

CORROSION INHIBITION OF MILD STEEL IN SULPHURIC ACID BY RICINUS COMMUNIS LEAVES

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ABSTRACT

The study of corrosion inhibition is significant in the field of research due to its usefulness in various industries. Increasing awareness of health and ecological risks have drawn attention in developing less expensive, eco-friendly inhibitors to retard the corrosion of mild steel in acid medium. In the present investigation Ricinus Communis Leaves (RCL) was used as corrosion inhibitor for mild steel in 0.5 M H₂SO₄ medium. Since temperature is one of the significant parameter in corrosion studies, the effect of temperature on the inhibitive property was studied gravimetrically. The inhibition efficiency (92.42%) was found to increase with increase in concentration of the extract (2.5%v/v) and with increase in temperature (323K). The inhibition by Ricinus Communis Leaves was found to obey Langmuir, Freundlich, Temkin adsorption isotherms. Thermodynamic parameters such as E_a, ΔG, ΔS, ΔH also have been calculated and discussed.

Keywords: Inhibitor, acid medium, adsorption isotherm, thermodynamic parameters.

INTRODUCTION

Steel is one of the major construction materials, which is extensively used in chemical and allied industries for the handling of acid, alkali and salt solutions. Sulphuric acid is the most difficult of the common acids to handle from the standpoints of corrosion and materials of constructions. Extreme care is required in the selection of materials to handle the acid by itself, even in relatively dilute concentrations or in process solutions containing appreciable amount of sulphuric acid. This acid is very corrosive to most of the common metals & alloys. Metals are exposed to the action of acids in many different ways and for many different reasons. Processes in which acids play a very important part are, acids pickling, industrial acid cleaning and oil well acidizing in order to stimulate of oil well. One of the most commonly used acids in today's industrialized world in sulphuric acid H₂SO₄, where some of its applications include chemical cleaning and processing, acid

treatment of oil wells and other applications². The wide use of this acid has led to the concentration of this study on the corrosive effects of this acid on carbon steel, which is a versatile component in many industrial structures³⁻¹¹. The Ricinus Communis under pharmacology is available as anti inflammatory, cytotoxic, antidiabetic, antibacterial and antifertility drugs. The aim of the present work is to find a naturally occurring cheap and environmentally safe substance that could be used for inhibiting the corrosion of mild steel. The use of natural product will establish, simultaneously, the economic and environmental goals.

EXPERIMENTAL METHOD

Preparation of the specimen

The sheets of cold rolled mild steel, which is commercially available in the market, were machined into coupons of area 5 x 1 cm². Holes were drilled on the center of one end of all the coupons for suspension and the

coupons are numbered for identification. These coupons were degreased, cleaned with emery paper and washed with distilled water and stored in desiccators in the absence of moisture before their use for the investigation.

Preparation of the extract

The leaves of Ricinus Communis Leaves were shade dried and powered. The extract was prepared by refluxing 50g of powered dry leaves in 1000 ml of 0.5 M H₂SO₄ for 3 hours and kept overnight. Then filtered and the volume of filtrate was made up to 1000 ml using the same acid. This solution was taken as the stock solution for further dilutions.

Mass loss method

Weighed samples are immersed in 100 mL of the acid (0.5 M H₂SO₄) without and with different concentrations of the inhibitor for a fixed immersion time ½ h. They are then taken out and immersed in saturated sodium bicarbonate solution to remove residual acids and then washed thoroughly with tap water, rinsed with distilled water, dried, stored in desiccators and reweighed. The parameters used for the present study are given below

- i) Concentration of the inhibitor: 0.005%, 0.01%, 0.05%, 0.10%, 0.15%, 0.2%, 0.5%, 1.0%, 1.5%, 2.5% (v/v)
- ii) Temperatures: (303, 313, 323, 333, 343) ± 2 K

The percentage of inhibitor efficiency (IE %) for various concentrations of the inhibitor were calculated as

$$IE\% = \left[\frac{W_0 - W}{W_0} \right] \times 100$$

Where W₀ and W are the corrosion rates of mild steel in 0.5 M H₂SO₄ in the absence and presence of definite concentrations of the inhibitor.

Adsorption isotherms

The degrees of surface coverage (θ) corresponding to different concentrations of the extract and at different temperatures have been extracted to deduce the best isotherm. The following isotherms were tested for their fit into the experimental data.

- Langmuir isotherm = Log(θ/1-θ) Vs log C
- Freundlich isotherm = Log(θ/C) Vs θ
- Temkin isotherm = θ Vs C

Surface examination

The mild steel specimens were immersed in various test solutions for a period of 168 h. The specimens were taken out and dried. Optical

microscope (NIKON-Model EPI-PHOT) was used for this investigation.

RESULTS AND DISCUSSION

Effect of temperature

The effect of temperature on the inhibitory action of the inhibitor was determined by weight loss method at various concentrations at different temperatures (303, 313, 323, 333 and 343) ± 2 K for a fixed immersion time ½ h. The tabulated data (Table 1) reveal that, as the concentration of the inhibitor increases the corrosion rate has decreased at all temperatures. There is no regular trend in the change of inhibition efficiency. This may be explained on the basis of the time lag between the process of adsorption and desorption. However, the inhibitor could be effectively used at 323K and maximum efficiency being 92.42%.

Interpretation of thermodynamic data

Putilova et al¹² have pointed out that for steel in acids the logarithm of the corrosion rate of steel "k" can be represented as a straight line function of 1/T (Arrhenius equation), where T is temperature in Kelvin's.

$$\ln k = \frac{-E_a}{RT} + B$$

where E_a is the activation energy, R is the Universal gas constant and B is a constant. The thermodynamic parameters such as free energy of adsorption (ΔG_{ads}), enthalpy change (ΔH) and entropy change (ΔS) were calculated using the well known relationships^{13,14}.

Activation energy (E_a) and thermodynamic data, such as change in free energy (ΔG_{ads}), enthalpy (ΔH) and entropy (ΔS) for mild steel in 0.5 M H₂SO₄ in the absence and in the presence of the inhibitor was calculated and listed in Table 2. The activation energy at different concentration of the inhibitor in 0.5 M H₂SO₄ is calculated by plotting Log C.R vs. 1/T (Figure 1). E_a values for inhibited systems are lower than those for uninhibited system indicating that all the inhibitors exhibit high I.E at elevated temperatures. The range of E_a is 40.86 – 45.07 kJ/mol for RCL in 0.5M H₂SO₄. The low and negative values of ΔG_{ads} (11.37-27.96 kJ) suggest the strong interaction of the inhibitor molecules whereas low value of ΔG_{ads} indicated spontaneous adsorption of inhibitors on mild steel surface. The ΔH values of (-20.306 - 0.127 kJ/mol) at all concentrations are found to be below 10 kJ/mol which indicate physical adsorption over the surface of mild steel. The change in entropy was found to be greater than zero (0.083-0.173 J/deg/mol). This indicates that the reaction is irreversible.

It is clear that, the complete desorption of the inhibitor is not possible.

Applicability of adsorption isotherms

The adsorption of the inhibitor is influenced by the nature and the charge of the metal, the chemical structure of the inhibitor, distribution of the charge in the molecule, and the type of electrolyte¹⁵⁻¹⁹. The surface coverage (θ) values for different concentrations of the inhibitor in 0.5 M H₂SO₄ have been evaluated from the weight loss data. The data were tested graphically to find a suitable adsorption isotherm.

A plot of $\text{Log}(\theta / (1 - \theta))$ against $\text{Log} C$ (Figure 2) shows a straight line ($R > 0.9$) indicating that adsorption follows the Langmuir adsorption isotherm. It is observed that although these plots are linear, the gradients are never unity, contrary to what is expected for ideal Langmuir adsorption isotherm equation. Organic molecules having polar atoms or groups which are adsorbed on the metal surface may interact by mutual repulsion or attraction and this may be advocated as the reason for the departure of the slope values from unity. The number of active sites of the surface occupied by one molecule of the inhibitor is given by the value of $(1/y)$. A straight line was obtained when the surface coverage was plotted against $\text{Log} C$ for the inhibitor. This shows that the adsorption obeys a Temkin adsorption isotherm, which is graphically represented in Figure 3. The plots of $\text{Log} \theta$ vs. $\text{Log} C$ are shown in Figure 4. The linearity shows that the

adsorption of the inhibitor on mild steel surface follows Freundlich isotherm.

Mechanism of inhibition

The probable mechanism can be explained on the basis of adsorption process and the structure 1 to 8 of the constituents present in the extract. The inhibition may be due to the adsorption of phytochemical constituents present in the extract through oxygen atoms on to the surface of the metal.

Constituents present in *Ricinus Communis* Leaves. their structures(1 – 7)

Surface Analysis

The polished specimen and the test specimens which are immersed in the blank (0.5 M H₂SO₄) and in certain concentrations of the inhibitor RCL for 24h were observed under a metallurgical microscope and photomicrographs are shown in the Figure 5-8. Figure 5 shows the polished mild steel surface before exposure to the acid medium, which is associated with polishing scratches. It is clear from the Fig. 6, that the surface of the mild steel was heavily corroded in 0.5 M H₂SO₄ medium, whereas in the presence of inhibitor, the surface condition was comparatively better (Figure 7 and 8). This depends on the concentration of the inhibitor solution suggesting that thereby the presence of a protective adsorbed layer of the inhibitor on mild steel surface which impedes corrosion rate of metal appreciably.

Table 1: Protection performance of RCL on mild steel in 0.5M H₂SO₄ (1/2 h) at different temperatures

| Conc. (%) | Inhibition Efficiency % | | | | |
|-----------|-------------------------|-------|-------|-------|-------|
| | 303 K | 313 K | 323 K | 333 K | 343 K |
| (v/v) | | | | | |
| Blank | - | - | - | - | - |
| 0.005 | 29.85 | 46.6 | 68.3 | 56.94 | 53.94 |
| 0.01 | 32.77 | 52.16 | 73.55 | 71.37 | 67.83 |
| 0.05 | 37.23 | 64.39 | 76.59 | 73.84 | 70 |
| 0.1 | 42.25 | 60.2 | 78.82 | 75.09 | 73.65 |
| 0.15 | 46.23 | 64.83 | 79.79 | 77.51 | 74.41 |
| 0.2 | 54.26 | 69.28 | 81.12 | 78.21 | 75.11 |
| 0.5 | 63.1 | 74.35 | 83.86 | 80.55 | 78.65 |
| 1.5 | 67.56 | 77.75 | 87.1 | 85.03 | 82.13 |
| 2 | 72.1 | 79.54 | 89.03 | 86.2 | 84.24 |
| 2.5 | 74.7 | 82.94 | 92.42 | 87.32 | 85.2 |

Table 2: Activation parameters for the dissolution of MS in the presence of RCL in 0.5M H₂SO₄

| Conc (%)(v/v) | Activation energy(Ea) | Free energy of adsorption (-ΔG) KJ/mol | | | | | Heat of adsorption(ΔH) KJ/mol | Entropy changes (ΔS) J/deg/mol |
|------------------|--------------------------|--|-------|-------|-------|-------|-------------------------------------|---|
| | KJ/mol | 303 K | 313 K | 323 K | 333 K | 343 K | | |
| Blank | 40.86 | - | - | - | - | - | - | - |
| 0.005 | 41.51 | 22.33 | 23.74 | 25.15 | 26.55 | 27.96 | -20.306 | 0.141 |
| 0.01 | 42.53 | 20.83 | 22.56 | 24.29 | 26.03 | 27.76 | 0.127 | 0.173 |
| 0.05 | 42.66 | 17.08 | 18.76 | 20.44 | 22.13 | 23.81 | 0.114 | 0.157 |
| 0.1 | 42.67 | 15.97 | 17.44 | 18.91 | 20.37 | 21.84 | 0.103 | 0.147 |
| 0.15 | 52.36 | 15.41 | 16.77 | 18.13 | 19.49 | 20.85 | 0.09 | 0.136 |
| 0.2 | 49.05 | 15.28 | 16.56 | 17.84 | 19.13 | 20.41 | 0.074 | 0.115 |
| 0.5 | 46.39 | 13.87 | 14.85 | 15.83 | 16.82 | 17.8 | 0.064 | 0.098 |
| 1.5 | 46.34 | 11.64 | 12.59 | 13.55 | 14.51 | 15.46 | 0.06 | 0.095 |
| 2 | 46.15 | 11.41 | 12.27 | 13.18 | 14.09 | 14.99 | 0.09 | 0.091 |
| 2.5 | 45.07 | 11.37 | 12.25 | 13.08 | 13.91 | 14.74 | 0.083 | 0.083 |

Constituents present in Ricinus Communis Leaves

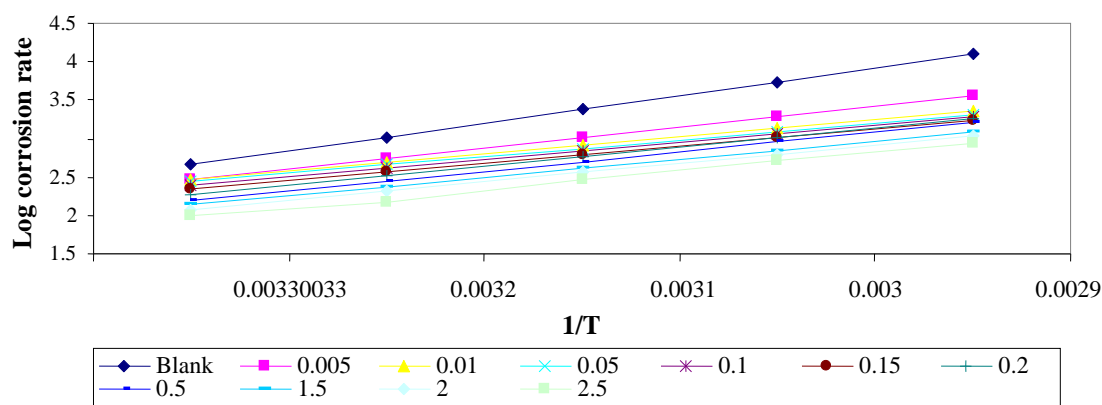
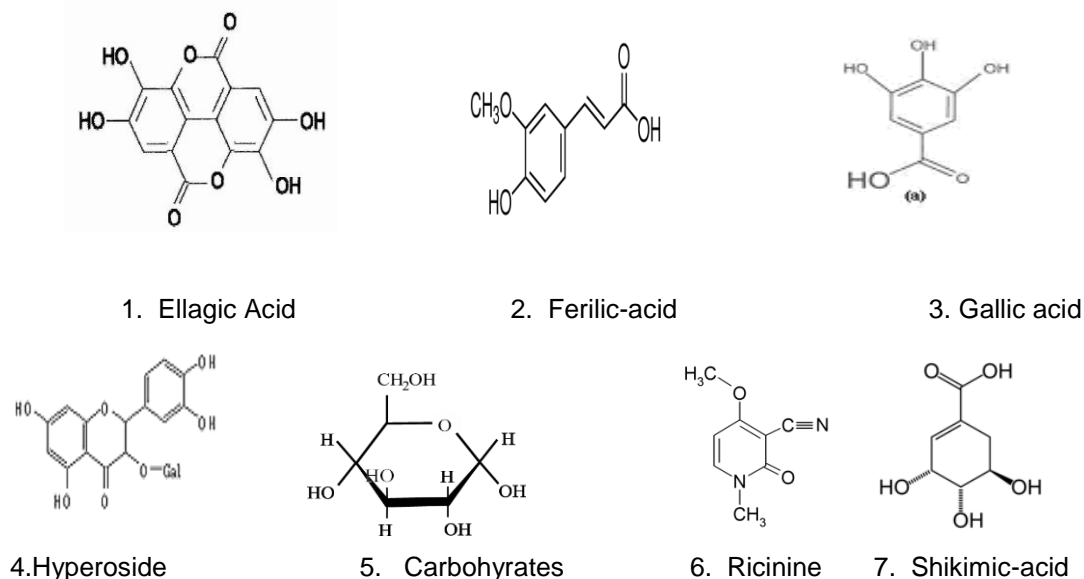


Fig. 1: Arrhenius plots for mild steel dissolution process in 0.5 M H₂SO₄

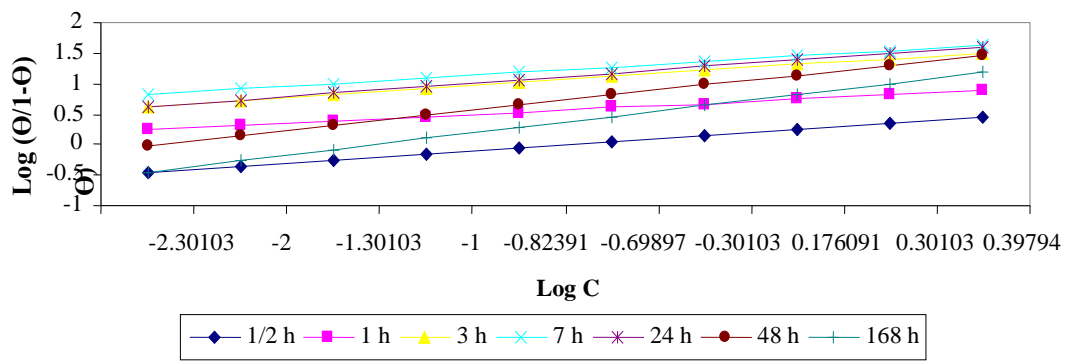


Fig. 2: Langmuir isotherm plots for the adsorption of various inhibitors in 0.5 M H₂SO₄

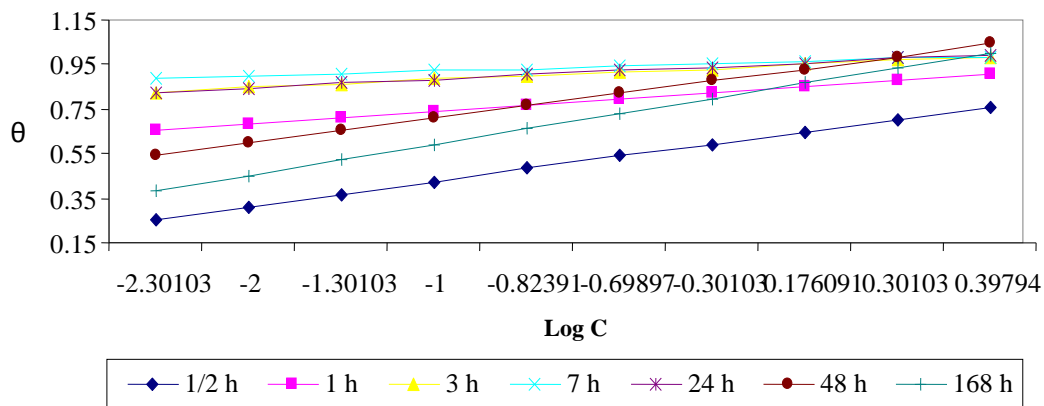


Fig. 3: Temkin isotherm plots for the adsorption of various inhibitors in 0.5 M H₂SO₄

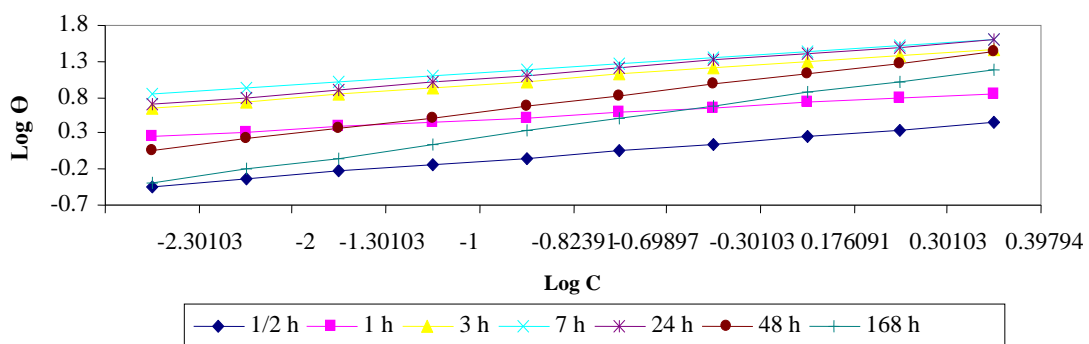


Fig. 4: Freundlich isotherm plots for the adsorption of various inhibitors in 0.5 M H₂SO₄



Fig. 5: Photomicrographs of Mild Steel Sample



Fig. 6: Sample Immersed in 0.5 M H₂SO₄



Fig. 7: Sample Immersed in 0.2% inhibitor solution



Fig. 8: Sample immersed in 2.5% inhibitor solution

CONCLUSION

1. The natural extract RCL was found to be effective inhibitor in the acidic medium giving up to 92.42% efficiency. The extracts under study resist corrosion at higher temperature in 0.5 M H₂SO₄, the optimum temperature being 323 K.
2. Adsorption Models-Langmuir, Temkin and Freundlich isotherm fit well as evident from the correlation coefficient values ($R > 0.9$ in all cases). This proves the applicability of all the models to the process.
3. The surface analysis study confirms the corrosion of mild steel and its inhibition by the inhibitor RCL.
4. The inhibitor RCL can be adsorbed on the metal surface through their oxygen atom of the constituents present in the extracts.

REFERENCES

1. Libin Tang, Xueming Li, Guannan Mu, Lin Li, Guangheng Liu. Applied Surf. Sci 2006; 253: 2367-2372
2. Subha R, Saratha R, Sivakamasundari S, International Conference on Recent Advancements in Chemistry, 2006; 40
3. Whittle J. E, Sci. Instrum. 1966; 43: 150-152
4. Hong T, Jepson W.P, Corrosion Science, 2001; 10(43): 1839-1849
5. Ehteram A Noor, Int. Electrochem J, Sci. 2007; 2: 996 - 1017
6. Bendahou, Benabdellah M, Hammouti B, Pigment & Resin Technology, 2006; 2(35): 95-100
7. Durnie W.H, Kinsella B.J, De Marco R, Jefferson A, Journal of Applied Electrochemistry, 2004; 11(31): 2001
8. Atul Kumar, E-Journal of Chemistry, 2008; 2(5): 275-280
9. James A.O, Oforka N.C, Abiola O.K, Ita B.I Eclat. Quim 2007; 3:(32)
10. Hosseini M.G, Arshadi M.R, Int.J. Electrochem. Sci. 2009; 4: 1339-1350
11. Khadom A.A, Aprael Yaro S, Abdul Amir H, Kadum, Ahmed S, Altaie, Journal of Applied Sciences, 2009; 9(13): 2457-2009
12. Putilova I.N, Bishop (ED), Metallic Corrosion Inhibitors, Pergoman, Oxford 1960; 139
13. Laidler K.J Chemical Kinetics Mc – Graw Hill Publishing Co.Ltd, 1965;
14. Al-Neami K.K, Mohammed A.K, Kenawy I.E and Fouda A.S

- Monatshefte für Chemie 1995; 126: 369.
15. Popova A, Sokolova E, Raicheva S, and Christov M, Corros. Sci, 2003; 45: 33–58.
 16. Rozenfeld I. L, Corrosion Inhibitors. New York: McGraw-Hill Inc, 1981; 182.
 17. Zhang D, Gao L, Zhou G, and Lee K, Appl J, Electrochem.,2008; 38: 71–76.
 18. Ueara J, and Aramaki K, Electrochem J. Soc., 1991; 138: 3245–3251.
 19. Granese I, Corrosion, 1988; 44: 322–327.