Electrodeposition of Nanocrystalline Zinc from Acid Sulphate Bath in the Presence of Aqueous Lawsonia Inermis Linn. Leaf Extract and Its Corrosion Study

A.Jaini Flora, R.Sangeetha, J. Felicita Florence

Abstract— Nanocrystalline zinc is electrodeposited on steel substrates from acid sulphate bath in the presence of aqueous Lawsonia inermis Linn leaf extract. The optimized bath composition in the presence of aqueous L.inermis leaf extract is used for this zinc electrodeposition. Potentiodynamic polarization study is carried out to find the effect of addition agent on zinc electrodeposition. The surface of the plated steel is examined using scanning electron microscopy (SEM); and Energy Dispersive Spectroscopy (EDS) for the surface elemental composition analysis. The crystal structure is studied by X-ray diffraction study. The inclusion of addition agent in the deposit is confirmed by FT-IR. Salt spray test and electrochemical measurements are carried out to find out corrosion resistance property of the deposits. Salt spray test and electrochemical measurements reveal the nanocrystalline zinc coatings have better corrosion resistance. SEM photomicrographs reveals fine-grained structure of the deposit from the optimized bath. IR and EDAX studies confirm the inclusion of addition agent. X-ray pattern of the deposit in the presence of aqueous extract shows a broadening of the diffraction peaks. This broadening can be attributed to the decrease in grain size.

Key words: Lawsonia inermis Linn leaf, Electrodeposition, current density, SEM, EDAX, XRD, IR

1 INTRODUCTION

The use of zinc-plated articles is increasing due to its sacrificial protection of steel from corrosion. Zinc has found widespread and used as the basis of a whole range of sacrificial coatings for ferrous substrates [1]. It is the most commonly used sacrificial coating [2] and can be applied by a variety of techniques, including hot- dipping, metal spraying, cementation, cladding and electrodeposition [1]. The role of electroplating parameters on the formation of different textures and microstructures is well established by several researchers [3] using various approaches, which has effectively lead to the preparation of coatings that differ in their macro and microstructure, texture density, uniformity and corrosion resistance [4,5].

Electrodeposition is a versatile technique for producing nanocrystalline materials [6]. It is a technologically and economically viable production route to metals, alloys and metal matrix composites, both in bulk form and as coatings. Properties of nano-structured electrodeposits such as hardness, wear resistance and electrical resistivity are strongly grain size dependent [7]. The grain size of the electrodeposits depends on the deposition parameters such as pH [8], deposition technique [9], current density [7] and substrate [10], as well as on the type and the amount of additives included in the electrolyte [11].The use of additives in electrodeposition solutions is extremely important due to their influence on the growth and structure of the resulting deposits. The presence of additives has been shown to influence physical and mechanical properties of electrodeposits such as grain size, brightness, internal stress, pitting and even chemical composition [12]. Electrodeposition technique can yield porous-free finished products that do not require subsequent consolidation processing. During the past decade, extensive work on the characterization of nanocrystalline materials has been conducted. However, there are only a few experimental tensile studies of nanocrystalline Materials with a grain size equal or less than 25 nm [13],[14].

In this present study, nanocrystalline zinc coating is obtained from simple acid sulphate bathin the presence of an additive aqueous Lawsonia inermis linn leaf extract. Felicita etal [15] has established the optimized bath with aqueous Lawsonia inermis Linn leaf extract by varying the components as well as the bath parameters. The effort has been made to study the effect of aqueous Lawsonia inermis Linn leaf extract on zinc deposit.

2. EXPERIMENTAL METHODS

2.1. Preparation of zinc coatings

All the solutions are prepared from AR grade chemicals and double-distilled water. The pH of bath solution is measured using a digital pH meter (Equipetronix, model: 7020) and adjusted with 10% sulphuric acid or sodium bicarbonate solution. Zinc plate of 99.99% purity is used as anode and activated each time by immersing in 10% HCl followed by water wash. Mild steel (AISI-1079, composition C 0.5%, Mn 0.5%, P and S 0.05% and rest Fe) plates of standard Hull cell size are mechanically polished using emery paper (320-800 grit size) to obtain a smooth surface and degreased by dipping in boiling

trichloroethylene. The scales and dust on the steel plates are removed by dipping in 10% HCl solution and then subjected to electrocleaning process. These steel plates are washed with distilled water and used for the experiments as such. After electrodeposition the plates are subjected to bright dip in 1% nitric acid for 2-3 s followed by water wash and drying. The optimized bath composition in the presence of aqueous L.inermis leaf extract is used for this zinc electrodeposition. Table1 shows optimized bath composition. Potentiodynamic polarization study is carried out to find the effect of addition agent on zinc electrodeposition. The surface of the plated steel is examined using scanning electron microscopy (SEM); and Energy Dispersive Spectroscopy (EDS) for the surface elemental composition analysis. The crystal structure is studied by X-ray diffraction study. The inclusion of addition agent in the deposit is confirmed by FT-IR. Salt spray test and electrochemical measurements are carried out to find out corrosion resistance property of the deposits.

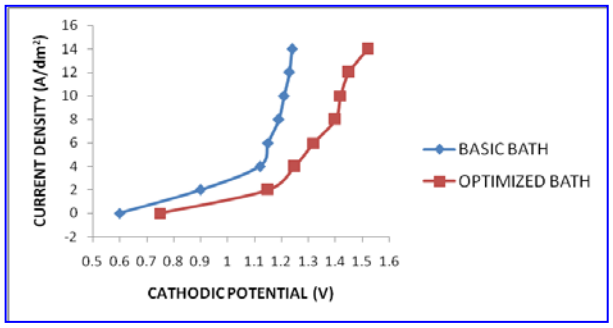
3. RESULTS AND DISCUSSION

The Zinc deposits on carbon steel obtained from this optimized bath with aqueous Lawsonia inermis linn leaf extract has shown better characteristic properties than the zinc deposits obtained from Basic Bath [15]. Matte white deposits are obtained at the current density of 0.8-4A/dm^2. This confirms the influence of Lawsonia inermis Linn. Leaf extract on electrodeposition of Zinc. The Current efficiency and the throwing Power of Zinc Electrodeposited carbon steel from optimized bath is found to be increased than in the case of zinc deposits on carbon steel from basic bath[15].

3.1 POTENTIODYNAMIC POLARISATION STUDY

The potential of steel cathode is measured galvanostatically with respect to saturated calomel electrode at different current densities. The variation of potential in Basic bath and optimized bath are shown in Fig 1. The shift in cathode potential towards negative direction is observed for Zinc electrodeposited carbon steel obtained from Basic bath and Optimized bath. This shows the effect of additive on the deposits

Fig 1
EFFECT OF CURRENT DENSITY ON CATHODIC POLARISATION



3.2 SEM ANALYSIS ON METAL SURFACE

The SEM image of Carbon Steel electroplated with Zinc from Basic bath and Optimized bath are shown in Fig 2A and 2B respectively. The SEM Micrograph of Zinc electro deposited Carbon steel surface from basic bath (Fig 2A) showed rough surface on the metal surface and it is also found that the crystal size is not uniform.The SEM Micrograph of Zinc electro deposited Carbon steel surface from Optimised bath (Fig 2 B) has shown uniform arrangement of crystals, refinement in the crystal size and hence give a bright deposit. This shows the effect of aqueous L.inermis extract on electrodeposition of zinc and the inclusion of leaf extract into metal surface.

Fig 2A
SEM PHOTO MICROGRAPHS OBTAINED FROM BASIC BATH

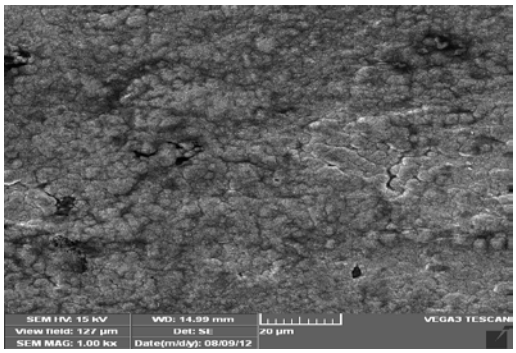
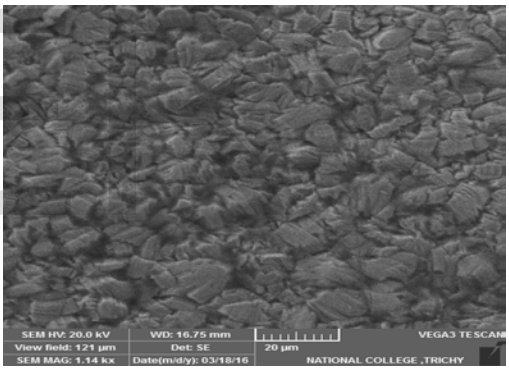


Fig 2B
SEM PHOTO MICROGRAPHS OBTAINED FROM OPTIMIZED BATH



3.3 EDAX ANALYSIS

An EDAX spectrum is used to find out the elements present in the deposit. EDAX spectra of Zinc electrodeposited carbon steel from Basic bath and Optimized bath are shown in Fig 3A and 3B respectively. EDAX spectra of Zinc electrodeposited carbon steel from Basic bath and optimized bath have shown the presence of Zinc, carbon and oxygen on the metal surface. The weight percentages of Zinc, Carbon and Oxygen in Zinc electrodeposited carbon steel from Basic bath are found to be 73.64%, 19.48 % and 6.88% respectively. But in the Zinc electrodeposited carbon steel from Optimized bath has only 59.59% of Zinc. This shows that the some of the active sites of Zinc are occupied by aqueous Lawsonia inermis Linn extract. The weight percentage of Carbon and Oxygen in the Zinc electrodeposited carbon steel from optimized bath is found to be increased to 29.52% and 10.86%. This confirms the inclusion of the addition agent during Zinc electrodeposition in the presence of extract.

Fig 3A

EDAX PHOTOGRAPH OBTAINED FOR ZINC ELECTRODEPOSITION FROM BASIC BATH

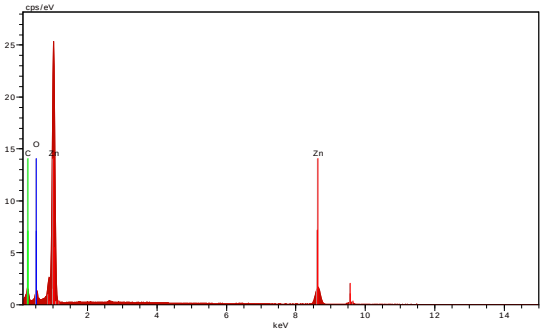
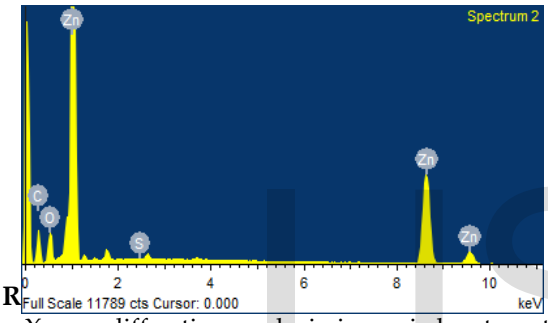


Fig 3B

EDAX PHOTOGRAPH OBTAINED FOR ZINC ELECTRODEPOSITION FROM OPTIMIZED BATH



3.4 X- R

X- ray diffraction analysis is carried out on the thin film of Zinc electroplated carbon steel obtained from basic bath and optimized bath are shown in Fig 4A and 4B. Intensity of peaks of Zinc electrodeposited carbon steel from optimized bath is decreased and the peak width is broader than that of Zinc electrodeposited carbon steel obtained from Basic bath. The average crystal size is found to be 0. 69 nm against 1.56nm of Zinc electrodeposited carbon steel obtained from Basic bath. The incorporation of leaf extract influences the growth of Zinc crystal such that it brought about a reduction in the crystal size. The extract included in the deposit acts as protrusions in a metal electrolyte interface resulting in a higher current density which increases the rate of nucleation and inhibited the growth of Zinc crystal and finally gives fine grained deposits.

3.5.FT-IR SPECTROSCOPY

The FT- IR spectrum of Pure L. Inermis extract is given in Figure 5A. The broad and medium intensity band near 3250 cm^{-1} is due to hydrogen bonded OH stretching vibration. The weak absorbtion at 3040 cm^{-1} is assigned to aromatic stretching vibration.

The aromatic overtones and combination bands in 2000-2700 cm^{-1} region confirms the presence of aromatic system, the absorbed pattern of finger like bands further suggests o-disubstituted and 1,2,3- trisubstitutedbenzene rings. The bands at 1630 and 1520 cm^{-1} are consistent with the skeletal vibrations of aromatic system. The bands at 1390, 1315 and 1275 cm^{-1} are due to OH in plane bending vibrations. The band at 1250 cm^{-1} is assigned to couple vibrations of OH in plane bending and CO stretching vibrations of OH group. The absorbtions at 1150 and 1050 cm^{-1} are due to CO stretching vibrations. The band at 860cm^{-1} represents OH out of plane bending vibration. The substitution pattern is established by strong CH out of plane bending absorptions at 800cm^{-1} (adjacent 3H) and 770cm^{-1} (adjacent 4H) suggests a α- substituted naphthalene ring. The weak band at 850 cm^{-1} represents 1, 4 substitutions

Fig 4A
XRD PHOTOGRAPH OBTAINED FOR ZINC EELCTRODEPOSITION FROM BASIC BATH

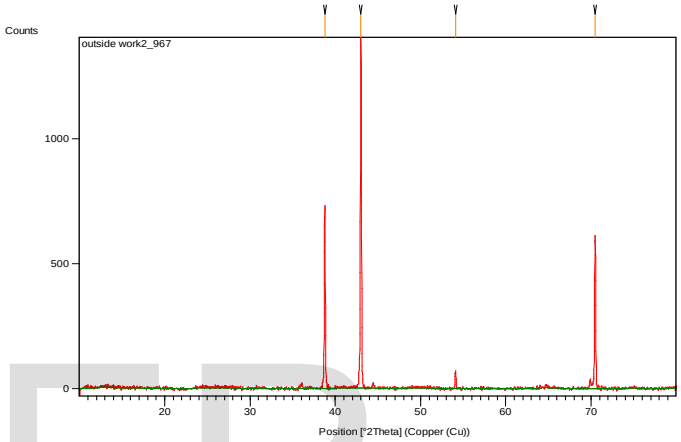
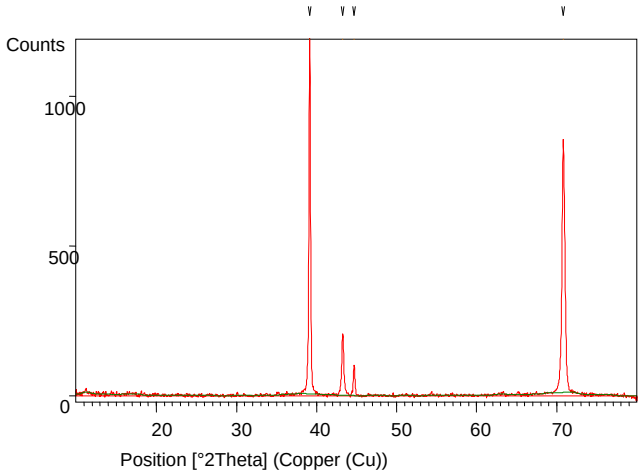


Fig 4B
XRD PHOTOGRAPH OBTAINED FOR ZINC ELECTRODEPOSITION FROM OPTIMIZED BATH



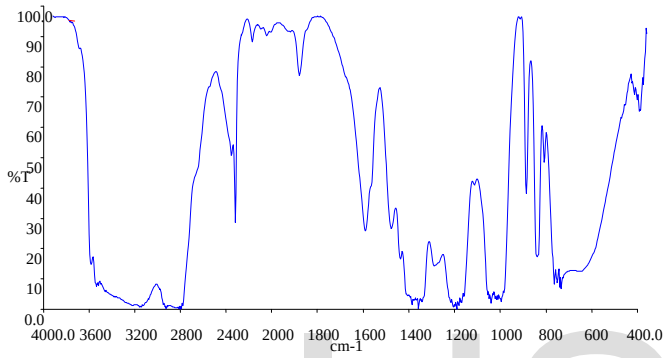
(Para) of an aromatic ring. These observations prove the presence of Major component, Lawsone in L. inermis extract.

The FT- IR Spectrum of the scrapped deposit obtained from optimized bath is given in Fig 5B. This spectrum is used to determine the inclusion of L. inermis extract in the deposit. It is observed that OH stretching frequency in the Free State has shifted from 3250- 3397 cm^{-1}. The C=C aromatic stretching

has shifted from 1598-1635 cm^{-1}. The CO stretching frequency has shifted from 1150- 1175 cm^{-1}. These observations indicate the inclusion of major component, Lawsone in L.inermis extract into the metal surface. These observations show that the major component has co ordinate with Zn^{2+} through oxygen atom of Lawsone and also through the π electrons of Naphthalene ring resulting in the formation of Zn^{2+} - Lawsone complex formed on the anodic sites of the metal surface. The peak at 1392 cm^{-1} is due to Zinc Hydroxide formed on the cathodic sites of the metal surface.

Fig 5A

FT-IR SPECTRUM OF PURE L. INERMIS LEAF EXTRACT



3.6 CORROSION STUDIES

3.6.1. SALT SPRAY TEST

Basic bath and Optimized bath are subjected to continuous spray of 5% sodium chloride solution. The Zinc electrodeposited carbon steel from Basic bath shows white rust within 48 hours. But the Zinc electrodeposited carbon steel from Optimized bath does not show any white rust even after 96 hours of testing. This study reveals the good corrosion resistance of the deposit. (Table 2)

3.6.2 POLARISATION STUDIES

Fig 6A and 6B show the effect of additive on corrosion behavior of Zinc deposits (Basic and Optimized Bath) in 3.5% NaCl Solution. The values are given in Table 3. The corrosion current (I_{corr}) for basic bath is 3.9514 x10^{-3} A/cm^2. It is decreased to 0.6694 x 10^{-3} for the optimized bath. The current of iron dissolution is decreased significantly, indicates that the surface is protected by the layer which is formed in the presence of additive, leaf Extract. The significant reduction in the corrosion current shows the adsorbtion of additive on the surface of carbon steel. It is also indicated that the protective film is formed on the metal surface. This gives protection from corrosion. Thus this protective layer by the additive controlled both the anodic and cathodic processes. Hence, the deposit obtained in the presence of additive, Henna extract shows maximum corrosion resistance.

FIGURE 5B

FT-IR SPECTRUM OF SCRAPPED ZINC DEPOSIT OBTAINED FROM OPTIMIZED BATH.

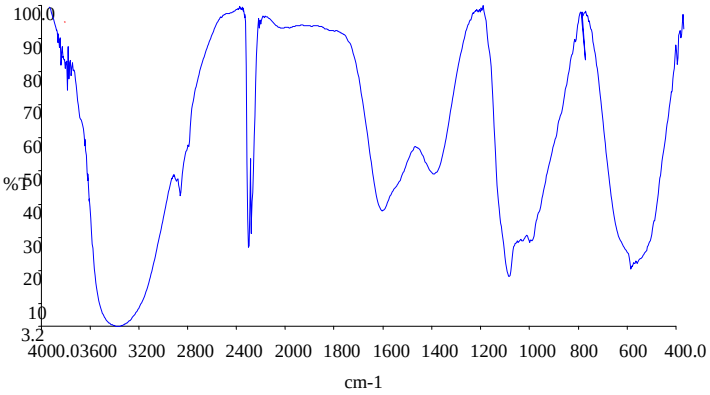


Table 2

Salt Spray Test Conducted at Different Time Intervals

Plating Bath Composition	Treatment (Hours)	Observation
BASIC BATH	24	No Rust
	48	White Rust
OPTIMIZED BATH	24	No Rust
	48	No Rust
	72	No Rust
	96	No Rust
	120	White Rust

TABLE 3

CORROSION PARAMETER OF ZINC ELECTRODEPOSITED MILD STEEL BY POTENTIODYNAMIC POLARISATION METHOD

System	Ecorr mV vs SCE	bc mV/ decade	ba mV/ decade	LPR Ω cm^2	Icorr X 10^{-3} A/cm^2
Basic Bath	-1.002	258.35	29.78	9.0323	3.9514
Optimised Bath	-1.029	66.94	30.854	4.8275	0.66944

3.6.3 AC IMPEDANCE SPECTRA

The AC impedance spectra of zinc plated carbon steel from Basic bath and optimized bath are shown in Fig 8A and 8B. The AC impedance parameters, namely the charge transfer resistance (R_t) and double layer capacitance (C_{dl}) are given in the Table 4. For Basic bath, Rt value is found to be 4.239 Ω cm^2 and the C_{dl} value is 1.869 x 10-3F/cm2. But for optimized bath R_t value has increased tremendously from 4.239 Ω cm^2 to 71.235 Ω cm^2 and the C_{dl} value has decreased to 0.1775 x 10^{-3} F/cm2. The increase in the R_t value and decrease in the C_{dl} value obtained from Ac impedance studies have shown the presence of protective layer in the presence of additive, aqueous Lawsonia inermis Linn. Extract. This particular study justifies the good Corrosion resistance power of the layer which is formed on the Carbon steel surface in the presence of leaf extract. The increase in the corrosion resistance of the deposit may be also due to fine grain struc-

ture of the deposit.

Fig 7A
POTENTIODYNAMIC POLARISATION CURVE FOR BASIC BATH

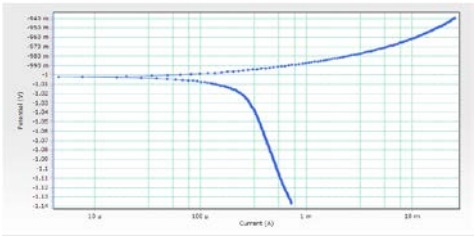


Fig 7B
POTENTIODYNAMIC POLARISATION CURVE FOR OPTIMIZED BATH

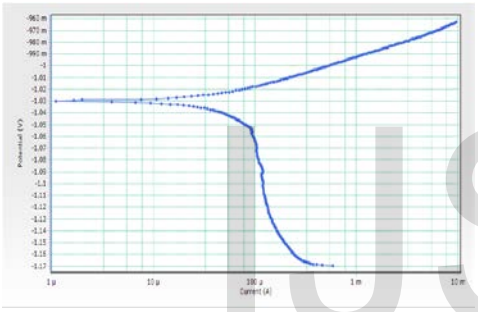


TABLE 4

CORROSION PARAMETER OF ZINC ELECTRODEPOSITED MILD STEEL BY AC IMPEDENCE STUDY

System	Rt Ω cm^2	Cdl μF/cm^2
Basic Bath	4.239	1.869 x 10^{-3}
Optimized Bath	71.235	0.1775 x 10^{-3}

Fig 8A

AC IMPEDENCE SPECTRA FOR BASIC BATH

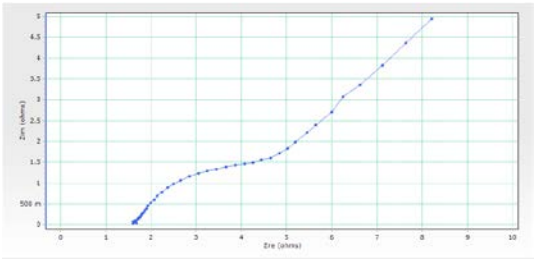
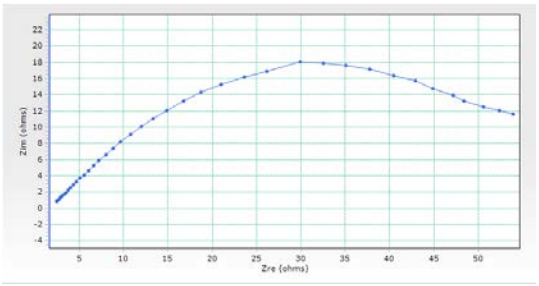


Fig 8B.
AC IMPEDENCE SPECTRA FOR OPTIMIZED BATH



4. CONCLUSION

The shift in cathodic potential towards negative direction is observed for zinc electrodeposited carbon steel from optimized bath on Polarization study confirms the effect of additive on electrodeposition. The fine grained deposits on Zinc electroplated carbon steel from optimized bath reveals the inclusion of addition agent on zinc electrodeposition. XRD spectra reveal the reduction in the particle size of Zinc deposits on carbon steel obtained from optimized bath. EDAX and FT-IR Spectroscopy confirm the inclusion of aqueous L.inermis Extract on zinc electroplated carbon steel from optimized bath.

Salt spray test confirms the greater corrosion resistance property of the deposits from optimized bath.

Polarization study reveals that the Zinc deposits obtained from optimized bath on carbon steel function as mixed inhibitor controlling both anodic and cathodic processes. From AC impedance spectra it is clear that a protective film is formed on the metal surface. From these corrosion studies the zinc electrodeposited carbon steel from optimized bath (in the presence of L.inermis extract) has greater corrosion resistant property.

REFERENCES

[1] G.D Wilcox, and D.R Gabe, Electrodeposited Zinc Alloy Coatings, *Corrosion Science*, 35(8), 1993, 1251-1258

[2] H.B. Muralidhara, and Y. Arthoba Naik, Electrochemical Deposition of Nanocrystalline Zinc on Steel Substrate from Acid Zincate bath, *Surface & Coatings Technology*, 202(14) 2008, 3403-3412

[3] R. Raiessi, A. Saatchi, M. A. Golozar and J.A. Szpunar, Effect of Surface Preparation on Zinc Electrodeposited Texture, *Surface and Coatings Technology*, 197, 2005, 229-237

[4] I. Zouari, and F. Lapicque, An electrochemical study of zinc deposition in a sulfate medium Electrochimica Acta, 37(3), 1992, 439–446

[5] Y. Xingpu, J. P. Celis, M. De Bonte and J. R. Roos, Ductility and Crystallographic Structure of Zinc Foils Electrodeposited from Acid Zinc Sulfate Solutions, *Journal of Electrochemical Society*, 141(10), 1994, 2698-2708

[6] F Ebrahimi, D Kong, TE Mattehews Q Zhai. in Processing and Fabrication of Advanced Materials by Srivastan and Khor, 7th Edition, TMS Publication, Warrendale, PA, **1998,** 509-521.

[7] F Ebrahimi; HQ Li, *Rev. Adv. Mater. Sci.*, **2003**, 5, 134-138.

[8] F Ebrahimi; GR Bourne; MS Kelley; TE Matthews, *Nano Structured Materials*, **1999,** 11,343-350.

[9] KL Morgan; Z Ahmed; F Ebrahimi, *MRS Proceeding*, **2001,** 634, B.3.11.1.

[10] F Ebrahimi; Z Ahmed; *Materials Characterization*, **2003,** 49, 373-379.

[11] AM Ei-Sherrik; U Erb, *Mater. Sci. Eng.*, **1995,** 30, 5743-5749.
[12] TV Venkatesha; J Balachandra; SM Mayanna; RP Dampal, *Met. Finish*, **1986,** 84, 29-31.
[13] JR Weertman; D Farkas; K Hemker, H Kung; Mayo; R Mitra; H Van Swygenhoven, *MRSBull.*, **1999**, 24, 44-50.
[14] F Ebrahimi; Z Ahmed; KL Morgan, *MRS Proceedings,* **2001,** 634, B.2.7.1.
[15] R. Sangeetha, J.Felicta Florence, IJSER, **2016**, vol 8, Issue 8.