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Effect of Green Corrosion Inhibitors on the Corrosion of Mild Steel C-1026 Pipeline in Seawater

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ABSTRACT *This study is about the corrosion inhibition of Mild Steel C-1026 behaviour in Seawater and soil environment using green inhibitors and weight loss method. The green plant extracts were Scent Leaf (SL) (Ocimum gratissimum), Cassava Leaf (CL) (Manihot Esculenta) and Neem Leaf (NL) (Azadirachta Indica). Some quantity of pineapple juice was added to boost inhibition effect on the MS surfaces. Parameters investigated include Weight Loss, Corrosion Rate, Inhibition Efficiency, pH analysis, Brinell Hardness test, Surface Roughness, Scanning Electron Microscopy, Potentiodynamic Polarization measurement and Fourier Transform Infrared Spectroscopy. The study revealed that the green plant extracts exhibited good inhibition efficiency on the Mild Steel C-1026. Neem Leaf was considered to have the maximum inhibition efficiency. Corrosion rate was reduced with the addition of green plant inhibitors. Furthermore, they affected the hardness and surface roughness of the Mild Steel surfaces. The results show that the chemical complexes in the green plant leave possess some inhibitive properties on oil and gas pipeline.*

KEY WORDS: *Chemical complex, Corrosion, Corrosion inhibitor, Mild Steel, Green plant leaves.*

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I. INTRODUCTION

Seawater is an environment where in most cases oil and gas pipeline transverses. Seawater is corrosive because it comprises some ions such as Chloride ion [1]. Transportation of oil and gas underground from the production site to the central processing base is through pipeline. Mild Steel is utilized for the fabrication of oil and gas pipelines which are predisposed to corrosion. Corrosion is the gradual dissolution of a metal by a slow chemical or electrochemical reaction between the metal and its environments. From previous investigations, soil is observed to be the most common cause of corrosion on underground pipeline [2,3,4,5]. Consequent upon the fact that soil is corrosive, various soils in three different locations in Bayelsa State were collected to characterize corrosivity area on pipeline in the state [2,8]. Corrosion is a cancer on metal due to thermodynamic instability [2,6,7]. However, threat by corrosion on oil and gas pipeline ought to be mitigated. In order to achieve this objective, inhibitor shall be employed. Inhibitor is a constituent when added in small concentration decreases the effective corrosion rate [2,8]. Previously, inorganic compounds were used as corrosion inhibitors in industry and they were predominantly composed of nitrogen, oxygen and sulphur atoms. Adsorption of the compounds onto the metal surface are faster with inhibitors that contain double or triple bonds [2,9,10]. Inorganic compounds like phosphates, chromates, dichromate and arsenates are discovered as effective inhibitors but they are highly toxic [2,12]. Green plant extracts are environmentally benign, readily available, ecologically acceptable and less costly which are unlike the inorganic compounds [2,11,12]. This study decided to investigate three green plant leaves; Ocimum gratissimum, Manihot Esculenta and Azadirachta indica behavourial characteristics of Mild Steel C-1026 in a predominately Seawater environment.

II. MATERIALS AND METHOD

ASTM G13 standard was used for the investigation. It is a recommended standard practice for laboratory immersion corrosion testing of materials [2,13].

Mild Steel grade C-1026 coupons of oil and gas pipeline were applied for the investigation throughout as control and inhibited samples. Seawater was the corrosive medium; Ocimum gratissimum, Manihot Esculenta and Azadirachta Indica were the corrosion inhibitors, while pineapple juice was added to boost inhibition effect on the MS surfaces. Plastic containers and ropes were used to suspend the coupons in the bath concentrations for the experiment. Tare M-200 electronic weighing balance was used to weigh the Mild Steel coupons before and after immersion in each experiment. Table 1 shows the elemental composition of the Mild Steel C-1026 utilized for the work [2].

Table 1: Elemental composition of the Mild Steel.

Element	Mn	Ti	As	Cu	Fe
Wt %	0.08	0.17	0.07	0.07	98.88

2.1 Sample Surface Preparation

The Mild Steel coupon surfaces were abraded with rough and smooth grit emery papers, rinsed in water, degreased in acetone, dried in air, weighed with a weighing balance and subsequently immersed in the test solutions for a period of 100 days or 2400 Hours [2].

2.2 Preparation of Leaf Paste Inhibitors

Fresh leaf inhibitors such as Ocimum gratissimum, Manihot Esculenta and Azadirachta Indica were gathered from Akenfa market and Agudama-epie forest in Bayelsa State, while the Seawater was collected from Furupa Community also in Bayelsa State. 31g each of the green plant leaves were weighed and thoroughly crushed with mortar and pestle, added with distilled water and filtered with filtration cloth. Thereafter, 150ml each of the leaf's solutions were added to 250ml of Seawater with addition of some quantity of pineapple juice [2].

2.3 Preparation of Mild Steel Coupons

Mild Steel C-1026 samples were cut into 4 x 2cm from cylindrical oil and gas of pipeline. These were abraded with emery papers, washed with acetone and subjected to the various bath concentrations for a period of 100 days or 2400 hours [2].

2.4 Preparation of Corrosive Media

250ml of Seawater was measured with calibrated cylindrical flask and poured into a plastic container.

2.5 Weight – Loss Analysis

The Mild Steel C-1026 coupons were first abraded with coarse and fine emery papers and treated with acetone. The initial weights of the coupons were obtained by using Tare M-200 electronic weighing balance before it was immersed in the corrosive medium with a specific concentration of inhibitors. Another bath was prepared as control for purpose of comparison.

The following formulae were used to compute the corrosion rate of the Mild Steel, MS coupons and inhibitor efficiency of the green plant extracts.

$$\text{Corrosion Rate, CR} = \frac{\text{K x Loss in weight (g)}}{\text{Surface Area x Period of immersion (Hours)of the specimen x Density of the Mild Steel.}} \quad 1$$

$$CR = \frac{\text{K (Wlost)}}{\text{AT}\rho}, = \frac{\text{K (W2}-\text{W1)}}{\text{AT}\rho}$$

Where, K is Constant, 87.6 and Density (ρ) of Mild Steel is 7.9 g/m, W_1 is Initial Weight and W_2 is Final Weight of coupons [2,6,12,13,14].

Corrosion Inhibition Efficiency, IE using the equation,

$$IE\ (\%) = 100\ \left[\frac{1-\text{W2}}{\text{W1}}\right]\% \quad 2$$

Where, W_1 is Weight Loss in the Absence of inhibitor and W_2 is Weight Loss in the Presence of inhibitor [2, 6,15,16].

2.6 Brinell Hardness Analysis

The Mild Steel C-1026 coupons were analysed with Mi-Tech MH180 instrument. The tip of the instrument was placed and stroke at three different positions to take the readings. The average of the readings was taken as the valid readings [2].

2.7 Surface Roughness Analysis

The Mild SteelC-1026 coupons were analysed with SRT 6100 Surface Roughness Tester instrument. Each coupon was test three times. The notches of the instrument were placed on the surface of each of the coupons. The reading continued until it clicked to stop. The readings were displayed on the glass screen of the instrument which was recorded as the surface roughness. This analysis was also conducted at Turret Engineering, Port Harcourt Rivers State. Fig. 5 shows the trend of surface roughness of the coupons in the absence and presence of corrosion inhibitors [2].

2.7 Electrochemical Potentiodynamic Polarization Measurement

This parameter was used to disclose the type of corrosion that took place in each of the coupons, whether it was anodic corrosion or cathodic corrosion or mixed corrosion as well as the type of corrosion inhibitors; anodic, cathodic or mixed inhibitor. It revealed the corrosion current intensity, Icorr and corrosion potential, Ecorr that might have taken place on the Mild Steel. CH Instrument Electrochemical Analyzer, CH604E Electrochemical Analyzer ⁻[1TAFel 1.bin] instrument was used for the analysis in University of Nigeria, Nsukka, Enugu.

2.8 Fourier Transform Infrared Spectroscopy

FTIR was carried out to show the functional group or type of compound present in a particular coupon. The FTIR analysis of the green plant leaves and those of the corrosion products (in the absence and presence of the inhibitors) were carried out using Carry-630 Agilent.

2.9 Scanning Electron Microscope Analysis

Scanning Electron Microscopy, SEM was used to determine the morphology of the various coupons. It was precisely employed to establish the disparity in surface morphology and microstructure of the inhibited and uninhibited coupons.

III.. RESULTS

3.1 Effect of immersion time on weight loss of the coupons for the different inhibitors.

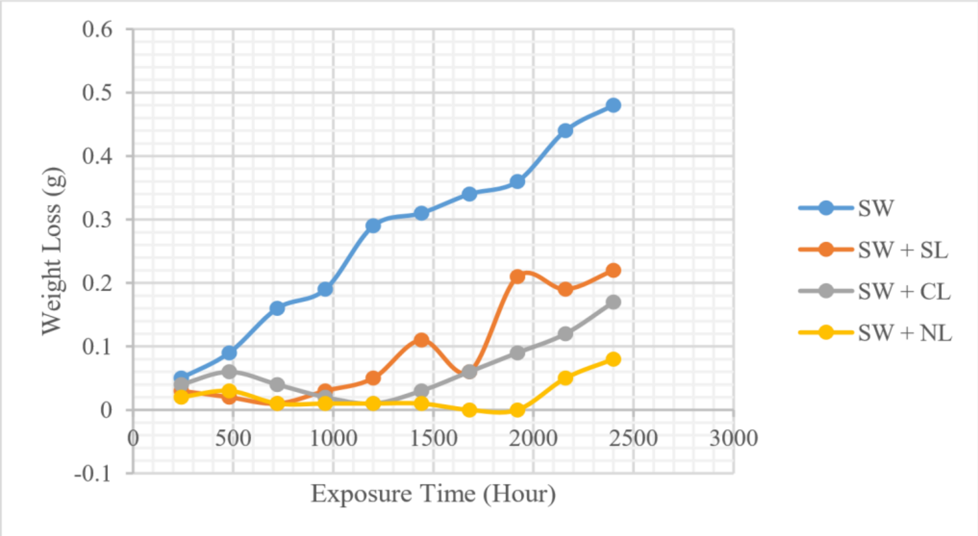

Figure 1: Effect of immersion time on weight loss of the coupons for the different inhibitors in Seawater

Fig. 1 shows the effect of exposure time on weight loss of both inhibited and uninhibited coupons. The results show that the coupons in Scent Leaf solution had average weight loss of 0.093g, Cassava Leaf coupon was 0.064g and Neem Leaf coupon had the least weight loss of 0.016g. However, there was decrease on weight loss in the presence of inhibitor as compared to the coupon in the Seawater solution with average weight loss value of 0.271g. It was evident that the disparity in weight loss for each of the coupons, the inhibitors may have exhibited some degree of passivation and surface coverage of the coupons. Weight loss gradually increased with increase in time.

3.2 Effect of immersion time on corrosion rate (CR) of Mild Steel C-1026 coupons with the different inhibitors

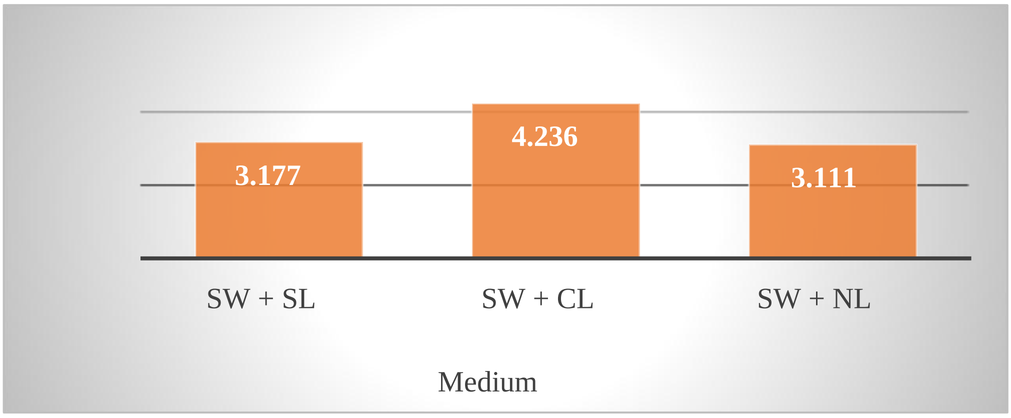

Figure 2: Average Corrosion Rate of Mild Steel C1026 in Seawater with different Corrosion Inhibitors.

Fig. 2 shows the effect of exposure time on corrosion rate of Mild Steel in seawater solution with different inhibitors. The investigation reveals that when the coupons were subjected to the Seawater and different inhibitors such as Scent Leaf, Cassava Leaf and Neem Leaf extracts for 100 days or 2400 hours, the coupon in Cassava Leaf solution had the highest Average Corrosion Rate of 4.236mpy, Scent Leaf 3.177mpy and Neem Leaf 3.111mpy. The Neem Leaf had the lowest value of Corrosion Rate. It was observed that Neem Leaf with low CR may be due to the high degree of adsorption of protective film of the complex chemical constituents in the plant extract on the coupon surface. Nevertheless, the way of inhibition is perhaps via adsorption of the inhibitor molecules onto the MS surface. According to Madawa *et al*., [2021] and Tuaweri and Ogbonnaya, [2, 12], the basis of inhibition is the adsorption of the phytochemical molecules in the plant on the surface of the metal consequent upon displacement of water molecules at the corroding surface. The rate of corrosion fluctuated with time might be due to the factors that influence the efficiency of inhibitor, such as temperature, water chemistry, surface condition of the steel, humidity, etc. [2,15].

3.3 Inhibition Efficiency (IE) for different inhibitors

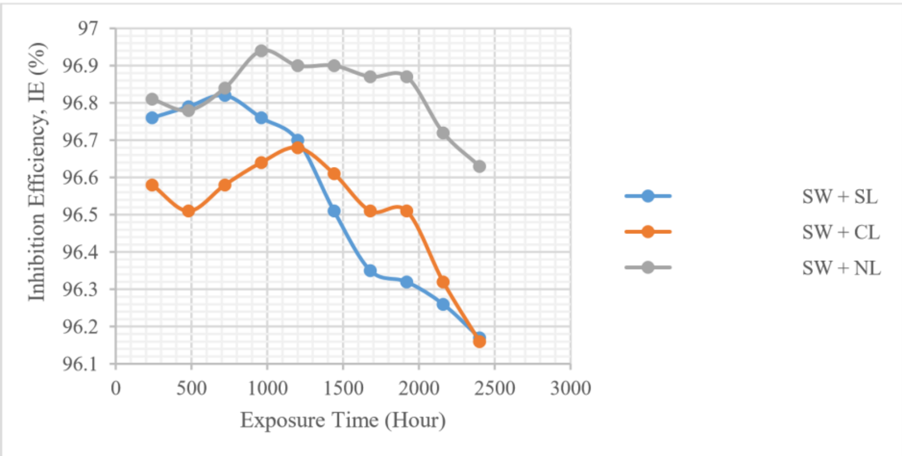

Figure 3: Corrosion Inhibition Efficiency (IE) of the coupons for the different inhibitors.

Fig. 4 shows that when the coupons were subjected to the SW containing different inhibitors for 2400 hours or 100 days, the coupons in NL solution had the highest Average Corrosion Inhibition Efficiency, E of 96.82%, SL was 96.54%, while coupon in CL had the least value of 96.51%. The NL was most efficiency because it contains tannin and has bitter taste. According to Lotto, 2003 [18], the corrosion inhibition efficiency of some plant extracts has been accredited to the presence of tannin in their chemical constituents in several cases [17]. Also related with the presence of tannin in the extracts is the bitter taste in the bark and/or leaves of the plants [16]. Neem is bitter in taste. The bitterness is owed to an arrangement of complex compounds called "triterpenes" or more precisely "limonoids" [18,20].

3.4 Phytochemical Analysis

Table 2 shows the result of Quantitative Phytochemical Analysis on the green plant extracts. It was evident that Tannin was abundant in Cassava and Neem leaf extracts, while Alkaloid, Tannin, Saponin, Flavonoid and Phenol was more in Scent Leaf, Cassava and Neem extracts, Alkaloid, Saponin, Flavonoid and Phenol was less in Scent Leaf, Cassava Leaf and Neem leaf, and there was none Phenol bioactive component in Neem leaf.

Table 2 Qualitative Method Analysis of Scent Leaf, Cassava Leaf and Neem Leaf

Sample	Alkaloid	Tannin	Saponin	Flavonoid	Phenol
Scent Leaf	+ +	+ +	-	+	+
Cassava Leaf	+	+ + +	+ +	+ +	+ +
Neem Leaf	+	+ + +	+	+ +	-

KEY: + = Less, + + = More, + + + = Abundant and **- = None**

3.5 Brinell Hardness Test

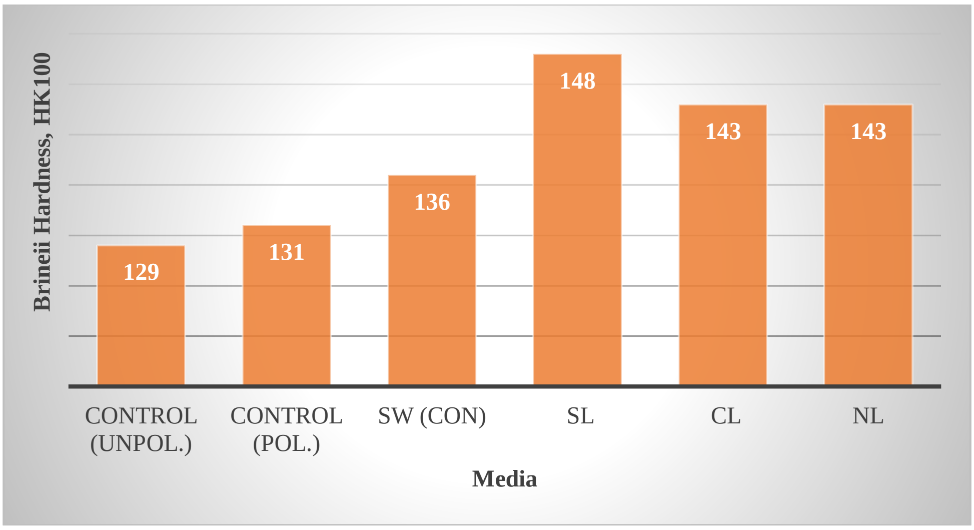

Figure 3: Brinell Hardness Test of Coupons.

Fig. 3 shows the hardness values of the coupons with or without inhibitors. The investigation reveals that the Control Sample (Unpolished) had the least hardness value of 129 HK_{100}, Control Sample (Polished) had 131HK_{100}, Seawater, SW had 136 HK_{100}, Cassava Leaf, CL and Neem Leaf, NL had the same value of 143HK_{100}, while SL had the highest value of 148HK_{100}. The Control Sample (Polished) having higher value than the Control Sample (Unpolished) might be evident to plastic deformation taking place during the polishing of the coupon. While Scent Leaf, SL having the highest value might be due to the coupon adsorbing much Scent Leaf chemical constituents.

3.6 Surface Roughness Analysis

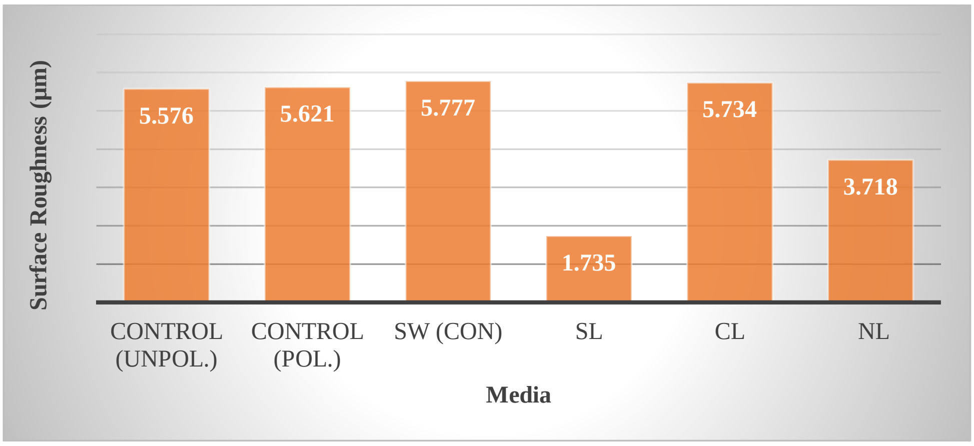

Figure 4: Surface Roughness Tests of Coupons

From the investigation, Fig. 4 reveals that SW (Con) had the highest surface roughness value of 5.777mµ, CL had 5.734mµ, Control sample (Pol) had 5.621mµ, Control sample (Unpol) was 5.576mµ, NL was 3.718mµ, while SL had the least roughness value of 1.735mµ. The SW (Con) having the highest surface roughness is probably because the macrocrystalline grain boundary is coarse which might be contributed to much corrosion on the coupon and it is without inhibitor, while the SL is evident to the microcrystalline grain boundary on the Mild Steel much dense because of adsorption of the inhibitor on the surface.

3.7 pH Analysis

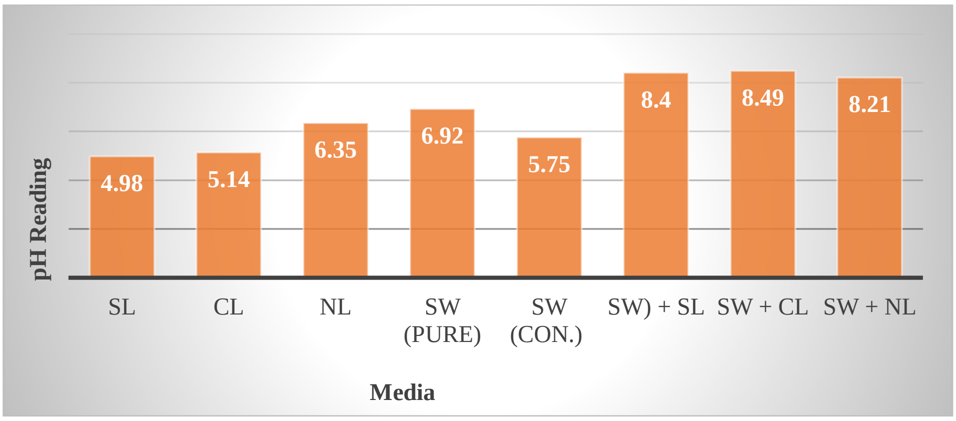

Figure 5: pH Analysis of Bath Concentrations

Investigation on the pH of the various Mild Steels on Fig. 5 shows that SL, CL, NL, SW (Pure) and SW (Con) solutions had the pH values less than 7 are acidic, while SL, CL and NL solutions had the pH values greater than 7 which are basic. Pure water is said to be neutral at pH 7, being neither an acid nor a base [18:19].

3.8 Electrochemical Potentiodynamic Polarization Measurement in Seawater

Seawater (SW)

The results obtained from the potentiodynamic polarization (anodic and cathodic) curve for the corrosion of Mild Steel in 250ml of Seawater solution in the absence of corrosion inhibitor is presented in Figure 8**.** The corrosion electrode potential (E_{corr}) was found to remain constant, while corrosion current density (Icorr) was found to increase. This proposes that Seawater behaves mainly as anodic corrosion.

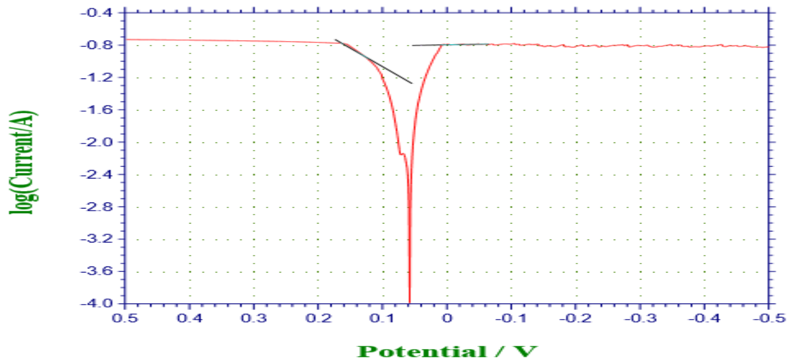

Figure 8: Potentiodynamic polarization curve for the Mild Steel in Seawater in the absence of inhibitor concentration.

Seawater (SW) solution in the presence of corrosion inhibitors

The results obtained from the potentiodynamic polarization (anodic and cathodic) curve for the corrosion of Mild Steel in 250ml of Seawater solution in the presence of Scent Leaf corrosion inhibitor is presented in Figure 9. The corrosion electrode potential (E_{corr}) was found to remain constant, while the corrosion current intensity (Icorr) was found to increase on addition of the 31g of corrosive inhibitor (Scent Leaf) into the Seawater solution. The values were shifted positively. This suggests that Scent Leaf extracts behave predominantly as anodic inhibitor. Similarly, potentiodynamic polarization (anodic and cathodic) curve for the corrosion of Mild Steel in 250 ml of Seawater solution in the presence of Cassava Leaf and Neem Leaf corrosion inhibitors are presented Figure 10 and 11. The corrosion electrode potentials (E_{corr}) were found to remain constant, while the corrosion current densities (Icorr) were found to decrease on addition of the 31g of corrosive inhibitor (Cassava Leaf and Neem Leaf) into the Seawater solution. The values were shifted negatively. This suggests that Cassava Leaf and Neem extracts behave predominantly as cathodic inhibitors.

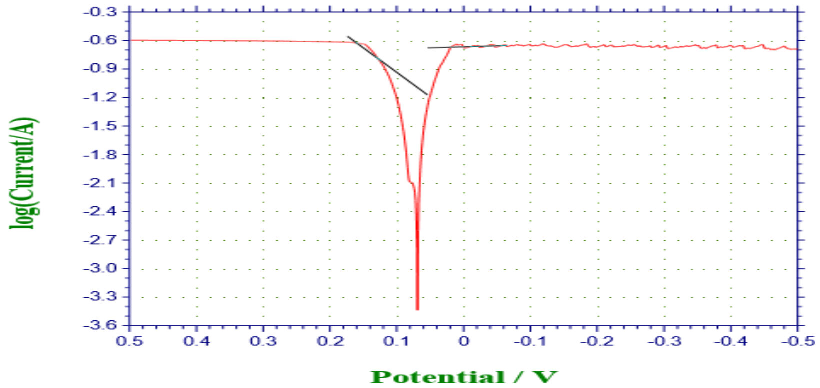

Figure 9: Potentiodynamic polarization curve for the Mild Steel in Seawater in the presence of Scent extract.

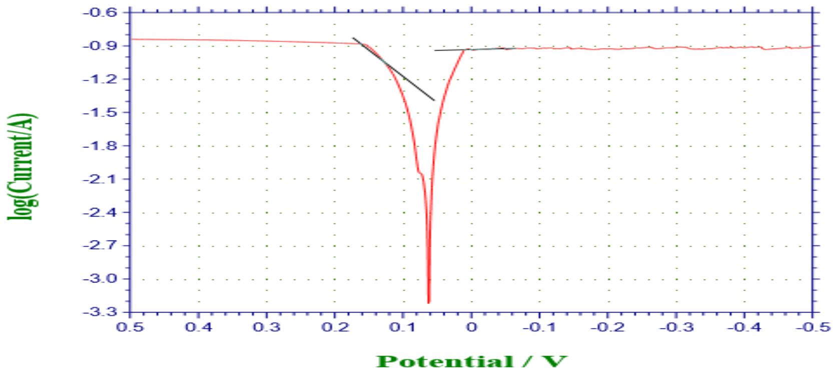

Figure 10: Potentiodynamic polarization curve for the Mild Steel in Seawater in the presence of Cassava extract.

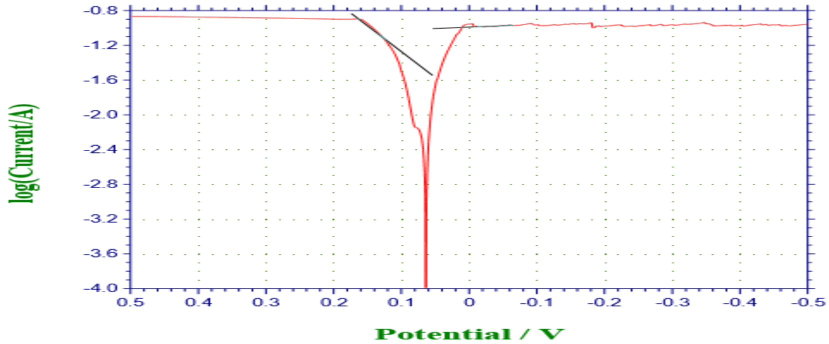

Figure 11: Potentiodynamic polarization curve for the Mild Steel in Seawater in the presence of Neem extract.

3.9 Fourier Transform Infrared Spectroscopy
Seawater (SW)

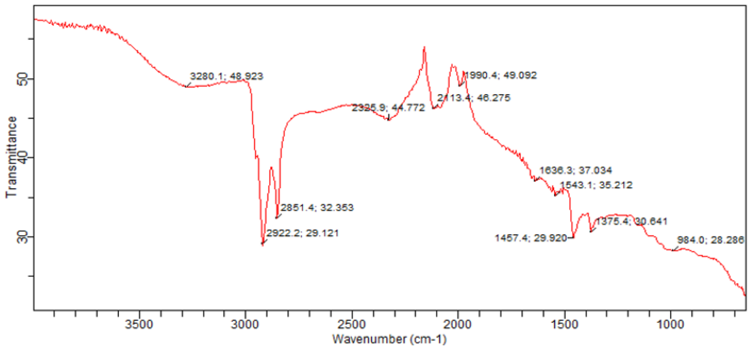

Figure 12: FTIR spectrum of film on Mild Steel surface in the absence of corrosion inhibitor in Seawater.

Fig.12 shows the FTIR spectrum of Seawater, SW corrosive media. Wave numbers and intensities of adsorption in terms of height of the different peaks, assembled from the FTIR spectrum of SW as well as vibration type and functional groups are presented in Figure 12. From the results obtained, C=C bending of alkene at 984.0 cm^{-1} and alkene, monosubstituted stretching at 1638.3 cm^{-1}, O–H phenol bending at 1375.4 cm^{-1}, stretching of hydrogen bonded carboxylic acids at 2922.2 and alcohol stretching at 3280.1 cm^{-1}, C–H bending of alkane, methylene group at 1457.4 cm^{-1}, N–O stretching of nitro compound at 1578.7 cm^{-1}, C=C=C stretching of alkene at 1990.4 cm^{-1}, N=C=S stretching isothiocyanate at 2113.4 cm^{-1}, N–H stretching of amine salt at 2851.4 cm^{-1}. **Seawater and Scent Leaf**

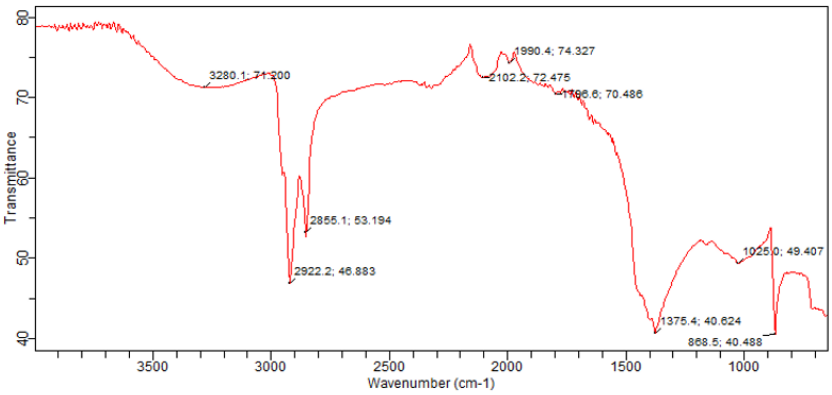

Figure 13: FTIR spectrum of film on Mild Steel surface after immersion in Seawater with Scent Leaf.

Fig. 13 shows the FTIR spectrum of Scent Leaf, SL extract as inhibitor in Seawater corrosive media. Wave numbers and intensities of adsorption in terms of height of the different peaks, collected from the FTIR spectrum of Seawater and Scent Leaf as well as vibration type and functional groups are presented in Figure 13. From the results obtained, C–H 1, 4 – disubstituted bending at 868.5 cm^{-1}, C–O stretching of primary alcohol at 1025.0 cm^{-1} and alkane stretching at 2855.1 cm^{-1}, O–H phenol bending at 1375.4 cm^{-1} and hydrogen bonded carboxylic acids stretching at 3280.1 cm^{-1}, C=O conjugated anhydride stretching at 1786.6 cm^{-1}, C=C=C alkene stretching at 1990.4 cm^{-1}, C≡C alkyne, monosubstituted stretching at 2102.2cm^{-1} and N–H amine salt stretching at 2922.2 cm^{-1}

Seawater and Cassava Leaf

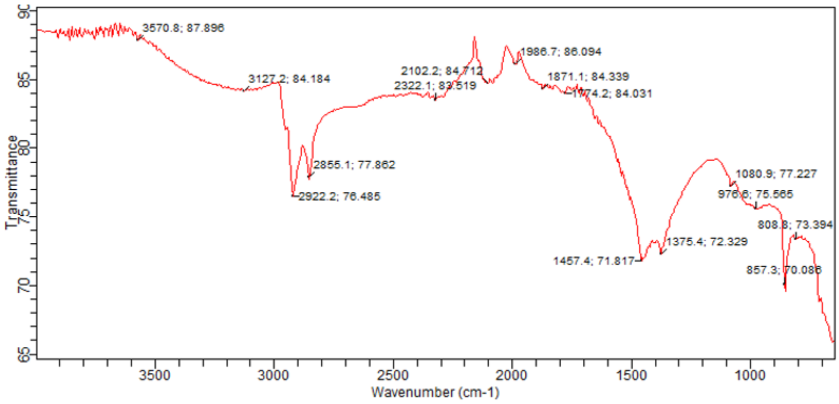

Figure 14: FTIR spectrum of film on Mild Steel surface after in Seawater with Cassava Leaf.

Fig.14 shows the FTIR spectrum of Cassava Leaf as inhibitor in Seawater corrosive media. Wave numbers and intensities of adsorption in terms of height of the different peaks, gathered from the FTIR spectrum of Seawater and Cassava Leaf, CL as well vibration type and functional groups are presented in Figure 14. From the results obtained, C–H 1, 4 – disubstituted bending at 808.8 cm^{-1}, 1, 3 – disubstituted bending at 857.3 cm^{-1}, alkane, methylene group bending at 1457.4 cm^{-1}, aromatic compound bending at 1871.1 cm^{-1} and alkane stretching 2865.1 cm^{-1}, C=C alkene, disubstituted (trans) bending at 976.6 cm^{-1}, C=O conjugated anhydride stretching at 1774.2 cm^{-1}, C=C=C alkene stretching at 1986.7 cm^{-1}, C≡C alkyne, monosubstituted stretching at 2102.2 cm^{-1}, O=C=O carbon dioxide at 2322.1 cm^{-1} and N–H amine salt stretching at 2922.2 cm^{-1}.

Seawater and Neem Leaf

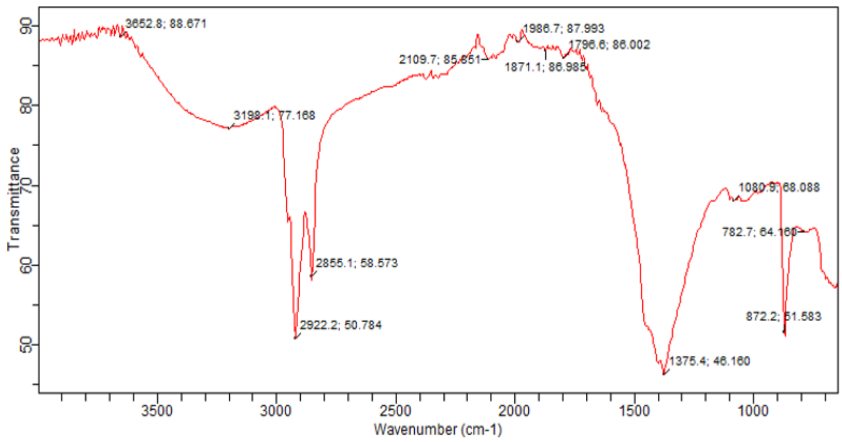

Figure 15: FTIR spectrum of film on Mild Steel surface after immersion in Seawater with Neem Leaf

Fig.15 shows the FTIR spectrum of Neem Leaf as inhibitor in Seawater corrosive media. Wave numbers and intensities of adsorption in terms of height of the different peaks, gathered from the FTIR spectrum of Seawater and Neem Leaf as well as vibration type and functional groups are presented in Figure 15. From the results obtained, C–H 1, 3 – disubstituted bending at 782.7 cm^{-1}, 1, 3 – disubstituted bending at 872.2 cm^{-1}, aromatic compound, overtone bending at 1871.1 cm^{-1} and alkane stretching 2855.1 cm^{-1}, C–O stretching of primary alcohol at 1080.9 cm^{-1}, O–H phenol bending at 1375.4 cm^{-1}, alcohol, intramolecular bonded stretching at 3198.1 cm^{-1} and alcohol, free, stretching at 3670.8 cm^{-1}, C=O conjugated anhydride stretching at 1786.8 cm^{-1}, C=C=C alkene stretching at 1985.7 cm^{-1}, C≡C alkyne, monosubstituted stretching at 2019.7 cm^{-1} and N–H amine salt stretching at 2922.2 cm^{-1}.

3.10 Microstructure or Morphological Studies

Figs show that in Seawater without inhibitor, the surface roughness on the coupon was very high. Cetin et al., 2009 [21] also affirmed to this factor. Deriving from the surface roughness analysis, Seawater coupon had

5.777µm, Scent Leaf coupon had 1.777µm, Cassava Leaf coupon had 5.734µm and Neem Leaf coupon had 3.718µm. This shows that the extracts inhibited corrosion on Mild Steel through adsorption of the inhibitor molecules on the surface [2, 22]. The Scent Leaf extracts molecules appear to have adsorb better yet Neem Leaf was observed to be the most efficient inhibitor probably due to its abundant tannin present. The reason why Seawater coupon corroded most is because of the presence of Cl^- ions in Seawater which is the main driving force of corrosion on MS [2, 12]. The presence of Chlorine in Seawater has much catastrophic effect on metals. As such, dipping them in Seawater causes loss in the metal quality and imminent failure.

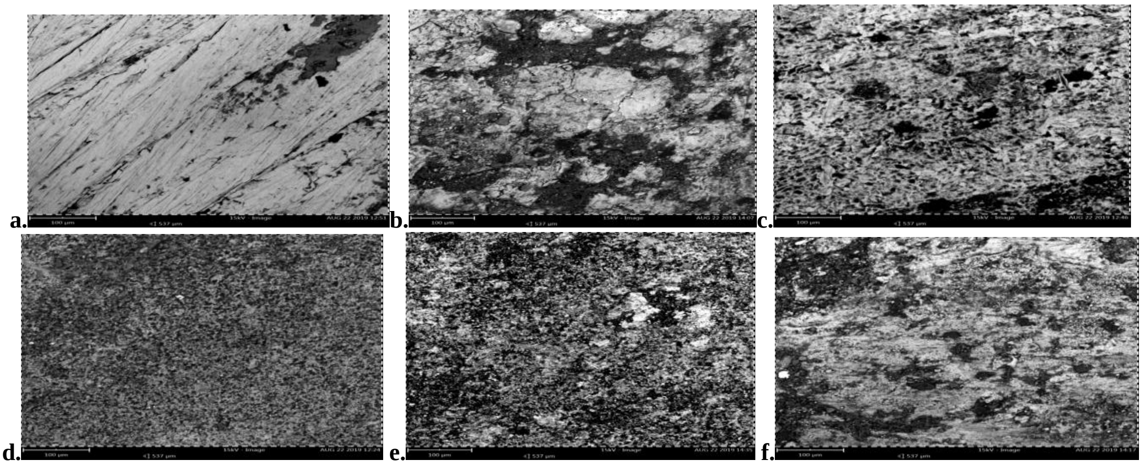

Figure 16:a. SEM analysis for Mild Steel (Polished) **b.** SEM analysis for the pure Mild Steel (Unpolished) **c.** SW **d.** SW and Scent Leaf **e.** SW and Cassava Leaf **f.** SW and Neem Leaf.

IV. CONCLUSION

The average weight loss of the coupons revealed that the Scent Leaf solution had the highest weight loss, while Neem Leaf had the least weight loss.

The corrosion rate was observed to increase on the coupon in the Cassava Leaf solution with the highest Average Corrosion Rate, CR of 4.236mpy.

The coupon in Neem Leaf solution had the highest Average Corrosion Inhibition Efficiency, IE of 96.82%.

The Brinell harness analysis revealed that the coupon in the Scent Leaf had the highest value of 148 HK_{100}, while the coupon Cassava Leaf, and Neem Leaves coupons had the least hardness value of 143 HK_{100}.

Surface Roughness analysis shows that Seawater coupon had the highest roughness value of 5.777 mµ, while Seawater and Scent Leaf had the least roughness value of 1.735 mµ.

The pH analysis disclosed that Scent Leaf, Cassava Leaf, Neem Leaf, Seawater (Pure) and Seawater (Con) solutions are acidic, while Scent Leaf, Cassava Leaf and Neem Leaf solutions are basic.

The SEM analysis indicates that there is adsorption of the protective film on the metal surface in the presence of the corrosion inhibitors as compared to the metal steel coupon in absence of inhibitor.

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