



ELECTROCHEMICAL INVESTIGATION ON INHIBITION EFFICIENCY OF *EICHHORNIA CRASSIPES* – Zn^{2+} SYSTEM IN NEUTRAL AQUEOUS MEDIUM

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ABSTRACT

The inhibition effect of *Eichhornia crassipes* (Water Hyacinth) leaves extract on corrosion of mild steel in 60 ppm Cl^- containing neutral aqueous medium was investigated using electrochemical techniques such as Potentiodynamic polarization (PDP) and Electrochemical Impedance spectroscopy (EIS) measurements. Polarization study demonstrate that the formulation consisting of *Eichhornia crassipes* leaves extract and Zn^{2+} behaves as mixed inhibitor with predominantly controlled anodic reactions. AC impedance spectra illustrate that a protective film is formed on the metal surface. Also, the presence of protective film is analysed by UV- Spectroscopic technique.

Keywords: *Eichhornia crassipes* (Water Hyacinth), Polarization, aqueous medium and UV

1. INTRODUCTION

Mild steel is a significant cost – effective material for engineering applications owing to its low cost, easy accessibility and high mechanical strength [1]. Many Inorganic compounds of chromates, phosphates, molybdates, etc., and the variety of organic compounds containing hetero atoms like nitrogen, sulphur, and oxygen can be used as corrosion inhibitors [2]. But the organic corrosion inhibitors are very much toxic and non-bio degradable in nature. Due to this reason the researchers are in the condition to prefer suitable green corrosion inhibitors like plant extracts, which are easily available, renewable, bio-degradable in nature. *E.crassipes* is commonly known as Water Hyacinth, noted as one of the most important noxious fresh water weeds [3], ranked 8th in the list of the world's ten most serious weeds [4] according to K.R.Reddy et al., (1984). It is a floating aquatic plant within flated petiols and native to tropical

America [5]. Because of its potent anti-oxidant and anti- microbial nature, many investigations were carried out on the corrosion inhibition nature of this plant [6,7]. The aim of the present work is to analyse the corrosion inhibition efficiency of water hyacinth leaves extract (WHLE) with Zn^{2+} on mild steel in 60 ppm Cl^- ion containing neutral aqueous medium which is normally present in the cooling water system.

Materials and methods

Preparation of Specimen

Mild steel specimens of size 1.0 cm ×4.0 cm ×0.2 cm and chemical composition 0.026 % sulphur, 0.06 % phosphorous, 0.4 % manganese, 0.1% carbon and the rest iron were polished to a mirror finish and degreased with acetone.

Preparation of the Water Hyacinth Leaves (WHLE) extract

In the present work, the Water Hyacinth leaves were collected from Shanmuga River in

Palani. Fresh leaves of this plant were cleaned, chopped into small pieces and shade dried. The extract was prepared by refluxing 5g of powdered leaves in 500ml dd water for 5hr and kept overnight. Then it was filtered and the volume of the filtrate was made up to 500ml using dd water and this was taken as stock solution [8].

Sodium Chloride Stock solution

Exactly 9.8g of Sodium chloride was dissolved in triple – distilled water and made up to one litre in a standard measuring flask. A hundred fold dilution yields 60ppm Cl⁻ ion concentration.

Zinc Sulphate Stock solution

Exactly 4.4g of Zinc sulphate was dissolved in triple – distilled water and made up to one litre in a standard measuring flask. A hundred fold dilution yields 10ppm Zn²⁺ ion concentration.

Potentiodynamic polarization study

This study was carried out using CHI 660A electrochemical impedance analyzer model a three-electrode cell assembly was used. The working electrode was used as a rectangular specimen of mild steel with one face of the electrode of constant 1cm² area exposed. A saturated calomel electrode (SCE) was used as a reference electrode. A rectangular platinum foil was used as the counter electrodes. Polarization curves were recorded after doing iR compensation. During the polarization study, the scan rate (v/s) was 0.01; Hold time at E_f (s) was zero and quiet time (s) was 2. The results such as Tafel slopes (b_a and b_c), I_{corr}, LPR and E_{corr} values were calculated.

$$\text{Inhibitor efficiency (\%)} = \frac{I_{\text{Corr}}^0 - I_{\text{Corr}}^i}{I_{\text{Corr}}^0} \times 100$$

Where, I_{Corr}⁰ = Corrosion current density without inhibitor (Blank) (A/cm²)

I_{Corr}ⁱ = Corrosion current density with inhibitor (A/cm²)

b_a = Anodic Tafel slope (mV / decade)

b_c = Cathodic Tafel slope (mV / decade)

E_{Corr} = Corrosion potential (mV vs SCE)

AC impedance measurements

CHI 660A electrochemical impedance analyzer model was used to record AC impedance measurements. The cell set up was the same as that used for polarization measurements. In X-axis real

part: (Z') and Y- axis imaginary part: (Z'') of the cell impedance were measured in ohms for various frequencies. The R_t (charge transfer resistance) and C_{dl} (double layer capacitance) values were calculated.

$$R_t = (R_s + R_t) - R_s$$

Here, R_s = solution resistance

$$C_{dl} = (2\pi f_{\text{max}} R_{ct})^{-1}$$

AC impedance spectra were recorded with initial E (v) =0; High frequency (Hz) =1x10⁵, Low frequency (Hz) = 1; Amplitude (v) = 0.05 and quiet time (s) =2.

Ultra Violet – Visible (UV- Vis) spectroscopy

The possibility of the formation of complexes between inhibitor solution and metal surface for one day immersion was studied and recorded by UV-Vis absorption spectra using Shimadzu UV-Vis Spectrophotometer- 1700 model.

Results and Discussion

Analysis of the results of potentiodynamic polarization (PDP) measurements for the WHLE – Zn²⁺ system

Electrochemical parameters such as corrosion potential (E_{corr}), corrosion current density (I_{corr}), cathodic and anodic Tafel slopes (b_c, b_a), LPR and percentage inhibition efficiency (IE%) according to polarisation studies are listed in Table1 and shown in Figure 1(a) and (b).

When mild steel immersed in aqueous medium containing 60ppm Cl⁻ ion, the corrosion potential is -550 mV vs SCE. The LPR value is -456 Ω cm². The corrosion current is 101.2 μA / cm². When inhibitor (10ppm WHLE and 50ppm Zn²⁺) is introduced into the system, the LPR value increases tremendously from 456 to 2297.9 Ω cm². Increase in LPR value is an indication of formation of protective film on the metal surface [9]. This is also supported by the fact there is a sharp decrease in the corrosion current value from 101.2 to 19.26 μA / cm². Such a significant reduction in corrosion current density indicated the decrease in corrosion rate in presence on the inhibitor and exhibits an inhibition efficiency of 81%. The formulation consisting of 50ppm Zn²⁺ and 10ppm of WHLE shifts the corrosion potential from -550 to -462 mV vs SCE. That is the corrosion potential shifts to the anodic (Noble) direction. This

suggests that the anodic region is controlled predominantly indicating the reduction in the dissolution of the metal as more WHLE molecules are transported to anodic sites in presence of Zn^{2+} ions.

Now, when the shifts in the anodic and cathodic slopes are to be compared, addition of 10ppm of WHLE and 50ppm Zn^{2+} shifts the anodic slope value from 245 to 165 mV/decade, while the

corresponding shift in the cathodic slope if from 187 to 227mV/decade. Thus the formulation of 10ppm WHLE and 50ppm Zn^{2+} controls anodic reaction predominantly and to some extents controlled the cathodic reaction by the formation of $Zn(OH)_2$ on the cathodic side of the metal surface. Both the anodic (b_a) and cathodic (b_c) Tafel slopes are varying from the blank values indicating the mixed mode of inhibition [10].

Table 1. Corrosion parameters of mild steel immersed in 60 ppm Cl^- containing aqueous medium in the presence and absence of inhibitor system by polarization study

System	$-E_{corr}$ mV vs SCE	b_c mV / decade	b_a mV / decade	LPR Ωcm^2	I_{corr} $\mu A / cm^2$	IE (%)
Blank:60 ppm Cl^- containing aqueous medium	550	187	245	456	101.2	-
60 ppm Cl^- ion + WHLE (10 ppm) + Zn^{2+} (50 ppm)	462	227	185	2297.9	19.26	81

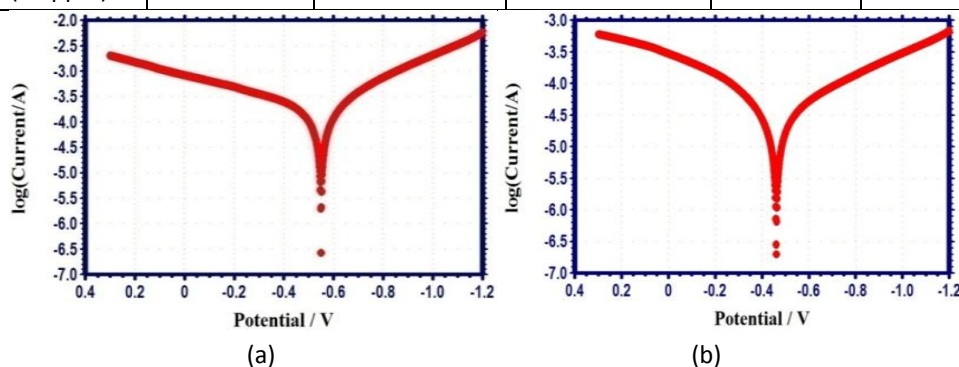


Figure 1. Polarisation curves of mild steel immersed in various test solutions (a) 60 ppm Cl^- ion(blank) (b) 60 ppm Cl^- ion + WHLE (10 ppm)+ Zn^{2+} (50 ppm)

Electrochemical Impedance Spectroscopy (EIS) measurements

EIS techniques provide valuable kinetic parameters for electro transfer reactions at the ion – electrolyte interface. The corrosion inhibition of mild steel with and without inhibitor by EIS parameters namely R_{ct} and C_{dl} represented in the Table 2 and their corresponding Nyquist plots are

shown in Figure2 (a) and (b).The charge transfer resistance R_{ct} obtained from the Nyquist plot increases from 968 Ωcm^2 to 1352 Ωcm^2 and the C_{dl} value decreases [11] from $4.433 \times 10^{-7} F/cm^2$ to $3.174 \times 10^{-7} F/cm^2$. These results lead to the conclusion that a protective film is formed on the metal surface by the inhibitor.

Table 2. Corrosion parameters of mild steel immersed in 60 ppm Cl^- containing aqueous medium in the presence and absence of inhibitor system by AC impedance spectra.

System	Nyquist plot	
	R_t ohm cm^2	C_{dl} F / cm^2
Blank:60 ppm Cl^- containing aqueous medium	968	4.433×10^{-7}
60 ppm Cl^- ion + WHLE (10 ppm) + 50 ppm Zn^{2+} ion	1352	3.1735×10^{-7}

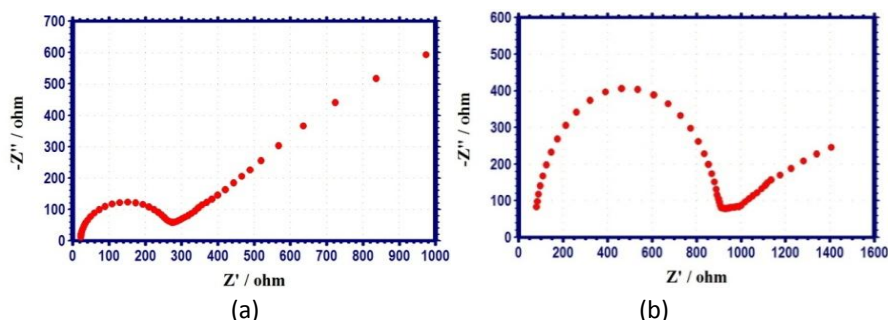


Figure 2. AC impedance spectra of mild steel immersed in various test solutions a) 60 ppm Cl^- ion(blank) b) 60 ppm Cl^- ion + WHLE (10 ppm)+ 50 ppm Zn^{2+} ion.

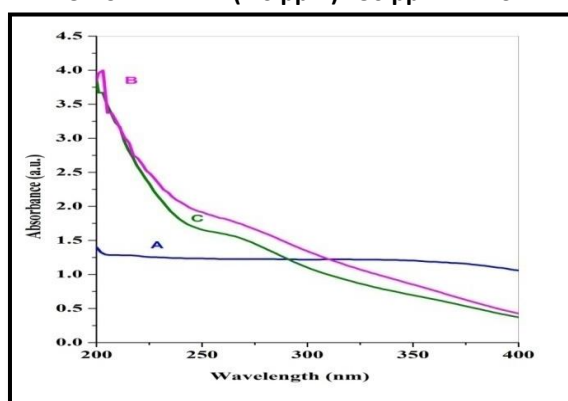


Figure 3. UV – Visible absorbance spectra of solutions of a)MS in 60 ppm Cl^- ion(Blank) b) Ms in WHLE (10 ppm) c) MS in WHLE (10 ppm) + Zn^{2+} (50 ppm)

Analysis of the UV –Visible Absorption spectra of WHLE- Zn^{2+}

The UV –Visible absorption spectra of various test solutions are given in Figure 4. The adsorption of inhibitor molecules at metal/ solution interface is supported by UV- Visible spectroscopy [12]. Mild steel immersed in 60ppm Cl^- ion containing aqueous corrosive medium in the presence of 10 ppm WHLE shows the absorption value λ_{max} at 208 nm and 268 nm respectively. When the mild steel immersed in WHLE (10 ppm) and Zn^{2+} (50 ppm) in corrosive medium containing 60 ppm Cl^- ion shows that the peaks appeared at 204 nm and 258 nm. This suggests that the possibility of formation of inhibitor complex between inhibitor WHLE molecules and Zn^{2+} ions in solution.

The observed shift in the λ_{max} values of 208nm to 204nm denotes aromatic $\pi - \pi^*$ transitions confirms the presence of alkyl substituted benzene compounds like toluene.

Similarly, λ_{max} shifts from 268nm to 258nm indicates the aromatic $\pi - \pi^*$ transitions confirms the presence of phenolic compounds [13] in the plant extract of *E. Crassipes* extract. The absorption on anodic sites occurred through long $\pi -$ electrons of aromatic rings and lone pair electrons of hetero atoms (N,O,P) which decreased the anodic dissolution of mild steel [14].

Conclusion

The present work concludes the followings:

- Polarization study reveals that, the inhibitor formulations are mixed type inhibitors and controlled anodic reactions predominantly.
- Linear Polarization Resistance (LPR) values increases with the presence of inhibitor formulations indicating a better corrosion protective ability of the inhibitors system under study.
- The AC impedance parameters obtained from Nyquist plots (R_{ct} and C_{dl}) in aqueous medium without and with the addition of

various concentrations of WHLE -Zn²⁺ system shows increase in R_{ct} value and decrease in C_{dl} value confirms the formation of protective film on the mild steel surface.

- The UV – Vis absorption spectroscopic study implies the formation of insoluble complex of Fe²⁺ - WHLE - Zn²⁺ in solution.

References

- [1]. Kumar Harish and Sunita, "ADS, ALS, AHDS and ADDBS Surfactants as Corrosion Inhibitors for Carbon Steel in acidic Solution", *Res.J.Chem.Sci.*, 2012, 2(7): 1-6.
- [2]. M. A. Quraishi, D. K. Yadav and I. Ahamad, "Green Approach to Corrosion Inhibition by Black Pepper Extract in Hydrochloric Acid Solution", *The Open Corrosion Journal*, 2009,2; 56-60.
- [3]. B.Gopal, *Water Hyacinth: Aquatic plant studies*, Elsevier Science Publishing Company, New York, 1987.
- [4]. K.R.Reddy, D.L.Sutton, "Water Hyacinth for Water Quality Improvement and Biomass Production", *J.of Environ.Quality*, 1984,13(1);1.
- [5]. O.A. Akinyemiju, "Invasion of Nigeria waters by water hyacinth", *Journal of Aquatic Plant Management*, 1987, 25; 24-26.
- [6]. S.B.Ulaeto, U.J.Ekpe. M.A. Chidie bere, E.E.Oguzie, Corrosion Inhibition of Mild Steel in Hydrochloric Acid by Acid Extracts of Eichhornia Crassipes *International Journal of Materials and Chemistry*, 2(4) (2012)158-164.
- [7]. Daniel. T. Oloruntoba, Jenny A. Abbas and Sunday J Olusegun, W.(Eds) *Procs 4th West Africa Built Environment Research (WABER) Conference*, 24-26 July, 2012, Abuja, Nigeria, 1131-1140.
- [8]. George E. Totten, *Fuels and lubricants handbook: technology, properties, performance, and testing*, ASTM International, West Conshohocken, PA.
- [9]. R. Hariharaputhran, A. Subramanian, Alice Arul Anthony, P. Manisankar, T. Vasudevan, and S. Venkatakrishna Iyer, "Influence of Nitrones on Corrosion Inhibition and Hydrogen Permeation Through Mild Steel in Acidic Solutions", *Anti Corros Methods and Mater.*, 1999, 46: 35–39.
- [10]. Y. Gonzalez, M. C. Lafont, N. Pebere and F. Moran, "A Synergistic Effect between Zinc Salt and Phosphonic Acid for Corrosion Inhibition of a Carbon Steel," *Journal of Applied Electrochemistry*, 1996, 26(12); 1259-1265. doi.org/10.1007/BF00249928.
- [11]. Ambrish Singh, Eno. E. Ebenso, M.A.Quraishi, "Boerhavia diffusa (Punarnava) Root Extract as Green Corrosion Inhibitor for Mild Steel in Hydrochloric Acid Solution: Theoretical and Electrochemical studies", *Int. J. Electrochem. Sci.*, 2012,7;8659 – 8675.
- [12]. V. Sribharathy and Susai Rajendran, "Corrosion Inhibition by Green Inhibitor: Sodium Metavanadate –Spirulina System", *Che. Sci. Rev. Lett.*, 2012, 1(1), 25 – 29.
- [13]. K. Jafarzadeh, T. Shahrabi, S. M. M. Hadavi and M. G. Hosseini, "Morphological characterization of AA5083-H321 aluminum alloy corrosion in NaCl solution under Hydrodynamic conditions", *Anti Corros. Met.Mater.*, 2009, 56(1); 35.
- [14]. S.A. Umoren, E.E. Ebenso, "The synergistic effect of polyacrylamide and iodide ions on the corrosion inhibition of mild steel in H₂SO₄", *Mater. Chem. Phys.*, 2007, 106; 387-393.