Corrosion Inhibition Studies on the Influence of *Colocasia esculenta* Leaves Extract on Mild Steel in 1.0 M HCl.

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Abstract

The ability of the ethanol extract of *Colocasia esculenta* leaves to inhibit mild steel corrosion in 1.0 M solution of HCl was examined using linear polarization along gravimetric methods at 303-333 K temperature range. Linear polarization experiments revealed *Colocasia esculenta* leaves extracts to retard mild steel dissolution in 1.0 M HCl by influencing both the anodic and cathodic half reactions on the steel surface. Inhibition efficiency of the leaves extract was a function of the concentration. Gravimetric data gave good fit with the Langmuir adsorption isotherm model while thermodynamic parameters derived from temperature evaluations showed the corrosion inhibition process to be spontaneous, exothermic and physisorptive.

1. Introduction

In a bid to getting rid of undesirable scales and rust when cleaning heat exchangers and boilers, acid solutions are usually employed. They are also used in acidizing oil wells and in oil recovery [1,2]. Corrosion of mild steel have been observed to take place after any of these processes leading to waste of materials and resources. The utilization of substances known as corrosion inhibitors is one of the ways of checkmating the dissolution of steel during any of these processes.

Corrosion inhibitors lower the rate of dissolution of metals/alloys when they are added in little amounts to corrosive environments. Corrosion inhibitors work by adsorbing on the metal surface hence preventing the aggressive ions in the electrolyte from attacking the metal [3].

Many man-made chemical substances have been researched upon as suitable inhibitors against the dissolution of steel [4,5]. However, the application of these chemical substances as corrosion inhibitors is becoming unpopular because of their high cost in addition to their toxic effects on humans leading to strict environmental regulations concerning their use. Hence, it behoves scientists to produce a group of efficient corrosion inhibitors that are not expensive and environmentally friendly as replacements to the toxic ones.

Plant extracts have proven to be promising green corrosion inhibitors for steel [3-5]. Plant extracts contain phytochemicals that bear heteroatoms such as oxygen, nitrogen, phosphorus, sulphur, and/or multiple bonds which function as centers for adsorption to the steel surface [3-5]. *Colocasia esculenta* leaves popularly known as cocoyam leaves contain alkaloids, tannins, saponins, flavonoids, phenols, terpenoids, quinines, coumarins, β-sitosterol and stigmasterol [6-7]. Adsorption of these phytochemicals especially β- sitosterol and stigmasterol on the steel surface can mitigate its corrosion in aqueous environments.

This paper reports on the application of the ethanolic extract of the leaves of *Colocasia esculenta* (CE) as a potential inhibitor against mild steel corrosion in 1.0 M HCl using gravimetric and linear polarization experiments.

2. Materials and Methods

2.1 Materials preparation

Experiments were conducted using mild steel (MS) coupons with composition (wt %): Fe-99.14; C-0.15; Mn-0.60; P- 0.04; & Si-0.03. Stock solution of *Colocasia esculenta* leaves extract was prepared as reported in a previous studies [8] by dissolving 500 g of powdered leaf parts of CE that have already been air-dried, in 95 % ethanol at room temperature for 72 hrs. The ethanol leaves extract was concentrated under vacuum at 40 ^{o}C until the solvent was completely removed. The dried alcoholic leave extract was used for corrosion inhibition studies by preparing inhibitor test solutions of 0.2-1.0 g/L concentration range. This was obtained by transferring 0.05 g - 0. 25 g of the extract into 250 mL of 1.0 M HCl solution.

2.2 Linear polarization

Linear polarization measurements were conducted as described elsewhere [9]. A three-electrode flask having a saturated calomel electrode (SCE) as reference electrode, platinum (Pt) as an auxiliary electrode and mild steel working electrode, was employed for the experiments. In quantifying the corrosion current densities (I_{corr}), the linear tafel segments of the anodic and cathodic curves were extrapolated to corrosion potential. Inhibition efficiency was calculated using equation 1 [9, 10]:

$$\%IE = \frac{I_{corr(blnk)} - I_{corr(inh)}}{I_{corr(blnk)}} \times 100 \qquad\qquad 1$$

where %IE is the inhibition efficiency of the extract of CE, $I_{corr(inh)}$ is the corrosion current density of mild steel with CE and $I_{corr(blnk)}$ is the corrosion current density of mild steel without CE.

2.3 Gravimetric measurements

Gravimetric experiments were done using methods reported in previous studies [8, 11-12]. Already cleaned and weighed coupons were suspended in the test solutions in glass jars [10]. Weight loss was calculated as the difference between the initial and final weights of the coupons at a fixed time interval. The effect of immersion time on the corrosion rate of the mild steel with and without CE extract was studied by conducting the experiment for 24 hours, 48 hours, 72 hours, 96 hours, 120 hours, 144 hours and 168 hours [13]. In like manner, temperature studies were conducted for 3 hours with the water bath maintained at 303 K, 313 K, 323 K, and 333 K respectively. Equations 2 and 3 were used to quantify the inhibition efficiency (% IE) and surface coverage (θ) of CE extract [8, 11]:

$$IE_{exp} = \left(1 - \frac{w_1}{w_2}\right)x100 \qquad\qquad 2$$

$$\theta = 1 - \frac{w_1}{w_2} \qquad\qquad 3$$

where w_1 and w_2 are the weight losses (g) for mild steel in the presence and absence of CE and θ is the degree of surface coverage of CE.

2.4. Optical microscopy

Optical micrographs of mild steel specimens in 1.0 M HCl with and without the leaves extract of CE were taken using Metallurgical microscope (TSVIEW Digital Metallurgical Microscope) model TUCSEN 0923502.

3. Results and Discussion

3.1. Linear polarisation

The values of change in current as a result of applied potential obtained from electrochemical measurements are used in this technique. A plot of the linear polarisation parameters measured for mild steel as the working electrode immersed in the test solutions is shown in Figure 1. The plot revealed that the introduction of CE to the free acid solution influenced both the anodic and cathodic half reactions by shifting both the anodic and cathodic curves of the Tafel plot to lesser values of I_{corr} (Figure 1). Thus showing CE behavior as a mixed inhibitor. Values of E_{corr} were however more negative at higher inhibitor concentration indicative of the mixed-type mechanism of the inhibitor with predominant cathodic effect at higher CE concentrations [14, 15].

The various electrochemical parameters such as E_{corr}, I_{corr} and %IE obtained by extrapolation of the tafel lines are presented on Table 1. The values given in Table 1 reveal that I_{corr} decreased with higher concentrations of the extract. This shows the inhibitive action of CE extract on mild steel in 1.0 M HCl solution. This observation is in agreement with studies by other researchers [14-16]
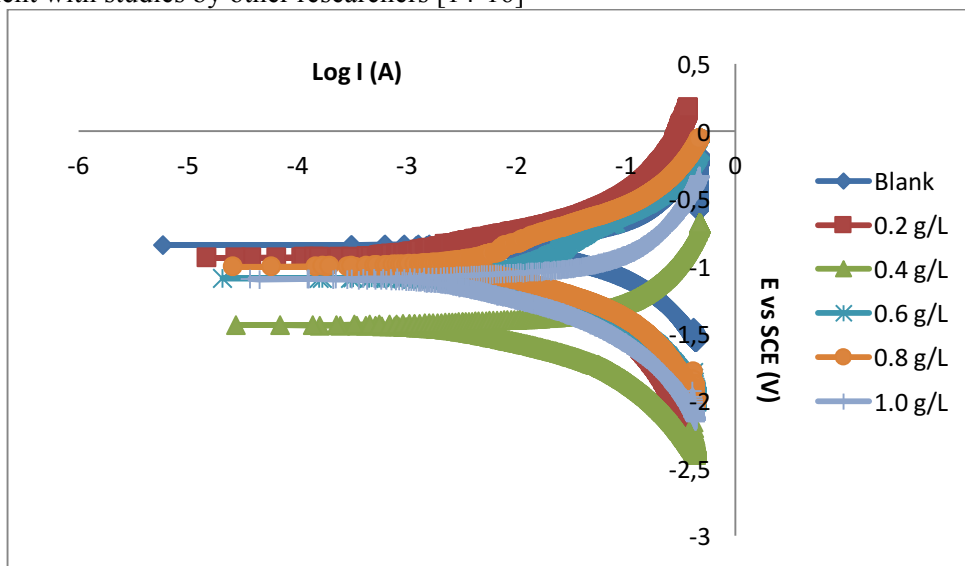
Figure 1: Linear polarisation plot for the corrosion of mild steel in 1.0 M HCl with and without *Colocasia esculenta*

Table 1: Linear polarisation parameters for the corrosion of MS in HCl with various concentrations of CE extracts

Conc (g/L)	E_{corr} (mV)	I_{corr} (µA/cm^2)	% I E
Blank	-1396.90	262.50	-
0.2	-940.80	23.17	91.08
0.4	-1598.40	42.36	83.84
0.6	-1104.80	8.36	96.81
0.8	-990.11	5.77	97.80
1.0	-1107.10	4.12	98.43

3.2. Gravimetric measurements
*3.2.1. Weight loss of mild steel and inhibition efficiencies of CE extract*
 Figure 2 shows the variation of the loss in weight of mild steel over time with and without different concentrations of CE. The plots reveal that the rates of corrosion of mild steel in the acid medium generally increased with time leading to greater loss in weights, with the blank giving the highest value of corrosion rate.
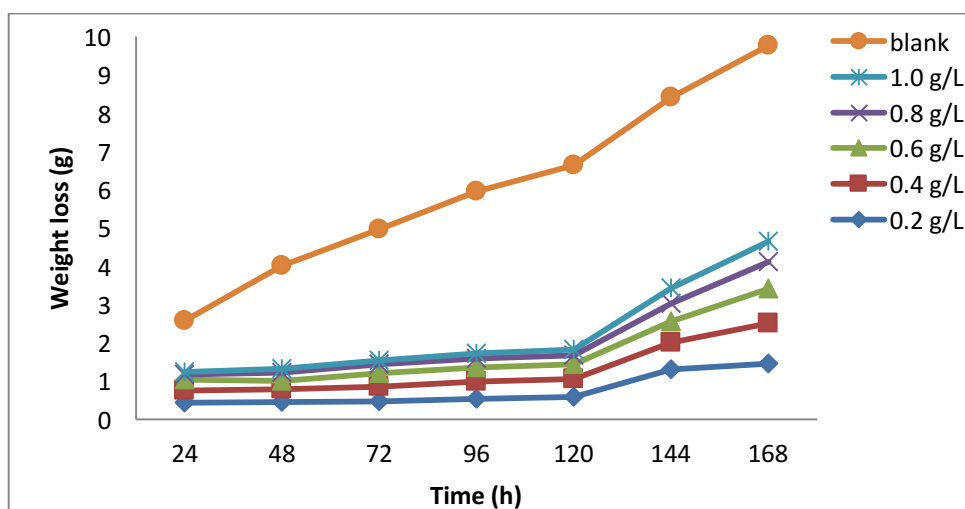
Figure 2: Weight loss (g) vs immersion time (h) for the corrosion of mild steel in HCl with and without CE extracts at 303 K

This observation can be attributable to the anodic dissolution of iron to produce hydrogen gas along with the high solubility of the metal oxides formed as corrosion products [14,17]. However, the release of hydrogen gas was considerably retarded on addition of CE extracts leading to a decrease in the rate of the anodic dissolution of iron and consequently a relative decrease in weight loss values of the steel in the presence of CE as reflected in Figure 2. Figure 3 illustrates the trend of % IE with immersion time for different concentrations of CE extract. The plots showed that CE extract retarded the dissolution of mild steel at the concentrations investigated with higher % IE values obtained at higher concentrations of CE. This observation may be due to the adsorption of CE constituents on the surface of the steel thereby preventing further dissolution of iron atoms from the steel surface. The decrease in % IE of CE after 120 h implies the desorption of the plant extract from the steel surface on prolonged exposure of the steel surface to the aggressive chloride ions in the acid solution [8, 11].
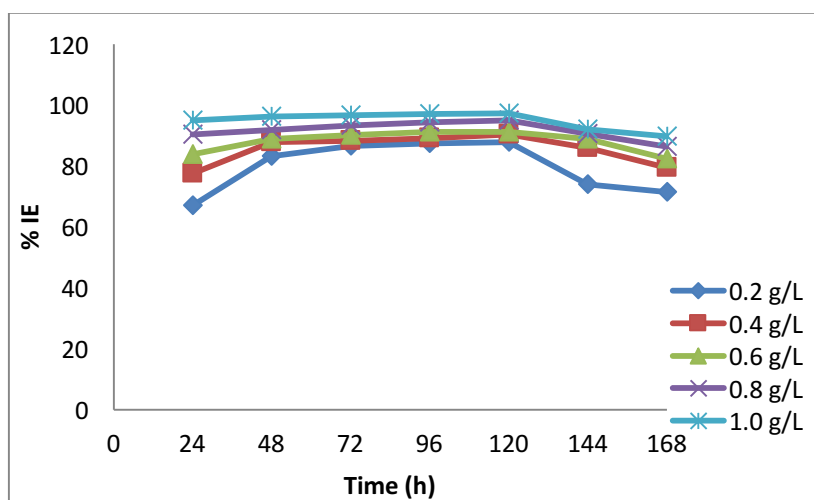
Figure 3: Inhibition efficiencies vs immersion time (h) for the corrosion of mild steel in 1.0 M HCl with and without CE extracts at 303 K

*3.2.2. Temperature and thermodynamics consideration*
The mean kinetic energy of the reactant species in any system is thermodynamically dependent on the temperature. Figure 4 illustrates the effect of temperature on the weight loss of mild steel in uninhibited and inhibited acid solutions.
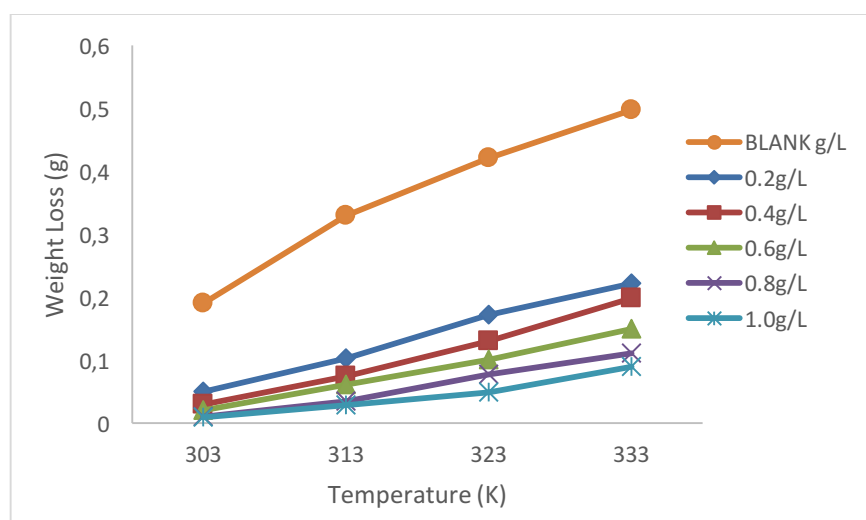
Figure 4: Weight loss (g) vs temperature (K) for the corrosion of mild steel in HCl with and without CE leaves extracts.

Figure 4 signifies the general increase in corrosion rates of the steel coupons at higher temperatures. This was observed in both the uninhibited HCl solution and on addition of CE extracts. Reacting species usually acquire more kinetic energy at higher temperatures, this explains the higher corrosion rates of the steel coupons in the test solutions as the temperature increased. Again, the presence of CE extract in the inhibited test solutions is seen to decrease the rate of corrosion of the mild steel coupons. The relationship between % IE of CE extract and temperature is shown in Figure 5. Figure 5 shows a decrease in % IE of CE extract with temperature at all

the concentration range investigated. This behavior has been reported by other researchers to be due to the agitation of the adsorbed inhibitor and its consequent desorption from the surface of the mild steel at higher temperatures, signifying physisorption [8,11]. From literature, the mechanism of physisorption has been linked with lower % IE values at higher temperatures [8-11, 14].
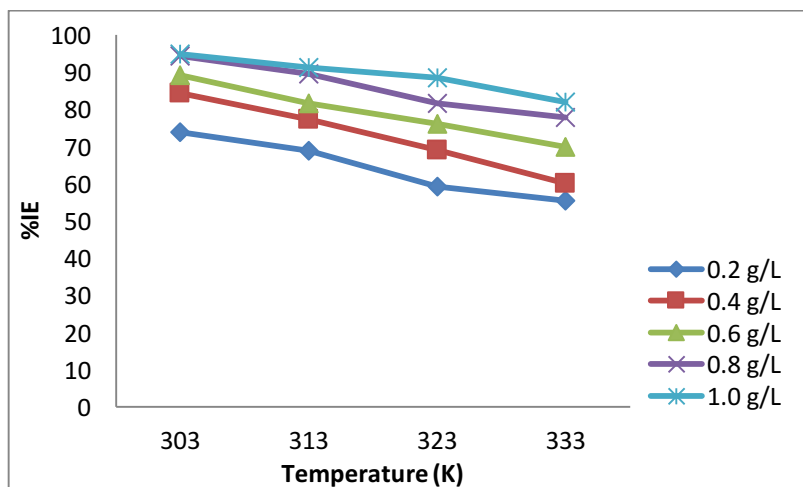
Figure 5: Inhibition efficiency vs temperature (K) for the corrosion of mild steel in HCl with and without CE extracts.

The effect of temperature on the corrosion of mild steel in the presence of CE can be understood by applying equations 4 and 5 below [8, 18, 19],

$$CR = A exp^{-E_a/RT} \qquad\qquad 4$$

$$log CR = log A - \frac{E_a}{2.303 RT} \qquad\qquad 5$$

where CR is the rate of corrosion of the mild steel, A is the Arrhenius constant, E_a is the activation energy, R is the universal gas constant and T is the absolute temperature of the system in Kelvin *(K)*.

A plot of *Log CR* versus $1/T$ represented on Figure 6 is linear with $\left(-\frac{E_a}{2.303 R}\right)$ as the slope and *Log A* as the intercept. The apparent activation energy (E_a) values were calculated from equation 5.
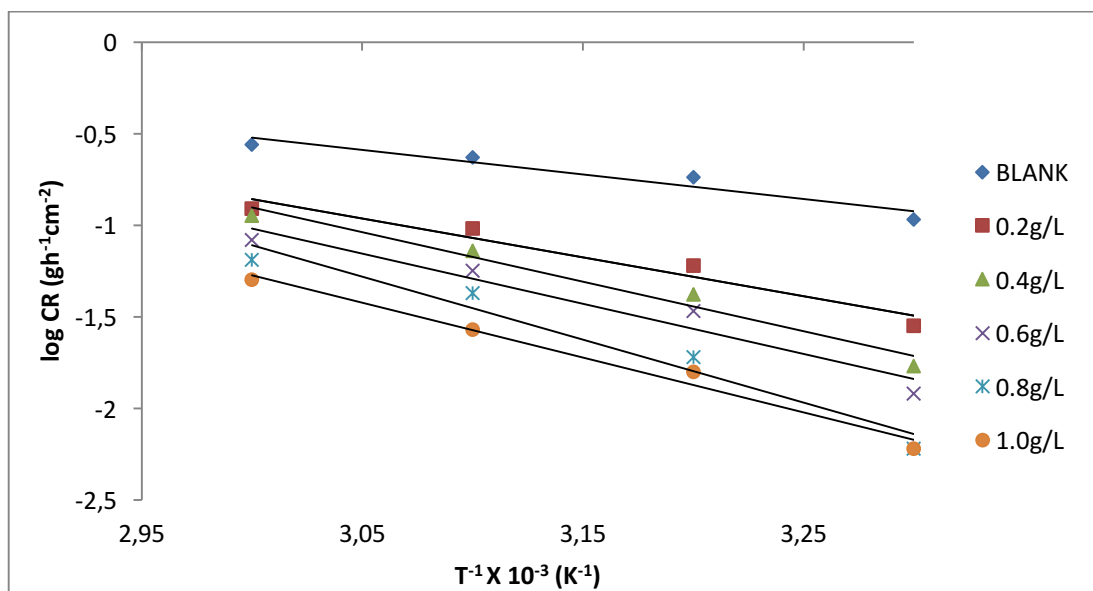
Figure 6: Arrhenius plot.

The transition state equation is given as equation 6 below [8, 18-20];

$$Log \, CR/T = \left[Log \left(R/nh \right) + \Delta S^*/2.303 \, R \right] - \Delta H^*/2.303 \, RT \qquad\qquad 6$$

where CR is the corrosion rate at temperature T, h is the Planck's constant $(6.6261 \times 10^{-34} Js)$, n is Avogadro's constant 6.0225×10^{23} and R is the molar gas constant. A plot of $Log\,{CR}/{T}$ versus ${1}/{T}$ is a straight line graph with slope $(-{\Delta H^*}/{2.303\,R})$ and an intercept $\left[Log\left({R}/{nh}\right) + {\Delta S^*}/{2.303\,R}\right]$ from which the values of ΔH^* and ΔS^* were calculated (Figure 7).

The values of the activation parameters presented on Table 2 show that the value of E_a in the free acid solution was less than those for the inhibited solutions. Also, Ea < 80 kJ/mol have been reported to reflect physical adsorption mechanism [20]. Physisorptive kind of adsorption is a phenomenon whereby an increase in temperature leads to the desorption of the adsorbed inhibitor from the steel surface thereby reducing the integrity of the steel by increasing the rate of corrosion of the steel [8, 14, 20].The values of ΔH^* were all found to be negative revealing the exothermic nature of the corrosion and corrosion inhibition process. The negative values of ΔS^* on Table 2 signifies the associative mechanism of the corrosion process whereby a decrease in disorder occurs in transiting from the reactants to the activated complex [18-19].
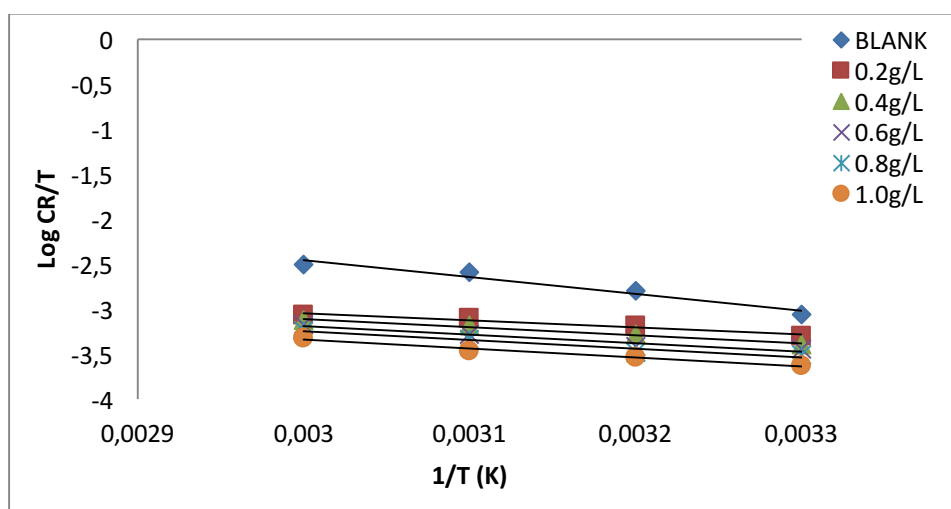

Figure 7: Transition state plot.

Table 2: Thermodynamic activation parameters.

Concentration (g/L)	E_a (kJ/mol)	ΔH^* (kJ/mol)	ΔS (kJ/mol)
Blank	10.47	-24.12	-189.25
0.2	17.27	-39.79	-142.67
0.4	21.56	-49.67	-114.02
0.6	21.82	-50.26	-114.44
0.8	23.97	-55.20	-104.45
1.0	27.31	-62.90	-78.46

3.2.3 Adsorption considerations

The ability of organic compounds to adsorb on to the surface of a metal/alloy to form a protective film has been reported to be responsible for their inhibition of corrosion processes [21].

In elucidating the adsorption mechanism of CE on the steel surface, surface coverage (Ө) values from weight loss data were adapted into different adsorption isotherms. Langmuir isotherm (Figure 8) best explained the adsorption pattern of CE on the steel surface. The plot has a slope that is linear with a regression coefficient value, $R^2 \geq 0.9$ [8, 14, 20]. Equation 7 is the linearized form of Langmuir [14],

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \qquad\qquad 7$$

where C is the concentration of CE in the entire electrolyte, K_{ads} is the adsorption equilibrium constant, Ө is the degree of surface coverage of CE. Table 3 presents the adsorption parameters evaluated from the plots.

It's evident that the natural extract contains infinite components at various contents; the higher protection of mild steel in HCl solution is due by a competitive action of several molecules and ions [22-24]. Then, the

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inhibitory effect is conducted by the intermolecular synergistic effect of several molecules / ions of extract [23-25].

3.3 Optical microscopy

Plate 1 is the micrograph of the mild steel (MS) coupon after immersion in 1.0 M HCl solution while Plate 2 is the micrograph of MS surface after immersion in the inhibited test solution. The surface of the steel coupon in Plate 1 appears to be more damaged and looked rough due to the presence of some pits and cracks on it. Plate 2 shows the presence of some protective films on the surface of the steel coupon. This confirms that CE inhibited the corrosion of the steel coupons in 1.0 M solution of HCl.
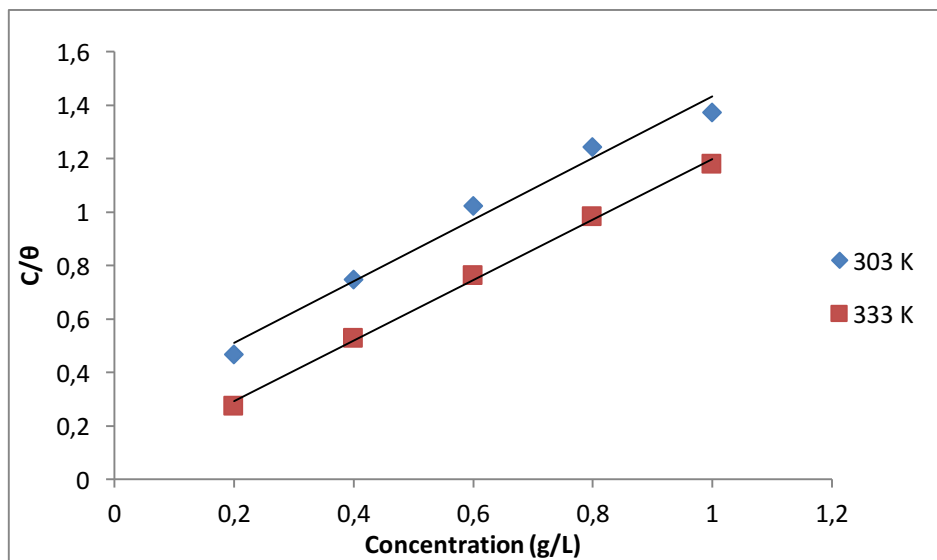

Figure 8: Langmuir isotherm.

Table 3: Langmuir adsorption parameters.

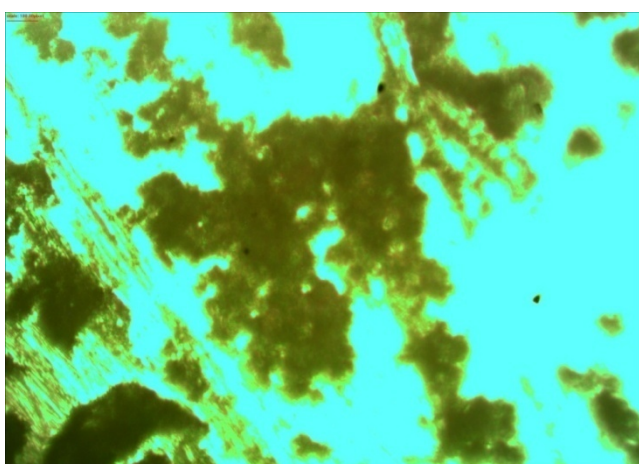| Temperature (K)	Intercept	Slope	K_{ads} (M^{-1})	R^2
303	0.280	1.152	3.571	0.981
333	0.065	1.132	15.385	0.997

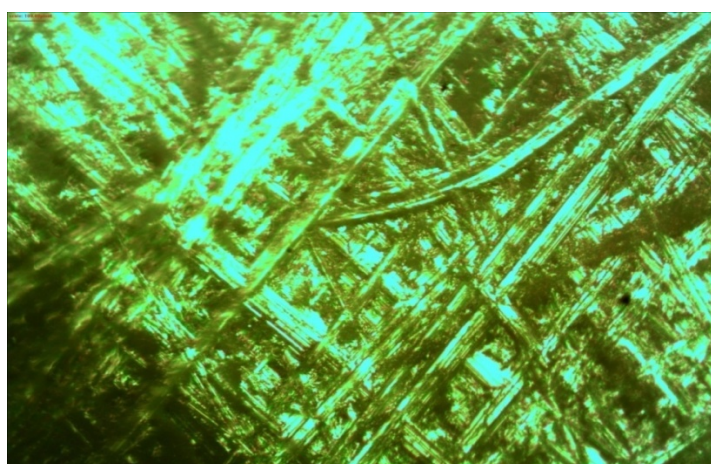Plate 1: Mild steel in 1.0 M HCl   Plate 2: Mild steel in 1.0 M HCl with 1.0 g/L CE.

Conclusion

The findings of this study show that CE leaves extracts inhibited mild steel corrosion in the acid medium and that % IE increased with increase in the concentration of the leaves extract. Linear polarisation measurements

revealed CE extracts behaved as a mixed-type inhibitor. Adsorption of CE extract on the steel surface was exothermic, spontaneous and physisorptive. Langmuir isotherm described the adsorption of CE extracts on the steel surface.

Competing Interests - Authors have declared that no competing interests exist.

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