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Synergistic Effect of Tobacco and Sugarcane Extracts on the Surface Morphology of Electrodeposited Zinc on Mild Steel

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Experimental investigations have been performed to determine the synergistic effect of *nicotiana tobaccum* (tobacco) and *saccharum officinarum* (sugarcane) extract additives on the electrodeposition of zinc on mild steel in acid chloride solution. The experiments were performed under different plating time, different additive concentrations and fixed pH conditions. Zinc electrodeposition on mild steel was performed using a DC – supply at defined operating parameters. 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 characteristics 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 the electroplating of zinc was good as indicated by the microstructural morphology of the plated surface. The electrodeposition process was sensitive to changes in additive concentration and plating time. Any variation in the plating parameter produced an entirely new and different surface crystal morphology.

Keywords: Synergistic effect; sugarcane; tobacco; electroplating; acid chloride; steel surface.

1. INTRODUCTION

In a previous study, the extracts of sugar cane (*Saccharum officinarum*) and tobacco (*Nicotiana tobaccum*) were separately investigated in acid chloride under the same test conditions as used in this present work [1, 2]. The results obtained were positively encouraging and that necessitated the present research interest; aimed at looking in to the possible reactions synergism of these extracts when used in different combinations at the same previous per cent concentrations.

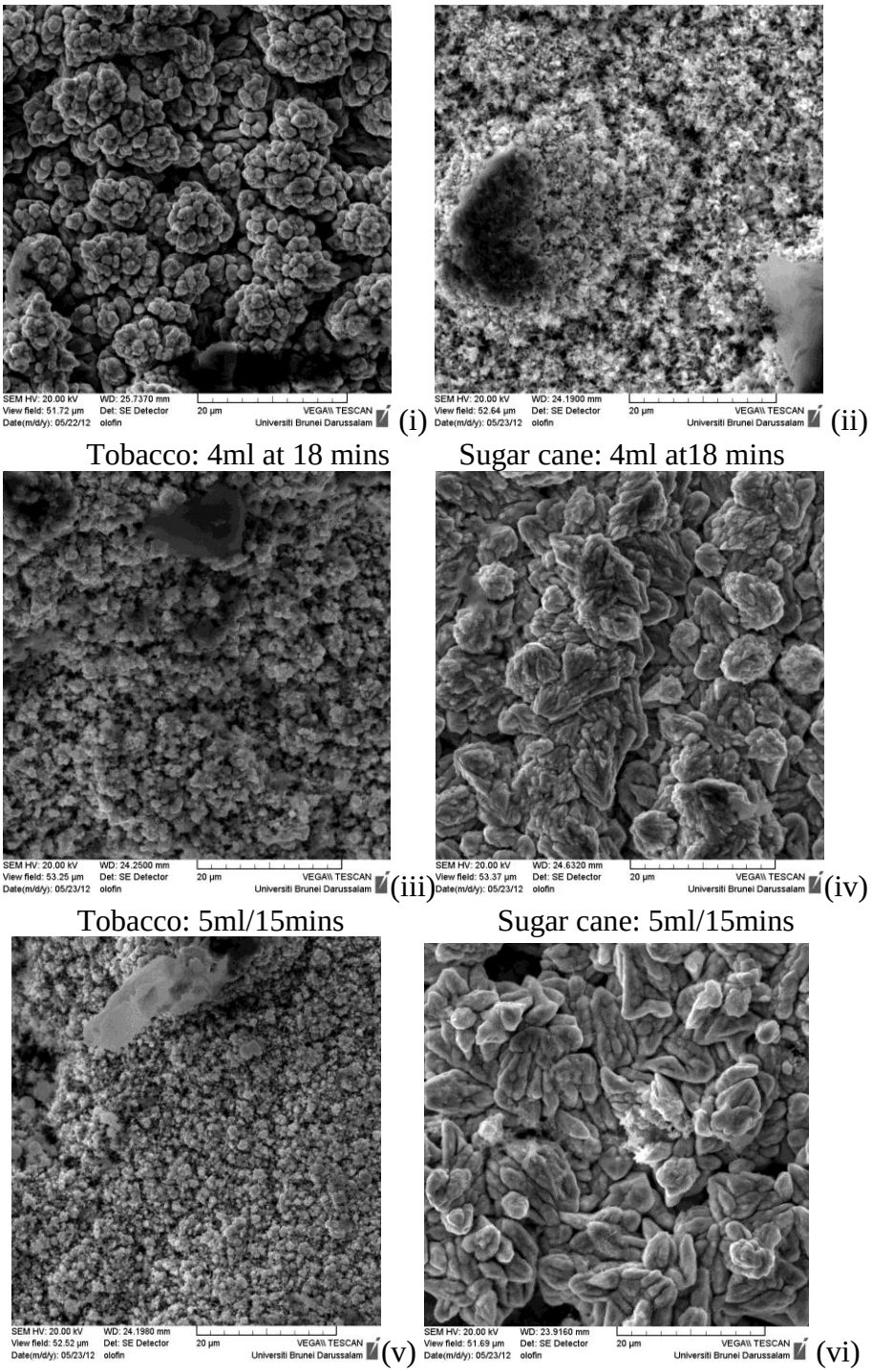


Figure 1. SEM micrographs of zinc plated mild steel using extracts of tobacco and sugar cane [1, 2]

A representative figure of some of the results of the previous plated surface morphology obtained is presented in Fig.1. Acid chloride solution has been widely used for zinc plating in recent time [3-7].

The application of plant extracts as additives in the electroplating of zinc on metallic alloy such as mild steel is relatively new. However, such experiments /reports have been documented by researchers in recent time [1-2, 8-10]. In addition, the use of extracts of tobacco (genus – *Nicotiana*:

family- *Solanaceae*), as an environmental benign corrosion inhibitor has been well reported [11-13]. It has been shown 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 [14-15]. Tobacco plants produce ~ 4,000 chemical compounds – including terpenes, alcohols, polyphenols, carboxylic acids, nitrogen – containing compounds (nicotine), and alkaloids [16]. These complex chemical compositions may exhibit electrochemical activity resulting in quality electroplating.

Similarly, the use of sugarcane (*saccharum officinarum*) juice as addition agent in zinc electrodeposition from acid based solution has been studied [1]. Sugarcane juice is obtained from the plant. The juice expressed from cane is an opaque liquid covered with froth due to air bubbles entangled in it. Its color varies from light grey to dark green, depending on the coloring matter in the rind of the cane crushed. It contains in solution all the soluble substances like sucrose, fine particles of bagasse, wax, clay (adhering to the cane), coloring matter and albumen. Chemically, it 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 [17-18]. The remaining 12% represents the insoluble cane fiber component. The cane juice has an acidic pH ranging from 4.9 to 5.5. The juice acidity corresponds to about 0.2%. About an equal quantity occurs in combination with the mineral bases as salts. 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. These colloids do not settle ordinarily unless conditions are altered. The juice is viscous owing to the presence of colloids as waxes, proteins, pentosans, gums, starch and silica. The gums belong to the polysaccharide group of carbohydrates. Sugarcane juice, considering its chemical constituents, is also expected to exhibit electrochemical activity of enhanced quality zinc electrodeposition on mild steel. It is also very environment friendly. A good result in this work will be of significant technological and economic benefit.

2. MATERIALS AND METHOD

The additives used were sugar cane (*saccharum officinarum*) and tobacco (*nicotiana tobaccum*) in mixed combinations. 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. The sugarcane was extracted as 100% natural juice from the mashed pulp of both. 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 fibers were squeezed through a sieve to obtain the juice. Both tobacco and sugar cane juice were kept in a refrigerator to ensure effective preservation.

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 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_3BO_4 (35g/l). Mixed solution extracts of *Nicotiana tobaccum* (Tobacco) and *saccharum officinarum* (sugar cane) of varying concentrations - 2, 2.5, 3 ml/50ml of acid chloride solution were used in turns as the addition agents (Table 1). 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.

Table 1. The bath addition agent and concentration used

Additive	Quantity of additive/ 50ml of acid chloride	% Concentration
Sugarcane + Tobacco	a. 2 ml (40 ml/L b. 2.5 ml (50 ml/L) c. 3 ml (60 ml/L)	4 5 6

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.

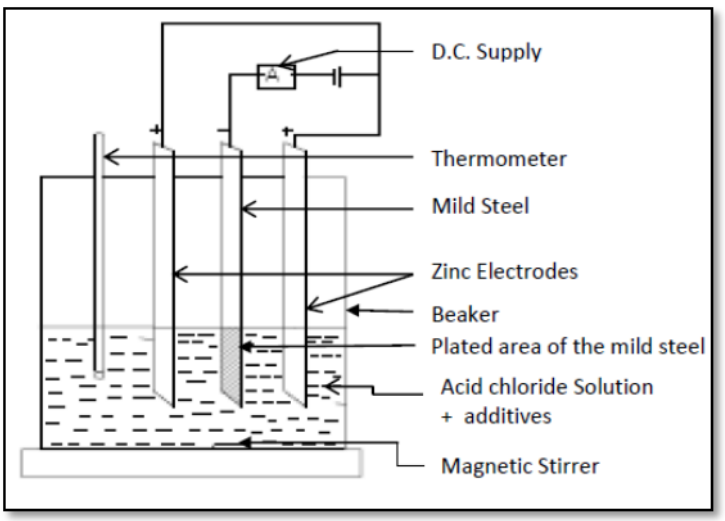


Figure 2. Schematic diagram of the experimental set-up

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 18minutes. 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).

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

Sample	Mass Deposited(g)
O2 (2 ml at 15 mins)	0.0251
P2 (2 ml at 18 mins)	0.0264
Q1 (2.5 ml at 15 mins)	0.0274
R1 (2.5 ml at 18 mins)	0.0278
S2 (3 ml at 15 mins)	0.0279
T2 (3 ml at 18 mins)	0.028I2

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^{o}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:

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

Where W is the weight loss in milligrams, 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

The Figure 1 is provided here in this work just to show, comparatively, the distinctive morphological structure between the tobacco extract additive alone and the sugar cane extract additive alone. Obviously, a finer grain microstructure was obtained with the use of tobacco alone than the sugar cane alone, though the sugar cane was brighter. A look at the combinations of these extracts below would show different morphological structure that emanated from their synergistic performance.

3.1.1. Unplated and zinc plated mild steel samples without additive

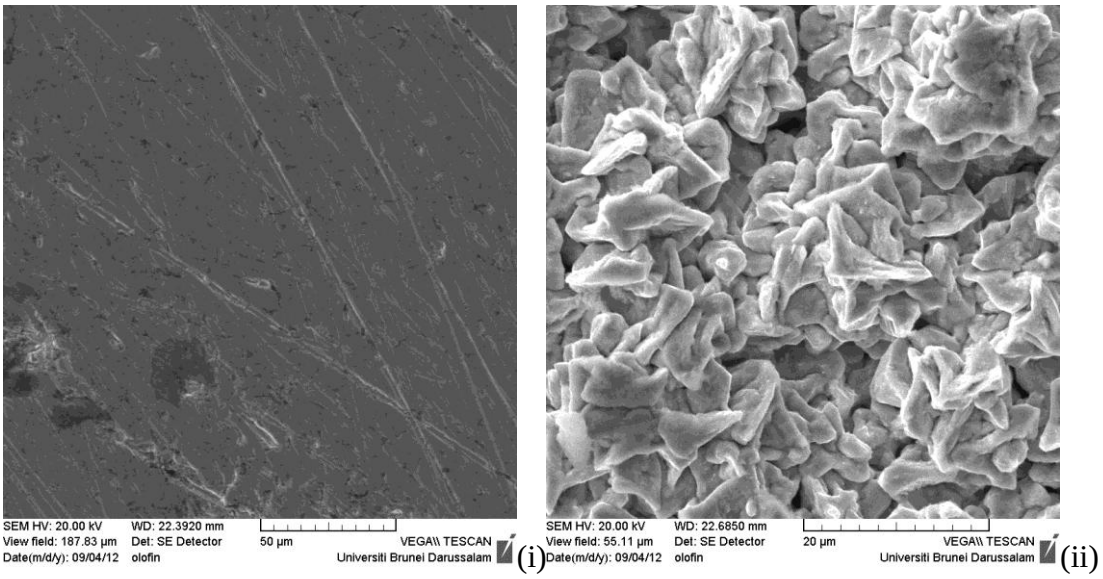


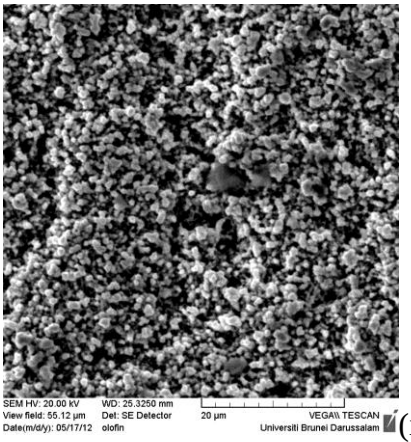
Figure 3. SEM micrographs of (i) unplated; and (ii) zinc plated mild steel sample without additive.

The SEM micrograph of the surface of the mild test sample before zinc plating is presented in Fig. 3(i). 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, Fig. 3(ii). Distinct crystals were obtained but the shapes are difficult to describe. Some coarse and fine particles were interspersed with each other and were closely packed. The crystals were very much different from those plated with additive as could be seen in the subsequent micrographs below. 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 observed coarse crystal morphological structure of the plated sample surface could be due to the poor throwing power of the acid solution.

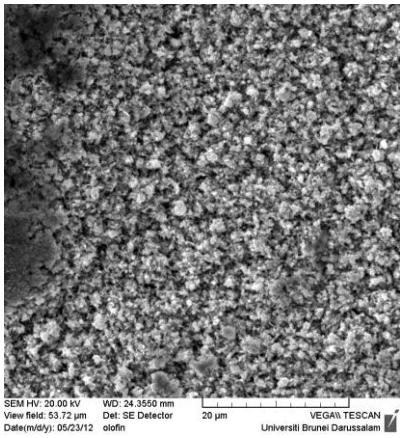
3.1.2 Plating with same additive concentration and different plating time

2 ml /50 ml additive at 15 and18 minutes plating time

The micrographs made with the plating at 15 and 18 minutes respectively with the combined tobacco and sugar cane extracts concentration of 2 ml/50ml of acid chloride solution are presented in Fig.4 (i and ii) respectively. The surface microstructure of each, is more of very fine grains, and very much leveled. The brightness of each micrograph is better than that of tobacco extract additive and less than the sugar cane extract additive alone as could be observed in Fig. 1.

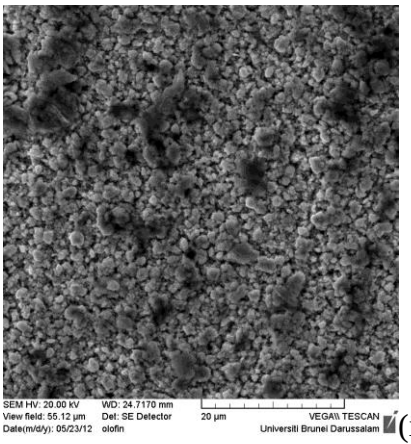


(i)

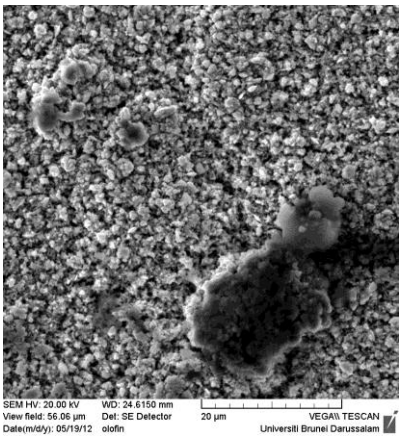


(ii)

O 2 ml 15 minutes P 2 ml 18 mins

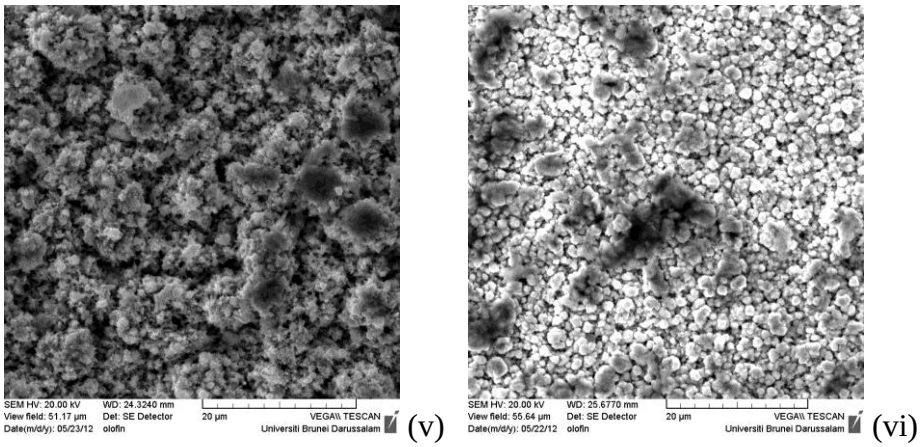


(iii)



(iv)

Q 2.5 ml 15mins R 2.5 ml 18 min



S 3 ml at 15 mins T 3 ml at 18 mins

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

But probably due to the difference in the plating time, the plating at 18 minutes presented finer grain morphology than the plating at 15 minutes. Also the mass of zinc deposited was more for the plating at 18 minutes (26.4 mg) than the plating at 15 minutes (25.1 mg) as presented in Table 2. At the portions examined, there was no and different plating time. All at the same magnification (x 5000) discernible porosity observed. 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, a significantly clear difference in surface structure could be observed. Obviously the observed very fine grains and leveling difference in surface morphology as evidenced in Fig. 4 (i-ii), emanated from the synergism exhibited by the combined extracts of tobacco and sugar cane additive. The complex chemical compositions of the tobacco and sugar cane extracts in combination would have impacted on the surface structure changes/modification. The unique microstructure observed in Fig.4 (i-ii), is clearly an evidence of good zinc electrodeposition.

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

The change in the extract additive concentration from 2 ml to 5ml tobacco/sugarcane extract/50 ml of acid chloride solution and for the plating time of 15 and 18 minutes provided a surface morphological structure that was compact and with fine grain particles, Fig. 4 (iii and iv), that did not look much different from those of Fig. 4 (i and ii). The increase in the plating time did not show any significant surface morphological changes. Here, the surface crystals remained very refined and levelled as could be observed. The deposition looked dense and very closely parked. However, at the 15 minutes plating time, the particles tend to be sperical in shape. The samples' surface was brighter than in the use of tobacco extract additve alone and less bright than the sugarcane's alone, Fig. 1, visually due to the tobacco extract strong darkish colour. The mass of zinc deposited was 27.4 and 27.8 mg respectively. There was no apparent porosity seen within the micrographs. The morphological structure obtained here could be associated with synergism effect of the mixed extact additives.

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 minutes respectively. There was no porosity observed in these micrographs. The surface microstructure show closed- packed, fairly bright and fine, levelled clustered-like grains, , as in Fig. 4 (v) and fine spherical-like grain particles as in Fig. 4 (vi) for 15 and 18 minutes plating time respectively and thus presenting a good surface morphology. It is thus plausible to associate the observed features here with concentration and plating time effect. A non-defective surface feature such as this has the positive implication of enhancing better surface corrosion protection. The plated zinc was expected to corrode sacrificially to protect the mild steel substrate. The mass of zinc deposited during the plating was 27.9 and 29.12 mg for the 15 and 18 minutes plating time respectively.

3.1.3 Plating with different additive concentrations and same plating time

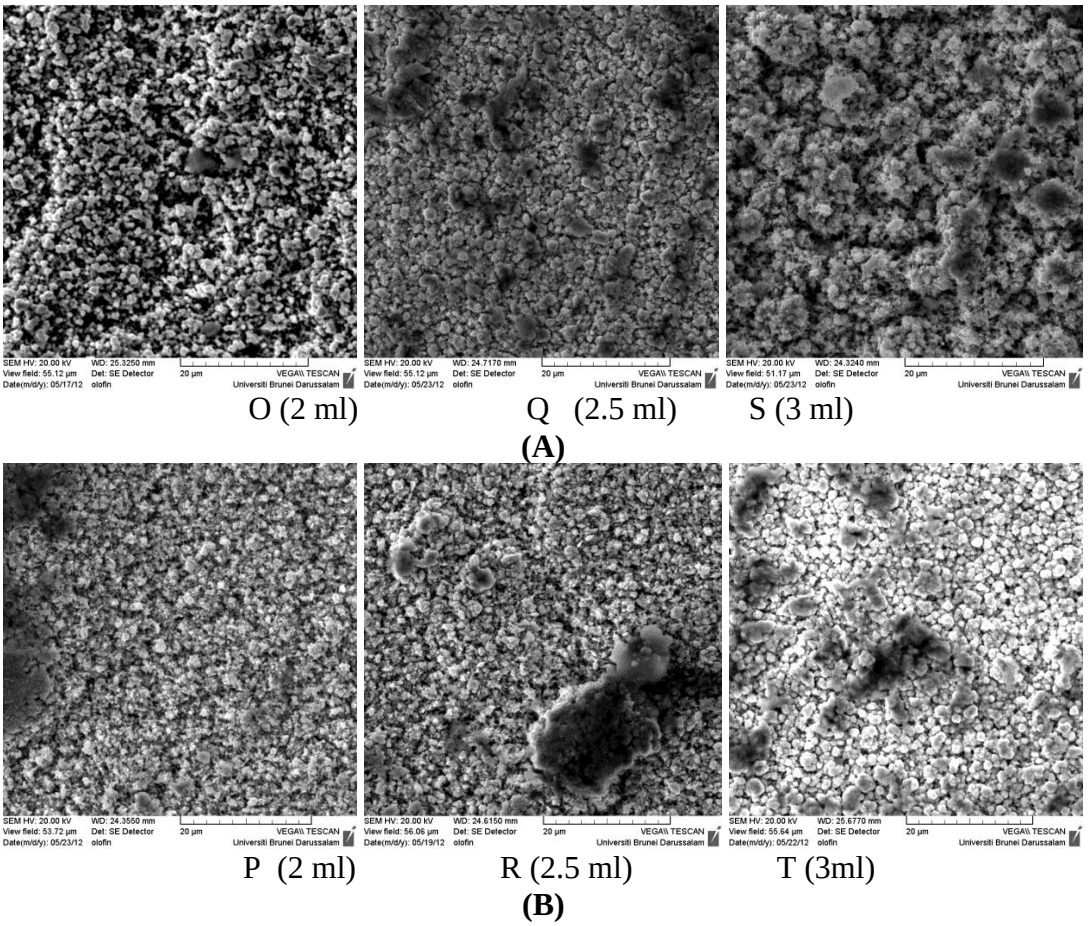


Figure 5. SEM micrographs of steel surface after zinc plating with the different additive concentration. (A) Plating at the same time (15 minutes); **(B)** plating at the same time (18 minutes). All the micrographs are at the same magnification (x 5000).

Presented in Figure 5, are the various SEM micrographs for the samples plated at different concentrations of 2, 2.5, and 3 ml/50ml and at the same plating time of: (**A)** 15 minutes and (**B**) 18 minutes respectively. The surface morphology of each of these micrographs had been described above. They are represented in Fig. 5 for surface structural comparison. All the micrographs used are at the magnification of x 5000.

Plating at 15 minutes with different concentrations show compact, dense and porosity free levelled and fine grain microstructure 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. It is difficult to say which is better morphologically.

Plating at 18 minutes for the same concentrations of extract additive, showed very similar microstructural features at all the concentrations used. Just as described above, the crystals were very fine, closely packed, levelled and no porosity observed. In general the plating time of 18 minutes at all the concentrations used seem to have finer microstructure and better levelling comparatively, though rather insignificant than the plating time of 15 minutes. The surface morphology for each of the plating time for the three different concentrations bears very close similarities.

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 and sugar cane that had been separately effective in electroplating process. All the results above regarding surface morphology are clearly in agreement with previous similar studies [19-20]

EDS Analysis

The result of energy dispersive analysis (EDS) of a plated sample in 2 ml/50 ml acid chloride concentration at 18 minutes plating time is presented in Fig. 6. The surface microstructure showed it to be mainly zinc. No other metallic element was indicated as co-deposited.

Adhesion test

The adhesion test that was performed confirmed that the plated zinc was adherent to the mild steel substrate surface. Visual inspection could not reveal any visible particle removed from the plated steel surface.

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. 8 shows the curves of the weight loss versus the exposure time at different concentrations of the combined tobacco and sugar cane extract additives 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. While the unplated sample recorded a weight loss of 39.70 mg on the 30^{th} day of the experiment, the sample plated with 2.5 ml tobacco and sugar extract /50 ml acid chloride solution recorded a weight loss value of 22.50 mg 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 after a long period of 30 days.

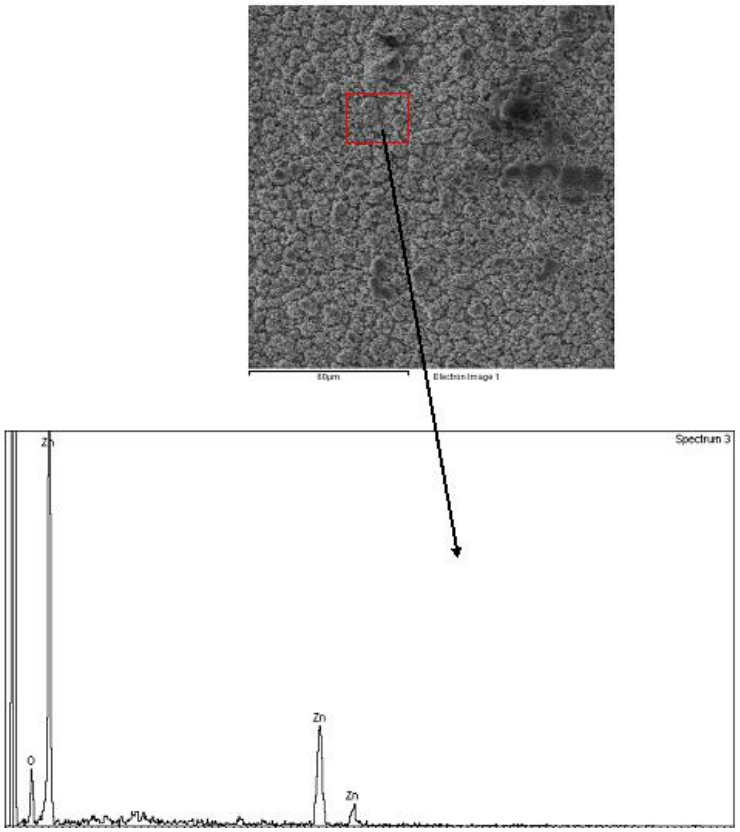


Figure 6. EDS analysis of the plated surface of sample in Fig. 4 (ii).

3.2. Corrosion resistance of the zinc plated mild steel

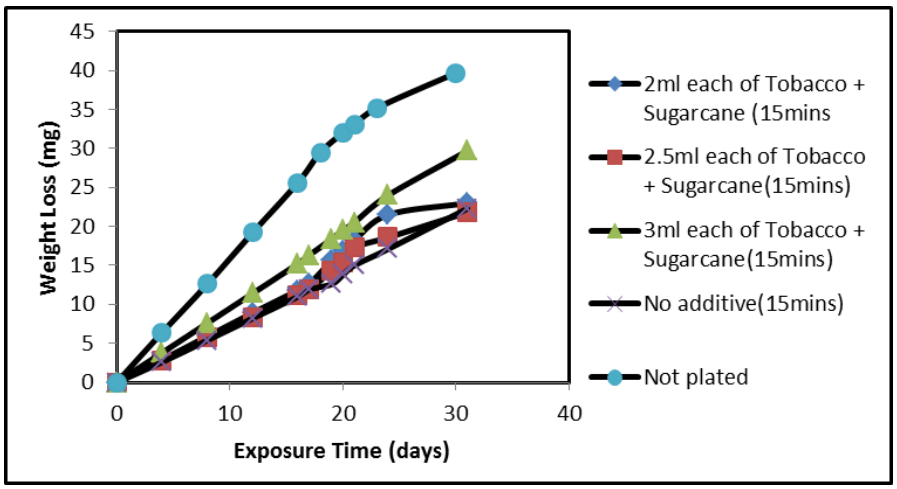


Figure 7. Variation of weight loss with exposure time for the zinc electrodeposited mild steel sample in seawater. (Different combined additive concentrations at 15 minutes plating time)

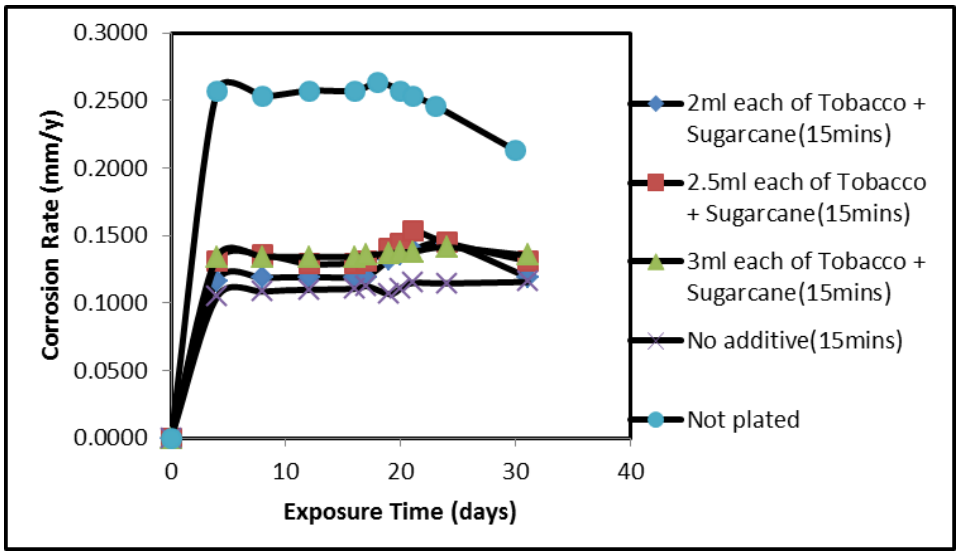


Figure 8. Variation of corrosion rate with exposure time for the zinc plated mild steel samples in seawater. (Different combined additive concentrations at 15 minutes plating time)

The corresponding corrosion rates curves, Fig. 8 followed the same trend as above. The unplated test sample recorded the highest corrosion rate (0.251 and 0.224mm/yr) on the 20th and 30th day of the experiment respectively; while the other samples plated with and without different concentrations of the combined extract additives / 50 ml acid chloride solution recorded very close corrosion rates ranging from 0.142 and 0.111 mm/yr at the same periods of the experiment. The extract additives in various concentrations seemed not to affect the corrosion resistance or susceptiblity performance of the electroplated surfaceof the mild steel substrate in any significant way. It should be noted that the extracts work mork more in levelling effect and in enhancing brightness of the plating and hence in morphological structure modification.

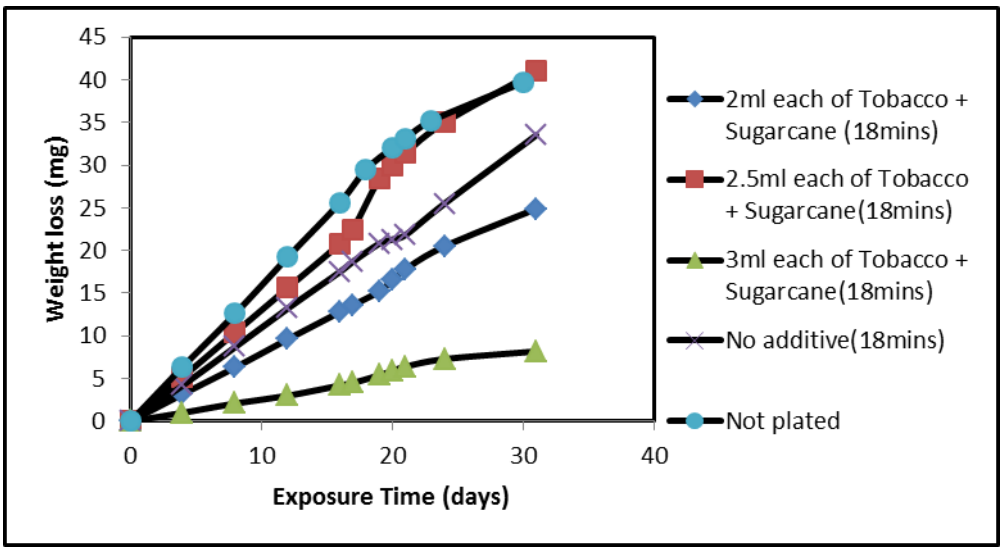


Figure 9. Variation of weight loss with exposure time for the zinc plated mild steel samples in seawater. (Different combined additive concentrations at 18 minutes plating time)

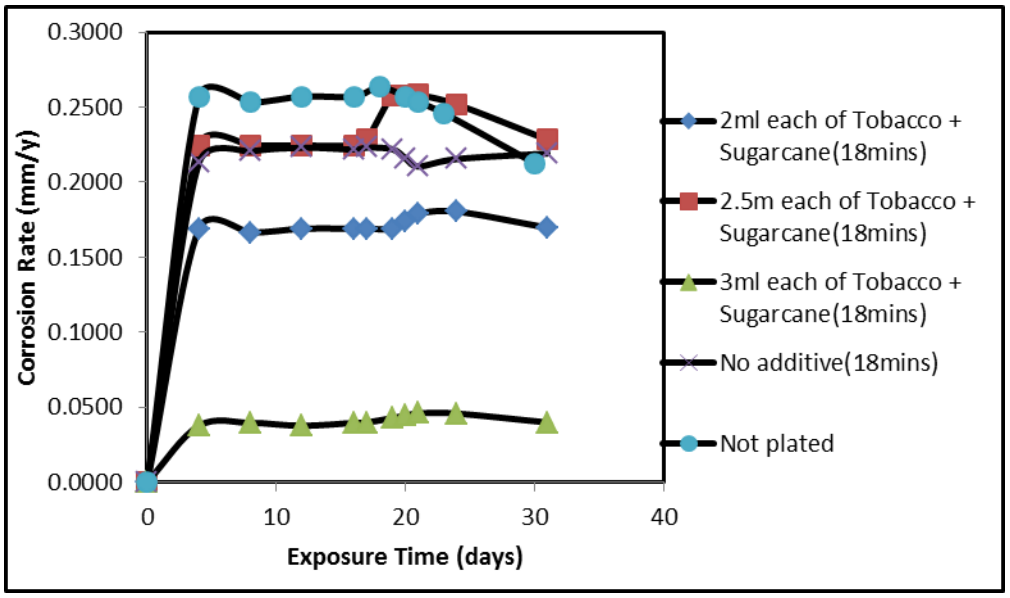


Figure 10. Variation of corrosion rate with exposure time for the zinc plated mild steel samples in seawater. (Different combined additive concentrations **at** 18 minutes plating time)

The results presented in the curves in Figs. 9 (weight loss) and Fig.10 (corrosion rates) were obtained with the plating time of 18 minutes, while maintaining the other plating parameters. Just as in Fig.8, the trend of corrosion resistance for the weight loss values looked similar. The samples plated with 3 ml solution extracts (as additive), gave the lowest weight loss (7.80 mg) on the 30th day of the experiment while the lowest corrosion rate. 0.026 mm/yr was recorded for the sample tested with 3 ml combined tobacco and sugar extract additive at the same period of the experiment. Results obtained here gavean indication that the plating time was a factor to consider. The weight loss values recorded for the specimens plated at 18 minutes plating time were much lower than those with the 15 minutes plating time. Like-wise, the corrosion rate values achieved were very much lower in the plating samples made at 18 minutes plating time than with the samples plated at 15 minutes plating time.

In all, as could be seen in the results as contained in the curves, the plated samples were more corrosion resistant and hence more protective. Again this is due to the dissolution of the deposited zinc in the test medium which sacrificially protected the mild steel substrate. In addition, from the results, it could be inferred that the rate/ magnitude of zinc dissolution was minimal.

From the above, it is important to mention 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 depodsited 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 better the morphological structure and the more the corrosion resistance performance.

4. CONCLUSIONS

1. The combination of tobacco (*Nicotiana tobaccum*) and sugarcane *(Saccharum officinarum)* extracts as the addition agent gave good zinc electrodeposition with fine, dense 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 different surface morphology depending upon the plating conditions.

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. The plated samples showed good corrosion resistance in seawater test when compared with the unplated samples and thus confirming their expected protective capabiliy.

5. The plating produced less than bright deposition due to the tobacco extract's colour that was difficult to decolourise using activated carbon. However, it was far brighter than the use of tobacco extract alone. The additives used in combination were non-toxic agricultural product that are environment friendly.

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