Available online www.jsaer.com

***Journal of Scientific and Engineering Research*, 2016, 3(4):339-345**

Research Article

ISSN: 2394-2630
CODEN(USA): JSERBR

Cathodic Protection of Charred Plantain (*Musa Paradisiaca*) Peels on Mild Steel Corrosion in Acidic Medium

Inemesit A Akpan, Idara N Obotowo

Physical and Materials Science Laboratory, Department of Chemistry, University of Uyo, Uyo, Akwa Ibom State, Nigeria

Abstract Cathodic protection of charred plantain peels oxide was investigated on mild steel surface in 0.1 M $_{H2SO4}$ corrodent at 30 °C. The results showed that the plantain peels oxide is effective as cathodic protection agent on mild steel surface by sacrificial electron donation from electropositive metals present in the charred plantain peels. Further enhancement of the sacrificial protection was achieved by introducing a synergy or conjoint action when the protected metal was wrapped with aluminium foil. Inhibition efficiencies of 24%, 50.4%, and 73.3% were attained for mild steel coupon coated with paint only; coated with paint mixed with charred plantain peels and coated with paint mixed with charred plantain peels followed by wrapping with aluminium foil respectively. It is proposed that charred plantain peels oxide be included in paint formulation so as to induce cathodic protection and prolong the life span of the iron structure.

Keywords Heat Exchanger, Cooling Fin, Plate Fin, Transient Thermal Analysis, Ansys, Film Coefficient, Cross Flow, Counter-Flow, Cross-Counter Flow. Heat Flux, Temperature Distribution

Introduction

Plantain (Musa paradisiaca)

Plantain peels are organic or agricultural wastes generated from plantain processing. These wastes are dumped in landfills or indiscriminately littered in the environment [1]. The peel of the fruit is discarded as waste after the inner fleshy portion has been removed to be eaten, thereby constituting a menace to the environment especially where its consumption is high. The leaves, pseudostem, fruit stalks, bracts and the peels have been considered for use as organic fertilizer in Somalia and Malaysia [2]. Various parts of the plant such as leaves, roots, fruit stalks and bract have been used for medicinal and domestic purposes. The juice from the leaf is used in the treatment of fresh wound cuts and insect bites while the leaves act as an arbortifacient. Its sap is used as a remedy for diarrhoea, dysentery, hysteria, and epilepsy. The fruit has been reported to be used as antiscorbutic, aphrodisiac and diuretic [3]. Adeniyi *et al.* [4] had reported that 100g edible portion of plantain contains 67.30g moisture, 0.40g crude fat, 31.15g carbohydrate, 0.95mg potassium, 35.10mg sodium, 71.5mg calcium, 28.00mg phosphorus, 2.40mg iron and yielded 116.00Kcal of energy.

Presently, the Federal Government of Nigeria policy on sourcing of local raw materials which are non-toxic and potentially suitable for alkali generation has given rise to an increased interest in research efforts geared towards exploiting locally available vegetable materials.

Cathodic Protection (Sacrificial Protection)

Cathodic protection involves coupling of metals which are more electropositive than steel to the structural members. These more reactive metals supply an electric current through the electrolytes (i.e. moisture and sea water) and in the process corrode instead. In other words, this is a general corrosion control practice in which a more base metal is attached electrically to the less base metal (i.e. metal being protected). The more base metals (sacrificial metal) such as alloys of Mg, Zn, or Al are forced to corrode in preference to the metal being protected. This means that the protected metal is made the cathode; hence electrons from the corroding sacrificial metal are supplied to the protected metal which is saturated with electrons that reduce the corrosion tendency of the protected metal. This arrangement continues to protect the less base metal so long as the sacrificial metal is still attached [5]. This is the principle of sacrificial anode protection which is used in the protection of buried pipes, steel storage tanks and even ships.

Sacrificial anode protection is anchored on the fact that metals have different rates of corrosion, i.e. one metal corrodes preferentially to another. Hence, the metal to be protected is electrically connected to a piece of more-active metal in the corrodent. This gives rise to a galvanic cell in which the active metal is the anode while the metal to be protected becomes the cathode. As Mg, Zn, and Al have higher electronegative potentials than iron, these are commonly used as sacrificial anodes for protecting iron and steel structures. However, these metals used as sacrificial anodes are quite expensive and need frequent replacement. Anodic reactions involve oxidation of metal to its ions; e.g. for steel, the following reaction occurs:

$$Fe \longrightarrow Fe^{2+} + 2e^{-} \quad 1.1$$

The cathodic process involves reduction and several reactions are possible [6].

In acidic water where hydrogen ions (H+) are plentiful, the following reaction occurs:

$$2H^{+} + 2e^{-} \longrightarrow H_2(g) \quad 1.2$$

In alkaline solutions, where hydrogen ions are rare, the reduction of water will occur to yield alkali and hydrogen

$$2H_2O + 2e^{-} \longrightarrow H_{2(g)} + 2OH^{-} \quad 1.3$$

However, unless the water is dearated, reduction of oxygen is the most likely process, again producing alkali at the surface of the metal

$$O_2 + 2H_2O + 4e^{-} \longrightarrow 4OH^{-} \quad 1.4$$

Coatings

The provision of an insulating coating to the structure will greatly reduce the current demand for cathodic protection [7]. When first applied, coatings will often contain flaws, and in service, further defects will develop over a period of time. The conjoint use of coatings and cathodic protection takes advantage of the most attractive features of each method of corrosion control. Thus, the bulk of protection is provided by the coating and cathodic protection provides protection to the flaws in the coating. As the coating degrades with time, the activity of the cathodic protection system develops to protect the deficiencies in the coating. A combination of coating and cathodic protection will normally result in the most economic protection system [8].

Calcareous scales

In sea water, cathodic protection of bare steel is economic because of the formation of calcareous deposits [9]. The alkali formed at the surface of a protected structure reacts with bicarbonate ions (reaction 1.5) which, in turn, precipitates as insoluble calcium carbonate (reaction 1.6) on the surface of the metal,

$$OH^{-} + HCO_3^{-} \longrightarrow CO_3^{2-} + H_2O \quad 1.5$$

$$CO_3^{2-} + Ca^{2+} \longrightarrow CaCO_3 \quad 1.6$$

The advantage of sacrificial anode systems is that it is simple to install; it is independent of any source of electric power; suitable for localised protection and less liable to cause interaction on neighbouring structures.

The corresponding author and his research team had previously carried out the study of cathodic protection potentials of selected electro-active anions on galvanised steel in acidic medium by weight-loss and hydrogen evolution technique [10]. The present research is focused on the cathodic protection potential of charred plantain peels oxide on mild steel surface in acidic medium. Charred plantain peel is naturally fortified with metals having higher electronegative potentials than mild steel. Some of the highly electropositive metals present in the charred plantain peels are magnesium, sodium, potassium, calcium, and zinc. The authors believe that the inclusion of the oxides of plantain peels in paint formulation can induce cathodic protection on the mild steel surface and hence prolong the life span of the metal surface. This research is intended to compare the extent of mild steel protection with ordinary paint coatings and the paint coatings mixed with plantain peels oxide.

Materials and Methods

Collection and Preparation of Plantain Peels

The plantain peels (Unripe) were collected from road side plantain roasters in Uyo metropolis, Akwa Ibom State, Nigeria. The samples were thoroughly washed with distilled water, sun-dried for 168 hours and then oven-dried at 100^{o}C to constant weight. The dried peels were ground into fine powder and stored in polyethylene containers until required for analysis

Charring of Samples

In the charring procedure, plantain peels powder (50g) were placed in a crucible and ignited with fire to ensure complete combustion [11]. The charred product was stored in air tight lid container for analysis.

Extraction of Ash

The plantain peel ash (20g) was dissolved with distilled water (100cm^3). The resulting solution was filtered and the filtrate kept in a sealed conical flask. The pH of the extract was determined and recorded.

Mineral Element Analysis

Potassium and sodium were determined using the digested extracts of the sample and readings were taken on Jenway Digital Flame Analyser PFP7. Calcium, magnesium, iron, manganese, and zinc were determined spectrophotometrically by using Buck 200 Atomic Absorption Spectrophotometer (AAS) and their absorption compared with absorption of standards of these metals.

Procurement and Preparation of Mild Steel Specimen

The mild steel coupons (98% Fe) used for this investigation were obtained and identified locally in a metal workshop in a mechanic village in Uyo metropolis, Akwa Ibom State, Nigeria. The metal sheets were mechanically press cut into square coupons of 4cm by 4cm. The thickness of the metal was 0.01cm and the total surface area of the square metal coupons each was 32.16cm^2. A set of four coupons were chosen. Each of the metal coupons was washed with distilled water and scrubbed with iron sponge to remove dirt. The coupons were then rinsed in acetone and dried in the oven at 100^{o}C, and then removed for coating as follows:

One coupon labelled A was maintained as blank coupon and left without painting. The second coupon labelled B was painted with car paint without any additive. The third coupon labelled C was painted with the car paint mixed with the charred plantain peels powder as the experimental cathodic protection agent. The fourth coupon labelled D was painted with the car paint mixed with the plantain peels powder and further wrapped with aluminium foil to form a conjoint or synergy of cathodic protection.

The coated or painted metal coupons were dried under the sun for 48 hours. A set of four beakers (500cm^3 capacity) were labelled A, B, C, and D and were filled with 0.1 M solution of H_2SO_4 (300cm^3). The prepared metal coupons were suspended by means of glass hooks in the acidic solutions corresponding to their labels and were ensured to be completely immersed in the acidic corrodent. The metals were allowed to corrode for three days interval progressively for twelve days. In every three days, weight loss measurements were taken and the corrodent solutions were also taken to determine the amount of Fe^{2+} ions present by means of Atomic Absorption Spectrophotometer (AAS).

Results and Discussion

Mineral Elements Analysis

The relevant mineral elements were detected using AAS. Table 3.1 records the types of metals having electropositive tendency than iron present in the charred plantain peels. Metals such as zinc, potassium, sodium, calcium, and magnesium present in the plantain peels oxide suggest that the charred powder can induce cathodic or sacrificial protection on ferrous metal surface to prolong its life span, if admixed with paint.

Table 1: Metal content of charred plantain peels extract

S/N	Mineral Element	Amount (mg/kg) Mean±S.D
1	Zinc (Zn)	0.3752 ± 0.0003
2	Potassium (K)	333.33 ± 0.002
3	Sodium (Na)	3725.00 ± 0.001
4	Calcium (Ca)	ND (Not Detected)
5	Magnesium (Mg)	0.3330 ± 0.004
6	Iron (Fe)	2.083 ± 0.003
7	Manganese (Mn)	ND (Not Detected)

Variation of Weight Loss with Time of Exposure (days)

The protected and unprotected metal coupons were immersed in the corrodent and the weight loss assessed after every three days progressively for twelve days. The variation of weight loss in grams with time (days) for the corrosion process is recorded in table 3.2 to 3.5 and depicted graphically in fig. 3.1. It was observed that the weight loss of all the metal steel coupons kept increasing as the days of exposure to the corrodent increased. The painting without and with the plantain peels powder actually protected the mild steel from corrosion as the curves for the protected coupons fell below the curve for the unprotected coupons which was highest signifying greatest weight loss.

Table 2: Variation of weight loss with time (days) of unpainted (blank) mild steel coupon in 0.1 M H_2SO_4 solution at 30^{o}C

Time (day)	Initial weight W_0(g)	Final weight W_1(g)	Weight loss ΔW (g)	Log W_1
3	3.2594	3.1367	0.1227	0.3297
6	3.2594	2.9158	0.3436	0.2824
9	3.2594	2.7441	0.5153	0.2416
12	3.2594	2.6459	0.6135	0.2164

Table 3: Variation of weight loss with time (days) of painted mild steel coupon in 0.1 M H_2SO_4 solution at 30°C

Time (Days)	Initial weight W_0 (g)	Final weight W_1 (g)	Weight loss ΔW (g)	Log W_1
3	3.743	3.1808	0.0935	0.3386
6	3.743	3.0125	0.2618	0.3037
9	3.743	2.8816	0.3927	0.2745
12	3.743	2.8068	0.4675	0.2569

Table 4: Variation of weight loss with time (days) of mild steel coupon coated with paint mixed with plantain peels oxide in 0.1 M H_2SO_4 solution at 30°C

Time (Days)	Initial weight W_0 (g)	Final weight W_1 (g)	Weight loss ΔW (g)	Log W_1
3	3.2815	3.2203	0.0612	0.3464
6	3.2815	3.1101	0.1714	0.3243
9	3.2815	3.0245	0.2570	0.3063
12	3.2815	2.9755	0.3060	0.2957

Table 5: Variation of weight loss with time (days) of mild steel coupon coated with paint mixed with plantain peels oxide and wrapped with aluminium foil in 0.1 M H_2SO_4 solution at 30°C

Time (Days)	Initial weight W_0 (g)	Final weight W_1 (g)	Weight loss ΔW (g)	Log W_1
3	3.2652	3.2324	0.0328	0.3488
6	3.2652	3.1734	0.0918	0.3371
9	3.2652	3.1274	0.1378	0.3279
12	3.2652	3.1012	0.1640	0.3225

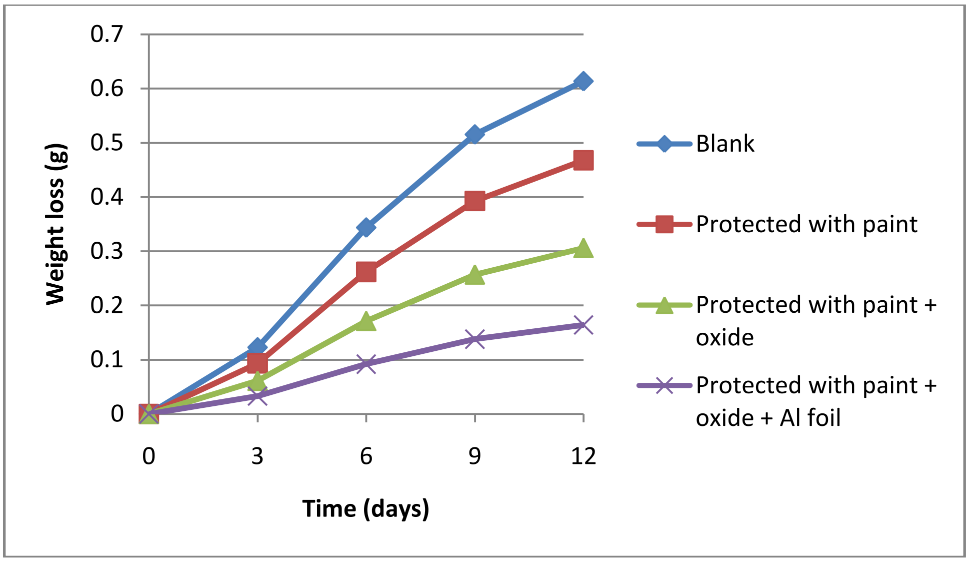

Figure 3.1: Variation of weight loss with time for the mild steel coupons in 0.1 M H2SO4 solution at 30°C

Kinetic Consideration of the Corrosion Process

The weight loss data were subjected to various integrated rate laws for different kinetic orders. The data fitted the first order integrated rate law model equation. Further kinetic plot of Log W_1 (W_1 = final weight) against time for the protected and unprotected mild steel specimens gave linear plots (fig. 3.2) slanting downwards form top left to bottom right indicating first order kinetics [12].

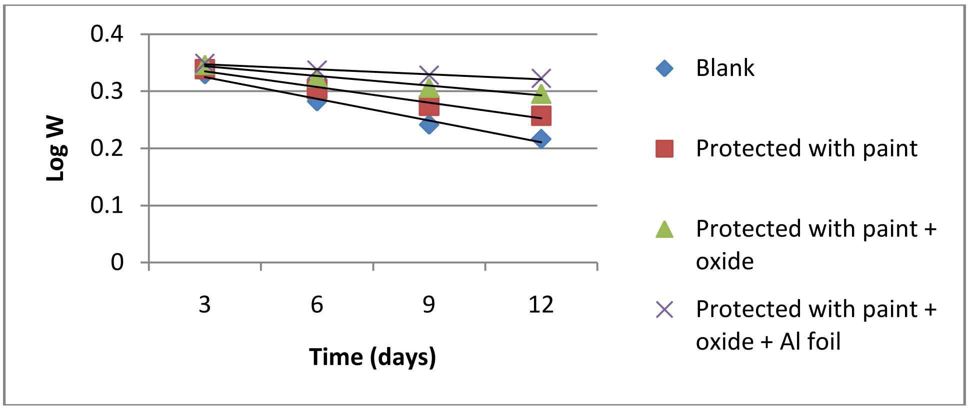

Figure 3.2: Kinetic plot of the weight loss for the mild steel coupons in 0.1 M H_2SO_4 solution at 30°C

Determination of the Amount of Fe^{2+} ions present in the Corrodent using AAS

Tables 3.6 records the extent of deterioration of the mild steel for 12 days in the four systems, while Fig. 3.3 depicts the amount of Fe^{2+} ions graphically with days of exposure. It was observed that the amount of Fe^{2+} ions dissipated into the blank or unprotected system was highest (33.46 mg/kg) for 12 days. The amount of Fe^{2+} ions present in the corrodent for the painted coupon was less than obtained for the unprotected system (27.24 mg/kg) for 12 days. Further reduction was obtained for the mild steel specimen coated with paint mixed with plantain peels oxide (23.86 mg/kg) for 12 days. The least amount of Fe^{2+} ions for 12 days was obtained for the steel specimen coated with paint mixed with the charred plantain peels and wrapped with aluminium foil. The observed trend corroborates the experimental results obtained in the weight loss method and confirmed that the experimental coatings had actually reduced the corrosion rate of the mild steel specimen [13].

Table 6: AAS data showing the amount of Fe^{2+} ions for the four types of steel coupons in mild steel corrodent 0.1 M H_2SO_4 at 30°C

Time (days)	[Fe2+] mg/kg			
	Blank	**Painted**	**Painted with palm bunch oxide**	**Painted with palm bunch oxide and wrapped with Al foil**
0	0	0	0	0
3	12.50	10.53	7.42	4.35
6	19.32	14.32	11.23	8.24
9	27.28	20.61	16.57	12.13
12	33.46	27.24	23.86	19.67

Table 7: Corrosion rate (mdd) and percentage inhibition of the unprotected and protected mild steel coupons in 0.1 M H_2SO_4 solution at 30°C

Label	Mild Steel Specimen	Corrosion rate (mdd)	Inhibition Efficiency (I%)
A	Blank (Unprotected)	108.00	-
B	Coated with paint	82.30	24
C	Coated with painted mixed with plantain peels oxide	53.87	50.4
D	Coated with paint mixed with the oxide and wrapped with Al foil	28.87	73.3

Proposed Mechanism of Protection on the Mild Steel Surface

The observed trend of reduction in corrosion rate is suggested to be due to physical adsorption or 100% surface coverage of the paint on the metal surface. The paint mixture contains atoms such as nitrogen (N) and sulphur (S) atoms which posses lone electron pairs to form coordinate bonds and chelate on the metal surfaces for effective coverage. The further reduction in corrosion rate is due to the induced cathodic protection activity of the highly electron-donating metals present in the plantain peels. The best corrosion rate reduction obtained for the mild steel coupon, coated with the paint mixed with charred plantain peels and wrapped with aluminium foil is due to synergy or conjoint action of sacrificial protection contributed by aluminium foil.

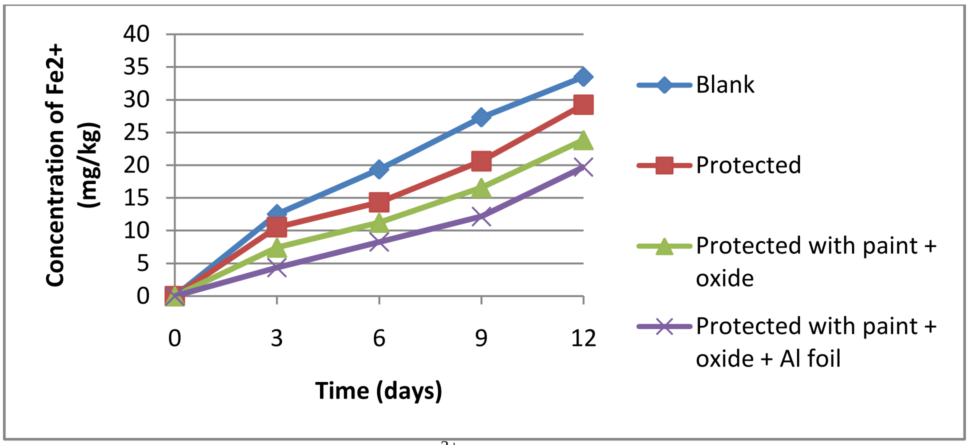

Figure 3: Concentration of Fe^{2+} ion (mg/kg) present in the corrodent

Effect of Coating (Painting) on the Corrosion Rate of Mild Steel Coupons in 0.1 M H_2SO_4 Corrodent

The four types of mild steel coupons were immersed in 0.1 M H_2SO_4 corrodent and the corrosion rate observed for 12 days. Table 3.7 records the corrosion rate of the mild steel coupons while Fig. 3.4 depicts the various corrosion rates in a pictogram. The corrosion rate (mdd) is usually determined using equation 3.1 which is given as follows:

$$\text{Corrosion Rate (mdd)} = \frac{534\Delta W}{DAT} \qquad 3.1$$

Where ΔW = weight loss (mg); D = Density of the mild steel specimen (g/cm^3); A = Total surface area of the metal specimen (cm^2) and T = Time of exposure (days). It was observed that the rate of corrosion was highest in the unprotected mild steel coupon (108.00 mdd). Appreciable reduction was observed for the painted coupon (82.30 mdd). Further reduction in corrosion rate was observed for the specimen coated with paint mixed with the plantain peels oxide (53.87 mdd); while the greatest corrosion rate reduction was observed for the mild steel specimen coated with paint mixed with the charred plantain oxide and wrapped with aluminium foil. The result indicates that the various coatings reduced the weight loss as well as the corrosion rate of the mild steel coupons.

Inhibition Efficiency arising from the type of Protection on the mild steel in the corrodent

Table 3.7 records the percentage inhibition efficiency of the three types of coatings on the surface of the mild steel coupon. The inhibition efficiency is usually calculated using the equation [14, 15] given below:

$$\text{Inhibition Efficiency (I\%)} = \frac{W_0 - W_1}{W_0} \times 100\% \qquad 3.2$$

where W_0 and W_1 represents weight loss in the unprotected and protected mild steel coupon respectively. For the mild steel coupon coated with paint only, 24% inhibition efficiency was achieved due to physisorption. For the mild steel specimen coated with paint mixed with plantain peels oxide, 50.4% inhibition efficiency was achieved. When the mild steel specimen was wrapped with aluminium foil after being coated with paint mixed with the plantain peels oxide, 73.3% inhibition efficiency was achieved. The various inhibition efficiencies are depicted in fig. 3.4 below.

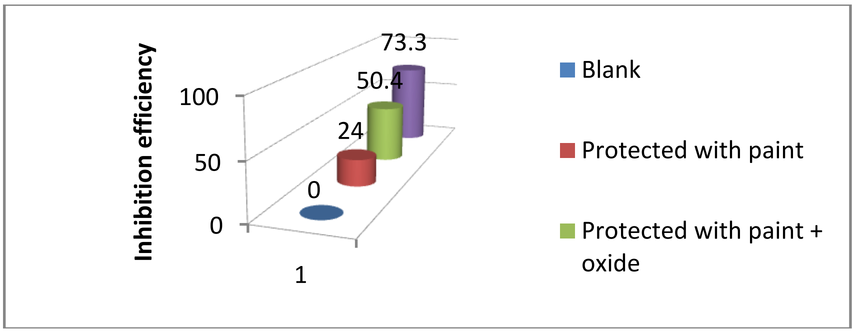

Figure 4: Inhibition efficiencies of the protected and unprotected mild steel coupons in 0.1 M H_2SO_4 solution at 30^oC.

Summary and conclusion

This research was carried out principally to investigate the extent of cathodic protection that could be induced by electropositive metal ions present in charred plantain peels. On the basis of this study, we have established that charred plantain peels when mixed with paint can offer cathodic protection on ferrous metal surfaces. The cathodic protection can further be enhanced through synergism or conjoint action by wrapping the metal with aluminium foil. We propose the inclusion of charred plantain peels in paint formulation such that the oxide could render cathodic protection to prolong the life span of the metal.

Acknowledgement

The authors have benefitted from the input from Professor Inimfon Udoetok of Akwa Ibom State University. We acknowledge his works on characterisation of some agricultural wastes [16]. We also acknowledge the expert advice of Prof. emeritus A. I. Onuchukwu for his advice on cathodic protection.

References

[1]. Osma, J. F.; Herreva, J. L. T. and Couto, S. R. (2007). Banana Skin: A Novel Waste for Lactase Production by Tramets Pubescens under Solid-state Conditions. Applications to Synthetic Dye Decolouration. *Dye Pigments*, 85, 32 – 37

[2]. Okareh, O. T.; Adeolu, A. T. and Adepoju, O. T. (2015). Proximate and Mineral Composition of Plantain (Musa paradisiaca) Waste Flour; A Potential Nutrients Source in the Formulation of Animal Feeds. *Afric J. Food Sci and Technol*, 6(2): 53 – 57

[3]. Gill, L. S. (1992). *Ethnomedicinal Uses of Plants in Nigeria*. University of Benin Press, Benin City, Nigeria, pp. 169 – 170

[4]. Adeniyi, T. A.; Sanni, L. O.; Barrimalaa, I. S. and Hart, A. D. (2006). Determination of Micronutrients and Colour Variability among New Plantain and Banana Hybrids Flours. *World J. Chem*, 1(1): 23 – 27

[5]. Onuchukwu, A. I. (2008). *Electrochemical Technology*. Spectrum Books Limited. Spectrum House, Ibadan, Nigeria, pp. 219 – 223

[6]. Akpan, I. A.; Onuchukwu, A. I.; Ayul, A. A. and Ejike, E. N. (2011). Electrochemical Study of the Cathodic Protection Efficiencies of Selected Anions on Galvanized Steel in Acidic Medium. *Bulletin of Pure and Applied Sciences*, 30C(1-2): 43 – 59.

[7]. Durham, M. O. and Durham, R. A. (2001). Ground System Design: Considerations for Vessels. *IEEE Ind. Applicat Mag*, 7(6): 41 – 49

[8]. Suzana, A. F.; Ferreira, E. A.; Benedetti, A. V.; Hudson, W. P.; Carvalho, C. V. and Santilli, S. H. (2016). Corrosion Protection of Chromium-coated Steel by Hybrid Sol-gel Coatings. *Surface and Coatings Technology*, 299, 71 – 80

[9]. Neville, A. and Morizot, A. P. (2002). Calcereous Scales formed by Cathodic Protection: An Assessment of Characteristics and Kinetics. *Journal of Crystal Growth*, 243(3): 490 – 502

[10]. Akpan, I. A.; Onuchukwu, A. I.; Ayuk, A. A. and Ejike, E. N. (2011). The Study of Cathodic Protection Potentials of Selected Electroactive Anions on Galvanized Steel in Acidic Medium by Weight Loss and Hydrogen Evolution Technique. *Bulletin of Pure and Applied Sciences*, 30C(1-2): 1 – 5

[11]. Akunna, T. O.; Ahaotu, E. O.; Oseji, C. N. and Ibeh, C. C. (2013). Production of Soap using Palm Bunch Ash. *Inter. J. Appl. Sci. Engr*. 1(2): 79 - 82

[12]. Ekpe, U. J.; Ibok, U. J.; Ita, B. I.; Offiong, O. E. and Ebenso, E. E. (1995). Inhibitory Action of Methyl and Phenyl Thiosemicarbazone Derivatives on the Corrosion of Mild Steel in Hydrochloric Acid. *Materials Chemistry and Physics*, 40, 87 – 93

[13]. Akpan, I. A.; Onuchukwu, A. I.; Ayuk, A. A. and Ejike, E. N. (2007). Spectrophotometric Assessment of Cathodic Protection Efficiencies of Selected Anions on Galvanised Steel in Acid Medium. *Bulletin of Pure and Applied Sciences*, 26C(2): 85 – 92

[14]. Akpan, I. A. and Offiong, N. O. (2013). Inhibition of Mild Steel Corrosion in Hydrochloric Acid Solution by Ciprofloxacin Drug. *International Journal of Corrosion*, 2013(301689), 1 – 5

[15]. Williams, E. E.; Akpan, I. A. and Francis, A. J. (2014). Corrosion Inhibition Potential of Ethylamine for Mild Steel Corrosion in Saline Water Environment. *Material Science, An Indian Journal*, 10(5): 173 – 181

[16]. Udoetok, I. A. (2012). Characterization of Ash made from Oil Palm Empty Fruit Bunches (OEFB). *International Journal of Environmental Sciences*, 3(1): 518 - 524