Azole Drug : A Novel Inhibitor for Corrosion

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Abstract

Heterocyclic compounds with atoms like N, O, and S are good corrosion inhibitors for metals and alloys. Molecules containing both N and S have good inhibition property when compared with molecules containing only N or S. A good inhibitor of corrosion should be alkaline. Azole drugs such as Fluconazole, Ketoconazole and Clotrimazole are good corrosion inhibitors due to the presence of aromatic rings, hetero-atoms and alkaline character. The rate of corrosion and inhibition efficiency of mild steel in the absence and presence of Fluconazole (FA) and Zn^{2+} containing 60ppm chloride ion has been studied by mass loss method. The inhibition efficiency of the system with 220ppm FA and 50ppm Zn^{2+} was high. AC impedance spectra, polarization study, Fourier Transform Infra Red spectra were analysed for knowing the nature of protective coating formed.

Keywords: Azoles, corrosion, green inhibitors, hetero-atom, mild steel.

Introduction

The irreversible interfacial reaction of a metal with its environment is called corrosion. The use of inhibitor is one of the best methods of protecting steel from corrosion. The capability of inhibitor depends on the environment, metal surface, interfacial electrochemical potential and structural aspect of inhibitor. The genuine material used in many industries is mild steel owing to its low cost and good mechanical properties. Corrosion of mild steel is an academic as well as industrial concern for the current years. Azoles are five-membered heterocyclic ring compounds with at least one hetero atom of nitrogen, sulphur or oxygen. The presence of free electron pairs play a significant role in inhibition due to the specific interaction between functional groups, metal surface and hetero atoms like N, O and S[1-3]. Increased inhibition takes place due to the combination of both factors[4-8]. Literature survey reveals that triazole derivatives has been used as inhibitors for corrosion in mild steel for a long time[9,10] as they adsorb on the mild steel and decrease the corrosion rate by blocking the active sites[11-13]. Fluconazole is a widely used bis-triazole antifungal drug. It has five-membered ring structures containing three nitrogen atoms[14].
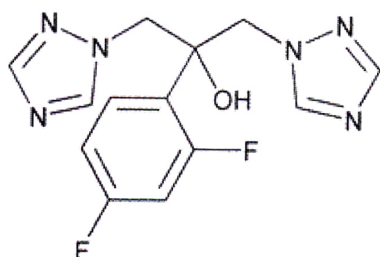
The current study is carried out to calculate the inhibition efficiency of FA-Zn^{2+} system by mass loss methods, identify the mechanism of corrosion inhibition by electrochemical studies and examine the type of protective coating formed on the surface of mild steel by FTIR spectra.

Material and Methods

Mass loss studies: Different concentrations of inhibitor with 60ppm Cl^{-} ion and Zn^{2+} ions were taken in 100ml glass beakers. Accurately weighed mild steel specimens in triplicate were immersed in the beaker for one day. After required time of immersion, the specimens were taken out, washed with clean water, dried and finally weighed. From the difference in weights of the specimen, the rate of corrosion is calculated using the relation:

$$\text{Corrosion rate} = \frac{\text{Loss in mass in milligrams}}{\text{Surface area of the metal specimen in } dm^2 \times \text{Period of immersion in days}}$$

The inhibition efficiency was calculated using the relation

$$IE = \frac{X_1 - X_2}{X_2} \times 100$$

Where: X_1 = Loss in weight of the specimen in the absence of inhibitor, X_2 = Loss in weight of the specimen in the presence of inhibitor.

Potentiodynamic polarization studies: Polarization study was carried out using three electrode cell assemblies. The reference electrode used was saturated calomel electrode (SCE) and the counter electrode is a rectangular platinum foil. The working

electrode is a metal piece with exposed area of 1cm². Corrosion parameters such as corrosion potential (E_{Corr}), corrosion current (I_{Corr}) and tafel slopes (anodic ba and cathodic ca) were calculated. The percentage of inhibition efficiency was calculated from I_{Corr} using the relationship[15].

$$IE \% = \frac{I^1_{Corr} - I^2_{Corr}}{I^1_{Corr}} \times 100$$

Where: I^1_{Corr} = Density of corrosion current in the absence of inhibitor, I^2_{Corr} = Density of corrosion current in the presence of inhibitor

AC impedance measurements: The real part (Z^1) and imaginary part (Z^{11}) of the cell impedance for various frequencies was measured in ohms. The charge transfer resistance (R_t) and double layer capacitance (C_{dl}) values were calculated. The inhibition efficiency of the inhibitor was calculated using the relation:

$$IE \% = \frac{R^1t - R^2t}{R^1t} \times 100$$

Where: R^1_t = Charge transfer resistance in the absence of inhibitor, R^2_t = Charge transfer resistance in the presence of inhibitor

Fourier Transform Infra Red spectral study: The mild steel specimens were immersed in a solution containing the inhibitor solution, 60ppm Cl⁻ ion and Zn^{2+} ions for 1 hour. After 1 hour, the specimens were taken out from the beaker and dried at room temperature. The protective film formed on the surface of the metal specimen was removed and mixed with KBr pellets in the form of a tablet. The FTIR spectra were recorded with a Perkin-Elmer 1600 Spectrophotometer.

Results and Discussion

Analysis of mass loss studies: Effect of concentration of inhibitor: Table-1 shows the rates of corrosion and inhibition efficiencies of mild steel in an environment containing 60ppm Cl⁻ ion. The solution with 50ppm Zn^{2+} ions and 20ppm FA has an inhibition efficiency of 2%. The solution with 50ppm Zn^{2+} ions and 140ppm has an IE of 43% but the solution containing 50ppm Zn^{2+} ions and 220ppm FA has 72% IE. When the inhibitor concentration increases above 220ppm the IE reduces to 53%. It is seen that as the inhibitor concentration increases, the protective film formed on the metal surface gets broken and mixes with the solution. Hence the best formulation with high inhibition efficiency is the system with 220ppm FA and 50ppm Zn^{2+} ion.

Effect of Immersion time: Table-2 shows the variation in the inhibition efficiency with the time of immersion. It was found that as the time of immersion increases, the inhibition efficiency decreases. This is due to the fact that the protective film formed

on the metal surface is not able to bear up the hit of Cl⁻ ion. The film is broken down and hence the IE decrease slightly with increase in the period of immersion.

Table-1
Effect of concentration of inhibitor on mild steel in neutral aqueous environment containing 60ppm of Cl⁻ ion

Inhibitor System : FA + Zn²⁺ Immersion Period : One Day									
Cl⁻ (ppm)	FA (ppm)	Corrosion Rate (mdd) Zn²⁺				Inhibition efficiency (%) Zn²⁺			
		0 ppm	10 ppm	25 ppm	50 ppm	0 ppm	10 ppm	25 ppm	50 ppm
60	0	24	18	17	21	-	21	33	3
60	20	25	19	18	23	-6	19	31	2
60	60	26	23	19	18	-10	2	24	31
60	100	20	25	15	15	-17	-4	36	57
60	140	24	25	19	14	-2	-4	24	43
60	180	24	2	17	9	0	13	28	62
60	220	23	22	17	7	2	9	28	72
60	260	22	24	17	11	6	0	28	53

Table-2
Effect of Immersion time on mild steel in neutral aqueous environment containing 60ppm of Cl⁻ ion

Inhibitor System : FA + Zn²⁺				
Immersion Period(Days)	1	3	5	7
CR in the absence of inhibitor	23.5	22	20	18.5
CR in the presence of inhibitor	6.5	6	5	4
IE %	63	57	50	48

Analysis of Potentiodynamic polarization study: Polarization study was used to identify the formation of protective coating on the surface of the metal. When such coating is formed the corrosion current (I_{Corr}) decreases [16-23]. The corrosion parameter of mild steel immersed in various test solutions obtained by polarization study is given in table-4 and the polarization curves are depicted in figure-1. When mild steel is immersed in neutral aqueous solution containing 60ppm Cl⁻ion, the corrosion potential is -644 mV Vs SCE. When 50ppm Zn^{2+} is added to the solution the corrosion potential decreases to -550 mV Vs SCE. The corrosion potential is slightly increased to -560 mV Vs SCE when 220ppm of inhibitor is added. But the formulation containing 60ppm Cl⁻ ion, 50ppm Zn^{2+} and 220ppm FA decreases the corrosion potential to -547 mV Vs SCE. The corrosion current for aqueous solution containing 60ppm Cl⁻ ion is 6.29×10^{-5} A/Cm² but it decreased to 1.31×10^{-5} A/cm² for the formulation consisting of 60ppm Cl⁻ ion, 220ppm FA and 50ppm Zn^{2+}. The IE% has increased. This is due to the formation of a protective coating on the surface of the metal.

Figure-1
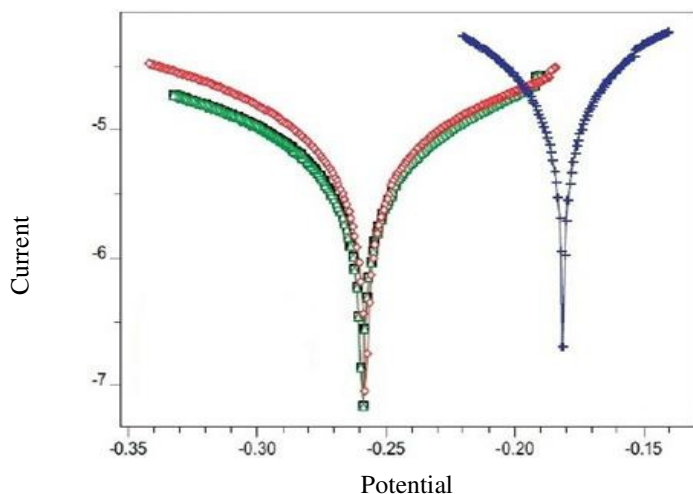**Polarization curves of low carbon steel immersed in various test solutions, - + - 60 ppm Cl⁻ ion, - ◇ - 60 ppm Cl⁻ ion + 50 ppm Zn²⁺ ion, - △ - 60 ppm Cl⁻ ion + 220 ppm Inhibitor, - □ - 60 ppm Cl⁻ ion + 220 ppm Inhibitor + 50 ppm Zn²⁺ ion**

Table-3
Effect of pH on mild steel in neutral aqueous environment containing 60ppm of Cl⁻ ion

Inhibitor System : FA + Zn²⁺					
Cl⁻(ppm)	FA (ppm)	Zn²⁺ (ppm)	pH	CR (mdd)	IE%
60	220	50	4	7	69
60	220	50	7	2	89
60	220	50	9.2	6.5	48

Table-4
Tafel polarization corrosion parameters of mild steel in neutral aqueous environment containing 60ppm of Cl⁻ ion obtained by potentiodynamic polarization study

System	Ecorr (mv Vs SCE)	bc (mv)	ba (mv)	Icorr (A/cm²)	IE %
Aqueous solution containing 60ppm Cl⁻ ion	-644	127	114	6.29×10^{-5}	-
Aqueous solution containing 60ppm Cl⁻ ion +50ppm Zn²⁺	-550	134	105	1.84×10^{-5}	71
Aqueous solution containing 60ppm Cl⁻ ion +220 ppm FA	-560	130	99	2.51×10^{-5}	60
Aqueous solution containing 60ppm Cl⁻ ion +220 ppm FA +50 ppm Zn²⁺	-547	114	101	1.31×10^{-5}	79

Table-5
Linear polarization resistance corrosion parameters of mild steel in neutral aqueous environment containing 60 ppm of Cl⁻ ion obtained by polarization study

System	Rp (Ohm)	IE %
Aqueous solution containing 60ppm Cl⁻ ion	1482	-
Aqueous solution containing 60ppm Cl⁻ ion +50ppm Zn²⁺	4936	70
Aqueous solution containing 60ppm Cl⁻ ion +220 ppm FA	3486	57
Aqueous solution containing 60ppm Cl⁻ ion +220 ppm FA +50 ppm Zn²⁺	6360	77

The Tafel slope for ba and bc are almost equal. The inhibitor showed the mixed inhibitor mainly cathodic. The anodic and cathodic tafel slopes are comparatively equal in the presence of inhibitor which indicates that the formulation containing FA and Zn²⁺ function as a mixed type inhibitor restricted by both anodic and cathodic reaction to the same extent. Conversely the cathodic tafel slope is somewhat higher as there was a shift in the corrosion potential to the cathodic side. The percentage of inhibition efficiency and linear polarization resistance parameters are shown in table-5.

The IE was calculated by the relation IE % = $\frac{Rp1 - Rp2}{Rp2} \times 100$

Where: R_p^1 = Polarization resistance in the absence of inhibitor, R_p^2 = Polarization resistance in the presence of inhibitor.

It is inferred from table-5 that as the polarization resistance increases from the system containing 60ppm Cl⁻ ion (1482 ohm) to the formulation containing 60ppm Cl⁻ ion, 50ppm Zn²⁺ and 220ppm FA (6360 ohm), the IE also increases with addition of inhibitor.

Study of AC impedance measurements: The AC impedance spectra of mild steel immersed in neutral aqueous solution consisting of 60ppm Cl⁻ ion, 60ppm Cl⁻ ion + 50ppm Zn²⁺, 60ppm Cl⁻ ion +220ppm FA and 60ppm Cl⁻ ion + 220 ppm FA + 50ppm Zn²⁺ are depicted in figure-2 (Nyquist Plot). The AC impedance parameters specifically double layer capacitance (C_{dl}) and charge transfer resistance (R_t) were calculated.

Table–6 shows that the solution with 60ppm Cl⁻ion has a charge transfer resistance value (R_t) of 678 ohm and double layer capacitance (C_{dl}) value of 9.53×10^{-5} F. In the presence of 220ppm FA and 50ppm Zn²⁺, R_t value increased from 678 to 2330 ohm and C_{dl} value decreased from 9.53×10^{-5} F to 3.02×10^{-8} F. This is due to the formation of a protective coating on the metal surface.
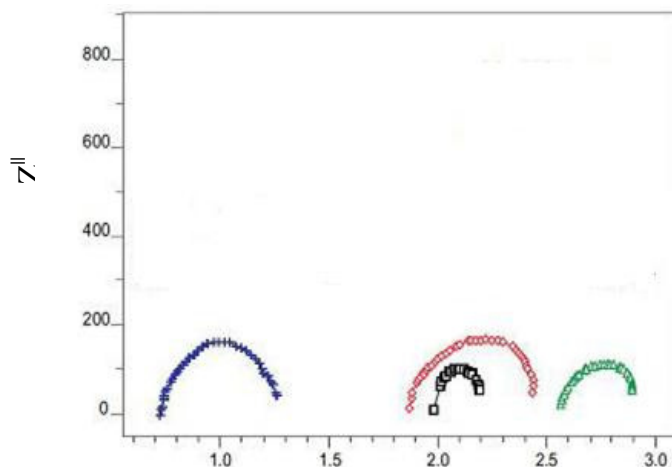
Figure-2
AC impedance spectra of low carbon steel immersed in various test solutions (Nyquist plots), - + - 60 ppm Cl⁻ ion, - - 60 ppm Cl⁻ ion + 50 ppm Zn²⁺ ion, -   - 60 ppm Cl⁻ ion + 220 ppm Inhibitor, -   - 60 ppm Cl⁻ ion + 220 ppm Inhibitor + 50 ppm Zn²⁺ ion

Table-6
Corrosion parameters of mild steel immersed in neutral aqueous environment containing 60ppm of Cl⁻ ion obtained by AC impedance spectra

System	R_t (Ohm)	IE %
Aqueous solution containing 60ppm Cl⁻ ion	678	9.53×10^{-5}
Aqueous solution containing 60ppm Cl⁻ ion +50ppm Zn²⁺	1500	3.88×10^{-8}
Aqueous solution containing 60ppm Cl⁻ ion +220ppm FA	1804	3.06×10^{-8}
Aqueous solution containing 60ppm Cl⁻ion +22 ppm FA +50ppm Zn²⁺	2330	3.02×10^{-8}

Analysis of FTIR Spectra: Figure 3a shows the FTIR spectrum (KBr) of pure FA. The C=N stretching frequency occurs at 1620cm⁻¹. The N-H stretching vibrations arise at 3069.84 and 3117.10 cm⁻¹ [24]. The C-F band stretching vibrations occurs at 1386.88, 1341.55 and 1277.90 cm⁻¹. The   C-OH frequency appears at 1214.24, 1140.94, 1103.33, 1078.25 and 1011.71 cm⁻¹.

Figure-3b depicts the FTIR Spectrum (KBr) of the film produced on the metal surface after immersion in the solution consisting of 60ppm Cl⁻ ion and 220ppm FA. There is a shift in the electron pair from C=N towards Fe²⁺ which resulted in Fe²⁺-FA complex on the anodic site of the surface of the metal. This is clear as the C=N stretching frequency has decreased from 1620 cm⁻¹ to1619.31 cm⁻¹.

Figure-3c shows the FTIR spectrum (KBr) of the layer formed on the surface of mild steel after immersion in the solution consisting of 60ppm Cl⁻ ion, 220ppm FA and 50ppm Zn²⁺. Due to the formation of Zn (OH)₂ on the cathodic site of the metal surface [25], there is a band at 1310 cm⁻¹. Thus a synergistic effect prevails in the FA-Zn²⁺ system and it functions as a mixed inhibitor system which is concluded from the FTIR spectral study.

Conclusion

The subsequent conclusions were made from the current study. The formulation consisting of 60ppm Cl⁻ ion, 220ppm FA and 50ppm Zn²⁺ has an IE of 72%. Synergistic effect exists in the FA-Zn²⁺ system. FA-Zn²⁺ system show a better IE in neutral medium. As the concentration of the inhibitor and the period of immersion increases the IE of the FA-Zn²⁺ system decreases.
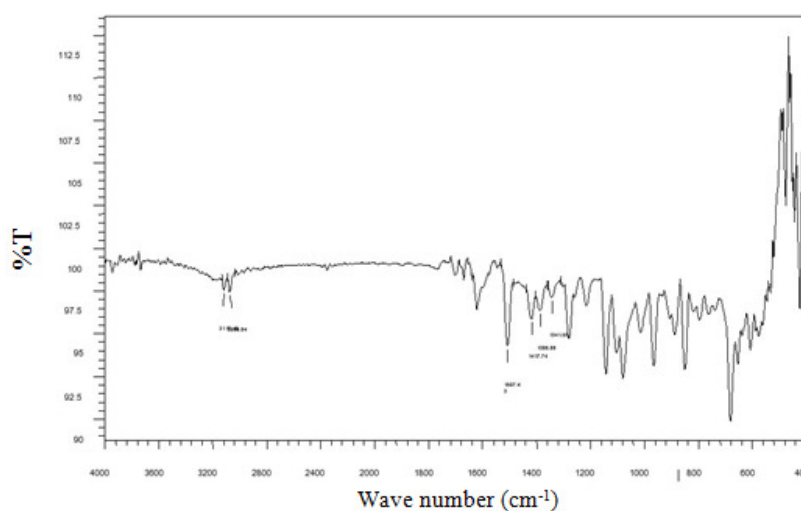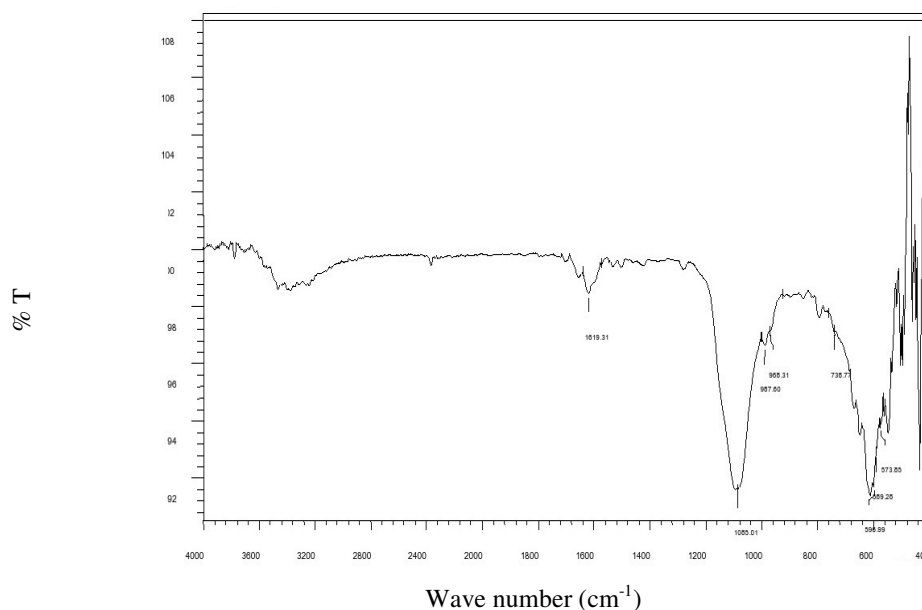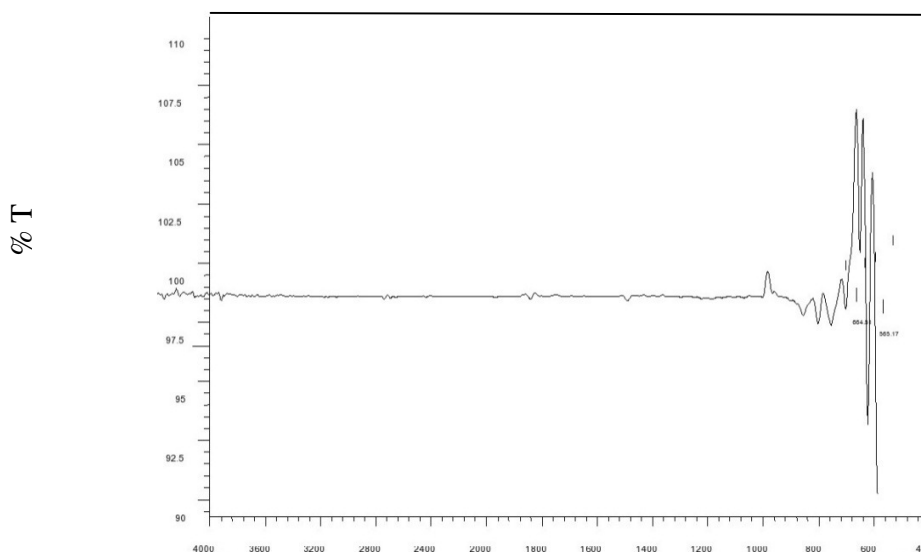

Figure-3a
FTIR spectra of pure FA

Figure-3b
FTIR spectra of the film formed on mild steel specimen, after immersion in the solution containing 60ppm Cl⁻ ion and, 220ppm FA

Figure-3c
FTIR spectra of the film formed on mild steel specimen after, immersion in the solution containing 60ppm Cl⁻ ion , 220ppm FA, and 50ppm Zn²⁺

The protective coating consists of Fe^{2+}- FA complex and Zn $(OH)_2$ as revealed from FTIR spectral studies. A protective coating is formed on the metal surface which is studied from AC impedance measurements. The protective coating consists of Fe^{2+}FA complex and Zn $(OH)_2$ as revealed from FTIR spectral studies.

References

1. Lashgari M., Arshadi M. and Biglar M., *Chem. Eng. Comm.*, **197,** 1303-1314 **(2010)**

2. Bentiss F., Traisnel M. and Lagrenee M., *Corros. Sci.*, **42,** 127-146 **(2000)**

3. Trabanelli G., Chemical Industries: Corrosion Mechanism", F.Mansfeld (Ed.), New York, Marcel

Dekker, P.120 **(1987)**

4. Yan Y., Li W., Cai L. and Hou B., *Electrochim. Acta*, **53,** 5953-5960 **(2008)**

5. Derya Loce H., Kaan C., Emregul and Atakol O., *Corrosion Sci.*, **50,** 1460-1468 **(2008)**

6. Bentiss F., Lgrenee M., Traisnel M. and Hornez J.C., *Corros. Sci*., **41,** 789-803 **(1999)**

7. Riggs O.L. Jr., Corrosion Inhibitors, Ed. C. C. Nathan, USA, NACE, 7, **(1973)**

8. Pattan S.R., Dighe N.S., Merekar A.N., Laware R.B., Shinde H.V. and Musmade D.S., *Asian J. Res. Chem*., (**2**), 196-201 **(2009)**

9. Ramesh S. and Rajeswari S., Corrosion Inhibition of mild steel in neutral aqueous solution by new Triazole derivatives, *Electrochimicat Acta*, 49(**5**), 811-820 **(2004)**

10. Bentiss F., Lagrene'e M., Traisnel M. and Gorenez J., The Corrosion Inhibition of Mild steel in acidic media by a new Traizole Derivative, *Corrosion Sci.*, **41(4)**, 789-803 **(1999)**

11. Bentiss F., Traisnel M., Gengembre L. and Lagrene'e M., A new Triazole Derivative as Inhibitor of the acid corrosion of mild steel, Electrochemical studies, weight loss determination, SEM AND XPS, *Applied surface Science*, **152(3-4),** 237-249 **(1999)**

12. Sudheer and Quraishi M.A., Effect of pharmaceutically active compound Omeprazole, on the corrosion of mild steel in hydrochloric acid solution, *J. Chem. Pharm. Res*, **3(5**), 82-92 **(2011)**

13. Manohar S.E., Environmental Chemistry (London, Sixth Edition, Lewis Publishers, **(1996)**

14. www.doctorfungus.org/thedrugs/fluconazole.php, **(2014)**

15. Ahamad I., Khan S., Ansari K.R., Quraishi M.A., *J .Chem. Pharm. Res*., **3,** 703-717 **(2011)**

16. Rajendran S., Uma V., Krishnaveni A., Jeyasundari J., Shyamaladevi B. and Maivannan M., Arabian, *J. Sci. Eng*., **34,** 147-158 **(2010)**

17. Rajendran S., Sumithra P., Devi B.S. and Jeyasundar J., *Zastita Materijala,* **50,** 223 **(2009)**

18. Rathish R.J., Rajendran S., Christy J.L., Devi B.S., Johnmary S., Manivannan M., Rajam K., Rengan P., *Open Corros. J*., **3,** 38-44 **(2010)**

19. Benita Sherine M., Mani R.K. and Rajendran S., *J. Electrochem, Soc*. India, **57,** 67-73 **(2008)**

20. Narayanasamy B. and Rajendran S., *Prog. org. coat*., **67,** 246-254 **(2010)**

21. Yesu Y., Thangam M., kalanithi C., Mary Anbarasi and Rajendran S., *The Arabian J. Sci. Eng*., **34,** 37- 47 **(2009)**

22. Kanimozhi S.A. and Rajendran S., *Arabian J. Sci. Eng*., **35,** 41-52 **(2009)**

23. Sathiyabama J., Rajendran S., Sundari J.J. and Shyamaladevi B., *J. Eng. Sci. Tech. Rev*., **3,** 27-31 **(2010)**

24. Silverstein R.M., Bassler G.C. and Morrill T.C., Spectometric Identification of Organic Compound, John wiley sons, Newyork, 134 **(1986)**

25. Sekine I., Hirakawa Y., *Corrosion,* **42,** 272 **(1986)**