# Corrosion Inhibition of Pipeline Steel in 0.5 M HCL Using Cotyledon of *Chrysophyllum cainito*

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***Authors' contributions***

*This work was carried out in collaboration between both authors. Author NCN designed and supervised the work. Author EPO carried the laboratory work and wrote the initial draft of the manuscript. Author NCN corrected the manuscript. Both authors read and approved the final manuscript.*

## ABSTRACT

The corrosion inhibition characteristics of *Chrysophyllum cainto* cotyledon aqueous extract was studied for the corrosion of pipeline steel in 0.5 M HCl using gravimetric technique. The corrosion surface morphology and corrosion surface film were studied using Scanning electron microscope and Fourier transform infrared spectroscopy respectively. The results obtained showed *Chrysophyllum cainto* aqueous extract as a good corrosion inhibitors of pipeline steel corrosion in acidic environment, recording an average corrosion inhibition efficiency above 90% at 303 K. The Scanning electron micrograph showed a smoother corrosion surface morphology in the presence of the extract while the Fourier transform infrared spectroscopic data showed the corrosion inhibition mechanism to be through adsorption.

*Keywords: Corrosion inhibition; gravimetric; adsorption; surface morphology; pipeline steel.*

## 1. INTRODUCTION

Corrosion of metallic materials has been of enormous cost to national gross domestic product of nations ranging to billions of USD. The global cost of corrosion was estimated to 2.5 trillion USD, which is about 3.4% of 2013 global Gross domestic product (GDP) [1]. The cost of

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corrosion is ever increasing hence the need for concerted effort to remedy its effects. Efforts to remedy corrosion is multifaceted, from material preparation and selection, design and construction to environment modification. One method of environmental modification is the introduction of corrosion inhibitors [2,3]. However most corrosion inhibitors raise environmental concerns, hence the need for inhibitors that will alley the environmental issues. Phyto materials has severally been used as eco-friendly corrosion inhibitors in addition to their re-new ability and been cheap [3-5].

The Chryosphyllum specie has been severally reported as a nutritional and medicinal species [6]. Also in literature is its corrosion inhibition characteristics [7]. An advancement of its corrosion mitigation activity will lead to a competitive demand with negative consequences especially in the developing countries. The Chryosphyllum species is a family of three notable fruit trees. Morphological, the barks of *Chryosphllum albidum* and *Chryosphllum subnudum* are pale-grayish brown while that of *Chryosphllum cainito* is scaly and brown. Fruits of the three are berries, while the fruit colour varies per species when ripe, for *C. albidum*, it is yellow; for *C. cainito*, purple-pink and for *C. subnudum* dark green [8].

The current work reports the corrosion inhibition characteristics of the cotyledon of *Chrysophyllum cainito* (CCC) on the corrosion of pipeline steel in hydrochloric acid. This part of the plant is usually discarded as waste after making use of the fruit. The success of this work will enhance the state of the environment as well as lessen the waste management burden.

## 2. METHODOLOGY

### 2.1 Materials Preparations

The Pipeline steel for this work was obtained from the System Metals Industries Limited, Port-Harcourt, Nigeria with thickness 2.5 mm and characterised, which has previously reported [9]. The steel plate was mechanically cut into 2cm by 3cm coupons and subjected to surface preparations by continuously polishing with different grades of emery papers (200 to 1000 mesh) until a smooth mirror like surface was achieved. It was washed in absolute ethanol, rinsed in acetone, dried and preserved till it was used in an active desiccator to prevent interaction with the environment.

The fresh fruits of *Chrysophyllum cainito* were washed, opened, the seeds removed and broken up to remove the cotyledon. This was allowed to air dry to prevent denaturing or loss of its phytochemicals. The dry sample was grounded using an electrical blender until a fine powder was formed. About 250 g of the sample was soaked in 4 litres of deionised water for 72 hours and the solutions was filtered and the filtrate concentrated to paste in a thermo stated water bath maintained at 30°C. This method has been previously reported [9]. The extract obtained was used to prepare various serial concentrations (1 g/l to 5 g/l) of the test solutions with 0.5 M HCl to ascertain its anti-corrosion properties in acid environment. All other reagents were of analytical grade

### 2.2 Weight Loss Technique

Pre-weighed and polished steel coupons were totally immersed in six 150 ml beakers containing same quantity of the test solution with and without the aqueous extract of CCC at 303 K in a water bath at a constant time interval for each temperature measurements. They were retrieved, after each interval, brushed under distilled water and absolute ethanol for cleaning off the corrosion products, dried in air after rinsing in acetone and weighed to determine the weight loss. The experiments were carried out in triplicate and the mean values of the weight loss were used for computation. The experiments were done at temperatures of 303, 313 and 333 K to determine the thermodynamics of corrosion process. Also, these methods have been severally reported [9,10].

The weight loss, degree of surface coverage ($\theta$), percentage inhibition efficiency (%), corrosion rate (mpy), and Rate constant (k) were determined using the equations below,

(a)  The weight loss ( W ) = $(W_i - W_f)$ g          1

Where: W = weight loss of pipeline steel coupon, and $W_i$ = Initial weight of the pipeline steel coupon before immersion, $W_f$ = Final weight loss of pipeline steel coupon after retrieval.

(b)  The corrosion inhibitor surface coverage ($\theta$)
$$= 1 - \frac{W_i}{W_o}$$          2

Where: $W_o$ = corrosion rates in the absence of CCC; $W_f$ = corrosion rates in the presence of CCC.

(c) The total surface area of pipeline steel coupon immersed in the solution was calculated as followed:  A = 2KM + Kt +2Mt +2∏rt - 2∏r$^2$ ....    3

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.

(d) The Corrosion inhibition efficiencies (%IE) $= 1 - \frac{Wi}{Wo}$ X 100    4

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.

(e) Corrosion rate (mpy) = $\frac{87.6\ (w1-w2)}{DAT}$    5

Where: $w_1$ and $w_2$ are the initial and final weights, D = density of the coupons (g/cm$^3$), A = surface area of coupons (cm$^2$) and T = exposure time (hours).

(f) Rate Constant (K)$= \frac{2.303}{Time} log \frac{w_1}{w_2}$    6

## 2.3 Surface Morphological Analysis (SEM)

The SEM micrograph for the corrosion inhibition of pipeline steel in 0.5 M HCl in the presence of CCC was carried out by immersing surface prepared coupons in 0.5 M HCl with 5 g/L CCC aqueous extract for 12 hours. While a reference micrograph was obtained by immersing a surface prepared coupon in 0.5 M HCL for 12 hours. Both coupons were retrieved dried and subjected to SEM examination using Oxford X-mass Scanning electron microscope.

## 2.4 Fourier Transform Infrared (FT-IR) Spectroscopy

The corrosion surface film of aqueous CCC extract on pipeline steel in 0.5 M HCl was determined by immersing pipeline steel coupons with prepared surface in 0.5 M HCl with 5 g/L CCC aqueous extract, for 24 hours. The pipeline steel coupons were retrieved, dried and the surface carefully scrapped off and subjected to FT-IR analysis using Magna-IR 560 Spectrometer ESP Nicolet with the aid of KBr disc provided by the instrument. These were compared with the FT-IR of aqueous CCC extract.

## 3. RESULTS AND DISCUSSION

### 3.1 Effect of Extract Concentration and Temperature on Weight Loss, Corrosion Rate, Inhibition Proficiency and Surface Coverage

Figs. 1 and 2 present the weight loss of pipeline steel in 0.5 M HCl in the presence and absence of CCC aqueous extract. The presence of CCC progressively retarded the weight loss of pipeline steel in the acid. The decrease in weight loss was pronounced with increase in the concentration of CCC while increase in temperature increased the weight loss progressively from 303 to 333 k. Previous researchers have reported this trend [9-12].

The effects of aqueous CCC on corrosion rate and corrosion inhibition efficiency on the corrosion of pipeline steel corrosion in 0.5 M HCl are presented in Figs. 3 and 4 respectively. The corrosion rate and corrosion inhibition efficiency showed inverse relationship in the presence of CCC extract, while the corrosion rate decreased, the corrosion inhibition efficiency increased with increase extract concentration. However, this trend was reversed with rise in temperature. Also, similar trends have been reported by researchers [4,12].

### 3.2 Adsorption Isotherm

Adsorption isotherms are usually applied to predict the adsorption behaviour of inhibitor molecules on metallic surface [13,14]. Though various adsorption isotherms were tested for the corrosion inhibition of CCC extract on pipeline steel in HCl, Temkin adsorption isotherm fitted better. The Temkin adsorption isotherm assumes a uniform distribution of adsorption energy, which increase with increased surface coverage is given by equation 7. and can be transformed to equations 8 to 10.

exp(-2aθ)  =  K$_{ads}$C    7

-2aθ = lnK$_{ads}$ + lnC    8
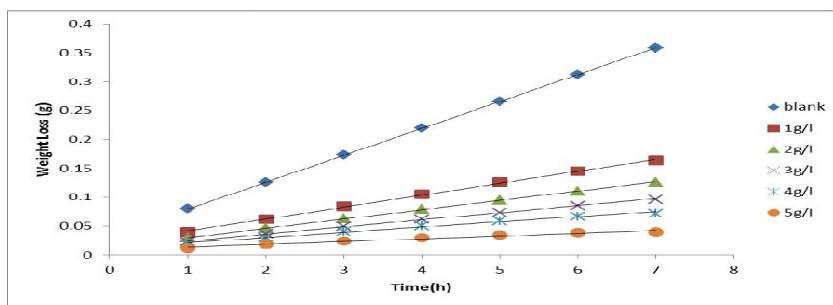
θ = (1/2a) Log K$_{ads}$ – (1/2a) ln C    9

**Fig. 1. Plot of weight loss against time for pipeline steel corrosion in 0.5 M HCl with varying concentrations of CCC aqueous extract at 303 K**
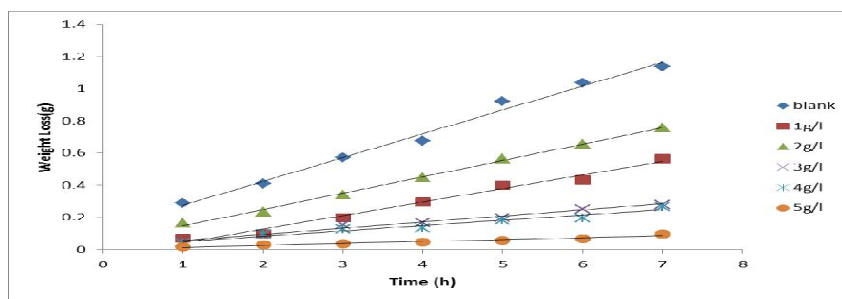


**Fig. 2. Plot of weight loss against time for pipeline steel corrosion in 0.5 M HCl with varying concentrations of CCC aqueous extract at 333 K**
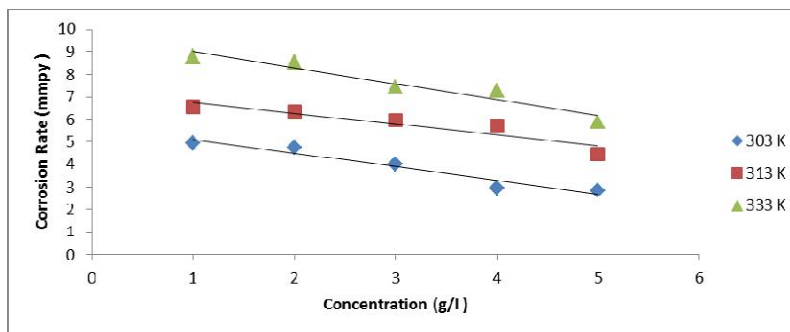


**Fig. 3. Plot of Corrosion Rate against Concentration of CCC extract on the corrosion of pipeline steel in 0.5 M HCl at different temperatures**
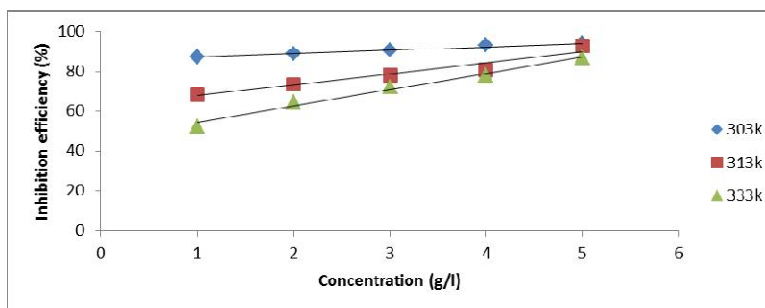


**Fig. 4. Plot of corrosion inhibition efficiency against concentration of CCC extract on the corrosion of pipeline steel in 0.5 M HCl at different temperature**

a represents the molecular interactions of the adsorption layer and heterogeneity of the coupons; $K_{ads}$ is the equilibrium constant, C concentration of extracts, θ degree of surface coverage. A Plot of surface coverage (θ) against In C at varying temperatures is presented in Fig. 5.

The coefficients of the linear regression ($R^2$) for the plots is greater than 0.951 at all studied temperatures which suggests good conformity of the adsorption data to the Temkin adsorption isotherm model. The data for Fig. 5 is presented in Table 1. The values of molecular interactions are all greater than zero (›0) which suggest lateral interaction between the pipeline steel and the extracts molecules.

## 3.3 Surface Morphological Analysis (SEM)

The results of the SEM examinations for the corrosion of pipeline steel in 0.5 M HCl in the absence and presence of CCC extracts are presented in Figs. 6 and 7 micrographs respectively. From the result obtained, the surface of the coupon immersed in 0.5 M HCl in absence of CCC extract showed badly corroded surface by HCl, due to metal dissolution in acid solution, Also, the surface was with more porosity resulting to the appearance of larger and deeper holes. While the contrary was observed in Fig. 7 with smoother surface attributed to the action of molecules of CCC aqueous extract. This has been reported to be due to the formation of a protective film on the metal surface, which is responsible for the inhibition or retardation of corrosion [14,15].

## 3.4 Fourier Transform Infrared Spectroscopy with and without the Extracts in HCl

The FT-IR of the surface film of aqueous CCC and aqueous CCC extract molecules on pipeline steel in HCl are presented in Figs. 8 and 9 respectively. Both spectra have the range of values of about 3350-1175cm$^{-1}$. The close relationship of the two spectra with few shift suggests that the molecules of CCC were adsorbed at the surface of the steel while the slight shifts suggests that new bonds were formed. This trend has been previously reported [16]. The following functional groups N-H at adsorption band 3290cm$^{-1}$, the band at 2929cm$^{-1}$ and 2121cm$^{-1}$ representing the O-H stretching and N=C=S stretching respectively. The Conjugated anhydride at 1726cm$^{-1}$. The bands at 1611-1413cm$^{-1}$ represents the C=C stretching, O-H bending, peak at 1380cm$^{-1}$ indicate C-H bending, while at 1324cm$^{-1}$ is an indication of C-O stretching. The ether functional group was observed at band 1022cm$^{-1}$ and the band 780cm$^{-1}$ indicates the C=C bending. The peak at 695 - 680cm$^{-1}$ shows mono and tri-substituted alkenes respectively.
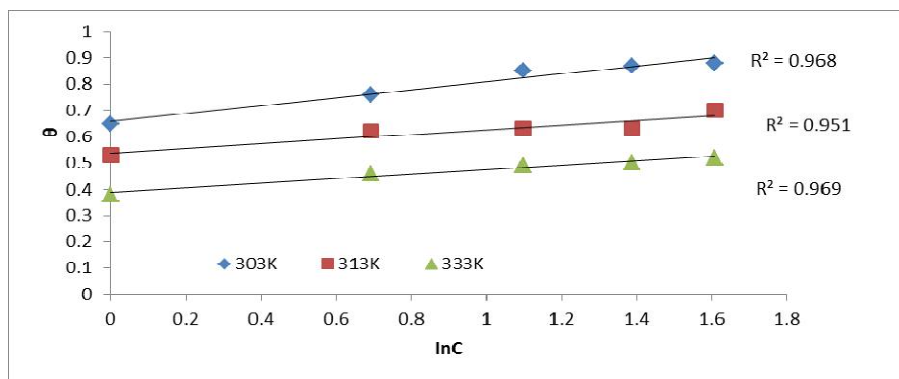


**Fig. 5. Temkin adsorption isotherm for the corrosion of pipeline steel in 0.5 M HCl in the presence of CCC extract at 303, 313 and 333 K**

**Table 1. Temkin adsorption parameters of the adsorption of CCC aqueous molecules on pipeline steel in 0.5 M HCL at 303, 313 and 333 K**

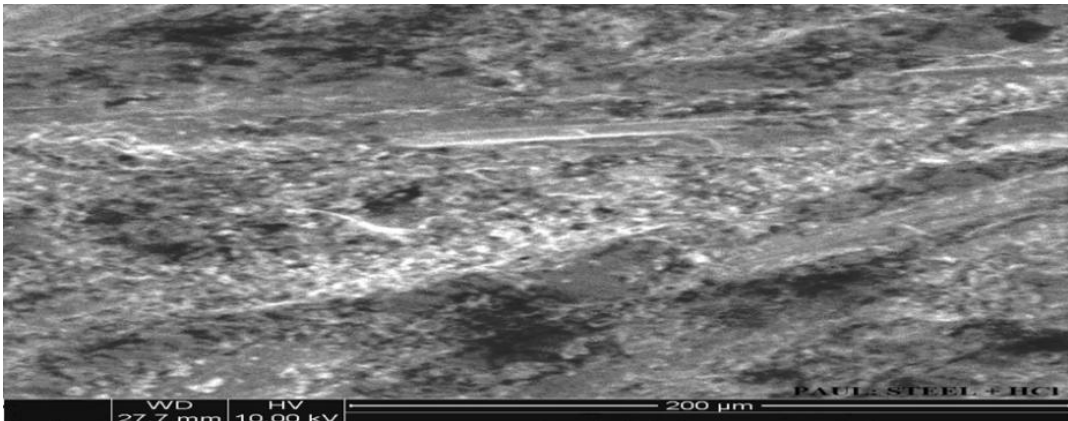| Tem (K) | $k_{ads}$ | a | $R^2$ |
|---------|-----------|-------|-------|
| 303 | 0.748 | 0.756 | 0.951 |
| 313 | 0.832 | 0.900 | 0.968 |
| 333 | 0.948 | 0.936 | 0.969 |

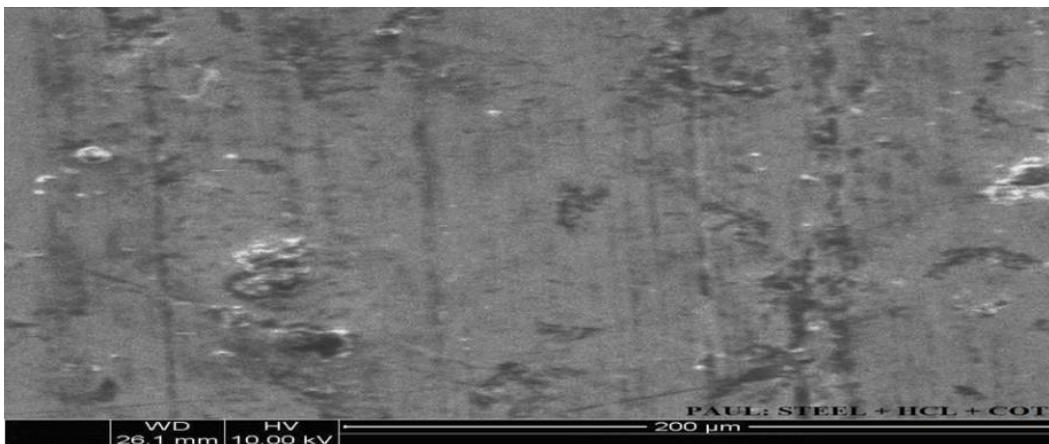**Fig. 6. SEM image of pipeline steel in 0.5 M HCl without CCC aqueous extract**



**Fig. 7. SEM image of pipeline steel in 0.5 M HCl with CCC aqueous extract**
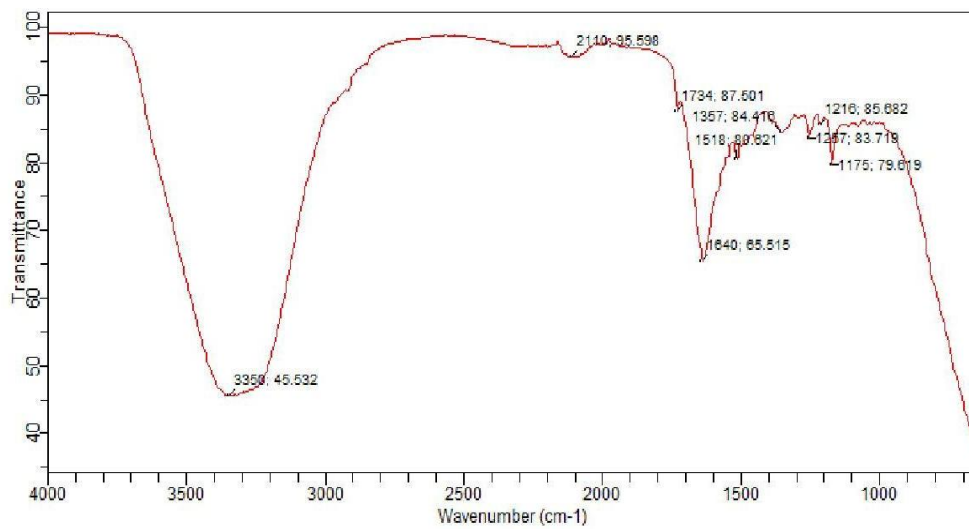


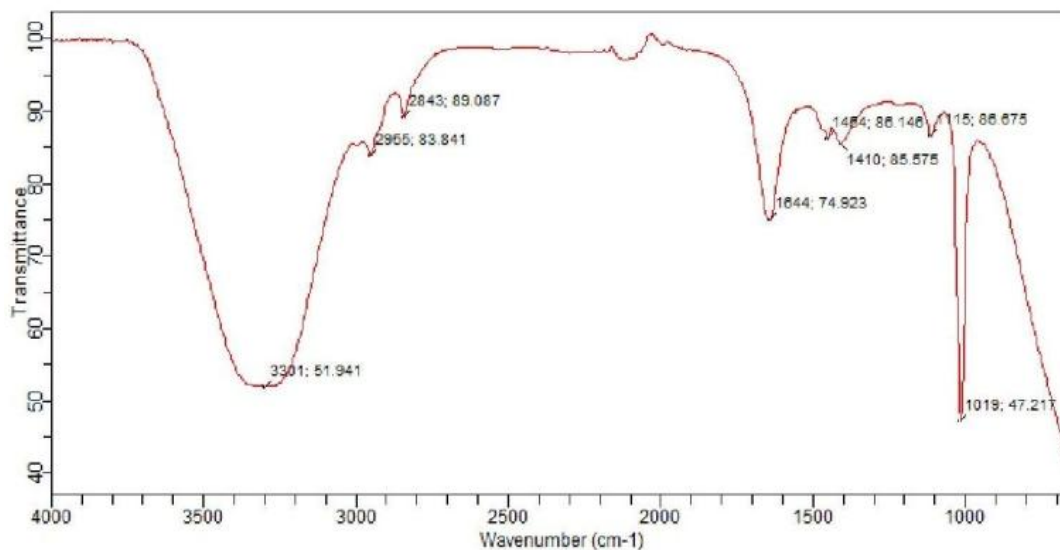**Fig. 8. FT-IR spectrum of aqueous CCC extract**

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**Fig. 9. FT-IR spectrum of the surface film of aqueous CCC on pipeline steel in HCl**

## 4. CONCLUSION

The work reported the application of aqueous extract of *Chrysophyllum cainto* cotyledon to inhibit the corrosion of pipeline steel in 0.5 M HCL solution containing serial concentrations of the extract. The extract exhibited good corrosion inhibition characteristics in the study environment. Also, the presence of the extract resulted in a smoother and cleaner corrosion surface morphology. While the inhibition mechanism was attributed to adsorption from the FT-IR and adsorption isotherm studies.

## COMPETING INTERESTS

Authors have declared that no competing interests exist.

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