# CAT'S WHISKERS (*Cleome gynandra*) AND GARDEN HUCLEBERRY (*Solanumscabrum*) LEAF EXTRACTS AS CORROSION INHIBITOR OF MILD STEEL IN HYDROCHLORIC ACID SOLUTIONS

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**Abstract:** The inhibition of corrosion of mild steel in hydrochloric acid solution by *Solanumscabrum* and *Cloeme gynandra* leaf extracts has been investigated via weight loss measurements and potentiodynamic polarization studies at 308, 318 and 328K. The inhibition efficiencies (%) increased with concentration of inhibitors and decrease with increasing temperature while activation energy of corrosion increases with increasing concentration. The average value of Ea (6.57 kJmol$^{-1}$and 4.18 kJmol$^{-1}$) for the two extracts, respectively were lower than 40.0 kJmol$^{-1}$; implying that the inhibitors are physically adsorbed on the mild steel surface. The mean values of Qads were found to be -12.22 and -4.57 kJmol$^{-1}$ for the inhibitors, respectively indicating that the adsorption process is exergonic. Inhibition of mild steel corrosion by *Solanumscabrum* and *Cloeme gynandra* follows first order kinetics. Physical adsorption mechanism is proposed for the inhibitors.

**Keywords:** *Cleome gynandra*; *Solanumscabrum;* inhibitory effect; potentiodynamic polarization; physisorption

## Introduction

Many synthetic compounds have shown good anticorrosion activity, though most of them are highly toxic to both human beings and environment. The safety and environmental issues of corrosion inhibitors arising from industries have always been a global concern. Such inhibitors may cause reversible (temporary) or irreversible (permanent) damage to organ system like kidneys or livers, disturb a biochemical processand enzyme system (Hammouti *et al*., 2013). The toxicity may manifest either during the synthesis of the compound or during its applications (Hammouti *et al*., 2013).

From the standpoint of safety, the development of non-toxic and effective inhibitors is considered more important and desirable nowadays, which are also called eco-friendly or green corrosion inhibitors (Manimegalai *et al*., 2000). These toxic effects have led to the use of natural products as anticorrosion agents which are eco-friendly and harmless. In recent years, many alternatives eco-friendly corrosion inhibitors have been studied and developed (Loto *et al*., 2014; Noor *et al*., 2016).

A compound or material deposited as a film on a metal surface that either provides physical protection against corrosive attack or reduces the open-circuit potential difference between local anodes and cathodes and increases the polarization is called 'corrosion inhibitor' (Sybil, 2003). Inhibitors are used to control the corrosion of metallic materials by controlling metal dissolution and consumption, generally by forming a film on the metal surface (Aggarwal and Avinash, 2002). Inhibitors are added to many systems, namely, cooling systems, refinery units, chemicals, oil and gas production units, boiler, and so forth. The use of chemical inhibitors has recently been limited because of the environmental threat they poseto the society. Due to the known hazardous effects of most synthetic corrosion inhibitors are the motivation for the use of some natural plant products as corrosion inhibitors (Cyril and Adams, 2012).

Plant extracts have become important corrosion inhibitors because they are environmentally acceptable, inexpensive, readily available and renewable sources of materials. Plant products are organic in nature, and some of the constituents including tannins, organic and amino acids, alkaloids, and pigments are known to exhibit inhibitory action. Moreover, they can be extracted by simple procedures with low cost. Many workers (Hammouti *et al*., 2013; Rajah and Sethuraman, 2008; Ebenso *et al*., 1998; El-Etre, 2006; Okafor and Ebenso, 2007; Oguzie *et al*., 2010) have contributed significantly to the green mitigation by investigating several plants and their different body parts as corrosion inhibitors.

In this study, the effect of extracts of the leafs of *Cleome gynandra* and *Solanumscabrum* as inhibitors are evaluated with a view to determining their effectiveness as corrosion inhibitors of mild steel in acidic medium.

## Materials and Methods

### *Sampling and sample preparation*

Mild steel sheets of AA120 and purity 98% was obtained from Mubi metropolis. Each sheet (0.1 cm in thickness) was mechanically press-cut into coupons of dimensions 3 x 4 cm. The coupons were descaled using wire brush and degreased in absolute ethanol, dried in propanone, weighed and stored in moisture-free desiccators prior to use. Methanol, ethanol, and distilled water were the solvents used for the extraction process. All solvents for this study were of analytical grade. The extracts (20, 40, 60, 80, and 100 mg/L) were prepared in 0.1M HCl and used as inhibitors. Similarly, concentrations of 0.02, 0.04, 0.06, 0.08 and 0.1M HCl solutions was prepared and used as corrodent.

### *Weight loss measurements*

The procedure reported earlier by Onen *et al.* (2013) and corroborated by Oguzie *et al.* (2014) was adopted for the weight loss measurement.

### *Corrosion protection efficiency measurements*

Corrosion rates were described by weight loss per density per unit area per unit time.These rates were calculated for different concentrations of inhibitors in HCl using the formula:

$$\text{The corrosion rate} = \frac{\Delta W_0 - \Delta W_i}{DAT} \quad (1)$$

**Where: $W_i$** and **$W_o$** are weight losses for mildsteel in the presence and absence, respectively of the inhibitor in HCl solution (Aydogdu and Aydinol, 2006); **D** is the density (g/cm$^3$), **A** is the area of mild steel bars (cm$^2$), **T** is the time of exposure (hours).

The percentage inhibition efficiency, $\%I_E$ was calculated using the expression;

$$\%I_E = \frac{W_0 - W_i}{W_0} \, x\,100 \qquad (2)$$

$$Surface\ coverage\ (\theta) = \frac{W_0 - W_i}{W_0} \qquad (3)$$

***Electrochemical measurement***

Electrochemical experiment was carried out using the procedure of Cang *et al.* (2013) with Autolab Instrument (model 302). All experiments were conducted at 308K. The exposed electrode area to the corrosive solution was 0.28 $cm^2$. Potentiodymic polarization curves were obtained by changing the electrode potential automatically from (-6000 to - 400mV) at open circuit potential. Measurement was performed using a computerinterface fitted with Demo version software.

**Results and Discussion**

***Effects of temperature on weight loss***

The percentage inhibition efficiencies, corrosion rate and surface coverage for different concentrations of HCl and inhibitors are given in Table1. The mean weight loss of mild steel in hydrochloric acid increases with time as the corrodent concentration and temperature were increased (Fig. 1). With an increase in corrodent concentrations and temperature, more active molecules of the reactants (acid and mild steel surface) become available for the reaction. Thus, the observed trend may also be due to the fact that rates of chemical reactions generally increase with acid concentration and temperature.

**Table 1: Corrosion Parameters for Mild steel Corrosion in 0.1M HCl with inhibitors (*Solanumscabrum* and *Cloeme gynandra*) at 308, 318 and 328K**

| Inhibitor Conc. | Inhibition Efficiency (%) | | | Corrosion Rate (x$10^{-7}$) | | | Surface Coverage (θ) | | |
|---|---|---|---|---|---|---|---|---|---|
| (mg/L) | 308K | 318K | 328K | 308K | 318K | 328K | 308K | 318K | 328K |
| Blank | - | - | - | 56.46 | 76.30 | 86.60 | - | - | – |
| *S. Sacabrum* | | | | | | | | | |
| 20 | 93.04 | 89.50 | 87.89 | 3.93 | 8.01 | 10.48 | 0.93 | 0.90 | 0.88 |
| 40 | 93.41 | 90.81 | 88.12 | 3.72 | 7.31 | 10.29 | 0.93 | 0.91 | 0.88 |
| 60 | 94.14 | 91.08 | 88.34 | 3.31 | 6.81 | 10.10 | 0.94 | 0.91 | 0.88 |
| 80 | 95.24 | 91.34 | 89.23 | 2.69 | 6.61 | 9.32 | 0.95 | 0.91 | 0.89 |
| 100 | 96.34 | 92.13 | 90.58 | 2.07 | 6.01 | 8.28 | 0.96 | 0.92 | 0. 91 |
| *C. gynandra* | | | | | | | | | |
| 20 | 91.58 | 89.76 | 88.57 | 4.76 | 7.81 | 9.90 | 0.92 | 0.90 | 0.89 |
| 40 | 92.67 | 90.81 | 88.79 | 4.14 | 7.01 | 9.71 | 0.93 | 0.91 | 0.89 |
| 60 | 93.04 | 91.60 | 89.01 | 3.93 | 6.41 | 9.52 | 0.93 | 0.92 | 0.89 |
| 80 | 93.77 | 92.13 | 89.46 | 3.52 | 6.01 | 9.13 | 0.94 | 0.92 | 0.89 |
| 100 | 94.14 | 92.65 | 89.91 | 3.31 | 5.61 | 8.74 | 0.94 | 0.93 | 0.90 |

The mean weight loss of mild steel decreased with increase in concentrationsof the additives (the two extract) and temperature as in Fig. 2. This establishes that the additives are corrosion inhibitors for the mild steel in 0.1M hydrochloric acid. These observations are in agreement with those made by several researchers (Ekpe *et al*., 1997; Onen, 2004, 2006) and may be attributed to an increase in the rate of ionization and diffusion of the active ions and also formation of film on the mild steel by the inhibitors, which passivates the alloy. Surface coverage increases with increase in inhibitor concentration and decreases with increase in temperature, as shown in Table1.

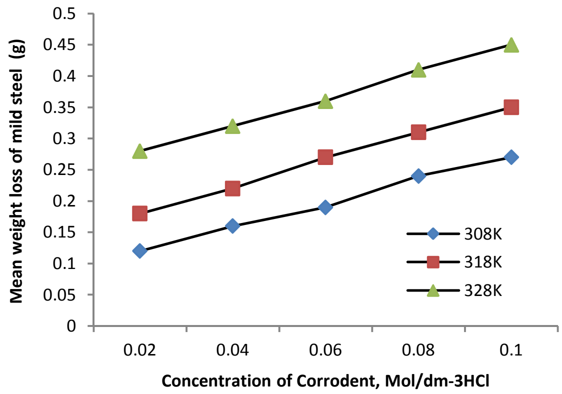


**Fig 1:** Plot of mean weight loss of mild steel against various concentration of corrodent, HCl at 308, 318 and 328K

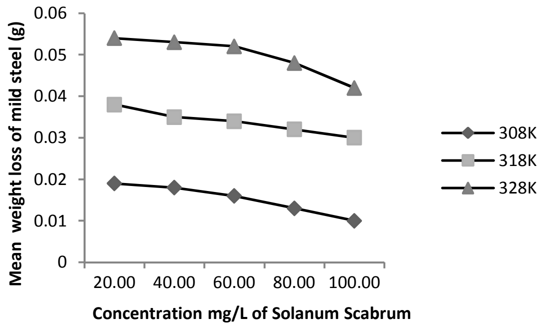


**Fig. 2:** Plot of mean weight loss of mild steel against various concentration of inhibitor *Solanumscabrum* at 308, 318 and 328K (Similar plot was obtained for *C. gynandra*).

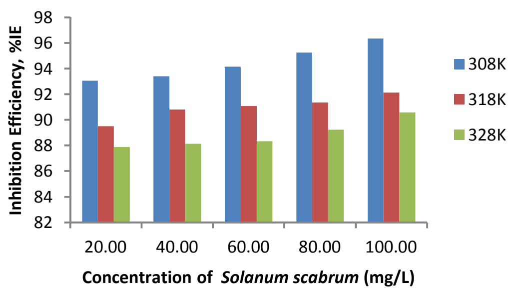


**Fig. 3:** Plot of percentage inhibition efficiency (%$I_E$) of mild steel against various concentrations of inhibitor (*Solanumscabrum)* at 308, 318 and 328K.

***Effect of inhibitor concentration on inhibition efficiency***

Inhibition efficiency was determined using equation (2) and reported in Table 1. Fig. 3 shows plot of inhibition efficiency (%) versus various concentrations of *Solanumscabrum* at 308, 318 and 328K and a similar plot was also obtained for *C. gynandra*. Inhibition efficiency (%) increased with increasing concentration of the inhibitors but decreased with increasing temperature (308-328K). This shows that the inhibitors function effectively at lower temperatures. This trend of inhibition effectiveness is also confirmed from the polarization studies (Table 3). The decrease in inhibition efficiencies with increasing temperature shows that the time lag for the process of adsorption of the inhibitor molecules on the mild steel surface becomes shorter. This observation is in agreement with report by Onen (2007).

***Kinetic and thermodynamic analysis of the results***

Plots of logarithm mean weight loss versus time (days) at 308K in different concentration of hydrochloric acid (without inhibitor) and with inhibitor are shown in Figs. 6 and 7, respectively. A linear variation was observed from these plots which signify first order kinetics for the inhibition process. The activation energies, Ea, recorded in Table 3 were determined using the equation;

$$Ea = 2.303R\frac{T1T2}{T2-T1}log\frac{\rho 2}{\rho 1} \quad (4)$$

**Where:** $\rho_1$ and $\rho_2$ are corrosion rates at 308K and 318K, respectively (Onen and Nwufo, 2007).

The average value of Ea 6.57 and 4.18 for the *Solanumscabrum* and *Cloeme gynandra*, respectively is lower than 40.0 $kJmol^{-1}$; implying that the inhibitors are physically adsorbed on the mild steel surface.

The values of heat of adsorption, Qads as depicted in Table 3 were determined from the relation:

$$Q_{ads} = 19.147\left(log\frac{\theta_2}{1-\theta_2} - log\frac{\theta_1}{1-\theta_1}\right)\left(\frac{T1T2}{T2-T1}\right) \quad (5)$$

**Where:** $\theta_1$ and $\theta_2$ are surface coverage at 308K and 318K, respectively for $T_1$ and $T_2$ (Onen *et al*., 2013).

All the values of Qads with mean values of -12.22 $kJmol^{-1}$ and -4.57 $kJmol^{-1}$ for *S. scabrum* and *C. gynandra,* respectively recorded in Table 2 indicated that both inhibition efficiency and heat of adsorption decreased with increase in temperature. This agrees with reports of (Onen, 2006; Onen and Nwufo, 2007). The negative values of Qads also suggest that repulsive interactions occurred between adsorbed inhibitor molecules and the mild steel. The negative values of $Q_{ads}$ equally signify that the adsorption is spontaneous; a property of strong inhibitor-metal surface interaction.

**Table 2: Kinetic and thermodynamic parameters for mild steel corrosion in 0.1M HCl with inhibitors (*Solanumscabrum* and *Cloeme gynandra*) at 308, 318 and 328K**

| Inhibitor Conc. (mg/L) | Mean weight loss | | | Activation energy, Ea($kJmol^{-1}$) 308–318K | Heat of adsorption Qads ($kJmol^{-1}$) 308–318K |
|---|---|---|---|---|---|
| | 308K | 318K | 328K | | |
| Blank | 0.273 | 0.381 | 0.446 | 2.44 | - |
| *S. Sacabrum* | | | | | |
| 20 | 0.019 | 0.038 | 0.054 | 5.81 | -0.36 |
| 40 | 0.018 | 0.035 | 0.053 | 5.14 | -6.11 |
| 60 | 0.016 | 0.034 | 0.052 | 5.89 | -10.18 |
| 80 | 0.013 | 0.032 | 0.048 | 7.33 | -17.52 |
| 100 | 0.100 | 0.025 | 0.042 | 8.67 | -26.97 |
| Average | | | | 6.57 | -12.22 |
| *C. gynandra* | | | | | |
| 20 | 0.023 | 0.039 | 0.051 | 4.03 | -0.39 |
| 40 | 0.020 | 0.035 | 0.050 | 4.27 | -5.14 |
| 60 | 0.019 | 0.032 | 0.049 | 3.98 | -4.48 |
| 80 | 0.017 | 0.030 | 0.047 | 4.37 | -6.36 |
| 100 | 0.016 | 0.028 | 0.045 | 4.27 | -6.47 |
| Average | | | | 4.18 | -4.57 |

**Table 3: Data obtained from potentiodynamic polarization curves shown in Fig. 5 and 10 for mild steel electrode in 0.1M HCl in different concentrations of the extracts at 308K**

| S/no. | Concentration | $i_{corr}$ ($x10^{-5}$) | $E_p$ (%) |
|---|---|---|---|
| Blank | 0.1M | 683.100 | - |
| *Solanum scabrum* | 20mg | 32.620 | 95.22 |
| " | 40mg | 7.227 | 98.94 |
| " | 60mg | 5.897 | 99.21 |
| " | 80mg | 4.412 | 99.35 |
| " | 100mg | 3.542 | 99.48 |
| *Cloeme gynandra* | 20mg | 43.65 | 93.61 |
| " | 40mg | 37.09 | 94.57 |
| " | 60mg | 33.88 | 95.04 |
| " | 80mg | 28.28 | 95.86 |
| " | 100mg | 25.68 | 96.24 |

***Adsorption analysis of the results***

It is clear from Table 1 and Fig. 3 that the inhibition efficiency (%) and surface coverage (θ) increased with inhibitor concentration and decreased with increasing temperature. This further confirms physical adsorption (physisorption) mechanism for the inhibition process (Onen and Nwufo, 2008). The high surface coverageobserved at high inhibitor concentrations is due to very strong interactions between the adsorbed species. The surface coverage values imply that the adsorption of the two extract (inhibitors) at the mild steel interface may be due to electrostatic force between the atoms on the metal surface and the adsorbates. This observation agrees with assertion made by earlier authors (Cang *et al*., 2013; Ekpe *et al*., 1997; Onen, 2006, 2007; Onen and Nwufo, 2007, 2008). Adsorption plays an important role in the inhibition of metallic corrosion by organic inhibitors. The efficiencies of inhibitors expressed as the relative reduction in corrosion rate can be quantitatively related by the amount of adsorbed inhibitors on the metal surface. It is assumed that the corrosion reaction are prevented from occurring over the active sites of the metal surface covered by adsorbed inhibitors species, whereas the corrosion reaction occurs normally on the surface at inhibitors free area (Chaurvedi *et al*., 2012).

Corrosion rate of the mild steel decreases with increasing concentration of the extracts (Fig. 4) and increases with temperature increasing. The inhibition efficiency also increases with increasing concentration of the extracts (Fig. 3), suggests that the extract molecules act by adsorption on the metal surface. Consequently, the increasing of the inhibition efficiency was ascribed to the increase in surface coverage. It was observed that corrosion inhibition efficiency decreased with increasing temperature and the bestefficiency was obtained at 308K as a result of a decrease in the adsorption of extract molecules.

The kinetics of the corrosion process is similar to the characteristics of a diffusion process; in which at highertemperature, the quantity of extract (inhibitor) molecules present at the metal surface is lower than at lower temperatures. The enhancement of inhibition efficiency at lower temperatures may be due to highactivation energy available for adsorption, and the higher rate of diffusion of inhibitor molecules. This assertion is supported by several authors (Aydogdu and Aydinol, 2006; Cang *et al*., 2013; Ekpe *et al*., 1997; Onen, 2004, 2006).

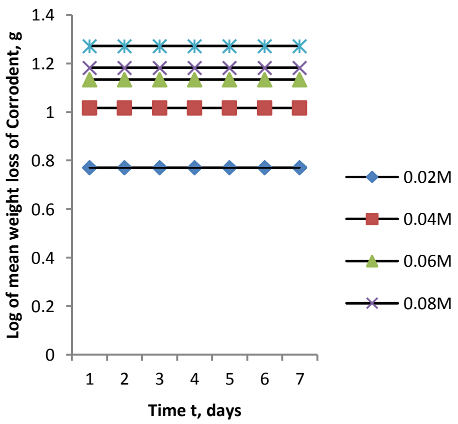


**Fig 4:** Plot of Log of mean weight loss of mild steel against various concentration of corrodent for 7 days at 318K.

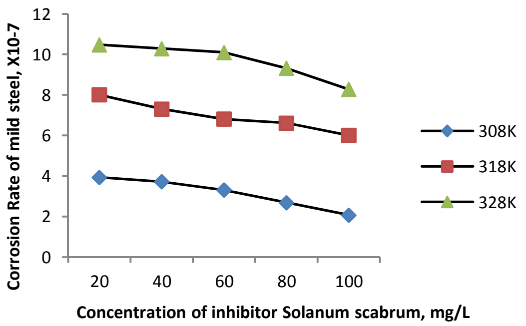


**Fig. 5:** Plot of corrosion rate of mild steel against various concentrations of *Solanumscabrum* at 308K, 318K and 328K (similar plot was obtained for *C. gynandra*)

**Polarization Measurements**

Figs. 6 and 7 show polarization curves for the inhibition characteristics of *C. gynandra* and *S. scabrum*. Anodic and cathodic polarization curves were recorded on mild steel electrode in 0.1M HCl at various concentrations of inhibitors and the blank. Both anodic and cathodic reactions of mild steel electrode corrosion were inhibited with an increase in concentrations of extracts. The results signify the mixed inhibition mode of the extracts. This results also suggest that the addition of the extracts reduces anodic and cathodic dissolution and retards the hydrogen evolution reaction. This agrees with the assertion made by Hammouti *et al.* (2013). Table 3 shows the calculated inhibition efficiency , $E_p$(%) using the equation (6) below:

$$E_\rho(\%) = \left(1 - \frac{i_{corr}}{i^o_{corr}}\right) x100 \qquad (6)$$

**Where:** $i^o_{corr}$ and $i_{corr}$ correspond to uninhabited and inhabited current densities, respectively.

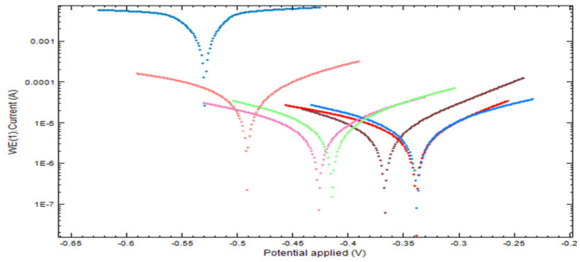


**Fig. 6:** Potentiodynamic polarization curves of mild steel electrode in 0.1M HCl without and with various concentrations of *C. gynandra.*

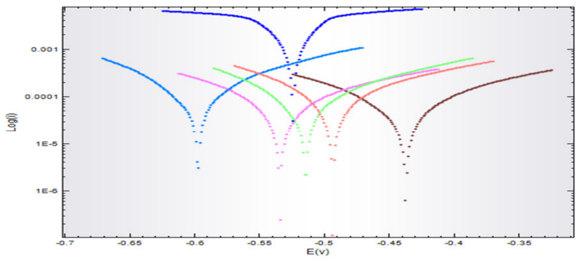


**Fig. 7:** Potentiodynamic polarization curves of mild steel electrode in 0.1M HCl without and with various concentrations of *S. scabrum.*

**Conclusions**

The inhibitors (*Solanumscabrum* and *Cloeme gynandra*) investigated retarded the acid corrosion of the mild steel; to some extent, being physically adsorbed on the metal surface. The inhibition efficiency (%) increased with increasing concentration but decreased with high temperature. A linear variation was observed from the plots which signify first order kinetics for the inhibition process. On the basis of Ea values, both extracts obeys the mechanism of physisorption. The values of Qads obtained at 308K and 318K were all negative indicating that the inhibitors are strongly adsorbed on steel surface and the adsorption was spontaneous.

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