Paper No.
SS25

CORCON 2017
17-20 September
Mumbai, India

CORROSION CONTROL OF MILD STEEL USED IN OIL AND NATURAL GAS INDUSTRIES BY TRIAZOLE DERIVATIVES IN 1 M HCl

Pratap P.Kamble
Chemistry Research Laboratory
Department of Chemistry, R.J.College,Ghatkopar,Mumbai,India
Email- pratapkamblerjc@gmail.com

Dr. R.S.Dubey
Chemistry Research Laboratory
Department of Chemistry, R.J.College,Ghatkopar,Mumbai,India

ABSTRACT:

Corrosion behaviour of mild steel and its control by bezotriazole and benzoyl benzotiazole in1M HCl has been investigated by weight loss, open circuit potential (OCP) and potentiodynamic polarization techniques. Microstructure of surface was analyzed by scanning electron microscopy (SEM) and energy dispersive analysis by X-ray (E-DAX).The polarization curves revealed that both the compounds behaved as mixed-type inhibitors. The inhibitors efficiency increased with increase in the concentration of both the inhibitors .The adsorption of inhibitor molecules on mild steel surface obeyed Langmuir adsorption isotherm .The presence of thin film formed due to adsorption may be responsible for decrease in corrosion rate of the mild steel.

Key words: *corrosion inhibition, Mild steel, HCl, triazole derivatives.SEM, E-DAX.*

INTRODUCTION:

Mild steel is the most common choice of material which is extensively used in the production and transportation of crude oil in the oil and natural gas industry[1].The main problem concerning mild steel application is its relatively low corrosion resistance in acidic solutions[2].The most commonly used media is hydrochloric acid. Hydrochloric acid solutions are widely used for acid cleaning, industry acid pickling,oil well acidizing and acid rescaling [3].The strong acid medium can cause structural damage to mild steel . Therefore the use of inhibitors is one of the most practical methods for the protection of metal against corrosion in acid media [4].There are several types of corrosion

inhibitors which are widely used to control corrosion problem of mild steel. Usually, an organic compound that exerts significant influence on the extent of adsorption on the metal surface can be used as effective corrosion inhibitors. Regarding the adsorption of inhibitors on the metal surface, Two types of interaction are possible .First is physical adsorption which involves electrostatic force between ionic charges or dipoles of the adsorbed species and electric charge of metal /solution interface and the second is chemical adsorption which involves charge sharing or charge transfer from the inhibitor molecules to the metal surface to form coordinated types of bonds[5].Organic compounds containing hetero atoms, pi electrons in the form of double and triple bonds and aromatic rings in there structures are mostly used as inhibitors. Several heterocyclic compounds such as Quinoline derivates, pyrazole derivatives, Imidazole derivatives, pyridine derivatives, pyridazine derivatives, Schiff base compounds can be used as effective corrosion inhibitors in various corrosion environments [6]

In present investigation an attempt have been made to study the inhibitive effects of Two synthesized triazole derivatives, benzotriazole and benzoyl benzotriazole ,on corrosion of mild steel in 1M HCL using weight loss and electrochemical techniques such as open circuit potential, potentiodynamic polarization. The passive film formed on the surface is further confirmed by SEM and EDX.

2. EXPERIMENTAL PROCEDURE:

2.1. MATERIAL AND SAMPLE PREPARATION

The weight loss and electrochemical experiment were performed on mild steel specimen having chemical composition, C-0.16%, Si-0.10%, Mn-0.40%, P-0.013%, S-0.02% and remaining iron. The exposed dimensions were 1cmx3cmx0.025cm and $1cm^2$ for the weight loss and electrochemical experiment respectively. Before exposure to test solution exposed areas were cleaned with different grades of metallographic emery paper,1/0,2/0.3/0,and 4/0, washed with doubled distilled water, degreased with acetone and finally dried and stored in desiccators.

TEST SOLUTION

1 M HCL was prepared by dilution of 36% HCI (analytical grades) in bi-distilled water.

2.2. SYNTHESIS OF INHIBITORS

Procedure for synthesis of benzotriazole:

10.8 gm of O-phenylenediamine was added to a mixture of 12 gm (11.5 ml) of glacial acetic acid and 30 ml of water, which was cooled to 15^0C.solution of 7.5 gm of sodium nitrite in 15 ml water was added all at ones, the mixture being stirred with the glass rod or by slow mechanical stirrer .The temperature increased slowly to 85^0C and then cooled slowly. When temperature was 45^0C the mixture was chilled in an ice bath for 30 minutes. A pale brown solid separated by filtration. Recystallisation was done using benzene as the solvent.

Procedure for synthesis of benzoyl benzotriazole:

To a solution of benzotriazole (11.9 g ,0.1 mole) in anhydrous dichloromethane (200 ml) at 0^0 C under nitrogen, triethyl amine (17 ml ,0.12 mol) was added drop wise, followed by addition of Benzoyl chloride (0.11 mol).The resulting mixture was stirred at room temperature for 1-2 hours. The reaction was quenched at this temperature with hydrochloric acid (2 N,200ml), and the organic

phase was separated with hydrochloric acid (2N,2x50 mi) and water (50 ml) sequentially .The organic extract were dried over anhydrous magnesium sulphate , filtered and evaporated to dryness to give a white powdery solid which was purified by recrystallisation from water.

The characterization data, IUPAC name, structure and abbreviation used for the synthesized compound are given below in Table 1.

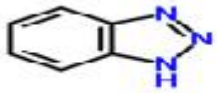
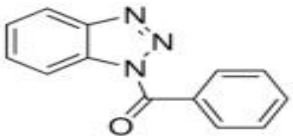
Sr.no	IUPAC name	Chemical structure	Analytical data
1	1,2,3-Benzotriazole		**MP** – 98^{0}C - 100^{0}C. **FT-IR- υ max/cm^3.** 1208,870,775,745,729,1615,1360.
2	Benzoyl bezotriazole		**MP** – 140^{0}C - 142^{0}C. **FT-IR- υ max/cm^3.** 1208,870,775,1775,750, 740,1355,1600.

Table 1: IUPAC name, molecular structure, melting point and analytical data of studied inhibitors.

2.3. Weight loss measurement:

The weight loss experiment was performed by immersing mild specimen in 50 ml of test solution with and without different concentration of inhibitors. After 24 h immersion time, the mild steel specimen were taken out, cleaned with distilled water, dried and accurately weighed. Each experiment was performed in triplicate to obtain good result and the mean value is reported. The inhibition efficiency was calculated by using the following relation.

$$\eta\% = \frac{W_0 - W_{corr}}{W_0}$$

Where W_0 and W_{corr} are the weight loss in absence and presence of inhibitors .The surface coverage is given by following relation

$$\theta = \eta\%/100.$$

2.4 Electrochemical measurement:

Polarization studies were carried out using electrochemical measurement system, DC 105, containing software of DC corrosion technique from M/S Gamery instrument, 734 Louis Drive, Warminster, PA, USA. For polarization studies, mild steel specimens having surface area of 1cm^2 were exposed to acid solution .Mild steel as working electrode, saturated calomel (SCE) as reference electrode and graphite as auxiliary electrode were used for all electrochemical measurement. Before each measurement the specimen were allowed to corrode freely, and their OCPs were measured as a function of time to obtain a steady-state potential. The anodic and cathodic Tafel curve were obtained by changing the electrode potential automatically from 0.5 and 0.5 v. at the scan rate of 5mv/s. polarization study was done with and without inhibitors in 1M HCl.

2.5 Surface measurement:

The surface film formed on the metal specimen was evaluated by SEM-EDX analysis. This was carried out by SEM/EDX model QUANTA-200 from the Netherlands. The spectra were recorded for a period of 24 hours in 1M HCl in the absence and presence of 500 ppm inhibitors. The energy of acceleration beam employed was 20 kv.

3. RESULT AND DISCUSSION

3.1 Weight loss experiment:

The loss in the weight of mild steel coupons in 1M HCl in absence and presence of different concentration of benzotriazole and benzoyl benzotriazole was determined after 24 hours immersion period at 25^0C+1^0C.The percentage inhibition efficiency (%E) and degree of surface coverage (θ) were calculated and presented in Table.2.In the two cases it can observed from the table that the inhibition efficiency increased with increase in concentration of inhibitors and the compounds acted as very good corrosion inhibitors for corrosion of mild steel in 1M HCl. The maximum efficiency for each compound was achieved at 500 ppm concentration. The parameter (θ) which represents the part of the metal surface covered by the inhibitors molecules increased as the inhibitors concentration increased. The corrosion inhibition can be attributed to the adsorption of inhibitors at the metal /acid interface.

Inhibitor	Concentration (ppm)	Weight loss(mg)	Surface coverage	Inhibition efficiency (%E)
Blank	**-**	**235**	**-**	**-**
Benzotriazole	**100**	**184**	**0.217**	**21.70**
	200	**136**	**0.419**	**41.90**
	300	**92**	**0.608**	**60.80**
	400	**51**	**0.784**	**78.40**
	500	**12**	**0.949**	**94.90**
Blank	**-**	**431**	**-**	**-**
Benzoyl	**100**	**190**	**0.559**	**55.90**
Benzotriazole	**200**	**135**	**0.687**	**68.70**
	300	**102**	**0.762**	**76.20**
	400	**88**	**0796**	**79.60**
	500	**71**	**0.835**	**83.50**

Table 2: The weight loss parameter obtained for mild steel in 1 M HCl containing different concentrations of Benzotriazole and Benzoyl Benzotriazole.

3.2. Adsorption isotherm:

The values of surface coverage θ were evaluated using the value of %IE resulted from weight loss experiment in 1M HCl .Figure 1 shows a plot C/θ v/s C gave a straight line with a coefficient $(R)^2$ value very close to unity. It indicates that corrosion control take place via adsorption. The adsorption of inhibitors molecules on mild steel surface obeys Langmuir adsorption isotherm. The equation can be represented as:

$$K_{ads} = \frac{\theta}{C(1-\theta)}$$

The equation can be rearranged to

$$C_{inh}/\theta = 1/K_{ads} + C_{inh}$$

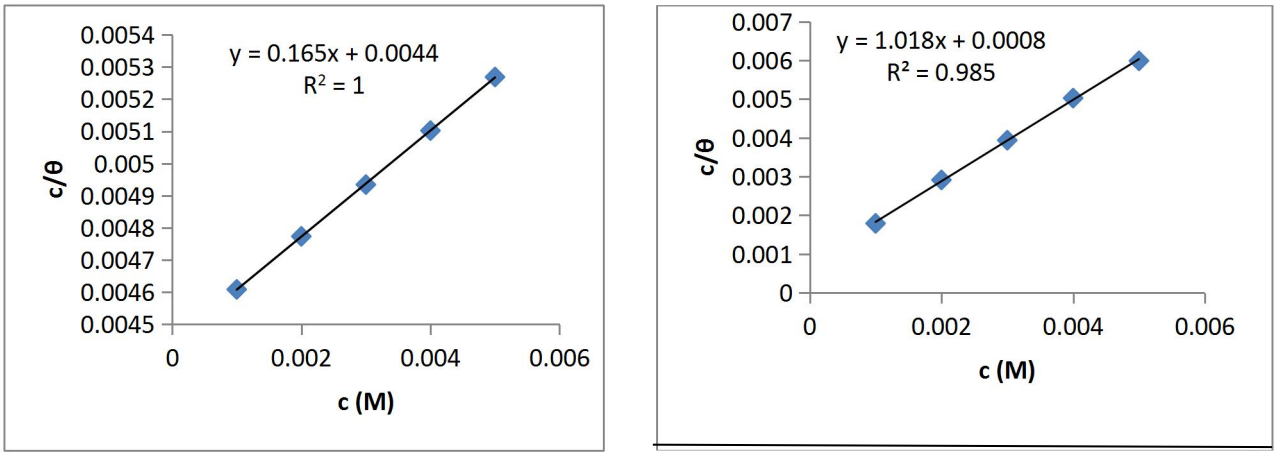
Where, C_{Inh} is the concentration of inhibitor, θ is surface coverage and K_{ads} is the equilibrium constant for adsorption – desorption process. The K_{ads} is related to standard free energy (ΔG^0_{ads}) of adsorption by following relation.

Free energy of adsorption: (ΔG^0_{ads}) =- 2.303 RT log (55.5 K_{ads}).

Where R is the universal gas constant, T is the absolute temperature in K ,and the numerical value 55.5 represent the molar concentration of water in acid solution.The calculated values of K_{ads} and ΔG^0_{ads} at studied temperature is listed in Table 3.

Compound	slope	K_{ads}	Regression coefficient	ΔG^0_{ads} (KJ.mol)
Benzotriazole	0.004	250	1	-23.635
Benzoyl Benzotriazole	0.0008	1250	0.985	-27.6232

Table 3: slope, equilibrium constant, regression coefficient and free enthalpy of adsorption of benzotriazole and benzoyl bezotriazole in 1 M HCl.



(a) **(b)**

Fig 1:Langmuir isotherm plot for adsorption of Benzotriazole (a) and Bezoyl Bezotriazole (b) on mild steel surface in 1 M HCl

Generally the magnitude of ΔG_{ads} around -20 kJ/mol less negative indicates physisorption and those around -40kJ/mol or more negative indicate chemisorptions. In the present case calculated values for both the inhibitors benzotriazole and benzoyl benzotriazole are – 23.635 and – 27.6232 respectively. This indicated the adsorption of inhibitors on the mild steel surface involved both physical and chemical process (7-8).

3.4Open circuit potential:

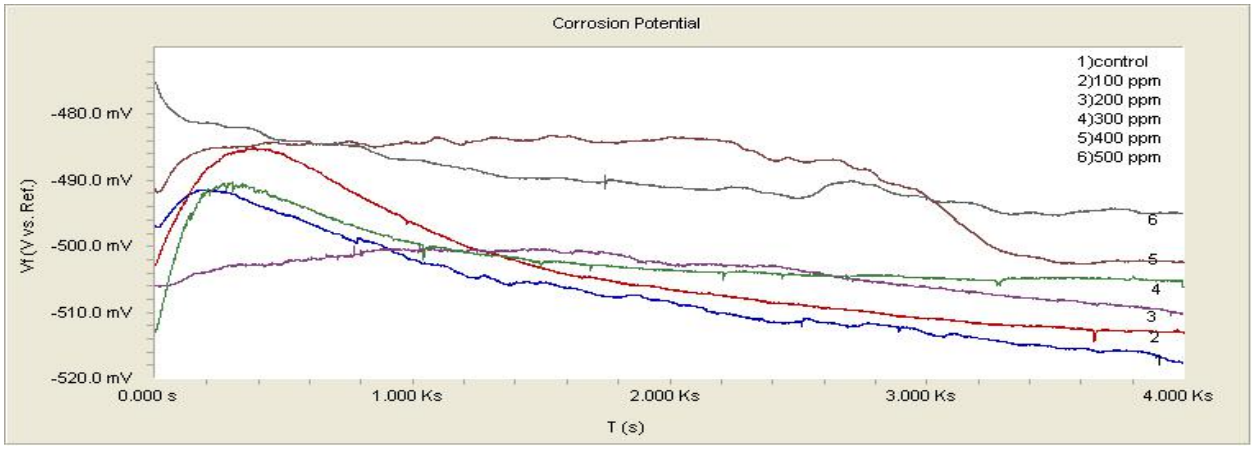


Fig 2(a): Open circuit potential diagram for mild steel in 1 M HCl without and with different concentrations of benzotriazole.

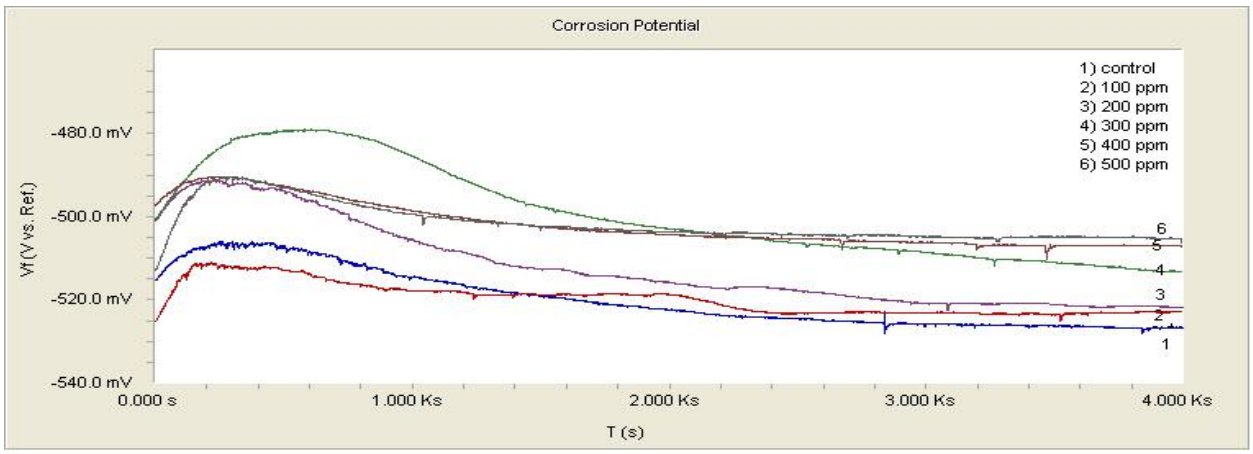


Fig 2 (b): Open circuit potential diagram for mild steel in 1 M HCl without and with different concentrations of benzoyl benzotriazole.

The evolution of open circuit potential with time for mild steel in 1M HCl solutions without and with benzotriazole and benzoyl benzotriazole is shown in figure 2(a) and figure 2 (b) respectively. The plot shows a clear change in the OCP curve due to the presence of the inhibitors.It is clear that the curve shifts in positive direction in the presence of benzotriazole and benzoyl benzotriazole. The inhibited solution exhibited higher positive open circuit potential value ,when compare with those obtained in blank solution, indicating formation of the protective film due to the adsorption of inhibitor on the mild steel surface. The continuous shift to the positive direction can be attributed to the formation of protective and inhibitive film,which increase with increasing the inhibitor concentration and immersion time[9].

3.5 Potentiodynamic polarization studies:

Polarization measurement were carried out in order to get information regarding kinetics of anodic and cathodic reactions. The obtained polarization curves for mild steel in 1M HCl in absence and presence of different concentration of benzotriazole and benzoyl benzotriazole are shown in figure3.corrosion kinetic parameter E_{corr}, I_{orr} ,Tafel (β_a ,β_c) and inhibition efficiency depicted in table

3.The lower current density (I_{corr}) values in the presence of inhibitors without causing significant changes in corrosion potential (E_{corr}) suggest that compound were mixed type inhibitors and adsorbed on the surface thereby blocking the corrosion reaction . The Tafel constants β_a and β_c were both affected and there were no definite trends in the shift of E_{corr} values. This indicates that compounds are mixed type inhibitors [10].

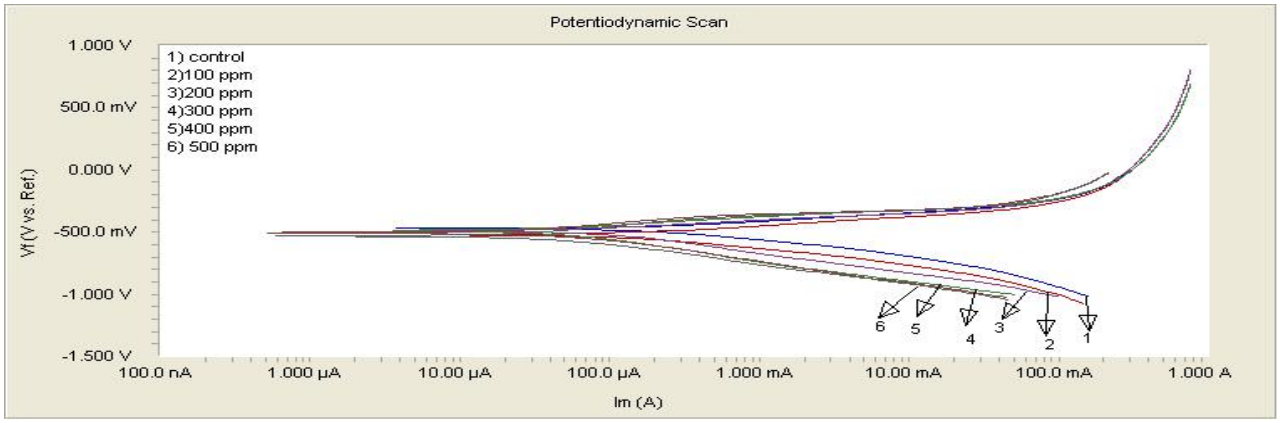


Fig. 3 (a): potentiodynamic polarization curve for mild steel in 1 M HCl without and with different concentrations of benzotriazole.

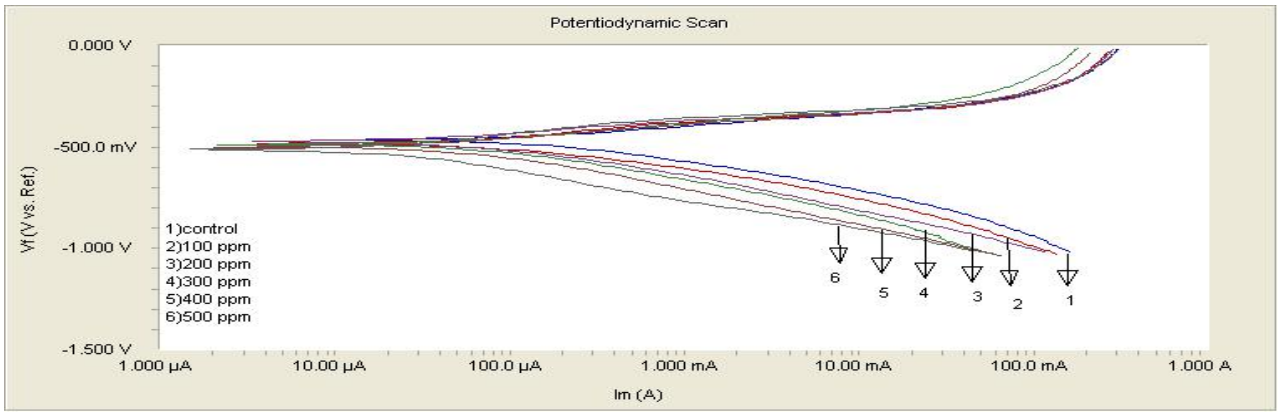


Fig. 3 (b): potentiodynamic polarization curve for mild steel in 1 M HCl without and with different concentrations of benzoyl benzotriazole.

Acid Medium	Concentration (ppm)	$-E_{corr}$ (mv)	I_{corr} ($\mu A/cm^2$)	β_a (v/dec)	β_c (v/dec)	IE %
1 M HCl	-	-471.0	197.0	91.30	163.4	-
	100	-524.0	157.0	86.80	142.8	20.30
	200	-488.0	108	70.40	160.2	45.18
	300	-495.0	74.60	66.10	155.8	62.13
	400	-483.0	46.70	85.60	100.8	76.29
	500	-504.4	12.50	82.40	109.3	93.65

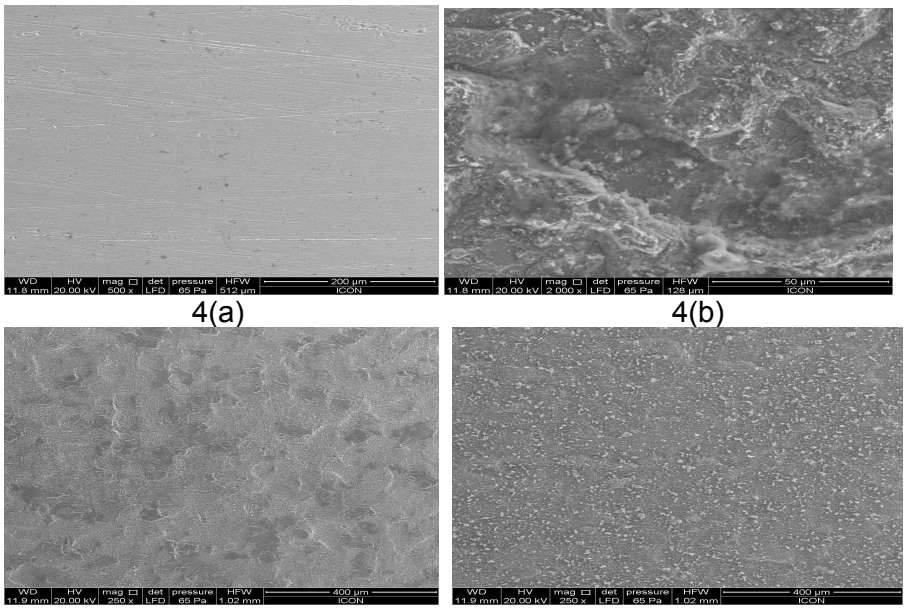
Table 4(a):potetiodynamic electrochemical parameter obtained for mild steel in 1 M HCl containing different concentration of benzotriazole.

Acid Medium	Concentration (ppm)	$-E_{corr}$ (mv)	I_{corr} ($\mu A/cm^2$)	β_a (v/dec)	β_c (v/dec)	IE %
1 M HCl	-	-464.0	178.0	78.00	157.2	-
	100	-483.0	76.30	94.10	129.6	57.13
	200	-487.0	58.60	83.30	142.5	67.07
	300	-471.0	46.90	80.00	139.4	73.65
	400	-499.0	38.00	84.00	138.2	78.65
	500	-513.0	25.40	111.2	151.6	85.73

Table 4(b): potentiodynamic electrochemical parameter obtained for mild steel in 1 M HCl containing different concentration of benzoyl benzotriazole.

3.6 SEM studies:

A photograph of the polished mild steel surface before immersion in 1M HCl is shown in figure 4aThe photograph shows the surface was smooth and without pits. The photograph of mild steel after immersion in 1M HCl is shown in figure 4b. The photograph indicates that surface was strongly damaged in absence of inhibitors. A photograph of mild steel after immersion in 1M HCl solution containing 500 ppm of benzotriazole and benzoyl benzotriazole is shown in figure 4(c-d) It is found that surface is free from pits and it was smooth. Thus we can conclude that in presence of both the inhibitors corrosion was inhibited strongly.



4(a) 4(b)

4(c) 4(d)

Fig.4 SEM micro graphs of mild surface-4(a) before immersion in 1 M HCl, 4(b) after one day immersion in 1 M HCl and 4(c) after one day of immersion in 1 M HCl+500 ppm of benzotriazole, 4(d) after one day immersion in 1 M HCl + 500 ppm benzoyl benzotriazole.

3.7 EDX studies:

Figures 5(a – d) show the EDX spectrum in the absence and presence of bezotriazole and benzoyl benzotriazole .Figure 5(c) show and additional peak characteristic for existence of nitrogen (N). Figure 5(d) shows additional peaks characteristic of N and O, indicating that the inhibitors molecule adsorbed on the metal surface.EDX investigation thus confirms the polarization data, that the presence of Triazole derivatives inhibits the corrosion of mild steel in 1M HCl due to adsorption of its molecules on the mild steel surface preventing it from being corroded easily.

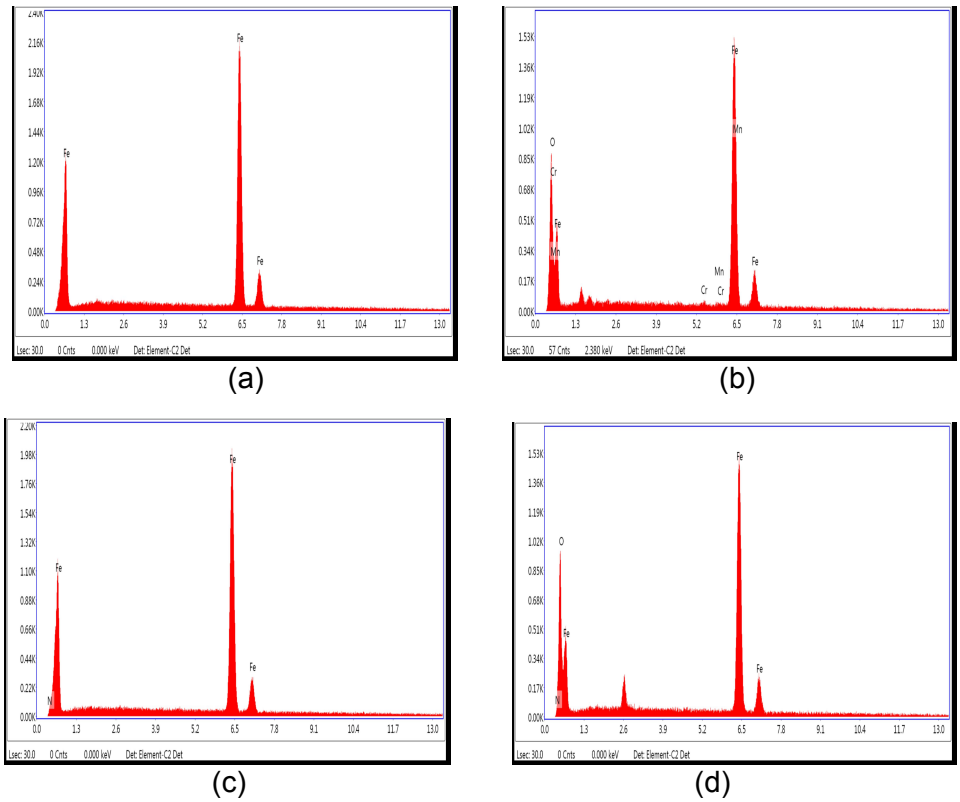


Fig.5 EDX of mild surface (a) before immersion in 1 M HCl, (b) after one day immersion in 1 M HCl and (c) after one day of immersion in 1 M HCl+500 ppm of benzotriazole, (d) after one day immersion in 1 M HCl + 500 ppm benzoyl benzotriazole.

3.7 MECHANISM OF INHIBITION:

The inhibition effect of benzotriazole and benzoyl benzotriazole derivatives towards the corrosion of mild steel in 1m HCl solution may be attributed to the adsorption of these compounds at the metal-solution interface. The inhibition process is a function of the metal, inhibitor concentration and temperature as well as inhibitor adsorption abilities which depends on adsorption sites[11] .The mode of adsorption (physisorption and chemisorption) observed could be attributed to the fact that inhibitors contains different donating atoms which can be adsorbed chemically and physically [12]. In case of benzotriazole the inhibition effect is due to interaction of pi electrons of benzene and triazole rings as well as the presence of electron-donating atoms such as nitrogen through which benzotriazole form bond with mild steel .similarly the inhibitive effect of benzoyl benzotriazole is because of pi electron of benzene and triazole ring, along with hetero atoms such as nitrogen and oxygen through which the inhibitor adsorbed on mild steel surface to form insoluble ,stable and uniform film.

4 CONCLUSIONS:

1) Benzotriazole and benzoyl benzotriazole were effective corrosion inhibitors and acted as mixed type inhibitors for mild steel corrosion in 1M HCl.
2) The corrosion process was inhibited by the adsorption of these molecules on mild steel surface and the inhibition efficiency increased with increase in concentration of both inhibitors.
3) In determining the corrosion rates, electrochemical studies and weight loss measurement gave similar result.
4) Adsorption of both the inhibitors for mild steel obeyed the Langmuir adsorption isotherm.
5) The value of ΔG^0_{ads} was low and negative, which indicated spontaneity of the adsorption process.
6) SEM-EDX analysis showed that there was improvement in surface morphology of inhibited mild steel as compared with uninhibited mild steel.

5 REFERENCES:

1. E. Guzie, F. Wing, “Corrosion inhibition and adsorption behavior of methionine on mild steel in sulfuric acid and synergistic effect of iodide ion”, J. Colloid interface sci.2007, 310, pp.90-98.
2. M.Seter, M.J.Thomson, J.Stoimenovski, D.R. Macfarlane, M.Forsyth, “Dual active ionic liquid and organic salt for inhibition of microbially influenced corrosion”. Chem.Commun.2012, 48, pp.5983-5985.
3. D. Gopi, K.Govindraju, L. Kavitha, “Investigation of triazole derived Schiff bases as corrosion inhibitor for mild steel in hydrochloric acid medium”.J.Appl.Electrochem.,2009,39,pp.269-276.
4. M. Ayman, A. Atta Gamal,El-Mahdy, A Hamad.Al-Lohedan and Abdel Rehman O.Ezzat, “A new Green Ionic Liquid-Based corrosion Inhibitors for steel in Acidic Environments”, Molecules 2015,20,p.11131.
5. N. labjar,S.El Hajjaji; M.Lebrini, M.Sarghini, C.Jama, F.Bentiss, “Enhanced corrosion resistance properties of carbon steel in hydrochloric acid medium by –(methylinephophonic):surface characterization”.J.M.Environ.Sci. 2(4) 2011, pp. 309-318.
6. A.S.Fouda, K.Shalabi, R.Ezzat, “Evaluation of some thiazole derivatives as acid corrosion inhibitors for carbon steel in aqueous solutions”. .J.M.Environ.Sci.6 (4)2015, pp.1022-1029.
7. P.N.S.Yadav, Br.Corrosion .Journal.34 (1) 1999 (51).
8. J.Shukla , K.S Pitre, “Electrochemical behavior of brass in acid solution and the inhibitor ffect of imidazole”. Corosion Rev., 2002, 20(3), pp.217-230.
9. A.S.Fouda,G.Y.Elewady ,K.Shalabi, S.Habbouba. “Gibberellic acid as green corrosion inhibitors for carbon steel in hydrochloric acid solutions”. J.M.Environ.Sci, 5 (3) (2014) pp.767-778.
10. N.P.Chakraverthy,K.N.Mohana,C.B.Pradeepkumar. “Corrosin inhibition effect and adsorption behavior of nicotinamide derivatives on mild steel in hydrochloric acid”. Int.J.Ind Chem (2014)5:19
11. K.U.Singh, R.S.Dubey, “Electrochemical investigation of some benzimidazole derivatives as corrosion inhibitors for mild steel in acid solution”. Int.J.Chem, Vol 3(1) (2014):pp.100-111.
12. Ahamad I,Khan, S. Ansari, M.A. Quraishi, J Chem Pharma Res.2011, 3 (2),p.703.