Recent Research in Science and Technology 2011, 3(12): 40-45
ISSN: 2076-5061
Available Online: http://recent-science.com/

Inhibition of mild steel corrosion in HCl solution using amino acid L-tryptophan

M. Mobin*, Mosarrat Parveen and M. Alam Khan

Corrosion Research Laboratory, Department of Applied Chemistry, Faculty of Engineering and Technology, Aligarh Muslim University, Aligarh-202002- India.

Abstract

The corrosion inhibition characteristics of nitrogen containing amino acid L-tryptophan on mild steel in 0.1 M HCl solution was studied by weight loss and potentiodynamic polarization measurements. L-tryptophan significantly reduces the corrosion rates of mild steel; the maximum inhibition efficiency being 83% at 50 ^oC in presence of inhibition concentration of 500 ppm. The adsorption of inhibitors on mild steel surface obeyed Langmuir's adsorption isotherm. The calculated thermodynamic parameters for adsorption reveal a strong interaction between the inhibitors and the mild steel surface. The results obtained by electrochemical studies are consistent with the results of the weight loss measurement. L-tryptophan acts more anodic than cathodic inhibitor.

Keywords: Mild steel, Corrosion inhibition, L-Tryptophan, Adsorption, Electrochemical technique.

INTRODUCTION

Organic compounds containing nitrogen, sulfur and oxygen have long been used as potential corrosion inhibitor in acid solutions [1-3]. These compounds get adsorbed, or form a protective layer/insoluble complex on the metal surface and block the active corrosion sites. However, most of these compounds are synthetic chemicals, are expensive and very hazardous to both human beings and the environments and needs to be replaced with nontoxic and eco-friendly compounds. Over the years, numerous classes of organic compounds have been investigated as corrosion inhibitors. However the trend in green chemistry is concentrated towards the replacement of most of these inhibitors with the nontoxic, cheap and eco-friendly compounds.

In recent years, a number of eco-friendly corrosion inhibitors have been exploited as green alternative to toxic and hazardous compound [4-7]. The amino acids which contain carboxyl and amino functionalities bonded to the same carbon atom are non-toxic, relatively cheap and easy to produce in purities greater than 99%. It has been shown by various authors that some amino acids can act as corrosion inhibitors, which has generated an increasing interest in these compounds as substitute to conventional corrosion inhibitors that are usually toxic [8-12]. The inhibition effect of three amino acids namely, alanine, glycine and leucine against steel corrosion in HCl solutions has been investigated by potentiodynamic polarization method. The inhibition effect was found to range from 28-91% [13]. The corrosion inhibition of Fe in 1M HCl using twenty two different common amino acids and four related compounds was investigated using potentiodynamic polarization curves [14]. In general, amino acids with longer hydrocarbon chains showed greater inhibition. Additional groups or groups which increased electron density on alpha amino group also increased the inhibition efficiency. The nitrogen containing amino acid L-tryptophan is a derivative of indole. The molecular structure of the compound suggests that it has strong potential to become an effective corrosion inhibitor. Moretti and Guidi [15] reported the corrosion inhibition of L-tryptophan on copper in aerated 0.5M H_2SO_4 in the temperature range of 20-50^oC. The corrosion rate did not rise as temperature increased. Corrosion inhibition behavior of low carbon steel by L-tryptophan was investigated using weight loss experiment and Tafel polarization curves [16]. The adsorption behavior of L-tryptophan at Fe surface was also investigated by the molecule dynamics simulation method and density functional theory. The results indicated that L-tryptophan could adsorb on Fe surface through the indole ring with π-electrons and nitrogen/oxygen atom with the lone pair electrons in its molecule.

A survey of literature indicates that only limited numbers of references are available dealing with the corrosion inhibition effect of L-tryptophan on mild steel. The present work was undertaken to investigate the corrosion inhibition behavior of L-tryptophan on mild steel in 0.1M HCl solution. The techniques used are weight loss measurements and potentiodynamic polarization measurements.

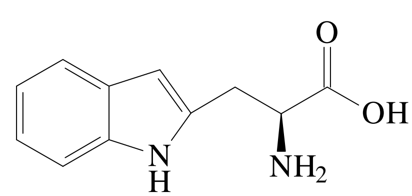

Fig1. Molecular Structure of L-Tryptophan

MATERIALS AND METHODS

Material preparation

The mild steel specimens having composition (weight %): 0.20 % C, 0.53 % Mn, 0.11 %S, 0.036 % Si and 0.098 % P and

Received: May 05, 2011; Revised: Aug 17, 2011; Accepted: Sept 15, 2011.

*Corresponding Author

M. Mobin
Corrosion Research Laboratory, Department of Applied Chemistry, Faculty of Engineering and Technology, Aligarh Muslim University, Aligarh-202002- India.

Tel: +91- 9411491161, Fax: +91-0571-2701895,
Email: drmmobin@hotmail.com

balance Fe were used for corrosion inhibition studies. The inhibitor L-tryptophan [(2S)-2-amino-3-(1-H-indol-3-yl) propanoic acid; molecular mass 204.23 g $mole^{-1}$], (CDH, India) was used as received. The stock solutions of 1000 ppm of L-tryptophan in 0.1mol L^{-1} HCl (MERCK, India) was prepared using double distilled water. The solution was diluted to get inhibitor L-tryptophan solution in the concentration range of 10 ppm to 500 ppm.

Weight loss measurements

The mild steel coupons of dimension 2.5 × 2.0 × 0.03 cm were used for weight loss measurements. The coupons were machined and abraded on different grit silicon carbide papers, washed with double distilled water, degreased with absolute ethanol and finally dried in acetone. To hold the specimens a hole of 1.5 mm diameter was made near the edge. The weight loss studies were carried out in the temperature range of 30-50^{o}C. The concentration of L-tryptophan was kept between 10 to 500 ppm in HCl. The weight loss experiments were performed for duration of 6 hrs, as per ASTM designation G1-90.The cleaned mild steel specimens were weighed on a microbalance (Model: Precisa 205A SCS) and suspended in 250 ml beakers containing 200 ml of test solution and placed in a digitally controlled water bath. The temperature of the water bath is controlled by a microprocessor based PID digital temperature indicator-cum-controller with an accuracy of $\pm$ 0.5^{o}C. The beakers were kept covered in order to avoid significant water loss. The inhibition efficiency (%IE) was calculated by using the following equation:

$$\%\ \mathrm{IE} = \frac{\mathrm{CR_o} - \mathrm{CR_i}}{\mathrm{CR_o}} \times 100 \qquad (1)$$

Where, CR_o = Corrosion rate of mild steel in blank HCl; CR_i =Corrosion rate of mild steel in presence of inhibitor

Potentiodynamic polarization measurements

The potentiodynamic polarization measurements were carried out using EG and G potentiostat/Galvanostat, model 263A. The experiments were carried out using a corrosion cell from EG and G; model K0047 with Ag/AgCl electrode (saturated KCl) as reference electrode, Pt wire as counter electrode and steel coupons as working electrode. The experiments were performed using a scan rate of 0.166 mV/S commencing at a potential above 250mV more active than the stable open circuit potential. All the measurements were carried out at 30^{o}C. Before starting the measurements the specimen were left to attain a steady state which was indicated by a constant potential. The inhibition efficiency was calculated using the relationship:

$$IE(\%) = \left(1 - \frac{i_{corr}}{i^o_{corr}}\right) \times 100 \qquad (2)$$

Where i_{corr}= inhibited current density and i^o_{corr}= uninhibited current density

RESULTS
Weight loss measurements

The corrosion of mild steel in 0.1M HCl in absence and presence of varying concentration of amino acid L-tryptophan was studied in the temperature range of 30-50^{o}C using weight loss technique. (Table. 1) shows the calculated values of corrosion rate and IE at different concentrations of L-tryptophan under varying temperature. From the data it is clearly seen that the corrosion rate of mild steel depends upon two factors namely, inhibitor concentration and temperature. The corrosion rates are significantly reduced in presence of L-tryptophan. The maximum increase in IE of 64% was observed at a concentration of 500 ppm at 30^{o}C which further increased to 83% on increasing the temperature from 30 to 50^{o}C. The plots of IE as a function of L-tryptophan concentration at 30-50^{o}C (Fig. 2) reveals that IE increases with increase in concentration. Except at very low concentration of L-tryptophan (up to 10 ppm) IE increases with increasing temperature.

Table 1. Corrosion parameters for mild steel in 0.1 M HCl in the absence and presence of L-tryptophan at 30-50^{o}C from weight loss measurements.

L-tryptophan Conc.	Corrosion rate (mpy)			Inhibition Efficiency (% IE)		
(ppm)	30^{o}C	40^{o}C	50^{o}C	30^{o}C.	40^{o}C	50^{o}C
Blank	102.14	253.62	874.47	-	-	-
10	57.42	131.32	551.57	44.29	47.98	36.15
50	55.03	101.46	348.80	46.43	60.12	60.14
100	47.68	80.25	207.21	53.57	68.21	76.18
200	46.93	78.79	200.94	54.29	68.79	76.86
400	42.53	88.46	154.01	58.57	65.32	82.26
500	36.67	75.52	146.67	64.29	70.23	83.11

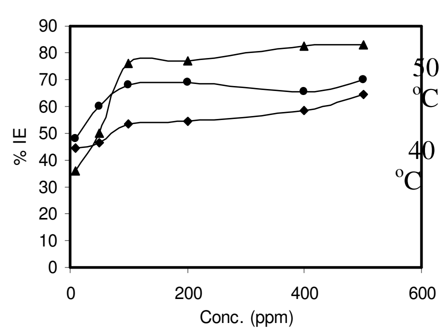

Fig 2. Plots of inhibition efficiency (IE) versus inhibitor concentration for mild steel in 0.1M HCl at different temperature of L-tryptophan.

The inhibition of mild steel corrosion in presence of various organic compounds have been attributed to their adsorption on the steel surface and are generally confirmed from the fit of the experimental data to various adsorption isotherms. The degree of surface coverage (θ) for various concentrations of L-tryptophan, in 0.1M HCl at 30-50 °C for 6 hrs immersion time has been evaluated by weight loss measurements. The data were tested graphically by fitting to various isotherms and the best result was obtained for Langmuir adsorption isotherm.

According to this isotherm, surface coverage (θ) is related to the inhibitor concentration C via

$$\frac{C}{\theta} = \frac{1}{K} + C \qquad (3)$$

where θ is the degree of surface coverage, K is the equilibrium constant of the adsorption process and C is the L-tryptophan concentration.

Enthalpy of adsorption, ΔH and entropy of adsorption, ΔS for the corrosion of mild steel in 0.1 M HCl in the presence of L-tryptophan was obtained by the equation:

$$CR = \frac{RT}{Nh}\exp\left(\frac{\Delta S}{R}\right)\exp\left(\frac{-\Delta H}{RT}\right) \qquad (4)$$

Where N is the Avogadro's number, h is the Plank' constant, R is the molar gas constant and T is the absolute temperature.

A plot of log θ/1-θ versus 1/T where, T is the solution temperature was also obtained for L-tryptophan (Fig. 3). The heat of adsorption (Q_d) was calculated from the slope of the plot ($-Q_d/2.303R$) and the values are listed in Table. 2. The plot of log (CR/T) versus 1/T in presence of L-tryptophan (Fig. 4) gave a straight line with slope of (–ΔH/2.303R) and an intercept of [(log(R/Nh) + (ΔS/2.303R)]. The values of ΔH obtained from the slope and ΔS evaluated from the intercept are given in Table. 2. The value of free energy of adsorption (ΔG_{ads}) was calculated using the following equation [17] and the values are listed in Table 3.

$$\Delta G_{ads} = -RT \ln (55.5\ K) \qquad (5)$$

Where, K is equilibrium constants and is given by

$$K = \frac{\theta}{C(1-\theta)} \qquad (6)$$

Where, θ is the degree of surface coverage, C the concentration of inhibitors in mol dm^{-3}, R gas constant and T is the solution temperature.

Table 2. Thermodynamic parameters for corrosion of mild steel in absence and presence of L-tryptophan.

Inhibitor conc. (ppm)	ΔH ($kJmol^{-1}$)	-ΔS ($kJk^{-1}mol^{-1}$)	-ΔQ ($kJmol^{-1}$)
Blank	86.54	78.49	-
500	54.95	33.76	41.8

Table 3. Thermodynamic parameters for mild steel in 0.1 M HCl in presence of L-tryptophan

Inhibitor conc. (ppm)	$-\Delta G_{ads}$ ($kJmol^{-1}$)		
	303 K	313 K	323 K
100	29.69	32.28	34.38
200	28.01	30.55	32.61
400	26.70	28.33	31.66
500	26.74	28.33	31.21

Potentiodynamic Polarization Measurements

The potentiodynamic polarization curves for the corrosion of mild steel in 0.1M HCl in absence and presence of varying concentration of L-tryptophan are shown in (fig.5). The values of electrochemical parameters as deduced from these curves e.g., corrosion potential (E_{corr}) corrosion current density (i_{corr}), the cathodic tafel slope (bc), the anodic tafel slope (ba) and % inhibition efficiency (% IE) are shown in Table. 4. The IE was calculated using the equation:

$$\%IE = \frac{i^o_{corr} - i_{corr}}{i^o_{corr}} \times 100 \qquad (7)$$

Where, i^o_{corr} and i_{corr} are the corrosion current density in absence and presence of inhibitors, respectively

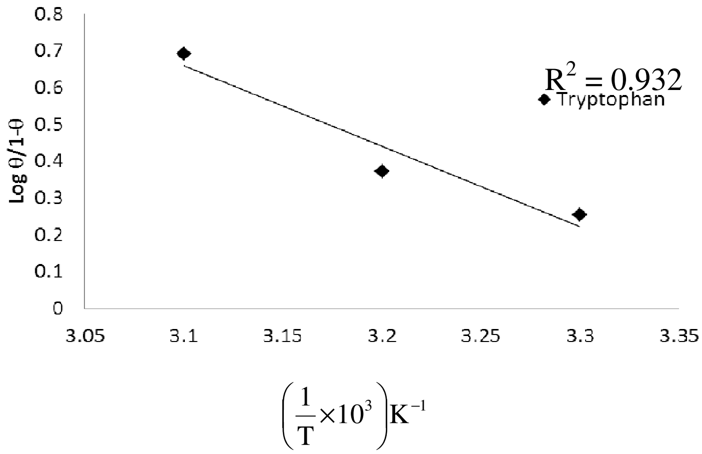

Fig 3. Arrhenius plot for log log θ/1-θ versus 1/T (■ L-tryptophan).

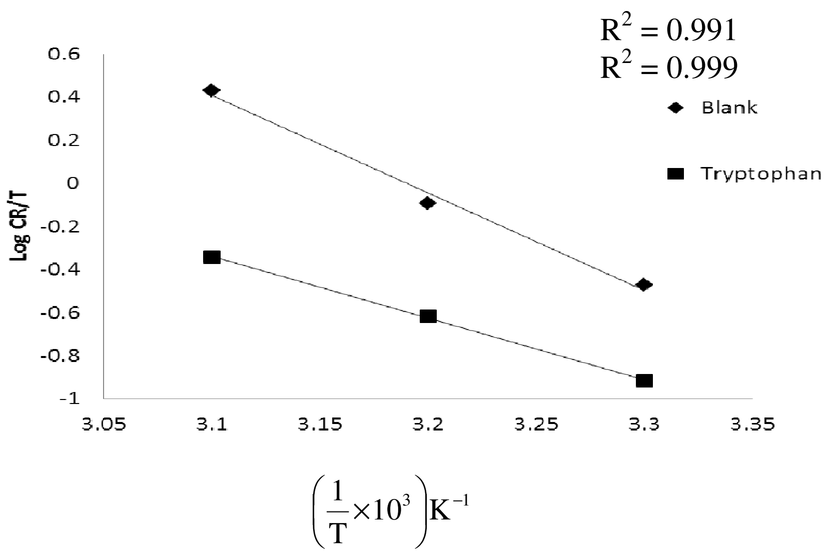

Fig 4. Arrhenius plot for log CR/T versus 1/T (♦ Blank; ■ L-tryptophan)

DISCUSSION

Weight loss measurements

The inhibition behavior of L-tryptophan on mild steel in 0.1 M HCl can be attributed to the adsorption of the molecules on the surface of steel. The effectiveness of the adsorption of L-tryptophan may be attributed to the presence of two nitrogen atoms in the molecule and its large volume [18]. The increased IE with increasing inhibitor concentration indicates that more inhibitor molecules are adsorbed on the steel surface leading to the formation of a protective film [19]. The increase in IE with increasing temperature suggests that at higher concentration L-tryptophan is chemically adsorbed on to the mild steel surface. At lower concentration the adsorbed film is not so stable and gets damaged at higher temperature, thus showing lower IE. The amino acid, L-tryptophan is easily protonated and expected to involve two ways of adsorption. Firstly, it may be adsorbed via donor-acceptor interactions between the π electrons of the indole rings and the unshared electrons pairs of the heteroatom to form a bond with vacant d-orbital of the metal surface [20]. Secondly, the $-NH_2$ group of amino acid in acid medium is readily protonated and might get adsorbed on the metallic surface via the negatively charged acid anions [21].

The plots of log θ/1-θ versus log C showed a linear correlation of slope close to unity suggesting that adsorption of L-tryptophan on mild steel interface obeys Langmuir adsorption isotherm [16].The values of heat of adsorption are less than - 40 KJ mol^{-1} suggesting the physical adsorption of the inhibitors [22]. The negative values of ΔG_{ads} suggest that the adsorption of L-tryptophan on mild steel is spontaneous. It is an established fact that values of ΔG_{ads} around -20 KJ mol^{-1} or less indicates physiosorption. The adsorption is attributed to the electrostatic attraction between the charged organic molecules and charged metal surface. The values of ΔG_{ads} around -40 KJ mol^{-1} or more are considered as chemisorptions. However, the values of ΔG_{ads} between -20 and -40 KJ mol^{-1} gives a disputed Judgment about the type of adsorption [23-26]. In the present investigation the values of ΔG_{ads} are in the range of -26.70 to -34.85 KJ mol^{-1} suggesting a mixed type of adsorption involving both physiosorption and chemisoprtion.

Potentiodynamic polarization measurements

The study of electrochemical data reveals that the value of i_{corr} continuously decreases in presence of L-tryptophan. The maximum IE of about 75% was observed at a concentration of 500 ppm indicating that a higher coverage of L-tryptophan on steel surface is obtained in the solution with highest concentration of inhibitor. The values of E_{corr} shifts to more positive value compared to the blank, indicating that L-tryptophan acts more anodic than cathodic inhibitor. The results as obtained by electrochemical studies are consistent with the results of the weight loss measurements.

Table 4. Potentiodynamic Polarization parameters for corrosion of mild steel in 0.1M HCl in absence and presence of various concentrations of L- tryptophan at 30^{o}C.

Inhibitor conc. (ppm)	E_{corr} (mV)	I_{corr} (µA)	β_c (mV)	β_a (mV)	C.R (mpy)	% IE
Blank	-622.96	666.1	283.19	134.63	58.59	-
100	-614.41	466.8	263.92	116.64	42.76	29.920
200	-603.23	435.6	271.522	117.146	39.90	34.60
500	-573.99	170.1	181.23	121.33	15.59	74.46

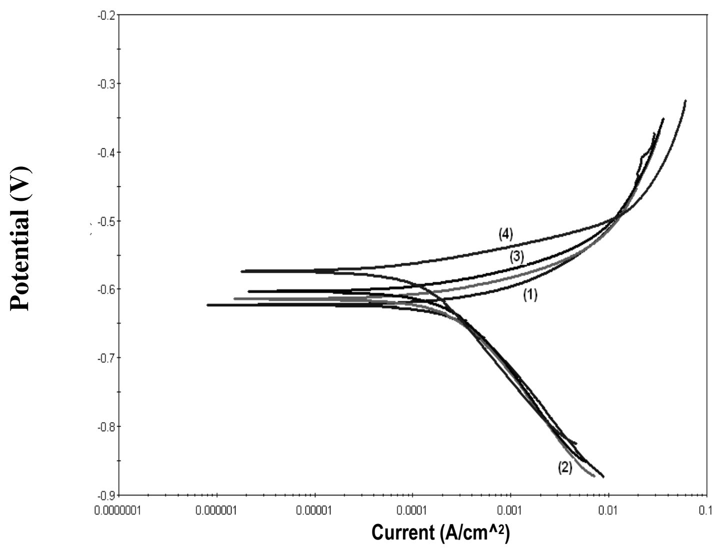

Fig 5. Potentiodynamic polarization curves of mild steel in 0.1MHCl in absence and presence of varying concentration of L tryptophan (1) Blank (2) 100ppm (3) 200ppm (4) 500ppm.

CONCLUSIONS

1. L-tryptophan showed good performance as corrosion inhibitor for mild steel in 0.1 M HCl.
2. The data obtained from weight loss measurements suggest corrosion inhibition by adsorption mechanism and fit well the Langmuir adsorption isotherm. The thermodynamic data suggest mixed type of adsorption involving both physiosorption and chemisoprtion.
3. L-tryptophan acts more anodic than cathodic inhibitor.

ACKNOWLEDGEMENT

Financial support from University Grants Commission, New Delhi, is gratefully acknowledged.

REFERENCES

[1] Lagrenee, M., B. Mernari, M. Bouanis, M. Trainel and F. Bentiss. 2002. Study of the mechanism and inhibiting efficiency of 3, 5-bis(4-methylthiophenyl)-4H-1,2,4-trizole on mild steel corrosion in acidic media. *Corros. Sci.* 44:573-588.

[2] Quraishi, M. A. and R. Sardar. 2002. Aromatic triazoles as corrosion inhibitors for mild steel in acidic environnements. *Corrosion.* 58(a):748-755.

[3] Quraishi, M. A. and F. A. Ansari. 2003. Corrosion inhibitions of fatty acid Trizoles for mild steel in Formic Acid. *J. Appl. Electrochem.,* 33:233-238.

[4] Eddy, N. O., F. E. Awe, E. Gimba, N. O.Ibisi and E. E. Ebenso. 2011. QSAR, Experimental and computational chemistry simulation studies on the inhibition potential of some amino acids for the corrosion of mild steel in 0.1M HCl. *Int. J. Electrochem. Sci.*6:931-957.

[5] Barouni, K., M. Mihit, L. Bazzi, R. Salghi, S. S. Al-Deyab, B. Hammouti and A. Albourine. 2010. The inhibited effect of cysteine towards the corrosion of copper in nitric acid solution. *The Open Corrosion Journal.* 3:58-63.

[6] Fu, J. J., S. N. Li, Y. Wang, X. L. Liu and L. D. Lu. 2011. Computational and electrochemical studies on the corrosion inhibition of mild steel by L-cysteine and its derivatives. *J. Mater. Sci.* 46:3550-3559.

[7] Bilgic, S. 2005. Corrosion inhibition effects of eco-friendly inhibitors in acidic media. *Korozyon.* 13(1):3-11.

[8] Silva, A. B., S. M. L. Agostinho, O. E. Baracia, G. G. O. Cordeiro and E. D'Elia. 2006. The effect of cysteine on the corrosion of

304L stainless steel in sulphuric acid. *Corros. Sci*. 48:3668-3674.

[9] Toufari, L., A. Kadri, A. Khalifa., N. Aimeeur and N. Benbrahim. 2008. The inhibition and adsorption process of L-cysteine against the corrosion of XC18 carbon steel in 2N H_2SO_4. *J. of Engg and Appl. Sci*. 3(a):688-696.

[10] Ognzie, E. E., Y. Li and F. H. Wang. 2007. Effect of 2-amino-3-mercaptopropanoic acid (cysteine) on the corrosion behavior of low carbon steel in sulphuric acid. *J. Electrochim. Acta*. 53(2):909-914.

[11] Umoren, S. A., I. B. Obot and N. O. Obi-Egbedi. 2009. Raphia hookeri gum as a potential eco-friendly inhibition for mild steel in sulphuric acid. *J. Mater. Sci.* 44(1):274-279.

[12] Morad, M. S. 2008. Corrosion inhibition of mild steel in sulfamic acid solution by S-containing amino acids. *J. Appl. Electrochem.* 38(11):1509-1518.

[13] Ashassi-Sorkhabi, H., M. R. Majidi and K.. Seyyedi. 2004. Investigation of inhibition effect of some amino acids against steel corrosion in HCl solution. *Appl. Surf. Sci*. 225:176-185.

[14] Hluchan, V., B. L. Wheeler and N. Hackerman. 1988. Amino acids as corrosoin inhibitors in hydrochloric acid solution. *Werkst, Korros.* 39:512-517.

[15] Moretti, G. and F. Guidi. 2002. Tryptophan as copper corrosion inhibitor in 0.5M aerated sulphuric acid. *Corros. Sci*. 44(9):1995-2011.

[16] Fu, J. J., S. N. Li, L. H. Cao, Y. Wang, L. H. Yan and L. D. Lu. 2010. L-Tryptophan as green corrosion inhibitor for low carbon steel in hydrochloric acid solution. *J. Mater. Sci.* 45:979-986.

[17] Cases, J. M and F. Villieras. 1992. Thermodynamic model of ionic and non-ionic surfactant adsorption-abstraction on heterogenous surface. *Langmuir,* 8(5):1251-1254.

[18] Ashassi-Sorkhabi, H., Z. Ghasimi and D. Seifzadeh. 2005. The inhibition effect of some amino acids towards the corrosion of aluminium in 1M HCl + 1M H_2SO_4 solution. *Appl. Surf. Sci.* 249(1-4):408- 418.

[19] Rao, V. S. and L. K.. Singhal. 2009. Corrosion behavior and passive film chemistry of 216L stainless steel in sulphuric acid. *J. Mater. Sci.* 49 (9):2327-2333.

[20] Olivares–Xometl, O., N. V. Likhanova, R. Martinez-Palou and M. A. Dominguez-Aguilar. 2009. Electrochemistry and XPS study of an imidazoline as corrosion inhibitor of mild steel in an acidic environment. *Mater. Corros.* 60 (1):14-21.

[21] Babic-Samarzija, K.., C. Lupu, N. Hackerman., A.R. Barron and A. Luttge. 2005. Inhibitive properties and surface morphology of a group of heterocyclic diazoles as inhibitors for acidic iron corrosion. *Langmuir.* 21(26):12187-96.

[22] Ha, L. J. 1990. Ph.D. Thesis, Faculty of Science, *Delhi University, Delhi.*

[23] de Souza, F. S. and A. Spinelli. 2009. Caffeic acid as a green corrosion inhibitor for mild steel. *Corros. Sci.* 51(3):642-649.

[24] Li, W. H., Q. He, S. T. Zhang, C. L. Pei and B. R. Hou. 2008. Some new triazole derivatives as inhibitors for mild steel corrosion in acidic medium. *J. Appl. Electrochem*. 38(3):289-295.

[25] Avci, G. 2008. Inhibitor effect of N, N'-methylenediacrylamide on corrosion behavior of mild steel in 0.5 M HCl. *Mater. Chem. Phys.* 112(1):234-238.

[26] Castellan, G.W. 1984. *Physical Chemistry,* Addison-Wesley, Reading, MA.