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Inhibitive Properties of MB –Zn^{2+} System and Its Synergism With SPT

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Abstract

The Inhibition Efficiency (IE) of Methylene Blue (MB) –Zn^{2+} system in controlling corrosion of carbon steel immersed in an aqueous solution has been evaluated by weight loss method. The formulation consisting of 250 ppm of MB and 25 ppm of Zn^{2+} has 84% inhibition efficiency (IE). The influence of SPT (Sodium Potassium Tartrate) on the IE of MB –Zn^{2+} system has been studied. 250 ppm of MB -25 ppm of –Zn^{2+} and 250 ppm of SPT has 94% inhibition efficiency (IE). Electro Chemical studies such as Potentiodymanic polarization and AC impedance have been used to find the mechanic aspects of corrosion inhibition.

Keywords:

Carbon steel, Corrosion inhibition, Methylene Blue (MB), Sodium Potassium Tartrate(SPT), AC impedance spectra, Potentio dynamic Polarization study.

"1. Introduction"

Several compounds such as molybdate [1,2], Phosphonic acids [3], Poly acryl amide [4] and Caffeine [5,6] have been used as corrosion inhibitions. Corrosion inhibition of mild steel in acidic media by some organic dyes has been investigated [7]. Qguzie has studied the inhibition of corrosion of mild steel in hydrochloric acid solution by methylene blue dye [8].Eriochrome black –T serves as a good corrosion inhibitor for carbon steel in well water [9]. At pH 11 methyl orange along with Zn^{2+} functions as a good inhibitor in controlling corrosion of Aluminum [10]. However, the stability of the inhibitor film formed over the metal surface depends on some physicochemical properties of the molecule, related to its functional groups, aromaticity, the possible steric effects, elec-tronic density of donors, type of the corrosive medium and nature of the interaction between the inhibitors with the d-orbital vacant of iron [11-12]. The present work is represent and studies the influence on the corrosion inhibition of mild steel in aqueous solution, of methylene blue dye (MB) which acts as a good inhibitor

"2. Experimental"

2.1. Preparation of specimens

Mild steel specimens were chosen from the same sheet of the following composition 0.1 percent C, 0.026 percent S, 0.06 percent P, 0.4 percent Mn and the balance Fe. Mild steel specimen of the dimensions 1.0x4.0x0.2 cm were polished to mirror trichloro ethylene and used for mass loss and surface examinations studies.

2.2. Weight loss study

The weighed specimen in triplicate were suspended by means of glass hooks in 100ml beakers containing 100ml of double distilled water in various concentration of inhibitors in the presence and absence of Zn^{2+} for 3 days of immersion. After 3days of immersion the specimens were taken out, washed in running water dried and weighed. From the change in weights of the specimen corrosion rates were calculated using the following relationship.

$$\text{Corrosion rate} = \frac{\text{Loss in weight (mg)}}{\text{Surface area of the specimen (dm}^2) \times \text{Period of immersion (days)}} \quad (1)$$

Corrosion inhibition efficiency (IE) was then calculated using the equation

$$IE = 100[1-W_2 / W_1] \% \quad (2)$$

Where W_1=corrosion rate in the absence of the inhibitors and W_2=corrosion rate in the presence of the inhibitors

2.3. Electrochemical study

Polarization studies carried out in a CHI electrochemical workstation with impedance, Model 660 A, a three electrode cell assembly was used. Saturated calomel electrode (SCE) was the reference electrode and platinum was the counter electrode from the polarization study, corrosion parameters such as corrosion potential (E_{corr}), corrosion current (I_{corr}) and tafel slopes (anodic= b_a and cathodic = b_c) were calculated.

2.4. AC impedance measurements

EG and G electrochemical impedance analyzer model 6310 was used to record AC impedance measurements. A three electrode cell assembly was used. The working electrode was a rectangular specimen of carbon steel with one face of the electrode of constant 1 cm^2 area exposed. A rectangular platinum foil was used as the counter electrodes. A time interval of 5 to 10 minutes was given for the system circuit potential. There over this steady state potential an AC potential of 10mV was superimposed. The AC frequency was varied from 100MHz to KHz. the real part (Z') and imaginary part (Z'') of the cell impedance were measure in ohm for various frequencies. The R_t (Charge transfer resistance) and C_{dl} (double layer capacitance) values were calculated. C_{dl} values were calculated using the following relationship.

$$C_{dl} = \frac{1}{2 \times 3.14 \times f_{max} \times R_t} \quad (3)$$

"3. Results and Discussion"

3.1. Weight loss study

The corrosion inhibition efficiencies (IE) of MB (Methylene Blue) in controlling the corrosion of carbon steel immersed in aqueous solution 60 ppm Cl^- in the absence and presence of zinc ion. The influence of SPT (Sodium Potassium Tartrate) on MB –Zn^{2+} was studied and IE was found to 94%. The values indicates that the ability of MB- Zn^{2+} - SPT as a good corrosion inhibition. The values are given in table (1-3) Corrosion rates (CR) of carbon steel in aqueous solution in the absence and presence of inhibitors and the efficiencies obtained by weight loss method.

"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."

Immersion period – Three days

MB ppm	Zn^{2+} ppm	CR mdd	IE %
0	0	17.27	-
50	0	15.45	32
100	0	11.82	48
150	0	9.09	60
200	0	7.27	68
250	0	6.36	72

"Table 2. 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"

MB ppm	Zn^{2+} ppm	CR mdd	IE %
50	25	18.18	20
100	25	13.63	52
150	25	8.18	64
200	25	5.45	76
250	25	3.63	84

"Table 3. 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"

MB ppm	Zn^{2+} ppm	SPT ppm	CR mdd	IE %
50	25	250	15.90	30
100	25	250	10.00	56
150	25	250	5.90	74
200	25	250	2.72	88
250	25	250	1.36	94

MB 250 ppm alone has inhibition efficiency 72% increasing the concentration of Zn^{2+} shown the increasing efficiency. 250 ppm of Methylene Blue (MB) and 25 ppm of Zn^{2+} has 84% of inhibition efficiency (IE).

3.2. Influence of SPT on the inhibition efficiency of MB-Zn^{2+} system

It is observed that when SPT is added the inhibition efficiency of MB –Zn^{2+} system increases. The increase in IE is more pronounced at 250 ppm of SPT. Synergistic effect exists between MB- Zn^{2+} system and SPT 250 ppm of MG alone has 74% inhibition efficiency (IE). 250 ppm of Methylene Blue (MB) and 100 ppm of Zn^{2+} has 84% IE. 250 ppm of SPT is added their combination has 94% IE. (Table 1-4).

3.3. Analysis of Potentio dynamic Polarization Curves.

Polarization study has been used to study the formation of protective film on the metal surface. The potentio dynamic polarization curves of carbon steel immersed in an aqueous solution in the absence and presence of inhibitor are shown Figure 1.

The corrosion parameters namely corrosion potential (E_{corr}) Tafel slopes b_c and b_a linear polarization resistance (LPR) and corrosion current (I_{corr}) are given in table 4. It is observed figure (1) that when carbon steel immersed in an aqueous solution, the corrosion potential is -578mV Vs SCE (Saturated Calomel Electrode). The LPR value is 1.46 $x10^{-3}$ohm cm^2. The corrosion current value is 4.293×10^{-5} A /cm^2.

When 250 ppm of Methylene Blue (MB), 25 ppm of Zn^{2+}, 250 ppm of SPT 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. There is not much change in the value of anodic Tafel slopes (221 and 124 mv/decade).But there is slight change in the anodic Tafel slope (415 and 296 mv/decade).

Hence MB –Zn^{2+} - SPT system functions as mixed inhibitor. It is observed from table-4. The LPR value was increases and the corrosion current decreases. These observations suggest the formation of protective film on the metal surface.

"Table 4. corrosion parameters of carbon steel immersed in aqueous solution obtained from Potentiodymanic polarization study"

System	E_{corr}	b_a mv / dec	b_c mv / dec	LPR ohm cm^2	I_{corr} A / cm^2
Aqueous solution (Blank)	-578	415	221	$1.46x10^{-3}$	$4.293x10^{-5}$
Aqueous solution containing MB(250ppm) + Zn^{2+}(100ppm)+SPT (250 ppm)	-411	296	124	$8.67\ x10^{-4}$	$4.389x10^{-7}$

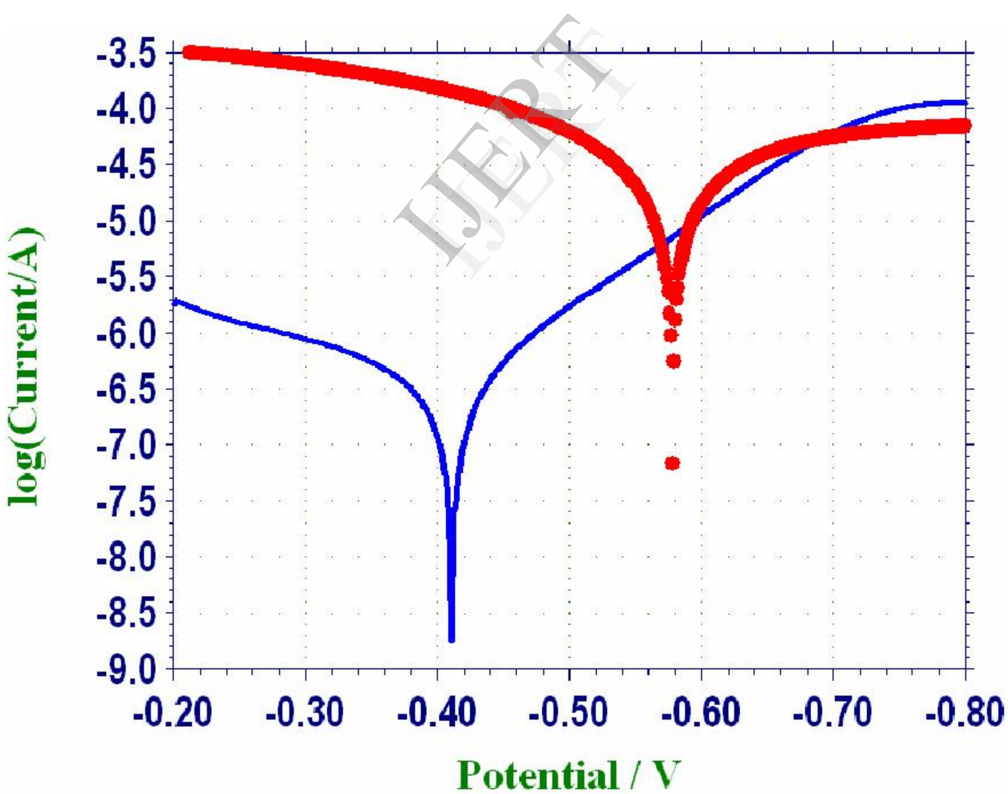

Figure 1. Polarization curves of mild steel immersed in various test solutions

a) **Aqueous solution (Blank) b) MB (250 ppm) + Zn^{2+} (25 ppm) + SPT (250 ppm)**

3.4. Analysis of AC impedance spectra

AC impedance spectra of carbon steel in aqueous solution in the absence and presence of inhibitors are shown in Fig (2) (Nyquist plot) Fig (3) (Bode plots).

The corrosion parameters namely charge transfer resistance (R_t) and double layer capacitance (C_{dl}) derived from Nyquist plots are given in table-5.

The impedance log (Z/ohm) values derived from bode plots are also given in table-5.

It is observed that when carbon steel immersed in an aqueous solution, the R_t value is 48 ohm cm^2. The (C_{dl}) value is 1.19 x 10^{-8} MF/cm^2.The impedance [log (Z/ohm] is 2.683.

When inhibitors 250 ppm of Methylene Blue (MB),25 ppm of Zn^{2+}, 250 ppm of SPT are added the R_t value increases from 428 to 1326 ohm cm^2. The C_{dl} value decreases from 1.19 x10^{-8} to 0.384 x 10^{-8} MF/cm^2. The impedance value increases from 2.683 to 3.939. This observation suggests that a protective film is formed on the metal surface.

Table 5. AC impedance parameters of carbon steel immersed in an aqueous solution and inhibitors"

System	R_t ohm cm^2	C_{dl} F/cm^2	Impedance (log Z/ohm)
Aqueous solution (Blank)	428	1.19 x 10^{-8}	2.683
Aqueous solution containing MB(250ppm) + Zn^{2+}(25 ppm) +SPT (250 ppm)	1326	0.3842 x 10^{-8}	3.939

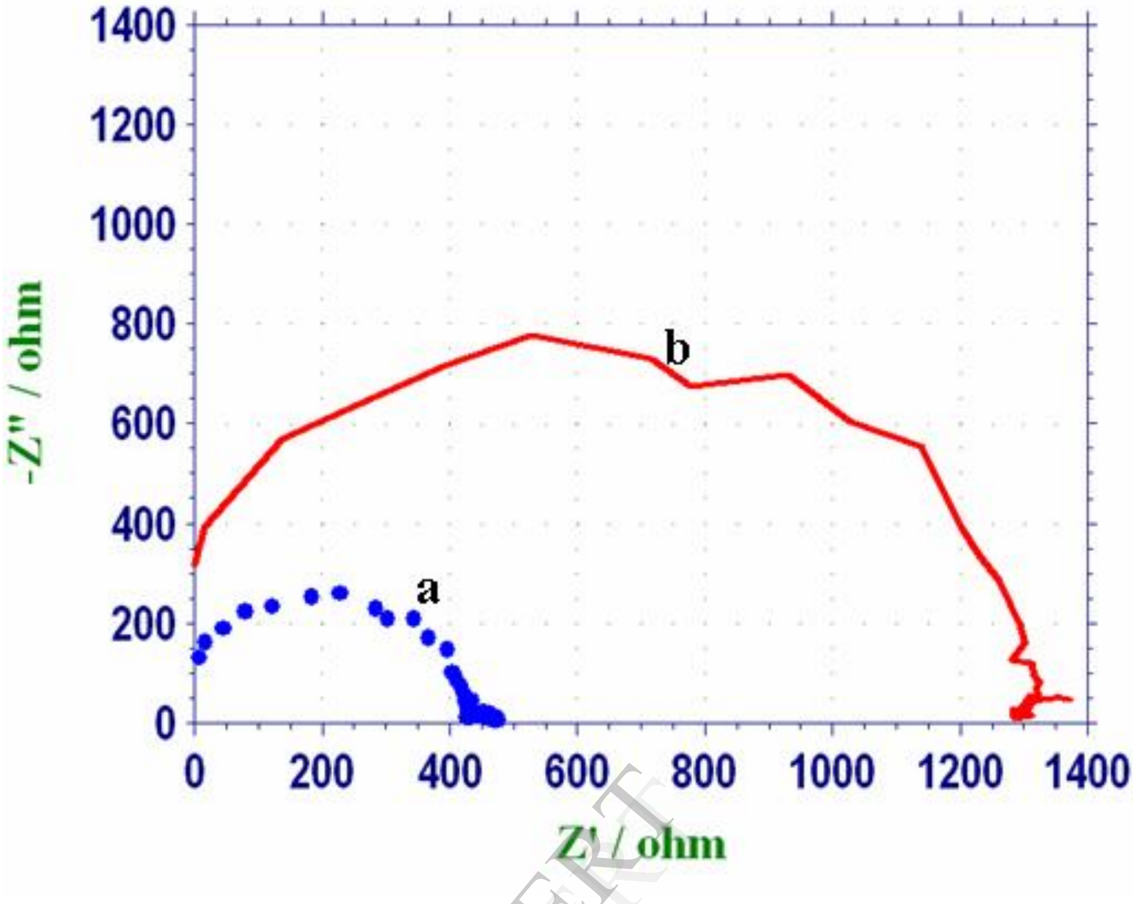

Figure 2. AC impedance spectra of mild steel immersed in various test solutions (Nquist Plot)

a) Aqueous solution (Blank)

b) MB (250 ppm) + Zn^{2+} (25 ppm) + SPT (250 ppm)

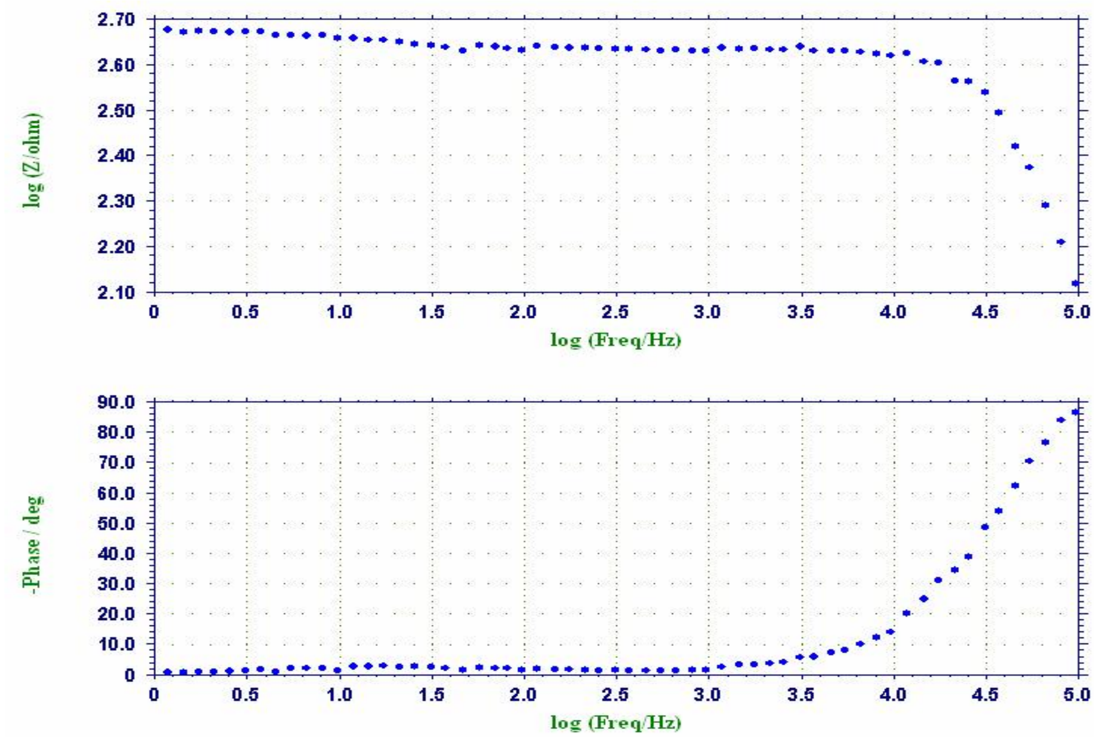

Figure 3a. AC impedance spectra of mild steel immersed in various test solutions (Bode Plot)

a) Aqueous solution (Blank)

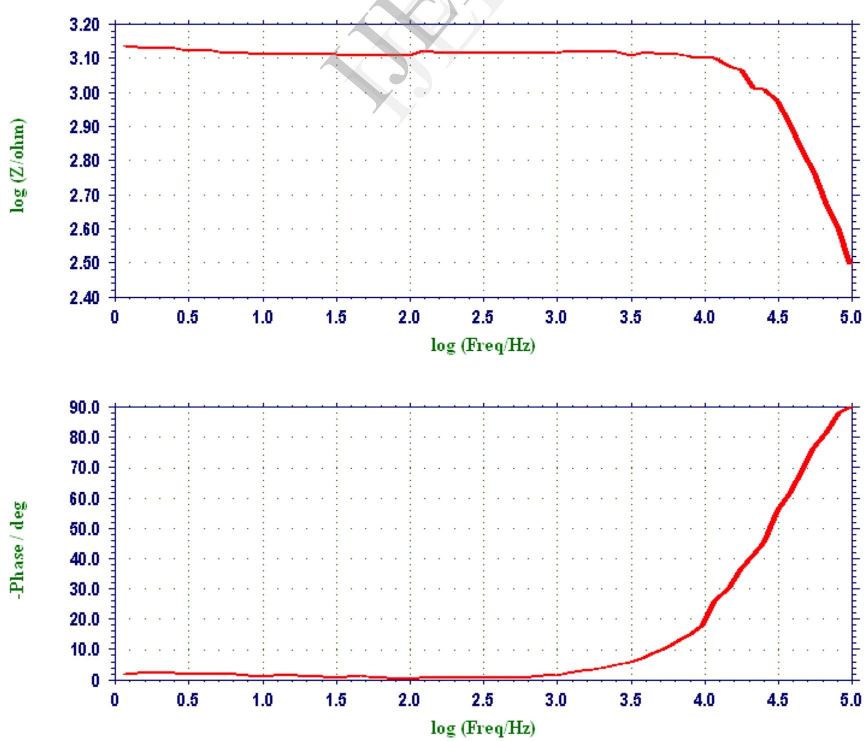

Figure 3b. AC impedance spectra of mild steel immersed in various test solutions (Bode Plot)

a) MB (250 ppm) + Zn^{2+}(25 ppm) + SPT(250 ppm)

"4. Conclusion"

The results of the weight loss study shows that the formulation consisting of 250 ppm of Methylene Blue (MB) and 25 ppm of Zn^{2+}, 250ppm of SPT has 94% inhibition efficiency (IE) in controlling corrosion of carbon steel in an aqueous solution. A synergetic effect exists between Zn^{2+} and Methylene Blue (MB) and SPT.

- Polarization study reveals that, this formulation function as anodic inhibitor. AC impedance spectra reveal that a protective film is formed on the metal surface.
- When the aqueous solution contains 250 ppm of Methylene Blue (MB), 25 ppm of Zn^{2+} and 250 ppm of SPT is prepared there is formulation of Zn^{2+}-MB and Zn^{2+}-SPT complex in solution.
- When carbon steel is immersed in this solution Zn^{2+}-MB and Zn^{2+}-SPT complex diffuses from the bulk of the solution towards metal surface.
- On the metal surface Zn^{2+}-MB-SPT complex is converted in to Fe^{2+}-MB, Fe^{2+}-SPT complex on the anodic sites. Zn^{2+} is released.
- Zn^{2+}-MB, Zn^{2+}-SPT+Fe^{2+} $\rightarrow$ Fe^{2+}-MB,Fe^{2+}-SPT +Zn^{2+}.
- The released Zn^{2+} combines with OH^- to form $Zn(OH)_2$ on the cathodic sites.
- $Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2\downarrow$

"5.References"

[1]. S. Rajendran , B.V.Apparao and N. Palaniswamy,Synergistic effect of molybdate and Zn^{2+} on the inhibition of corrosion of mild steel in neutral aqueous environment, J Electrochem Soc 47(1998) 43.

[2].S. Rajendran , B.V. Apparao , A. Mani and N. Palaniswamy, Corrosion inhibition by ATMP-molybdate-Zn^{2+} system in low chloride media, Anti Corrosion Methods Mater 45(1998)25-30.

[3].S.Rajendran , B.V. Apparao and N. Palaniswamy. Synergistic effect of 2-chloro ethyl phosphonic acid and Zn^{2+}, Anti Corrosion Methods Mater 47(2000)294-297.

[4].S. Rajendran , B.V.Apparao and N. Palaniswamy, Synergistic, biocidal effects of amino (trimethylene phosphonic acid) Polyacrylamide and Zn^{2+} on the inhibition of corrosion of mild steel in neutral aqueous environment, Anti Corrosion Methods Mater 44(1997) 308-313.

[5].S. Rajendran, S. Vaibhavi , N. Anthony and D.C. Trivedi,Transport of inhibitors and corrosion inhibition efficiency, Corrosion 59(2003)529-534.

[6].S.Rajendran,A.John Amalraj, M. Jasmine Joice, A. Moreen, D.C.Trivedi and M.Sunderavadivelu, Corrosion inhibition of the caffeine –Zn^{2+} system, Corrosion Rev 22(2004)233.

[7].E.E.Ebenso,and E.E. Oguzie, Corrosion inhibition of mild steel in acidic media by some organic dyes, Mat. Letters 59(2005)2163- 2165.

[8].Qguzie, Corrosion inhibition of mild steel in hydro chloric acid solution by methylene blue dye Mat. Letters 599(2005)1076-9.

[9]. J.Sathiya Bama, S.Rajendran, J.Arockia Selvi, Eriochrome Black –T as Corrosion inhibitor for carbon steel in well water, Bulletin of Electro Chemistry, 22(2006) 363

[10]. Susai Rajendran, M. Manivannan, J. Wilson Sahayaraj, J. Arockia Selvi, J. Sathyabama, A.J. Amalraj and N. Palaniswamy, Corrosion behaviour of Aluminium in Methyl orange solution at pH 11, Transaction of the SAEST, 63(2006)41.

[11]. D.A. Jones, Principles and Prevention of Corrosion, second ed., Prentice-Hall Inc., New Jersey, 1996.

[12].V.S. Sastry, Corrosion Inhibitors. Principles and Applications, John Wiley & Sons, New York, 1998.