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Influence of the TSC (Trisodium Citrate) on the corrosion inhibition of mild steel in MGD-Zn^{2+}

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ABSTRACT

The inhibition effect of MGD (Malachite green dye) on the corrosion of mild steel was studied by weight loss, Potentiodymanic polarization and FTIR spectra. The absence and presence of Zn^{2+} was studied. MGD alone has some inhibition efficiency of 76%. Increasing the concentration of MGD and Zn^{2+}, the efficiency has increases. The influence of the TSC (Trisodium citrate) on the corrosion inhibition of MGD+Zn^{2+} system was studied and the IE is 100%. Present study was aimed to investigate the inhibition efficiency of MGD-Zn^{2+}-TSC in controlling the corrosion of carbon steel immersed in aqueous solution containing 60 ppm Cl$^-$. Potentiodymanic polarization study and FTIR shows that protective film formed on the metal surface.   © 2013 Trade Science Inc. - INDIA

INTRODUCTION

A survey of literature reveals that the applicability of organic compounds as corrosion inhibitors for mild steel in acidic media has been recognized for a long time. A large number of organic compounds, particularly those containing nitrogen, oxygen or sulphur in a conjugated system, are known to be applied as inhibitors to control acid corrosion of iron and steel. The inhibition process has been shown to occur via inhibitor adsorption isotherm and the efficiency of the inhibitors strongly depends on the structure and chemical characteristics of the adsorbed inhibitor layer formed under particular experimental conditions. Although dyes have been extracted from natural sources for centuries, it was not until 1856 that a synthetic dye was produced commercially[1,2]. Different kinds of dyes are known viz. heterocyclic dyes (e.g. safranine T, methylene blue); xanthene dyes (e.g. eosin, thymol blue, phenolphthalein, phenol red) ; an-

thraquinone dyes (e.g. alixarin red S) and azo dyes (e.g. methyl red, congo red, methyl orange). Of all the dyes, azo dyes are a class of compounds that are strongly coloured. They can be intensely yellow, red, orange, blue or even green, depending on the exact structure of the molecule. Because of their colour, azo compounds are of tremendous importance as dyes. Infact, about half of the dyes in industrial use today are azo dyes, which are mostly prepared from diazonium salts[3]. The adsorption of corrosion inhibitor depends mainly on physico-chemical properties of the molecules such as functional group, steric factor, molecular size, molecular weight, molecular structure, aromaticity, electron density at the donor atoms and orbital character of donating electrons[4-8] and also, on the electronic structure of molecules[9-13]. Inhibitors are generally used for reduce the corrosive attack on metallic material to control the metal dissolution. Most of the well-known inhibitors are organic compounds containing nitrogen, sulphur and /or oxygen atoms. It has

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been observed that the most of the organic inhibitors act by adsorption on the metal surface[14].

EXPERIMENTAL PROCEDURE

Preparation of specimens

Carbon steel specimens (S, 0.0267%; P 0.067%; Mn 0.4%; C 0.1% and rest iron) of the dimensions 1.0 x 4.0x0.2 cm were polished to mirror finish, degreased with acetone and used for weight loss method and surface examination studies.

Weight loss

Carbon steel specimens were immersed in 100 ml of an aqueous solution containing 60 ppm Cl⁻ and various concentration of MGD in the presence and absence of Zn^{2+} (as $ZnSO_4.7H_2O$) for a period of one day. Influence of TSC (Trisodium citrate) on the inhibition efficiency of MGD + Zn^{2+} system. The weight of the specimen before and after immersion was determined using Shimadzu balance AY62. The corrosion inhibition efficiency was calculated using equation

IE=100(1-w_2/w_1)%

Where w_1 is the corrosion rate in the absence of inhibitor and w_2 is the corrosion rate in the presence of inhibitor.

Potentiodymanic dynamic polarization study

This study was carried out in a three electrode cell assemble connected to electrochemical analyzer. The standard calomel electrode (SCE) was used as reference electrode, platinum electrode was used as a counter electrode and working electrode. All potentials were measured versus SCE.

FTIR spectra

The carbon steel specimens immersed in various test solutions for one day were taken out and dried. The film formed on the metal surface was carefully removed and thoroughly mixed with KBr, so as to make it uniform throughout. The FTIR spectra were recorded in a Perkin Elmer 1600 spectro photometer.

RESULTS AND DISCUSSION

Weight loss study

The corrosion inhibition efficiencies (IE) of Mala-

chite green dye (MGD) in controlling the corrosion of carbon steel immersed in aqueous solution containing 60 ppm Cl⁻ both in the absence and presence of zinc ion. The influence of TSC of MGD-Zn^{2+} was studied and IE was found to 100%. The values indicate that the ability of MGD-Zn^{2+}-TSC as a good corrosion inhibitor. The values are given in TABLE 1 to 4. MGD (250 ppm) alone has inhibition efficiency (IE) 76% increasing the concentration of Zn^{2+} shown the increasing efficiency. 250 ppm of MGD and 200 ppm of Zn^{2+} has 97% efficiency. Increasing the concentration of MGD-Zn^{2+} shows the higher efficiency.

TABLE 1 : Corrosion rates (CR mdd) carbon steel immersed in an aqueous solution containing 60 ppm of Cl⁻ and the inhibition efficiencies (IE) obtained by weight loss method.

Cl⁻ ppm	MGD ppm	Zn^{2+} ppm	CR mdd	IE %
60	0	0	18	-
60	50	0	7.74	57
60	100	0	6.84	62
60	150	0	5.58	69
60	200	0	4.86	73
60	250	0	4.32	76

TABLE 2 : Corrosion rates (CR mdd) carbon steel immersed in an aqueous solution containing 60 ppm of Cl⁻ + MGD + Zn^{2+} and the inhibition efficiencies (IE) obtained by weight loss method.

Cl⁻ ppm	MGD ppm	Zn^{2+} ppm	CR mdd	IE %
60	50	200	13.14	27
60	100	200	9.90	45
60	150	200	6.30	65
60	200	200	2.70	85
60	250	200	0.54	97

TABLE 3 : Corrosion rates (CR mdd) carbon steel immersed in an aqueous solution containing 60 ppm of Cl⁻ + MGD + Zn^{2+} + TSC and the inhibition efficiencies (IE) obtained by weight loss method.

Cl⁻ ppm	MGD ppm	Zn^{2+} ppm	TSC ppm	CR mdd	IE %
60	50	50	50	11.25	37
60	100	50	100	6.30	65
60	150	50	150	0.90	95
60	200	50	200	-	100
60	250	50	250	-	100

Influence of TSC on the inhibition efficiency of MGD-Zn^{2+} system

It is observed that when TSC is added the inhibi-

tion efficiency of MGD-Zn^{2+} system increases. The increase in IE is more pronounced at 250 ppm of TSC. Synergistic effect exists between MGD-Zn^{2+} system and TSC (250 ppm MGD) alone has 76%. 250 ppm of MGD and 200 ppm of Zn^{2+} has 97% IE. When 250 ppm of TSC is added, their combination has 100% inhibition efficiency.

TABLE 4 : Influence of increasing concentration of inhibitors. Immersion period-two days.

Inhibition	CR mdd	IE %
MGD(250 ppm) alone	4.32	76
MGD(250 ppm)+ Zn^{2+} (200 ppm)	0.54	97
MGD(250 ppm)+ Zn^{2+} (200 ppm)+TSC(250 ppm)	Nil	100

Influence of immersion period on inhibition efficiency

The IE of MGD (250 ppm)-Zn^{2+}(200 ppm)-TSC (250 ppm) system is found to TABLE 5. The inhibition efficiency decreases as the immersion period increases. This indicates that the protective film formed on the metal surface is unable to withstand the continuous attack of corrosive ions present in aqueous solution containing 60 ppm Cl^-.

TABLE 5 : Influence of immersion period on the inhibition efficiency of the MGD (250 ppm)-Zn^{2+}(200 ppm) +TSC (250 ppm).

| Immersion period (Days)	2	3	6	8
Aqueous solution containing 60 ppm Cl^- CR mdd	18	16.28	13.39	8.68
Aqueous solution containing 60 ppm Cl^-+MGD (250ppm) +Zn^{2+}(200 ppm) + TSC(250 ppm) CR mdd	-	0.72	2.16	3.24
IE%	100	96	88	82

Open circuit potential (OCP)

One simple way to study the film formation and passivation of mild steel in a solution is to monitor the open-circuit electrode potential as a function of time. A rise of potential in the positive direction indicates the formation of a passive film and a steady potential indicates that the film remains intact and protective. A drop of potential in the negative direction indicates breaks in the film, dissolution of the film, or no film formation.

Analysis of potentiodymanic polarization curves

Polarization study has been used to study the formation of protective film on the metal surface. The Potentiodymanic polarization curves of carbon steel

immersed in an aqueous solution containing 60 ppm of Cl^- in the absence and presence of inhibitors shown in Figure 1.

The corrosion parameters namely corrosion potential (E_{corr}) Tafel slopes b_c (cathodic) and b_a (anodic) linear polarization resistance (LPR) and corrosion current (I_{corr}) are given in TABLE 6 that when carbon steel immersed in an aqueous solution containing 60 ppm of Cl^-, the corrosion potential is -612mv VS SCE (Saturated calomel electrode). The LPR value is 2.09×10^5 ohm cm^2. The corrosion current value is 2.075×10^{-6} A/cm^2. When 250 ppm of MGD, 200 ppm of Zn^{2+} and 250 ppm of TSC are added to the above environment, the corrosion potential is shifted to the noble side due to the formation of protective film on the metal surface. It is observed from TABLE 6 that the LPR value increases and the corrosion current value decreases. These observations suggest the formation of a protective film on the metal surface. This prevents the corrosion of metal.
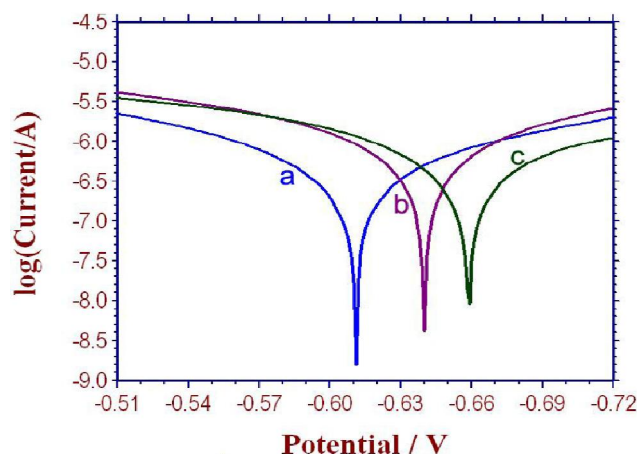

Figure 1 : Polarization curves of carbon steel immersed in various test solutions a) 60 ppm Cl(Blank) b) 60 ppm Cl^- + MGD (250ppm) +Zn^{2+} (200 ppm) c) 60 ppm Cl^- + MGD (250ppm) +Zn^{2+} (200 ppm) + TSC (250ppm).

Analysis of FTIR spectra

FTIR spectra have been used to analyze the protective film formed on the metal surface. The FTIR spectrum of pure MGD, MGD-Zn^{2+} and MGD-Zn^{2+}-TSC is shown in Figure 2a, 2b, 2c. FTIR spectra of control malachite green showed the specific peak in finger print region (1500 to 500 cm^{-1}) for the mono substituted para di substituted benzene rings which is supporting to the peaks at 1564 cm^{-1} for the C=C

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stretching of the benzene ring. Also the peak at 1168 cm⁻¹ for C-H stretching of asymmetric CH_3 group is given the perception of structure of malachite green.
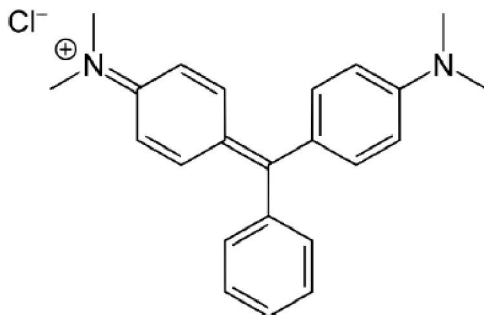
Scheme 1 : Structure of MGD.

The FTIR spectra showed peak at 1278 cm⁻¹ for C-N stretching with supporting peak at for NH stretch

represents the formation of primary and secondary amines. The sharp peak at 790 cm⁻¹ for distributed benzene derivatives indicates aromatic nature of amines. The C=C stretching frequency appears at 1599 cm⁻¹. This suggest that MG coordinated with Fe^{2+}-MG complex.

The peak at 1384 cm⁻¹ is due to Zn-O stretching. The –OH stretching frequency appears at 3350 cm⁻¹. This suggest that the formation of $Zn(OH)_2$ On the metal surface. The C=O stretching frequency of TSC has shifted from 1599 cm⁻¹ to 1590 cm⁻¹. This shift indicates that the carbonyl oxygen atom was coordinated to Fe^{2+} results in the formation of Fe^{2+}-MGD, Fe^{2+}-TSC complex on the anodic sides of the metal surface[15,16].

TABLE 6 : Corrosion parameters of carbon steel immersed in an aqueous solution containing 60 ppm of Cl⁻ obtained from potentio dynamic polarization study.

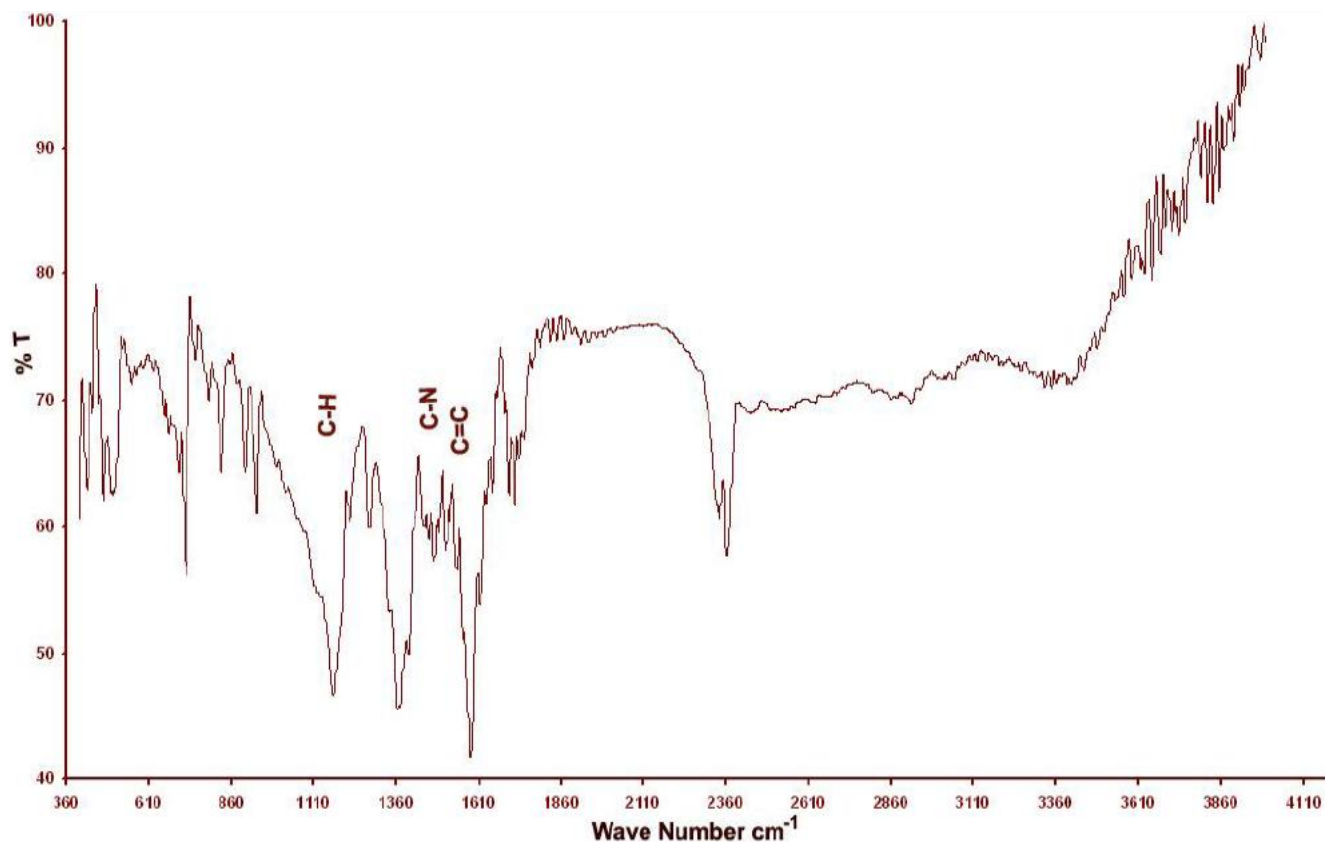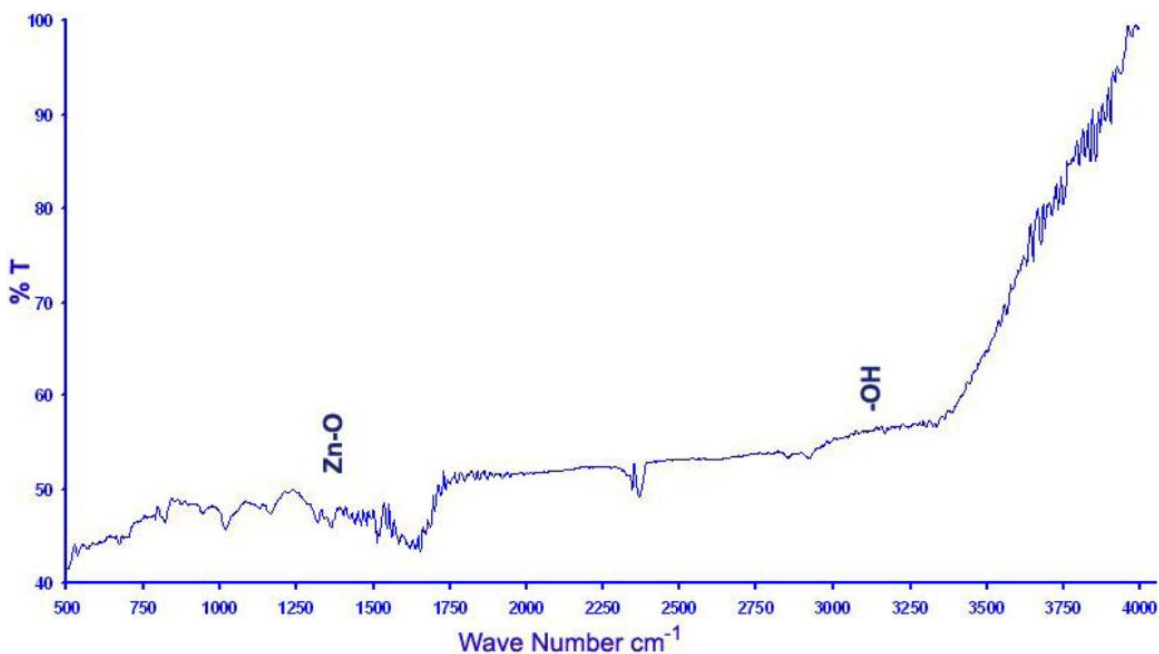| System	E_{corr} mV vs SCE	b_a mV/decade	b_c mV/decade	LPR ohm cm²	I_{corr} A/cm²
Aqueous solution containing 60 ppm Cl⁻	-612	210	189	2.09×10^5	2.075×10^{-6}
Aqueous solution containing 60 ppm Cl⁻ + MGD (250ppm) +Zn²⁺ (200 ppm)	-640	196	204	3.11×10^5	1.397×10^{-6}
Aqueous solution containing 60 ppm Cl⁻ + MGD (250ppm) +Zn²⁺ (200 ppm) + TSC (250ppm)	-659	419	211	4.38×10^5	1.312×10^{-6}

Figure 2a : Pure MGD.

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Figure 2b : Pure MGD + Zn^{2+}.
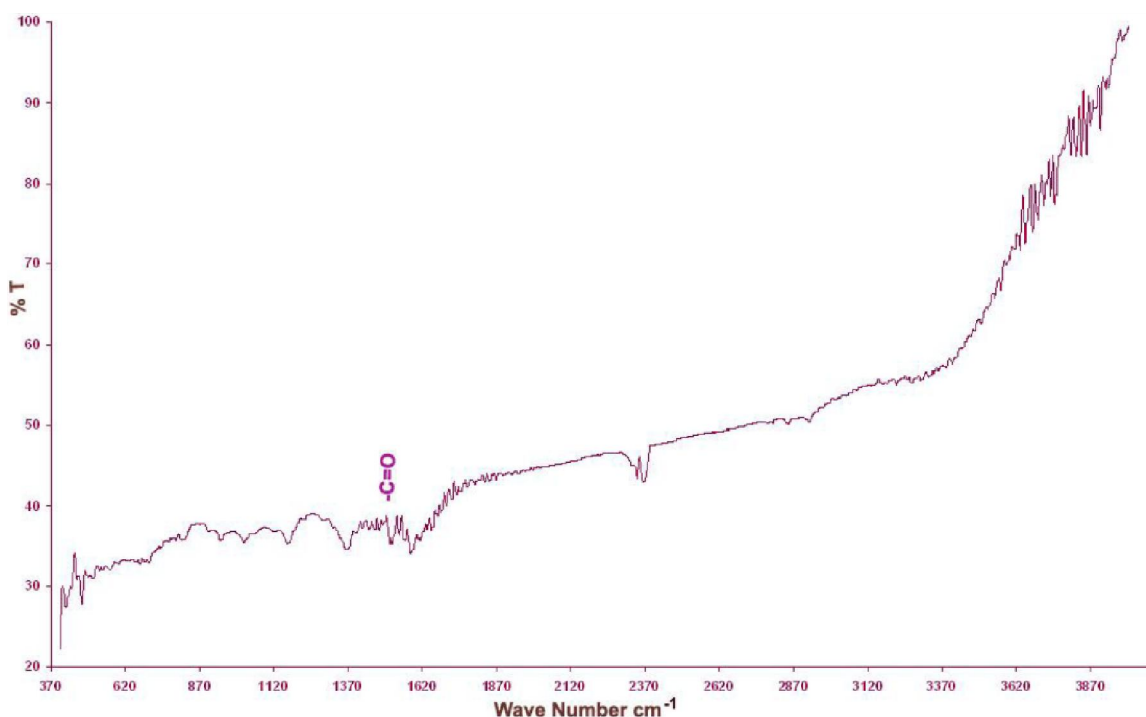
Figure 2c : Pure MGD + Zn^{2+} + TSC.

Mechanism of corrosion inhibition

In view of the above results, the following mechanism may be proposed for the corrosion inhibition of carbon steel immersed in an aqueous solution containing 60 ppm Cl$^-$.

The formulation consisting of 250 ppm of MGD and 200 ppm of Zn^{2+}, 250 ppm of TSC in aqueous solution containing 60 ppm Cl$^-$ containing MGD-Zn^{2+}, TSC-Zn^{2+} complex in solution.

(i) When carbon steel is immersed in this solution MGD-Zn^{2+}, TSC-Zn^{2+} complex diffuses from the bulk of the solution towards the metal surface.

(ii) On the metal surface MGD-Zn^{2+}, TSC-Zn^{2+} complex is converted in to Fe^{2+}-MGD, Fe^{2+}-TSC complex

Research & Reviews On
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(iii) Zn^{2+}-MGD, Zn^{2+}-TSC+$Fe^{2+}\rightarrow Fe^{2+}$-MGD, Fe^{2+}-TSC+Zn^{2+}

(iv) The released Zn^{2+} combines with OH^- to form $Zn(OH)$ on the cathodic sites.

$$Zn^{2+}+2OH^-\rightarrow Zn(OH)_2$$
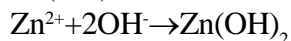
CONCLUSION

Malachite green along with Zn^{2+} and TSC (Trisodium citrate) acts as a corrosion inhibitor system for carbon steel in aqueous solution containing 60ppm Cl^-. Its efficiency increased due to the transporting ability for Zinc ion through the formation of MGD-Zn^{2+}, MGD-Zn^{2+}-TSC system is found to decrease as the immersion period increases. A suitable mechanism has been proposed for the corrosion inhibition based on the results of polarization study and FTIR spectra.

REFERENCES

[1] N.Putilova, V.P.Barranik, S.A.Balezin; Metallic corrosion inhibitors, Oxford; Newyork, **(1960)**.

[2] K.Venkataraman; The chemistry of synthetic dyes, Academic Press; New York, **(1970)**.

[3] J.D.Roberts, M.C.Caserio; Basic principles of organic chemistry, 2nd Edition, W.A.Benjamin Inc., California, **(1979)**.

[4] I.Dehri, M.Ozcan; Mater.Chem.and Phys., **98**, 316 **(2006)**.

[5] M.G.Hosseini, M.Ehteshamzadeh, T.Shahrabi; Electrochim Acta., **52**, 3680 **(2007)**.

[6] I.L.Rosenfelld; Corrosion inhibitors, Mc Graw- Hill; New York, **(1981)**.

[7] M.M.El-Naggar; Corrosion Science, **49**, 2226 **(2007)**.

[8] S.T.Selvi, V.Raman, N.Rajendran; J.Appl. Electrochem, **33**, 1175 **(2003)**.

[9] M.Ozcan, I.Dehri, M.Erbil; App.Surf.Science, **236**, 155 **(2004)**.

[10] S.L.Granese; Corrosion, **44**, 322 **(1998)**.

[11] S.L.Granese, B.M.Rosales, G.Oviedo, J.O.Zerbino; Corrosion Science, **33**, 1439 **(1992)**.

[12] A.S.Fouda, H.A.Mostafa, F.El-Taib, G.Y.Elewady; Corrosion Science, **47**, 1988 **(2004)**.

[13] M.Abdallah; Corrosion Science, **46**, 1981 **(2004)**.

[14] S.S.Abd El-Rehim, M.A.M.Ibrahim, K.F.Khaled; J.Appl.Electrochem., **29**, 593 **(1999)**.

[15] R.M.Silverstein, G.C.Basler, T.C.Morrill; Spectroscopic identiûcation of organic compounds, 4th Edition-John Wiley and Sons; Newyork, **(1981)**.

[16] A.D.Cross; Introduction to practical infrared spectroscopy, Butterworths Scientific Publication; London, **(1990)**.