Corrosion Inhibition of Stainless Steel (316l) Using Cola Nitida,Cola Acuminata and Cola Garcinia
BY

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---**Abstract**---
Recently, investigations have been made into the corrosive characteristics and inhibitive properties of natural plants. In order to make a meaningful contribution to the contemporary interest, the corrosion inhibitive effects of Cola Nitida (Red Cola/Native Cola), Cola Acuminata (White Cola) and Cola Garcinia (Bitter Cola) solution extracts on the corrosion of austenitic stainless steel (316L) immersed in soil (pH 5.4), seawater (3% NaCl), 1M and 2M hydrochloric (HCl) acids environments were studied at ambient temperature. The corrosion rates of the stainless steel specimens were determined using the weight loss method for a period of forty-two days. The solution extracts inhibited the corrosion of the stainless steel specimens to an extent depending on the composition of the extracts and the type of the environment. The results obtained showed that the lowest and highest corrosion rates were observed in the soil and 2M HCl acid environments respectively. Cola Garcinia (Bitter Cola) exhibited the best inhibitor extract in the soil and 2M HCl acid environments while Cola Acuminata (White Cola) showed the best inhibitor in the seawater and 1M HCl acid environments. The inhibition was attributed to the adsorption of the inhibitors on the surfaces of the stainless steel specimens.
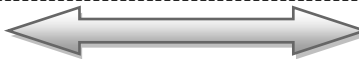
I.   INTRODUCTION

The corrosion of engineering materials especially metals has been a major industrial problem which   has attracted a serious concern to engineers and researchers who are committed to the study, monitor and control of corrosion. Oforka (2004) opined that metals are exposed to the action of acids, bases   and brine solutions in different ways and for various reasons. Most often, the severity of the corrosion rates   are controlled using corrosion inhibitors (Fontana, 1987).An inhibitor is a substance which when added in small concentrations to an environment decreases the corrosion rate (Ijomah, 1991). It is commonly added in small amounts either continuously or intermittently to acids, cooling waters, and other environments/media to minimize or control serious corrosion. Most of the well-known inhibitors useful in several industries today are natural products of plant origin containing different organic compounds such as alkaloids, tannins, pigments and   amino acids (Ebenso, et al, 2004). These inhibitors are known for their efficient characteristics which include non-expensive, ecologically tolerable and non-toxic to the environment.In view of the research interest in recent times into possible natural corrosion inhibition,

this work aims at determining the inhibition efficiency of Cola Nitida, Cola Acuminata and Cola Garcinia on the corrosion of austenitic stainless steel (316L) in soil, seawater and acidic (HCl) environments.

According to Burdock, et al (2009), cola nut/seed is caffeine containing nut of evergreen trees of the genus cola primarily the species cola acuminate and cola nitida. From the age long investigation by Booth and Mercer (1964), the inhibitive effects of some plants' solution extract has been attributed to the presence of tannin in the chemical composition. Walker (1975), observed that the bitter taste in plants' barks, seeds or leaves is attributed to the presence of tannins. Thus, tannins could be obtained by water extraction from a variety of barks, stems, seeds and fruits. The corrosion inhibition action of cola spp and other natural/plant inhibitors include the following mechanisms:

- Adsorbing themselves on the metallic surfaces, hence protecting the metallic surfaces by forming a thin film (passivation)
- Increasing the anodic or cathodic polarization behaviours (Tafel slopes)
- Increasing the electrical resistance of the metallic surface
- Reducing the movement of diffusion of ions to the metallic surface.

II. MATERIALS AND METHODS

2.1 Preparation of specimens

The austenitic stainless steel (316L) used in this study was obtained as sheet steel bar from Universal Steel Company, Lagos. The sheet was cut into various rectangular coupons (specimens) of uniform dimension, 4.0 X 3.0 X 0.15 cm. a hole of 0.3 cm was drilled on each coupon through which a twine was passed to aid suspension and total immersion in the environments.

The chemical composition of the austenitic steel sample is as shown in table 1.0.

Table 1.0: Chemical Composition of the austenitic Stainless Steel

Element	C	Si	S	P	Mn	Ni	Cr	Mo	V	Cu
% Composition	0.037	0.050	0.006	0.004	1.285	10.104	18.860	0.866	0.074	0.577
Element	W	As	Sn	Co	Al	Pb	Ca	Zn	Fe	
% Composition	0.099	0.034	0.012	0.126	0.016	0.028	0.001	0.037	66.784	

2.2 Preparation of Environment

Four different environments were used for the study. They are :

[1]   Soil (pH 5.40)
[2]   Seawater (3% NaCl solution)
[3]   1M HCl Acid
[4]   2M HCl Acid

A small portion of land (soil environment) at Ihiagwa, an outskirt of federal University of Technology, Owerri, Nigeria was mapped out and used for the study.

The seawater used in the study was obtained from high sea creek, Port-Harcourt, Nigeria. The chemical analysis of the sample was performed at SAAT laboratory, federal University of Technology, Owerri (FUTO), Nigeria. The different concentrations of the HCl acid solution was prepared in the chemistry department laboratory, FUTO, Nigeria

Table 2.0: Chemical Analysis of the Seawater

Composition	Ca^{2+}	Mg^{2+}	Na^+	CO_3^{2-}	Cl^-	O^{2-}	SO_4^{2-}	Fe^{2+}	NO_3^{2-}
Amount	7.10	3.12	4.70	0.31	54.36	0.55	2.99	0.29	0.001

2.3 Preparation of Inhibitors

The cola spp seeds; Nitida, Acuminata and Garcinia used as inhibitors were obtained in their fresh forms from a local market situated in the eastern region of Nigeria. These seeds/nuts were ground using small amount of distilled water to extract the juice (solution) from the nuts at a ratio of 0.2 ml (distilled water) to 2 grams (seed). The mixture was poured into a sieve where the juice was extracted..

Finally, the inhibited environment was prepared with 20 ml of each inhibitor as a solution per a litre of the environment.

Table 3.0: Composition of the Inhibitors

Cola Nitida	Cola Acuminata	Cola Garcinia
Caffeine	Caffeine	Biflavonoid
Epicatechin	Glucose	Xanthones
Tannins	Kolanin	Benzophenones
Kola Red	Starch	Flavanones
Choline & Bentaine	Fatty matter	Water (4.6%)
Starch	Sugar	Protein (14.3g)
sugars	Fat depositing enzyme	Fats (66.9g)
Potassium	-	Carbohydrates (10.9g)
Amino acid	-	Fibres (3.1g)
-	-	Ash (3.3g)
-	-	Minerals (Fe, Ca, P, Na, K)
-	-	Energy (654 cal)

Sources: http://www.spring4health.com; http://www.henriettesherbal.com. Accessed Sept 20, 2012

2.4 Experimental Set-Up and Monitoring

The initial weights of the coupons were taken to the nearest 0.001g on a digital electronic weighing machine, degreased and dried in acetone of analar grade before usage. These sample coupons were totally immersed in a plastic bowls containing each of the prepared corrosive environments. Six (6) uniformly spaced coupons were suspended differently in each of the environment. The set-up was achieved with the aid of a polymeric twine tied to a smooth stick and passed through the 0.3cm diameter holes in the coupons. The weight loss of each coupon in the soil and seawater environments was determined at intervals of seven (7) days for a total period of forty-two (42) days. Moreso, the weight loss of the coupons in the acidic environments (1M HCl & 2M HCl acids) was determined at intervals of two (2) hours for a total of twelve (12) hours. Thus, the weight loss within the immersion period was determined as the difference between the initial weight prior to immersion and the final weight after immersion, and the corresponding corrosion rate calculated.

2.5 Determination of Corrosion Rates

The corrosion rates of metals in service environment are usually expressed in quantitative terms. Therefore, the corrosion rates were calculated using weight loss measurement obtained over the total period of this study.

According to Wranglen (1988) in Adindu and Ovri (2012), the following relationship was adopted for the corrosion rate calculations:

$$CR = \frac{534}{}$$

Where; CR = Corrosion Rate in mils penetration per year (mpy)
W = Weight loss (g)

D = Density of coupon (g/cm^3)

A = Area of coupon (cm^2)

T = Time of exposure (days/hours)

2.6   Calculation of Inhibition Efficiency

The percentage inhibitor efficiency, I% was calculated for all the environments and it is given by (Loto, 1998):

$$I\% = \frac{W_o - W_i}{W_o}$$

Where; W_o = weight loss without inhibitor

W_i = Weight loss with inhibitor

2.7 PRESENTATION OF RESULTS

The detailed experimental results of the study are given in tables 4.0 – 9.0 while figures 1.0 – 8.0 illustrate all the results.

Table 4.0: Weight Loss (mg) and Corrosion Rate (mpy) values of stainless Steel Exposed to Soil Environment

C/N	7th day		14th day		21st day		28th day		35th day		42nd day	
	Wt Loss	CR X 10^{-3}	Wt Loss	CR X 10^{-3}	Wt Loss	CR X 10^{-3}	Wt Loss	CR X 10^{-3}	Wt Loss	CR X 10^{-3}	Wt Loss	CR X 10^{-3}
A$_1$	84.00	1.28	88.00	0.67	91.00	0.46	95.00	0.36	99.00	0.30	103.00	0.26
A$_2$	80.00	1.22	83.00	0.63	87.00	0.44	91.00	0.31	94.00	0.29	100.00	0.25
A$_3$	81.00	1.23	84.00	0.64	86.00	0.43	89.00	0.34	93.00	0.28	98.00	0.25
A$_4$	78.00	1.19	80.00	0.61	83.00	0.42	88.00	0.34	90.00	0.27	94.00	0.24

Key:

A$_1$ – Steel samples without inhibitor (Control)

A$_2$ – Steel samples inhibited with Cola Nitida

A$_3$ – Steel samples inhibited with Cola Acuminata

A$_4$ – steel samples inhibited with Cola Garcinia

Wt Loss – Weight loss (mg)

CR – Corrosion Rate (mpy)

Table 5.0: Weight Loss (mg) and Corrosion Rate (mpy) values of stainless Steel Exposed to Seawater Environment

C/N	7th day		14th day		21st day		28th day		35th day		42nd day	
	Wt Loss	CR X 10^{-3}	Wt Loss	CR X 10^{-3}	Wt Loss	CR X 10^{-3}	Wt Loss	CR X 10^{-3}	Wt Loss	CR X 10^{-3}	Wt Loss	CR X 10^{-3}
B$_1$	18.00	0.27	21.00	0.16	27.00	0.14	30.00	0.11	35.00	0.11	39.00	0.099
B$_2$	17.00	0.26	19.00	0.15	25.00	0.13	29.00	0.11	32.00	0.097	35.00	0.088
B$_3$	15.00	0.15	17.00	0.13	21.00	0.11	26.00	0.099	29.00	0.088	32.00	0.081
B$_4$	17.00	0.15	19.00	0.15	21.00	0.11	26.00	0.099	29.00	0.088	30.00	0.076

Key:

B$_1$ – Steel samples without inhibitor (Control)

B$_2$ – Steel samples inhibited with Cola Nitida

B$_3$ – Steel samples inhibited with Cola Acuminata

B$_4$ – steel samples inhibited with Cola Garcinia

Wt Loss – Weight loss (mg)

CR – Corrosion Rate (mpy)

Table 6.0: Weight Loss (mg) and Corrosion Rate (mpy) values of stainless Steel Exposed to 1M HCl Acid Environment

C/N	2 Hours		4 Hours		6 Hours		8 Hours		10 hours		12 Hours	
	Wt Loss	CR	Wt Loss	CR	Wt Loss	CR	Wt Loss	CR	Wt Loss	CR	Wt Loss	CR
C$_1$	79.00	0.100	90.00	0.058	106.00	0.045	160.00	0.051	211.00	0.054	250.00	0.053
C$_2$	73.00	0.093	84.00	0.054	101.00	0.043	154.00	0.049	206.00	0.053	246.00	0.052
C$_3$	70.00	0.090	83.00	0.053	99.00	0.042	151.00	0.048	201.00	0.051	233.00	0.050
C$_4$	69.00	0.088	84.00	0.054	103.00	0.044	156.00	0.050	208.00	0.053	247.00	0.053

Key:

C$_1$ – Steel samples without inhibitor (Control)

C$_2$ – Steel samples inhibited with Cola Nitida

C$_3$ – Steel samples inhibited with Cola Acuminata

C$_4$ – steel samples inhibited with Cola Garcinia

Wt Loss – Weight loss (mg)

CR – Corrosion Rate (mpy)

Table 7.0: Weight Loss (mg) and Corrosion Rate (mpy) values of stainless Steel Exposed to 2M HCl Acid Environment

C/N	2 Hours		4 Hours		6 Hours		8 Hours		10 hours		12 Hours	
	Wt Loss	CR	Wt Loss	CR	Wt Loss	CR	Wt Loss	CR	Wt Loss	CR	Wt Loss	CR
D$_1$	98.00	0.130	109.00	0.070	177.00	0.075	225.00	0.072	279.00	0.071	318.00	0.068
D$_2$	93.00	0.120	106.00	0.068	139.00	0.059	210.00	0.067	272.00	0.070	310.00	0.067
D$_3$	91.00	0.120	104.00	0.067	13300	0.057	200.00	0.064	266.00	0.068	308.00	0.066
D$_4$	89.00	0.110	105.00	0.067	130.00	0.054	218.00	0.069	274.00	0.070	313.00	0.067

Key:

D$_1$ – Steel samples without inhibitor (Control)

D$_2$ – Steel samples inhibited with Cola Nitida

D$_3$ – Steel samples inhibited with Cola Acuminata

D$_4$ – steel samples inhibited with Cola Garcinia

Wt Loss – Weight loss (mg)

CR – Corrosion Rate (mpy)

Table 8.0: Inhibition Efficiency, I% distribution of Steel samples in Soil and Seawater Environments

Environment	Efficiency Distribution, I%					
	7th day	14th day	21st day	28th day	35th day	42nd day
A$_1$	-	-	-	-	-	-
A$_2$	4.80	5.70	4.40	4.20	5.10	2.90
A$_3$	3.60	4.50	5.50	6.30	6.10	4.90
A$_4$	7.10	9.10	8.80	7.40	9.10	8.70
B$_1$	-	-	-	-	-	-
B$_2$	5.56	9.52	7.41	3.30	8.57	10.26
B$_3$	16.66	19.05	22.22	13.33	17.14	17.95
B$_4$	5.56	9.52	22.22	13.33	17.14	23.08

Table 9.0: Inhibition Efficiency, I% distribution of Steel samples in 1M and 2M HCl Acid Environments

Environment	Efficiency Distribution, I%					
	2 Hours	**4 Hours**	**6 Hours**	**8 Hours**	**10 Hours**	**12 Hours**
C_1	-	-	-	-	-	-
C_2	7.59	6.67	4.72	3.75	2.37	1.60
C_3	11.39	7.78	6.60	5.63	4.74	6.80
C_4	12.66	6.67	2.83	2.50	1.42	1.20
D_1	-	-	-	-	-	-
D_2	5.10	4.75	4.23	3.67	2.55	2.59
D_3	7.14	6.59	5.86	4.11	4.06	4.14
D_4	9.18	8.67	6.55	5.11	4.79	5.57
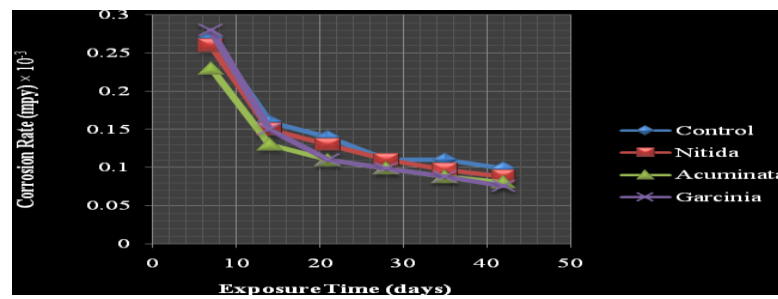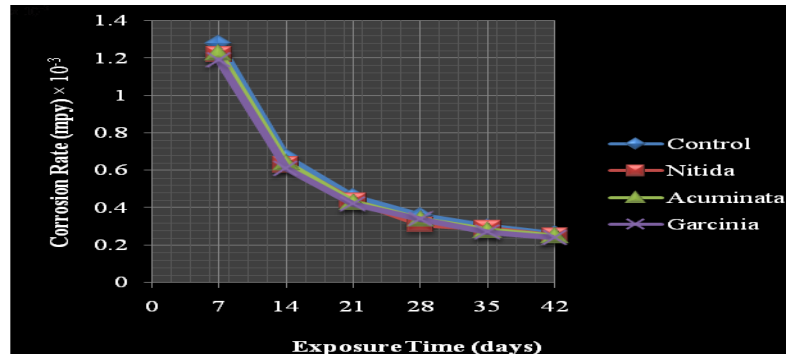
Figure 1.0: Fig 1.0: Corrosion Rate (mpy) $\times 10^{-3}$ Versus Exposure Time (days) for Stainless Steel Exposed to the Soil Environment

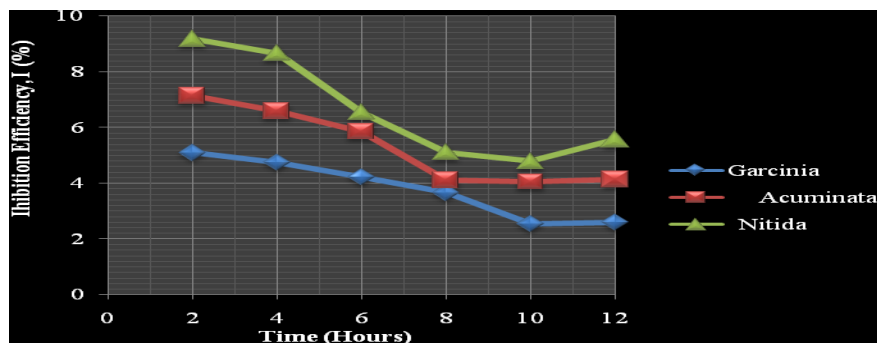Fig.7.0. Inhibition Efficiency Variation, % versus Time (Hours) for the Inhibitors in 1M HCl Acid Environment

Figure 8.0: Inhibition Efficiency Variation, I (%) Versus Time (days) for the Inhibitors in 2M HCl Acid Environment

IV. DISCUSSION OF RESULTS

4.1 The Soil Environment

Table 4.0 shows the corrosion rates of the steel samples buried in the soil environment while figure 1.0 depicts the plot of the corrosion rate (mpy) as a function of exposure time (days). Both table 4.0 and fig.1.0 showed that the corrosion the corrosion rate decreases sharply with increase in exposure time in all the different inhibited soil environments. Generally, the control experimental set-up (soil environment without inhibitor) recorded high corrosion rates more than all the inhibited soil environments. The extent of decrease in corrosion rate was observed to depend partly on the type of inhibitor used. The lowest average corrosion rate of 0.51×10^{-3} mpy was observed in Cola Garcinia as against 0.52×10^{-3} mpy and 0.53×10^{-3} mpy for Cola Nitida and Cola Acuminata respectively.This gradual decrease in corrosion rate with exposure time was attributed to the formation of an oxide film on the steel surface creating a barrier between the metal substrate and the environment, thereby reducing the corrosion rate.

4.2 The Seawater Environment

The plot of corrosion rate (mpy) against exposure time (days) for seawater environment is shown in figure 2.0. this figure shows that the corrosion rate values of the steel samples in seawater environment are lower (0.28×10^{-3} – 0.076×10^{-3} mpy) than the steel samples in the soil environment (1.28×10^{-3} – 0.24×10^{-3} mpy).

These inhibitors (cola Spp extracts) functioned effectively in the seawater environment. This is attributed to the fact that the inhibitors are organic in nature, hence an adsorption type of inhibitors that adsorb on the metal surface and depress metal dissolution and reduction reactions (Adeyemi and Benjamin, 2001). Therefore, this blocking effect is due to the blanketing of the metal surface which reduces the active sites on the metal surface upon which anodic and cathodic reactions could occur.

The average corrosion rates recorded in decreasing order are as follows: 0.15×10^{-3} mpy (control), 0.14×10^{-3} mpy (Cola Nitida), 0.13×10^{-3} mpy (Cola Garcinia) and 0.12×10^{-3} (Cola Acuminata).

4.3 The Hydrochloric Acid (HCl) Environment

The plots of corrosion rates (mpy) versus exposure time (hours) as represented in figures 3.0 and 4.0 show that the corrosion rates increase with exposure time. The figures also reveal that the corrosion rates increase as the concentration of the HCl acid increases. For instance, in 1M HCl (control), the corrosion rate is 0.053 mpy at 12 hours while in 2M HCl (control), the corrosion rate at 12 hours is 0.068 mpy. This is attributed to the generation of more H^+ ions which increase the corrosion process. It agreed with the result of Osarolube, et al (2004) which states that the higher the concentration of acids, the faster the rate of dissolution (corrosion rate) of materials and the longer the time, the more the reaction.The addition of the cola spp solution extracts shows a decrease in the corrosion rate which confirms their inhibition capabilities. In 1M HCl acid environment, Cola Acuminata recorded the least average corrosion rate (0.056 mpy) against 0.057 mpy each for Cola Nitida and Cola Garcinia respectively. In 2M HCl environment, Cola Garcinia exhibited the least average corrosion rate (0.072 mpy) against the higher corrosion rates of 0.073 mpy and 0.075 mpy for Cola Acuminata and Cola Nitida respectively.

4.4 Inhibition Efficiency

Tables 8.0 and 9.0 show the inhibition efficiency, I% distribution of the steel samples in the test environments whilst figs 5.0 – 8.0 represent the variation of inhibition efficiency, I% with time.As observed from the graphs, there is an initial rapid increase in inhibition efficiency, followed by a sharp decrease and consequently, a prompt rise in inhibition efficiency in the final stage of the experiment. The decrease could be attributed to the contamination of the inhibitors by the corrosion products formed. Thus, in order to keep the concentration of the inhibitors constant, more inhibitors should have been added at the point of noticeable decrease in inhibition efficiency.In the soil and 2M HCl acid environments, Cola Garcinia exhibited the best inhibition efficiency with average values of 8.37% and 6.65% respectively. Cola Acuminata showed the best inhibition efficiency in the

seawater and 1M HCl acid environments with average inhibition efficiency values of 17.73% and 7.16% respectively.The inhibition (decrease in corrosion rate) is attributed to the adsorption of the aggressive molecular species/ ions of the environments by the cola spp solution extracts.

V. CONCLUSION

Based on the results obtained from this study, the following conclusions can be deduced:

- The solution extracts of Cola Nitida, Cola Acuminata and Cola Garcinia could serve as corrosion inhibitors in the soil, seawater and HCl acid environments.
- The Cola Spp extracts inhibited the corrosion reactions through the mechanism of physical adsorption on the metal surface
- Cola Garcinia proved to be the best inhibitor in the soil and 2M HCl acid environments, while Cola Acuminata showed the best inhibition efficiency in the seawater and 1M HCl acid environments.
- The corrosion rate of the steel in HCl environment was a function of concentration of the HCl. The corrosion rate increases as the concentration of the HCl increases
- Soil, seawater and HCl acid environments manifested varying degrees of corrosion attack on the austenitic stainless steel (316L) with HCl exhibiting the highest attack.

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