

Corrosion Inhibition by Extract of Leaves – Stability and Durability Study

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Abstract

Metals which are to be subjected to further treatment such as painting, enamellings, galvanizing, electroplating, phosphate coating, cold rolling, etc., must exhibit a clean surface, free of salt or oxide scales. To remove undesirable scales the particular piece of metal is subjected to pickling. The process involves immersing the metal in a pickling bath containing an acid solution of suitable strength. Rather than the advantages, the disadvantages like huge consumption of acid, acid mist formation, hydrogen evolution, base metal loss (corrosion), heavy expenditure for effluent treatment, etc., are plenty in this process. In order to overcome most of these problems, inhibitors are used. The scientific and technical corrosion literature has descriptions and lists of numerous chemical compounds that exhibit inhibitive properties. Unfortunately many of these inhibitors are toxic, less soluble and cause environmental pollution and also too expensive. Increasing awareness of health and ecological risks has led to finding more suitable non-toxic inhibitors. Due to the diversity in their structures of the phytochemical constituents present in the plant extracts, many extracts of common plants have been used as corrosion inhibitors for materials in pickling and cleaning process. The present study was undertaken to verify the inhibition of mild steel corrosion in 1M HCl and 0.5M H₂SO₄ by extract of *Ricinus Communis* through gasometric method and to find the stability of the extract under different storage conditions and during prolonged storage period (durability) through weight loss method. The effective corrosion inhibition nature of *Ricinus Communis* on mild steel in acid solution has been confirmed through gasometric method. The acid extract (both HCl and H₂SO₄) are stable at room temperature upto a storage period of 45 days. FTIR studies revealed that the inhibition of corrosion is due to the adsorption of phytochemical constituents present in the extract on the metal surface.

Keywords: *Ricinus Communis*, corrosion inhibitor

Introduction

Pickling is a metal surface treatment used to remove impurities such as stains, inorganic contaminants, rust or scale, from metals and alloys. An effective acid inhibitor [1-4] minimizes acid attack on the base metal once the scale has been removed, protecting the surface and optimizing acid utilization. Most corrosion inhibitors are organic compounds having hetero atoms in their aromatic or long carbon chain [5-10]. However, there is increasing concern about the toxicity and cost of most corrosion inhibitors. There has been a growing trend in the use of natural products such as leaves, seed and flowers of plants as corrosion inhibitors for metals in acid cleaning processes [11-20]. In continuation of

previous work in developing eco-friendly corrosion inhibitor [21], the present work is carried out to confirm the inhibiting effect of *Ricinus comunis* leaves (RCL) through gasometric method and to find out the stability and durability of the extract. The surface morphology was studied using FTIR technique.

Materials and methods

Preparation of specimen

Experiments were performed with commercial grade mild steel sheets available in the local market and the elemental analysis was carried out using vacuum emission spectrometer. Mildsteel (C=0.176%, Mn=0.431%, Si=0.00, S=0.029%, P=0.03%Cr=0.006%, Mo=0.023%, Ni=0.011% and Fe=99.3%) of area 5×1 cm² were used. The specimens were degreased, cleaned with fine quality emery sheet, washed with distilled water and stored in desiccator before use.

Preparation of the extract

Extract was prepared by using the same method material in our previous paper. The extract was divided into two portions one kept at lab temperature another under refrigerator condition (RC).

Weight loss method

Mild steel specimens were accurately weighed and fully immersed in 100ml of 1M HCl and 0.5M H₂SO₄ solutions for different concentrations {1, 3, 5, 7, 9, 11, 13 (% V/V)} of the inhibitor and at different time intervals {1/2, 1, 3, 5, 7, 12, 24, 48 (hours)}. Test specimens were removed after the correct interval of time and dipped in sodium bicarbonate solution for neutralization of remaining acid in the specimen. Then washed with distilled water, dried and reweighed. The loss in weight was determined in triplicate and the results were averaged. Similar procedure was followed for the extract kept under RC after attaining the room temperature.

Storage Period of the Inhibitor (Days) : 7, 14, 21, 28, 45, 60, 90

Storage condition : Lab temperature and refrigerated condition

From the weight loss, the corrosion rate (CR) and the inhibition efficiency (I.E%) were calculated using the following equations.

$$\text{Corrosion rate (CR)} = 534 \times W/DAT \text{ (mpy)} \quad (1)$$

where, mpy is Miles per year, W is weight loss in mg, D is density of specimen in g/cm³ (7.9 g/cm³), A is surface area of specimen in square inch, T is exposure time in hours.

$$I.E(\%) = \frac{CR_b - CR_{inh}}{CR_b} \quad (2)$$

where CR_b and CR_{inh} are corrosion rate of mild steel in the absence and presence of the inhibitor respectively.

Gasometric Technique

A flask with a side tube was connected to a delivery tube to a graduated gas collector which is a reservoir of water. 100ml of the test solution were then introduced into the flask and the initial volume of the air in the graduated gas collector was set to zero. Thereafter one mild steel coupon was dropped into the test solution and the reaction vessel immediately closed. The volume of the hydrogen gas evolved by the corrosion reaction was estimated from the change in volume of the water in the reservoir. The progress of the reaction was monitored by careful measurement of the evolved hydrogen gas at fixed time intervals. The experiment was conducted at room temperature.

$$I.E(\%) = \frac{V(h) - V(inh)}{V(h)} \times 100$$

Where, V (inh) is the volume of hydrogen evolved at time 't' for inhibited solution.

V (b) is the volume of hydrogen evolved at time 't' for uninhibited solution

FT-IR

The mild steel specimen was immersed in 100ml of 1M HCl and 0.5M H₂SO₄ in the presence and absence of the inhibitor (Concentration of the inhibitor 1,3,5,7,9,11,13 % w/v) for 24 hours. They are taken out and immersed in saturated sodium bi carbonate solution to remove residual acid and washed thoroughly with distilled water and dipped in acetone then dried, scratched the specimen and collected the powder. The powder was analyzed by using SHIMADZU FT-IR spectrometer.

Results and discussion

At different storage period of the extracts (7,14,21,28,45 and 60 days) weight loss method was carried out using the extract stored under room temperature (RT) and refrigerated condition (RC) over a period of time. The inhibition efficiency for mild steel in 1M HCl and 0.5 M H₂SO₄ in the absence and presence of various concentrations of the RCL extract stored for a prolonged period are determined. The results of the study are given in table (1 and 2) respectively.

Table 1 IE of RCL extract on Mild Steel in 1M HCl At Room Temperature And Refrigerated Condition

Conc. % (w/v)	Inhibition efficiency (%)											
	Storage period of the extract (Days)											
	7 days		14 days		21 days		28 days		45 days		60 days	
	RT	RC	RT	RC	RT	RC	RT	RC	RT	RC	RT	RC
1	30.1	20.5	30.5	25.7	25.1	24.4	23.5	23.5	22.5	11.6	-	-
3	41.2	46.6	40.8	45.0	39.7	39.4	38.9	37.9	34.9	33.8	-	-
5	52.5	51.8	50.6	50.0	51.6	50.0	50.3	49.4	46.3	46.6	-	-
7	76.6	76.1	76.2	70.3	52.1	61.8	62.6	51.7	59.7	50.0	-	-
9	83.1	81.1	81.1	80.3	75.0	73.5	71.5	71.6	67.8	60.3	51.0	-
11	87.0	87.1	81.7	84.2	81.9	81.0	81.0	83.0	84.4	74.0	69.0	65.0
13	91.1	89.7	90.9	88.3	90.2	87.6	89.7	86.4	88.1	86.2	75.9	78.2

Table-2 IE of RCL extract on Mild Steel in 0.5M H₂SO₄ At Room Temperature And Refrigerated Condition

Conc. % (w/v)	Inhibition efficiency (%)											
	Storage period of the extract (Days)											
	7 days		14 days		21 days		28 days		45 days		60 days	
	RT	RC	RT	RC	RT	RC	RT	RC	RT	RC	RT	RC
1	15.4	19.4	28.1	28.2	24.5	25.3	24.2	24.2	24.2	24.2	20.9	-
3	19.7	22.2	27.9	34.5	17.2	15.3	16.4	14.6	11.4	11.6	-	-
5	61.8	70.0	52.3	48.6	50.0	47.3	49.6	45.6	41.2	40.0	-	-
7	80.3	82.1	75.2	73.6	73.6	70.9	61.1	61.7	61.7	60.5	-	-
9	83.0	85.2	79.2	75.6	74.1	74.1	73.7	71.0	72.3	70.1	60.0	-
11	87.1	90.4	86.1	81.1	81.9	81.0	82.4	78.6	87.6	77.5	72.6	68.4
13	92.5	92.4	87.4	87.8	87.3	87.7	87.3	87.9	87.7	85.5	78.4	75.4

There was a variation in IE with storage period. However, the inhibition efficiencies are found to increase with increasing extract concentration at all storage periods. Since the IE decreased with storage period study was carried out for 60 days only for higher concentration of the inhibitor. From the values of IE, it is clear that the corrosion inhibition may be due to increase in the adsorption of phytochemical constituent of extract on the metal surface. The decrease in IE with storage period may be due to the desorption of the adsorbed photochemical constituents from the surface of the metal surface.

Stability Test

The development of any product depends on various factors. Storage condition of the product, i.e whether it should be kept under refrigerated condition or on the table is very important. Storage at room temperature will reduce the storage cost (cost of electricity). Every time the extract was taken from the refrigerator kept outside for some time to attain room temperature then the weight loss study was carried out. The results of weight loss measurements using the RCL extract in 0.5 M H₂SO₄ and 1 M HCl stored in refrigerator and on table condition are given in Table (1 and 2 respectively). The comparison of %IE of RCL under RT and RC in 1 M HCl and 0.5 M H₂SO₄ shows that there is no significant change in the inhibition efficiency of the extract stored at room temperature as well as in refrigerator condition.

Gasometric Technique

Table 3 Inhibition Efficiency of Extract (RCL) for the corrosion of Mild Steel in Acid Medium (Gasometric Method)

Conc of the extract % (V/V)	RCL			
	HCl		H ₂ SO ₄	
	Vol. of Gas	I.E	Vol. of Gas	I.E
Blank	64	-	68	-
1	50	22	48	29.4
7	28	56	32	52.9
13	20	69	20	70.5

The volume of hydrogen gas evolved, during the corrosion reaction of mild steel in 1M HCl and 0.5M H₂SO₄ in the absence and presence of different concentrations extract (RCL) at room temperature were measured as a function of the reaction time (Table-3), and the data are represented in Fig.(1 and 2 respectively). The volume of hydrogen evolved at different concentrations of acid extract of RCL is lower than volumes evolved for the blank solution (1M HCl and 0.5M H₂SO₄) indicating that different concentrations of these extracts retard the corrosion of mild steel. From Table (3), it is clear that the volume of hydrogen gas evolved decreases as the concentration of extract increases, confirm

the inhibition efficiency increases with concentration of the derivatives.

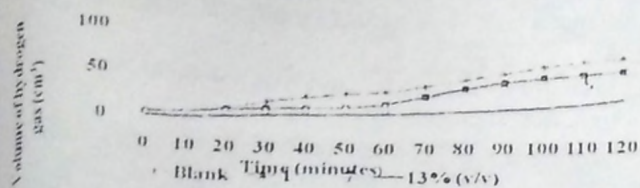


Fig. 1 Variation of the volume of hydrogen gas evolved with time during the inhibition of the corrosion of mild steel in 1 M HCl by various concentrations of the extract

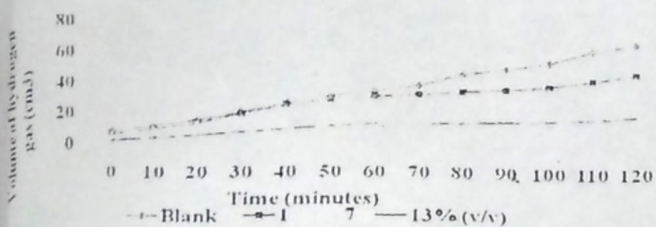


Fig. 2 Variation of the volume of hydrogen gas evolved with time during the inhibition of the corrosion of mild steel in 0.5 M H₂SO₄ by various concentrations of the extract

FT-IR Technique

The respective FT-IR peaks of the powder form of RCL mild steel immersed in blank, mild steel sample immersed in 1 M HCl and 0.5 M H₂SO₄ containing 13% (v/v) of RCL are given in Table (4) and corresponding spectra are shown in Fig.(3,4,5). From the Table it is clear that there is shift in IR peak from powdered form of the plants and mild steel immersed in acid medium containing plant extracts which shows there is formation of metal-plant extract complex.

The peaks at 3333, 2856, 2854 cm⁻¹ can be assigned to the presence of superficial adsorbed water, stretching mode of an O-H and/or N-H and aromatic C-H groups (from plant extract). The peaks at 1612, 1635 cm⁻¹ corresponds to C=O, R₂-C=N, C=C; this shows that the plant extracts contains mixtures of compounds. Almost all peaks observed for plant extract is also noticed for mild steel immersed in 1 M HCl and 0.5 M H₂SO₄ containing 13% (v/v) volume of plant extracts. However, the spectra shows the reduced intensity of the broad peak around 3392 (RCL) designates the reduction of the free O-H groups, since it is proximity of hydroxyl groups on the aromatic rings which enables the compound to form iron-plant extract complex.

Table 4 IR Frequencies of Inhibitor and Mild Steel in Acid Extracts

RCL powder	Mild steel in		Possible groups
	RCL extract in HCl	RCL extract in H ₂ SO ₄	
3392	3333	3356	O-H/N-H Aromatic C-H C=C, esters, NH ²⁺ , NH ³⁺ C=O, Phenols C-OH, C-H Fe ₂ O ₃
2852	2856	2854	
1635	1612	-	
1261	1319	-	
1026	1028	1116	
-	648	651	

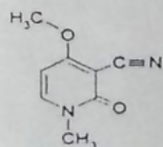
Fig. 3 IR spectra of RCL

Fig. 4 IR spectra of RCL in 1M HCl

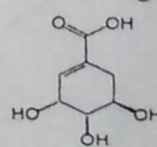
Fig. 5 IR spectra of RCL in 0.5M H₂SO₄

Mechanism of Inhibition

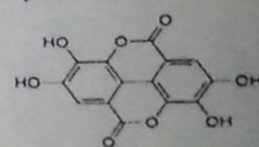
The acid extracts investigated in the study are organic in nature and found to contain the following compounds.



Ricine



Shilimic acid



Ellagic acid

The mechanism of corrosion inhibition of mild steel in acidic solution can be explained on the basis of one or more of these compounds on the metal surface. The inhibitor possesses electroactive nitrogen, oxygen atoms and aromatic rings which favour the adsorption on metal surface. In the presence of inhibitor a thin greenish black film has always been observed on the surface of the specimens. This shows that the inhibition is due to the formation of some complex film formed between plant extract and the metal ions, which is confirmed from the spectral studies.

Conclusion

- The gasometric method confirmed the inhibitive nature of the extract RCL for corrosion of mild steel in acid medium.
- Corrosion inhibition increases with increase in the concentration of the extract.
- The extract (RCL) could be stored at room temperature (no need to store under refrigerated condition) up to 45 days.

- FT-IR study shows that inhibitor prevent corrosion by adsorption of the phytoconstituents of the extract on the metal surface.

Acknowledgments

The authors sincerely thank the authorities of Avinashilingam Deemed University for Women, Coimbatore, Tamilnadu, India for providing the facilities to carry out the study.

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