Inhibition of Pipeline Steel Corrosion in 0.5 M H₂SO₄ Using Cotyledon of *Chrysophyllum Albidum*

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ABSTRACT: The corrosion inhibition characteristics of *Chrysophyllum albidum* cotyledon extract was studied as a green and sustainable corrosion inhibitors for pipeline steel in acidic environment at temperatures, 303, 313 and 323K using gravimetric technique. The results obtained showed that the inhibition efficiency increased with increase in extract concentration but decrease with increase in temperature. The extract attained an inhibition efficiency of 94 % with 5 g/L at 303 K and 52.2 % with 1 g/L at 333K. Also increase in concentration of the extract lead to increase in activation energy depicting an exothermic process. Fourier transform infrared spectroscopy (FT-IR) studies showed the mode of inhibition as adsorption of phytochemicals from the extract on pipeline steel surface. Langmuir adsorption isotherm best fitted into the adsorption process which is spontaneous and physical.

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Corrosion of metallic structures has persistently been a source of down turn to the economy. However, the use of metallic materials for construction presently seems inevitable due to its physical properties and cost. Importantly, iron and its alloy, used for construction poses a great challenge for corrosion scientists and manufacturing industries. More so as a result of regular contact with mineral acids such as HCl, H₂SO₄, CH₃COOH, etc. The exposed part of a metallic structure is more affected by external corrosion due to acidic effect of most industrial environment (Ejekeme et al., 2015). While the inner metallic surfaces are affected by the corrosive industrial fluids they convey (Ngobiri et al., 2013).

However, several methods of corrosion mitigation have been employed. The use of inhibitor to mitigate the metallic degradation process is a veritable one because of the ease of application in some difficult processes and areas. (Akalezi et al., 2015, Rajaei et al., 2013, Loto and Mohammed, 2000).

The present work evaluates the corrosion inhibiting properties of the Cotyledon of *Chrysophyllum albidum* (CA) extract by gravimetric technique. The fruit is seasonal from December to April and has immense economic potential, especially following the report that jams obtained from the fruit-pulp could compete with raspberry jams and jellies. Also the oil from the seed has been used for diverse purposes. In Nigeria, *Chrysophyllum albidum* is known as ‘‘agbalumo’’ in South Western and ‘‘Udara’’ in South Eastern, Nigeria. It rich sources of natural antioxidants have been established to promote health by acting against oxidative stress related diseases such as diabetes, cancer and coronary heart diseases (Abiodun and Oladapo 2011, Akbariet al., 2012, Akaleziet al.2015). The GC-Mass spectra of the crude extract of the cotyledon was used to identify the various phytochemical components. The *Chrysophyllum albidum* cotyledon was used because of its unique phytochemical constituents which have bonding sites to metallic surface. Importantly the cotyledon is usually discarded arbitrarily as waste constituting environmental nuisance. The success of this project is anticipated to not only to aid in waste management but convert waste to wealth.

MATERIALS AND METHODS

Materials: The Pipeline steel was procured from System Metals Industries Limited, Port-Harcourt, Nigeria. The pipeline coupons were cut to a dimension of 2cm by 3cm used for weight loss measurement studies. All other reagents were of analytical grade.

Plant extraction: Chrysophyllum albidum was washed, the cotyledon removed and sun dried for seven days. It was ground and sieved before extraction. The extract was obtained using the procedure already reported (Ebenso et al., 2002, Edidong et al., 2018, *Corresponding Author Email: nnaemeka.ngobiri@uniport.edu.ng*
Weight Loss Measurements: The pipeline coupons were cut to a dimension of 2cm by 3cm for weight loss measurement studies. The serial dilutions of the 0.5 M H₂SO₄ and extract concentrations were 1g/dm³, 2g/dm³, 3g/dm³, 4g/dm³, 5g/dm³ and blank/control with no additive. The experiment was repeated at higher temperatures in a J.P. SELECTA 6001197 thermo stated water bath at 313 K and 323 K respectively. The tests were conducted in triplicate and the mean value of the weight loss obtained at each temperature was used to determine the following parameters.

\[ W = \frac{w_i - w_f}{g} \quad (1) \]

Where, \( W \) = weight loss of pipeline steel coupon, \( w_i \) = Initial weight of the pipeline steel coupon, \( w_f \) = Final weight loss of pipeline steel coupon, and all unit in grams.

The surface coverage (\( \theta \)) CA-C in 0.5M H₂SO₄ at different concentrations was obtained by using the equation below.

\[ \theta = 1 - \frac{w_f}{w_o} \quad (2) \]

Where; \( w_o \) = corrosion rates in the absence of inhibitor; \( w_f \) = corrosion rates in the presence of inhibitor.

The inhibition efficiencies were calculated using the formula

\[ \% IE = 1 - \frac{w_i}{w_o} \times 100 \quad (3) \]

Where \( w_o \) and \( w_i \) is weight loss in grams of metal coupon in the presence and absence of various concentration of the extract respectively.

The total surface area of pipeline steel coupon immersed in the solution was calculated as follows:

\[ A = 2K + M + 2r [t - 2r]^2 \quad (4) \]

Where \( A \) = Total surface area of the coupon immersed in solution, \( K \) = length of coupon, \( M \) = Width of coupon, \( T \) = Thickness of coupon, \( r \) = Radius of the hole drilled on coupon.

The corrosion rate, half-life and rate constant were obtained as showed below.

\[ CR \text{ (mpy)} = \frac{97.6 \cdot \Delta W}{DA \cdot T} \quad (5) \]

Where; \( CR \) = Corrosion rate (mpy); \( \Delta W \) = change in weight loss, \( D \) = density of specimen (g/cm³), \( A \) = surface area of specimen cm² and \( T \) = exposure time (hours).

RESULTS AND DISCUSSION

Weight Loss, Corrosion Rate, Inhibition Efficiency and Surface coverage and effect of Temperature: The effect of different concentration of the extract of CA cotyledon extract on pipeline steel in 0.5M H₂SO₄ was investigated by weight loss method at varied temperatures of 303 K, 313 K and 333 K respectively, after 168hours of immersion period and presented in Figures 1-3.
The figures clearly show a reduction in weight loss of the metal coupons in the presence of extract compared to its blank. The figure further revealed decreases in weight loss of the pipeline steel as the concentration of the inhibitors increases. This trend reversed at higher temperature. The least weight loss was recorded at 5 g/L extract concentration and inhibition efficiency of 94 %. This behaviour of flora extracts in steel corrosion in acid environment has been previously reported (Madufor et al., 2013, Ejikeme et al., 2015).

Notably, is the decrease in corrosion inhibiting capacity of the extract with increase in temperature from 303 to 333 K. This trend has been reported by researchers (Iloomaeke et al., 2013, Li et al., 2014). Thermodynamically, increase in temperature increases the kinetic energy of reacting entities. Therefore, it is expected to increase the rate of oxidation of the steel in acidic environment, reducing the efficacy of the extract in inhibiting corrosion. However, there is a balance of the increased oxidation of the iron in acid environment and the inhibitive action of the CA cotyledon extract at higher temperature. The constituents of CA extract contains phytochemicals such as alkaloids, terpenes, flavonoids, tannins, etc. These have fused benzene rings and heteroatoms in the rings, the chemical complexity of the extracts makes it difficult to assign the inhibiting action to a particular constituent. (Awizar et al., 2013, Li et al. 2014; Nnanna et al., 2014). Increase in corrosion rate as the temperature increase has been attributed to desorption of the inhibitive molecules at higher temperature (Ngobiri et al., 2019). This corroborated with the surface coverage data in Table 1. The overall consequence is increased corrosion rate at higher temperature though the extract still shows active inhibitive presence.

**Table 1.** Corrosion rate, Inhibition efficiency and degree of surface coverage deduced from weight loss measurements in H$_2$SO$_4$ for cotyledon extracts.

| Corrosion Rate | Inhibition Efficiency(%IE) | Degree of surface coverage(θ) |
|----------------|---------------------------|-------------------------------|
|                | 30°C | 40°C | 60°C | 30°C | 40°C | 60°C | 30°C | 40°C | 60°C |
| Blank          | 5.05 | 6.59 | 9.87 |      |      |      |      |      |      |
| 1              | 4.32 | 6.15 | 8.91 | 87.20| 68.3 | 52.2 | 0.87 | 0.68 | 0.52 |
| 2              | 3.68 | 5.79 | 8.47 | 89.1 | 73.4 | 64.0 | 0.89 | 0.73 | 0.64 |
| 3              | 2.87 | 4.79 | 7.98 | 90.6 | 78.3 | 72.0 | 0.91 | 0.78 | 0.72 |
| 4              | 2.42 | 3.70 | 6.98 | 93.3 | 80.7 | 77.6 | 0.93 | 0.81 | 0.78 |
| 5              | 1.95 | 2.97 | 6.82 | 94.0 | 92.7 | 86.7 | 0.94 | 0.93 | 0.87 |

**Adsorption Study:** Table 1 indicates high degree of surface coverage of the corrosion inhibiting molecules. The mode of their action has been severally attributed adsorption on the metallic surface (Kalpana et al., 2003, Li et al., 2014). In order to determine a suitable mode of adsorption, the corrosion data was fitted into various adsorption isotherms. This is to determine the best fit. The linearity of the plot and good correlation coefficient may suggest that the experimental data for the studied extract fits better a particular adsorption isotherm but consideration of the deviation of the slope from unity shows that the isotherm may not be strictly applied. Several adsorption isotherms were tested, the corrosion of pipeline steel in 0.5 M H$_2$SO$_4$ in the presence of CA-cotyledon extract fitted more to Temkin and Langmuir isotherms.

**Temkin adsorption isotherm** which assumed a uniform distribution of adsorption energy with increase in surface coverage is given by equation (Bolaji, 2012).

\[
\text{Exp} (-2aθ) = K_{ads}C \quad (6)
\]

\[-2aθ = \ln K_{ads} + \ln C \quad (7)\]

\[θ = (1/2a) \ln K_{ads} - (1/2a) \ln C \quad (8)\]

Where: \(a\), is the molecular interactions of the adsorption layer and heterogeneity of the surface of the coupons; \(K_{ads}\) is the equilibrium constant, \(C\) is the concentration of the extracts, \(θ\) is the degree of surface coverage. Plots of surface coverage (θ) against lnC at 30°C,40°C and 60°C are shown in Figure 6 and coefficients (R$^2$) value greater than 0.835 in H$_2$SO$_4$ are...
shown in Table 2. These suggest some measure of conformity of the data to the Temkin adsorption isotherm model. The values of molecular interactions are all greater than zero (0) which suggest lateral interaction between the pipeline steel and the extract.

Figure 7 shows the linear plot of C/θ against C obtained by Langmuir adsorption isotherm equation as shown:

\[
\frac{C}{\theta} = \frac{1}{K} + \frac{C}{R^2}
\]

Where: K is the equilibrium constant, C is the concentration of the extracts and θ is the degree of surface coverage. The CA cotyledon extract fitted into the Langmuir adsorption isotherm with correlation coefficient (R²) value of 0.999 which shows a better fit than Temkin isotherm, as shown in Table 3. The values of ΔG°ads are all negative ranging from -10.533 and -10.797 kJ mol⁻¹ in H₂SO₄ medium. The values of ΔG°ads are often used to suggest either chemisorptions, physisorption or both adsorption modes. Physisorption is linked to electrostatic interactions between charged extracts molecules and charged metal surface, while chemisorptions has to do with charge sharing between the metal surface and the extracts molecules resulting in special kind of coordinate bond (Li et al., 2012). A value of ΔG°ads around -20 kJ mol⁻¹ or less implies physisorption while around -40 kJ mol⁻¹ or greater suggest chemisorptions.

However, the values of ΔG°ads obtained as showed in Table 4 are less negative than -20 kJ mol⁻¹, suggesting physisorption mechanism. Plots of ΔG°ads against T are shown in figure 10 from which the ΔH°ads and ΔS°ads values were obtained. ΔH°ads representing the slope and ΔS°ads as the intercept and the values were -1.96 and -65 kJ mol⁻¹ in H₂SO₄.

![Figure 6: Temkin adsorption isotherm for pipeline steel corrosion cotyledon in 0.5MH₂SO₄ at 303, 313 and 333 k](image)

![Figure 7: Langmuir adsorption isotherm for pipeline steel corrosion cotyledon in 0.5MH₂SO₄ at 303, 313 and 333 k](image)

**Figure 6:** Temkin adsorption isotherm for pipeline steel corrosion cotyledon in 0.5MH₂SO₄ at 303, 313 and 333 k

**Table 3:** Some parameters of the linear regression between θ and InC

| Temp(K) | H₂SO₄ COTYLEDON | K_ads | θ | R² |
|---------|----------------|-------|---|----|
| 303     | 0.863          | 0.796 | 0.978 |
| 313     | 0.986          | 0.903 | 0.970 |
| 333     | 1.077          | 1.051 | 0.835 |

The standard enthalpy (ΔH°ads) and entropy (ΔS°ads) were obtained from the equation below:

\[
\Delta G°ads = \Delta H°ads - T\Delta S°ads \tag{10}
\]

![Figure 8: Plot of ΔG°ads against T (K) for the adsorption of CA-cotyledon extracts in acid medium on pipeline steel surface](image)

![Figure 9: Plot of ΔG°ads against T (K) for the adsorption of CA-cotyledon extracts in acid medium on pipeline steel surface](image)

From literature report of Madufor et al., 2013 that the values obtained confirm exothermic adsorption to be either by physical adsorption or chemical adsorption while endothermic is only by chemical adsorption. Base on numerical values only, physisorption only manifest when ΔH°ads value is lower than -40 kJ mol⁻¹ while chemisorptions is -100 kJ mol⁻¹ (Edidong et al.,...
2018). The value of $\Delta H_{ads}$ obtained confirmed physisorption mechanism while the negative values of $\Delta S_{ads}$ implies adsorption of the extract on the surface of the coupons resulting in a reduction of the entropy, which agreed with basic thermodynamic principle of lower in entropy for exothermic reaction.

Kinetic and Thermodynamic Parameters: The values were obtained by Arrhenius equation shown below:

$$\log CR = \log A - \left( \frac{E_a}{2.303RT} \right) 11$$

$$\log \frac{CR}{T} = \left( \frac{R}{Nh} \right) + \left( \frac{\Delta S^*}{2.303RT} \right) - \left( \frac{\Delta H^*}{2.303RT} \right) 12$$

Where $E_a$ represent activation energy, $A$, frequency factor, $R$ gas constant and $T$, absolute temperature, $\Delta H^*$, enthalpy of activation, $\Delta S^*$ entropy of activation.

The value of $E_a$ were obtained from the plot of logCR against 1/T as shown in figure 10, while $\Delta S^*$ and $\Delta H^*$ where gotten from the intercept and slope of the plot of log CR/T against 1/T shown in figure 11. Generally, physisorption is noted when $E_a$ and $\Delta H^*$ value in the presence of extract is greater than in the absence of extract while opposite is for chemisorption.

From Table 5, it is observed that $E_a$ and $\Delta H^*$ values in the presence of extract are greater than in the absence validating that physisorption occur against chemisorption. The activation energy calculated show an increase with increased concentration compared to the blank. The value of $\Delta S^*$ were noted to be negative both in the absence and presence of the extract. The negative value of energy of activation for inhibited system has already being reported with hydrogen evolution reaction by Zhang QB et al. 2009. With increase in negative value of the activation energy in the presence of extract, which increased as the concentration increased (Table 5). The negative value of $\Delta S^*$ signified association rather than dissociation step of activated complex in the rate determining step, signifying a reduction in the degree of disorderliness. (Edidiong et al., 2018).

Table 5. Activation parameters for pipeline steel in 0.5M $\text{H}_2\text{SO}_4$ of the extract

| Concentration (g/l) | $E_a$(kJmol$^{-1}$) | $\Delta H^*$(kJmol$^{-1}$) | $\Delta S^*$(Jmol$^{-1}$K$^{-1}$) | $R^*$ (Arrhenius) | $R^*$ (Transition) |
|--------------------|--------------------|-----------------------------|-----------------------------|-----------------|-------------------|
| Blank              | 45.17              | -105.45                     | 0.999                       | 0.992           |
| 1                  | 49.39              | -102.64                     | 0.997                       | 0.940           |
| 2                  | 51.88              | -98.34                      | 0.975                       | 0.996           |
| 3                  | 54.50              | -95.68                      | 0.953                       | 0.969           |
| 4                  | 57.19              | -92.42                      | 0.982                       | 0.935           |
| 5                  | 59.92              | -86.76                      | 0.999                       | 0.999           |

FT-IR Studies of surface film of pure CA-cotyledon and CA-cotyledon on pipeline steel surface in $\text{H}_2\text{SO}_4$: The FT-IR spectra of the surface film on pipeline steel in the absence and presence of CA-cotyledon extract are presented in Figures 12 and 13. The functional group(s) in the extract involved in the adsorption process were identified using this method. Before the immersion of the metals, the projecting spectral peaks provide evidence on the functional groups in the pure extract. After absorption for 12 hours, the peaks were either vanished or are less prominent due to the participation of the compliant of the functional group(s) in adsorption. The absorption spectra of both surfaces (pure CA-cotyledon and CA-cotyledon on
pipeline steel surface in H₂SO₄ were similar but for some striking differences. The pure CA-cotyledon extract spectra have the range of values of 3290-1022, the cotyledon extract on pipeline steel coupon environment.

Figure 13, compared to the absence of the extract for cotyledon extract with the coupon in H₂SO₄, shows a peak at 3983-3744 indicated a strong and broad band indicating O-H stretching vibration. A peak around 2929 O-H intermolecular bonded alcohol stretching mode. The peak at 2854 linked to stretching vibration of O=C=O. The peak at 1987 indicated the presence of C-O, 1640 suggest C=C (alkene disubstituted), stretching frequency. The peak at 1378 confirmed O-H stretch. The peak at 717 confirms C-H stretching (aromatic triple boded compound) while at 672 represent C-H stretching (aromatic compound).

**Conclusion:** Chrysophyllum abildum cotyledon extracts was tested for inhibition of pipeline steel corrosion in 0.5M H₂SO₄ acid solution. The results obtained showed good corrosion inhibition activity of the extract. The inhibition values increases with increasing concentration of Cotyledon extract but decreased as the temperature increase. The FT-IR studies showed the presence of functional groups such as O-H, N-H and C=O was adsorbed on the surface of pipeline steel. The adsorption of inhibitor molecules on pipeline steel obey the Langmuir adsorption isotherm. The CA cotyledon extract acted as a good inhibitor of pipeline steel corrosion in 0.5 M H₂SO₄ solution.

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