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Corrosion Inhibition Performance of Selected Green Plants and Their Blends on Stainless Steel in Cassava Pulp Filtrate

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ABSTRACT

A comparative study of the corrosion inhibition performance of Neem (NM) and bitter leaf (BL) extracts when used individually and in combined form (NMBL 1:1, NMBL 1:3 and NMBL 3:1) to mitigate the corrosion of stainless steel in cassava pulp filtrate was undertaken. The corrosion rates obtained in the presence of Neem (NM) extract were lower compared to corrosion rates obtained in environments containing blends of the extracts (NMBL 1:1, NMBL 1:3, NMBL 3:1). This implies that the inhibition efficiency of Neem (NM) extract was better than blends of Neem (NM) and bitter leaf (BL) in ratios of 1:1, 1:3 and 3:1. Also, the corrosion rates obtained in environments containing Bitter leaf (BL) extract are lower compared to corrosion rates obtained in environments containing blends of extracts (NMBL 1:1, 1:3 and 3:1). This is an indication that the corrosion inhibition performance of Bitter leaf (BL) extract is better than the blends of Neem (NM) and Bitter leaf (BL) in ratios of 1:1, 1:3 and 3:1. The adsorption of the extracts (Neem (NM), Bitter leaf (BL) and blend of Neem and Bitter leaf extracts in ratio of 1:3) obeyed Langmuir adsorption isotherm. The adsorption of the extracts (blends of Neem and Bitter leaf extracts in ratios of 1:1 and 3:1) did not obey Langmuir adsorption isotherm. The extracts inhibited the corrosion of the metal samples by physical adsorption.

KEYWORDS: Neem, bitter leaf, corrosion rate, adsorption, Inhibition.

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1. INTRODUCTION

An assessment of the traditional methods of processing cassava reveals that the problems of corrosion are very severe. Local processing of cassava produces a poisonous compound called hydrogen cyanide and also reduces the total cyanogen's content (Kendirim *et al.*, 2005). Hydrogen cyanide is very corrosive and is mostly responsible for the corrosion of most cassava processing equipment. The corrosive action of cassava fluid is mostly due to the cyanide ions whose concentrations vary due to genetic and environmental factors, location, season and soil type (JECFA, 1993). Several studies have been conducted to investigate the effect of cassava fluid on corrosion of metals and alloys. Jekayinfa *et al.* (2005) investigated the effect of cassava fluid on the corrosion performance of mild steel. The results showed that 0.36 % carbon steel was less affected by corrosion than 0.18 % carbon steel. According to Kareem (2009), mild steel is more susceptible to corrosion in cassava fluid, sodium chloride and distilled water than in lubricating oils and atmospheric air. Ofoegbu *et al.* (2011) investigated the corrosion behaviour of 304L stainless steel in Nigerian food processing environments. The results showed that the average corrosion rates of 304 stainless are: in ground melon (1.98×10^{-3} mpy); in cassava pulp (3.68×10^{-3} mpy); in mashed palm fruit (4.75×10^{-3}mpy) and in tomato (5.46×10^{-3}mpy).

Corrosion reduction in metallic materials used for the processing of cassava can be affected by the use of inhibitors. Alagbe (2009) studied the effect of some amino acid derivatives (leucine, alanine, methionine and glutamic acid) on the corrosion behaviour of NST-44 mild steel in cassava and lime fruits. The results revealed that the inhibitive power of the derivatives in cassava solution followed the order; alanine > leucine > methinonine > glutamic acid. Amuda *et al.* (2006) studied the effects of two inorganic inhibitors (zinc oxide and sodium sulphite) on the corrosion behaviour of mild steel in cassava

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extract. The corrosion rate averaged 0.0799 mm/yr and 1.1841 mm/yr in the presence of zinc oxide and sodium sulphite inorganic inhibitors respectively. Extracts of neem and bitter leaf successfully mitigated the corrosion of stainless steel in cassava extract (Elachi *et al*., 2016).

This work now focuses attention on the comparative analysis of Neem and Bitter leaf extracts when used individually and in combined form to mitigate the corrosion of stainless steel in cassava pulp filtrate. Also, to study the effect of exposure time on the corrosion of stainless steel in cassava pulp filtrate.

2. MATERIALS AND METHODS

2.1 Materials

The materials used for this work are fully described in Elachi *et al.* (2016).

2.2 Methods

2.2.1 Processing of plant materials

Neem (NM) leaves were obtained from a Neem tree at the premises of University of Agriculture, Makurdi, Benue State. Bitter leaves (BL) were procured from a farm at the bank of River Benue. The leaves were separately washed with distilled water to remove dust and sand particles. The washed leaves were shade dried for two weeks. The leaves were then separately converted into powder and stored in air tight containers.

2.2.2 Preparation of blend of extracts

Powdered samples of Neem and Bitter were combined in the ratios of 1:1 (i.e 30 grammes of Neem and 30 grammes of Bitter leaf); 1:3 (i.e 15 grammes of Neem and 45 grammes of Bitter leaf) and 3:1(i.e 45 grammes of Neem and 15 grammes of Bitter leaf.). The powdered samples of Neem and Bitter leaf combined in the ratios of 1:1, 1:3 and 3:1 were placed in three round bottom flasks. 1000 mL of distilled water was added to each flask containing the samples. The resulting mixture in each flask was boiled for two hours. After boiling, the mixtures in the flasks were allowed to cool completely in open air. After cooling the content of each flask was filtered using a filter paper. The filtrates were taken as the stock solutions.

2.2.3 Phytochemical analyses of blends of plant extracts.

Phytochemical analyses of the blends of plant extracts were carried using methods as described by Onwuka (2005), Aliyu *et al.* (2008), and Ademorati (1996).

2.2.4 Preparation of corrosion test specimens (coupons)

Corrosion test specimens each of dimension 79 mm × 25 mm × 3 mm were produced from a stainless-steel sheet with percentage chemical composition of 70.6 Fe, 0.054 C, 0.28 Si, 9.96 Cr, 6.60 Ni, 0.095 Mo, 0.0107 Cu, 0.113 Co, 0.023 P, 0.08 Va and 0.0019 Ca (Elachi *et al.*, 2016). A 3 mm diameter hole was drilled on each specimen to facilitate easy suspension and withdrawal from the environment. The test specimens were finely polished with abrasive papers followed by washing with deionized water and drying. The dried samples were weighed to obtain the initial weight of the test specimens. The percentage chemical composition of the stainless-steel sheet is:

2.2.5 Preparation of Corrosion medium

The method used by Elachi *et al.* (2016) was adopted for the preparation of the corrosion medium. The bitter variety of cassava roots obtained from a farm in Makurdi, Benue State were peeled and sliced into smaller pieces. The sliced roots were washed thoroughly in water to remove sand particles. Fourty- five thousand grammes of the sliced roots were measured and placed in a rubber container containing thirty litres of water. The roots were left in the water for seven days to ensure maximum extraction of the cyanide from the cassava roots. After seven days, the liquid was decanted, filtered using a nylon cloth to remove tiny particles present in it.

2.2.6 Corrosion Measurement

The corrosion rates of the metal samples in environments containing Neem (NM) and Bitter leaf (BL) extracts as inhibitors were generated by Elachi *et al.* (2016). Fifteen (15) rubber containers each containing 1000 mL of the corrodent were arranged on a table. The required

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concentrations (0.2 g/L, 0.4 g/L, 0.6 g/L, 0.8 g/L and 1.0 g/L) were respectively prepared from the stock solutions of blends of Neem and Bitter leaf in ratios of 1:1, 1:3 and 3:1. After measurement, the blends of extracts (Neem and Bitter leaf in ratios of 1:1, 1:3 and 3:1) were respectively added to each of the containers containing the corrodent.

Pre- weighed test samples were totally immersed in each of the plastic containers containing both the corrodent and the extracts. The coupons were suspended in the corrodents by cotton threads from wooden rods placed across the top of each of the beakers for a period of thirty-five days. After every seven days, samples were retrieved from the corrodents, observed, washed thoroughly with in water with a sponge and brush to remove corrosion products. Samples were again subjected to absolute washing in absolute ethanol with a cotton wool, dried under the sun and weighed to determine the final weight. The difference in weight of the coupons was taken as the weight loss. The experiment was repeated again. The weight loss value obtained from each coupon in the first experiment was added to the corresponding weight loss value obtained from each coupon in the second set of experiment and the average weight loss value determined. The average value was recorded as the weight loss. The corrosion rate was computed using equation (1) (Umoren *et al.*, 2008)

$$Corrosion\ rate = \frac{87.6W}{pAT} \quad (1)$$

Where W is the weight loss in grammes, p is the density of the specimen in gcm^{-3}, A is the area of the specimen in cm^2 and T is the exposure time in hours.

The inhibition efficiency (I%) of the extracts was computed using equation (2) (Umoren et al., 2008).

$$I\% = \left(1 - \frac{Wi}{Wo}\right) \times 100 \quad (2)$$

Where

Wi = weight loss in the presence of the inhibitor

Wo = weight loss in the absence of the inhibitor

3. RESULTS AND DISCUSSION

3.1 Effect of exposure time on corrosion rate.

The results of the effect of exposure time on corrosion rate of stainless steel in cassava pulp filtrate with different concentrations (0.0 g/L, 0.2 g/L, 0.4 g/L, 0.6 g/L, 0.8 g/L and 1.0 g/L) of the extracts are presented in Figures 1 to 5. From all the Figures, the corrosion rates at 0.0 g/L (in an environment without any extract) is higher compared to the corrosion rates obtained at different concentrations (0.2 g/L, 0.4 g/L, 0.6 g/L, 0.8 g/L and 1.0 g/L) of the extracts and their blends. This is an indication that the extracts and their blends mitigated the corrosion of the metal(s) in cassava pulp filtrate. This could the attributed to the presence of the extracts in the environment(s) which created a barrier between the metals and the environment(s), thereby limiting contact between them.

Figure 1 is the observable pattern of the behaviour of stainless steel in cassava pulp filtrate with 0.0 g/L, 0.2 g/L, 0.4 g/L, 0.6 g/L, 0.8 g/L and 1.0 g/L of Neem extract. It was observed from the Figure that at 0.0 g/L, 0.2 g/L, 0.4 g/L, 0.6 g/L and 1.0 g/L of Neem extract, corrosion rate increased in the first seven (7) days, reaching a peak on day seven and after that corrosion rate began to reduce till the end of exposure time. The cyanide ions in the initial period of exposure of the metal sample(s) were very aggressive and reacted readily with the metal(s), which resulted in the depletion of the concentration of iron in the metal sample(s) (Amuda *et al.*, 2008). At 0.8 g/L of Neem extract, a slightly different pattern was observed. Corrosion rate increased from day zero (0), reaching a peak on the fourteenth (14th) day and subsequently corrosion rate began to decline till the end of the exposure time.

This could be due to the release of more cyanide ions into the corrosive environment due to the fermentation of minute particles of cassava present in the environment that did not ferment completely during the period of soaking. The cyanide ions released increased the aggressiveness of the corrodent and that led to

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massive depletion of the metal sample in the first fourteen (14) days. The increase in corrosion rates with increased exposure time observed at all concentrations of Neem extract could be explained in terms of the chemistry of the cyanide ions (Amuda *et al.*, 2008). As the exposure time is increased, the environment becomes weaker due to the dilution and reduction in the concentration of the cyanide ions (Nartey, 1978 as cited in Amuda *et al*., 2008).

As a result, the corrosion reactions were greatly reduced and that could be responsible for the low corrosion rates observed at all concentrations of Neem extract with increased exposure time. Figures 2 to 5 are the observable patterns of the behaviour of stainless steel in cassava pulp filtrate with various concentrations (0.0 g/L, 0.2 g/L, 0.4 g/L, 0.6 g/L, 0.8 g/L and 1.0 g/L) of Bitter leaf (BL), blends of Neem (NM) and Bitter leaf (BL) in the ratios of 1:1, 1:3 and 3:1 respectively. From the Figures, corrosion rates were observed to increase steadily from day zero (0) to seven (7), reaching a maximum on the seventh day and subsequently began to decline till the end of the exposure time. The same reasons given for the trends observed in Figure 1 still applies to the trends observed in Figures 2 to 5

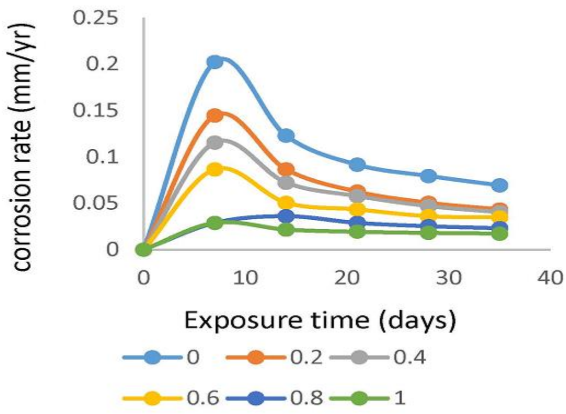

Fig 1 Effect of exposure time on the corrosion rate of stainless steel in cassava pulp filtrate with Neem extract as an inhibitor

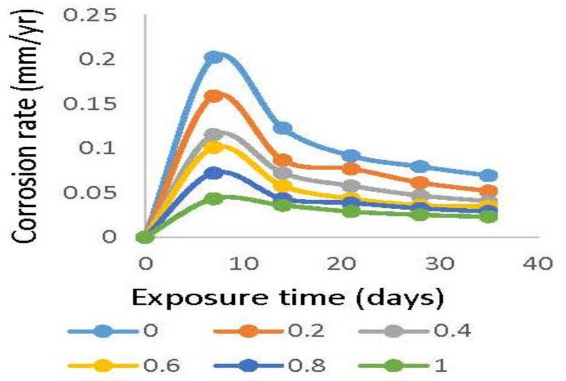

Fig 2 Effect of exposure time on the corrosion rate of stainless steel in cassava pulp filtrate with Bitter leaf extract as an inhibitor

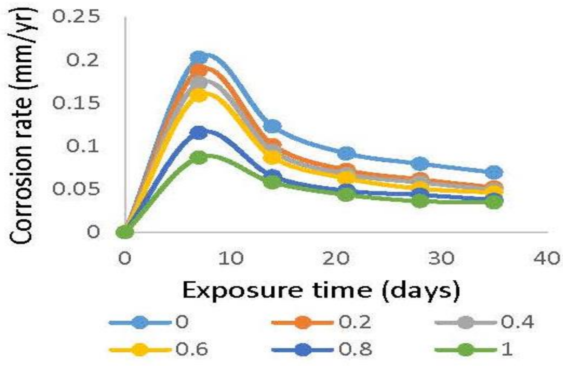

Fig 3 Effect of exposure time on the corrosion rate of stainless steel in cassava pulp filtrate with Neem and Bitter leaf extracts blended in ratio of 1:1 as an inhibitor

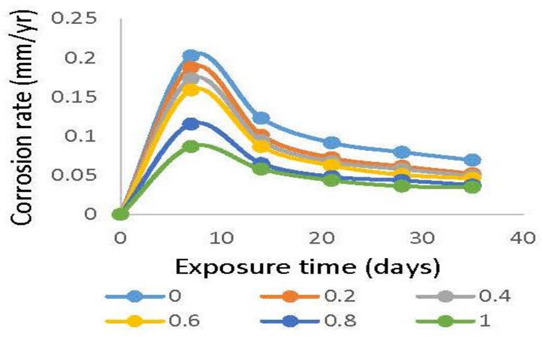

Fig 4 Effect of exposure time on the corrosion rate of stainless steel in cassava pulp filtrate with Neem and Bitter leaf extracts blended in ratio of 1:3 as an inhibitor

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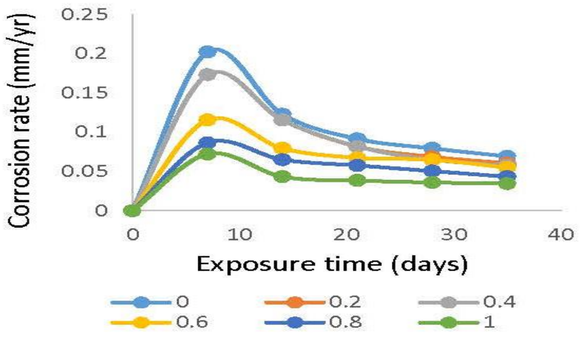

Fig 5 Effect of exposure time on the corrosion rate of stainless steel in cassava pulp filtrate with Neem and Bitter leaf extracts blended in ratio of 3:1 as an inhibitor

3.2 Comparison of the corrosion rates obtained in environments with extracts used individually and in blended forms

Figure 6 compares the corrosion rates obtained in an environment with Neem extract and in environments with blends of Neem and Bitter leaf in the ratios of 1:1, 1:3 and 3:1. Corrosion rates at 0.2 g/L, 0.4 g/L, 0.6 g/L, 0.8 g/L and 1.0 g/L were lower compared to the corrosion rates obtained at the same concentrations of Neem and Bitter leaf blended in ratios of 1:1, 1:3 and 3:1. This could likely be due to the variations in the concentrations of the phytochemical constituents present in the extracts (Neem, blends of Neem and Bitter leaf in ratios of 1:1, 1:3 and 3:1) as shown in Tables 1 to 3. The inhibitive effect of plant extracts is likely due to the presence of some phytochemical constituents present in the extracts (Umoren *et al*., 2008). Abdallah (2004) also reported that phytochemical components in plants perform the inhibitive action and their adsorption on the metal surface reduces the surface area available for corrosion. From the results in Tables 1 to 3, the concentrations of the phytochemicals in neem (cyanogenic glycosides, flavonoids, saponins, alkaloids and phenols) are higher compared to the concentration of the same phytochemicals in Neem and Bitter leaf blended in ratios of 1:1, 1:3 and 3:1. Therefore, the surface area available for corrosion (Abdallah, 2004) is greatly reduced in an environment with Neem extract compared to environments with Neem and Bitter leaf in blended forms (NMBL 1:1, NMBL 1:3 and NMBL 3:1). This could be the likely reason for the low corrosion rates obtained in environments with neem extracts. The concentration of the phytochemical constituent (tannins) is higher in neem compared to blends of Neem and Bitter leaf in ratios of 1:1 and 1:3. The concentration of tannin in Neem and Bitter leaf blended in ratio of 3:1 is higher compared to the concentration of tannin in Neem extract. Also, the concentration of oxalate in the blend of extracts (NMBL 1:1, 1:3 and 3:1) are higher compared to what was obtained for Neem. But that did not improve the inhibition performance of the blend of extracts when compared to Neem. This could mean that the corrosion inhibition performance of Neem extract was mostly influenced by cyanogenic glycosides, flavonoids, saponins, alkaloids, phenols and not oxalate.

Figure 7 compares the corrosion rates obtained in environments with Bitter leaf extract and blends of Neem and Bitter leaf in the ratios of 1:1, 1:3 and 3:1. The corrosion rates obtained at all concentrations of bitter leaf were observed to be lower compared to the corrosion rates obtained at the same concentrations of blends of Neem and Bitter leaf in ratios of 1:1 and 3:1. Corrosion rate at 0.2 g/L of Bitter leaf was observed to be the same when compared to the corrosion rate at 0.2 g/L of Neem and Bitter leaf blended in ratios of 1:3. At 0.4 g/L, 0.6 g/L, 0.8 g/L and 1.0 g/L of Neem and Bitter leaf blended in ratio of 1:3, the corrosion rates were higher than the corrosion rates at the same concentrations of Bitter leaf extract. Results of phytochemical analysis in Tables 1 to 3 showed that the concentrations of the phytochemical constituents (cyanogenic glycosides, flavonoids, saponins, alkaloids, phenols and tannins) are higher in Bitter leaf extract compared to Neem and Bitter leaf blended in ratios of 1:1 and 1:3. This implies that the surface area available for corrosion reactions in environment with Bitter

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leaf is greatly reduced. Therefore, there is reduced corrosion reactions in environment with bitter leaf compared to environments with blends of Neem and Bitter leaf in ratios of 1:1 and 1:3. Also, the concentrations of the phytochemical constituents (cyanogenic glycosides, saponins, alkaloids and phenols) are higher in Bitter leaf than in the blend of Neem and Bitter leaf in the ratio of 3:1. This could be responsible for the superior corrosion inhibition performance of bitter leaf compared to blend of Neem and bitter in ratio of 3:1.

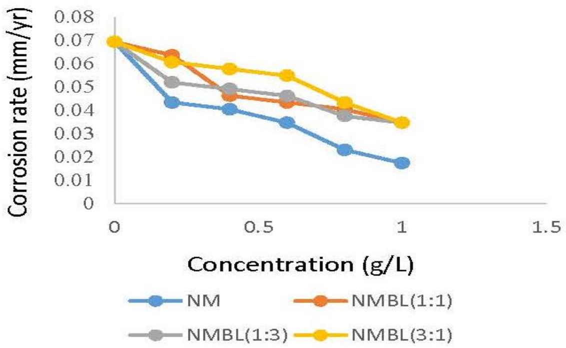

Fig 6 Effect of concentration of Neem and blend of Neem and Bitter leaf in the ratios of 1:1, 1:3 and 3:1 on the corrosion rate of stainless steel in cassava pulp filtrate

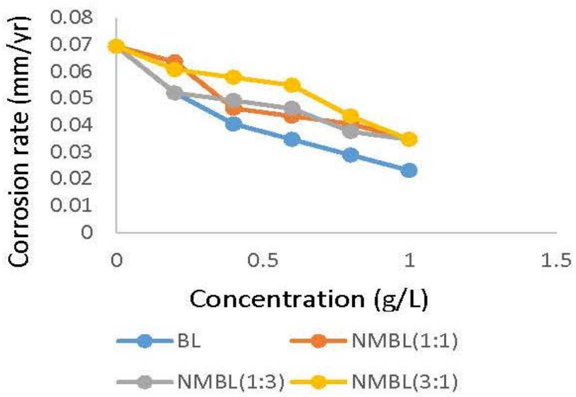

Fig 7 Effect of concentration of Bitter leaf and blend of Neem and Bitter leaf in the ratios of 1:1, 1:3 and 3:1 on the corrosion rate of stainless steel in cassava pulp filtrate

Table 1: Phytochemical Analyses of Neem and Bitter Leaf Extracts

Phytochemical	Extracts	
	NM	BL
Cyanogenic glycoside (mg/L)	466.66 ± 4.24	466.66 ± 0.0
Flavonoids (%)	1.197 ± 0.00	0.619 ± 0.01
Saponins (%)	51.290 ±1.54	13.500 ± 0.00
Alkaloids (%)	1.320 ± 0.01	2.560 ± 0.09
Phenols (%)	1.25 ± 0.06	1.14 ± 0.01
Tannin (%)	5.67 ± 0.04	5.39 ± 0.01
Oxalate (%)	9.031 ± 0.04	12.640 ± 0

Source:(Elachi *et al*., 2016)

Table 2: Phytochemical Analyses of Neem and Bitter Leaf Blended in ratios of 1:1 and 1:3

Phytochemical	Extracts	
	NMBL(1:1)	NMBL(1:3)
Cyanogenic glycoside (mg/L)	400.00±7.07	66.67±0.00
Flavonoids (%)	0.439±0.01	0.548±0.03
Saponins (%)	12.660±0.09	12.320±0.45
Alkaloids (%)	0.894±0.05	1.050±0.07
Phenols (%)	1.04±0.00	0. 57 ±0.10
Tannin (%)	4.54±0.00	4.96±0.09
Oxalate (%)	12.640±0.00	15.80±1.14

Table 3: Phytochemical Analysis of Neem and Bitter Leaf Extracts Blended in ratio of 3:1

Phytochemical	Extracts
	NMBL (3:1)
Cyanogenic glycoside (mg/L)	300.00 ± 7.07
Flavonoids (%)	0.957 ± 0.00
Saponins (%)	12.130 ±0.00
Alkaloids (%)	0.506 ± 0.00
Phenols (%)	0.52 ± 0.10
Tannin (%)	6.52 ± 0.00
Oxalate (%)	31.608 ± 0.01

3.3 Effect of concentration of extracts on inhibition efficiency

The effect of concentration on the inhibition efficiencies of Neem (NM), Bitter leaf (BL) and blends of Neem (NM) and Bitter leaf (BL) in the ratios of 1:1, 1:3 and 3:1 are presented in Figures 8 and 9. The inhibition efficiencies of the

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extracts (Neem (NM), Bitter leaf (BL) and blends of Neem (NM) and Bitter leaf (BL) in the ratios of 1:1, 1:3 and 3:1) were observed to increase with increase in the concentration of the extracts from 0.2 g/L to 1.0 g/L. The increase in inhibition efficiency with increase in the concentration of the extracts could be attributed to increase in the metal surface area covered by the extracts (Umoren *et al*., 2008). With increase in the surface area of the metal covered by the extracts, the surface area of the metal available for corrosion reactions is greatly reduced.

Consequently, corrosion rates at high extract concentrations were greatly minimized and as such the efficiency of the extracts is increased. Figure 8 compares the inhibition efficiency of Neem (NM) and blends of Neem and Bitter leaf in the ratios of 1:1, 1:3 and 3:1. It was observed from the Figure that the inhibition efficiency of Neem is higher compared to the extracts in blended forms. Figure 9 compares the inhibition efficiency of Bitter leaf and blends of Neem and Bitter leaf in the ratios of 1:1, 1:3 and 3:1. Bitter leaf was observed to be more efficient as an inhibitor in cassava pulp filtrate compared to the extracts used in blended forms (NMBL (1:1), NMBL (1:3) and NMBL (3:1)). This could be attributed to variations in the concentrations of the phytochemicals present in the extracts as explained in section 3.2.

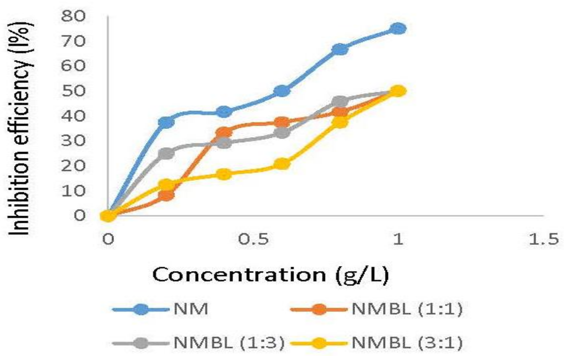

Fig 8 Effect of concentration on the inhibition efficiencies of Neem and blends of Neem and Bitter leaf in the ratios of 1:1, 1:3 and 3:1

3.4 Effect of exposure time on inhibition efficiency

The effects of exposure time on inhibition efficiency of the extracts are presented in Figures 10 to 14.

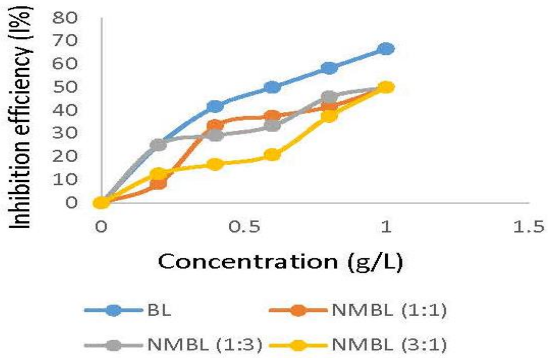

Fig 9 Effect of concentration on the inhibition efficiencies of Bitter leaf and blends of Neem and Bitter leaf in the ratios of 1:1, 1:3 and 3:1

It was observed from all the Figures that the inhibition efficiencies of the extracts did not follow any regular pattern as the exposure time increases. The effect of exposure time on the inhibition efficiency of Neem extract is presented in Figure 10. The extract exhibited maximum inhibition efficiency on the thirty fifth day at concentration of 0.2 g/L. The extract exhibited maximum inhibition efficiency on the seventh day at concentrations of 0.4 g/L, 0.6 g/L, 0.8 g/L and 1.0 g/L. Figure 11 presents the effect of exposure time on the inhibition efficiency of Bitter leaf extract. Bitter leaf extract exhibited maximum inhibition efficiency on the thirty fifth day at extract concentration of 0.2 g/L. Maximum inhibition efficiency was exhibited by the extract at concentrations of 0.4 g/L and 1.0 g/L on the seventh day. The extract attained a maximum efficiency on the fourteenth day of immersion at concentrations of 0.6 g/L and 0.8 g/L. Figure 12 shows the effect of exposure time on the inhibition efficiency of Neem and Bitter leaf blended in the ratio of 1:1.

It was observed from the Figure that the inhibition efficiency of the extract was maximum on the seventh day of exposure at all extract concentrations. Presented in Figure 13 is the effect of exposure time on the inhibition efficiency of Neem and Bitter leaf blended in ratio of 1:3. The extract exhibited maximum inhibition efficiency on the thirty fifth day at

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concentrations of 0.2 g/L and 0.4 g/L. Inhibition efficiency was maximum on the twenty eighth, twenty first and seventh day of immersion at extract concentrations of 0.6 g/L, 0.8 g/L and 1.0 g/L respectively. Figure 14 shows the effect of exposure time on the inhibition efficiency of Neem and Bitter leaf blended in the ratio of 3:1. Maximum efficiency was attained on the seventh day of exposure at concentrations of 0.2 g/L, 0.6 g/L and 0.8 g/L. The inhibition efficiency of the extract was maximum on the twenty eighth and fourteenth day at concentrations of 0.4 g/L and 1.0 g/L respectively.

3.5 Adsorption isotherm

The Langmuir adsorption isotherm model is based on the assumption that the adsorption takes place at specific homogenous sites within the adsorbent (Noor *et al*., 2009). The Langmuir adsorption isotherm is given equation 3 (Gaidhani *et al*., 2020).

$$\frac{C}{\theta} = C + \frac{1}{Kads} \qquad (3)$$

Where C is the concentration of the inhibitor in g/L, θ is the fraction of the metal surface covered with the inhibitor and K_{ads} is the equilibrium adsorption constant in L/g

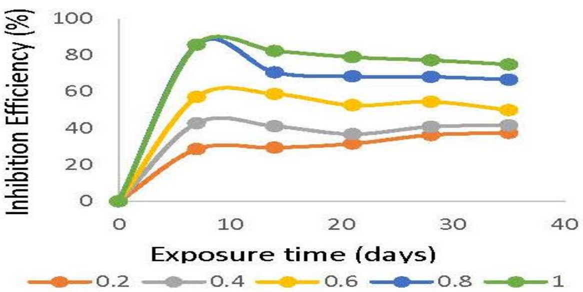

Fig 10 Effect of exposure time on the inhibition efficiency of Neem extract in cassava pulp filtrate

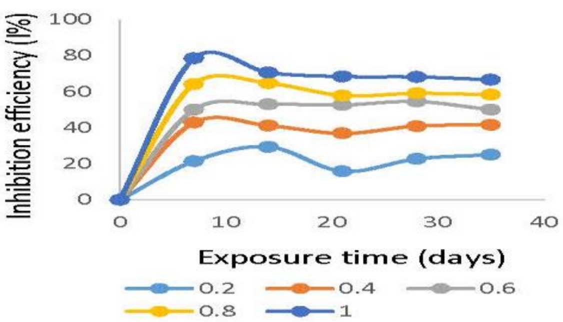

Fig 11

Effect of exposure time on the inhibition efficiency of Bitter leaf extract in cassava pulp filtrate

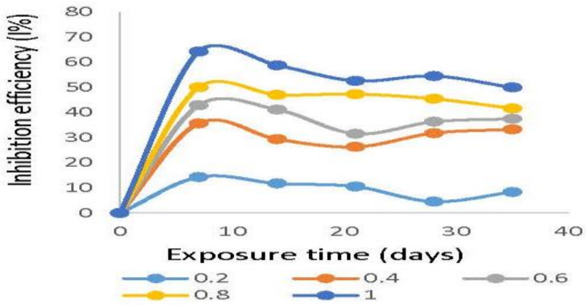

Fig 12 Effect of exposure time on the inhibition efficiency of Neem and Bitter leaf extracts blended in ratio of 1:1 in cassava pulp filtrate

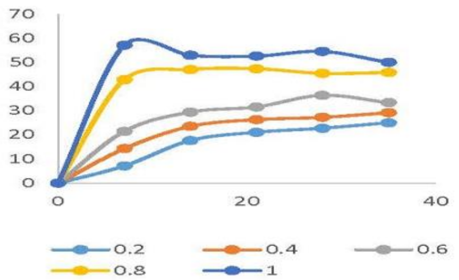

Fig 13 Effect of exposure time on the inhibition efficiency of Neem and Bitter leaf extracts blended in ratio of 1:3 in cassava pulp filtrate

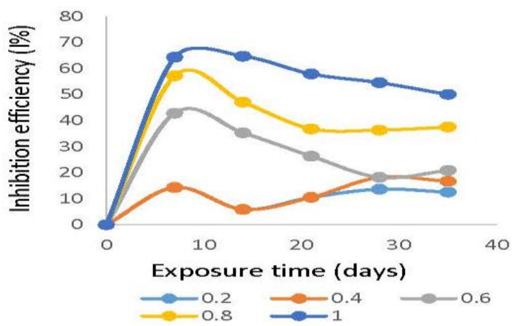

Fig 14 Effect of exposure time on the inhibition efficiency of Neem and Bitter leaf extracts blended in ratio of 3:1 in cassava pulp filtrate

The linear plots of Langmuir adsorption isotherm of Neem, Bitter leaf and Neem and Bitter leaf blended in ratios of 1:1, 1:3 and 3:1 are presented in Figures 15 and 16. Values of the Langmuir adsorption isotherm parameters are presented in Table 4. The R^2 values and slopes obtained from the plots for Neem extract, Bitter leaf extract and blend of Neem and Bitter leaf in ratio 1:3 are close to unity, therefore the adsorption of the extracts (Neem extract, Bitter leaf extract and blend of Neem and Bitter leaf in ratio of 1:3) on the metal surface strongly adheres to the Langmuir adsorption model (Eddy *et al*., 2011). The R^2 values and slopes for blends of Neem and Bitter leaf in ratios of 1:3 and 3:1 were not close to unity; therefore, the adsorption of the extracts on the metal surface did not adhere to Langmuir adsorption isotherm model. Presented in Table 5 are the adsorption equilibrium constant (K_{ads}) and the standard free energy of adsorption of the extracts (ΔG^o_{ads}).

The efficiency of an inhibitor is mostly a function of the adsorption constant (K_{ads}), large values of K_{ads} indicate better and stronger interaction, while small values of K_{ads} mean weak interaction between the metal and the inhibitor molecule (Khalil *et al*., 2003; Abd- El-Nabey *et al*., 1996 as cited in Fetouh *et al*., 2014). Based on the numerical values of the adsorption equilibrium obtained from the Langmuir adsorption isotherm (Table 5), Neem extract was more efficient as an inhibitor compared to blends of Neem and Bitter leaf in ratios of 1:1, 1:3 and 3:1. The inhibition efficiency follows the order: Neem > blend of Neem and Bitter leaf in ratio of 1:3 > blend of Neem and Bitter leaf in ratio of 1:1 > blend of Neem and Bitter leaf in ratio of 3:1. Also, based on the values of the equilibrium constant (K_{ads}) in Table 5, Bitter leaf was more as an inhibitor compared to the extracts in blended forms. The inhibition efficiency of the extracts followed the order: Bitter leaf > blend of Neem and Bitter leaf in ratio of 1:3 > blend of Neem and Bitter leaf in ratio of 1:1 > blend of Neem and Bitter leaf in ratio of 3:1.

The adsorption equilibrium constant is related to the free energy of adsorption according to equation 4 (Eddy *et al*., 2011)

$$\Delta G^o_{ads} = -2.303RT\log(55.5K_{ads}) \quad 4$$

Where ΔG^o_{ads} is the standard free energy of adsorption of the extracts on the metal surface, R is the universal gas constant and K_{ads} is the adsorption constant.

The values of the standard free energy of adsorption (ΔG^o_{ads}) for Neem, Bitter leaf and the extracts in blended forms are presented in Table 5. The negative values of ΔG^o_{ads} for the extracts and their blends ensure the spontaneity of the adsorption process and the stability of the adsorbed layer on the surface of the metal (Onuegbu *et al*., 2013). Generally, the values of ΔG^o_{ads} up to -20KJ/mol or lower are consistent with physical adsorption (Eddy *et al.*, 2011; Onuegbu *et al*., 2013). Therefore, the adsorption of the extracts and their blends onto the metal surfaces occurred by physical adsorption.

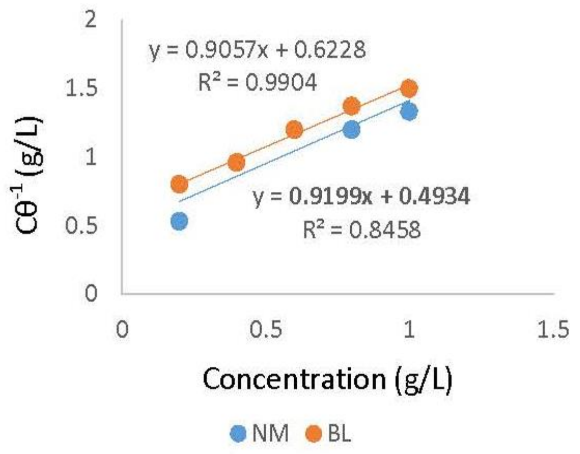

Fig 15 Langmuir isotherm for the adsorption of Neem and Bitter leaf extracts on stainless steel surface.

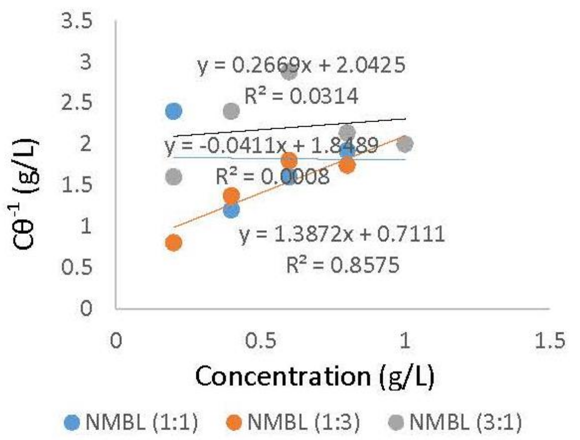

Fig 16
Langmuir isotherm for the adsorption of Neem and Bitter leaf extracts blended in the ratios of 1:1, 1:3 and 3:1 on stainless steel surface.

Table 4: Values of Langmuir Adsorption Isotherm Parameters for the Adsorption of the Extracts leaf on the Metal Surface

Extract	R^2	Slope
NM	0.8458	0.9199
BL	0.9904	0.9057
NMBL(1:1)	0.0008	-0.0411
NMBL(1:3)	0.8575	1.3872
NMBL(3:1)	0.0314	0.2669

Table 5: Values of Adsorption Equilibrium Constant and the Standard Free Energy of Adsorption

Extract	K_{ads} (L/g)	ΔG^o_{ads}
NM	2.027	-11.70
BL	1.606	-11.13
NMBL(1:1)	0.541	-8.43
NMBL(1:3)	1.406	-10.79
NMBL(3:1)	0.490	-8.19

3.6 Probable mechanism of corrosion inhibition by the extracts

From the results of phytochemical analyses in Tables 1 to 3, the extracts (Neem, Bitter leaf and Neem and Bitter leaf extracts blended in the ratios of 1:1, 1:3 and 3:1) contained the following phytochemicals in varying concentrations: cyanogenic glycosides, flavonoids, saponins, alkaloids, phenols, tannins and oxalates. These compounds have complicated molecular structures, large molecular weights and heteroatoms incorporated in their structures (Okafor *et al*., 2010). Apart from heteroatoms, aromatic rings are also present in the structures of these compounds (Shah *et al*., 2011; Amar *et al*., 2017 as cited in Marzorati *et al*., 2018). The free electron pairs on the heteroatoms [i.e oxygen (O), Sulphur (S) and nitrogen (N)] form bonds with the electrons on the metal surface (Rani & Basu, 2010). Therefore, a barrier to mass and charge transfer is created leading to a decrease in the interaction between the metal and the corrodent (Okafor *et al*., 2010). Consequently, the rate of the metal is reduced. Similarly, the π electrons available on the aromatic ring systems present in the structures of these compounds also increase adsorption and consequently enhance the inhibition efficiencies of the extracts (Ali *et al*., 2003)

4. CONCLUSION

The corrosion rates obtained in the presence of the extracts used individually (neem and bitter leaf) were lower compared to the corrosion rates obtained in environments containing the extracts in blended forms (NMBL 1:1, NMBL 1:3 and NMBL 3:1). The inhibition efficiencies of the extracts used individually (Neem and Bitter leaf) were higher compared to the extracts used in blended forms (NMBL 1:1, NMBL 1:3 and NMBL 3:1). This is an indication that the extracts were more efficient in corrosion inhibition of the metals in cassava pulp filtrate when used individually than in blended form. The adsorption of the extracts (Neem (NM), Bitter leaf (BL) and blend of Neem and Bitter leaf extracts in ratio of 1:3) obeyed Langmuir adsorption isotherm. The adsorption of the extracts (blends of Neem and Bitter leaf extracts in ratios of 1:1 and 3:1) did not obey Langmuir adsorption isotherm. The extracts inhibited the corrosion of the metal samples by physical adsorption.

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