

Effect of Temperature on Corrosion Inhibitive Property of *Trigonella foenum graecum* Seeds

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ABSTRACT: The effect of temperature on the inhibitive property of the *Trigonella foenum graecum* seeds (*TfgS*) on the acid corrosion of aluminum has been investigated. The experimentation was carried out by the weight loss method. The results reveal that *TfgS* inhibit corrosion of aluminum very efficiently. The inhibition efficiency (IE %) was found highest 95.65% at the optimum concentration of *TfgS* at elevated temperature which decreases with further increase in temperature. The corrosion and thermodynamic parameters were determined in the studied temperature range for different concentrations of *TfgS*. The ΔG values indicate that the adsorption of *TfgS* on aluminum is physical in nature. The adsorptive behavior of the inhibitor at room and elevated temperatures was further studied by the FTIR spectroscopy and Optical micrography techniques. It can be inferred that the *TfgS* may be a better substitute of the chemical inhibitors used for acid corrosion of aluminum.

KEYWORDS: Aluminum, *Trigonella foenum graecum* seeds (*TfgS*), Kinetic and Thermodynamic Parameters, FT-IR Spectroscopy.

I. INTRODUCTION

Aluminum and its alloys have high corrosion resistance in many environments. Large parts of the metal surface are covered with a protective film and are in the passive state, while other small parts of the surface are in the active state. The Cl^- ions cause the passive film to break down at certain weak spots on the metal surface [1]. It has been found that one of the best practical and preferred methods of protecting metal against corrosion involves the use of corrosion inhibitor, the substances that slow down the rate of corrosion [2]. Most of the corrosion inhibitors used are synthetic chemicals (organic compounds) containing electronegative functional group and pi-electrons in triple or conjugated double bonds. The heteroatoms such as sulphur, phosphorus, nitrogen, and oxygen as well as aromatic rings present in their structure are the major adsorption centre. These synthetic chemicals show good anticorrosive activity but most of them are expensive, non-biodegradable, and highly toxic [3-5]. It is necessary to explore environment friendly and less expensive inhibitors. Plant products have constituents like tannins, organic and amino acids, alkaloids, and pigments are known to exhibit inhibiting action [6-17] Moreover, they are easily available, bio degradable and can be extracted by simple procedure at low cost.

The aim of this study is to investigate inhibitive property of the ethanolic extract of *Trigonella foenum graecum* seeds (*EETfg*) to inhibit the corrosion of aluminum in Hydrochloric acid (HCl). Fenugreek [*Trigonella foenum graecum* (*Tfg*)] is a plant in the family fabaceae having active constituents like Lipids, Polyscharrides, Aminoacid, Alkaloid, Fiber, and Volatile compounds as -g-lactone, sotolone etc. [18-19]. Major *Tfg* producing countries are India, Argentina, Egypt, France, Spain, Turkey, Moraco and China. India is the largest producer in the world and Rajasthan, Gujarat, Uttaranchal, Uttarpradesh, Madhyapradesh, Maharashtra, Haryana and Punjab are the major fenugreek producing states among which Rajasthan has maximum area and production of about more than 80% of India's total production. *Tfg* is an annual plant widely cultivated for both medicinal and culinary uses [20].

This work presents the study of the temperature effect on inhibition efficiency of acid corrosion of aluminum in 0.5N HCl in the absence and presence of various concentrations of *EETfgS* by using weight loss method. The specimens were also examined using FTIR and optical microcopies.

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II. MATERIALS AND METHOD

2.1 Weight loss measurements

The weight loss measurements were performed following standard method, explained in detail elsewhere [21].

2.1.1 Preparation of aluminum coupons:

The industrial aluminum of 98.99% purity (AA6063), mechanically press cut as rectangular coupons (3cm x 2cm x 0.16cm) with a hole of about 0.12mm diameter near the upper edge has been used as specimen. After check for rough edges, the surface treatment was carried out by using various grades of emery paper (110 to 410) until the surface appeared free from scratches and other apparent defects. These were degreased with water and finally with acetone and then dried and stored in vacuum desiccators containing CaCl_2 , until cooled to room temperature and then weighed accurately using a digital balance. The specimen were subjected to further heating, cooling and weighing till a constant weight obtained and then stored in desiccators.

2.1.2 Ethanolic extraction of *Trigonella foenum graecum* seeds (EETfgS)

The stock solutions of the *Tfg* seeds were prepared by soaking the weighed amount of room temperature dried and finely powdered seeds of *Tfg* in a properly corked container having distilled ethanol. On completion of soaking period, the ethanolic solutions were refluxed for 24h to concentrate the inhibiting chemicals and then filtered to remove any suspended impurities. This stock solution of the extract was stored in a clean corked bottle. From this dried liquid extract was used as inhibitor.

2.1.3 Preparation of test solutions

The aggressive solutions used were made of AR grade reagent (0.5N HCl) and deionized water. 100ml of the aggressive solutions was measured in 7 separate solutions and labeled as S0, S1, S2, S3, S4, S5 and S6. EETfgS was added in order of increasing concentration as to have 0.022, 0.066, 0.154, 0.264, 0.528 and 1.056g/L respectively in S1, S2, S3, S4, S5 and S6. No extract was added to the S0, i.e., the first beaker solution. All the beakers were covered with Teflon tape and kept unstirred throughout the experiment.

2.2 Surface analysis

2.2.1 Fourier – Transform infrared (FITR) spectroscopy

The spectra were recorded with the 8400s Shimadzu, Japan spectrometer. The samples were prepared using KBr and the analysis was done by scanning the samples through a wave number range of 400 to 4000 cm^{-1} .

2.2.2 Optical micrography

Optical adsorption measurements have been performed by using LABOMED microscope. The measuring scale attached with the eyepiece has an accuracy of 0.1 μm . In the present work 40X magnification has been used.

III. RESULTS AND DISCUSSION

3.1 Corrosion rates and inhibition efficiency by weight loss measurements:

The effect of inhibitor on the corrosion of aluminum in 0.5 N HCl solutions was studied using the weight loss technique. Fig. 1 shows the variation of weight loss with immersion time periods at room temperature (303 \pm 1K). It is seen that it changes linearly with immersion time period in uninhibited and inhibited acid solutions. The magnitude of weight loss in the presence of the additive is significantly less than that of with only HCl which indicates that insoluble film has been developed on the surface of the coupons.

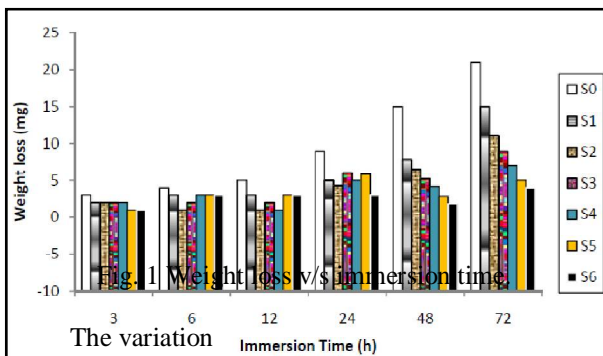


Fig. 1 Weight loss v/s immersion time

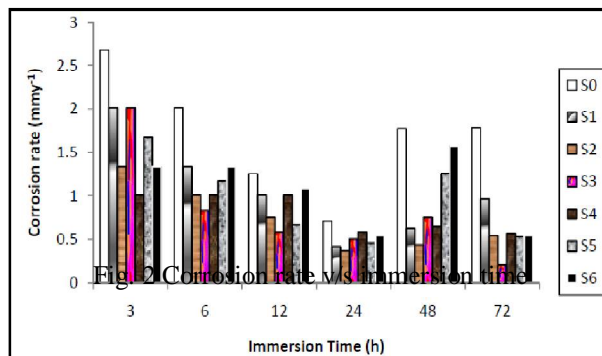


Fig. 2 Corrosion rate v/s immersion time

of corrosion rate with time period has been shown in Fig 2 which decreased with increase in the period of contact while if inhibitor concentration is increased it decreases. This behavior could be attributed to the increase in adsorption of EETfgS at the metal solution interface. The minimum corrosion rate 0.0754 mm.y^{-1} has been observed for S6 solution in which the concentration of inhibitor added is 1.056 g/L .

The effect of exposure time on inhibition efficiency (IE%) has been shown in Fig. 3. It reveals a small decrease in IE% from 88% to 80% as exposure time increases from 48 to 72h. A slight decrease in inhibition after 48h is probably due to decrease in adsorption and increase in desorption. This behavior may be attributed to the increase of the surface area covered by the adsorbed molecules of EETfgS with the increase in concentration of inhibitor. Organic compounds (mainly heterocyclic compounds having N, O present in the ring) present in EETfgS can easily be adsorbed on the corroding alloy surface giving rise to such inhibition and the inhibition may be due to their synergistic action.

The effect of concentration on inhibition efficiency is shown in Fig. 4. Maximum inhibition efficiency was found 88% at concentration of inhibitor 1.056 g/L for immersion time of 48 hours. From Fig. 3 and Fig. 4 an irregular trend has been observed at lower immersion time periods i.e. 3 to 12h and lower concentrations of the inhibitor which improves when the immersion time and the concentration of the inhibitor are increased. This can be attributed to the desorption of the metal for lower concentrations and lower immersion time periods, whereas as the time of immersion and concentration are increased, the formation of monolayer on the surface of the sample diminishes the rate of corrosion.

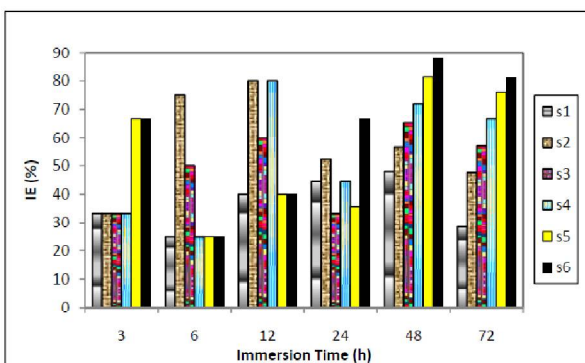


Fig. 3 IE% v/s immersion time

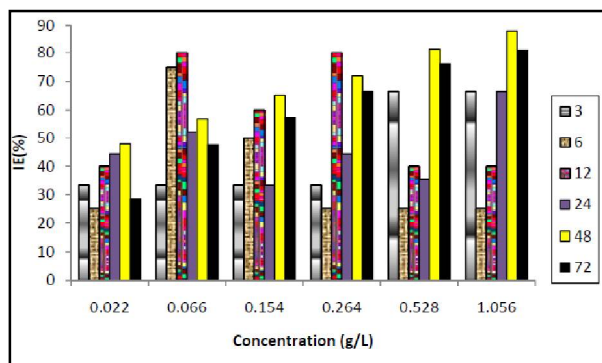


Fig. 4 IE% v/s various concentrations

3.2 Temperature Effect:

The effect of temperature (in the range 303-353K), the adsorption of EETfgS and activation parameter of the acid corrosion of aluminum in 0.5N HCl were also studied. Weight loss measurements were carried out in the absence and presence of various concentrations of EETfgS at immersion time 72h.

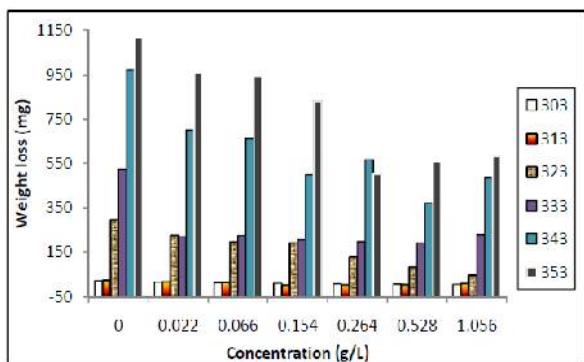


Fig. 5 Weight loss (mg) v/s concentration

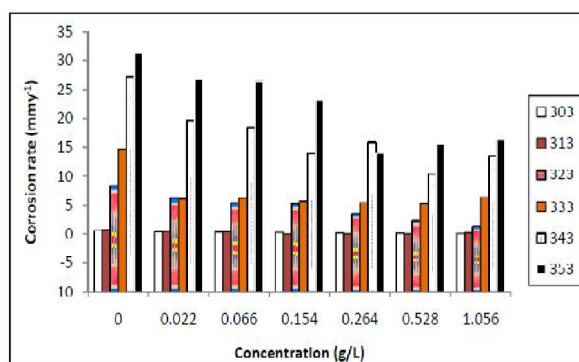


Fig. 6 Corrosion rate v/s concentration

Fig. 5 shows effect of variation of concentration of EETfgS on weight loss showing a general decrease. Fig. 6 shows effect of variation of concentration of EETfgS on corrosion rate. This represents that there is a progressive increase in the corrosion rate as the temperature is increased from 303 to 353K for immersion time period of 72h. The minimum corrosion rate was observed to be 0.0279 mmy^{-1} for solution having concentration of inhibitor 0.154 g/m at room temperature ($303 \pm 1\text{K}$).

Fig. 7 and Fig. 8 illustrate the variation of IE% with EETfgS concentrations and temperatures, respectively. It is seen that the IE% (at optimum concentration 0.154g/L) increased for temperature 313K to 95.65% but decreased to 55.06% if the temperature is further increased up to 353K. The decreased protection efficiency at high temperature might be explained from the fact that increase of temperature affected the rate of adsorption and desorption was faster than the rate of adsorption.

The combined effect of EETfgS concentration and temperature seems to be more complex. No regular trend was observed in corrosion parameters as a function of increase in temperature.

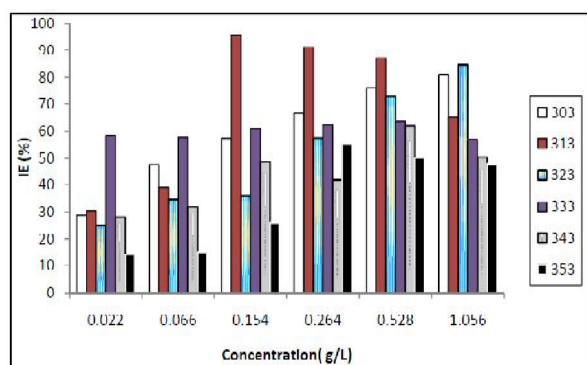


Fig. 7: IE% v/s concentration.

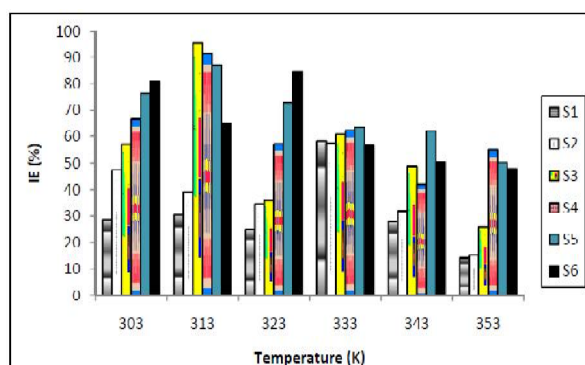


Fig. 8: IE% v/s temperature.

3.3 Thermodynamic parameters

Thermodynamic parameters were also determined using standard formulas which are tabulated in Table 1. The negative free energy values (ΔG) indicate spontaneous adsorption and a strong interaction between the inhibitor molecules and the metal surface. The value at room temperature was found much lower than -20kJ/mol which shows physical adsorption of the molecule on aluminum surface. While at slightly high temperature (313K) value is increasing (23.46kJ/mol) which is an indicative of chemisorptions of inhibitor at metal surface. The negative sign of enthalpy (ΔH) reveals that the adsorption of inhibitor molecules is an exothermic process. The absolute values are relatively lower, approaching those typical of chemisorptions. The shift towards positive value of entropies (ΔS) imply that the spontaneous adsorption and activated complex formation in the rate determining step represents dissociation rather than association, it is clearly indicated that the disordering increases on going from reactant to the activated complex.

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Table 1:- Thermodynamic parameters of acid corrosion of aluminum.

Test solution	(-) $\Delta G =$ (kJ/mole)						ΔH (kJ/mole)	ΔS (J/mol.K)
	303K	313K	323K	333K	343K	353K		
S1	17.42	18.23	18.07	22.61	19.63	17.69	-9.48	-28
S2	16.72	16.37	16.38	19.48	17.06	14.70	-21.44	14
S3	15.58	23.36	14.27	17.53	16.65	14.17	-39.22	68
S4	15.22	20.04	15.14	16.21	14.32	16.29	-26.25	30
S5	14.65	17.05	15.13	14.43	14.67	13.69	-26.82	36
S6	13.62	11.94	15.19	11.71	11.31	11.39	-27.96	47

3.4 Adsorption isotherm

The action of inhibitor in acid solutions is generally agreed to be adsorption on to the metal surface which is usually oxide free in acid solutions. Langmuir isotherm was tested for its fit to the experimental data.

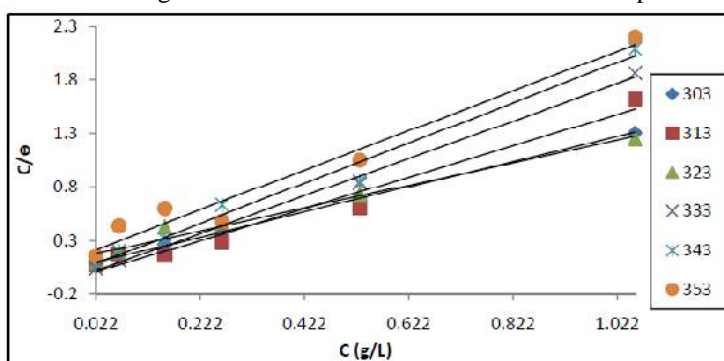


Fig. 9 C/ θ v/s C at different temperatures.

The plot of C/ θ versus C shows a linear behavior (Fig. 9) which proves that Langmuir adsorption isotherm is obeyed for each temperature over the range of concentration studied. The correlation coefficient, slopes, obtained from Langmuir isotherm plots are given in Table 2

Table 2 The correlation coefficient and slopes from Langmuir adsorption isotherm at different temperatures

Temperature (K)	Slope	Correlation coefficient(R^2)	k
303	1.17	0.999	14.285
313	1.47	0.971	00.972
332	1.06	0.974	06.493
333	1.70	0.996	00.780
343	1.80	0.982	24.390
353	1.80	0.960	05.747

The degree of linearity of Langmuir adsorption isotherm as measured by value of R^2 in the range ($0.999 \geq r^2 \geq 0.960$) which is nearly equal to one and slope is almost unity at room temperature At higher temperature the deviation of the slopes from unity can be attributed to the molecular interaction among the adsorbed inhibitor species.

3.5 Surface- analysis:

3.5.1 FTIR spectroscopy

The adsorption of EETfgS on aluminum was further examined by FTIR spectral studies using KBr pellet method. The peaks in the spectra were identified for various functional groups present in the EETfgS and that of the corrosion product of aluminum (only those are shown which have shifted) in Table 3. It has been found that the N-H stretching at

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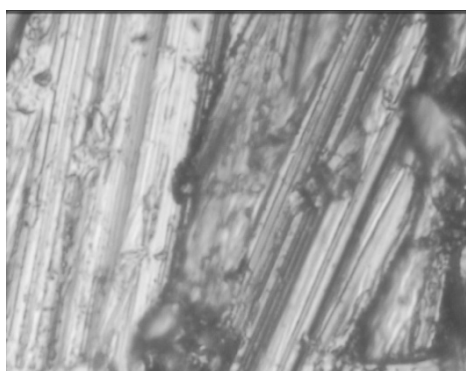
2350cm⁻¹ and was shifted to 2360cm⁻¹, and cyclic five membered aldehyde and ketone at 1750 cm⁻¹ shifted to 1860 cm⁻¹, C=C benzene ring at 1650 cm⁻¹ shifted at 1620 cm⁻¹. These values indicate an interaction between EETfgS and metal surface and that these functional group are involved in the formation of bond with aluminium [23-24].

Table -3 Peaks of IR adsorbed on aluminum and ethanol extract of *Trigonal foenum graecum* seeds.

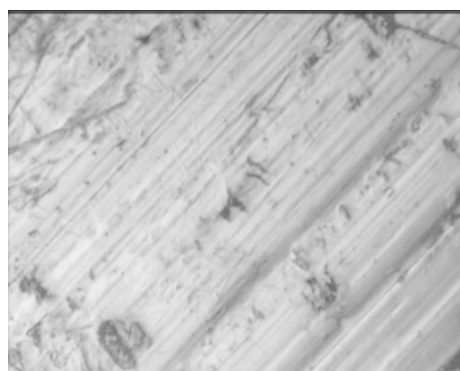
Pure extract of EETfgS		Extract adsorbed on aluminum alloy (AA6063)	
Frequency (cm ⁻¹)	Assigned peak	Frequency (cm ⁻¹)	Assigned peak
3010	Trisubstituted C-H str.		
2940	C-H str.		
2850	C-H stretching		
2350	N-H stretching	2360	N-H stretching
1750	Cyclic five membered aldehyde and ketone	1860	Cyclic five membered aldehyde and ketone
1650	Aromatic C=C with benzene rings	1620	N-H def.
1450	Aromatic C=C		
1350	C-O stretching primary alcohol		
1150	C-O stretching in aromatic ether	1160	C-O stretching in aromatic ether
1020 to 1200	tertiary alcohol		
900	aliphatic amine	930	aliphatic amine
800 to 850	mono substituted alkenes		
650	para di substituted benzene		

3.5.2 Optical micrography

Fig. 10A shows the surface of aluminium coupon while the Fig. 10B is the surface after various treatments. It is clear from the Figs. 10 (C, E, G, I, K, M) that the surface of aluminum was heavily corroded in 0.5N HCl, while in the presence of inhibitor the surface condition was comparatively better as seen in Figs. 10 (D, F, H, J, L, N).



Aluminium coupon 10 (A)



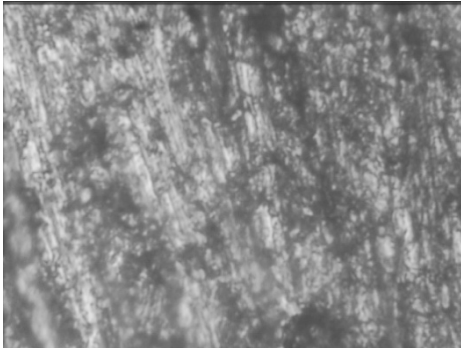
Al coupon after the surface treatment 10 (B)

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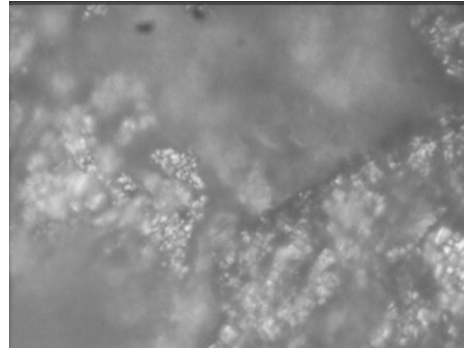
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AT 303K

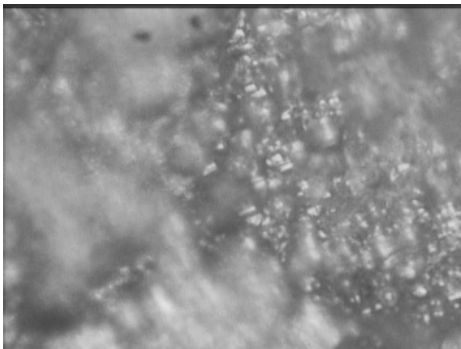


Immersed in 0.5N HCl 10 (C)

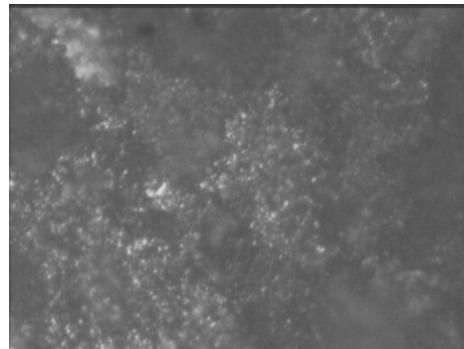


Highest concentration S6 (1.056g/L) 10(D)

AT 313K

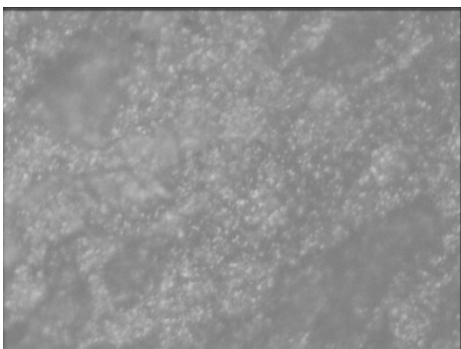


Immersed in 0.5N HCl 10 (E)

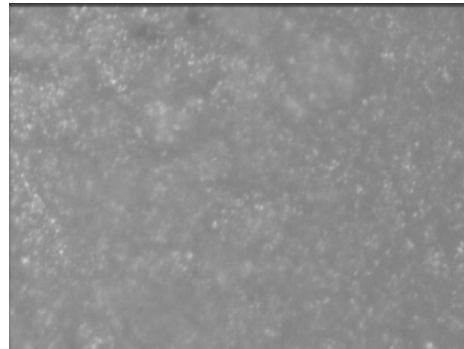


Optimum concentration S3 (0.154g/L) 10 (F)

AT 323K



Immersed in 0.5N HCl 10 (G)



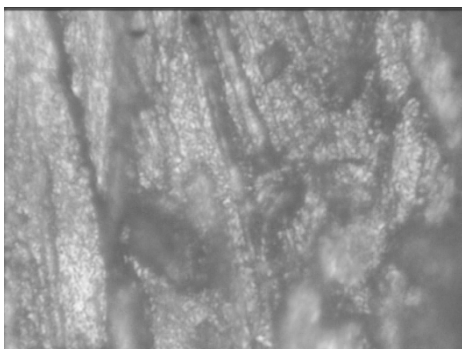
Highest concentration S6 (1.056g/L) 10 (H)

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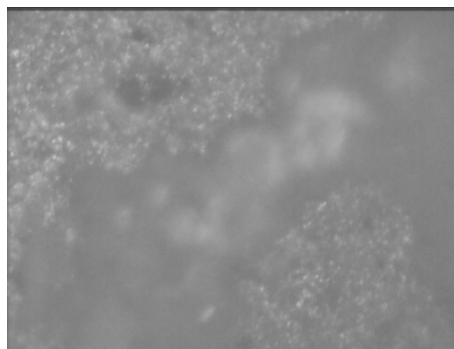
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AT 333K

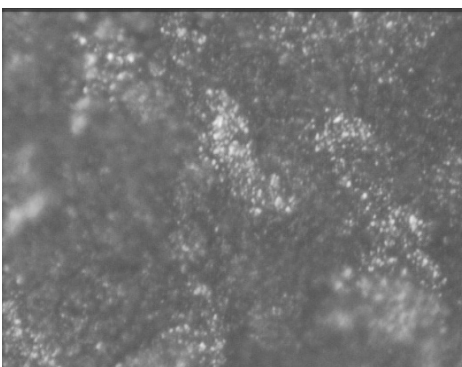


Immersed in 0.5N HCl 10 (I)

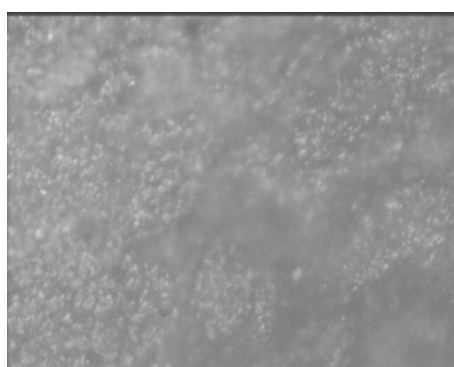


Optimum concentration S5 (0.528 g/L) 10 (J)

AT 343K

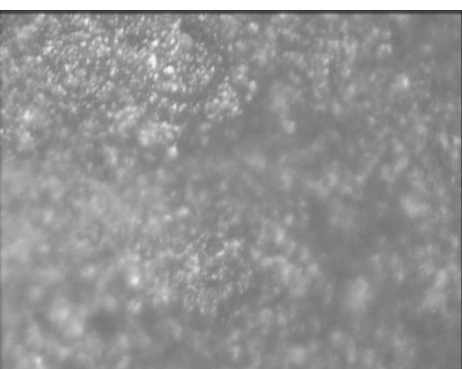


Immersed in 0.5N HCl 10 (K)

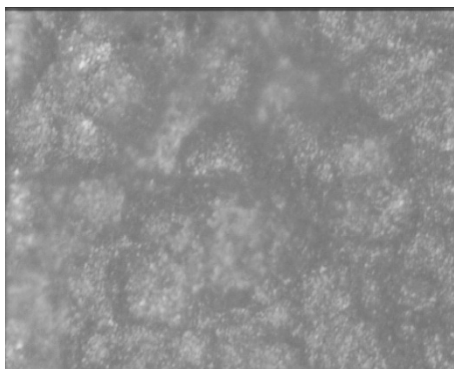


Optimum concentration S6 (1.056g/L) 10 (L)

AT 353K



Immersed in 0.5N HCl 10 (M)



Optimum concentration S4 (0.264 g/L) 10 (N)

Fig-10 (A-N) Optical micrographs of aluminium coupons before and after surface treatment at various temperature.

Dependence on the concentration of the inhibitor solution and temperature suggests the presence of a protective adsorbed layer of the inhibitor on aluminum surface which impedes corrosion rate of metal appreciably [24].

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IV. CONCLUSION

From the study it has been concluded that:

- a. EETfgS has been found to act as a good inhibitor for corrosion of aluminum alloy (AA6063) in 0.5N HCl.
- b. The values of the free energy of adsorption calculated indicate strong, spontaneous and physical adsorption of the extract on the aluminum alloy (AA6063) surface.
- c. The presence of the EETfgS extracts increases the activation energy of the corrosion process.
- d. Inhibition efficiency of EETfgS increases with increasing concentration, while an increase or decrease in the Inhibition efficiency is detected with increasing temperature depending on EETfgS concentration. The EETfgS inhibit corrosion up to 95.17% in acidic medium at an optimum concentration 0.154g/L, at an elevated temperature (313K).
- e. The EETfgS was found to obey Langmuir adsorption isotherm from the fit of experimental data at room temperature while at elevated temperature deviation from ideal Langmuir adsorption isotherm was observed.
- f. Results let to suggest the occurrence of physical adsorption for the inhibitor species.
- g. FTIR spectra show most of the organic molecules present in the inhibitor and some complexes formed between inhibitor and metal surface.
- h. Optical micrographs further confirm the formation of the protective film over the aluminum alloy surface by the green inhibitor used.

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