



Synergistic Effect of Zinc ion on Corrosion Inhibition of Carbon Steel in aqueous solution using L- Methionine

V.Prathipa^{1*}, A.Sahaya Raja²

¹Department of chemistry, PSNA College Engineering and Technology, Dindigul, Tamilnadu, India

²PG& Research Department of Chemistry, G.T.N. Arts College, Dindigul, Tamilnadu, India

Abstract : The corrosion and inhibition behaviors of carbon steel in the presence of L-Methionine and ZnSO₄ have been studied using gravimetric method and electrochemical techniques. Results obtained by various techniques are close to each other and maximum Inhibition efficiency is 93%. Synergistic parameters and Statistical study of “F” test suggest that a synergistic effect exists between L-Methionine and Zn²⁺. The protective film on the metal surface has been analyzed by FT – IR spectra. A suitable mechanism of corrosion inhibition is proposed based on the results obtained from weight loss study, electrochemical study and surface analysis technique. The inhibitor L-Methionine – Zn²⁺ system may find application in cooling water system.

Keywords : Carbon steel, L-Methionine, ZnSO₄, synergistic effect, F-Test, FT-IR spectra.

Introduction:

Carbon steel finds a lot of application in industries like metal finishing, boiler scale removal, pickling baths etc. It gets rusted when it comes in contact with any aqueous medium. The use of inhibitors is one of the best methods for protecting metals against corrosion. Corrosion is a chemical or electrochemical process in nature with four components are: an anode, a cathode, an electrolyte and some direct electrical connection between the anode and cathode, the adsorbed inhibitor then acts to slow corrosion process by either: 1. Increasing the anodic or cathodic polarization behaviour; 2. Reducing the movement or diffusion of ions to the metallic surface. Corrosion inhibitors are used to prevent the effect of corrosion in such cases. The majority of well-known inhibitors are organic compounds containing heteroatom, such as O, N, S and multiple bonds¹. Most of the organic compounds are not only expensive but also toxic to both human beings and environments² and therefore the use of hazardous chemical inhibitors is totally reduced because of environmental regulations. It is better to look for environmentally safe inhibitors. Many researchers investigated the inhibition effect of environment friendly inhibitors like amino acids on metal corrosion³⁻¹³. This is due to the fact that amino acids are non-toxic, biodegradable, relatively cheap, and completely soluble in aqueous media and produced with high purity at low cost. Various amino acids have been used to inhibit the corrosion of metals and alloys¹⁴⁻¹⁷. Eco-Friendly Inhibitor L-Cysteine-Zn²⁺ System to control corrosion of carbon steel in Aqueous Medium⁶. The corrosion of SS 316L has been inhibited by glycine, leucine, valine, and arginine⁷. Sivakumar et al have used L-Histidine to prevent corrosion on carbon steel⁸. Cystein, glycine, glutamic acid, and glutathione have been used as corrosion inhibitor to prevent the corrosion of copper in HCl⁹. Amino acid such as DL-Phenylalanine has been used to prevent corrosion of carbon steel¹⁰. The corrosion of brass in O₂-free NaOH has been prevented by methionine¹¹. Sahaya Raja *et al* have used Glycine along with Zn²⁺ to prevent

corrosion of carbon steel in well water¹². Synergistic and Antagonistic Effect of L – Alanine for carbon steel in aqueous medium has been investigated¹⁸. Prathipa et al was studied corrosion inhibition of carbon steel using green inhibitor (L-Alanine)¹⁹. Arginine - Zn²⁺ system has been used to inhibit corrosion of carbon steel^{13,20}. L – Alanine as inhibitor for carbon steel in well water was studied²¹.

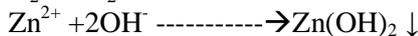
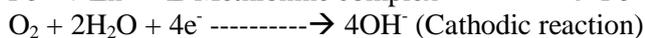
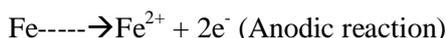
2. Material and Methods:

Determination of corrosion rate - All the weight of the carbon steel specimens before and after corrosion was carried out using Shimadzu Balance-AY62. Corrosion rates were calculated using the following relationship. Corrosion Rate (mm/y) = [loss in weight (mg) X 1000 / surface area of the specimen (dm²) X period of the immersion (days)] X (0.0365/ ρ). **Electrochemical and Impedance measurements** - Potentiodynamic polarization studies and AC Impedance measurements are carried out using CHI electrochemical impedance analyzer (model 660A). **Surface characterization studies- FTIR Spectra** were recorded in a Perkin – Elmer 1600 spectrophotometer. All solutions were prepared using well water collected from N.S.Nagar, Dindigul, Tamil Nadu, India. The study was carried out at room temperature (303K). The chosen environmental well water and its physicochemical parameters are pH – 8.0, Conductivity 1770 μmhos/cm, TDS – 1219ppm, TH - 424ppm, Chloride – 669ppm

3. Result and discussion

3.1. Analysis of the weight loss method and Influence of Zn²⁺ on the inhibition efficiencies of L-Methionine

L-Methionine shows some inhibition efficiencies. 50 ppm of L-Methionine has 24 percent IE, as the concentration of L-Methionine increases, IE increases some extent but the influence of Zn²⁺ on the inhibition efficiencies of L-Methionine is shown in **Fig - 1**. It is observed that as the concentration of L-Methionine increases the IE increases. Similarly, for a given concentration of L-Methionine the IE increases as the concentration of Zn²⁺ increases. It is also observed that a synergistic effect exists between L-Methionine and Zn²⁺. For example, 5 ppm of Zn²⁺ has 10 percent IE; 250 ppm of L-Methionine has 59 percent IE. Interestingly their combination has a high IE, namely, 93 percent. In presence of Zn²⁺ more amount of L-Methionine is transported towards the metal surface. Thus the anodic reaction and cathodic reaction are controlled effectively. This accounts for the synergistic effect existing between Zn²⁺ and L-Methionine.



3.2 Synergism parameters (S_I)

Synergism parameter (S_I) have been used to know the synergistic effect existing between two inhibitors²²⁻²⁴. Synergism parameter (S_I) can be calculated using the following relationship. Synergism parameters (S_I) = $1 - \theta_{1+2} / 1 - \theta_{1+2}$

Where $\theta_{1+2} = (\theta_1 + \theta_2) - (\theta_1 \theta_2)$, θ_1 = Surface coverage by L-Methionine,

θ_2 = Surface coverage by Zn²⁺,

θ_{1+2} = Surface coverage by both L-Methionine and Zn²⁺,

θ = surface coverage = IE%/100

The synergism parameters of L-Methionine -Zn²⁺ system is shown in **Fig - 1**. For different concentrations of inhibitors, S_I approaches 1 when no interaction between the inhibitor compounds exists. When S_I > 1, it points to synergistic effects. In the case of S_I < 1, it is an indication that the synergistic effect is not significant²³. From **Fig - 1**, it is observed that value of synergism parameters (S_I) calculated from surface coverage were found to be one and above. This indicates that the synergistic effect exists between L-Methionine and Zn²⁺. Thus, the enhancement of the inhibition efficiency caused by the addition of Zn²⁺ ions to L-Methionine is due to the synergistic effect.

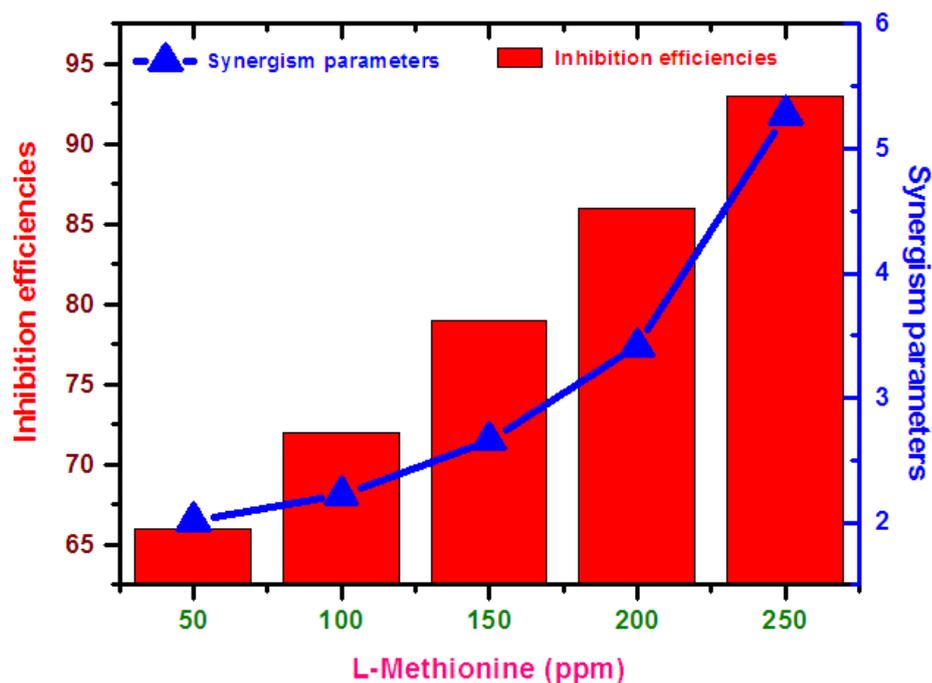


Figure – 1: Inhibition efficiencies of L-Methionine and Synergism parameters

3.3 'F'-test

To know whether the synergistic effect existing between L-Methionine and Zn^{2+} is statistically significant or not, F-test was used^{19,22-24}. The results are given in **Table 1**. It is observed that the calculated F-value 25.04 is greater than the table value 5.32 for 8 degrees of freedom at 0.05 level of significance. Hence it is concluded that the synergistic effect existing between L-Methionine and Zn^{2+} (5 ppm) is statistically significant. Therefore, it is concluded that the synergistic effect existing between L-Methionine and Zn^{2+} (5 ppm) is statistically significant.

Table 1: Distribution of F-Value between the inhibition efficiency of various concentration of L-Methionine (0ppm of Zn^{2+}) and the inhibition efficiencies of L-Methionine in the presence of 5 ppm of Zn^{2+} .

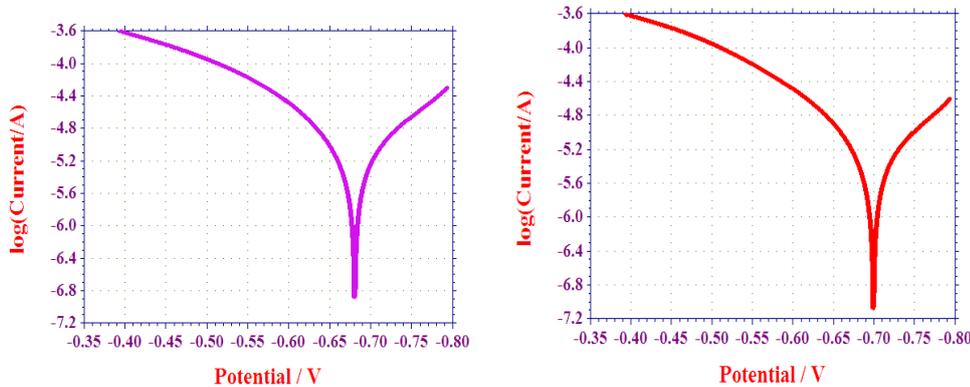
Source of variance	Sum of squares	Degrees of freedom	Mean square	F-value	Level of significance
Between the sample	760.5	1	760.5	< 0.05	25.04
Within the sample	243	8	30.3745		

3.4 Analysis of potentiodynamic polarization study

Polarization study has been used to confirm the formation of protective film formed on the metal surface during corrosion inhibition process^{6,8,10}. If a protective film is formed on the metal surface, the corrosion current value (I_{corr}) decreases. The potentiodynamic polarization curves of carbon steel immersed in well water in the absence and presence of inhibitors are shown in **Fig-2**. The corrosion parameters are given in **Table 2**. When carbon steel was immersed in well water the corrosion potential was -680 mV vs SCE. When L-Methionine (250 ppm) and Zn^{2+} (5 ppm) were added to the above system the corrosion potential shifted to -699 mV vs SCE. This suggests that a protective film is formed on the metal surface. Further the corrosion current decreases from $8.476 \times 10^{-6} \text{ A/cm}^2$ to 5.956×10^{-6} . Thus polarization study confirms the formation of a protective film on the metal surface.

Table 2: Corrosion parameters of carbon steel immersed in well water in the absence and presence of inhibitor system obtained from potentiodynamic polarization study

System	Tafel Results	
	E_{corr} mV vs SCE	I_{corr} A/cm ²
Well water	-680	8.476×10^{-6}
Well water+ L-Methionine (250ppm)+ Zn ²⁺ (5ppm)	-699	5.956×10^{-6}



a) Well water (Blank)

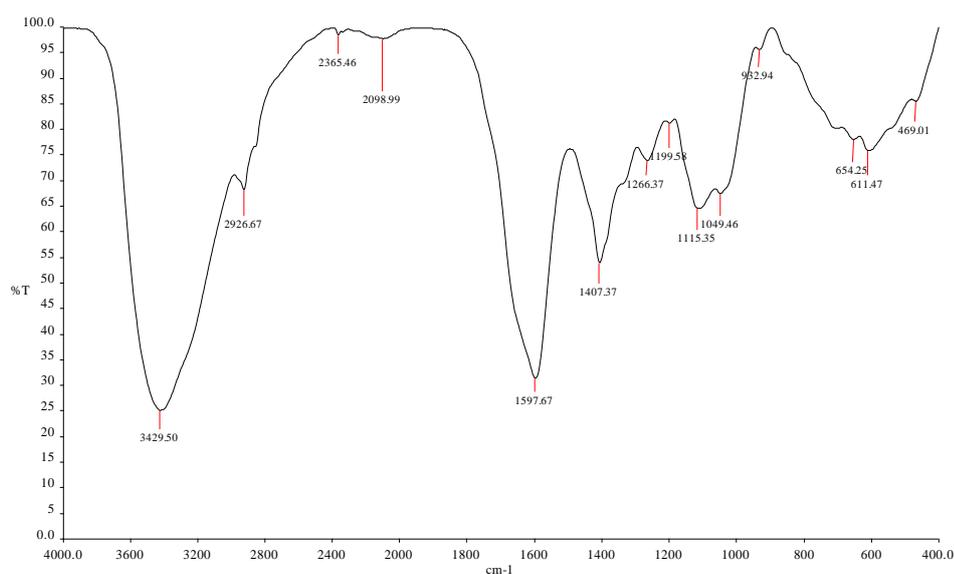
b) Well water + L- Methionine (250 ppm) + Zn²⁺ (5 ppm)**Fig 2: Polarization curves of carbon steel immersed in various test solutions**

3.5 Analysis of AC Impedance spectra

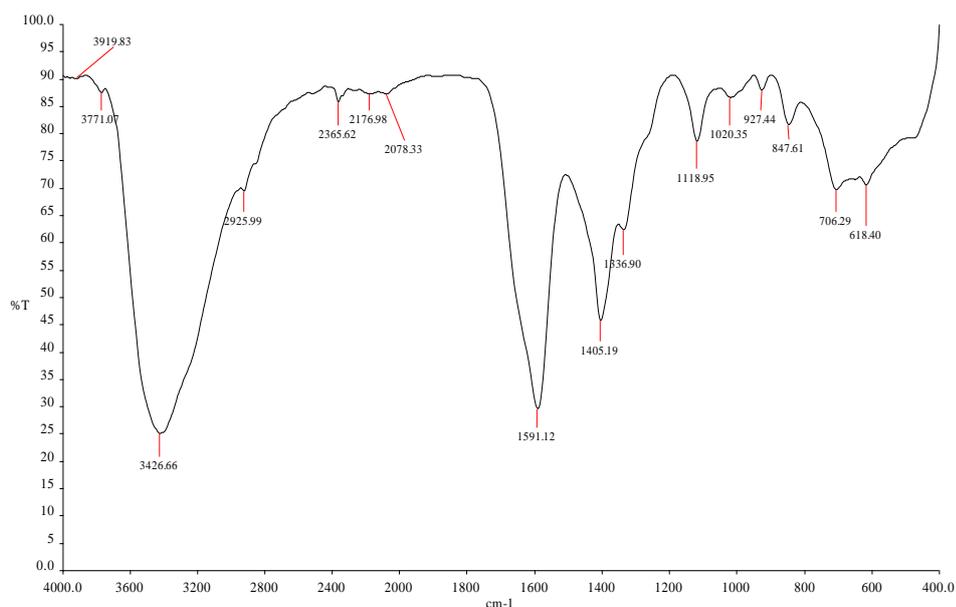
AC impedance spectra (electro chemical impedance spectra) have been used to confirm the formation of protective film on the metal surface^{11,13}. If a protective film is formed on the metal surface, charge transfer resistance (R_t) increases; double layer capacitance value (C_{dl}) decreases. The AC impedance spectra of carbon steel immersed in well water in the absence and presence of inhibitors (L-Methionine -Zn²⁺) are shown in **Fig-3** (Nyquist plot). The AC impedance parameters namely charge transfer resistance (R_t) and double layer capacitance (C_{dl}) derived from Nyquist plot are given in **Table 3**. It is observed that when the inhibitors (L-Methionine (250 ppm) +Zn²⁺ (5 ppm)) are added the charge transfer resistance (R_t) increases from 1184 Ω cm² to 1830 Ω cm². The C_{dl} value decreases from 1.6297×10^{-9} F/cm² to 1.0544×10^{-9} F/cm². These results lead to the conclusion that a protective film is formed on the metal surface.

Table 3: Corrosion parameters of carbon steel immersed in well water in the absence and presence of inhibitor system obtained from AC impedance spectra.

System	Nyquist plot	
	R_t Ω cm ²	C_{dl} F/cm ²
Well water	1184	1.6297×10^{-9}
Well water+ L-Methionine (250ppm)+Zn ²⁺ (5ppm)	1830	1.0544×10^{-9}



4(a) FTIR Spectra for Pure L- Methionine



4 (b) FTIR Spectra for Film formed on Metal Surface immersion in test solution containing 250ppm L Methionine + 5ppm Zn²⁺

4. Mechanism of Corrosion inhibition

The results of the weight-loss study show that the formulation consisting of 250 ppm L-Methionine and 5 ppm of Zn²⁺ has 93% IE in controlling corrosion of carbon steel in well water. A synergistic effect exists between Zn²⁺ and L-Methionine. Polarization study reveals that this formulation functions as cathodic inhibitor. AC impedance spectra reveal that a protective film is formed on the metal surface. FTIR spectra reveal that the protective film consists of Fe²⁺- L-Methionine complex and Zn(OH)₂. In order to explain these facts the following mechanism of corrosion inhibition is proposed.

- When the solution containing well water, 5 ppm of Zn²⁺ and 250 ppm of L-Methionine is prepared, there is formulation of Zn²⁺ - L-Methionine complex in solution. When carbon steel is immersed in this solution, the Zn²⁺ - L-Methionine complex diffuses from the bulk of the solution towards metal surface.

- Zn^{2+} - L-Methionine complex diffuses from the bulk solution to the surface of the metal and is converted into a Fe^{2+} - L-Methionine complex, which is more stable than Zn^{2+} - L-Methionine.
- On the metal surface Zn^{2+} - L-Methionine complex is converted in to Fe^{2+} - L-Methionine and Zn^{2+} is released.

$$Zn^{2+} - L-Methionine + Fe^{2+} \text{ -----} > Fe^{2+} - L-Methionine + Zn^{2+}$$
- The released Zn^{2+} combines with OH^- to form $Zn(OH)_2$.

$$Zn^{2+} + 2OH^- \text{ -----} > Zn(OH)_2 \quad \downarrow$$
- Thus the protective film consists of Fe^{2+} - L-Methionine complex and $Zn(OH)_2$.

5. Conclusion

Weight loss study reveals that the formation consisting of 250ppm of L-Methionine and 5ppm of Zn^{2+} has 93% inhibition efficiency, in controlling corrosion of carbon steel in well water. A Synergistic effect exists between Zn^{2+} and L-Methionine system. Statistical study of F-test revealed that the synergistic effect existing between L-Methionine and Zn^{2+} is statistically significant. Polarization study reveals that L-Methionine system function as cathodic inhibitor. AC impedance spectra reveal that a protective film is formed on the metal surface. FTIR spectral study suggests that L-Methionine has coordinated with Fe^{2+} through the oxygen atom of the carboxyl group, nitrogen atom of the amine group and sulphur atom of the thiol group resulting in the formation of Fe^{2+} - L-Methionine complex and $Zn(OH)_2$ is formed. Thus the FTIR spectral study leads to the conclusion that the protective film consist of Fe^{2+} - L-Methionine complex and $Zn(OH)_2$ on the metal surface thereby inhibiting the corrosion of carbon steel, which is protective in nature.

Acknowledgement

The authors are thankful to their respective management, Principal, G.T.N.Arts College, Dindigul, Tamil Nadu, India for providing the required facilities for completion of the work.

References

1. P. Bothi Raja, M.G. Sethuraman, Inhibitive effect of black pepper extract on the sulphuric acid corrosion of mild steel, Mater. Lett. 62, 2977 (2008)
2. A.Y. El-Etre, Khillah extract as inhibitor for acid corrosion of SX 316 steel, Appl. Surf. Sci. 252, 8521 (2006)
3. Ashassi-Sorkhabi, M.R. Majidi and K. Seyyedi, Investigation of inhibition effect of some amino acids against steel corrosion in HCl solution, Appl. Surf. Sci. 225, 176 (2004)
4. Z. Ghasemi and A. Tizpar, The inhibition effect of some amino acids towards Pb-Sb-Se-As alloy corrosion in sulfuric acid solution, Appl. Surf. Sci. 252, 3667 (2006)
5. N. O. Eddy, U. J. Ibok, and B. I. Ita, QSAR and quantum chemical studies on the inhibition potentials of some amino acids for the corrosion of mild steel in H_2SO_4 , J. Comp. Methods. Sci. Engg. 11, 25 (2011)
6. A.Sahaya Raja, J. Sathiyabama , R. Venkatesan , V. Prathipa, Corrosion Control of Carbon Steel by Eco-Friendly Inhibitor L-Cysteine- Zn^{2+} System in Aqueous Medium, J. Chem. Biol. Phy. Sci. 4, 3182 (2014)
7. N. A. Abdel Ghany, A. E. El-Shenawy, and W. A. M. Hussien, The inhibitive effect of some amino acids on the corrosion behaviour of 316L stainless steel in sulfuric acid solution, Modern Appl. Sci. 5, 19 (2011)
8. S.Sivakumar, A.Sahaya Raja, J.Sathiyabama, V.Prathipa, Spectroscopic methods used for analyzing protective film formed by L-Histidine on carbon steel, Int. J. Pharm. Drug Anal. 2, 601 (2014)
9. D.-Q. Zhang, B. Xie, L.-X. Gao, Q.-R. Cai, H. G. Joo, and K. Y. Lee, Intramolecular synergistic effect of glutamic acid, cysteine and glycine against copper corrosion in hydrochloric acid solution, Thin Solid Films., 520, 356 (2011)
10. A. Sahaya Raja, S. Rajendran, and P. Satyabama, Inhibition of Corrosion of Carbon Steel in Well Water by DL-Phenylalanine- Zn^{2+} System, J. Chem. 2013, 1 (2013)

11. A.Sahaya Raja, S. Rajendran, J. Nagalakshmi, Angelin Thangakani and M. Pandiarajan, Eco-Friendly Inhibitor Glycine-Zn²⁺ System Controlling Corrosion of Carbon Steel in Well Water, Euro. Chem. Bull. 1, 130 (2012)
12. J. Wu, Q. Wang, S. Zhang, and L. Yin, Wu, Q. Wang, S. Zhang, and L. Yin, Methionine as corrosion inhibitor of brass in O₂-free 1M NaOH solution, Adv. Mat. Res. 308, 241 (2011)
13. Anthony Samy Sahaya Raja and Susai Rajendran, Inhibition of corrosion of carbon steel in well water by arginine - Zn²⁺ system, J. Electrochem. Sci. Engg. 2, 91 (2012)
14. A.Sahaya Raja, P.Angel, R.Sonisheeba, J.Thomas Paul raj, S.Sivakumar, R.Venkatesan, J.Sathiyabama, Corrosion Control by Green Solution – An Overview, International Journal of Advanced research in Chemical Science (IJARCS), 1, 10 (2014),
15. A.Sahaya Raja, R.Venkatesan, R.Sonisheeba, J.Thomas Paul raj, S.Sivakumar, P.Angel, J.Sathiyabama, Corrosion Inhibition by Cysteine– An Overview, International Journal of Advanced research in Chemical Science(IJARCS), 1, 101 (2014).
16. A.Sahaya Raja, S. Rajendran, J.Sathiyabama and P. Angel, Corrosion Control by Aminoacetic acid (Glycine) – An Overview, International Journal of Innovative research in Science, Engineering and Technology., 3, 11455 (2014)
17. V.Prathipa, A.Sahaya Raja, A Review on the Assessment of Amino Acids Used As Corrosion Inhibitor of Metals and Alloys, J. Chem. Bio. Phy. Sci., 5, 1585 (2015)
18. V. Prathipa, A. Sahaya Raja, Synergistic and antagonistic effects of L–alanine as green corrosion inhibitor for carbon steel in aqueous medium, J. Adv. Chem. Sci. , 1,45 (2015).
19. V.Prathipa, A. Sahaya Raja, S. Rajendran, Electrochemical study and spectroscopic methods used for analyzing protective film formed by L-alanine on carbon steel in well water: A green approach, J. Adv. Chem. Sci., 1, 59 (2015),.
20. A.Sahaya Raja, S.Rajendran, J.Sathiyabama, T.S.Muthumegala, A.Krishnaveni, N.Palaniswamy, P. Prabhakar, Corrosion Inhibition by Arginine – Zn²⁺ system, Zastita Materijala., 52, 101 (2011).
21. A.Sahaya Raja, N.Rajendran, V.Prathipa, S. Rajendran, Nano analyses of protective film formed by L-alanine-zinc ion system onto carbon steel, J. Adv. Chem. Sci., 1, 78 (2015).
22. P.Angel, A. Sahaya Raja, J. Sathiyabama and V. Prathipa, Corrosion inhibition of *Vitex Negundo* Extract as a green corrosion inhibitor for carbon steel in well water, International Journal of Chemical Studies., 2, 31 (2014).
23. J.ThomasPaulraj, A.Sahaya Raja, J.Sathiyabama, V.Prathipa, A Study of *Acalypha Indica* Extract as a Novel Green Inhibitor for Carbon Steel in Aqueous Medium International Journal of Green and Herbal Chemistry., 3, 1033 (2014).
24. R.Soni Sheeba, A Sahaya Raja, J.Sathiyabama and V.Prathipa, Green approach to corrosion inhibition of carbon steel by the extract of *Polyalthia Longifolia*, Journal of Applicable chemistry,3, 2055 (2014).
25. A.Sahaya Raja, Corrosion inhibition by Amino Acids, Ph.D.thesis,PG and Research department of chemistry, G.T.N. Arts college, Affiliated to Madurai Kamaraj University, (2011).
26. R.M.Silverstein, G.C. Bassler, T.Moril, “Spectrometric Identification of Organic Compound”, John Wiley and Sons, New York, 1981.
27. A.D. Cross, “Introduction to practical infrared spectroscopy”, Butterworths Scientific Publications, London, 1990
28. Kzauo Nakamoto, Infrared and Raman spectra of inorganic coordination compound, Wiley Interscience, New York, 1986.
