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Inhibition of Pipeline Steel Corrosion in 0.5 M H_2SO_4 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 attemperatures, 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 energydepicting 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, H_2SO_4, CH_3COOH, 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, Raja*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 immerse 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,Akbari*et al.*, 2012,Akalezi*et al.*2015). The GC-Mass spectra of the crude extract of the cotyledon was used to identify the various pytochemical 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,

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Ejikeme *et al*., 2015, Ngobiri and Okorosaye-Orubite, 2018).

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 H_2SO_4 and extract concentrations were $1g/dm^3$, $2g/dm^3$, $3g/dm^3$, $4g/dm^3$, $5g/dm^3$ 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 theweight loss obtained at each temperaturewas used to determine the following parameters.

$$W = \frac{w_1 - w_g}{g} (1)$$

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 (θ) CA-C in 0.5M H_2SO_4at different concentrations was obtained by using the equation below.

$$\theta = 1 - \frac{Wi}{Wo} (2)$$

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

$$\% IE = 1 - \frac{Wi}{Wo} \text{ X } 100 \quad (3)$$

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 asfollows:

$$A = 2KM + Kt + 2Mt + 2\prod rt - 2\prod r^2 \quad (4)$$

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.

$$CR\ (mpy) = \frac{87.6\,\Delta w}{DAT} (5)$$

Where; CR = Corrosion rate (mpy); ΔW = change in weight loss, D = density of specimen (g/cm^3), A =surface area of specimen cm^2) 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 H_2SO_4 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.

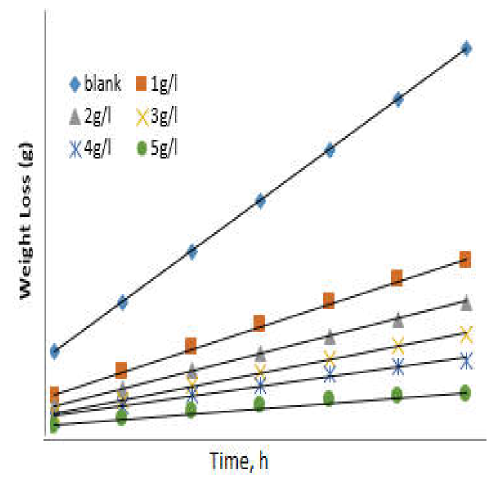

Fig 1. Plot of weight loss against time for pipeline corrosion in $0.5MH_2SO_4$ containing different concentration of CA cotyledon at 303k

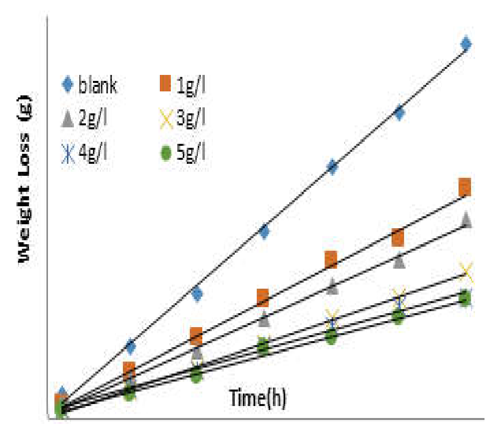

Fig 2.Plot of weight loss against time for pipeline corrosion in $0.5MH_2SO_4$ containing different concentration of CA cotyledon at 313k.

The figures clearly shows 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).

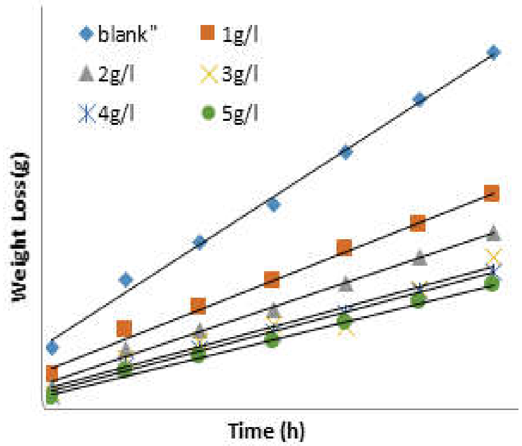

Fig 3.Plot of weight loss against time for pipeline corrosion in 0.5MH_2SO_4 containing different concentration of CA cotyledon at 333k.

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 (Iloamaeke *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.

Table1. Corrosion rate, Inhibition efficiency and degree of surface coverage deduced from weight loss measurements in H_2SO_4 for cotyledon extracts.

	Corrosion Rate			Inhibition Efficiency(%IE)			Degree of surface coverage(θ)		
	30^{O}C	40^{O}C	60^{O}C	30^{O}C	40^{O}C	60^{O}C	30^{O}C	40^{O}C	60^{O}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_2SO_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).

$$\text{Exp}(-2a\theta) = \text{KadsC} \quad (6)$$

$$-2a\theta = \text{In}K_{ads} + \text{InC} \quad (7)$$

$$\theta = (1/2a)\,\text{Log}\,K_{ads} - (1/2a)\,\ln C \quad (8)$$

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 InC at 30^{O}C,40^{O}Cand 60^{O}C are shown in Figure 6and coefficients (R^2)value greater than 0.835 in H_2SO_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.

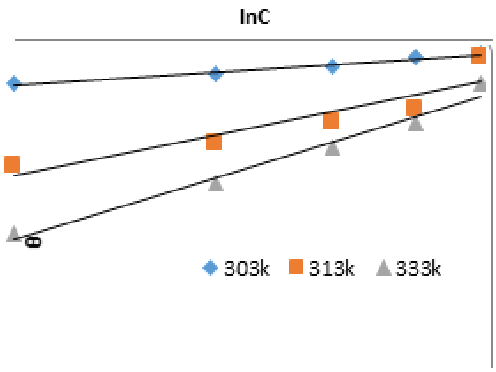

Fig 6: Temkin adsorption isotherm for pipeline steel corrosion cotyledon in 0.5MH_2SO_4 at 303, 313 and 333 k

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

Tem(K)	H_2SO_4 COTYLEDON		
	K_{ads}	a	R^2
303	0.863	0.796	0.978
313	0.986	0.903	0.970
333	1.07	1.051	0.835

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

$$\frac{C}{\theta} = \frac{1}{K} + C \quad (9)$$

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 (R^2) value of 0.999 which shows a better fit than Temkin isotherm, as shown in Table 3. The values of$\Delta G^o_{ads}$are all negative ranging from -10.533 and -10.797kJmol^{-1} in H_2SO_4 medium. The values of ΔG^o_{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 -20kJmol^{-1} or less implies physisorption while around -40kJmol^{-1} or greater suggest chemisorptions.

However the values of ΔG^o_{ads}obtained as showed in Table 4are less negative than -20kJmol^{-1}, suggesting physiosorption mechanism. Plots of ΔG^o_{ads} against T are shown in figure 10 from which the ΔH^o_{ads} and ΔS^o_{ads} values were obtained. ΔH^o_{ads} representing the slope and ΔS^o_{ads} as the intercept and the values were -1.96 and -65 kJmol^{-1} in H_2SO_4.

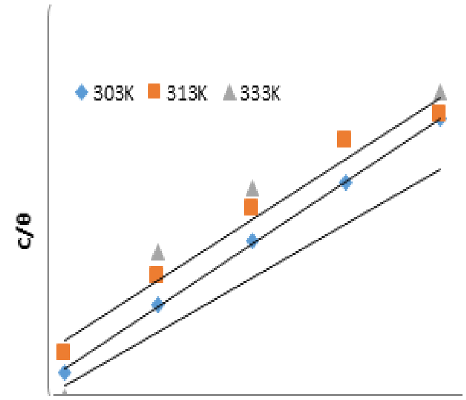

Fig 7. Langmuir adsorption isotherm for pipeline steel corrosion cotyledon in 0.5MH_2SO_4 at 303, 313 and 333 K in the presence of CA-cotyledon extract

Table 4. Calculated parameters from Langmuir adsorption isotherm plot for pipeline steel in 0.5MH_2SO_4 of the presence of CA cotyledon extracts.

Temp(K)	H_2SO_4 COTYLEDON			
	K_{ads}	ΔG_{ads}	Slope	R^2
303	1.154	-10.533	0.99	0.999
313	1.123	-10.615	0.99	0.977
333	0.86	-10.797	1.025	0.334

The standard enthalpy (ΔH^o_{ads}) and entropy (ΔS^o_{ads}) were obtained from the equation below:

$$\Delta G^o_{ads} = \Delta H^o_{ads} - T\Delta S^o_{ads} \quad (10)$$

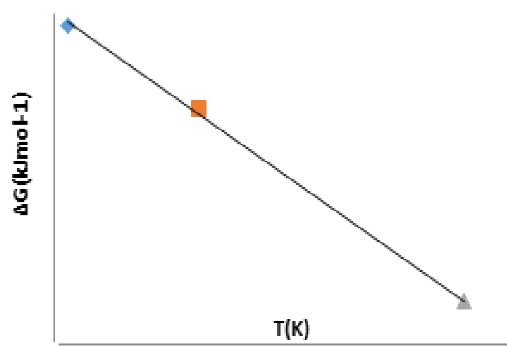

Fig9. Plot of ΔG^o_{ads} against T (K) for the adsorption of CA-cotyledon extracts in acidmedium on pipeline steel surface

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, physiosorption only manifest when ΔH^o_{ads} value is lower than -40 kJmol^{-1} while chemisorptions is -100 kJmol^{-1} (Edidong et al., 2018). The value of ΔH^o_{ads} obtained confirmed physiosorption mechanism while the negative values of ΔS^o_{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:

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

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

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

The value of E_a were obtained from the plot of logCR against 1/T as shown in figure 10, while ΔS^* and ΔH^* where gotten from the intercept and slope of the plot of log CR/T against I/T shown in figure 11. Generally, physisorption is noted when E_a and ΔH^*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 ΔH^* values in the presence of extract are greater than in the absence validating that physiosorption occur against chemisorption. The activation energy calculated show an increase with increased concentration compared to the blank. The value of ΔS^* 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 ΔS^* 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).

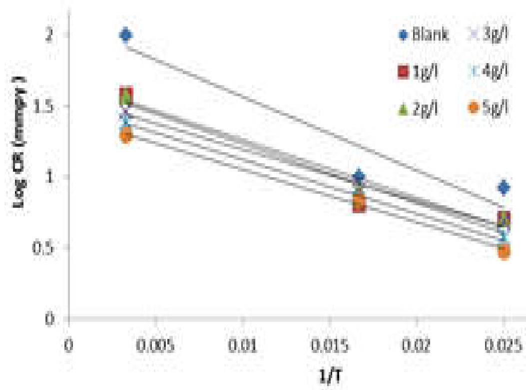

Fig10. Arrhenius plot in the absence and presence of different concentration of the extract in H_2SO_4

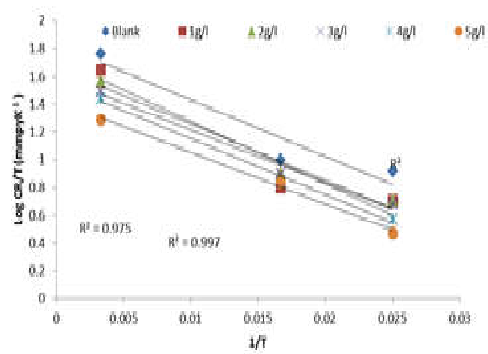

Fig11. Transition state plots for pipeline steel in 0.5 M H_2SO_4 in the absence and presence of different concentrations of the extract.

Table 5. Activation parameters for pipeline steel in 0.5MH_2SO_4 of the extract

Con(g/l)	H_2SO_4 COTYLEDON				
	E_a(kJmol^{-1})	ΔH*(kJmol^{-1})	ΔS*(Jmol-1)	R^2(Arrehius)	R^2(Transition)
Blank	45.17	40.45	-105.45	0.999	0.992
1	49.39	45.63	-102.64	0.997	0.940
2	51.88	48.85	-98.34	0.975	0.996
3	54.50	51.56	-95.68	0.953	0.969
4	57.19	54.83	-92.42	0.982	0.935
5	59.92	58.96	-86.76	0.999	0.999

FT- IR Studies of surface film of pure CA-cotyledon and CA-cotyledon on pipeline steel surface in H_2SO_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 and13. 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 H_2SO_4) were similar but for some striking differences. The pure CA-cotyledonextract spectra have the range of values of 3290-1022, the cotyledon extract on pipeline steel coupon environment.

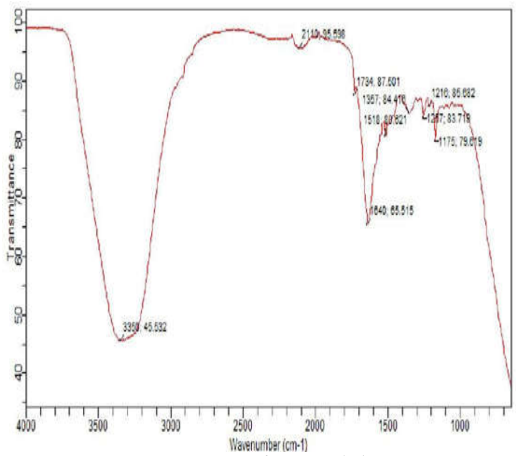

Fig12: FT-IR spectra of CA-cotyledon extract

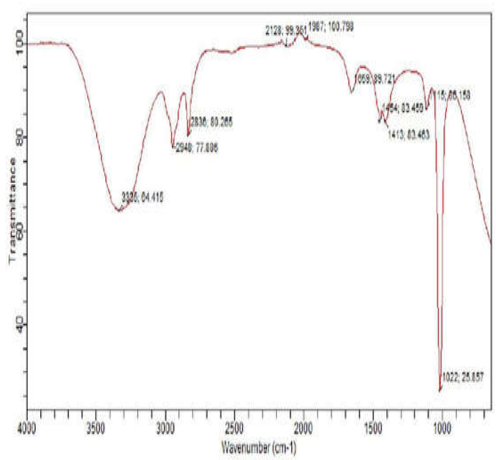

Fig 13: FT-IR spectra formed on the pipeline steel after immersion in 0.5M H_2SO_4 with inhibitor (CA-cotyledon extract).

Figure 13, compared to the absence of the extract for cotyledon extract with the coupon in H_2SO_4, 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 band 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 abldum* cotyledon extracts was tested for inhibition of pipeline steel corrosion in 0.5M H_2SO_4 acid solution. The results obtained showed good corrosion inhibition activity of the extract. The inhibition values increases with increasing concentration of Cotyledon extractbut 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 obeys the Langmuir adsorption isotherm. The CA cotyledon extract acted as a good inhibitor of pipeline steel corrosion in 0.5 M H_2SO_4 solution.

REFERENCE

Abiodun, OA; Oladapo, AS (2011). Physicochemical properties of African Star Apple (*Chrysophyllum albidum*) components. Nutrition and food science 41:8-11

Akalezi, CO; Oguzie, EE, (2015). Evaluation of anticorrosion properties of *Chrysophyllum albidum* leaves extract for mild steel protection in acidic media, International Journal of industrial chemistry, 7 (1), 81-92.

Akbari, V; Jamei, R; Heidari, R; Esfahlan, AJ (2012). Antiradical activity of different parts of chrysophyllum albidum (Juglans regia L.) fruit as a function of genotype. *Food chemistry*, *135*(4), 2404-2410

Awizar, DA; Othman, NK; Jalar, A; Daud, AR; Rahman, IA; Al-hardan NH,(2013).Nanosilicate Extraction from Rice Husk as Green Corrosion Inhibitor, International *Journal of Electrochemical Science*, 8, 1759 - 1769.

Bolaji Aremo, (2012). Development of a spongy metal gas diffusion system for alkaline fuel cells, Ph.D. Thesis, Obafemi Awolowo University, Ile – Ife, Nigeria.

Ebenso, EE; Okafor, PC; Ekpe, UJ, (2002).Studies on the inhibition of aluminium corrosion by 2-acetylphenothiazine in chloroacetic acids. *Bulletin of electrochemistry*, 18(12), 551-558.

Edidong, A; Essien, Doga Kavaz; Ekemini BI; Umoren SA (2018). Synthesis, characterization and anticorrosion property of olive leaves extract-titanium nano-particles composite. *Journal of adhesion science and technology*, 1-19.

Ejikeme,PM; Umana, SG; Menkiti, MC; Onukwuli, OD, (2015).Inhibition of mild steel and aluminium corrosion in 1M H_2SO_4 by leaves extract of African breadfruit. *International Journal of material and chemistry* 5(1), 14-23.

Iloamaeke, IM; Onuegbu, TU; Umeobika, UC; Umedum, NL, (2013).Green approach to corrosion inhibition of mild steel using emiliasonchifolia and *Vitexdoniana* in 2.5 M HCl medium. *International Journal of Science and Modern Engineering (IJISME)*, *1*(3), 48-52.

Li, X; Deng, S; Fu, H, (2012). Inhibition of the corrosion of steel in HCl, H_2SO_4solutions by bamboo leaf extract. *Corrosion Science*, *62*, 163-175.

Loto, CA; Mohammed, AI, (2000). The effect of *Anacardium Occidentale* (cashew) juice extract on the corrosion of mild steel in hydrochloric acid. *Corro. Prev. Control*, *47*(2), 50-56.

Madufor, IC; Itodoh, UE; Obidiegwu, MU; Nwakaudu, MS, (2013).*Chrysophyllum albidum* (African star apple) fruit extract as environmentally friendly inhibitor on the corrosion of aluminium in acidic medium, 4. 1-142.

Nnanna, LA; Uchendu, KO; Nwosu, FO; Ihekoronye, U; Eti, PE, (2014),*Gmelina arborea* bark extracts as corrosion inhibitor for mild steel in an acidic environment,Int.J.Mater.Chem.,4(2):34-39

Ngobiri, NC; Akaranta, O; Oforka, NC; Oguzie, EE; Ogbulie, SU, (2013). Inhibition of pseudo-anaerobic corrosion of pipeline steel in pipeline water using biomsa-derived molecules, *Advances in materials and corrosion* 2, 20-25

Ngobiri, NC; Oguzie, EE; Oforka, NC; Akaranta, O. (2019). Comparative study on the inhibitive effect of Sulfadoxine–Pyrimethamine and an industrial inhibitor on the corrosion of pipeline steel in petroleum pipeline water. *Arabian Journal of Chemistry*, 12, 1024-1034

Ngobiri, NC; Orubite, KO, (2018). Corrosion pattern of pipeline steel in petroleum pipeline water in the presence of biomass derived extracts of *Brassica oleracea* and *Citrus paradise* mesocarp, *Mat. Sci. Applica.* 9,126-141

Raja, PB; Qureshi, AK; Rahim, AA; Awang, K., Mukhtar, M. R; Osman, H. (2013). Indole alkaloids of *Alstonia angustifolia var. latifolia* as green inhibitor for mild steel corrosion in 1 M HCl media. *J. Mat. Engineer. Perform. 22*(4), 1072-1078

Zhang QB; Hua, YX, (2009). Corrosion inhibition of mild steel by alkylimidazolium ionic liquids in hydrochloric acid. *Electrochim Acta*54:1881-160.