

# Adsorption and Anticorrosion Performance of *Ocimum Canum* Extract on Mild Steel in Sulphuric Acid Pickling Environment

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**Abstract** The corrosion inhibitory effect of extracts from *Ocimum Canum* (OC) on mild steel was studied in 0.5 M H<sub>2</sub>SO<sub>4</sub> using gasometric and weight loss methods of monitoring corrosion. The result shows that the OC extract functioned as an effective inhibitor for mild steel corrosion in H<sub>2</sub>SO<sub>4</sub> solutions. The inhibition efficiency of OC on mild steel corrosion in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution increases on increasing its concentration but decreases when temperature is increased. The inhibition is attributed to the adsorption on the mild steel surface by constituents of OC extract and conforms to Langmuir adsorption isotherm. Mechanisms of inhibition were deduced using the dependence of the inhibition efficiency on temperature and also from assessment of kinetic and activation parameters which govern the processes and it was discovered that the adsorption of the extract's organic constituents on the corroding mild steel were by physical adsorption.

**Keywords** *Ocimum Canum*, Corrosion Inhibitor, Mild Steel, Gravimetric, Gasometric, Physical adsorption

## 1. Introduction

In chemical industries, acidic solutions are usually used for industrial cleaning and to remove scales from metal surfaces, these processes lead to significant metal dissolution. In order to prevent and minimize the dissolution of metals in acidic environments, different corrosion inhibitors are used, especially organic compounds, which in their structure contain some of the following atoms; nitrogen, sulphur, oxygen, phosphor etc. [1-4].

Most corrosion inhibitors that are synthesized are usually hazardous and this has favoured using environmentally acceptable inhibitors. Natural products are renowned corrosion inhibitors, being environmentally friendly. The extracts from various parts of some plants have been revealed to inhibit corrosion of mild steel in acidic solutions [5-8]. These natural inhibitors studied have been discovered to be highly eco-friendly and possess no threat to the environment.

*Ocimum Canum* (OC) belongs to the Lamiaceae family. It is also called the African basil with a distinct mint flavor, with hairy leaves and scented flowers. OC was used specially for treating diabetes. OC is common in Africa, usually in the

tropics and other areas of the equatorial region and was after some time introduced to the Americas. The stems of the plant are angled and the branches are from its base and the leaves are oval. The leaves are fuzzy and tiny and have flowers which are beautiful violet or white, with a pleasant scent like that of a clove. The leaves are opposite and toothed [9].

The present study is directed at the evaluation of extracts from OC as an inhibitor for the corrosion of mild steel in sulphuric acid pickling environment employing gasometric and weight loss techniques. Phytochemical screening of the extract of the inhibitor reveals that the OC extract contains alkaloid, saponin, anthraquinone, tannin, phlobatanins, steroids, flavanoids, among others [10].

## 2. Materials and Methods

### 2.1. Material Preparation

Mild steel sheets with weight percentage composition as follows: C, 0.05; Mn, 0.6; P, 0.36; Si, 0.03 were used. The sheets with thickness 0.14 cm, was pressed-cut mechanically into coupons 2cm × 4cm dimension. These coupons were utilized as procured without polishing, but were however degreased in ethanol, dried with acetone, weighed and kept in a desiccator before use [11].

### 2.2. Inhibitor Preparation

Weighed quantity of the dried and ground OC were refluxed with ethanol for about 4 hours and was kept overnight to completely extract the basic components. The

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resulting solutions were filtered and the ethanol evaporated followed by drying in an oven for one night. The solid extract was stored after weighing and used as inhibitor for the corrosion study. From the weighted solid extract, test solutions of the inhibitor were prepared in the concentration range 0.1 – 2.0 g/L.

### 2.3. Weight Loss Measurement

Tests were carried out by totally immersing the coupons into the test solutions and maintained at 30, 40 and 50°C. The previously cleaned and weighed mild steel coupons were hung with glass hook and rod inside beakers containing inhibitor test solutions. The entire test was conducted in solutions that are aerated. To determine weight loss against time, the mild steel coupons were removed from the test solution after every 24 hours progressively for a period of 120 hours, scrubbed with brush and rinsed with water, dried with acetone and re-weighed. The difference in weight between the coupons at a particular time and the initial weight of the coupons were taken to be the weight loss. From the data gotten from weight loss, the corrosion rates (CR) were calculated from equation (1):

$$CR = \frac{\Delta W}{At_{\infty}} \quad (1)$$

Where  $\Delta W$  is weight loss in grams,  $A$  represents the surface area of the specimen in  $\text{cm}^2$  and  $t_{\infty}$  is the end time of each experiment in days. From the corrosion rate, the surface coverage ( $\theta$ ) resulting from adsorption of the inhibitor molecules, and inhibition efficiency of the molecule (IE%) were determined using equ. (2) and (3), respectively.

$$\theta = \frac{CR_{\text{blank}} - CR_{\text{inh}}}{CR_{\text{blank}}} \quad (2)$$

$$IE\% = \frac{CR_{\text{blank}} - CR_{\text{inh}}}{CR_{\text{blank}}} \times \frac{100}{1} \quad (3)$$

where  $CR_{\text{inh}}$  and  $CR_{\text{blank}}$  are the corrosion rates in the presence and absence of the inhibitor respectively.

### 2.4. Gasometric Measurement

Gasometric measurement was carried out by using the gasometric assembly which is similar to the set-up described by Oguzie [12]. It consist basically two necked round-bottom flask which serves as the medium for the reaction containing the metal coupons and the corrodent. Other parts are a separating funnel, a burette fitted with taps, and an outer glass jacket which serves as a water condenser. A two-necked round-bottom flask was connected to a burette through a delivery tube which was also connected to a reservoir containing paraffin oil. About 200ml of the test solution was then introduced inside the flask and the initial volume of air in the burette recorded. Thereafter, the reaction vessel was immediately closed after two coupons were dropped in the solution. The change in volume of the paraffin oil level was used to estimate the volume of hydrogen gas evolved by the corrosion reaction. The evolved gas was carefully measured at fixed time interval to monitor the progress of the corrosion reaction. Experiments were carried

out at 30°C, 40°C and 50°C. The hydrogen evolution rate ( $RV_H$ ) is determined from the ratio of the volume of evolved gas ( $V$ ) to time ( $t$ ), according to equation (4)

$$RV_H = \frac{\Delta V}{\Delta t} \quad (4)$$

and the surface coverage of the inhibitor ( $\theta$ ) and efficiencies (IE%) determined using equations (5) and (6), respectively.

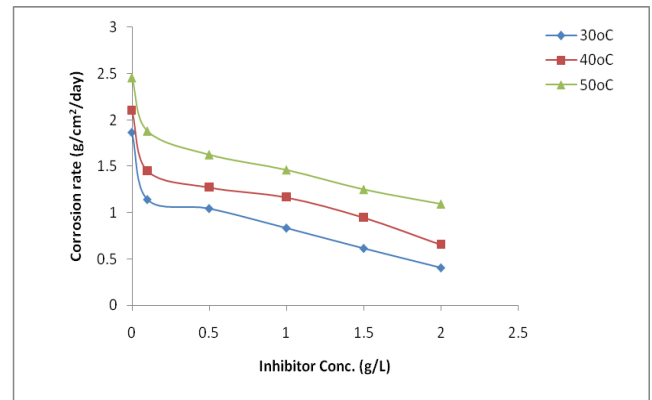
$$\theta = \frac{RV_{H \text{ blank}} - RV_{H \text{ inh}}}{RV_{H \text{ blank}}} \quad (5)$$

$$IE\% = \frac{RV_{H \text{ blank}} - RV_{H \text{ inh}}}{RV_{H \text{ blank}}} \times \frac{100}{1} \quad (6)$$

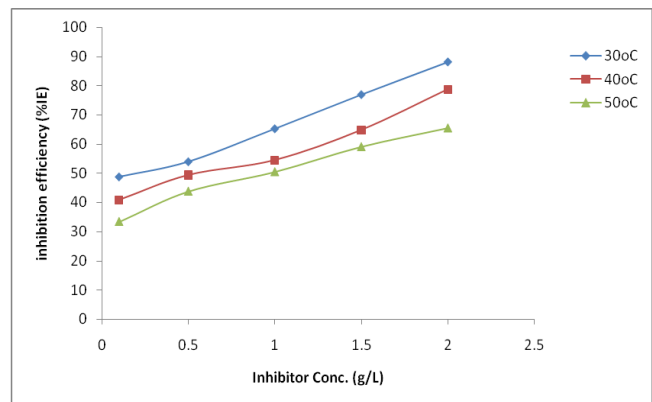
where  $RV_{H \text{ inh}}$  and  $RV_{H \text{ blank}}$  are the hydrogen evolution rate in the presence and absence of the inhibitor molecules, respectively. All the test from the gasometric and weight loss and measurements were run in triplicate and the average of the measurements presented.

## 3. Results and Discussion

### 3.1. Weight Loss Experiment



**Figure 1.** Variation of corrosion rate with concentration for mild steel with and without different concentrations of OC in 0.5 M  $\text{H}_2\text{SO}_4$  solution at different temperatures



**Figure 2.** Variation of inhibition efficiency (%IE) with OC concentration for mild steel in 0.5 M  $\text{H}_2\text{SO}_4$  solution at different temperatures from gravimetric measurements

The plot of the rate of corrosion and efficiency of the inhibitor with inhibitor concentration for mild steel corrosion in 0.5 M  $\text{H}_2\text{SO}_4$  at 30°C, 40°C and 50°C is shown in Figure

1 and 2. It is evident from Fig. 1 that the rate of corrosion decreased in the presence of the inhibitors compared to blank solution. This clearly indicates that OC extract retarded mild steel corrosion in  $H_2SO_4$  environment. It is also noticed that corrosion rate is increased as the temperature is elevated from 30 to 50°C both in the presence and absence of the inhibitors. This shows that the metal is susceptible to faster dissolution with increasing thermal agitation of the corrosive environment [13]. From Figure 2, it is observed that inhibition efficiency increased with an increase in OC extract concentration. The increase in inhibition efficiency and the decrease in corrosion rates with the increase in inhibitor concentration could be ascribed to the adsorption of the molecules of the inhibitor on the mild steel surface. The surface coverage occupied by the adsorbed molecules increases by increasing the concentration of the inhibitor which leads to better protection.

In the present corrosion study of mild steel in 0.5 M  $H_2SO_4$  solutions using gravimetric method, weight at time  $t$ , is designated  $W_t$ . When  $\log W_t$  was plotted against time (in days) at 30°C and other temperatures studied, a linear plot was observed with a slope of  $(-k/2.303)$ , which confirms first-order reaction kinetics with respect to mild steel in  $H_2SO_4$  solutions, as presented in equation 7:

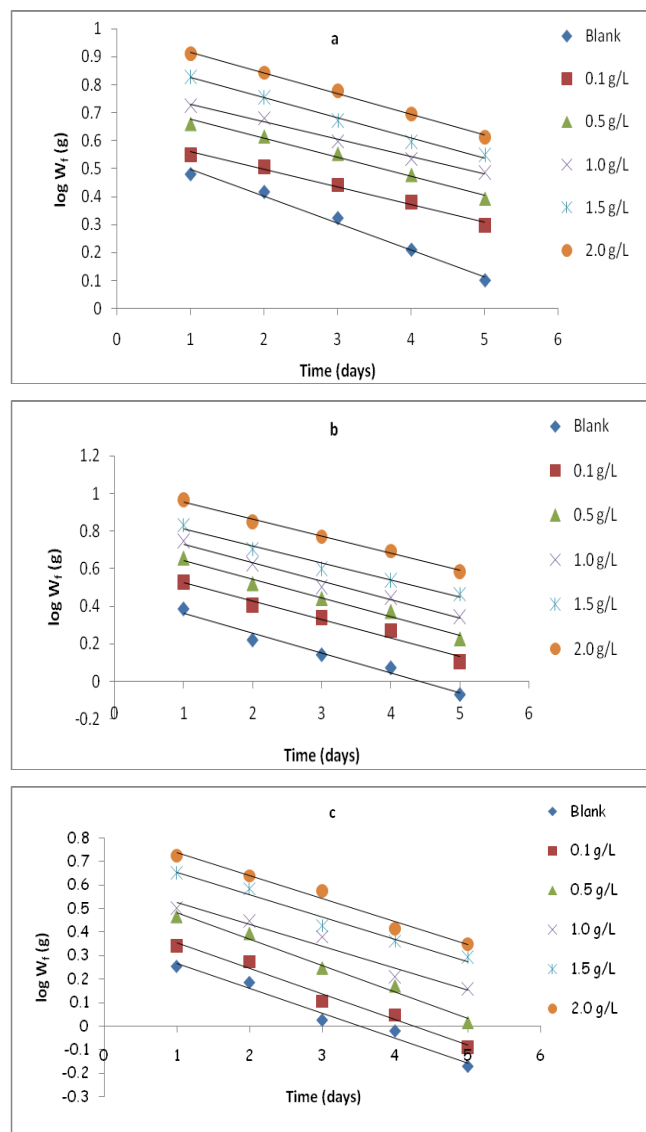
$$\log w_t = \log w_i - \frac{kt}{2.303} \quad (7)$$

where  $W_i$  is the initial weight before immersion,  $k$  is the rate constant while  $t$  is the time. The rate constant values,  $k$ , gotten from the slopes of the plots in Figure. 3 are shown in Table 1. The obtained results reveal that the rate constant decreases with increase in OC concentration.

From the values of the rate constant, the values of the half-life,  $t_{1/2}$ , of the mild steel in the test solutions were calculated using the equation:

$$t_{1/2} = \frac{0.693}{k} \quad (8)$$

The resultant data are also shown in Table 1. It was observed that the half-life values increased with an increase in OC concentration, indicating decrease in the dissolution rate of the metal in the solutions with increase in OC concentration [14].



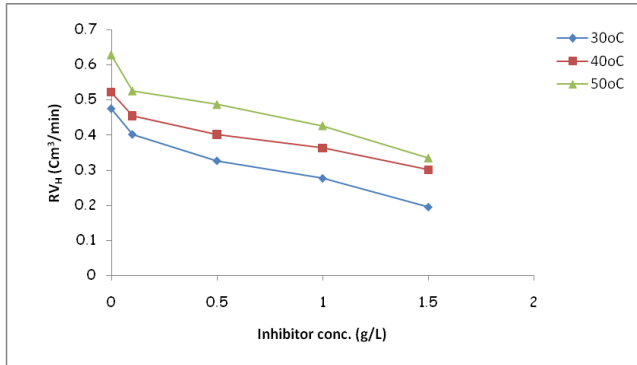
**Figure 3.** Variation of  $\log W_t$  with time for mild steel in 0.5 M  $H_2SO_4$  solution containing various concentrations of ethanol OC extract at (a) 30°C (b) 40°C and (c) 50°C

**Table 1.** Kinetic data and heat of adsorption ( $Q_{ads}$ ) for mild steel corrosion in  $H_2SO_4$  containing different concentrations of OC using gravimetric

Conc (g/L)	Rate constant, $K \text{ (day}^{-1}) \times 10^{-2}$			Half-life, $t_{1/2}$ , day			$E_a$ , KJ/mol 40–50°C	$Q_{ads}$ , KJ/mol
	30°C	40°C	50°C	30°C	40°C	50°C		
Blank	3.68	5.78	14.20	18.83	11.99	4.88	25.82	-
0.1	3.02	5.21	15.73	22.95	13.30	4.41	30.91	-17.24
0.5	2.27	4.53	13.22	30.53	15.30	5.24	34.20	-19.36
1.0	2.03	4.39	12.68	34.14	15.79	5.47	35.45	-18.91
1.5	1.60	3.94	11.09	43.31	17.59	6.25	36.17	-21.13
2.0	1.46	3.76	10.44	47.47	18.43	6.64	38.27	-23.35

### 3.2. Gasometric Measurement

Fig. 4 shows the variation of hydrogen gas evolved rate with inhibitor concentration for mild steel corrosion in 3 M  $H_2SO_4$  containing different concentrations of OC extract at different temperatures. The figure revealed higher rate of evolution of hydrogen gas by the blank solutions as compared to the evolution by solutions containing different concentrations of OC extract indicating that OC extract functioned as an inhibitor for mild steel corrosion in  $H_2SO_4$  at the studied temperatures. It is equally observed that the hydrogen gas evolution rate decreases with an increase in the concentration of OC extract.



**Figure 4.** Variation of rate of hydrogen gas evolved with inhibitor concentration for mild steel corrosion in 3 M  $H_2SO_4$  containing different concentrations of OC extract

### 3.3. Effect of Temperature

Evaluating the effect of temperature on the rate of corrosion and inhibition efficiency of OC extract in  $H_2SO_4$  has given insight into the stability and adsorption mechanism of the inhibitor on the surface of the mild steel. From weight loss measurement, it is observed from Fig. 1 that at all of the temperatures studied the rate of corrosion increases with temperature rise. However, inhibition efficiency of the OC extract decreases as the temperature increases. This trend is consistent with both gasometric and weight loss methods employed in this study as presented in Fig. 1 and Table 2 respectively. Decrease in inhibition efficiency with temperature rise is suggestive of physical adsorption of OC extract onto the surface of the mild steel [15].

The activation energies ( $E_a$ ) for the corrosion reaction in presence and absence of the OC extract were calculated from Arrhenius equation:

$$\ln k = \ln A - \frac{E_a}{RT} \quad (8)$$

where A represent the pre-exponential factor, T represent absolute temperature, R represent the gas constant and k represent the corrosion rate of mild steel. Arrhenius plot of  $\ln k$  versus  $1/T$  is presented in Fig. 5. The  $E_a$  values evaluated from the slope of the graph are presented in Table 1.

An estimated heat of adsorption ( $Q_{ads}$ ) was calculated from the trend of surface coverage with temperature as follows [6]:

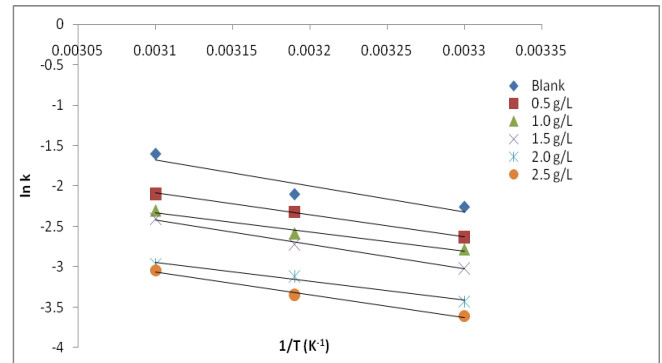
$$Q_{ads} = 2.303R \left[ \log \left( \frac{\theta_2}{1-\theta_2} \right) - \log \left( \frac{\theta_1}{1-\theta_1} \right) \right] \times \frac{T_1 T_2}{T_2 - T_1} \quad (9)$$

where  $\theta_1$  and  $\theta_2$  are the degrees of surface coverage at temperatures  $T_1$  and  $T_2$ . The calculated values are presented in Table 1.

It is observed that the  $E_a$  values ranged from 25.82 KJ/mol to 38.27 KJ/mol for all concentrations of OC extract studied and values of  $E_a$  between 20 – 40 KJ/mol is indicative of physical adsorption while  $E_a > 80$  KJ/mol is indicative of chemical adsorption. Thus the values of activation energy support the fact that OC extract was physically adsorbed on the surface of the mild steel. The negative values of  $Q_{ads}$  show that the degree of surface coverage decreased with increase in temperature, also supporting the proposed physisorption mechanism for OC extract.

**Table 2.** Rate of hydrogen evolution ( $RV_H$ ) and Inhibition efficiency (IE %) for the mild steel in  $H_2SO_4$  containing different concentrations of OC using gasometric measurement

Conc (g/L)	RV <sub>H</sub> (cm <sup>3</sup> /min)			%IE		
	30°C	40°C	50°C	30°C	40°C	50°C
Blank	0.475	0.522	0.627	-	-	-
0.1	0.402	0.455	0.525	43.5	43.4	36.7
0.5	0.327	0.402	0.487	54.3	47.7	45.7
1.0	0.277	0.363	0.427	60.6	57.6	54.6
1.5	0.195	0.302	0.335	77.0	65.9	61.3
2.0	0.123	0.225	0.263	89.2	77.9	70.8



**Figure 5.** Arrhenius plots for the corrosion of mild steel in 0.5 M  $H_2SO_4$  with and without different concentrations of OC

### 3.4. Adsorption Behaviour

To further elucidate the adsorption behaviour of OC extract in 0.5 M  $H_2SO_4$  solution, different isotherm models were employed, such as Freundlich, Langmuir, Flory-Huggins, Frumkin, and Temkin, but the best fit was the Langmuir isotherm model as presented in Figure 6, obtained by using the weight loss data. The Langmuir adsorption isotherm is represented by equation 10:

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \quad (10)$$

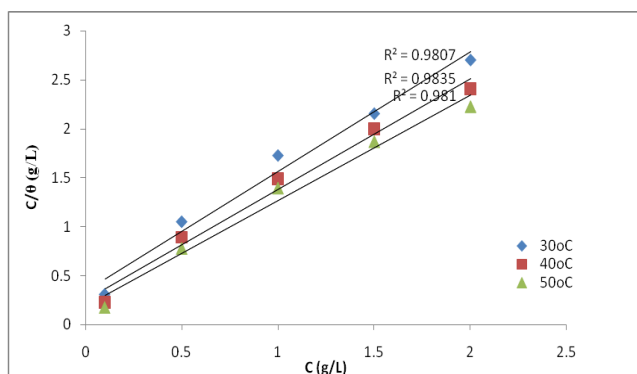
where  $\theta$  is the degree of surface coverage, C is the inhibitor concentration,  $K_{ads}$  is the equilibrium constant of the adsorption process. The variation of  $C/\theta$  against C is linear

with good correlation coefficient ( $R^2$ ) which suggests that the adsorption of OC extract follow Langmuir adsorption isotherm. This implies that the adsorption of OC extract on the surface of the mild steel is a monolayer adsorption. As seen from Table 3, there is a steady decrease in the equilibrium constant of adsorption  $K_{ads}$  with rise in temperature, which indicates that the interactions between mild steel surface and the adsorbed inhibitor molecules are weakened and as a result, the adsorbed inhibitor molecules could be removed easily. Such data gives an insight to why increasing temperature decreases the inhibition efficiency [16].

The free energy of adsorption values  $\Delta G_{ads}$ , were calculated from the relationship:

$$\Delta G_{ads} = -RT \ln(55.5 K_{ads}) \quad (11)$$

where  $R$  is the gas constant,  $T$  is the temperature in Kelvin and 55.5 is the concentration of water in solution. The calculated values are shown in Table 1. The  $\Delta G_{ads}$  values are observed to be negative in every case, implying that the OC extract is strongly adsorbed on the surface of the mild steel [17]. The values of  $\Delta G_{ads}$  obtained imply that OC extract adsorption occurs by way of physical adsorption mechanism. Generally, values of  $\Delta G_{ads}$  less negative or equal to  $-20 \text{ kJmol}^{-1}$  (as obtained in this study) are consistent with electrostatic interaction between the charged metals and charged molecules which signifies physical adsorption while values more negative than  $-40 \text{ kJmol}^{-1}$  signify chemical adsorption [18, 19].



**Figure 6.** Langmuir Isotherm for the adsorption of OC extracts on mild in 0.5 M  $\text{H}_2\text{SO}_4$  at different temperatures

**Table 3.** Calculated thermodynamic parameters from Langmuir adsorption isotherm

Temperature ( $^{\circ}\text{C}$ )	$K_{ads}$	$\Delta G_{ads}$ (kJ/mol)	$R^2$
30	1.12	-10.40	0.9807
40	1.08	-10.65	0.9835
50	0.67	-9.71	0.9810

## 4. Conclusions

The results presented in this paper show that *Ocimum Canum* (OC) inhibits mild steel corrosion in  $\text{H}_2\text{SO}_4$  solutions to reasonable extent. The corrosion rate of the mild

steel in 0.5 M  $\text{H}_2\text{SO}_4$  is dependent on the concentration of the inhibitor. This rate decreased as the concentration of the inhibitor is increased. The percentage inhibition efficiency of this inhibitor decreased with temperature rise which indicate that physical adsorption was the predominant inhibition mechanism. OC extract can be considered as an eco-friendly corrosion inhibitor for mild steel in 0.5M  $\text{H}_2\text{SO}_4$  solution.

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