

INHIBITIVE EFFECT OF HEXAMETHYLENETETRAMINE ON MILD STEEL IN EFFLUENT WATER

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1.1 Abstract

Corrosion of mild steel in effluent water (EFW), producing severe destructive problems in systems such as equipment and piping systems as well as pipelines. The use of chemical treatment has found to be an inexpensive and easiest method for corrosion protection in EFW. The corrosion inhibition of mild steel in oilfield effluent water has been studied in relation to the concentration of the hexamethylenetetramine (as corrosion inhibitor) as well as the temperature using weight loss method. The mild steel corrosion coupons were processed and evaluated as per 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.

Key Words: Hexamethylenetetramine (HMTA), effluent water (EFW), corrosion inhibitors, infrared spectroscopy (IR), scanning electron microscopy (SEM), mild steel.

1.2 INTRODUCTION

In oil and gas industries corrosion due to effluent water in mild steel is a severe and foremost problems. Oil and gas pipelines are generally made of mild steel which has its excellent desirable properties and it is extensively used in various types of vessels, tanks, pipes and many other equipment.[1] **Elron Edgar Gomes (2015)**. But it is susceptible to undergo severe corrosion. Effluent water is also called as waste water and it is defined by the United States Environmental Protection Agency as "wastewater - treated or untreated that flows out of a treatment plant, sewer, or industrial outfall. Wastewater problem is huge in oil and gas industry, more than 10 times of wastewater produced during oil and gas production in some well. To study corrosion in effluent water is a challenging task in this field. Effluent water discharge from gathering centres shows high corrosivity due to its high total dissolved solids more or less same as produced water and high contents of sodium chloride, which could lead to premature failures in effluent water disposal plant and injection lines.[2] **Bhagure, Ganesh Ramdas, Mirgane, S.R, (2010)**. There are numerous types of chemicals used to prevent corrosion, scales and microbial growth in these facilities. Hence, it was decided to evaluate the chemicals on basis of their efficiency in decreasing the general and pitting corrosion. [3] **Abdul Wahab Al-Mithin, Amer Jarragh, Sandip Kuthe, Sharad Londhe (2013)** Corrosion can be defined as "the spontaneous process of degradation and deterioration or destruction of metallic construction in the course of their chemical, biochemical or electrochemical interactions with the surroundings." [4] **Parekh, Sunilkumar Punambhai (2015)**. Corrosion can be slow or fast depends on the environment to which it is exposed. The destruction caused by corrosion may result in the appearance of undesirable product, which may result in the form of very high cost on operation and maintenance and unexpected shut down of the operating equipment, loss of valuable products, safety risk and low reliability, customer disappointment and over consumption of raw material. All the above facts combine together and put the industry in excessive loss. [5] **Meyer, G. R et al, (2013)**. 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 Effluent water (EFW). Weight loss method was used for corrosion inhibition efficiency evaluation at different inhibitor concentration and 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.[6] *Dubey, A. K., & Singh, G. (2007)* 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.[7] *Kazaure, Z. S., Agbogo, U. V., Bognet, O., & Adeyemi, O. O. (2015).*

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:

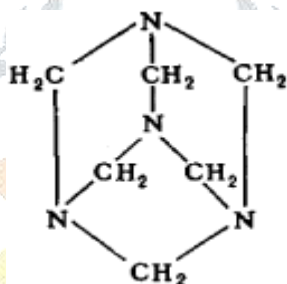


Figure 1: Molecular Structure of Hexamethylenetetramine

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

Effluent water used to make different concentration of 0.1, 0.2 and 0.3 Molarity solution prepared in EFW 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 EFW. From the prepared solution of Hexamethylenetetramine and Sulfanilamide, volume used in the ratio of 60:40.

Effluent water was used for weight loss corrosion rate and corrosion efficiency determination. From the physicochemical properties of the effluent 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 effluent 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 Effluent 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 (SFA) 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 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 Effluent 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 concentration was estimated on the basis of highest inhibition efficiency of Hexamethylenetetramine was found to be in 0.3M are 70.83 % in 1 day and 95.35 % in 30 days respectively in EFW. The corrosion rate was calculated in 0.3M are 0.18 mpy in 1 day and 0.26 mpy in 30 days respectively. HMTA is an organic corrosion inhibitor with aromatic ring of carbon and nitrogen atoms which facilitate electronic interactions between lone pair of electrons of nitrogen and mild steel surface that form protective films either by physisorption or chemisorption or both leading to increase the adsorption on the surface of metal [8] **Reza Javaherdashti (2013)** 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] High inhibition efficiency of HMTA at the highest concentration reveal that the HMTA is fairly good corrosion inhibitor. Hexamethylenetetramine with 4 ppm of KI was found achieved maximum inhibition efficiency in 0.3M are 72.5 % in 1 day and 97.02 % in 30 days respectively in EFW. The corrosion rate was calculated in 0.3M are 0.17 mpy in 1 day and 0.17 mpy in 30 days respectively. It has been observed by the addition of little amount of potassium iodide

to solutions containing organic inhibitors enhances the inhibition efficiency onto the metal surface by synergistic effect. [9]K. S. Shaju et al. (2012). The halide ions are first adsorbed by chemisorption covering the covering greater surface by means of electrostatic interaction and ease of polarizability of iodide ion (I^-) facilitate electron pair bonding adhere firmly on the steel surface. The inhibitor is then drawn in to the double layer by the adsorbed halide ion, such that the ion pair formation occurs directly on the metal surface. The synergistic ability of the halide increases in the order $Cl^- < Br^- < I^-$. [10] Khan, S., & Quraishi, M. A. (2010). 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 70 % in 1 day and 96.81 % in 30 days respectively and the corrosion rate was calculated in 0.3M are 0.18 mpy in 1 day and 0.18 mpy in 30 days respectively. This observation can be explained, that adsorption depends on the size, shape and orientation of organic inhibitors molecule. The presence of hetero atoms with nitrogen, sulphur and/or oxygen atoms, π -electrons, double or triple bonds in the conjugated system in SFA are active centers of the inhibitor molecules which take part in bond formation and act as electron donors, while the corroding metal acts as an electron acceptor thus forming the multi- dimensional protective layers on the metal surface and hence, inhibitor is effective due to high molecular size and high electron density. [11][12] Olamide, O., Festus, A. O., Adeolu, A. A., (2016) and Malik, M. A., Hashim, M. A., Nabi, F., Al-Thabaiti, S. A., Khan, Z., (2011).

1.4.2 Comparison of 1 day and 30 days weight loss measurements in HMTA, HMTA +KI and HMTA + SFA in Effluent 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 case of 1 day HMTA + KI efficiency increased than HMTA and HMTA +SFA due to the action of iodide ions which is bigger in size and increased the surface coverage on the surface of metal. HMTA and HMTA + SFA efficiency is more or less same in case of 1 day, comparing the values of highest IE in 0.3M in 1 day are 70.83% in HMTA, 72.50% in HMTA + KI and 70% in HMTA + SFA respectively, but in 30 days the values of highest IE are 95.35% in HMTA, 97.02% in HMTA + KI and 96.81% 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 EFW 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.

Effluent Water(EFW)							
Blank/Inhibitor	Time (days)	Conc. (ppm)	Initial Wt.	Final Wt.	Wt. Loss (mg)	CR (mpy)	IE (%)
Blank	1	0	9.0560	9.0548	0.0012	0.60	0.00
HMTA		0.10	9.6967	9.6962	0.0006	0.28	54.17
		0.20	9.1866	9.1862	0.0004	0.22	64.17
		0.30	9.5952	9.5949	0.0003	0.18	70.83
Blank		0	9.0560	9.0548	0.0012	0.60	0.00
HMTA + KI		0.10	9.4823	9.4818	0.0005	0.26	56.67
		0.20	9.2433	9.2429	0.0004	0.21	65.00
		0.30	9.0935	9.0932	0.0003	0.17	72.50
Blank		0	9.0560	9.0548	0.0012	0.60	0.00
HMTA + SFA		0.10	9.2112	9.2106	0.0006	0.28	53.33
		0.20	9.2112	9.2108	0.0004	0.22	64.17
		0.30	9.2112	9.2108	0.0004	0.18	70.00
Blank	30	0	9.7058	9.2668	0.4390	7.35	0.00
HMTA		0.10	11.9620	11.9310	0.0310	0.40	92.94
		0.20	10.2276	10.2053	0.0223	0.29	94.92
		0.30	11.5722	11.5518	0.0204	0.26	95.35
Blank		0	9.7058	9.2668	0.4390	7.35	0.00
HMTA + KI		0.10	10.1969	10.1738	0.0231	0.30	94.74
		0.20	9.1866	9.1727	0.0139	0.23	96.83
		0.30	10.1628	10.1497	0.0131	0.17	97.02
Blank		0	9.7058	9.2668	0.4390	7.35	0.00
HMTA + SFA		0.10	11.5779	11.5582	0.0197	0.25	95.51
		0.20	10.6023	10.5858	0.0165	0.21	96.24
		0.30	11.6720	11.6580	0.0140	0.18	96.81

1.4.1 Effect of temperature of Hexamethylenetetramine on Mild Steel in Effluent water (EFW)

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 EFW 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. [13] *Ebenso, N. O., & Eddy, E. E. (2010)*. 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 EFW 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 $\ln (CR/T)$ 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 was observed that the values of E_a^* is high in the presence of inhibitor than in the absence of inhibitor on mild steel in EFW which supports the physical adsorption of HMTA molecules on the metal surface during first step of adsorption processes. [14] **Chandrabhan Verma, P. Geethamani**. By increasing concentration also increases the E_a^* determined the strong adsorption of HMTA molecules on mild steel. [15] **Karumalaiyan Palanisamy** The temperature effect on the rate of corrosion in the uninhibited and inhibited additives was used to clarify the nature of adsorption of the inhibitors onto the steel surface. [16] **B.I. Ita** With increasing temperature, the corrosion rates also increases. Therefore, it can be explained that inhibitor is dependant on temperature, as the temperature increases, the IE decreases due to desorption of inhibitor molecules and mild steel exposed to aggressive environment. The reaction between adsorption and desorption of molecules occur until equilibrium is established again at a different value of equilibrium constant. Hence lower values of IE are attained at elevated temperatures. As the process of physisorption which disappear at higher temperatures. The increase value of E_a^* is given in the **Table.3** The reaction process is endothermic in nature which can be explained by the positive values of activation enthalpy (ΔH^*) and dissolution of mild steel is difficult [17] **R. Karthikaiselvi**, Negative values of (ΔS_a^*) which represent association rather than dissociation indicates that a decrease in disordering on going from reactants to the activated complex in the rate determining step.

Table. 3 Activation parameters for mild steel in EFW in the absence and presence of different concentrations of TU, TU with KI and TU with SFA

Inhibitor (EFW)	CONC. m/l	E_a^*R kJ mol ⁻¹	K (mg cm ⁻² h ⁻¹)	ΔH_a kJ mol ⁻¹	ΔS_a J mol ⁻¹ K ⁻¹
HMTA	0.0	28.41	6*10 ⁴	26.15	-160.94
	0.1	38.33	1*10 ⁶	36.20	-133.68
	0.2	42.69	7*10 ⁶	40.54	-120.44
	0.3	47.48	4*10 ⁷	45.44	-106.19
HMTA+KI	0.0	28.41	6*10 ⁴	26.15	-160.94
	0.1	39.45	2*10 ⁶	37.32	-130.26
	0.2	42.46	6*10 ⁶	40.31	-121.42
	0.3	48.04	4*10 ⁷	46.02	-104.76
HMTA+SFA	0.0	28.41	6*10 ⁴	26.15	-160.94
	0.1	38.19	1*10 ⁶	36.06	-134.01
	0.2	43.07	9*10 ⁶	40.91	-119.06
	0.3	47.51	4*10 ⁷	45.48	-105.85

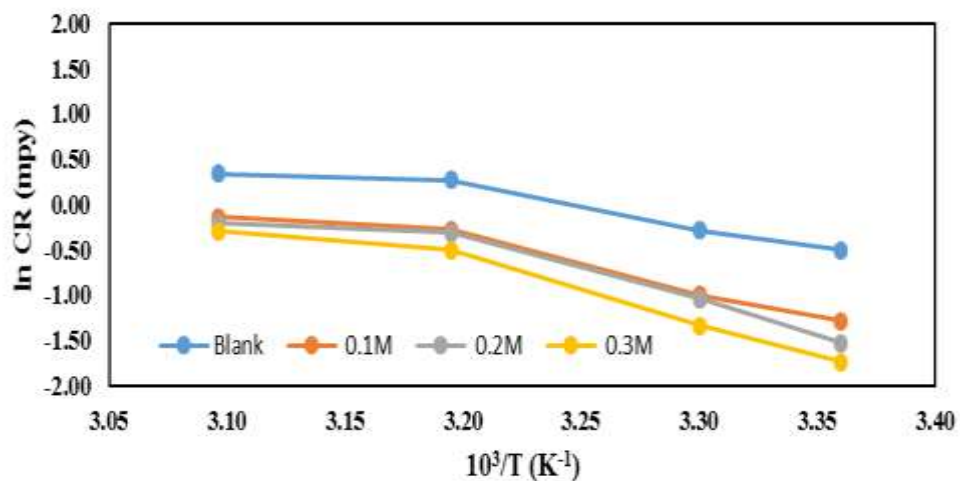


Figure 2: Arrhenius plots for the corrosion of mild steel in EFW in the absence and presence of different concentrations of HMTA

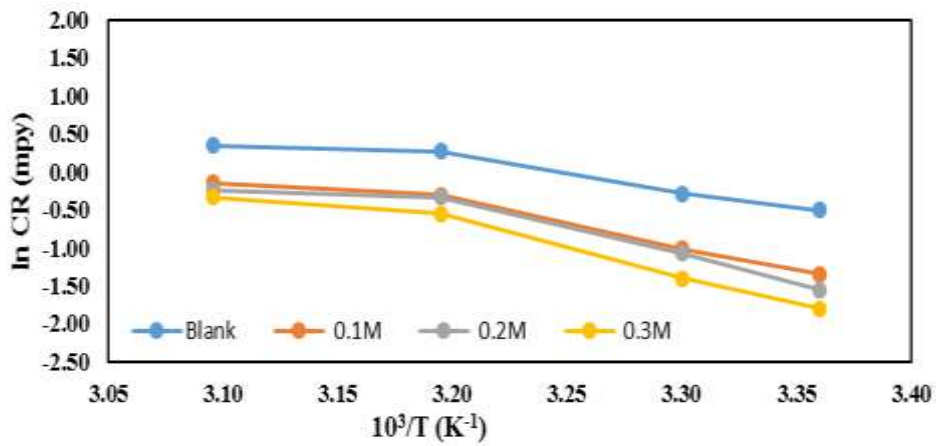


Figure 3: Arrhenius plots for the corrosion of mild steel in EFW in the absence and presence of different concentrations of HMTA with KI

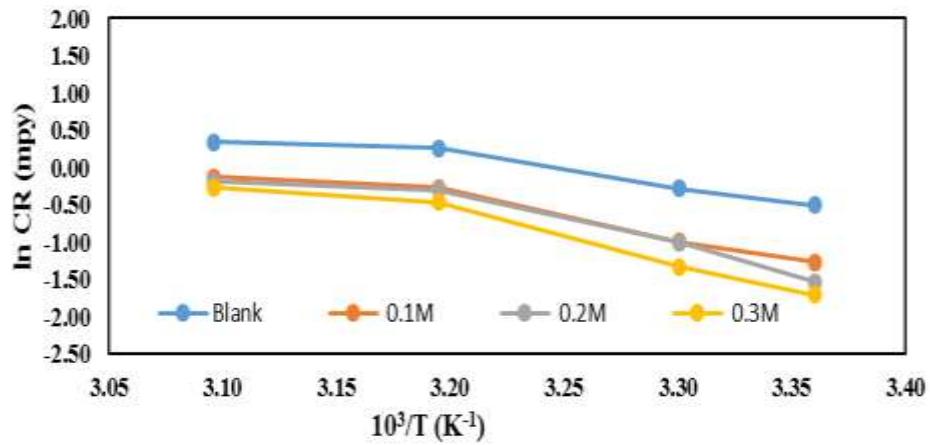


Figure 4: Arrhenius plots for the corrosion of mild steel in EFW in the absence and presence of different concentrations of HMTA with SFA

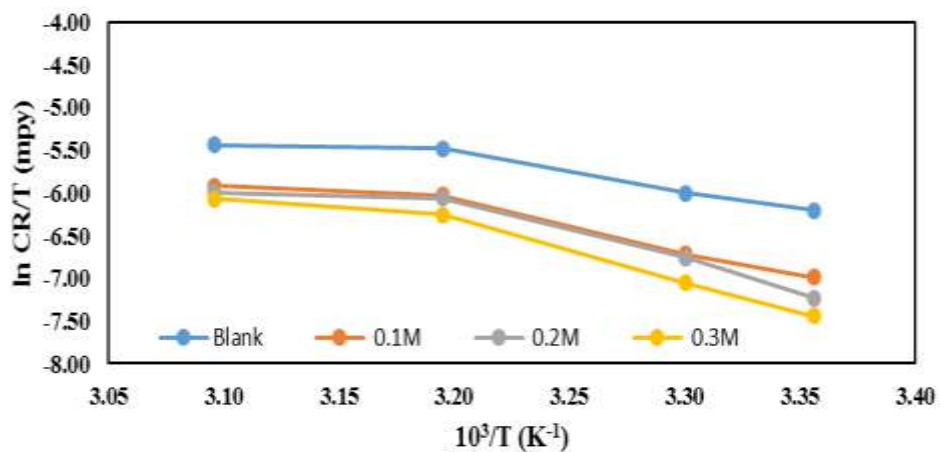


Figure 5: Alternative Arrhenius plots for the corrosion of mild steel in EFW in the absence and presence of different concentrations of HMTA

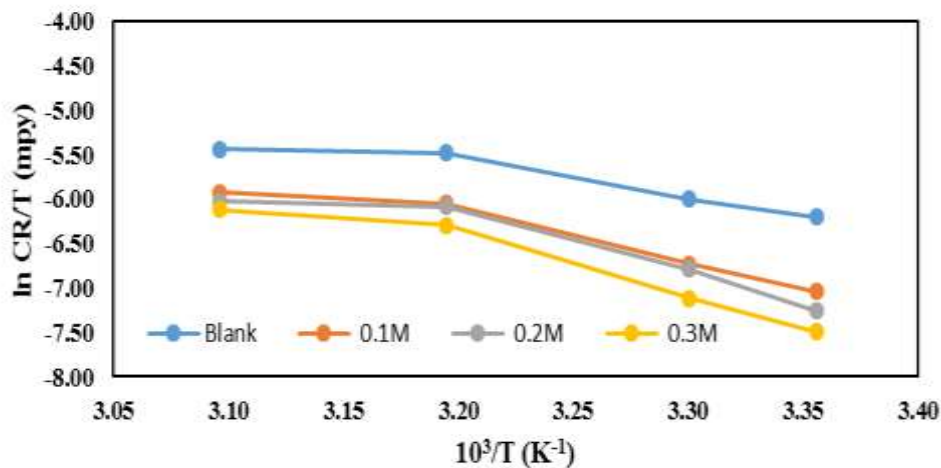


Figure 6: Alternative Arrhenius plots for the corrosion of mild steel in EFW in the absence and presence of different concentrations of HMTA with KI

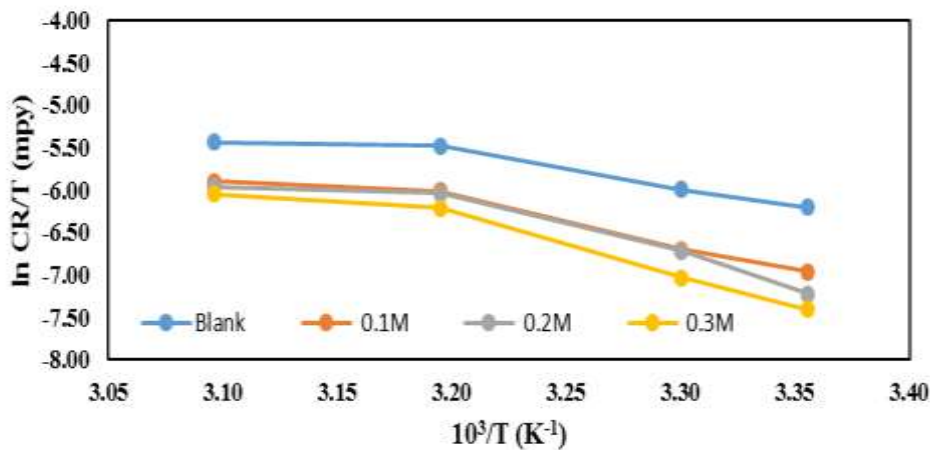


Figure 7: Alternative Arrhenius plots for the corrosion of mild steel in EFW in the absence and presence of different concentrations of HMTA with SFA

1.4.3 Adsorption isotherm

The higher corrosion inhibition efficiency is due to the higher surface coverage.[18] *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,* The fraction of surface covered (θ) depend on the concentration C of the inhibitor can be explained by Langmuir’s 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 ($\theta=IE\%100$) can 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)

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \tag{5}$$

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 EFW

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)

$$K_{ads} = 1/55.5 \exp[-\Delta G_{ads}/RT] \quad (6)$$

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 the **Table.4** 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. 4** 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.[19] *Jonnie, N., Asegbeloyin, Ejikeme P., M., Olasunkanmi L., O., Adekunle A., S., Ebenso E., E., (2015).*

Table. 4 Thermodynamic parameters for adsorption of HMTA, HMTA +KI and HMTA + SFA on mild steel in EFW at different temperatures from Langmuir adsorption isotherm

Water	Inhibitor	T (K)	K_{ads} (L mol ⁻¹)	$-\Delta G_{ads}$ (kJ mol ⁻¹)	ΔH_{ads} (kJ mol ⁻¹)	$-\Delta S_{ads}$ (J mol ⁻¹ K ⁻¹)
EFW	HMTA	298	14771	-16.6	-5.98	-35.00
		303	12723	-16.5		
		313	10132	-16.5		
		323	12438	-17.6		
EFW	HMTA+KI	298	16129	-16.8	-10.60	-20.00
		303	12300	-16.4		
		313	10515	-16.6		
		323	11173	-17.3		
EFW	HMTA+SFA	298	14663	-16.6	-5.80	-35.50
		303	11947	-16.4		
		313	11038	-16.7		
		323	11834	-17.4		

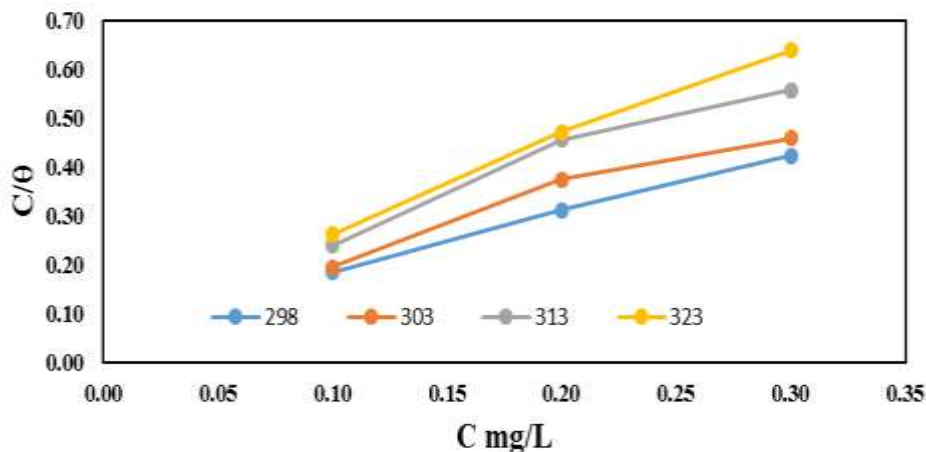


Figure 8: Langmuir isotherm for the adsorption of HMTA on mild steel in EFW at different temperatures.

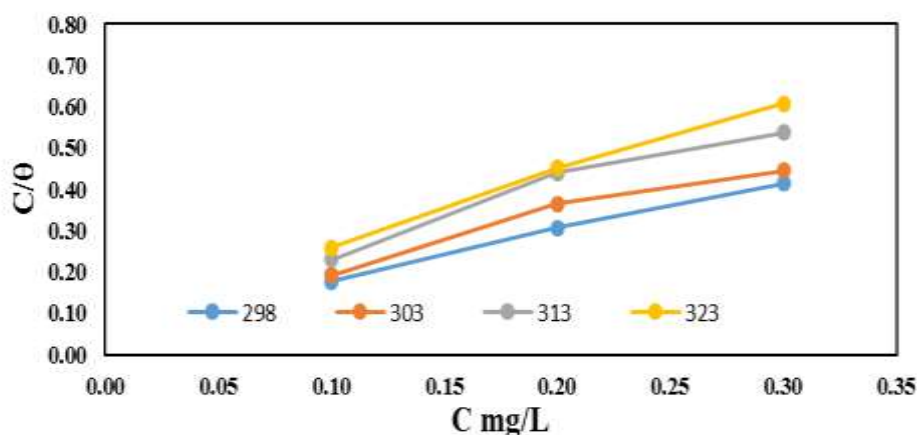


Figure 9: Langmuir isotherm for the adsorption of HMTA and KI on mild steel in EFW at different temperatures.

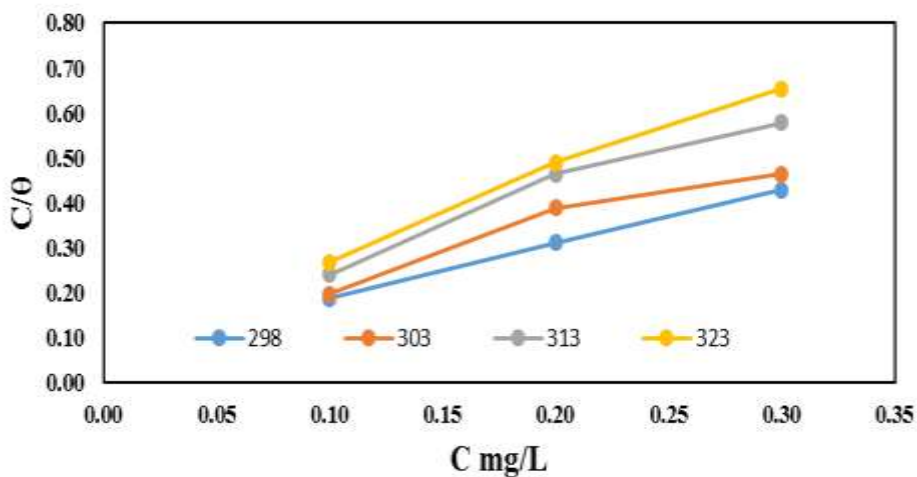


Figure 10: Langmuir isotherm for the adsorption of HMTA and SFA on mild steel in EFW at different temperatures.

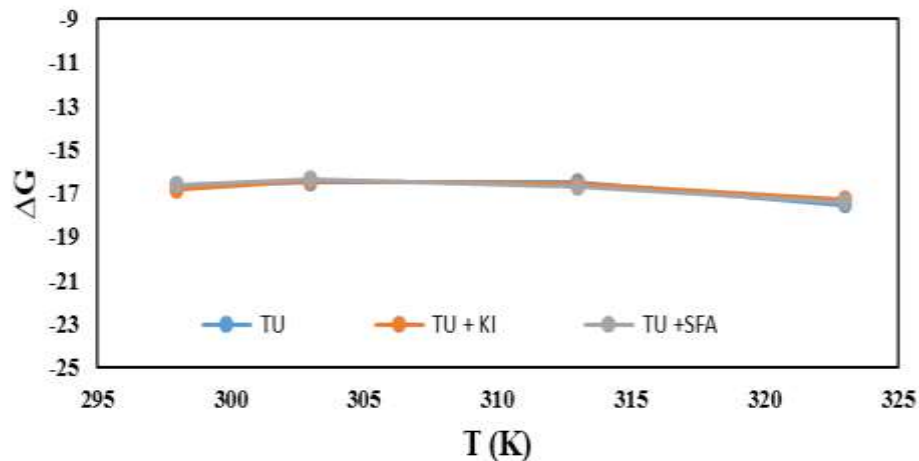
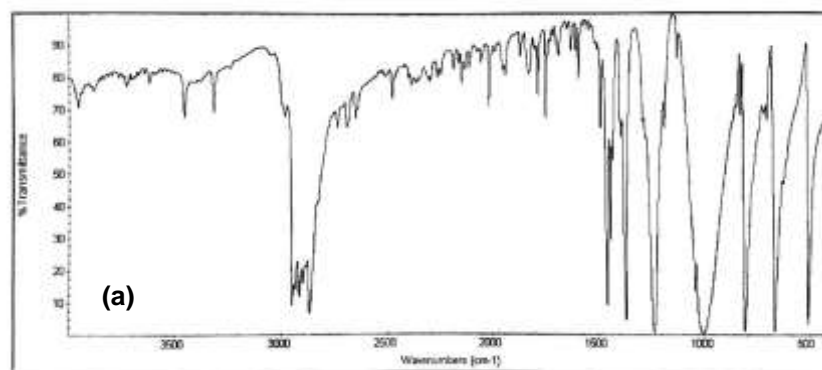


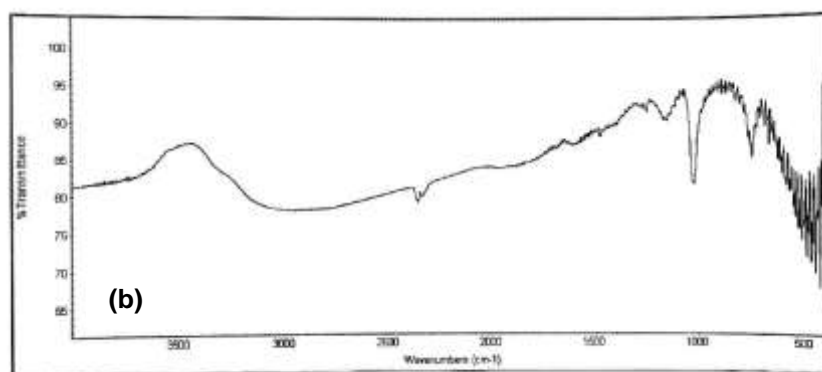
Figure 11: Plot of ΔG_{ads} vs. absolute temperature for TU, TU+KI AND TU+SFA in EFW

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.[20]



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 $-\text{CH}_2$ 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 $-\text{CH}_2$ stretching and bending vibrations, and broad hump is observed in region between $2500\text{--}3500\text{ cm}^{-1}$ due to the merging of $-\text{CH}$ 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 Effluent 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.

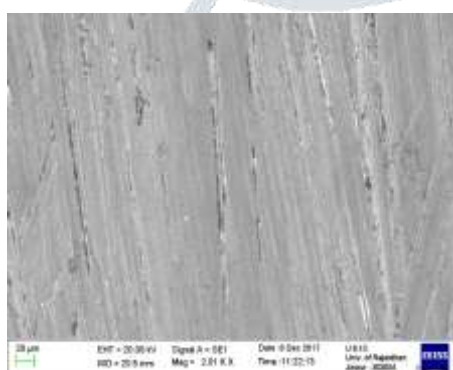


Figure 14: Blank

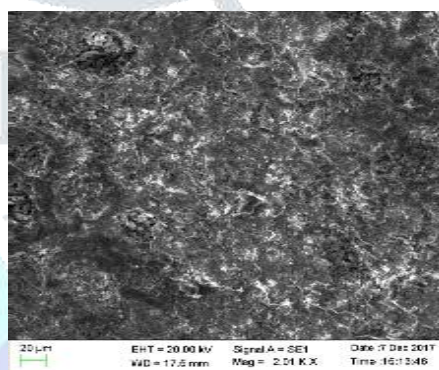


Figure 15: EFW Blank

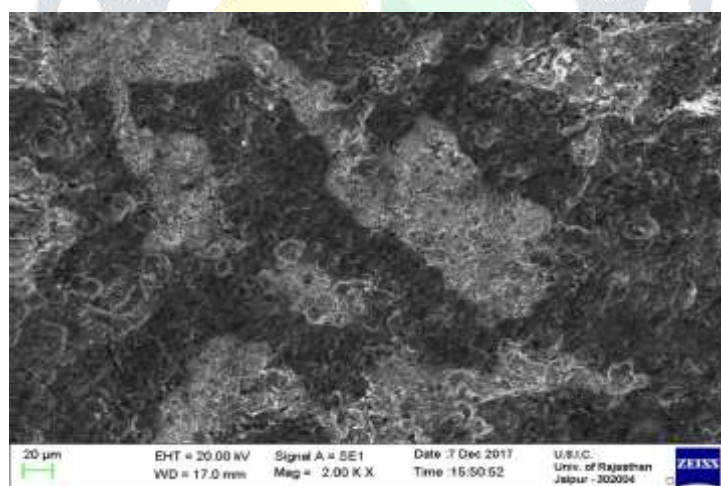


Figure 16: Hexamethylenetetramine EFW

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 effluent water (EFW) 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 EFW 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 EFW and corrosion inhibition efficiency reaches to 95.35 in HMTA & 97.02 in HMTA with KI and 96.81 HMTA with SFA in EFW 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.



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