



Corrosion inhibition of Aluminum by *Trigonella foenum graecum* seeds in 0.5N HCl

Shashi Sharma

Department of Chemistry, University of Rajasthan, Jaipur (Rajasthan) India- 302 015.

Received on: 24-Apr-2016 Accepted and published on 07-June-2016

ABSTRACT

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 88% for concentration of inhibitor 1.056g/L at immersion time of 48 hours. The adsorptive behavior of the inhibitor was further studied by the FTIR spectroscopy and Optical micrography techniques. It is 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), FT-IR Spectroscopy, Optical Micrography.

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 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 which are known to exhibit inhibitory 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 0.5N

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, Uttar Pradesh, Madhya Pradesh, 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.

MATERIALS AND METHODS

Weight loss measurements

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

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 have 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

Dr. Shashi Sharma
Email: shashe.sharma@gmail.com

Cite as: J. Integr. Sci. Technol., 2016, 4(1), 37-40.

© IS Publications JIST ISSN 2321-4635

CaCl₂, 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.

Ethanolic extraction of *Tfg*S

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.

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.

Surface analysis

Fourier – Transform infrared (FTIR) 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.

Optical micrography

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

RESULTS AND DISCUSSION

The effect of inhibitor on the corrosion of aluminum in HCl solutions was studied using the weight loss technique at room temperature at various immersion time periods. Corrosion and adsorptive parameters like corrosion rate (ρ_{corr} in mmy⁻¹), percentage inhibition efficiency (IE%), fractional surface coverage (θ), adsorption equilibrium constant (K_{ad}) etc. have been calculated and are tabulated in table 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. Figure 1 shows the variation of weight loss with immersion time periods at room temperature (303±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. The variation of corrosion rate with time period has been shown in Figure 2 which decreased with increase in the period of

contact while if inhibitor concentration is increased it decreases.

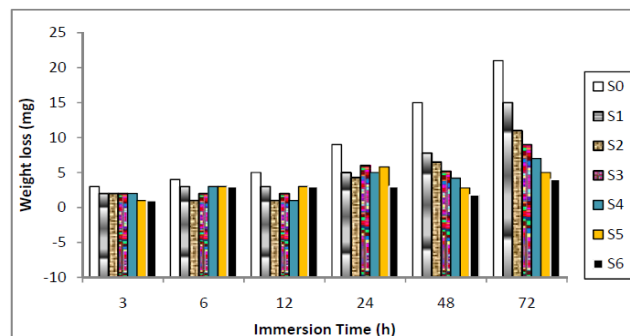


Figure 1. Weight loss v/s immersion time.

This behavior could be attributed to the increase in adsorption of EETfgS at the metal solution interface. The minimum corrosion rate 0.0754 mmy⁻¹ has been observed for S6 solution in which the concentration of inhibitor added is 1.056g/L.

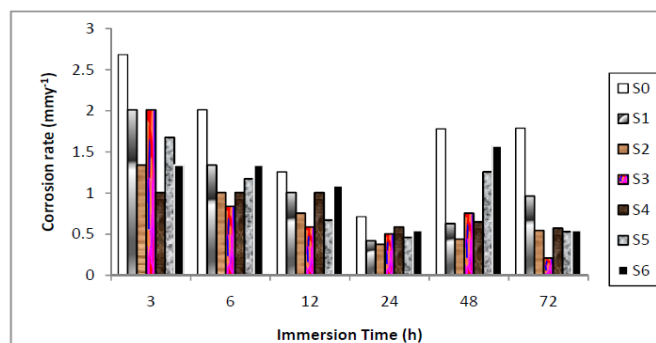


Figure 2. Corrosion rate v/s immersion time

The effect of exposure time on inhibition efficiency (IE%) has been shown in Figure 3. It reveals that 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 in the ring) present in EETfgS can easily be adsorbed on the sample surface giving rise to such inhibition. The effect of concentration on IE% is shown in Figure 4 which was 88% at concentration of inhibitor 1.056g/L for immersion time of 48 h. From Figure 3 and Figure 4 an irregular trend has been observed at lower immersion time periods when the immersion time and the concentration of the inhibitor are increased. This can be attributed to desorption of the metal for lower concentrations and lower immersion time periods, whereas with increase, the formation of monolayer on the surface of the sample diminishes the rate of corrosion.

Table 1 Corrosion parameters of acid corrosion of aluminium without and with various concentrations of EETfGS for various immersion times (h) at temperature 303±1K.

Time (h)	EETfGS concentration (g/L)	Weight loss (mg)	Corrosion rate (ρ_{cor} in $\text{mm} \cdot \text{y}^{-1}$)	Inhibition Efficiency (IE%)	Fractional Surface coverage (θ)	Adsorption Equilibrium Constant (K_{ad})
3	S0	3.0	2.0117	-	-	-
	S1 (0.022)	2.0	1.3411	33.33	0.3333	22.727
	S2 (0.066)	2.0	1.3411	33.33	0.3333	7.575
	S3 (0.154)	2.0	1.3411	33.33	0.3333	3.246
	S4 (0.264)	2.0	1.3411	33.33	0.3333	1.893
	S5 (0.528)	1.0	0.6706	66.67	0.6667	3.787
	S6 (1.056)	1.0	0.6706	66.67	0.6667	1.893
6	S0	4.0	1.3411	-	-	-
	S1 (0.022)	3.0	1.0058	25.00	0.2500	15.152
	S2 (0.066)	1.0	0.3353	75.00	0.7500	45.455
	S3 (0.154)	2.0	0.6706	50.00	0.5000	6.493
	S4 (0.264)	3.0	1.0058	25.00	0.2500	1.262
	S5 (0.528)	3.0	1.0058	25.00	0.2500	0.631
	S6 (1.056)	3.0	1.0058	25.00	0.2500	0.315
12	S0	5.0	0.8382	-	-	-
	S1 (0.022)	3.0	0.5029	40.00	0.4000	30.303
	S2 (0.066)	1.0	0.1676	80.00	0.8000	60.606
	S3 (0.154)	2.0	0.3353	60.00	0.6000	9.740
	S4 (0.264)	1.0	0.1676	80.00	0.8000	15.152
	S5 (0.528)	3.0	0.5029	40.00	0.4000	1.262
	S6 (1.056)	3.0	0.5029	40.00	0.4000	0.631
24	S0	9.0	0.7544	-	-	-
	S1 (0.022)	5.0	0.4191	44.44	0.4444	36.364
	S2 (0.066)	4.3	0.3604	52.22	0.5222	16.561
	S3 (0.154)	6.0	0.5029	33.33	0.3333	3.246
	S4 (0.264)	5.0	0.4191	44.44	0.4444	3.030
	S5 (0.528)	5.8	0.4862	35.56	0.3556	1.044
	S6 (1.056)	3.0	0.2515	66.67	0.6667	1.893
48	S0	15.0	0.6287	-	-	-
	S1 (0.022)	7.8	0.3269	48.00	0.4800	41.958
	S2 (0.066)	6.5	0.2724	56.67	0.5667	19.814
	S3 (0.154)	5.2	0.2179	65.33	0.6533	12.238
	S4 (0.264)	4.2	0.1760	72.00	0.7200	9.740
	S5 (0.528)	2.8	0.1173	81.33	0.8133	8.252
	S6 (1.056)	1.8	0.0754	88.00	0.8800	6.944
72	S0	21.0	0.5867	-	-	-
	S1 (0.022)	15.0	0.4191	28.57	0.2857	18.182
	S2 (0.066)	11.0	0.3073	47.62	0.4762	13.774
	S3 (0.154)	9.0	0.2515	57.14	0.5714	8.658
	S4 (0.264)	7.0	0.1956	66.67	0.6667	7.575
	S5 (0.528)	5.0	0.1397	76.19	0.7619	6.060
	S6 (1.056)	4.0	0.1118	80.95	0.8095	4.024

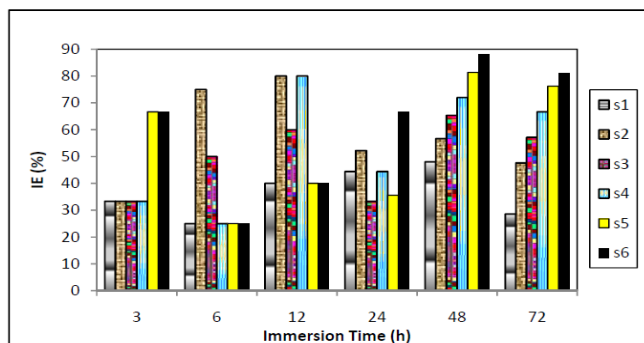


Figure 3. IE% v/s immersion time

Surface- analysis:

FTIR spectroscopy

The adsorption of EETfGS on aluminium was 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

aluminium as provided in Table (supporting information). It has been found that the N-H stretching at 2350cm^{-1} and was shifted to 2360cm^{-1} , and cyclic five membered aldehyde and ketone at 1750cm^{-1} shifted to 1860cm^{-1} , C=C benzene ring

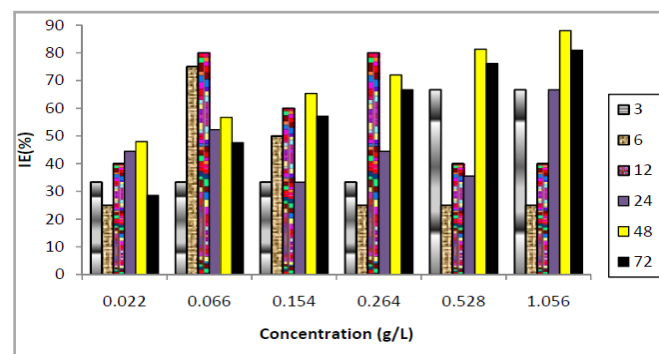


Figure 4. IE% v/s various concentrations

at 1650 cm^{-1} shifted to 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

Optical micrography

Figure 4A and B are coupons with and without surface treatment. It is clear from the Fig. 4C 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 Figure 4D. 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

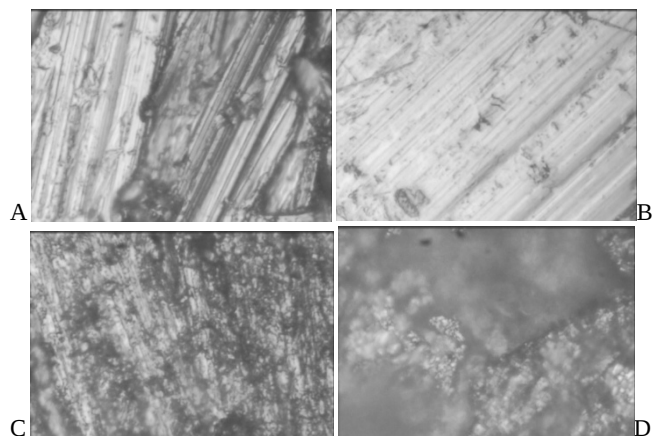


Figure 4. (A) Aluminum coupon (B) Al coupon after the surface treatment (C) Immersed in 0.5N HCl (D) Highest concentration S6 (1.056g/L)

CONCLUSIONS

From the study it has been concluded that:

- EETfgS has been found to act as a good inhibitor for corrosion of aluminum alloy (AA6063) in 0.5N HCl.
- FTIR spectra show most of the organic molecules present in the inhibitor and some complexes formed between inhibitor and metal surface.
- Optical micrographs further confirm the formation of the protective film over the aluminum alloy surface by the green inhibitor used.

ACKNOWLEDGMENTS

Author is thankful to Head, Department of Physics and Chemistry, University of Rajasthan; Dr. P. K. Singh, Head, Solar cell Division, NPL, New Delhi for their support.

REFERENCES

- M. Schütze, D. Wieser and R. Bender. Corrosion Resistance of Aluminium and Aluminium Alloys, Wiley-VCH, Weinheim **2010**.
- E. Ghali and R. W. Revie. Corrosion Resistance of Aluminum and Magnesium Alloys: Understanding, Performance, and Testing, John Wiley and Sons, New York **2010**.
- A. M. Fekry and M. A. Ameer. Corrosion inhibition of mild steel in acidic media using newly synthesized heterocyclic organic molecules, *Int. J. Hydro. Ener.*, **2010** 35 7641.

- Y. Abboud, A. Abourriche, T. Saffaj, M. Berrada, M. Charrouf, A. Bennamara and H. Hannache. A novel azo dye, 8-quinolinol-5-azoantipyrine as corrosion inhibitor for mild steel in acidic media, *Desalination*, **2009** 237 175.
- S. N. Banerjee. An Introduction to Science of Corrosion and its Inhibition, Oxonian Press, New Delhi **1985**.
- V. S. Sastri, E. Ghali and M. Elboudjaini. Corrosion prevention and protection: practical solutions, John Wiley and Sons, New York **2007**.
- O. K. Abiola, J.O.E. Otaigbe and O.J. Kio. Gossipium hirsutum L. extracts as green corrosion inhibitor for aluminum in NaOH solution, *Corros. Sci.*, **2009** 51 1879.
- S. A. Umoren, I. B. Obot, E. E. Ebenso and N. O. Obi-Egbedi. The Inhibition of aluminium corrosion in hydrochloric acid solution by exudate gum from *Raphia hookeri*, *Desalination*, **2009** 247 561.
- E. A. Noor. Potential of aqueous extract of *Hibiscus sabdariffa* leaves for inhibiting the corrosion of aluminum in alkaline solutions, *J. App. Electrochem.*, **2009** 39 1465.
- S. Rajenderan, J. Jeyasundari, P. Usha, J. A. Selvi, B. Narayanasamy, A. P. P. Regis and P. Renga. Corrosion behavior of aluminum in the presence of an aqueous extract of *hibiscus rosasinensis*, *Port. Electrochimica Acta*, **2009** 27(2) 153.
- R. Rajalakshmi, S. Subhashini, M. Nanthini and M. Srimathi. Inhibiting effect of seed extract of *abrus precatorius* on corrosion of aluminum in sodium hydroxide, *Ori. J. Chem.*, **2009** 25(2) 313.
- J. Dubey, P. Sharma, A. Chaturvedi and R. K. Upadhyay. Effect of Temperature on Corrosion Inhibition Efficiency of *Withania Somnifera* (Ashwagandha) on aluminum in HCl Solution, *J. Corros. Sci. Eng.*, **2010** 13 (Preprint).
- R. Khandelwal, S. Sahu, S. K. Arora and S. P. Mathur. Study of corrosion inhibition efficiency of naturally occurring plant *Cordia Dicotoma* on aluminum in acidic media, *J. Corros. Sci. Eng.*, **2010** 13 (Preprint).
- O. K. Abiola and Y. Tobun. *Cocos nucifera* L. water as green corrosion inhibitor for acid corrosion of aluminum in HCl solution, *Chin. Chem. Lett.*, **2010** 21 1449.
- E. I. Ating, S. A. Umoren, I. I. Udousoro, E. E. Ebenso and A. P. Udoh. Leaves extract of *ananas sativum* as green corrosion inhibitor for aluminum in hydrochloric acid solutions, *Green Chem. Lett. Rev.*, **2010** 3(2) 61.
- I. B. Obot, N. O. Obi-Egbedi, S. A. Umoren and E. E. Ebenso. Synergistic and antagonistic effects of anions and *ipomoea invulcrata* as green corrosion inhibitor for aluminum dissolution in acidic medium, *Int. J. Electrochem. Sci.*, **2010** 5(7) 994.
- O. O. Ajayi, O. A. Omotosho, K. O. Ajanaku and B. O. Olawore. Degradation Study of Aluminum Alloy in 2 M Hydrochloric Acid in the Presence of *Chromolaena odorata*, *J. Eng. App. Sci.*, **2011** 6 10.
- G. M. S. El-Bahy. FTIR and Raman spectroscopic study of fenugreek (*Trigonella foenum graecum* L.) Seeds, *J. App. Spec.*, **2005** 72(1) 111.
- P. R. Petit, Y. D. Sauvage, D. M. H. Buys, O. M. Leconte, Y. G. Baissac, G. R. Ponsin and G. R. Ribes. Steroid saponins from fenugreek seeds extractions, purifications and pharmacological investigation on feeding behavior and plasma cholesterol *steroids*, **1995** 60(10) 674.
- J. K. Grover, S. Yadav and V. Vats. Medicinal plants of India with antibiotic potential, *J. Ethnopharmacol.*, **2002** 81(1) 81.
- E. A. Noor. Comparative study on the corrosion inhibition of mild steel by Aqueous extract of *Fenugreek* seeds and leaves in acidic solution, *J. Eng. Appl. Sci.*, **2008** 3(1) 23.
- B. C. Smith. Fundamentals of Fourier transform infrared spectroscopy, CRC Press, London, UK **1996**.
- P. S. Kalsi. *Spectroscopy of Organic Compounds* (6th ed.), New Age Int. Publ. (India), New Delhi **2004**.
- J. Mertz. Introduction to optical microscopy, Roberts, Greenwood Village, Colorado **2010**.

SUPPORTING INFORMATION

The IR peaks table and their identification is provided as supporting information and can be downloaded from journal article site.