

INHIBITIVE EFFECT OF HEXAMETHYLENETETRAMINE ON MILD STEEL IN BRACKISH WATER

Saifee K. Fatima. ^{1*}, Filmwala Zoeb. A² and Hussain Kaneez. F³

¹ & ² Chemistry Department, JJT University, Jhunjhunu, Rajasthan (India).

³Chemical Engineering Department, College of Engineering & Petroleum, Kuwait University (Kuwait).

1.1 Abstract

Hexamethylenetetramine (HMTA) was found suitable as corrosion inhibitor on mild steel in Brackish Water (BRW) by weight loss methods with respect to time, concentration and temperature measurements. Corrosion Inhibitor film efficiency depends on the chemical concentration and contact time with the surface of mild steel. As the temperature increases Corrosion Rate increases but mostly Inhibition Efficiency decreases. Thermodynamic factors show that the adsorption on mild steel followed both physio-chemical adsorption mechanisms. Synergetic effect of potassium iodide (KI) in corrosive media has been found to stabilize the adsorption, leading to improved inhibition efficiency and found to control general and pitting corrosion rate to maximum extent. Hexamethylenetetramine has been studied by keeping consideration of International Standard procedures i.e. NACE SP-0775 2013 and ASTM G1-03. The results were supplemented with scanning electron microscopy (SEM) and infra-red (IR) spectroscopy. The results showed that HMTA is a good corrosion inhibitor.

Key Words: Hexamethylenetetramine (HMTA), Brackish Water (BRW) Potassium Iodide (KI), scanning electron microscopy (SEM).

1.2 INTRODUCTION

In oil and gas production, corrosion is a major factor in aqueous environments. Brackish water utilized in the production is normally defined as fresh water and little salty but comparatively less salty-water than seawater, which contains soluble and insoluble salts, has low total dissolved solids (TDS), low concentration of cations and pH is slightly basic. If pH of brackish water is lower than 7.5 can be corrosive on mild steel resulting in catastrophic failures of piping, elbows, reducers and tees. [1] In oil production, wash water routed through brackish water storage tanks and utilized in the 2nd stage desalter which collects incomplete cleaned crude oil from the 1st stage desalter. It is also used for pressure maintenance or secondary recovery. Brackish water is found in the depth of 4,000 feet or more and sometime it is found in aquifers of coastal areas.[2] Mild steel is widely used in many industries because of economically cost-effective and easy fabrication, but it is prone to undergo severe corrosion in aggressive environmental conditions.

Corrosion is a naturally occurring process an unwelcome occurrences, caused by the dissolution of metal through an accidental chemical or electrochemical reactions at the interface between the metal and electrolyte and reduce their life.[3] The natural state of iron in the form of reddish brown color (Fe₂O₃) ferric oxide ore, which also called as rust, produced during corrosion of iron and steel which tend to revert back to iron oxide Fe₂O₃ (Iron oxide) and weakens the iron and steel.[4] The main concern is our everyday problem that came across due to corrosion. Corrosion, in general, and pitting corrosion, in particular, need to be protected to increase the life of material.[5] The factors which affects corrosion in brackish water is low concentration of dissolved solids, low conductivity, and high concentration of dissolved oxygen, other

parameters, such as temperature, flowing velocity and exposure duration, have also important influences on the corrosion processes.[6] Bacterial activity is the main factor of localized corrosion in brackish water, which depends heavily on water chemistry. The aim of the present investigation was to obtain reliable information regarding the composition of Brackish Water and their corrosion causing capacity on mild steel. Water is a chief constituent in all stages of oil and gas production. Injection of corrosion inhibitor through different sites are important to inhibit from corrosion during the production, transportation, storage, and separation of crude oil and natural gas. The key role is to maintain the pipelines other equipment, piping system and connected pipelines in good condition in oilfield is depend on the proper corrosion protection technology.

The aim of this work is to study the corrosion inhibition of HMTA with Synergistic Effect of Potassium Iodide (KI) and sulfanilamide (SFA) on mild steel in Brackish Water (BRW). Weight loss method was used for corrosion inhibition efficiency evaluation at different inhibitor concentration and at different temperatures. The results were supplemented by SEM and IR studies.

1.3 EXPERIMENTAL

1.3.1 Materials and methods

1.3.1.1 Surface Preparation of the Corrosion coupon:

In the present work, mild steel was used as material for the corrosion studies. The specimens used for corrosion tests with a dimension of 2 x 2 cm. Chemical composition of mild steel coupons (C=0.20%, Mn=1.00%, Si=0.05%, S=0.025%, P=0.25% and Fe=98%) have been used.[7] The surface of the specimens was polished using emery paper (Silicon carbide, grade 200 - 800), rinsed with distilled water, dried and immersed in acetone for 5 seconds, and finally dried at room temperature and then weighed. These polished coupons were subjected to water test in agreement as per international standards i.e. NACE SP-0775 2013 and ASTM G1-03 to make sure the metal surfaces were free of scratches and other apparent defects like pits. All reagents that were used for the study were of analytical grades and double distilled water.[8]

1.3.1.2 Organic Compound

Hexamethylenetetramine is white crystalline compound is highly soluble in water, chloroform, ethanol, and some other organic solvents. It has a cage-like structure similar to adamantane. The molecular formula of Hexamethylenetetramine is $C_6H_{12}N_4$. The molecular structure of Hexamethylenetetramine compound is:

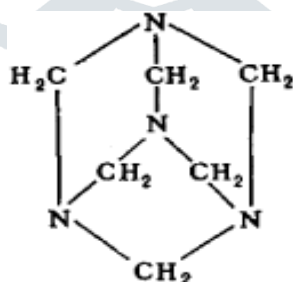


Figure 1: Molecular Structure of Hexamethylenetetramine

1.3.1.3 Preparation of Hexamethylenetetramine (HMTA), Potassium Iodide and Sulfanilamide (SFA) solutions.

Brackish water used to make different concentration of 0.1, 0.2 and 0.3 Molarity solution prepared in BRW for Hexamethylenetetramine in 50 ml volume. Potassium Iodide solution used during the experiment is 4 ppm. 0.1 Molarity of Sulfanilamide solution prepared in 50 ml volume in BRW. From the prepared

solution of Hexamethylenetetramine and Sulfanilamide, volume used in the ratio of 60:40. Brackish water was used for weight loss corrosion rate and corrosion efficiency determination.

Brackish water was used for weight loss corrosion rate and corrosion efficiency determination. From the physicochemical properties of the brackish it was determined that oil field fluids, the higher the concentration of the inorganic ions present, the higher the chances of corrosion and it is influenced by the following corrosion variables, namely: conductivity, Total dissolved solids, pH, dissolve gases, intensity of microbiological activities, temperature, pressure, and velocity. The most parameters to check water quality in brackish water are chlorides, carbonate, bicarbonate, sulfates, calcium, magnesium, iron and sodium are present. Chloride typically represents the most significant percentage of the total dissolved solids to promote extremely aggressive corrosion, particularly localized (pitting, crevice, etc.) corrosion.

1.3.2 Weight Loss Corrosion Coupon Analysis

The mild steel corrosion coupons were used during weight loss experiment, immersed in Brackish Water at different concentrations of 0.1, 0.2 and 0.3 Molarity of HMTA for 1 day and 30 days weight loss. The experiments were carried out to study the corrosion inhibition effects of Hexamethylenetetramine (HMTA) with and without corrosion inhibitor, synergistic effect of Potassium Iodide (KI) and Sulfanilamide at different concentrations and at different temperatures. Mild steel coupons were accurately weighed and then immersed in 50 ml test solution contained in a plastic bottle. The first bottle was used as blank and rest were used as blank without inhibitor and rest were used to contained as with corrosion inhibitor kept at constant temperature $25 \pm 1^\circ\text{C}$ throughout the experiment. After the period of 1 day and 30 days, the mild steel coupons were removed, scrubbed with 000 grade steel wool in soap solution, degreased with acetone, dried in warm air and re-weighed. Corrosion coupon test specimens were prepared, cleaned and analyzed as per international standards i.e. NACE SP-0775 2013 and ASTM G1-03. A calculation of average corrosion rate (CR), expressed as uniform rate of thickness loss per unit time in mils per year (mpy) is shown in equation (1)

$$CR = \frac{WX365X1000}{ATDX(2.54)^3} = \frac{2.227X10^4 XW}{ATD} \quad (1)$$

Table. 1 Classification of Corrosion and Pitting Rates as per NACE SP0775-2013

(mpy = mils per year)

General Corrosion	Corrosion rate	Pitting Corrosion Rate	Pitting Rate
Low	<1 mpy	Low	<5 mpy
Moderate	1-4.9 mpy	Moderate	5-7.9 mpy
High	5-10 mpy	High	8-15 mpy
Severe	>10 mpy	Severe	>15 mpy

The corrosion inhibition efficiency IE (%) was calculated using the equation (2)

$$IE (\%) = \frac{W_0 - W}{W_0} \times 100 \quad (2)$$

Where W_0 is the weight loss in the absence of inhibitor in solution and W is the weight loss in the presence of inhibitor in the solution.

1.4 RESULTS AND DISCUSSION

1.4.1 Analysis of 1 day and 30 days Weight Loss Study

The weight loss study of mild steel immersed in Brackish water for a period of 1 day and 30 days of varying concentration in the absence and presence of inhibitor concentration from 0.1 to 0.3 M at $25\pm 1^\circ\text{C}$ temperature and it is given in **Table 2**. From the weight loss study it was observed that inhibitor concentration increased and it was accompanied by a decrease in corrosion rate (CR) of mild steel and an increase in the percentage inhibition efficiency (% IE) for each compound studied. The concentrations was estimated on the basis of highest inhibition efficiency of Hexamethylenetetramine was found to be in 0.3M are 78.4 % in 1 day and 85.98 % in 30 days respectively in BRW. The corrosion rate was calculated in 0.3M are 0.27 mpy in 1 day and 0.33 mpy in 30 days respectively. HMTA is an organic inhibitor containing polar functional groups with the nitrogen atoms in the conjugated system have been stated to exhibit good inhibiting properties due to strong electrostatic interaction between the mild steel surface and inhibitor through physio-chemical adsorption. The degree of adsorption depends on the nature of surface condition of mild steel, the type of corrosive media and concentration of the corrosion inhibitor.[9] Hexamethylenetetramine with 4 ppm of KI was found achieved maximum inhibition efficiency in 0.3M are 80 % in 1 day and 86.36 % in 30 days respectively in BRW. The corrosion rate was calculated in 0.3M are 0.25 mpy in 1 day and 0.33 mpy in 30 days respectively. It has been observed by the addition of little amount of potassium iodide enhances the inhibition efficiency which showed the synergistic effect of Hexamethylenetetramine in BRW. The halide ions are first adsorbed by chemisorption covering greater surface by means of electrostatic interaction involve in bonding between the iodide ions, which are able to increase adsorption of the organic cations by forming the intermediate bonds between the positively charged metal surface and the positive end of the inhibitor which facilitates corrosion inhibition synergism on the metal surface.[10] Study on mix effect of HMTA and SFA gives the idea that addition of another organic compound enhances the adsorption onto the metal surface in an aqueous solution. The highest inhibition efficiency of HMTA and SFA was found to be in 0.3M are 74 % in 1 day and 86.80 % in 30 days respectively and the corrosion rate was calculated in 0.3M are 0.33 mpy in 1 day and 0.31 mpy in 30 days respectively. This observation can be explained, that inhibitors are adsorbed on the metal surface immersed in an aqueous phase replacing water molecules and non-uniform distribution of electrical charges at the interface protecting by double layer onto the metal surface by adsorption process.[11]

1.4.2 Comparison of 1 day and 30 days weight loss measurements in HMTA, HMTA +KI and HMTA + SFA in Brackish Water

From the table. 2 It is evident that inhibition efficiency (IE) of HMTA + KI and HMTA + SFA is more than HMTA in 30 days but in 1 day HMTA + SFA showed less efficiency. In case of HMTA + KI efficiency increased due to the action of iodide ions which is bigger in size and increased the surface coverage on the surface of metal but in case of HMTA + SFA, results are more good in 30 days than in 1 days which explained that SFA will stabilize with time and show inhibiting effect, comparing the values of highest IE in 0.3M in 1 day are 78.4% in HMTA, 80% in HMTA + KI and 74% in HMTA + SFA respectively, but in 30 days the values of highest IE are 85.98% in HMTA, 86.36% in HMTA + KI and 86.80% in HMTA + SFA, which indicates that HMTA is fairly good to control corrosion on mild steel. IE is higher in 30 days than in 1 days results indicate that HMTA inhibitor adhere strongly to the metal surface.

Table. 2 Weight Loss Parameters of Mild Steel in BRW in the absence and presence of various concentrations of HMTA, HMTA + KI and HMTA + SFA for 1 Day and 30 Days exposure at room temperature 25±1°C.

Brackish Water(BRW)								
Blank/ Inhibitor	Time (days)	Conc. (ppm)	Initial Wt.	Final Wt.	Wt. Loss (mg)	CR (mpy)	IE (%)	
Blank	1	0	9.3002	9.2977	0.00250	1.26	0.00	
HMTA		0.10	9.3762	9.3754	0.00078	0.39	68.80	
		0.20	9.6987	9.6980	0.00068	0.34	72.80	
		0.30	9.6334	9.6329	0.00054	0.27	78.40	
		Blank	0	9.3002	9.2977	0.00250	1.26	0.00
HMTA + KI		0.10	8.8278	8.8270	0.00077	0.39	69.20	
		0.20	9.1069	9.1063	0.00064	0.32	74.40	
		0.30	9.1535	9.1530	0.0005	0.25	80.00	
Blank		30	0	9.3002	9.2977	0.00250	1.26	0.00
HMTA + SFA			0.10	9.1537	9.1528	0.00090	0.45	64.00
			0.20	9.1538	9.1531	0.00072	0.36	71.20
			0.30	9.2687	9.2681	0.00065	0.33	74.00
	Blank		0	9.3002	9.1154	0.1848	2.38	0.00
HMTA	0.10		9.3762	9.3439	0.0323	0.54	82.52	
	0.20		9.6334	9.6032	0.0302	0.51	83.66	
	0.30		11.8386	11.8127	0.0259	0.33	85.98	
	Blank		0	9.3002	9.1154	0.1848	2.38	0.00
HMTA + KI	0.10		11.6423	11.6145	0.0278	0.36	84.96	
	0.20		11.3254	11.2987	0.0267	0.34	85.55	
	0.30		11.7785	11.7533	0.0252	0.33	86.36	
Blank	HMTA + SFA	0	9.3002	9.1154	0.1848	2.38	0.00	
0.10		11.0445	11.0070	0.0375	0.48	79.71		
0.20		11.7409	11.7087	0.0322	0.42	82.58		
0.30		11.4677	11.4433	0.0244	0.31	86.80		

1.4.1 Effect of temperature of Hexamethylenetetramine on Mild Steel in Brackish Water (BRW)

Corrosion on mild steel is affected by temperature. In order to study the effect of temperature on the inhibition efficiencies of the inhibitor on mild steel in BRW in absence and presence of different concentrations from 0.1M to 0.3M of Hexamethylenetetramine, synergistic effect of Hexamethylenetetramine with Potassium Iodide (KI) and Hexamethylenetetramine with Sulfanilamide was studied in the temperature range of (25°C, 30°C, 40°C and 50°C) for 1 day using weight loss measurements. The corrosion rate increases with the rise in temperature from 25°C to 50°C. As the temperature increases, the rate of corrosion increases. This may be attributed to desorption of the inhibitors molecules at higher temperatures, thus exposing the metal surface to further attack. Inhibition efficiency decreases as temperature increases, at the same time it was observed that increase in concentration was accompanied by a decrease in corrosion rate and an increase in the percentage inhibition efficiency.

1.4.2 Thermodynamic Studies for corrosion parameter

In order to study the effect of temperature on the inhibited corrosion reaction of mild steel can be best represented by Arrhenius and transition state equations.[12] The activation energy of the metal dissolution in the absence and presence of inhibitor can be calculated using the equation (3)

$$CR = K \exp \left(-\frac{E_a^*}{RT} \right) \quad (3)$$

Alternative formulation of the Arrhenius equation (4)

$$CR = \frac{RT}{Nh} \exp \frac{\Delta S_a^*}{R} \exp \left(-\frac{\Delta H_a^*}{RT} \right) \quad (4)$$

Where, k is Arrhenius pre-exponential constant, N is Avogadro's number, h is Planck's constant, T is the absolute temperature and R is the molar gas constant.

Thermodynamic parameters such as the E_a^* apparent activation energy, ΔS_a^* is the entropy of activation and ΔH_a^* is the enthalpy of activation for the corrosion of mild steel of different concentrations for the corrosion of mild steel in BRW in the absence and presence of HMTA, HMTA with KI and HMTA with SFA, at different temperature were calculated and values are tabulated in **Table.3**

Using **Eq. (3)** and from a plot of the $\ln CR$ versus $1/T$ (**Figs. 2 - 4**), the values of E_a^* and k at various concentrations of HMTA, HMTA with KI and HMTA with SFA were computed from slopes and intercepts. Further, using **Eq. (4)**, plots of $\ln (C_R/T)$ versus $1/T$ gave straight lines (**Figs. 5 - 7**), with a slope of $(-\Delta H_a^*/R)$ and an intercept of $[\ln (R/Nh) + \Delta S_a^*/R]$, from which the values of ΔH_a^* and ΔS_a^* were calculated and are listed in **Table.3** In the present study, It is observed that E_a^* is much lower in absence of inhibitor than in the presence of inhibitor in BRW the value of activation energy increased in the presence of the increased concentration of inhibitor, indicate that physical adsorption between the surface of mild steel and the inhibitor molecules, which build a physical barrier to charge and mass transfer, leading to reduction in the corrosion rate but at the same time activation energy is more at higher temperature because of higher corrosion rate. Therefore, it can be explained that inhibitor is dependant on temperature, when temperature increases corrosion rate also increases combined with increased concentration corrosion rate decreased. The increase value of E_a^* is given in the table. 3 This supports physical adsorption of HMTA, HMTA with KI and HMTA with SFA on mild steel surface.[13]

The positive sign of enthalpies (ΔH_a^*) indicates the endothermic nature of mild steel signifying that additional energy was required for the activated state and the inhibitor adhere firmly to metal surface at high temperature. Therefore, dissolution of mild steel is difficult in aqueous medium. The negative values of (ΔS_a^*) imply that the activated complex represents an association rather than a dissociation step suggesting that decrease in disordering takes place on going from reactant to the activated complex in the rate determining step.

Table. 3 Activation parameters for Mild Steel in BRW in the absence and presence of different concentrations of TU, TU with KI and TU with SFA

Inhibitor	Conc. m/l	$E_a^* R$ kJ mol ⁻¹	K (mg cm ⁻² h ⁻¹)	$\Delta H_a^* kJ$ mol ⁻¹	$\Delta S_a^* J$ mol ⁻¹ K ⁻¹
HMTA	0.0	27.620	9*10 ⁴	28.00	-148.65
	0.1	45.291	4*10 ⁷	45.65	-98.06
	0.2	50.789	3*10 ⁸	51.31	-81.06
	0.3	55.111	1*10 ⁹	55.64	-68.02
HMTA+KI	0.0	27.620	9*10 ⁴	25.47	-156.86
	0.1	45.423	4*10 ⁷	43.27	-106.05
	0.2	45.828	4*10 ⁷	43.73	-106.51
	0.3	52.558	4*10 ⁸	50.54	-85.66
HMTA+SFA	0.0	27.620	9*10 ⁴	25.47	-156.86
	0.1	42.702	1*10 ⁷	40.54	-114.17
	0.2	49.842	2*10 ⁸	47.83	-92.05
	0.3	50.688	2*10 ⁸	48.68	-90.03

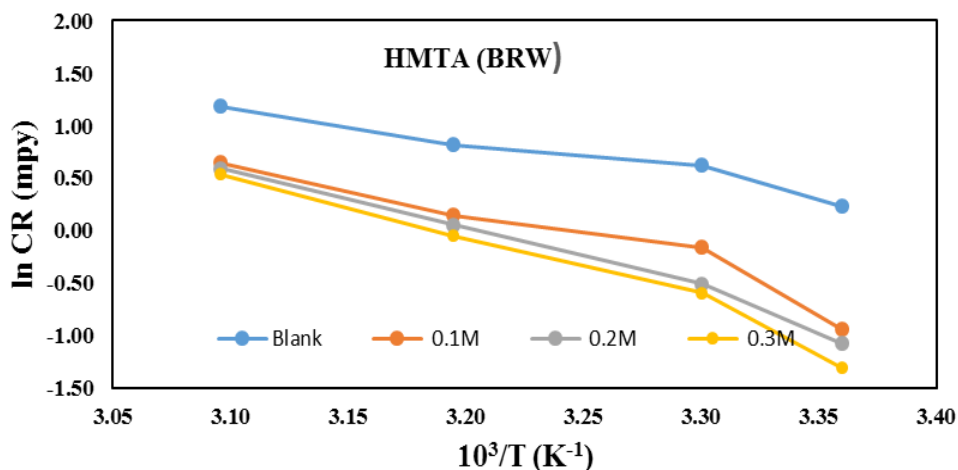


Figure 2: Arrhenius plots for the corrosion of mild steel in BRW in the absence and presence of different concentrations of HMTA

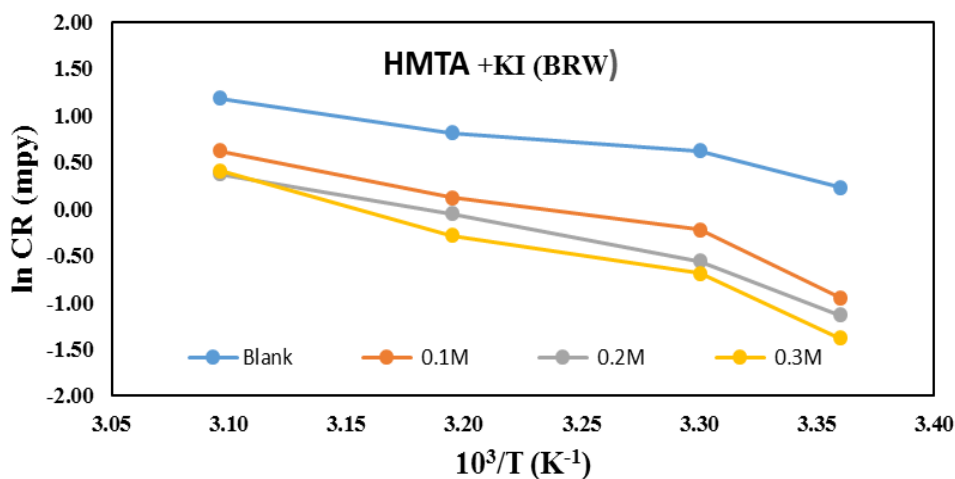


Figure 3: Arrhenius plots for the corrosion of mild steel in BRW in the absence and presence of different concentrations of HMTA with KI

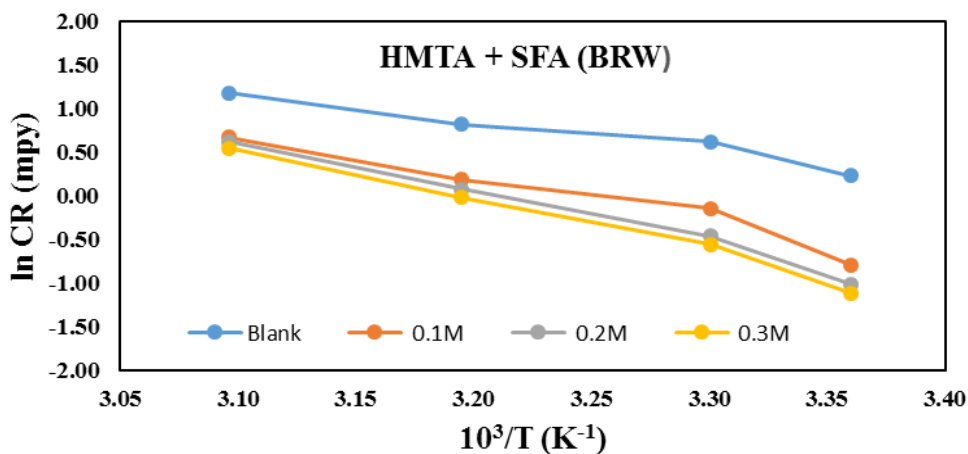


Figure 4: Arrhenius plots for the corrosion of mild steel in BRW in the absence and presence of different concentrations of HMTA with SFA

1.4.3 Adsorption isotherm

The higher corrosion inhibition efficiency is due to the higher surface coverage.[14] The surface coverage (θ) data are very useful while discussing the adsorption characteristics. The dependence of the fraction of the surface covered (θ) on the concentration C of the inhibitor can be explained by adsorption isotherm, which assumes that the solid surface contains a fixed number of adsorption sites and each site holds one layer of adsorbed species. The fraction of surface covered with inhibitor species ($\theta=IE\%$) can be followed as a function of inhibitor concentration and solution temperature and it was found best to obey Langmuir adsorption isotherm which can be expressed by the following equation (5)

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \quad (5)$$

Where, C is the concentration (g/L) of inhibitor, θ is the degree of surface coverage, K_{ads} is the equilibrium constant for the adsorption process. A plot of C/θ versus C gave a straight line (Figs. 8 – 10) with a slope almost equal to unity which confirm that the adsorption of TU on mild steel surface in BRW and EFW obeys the Langmuir adsorption isotherm with intercept equal ($1/K_{ads}$). The equilibrium adsorption constant, K_{ads} is related to the standard Gibb's free energy of adsorption (ΔG_{ads}) by the expression below (6)

$$K_{ads} = 55.5 \exp[-\Delta G_{ads}/RT] \quad (6)$$

Where, 55.5 is the molar concentration of water in solution ($mol L^{-1}$), R is the gas constant and T is the temperature in kelvin. The calculated ΔG_{ads} values of TU are tabulated in Tables 4. The enthalpy and entropy of adsorption (ΔH_{ads} and ΔS_{ads}) can be calculated using the equation (7).

$$\ln K_{ads} = \ln \frac{1}{55.5} - \frac{\Delta H_{ads}}{RT} + \frac{\Delta S_{ads}}{R} \quad (7)$$

The Gibb's free energy of adsorption can be calculated based on the following thermodynamic equation. (8)

$$\Delta G_{ads} = \Delta H_{ads} - T\Delta S_{ads} \quad (8)$$

Using equation (8) and from a plot of ΔG_{ads} vs. T (Fig 11) the values of ΔS_{ads} and ΔH_{ads} were computed from slopes and intercepts, respectively and the results are presented in Table. 3 The values of ΔS_{ads} and ΔH_{ads} give information about the mechanism of corrosion. The consistent negative values of ΔG_{ads} confirms the adsorption process of inhibitor molecules onto metal surface is spontaneous and good stability of adsorbed layer on mild steel surface.

When $\Delta H_{ads} > 0$ signifies an endothermic adsorption process while $\Delta H_{ads} < 0$ is attributed to an exothermic adsorption process which may involve either physisorption or chemisorption or mixture of both processes. The ΔS_{ads} values for all inhibitors are negative, which represent that the activated complex in the rate determining step characterizes an association rather than a dissociation step, meaning that a decrease in disordering takes place on going from reactants to the activated complex.[15]

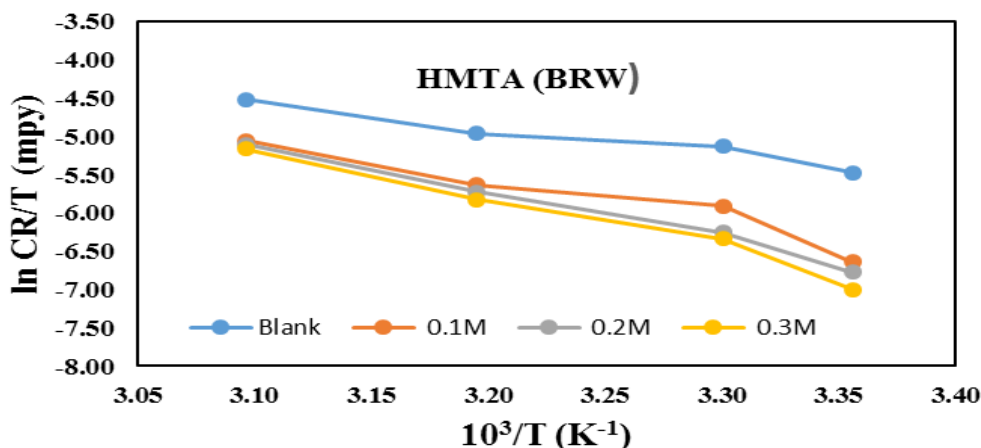


Figure 5: Alternative Arrhenius plots for the corrosion of mild steel in BRW in the absence and presence of different concentrations of HMTA

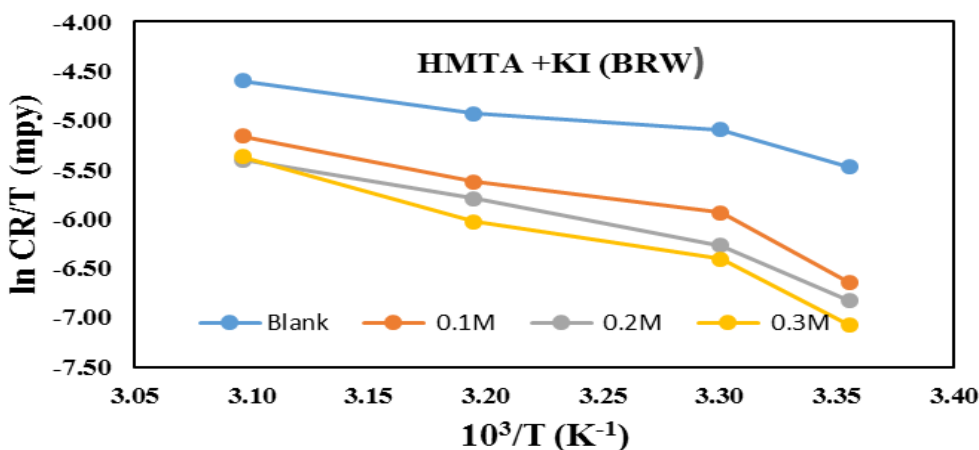


Figure 6: Alternative Arrhenius plots for the corrosion of mild steel in BRW in the absence and presence of different concentrations of HMTA with KI

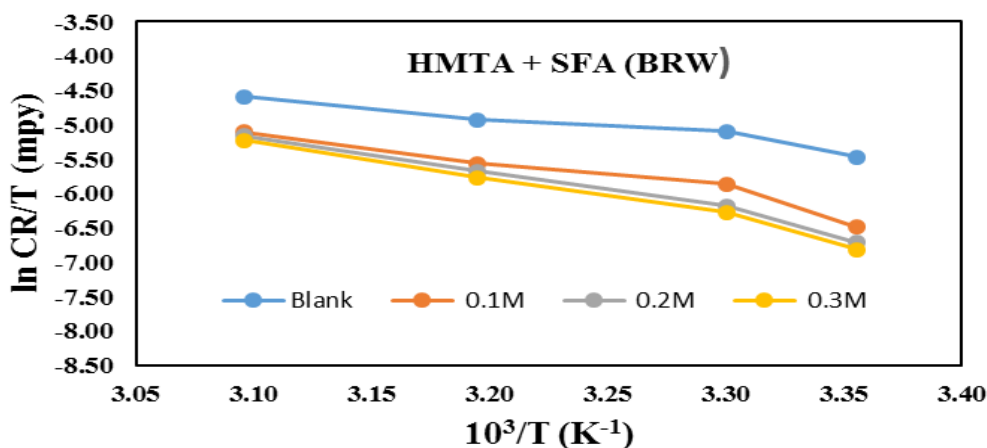


Figure 7: Alternative Arrhenius plots for the corrosion of mild steel in BRW in the absence and presence of different concentrations of HMTA with SFA

Table. 4 Thermodynamic parameters for adsorption of HMTA, HMTA +KI and HMTA + SFA on Mild Steel in BRW at different temperatures from Langmuir adsorption isotherm

Water	Inhibitor	T (K)	K_{ads} (L mol ⁻¹)	ΔG_{ads} (kJ mol ⁻¹)	ΔH_{ads} (kJ mol ⁻¹)	ΔS_{ads} (J mol ⁻¹ K ⁻¹)
BRW	TU	298	32362	-18.6	-9.76	-27.2
		303	16340	-17.2		
		313	19380	-18.2		
		323	19569	-18.8		
BRW	TU+KI	298	30960	-18.5	-17.12	-2.2
		303	17483	-17.3		
		313	12180	-17.0		
		323	17094	-18.4		
BRW	TU+SFA	298	31546	-18.5	-17.12	-2.2
		303	16447	-17.2		
		313	16556	-17.8		
		323	16155	-18.3		

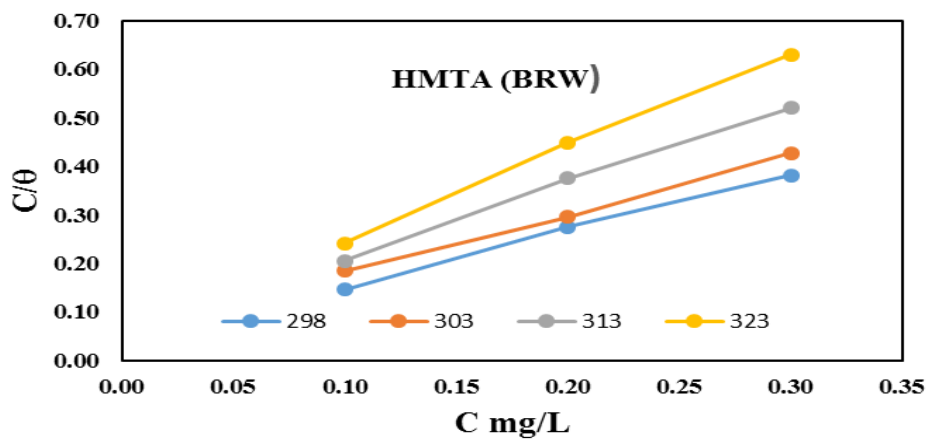


Figure 8: Langmuir isotherm for the adsorption of HMTA on mild steel in BRW at different temperatures.

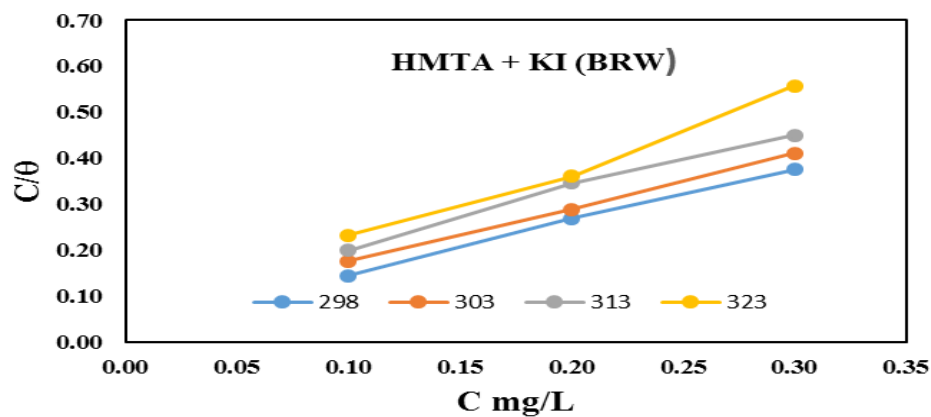


Figure 9: Langmuir isotherm for the adsorption of HMTA and KI on mild steel in BRW at different temperatures.

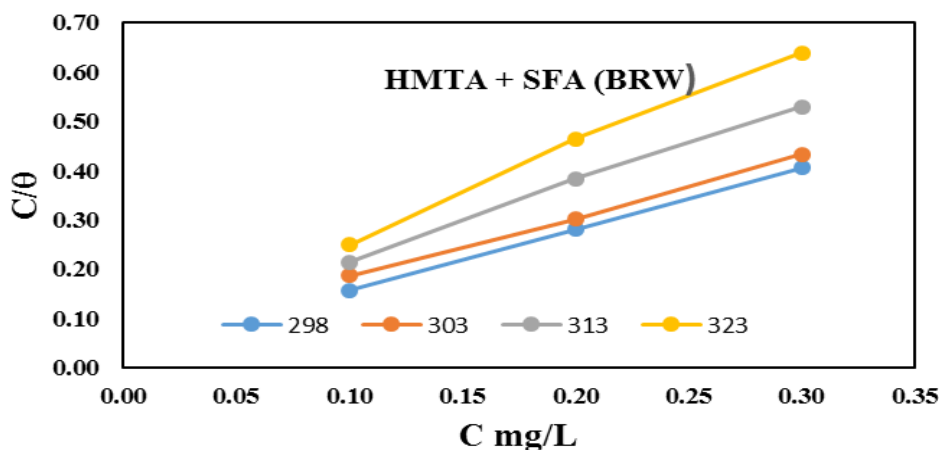


Figure 10: Langmuir isotherm for the adsorption of HMTA and SFA on mild steel in BRW at different temperatures.

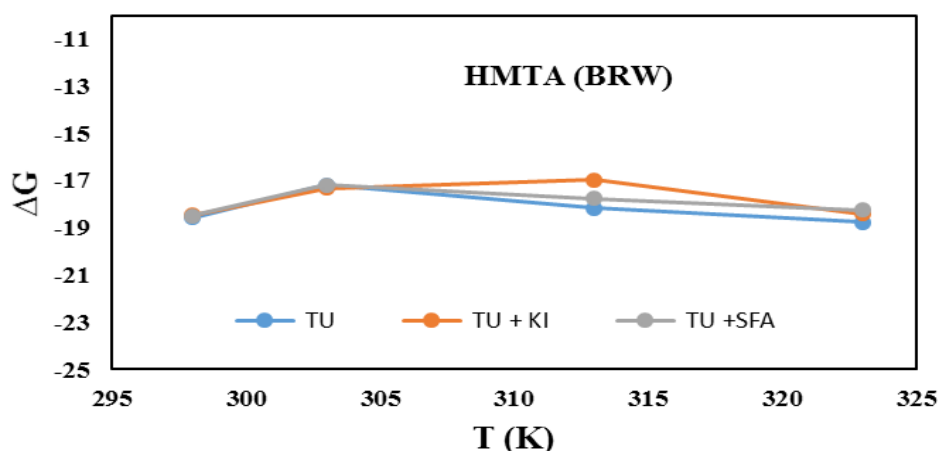
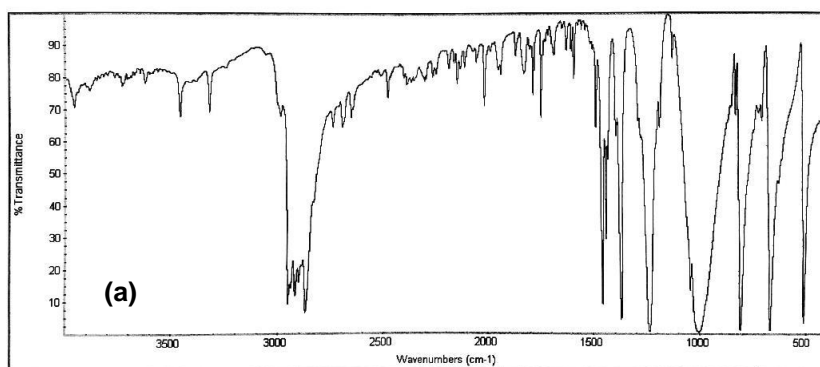


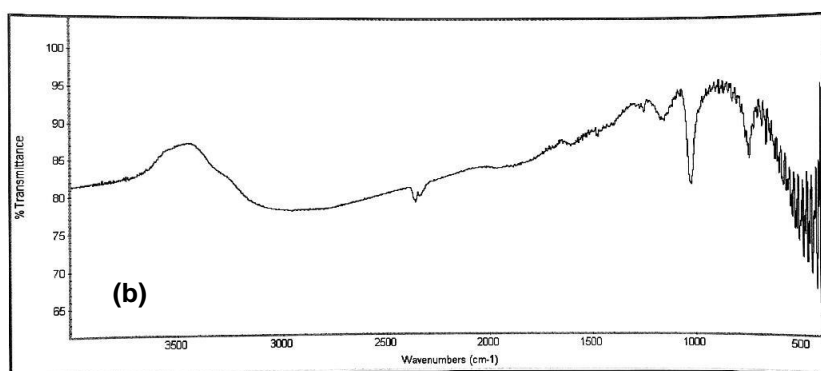
Figure 11: Plot of ΔG ads vs. absolute temperature for TU, TU+KI AND TU+SFA in BRW

1.5 Analysis of FTIR spectra:

Fourier transform infra-red spectroscopy Perkin-Elmer ‘Spectrum Two’ Spectrophotometer (spectral resolution 0.5 cm^{-1}) was used to record the FT-IR spectra of pure Hexamethylenetetramine (HMTA) and Hexamethylenetetramine adsorbed on the mild steel surface. The mild steel specimens were immersed in various test solutions for one week were taken out cleaned and dried first, and the thin film formed on the metal surface was carefully removed. To record the FT-IR spectra of pure, the powder was mixed with Potassium Bromide (KBr) and made into the disc. The spectra were recorded in the frequency range of $4000\text{--}500\text{ cm}^{-1}$. Data was collected and interpreted by the Spectrum Software. [16].



Figures 12: (a) FTIR Spectrum of pure HMTA



(b) FTIR Spectrum of HMTA film formed on the metal surface

On comparing the spectra pure HMTA (**Figure 12a**), it exhibits several peaks attributed to the various functional groups, which are similar to those previously reported. Peaks in between $2800\text{--}3000\text{ cm}^{-1}$ is attributed to symmetric and asymmetric -CH_2 stretching vibrations. Peaks at 1450 , 1392 , and 1053 cm^{-1} corresponds to C-H bending vibrations and the peak at 813 cm^{-1} attributed to CN heterocycle group. The peak at 1007 cm^{-1} is due to C-N stretching vibration and at 687 cm^{-1} and 720 cm^{-1} corresponds to N-H or C-H bands. Whereas in Hexamethylenetetramine adsorbed on the mild steel surface (**Figure 12b**) there is a complete disappearance of sharp peaks due to -CH_2 stretching and bending vibrations, and broad hump is observed in region between $2500\text{--}3500\text{ cm}^{-1}$ due to the merging of -CH stretching and C-OH peaks with reduced intensity indicating the involvement of C-C bond in adsorption process. Besides the peak at 1007 cm^{-1} due to C-N stretching vibrations is completely reduced in intensity confirming the adsorption process.

1.6 Scanning Electron Microscopy (SEM)

Surface Morphological Studies Surface analysis was performed using scanning electron microscope. Polished mild steel coupons was tested after the immersion in 0.3M in the absence and presence of HMTA for 30 days at room temperature in Brackish Water to check efficiencies of corrosion inhibitor. Then the corrosion coupons washed with distilled water, dried in desiccator and therefore subjected to scanning electron microscopic examination.

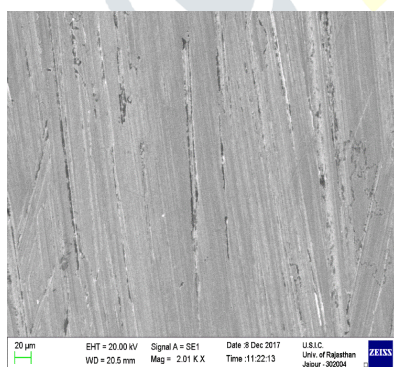


Figure 14: Blank

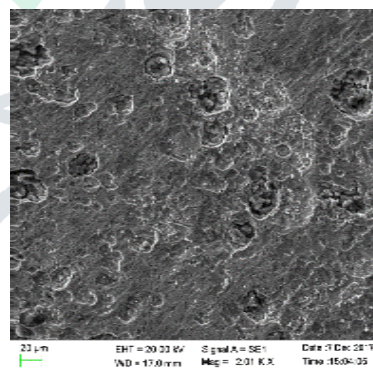


Figure 15: BRW Blank

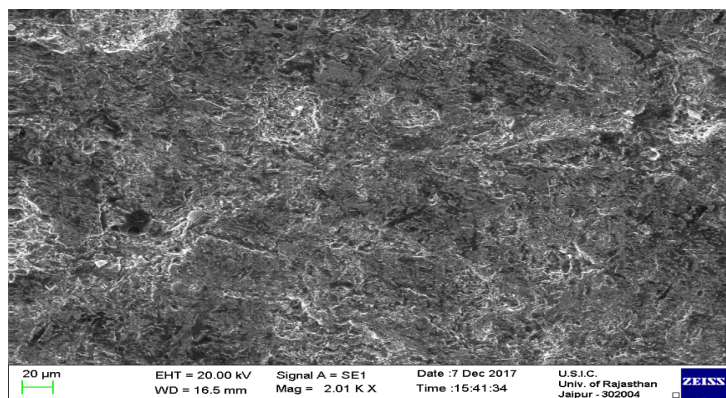


Figure 16: Hexamethylenetetramine BRW

Flakes which show corrosion products are observed in the micrographs. The electron micrographs (SEM) reveal that the surface was strongly damaged owing to corrosion in absence of the HMTA, but in the presence of the HMTA there is a much smaller damage on the surface. This is ascribed to the formation of a good protective film on the mild steel surface. It is quite apparent from the micrographs the uniform products like metal hydrides, and their oxides are also visible.

1.7 Conclusions

This research investigated the phenomenon of corrosion of mild steel metal in brackish water (BRW) system. Weight loss method, temperature measurements FT-IR, and SEM were used in this study. From the result and discussions, the following conclusions were derived:

1. HMTA chemical compound acts as good inhibitor for mild steel in BRW either alone or with KI or with SFA.
2. From the weight loss study, it is showed that strong electrostatic interaction between the mild steel surface and HMTA/ KI/ SFA through physio-chemical adsorption occurred in the inhibition process.
3. The corrosion rates of mild steel generally increased with increasing temperature.
4. Corrosion rate decreased with HMTA addition in BRW and corrosion inhibition efficiency reaches to 85.98 in HMTA & 86.36 in HMTA with KI and 86.80 HMTA with SFA in BRW respectively..
5. Inhibition efficiency increased with increase in HMTA concentration and exposure duration
6. The combination of HMTA and KI indicates a synergistic effect exists between them which enhance the corrosion inhibition synergism on the metal
7. The metallographic micrographs showed that the morphology pits of mild steel in the absence of HMTA/KI/SFA demonstrated a higher number than that in the presence of these chemicals.

1.8 Bibliography

1. *Whittaker, J., Liu, Q., Brown, D. J., & Mar, R. (2014). Corrosion Management and Mechanism Study on SAGD Brackish. Corrosion 2014, 1-14.*
2. *Nicota, J. P., & Chowdhury, A. H. (2005). Disposal of Brackish Water Concentrate into Depleted Oil and Gas Fields: A Texas study,. Desalination 181, 61-74.*
3. *Parekh, & Punambhai, S. (2015). Corrosion Studies of Some Metals by Different Environmental Conditions in Ahmedabad Central Gujarat. Kadi Sarva Vishwavidyalaya, 11.*
4. *Gurudatt, D. M., & Mohana, K. N. (2014). Synthesis of Some Novel Nitrogen Containing Heterocycles and Study of their Antioxidant Activity and Corrosion Inhibition Performance on Mild Steel, University of Mysore, 176-210.*
5. *Raheem, ., D. (2011). Effect of Mixed Corrosion Inhibitors in Cooling Water System. Al-Khwarizmi Engineering Journal, 7(4), 76- 87.*
6. *Aromaa, J., & Forsen, O. (2016). Factors Affecting Corrosion in Gulf of Finland Brackish Water, International Journal of Electrochemistry, 1-10.*
7. *Dubey, A. K., & Singh, G. (205-219). Corrosion Inhibition of Mild Steel Using Brij-30. Portugaliae Electrochimica Acta 25, 2007.*

8. Kazaure, Z. S., Agbogo, U. V., Bognet, O., & Adeyemi, O. O. (2015). Kinetics and Thermodynamic Study of Inhibition Potentials by Ethoxyethane Extracts of *Cochlospermum tinctorium* for the Oxoacid Corrosion of Mild Steel. *Inter J. of Materials and Chem*, 5(3), 64-76.
9. Olamide, O., Adekunle, O. F., & Adediran. (2016). Corrosion Inhibition of Mild Steel in Seawater using *Jatropha Stem*. *analele universității "efimie murgu" reșița*, ISSN 1453 – 7397, 228-238.
10. Khan, S., & Quraishi, M. A. (2010). Synergistic Effect of Potassium Iodide on Inhibitive Performance of Thiadiazoles during Corrosion of Mild Steel in 20% Sulfuric Acid. *Arabian journal for science and engineering*, 1-13.
11. Fouda, S., Abd El Mgeed, A., & Abd El-Salam, S. (2015). *Melissa Officinalis* Aqueous Plant Extract as Eco-Friendly Corrosion Inhibitor for Carbon Steel in Aqueous Solutions. *Der Pharma Chemica*, 7(7), 27-38, ISSN 0975-413X
12. Ebenso, N. O., & Eddy, E. E. (2010). Corrosion Inhibition and Adsorption Characteristics of Tarivid on Mild Steel in H_2SO_4 , 7(S1). CODEN ECJHAO *E-Journal of Chemistry*, ISSN: 0973-4945, S442-S448.
13. Gurudatt, D. M., & Mohana, K. N. (2014). Synthesis of Some Novel Nitrogen Containing Heterocycles and Study of their Antioxidant Activity and Corrosion Inhibition Performance on Mild Steel, *University of Mysore*, 176-210.
14. Verma, C. Singh, Quraishi, P. M. A., (2015). A Thermodynamical, Electrochemical and Surface Investigation of Bis (indolyl) Methanes as Green Corrosion Inhibitors for Mild Steel in 1 M Hydrochloric Acid Solution, *Journal of the Association of Arab Universities for Basic and Applied Sciences*. 24–30,
15. Jonnie, N., Asegbeloyin, Ejikeme P., M., Olasunkanmi L., O., Adekunle A., S., Ebenso E., E., (2015). A Novel Schiff Base of 3-acetyl-4-hydroxy-6-methyl-(2H) pyran-2-one and 2,2'-(ethylenedioxy) diethyl amine as Potential Corrosion Inhibitor for Mild Steel in Acidic Medium, *Materials* 8, 2918-2934.
16. Mobin, R. M. (2017). Polysaccharide from *Plantago* as a Green Corrosion Inhibitor for Carbon Steel in 1 M HCl Solution. *Carbohydrate Polymers*, 172–183.

