | 0.614 | 61.4 | 0.422 | 0.617 | 61.7 | 0.511 | 0.551 | 55.1 |
| **2.0 g/L** | 0.344 | 0.685 | 68.5 | 0.344 | 0.688 | 68.8 | 0.509 | 0.553 | 55.3 |
| **3.5 g/L** | 0.197 | 0.820 | 82.0 | 0.245 | 0.777 | 77.7 | 0.483 | 0.576 | 57.6 |
| **5.0 g/L** | 0.142 | 0.870 | 87.0 | 0.1801 | 0.836 | 83.6 | 0.374 | 0.671 | 67.1 |
| **7.5 g/L** | 0.109 | 0.900 | 90.0 | 0.1792 | 0.837 | 83.7 | 0.223 | 0.804 | 80.4 |
| **10.0 g/L** | 0.027 | 0.975 | 97.5 | 0.2 | 0.841 | 84.1 | 0.218 | 0.808 | 80.8 |

*Table 2: Effect of temperature on corrosion rate of metal, surface coverage and inhibition efficiency of Alkaloid extracts on corrosion of Iron in $H_2SO_4$ environment*

| | **313K** | | | **323K** | | | **333K** | | |
|---|---|---|---|---|---|---|---|---|---|
| **Inhibitor Conc.** | CR ($mg/cm^2/min$) | θ | IE (%) | CR ($mg/cm^2/min$) | θ | IE (%) | CR ($mg/cm^2/min$) | θ | IE (%) |
| **Control** | 1.093 | - | - | 1.101 | - | - | 1.138 | - | - |
| **0.5 g/L** | 0.614 | 0.438 | 43.8 | 0.658 | 0.402 | 40.2 | 0.662 | 0.418 | 41.8 |
| **1.0 g/L** | 0.529 | 0.516 | 51.6 | 0.613 | 0.443 | 44.3 | 0.621 | 0.454 | 45.4 |
| **2.0 g/L** | 0.517 | 0.527 | 52.7 | 0.539 | 0.510 | 51.0 | 0.588 | 0.483 | 48.3 |
| **3.5 g/L** | 0.245 | 0.776 | 77.6 | 0.384 | 0.651 | 65.1 | 0.479 | 0.579 | 57.9 |
| **5.0 g/L** | 0.211 | 0.807 | 80.7 | 0.252 | 0.771 | 77.1 | 0.384 | 0.663 | 66.3 |
| **7.5 g/L** | 0.196 | 0.821 | 82.1 | 0.227 | 0.794 | 79.4 | 0.302 | 0.735 | 73.5 |
| **10.0 g/L** | 0.163 | 0.851 | 85.1 | 0.211 | 0.808 | 80.8 | 0.297 | 0.739 | 73.9 |

*Table 3: Effect of temperature on corrosion rate of metal, surface coverage and inhibition efficiency of saponin extracts on corrosion of Iron in $H_2SO_4$ environment*

| | **313K** | | | **323K** | | | **333K** | | |
|---|---|---|---|---|---|---|---|---|---|
| **Inhibitor Conc.** | CR ($mg/cm^2/min$) | θ | IE (%) | CR ($mg/cm^2/min$) | θ | IE (%) | CR ($mg/cm^2/min$) | θ | IE (%) |
| **Control** | 1.093 | - | - | 1.101 | - | - | 1.138 | - | - |
| **0.5 g/L** | 0.517 | 0.527 | 52.7 | 0.627 | 0.431 | 43.1 | 0.714 | 0.373 | 37.3 |
| **1.0 g/L** | 0.444 | 0.594 | 59.4 | 0.539 | 0.510 | 51.0 | 0.639 | 0.438 | 43.8 |
| **2.0 g/L** | 0.344 | 0.685 | 68.5 | 0.513 | 0.534 | 53.4 | 0.581 | 0.489 | 48.9 |
| **3.5 g/L** | 0.245 | 0.776 | 77.6 | 0.346 | 0.686 | 68.6 | 0.492 | 0.568 | 56.8 |
| **5.0 g/L** | 0.217 | 0.801 | 80.1 | 0.301 | 0.727 | 72.7 | 0.376 | 0.670 | 67.0 |
| **7.5 g/L** | 0.216 | 0.802 | 80.2 | 0.275 | 0.750 | 75.0 | 0.307 | 0.730 | 73.0 |
| **10.0 g/L** | 0.210 | 0.808 | 80.8 | 0.255 | 0.768 | 76.8 | 0.3 | 0.737 | 73.7 |

*Table 4: Effect of temperature on corrosion rate of metal, surface coverage and inhibition efficiency of flavonoid extracts on corrosion of Iron in $H_2SO_4$ environment*

### *3.3. Thermodynamic Considerations*

The temperature of the system was varied across the inhibitor concentrations from which the activation energy for the corrosion of Iron sheets in solutions of $H_2SO_4$ was evaluated using the Arrhenius equation given by equation 3.

$$\ln R_c = \ln A - \frac{E_o}{RT} \qquad 3$$

Where $R_c$ is the corrosion rate, $E_o$ is the apparent effective activation energy, R is the general gas constant, and A is the Arrhenius pre-exponential factor (Singh et al., 2012;). Thermodynamic parameters; Enthalpy, $\Delta H_{ads}$, Entropy $\Delta S_{ads}$ of alkaloid, saponins and flavonoid extracts of *Ocimun basilicum* leaves on Iron sheets was calculated using equations 4 (transition state equation), which can be written as follows (Ugi et al., 2016; Khaled and El-Sharik 2013).

$$R_c = \frac{KT}{h}\exp\left(\frac{\Delta S^*_i}{R}\right)\exp\left(\frac{-\Delta H}{RT}\right) \qquad 4$$

Calculated values of activation energy between 313 and 333 K were obtained from the slope of Figure 4 – 6 and presented in Table 5. The values obtained are greater than the value obtained for the blank solution indicating that alkaloid, saponins and flavonoid extracts of *Ocimun basilicum* leaves retards the corrosion of Iron. Since the Activation energy which is the energy required to oxidize metal is increased with inhibitor concentration, it implies that more energy has to be supplied to the system for the corrosion to take place thus, the observed decrease in corrosion rate. The values are also consistent with the data expected for the mechanism of physical adsorption (<80 $kJmol^{-1}$) according to Shalabi et al., (2013); Khaled and El-mobarak (2012). The reaction is exothermic and the reaction becomes less exothermic with increase in inhibitor concentration. The negative values for $\Delta S_{ads}$ (Table 5) shows the non-spontaneous dissolution of the Iron sheet and the increase in its value suggests decrease in disordering in the rate determining step. From equation 4 and 5 values of log ($R_c$/T) were plotted against 1/T, and from the slope and intercept of the plot (Figs. 7 – 9), values of enthalpy and entropy of adsorption were calculated as shown in Table 5 (Santhini and Jeyara 2012; Kadlum et al., 2014). From the calculated values of $\Delta H_{ads}$ (Table 5), it can be deduced that the adsorption of the inhibitor on Iron sheet surface is exothermic.

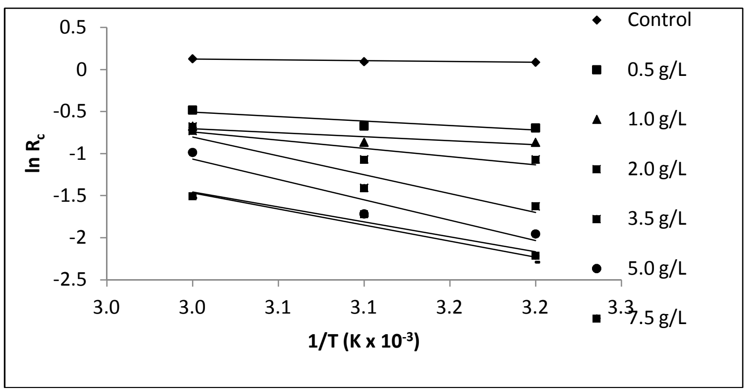


*Figure 4: Arrhenius plot for Alkaloid extracts of Ocimun basilicum leave on Iron in 1 M $H_2SO_4$*

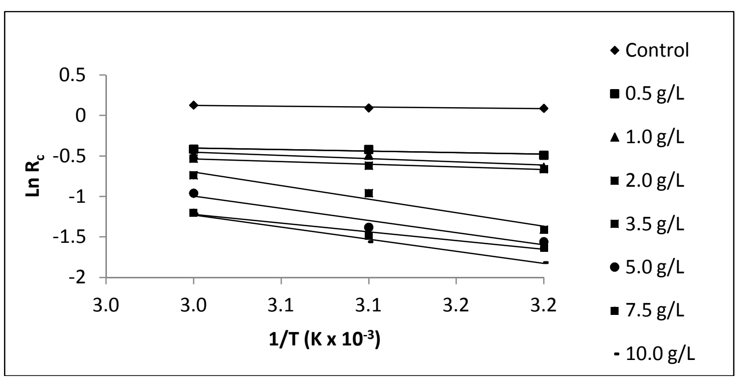


*Figure 5: Arrhenius plot for saponins extracts of Ocimun basilicum leave on Iron in 1 M $H_2SO_4$*

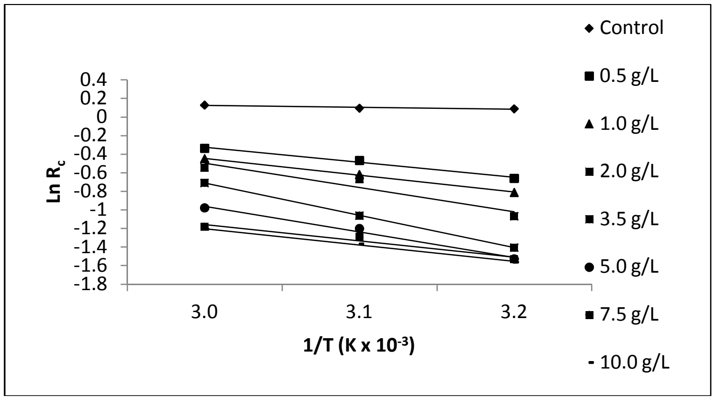


*Figure 6: Arrhenius plot for flavonoids extracts of Ocimun basilicum leave on Iron in 1 M $H_2SO_4$*

| | Alkaloid extract | | | Saponins extract | | | Flavonoids extract | | |
|---|---|---|---|---|---|---|---|---|---|
| **Conc. (g/L)** | $E_o$ | $\Delta H_{ads}$ kJ/mol | $-\Delta S_{ads}$ kJ/mol | $E_o$ | $\Delta H_{ads}$ kJ/mol | $-\Delta S_{ads}$ kJ/mol | $E_o$ | $\Delta H_{ads}$ kJ/mol | $-\Delta S_{ads}$ kJ/mol |
| **Control** | 16.6 | -12.03 | 27.2 | 16.6 | -12.03 | 27.2 | 16.6 | -12.03 | 27.2 |
| **0.5 g/L** | 18.9 | -19.73 | 34.9 | 17.7 | -22.25 | 37.5 | 19.4 | -15.656 | 30.9 |
| **1.0 g/L** | 20.0 | -21.26 | 36.5 | 19.6 | -32.24 | 47.4 | 21.0 | -18.162 | 33.4 |
| **2.0 g/L** | 23.3 | -39.09 | 54.3 | 19.6 | -32.36 | 47.6 | 21.3 | -27.784 | 43.0 |
| **3.5 g/L** | 29.6 | -49.31 | 64.5 | 26.0 | -36.57 | 51.8 | 21.9 | -38.128 | 53.3 |
| **5.0 g/L** | 37.3 | -54.49 | 69.7 | 26.1 | -44.50 | 59.7 | 31.5 | -41.256 | 56.5 |
| **7.5 g/L** | 40.7 | -76.98 | 92.2 | 36.1 | -58.94 | 74.1 | 33.1 | -49.435 | 64.6 |
| **10.0 g/L** | 48.1 | -90.02 | 105.2 | 40.3 | -72.17 | 87.4 | 41.9 | -55.208 | 70.4 |

*Table 5: Thermodynamic parameters obtained from the adsorption of Ocimun basilicum leave extracts on Iron in 1 M $H_2SO_4$ acid*

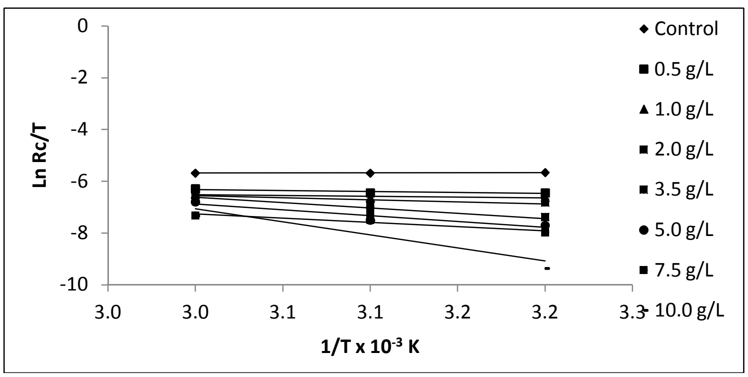


*Figure 7: Transition state plot for Alkaloid extracts of Ocimun basilicum leave on Iron in 1 M $H_2SO_4$*

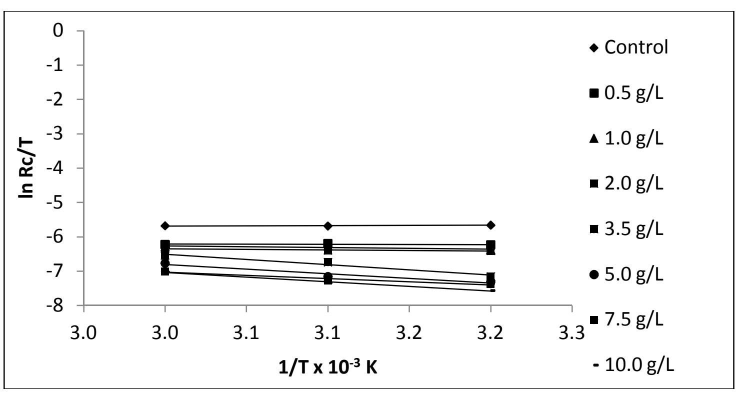


*Figure 8: Transition state plot for saponins extracts of Ocimun basilicum leave on Iron in 1 M $H_2SO_4$*

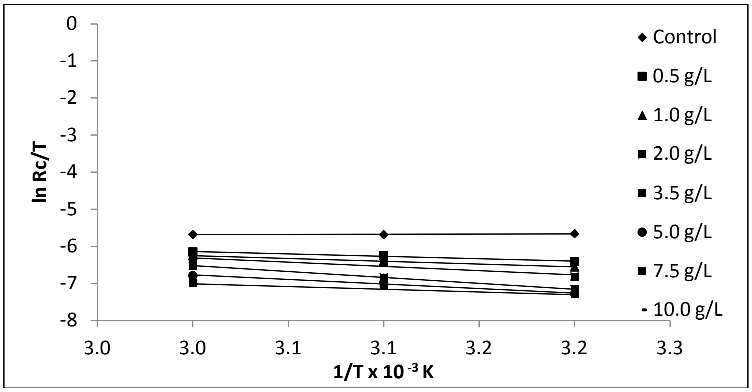


*Figure 9: Transition state plot for flavonoid extracts of Ocimun basilicum leave on Iron in 1 M $H_2SO_4$*

*3.4. Adsorption Consideration*

According to Langmuir adsorption isotherm, surface coverage, θ is related to equilibrium adsorption constant ($K_{ads}$) and concentration, C by the equation 5 (Saratha and Meenakshi 2010; Grubben and Denton 2004):

$$\frac{C}{\theta} = \frac{1}{Kads} + C \qquad 5$$

Figure 10 – 12 shows the straight lines of C/θ vs. C at different temperatures. The parameters obtained from C/θ vs. C plots were listed in Table 6. These results show that all the linear correlation coefficients ($R^2$) are almost equal to unity. This indicates strict adherence to the principles underlying the derivation of Langmuir isotherm. However, these values were not equal to 1, this indicates a slight deviation from Langmuir theory of adsorption according to Hui et al., (2013) and Pradeep&Mohana, (2013). Adherence to Langmuir suggests formation of monolayer of adsorption and no interaction between the adsorbed species. From Table 6, $K_{ads}$ represents the strength between adsorbate and adsorbent. Larger values of the $K_{ads}$ (> 1) imply more efficient adsorption and hence better inhibition efficiency. $K_{ads}$ value decreased in this study with increase in the temperature indicating that adsorption of inhibitors on the Iron surface was unfavourable at higher temperatures which is also an indication of a physical adsorption mechanism. (Murthy and Vijayaraganan 2014; Ghulamullah et al., 2015; Peter et al., 2015; Gustat and Singh 2004). Negative values of $\Delta G_{ads}$ indicate spontaneity and stability of the adsorption layer. The values of the free energy obtained which were below -40kJ/mol also suggests a physical adsorption mechanism for the adsorption of the inhibitor on the Iron surface in 1.0 M $H_2SO_4$ solution (Murthy and Vijayaraganan 2014; Ghulamullah et al., 2015; Peter et al., 2015).

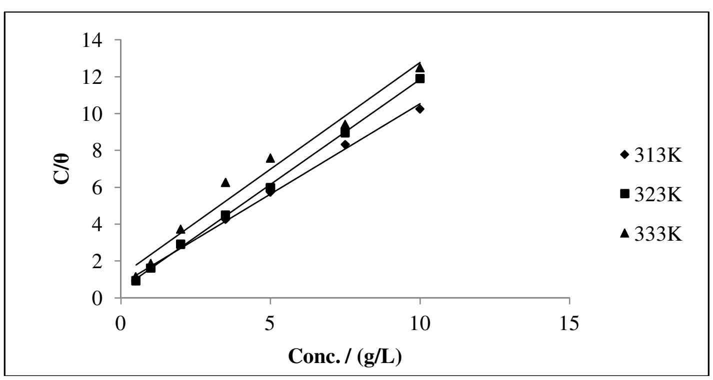


*Figure 10: Langmuir isotherm plots for the adsorption of AEOBL on Iron in 1 M $H_2SO_4$*

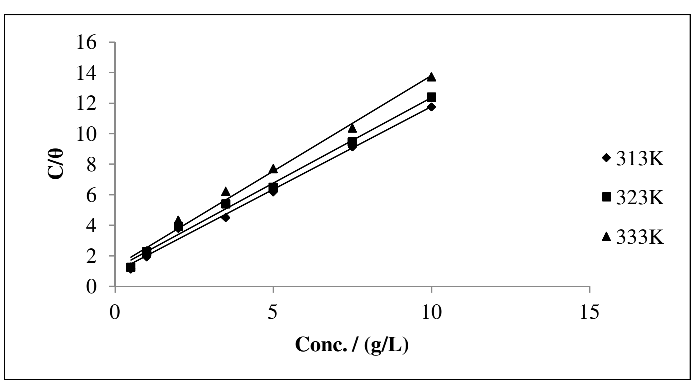


*Figure 11: Langmuir isotherm plots for the adsorption of SEOBL on Iron in 1 M $H_2SO_4$*

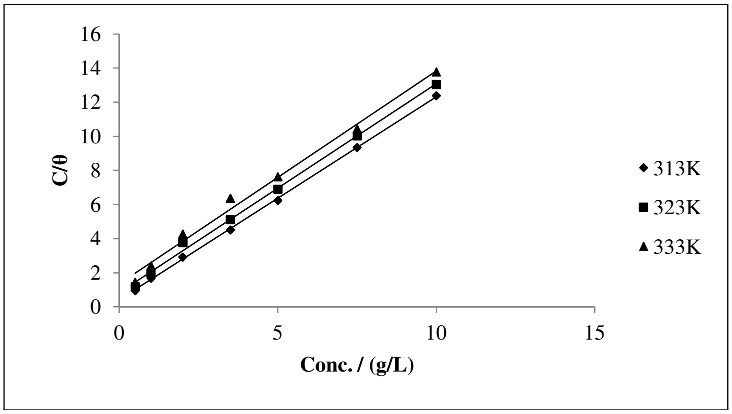


*Figure 12: Langmuir isotherm plots for the adsorption of FEOBL on Iron in 1 M $H_2SO_4$*

| | Alkaloid | | | | Saponin | | | | Flavonoid | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Temp (K)** | $k_{ads}$ | $R^2$ | Slope | $\Delta G_{ads}$ | $k_{ads}$ | $R^2$ | Slope | $\Delta G_{ads}$ | $k_{ads}$ | $R^2$ | Slope | $\Delta G_{ads}$ |
| **313** | 0.731 | 0.995 | 0.981 | -9.636 | 0.921 | 0.992 | 1.085 | -10.238 | 0.415 | 0.999 | 1.190 | -8.163 |
| **323** | 0.471 | 0.999 | 1.137 | -8.763 | 1.171 | 0.992 | 1.119 | -11.21 | 0.841 | 0.997 | 1.224 | -10.32 |
| **333** | 1.203 | 0.976 | 1.157 | -11.631 | 1.277 | 0.989 | 1.254 | -11.797 | 1.359 | 0.991 | 1.246 | -11.97 |

*Table 6: Results from Langmuir isotherm showing parameters for the adsorption of AEOBL, SEOBL and FEOBL on Iron in 1 M $H_2SO_4$*

## 4. Conclusion

1. The highest valuable result for corrosion inhibition performance was achieved at concentration of 10.0 g/L for both extracts at 30$^o$C. Both extracts of *Ocimun basilicum* leaves acts as good corrosion inhibitors for Iron in 1 M $H_2SO_4$ solution.
2. The increase in concentration of the inhibitors to the corrosive medium, improved the inhibition efficiency in the order AEOBL (98.4 %) > > SEOBL (92.4 %) > FEOBL (92.5 %).
3. Temperature dependent result revealed that the inhibitors function effectively at lower temperatures and that the time lag for the adsorption and desorption of the inhibitor molecules on Iron sheet surfaces become shorter at higher temperature.
4. The adsorption of extracts of *Ocimun basilicum* leaves obeyed Lamgmuir adsorption isotherm and a physical adsorption mechanism has been proposed for the adsorption process.

## 5. References


i. Adeniran OI, Olajide OO, Igwemmar NC, Orishadipe AT. Phytochemical constituents, antimicrobial and antioxidant potentials of tree spinach Cnidoscolus aconitifolius (Miller) I. M. 2012;4(7):3550-3556.
ii. Al-Amiery AA, Abdul A, Kadhum H, Kadihum A, Mohamad AB, How CK, Junaedi S. Inhibition of mild steel corrosion in sulphuric acid solution by new Schiff base. Materials. 2014;7:787-804.
iii. Allaoui M, Cheriti A, Gherraf N, Chebouat E, Dadamoussa B, Salhi R. Inhibition of mild steel corrosion in 1 M HCl medium by acid extract of Haloxylon scoparium pommel. Int. J. Eletrochem. Sci. 2013;8(7):9429–9434.
iv. Al-Otaibi MS, Al-Mayouf AM, Khan M, Mousa AA, Al-Mazroa SA, Alkhathlan HZ. Corrosion inhibitory action of some plant extracts on the corrosion of mild steel in acidic media. Arabian Journal of Chemistry; 2012. DOI: 10.1016
v. Atta AM, El-Mahdy GA, Al-Lohedan HA, Al- Hussain SA. Inhibition of mild steel in acidic medium by magnetite myrrh nanocomposite. International Journal of Electrochemical Science. 2014;9(12):8446–8457.
vi. Dada AO, Olalekam AP, Olatunya AM, Dada O. Langmuir, Freundlich, Temkin and Dubinin – Radushkevich isotherms studies of equilibrium sortion of Zn2+ unto Phosphoric acid modified rice husk. ISOR Journal of Applied Chemistry. 2012;3(1):38–45.
vii. Dada, A. O., Olalekam, A. P., Olatunya, A. M. & Dada, O. (2012). “Langmuir, Freundlich, Temkin and Dubinin – Radushkevich isotherms studies of equilibrium sortion of Zn2+ unto Phosphoric acid modified rice husk.” ISOR Journal of Applied Chemistry. 3(1): 38 – 45
viii. Eddy NO, Momoh-Yahaya H, Oguzie EE. Theoretical and experimental studies on the corrosion inhibition potentials of some purines for aluminum in 0.1 M HCl. Journal of Advance Research. 2015;6(2):203–217.
ix. Ghulamullah K, Kazi M, Newaz N, Wan J, Basiru H, Binti MA, Fadhil LF, Ghulam MK. Application of natural product extracts as green corrosion inhibitors for metals and alloys in acid Johnston]. J. Med. Plants Res. 2013;7(19): 1317–1322.
x. Gopal J, Sudish KS, Priyanka D, Shanti S, Ebenso EE, Rajiv P. Parthenium hysterophorus plant extract as an efficient green corrosion inhibitor for mild steel in acidic environment. Int. J. electrochem. Sci. 2012;7(10):9933-9945.
xi. Grubben G. J. & Denton O. A. (2004). Plant Resources of Tropical Africa. 2: Vegetables. PROTA Foundation. Wisley pub. pp. 201.

xii. Gustaf B. & Singh P. M. (2004) "Susceptibility of Stainless Steel Alloys to Crevice Corrosion in Chlorine Dioxide Bleach Plants", Corrosion Science, 46(9), 2159-2182.

xiii. Habib A, Mirzaee S, Rostamikia T, Bagheri R. Pomegranate (Punica granatum) peel extract as a green corrosion inhibitor for mild steel in hydrochloric acid solution. International Journal of Corrosion; 2015. Article ID 197587, 6 pages.

xiv. Hui, C., Zhenghao, F., Jinling, S., Wenyan, S. & Qi, X. (2013). " Corrosion inhibition of mild steel by Aloes extract in HCl solution medium.," Int. J. electrochem. Sci., 8(2013): 720 – 734

xv. Jamal J. Khalighi A. KashiA A. Bais P.H. Vivanco J.M. (2002) Chemical characterization of Basil found in local accessions and used in traditional medicine in Iran. Journal of Agric. And food chemistry 50(21): 5878 – 5883

xvi. Jayasinghe C. Gotoh N. Aoki Y. Wada S. (2003) Phenolics composition and antioxidant activity of sweet Basil. Journal of Agric. And food chemistry. 51(15): 4442 – 4449

xvii. Jeeva1 PA, Harikumar S, Karthikeyan S, Narayanan S, Mukherjee A, Chandrasekaran N. Quantum mechanical studies of Thio compunds on the corrosion inhibition of mild steel in acidic media. International Journal of Pharm Tech Research. 2014;4(4):1422-1427.

xviii. Kadhum AH, Mohamad AB, Hammed LA, Al- Amiery AA, San NH, Musa YA. Inhibition of mild steel corrosion in hydrochloric acid solution by new coumarin. Materials. 2014;7: 4335-4348.

xix. Kamal C, Gopolakrishma LM. Caulerpin-A bis-indole as a green inhibitor for the corrosion of mild steel in 1M HCl solution from the marine alga Caulerpa racemosa. Ind. Eng. Chem. Res. 2012;51:10399–10407.

xx. Khaled KF, Al-Mobarak NA. A predictive model for corrosion inhibition of mild steel by thiophene and its derivatives using artificial neural network. International. Journal of Electrochemical Science. 2012;7:1045–1059.

xxi. Khaled KF, El-Sherik AM. Using molecular dynamics simulations and genetic function approximation to model corrosion inhibition of iron in chloride solutions. International. Journal of Electrochemical Science. 2013;8:10022- 10043.

xxii. Loto, C. A. (2011) "Inhibition effect of Tea ( Camellia Sinensis) extract on the corrosion of Mild steel in dilute sulphuric acid" Journal of Material & Environmental Science. 2 ( 4) : 335 – 344

xxiii. Murthy ZV, Vijayaragavan K. Mild steel corrosion inhibition by acid extract of leaves of Hibiscus sabdariffa as a green corrosion inhibitor and sorption behavior. Green Chemistry Letters and Reviews. 2014;7(3): 209- 219.

xxiv. Nnanna L. A., Onwuagba B. N., Mejeha I. M. and Okeoma K. B. ( 2010) " Inhibition effects of some plant extracts on the acid corrosion of aluminium alloy" African Journal of Pure & Applied Chemistry. 4 (1): 011 – 016.

xxv. Okafor, P.C., Ebiekpe, V.E., Azike, C.F., Egbung, G.E., Brisibe, E. A. & Ebenso, E.E. (2012) "Inhibitory action of Artemisia annua extracts and artemisinin on the corrosion of mild steel in H2SO4 solution", International Journal of Corrosion, 12: 132-137

xxvi. Patel N. S., Jauhariand S., Mehta G. N., Ad-Deyab S. S., Warad I. & Hammouti B. (2013). "Mild Steel Corrosion by Various Plant Extracts in 0.5 M Sulphuric acid". Int. J. of Electrochem. Sci., 8(2013): 2635 – 2655.

xxvii. Peter A, Obot IB, Sharma SK. Use of natural gums as green corrosion inhibitors: An overview. International Journal of Industrial Chemistry. 2015;6(3):153-164.

xxviii. Pradeep, K. C. B. & Mohana, K. N. (2013). "Adsorption and thermodynamic characteristics of Plumeria rubra plant extracts on mild steel corrosion in industrial water medium". International Research Journal of Pure & Applied Chemistry, 3(4): 330 – 346.

xxix. Saedah R. Al-Mhyawi. Inhibition of mild steel corrosion using Juniperus plants as green inhibitior. African Journal of Pure and Applied Chemistry. 2014;8(1):9-22.

xxx. Santhini N, Jeyaraj T. The inhibition effect of [3-(4-hydroxy-3-methoxy-phenyl)-1- phenylpropenone] on the corrosion of the aluminium in alkaline medium. J. Chem. Pharm. Res.

xxxi. Saratha R., & Meenakshi R. (2010) " Corrosion inhibitor: A plant extract. Der Pharma. Chemica. 2(1): 287 – 294

xxxii. Shalabi1 K, Abdallah YM, Hassan HM, Fouda AS. Adsorption and corrosion inhibition of Atropa belladonna extract on carbon steel in 1 M HCl solution. International Journal of Electrochemical Science. 2014;9:1468-1487.

xxxiii. Sharma KS, Anjali Peter, Obot IB. Potential of Azadirachtaindica as a green corrosion inhibitor against mild steel, aluminium and tin: A review. Journal of Analytical Science and Technology. 2015;6:26–41.

xxxiv. Sudhish K. Shukla, and Eno E. Ebenso (2011) Corrosion Inhibition, Adsorption Behavior and Thermodynamic Properties of Streptomycin on Mild Steel in Hydrochloric Acid Medium. Int. J. Electrochem. Sci. 6 (2011): 3277 - 329

xxxv. Ugi, B.U., Obeten, M.E., Magu T.O. and Uwah I.E. (2016) Corrosion Inhibition Performance Of Alkaloid Extracts Of Calendula officinalis (Pot Marigold) Plant On Aluminium, Carbon Steel And Zinc In 5 M Nitric Acid Solution. International Journal of Innovative Research and Advanced Studies. 3(12): 34 - 40
gu, I. E. Uwah, Inter. J. Inn. Res. Adv. Stud. 2016,3, 12, 34 - 40