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LEAF EXTRACT OF LUFFER CYLINDERICAL FOR THE DEVELOPMENT OF AN ANTI CORROSIVE PAINT

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ABSTRACT

Metallic materials are the most widely used materials in various industries. They are useful due to their excellent mechanical properties. However, they are susceptible to corrosion. Many of the corrosion problems in industries comes from the frequent use of acids such as HCl and H_2SO_4 for acid cleaning, descaling, pickling, acidizing in mining and oil wells. Therefore, corrosion inhibitor needs to be introduced to these solutions to mitigate this challenge. Many synthetic compounds which have been used as corrosion inhibitors are expensive and toxic, posing threat in our ecosystem. This paper describes a paint incorporated with organic inhibitor, i.e., luffa cylindrica leaf extract. This paint was formulated to enhance its anticorrosive property. Luffa cylindrica (sponge) leaf extract was chosen as the corrosion inhibitor as it is organic, readily available, environmentally acceptable, and a renewable source of material for a wide range of corrosion problems. The inhibitive action of luffa cylindrica extract in HCl and Pipeline water were investigated by weight loss method. The inhibitive effects of luffa cylindrica extract were investigated with percentages of 1g/l, 2g/l, 3g/l, 4g/l and 5g/l incorporated into paint. The inhibition efficiency increased with concentration of luffa cylindrica extract reaching a maximum value of 97.39% with pipeline water whereas HCl had a maximum value of 74.89% at 5g/l. The results showed that at 5g/l has the highest corrosion rate of 0.042 mm/yr in pipeline water as compared to Paint 1 with 0.0477 mm/yr. Paint 5 with inhibitor concentration of 5g/l was proposed as the most effective paint that contains a natural inhibitor for pipeline steel in all the media.

Keywords: Luffa cylindrica; Corrosion inhibition; gravimetric; adsorption; pipeline steel.

INTRODUCTION

In many industrial operations, the addition of inhibitors to process fluids to minimize the rate of metal corrosion is very common. Chemicals are usually applied on metal surfaces as part of the final finishing procedures prior to plating, painting, or storage (Abdel-Gaber et al., 2011). According to Ahmad, et al. (2021), the chemicals are capable of removing scales, soil and light rust from the metal surfaces. Apart from this, they often contain about 1 % organic corrosion inhibitors by volume of the acid used, such as hydrochloric acid. Synthetic inhibitors have been widely applied to protect metal surfaces against corrosion (Al-Amiery et al., 2022; Al-Otaibi et al., 2012). However, these inhibitors are toxic, expensive with environmental and safety issues. Alternative sources including natural products, extracts from plants, and other environmental benign organic sources have been widely reported (Awizar et al., 2013).

Many organic compounds have been tested for corrosion inhibition. The functionality of these compounds has been attributed to their electronegative functional groups and presence of π electrons in triple bonds or conjugated double bonds. They also contain nitrogen, sulphur or oxygen atoms in their structures. Their mode of operation is by physical or chemical interactions between their molecules and the metal surfaces (Al-Amiery et al., 2022). Several plant extracts including an extract from Carica papaya, Rosmarinus Officinalis, Damsissa, Murrayakoenigii, cashew, mango, Uncaria gambir and Fiscusycomorus had been investigated (Bahrami et. al., 2010; Bhat et. al., 2001; Cwalina et. al., 2014; Chris et. al., 2015). According to Helen et al. (2014), these plants possess adequate cyclic organic phytochemicals, nitrogen, sulphur and oxygen atoms that are responsible for their inhibition properties. The large scale synthesis of various natural plant extract is faced with many challenges. The chief of which is the isolation of specific components of the plant extract with inhibitory characteristics. Nevertheless, many natural plant extracts have proven efficient as corrosion inhibitors (Damborenea et al., 2014; E.P. Othaki and N.C. Ngobiri (2020) ; Edidiong, et al., 2018). To gain insight on the working and applicability of natural extracts for commercial purposes, inhibition mechanism, kinetics and process thermodynamics was investigated on a pilot scale. The extract, after careful concentration under controlled temperature, may however, be added in the right mix to paints of organic solvent base for easy dissolution and dispersion.

Corrosion of metal takes place whenever there is an interaction of two different electrochemical reactions on the material surface. With detailed knowledge of these electrochemical processes, potential theory is commonly applied for the prediction of corrosion rate. In many cases, these data are not available which limit the application of mixed potential theory with confidence. Laboratory measurements are therefore made and interpreted in terms of mixed potential theory such as polarization resistance, electrochemical impedance spectroscopy (EIS) and electrochemical noise (Ejikeme et al., 2015; Elemo, et al., 2011; Kliskic et al., 2000). These methods involve the use of advanced instruments with expert advice that are often not available to many researchers. Gravimetric-based method such as weight loss provides integrated mass loss information from corrosion that has occurred over some period of time. Because of simplicity and economic friendliness, gravimetric techniques are commonly used to measure general corrosion rate (Figueira, et al., 2020). However, gravimetric-based techniques are unsuitable for continuous field monitoring of corrosion rates.

This present study deployed gravimetric and qualitative techniques to evaluate another eco-friendly material (LCLE), for use as an engineering inhibitor on Pipeline steel submerged in a 0.5 M HCl and Pipeline water solution. The optimum condition, the kinetics and thermodynamic parameters for maximum corrosion inhibition using LCLE were established.

The *Luffa aegyptiaca (sponge gourd)* specie has been severally reported as a nutritional and medicinal species (Galio, A.F., and Dariva, C.G. (2014). Also in literature is its corrosion inhibition characteristics. An advancement of its corrosion mitigation activity will lead to a competitive demand with negative consequences especially in the developing countries. *Luffa aegytiaca* also known as *luffa cylindrica,* sponge gourd, loofa, dish cloth gourd, bath sponge, and vegetable sponge is an essential vegetable and medicinal plant that belongs to the genus Luffa and plant family Cucurbitaceae. It's origin can be traced to tropical Asia. It is a crawling plant that grows in the wild and on abandoned buildings, structures and fence was in towns and villages in Nigeria. It is a climbing annual wild vine with lobed cucumber like leaves that are dark green in colour with rough surface. The plant with yellow flowers bear fruits that are cucumber shaped but larger in size and contain

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fibrous sponge in which holds the hard black seeds (Goni et.al., 2019; Grundmeier et. al., 2000; Hansson, C.M. (2011).). It is an important source of carbohydrates, vitamin C, several minerals (such as Mg, Ca, Na, K, Cu, Zn, and Mn), tannin, phytin phosphorus, phytic acid and protein.

The leaves, seeds, and fruits of sponge gourd are used in treating various ailments such as viral infections, diarrhea, fever, swells, inflammatory diseases, etc (Ju et.al., 2008). Immature fruits are consumed as vegetables which is effective in treating diabetes. The extracts from living vines are used as constituents in cosmetics and medicine. They are used as fillers in producing composite materials. In some cultures , the mature fibrous skeleton of the of the luffa fruit is used as a natural scrubbing spong for cleaning and bathing. It has been used for centuries as an eco-friendly alternative to synthetic sponges.

Matured *Luffa cylindrica* (Sponge gourd) fruit Dried Matured *Luffa cylindrica (* Sponge gourd) leaf. The chemical components of *Luffa aegytiaca* include various bio active compounds such as flavonoids, phenolic acids, and other phytochemicals. These compounds contribute to the several potential health benefits and therapeutic properties of the plant. However, it's important to note that there is limited research on the inhibitory properties of sponge gourd and this work will aid in showing how effective this plant can be in inhibiting corrosion of pipeline steel.

The current work reports the corrosion inhibition characteristics of the fruits of *Luffa aegyptiaca (sponge gourd)* fruit 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.

METHODOLOGY

Materials

Pipeline Steel (AA5083) specimens were used for this study due to their extensive usage in marine, oil and gas industry, particularly as a plate for ship, pipeline construction. Pipeline Steel (PS) metal sheets were obtained from Metal section of Mile 3 Market Port Harcourt, Rivers State. The specimen were cut into square shapes with dimension of 2.96 cm x 2.5 cm x 0.9 cm. The AA5083 has percentage composition of 0.42% Si, 0.45% Fe, 0.12% Cu, 0.40-1.0% Mn, 4.0-4.9% Mg, 0.05-0.25% Cr, 0.25% Zn and 0.15% Ti. (Kadafa, A. (2012); Kalpana, M., and Mehta, G. (2003). Lebrini et. al., 2011). The specimens were polished with 400, 800 and 1200 grade of abrasive paper. The polished specimens were cleaned by using acetone (according to SSPC-SP1 Standard) to remove all visible oil, grease, soil, drawing and cutting compounds, and other soluble contaminants until a mirror like surface was achieved, washed in absolute ethanol and distilled water, rinsed in acetone , dried in air and preserved in desiccators to prevent interaction with the environment. The elemental composition of the metal coupons was analysed using optical electronic spectroscopy (OES) in the Department of Metallurgical and Material Engineering, University of Lagos.

Plant extraction

The *luffa cylindrica* (leaves) were harvested in uncompleted buildings at different locations (such as Rumuigbo, Ipo, and University of Port Harcourt), Rivers State; washed to remove any earthly materials and contaminants, allowed to dry for seven days. The plant was taxonomically identified at Plant Science and Biotechnology Department, University of Port Harcourt, Nigeria where a voucher specimen submitted. (Ngobiri, et.al., (2019). The fresh fruits were washed with running water, rinsed with distilled water. The fresh fruit samples were grounded using manual blender. The extract were obtained by soaking 100 g of grounded leaf samples for 7 days in 1000 cm^3 beaker containing 500 cm^3 of ethanol. The mixture were first sieve with muslin cloth, the liquid obtained were subsequently filtered using Whatman No 1 filter paper and the filtrate was then_concentrated using a water bath until a solid residue was obtained at 60^{o}C.

The percentage yield of plant extract was found to be 7.25% for LCL. The stock solutions of the extracts so obtained were used in preparing different concentration of the extract ranging in from 1- 5g/l of the inhibitor.

Paint Preparation

WW rosin type resin (colophony) was used as a binder and oleic acid as the plasticiser. The paint was prepared by using a magnetic stirrer to blend all the ingredients together and also to achieve an efficient dispersion. WW rosin and oleic acid were dissolute in a xylene/white spirit mixture (1:1) by using a high speed disperser. They were then mixed with the pigments and additives (zinc oxide and calcium carbonate), and dispersed for 24 hours (Norsworthy, R. (2014). The paints were diluted with different concentrations of *luffa cylindrica (sponge)* leaf extract. The specimens (pipeline steel) were then coated with epoxy-based paint with the aid of paint brush until a uniform surface was obtained. There are five types of paints used in this study, in which Paint 1 without luffa fruits extract (zero inhibitor) acts as the control paint. Besides that, there are Paint 2, Paint 3, Paint 4 and Paint 5 incorporated with different concentration of *luffa cylindrica (sponge)* leaf extract.

Weight Loss Measurements

Pre-weighed and polished Pipeline steel coupons were totally immersed in six 150 ml beakers with the ame quantity of the test solution with and without the aqueous extract of *Luffa aegyptiaca (sponge gourd)* leaf *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 303k, 313k and 333k to determine the thermodynamics of corrosion process. Also, these methods have been severally reported (Nunez, L (2005)).

The weight loss, degree of surface coverage (θ), 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)

The fractional surface coverage

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

Where: W_o = corrosion rates in the absence of inhibitor; W_f = corrosion rates in the presence of inhibitior.

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

Where A = Total surface area of the coupon immersed in solution, K = length of coupon, M = Width of coupon,

Corrosion Rate, Inhibition Proficiency and Surface Coverage

(d). The Corrosion inhibition efficiencies

$$(\%IE) = 1 - \frac{Wi}{Wo} \quad (4)$$

Where: W_o and Wi 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).

$$\text{(f) Half Life } (t_{1/2}) = \frac{0.693}{k} \quad (6)$$

(g)Rate Constant

$$(K) = \frac{2.303}{Time} \log \frac{w_1}{w_2} \quad (7)$$

RESULTS AND DISCUSSION

Weight Loss, Corrosion Rate, Inhibition Efficiency and Surface coverage and effect of Temperature: The effect of different

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concentration of the extract of Luffa cylindrical leaf extract on pipeline steel in 0.5M HCl and Pipeline water were 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- 5

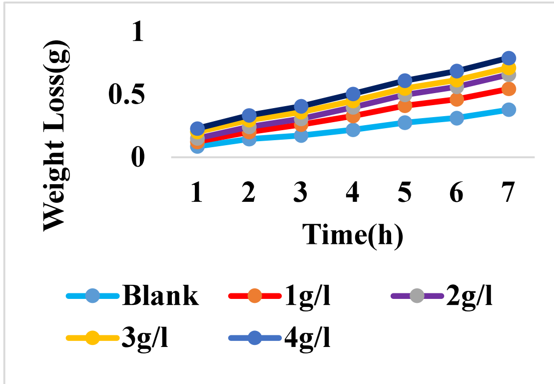

Figure 1: Plot of weight loss against time for pipeline steel corrosion in 0.5 M HCl with different concentrations of Leaf extract at 303 K.

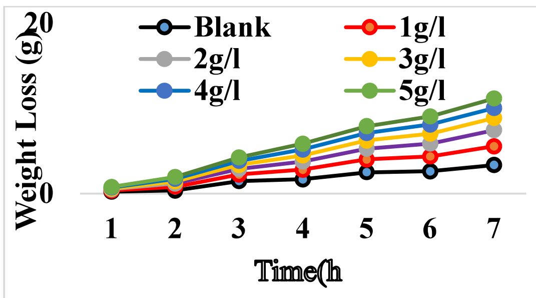

Figure 2: Plot of weight loss against time for pipeline steel corrosion in 0.5 M HCl with different concentrations of Leaf extract at 313 K.

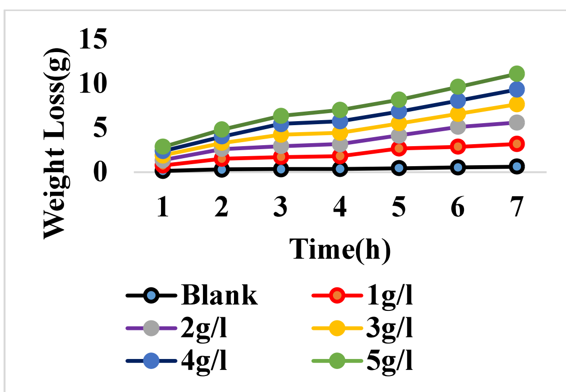

Figure 3: Plot of weight loss against time for pipeline steel corrosion in 0.5 M HCl with different concentrations of Leaf extract at 333 K.

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 in both acidic media and pipeline water. The least weight loss was recorded at 5 g/L extract concentration and inhibition efficiency of 74.89% in HCl and 97.39

% in Pipeline water. This behaviour of flora extracts in steel corrosion in acid and pipeline water environment has been previously reported (Madufor *et al.,* 2013, Ejikeme *et al.,* 2015).

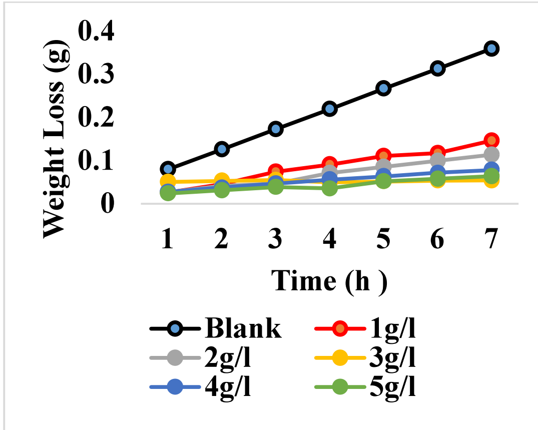

Figure 4: Plot of weight loss against time for pipeline steel corrosion in pipeline water with different concentrations of luffa cylindrica leaf at 303 K.

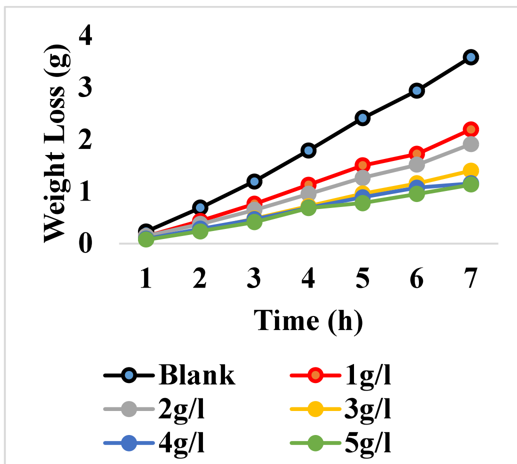

Figure 5: Plot of weight loss against time for pipeline steel corrosion in pipeline water with different concentrations of luffa cylindrica leaf at 313 K

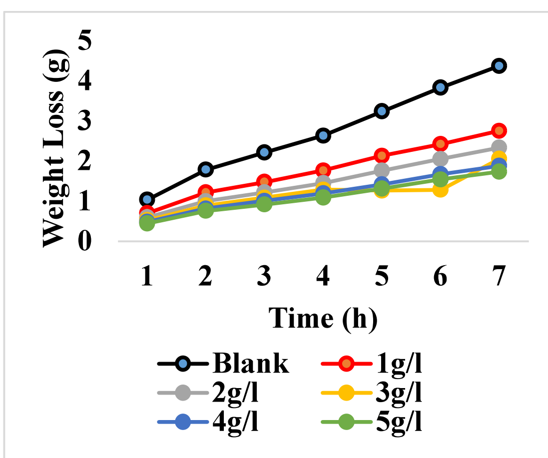

Figure 6: Plot of weight loss against time for pipeline steel corrosion in pipeline water with different concentrations of luffa cylindrica leaf at 333 K

Scientia Africana, Vol. 25 (No. 1), February, 2026. Pp 123-140
 ISSN 1118 – 1931

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 pipeline steel in acidic and pipeline water environment, reducing the efficacy of the extract in inhibiting corrosion. However, there is a balance of the increased oxidation of the iron in acid and pipeline water environment and the inhibitive action of the Luffa Cylindrica extract at higher temperature. The constituents of luffa cylindrica 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 1-2. The overall consequence is increased corrosion rate at higher temperature though the extract still shows active inhibitive presence.

Table 1-2. Corrosion rate, Inhibition efficiency and degree of surface coverage deduced from weight loss measurements in HCl and Pipeline water for Luffa cylindrica extracts.

Conc.(s) of Luffa Leaf (g/l)	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
Paint (blank)	1.854	1.866	2.037	-	-	-			
Paint 1	0.509	0.530	0.543	75.01	80.97	71.521	0.750	0.810	0.715
Paint 2	0.049	0.056	0.346	97.59	81.32	72.422	0.976	0.813	0.724
Paint 3	0.049	0.049	0.338	97.61	81.79	72.551	0.976	0.818	0.726
Paint 4	0.048	0.048	0.323	97.64	82.59	72.690	0.976	0.826	0.727
Paint 5	0.044	0.047	0.306	98.99	83.51	72.760	0.977	0.835	0.728

Table 1: Corrosion rate, Inhibition efficiency and degree of surface coverage values deduced from weight loss measurements in HCl solution with luffa leaf extracts.

Conc.(s) of Luffa Leaf (g/l)	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
Paint (blank)	2.782	2.868	3.391	-	-	-			
Paint 1	0.731	0.789	0.891	73.71	73.73	72.47	0.737	0737	0.723
Paint 2	0.720	0.783	0.885	73.90	74.10	72.71	0.739	0.741	0.727
Paint 3	0.712	0.774	0.874	74.22	74.41	73.01	0.742	0.744	0.730

Paint 4	0.710	0.766	0.858	74.70	74.47	73.28	0.747	0.745	0.733
Paint 5	0.709	0.741	0.851	74.89	74.51	74.16	0.749	0.745	0.742

Table 2: Corrosion rate, Inhibition efficiency and degree of surface coverage values deduced from weight loss measurements in Pipeline water with luffa leaf extracts.

Adsorption Study

Table 1-2 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 HCl and in Pipeline water in the presence of LC-fruit 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).

Exp (-2aθ) = KadsC (8)

-2aθ =InK_{ads}+ InC (9)

θ = (1/2a) Log K_{ads} – (1/2a) lnC (10)

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}C and 60^{O}C are shown in Figure 7-8; and coefficients (R^2) value greater than 0.923 in HCl and 0.954 in Pipeline water shown in Table 3. 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.

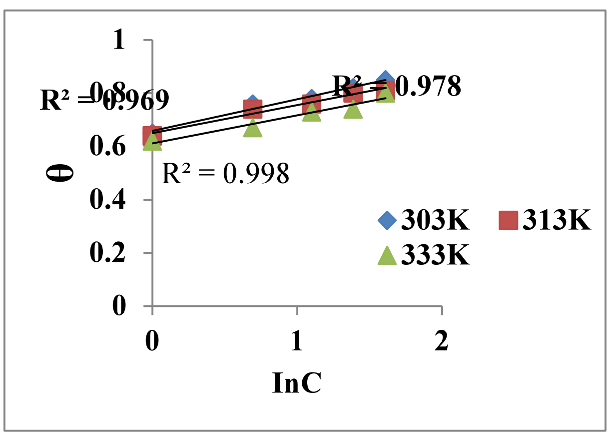

Figure 7: Temkin adsorption isotherm for pipeline steel corrosion in 0.5M HCl with Luffa leaf extract at 303 K, 313 K and 333 K

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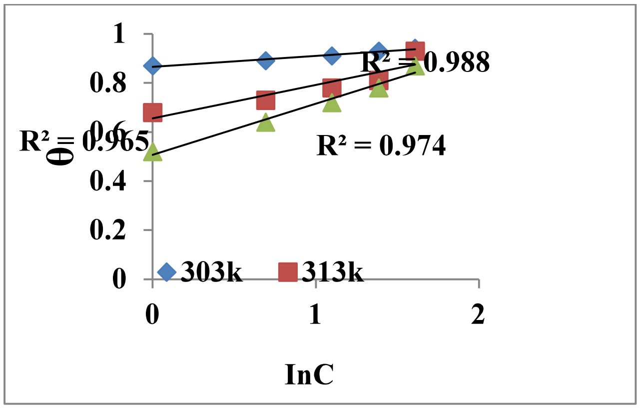

Figure 8: Temkin adsorption isotherm for pipeline steel corrosion in pipeline water with Luffa leaf extract at 303 K, 313 K and 333 K

Table 3: Some parameters of the linear regression between θ and In C.

Tem (K)	HCl Leaf			Luffa leaf extract in pipeline water		
	K_{ads}	A	R^2	K_{ads}	A	R^2
303	0.751	0.730	0.923	0.782	0.752	0.999
313	0.874	0.851	0.945	0.894	0.866	0.966
333	0.973	0.967	0.942	0.984	0.977	0.975

Figure 9-10; shows the linear plot of C/θ against C obtained by Langmuir adsorption isotherm equation as shown:

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \qquad (11)$$

Where: K is the equilibrium constant, C is the concentration of the extracts and θ is the degree of surface coverage. The LC leaf 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. This Isotherms are commonly used to model adsorption processes. Langmuir isotherm assumes monolayer adsorption on a homogeneous surface, while Temkin isotherm accounts for adsorbent-adsorbate interactions. Using both helps determine the adsorption mechanism and surface characteristics. The values of ΔG^o_{ads} are all negative ranging from -10.680 and 10.780kJmol^{-1} in HCl medium and -10.691 and -10.786kJmol^{-1} in Pipeline water. The values of ΔG^o_{ads} are often used to suggest either chemisorptions, physiosorption or both adsorption modes.

Physiosorption 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^oads around 20kJmol^{-1} or less implies physiosorption while around 40kJmol^{-1} or greater suggest chemisorptions.

However, the values of ΔG^o_{ads} obtained as showed in Table 4 are less negative than -20kJmol^{-1}, suggesting physiosorption mechanism. Plots of ΔG^o_{ads} against T are shown in figure 11 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 - 1.95 and -64 $kJmol^{-1}$ in HCl and -1.98 and -68$kJmol^{-1}$ in pipeline water.

Con (g/l)	Luffa leaf extract in pipeline water					HCl Leaf				
	E_a ($kJmol^{-1}$)	ΔH*($kJmol^{-1}$)	ΔS*(Jmol-1)	R^2(Arrhenius)	R^2(Transition)	E_a($kJmol^{-1}$)	ΔH*($Kjmol^{-1}$)	ΔS*($Jmol^{-1}$)	R^2(Arrhenius)	R^2(Transition)
Paint (blank)	43.72	40.46	-102.08	0.950	0.925	43.60	40.34	-102.24	0.930	0.915
Paint 1	44.91	44.47	-98.89	0.998	0.996	44.90	43.52	-100.23	0.996	0.996
Paint 2	46.59	45.68	-96.56	0.965	0.967	46.09	45.46	-96.42	0.947	0.957
Paint 3	48.67	48.97	-94.82	0.973	0.968	47.65	48.97	-93.71	0.972	0.936
Paint 4	51.98	52.67	-91.56	0.987	0.985	50.96	50.46	-90.46	0.986	0.986
Paint 5	52.87	54.55	-90.78	0.988	0.989	52.67	53.65	-90.17	0.988	0.988

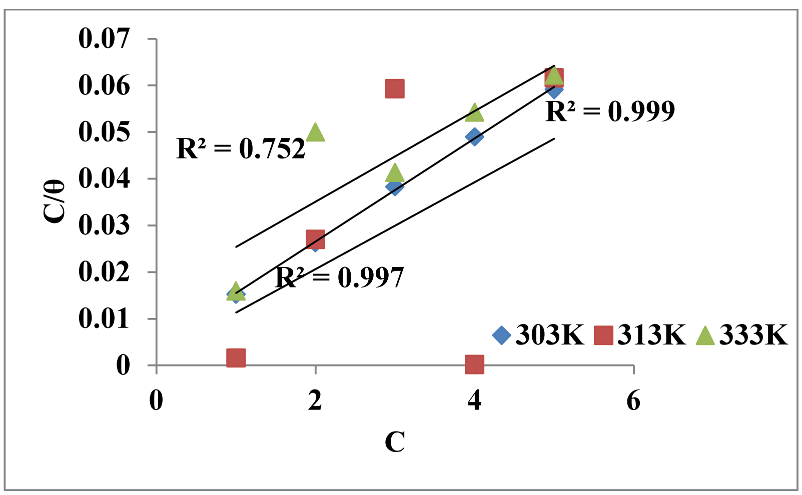

Figure 9: Langmuir adsorption isotherm of pipeline steel in 0.5M HCl with Luffa leaf extract at 303 K, 313 K, and 333 K.

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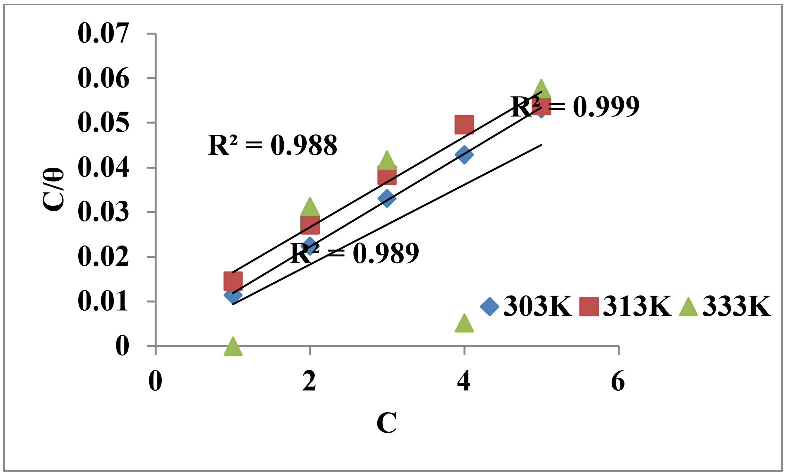


Figure 10: Langmuir adsorption isotherm of pipeline steel in 0.5M pipeline water with Luffa leaf extract at 303 K, 313 K, and 333 K

Table 4: Calculated parameters from Langmuir adsorption isotherm plot for pipeline steel in 0.5M HCl of the extracts.

Temp(K)	HCl Leaf				Luffa fruit extract in pipeline water compared			
	K_{ads}	ΔG_{ads}	Slope	R^2	K_{ads}	ΔG_{ads}	Slope	R^2
303	1.172	-10.680	0.95	0.845	1.172	-10.691	0.97	0.858
313	1.156	-10.766	0.98	0.990	1.156	-10.768	0.98	0.991
333	0.896	-10.780	0.99	0.995	0.896	-10.786	0.99	0.996

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

$$\Delta G^o_{ads} = \Delta H^o_{ads} - T\Delta S^o_{ads} \qquad (12)$$

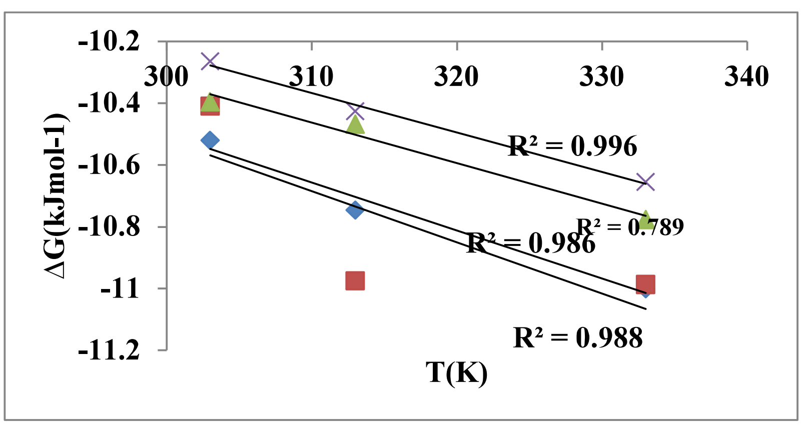


Figure 11: Freundlich Isotherm plot of ΔG^o_{ads} against T (K) for the adsorption of Luffa Fruit extracts in HCl acid medium and pipeline water

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.

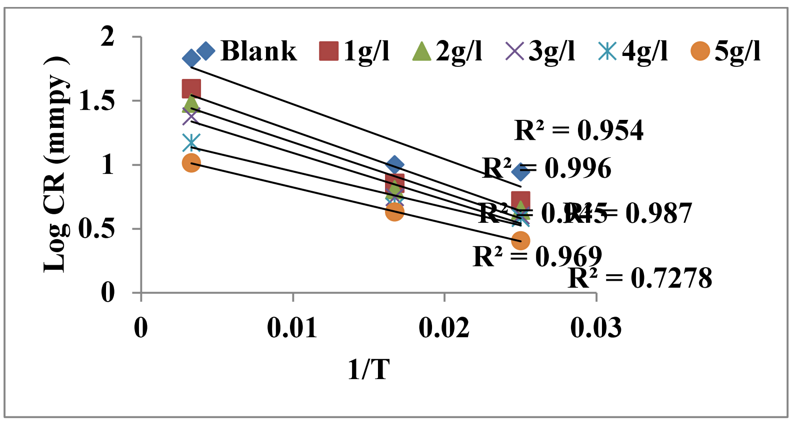
Kinetic and Thermodynamic Parameters

The values were obtained by Arrhenius equation shown below:

$$\log CR = \log A - \left(\frac{Ea}{2.303\,RT}\right) \qquad (13)$$

$$\log\frac{CR}{T} = \left[\left(\frac{R}{Nh}\right) + \left(\frac{\Delta S*}{2.303R}\right)\right] - \frac{\Delta H*}{2.303RT} \qquad (14)$$

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 12-13, while ΔS^* and ΔH^* where gotten from the intercept and slope of the plot of log CR/T against I/T shown in figure 14-15. Generally, physiosorption 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).

Figure 12: Arrhenius plot in the absence and presence of different concentrations of Luffa leaf extract in HCl

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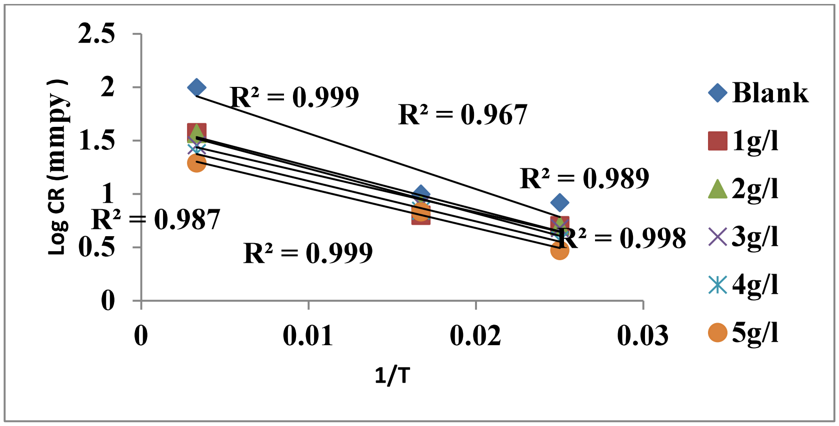

Figure 13: Arrhenius plot in the absence and presence of different concentrations of Luffa leaf extract in pipeline water

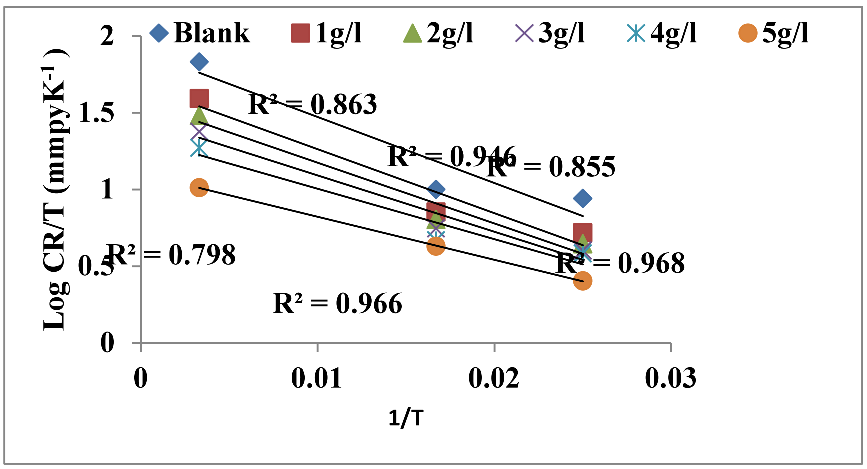

Figure 14: Transition state plots of pipeline steel in the absence and presence of different concentrations of Luffa leaf extract in 0.5M HCl

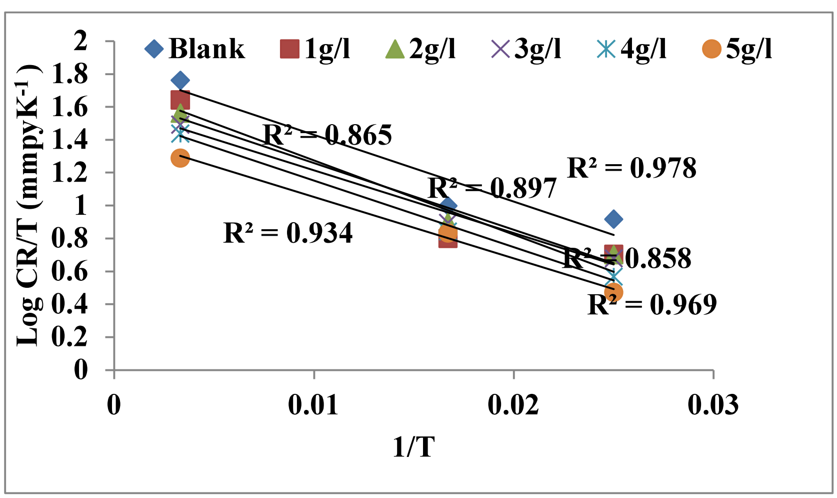

Figure 15: Transition state plots of pipeline steel in the absence and presence of different concentrations of Luffa leaf extract in pipeline water

Table 5: Activation parameters for pipeline steel in 0.5M HCl and Pipeline water

Con	Luffa leaf extract in pipeline water					HCl Leaf				
(g/l)	E_a (kJmol^{-1})	ΔH* (kJmol^{-1})	ΔS* (Jmol-1)	R^2 (Arrhenius)	R^2 (Transition)	E_a (kJmol^{-1})	ΔH* (Kjmol^{-1})	ΔS* (Jmol^{-1})	R^2 (Arrhenius)	R^2 (Transition)
Paint (blank)	43.72	40.46	-102.08	0.950	0.925	43.60	40.34	-102.24	0.930	0.915
Paint 1	44.91	44.47	-98.89	0.998	0.996	44.90	43.52	-100.23	0.996	0.996
Paint 2	46.59	45.68	-96.56	0.965	0.967	46.09	45.46	-96.420	0.947	0.957
Paint 3	48.67	48.97	-94.82	0.973	0.968	47.65	48.97	-93.71	0.972	0.936
Paint 4	51.98	52.67	-91.56	0.987	0.985	50.96	50.46	-90.46	0.986	0.986
Paint 5	52.87	54.55	-90.78	0.988	0.989	52.67	53.65	-90.17	0.988	0.988

FT- IR Studies of surface film of pure LC-Leaf and LC-Leaf on pipeline steel surface in HCl and Pipeline water: This method was used to identify the functional group (s) in the extracts involved in the adsorption process, by measuring infrared radiation absorption.

Sample Preparation: The sample was prepared by grinding it into a fine powder and mix with KBr (potassium bromide) to form a pellet.

Scanning: The prepared sample is then placed in the FTIR spectrometer, and infrared radiation was passed through it. The spectrometer measures the absorption of radiation by the sample at different wavelengths.

Spectrum Generation: The result is a spectrum showing the percentage transmittance (%T) or absorbance (A) of the sample versus wavenumber (cm^{-1}).

Analysis: The spectrum is the analysed to identify the functional groups present in the sample. This was done by matching the absorption peaks to know absorption frequencies of different functional groups, such as O-H, C=O or C-H bonds.The projecting spectra peaks provided evidence of the functional groups in the complex. After adsorption for a particular period of time, peaks were either vanished or are less prominent due to the participation of the functional group(s) in adsorption. Three adsorption spectrum were obtained which look very much alike but with little differences. The pure extract spectrum are shown figure 16a, The FT-IR spectra of the surface film on pipeline steel in the absence and presence of LC-leaf extract are presented in Figures16a-16c. The functional group(s) in the extract involved in the adsorption process were identified using this method. Before the some striking differences. The pure LC-leaf extract spectra have the range of values of 3290-1022, the leaf extract on pipeline steel coupon environment. 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 LC-leaf and LC-leaf on

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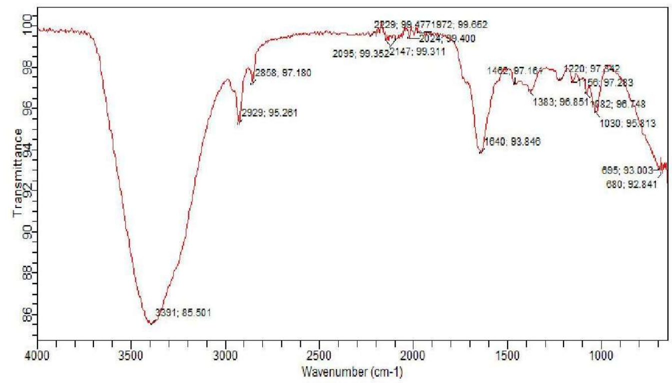

Figure 16a: FT-IR spectrum of pure pericarp extract

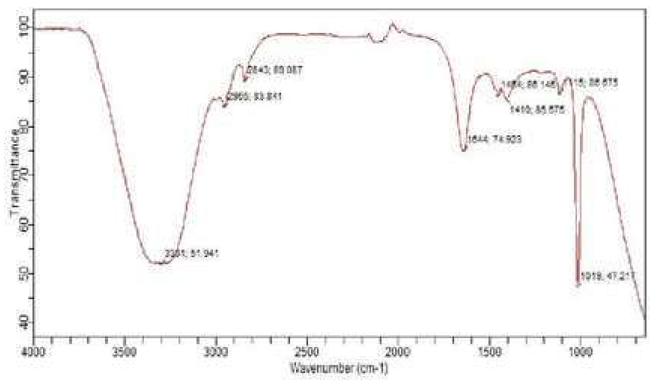

Figure 16b: FT-IR spectrum of LCL surface film after pipeline steel immersion in 0.5 M HCl solution with extract.

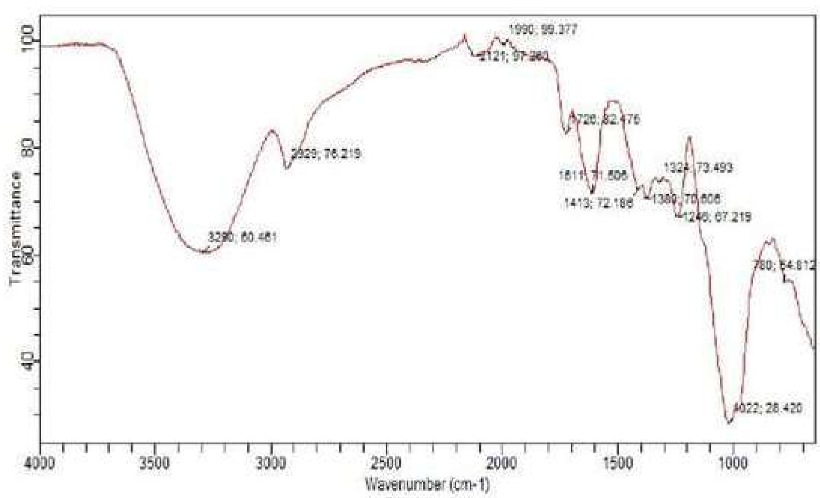

Figure 16c: FT-IR spectrum of LCL surface film after pipeline steel immersion in 0.5 pipeline water solutions with extract

Figure 13, compared to the absence of the extract for leaf extract with the coupon in HCl and Pipeline water, 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 OH stretch. The peak at 717 confirms C-H stretching (aromatic triple boded compound) while at 672 represent C-H stretching (aromatic compound).

CONCLUSION

Luffa cylindrica leaf extracts were tested for inhibition of pipeline steel corrosion in 0.5M HCl acid medium and pipeline water solution. The results obtained showed good corrosion inhibition activity of the extract. The inhibition values increase with increasing concentration of leaf 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 obeys the Langmuir adsorption isotherm. The LC-leaf extract acted as a good inhibitor of pipeline steel corrosion in 0.5 M HCl medium and with a higher value in pipeline water solution.

Competing Interests

Authors have declared that no competing interests exist.

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