Research Article

Cleome gynandra and *Solanum scabrum* Leaf Extracts as Corrosion Inhibitor of Mild Steel in Hydrochloric Acid Solutions

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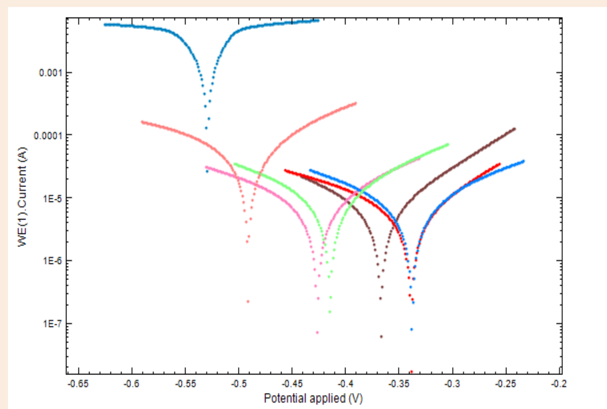
Abstract

The inhibition of corrosion of mild steel in hydrochloric acid solution by *Solanum scabrum* and *Cloeme gynandra* leaf extracts has been investigated via weight loss measurements and potentio-dynamic polarization studies at 308, 318 and 328K. The inhibition efficiencies (%) increase 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 is lower than 40.0kJmol^{-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 *Solanum scabrum* and *Cloeme gynandra* follows first order kinetics. Physical adsorption mechanism is proposed for the inhibitors.



Keywords: *Cleome gynandra*; *Solanum scabrum;* inhibitory effect; potentiodynamic polarization; physisorption

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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 has always been a global concern. Such inhibitors may cause reversible (temporary) or irreversible (permanent) damage to organ system like kidneys or livers, or to disturb a biochemical process or to disturb an enzyme system. The toxicity may manifest either during the synthesis of the compound or during its applications, [1].

Although, the most effective and efficient organic inhibitors are compounds that have multiple bonds, the biological toxicity of these products, especially organic phosphates, is documented specifically about their environmental harmful characteristics. 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, [2]. These toxic effects have led to the use of natural products as anticorrosion agents which are eco-friendly and harmless. In recent years, many alternative eco-friendly corrosion inhibitors have been studied and developed.

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*, [3]. 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, [4].

Among the several methods of corrosion control and prevention, the use of corrosion inhibitors is very popular. Corrosion inhibitors are substances which when added in small concentrations to corrosive media decrease or prevent the reaction of the metal with the media. 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 used contain heteroatom such as O, N, and S and 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 group, such as functional groups, electron density at the donor atom, π-orbital character, and the electronic structure of the molecule. Though many synthetic compounds showed good anticorrosive activity, most of them are highly toxic to both human beings and the environment, [5].

The use of chemical inhibitors has recently been limited because of the environmental threat they pose to the society. These inhibitors may cause reversible (temporary) or irreversible (permanent) damage to organs, namely, kidneys or liver, or disturbing biochemical processes and enzymic reactions at some site in the body. The toxicity may manifest either during the synthesis of the compound or during its applications. These known hazardous effects of most synthetic corrosion inhibitors are the motivation for the use of some natural plant products as corrosion inhibitors, [6].

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 [1, 7-11] 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 leaf of ***Cleome gynandra*** and ***Solanum scabrum*** as inhibitors are evaluated and studied in detail with a view to determining their effectiveness as corrosion inhibitors of mild steel in acidic medium.

Experimental

Sampling and Sample Preparation

Mild steel sheets of AA120 and purity 98% was obtained from Mubi metropolis. Each sheet (0.1cm in thickness) was mechanically press-cut into coupons of dimensions 3 x 4cm. 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 respectively were solvents used for the extraction process. All solvents for this study were of analytical grade.

Extraction Technique(s)

Sample leaf of *Cleome gynandra* and *Solanum scabrum* was collected from nearby bush in Mubi Metropolis, Adamawa State, Nigeria. The leaf samples was air dried in the Chemistry Laboratory, Adamawa State University, Mubi, and pulverized to fine powder, stored in air tight container with labels for the analysis. 50g of each sample of the leaf was used for the extraction with Soxhlet extractor for three (3) hours using Methanol, Ethanol, and distilled water respectively. Methanol gave the best yield and was subsequently used for the extraction. After extraction, the samples were allowed to cool then filtered. The filtrate was used to prepare the inhibitor concentrations between 20, 40, 60, 80, and 100mg/L in 0.1MHCl.

Similarly, a concentration range 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 [11] and corroborated by oguzie *et al* [12], was adopted for the weight loss measurement.

Corrosion protection efficiency measurements

Corrosion rates was described by weight loss per density per unit area per unit time, for mild steel in HCl and the different concentrations of the extracts for the period of immersion using the formula, [11].

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

where W_i and W_o are weight losses for mild steel in the presence and absence, respectively of the inhibitor in HCl solution.

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

$$\%I_E = \frac{W_0 - W_i}{W_0} \times 100 \quad (2)$$

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

Electrochemical Measurement

Electrochemical experiment was carried out using a conventional electrolytic cell with three-electrode arrangement; saturated potassium chloride reference electrode (KClE), platinum mesh as counter electrode (CE), and the mild steel bar as the working electrode (WE). Prior to each experiment, the specimens were polished with a series of emery papers of different grit sizes up to 1000 grit size, polished with Al_2O_3 (0.5mm particle size), washed several times with bi-distilled water then with acetone and dried using a stream of air. The electrode potential was allowed to stabilize 30 minute before starting the measurements. The aggressive environment used was 0.1M HCl solution with different concentrations of the extracts. All experiments were conducted at 308K. The exposed electrode area to the corrosive solution was 0.28cm^2.

Potentiodymic polarization curves were obtained by changing the electrode potential automatically from (-6000 to - 400mV) at open circuit potential. Measurement was performed with Autolab Instrument (model 302) using a computer interface fitted with Demo version software.

Results and Discussion

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

Inhibitor concentration (mg/L)	**Inhibition efficiency (%)**			**Corrosion Rate (x10^{-7})**			**Surface coverage (θ)**		
	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

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 are increased (figure 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.

The mean weight loss of mild steel decreases with increasing concentrations of the additives (the two extract) and as well as increase in temperature as seen in figures 2 and 3. 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 [13-16] 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 metal/ alloy. Surface coverage increases with increase in inhibitor concentration and decreases with increase in temperature, as shown in Table1.

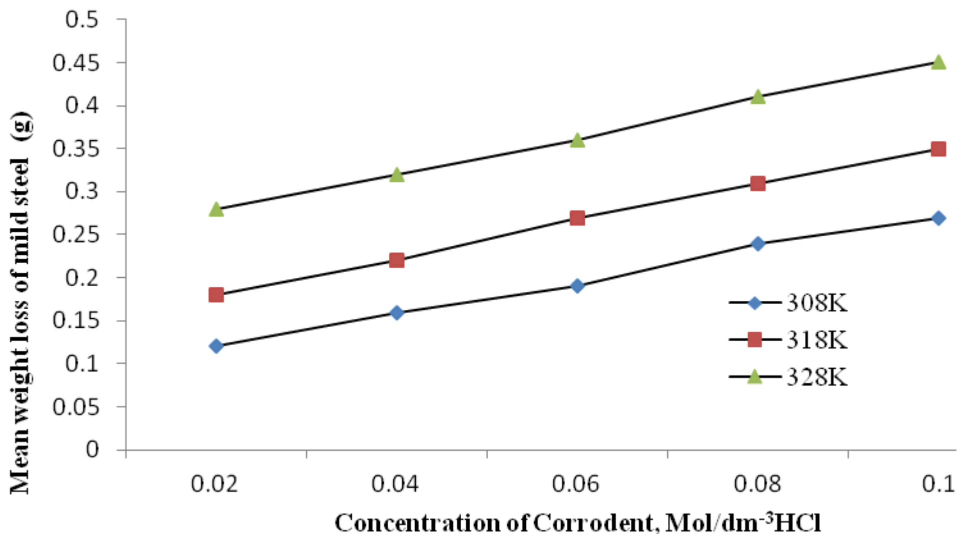

Figure 1 Plot of mean weight loss of mild steel against various concentration of corrodent, HCl at 308, 318 and 328K

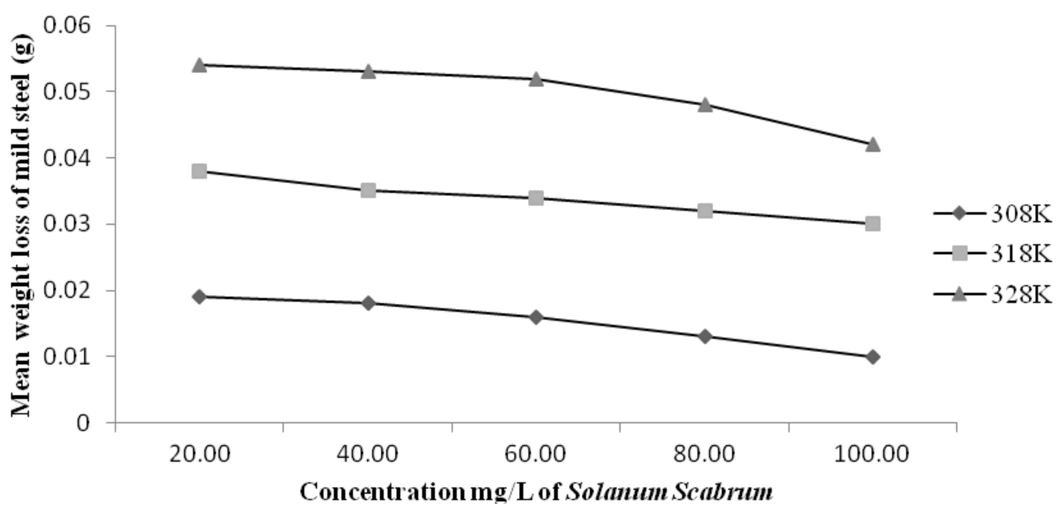

Figure 2 Plot of mean weight loss of mild steel against various concentration of inhibitor *Solanum scabrum* at 308, 318 and 328K

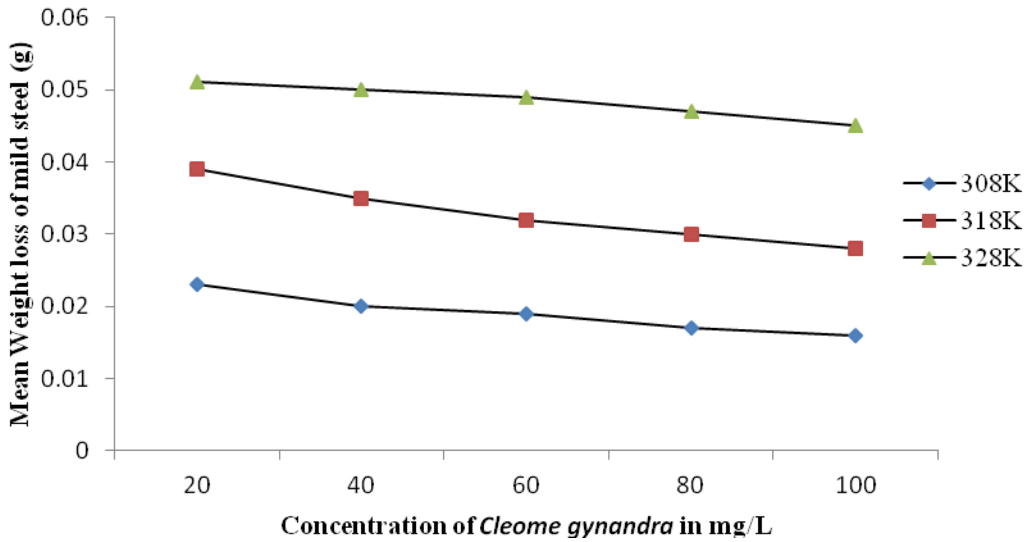

Figure 3 Plot of mean weight loss of mild steel against various concentration of inhibitor *Cleome gynandra* at 308, 318 and 328K.

Effect of Inhibitor Concentration on Inhibition Efficiency

Inhibition efficiency was determined using equation (2) and depicted in Table-1. Figures 4 and 5, show plots of inhibition efficiency (%) versus various concentrations of *Solanum scabrum* and *Cleome gynandra* respectively at 308, 318 and 328K. It can be seen that inhibition efficiency (%) increase with increasing concentration of the inhibitors but decrease 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 [17].

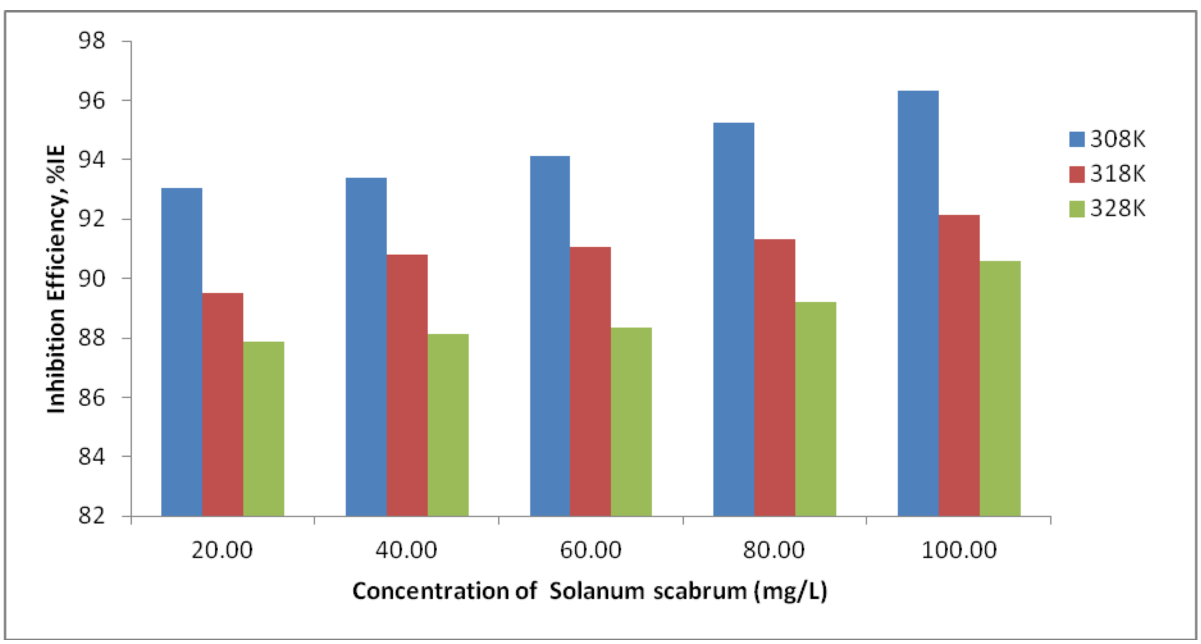

Figure 4 Plot of Percentage Inhibition Efficiency (%I_E) of Mild steel against various Concentrations of Inhibitor (*Solanum scabrum)* at 308, 318 and 328K.

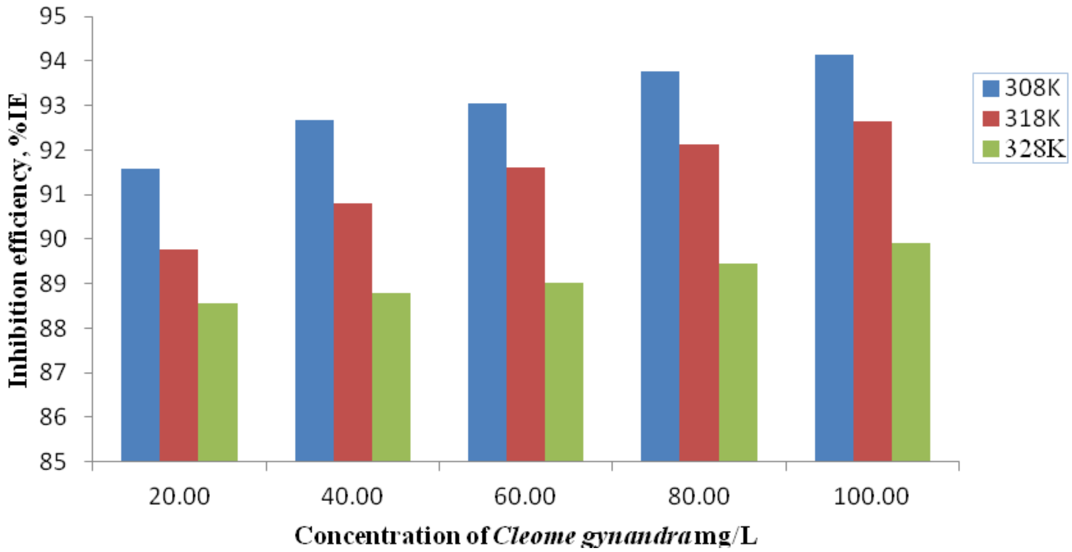

Figure 5 Plot of Percentage Inhibition Efficiency (%I_E) of Mild steel against various Concentrations of Inhibitor (*Cleome gynandra)* at 308, 318 and 328K

Table 2 Kinetic and Thermodynamic Parameters for mild steel corrosion in 0.1M HCl with inhibitors (*Solanum scabrum and Cloeme gynandra*) at 308, 318, and 328K

Inhibitor concentration (mg/L)	**Mean weight loss 308K**	**318K**	**328K**	**Activation energy, Ea(kJmol^{-1}) 308-318K**	**Heat of adsorption Qads(kJmol^{-1}) 308-318K**
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**

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 figures (6 and 7). 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 ρ_1 and ρ_2 are corrosion rates at 308K and 318K respectively, [18].
The average value of Ea 6.57 and 4.18 for the *Solanum scabrum* and *Cloeme gynandra* respectively is lower than 40.0kJmol^{-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 θ_1 and θ_2 are surface coverage at 308K and 318K respectively for T_1 and T_2 [11].

All the values of Qads with mean values of -12.22kJmol^{-1} and -4.57 kJmol^{-1} for *S. scabrum* and *C. gynandra* recorded in Table-2 indicates that both inhibition efficiency and heat of adsorption decrease with increase in temperature. This agrees with reports of [16, 18].

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.

Adsorption Analysis of the Results

It is clear from table-1 and figures (4 and 5) 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, [19]. The high surface coverage observed at high inhibitor concentrations is due to very strong interactions between the adsorbed species. The surface coverage values implies 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 [13, 14, 16 -19].

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, [20].

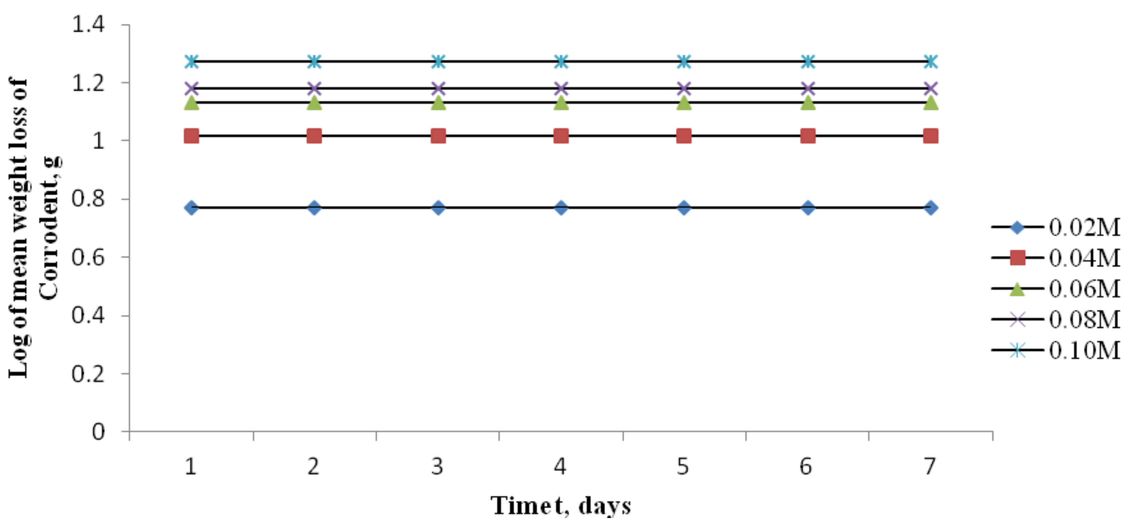

Figure 6 Plot of Log of mean weight loss of mild steel against various concentration of corrodent for 7 days at 318K.

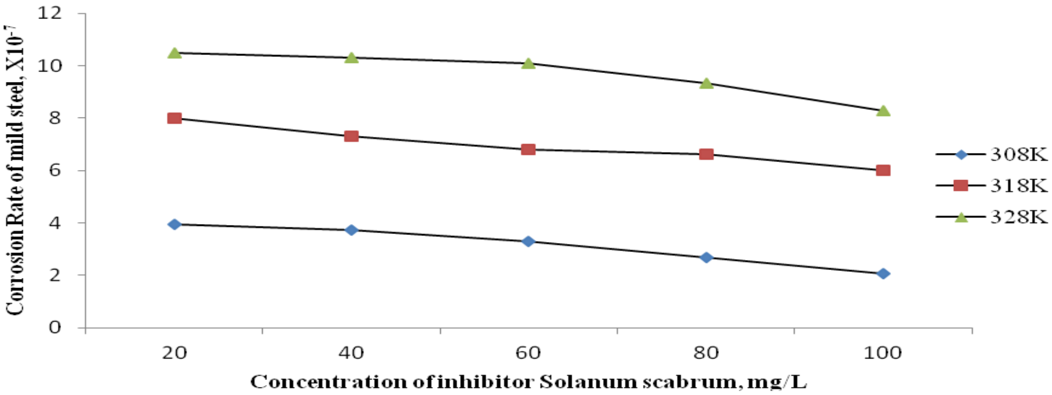

Figure 7 Plot of Corrosion Rate of mild steel against various Concentrations of *Solanum scabrum* at 308K, 318K and 328K

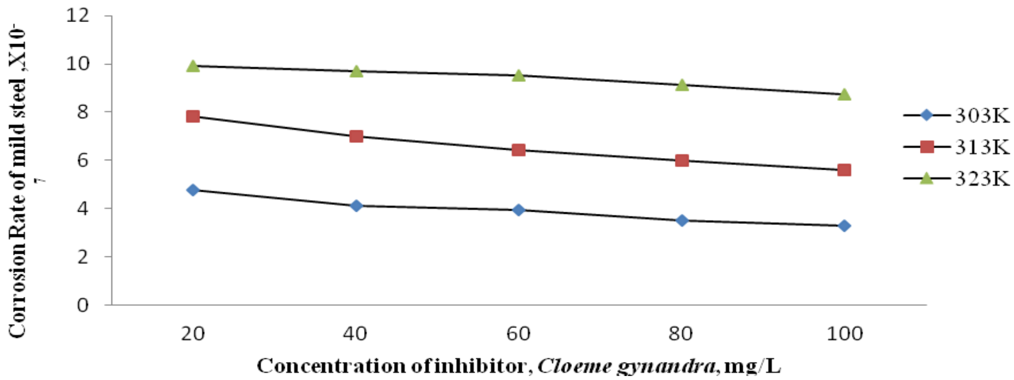

Figure 8 Plot of Corrosion Rate of mild steel against various Concentrations of *C. gynandra* at 308K, 318K and 328K

Corrosion rate of the mild steel decreases with increasing concentration of the extracts (figure 7 and 8), and increases with temperature increasing. The inhibition efficiency also increases with increasing concentration of the extracts (figures 4 and 5), 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 best efficiency was obtained at 308K as a result of a decrease in the adsorption of extract molecules.

The corrosion process kinetics acquire the character of a diffusion process, in which at higher temperature, 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 high activation energy available for adsorption, and the higher rate of diffusion of inhibitor molecules. This assertion is supported by several authors [12-16].

Polarization Measurements

Figures 9 and 10 are show polarization curves for the inhibition charteristics of *C.gynandra* and *S. scabrum***.** Anodic and cathodic polarization curves were recorded on mild steel electrode in 0.1MHCl at various concentrations in the presence and absence of the extracts. 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 result also suggests that the addition of the extracts reduces anodic and cathodic dissolution and retards the hydrogen evolution reaction. This agrees with the assertion made earlier by Hammouti *et al* [1]. Table 3 shows the calculated inhibition efficiency, E_p (%) using the equation (6) below:

$$E_p(\%) = \left(1 - \frac{i_{corr}}{i^o_{corr}}\right) X\ 100 \qquad (6)$$

where i^o_{corr} and i_{corr} correspond to uninhabited and inhabited current densities, respectively.

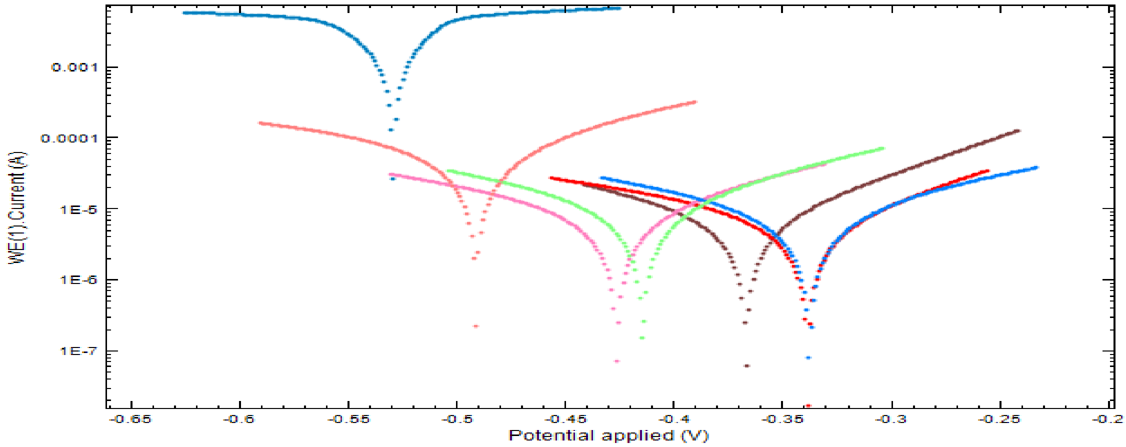

Figure 9 Potentiodynamic Polarization curves of Mild steel Electrode in 0.1M HCl without and with various Concentrations of *C. gynandra*

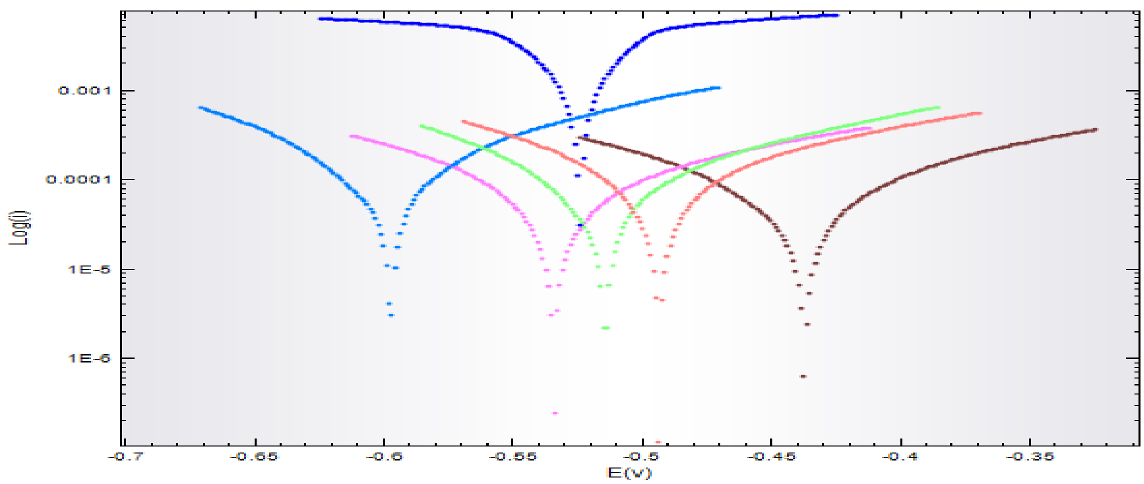

Figure 10 Potentiodynamic Polarization curves of Mild steel Electrode in 0.1M HCl without and with various Concentrations of *S. scabrum*

Conclusions

The study shows that the inhibitors (*Solanum scabrum* and *Cloeme gynandra*) investigated retarded the acid corrosion of the mild steel to some extent being physically adsorbed on the metal surface with the inhibition efficiency (%) increase with increasing concentration but decrease with 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, as seen from the experimental observation. The values of Q_{ads} obtained at 308K and 318K are all negative indicating that the inhibitors are strongly adsorbed on steel surface and the adsorption is spontaneous.

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