

Technical Report

Effect of *Manihot Esculenta* C. Leaf Extract Additive on the Zinc Electroplating on Mild Steel in Acid Chloride Solution

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The plating quality effect of *manihot esculenta* c. (cassava) leaf extract as addition agent on the electroplating of zinc on mild steel in acid chloride solution was investigated in the laboratory. The experiments were performed using different extract additive concentrations, different plating time and fixed pH conditions. A DC – supply at defined operating parameters was used to perform the electroplating of zinc on mild steel. The surface of the plated steel was examined using a scanning electron microscope (SEM) equipped with Energy Dispersive Spectroscopy (EDS). This was used to examine the surface of the plated steel for surface morphology and for surface elemental composition analysis. Distinct variable 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 gravimetric, potential measurement and corrosion current methods. The coating efficiencies were also determined. Variations in the plating parameters produced entirely new and different surface morphology. The quality of the electro-deposition of zinc was good as showed by the microstructural features of the plated surfaces. The electrodeposition process was sensitive to changes in additive concentration and plating time.

Keywords: Electroplating, cassava leaf, steel surface, acid chloride solution, corrosion.

1. INTRODUCTION

Electroplating of zinc on mild steel has been of very vital importance in surface engineering research and in metals' industry. This is necessitated by the need not only to prevent corrosion but also to enhance the aesthetic value of steel components in different manufacturing productions, industries

and in our daily lives. In spite of the fairly long period of time that the commercially-available proprietary additives have been used [1-4], the need to develop other environment –friendly non-commercial proprietary additives for the acid chloride bath has been generating increased research interest. This includes the present investigation. This work therefore aims at a further contribution to the recent investigations [5-9] which characterized the surface effects of additives on the electrodeposition of zinc on mild steel in acid-chloride solution under different conditions. 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.

Chloride zinc solution in addition to eliminating cyanide in plating, 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. 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].

Various researchers have reported and /or documented the use of plant extracts as inhibitors for the corrosion of metals/alloys in recent time [14-22]. However, the application of these plant extracts to electroplating of zinc on metallic alloy such as mild steel is very new. The extract of leaves of *manihot esculenta c.* (cassava) is used in this work as the addition agent. Cassava is a woody shrub of the Euphorbiaceae family. The phytochemical, nutritive and antinutritive composition of Cassava (*Manihot esculenta C.*) tubers and leaves had been investigated [23]. The aqueous and ethanolic extracts of raw cassava leaves consists of alkaloids, flavonoids, tannins, anthraquinone, phlobatinnins, saponins, reducing sugars and anthrocyanosides. Raw cassava leaves contain crude fibre and protein. The leaves also contain Vitamins A, C and E and minerals, namely, calcium, magnesium, phosphorus, iron, sodium, and chloride ions. Raw cassava leaves contain antinutrients, such as tannins, oxalate, phytate and trypsin inhibitor activity. The high contents of the antinutrients in the raw cassava leaves make them unsafe and unsuitable for human consumption, except after processing.

The toxic and antinutritional cassava extracts contain mainly the cyanogenic glycoside linamarin – 2 (β -d- glucopyranosyloxy isobutyronitrile with a little of the closely related lotaustralin - 2 (β - d glucopyranosyloxy) 2 – methylbutyronitrile [24-26]. These substances hydrolyse under the influence of the endogeneous enzyme linamarase to liberate hydrogen cyanide [24].

These complex chemical compositions may exhibit electrochemical activity such as zinc electroplating on mild steel. A good result in this work will be of economic and technological benefit.

2. MATERIALS AND METHODS

The cassava leaf 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 cassava leaves weighing 165 g each were soaked in 450 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. 45 g of concentrated cassava leaf extract was obtained after the distillation process. The extract

filtrate was then dissolved in 300 ml of distilled water to obtain a concentration of 0.18g/ml (180mg/l). The solution was stirred vigorously to ensure that the leaf extract was properly dissolved.

2.1 Experimental set-up

The experimental set up was just as previously described [27-30]. 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, 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). Solution extracts of *manihot esculenta* (cassava) of varying concentrations: 5, 10 and 15 ml/50ml of acid chloride solution were used in turns as the addition agents.

Electroplating of zinc on steel was performed following the previous experimental procedures [26-27] by partially immersed the steel specimen and the zinc electrodes in the plating solution (20 mm deep) through the rectangular hole made on a machine prepared flat 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 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. The results obtained are graphically presented in Figure 2.

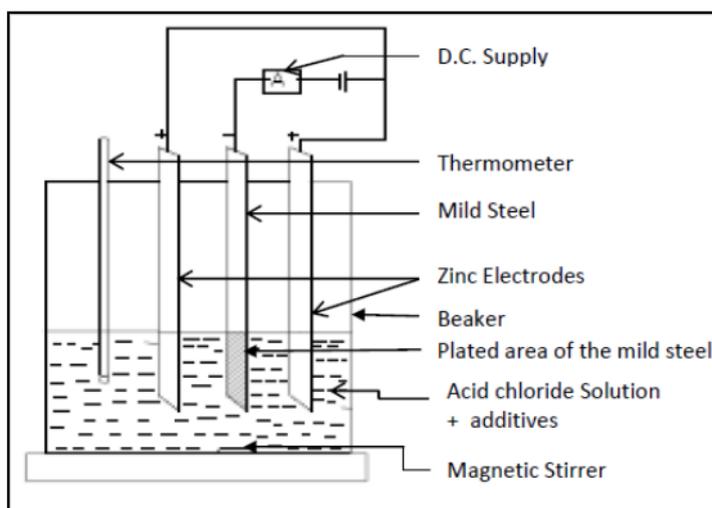


Figure 1. Schematic diagram of the experimental set-up

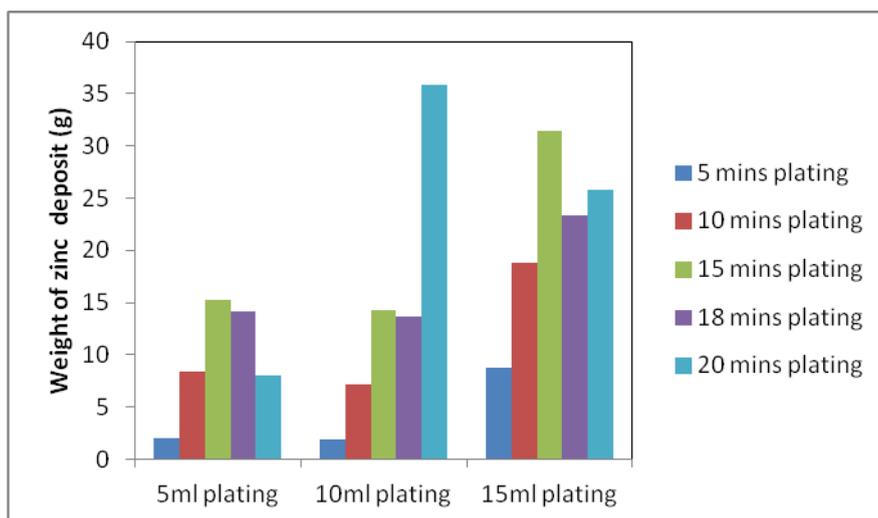


Figure 2. Weight of zinc deposited on mild steel samples versus additives concentrations and the different plating time

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. The respective samples were labelled as presented in Table 1.

Table 1. Plated samples identification

A	Nil (15mins)
B	5ml Cassava Leaf Extract (15mins)
C	5ml Cassava Leaf Extract (18mins)
D	10ml Cassava Leaf Extract (15mins)
E	10ml Cassava Leaf Extract (18mins)
F	15ml Cassava Leaf Extract (15mins)
G	15ml Cassava Leaf Extract (18mins)

2.2. SEM/EDS characterisation

The surface morphology of each of the plated test specimens was examined with a scanning electron microscope (SEM) equipped with energy dispersive spectroscopy (EDS). 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 on the selected surface portions to determine the elemental composition of the metal plated surface.

2.3. Adhesion test

The adhesion of the zinc plating to the steel substrate was tested by the use of cellotape fastened to the surface and then pulled off. The cellotape was visually observed for any zinc stripping from the plated steel's surface. Also, 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 and by potential and current measurements. Each of the plated mild steel test specimens was partially immersed in the 0.5M HCl test environment. The hydrochloric acid 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:

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

- where W is the weight loss in milligrams, D is the density in g/cm², A is the area in cm², and T is the time of exposure in hours.

2.5. Potential and Current measurements

Mild steel samples were cut into small coupons and welded/soldered with copper wires to each of them. They were then mounted in resins (araldite); to expose only the plated sample surface area to the acid test medium. The measurements were performed with multimeter (for voltage) and zero resistance ammeter (for current) measurements. All the experiments were performed using 75 ml each in a beaker of 0.5M HCl. In all the corrosion tests, only few selected specimens were used.

2.6. Efficiency of Coating

The coating efficiency was determined with the use of this formula:

$$EC\% = \frac{R_{cn} - R_{ca}}{R_{ca}}$$

where R_{ca} is corrosion rate of sample plated with additive, and R_{cn} is the corrosion rate of samples plated without additives.

3. RESULTS AND DISCUSSION

3.1. Electrodeposition of zinc

Plating with no additive

The SEM micrograph of the surface of the mild test sample before zinc electroplating is presented in Fig. 3 (i). Fig. 3 (ii) shows the photomicrograph of the zinc electroplated mild steel test

samples from acid–chloride solution without any additive. The slipped-stack-like crystals were distinctly and uniformly distributed throughout the plated surface, closely packed and with very low microscopic porosity in just two places. The surface crystals feature was not smooth. The structure was coarse and this could be due to the absence of levelling agents in the acid solution and the poor throwing power of the acid solution. The surface morphological structure was however, uniquely patterned in shape.

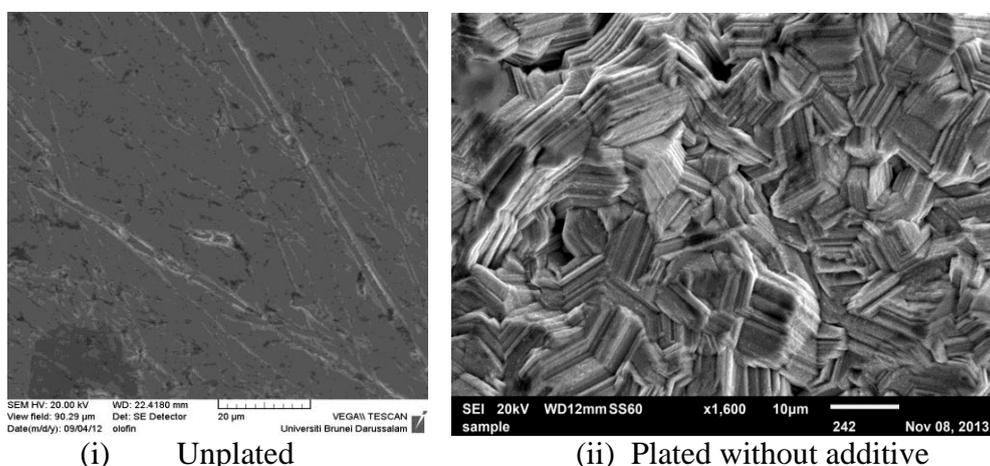


Figure 3. SEM micrographs of mild steel test sample: (i) Unplated sample (ii) Plated without cassava leaf extract addition .

*Plating with same additive concentration and different plating time
5 ml /50 ml additive at 15 and 18 minutes plating time*

In Fig.4, the micrographs made with plating at 15 and 18 minutes respectively with the extract concentration of 5ml/50ml of acid chloride solution are presented.

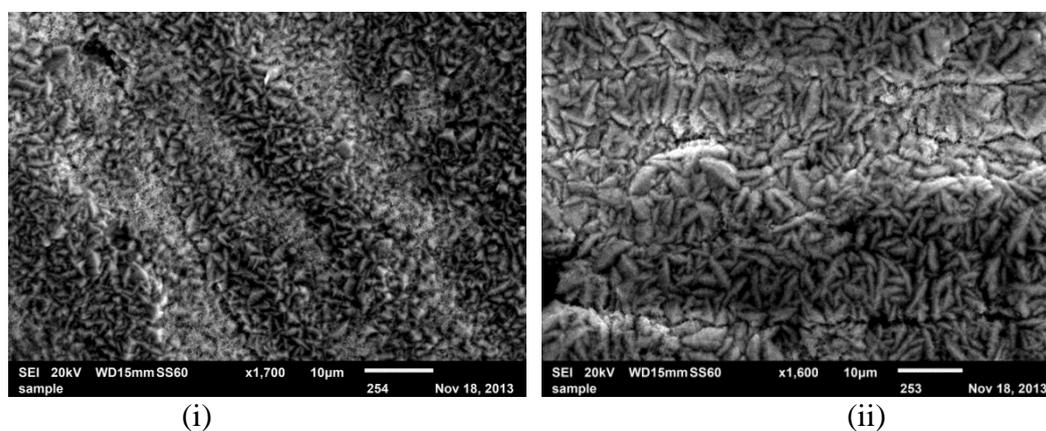


Figure 4. SEM micrographs of steel surface after zinc plating with 5ml /50ml of acid- chloride solution at (i) 15 and (ii) 18 minutes respectively.

The microstructure in Fig. 4 (i) appears finer than in Fig. 4 (ii) though they both have fine small grains with rod-like appearance. The surface microstructure is levelled and looks bright. The crystal particles were very close-packed and no porosity observed. Obviously, the observed very fine grains and levelling difference in surface morphology as evidenced in Fig. 4(i-ii), when compared with those in Fig. 3 (i-ii), emanated from the addition of the cassava leaf extract which has complex chemistry including low CN^- ion concentration but could exhibit electrochemical activity of electro-deposition. The difference in surface morphology in Figures 4 (i) and (ii) seems insignificant but the grains of the latter (the 18 minutes plating time) are bigger and more defined. The unique microstructure observed in Fig.4 (i-ii), is evidence of good zinc electroplating. The mass of zinc deposited was weighed to be 15 and 14 g respectively, Fig. 2.

10ml /50ml of additive at 15 and 18 minutes plating time

Another different surface morphological structures as shown in Fig. 5 (i - ii) were obtained when the concentrations of the ecassava lef xtract additive were changed from 5ml to 10ml cassava leaf extract/50 ml of acid chloride solution at both the 15 and 18 minutes plating time. The very little increase in the volume/concentration of the extract brought about very significant surface morphological changes. Here, the surface crystals remained not just very refined and levelled but equally smooth as could be observed. In these micrographs, no porosity was observed at the portions examined. The surface microstructures show a densely and closed- packed feature and thus presenting a good surface morphology. However, the surface feature for the 18 minutes plating time was smoother than the 15 minutes'. The ripple/ridges feature of the surface morphology of the 15 minutes plating time, Fig. 5 (i), is difficult to explain. The observed features here could thus be plausibly associated 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. Curiously, just as in Fig. 4 (i-ii), the same mass of zinc was deposited: 15 and 14 g respectively for the 15 and 18 minutes plating time. The deposition was bright.

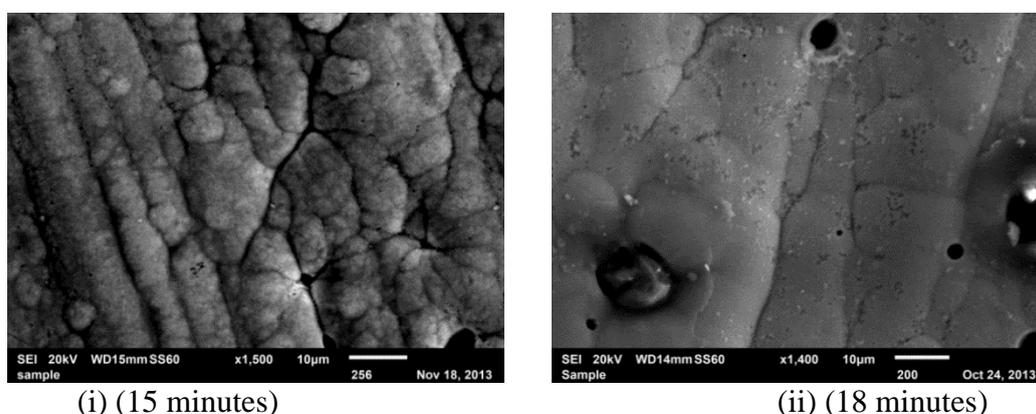


Figure 5. SEM micrographs of steel surface after zinc plating with 10ml /50ml of acid chloride solution at (i) 15 minutes and (ii) 18 minutes respectively.

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

Presented in Fig. 6 (i - ii) are the scanning electron microscopy micrographs of steel surface after zinc electroplating with 15 ml /50ml of acid chloride solution at 15 and 18 minutes respectively. The crystal grains were very refined, well levelled and are closely similar in shape. The grains were well close-packed and thus presenting a smooth surface characteristics. In spite of the low brightness of the deposition, this plating was expected to give very good surface protection to the mild steel substrate. The mass of zinc deposited was 31 g for 15 minutes plating time and 26 g for 18 minutes plating time. The reduced plating time seemed to have no apparent adverse effect on the obtained zinc deposition. The increase in the additive concentration seemed to have made significant contribution to the observed fine-grained, smooth and levelled surface morphology. It is important to mention here gain that the chemical composition of cassava leaf is indeed very complex as mentioned above. Undoubtedly this would have very great beneficial impact on the positive results that were recorded in this work.

The fineness and the compactness of the surface morphology in the plated steel substrate were therefore expected to give a better surface protective property in terms of corrosion resistance. It is also important to mention that the 18 minutes plating time enhanced its levelling behaviour though the obtained micrograph is cloudy.

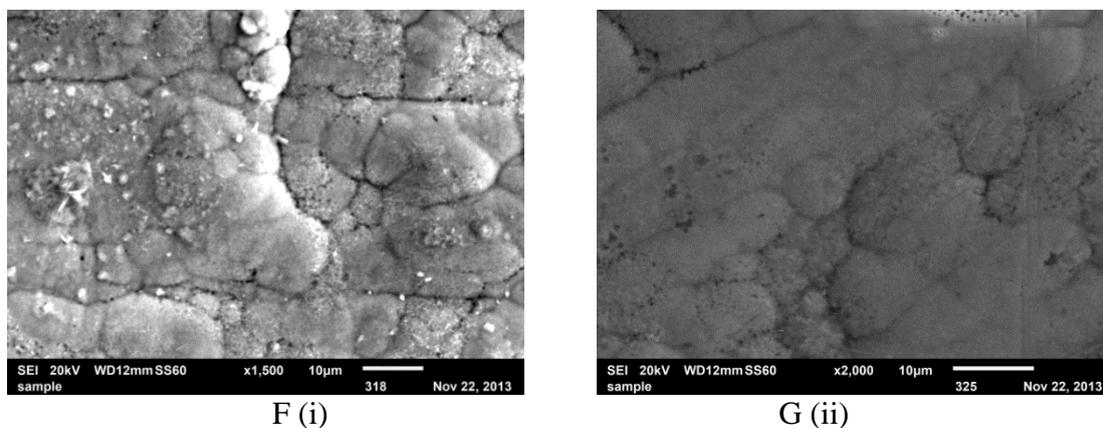


Figure 6. SEM micrographs of steel surface after zinc plating with 15 ml /50ml of acid chloride solution at (i) 15 min. and (ii) 18 minutes respectively.

Different additive concentrations and same plating time

The various SEM micrographs for the samples plated at different concentrations of 5, 10, and 15 ml/50ml and at the same plating time of: (A) 15 minutes and (B) 18 minutes respectively, are presented in Fig. 7. The surface morphology of each of these micrographs had been described above. They are represented in Fig. 7 for surface structural comparison. There seems to be no significant difference, in general, in the structural morphology for the plating time of 15 and 18 minutes at each of the concentrations used. However, the finest surface microstructure was achieved for the plating with 10 ml/50ml concentration at 18 minutes plating time. The surface morphology for each of the plating

time for the three different concentrations shows different features with good levelling and dense packing.

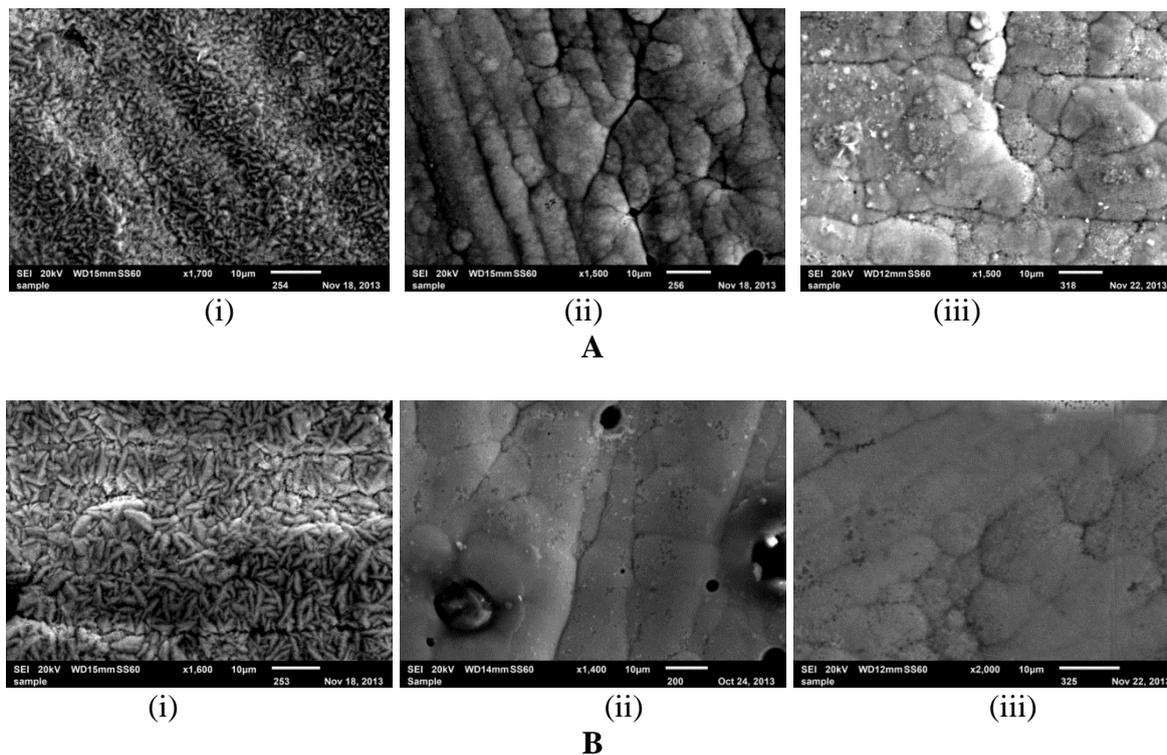


Figure 7. SEM micrographs for the samples plated at different concentrations and at the same plating time: **(A)** – (i) 5 ml, (ii) 10ml and (iii) 15ml/50ml for 15 minutes; **(B)** (i) 5 ml, (ii)10 ml, and (iii) 15ml at 18 minutes respectively.

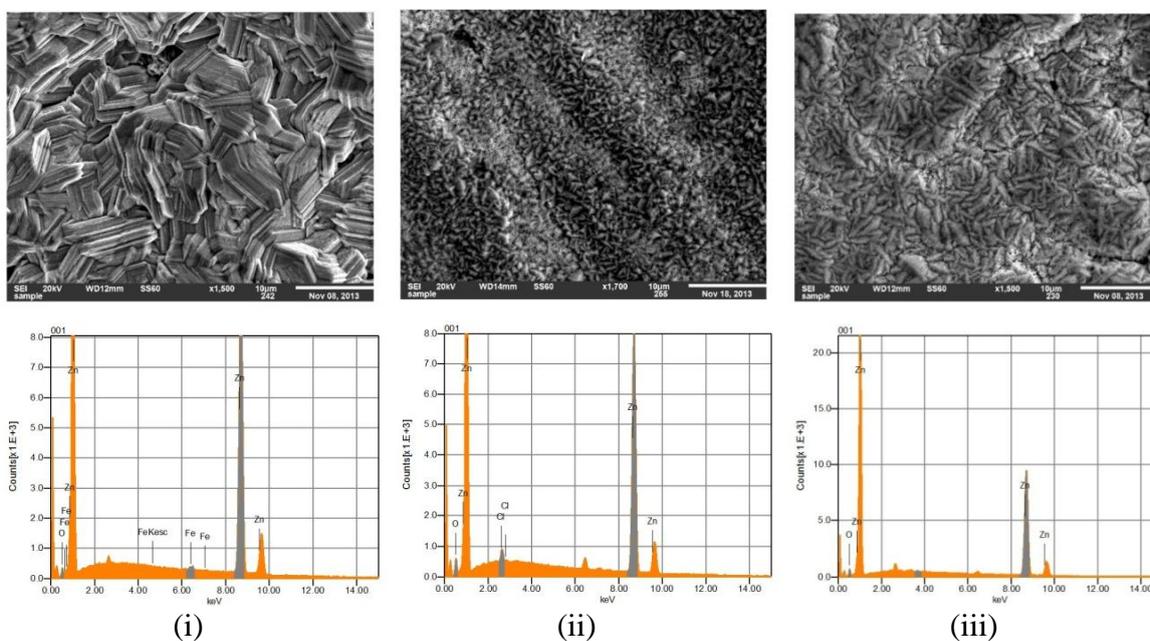


Figure 8. EDS analysis of the plated surface of samples in (i) Fig.3 (ii) (without additive), (ii) Fig. 4 (i) (with additive) and (iii) 4 (ii) (with additive).

EDS Analysis

The results of energy dispersive analysis (EDS) of Fig. 3 (ii) and Fig. 4 (i and (ii)) are presented in Fig. 8. The surface microstructure was predominantly zinc and a little amount of iron in the plating without additive which apparently was in trace form. The EDS analysis confirmed the effective coverage of the zinc deposition and the dense packing that left no room for porosity.

3.2. Corrosion resistance of the zinc plated mild steel

All the plated samples with additives showed better corrosion resistance than the plated samples without the cassava leaf extract additive. While the plated sample without additive recorded a corrosion rate value of 171 mm/yr on the 22nd day of the experiment, the corrosion rate for all the zinc plated metals with additives ranged between 153 mm/yr for the 10 ml- (at 15 minutes plating time) and 75 mm/yr for the 15 ml//50ml of acid chloride solution at 18 minutes plating time.. The latter has the lowest corrosion rate of all the samples at all the plating time and at all the concentrations used as presented in Fig. 9. The difference in corrosion rate is apparent. However, any porosity as could be observed in Fig. 3 (ii) would provide a small anodic site on the mild steel substrate in comparison with a large cathodic zinc plated portion with the consequence of increased rate of corrosion reactions such as observed. It should be noted also that additives function more as levelling and brightening agents.

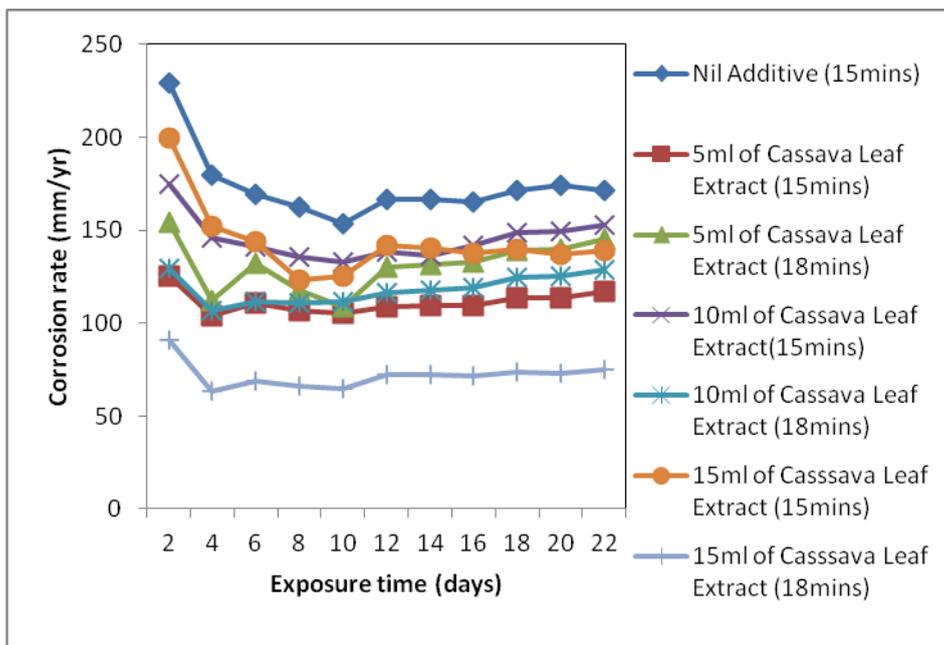


Figure 9. Variation of corrosion rate with exposure time for the zinc plated mild steel samples in 0.5M HCL (Variable additive concentrations – 5, 10 and 15 ml/50ml acid chloride solution); and 15 and 18 minutes plating time)

The results obtained for variation of potential with the exposure time for the zinc plated mild steel in 0.5 M HCl with variable plating time of 15 and 18 minutes and 5, 10 and 15ml/50 ml acid chloride solution concentrations of cassava leaf extract additive are presented in Fig. 10. All the results

appeared to be in the active corrosion reactions potentials ranging between -0.4820 (-482 mV) and -0.5890V (-589 mV) while maintaining an almost steady state corrosion reactions phenomena as the potential fluctuations are minimal. These very close results were not unexpected due to the anodic dissolution of the plated zinc in the acidic test medium. The zinc corroded to cathodically protect the mild steel substrate. There was no particular or significant effect of the plating time variation nor the additive concentration exhibited from the potential measurement values. As mentioned above, the additives function mainly for surface microstructural levelling and as brightener for the zinc electrodeposit on the metal substrate.

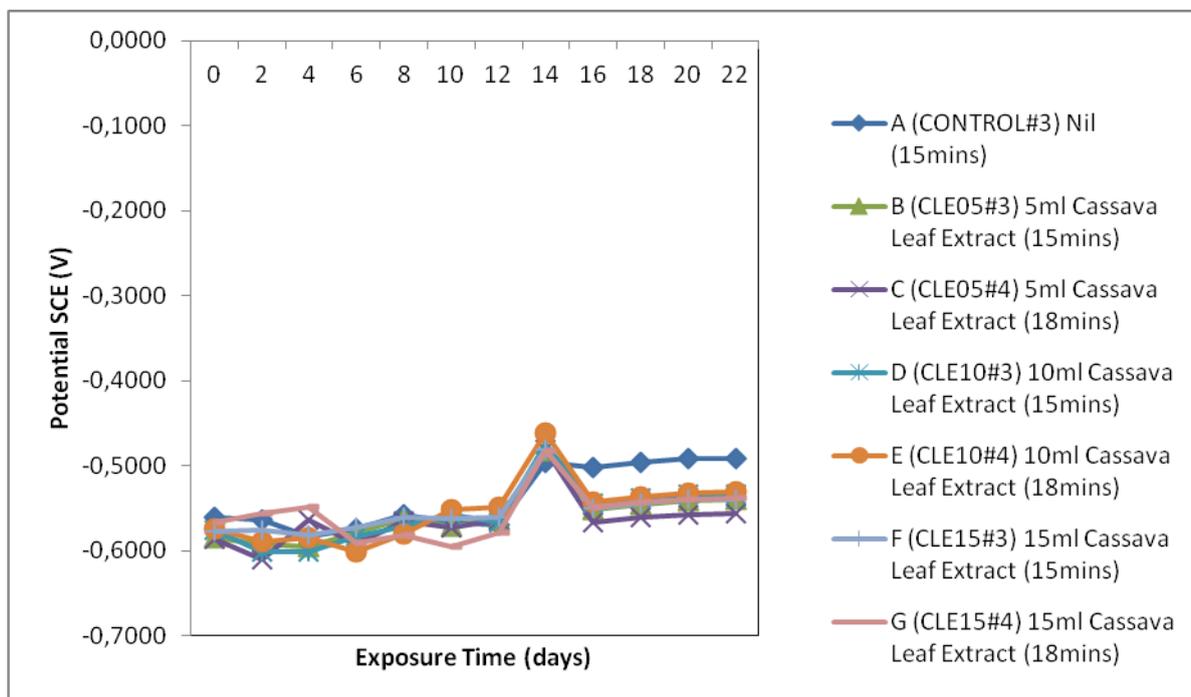


Figure 10. Variation of potential with the exposure time for the zinc plated mild steel in 0.5 M HCl with variable plating time and cassava leaf extract additive concentrations.

Presented in Fig. 11 are the results obtained for variation of corrosion current density with the exposure time for the zinc plated mild steel in 0.5 M HCl with variable plating time of 15 and 18 minutes and 5, 10 and 15ml/50 ml acid chloride solution concentrations of cassava leaf extract additive. Though fluctuating, the general trend was that of reducing corrosion current density from the beginning with time of exposure throughout the experimental period. This observed trend of results indicates reducing corrosion rates reactions as the experiment proceeded. In spite of the fact that a clear trend of non-strict association with the plating parameters in terms of plating time and extract additive concentrations was exhibited, it is very distinct that the plating without additive had the highest corrosion current density and hence the highest corrosion rate. Also, 15ml/50 ml acid chloride solution of cassava leaf extract concentration at 18 minutes plating time had the lowest corrosion current density and hence the lowest corrosion rate. These trends of results are in agreement with the results obtained for corrosion rate gravimetrically.

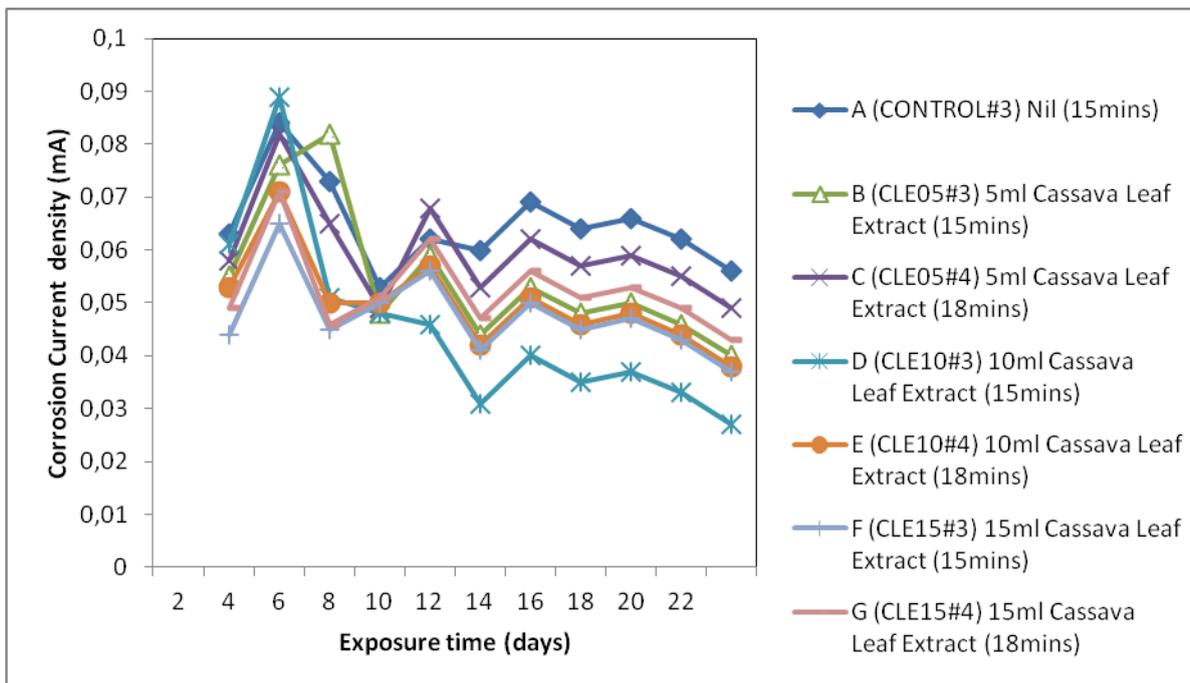


Figure 11. Variation of corrosion current density with the exposure time for the zinc plated mild steel in 0.5 M HCl.

Fig. 12 shows the variation of coating efficiency with the exposure time for the plated test samples immersed in 0.5M HCL. At an efficiency that ranges between 56.44 and

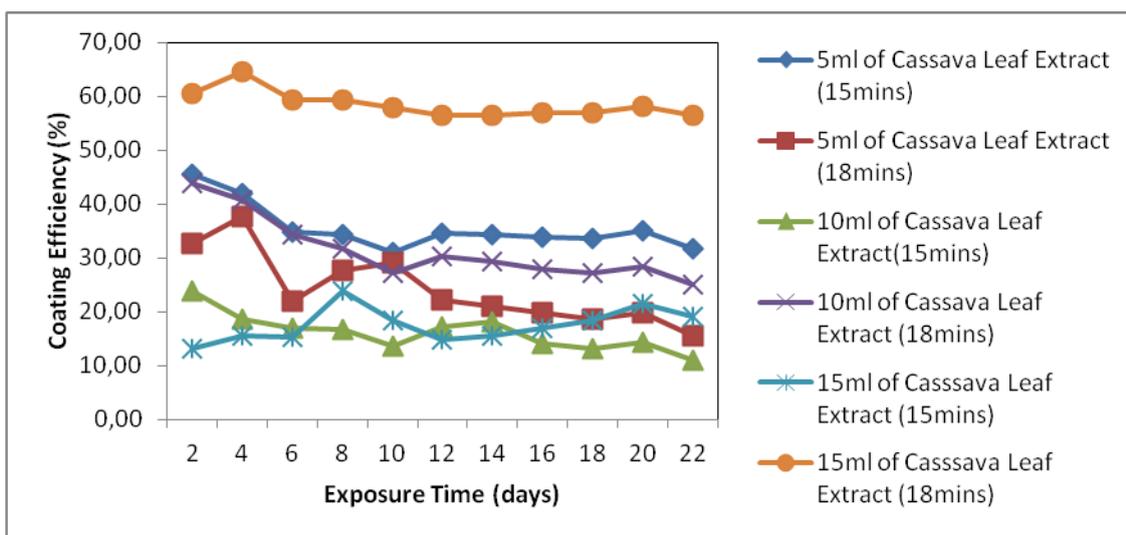


Figure 12. Variation of corrosion current density with the exposure time for the zinc plated mild steel in 0.5M HCl.

64.57%, the leaf extract additive concentration of 15ml/50ml of acid chloride solution and the plating time of 18 minutes, could be described as the most effective and hence providing the best electroplating quality in terms of levelling and surface integrity that is devoid of porosity. This result

bears very good correlation with the result obtained for the corrosion current density and the corrosion rate from the gravimetric method.

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 deposited 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 observed.

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

1. The use of cassava leaf (*manihot esculenta*) extract as the addition agent gave good quality zinc electroplating with fine, dense, levelled and close- packed crystal grains on mild steel surface in the acid zinc chloride solution.
2. Depending upon the plating conditions, characterisation of the zinc plated surface of the mild steel substrate showed different but good surface morphology.
3. The protective capability of the zinc plated metal was confirmed by the good corrosion resistance of the tested samples in the strong acid (HCL) test when compared with the unplated samples.
4. With variation in the plating parameters an entirely new and different surface crystal structure is produced. The electrodeposition process was sensitive to changes in additive concentration and plating time.
5. The plating produced bright deposition as expected.
6. The additive used was an agricultural product that is environment friendly.

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