JOURNAL OF SCIENCE AND TECHNOLOGY VOL. 12 NO. 2 (2020) 75-83

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JST

Journal homepage: http://penerbit.uthm.edu.my/ojs/index.php/jst
ISSN : 2229-8460 e-ISSN : 2600-7924

Journal of Science and Technology

Corrosion Inhibition of Mild Steel in Tetraoxosulphate (VI) Acid Using *Mangifera Indica* and *Citrus Sinensis* Peels Extracts

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DOI: https://doi.org/10.30880/jst.2020.12.02.008
Received 23 July 2020; Accepted 10 December 2020; Available online 24 December 2020

Abstract: The problem of corrosion and inhibitive effect by two plants peel extracts of mango (*Mangifera indica*) and orange (*Citrus sinensis*) were comparatively investigated on mild steel samples immersed in 1 M tetraoxosulphate (VI) acid at ambient temperature. Statistical probe with Analysis of Variance (ANOVA) together with Bonferroni-Holm Posthoc Significance Test were used. The inhibitive effect of *Mangifera indica* and *Citrus sinensis* peels extracts on the corrosion of mild steel in H_2SO_4 solution was investigated with the loss in weight techniques for ten days. From the results obtained, the inhibition efficiency increased with increase in the concentration of the two plant peels extracts over a concentration range of 0.2 to 1.0 g/L of solution. Highest inhibition efficiency of 50.54% and 50.21% was observed in the concentration of 1.0 g/L of *Mangifera indica* and *Citrus sinensis* peels extracts respectively. Investigations showed that the corrosion inhibition of mild steel inside H_2SO_4 solution depends on the proportion of the inhibitors applied. *Mangifera indica* peel extract was found to be slightly more effective against corrosion in the 1 M H_2SO_4 solution for mild steel.

Keywords: *Mangifera indica*, *citrus sinensis*, corrosion inhibition, mild steel, tetraoxosulphate (VI) acid

1. Introduction

Corrosion inhibition in metals especially steel is a field of study that has been explored for many years. An interesting aspect of this research area is the engagement of biomaterials like agricultural products or wastes in producing materials for corrosion inhibition. Some practical applications of corrosion inhibition in some industries such as oil and construction industries had been reported [1-2]. Corrosion control of metals and alloys, removal of scales in boilers and heat exchangers, as well as rust prevention in metal finishing processes are done with inhibitors.

Some recent and previous studies published in the subject area gave varying degrees of achievements by using extracts of *Thevetia peruviana*, cocoa leaf, *Pterocarpus santalinoides* leaves, *areca* flower, bitter leaf, *Alstonia boonei*, *Pterocarpus santaliniodes* leaves, *Chysophyllum albidum* plant, *Parinari polyandra, Alchornea cordifolia*, *Bridelia ferruginea*, *Citrus paradise*, *Jathropha curcas* leaves, *Citrus aurantifolia* seed, and saponins from crude extracts of *Gongronema latifolium* [3-17]. Heteroatoms like sulphur, nitrogen, oxygen, and phosphorus attached to organic compounds are available in the extracts of some plants. Protective films formed on surfaces by these heteroatoms through effective coordination of their electrons with the metal ions assists in inhibiting corrosion. [4, 15].

Corrosion inhibitors works by reducing reduction at the cathode or oxidation at the cathode. Hydroxyl (-OH) or nitro (-NO_2) functional groups are available in potential corrosion inhibitors. Thus, in finding readily available, environmentally friendly as well as safe compositions, natural products like leaves or plant extracts are being explored

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as corrosion inhibitors. The hazardous effects associated with most synthetic corrosion inhibitors which includes non-biodegradability, toxicity and bioaccumulation also motivated researchers to look for naturally occurring corrosion inhibitors which are non-toxic, cheap, easily-sourced, ecologically adaptable, renewable and friendly to the environment. The banning of some inhibitors that contained chromates had been affected due to the toxic problem they possess and their hazardous effects on the environment [12, 16, 18]. Therefore, there has been enhanced activities in the use of suitable environmentally friendly with non-toxic attributes extracts from natural materials for corrosion inhibition applications.

Comparison of maize husk polar extract in corrosion inhibition of two different acidic media had been reported [19]. The study entailed comparative assessment of the inhibition efficiency of a maize husk polar extract in HCl and H_2SO_4 acidic solutions for corrosion retardation of mild steel. After 48 hours, a maximum inhibition efficiency of 96% was reported in 1.5 M H_2SO_4 solution.

With the abundant availability of orange and mango fruits, this particular work is concerned with comparative studies on the corrosion inhibition achievable with mild steel in tetraoxosulphate (VI) acidic solution, using peels extracts of orange (*Citrus sinensis*) and mango (*Mangifera indica*).

2. Experimental

2.1 Apparatus and Reagents

JPI 8007 measuring cylinder, JPI 8022 beakers, India manufactured model number AVI 567 water bath, USA model number ASTM E11 sieve, Linthotech India model number CST 1121 grinder, India model number G-1502 weighing balance, sand paper, mild steel coupons (dimensions 5 cm, 4 cm, and 0.5 cm of length, breadth, and height respectively) were obtained from Mechanical Engineering Department, University of Lagos. Also used are tetraoxosulphate (VI) acid, ethanol, acetone, *Citrus sinensis* and *Mangifera indica* obtained from Ketu fruits market, Lagos state, Nigeria.

2.2 Preparation of Inhibitor

Two kilograms of sweet orange (*Citrus sinensis*) peels together with the same amount of mango (*Mangifera indica*) peels were weighed, then sundried until a constant value was obtained. They were then grounded and sieved until fine particles were obtained. The fine particles were soaked thereafter in 500 ml of 1.0 M ethanol solution for 48 hours to form the corrosion inhibitor.

2.3 Experimental Results Reproducibility

Average of three runs were recorded for each run.

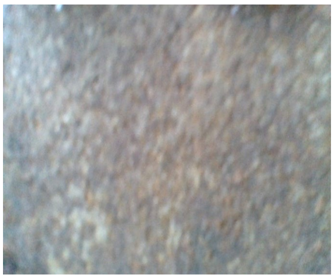
2.4 Weight Loss Measurement

Certain amount of six samples of mild steel were weighed. The mild steel was suspended and immersed completely in the test solution (1 M H_2SO_4) with and without inhibitors for 10 days (24, 48, 72, 96, 120, 144, 168, 192, 216, 240 hours respectively). However, the mild steel was withdrawn at 24 hours intervals, rinsed severally in a solution of sodium hydroxide until a clean and constant mass was obtained, immediately dried by means of acetone solvent and re-weighed. The weight loss was then determined for each of the mild steel using a solution of H_2SO_4 with varying mass of the citrus sinensis inhibitors (from 0-1 kg of citrus sinensis using 0.2 kg intervals). The same procedure was repeated using *Mangifera indica*. The formulation described was obtained from the Standard Organisation of Nigeria (SON). Fig. 1 and 2 show the procedure.


(a)


(b)

Fig. 1 - Mild steel; (a) about to be inculcated into prepared solutions; (b) corrosion taking place in solutions.


(a)


(b)

Fig. 2 - One side of mild steel; (a) before corrosion; (b) slightly corroded after 10 days.

Following the data from the weight loss obtained, the rate of corrosion was calculated using Eq. 1, while the weight loss calculation is given in Eq. 2:

$$CR = \frac{WL}{At} \quad (1)$$

$$WL = Initial\ weight\ (W_1) - Final\ weight\ (W_2) \quad (2)$$

where CR is the corrosion rate, *WL* is the weight loss in grams, *A* is the surface area of specimen, *t* is the immersion time in hours or days.

After the corrosion rate determination, the surface coverage (θ) caused by the inhibitor molecules adsorption, as well as the molecules inhibition efficiency (μ%) were evaluated with Eq. 3 and 4:

$$\theta = \frac{CR_{\text{blank}} - CR_{\text{inhibitor}}}{CR_{\text{blank}}} \quad (3)$$

$$\mu\ \% = \frac{CR_{\text{blank}} - CR_{\text{inhibitor}}}{CR_{\text{blank}}} \times 100 \quad (4)$$

where $CR_{inhibitor}$ and CR_{blank} are the corrosion rates in the presence and absence of the inhibiting molecules respectively.

3. Results and Discussion

3.1 Estimation of Weight Loss with Corrosion Rate, Inhibition Efficiency and Surface Coverage

The weight loss evaluation of mild steel in 1.0 M H_2SO_4 solution with various concentrations of the plant extracts (PE) as time progresses is presented as follows:

$$Surface\ Area = 2\ (\ lb + lh + bh\ )$$
$$\therefore Surface\ Area = 2\ (\ 5\ cm \times 4\ cm + 5\ cm\ \times 0.5\ cm + 4\ cm\ \times 0.5\ cm\ )$$
$$= 2\ (\ 20\ cm^2 + 2.5\ cm^2 + 2cm^2)$$
$$= 2(\ 24.5\ cm^2\ )$$
$$Surface\ Area = 49\ cm^2$$

Based on the weight loss data, the CR can be estimated from Eq. 1. From the CR, θ and μ% were determined using Eq. 3 and 4.

The weight loss calculations for *Mangifera indica* was calculated with Eq. 2 and presented in Fig. 3. The corrosion rate calculations for *Mangifera indica* was calculated with Eq. 1 and the obtained values were plotted in Fig. 4. The surface coverage calculations for *Mangifera indica* was calculated using Eq. 3 and the values obtained are shown in Fig. 5. The inhibition efficiency calculations for *Mangifera indica* was calculated with Eq. 4 and the obtained data are presented in Fig. 6.

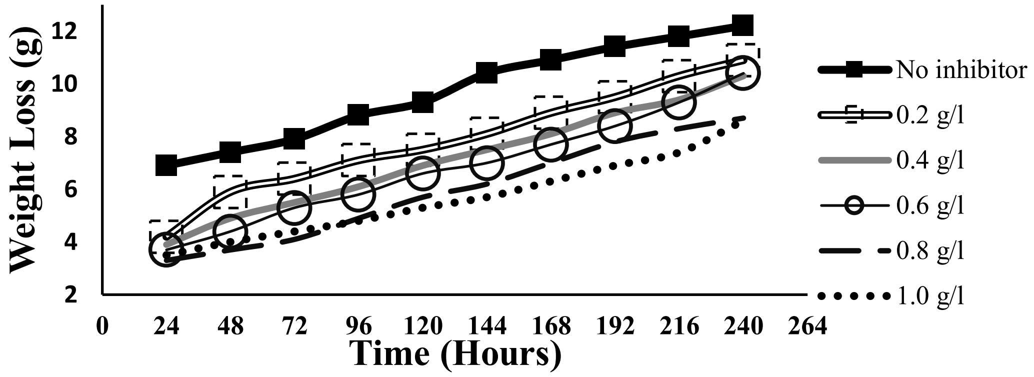


Fig. 3 - Weight loss of mild steel coupons propagation with time in 1.0 M H_2SO_4 solution plus *Mangifera indica* peels extract.

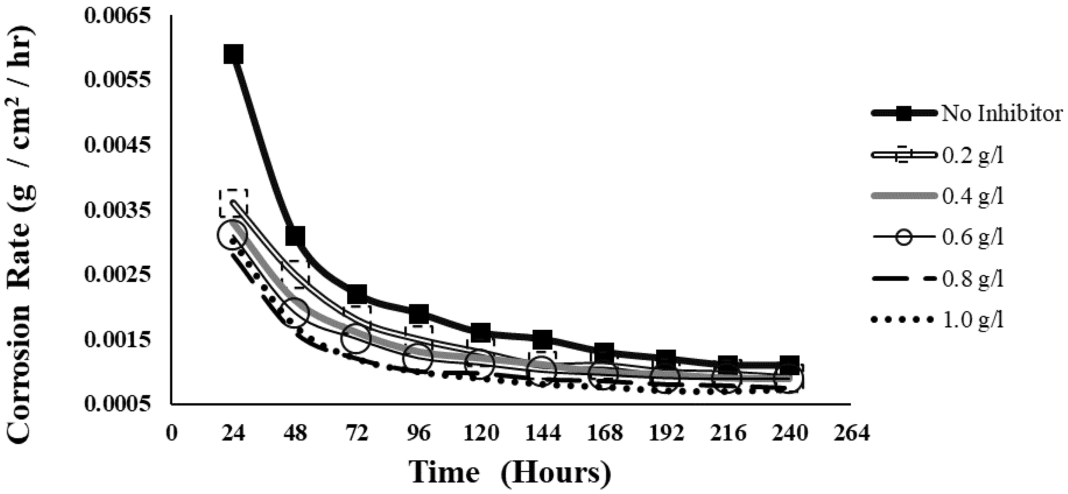


Fig. 4 - Corrosion rate of mild steel coupons propagation with time in 1.0 M H_2SO_4 solution plus *Mangifera indica* peels extract.

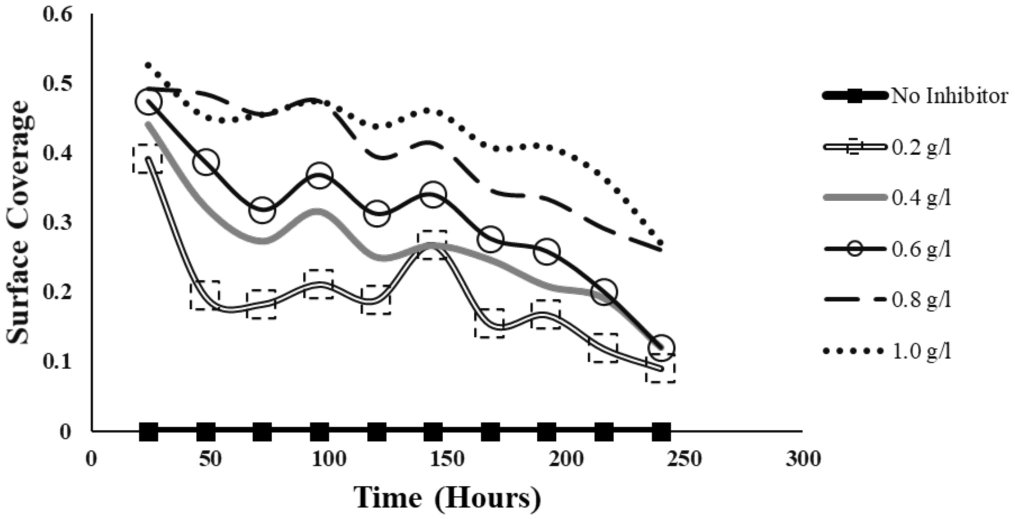


Fig. 5 - Surface coverage of mild steel coupons propagation with time in 1.0 M H_2SO_4 solution plus *Mangifera indica* peels extract.

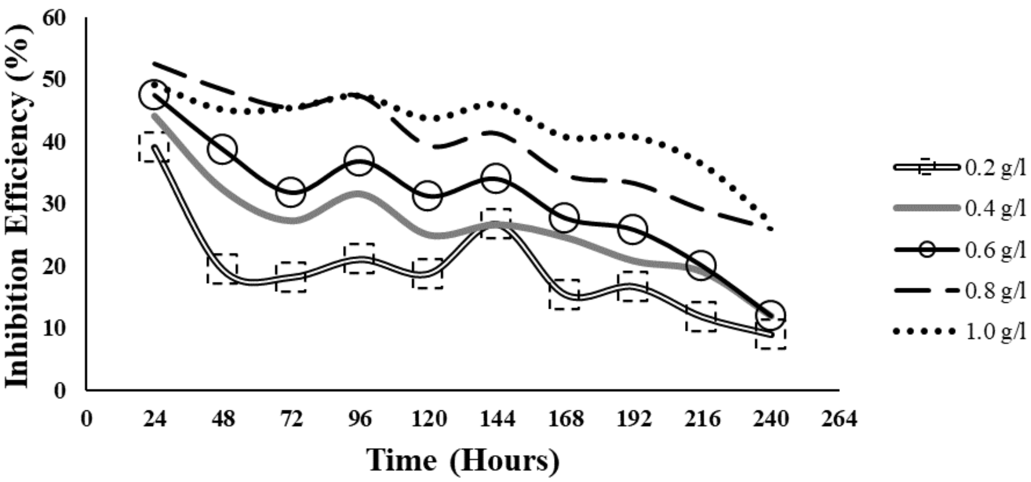


Fig. 6 - Inhibition efficiency of mild steel coupons propagation with time in 1.0 M H_2SO_4 solution plus *Mangifera indica* peels extract.

The weight loss calculations for *Citrus sinensis* was calculated with Eq. 2 and presented in Fig. 7. The corrosion rate calculations for *Citrus sinensis* was calculated with Eq. 1 and the values obtained were plotted in Fig. 8. The surface coverage calculations for *Citrus sinensis* was calculated with Eq. 3 and the values obtained are presented in Fig. 9. The inhibition efficiency calculations for *Citrus sinensis* was calculated with Eq. 4 and the values obtained are presented in Fig. 10.

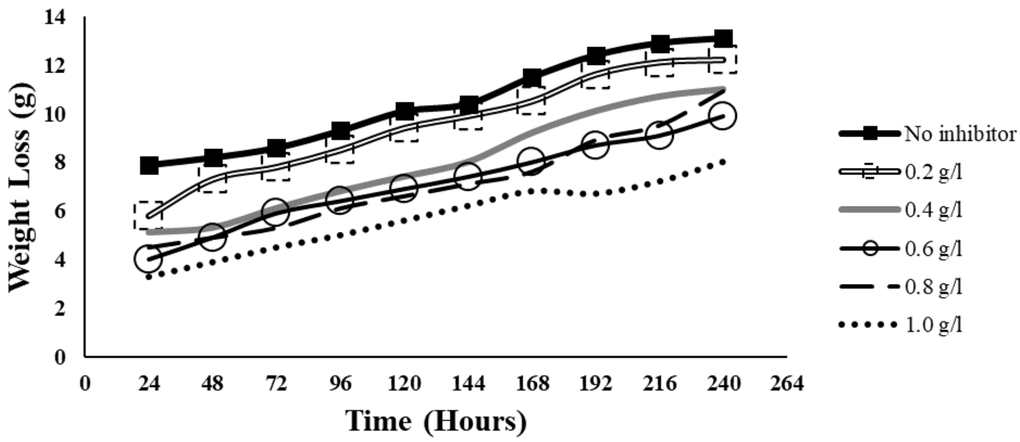


Fig. 7 - Weight loss of mild steel coupons propagation with time in 1.0 M H_2SO_4 solution plus *Citrus sinensis* peels extract.

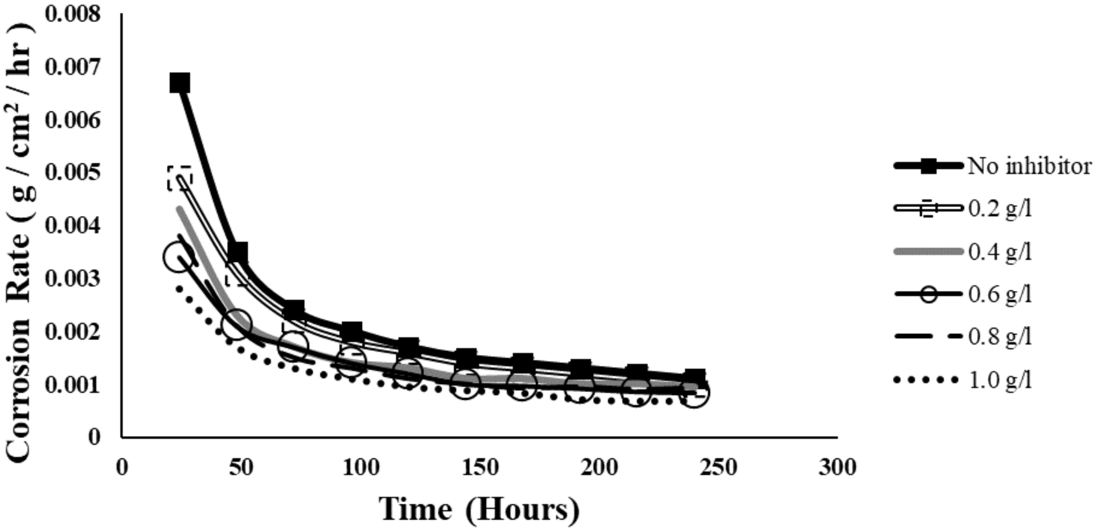


Fig. 8 - Corrosion rate of mild steel coupons propagation with time in 1.0 M H_2SO_4 solution plus *Citrus sinensis* peels extract.

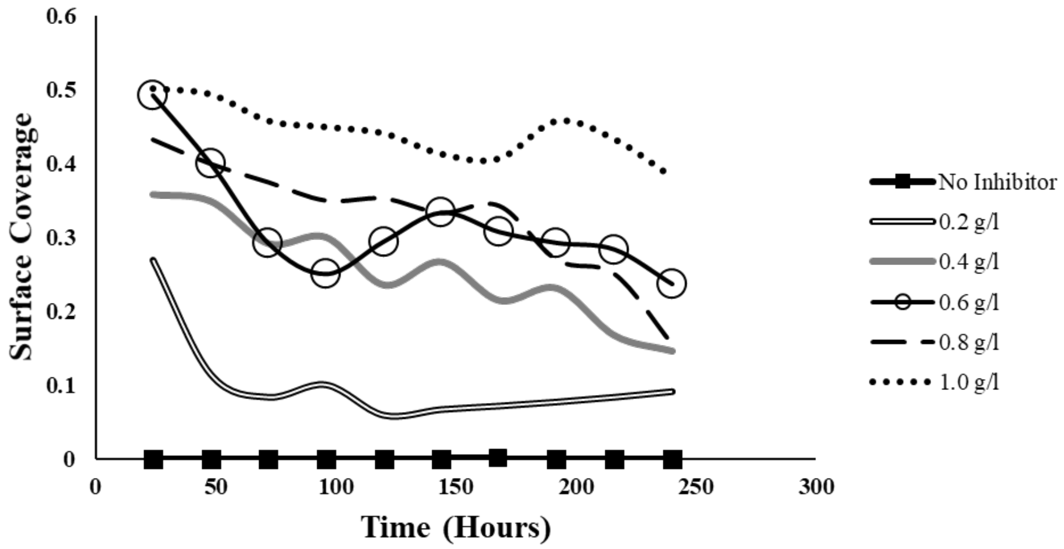


Fig. 9 - Surface coverage of mild steel coupons propagation with time in 1.0 M H_2SO_4 solution plus *Citrus sinensis* peels extract.

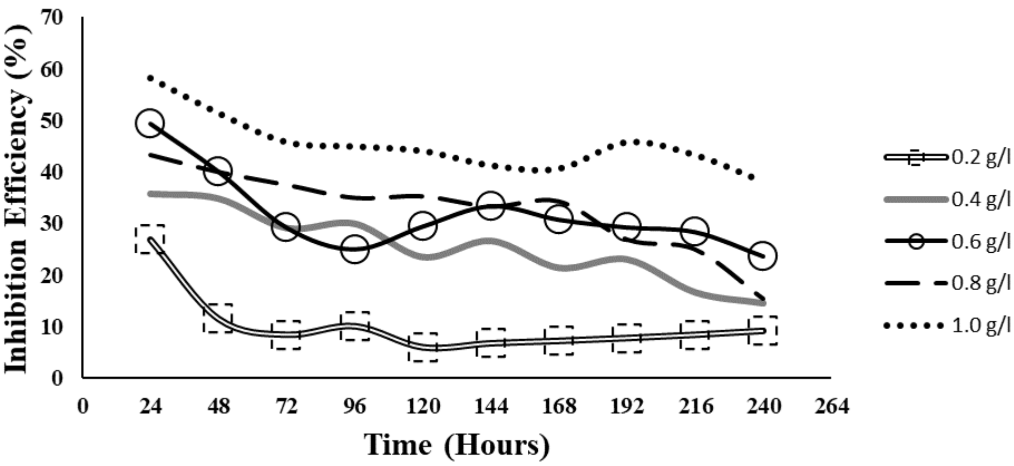


Fig. 10 - Inhibition efficiency of mild steel coupons propagation with time in 1.0 M H_2SO_4 solution plus *Citrus sinensis* peels extract.

3.2 Statistical Assessment of Inhibition Efficiency with Time

A statistical examination of the inhibition efficiency with respect to time for both extracts were investigated with Analysis of Variance (ANOVA) followed by Bonferroni-Holm posthoc significance test with the aid of the Daniel's XL Toolbox Version 6.70 statistical software. Relatively to other parameters estimated in this work which are WL, CR, θ and μ%; the inhibition efficiency (μ%) is most suitable in describing the corrosion prevention rate measurement.

For the *Mangifera indica* peels extracts, the degrees of freedom between the groups (DFB) value was 5, the degrees of freedom within the groups (DFW) value was 54, the Fisher's ratio (F) value was 18.59, which is a desirable high and commendable value signifying good relationship among the variables. The probability factor (P) was 1.07×10^{-10}, which was less than the critical probability factor (PC) with a value of 0.05 in the 95% confidence interval depicting good statistical relevance as well.

Table 1 - Bonferroni-Holm posthoc significance test for inhibition efficiency at various concentrations of *Mangifera indica* peels extracts.

Group 1	Group 2	Critical P value	P value	Significant
Time (Hours)	0.2 g/l	0.003846	0.000126	Yes
Time (Hours)	0.4 g/l	0.004545	0.000239	Yes
Time (Hours)	0.6 g/l	0.005	0.000366	Yes
Time (Hours)	0.8 g/l	0.005556	0.000834	Yes
Time (Hours)	1.0 g/l	0.00625	0.001107	Yes

Likewise, for the *Citrus sinensis* peels extracts, the D_{FB} value was 5, the D_{FW} value was 54, the F value was 20.67, another desirable high and suitable value signifying good relationship of variables. The P value was 1.78×10^{-11}, which was also less than the critical probability factor with a value of 0.05 in the 95% confidence interval confirming good statistical relationship of variables.

Table 2 - Bonferroni-Holm posthoc significance test for inhibition efficiency at various concentrations of *Citrus sinensis* peels extracts.

Group 1	Group 2	Critical P value	P value	Significant
Time (Hours)	0.2 g/l	0.004545	0.0000504	Yes
Time (Hours)	0.4 g/l	0.00625	0.000218	Yes
Time (Hours)	0.6 g/l	0.007143	0.000397	Yes
Time (Hours)	0.8 g/l	0.008333	0.000432	Yes
Time (Hours)	1.0 g/l	0.0125	0.00129	Yes

The Bonferroni-Holm posthoc significance test of all the inhibitor concentrations with respect to time for both extracts shown in Tables (1) and (2) were significant. This showed that the inhibition efficiency was highly controlled by the extracts in the observed range of concentration from 0.2 – 1.0 g/l.

The results obtained are comparable with that of Okewale and Adesina [4], Ofoma *et al.* [9], as well as that of Amini *et al.* [20]. The results showed similar trend of effectiveness and accuracy, but not equal in values due to different inhibiting substances used which are leaf extract of *Pterocarpus santaliniodes*, cocoa leaf extract and benzotriazole used for investigations respectively. As observed, WL increased with time but decreased with increase in concentration for both plant extracts. The decrease is caused by the inhibitive effects posed by the plant extracts, which increased as plant extracts concentration increased. Fig. 4 and 8 showed that the rate of corrosive activity of mild steel in 1.0 M H_2SO_4 decreased with increase in the inhibitor concentrations for all times. The decrease observed in the inhibition efficiency as time progresses could be explained on the basis of increased desorption of the inhibitor molecules on the metal surface [4, 9, 13]. The reduction in rate of corrosion of the mild steel in combination with the plant extracts was concentration dependent. The H_2SO_4 test solutions that contained no inhibitor showed a greater mass loss after 240 hours.

As observed in Fig. 6 and 10, mango peels extract has a higher inhibition efficiency capability than that of orange peels extract. This is an indication of mango peels extract's superiority compared to that of orange. This also suggests that mango peels extract has higher quantities of polar heterosides like catechin, procyanidins polyglycosides and flavanodiols, as well as sugar molecules that contains hydroxyl groups, which forms protective layers on the surface of the metals through hydrogen bonding as observed by Rocha *et al.* [21]. However, the CR value of 4.9×10^{-3} g cm^{-2} h^{-1} after 24 hours for the *Mangifera indica* inhibitor is a bit higher than that of 3.6×10^{-3} g cm^{-2} h^{-1} obtained for *Citrus sinensis*. After 240 hours, the least corrosion rate of the *Citrus sinensis* inhibitor (9.09×10^{-2} g cm^{-2} h^{-1}) was a bit higher also than that of the *Mangifera indica* (9×10^{-3} g cm^{-2} h^{-1}). The corrosion rate values for *Mangifera indica* were all slightly lower than those of *Citrus sinensis*. This confirmed that *Mangifera indica* peels extract performance was slightly better than that of *Citrus sinensis* peels extract regarding inhibition strength in H_2SO_4 solutions as a result of its chemical composition behaviour in acidic medium concentrations as observed.

The surface coverage plots in Fig. 5 and 9 for both extracts followed the same trend as that of their respective inhibition efficiencies, with that of no inhibitor having a perpetual zero value. The plots of weight loss and inhibition efficiency with respect to time for both plant extracts are shown in Fig. 3, 6, 7 and 10. The weight loss increased with time for both extracts as shown in Fig. 3 and 7 over the ten days period. The figures also revealed that the efficiency of corrosion inhibition decreased as quantity of the inhibitors decreased and also decreased as time increased. The decrease observed in the inhibition efficiency as time increased could also be accounted for as a result of increase in the protective films solubility, as well as that of any reacting material that is precipitated on the metal surface, which may inhibit the corrosion. The results obtained suggested that optimization of variables might lead to better corrosion inhibition and understanding.

4. Conclusion

This study has been able to clearly demonstrate that both *Citrus sinensis* and *Mangifera indica* peels extracts can be utilised successfully for mild steel corrosion inhibition in 1 M H_2SO_4 solutions at ambient temperature. They could be employed by scientists and engineers due to their environmental-friendliness, non-toxicity, relatively less expensive nature, and biodegradability. The statistical examinations with ANOVA as well as Bonferroni-Holm Posthoc Significance Test justified the suitability of the studies. For emphasis, because the peels extracts used for this study were retrieved plants, their potency could diminish slightly with time. From the study, *Mangifera indica* peel extracts was demonstrated to be a bit highly effective than *Citrus sinensis* for effective inhibition of corrosion of mild steel in 1 M H_2SO_4 solution. The inhibition efficiencies of both plant extracts decreased with time, but increased with extracts concentration. The plant extracts studied in this work indicated the possibility of considering agro-wastes as a source of eco-friendly, relatively cheap, and suitable acid anti-corrosion inhibitor. In addition, *Citrus sinensis* and *Mangifera indica* peels extracts can be evaluated further for corrosion inhibitors which can be useful in controlling corrosion of metallic objects including alloys in acid environment, as well as for scales removal and in metal finishing industries anti-rust agents. They could also be utilised in heat exchangers and boilers cleaning.

5. Acknowledgement

The author would like to thank Department of Chemical and Petroleum Engineering, University of Lagos, Akoka, Lagos, Nigeria for aiding the research work.

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