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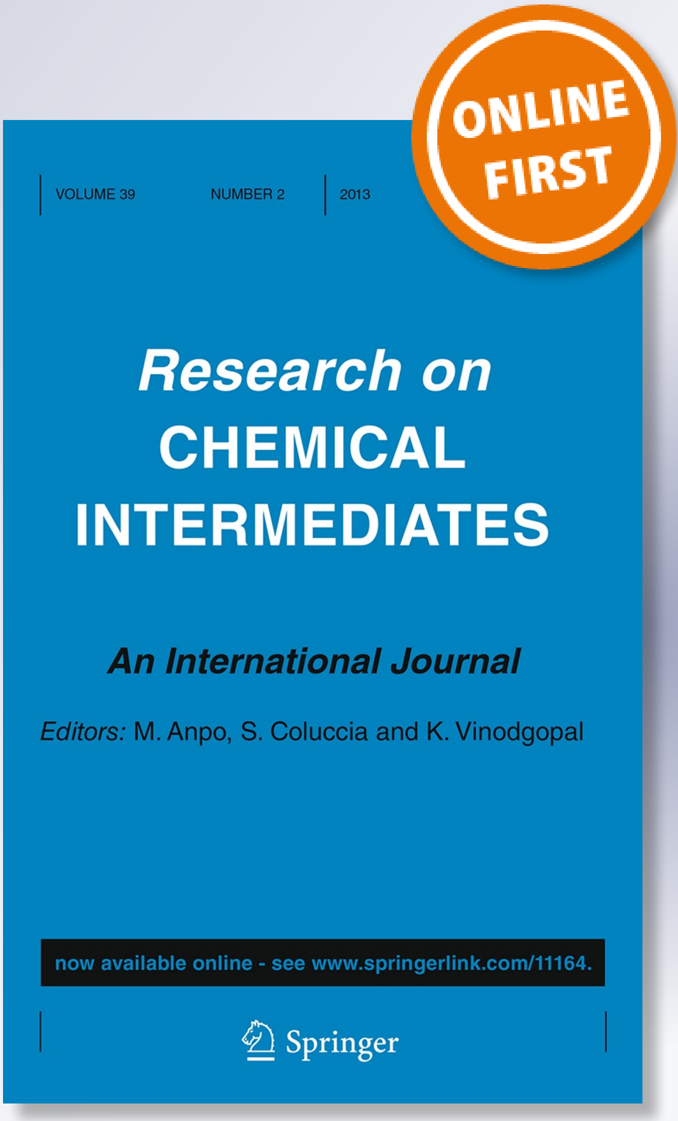

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Synergism of *Saccharum officinarum* and *Ananas comosus* extract additives on the quality of electroplated zinc on mild steel

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Abstract Synergism of *Saccharum officinarum* (sugarcane) and *Ananas comosus* (pineapple) extract additives on the quality of electroplated zinc on mild steel in acid chloride solution was investigated experimentally at ambient temperature (~28 °C). The experiments were performed at different plating times (15 and 18 min), additive concentrations (2, 2.5, 3 ml/50 ml of acid chloride solution), pH 5, temperature (27–30 °C), current (0.08 A), and voltage (13 V DC) conditions. Zinc electroplating on mild steel was performed using a DC-supply. The surface of the plated steel was examined with scanning electron microscopy, and energy dispersive spectroscopy 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 a gravimetric method. Microstructural morphology of the plated surface indicated a good quality electroplating that was better than either the sugarcane or pineapple extracts alone. The electroplating 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 Synergism · Sugarcane · Pineapple · Electroplating · Acid chloride · Steel surface

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Introduction

In a previous study, the extracts of sugarcane (*Saccharum officinarum*) and pineapple (*Ananas comosus*) 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 this produced the present research interest, aimed at looking into the possible plating reactions 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. Acid chloride solution has been widely used for zinc plating in recent times [3–7]. Research investigations using plant extracts as additives in zinc chloride plating medium have also been reported [8–11].

The pineapple juice extract used was obtained from the plant, a tropical fruit which grows in countries which are situated in the tropical and sub-tropical regions. Scientifically, it is known as *A. comosus* and belongs to the family of Bromeliaceae. It grows on the ground and can grow up to 1 m in height and 1.5 m wide.

Pineapple contains water, carbohydrates, sugars, sucrose, fructose, glucose, ash, vitamins A, C, and phytonutrients such as carotene-ß and crypto-xanthin-ß. The juice is particularly high in vitamin C, manganese, and vitamin B [12, 13]. In addition, the juice contains protein, fat, dietary fiber, and other vitamins such as folates, niacin, pyridoxine, riboflavin, thiamin, vitamin E, and 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

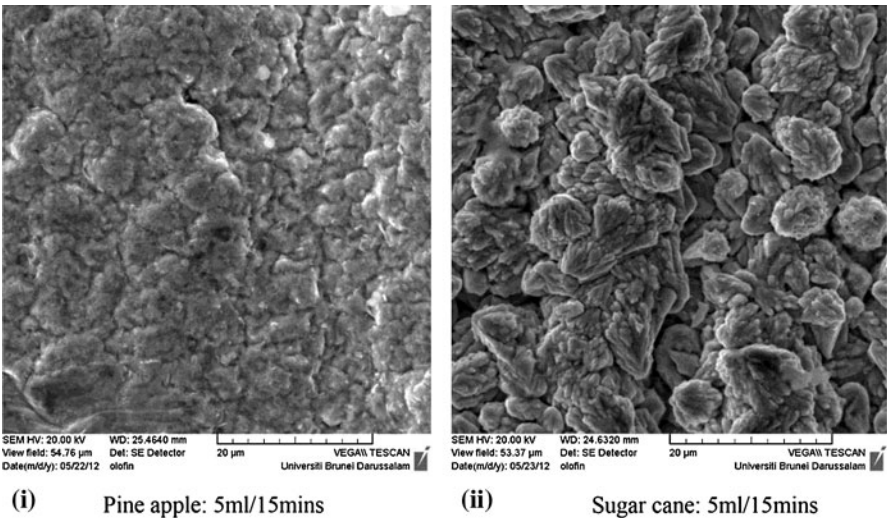

Fig. 1 **a**, **b** SEM micrographs of zinc plated mild steel using, separately, extracts of sugarcane and pineapple at the same plating time and concentrations [1, 2]

contains peroxidase, acid phosphate, several protease inhibitors and organically bound calcium, and is found in peak concentration within the pineapple rind [14].

Similarly, the use of sugarcane (*S. officinarum*) juice as addition agent in zinc electrodeposition from acid-based solution has been studied [1, 2]. 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 gray 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 [12, 13]. Further compositions are shown in Tables 1 and 2 [12]. 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. The juice is viscous owing to the presence of colloids such as waxes, 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. A good result here will be of technological and economic benefit.

Materials and methods

The additives used were sugarcane and pineapple in mixed combinations. The pineapple 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 sugarcane. The mashed fibers were squeezed through a sieve to obtain the juice. Both pineapple and sugarcane juice were kept in a refrigerator to ensure effective preservation.

Table 1 Composition of sugarcane juice [12]

Parameter	Value (%)
Water	70–75
Sucrose	11–16 (avg. = 13.0 %)
Reducing sugars	0.4–2
Organic non-sugars	0.5–1
Mineral matters	0.5–1
Fiber	10–16

Table 2 Composition of non-sugars in sugarcane juice [12]

Acids	Nitrogen compounds	Coloring matters	Other organic non-sugars	Mineral matters
Organic acids: glycolic, malic, oxalic, succinic, tannic	Organic compounds: albumin, albumoses, amines, amino-acids, nuleins, peptones, xanthene compounds	Soluble: anthocyanin, saccharetin	Soluble: pectin, gum (xylan)	Mostly soluble: alumina, lime, magnesia, potash, soda, sulphur, chlorine
Inorganic acids: phosphoric, sulphuric	Inorganic compounds: ammonia, nitrogen	Insoluble: chlorophyll	Insoluble: cane fiber, cane wax	Insoluble: silicates

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 10.0 cm long and 1.0 cm 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 min 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 s in 3 M 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 (71 g/l), KCl (207 g/l) and H_3BO_4 (35 g/l). Mixed solution extracts of sugarcane and pineapple of varying concentrations (2, 2.5, 3 ml/50 ml) of acid chloride solution were used in turn as the addition agents (Table 3). Electroplating of zinc on steel was performed by partially immersing the steel specimen and the zinc electrodes in the plating solution (20 mm deep) through the rectangular hole made on a prepared plastic cover for the 250-ml 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).

The plating solutions were put in turn 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

Table 3 The bath addition agent and concentration used

Additive	Quantity of additive/ 50 ml of acid chloride (ml)	% Concentration
Pineapple + sugarcane	2.0	4
	2.5	5
	3.0	6

taken before and after the electroplating process in order to determine the weight of zinc deposit by finding the difference in the two weight readings (Table 4).

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 0.08 A; voltage, 13 V DC; plating times, 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.

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.

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.

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

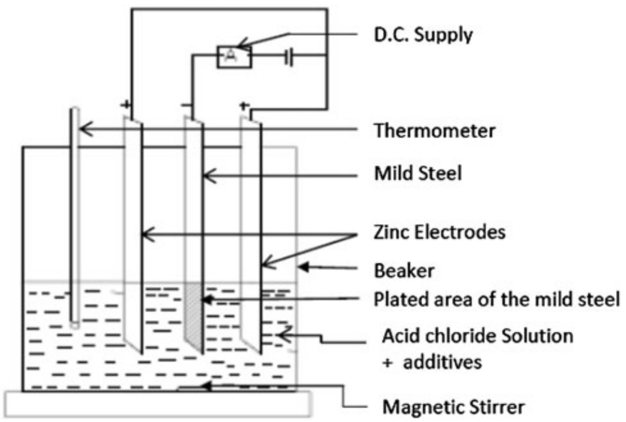

Fig. 2 Schematic diagram of the experimental set-up

Table 4 Mass of zinc deposited on steel substrate during plating

Sample	Mass deposited (g)
VIIB	0.0242
VIIIB	0.0244
IX	0.0265
XA	0.0323
XIB	0.0274
XIIB	0.0241

environment. The seawater was topped up to replace the amount lost due to evaporation. Weight loss measurements were taken every 2 days for a period of 24 days. Corresponding corrosion rate values were determined from these weight loss values by calculation using this formula:

$$\text{C.R.} = 87.6W/\text{DAT} \tag{1}$$

where W is the weight loss in 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.

Results and discussion

Electrodeposition of zinc

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

Not plated and zinc plated mild steel samples without additive

The SEM micrographs of the surface of the mild test sample before zinc plating and after plating but without additive are presented in Fig. 3a and b, respectively. 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. 3b). 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. The crystals were very different from those plated with additive as can 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.

Plating with same additive concentration and different plating times

Additive of 2 ml/50 ml at 15 and 18 min plating times The micrographs made with the plating at 15 and 18 min with, respectively, the combined sugarcane and pineapple juice extracts at a concentration of 2 ml/50 ml of acid chloride solution are presented in Fig. 4a and b, respectively. The surface microstructure of each is of more compact and dense grains, and very level. However, the morphological structure of Fig. 4a, plating at 15 min, looks very much different from that of Fig. 4b, plating at 18 min. This morphological difference could be due to the difference in the plating time. The brightness of each micrograph is better than that of the pineapple extract additive alone and also better than the sugarcane extract additive alone. The grain structures as presented in the micrographs are difficult to describe. The mass of zinc deposited for each of the plated sample was very close but slightly more in the plating at 18 min (24.40 mg) than the plating at 15 min (24.2 mg) as presented in Table 2.

At the portions examined, no discernible porosity was observed. The crystal particles were densely packed, creating a well-defined surface microstructure. When compared with the Fig. 3b, that is, with the one without added juice, a significantly clear difference in surface structure can be observed. It is apparent that the observed very closely packed grains and leveling difference in surface morphology, as shown in Fig. 4a, b, resulted from the synergism exhibited by the combined extracts of sugarcane and pineapple additives. The complex chemical compositions of the pineapple and sugarcane extracts in combination could, plausibly, be associated with the surface structure changes/modification obtained. The unique microstructure observed in Fig. 4a, b, shows good quality zinc electroplating.

Additive of 2.5 ml/50 ml at 15 and 18 min plating times The change in the combined extract additive concentration from 2 ml to 2.5 ml extract/50 ml of acid

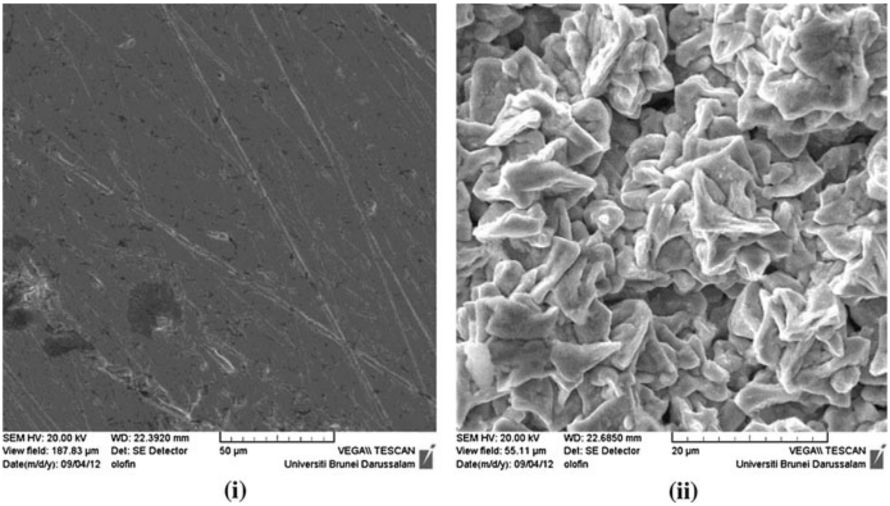

Fig. 3 SEM micrographs: **a** not plated; **b** zinc plated mild steel sample without additive

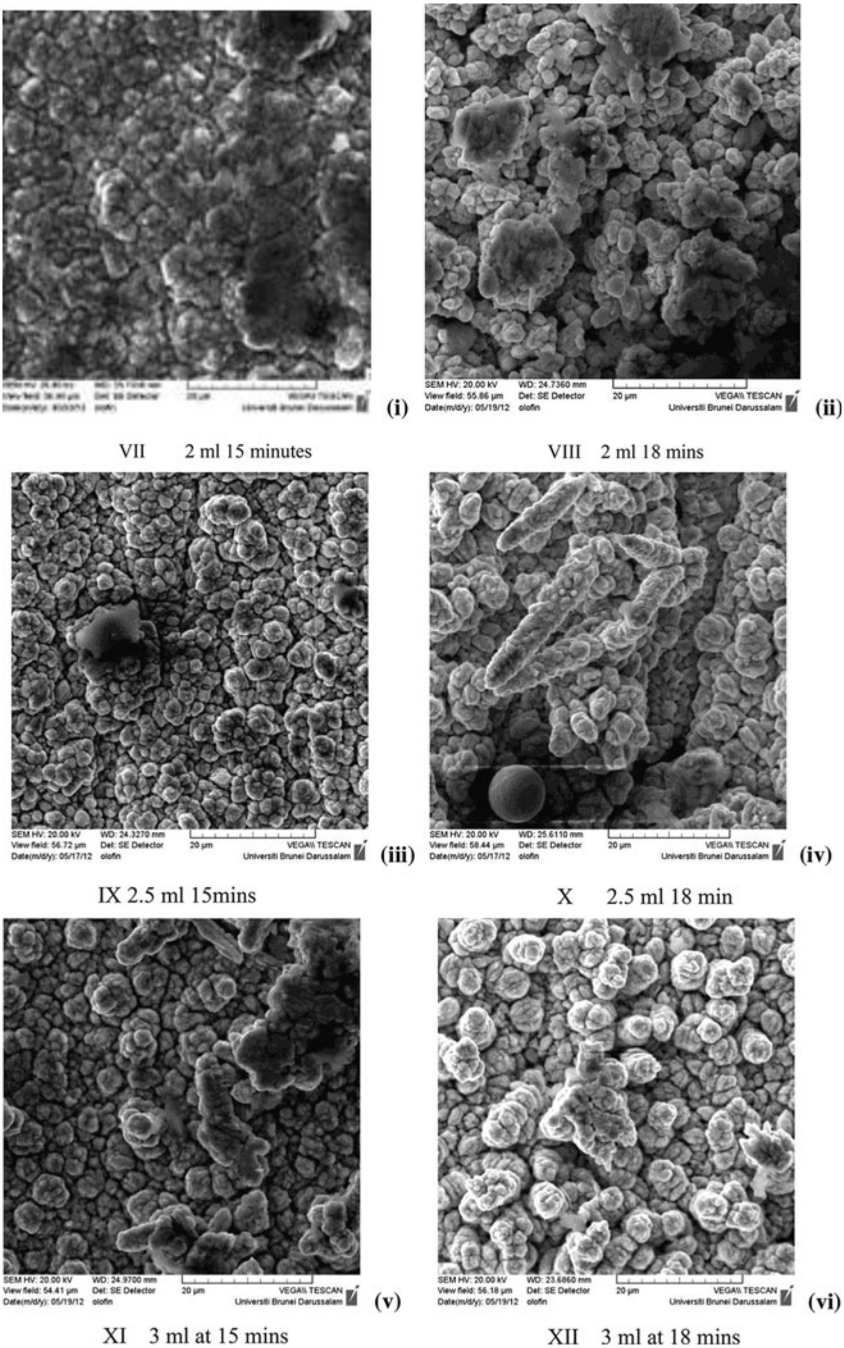

Fig. 4 SEM micrographs of the steel surface after zinc plating with the same additive concentration and different plating time. All at the same magnification (×5,000)

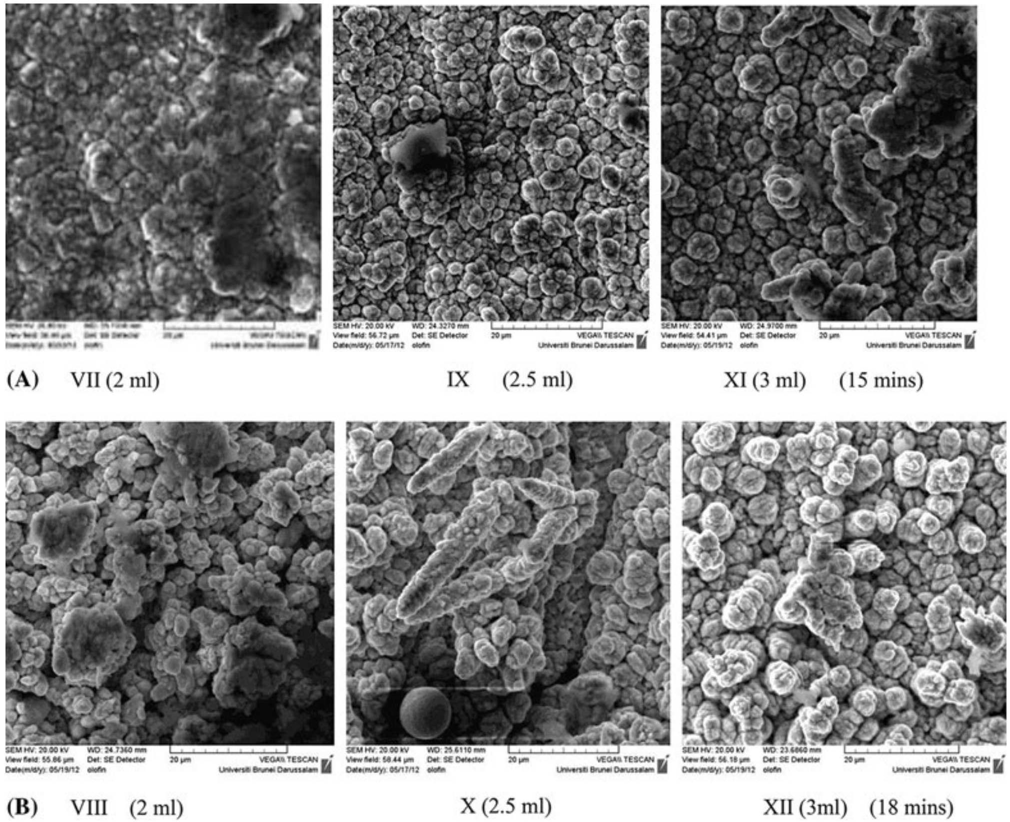

Fig. 5 SEM micrographs of steel surface after zinc plating with the different additive concentrations. **a** Plating at the same time (15 min); **b** plating at the same time (18 min). All the micrographs are at the same magnification (×5,000)

chloride solution and for the plating times of 15 and 18 min provided a surface morphological structure that was compact and closely packed (Fig. 4c, d) that look different from those of Fig. 4a, b. The increase in the plating time clearly show significant surface morphological changes between the two micrographs. Finer spherical surface crystals with very good levelled appearance can be observed in Fig. 4c. Except for some rod-like crystal structures obtained, the structure for the 18 min plating time also appeared finer, compact and levelled. The deposition looked dense and very closely packed. The sample surface was brighter than with the use of tobacco extract additive alone and also brighter than the sugarcane alone. The masses of zinc deposited were 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 a synergism effect of the mixed extract additives.

Additive of 3 ml/50 ml at 15 and 18 min plating times Figure 4e, f shows the SEM micrographs of steel surface after zinc plating with 3 ml/50 ml of acid chloride solution at 15 and 18 min, respectively. There was no porosity observed in these micrographs. The surface microstructure show closed-packed, fairly bright and fine, levelled clustered grains, as in Fig. 4e, and fine spherical-like grain particles as in Fig. 4f for 15 and 18 min plating times, respectively, and thus presenting a good surface morphology. It is thus plausible to associate the observed features here with concentration and plating time effects. 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 min plating times, respectively.

Plating with different additive concentrations and same plating time

The various SEM micrographs for the samples plated at different concentrations of 2, 2.5, and 3 ml/50 ml and at the same plating time of 15 and 18 min, respectively, are presented in Fig. 5.

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 $\times 5{,}000$.

Plating at 15 min with different concentrations shows a compact, dense and porosity-free, leveled and fine grain microstructure that indicated good plated surface morphology. However, the microstructure looked different in shape from 2 to 3 ml/50 ml concentrations of extract additive. It is difficult to say which is better morphologically. One unique striking 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. Just as described above, the crystals were very fine, closely packed, leveled, morphologically similar in shape and with no porosity observed. In general, the plating time of 18 min at all the concentrations used seems to have a comparatively more unique microstructure. The plating at 15 min also shows the same similarity characteristics as described above for the 18 min zinc plating time. The surface

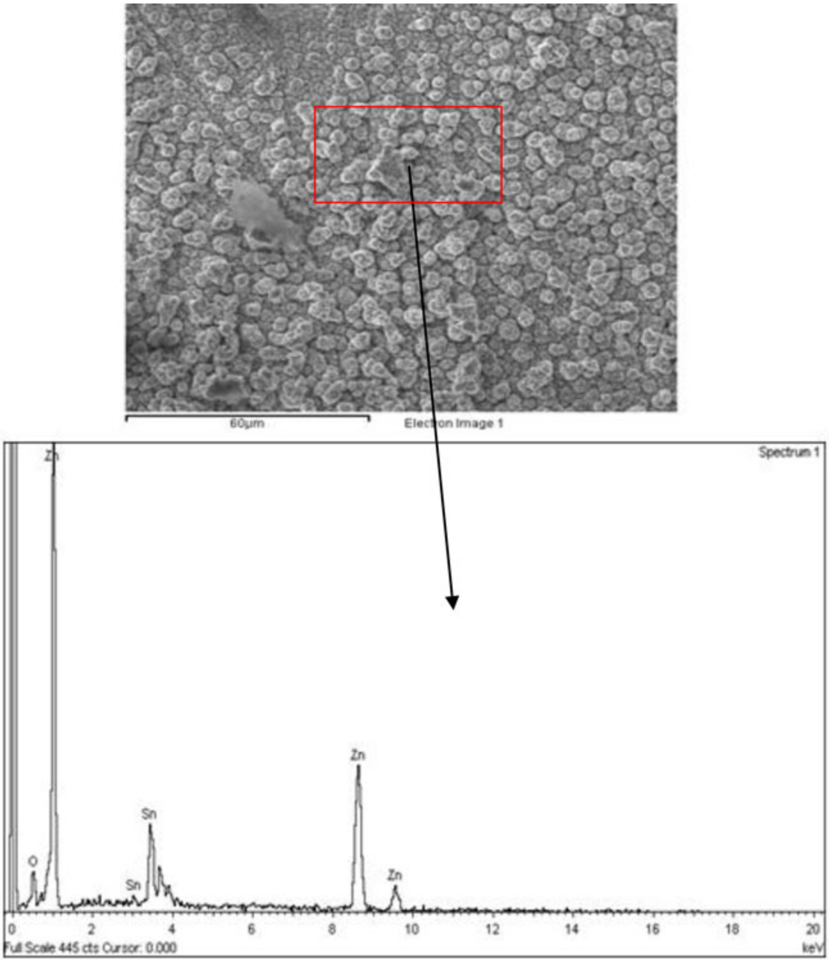

Fig. 6 EDS analysis of the plated surface of sample in Fig. 4f

morphology for each of the plating times 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 pineapple and sugarcane, that had been separately effective in the electroplating process in the previous studies.

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 particles removed from the plated steel surface. It is therefore expected that the electroplated mild steel surface will be suitable for the corrosion protection

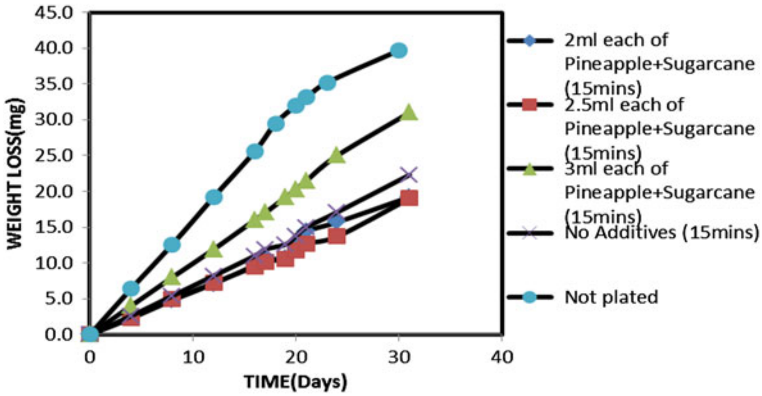

Fig. 7 Variation of weight loss with exposure time for the zinc electrodeposited mild steel sample in seawater. (Different combined additive concentrations at 15 min plating time)

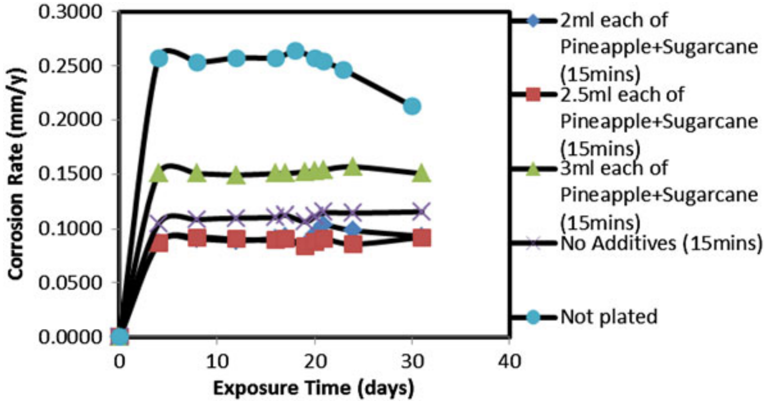

Fig. 8 Variation of corrosion rate with exposure time for the zinc plated mild steel samples in seawater. (Different combined additive concentrations at 15 min plating time)

of the steel surface. It was expected to sacrificially protect the substrate from corrosion in a corrosive medium.

EDS Analysis The result of energy dispersive analysis (EDS) of a plated sample in 2 ml/50 ml acid chloride concentration at 18 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 was present. Just as written above, the surface microstructure here was closely packed and with roundish crystal grains which indicate good morphological structure and a good evidence of the combined extracts effective synergism.

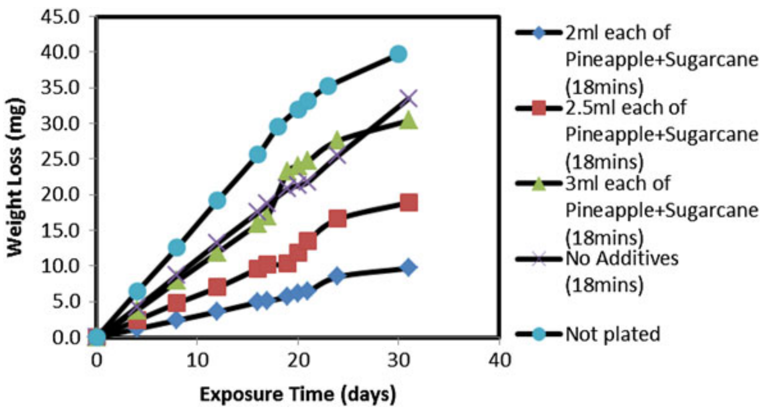

Fig. 9 Variation of weight loss with exposure time for the zinc plated mild steel samples in seawater. (Different combined additive concentrations at 18 min plating time)

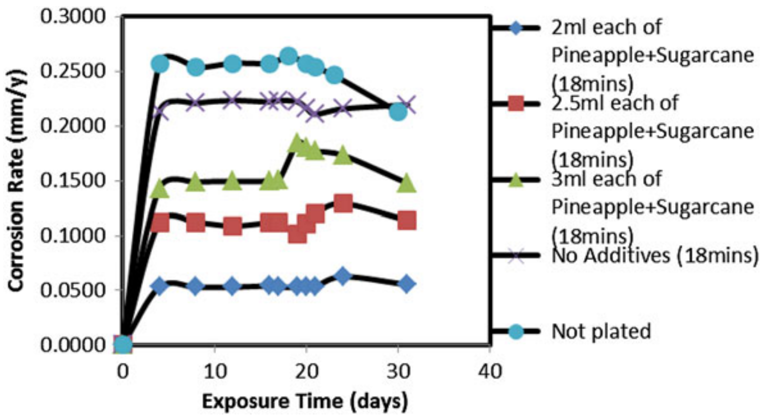

Fig. 10 Variation of corrosion rate with exposure time for the zinc plated mild steel samples in seawater. (Different combined additive concentrations at 18 min plating time)

Corrosion resistance of the zinc plated mild steel

Presented in Figs. 7, 8, 9, 10 are 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 seawater medium. Figure 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.

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 30th day of the experiment, the sample plated separately with 2 and 2.5 ml pineapple and sugarcane extract/50 ml acid chloride solution recorded the same weight loss value of 18.50 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.

The corresponding corrosion rates curves are presented in Fig. 8. The unplated test sample recorded the highest corrosion rate (0.252 and 0.225 mm/year) 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 0.0.081 to 0.150 mm/year at the same periods of the experiment. The corrosion resistance or susceptibility performance of the electroplated surface of the mild steel substrate was not in any significant way affected by the various extract additives used. In fact, the extracts function mainly in levelling effect and in enhancing brightness of the plating and hence in morphological structure modification.

Figures 9 and 10 show 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. Just as in Fig. 8, the trend of corrosion resistance for the weight loss values looked similar. The samples plated with 2 ml solution extracts (as additive) gave the lowest weight loss (10.00 mg) on the 30th day of the experiment, followed by the 2.5 ml additive concentration. The same trend was also followed in the corrosion rate. The lowest corrosion rate. 0.055 mm/year, was recorded for the sample tested with 2 ml combined pineapple and sugar extract additive at the same period of the experiment. Results obtained here showed that the plating time was 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. Likewise, the corrosion rate values achieved were very much lower in the plating samples made at 18 min plating time than with the samples made at 15 min plating time.

The overall results obtained here showed 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.

In summary, 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 more compact and levelled the surface crystal particles; the finer the crystal and morphological structure, the better the corrosion resistance of the plated samples.

Conclusions

1. The combination of sugarcane (*S. officinarum*) and pineapple (*A. comosus*) extracts as the addition agent gave good zinc electroplating with fine, dense and closely packed crystal grains on mild steel surface in the acid zinc chloride solution.
2. Depending upon the plating conditions, the zinc plated surface of the mild steel substrate showed 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. The plated samples showed good corrosion resistance in a seawater test when compared with the unplated samples and thus confirming their expected protective capability.
5. The plating produced a bright deposition that was brighter than either the pineapple or sugar alone and thus exhibiting synergism characteristic. The additives used in combination were non-toxic agricultural products that are environmentally friendly.

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