

Technical Report

## **Influence of *Ananas comosus* Juice Extract as Additive on the Electrodeposition of Zinc on Mild Steel in Acid Chloride Solution**

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Electrodeposition of zinc on mild steel in acid chloride solution using as additive, different concentrations of *ananas comosus* (pineapple) juice extracts, was investigated. Different additive concentrations, plating time, and constant pH conditions were used for the experiments. The electrodeposition of zinc on mild steel was performed using a DC – supply. The surface of the plated steel was examined using scanning electron microscopy (SEM); and Energy Dispersive Spectroscopy (EDS) for surface elemental composition analysis. Different surface microstructural features were obtained depending upon the concentration of the additive and the plating time. The corrosion resistance of the plated surface was also determined by gravimetric method. The quality of electrodeposition of zinc was good as indicated by the plated surface morphology.

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**Keywords:** Electrodeposition, pineapple, steel, acid chloride, corrosion, surface characteristics

### **1. INTRODUCTION**

Acid zinc-based baths have grown in popularity in the past few years. This phenomenal growth has resulted from the need to avoid the toxicity of cyanide –based baths and their costly effluent following stringent regulation against water pollution. For some years, the commercially–available proprietary additives have been used [1-4]. However, the present interest in further research necessitates the need to develop other environment –friendly non-commercial proprietary additives for the acid chloride baths. The importance of electrodeposition (electroplating) in engineering products/facilities and in our daily lives is further made significant by the need to prevent corrosion and toxicity, and to enhance the aesthetic value of steel components in the automotive, construction,

electronics, electrical appliances, recreational and materials handling industries and in our daily lives. This has, in addition, led to an enlarged interest in the field of electrodeposition.

In recent works [5-7], surface characterisation of the effects of organic additives on the electrodeposition of zinc on mild steel and the influence of organic additives on the surface characteristics of zinc electrodeposition on mild steel in acid-chloride solution under different conditions were performed. The use of *ananas comosus* (pineapple) under different experimental working parameters/conditions in this study is an attempt to further extend these previous investigations.

Two types of non-cyanide zinc plating solutions are in use – mildly acid solution using chloride or sulphate anions, and alkaline-zincate solutions [8]. The mild baths generally consist of zinc chloride dissolved in solution of excess ammonium chloride. More recently, potassium chloride processes, which are far less corrosive, have been marketed and ammonia free-formulation is now the most popular in production [4]. Zincate baths consist solely of a small concentration of zinc metal dissolved in approximately 100g/l of sodium hydroxide solution [9]. Chloride zinc solution does not only eliminate cyanide in plating, it also gives improved bath efficiency and exceptional brightness. And zinc baths are used where it is desirable to have a high plating rate and low cost. Chloride zinc plating offers considerable advantages over cyanide-based systems, although it is not without its share of routine operating problems [3]. Use of the acid sulphate process is increasing due to its relatively low cost, safety features and pollution control characteristics, but throwing power and insufficient brightness from an acid sulphate bath are disadvantages [9]. Many other authors [10-13] have also reported in different areas of zinc and zinc alloys electrodeposition and on synergistic effect of electrodeposited alloys / effect of addition agents and also on their corrosion resistance characteristics using different bath solutions.

The use of local plant, pineapple juice, as addition agent in zinc electrodeposition from acid based solution, in this work, makes this study significant. Pineapple juice is obtained from the plant. Pineapple is a tropical fruit which grows in countries which are situated in the tropical and sub-tropical regions. Scientifically, it is 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.

Raw pineapple juice is high in vitamin C, manganese, and vitamin B [14-15]. Pineapple mainly contains water, carbohydrates, sugars, sucrose, fructose, glucose, ash, vitamins A, C and phytonutrients such as carotene- $\beta$  and crypto-xanthin- $\beta$ . In addition, the juice contains also, 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.

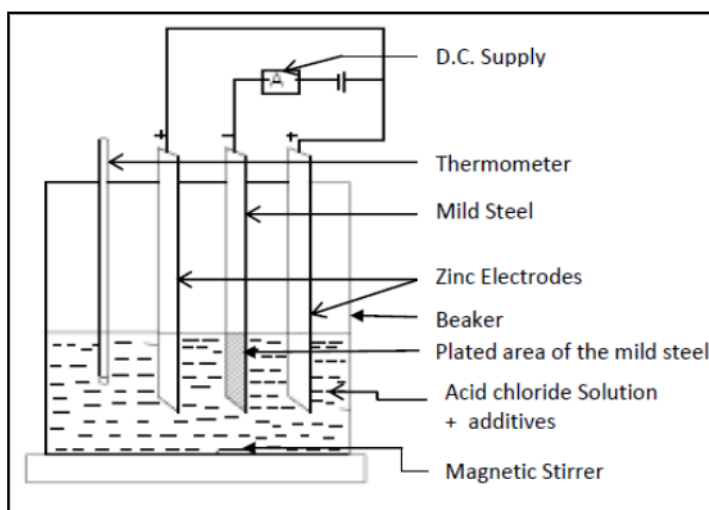
Pineapples contain antioxidants namely flavonoids, vitamin A and C (already mentioned above). These antioxidants reduce the oxidative damage such as that caused by free radicals and chelating metals. The juice also contains the enzyme bromelain, which is a natural digestive enzyme with anti-inflammatory properties. Bromelain contains peroxidase, acid phosphate, several protease inhibitors and organically bound calcium and is found in peak concentration within the pineapple rind [16].

Considering the chemical constituents of pineapple juice as written above, it is expected to exhibit electrochemical activity of enhanced quality zinc electrodeposition on mild steel. As an edible natural compound it is also very environment friendly. Its successful use as an additive, in the improved deposition of zinc on mild steel, will be technologically and economically beneficial.

## 2. MATERIALS AND METHODS

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 electrodeposition of zinc. The test specimens were degreased ultrasonically for 5 minutes with an alkaline degreasing chemical – Henkel VR 6362-1, 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 H<sub>3</sub>BO<sub>4</sub> (35g/l). Extracted *Ananas comosus* (pineapple) juice of varying concentration: 4, 5, 6 ml/50ml of acid chloride solution (80, 100, 120ml/l) were used in turns as the addition agents (Table 1).



**Figure 1.** Schematic diagram of experimental set-up.

Electrodeposition 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 prepared Perspex 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. 1. 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 minutes. 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 between both weight readings, (Table 2). 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.

**Table 1.** The bath addition agent and the concentration used

Additive	Quantity / 50ml of acid chloride	% Concentration
Pineapple juice - (extracted)	a. 4.0ml	0.08
	b. 5.0ml	0.10
	c. 6.0ml	0.12

### 2.1. SEM/EDS characterisation

A scanning electron microscope (SEM) equipped with energy dispersive spectroscopy (EDS) was used to examine the surface topology and 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.

### 2.2. Adhesion test

The adhesion of the zinc coating to the steel substrate was tested by using cellotape fastened to the surface and later pulled off and visually observed for any zinc stripping from the plated steel's surface. The plated surface was scratched with a scalpel to test for the zinc adhesion. The specimens were too small for a bending test.

### 2.3. Corrosion resistance testing of electroplated specimen

Corrosion resistance of the electroplated mild steel was tested in sea water gravimetrically. The water was obtained at the Alpha Beach, Lekki, Lagos, Nigeria from the Atlantic Ocean. Each of the test 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:

$$\text{C.R.} = \left[ \frac{87.6W}{\text{DAT}} \right] \quad \text{eqn. 1}$$

Where W is the weight loss in milligrams, D is the density in  $\text{g/cm}^2$ , A is the area in  $\text{cm}^2$ , and T is the time of exposure in hours.

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

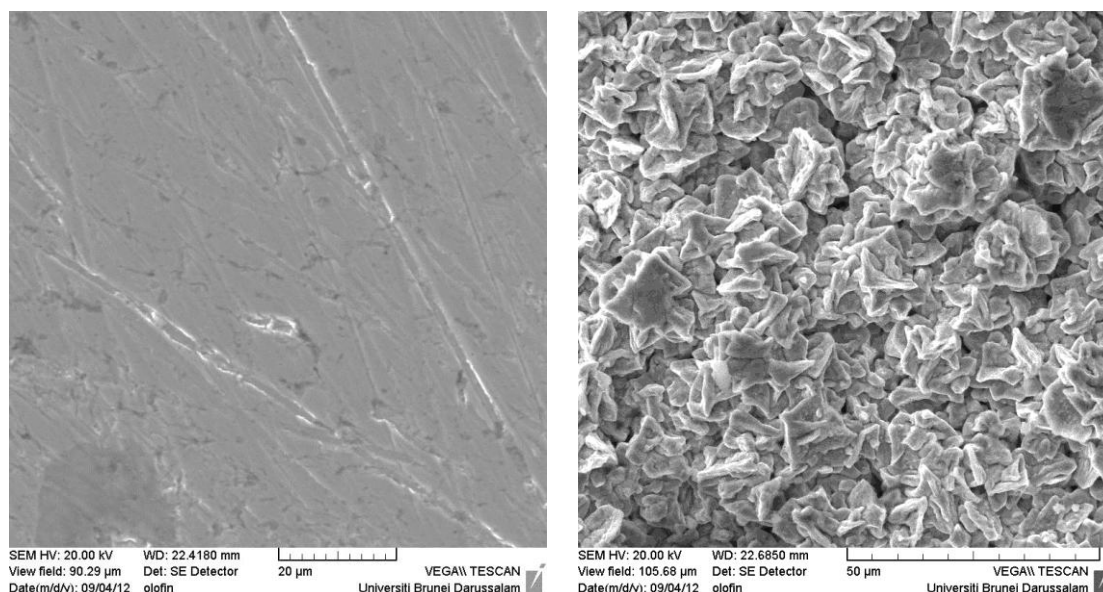
Sample	Mass Deposited (g)
U2	0.0232
V2	0.0499
W1	0.0228
X2	0.0373
Y2	0.029
Z2	0.0253

### 3. RESULTS AND DISCUSSION

It is important to state here that the major variables that will describe and explain the results obtained in this work will be the electrodeposition time effect and the amount of the sugarcane extract additive used in the acid chloride solution.

#### 3.1. Electrodeposition of zinc in acid chloride solution without additive

The SEM micrograph of the surface of the mild test samples before zinc electrodeposition is presented in Fig. 2(i). Electrodeposition of zinc on mild steel test samples from acid – chloride solution without any additive showed little apparent porosity, Fig. 2(ii). The crystals were not clearly defined in shape with some coarse but closely packed. The surface crystals feature was not particularly smooth. This observation seems to indicate that zinc – electroplating of ferrous metals in acid chloride solution without any additives may not be strongly corrosion resistant. The slightly coarse structure could be due to the absence of levelling agents in the acid solution. The viability of this type of zinc plating will certainly depend on the conditions under which the experiments are performed. The observed amorphous crystal structure of the plated sample surface could be due to the poor throwing power of the acid solution.



**Figure 2.** SEM micrographs of mild steel test sample: (i) Before zinc electrodeposition (ii) Plating without additive.

### 3.2. With Addition of Pineapple (*Ananas comusus*) juice extracts

#### 3.2.1. 4ml pineapple juice/50ml of acid chloride solution at 15 minutes plating time

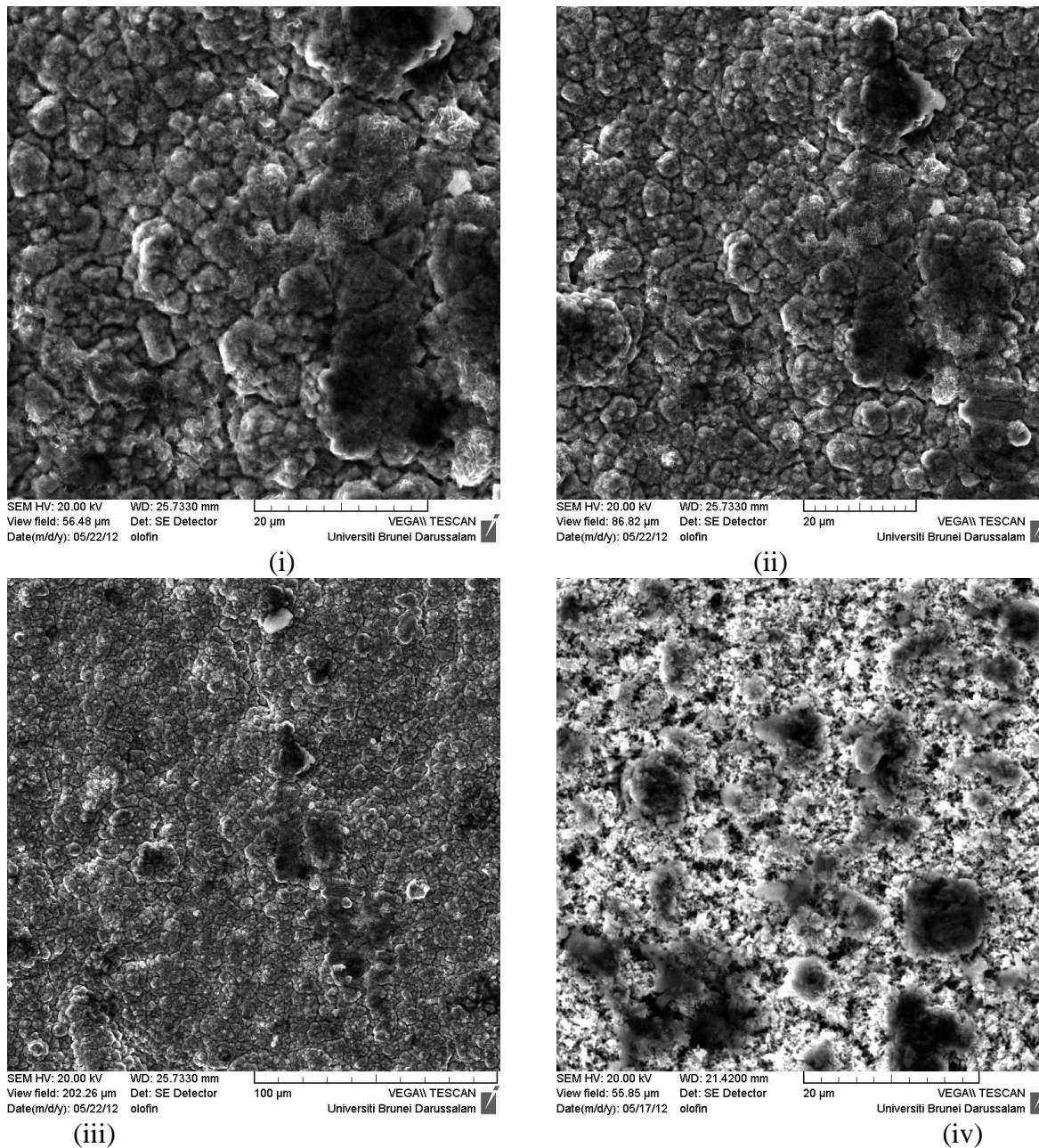
Fig.3 (i-iii) shows the SEM micrographs obtained for the addition of the pine apple juice extracts - 4ml /50ml of acid chloride solution at 15 minutes plating time and at the magnifications of x7000, x5000 and x1000 respectively. At the portions examined, there was no discernible porosity observed. The crystal particles were very close-packed and creating a well-defined surface microstructure. When compared with the Fig. 2 (ii), that is, with the one without added juice, a significantly clear difference in surface structure could be observed. Obviously the observed grain refining and levelling difference in surface morphology as evidenced in Fig. 3(i-iii), emanated from the addition of the pineapple juice extract. The complex chemical composition of the juice extract would have certainly caused the difference in surface structure changes/modification. The unique structure observed in Fig.3 (i-iii), is evidence of good zinc electrodeposition. Within the plating period, a mass of 23.2mg zinc was deposited on the steel substrate, Table 2.

#### 3.2.2. 4ml pineapple juice /50ml of acid chloride solution at 18 minutes plating time

The micrograph made with the plating at 18min with the same juice concentration of 4ml/50ml of acid chloride solution and magnification of x5000 is presented in Fig.3 (iv). Here the surface microstructure is more of refined grains, levelled and looks brighter. The longer time of plating (electrodeposition) process could be associated with the difference in surface feature obtained. A shift in the plating time from 15 to 18 minutes gave rise to this significant zinc electrodeposition feature. The implication then, is that zinc electrodeposition on mild steel in acid solution bath is very time

sensitive/dependent. It could also be said that the addition agent worked differently with electrodeposited zinc on mild steel substrate as the plating time varies. A densely packed surface structure, as just seen in Fig.3 (iv), is expected to give appreciable corrosion resistance performance. The brightening effect of the added juice extract was good. The mass of zinc deposited was weighed to be 49.9mg, Table 2. The increase in mass deposited at this plating time was far more significant than in the former where the plating time was 15 minutes and the mass deposited was 23.3mg.

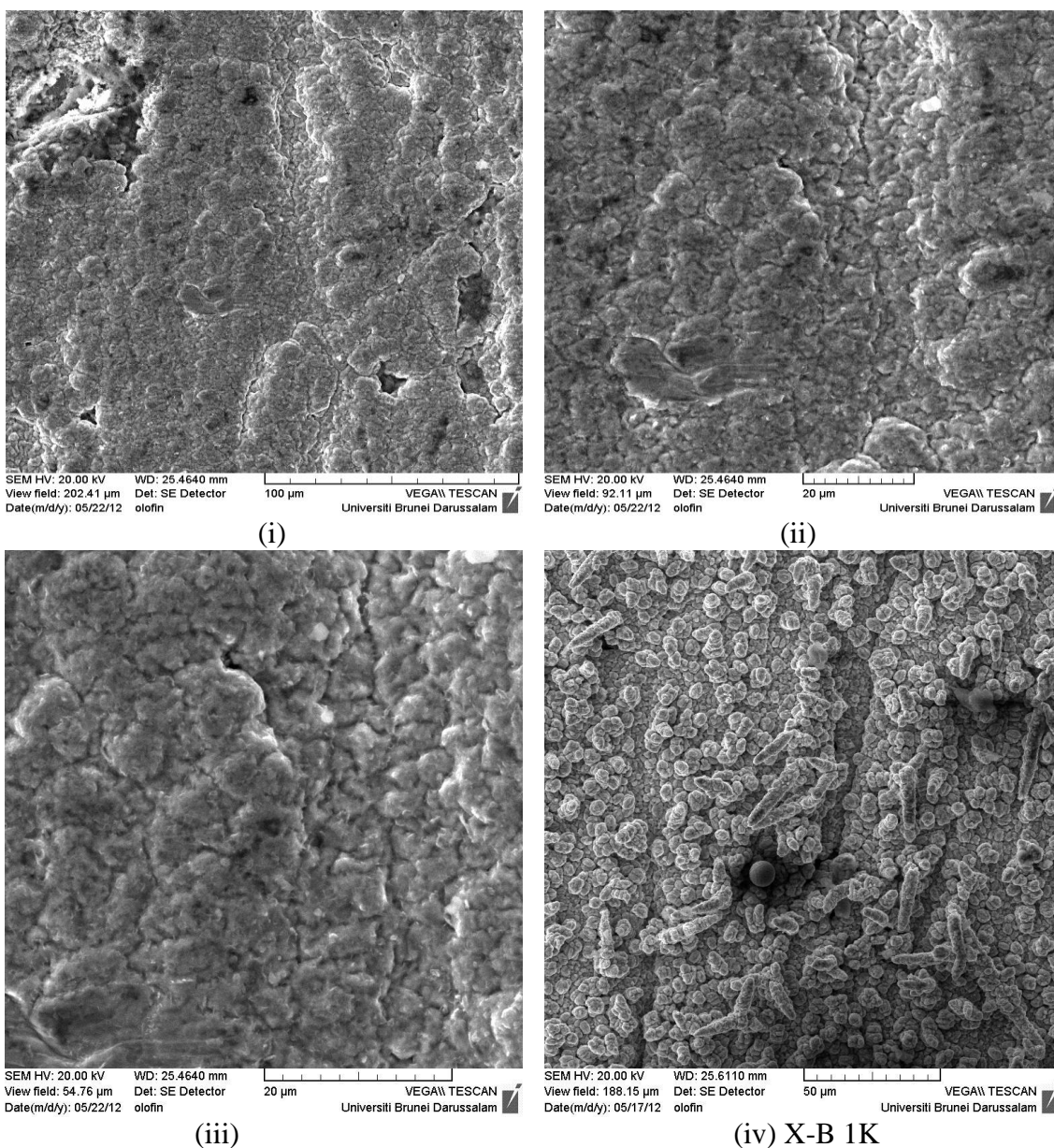
3.2.3. 5ml pineapple juice /50ml of acid chloride solution at 15 minutes plating time



**Figure 3.** SEM micrographs of steel surface after zinc electrodeposition with 4ml /50ml of acid chloride solution at 15 min. (i) x7000, (ii) x5000 (iii) x1000 magnification respectively; and (iv), plating at 18min; and magnification of x5000.



A change in the juice additive concentration from 4ml to 5ml pineapple juice extract/50 ml of acid chloride solution at 15 minutes provided another different surface feature/characteristic as presented in Fig. 4 (i – iii). The very little increase in the volume/concentration of the juice extract brought about very significant surface morphological changes. Here, the surface crystals have become very refined and levelled as could be observed even from very high magnification of x5000. The samples surface was bright visually. The mass of zinc deposited was 22.8 mg. There was no apparent porosity seen within the micrographs. It is expected that the plating will exhibit good corrosion protection sacrificially. Fig.4 (iv) shows plating at 18min; with the same - concentration and at a magnification of x1000. This will be discussed in the next section.



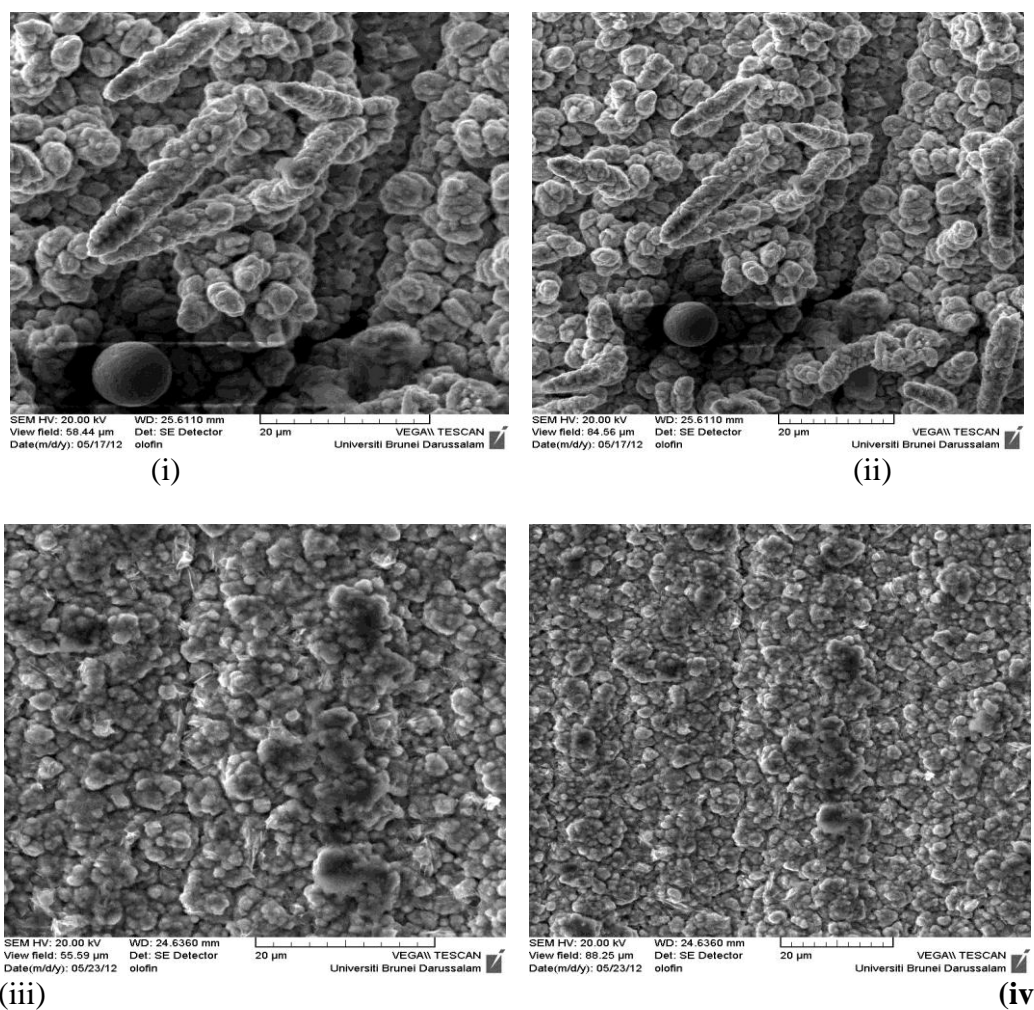
**Figure 4.** SEM micrographs of steel surface after zinc electrodeposition with 5ml /50ml of acid chloride solution at 15 min. (i) x1000 and (ii) x3000 (iii) x5000 magnification respectively; (iv) plating at 18min; and magnification x1000.



3.2.4. 5ml pineapple juice /50ml of acid chloride solution at 18 minutes plating time

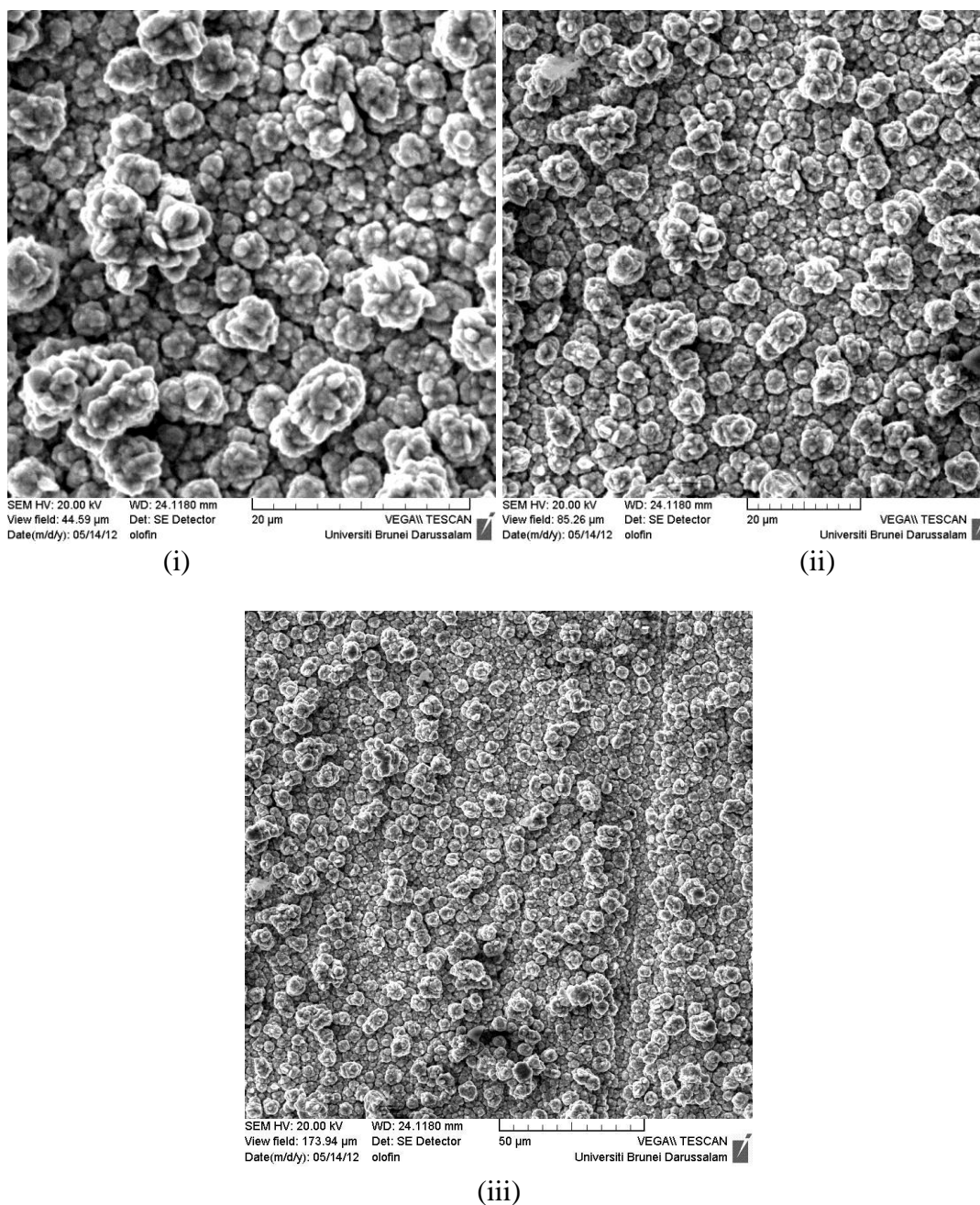
Presented in Figs. 4 (iv) and 5 (i-ii) are the micrographs made for the samples plated in 5ml /50ml of acid chloride solution at 18 min. and at the magnifications of (i) x1000, (ii) x5000 and (iii) x3000 respectively. The surface microstructure shown here are very much different from others earlier discussed. The additive concentration and the plating time changed and these changes affected the surface structure very much. It is a mixture of predominantly roundish and very little rod-like surface crystals. The crystals were densely/compactly packed with little porosity and grooves as shown in Fig. 4 (iv). The surface plating was bright and the crystals were fine particularly the predominant round crystals. It could also be described as a levelled surface though the characteristic poor throwing power of the acid solution could cause the porosity and the grooves observed. Nevertheless, it was good plating that was expected to be sacrificially corrosion protective. The mass of zinc deposited at the plated portion was 37.3 mg

3.2.5. 6ml pineapple juice /50ml of acid chloride solution at 15 minutes plating time



**Figure 5.** SEM micrographs of steel surface after zinc electrodeposition with 5ml /50ml of acid chloride solution at 18 min. (i) x5000 and (ii) x3000; (iii) with 6ml/50ml of acid chloride plating at 15min: x5000 and( iv) x3000 magnifications respectively.

Fig.5 (iii-iv) shows the obtained SEM micrographs for the zinc electrodeposition on mild steel substrate 6ml/50ml of acid chloride solution and at the plating time of 15minutes.



**Figure 6.** SEM micrographs of steel surface after zinc electrodeposition with 6ml /50ml of acid chloride solution at 18 min. (i) x6000, (ii) x3000 and (iii) x1000.

Here there was a phenomenal difference in surface microstructural features when compared with the plating of the different additive concentration and different plating time as in section 3.2.4. The surface morphology in this electrodeposition, even at the very high magnifications of x3000 and x5000 respectively, was that of fine grain particles with very good levelling and absolutely no porosity

within the micrographs. Visually the plating was bright; and surprisingly, the throwing power of the plating solution could then be considered as good here. The major change in plating parameters here was the use of 6ml-, instead of the previous 4ml- and 5ml//50ml of acid chloride solution. It can then be inferred that increase in the juice additive concentration improves the plating quality as indicated by the surface features. The mass of zinc deposited at the plated portion was 29mg.

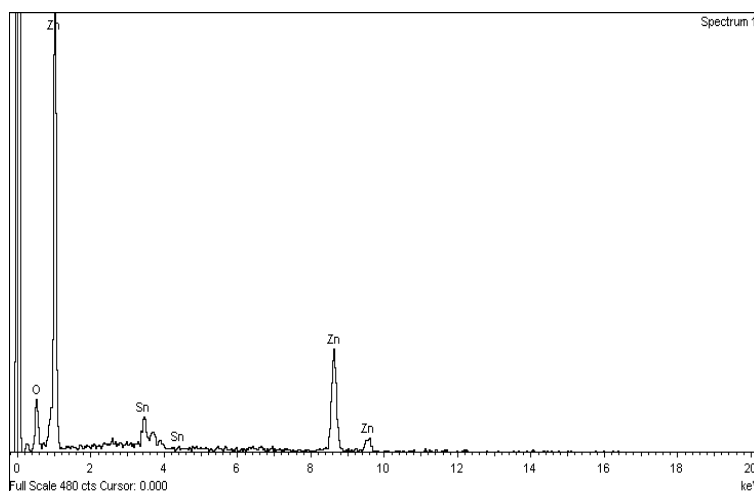
Just as explained previously, the chemical compositions of the pineapple juice was complex and consist of various chemical compounds and minerals. Some of these, such as glucose and sucrose were already known to be good addition agents for zinc electrodeposition in acid chloride solution. The phytonutrients and flavonoids and other vitamin compounds could also make a contribution to good zinc electrodeposition on mild steel substrate.

### 3.2.6. 6ml pineapple juice /50ml of acid chloride solution at 18 minutes plating time

With 6ml /50ml of acid chloride solution at 18 minutes plating time, Fig. 6 (I - iii) a very well defined round crystal structure could be observed. The increase in plating time from 15 to 18 minutes has again changed the surface microstructure from that of Fig. 5. This unique structure, which was evidence of good zinc electrodeposition, arose mainly from the addition of the pineapple juice and increased plating time while maintaining the concentration at 6ml/50ml of acid chloride solution. In spite of the very high magnification of the SEM used, a closed crystal structure could be seen and no porous defect observed. Within the plating period, a mass of 25.3 mg zinc was deposited on the steel substrate at the plated portion, Table 2. The zinc plated surface was bright. The plated sample was also expected to provide good corrosion protection sacrificially.

### 3.3 EDS Analysis

The result of energy dispersive analysis (EDS) of Fig. 3 (iii) is presented below as Fig. 7; and a Table of analysis as Table 3. The surface microstructure showed it to be mainly zinc and a little amount of tin which could be in trace form in the zinc metal that was co-deposited.



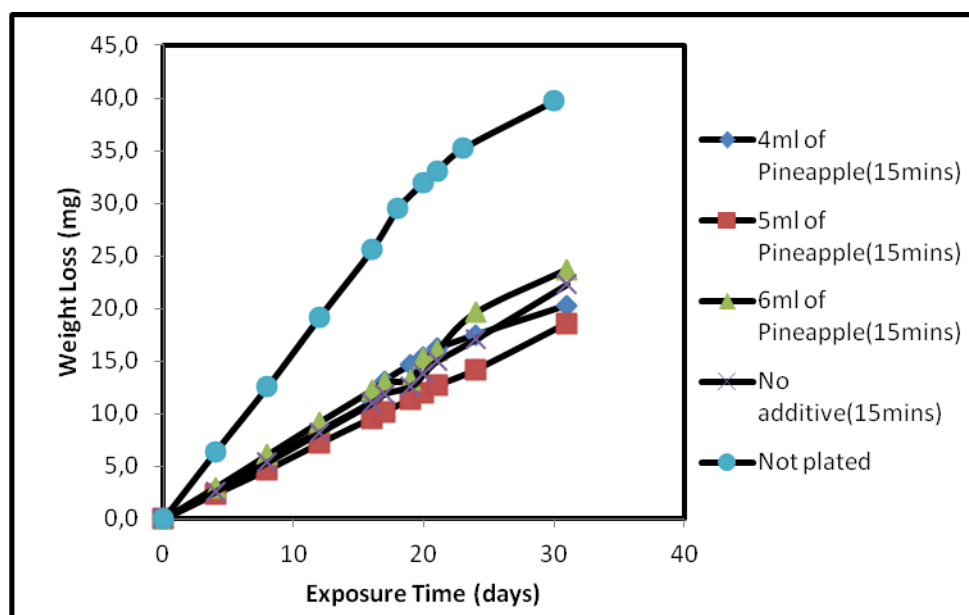
**Figure 7.** EDS analysis of the plated surface of sample in Fig. 3 (iii)

**Table 3.** EDS analysis of the plated surface of sample in Fig. 3 (iii)

Element	App Conc	Intensy Corr.	Weight%	Weight% Sigma	Atomic%
O K	2.17	0.9143	12.49	1.76	37.92
Zn K	14.50	0.9698	78.74	2.06	58.49
Sn L	1.38	0.8302	8.77	1.36	3.59
Totals			100.00		

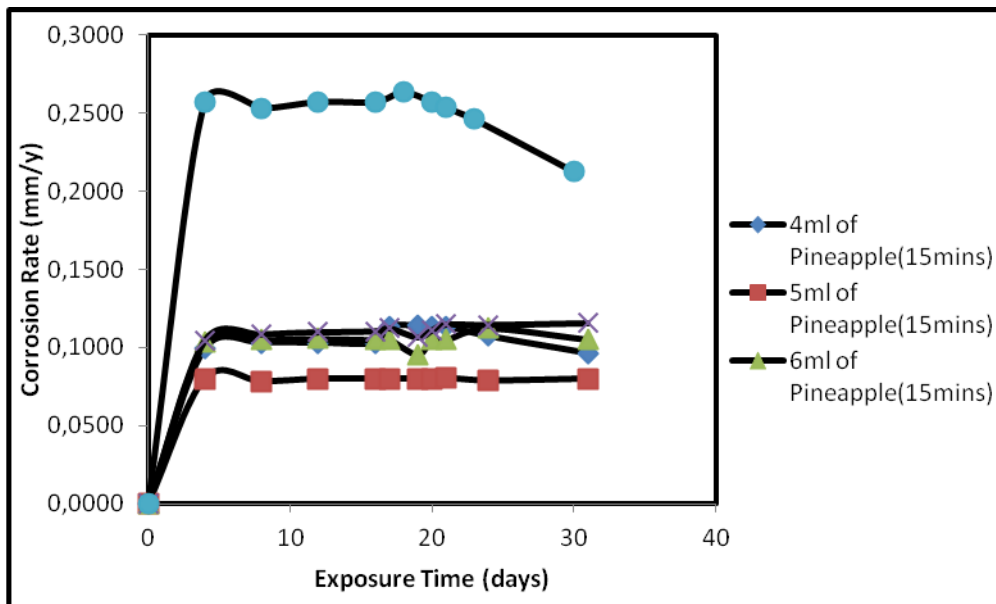
*3.4. Corrosion resistance of the zinc plated mild steel substrate*

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 environment are presented in Figs. 8 to 11. Fig. 8 shows the curves of the weight loss versus the exposure time at variable additive concentrations and at the plating time of 15 minutes for each of the test samples. All the plated samples showed better corrosion resistance than the unplated samples. For example, the sample plated with 6ml juice extract/50ml acid chloride solution recorded a weight loss value of 18.60mg on the 30<sup>th</sup> day of the experiment while the unplated sample recorded a weight loss of 39.70mg at the same period of 30 days of the experiment. However, the trend of corrosion resistance performance did not, in general, followed the amount of the juice extracts used as additive; the sample plated with 5ml juice extract/50ml acid chloride solution showed less weight loss (18.60mg) than the one plated with 6ml extract /50ml acid chloride solution (22.30mg) on the 30<sup>th</sup> day of the experiment. The weight loss recorded for the plated samples was due to the anodic zinc dissolution in the test environment after a long period of 30 days; zinc corroded sacrificially to protect the mild steel substrate.

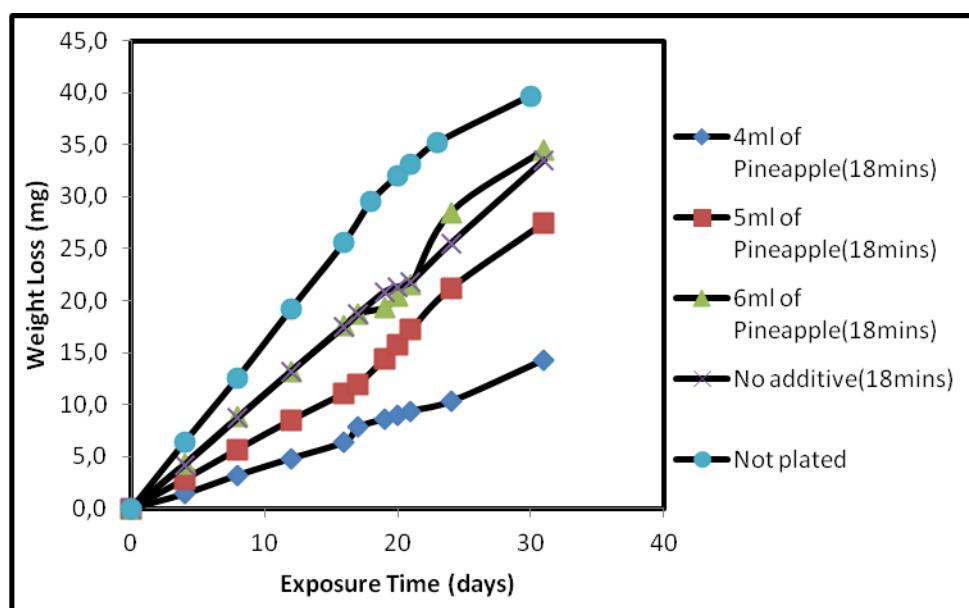


**Figure 8.** Variation of weight loss with exposure time for the zinc electrodeposited mild steel - sample in seawater. (Variable additive concentrations and 15 minutes plating time)

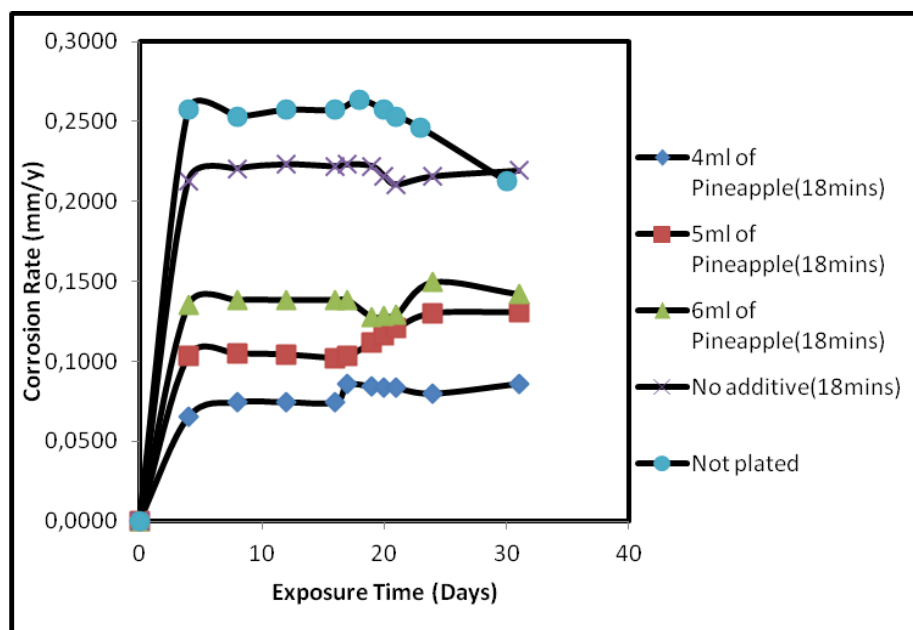
The corresponding corrosion rates curves, Fig.9 followed the same trend as above. The unplated test sample recorded the highest corrosion rate (0.2572 and 0.2127mm/yr) on the 12<sup>th</sup> and 30<sup>th</sup> day of the experiment respectively; while the sample plated with 4ml juice extract/50ml acid chloride solution recorded the corrosion rates of 0.0799 mm/yr at the same periods of the experiment respectively. The corrosion rate in the latter was indeed very low comparatively.



**Figure 9.** Variation of corrosion rate with exposure time for the zinc plated mild steel samples in seawater. (Variable additive concentrations and 15 minutes plating time)



**Figure 10.** Variation of weight loss with exposure time for the zinc plated mild steel samples in seawater. (Variable additive concentrations and 18 minutes plating time)



**Figure 11.** Variation of corrosion rate with exposure time for the zinc plated mild steel samples in seawater. (Variable additive concentrations and 18 minutes plating time)

While other plating parameters remain the same, the results presented in the curves in Figs. 10 (weight loss) and Fig.11 (corrosion rates) versus the exposure time, were obtained with the plating time of 18 minutes. The trend here was as in Fig. 8 for the weight loss values; however, the samples plated with 4ml juice extracts (as additive) gave the lowest weight loss (14.30mg) on the 30<sup>th</sup> day of the experiment. The unplated sample recorded a weight loss value of 39.70mg at the same period of the experiment while with the use of 5ml and 6 ml juice extract /50ml acid chloride solution the weight loss values were 27.50 and 33.50mg respectively. The corrosion rate for the sample with 4ml juice extract additive recorded 0.0861 mm/yr. Those with 5ml and 6 ml juice extracts, recorded corrosion rate values of 0.1307 and 1422 mm/yr respectively. The unplated sample and the one without additive respectively recorded the same value of corrosion rate of 0.2127 at the 30<sup>th</sup> day (end) of the experiment. In all, the plated samples were more corrosion protective.

It is observed 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, in some cases, on the plated portions. The more compact the surface crystal particles, the finer the crystal structure; and the less amount of porosity in the plated samples, the more the corrosion resistance/protective tendency of the zinc plated surface observed.

Cellotape test: The cellotape test confirmed the strong adhesion of the zinc to the steel surface. Visual inspection could not reveal any visible particle removed from the plated steel surface.

#### 4. CONCLUSIONS

- Using the pineapple (*Ananas comusus*) juice as the addition agent, the experiments produced good zinc electrodeposition on mild steel surface in the acid zinc chloride solution.



2. Characterisation of the zinc plated surface of the mild steel substrate showed different surface features depending upon the plating conditions and variations.
3. The electrodeposition process was very sensitive to any changes in additive concentration and plating time. Any variation produced an entirely new and different surface microstructure/morphology.
4. When compared with the unplated samples, the plated specimens showed good corrosion resistance in seawater test and thus confirming their protective capability as expected.
5. The electrodeposition process produced very fairly bright deposition. The surface structures obtained indicate that the plating could serve several useful protective purposes that could be technologically and economically viable.
6. The juice extract additive used was environment friendly.

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