

Synergism of *Saccharum Officinarum*, *Nicotiana Tobaccum* and *Ananas Comusus* Extract Additives on the morphological structure and Quality of Electroplated Zinc on Mild Steel

C.A. Loto^{1,2,*}, A.O. Olofinjana³, Y.N. Allana¹

¹Department of Mechanical Engineering, Covenant University, Ota, Nigeria

²Department of Chemical, Metallurgical and Materials Engineering, Tshwane University of Technology, Pretoria, South Africa

³Faculty of Science, Universiti Brunei Darussalam, Brunei Darussalam

*E-mail: akinloto@gmail.com, cleophas.loto@covenantuniversity.edu.ng, akinloto@yahoo.com

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Synergism of the combined *Saccharum Officinarum* (sugar cane), *Nicotiana Tobaccum* (tobacco) and *Ananas Comusus* (pine apple) extract additives on the surface morphology and quality of electroplated zinc on mild steel in acid chloride solution was investigated at ambient temperature (~28°C). The experiments were performed at different plating time (15 and 18 min), additive concentrations (2, 2.5, 3 ml/50ml of acid chloride solution), pH5, temperature (27-30°C), current (0.08A) and voltage (13 V DC) conditions. Zinc electroplating on mild steel was performed using a DC – supply. Examination of the steel plated surface was performed with scanning electron microscopy (SEM) and Energy Dispersive Spectroscopy (EDS) for surface elemental composition analysis. Different surface characteristics were obtained depending upon the concentration of the additive and the plating time. The corrosion resistance of the plated surface was determined by weight loss method. Surface morphology of the plated surface indicated a good electroplating that was better than either of the extracts alone. The electroplating process was sensitive to changes in additive concentration and plating time as any variation in the plating parameter produced a new and different surface crystal morphology.

Keywords: Synergism, sugarcane, tobacco, pineapple, electroplating, acid chloride, steel surface.

1. INTRODUCTION

The extracts of sugar cane (*Saccharum officinarum*), tobacco (*Nicotiana Tobaccum*) and pine apple (*Ananas comusus*) were separately investigated, in a previous study, in acid chloride under the

same test conditions as used in this present work [1-3]. The positive results obtained encouraged and necessitated the present research interest; looking at the plating reactions and the

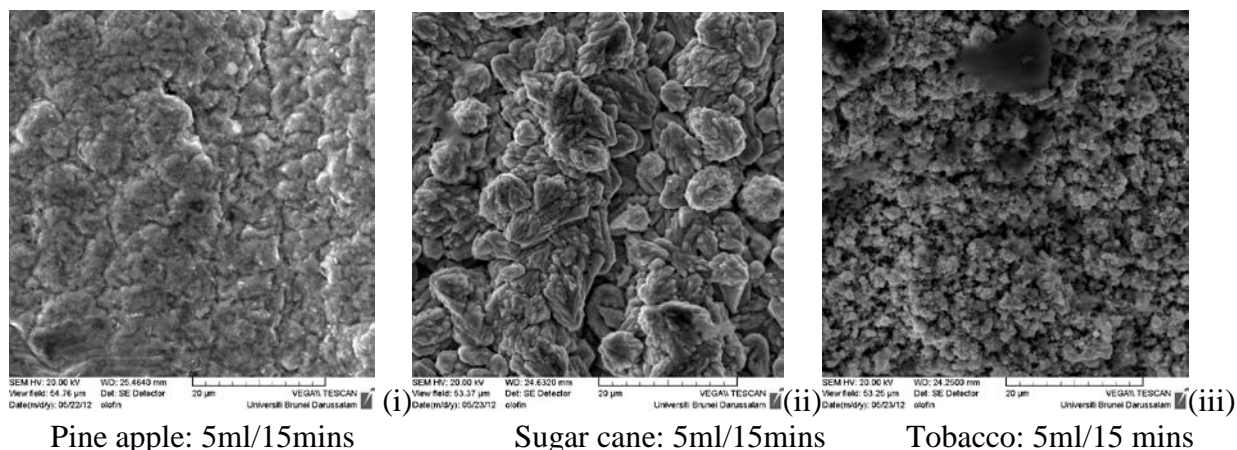


Figure 1. (i-iii): SEM micrographs of zinc plated mild steel using separately, extracts of sugar cane pineapple and tobacco at the same plating time and concentrations [1- 3]

synergism of these extracts when used in different combinations at the same previous plating time and varied concentrations. A summary of some of the results of the plated surface morphology obtained are presented in Fig.1. The use of acid chloride solution for zinc plating in recent time has been widely reported [4- 9] There are also various research reports on the use of plant extracts as additives in zinc chloride plating medium [9-12].

The use of sugarcane (*saccharum officinarum*) juice as addition agent in zinc electroplating from acid based solution has been studied [1 -2]. Sugarcane juice is obtained from the plant. It contains in solution all the soluble substances like sucrose, fine particles of bagasse, wax, clay (adhering to the cane), colouring matter and albumen. The chemical composition contains glucose and fructose, vitamin B2, potassium, etc. Sugarcane contains about 70% of water, in which sucrose and other substances are held in solution, forming about 88% by weight of juice in the stem [12– 13]. Further compositions had been previously mentioned [12]. The remaining 12% represents the insoluble cane fibre component. The cane juice has an acidic pH ranging from 4.9 to 5.5. The juice acidity corresponds to about 0.2%. Another major component of the juice is the colloids. The colloids are particles existing in a permanent state of fine dispersion and they impart turbidity to the juice. The presence of colloids as waxes makes the juice viscous owing to the proteins, pentosans, gums, starch and silica. Sugarcane juice, with its chemical constituents, is expected to exhibit electrochemical activity of enhanced quality zinc plating on mild steel. It is environment friendly.

Similarly, the pineapple juice extract used was obtained from the plant, which is scientifically, known as "*Ananas comosus*" and belongs to the family of *Bromeliaceae*, of the genus *Ananas* and grows on the ground. It can grow up to 1m in height and 1.5m wide. Pineapple contains water, carbohydrates, sugars, sucrose, fructose, glucose, ash, vitamins A, C and phytonutrients such as carotene- β and crypto-xanthin- β . The juice is particularly high in vitamin C, manganese, and vitamin B

[14]. In addition, the juice contains protein, fat, dietary fibre, other vitamins such as folates, niacin, pyridoxine, riboflavin, thiamin, vitamin E, vitamin K. It also contains electrolytes like sodium and potassium and other minerals such as calcium, copper, iron, magnesium, manganese, phosphorus, selenium and zinc. Pineapples contain antioxidants namely flavonoids. The juice also contains the enzyme bromelain, a natural digestive enzyme with anti-inflammatory properties. Bromelain contains peroxidase, acid phosphate, several protease inhibitors and organically bound calcium and is found in peak concentration within the pineapple rind [14].

The use of tobacco extract in the electroplating of zinc on mild steel has been investigated and reported [3]. Some previous work on extracts of tobacco (genus – *Nicotiana*: family- *Solanaceae*), as an environmental benign corrosion inhibitor [15-18, 20] had shown it to be effective in preventing the corrosion of steel and aluminium in saline environments; and in fact, exhibiting a greater corrosion inhibition effect than chromates [18-19]. Tobacco plants produce ~ 4,000 chemical compounds – including terpenes, alcohols, polyphenols, carboxylic acids, nitrogen – containing compounds (nicotine), and alkaloids [20]. These complex chemical compositions may exhibit electrochemical activity such as electrodeposition. A good result here will be of technological and economic benefit.

2. MATERIALS AND METHODS

The experimental procedures here follow the same methods that were previously used [1-3]. The additives used were sugar cane (*Saccharum officinarum*), tobacco (*Nicotiana tobaccum*) and pine apple (*Ananas comusus*) in mixed combinations. The pine apple was extracted as 100% natural juice from the mashed pulp. The skin of the fresh pineapple as well as the crown was removed. The pineapple was cut into chunks and placed in a juice extractor for a few minutes. This juice was obtained and the residue was discarded. The sugarcane was similarly extracted as 100% natural juice from the mashed pulp. The sugarcane juice was obtained by peeling the skin off the sugarcane and cutting into small pieces. These pieces were then pounded to soften the sugar cane. The mashed fibres were squeezed through a sieve to obtain the juice. Both pine apple and sugar cane juice were kept in a refrigerator to ensure effective preservation.

The tobacco extract was obtained from the leaves which were sun dried for 10 days before being ground to powder form in order to increase the surface area for extraction. Two portions of ground tobacco leaves weighing 137 g each were soaked in 420 ml of ethanol for 5 days. The ethanol was then boiled off on a heating mantle using a simple distillation set to collect the ethanol that was used. 30 g of concentrated tobacco extract was obtained after the distillation process. The gelatinous extract was then dissolved in 300 ml of distilled water to obtain a concentration of 0.10g/ml (100g/l). The solution was stirred vigorously to ensure that the tobacco was properly dissolved.

2.1 Experimental set-up

Flat mild steel, SIS 14147, 0.1 cm thick, with a nominal composition of 0.038% C, 0.195 Mn and the remainder Fe, was cut into several test specimens of 10.0 cm long and 1.0cm wide. A portion

of 1.0 cm in length was marked off at one end for the electroplating of zinc. The test specimens were degreased ultrasonically for 5 minutes and then removed from the solution, rinsed in distilled water, immersed in methanol, and air dried. The specimens were, in turns, etched for 50 seconds in 3M HCl, rinsed in distilled water, immersed in methanol, air dried and stored in a desiccator for further experimental process. The acid chloride solution for the electrodeposition consisted of ZnCl (71g/l), KCl (207g/l) and H₃BO₄ (35g/l). Mixed solution extracts of *saccharum officinarum*, *nicotiana tobaccum* and *ananas comusus* (pineapple) of varying concentrations - 2, 2.5, 3 ml/50ml of acid chloride solution were used in turns as the addition agents (Table 1).

Table 1. The bath addition agent and concentration used

Additive		Quantity of additive/ 50ml of acid chloride		% Concentration
Sugarcane + Pineapple	+ Tobacco	a.	2 ml	4
		b.	2.5 ml	5
		c.	3 ml	6

Electroplating of zinc on steel was performed by partially immersing the steel specimen and the zinc electrodes in the plating solution (20mm deep) through the rectangular hole made on a prepared plastic cover for the 250ml beaker used as the plating bath. The steel specimen was connected to the negative side of a DC supplier while the zinc electrodes were also connected with a wire to the positive side, Fig. 2.

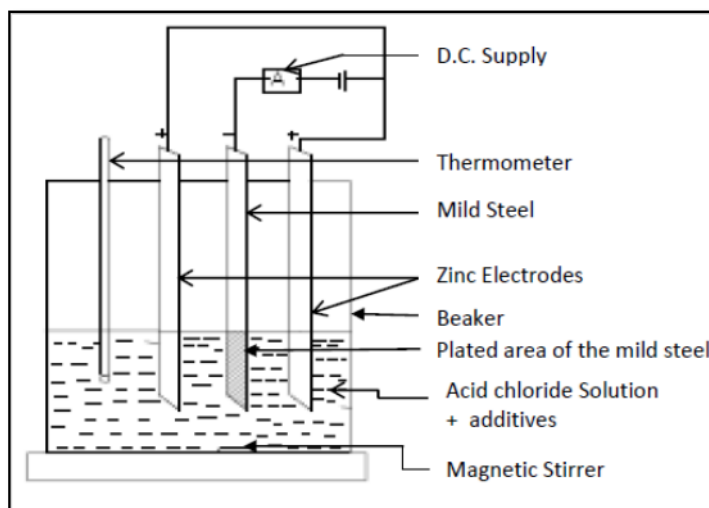


Figure 2. Schematic diagram of the experimental set-up

The plating solutions were put in turns into the beaker and their respective pH was obtained by adjusting the original solution with potassium hydroxide. The plating times used for each bath were 15 and 18 min. The weight of the steel specimen was taken before and after the electroplating process in

order to determine the weight of zinc deposit by finding the difference in both weight readings, (Table 2).

Table 2. Mass of zinc deposited on steel substrate during plating

Sample	Mass Deposited (g)
19A	0.0253
20A	0.0301
21A	0.0239
22A	0.0306
23A	0.0226
24A	0.0279

The plating solution was stirred gently while the plating was being carried out to ensure even plating. The other operating conditions were: pH of the solution, 5; temperature, 27-30°C; current 0.08A; Voltage, 13V DC; plating time, 15 and 18 min. After each plating experiment, the specimen was taken out, rinsed in distilled water, immersed in methanol, and quickly air-dried. The specimens were stored in a desiccator for further analysis.

2.2. SEM/EDS characterisation

A scanning electron microscope (SEM) equipped with energy dispersive spectroscopy (EDS) was used to examine the surface morphology of each of the plated test specimens. A small portion of each of the specimens was cut and mounted on a stub. The specimens were examined in turn in the SEM, and electron micrographs were made of the representative areas of the surface at different magnifications. The EDS analysis was also done to determine the composition of the surface of the plated metal.

2.3. Adhesion test

Adhesion of zinc coating to the steel substrate was tested by using cellotape fastened to the surface and later pulled off. This was then visually observed for any zinc stripping from the plated steel's surface. The plated surface was further scratched with a scalpel to test for the zinc adhesion.

2.4. Corrosion resistance testing of electroplated specimen

Corrosion resistance of the electroplated mild steel was tested gravimetrically. Each of the plated mild steel test specimens was partially immersed in the seawater test environment. The seawater was topped up to replace the amount lost due to evaporation. Weight Loss measurements were taken every two days for a period of 24 days. Corresponding corrosion rates values were determined from these weight loss values by calculation using this formula:

$$C.R. = 87.6W/DAT \dots (1)$$

Where W is the weight loss in milligrams (mg), D is the density in g/cm^2 , A is the area in cm^2 , and T is the time of exposure in hours.

3. RESULTS AND DISCUSSION

3.1. Electrodeposition of zinc

Figure 1 shows comparatively, the distinctive morphological structures that were previously observed separately in the extracts of sugar cane, pine apple and tobacco additives alone. Obviously, a finer grain microstructure was obtained with the use of tobacco alone than the sugar cane and the pine apple alone, though the sugar cane and pine apple extracts provided far brighter electroplating. The combinations of these extracts as presented below would show different morphological structures that emanated from their synergistic performance.

3.1.1. Not plated and zinc plated mild steel samples without additive

The SEM micrographs of the surface of the mild test samples before zinc plating and after plating, (without additive) are presented in Fig. 3 (i and ii) respectively. Fig. 3(ii) shows that there was no apparent porosity observed when zinc was electroplated on the steel test samples from acid–chloride solution without any additive at the portion photographed with the SEM. The crystals were distinct but the shapes are difficult to describe. Some coarse and fine particles were interspersed with each other and were closely packed. Subsequent micrographs below show the crystals to be very much different from those plated with additive. The surface crystals feature was not particularly smooth. The surface crystal coarse structure could be due to the absence of levelling agents in the acid solution. The poor throwing power of the acid plating solution could also cause the observed coarse crystal morphological structure of the plated sample surface [1-3, 21]

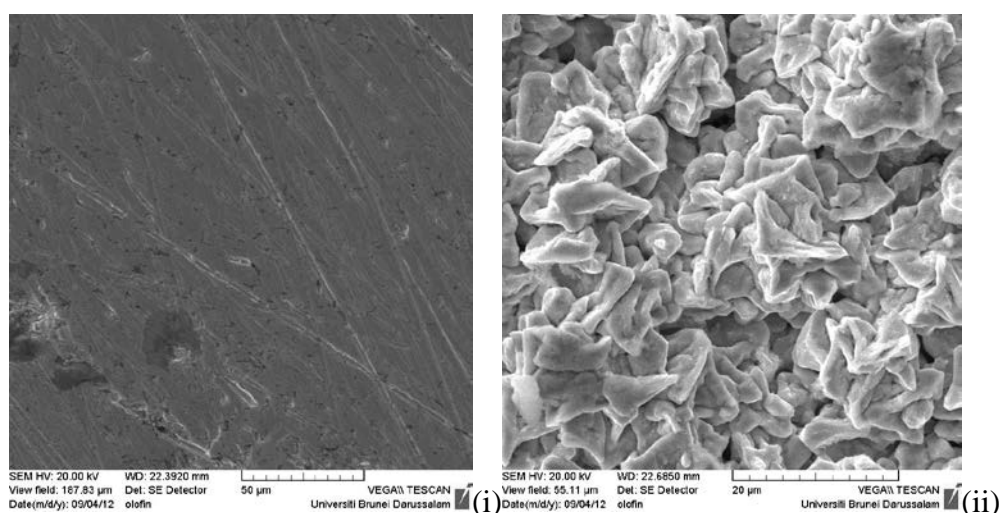


Figure 3. SEM micrographs: (i) Not plated; (ii) zinc plated mild steel sample without additive.

3.1.2 Plating with same additive concentration and different plating time

2 ml /50 ml additive at 15 and 18 minutes plating time

Fig.4 (i and ii) shows the micrographs made with the plating at 15 and 18 min respectively with the combined sugar cane, tobacco and pineapple juice extracts concentration of 2 ml/50ml of acid chloride solution. The surface microstructure of each is fine, and more of compact and dense grains, and very much levelled. However, the morphological structure for Fig. 4(ii), plating at 18 min looks finer than that of Fig. 4(i), the plating at 15 min. It shows that the plating time affected the surface morphological difference, though minimally. The brightness of each micrograph was not better than that of pine apple extract additive alone and also the sugarcane extract additive alone but much better than the tobacco extract alone. The mass of zinc deposited for each of the plated sample was close in value but more in the plating at 18 min (30.60 mg) than the plating at 15 min (23.9 mg) as presented Table 2.

There was no discernible porosity observed at the portions examined. The crystal particles were densely packed and creating a well-defined surface microstructure. When compared with the Fig. 3 (ii), that is, with the one without added juice extract, a significantly clear difference in surface structure could be observed. It is apparent that the observed very closely packed grains and levelling difference in surface morphology as shown in Fig. 4 (i-ii), resulted from the synergism exhibited by the combined extracts of sugar cane, tobacco and pine apple additive.

The complex chemical compositions of each of the extracts in combination could, plausibly, be associated with the surface structure changes/modification obtained. The microstructure observed in Fig.4 (i-ii), is unique and shows good quality zinc electroplating with clearly refined surface grain structure.

2.5ml /50ml of additive at 15 and 18 minutes plating time

Fig. 4 (iii and iv) showed a surface morphological structure that was compact and closely packed when the combined extract additive concentration was changed from 2 ml to 2.5 ml extract/50 ml of acid chloride solution and for the plating time of 15 and 18 min. The surface structure also look different from those of Fig. 4 (i and ii). The micrographs are also very much different from those in Fig.1 that show separate extracts alone. The increase in the plating time clearly show significant surface morphological changes between the two micrographs. Fine spherical surface crystals with very good levelled appearance could be observed in Fig. 4 (iii). The structure for the 18 min plating time, Fig. 4 (iv), also appeared finer, compact and more levelled. The deposition looked dense and very closely parked. The samples' surface was brighter than in the use of tobacco extract additive alone and also brighter than the sugarcane's and pine apple's extracts alone [1-3].

The mass of zinc deposited for 15 min plating time was 22.6 mg (Fig 4 (iii)) and for the 18 min plating time, it was 27.9 mg (Fig. 4 (iv)) respectively. Their micrographs showed no apparent porosity. The morphological structure obtained here could be associated with synergism effect of the mixed extract additives and the longer plating time gave finer and more levelled appearance.

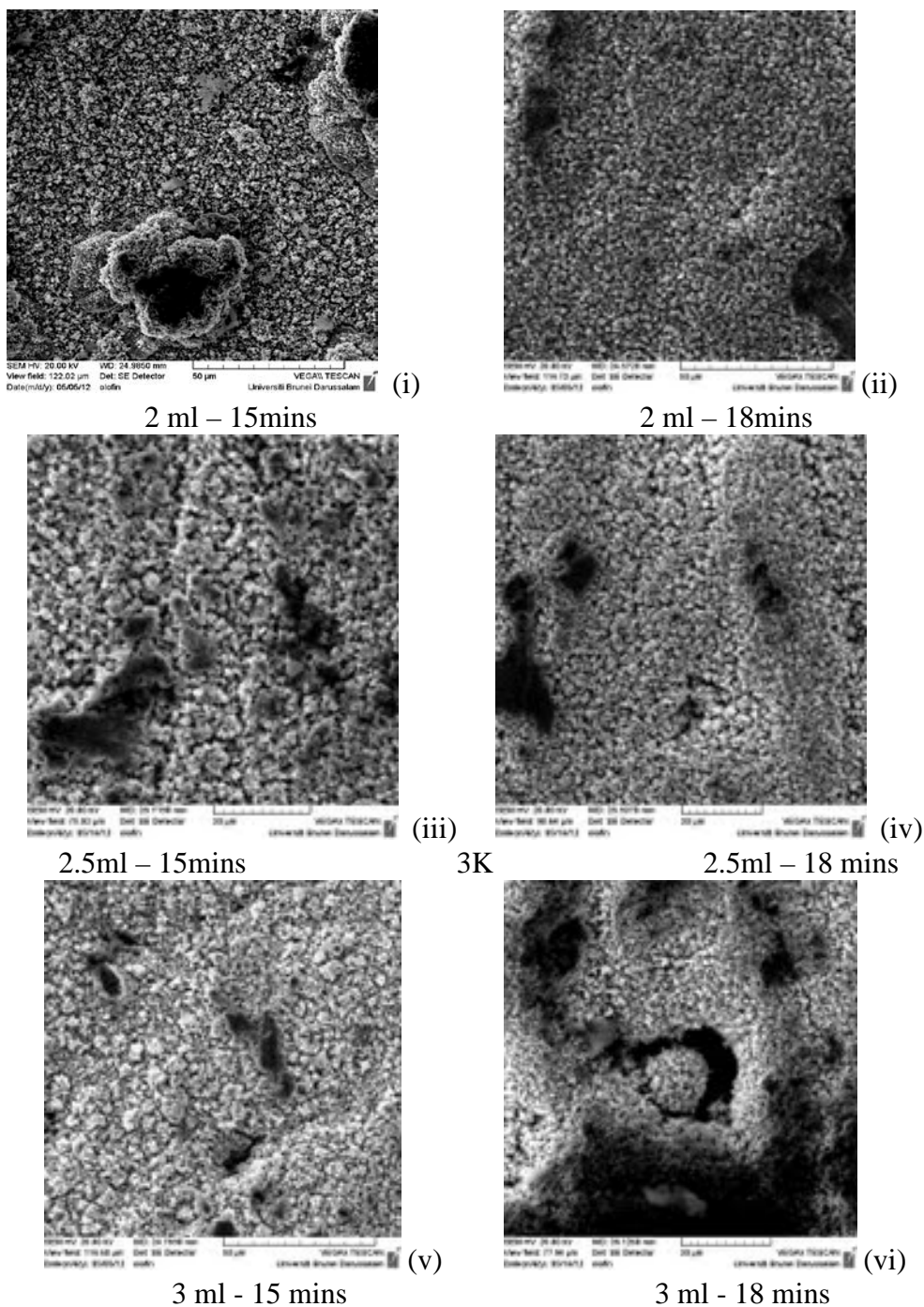


Figure 4. SEM micrographs of steel surface after zinc plating with the same additive concentration and different plating time.

3 ml /50ml of additive at 15 and 18 minutes plating time

Figure 4 (v and vi) show the SEM micrographs of steel surface after zinc plating with 3 ml /50ml of acid chloride solution at 15 and 18 min respectively. There was insignificant porosity observed in the micrographs. The surface microstructure show closed- packed, fairly bright and fine, levelled grains, as in Fig. 4 (v) and finer sand-like grain particles as in Fig. 4 (vi) for 15 and 18 min plating time respectively. A good plated surface morphology was observed. It is thus appropriate to

associate the observed surface features here with concentration and plating time effect. The plated zinc was expected to corrode sacrificially to protect the mild steel substrate. The mass of zinc deposited during the plating was 25.3 and 30.10 mg for the 15 and 18 min plating time respectively. A clear observation in this section is the concentration effect. The more the concentration of the additives used, the clearer the definition of the surface grain crystals and the brighter the plating appearance. In addition, the mass of zinc deposited for each of the plating was more for the plating at 18 minutes.

3.1.3 Plating with different additive concentrations and same plating time

Presented in Fig. 5, are the various SEM micrographs for the samples plated at different concentrations of 2, 2.5, and 3 ml/50ml at the same plating time of: (A) 15 min and (B) 18 min respectively.

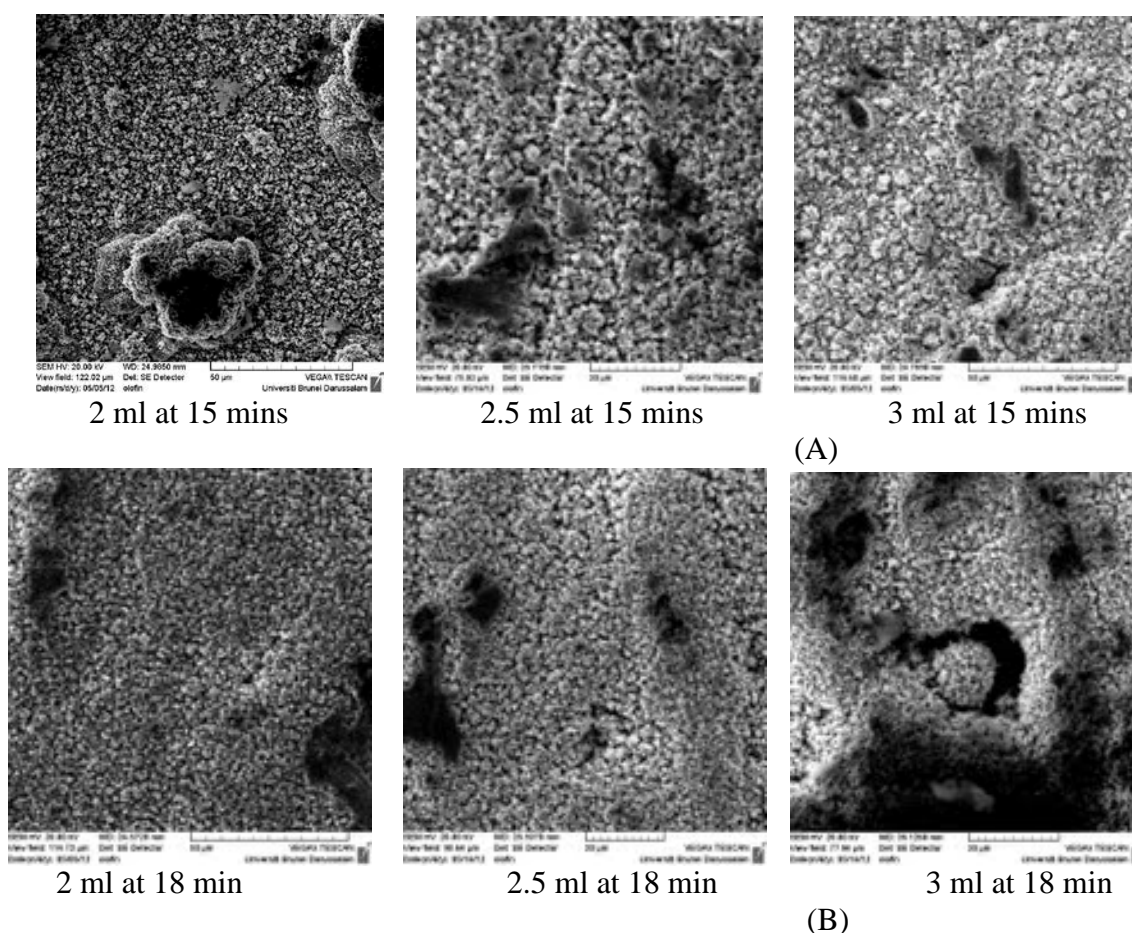


Figure 5. SEM micrographs of steel surface after zinc plating with the different additive concentration. (A) At 15 min); (B) at 18 min

The surface morphology of each of these micrographs had been described above in Fig. 4. For surface structural comparison they are re-presented in Fig. 5 in re-arranged form. Plating at 15 min with different extracts concentrations show compact, dense and almost porosity free, levelled and fine grain morphological surface structure that indicated good plated surface morphology. However, the

microstructure looked different in shape from 2 ml /50ml to 3 ml /50 ml extract additive concentrations. A unique observation here is that the plating at 18 min for the same concentrations of extract additive, show very similar microstructural features at all the concentrations used. In addition, the finest grain crystals, in general, were obtained with extractive additive concentration of 3 ml/50 ml for the plating. Just as described above, the crystals were very fine, closely packed, levelled; very similar in shape and no significant porosity observed. The plating time of 18 min at all the concentrations used seem to have more unique microstructure comparatively.

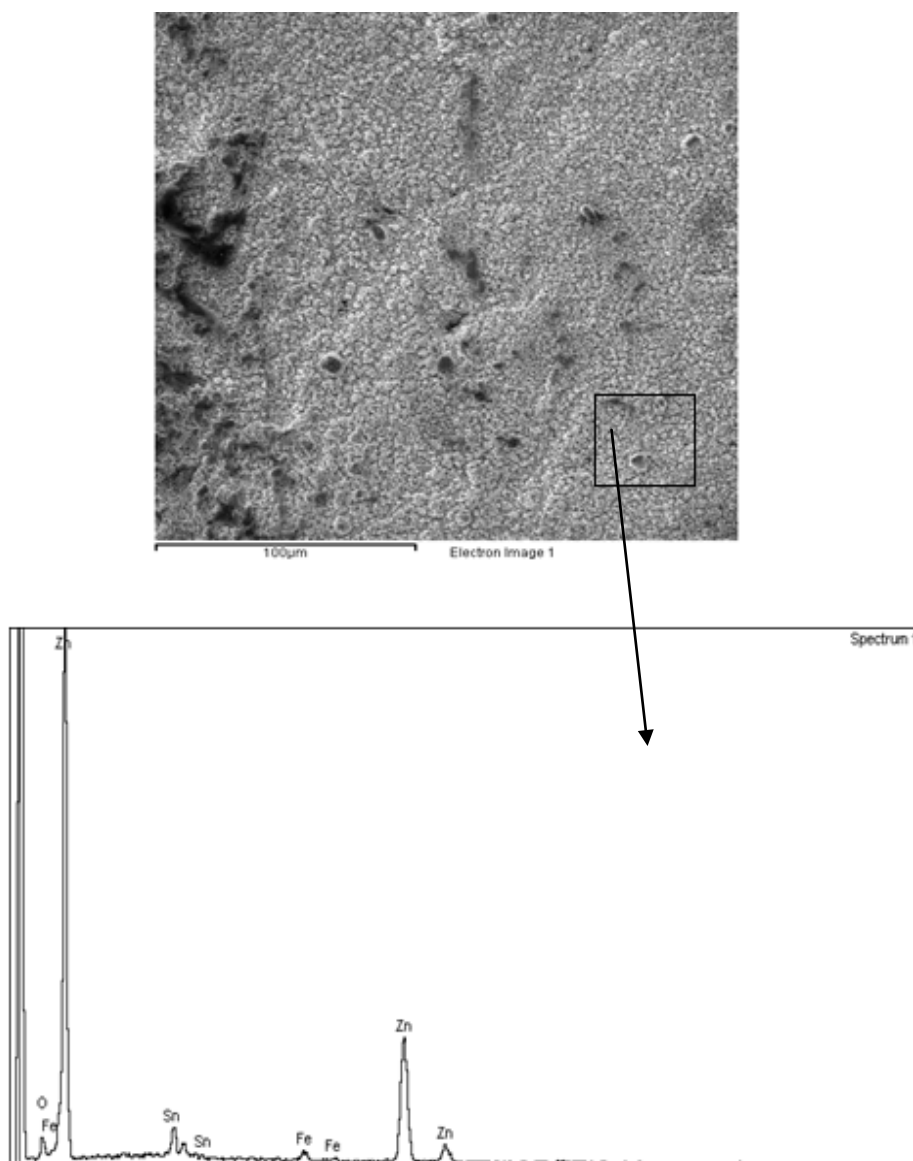


Figure 6. EDS analysis of the zinc plated surface of sample in Fig. 4 (v).

Just as described above, the plating at 15 min also gave the same similar characteristics for the 18 min zinc plating time. The surface morphology for each of the plating time for the three different concentrations bears very close similarities in grain structure. The grains were fine, the surface was levelled and the plating was bright. The surface crystal morphology showed good zinc electroplating

on the mild steel substrate. The quality electroplating observed generally with these combined extracts is a good indication of their synergistic performance that emanated from the different combined chemical constituents of tobacco, pineapple and sugar cane. These when separately used previously showed very effective and good quality electroplating performance.

Adhesion test

The adhesion test confirmed the strong adherence of the plated zinc to the mild steel substrate surface. Also there was no visible particle removed from the plated steel surface when it was visually inspected. In anticipation, the electroplated mild steel surface would, most likely, provide corrosion protection of the steel surface; the plated zinc will sacrificially protect the substrate from corrosion in a corrosive medium.

EDS Analysis

The result of energy dispersive analysis (EDS) of a zinc plated sample in 3 ml/50 ml acid chloride concentration at 15 min plating time is presented in Fig. 6. The surface microstructure showed it to be mainly zinc; there are also minor traces of tin co-deposited. There was no porosity at the portion of the sample examined and no any other metallic impurity except iron in trace form was present. The surface microstructure of the EDS analysed plated sample was closely packed, bright, levelled and with fine crystal grains which indicate good morphological structure and a good evidence of the combined extracts effective synergism.

3.2. Corrosion resistance of the zinc plated mild steel

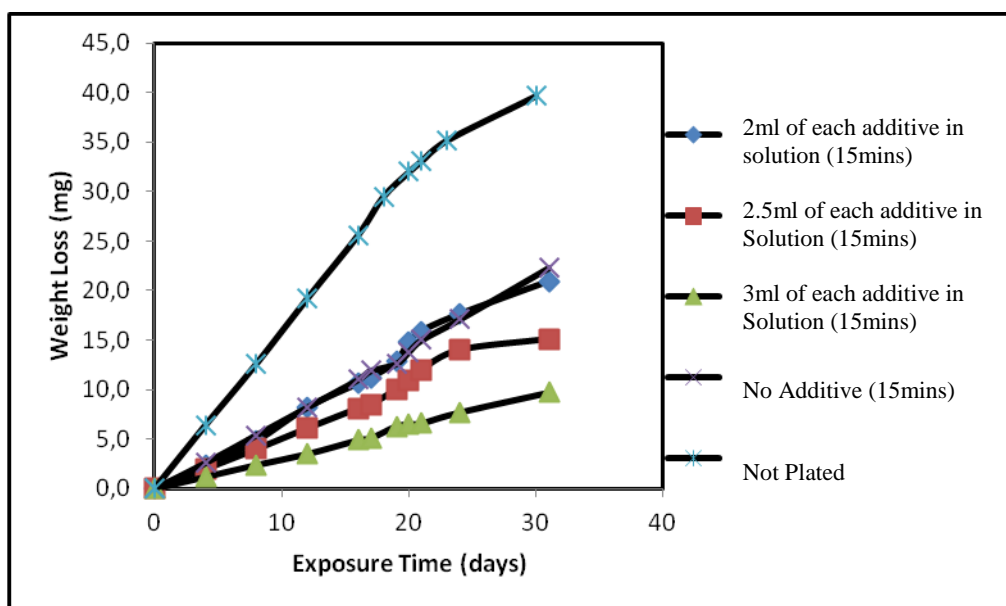


Figure 7. Variation of weight loss with exposure time for the zinc electrodeposited mild steel sample in seawater. (Different combined additive concentrations at 15 min plating time)

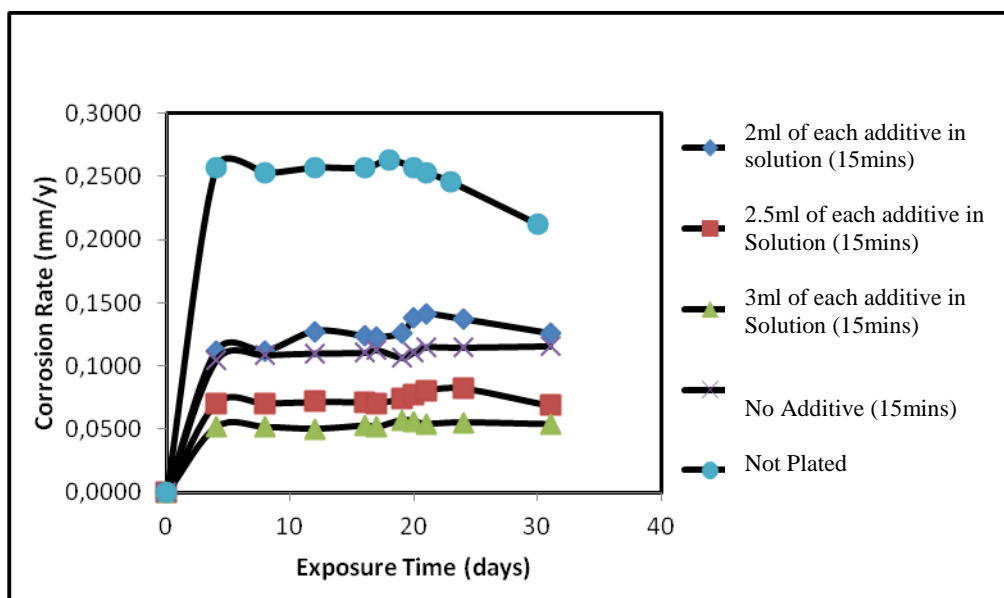


Figure 8. Variation of corrosion rate with exposure time for the zinc plated mild steel samples in seawater. (Different combined additive concentrations at 15 min plating time)

The results of the weight-loss method and the calculated corresponding corrosion rates of some of the zinc plated mild steel samples that were tested in the sea water medium are presented in Figs. 7 to 10. Fig. 7 shows the curves of the weight loss versus the exposure time at different concentrations of the combined pineapple and sugarcane extract additives and at the plating time of 15 min for each of the test samples.

There was better corrosion resistance of all the plated samples than the unplated sample. While the unplated sample recorded a weight loss of 39.70 mg on the 30th day of the experiment, the sample plated separately with 2 ml, 2.5 ml and 3 ml combined pineapple, tobacco and sugarcane extract /50 ml acid chloride solution recorded the different weight loss values of 21.10, 15.1 and 9.7 mg respectively at the same period of 30 days of the experiment. The weight loss recorded for the plated samples was due mainly to the anodic zinc dissolution in the test environment [3] after a long period of 30 days. The plated sample without additive also performed fairly well.

The corresponding corrosion rates curves are presented in Fig. 8. The unplated test sample recorded the highest corrosion rate (0.213mm/yr) on the 30th day of the experiment; while the other samples plated with 2, 2.5 and 3ml different concentrations of the combined extract additives / 50 ml acid chloride solution recorded 0.1156, 0.0688 and 0.0540 mm/yr respectively at the same periods of the experiment on the 30th day. The corrosion resistance or susceptibility performance of the electroplated surface of the mild steel substrate was not significantly affected by the different concentrations of the extract additives used. However, there was a tendency towards improved better corrosion resistance with increase in extract concentration. The extracts function mainly in levelling effect and in enhancing brightness of the plating and hence in morphological structure modification.

The results obtained for the weight loss and the corresponding corrosion rates respectively for the zinc plated mild steel in sea water at the plating time of 18 min while maintaining the other plating parameters are presented in Figs 9 and 10. The samples plated with 2 ml solution extracts (as additive),

gave the lowest weight loss (8.00 mg) on the 30th day of the experiment and followed with the 3 ml additive concentration (13.4 mg); the 2.5 ml concentration extract additive recorded 16.9 mg weight loss. In comparison, the sample plated without additive achieved a weight loss value of 33.5 mg during the same plating period while the unplated sample had a value of 39.7 mg. The same trend was also followed in the corrosion rate.

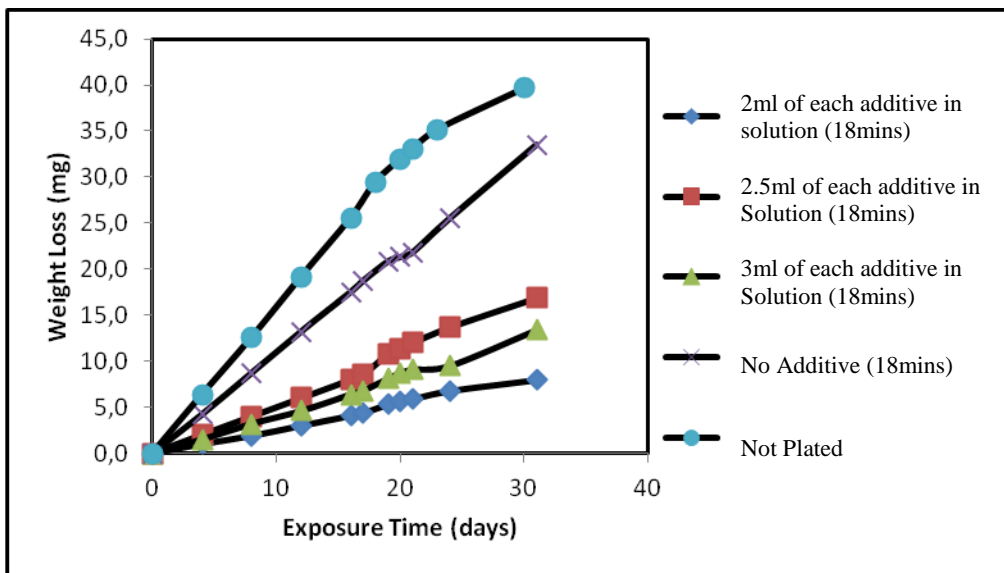


Figure 9. Variation of weight loss with exposure time for the zinc electrodeposited mild steel sample in seawater. (Different combined additive concentrations at 18 min plating time)

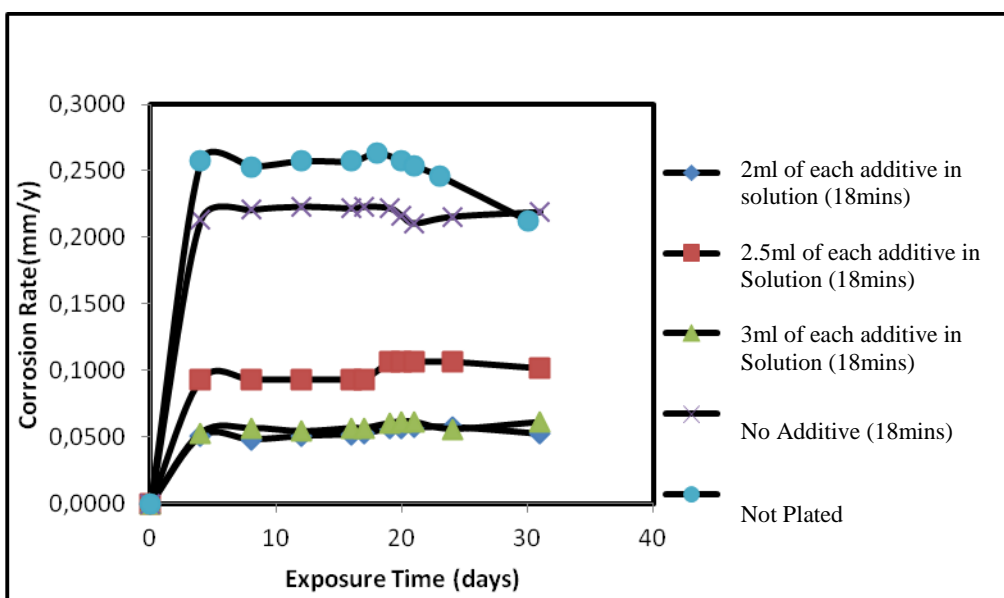


Figure 10. Variation of corrosion rate with exposure time for the zinc plated mild steel samples in seawater. (Different combined additive concentrations at 18 min plating time)

The lowest corrosion rate, 0.0610 mm/yr was recorded for the sample tested with 2 and 3 ml combined pineapple, tobacco and sugar extract additive at the same period of the experiment; while the

value of 0.1017 mg was achieved for the 2.5 ml extract concentration. Much higher values of corrosion rate for the sample without additive of 0.2160 (20th day) and 0.2192 (30th day) were recorded and for the unplated sample, the corrosion rates achieved were 0.2572 (20th day) and 0.2127 (30th day). These results confirmed the plating time to be a factor to consider.

The weight loss values recorded for the specimens plated at 18 min plating time were much lower than those with the 15 min plating time. Like-wise, the corrosion rate values achieved were very much lower in the plating samples made at 18 min plating time than with the samples plated at 15 min plating time.

The overall results obtained confirmed the plated samples to be more corrosion resistant and hence more protective. The corrosion of the plated samples was apparently due to the dissolution of the deposited zinc in the test medium which sacrificially protected the mild steel substrate

It can be summarised that the results obtained for corrosion resistance performance of the samples bear very close correlation with the surface microstructure in the micrographs and also to the mass of zinc deposited on the plated portions. The inference from the above is that the more compact and levelled the surface crystal particles and the finer the crystal hence the morphological structure are, the better the corrosion resistance of the plated samples [3].

4. CONCLUSIONS

1. The combination of sugar cane (*Saccharum officinarum*), tobacco (*Nicotiana tobaccum*) and pineapple (*Ananas comusus*) extracts as the addition agent gave good zinc electroplating with fine, dense, levelled and close- packed crystal grains on mild steel surface in the acid zinc chloride solution.
2. The zinc plated surface of the mild steel substrate showed minimal different surface morphology.
3. The electrodeposition process was less sensitive to changes in additive concentration and plating time when compared with the previous use of the additives separately, thus indicating effective synergistic plating quality.
4. When compared with the unplated samples, the plated samples showed good corrosion resistance in seawater test and thus confirming their expected mild steel protection in the tested environment.
5. The plating produced bright deposition that was brighter than either of the combined extracts of pineapple, tobacco and sugar alone and thus exhibiting synergism characteristic. The additives used in combination were non-toxic plant products; they are eco- friendly.

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