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# CORROSION INHIBITIVE EFFECTS OF COCONUT (COCOS NUCIFERA LINN) WATER FOR MILD STEEL IN ACIDIC MEDIUM

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**ABSTRACT**: The corrosion inhibitive effect of coconut water as an eco-friendly inhibitor for the corrosion control of mild steel in 0.5 Molar solution of  $H_2SO_4$  acid have been investigated using the weight loss method which is considered more informative than other laboratory techniques. The studies were carried out using 30-110ml of the coconut water. The test coupons were totally immersed in the corroding medium containing various concentration of the inhibitor at the time intervals of 24-192 hours. The results obtained showed that the concentration of the inhibitor in the corrodent impacted differently on the test coupons. The corrosion rate was found to decrease while the inhibitor efficiency increases as the inhibitor concentration was increased. The plateau of maximum inhibition efficiency of 89.07% and 81.57% was obtained at the concentration of 90ml and 110ml for 24hours and 48hours immersion time respectively. The study showed that coconut water possesses inhibiting properties for reducing the corrosion of mild steel in the acidic medium.

**KEYWORDS:** Coconut water, inhibitive effect, mild steel, H<sub>2</sub>SO<sub>4</sub>, corrosion rate

## **INTRODUCTION**

Corrosion is defined as the physio-chemical interaction between metal and its environment which may results in selective dissolution of the metal surfaces leading to deterioration of the mechanical properties of the metal/alloy [1]. If this destructive phenomenon is not properly checked the metal which forms part of the structure may fail prematurely before it service life. Report [2] has demonstrated that the occurrence of corrosion in industrial plant has effects on the chemistry of a chosen process, and the products of corrosion can affect reaction and purity of the reaction product.

Corrosion has gained so much importance that an engineer, while selecting an alloy for an application also takes into consideration the corrosion resistance of the alloy in the specific environment. Corrosion is an enemy to mankind and is also one of the major causes of technological problems of modern society [3]. Corrosion processes are responsible for the numerous losses of materials occurring every year and worldwide involving billions of dollars annually. It is very obvious that the appropriate way to mitigate it is prevention [4].

Several studies conducted over the past 30 years on the economy issue of corrosion have shown that the annual direct cost of corrosion to an industrial economy ranges from 3-5% of Gross National Product. In the United State of America, this cost is estimated to be over \$276 billion per year, while in Japan it is estimated to be 5258 trillion Yen per year [5] and [6].

The consequences of corrosion are of great concerns to the world, therefore efforts must be made to prevent the corrosion of metals/alloys. The practical solutions to the problems of

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corrosion lie in controlling it by reducing the rate at which corrosion reaction proceed. Among the various conventional methods available to prevent the corrosion of metals in corrosive environments is the used of corrosion inhibitors. This method is gaining wide industrial acceptance due it low processing cost and ease of application. [7], [8], [9] and [10]. Corrosion inhibitors are chemical substances that, when added in small concentration to an environment, effectively decreases the corrosion rate [11] and [12].

Available report has shown that corrosion inhibitors have been applied in diverse areas ranging from petroleum refining, where they are used not only in the refining process, but also in products such as lubricants and fuels, cement and concrete, where they are used to prevent the reinforced bar in many structures from degrading. They are also used as product additives to extend the useful lifetime of many components such as radiators where they are added to heat transfer fluids.

A corrosion inhibitor may act in a number of ways: It may restrict the rate of the anodic process or the cathodic process by simply blocking active sites on the metal surface. Alternatively, it may act by increasing the potential of the metal surface so that the metal enters the passivation region where a natural oxide film forms. A further mode of action of some inhibitors is that the inhibiting compound contributes to the formation of a thin layer on the metal surface which represses the corrosion process [2].

Corrosion inhibitors are group as either synthetic or natural [4]. The synthetic corrosion inhibitors have been widely used in the petrochemical industries to control the corrosion rate of carbon steels but the environmental concerns and recent spike in their prices have spurred the development of inorganic corrosion inhibitors replacement and thus, demand in volume terms will continue to be low [13]. The development of green inhibitors is expected to open opportunities for the growth of the market over the next few years. Corrosion inhibitors of plant origin are fast gaining attention worldwide and are extensively been developed. Report by several authors have demonstrated that corrosion inhibitors of plant origin offers more protection at lower treat rates, eco-friendly, biodegradable and non toxic. [14], [15], [16] and [17].

There are several documented works on corrosion inhibitors of plant origin, however, there are lots of other plants whose corrosion inhibitive potential are yet to be explored. Therefore, the authors concern is to develop a novel green inhibitor that is cost effective and could serve as a possible replacement to other alternatives inhibitors in the scientific world.

Adzor *et al.* [14], investigated the corrosion inhibitive potential of *Hibiscus Sabdariffa calyx* extract for low carbon steel in 0.5M H<sub>2</sub>SO<sub>4</sub> acidic solution using the weight loss method and concluded that the dry calyx extract effectively decreases the corrosion rate of the carbon steel in the acidic medium. The concentration of the extract and immersion time impacted differently on the corrosion rate of the steel. Mangai and Ravi [15], studied the comparative effect of imidazole compounds and *trichodesma indicum Linn R. Br.* On C38 steel in 1M HCL medium using the weight loss at various temperatures. The study showed that the alkaloid part of the plant extract acts as a better inhibitor in comparison to the selected organic inhibitors. Prabhu and Rao [18], investigated *Coriandrum Sativum L*: A novel green inhibitor for the corrosion inhibition of aluminum in 1.0M phosphoric acid solution using potentiodynamic polarization and electrochemical impedance spectroscopy techniques. The results that the aqueous extract of seeds of *coriandrum sativum* acted as a mixed inhibitor in 0.5M and 2.0M phosphoric acid solution. Singh *et al.* [19], studied the corrosion inhibition of

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carbon steel in HCL solution by some plant extracts and concluded that the leaves extract of *Andrographis Paniculata, Murraya koenigii* and *Aegle marmelos* were investigated as corrosion inhibitors by weight loss and electrochemical methods. The study showed that all the leaves extracts exhibited better inhibition characteristics. Ogoko, *et al.* [20] reported that the initial step in any corrosion inhibition process is the adsorption of the inhibitor on the surface of the metal, and thus, suppress the metal dissolution and reduction reactions. Although, the stability of the inhibitor film formed over the metal surface depends on some physiochemical properties of the molecules related to its functional groups such as aromaticity, type of the corrosive medium and nature of the interaction between the inhibitors with the d-orbital vacant of iron. Grafen, *et al.* [21], posited that the effectiveness of corrosion inhibitors depends on the fluid composition, quantity of water, and flow regime and a common mechanism is a formation of a passivation layer which prevent access of the corrosive substance.

The aim of this research work is to investigate the inhibitive potential of coconut water as a cost effective, eco-friendly, non-toxic and biodegradable corrosion inhibitor for mild steel in 0.5M H<sub>2</sub>SO<sub>4</sub> acid solution. Several laboratory techniques have been used to investigate the relative resistance of metals/alloys in various corrosive environments. The weight loss technique though long and tedious is by far more informative than other laboratory techniques [22] and [23]. Mild steel is a major material of construction. It is widely used in the chemical and allied industries for handling of alkalis, acids and salt solutions [24]. However, mild steel has poor corrosion resistance when it comes in contact with acidic solutions during acid cleaning, transportation of acid, de-scaling, storage of acids and other chemical processes. [14] and [25]. Corrosion inhibitors have been found to be very effective in repressing the corrosion rate of low carbon steel after dissolution of the fouling oxides [26].

Coconut plant has long been recognized as a valuable source of various commodities for human life. It is one of the most useful plants in the world, providing a multitude of uses, from arrack to food staple, sugar to vinegar, fibers and fodder, thatching and lumber, and virgin coconut oil among many others. In addition, it yields 3 to 4 tons of copra (nut meat) per hectare and over two tons of oil [27]. Coconut water (liquid endosperm) has been extensively studied since its introduction to the scientific community in the 1940s. In its natural form, it is a refreshing and nutritious beverage which is widely consumed due to its beneficial properties to health, some of which are based on cultural/traditional beliefs [28], [29], [30], [31], [32], [33], [34] and [35]. It is also believed that coconut water could be used as an important alternative for oral rehydration and intravenous hydration of patients in remote regions [33]. Coconut water may also offer protection against myocardial infarction [35]. Interestingly, a study has shown that regular consumption of either coconut water or mauby (a liquid extracted from the bark of the mauby tree (Colubrina arborescens), or a mixture of both, is effective in bringing about the control of hypertension [36]. Coconut water has also been widely used in the plant tissue culture industry [37], [38], [39] and [40]. The extensive use of coconut water as a growth-promoting component in tissue culture medium formulation can be traced back to more than half a century ago, when Overbeek et al [1941], first introduced coconut water as a new component of the nutrient medium for callus cultures [37].

The phytochemical analysis of coconut water showed the presence of the following micro and macro nutrients: phytohormones, auxin, cytokinins, gibberellins, inorganic ions, sugars,

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vitamins, fibers, proteins, antioxidants and minerals with isotonic electrolyte balance [27] and [41]. Recent research evidences revealed that the presences of these chemical species in the aqueous solution of plant extracts are responsible for the stifling of oxidation of metals/alloys in various corrosive environments [42].

# **Materials and Equipment**

The materials and equipment used for this study were: coconut water, distilled water, 0.5M H<sub>2</sub>SO<sub>4</sub> solution, emery paper of various grades, acetone, measuring cylinders, beakers, mild steel, desiccator, air gun dryer and analytical weighing balance.

# **Preparation of the inhibitor**

The matured coconuts were purchased from Ochanja market, Onitsha. They coconuts were broken into two halves and the aqueous solution of the endosperm was poured into a bowl and then filtered to remove residues present. The aqueous solution was then measured into varying concentrations ranging from 30-110ml. Each of this concentration was mixed with the already prepared 0.5M H<sub>2</sub>SO<sub>4</sub> solution and was labeled for identification.

# **Experimental procedures**

The commercial grade of the mild steel used for this research work was collected from the central store of the Metallurgical Training Institute, Onitsha. The chemical composition of the mild steel as- received is presented in Table 1 while the photograph of the matured *cocos nucifera Linn* used for the study is shown in Figure 1. A total of 144 test coupons with average surface area of 4.84cm<sup>2</sup> with dimension 2.2x2.2x6cm were used for the study. There were divided into eight (8) groups for the six (6) media. Each group was immersed in sufficient volume of the appropriate medium to cover the coupons for a period ranging from 24 - 192hrs, for a maximum of eight (8) days. A set of coupons from the media were withdrawn, washed in distilled water, clean with acetone, dried and the final weight recorded. This was done at the intervals of 24hrs, 48hrs, 72hrs, 96hrs, 120hrs, 144hrs 168hrs and 192hrs respectively. From the results obtained, the average corrosion rate and inhibition efficiency were computed.

Elements	% Composition	
С	0.158	
Si	0.219	
Mn	0.493	
Р	0.025	
S	0.006	
Cr	0.087	
Ni	0.011	
Мо	0.002	
Al	0.030	
Cu	0.051	
Со	0.003	
Ti	0.001	
Nb	0.003	

Table 1: Chemical composition	of the mild steel as- received
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V	0.002
W	0.033
Pb	0.003
В	0.001
Sn	0.003
Zn	0.002
As	0.005
Bi	0.002
Са	0.001
Се	0.003
Zr	0.002
La	0.002
Fe	98.9



Figure 1: Photograph of the matured coconut

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## Corrosion rate (mpy) and inhibitor efficiency (%)

The corrosion rate was determined from the standard expression for measurement of corrosion rate in mils per year (mpy), [12].

 $mpy = \frac{534W}{DAT}$  ------ (1)

**DAT** Where; W = weight loss (g), D = density of the material  $(g/cm^3)$ ,T = time of exposure (hours), A = total surface area  $(cm^2)$ .

## **Inhibitor efficiency**

The inhibition efficiency (IE) was evaluated using the expression [43].

$$IE = (rate_{no Inhib.} - rate_{with inhib.})$$

rateno inhib.

\_\_\_\_\_ X 100% ------ (2)

Where; rate<sub>no Inhib.</sub> and rate<sub>with inhib</sub> are corrosion rate without and with inhibitors respectively.

## **RESULTS AND DISCUSSION**

The results of the study are shown in Tables 2-8. The visual examination of the coupons in the studied media revealed changes in the colour of the coupons from bright shiny surfaces to dull ones. Macro-cracks and pits were observed on the surfaces of all the coupons, indicating corrosion attack by the acidic medium. However, the changes in colour, the presence of macro-cracks and pits were more intense on the coupons immersed in the blank corrodent.

Table 2 show the variation of corrosion rate with time of immersion of the coupons in 0.5M H<sub>2</sub>SO<sub>4</sub> acid solution. It is evident that the coupons immersed in the acidic medium without inhibitor exhibited the highest corrosion rates compared to those immersed in the acidic medium containing various concentration of the inhibitor. A progressive increase in the corrosion rate was observed as the time of immersion was increased from 24h - 48hours, a pronounced decrease in the corrosion rate as the immersion time was increased from 72-120hours, a gradual increase in the corrosion rate was observed at 144hours of immersion and a subsequent decrease in the corrosion rate as the duration of the coupons in the blank corrodent was further increased from 168-196hours. The loss of chemical reactivity (passivity) experienced by the coupon at 144hours of immersion in the acidic solution could be attributed to the fact that the oxide film formed on the metal surface which was relatively stable at 120hours and subsequently destroyed as the immersion time was further increased to 144hours was growing under tension, hence, the formation of a discontinuous, porous film possessing low protective properties. The broken and spall oxide film further create room for the oxygen in the acid solution to gain more access to the metal surfaces resulting to further oxidation reaction, with new oxide film been formed on the metal surfaces, which gradually thicken. The new thin oxide film formed is responsible for the decreasing corrosion rate observed at 168-192hours of immersion. The unusual, active, passive and transpassive behaviour exhibited by the steel coupons in the acidic solution at different time of immersion is in consonance with several reports [11], [12] and [14].

Coupon	Immersion	Initial	Final	Weight	Corrosion
	Time(hours)	Weight(g)	Weight(g)	Loss(g)	Rate(mpy)
A1	24	22.910	20.403	2.507	1.464
A2	48	22.910	17.294	5.616	1.640
A3	72	22.910	15.223	7.687	1.497
A4	96	22.910	12.715	10.195	1.488
A5	120	22.910	11.026	11.884	1.388
A6	144	22.910	8.308	14.602	1.422
A7	168	22.910	6.875	16.035	1.338
A8	192	22.910	5.971	16.939	1.237

 Table 2: Variation of corrosion rate with time of immersion in 0.5M H<sub>2</sub>SO<sub>4</sub>.

Tables 3-8 show the variation of corrosion rates with time of immersion of the steel coupons in the acidic solution containing various concentration of the inhibitor. The results showed that the concentration of the inhibitor in the corrodent impacted differently on the coupons. The remarkable decrease in the corrosion rates of the test coupons as the concentration of the inhibitor in the corrodent was increased implies that the more the concentration of the inhibitor in the corrodent, the more readily the inhibitor molecules get adsorbs on the metal surfaces and the smaller the residual anodic areas becomes, thus favouring anodic polarization. Reports by Ayeni et al [17] and Asuke et al [43] showed that the degree of inhibition of inhibitors of plant origin depends on the surface coverage of the metal surfaces by the inhibitor molecules. Therefore, the variation in the corrosion rates with time of immersion of the test coupons in the corrodent containing various concentration of the coconut water could be attributed to the presence of some inorganic ions (e.g Zn, Mg Mn, etc.), antioxidant (ascorbic acid) and some other chemical species in the the phytochemical composition of the coconut water, may have worked in synergy to inhibit both the anodic and cathodic reactions. The net absorption of the chemical constituents on the metal surfaces creates a protective barrier that isolates the metal surfaces from the corrodent. Studies carried out by Dutra et al [45] and Bardal [46] showed that when the concentration of an inhibitor becomes high enough, the cathodic current density at the primary passivation potential becomes higher than the critical anodic density, that is shift the potential for a noble sense and, consequently, the metal is passivated, hence the lower corrosion rate exhibited by the coupons at higher inhibitor concentration. The inhibition efficiency increases as the concentration of the coconut water in the acid solution was increased. At certain concentration and time of immersion, the inhibition efficiency reached a plateau of maximum protection. The maximum inhibition efficiency of 89.07 and 81.57 was obtained at 24 and 48hours of immersion time in the 0.5M H<sub>2</sub>SO<sub>4</sub> solution containing 90ml and 110ml of coconut water respectively. Beyond 24hours (between 48-92hours), the inhibitor concentration of 110ml showed better inhibiting efficiency compared to the inhibitor concentration of 90ml. The variation of the inhibitor efficiency could be attributed to the variation in the anodic and cathodic reactions which are been affect by the concentration of the corrosion inhibitor, thus affecting their stability.

Coupon	Immersion Time(hrs)	Initial Weight(g)	Final Weight(g)	Weight Loss(g)	Corrosion Rate(mpy)	Inhibition Efficiency
						%
B1	24	22.910	22.097	0.813	0.465	68.25
B2	48	22.910	21.261	1.649	0.482	70.64
B3	72	22.910	19.991	2.919	0.568	62.03
B4	96	22.910	19.153	3.757	0.549	63.13
B5	120	22.910	18.100	4.810	0.562	59.53
B6	144	22.910	17.382	5.528	0.538	62.14
B7	168	22.910	16.655	6.255	0.522	60.99
B8	192	22.910	14.720	8.190	0.598	51.65

# Table 3: Variation of corrosion rate with time of immersion in 30ml of coconut water plus $0.5M~H_2SO_4$

# Table 4: Variation of corrosion rate with time of immersion in 50ml of coconut waterplus 0.5M H2SO4.

Coupon	Immersion	Initial	Final	Weight	Corrosion	Inhibition
	Time(hrs)	Weight(g)	Weight(g)	Loss(g)	Rate(mpy)	Efficiency
						%
C1	24	22.910	22.134	0.776	0.453	69.05
C2	48	22.910	21.551	1.359	0.397	75.80
C3	72	22.910	21.078	1.832	0.357	76.17
C4	96	22.910	20.302	2.608	0.381	74.41
C5	120	22.910	18.899	4.011	0.469	66.25
C6	144	22.910	18.293	4.617	0.449	68.38
C7	168	22.910	18.425	4.485	0.374	72.03
C8	192	22.910	17.093	5.817	0.425	65.66

Coupon	Immersion Time(hrs)	Initial Weight(g)	Final Weight(g)	Weight Loss(g)	Corrosion Rate(mpy)	Inhibition Efficiency
	Time(ms)	Weight(g)	Weight(g)	L035(g)	Rute(mpy)	%
D1	24	22.910	22.400	0.510	0.298	79.66
D2	48	22.910	21.725	1.185	0.346	78.90
D3	72	22.910	20.985	1.925	0.375	74.96
D4	96	22.910	20.936	1.974	0.288	80.63
D5	120	22.910	20.667	2.243	0.262	81.24
D6	144	22.910	19.809	3.101	0.302	78.76
D7	168	22.910	18.878	4.032	0.336	74.86
D8	192	22.910	18.859	4.051	0.296	76.08

# Table 5: Variation of corrosion rate with time of immersion in 70ml of coconut water plus $0.5M~H_2SO_4$

Table 6: Variation of corrosion rate with time of immersion in 90ml of coconut water plus  $0.5M~H_2SO_4$ 

Coupon	Immersion	Initial	Final	Weight	Corrosion	Inhibition
	Time(hrs)	Weight(g)	Weight(g)	Loss(g)	Rate(mpy)	Efficiency
						%
E1	24	22.910	22.636	0.274	0.160	89.07
E2	48	22.910	21.650	1.260	0.368	77.56
E3	72	22.910	21.386	1.524	0.297	80.17
E4	96	22.910	20.829	2.081	0.304	79.59
E5	120	22.910	20.641	2.269	0.265	80.91
E6	144	22.910	19.861	3.049	0.297	79.11
E7	168	22.910	19.341	3.569	0.298	77.74
E8	192	22.910	17.949	4.961	0.362	70.71

Coupon	Immersion	Initial	Final	Weight	Corrosion	Inhibition
	Time(hrs)	Weight(g)	Weight(g)	Loss(g)	Rate(mpy)	Efficiency
						%
F1	24	22.910	22.424	0.486	0.284	80.61
F2	48	22.910	21.875	1.035	0.302	81.57
F3	72	22.910	21.477	1.433	0.279	81.36
F4	96	22.910	21.015	1.885	0.275	81.55
F5	120	22.910	20.197	2.713	0.317	77.17
F6	144	22.910	19.670	3.240	0.315	77.81
F7	168	22.910	19.323	3.587	0.299	77.63
F8	192	22.910	19.124	3.786	0.276	77.65

 Table 7: Variation of corrosion rate with time of immersion in 110ml of coconut water plus 0.5M H<sub>2</sub>SO<sub>4</sub>.

# CONCLUSION

The study showed that the aqueous solution of the coconut water (liquid endosperm) exhibited better corrosion characteristics. The interaction between the chemical species in the coconut liquid endosperm with the anodic and cathodic reactions accounts for the lower corrosion rates exhibited by the test coupons in the corroding media. A new novel green corrosion inhibitor has been developed for industrial use.

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