Hexamine as Corrosion Inhibitor for Mild Steel in Acidic Medium

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ABSTRACT

The corrosion inhibition of mild steel in 1.0 M HCl solution was investigated using Hexamethylene tetramine (hexamine) as a corrosion inhibitor by using different techniques i.e. weight loss method, potentiodynamic polarization and Electrochemical Impedance Spectroscopic (EIS) at 35.0^o C. Further, the surface study of corroded specimen was carried out by inverted trinocular metallurgical research microscopy. It was observed that the percentage corrosion inhibition efficiency increases with increase in the concentration of inhibitor. The maximum percentage corrosion inhibition efficiency was 93.0 % at a concentration of 800 ppm. Impedance study shows the increases in R_{ct} value with increase in the concentration of inhibitor. Potentiodynamic polarization studies showed that Hexamine behave as mixed type of corrosion inhibitor. Results obtained from corrosion experiments shows that Hexamine is a very good corrosion inhibitor for mild steel in 1.0 M HCl.

Introduction

Mild steel is widely used as material in a variety of industrial application such as petroleum; production, pipeline, construction etc. It also used in fabrication purpose due to its good mechanical properties and low cost and easy availability. The main drawback of mild steel is that it is highly responsive to corrosion attack and it is also dissolute in acidic medium [1]. Most of the acids with sufficient dilution are commonly used in industries. Chemical cleaning, acid descaling and in acid pickling which causes corrosion attack on mild steel [2, 3]. Corrosion process is responsible for the deterioration of valuable properties of mild steel and destruction the metal surface. There are many methods to protect the metal surface from these attacks but one of best selected method is use of corrosion inhibitors [4, 5]. There are different type of organic and inorganic compound, pharmaceutical drugs like tryptamine [6], thiazole derivatives [7,8], benzimidazole [9-13], and 1,3,4-oxadiazloe derivative [14] which are used as corrosion inhibitor to control corrosion on metals and their alloys [15]. The organic inhibitors are preferred over inorganic inhibitor as they contains electronegative group, π electron in multiple bonds and aromatic ring in their structure, which act as the main adsorption centers [16-18]. The effectiveness of organic inhibitor also depends on electron density of donor atom size and structure of inhibitor [19-21].

In continuation to our earlier study [22-26], the present study aims to investigate the inhibitive properties of hexamine as corrosion inhibitor on mild steel in acidic solution at 35.0^0C. All corrosion kinetics parameters have been studied by using four techniques i.e. Weight loss technique, EIS (Electrochemical Impedance Spectroscopy), Potentiodynamic polarization techniques and Mettallurgical research microscopy technique.

Experimental details :

Preparation of Materials

All Experiments were carried out on mild steel coupons. The composition (weight %) of mild steel used was : C 0.054%, Mn 0.26%, Si 0.015% , Ni 0.0098 % , Cr 0.056% , S 0.017%, P 0.019% ,Cu 0.010, Mo 0.018, Ti 0.002 and balance Fe. Metal specimens were cut into size 3.0×1.0 cm^2. Prior to the corrosion study, the surface of these coupons were polished with emery paper (Si C grade 100-1000), washed with double distilled water, dried with hot air dryer and then degreased with acetone and dried again before storing in desiccator.

Inhibitor:

Hexamethylene tetramine (Hexamine) was purchased from CDH, New Delhi (AR). The Structure of hexamine with molecular formula $C_6H_{12}N_4$ is shown below:
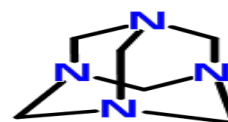
Weight loss techniques

The weight loss study was carried at 35.0 ^{0}C temperature with immersion time 12.0 & 24.0 hours. After the completion of experiment the sample were removed from corroding solution i.e. 1.0 M HCl & washed with double distilled water and degreased with acetone then dried and weighed again.

In each case triplicate experiments were carried out and the average weight loss value was recorded. Through the weight loss results, Percentage corrosion inhibition efficiency (PCIE %), corrosion rate (C_R) and surface coverage (θ) were calculated by using following equations:

$$\text{PCIE (\%)} = \frac{w_o - w_i}{w_o} \times 100 \qquad ... (1)$$

$$\theta = \frac{w_o - w_i}{w_o} \qquad ... (2)$$

Where, w_0 and w_i are the weight loss value of mild steel sample in absence and presence of inhibitor, respectively.

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The corrosion rate (C_R) of mild steel was calculated using the relation :

$$C_R \ (mpy) = \frac{87.6 \times w}{A \ t \ D} \qquad \qquad .... (3)$$

Where, 'w' is weight loss of mild steel in 'mg', A is the area of the coupon (cm^2), t is the exposure time (h) and D is the density of mild steel (g cm^{-3}).

Electrochemical measurements

Electrochemical impedance spectroscopy and Potentiodynamic polarization measurements were performed using Metrohm Autolab Model PGSTAT 128N potentiostat. Electrochemical measurements were carried out in a conventional three electrodes electrochemical cell with the mild steel as a working electrode, a platinum counter electrode and saturated calomel electrode as reference electrode. Before the electrochemical experiments, the surface of mild steel was polished with different grades emery paper (100-1000) and surface area was taken in range $1.0 \times 1.0 \ cm^2$.

EIS measurements were carried out in frequency range of 10 kHz to 0.01Hz with signal amplitude of 10 mV at the corrosion potential. The experiments were carried out in the absence and presence of different concentrations of inhibitor which were previously used in weight loss experiments. The measurements were automatically controlled by Z-view software and the impedance diagrams were given in the Nyquist representation. electrochemical impedance parameters such as Charge Transfer Resistance (R_{ct}) and Double Layer Capacitance (C_{dl}) were calculated from EIS data.

The potentiodynamic polarization measurements were made after EIS studies in the same cell setup, in a potential range of -200 mV to +200 mV with respect to open circuit potential, at a scan rate of 1.0 mV/ sec. From the Tafel plots, the corrosion potential E_{corr}, corrosion current density I_{corr}, Tafel slopes β_a and β_c were obtained in the absence and presence of inhibitors at different concentrations.

Surface Analysis (Metallurgical Research Microscopy Technique) :

The Surface morphology of mild steel coupons after its weight loss measurement in presence and absence of different concentration of inhibitor in 1.0 M HCl for 24.0 h at 35.0 ^{0}C were examined by trinocular inverted Metallurgical Research Microscopy technique. Percentage porosity (PP), total object (TO), maximum perimeter and maximum area of corroded surface at different concentrations of inhibitor was also calculated using the Metallurgical software provided with instrument.

Result and Discussion

Weigh loss measurement

The relationship between percentage corrosion inhibition efficiency and corrosion rates with varying concentrations of inhibitor for different immersion time at 35.0 ^{0}C are shown in Figure 1. The weight loss data values such as inhibition efficiencies (IE%), corrosion rates (CR), weight loss (mg) and the surface coverage (θ) are calculated for different concentrations of hexamine in 1.0 M HCl for different immersion time at 35.0 ^{0}C and values that obtained from these calculations are listed in Table 1. Table 1 shows that there is increased in percentage corrosion inhibition efficiency, surface coverage (θ) and decreased corrosion rate with increase in concentration of inhibitor i.e. 100 to 800 ppm that might be due to the increased adsorption of inhibitor on the mild steel surface with increase in inhibitor concentration at 35.0 ^{0}C [27]. It is also clear that there is variation of PCIE% and

corrosion rates (CR) with immersion time from 12 to 24 h, the PCIE% slightly increased with immersion time from 91.67 to 93.35 at 800 ppm and corrosion rate also increased with immersion time. Thereby weight loss experiments results suggests that hexamine is an effective inhibitor for mild steel in 1.0 M HCl up to 24.o h of immersion time.
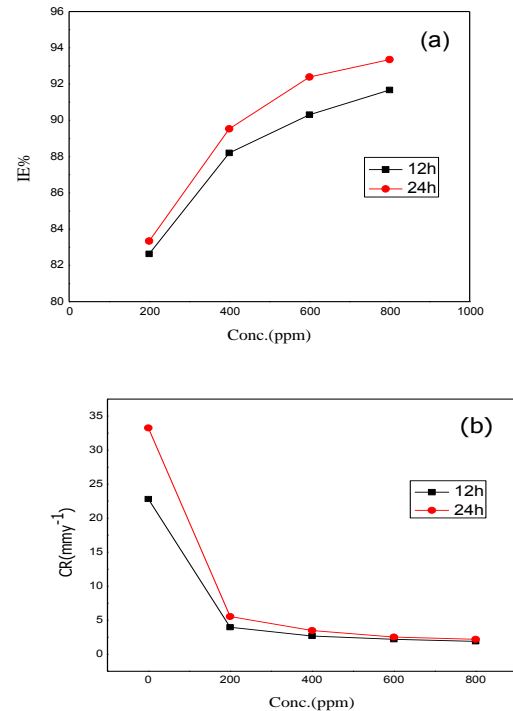

Fig 1. Variation of Percentage corrosion inhibition efficiency (a) and corrosion rates (b) with different concentrations of corrosion inhibitor at different time of exposure at 35.0 ^{0}C.

Electrochemical Impedance Spectroscopy Experiments :

The result obtained from impedance spectroscopy experiments were presented in the form of Nyquist plot for mild steel in 1.0 M HCl in the presence and absence of different concentration of hexamine as corrosion inhibitor are shown in Figure 2. The Nyquist plots are semicircle in nature and it can be seen from the plots that diameter of semicircle increases with increase in the inhibitor concentration in 1.0 M HCl solution. It shows that the impedance of mild steel is increased with increase in concentration of inhibitor which further supports the adsorption of inhibitor molecule on surface of mild steel.
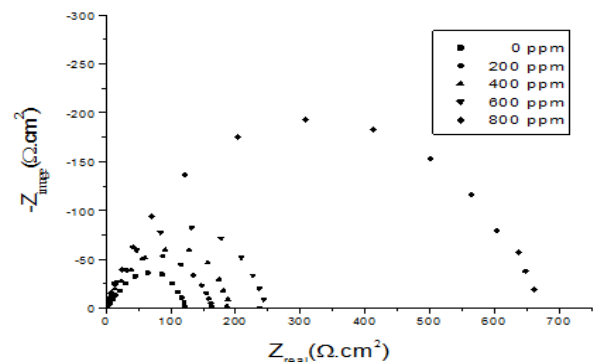

Figure 2. Nyquist plots for mild steel samples in 1.0 M HCl with presence and absence of different concentrations of hexamine as corrosion inhibitor.

Before the impedance spectroscopy experiments, the mild steel sample which used as working electrode were immersed in test solution about 30 minutes for each concentration to obtain a static OCP value. All the impedance parameters that are obtained from impedance experiments such as Charge Transfer Resistance (R_{ct}), Double Layer Capacitance (C_{dl}) and Percentage corrosion inhibition efficiency are shown in Table 2. The value obtained for charge transfer resistance (R_{ct}) was calculated from the difference in impedance (Z_{real}) lower and higher frequencies.

From the Table 2, it is observed that the charge transfer resistance (R_{ct}) value increases with increase in the concentration of inhibitor in the solution. The decrease in C_{dl} (double layer capacitance) with increase in the concentration of inhibitor, indicates the increase in the thickness of double layer [28] which cover the metal surface electrode or decrease in local dielectric constant [29,30] which also leads to an increase in the PCIE%. The C_{dl} value is calculated by using following equation [31]

$$C_{dl} = \frac{1}{2\pi f_{max} R_{ct}} \qquad \text{.... (4)}$$

f_{max} is the frequency value at the top of semicircle and it is mid way of Z_{real} and also at which Z_{image} component is maximum.

The percentage corrosion inhibition efficiency of different tested samples are calculated from R_{ct} value using following equation [32].

$$I.E.\% = \frac{R_{ct\,(inh)} - R_{ct}}{R_{ct\,(inh)}} \qquad \text{... (5)}$$

Where, R_{ct} and $R_{ct\,(inh)}$ are the charge transfer resistance in absence and presence of different concentrations of inhibitor. Therefore, all these results shows that there is formation of insoluble protective inhibitor molecule film due to the adsorption of hexamine on the surface of mild steel. It is important to notify that the significant difference in corrosion inhibition efficiency between weight loss measurement and electrochemical impedance measurement, probably due to the different immersion time of sample for weight loss 12 and 24 h and impedance 30 min (to stabilized the OCP).

Potentiodynamic Polarization Experiments:

Potentiodynamic Polarization curves of mild steel in 1.0 M HCl solution in absence and presence of different concentration of inhibitor are shown in Figure 3. From the Figure 3, it can be seen that the inhibitor effect the both cathodic and anodic polarization curves to the same extent.

First of all the inhibitor adsorbed on the surface of electrode and decrease the anodic dissolution and also retarded the hydrogen evolution reaction at cathode that shows both cathodic and anodic reaction were suppressed with addition of inhibitor. The electrochemical polarization parameters values such as corrosion potential ($-E_{corr}$), corrosion current density (I_{corr}), anodic (β_a) and cathodic (β_c) Tafel constant, polarization resistance (R_p) and percentage corrosion inhibition efficiency (PCIE %) are listed in Table 3. It is observed from the Table 3 that I_{corr} values decreased, polarization resistance (R_p) and Percentage corrosion inhibition efficiency increased with increase in the concentration of inhibitor. It is also seen that there is large difference in inhibition efficiency between weight loss measurement and polarization study that is higher for weight loss than polarization due to effect of immersion time and different units of expressing corrosion rates in the two experiments.

The values of polarization resistance, cathodic and anodic Tafel constant are used to calculate the corrosion current (I_{corr}) by using following equation (Stern-Geary equation):

$$I_{corr} = \frac{\beta_a X \beta_c}{2.303(\beta_a + \beta_c)} X \frac{1}{R_p} \qquad \text{... (6)}$$

The percentage corrosion inhibition efficiency (PCIE %) for each concentrations of inhibitor are calculated by using following equation :

$$PCIE\% = (1 - \frac{I_{corr}{}^i}{I_{corr}{}^0}) \times 100 \qquad \text{... (7)}$$

Where, $I_{corr}{}^0$ & $I_{corr}{}^i$ are the current density of uninhibited or inhibited solution.
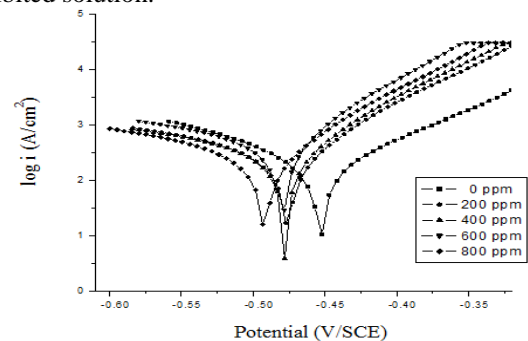

Figure 3. Potentiodynamic polarization curves for the corrosion of mild steel in 1.0 M HCl with and without different concentrations of hexamine as corrosion inhibitor.
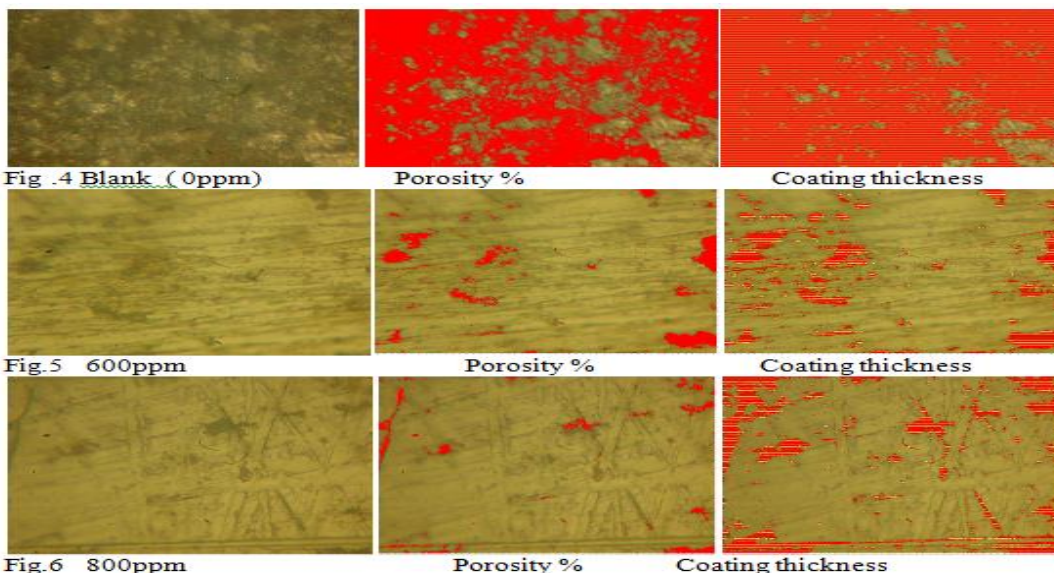

Fig 4-6. Surface image of mild steel coupons at different concentrations (0, 600, 800 ppm) of inhibitor.

According to Riggs [33], (a) if the value of displacement in ($-E_{corr}$) is higher than 85 mV with respect to ($-E_{corr}$), the inhibitor can be seen as anodic or cathodic type inhibitor, and (b) if value of displacement in ($-E_{corr}$) is lower than 85 mV, the inhibitor can be acts as mixed type inhibitor. In present work, the maximum displacement in (E_{corr}) is 41 mV, which clearly indicates that hexamine act as mixed type inhibitor or exhibited both anodic and cathodic type inhibitor.

Surface Analysis

Metallurgical research microscopy technique was used for mild steel samples in absence and presence of different concentrations of hexamine as corrosion inhibitor and shown in Figures 4-6. It is clear from the Figure 4-6 that the surface of mild steel sample becomes more clear and smooth with increase in the concentration of inhibitor. Other surface analysis parameters such as percentage porosity, coating thickness, total object present on mild steel sample with and without the presence of inhibitor concentration are shown in Table 4. The results obtained from the Table 4 shows that the percentage porosity and total object decreases with increase in concentration of inhibitor [30] hence shows that there is

formation of thin protective layer on the surface of mild steel that protect metal from the corrosion.

Conclusion

Hexamine was found to be an effective corrosion inhibitor for mild steel in 1.0 M HCl solution. Weight loss study have shown that the percentage corrosion inhibition efficiency increases with increase in concentration of inhibitor and maximum inhibition efficiency was found to be 91.90 % at 800 ppm with immersion time 24 hours. The results obtained from impedance study indicates that there is formation of continuous protective film on mild steel surface to reduce corrosion and increased percentage corrosion inhibition efficiency with increase in concentration of hexamine as corrosion inhibitor. Polarization studies have shown that hexamine act as a mixed type inhibitor. Metallurgical research microscopy technique shows that the surface of mild steel get more clear and smoother with increase in concentrations of hexamine and it indicates that there is formation of protective layer on the surface of mild steel sample.

Table 1. Percentage corrosion inhibition efficiency (PCIE) values for the corrosion of mild steel in 1.0 M HCl solution in the absence and in presence of different concentrations of hexamine from weight loss experiments at 35.0 ^{0}C at 12.0 h and 24.0 h of immersion times.

Inhibitor	Conc.(ppm)	Weight loss (mg)	Surface coverage (θ)	CR (mpy)	PCIE
Hexamine (12.0 h)	Blank	144	-	22.81	-
	200	25	0.82	3.96	82.63
	400	17	0.88	2.69	88.20
	600	14	0.90	2.21	90.31
	800	12	0.91	1.90	91.67
(24.0 h)	Blank	210	-	33.26	-
	200	35	0.83	5.54	83.34
	400	22	0.89	3.48	89.53
	600	16	0.92	2.53	92.39
	800	14	0.93	2.21	93.35

Table 2. Different Impedance parameters and PCIE in presence and absence of different concentrations of hexamine as corrosion inhibitor at 35.0 ^{0}C.

Inhibitor name	Conc. (ppm)	R_{ct} (Ω.cm^2)	C_{dl} (μF.cm^{-2})	PCIE
Hexamine	Blank	119.47	191.77	-
	200	162.36	141.11	26.47
	400	193.85	118.92	38.37
	600	242.65	94.42	50.76
	800	660.59	34.68	81.91

Table 3. Potentiodynamic polarization experiments data for mild steel samples in 1.0 M HCl solution with and without different concentration of hexamine as corrosion inhibitor at 35.0 ^{0}C.

Inhibitor name	Conc. (ppm)	β_a(mVd^{-1})	β_c(mVd^{-1})	R_p(Ω.cm^2)	$-E_{corr}$(mV vs.SCE)	i_{corr}(μA cm^{-2})	%I.E
Hexamine	Blank	534	373	42.5	-458	2.24	-
	200	422	468	56.5	-486	1.70	24.10
	400	352	476	67.4	-488	1.30	41.96
	600	465	476	108	-485	0.94	58.03
	800	362	350	131	-499	0.58	74.10

Table 4. Surface parameters study of mild steel samples after weight experiment with and without presence of different concentration of hexamine for 24.0 h at 35.0 ^{0}C.

Conc. (ppm)	Maximum area (micron)	Maximum perimeter (micron)	Coating thickness (micron)		Total object	Percentage Porosity
			Maximum Thickness	Avg. Thickness		
Blank	719771.46	12308.38	676.316	68.193	564	88.03
600	9300.00	726.60	173.684	12.493	315	5.12
800	3164.81	695.84	181.579	12.763	196	2.67

References :

1. Singh A K, Quraishi M A. Inhibitive effect of diethylcarbamazine on the corrosion of mild steel in hydrochloric acid. Corros Sci 2010; 52:1529–1535.

2. Laamari R, Benzakour J, Berrekhis F, Abouelfida A, Derja A, Villemin D. Corrosion inhibition of carbon steel in hydrochloric acid 0.5 M by hexa methylene diamine tetramethyl-phosphonic acid. Arabian J of Chem 2011; 4:271–277.

3. Bahrami M J, Hosseini S M A, Pilvar P Experimental and theoretical investigation of organic compounds as inhibitors for mild steel corrosion in sulfuric acid medium. Corros Sci 2010; 52:2793–2803.

4. Fouda A S, Ibrahim A A, El-behairy W T. Thiophene derivatives as corrosion inhibitors for carbon steel in hydrochloric acid solutions. Der Pharma Chemica 2014; 6:144-157.

5. Stanly Jacob K, Parameswaran G. Corrosion inhibition of mild steel in hydrochloric acid solution by Schiff base furoin thiosemicarbazone. Corros Sci 2010; 52:224–228.

6. Lowmunkhong P, Ungthararak D, Sutthivaiyakit P. Tryptamine as a corrosion inhibitor of mild steel in hydrochloric acid solution. Corros Sci 2010; 52:30–36.

7. Quraishi M A, Sharma H K. Thiazoles as corrosion inhibitors for mild steel in formic and acetic acid solutions. J of Appl Electrochem 2005; 35:33–39.

8. Lian H Q, Liu R Q, Zhu L Q, Wang J D. Inhibition corrosion of thiazole derivatives on A3 steel in 1 mol/L HCl solution. Chinese J of Appl Chem 2006; 23:676–681.

9. Wang L. Evaluation of 2-mercaptobenzimidazole as corrosion inhibitor for mild steel in phosphoric acid. Corros Sci 2001; 43:2281–2289.

10. Popova A, Christov M, Deligeorigiev T. Influence of the molecular structure on the inhibitor properties of benzimidazole derivatives on mild steel corrosion in 1 M hydrochloric acid. Corros Sci 2003; 59:756–764.

11. Popova A, Christov M, Raicheva S, Sokolova E. Adsorption and inhibitive properties of benzimidazole derivatives in acid mild steel corrosion. Corros Sci 2004; 46:1333–1350.

12. Khaled K F. The inhibition of benzimidazole derivatives on corrosion of iron in1 M HCl solutions. Electrochimica Acta 2003; 48:2493–2503.

13. Wahdan M H. The synergistic inhibition effect and thermodynamic properties of 2-mercaptobenzimidazol and some selected cations as a mixed inhibitor for pickling of mild steel in acid solution. Materials Chemistry & Physics 1997; 49:135–140.

14. Bentiss F, Traisnel M, Lagreneé M. The substituted 1,3,4-oxadiazoles: a new class of corrosion inhibitors of mild steel in acidic media. Corros Sci 2000; 42:127–146.

15. Aejitha L S, Kasthuri PK. Inhibition Action of Mild Steel Corrosion in HCl Acid Medium by Extract of Digera Muricata. Inter J of Sci & Res 2014; 3:607-611.

16. Dean Jr S W, Derby R, Von dem bussche GT. Inhibitor types. Materials Performance 1981; 20:47-51.

17. O L Riggs Jr., Corrosion Inhibitors, secnd ed., C.C. Nathan, Houston, TX, 1973

18. Hosseini S M A, Azimi A. The inhibition of mild steel corrosion in acidic medium by 1-methyl-3-pyridin-2-yl-thiourea. Corros Sci 2009; 51:728–732.

19. Doner A, Kardas G. N-Aminorhodanine as an effective corrosion inhibitor for mild steel in 0.5 M H$_2$SO$_4$. Corros Sci 2011; 53:4223–4232

20. Deng Li X, Fu S H. Triazolyl blue tetrazolium bromide as a novel corrosion inhibitor for steel in HCl and H$_2$SO$_4$ solutions. Corros Sci 2011; 53:302-309.

21. Bentiss F, Traisnel M, Gengembre L, Lagrenee M A. new triazole derivative as inhibitor of the acid corrosion of mild steel: electrochemical studies, weight loss determination, SEM and XPS. Appl Surf Sci 1999; 152:237–249.

22. Kumar H and Kumari M Corrosion Characteristics of Cetyl Trimethyl Ammonium Bromide for Carbon Steel in Hydrochloric Acid Solutions Elixir Corrosion & Dye 2016; 93:39321-39330.

23. Kumar H, and Kumari M Corrosion Characteristics of 1,2,3-benzotriazole for carbon steel in hydrochloric acid solutions. Int J Chemical Studies 2016; 4:32-39.

24. Kumar H and Yadav V. Citrus sinensis peels as a Green Corrosion Inhibitor for Mild Steel in 5.0 M Hydrochloric Acid Solution. Res J of Chem Sci 2016; 6:53-60.

25. Saini V and Kumar H. N, N, N, N-Tetramethylethylenediamine (TMEDA) and 1, 3-Diaminopropane (DAP) as Vapour Phase Corrosion Inhibitor (VPCI) for mild steel under Atmospheric conditions. Res J of Chem Sci 2014; 4:45-53.

26. Ahamad I, Prasad R and Quraishi MA. Inhibition of mild steel corrosion in acid solution by Pheniramine drug: Experimental and theoretical study. Corros Sci 2010; 52:3033–3041

27. Naqvi I, Saleemi A R, Naveed S. Cefixime: A drug as Efficient Corrosion Inhibitor for Mild Steel in Acidic Media.Electrochemical and Thermodynamic Studies. Intern J of Electrochemical Sci 2011; 6:146 – 161.

28. McCafferty E, Hackerman N. Double Layer Capacitance of Iron and Corrosion Inhibition with Polymethylene Diamines. J of the Electro Soc 1972; 119:146–154.

29. Babic-Samardzija K, Lupu C, Hackerman N, Barron AR, Luttge A. Inhibitive properties & surface morphology of a group of hetrocyclic   diazoles as inhibitors for acidic iron corrosion. Langmuir 2005; 21:12187–12196.

30. Kumar H, Yadav V. Citrus sinensis peels as a Green Corrosion Inhibitor for Mild Steel in 5.0 M Hydrochloric Acid Solution. Res J of Chemical Sci 2016; 6:1-19.

31. Machnikova E, Kenton W H, Hackerman N. Corrosion inhibition of carbon steel in hydrochloric acid by furan derivatives. Electrochimica Acta 2008; 53:6024–6032.

32. Torres V V, Rayol V A, Magalhães M, Viana G M, Aguiar L C S, Machado S P, Orofino H, D'Elia E. Study of thioure as derivatives synthesized from a green route as corrosion inhibitors for mild steel in HCl solution. Corros Sci 2014; 79:108–118.

33. A Mamari K, Zarrok H, Zarrouk A, Salghi R, Ebensoc E E, Hammouti B, Chaouch A, Oudda H, Essassi E M, E Bakri M. Anti-corrosion properties of indole derivative for carbon steel in HCl solution. Der Pharmacia Lettre 2013; 5:319-326.