



Corrosion Inhibition of mild steel in Formic acid using Tamarindus Indica Extract

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Abstract

Heat of Adsorption of Tamarindus indica leaves extract and mild steel corrosion inhibition in formic acid solutions using Tamarindus Indica as natural inhibitor have been studied using gravimetric technique. Inhibition efficiency was observed to increase with an increase in Tamarindus indica leaf extract concentration. Temperature effect on the corrosion behavior of mild steel in 0.5M, 1M and 2M Formic acid solutions with addition of plant extracts was studied at the temperatures 30°C and 45°C. Optimum Inhibition efficiencies at 45°C are 76.18% for 0.5M, 74.88% for 1M, and 70.82% for 2M. Very low inhibition efficiencies are observed at 30°C. The adsorption mechanism proposed from the heat of adsorptions for 1M and 2M formic acid solutions is physisorption while 0.5M shows chemisorption based on the calculated values of the heat of adsorption.

Keywords: Corrosion Inhibition, Tamarindus indica, Formic acid, Adsorption.

Introduction

Metallic materials are widely used in the storage and transportation of various chemicals however, corrosion limits the usefulness of metals and alloys. Corrosion involves the deterioration or degradation of materials especially metals by reaction with the environment¹. Corrosion damages metals leading to economic consequences in terms of replacement of engine parts, repairs, product losses and environmental pollution. This has made the mitigation of corrosion an important area of study.

The use of corrosion inhibitors to limit corrosion rates of metals placed in very corrosive media is acceptable in corrosion prevention. Corrosion inhibitors are substances which when added in small concentrations, effectively reduce the corrosion rate of a metal exposed to a corrosive environment. Broad categories of corrosion inhibitors are those that enhance the formation of a protective film through an oxidizing effect and those that inhibit by selectively adsorbing on the metal surface thereby forming a barrier that limits access of corrosive agents to the metal surface¹. Another mechanism reported is the inhibitor reacting with a potential corrosive component present in aqueous media to form a complex product². The efficiency of an inhibitor depends largely on the interactions between the metal surface and the inhibitor. Nitrogen based organic compounds such as imidazolines have been applied successfully as corrosion inhibitors in oil industries even without an understanding of the mechanisms of interaction³.

Mild steel corrosion is common in acidic media with its practical importance in acid pickling of iron, cleaning of scales

of boilers using chemicals, petrochemical and oil industries²⁻⁴. Corrosion inhibition of mild steel in acid solutions using various types of organic extracts has been studied⁵. Very few among them that are environmentally friendly include extracts of various parts of plants⁶⁻⁹.

Tamarindus Indica is part of the Dicotyledonous family Leguminosae and belongs to the Subfamily Caesalpiniaceae. It is a tropical fruit which is commonly found everywhere in Asia and Africa. The seed contains tannin and dyeing matters which make it unsuitable for consumption. Phytochemical screening shows that Tamarindus indica extract has a positive result for tannin, alkaloid, flavonoids and glycosides¹⁰.

This work evaluates the efficacy of Tamarindus Indica in inhibiting corrosion of mild steel in 0.5M, 1M and 2M Formic acid solutions. The heat of adsorption and activation energy of the corrosion behavior of mild steel in Formic acid media are also calculated to ascertain the adsorption mechanism for the reaction.

Materials and Methods

Materials preparation: The mild steel bars used for this study were obtained from American University of Nigeria, Yola with an estimated composition of Si-0.051%, Cu-0.185%, Mn-1.102%, P-0.919%, Pb-0.074%, S-0.783%, Mo-0.027%, V-0.014% and the Fe being the major component. The metal bar was cut into equal cuboids with an area of 6cm² each. The metal bars were polished mechanically with silicon carbide paper, degreased in ethanol and dried in acetone before storage in moisture free desiccators for the corrosion study.

Tamarindus indica leaves were collected from Yola, Nigeria. They were dried in a Genlab oven at 50°C and ground to powder form. Stock solutions of the plant extracts were prepared by soaking known amount of the dried and ground leaves of Tamarindus indica in 99.5% JHD absolute ethanol. The sample is filtered after 48hrs and the filtrate is heated to concentrate the extract. From the stock material, test concentrations of 0.5M, 1M, and 2M formic acid with inhibitor concentrations of 1mg/ml and 3mg/ml were prepared by diluting with appropriate concentrations of the 85% Fisher Scientific formic acid. A blank solution of only the acid was also prepared.

Weight loss measurements: The initial weights of mild steel are taken and the steel is then immersed in 100ml of the blank, 1mg/ml inhibitor in acid and 3mg/ml inhibitor in acid solutions. The study is done at 303K and 318K with each sample taken out weekly, cleaned in water and acetone is used to rinse. The metal is dried in air and then weighed. Total weight loss after 804 hours was used for calculations. The parameters calculated included the corrosion rates (CR), percentage inhibition efficiency (IE%) of the inhibitor, and the degree of surface coverage (θ) using equations (1) – (3). To study how temperature affects corrosion behavior, the activation energy and heat of adsorption were determined using equations (4) and (5).

$$IE\% = \left(1 - \frac{W_1}{W_2}\right) \times 100 \quad (1)$$

$$\theta = \left(1 - \frac{W_1}{W_2}\right) \quad (2)$$

$$CR = \frac{K\Delta W}{\rho A t} \quad (3)$$

$$\log \frac{CR_2}{CR_1} = \frac{E_a}{2.303 R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad (4)$$

$$Q_{ads} = 2.303R \left[\log\left(\frac{\theta_2}{1-\theta_2}\right) - \log\left(\frac{\theta_1}{1-\theta_1}\right)\right] \quad (5)$$

Results and Discussion

Corrosion Studies and Effect of Temperature: The results in Table-1 illustrate a decrease in weight loss and corrosion rates as the concentration of inhibitor increases from 1mg/ml to 3mg/ml at 45°C. The decrease in weight loss is attributed to the ethanolic extract of Tamarindus indica limiting the rate of corrosion. The surface area coverage which demonstrates the area of the mild steel covered by the inhibitor increases with an increase in the concentration of the inhibitor in the acid solution. This is also observed in the inhibition efficiency from 0 for the blank, 38.27% for 1mg/ml and an optimum of 76.19% for 3mg/ml inhibitor concentration. A similar trend is observed in Table-2 however, the weight loss values and corrosion rates are higher compared to the values in 0.5M acid. This is attributed to the increase in the concentration of the acid. As a consequence, the % surface area covered as well as the % Inhibition

efficiency decreased compared to the 0.5M formic acid. To further study the effect of the concentration of the acid, the study at 2M formic acid illustrated in Table-3 shows higher corrosion rates, lower surface area coverage and lower inhibition efficiencies. Therefore, despite the inhibitor presence, an increase in the concentration of the acid will lead to higher corrosion rates and weight loss. This result in a corresponding decrease in the surface area covered for the 3mg/ml inhibitor concentration.

To further ascertain the effect of temperature on corrosion behavior of mild steel in Formic acid media, the study is done at 30°C with results illustrated in Tables 4-6 for the concentrations 0.5M, 1M and 2M respectively. From the results obtained at 30°C, it was observed that corrosion of mild steel is higher at increased temperature of 45°C. Therefore, heat plays a vital role in corrosion inhibition of mild steel in solutions of formic acid and Tamarindus indica.

Table-1
Weight loss, Corrosion rates, Surface area coverage and Inhibition Efficiency of Tamarindus Indica in 0.5M Formic acid at 45°C

	ΔW (mg)	CR (mm/yr)	θ	%IE
Blank	886.5	1.960332606	0	0
1mg/ml INH	547.2	1.210032715	0.3827411 17	38.274111 68
3mg/ml INH	211.1	0.466809039	0.7618725 32	76.187253 24

Table-2
Weight loss, Corrosion rates, Surface area coverage and Inhibition Efficiency of Tamarindus Indica in 1M Formic acid at 45°C

	ΔW (mg)	CR (mm/yr)	θ	%IE
Blank	1280.9	2.832476069	0	0
1mg/ml INH	1092.8	2.416527323	0.14685	14.68499
3mg/ml INH	321.7	0.71138071	0.748848	74.88485

Table-3
Weight loss, Corrosion rates, Surface area coverage and Inhibition Efficiency of Tamarindus Indica in 2M Formic acid at 45°C

	ΔW (mg)	CR (mm/yr)	θ	%IE
Blank	1526.8	3.376238943	0	0
1mg/ml INH	803	1.775687629	0.474063	47.40634
3mg/ml INH	445.4	0.984920635	0.708279	70.82788

Table-4

Weight loss, Corrosion rates, Surface area coverage and Inhibition Efficiency of Tamarindus Indica in 0.5M Formic acid at 30°C

	ΔW (mg)	CR (mm/yr)	θ	%IE
Blank	363.4	0.803593	0	0
1mg/ml INH	358.7	0.793199	0.012933	1.293341
3mg/ml INH	348	0.769538	0.042378	4.237755

Table-5

Weight loss, Corrosion rates, Surface area coverage and Inhibition Efficiency of Tamarindus Indica in 1M Formic acid at 30°C

	ΔW (mg)	CR (mm/yr)	θ	%IE
Blank	452.8	1.001284381	0	0
1mg/ml INH	406.9	0.899784927	0.101369	10.13693
3mg/ml INH	393.5	0.870153278	0.130963	13.09629

Table-6

Weight loss, Corrosion rates, Surface area coverage and Inhibition Efficiency of Tamarindus Indica in 2M Formic acid at 30°C

	ΔW (mg)	CR (mm/yr)	θ	%IE
Blank	406.7	0.899342663	0	0
1mg/ml INH	331.4	0.732830486	0.185149	18.51488
3mg/ml INH	261.7	0.578701684	0.356528	35.65282

Heat of Adsorption and Activation energy: A thermodynamic comparative study of the corrosion behavior of mild steel in formic acid to determine the heat of adsorption and energy of activation was done at 30°C and 45°C. The results are illustrated in Tables (7) – (9) for 0.5M, 1M and 2M Formic acid respectively. The heat of adsorption increases with increase in the concentration of inhibitor and decreases as the concentration of the acidic media increases from 0.5M to 2M. The activation energy is observed to decrease with increase in the inhibitor concentration. The positive values observed for the heat of adsorption indicate that the process is endothermic. If the values of the heat of adsorption are less than 40kJ/mol, the adsorption process is physical adsorption (physisorption) while it is chemical adsorption for values above 60kJ/mol. The process is termed pseudo-chemisorption for values between 40kJ/mol and 60kJ/mol¹¹⁻¹². In the present study, for 0.5M formic acid, the values of the heat of adsorption are above 60kJ/mol indicating chemisorption while 1M and 2M indicated physisorption.

Table-7

Heat of Adsorption and Activation Energy for corrosion inhibition in 0.5M Formic acid

	Qads (kJ/mol)	Ea (kJ/mol)
Blank	0	109.6828433
1mg/ml INH	73.85041528	51.94363098
3mg/ml INH	81.96524101	-61.48086607

Table-8

Heat of Adsorption and Activation Energy for corrosion inhibition in 1M Formic acid

	Qads (kJ/mol)	Ea (kJ/mol)
Blank	0	127.8970535
1mg/ml INH	8.091153034	121.509176
3mg/ml INH	57.15329849	-24.77848782

Table-9

Heat of Adsorption and Activation Energy for corrosion inhibition in 2M Formic acid

	Qads (kJ/mol)	Ea (kJ/mol)
Blank	0	162.7025
1mg/ml INH	26.38488	108.8528
3mg/ml INH	28.28998	65.40478

Conclusion

Tamarindus indica of concentrations 1mg/ml and 3mg/ml act as good inhibitors of mild steel corrosion in formic acid solution of 0.5M, 1M and 2M. The inhibition efficiency increases with increase in inhibitor concentration. The surface area coverage also increases with an increase in the inhibitor concentration and this is as a result of more phytochemical constituents adsorbed on the metal surface when the extract increased. Optimum Inhibition efficiencies at 45°C are 76.18% for 0.5M, 74.88% for 1M, and 70.82% for 2M were obtained at 45°C. Lower inhibition efficiencies are observed at a lower temperature of 30°C which also has low values for the corrosion rates. An adsorption mechanism involving physisorption of extract constituents at both temperatures has been proposed from the trend of adsorption free energies for the 1M and 2M solutions while 0.5M shows chemisorption based on the calculated values of the heat of adsorption.

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