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Inhibitive effect of Grapefruit peels on Titanium steel in acidic solutions

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Abstract. The corrosion inhibitive effect of *Citrus* × *Paradisi* (CP) (grapefruit) inhibitor, has been experimented on Ti steel samples in 0.5 M HCl and 0.25 M H_2SO_4 solutions by weight loss method and open circuit potential. Result revealed that the presence of active components in *Citrus* × *Paradisi* inhibitor supported the inhibitive nature and its potency by mitigating corrosion effect on the Ti steel samples in both acidic solutions. The corrosion rate values decreased drastically for all the steel samples as both CP inhibitor and inhibitor efficiency increases. The highest inhibitor efficiency (IE) occurred in HCl solution with 91% at the maximum CP inhibitor concentration. Also, the open circuit potential shows that CP inhibitor performed like a mixed type of inhibitor. This confirms excellent adsorption behaviour of CP inhibitor on the Ti steel samples.

Keywords: Corrosion rate; corrosion inhibitor; active components; acidic media

Introduction

Corrosion is a chemical or electrochemical reaction between a material and the environment that causes deterioration of the metal. [1,2]. It is an oxidation reaction. Corrosion is initiated when the surface of a metal is exposed, thereby getting in contact with a gas or liquid, and it increases in the presence of high temperature, acid and salts Most metals are sensitive to corrosion, according to research [3-12], although all materials are liable to deterioration. It is an ongoing issue that is frequently difficult to totally remove. Complete eradication would be more feasible and possible than prevention.

Inhibitors protect cells against acid damage by the formation of a barrier of one or more molecular layers. Though, inorganic and synthetic inhibitors inhibit metals, yet they have been banned by several environmental regulations because they are toxic and cannot be easily disposed [13]. This has brought about the development of green inhibitors that are environmentally benign, affordable, and biodegradable to replace inorganic and synthetic organic inhibitors. Plant extracts, amino acids, proteins, and biopolymers have all been reported to be effective corrosion inhibitors [14]. Plant extracts are thought to be a significant means of getting chemical substances that are formed naturally which may be extracted by simple, low-cost processes [15]. These natural extracts are similar to synthetic organic inhibitors, and are also found as good inhibitors on corroded metals like the synthetic inhibitors [14].

Heteroatoms are common in organic inhibitors. Because of their increased basicity and electron density, N and S are corrosion inhibitors. The active centres for the adsorption process on the metal surface are N and S [16,17]. The inhibition efficiency should be in this order: O N S P. Researches have shown that the organic inhibitors displace water molecules and form a compact barrier when they are absorbed on surface of the metal,

Green corrosion inhibitors do not contain heavy metals and toxic elements, they are biodegradable and environmentally friendly. Several reports on the numerous natural compounds used as green inhibitors are available. The Grapefruit peel oil extract employed as an inhibitor in this study is a green inhibitor that is non-toxic and ecologically beneficial. Grapefruit is a citrus fruit that can have a bittersweet or sour flavor. It includes a variety of vitamins and minerals. It can be eaten whole or in juice or pulp form. They may also help with weight management [18]. Grapefruit is nutrient-dense yet low in calories. It also contains high levels of vitamins A and C. Grapefruit is high in fiber and water. For a healthy digestive tract, both water and fiber can help avoid constipation and promote regularity. Vitamin C is essential for the development of collagen, the skin's major support system. This study examines the use of Citrus Paradisi as an oil-based inhibitor to prevent Ti steel corrosion in a 0.5 M HCl and 0.25 M H2SO4 environment. Weight loss and open circuit potential techniques were used to investigate the inhibitory impact of Citrus Paradisi surfactant inhibitor.

2 Experimental Methods

Oil extract from *Citrus* × *Paradisi* (grapefruit) peels was bought from a market in Ota, Ogun State, Nigeria. The grape fruit peels were cut into pieces and dried in an oven for two days at 150°C to remove its moisture. The dried peels were grinded into fine particles. 800g of the grinded grape peels was loaded on the filter paper, positioned into the simple distillation flask equipment and saturated with n-hexane (C_6H_{14}) extractor solvent which was added underneath the flask. Thereafter, the flask equipment was heated for the extraction of *Citrus* × *Paradisi* oil. The C_6H_{14} was removed after being boiled. The chemical composition test and phytochemical analysis of the extracted oil of *Citrus* × *Paradisi* was done at the department of Chemistry, Covenant University.

The acid solutions were prepared into 200 ml of 0.25 M H_2SO_4 and 0.5 M HCl solution with distilled H_2O. *Citrus* × *Paradisi* inhibitor was administrated into the acidic solutions in the proportion of 5ml, 4ml, 3ml, 2ml and 1ml respectively. Ti stainless steel samples were prepared and cut into samples of average dimensions of 10 x 10 x 3 mm and analysed in the laboratory with X-ray Fluorescence spectroscopy equipment at the University of Ibadan, for the weight loss and polarization measurement. This analysis was carried out for a time duration of 336 hours (14 days). The sample was removed every 24 h from the mixture of acid and inhibitor, washed in water and acetone, dried, and weighed appropriately.

The mathematical expressions in equations 1 and 2 were used to generate the corrosion rate and inhibition efficiency, respectively.

$$CR = \left[\frac{87.6W}{\mathrm{DAT}}\right] \quad (1)$$

Where, W represents weight loss (g), D represents density (g/cm^2), A represents area (cm^2), and T represents immersion time (h). Inhibition efficiency (η) was approximated from the mathematical expression;

$$\eta = \left[\frac{\omega_1 - \omega_2}{\omega_1}\right] \times 100 \qquad (2)$$

ω_1 represents weight loss of the alloys without *Citrus* × *paradisi* inhibitor in the electrolyte while ω_2 represents weight loss of the alloys at definite *Citrus* × *paradisi* concentrations.

The table 1 shows the phytochemical constituents present in *Citrus* × *paradisi* inhibitor.

Table 1: Phytochemical constituents present in *Citrus* × *paradisi*

S/N	Phytochemical compound	Result
1	Tannin	+
2	Saponin	-
3	Flavonoids	+
4	Quinones	-
5	Coumarin	-
6	Terpenoids	+
7	Glycoside	+
8	Alkaloids	+
9	Steroids	+
10	Phenol	+
11	Carbohydrate	+

Key: "+" active compound present, "-" active compound absent.

3 Results and discussion

3.1 Weight loss (WL) study

Observations from the weight loss experiment showed the difference in samples with and without *Citrus* × *paradisi* inhibitor (CP inhibitor). Figure 1 and 2 reveal the comprehensive results by curves, after 336 h exposure time with values of weight loss (WL), inhibitor efficiency (IE) and corrosion rate (CR) of Ti steel samples in both HCl and H_2SO_4 solutions. Evidence in figure 1 shows severe corrosion degradation on the steel sample after introduced to 0.5 M HCl solution with corrosion rate of 0. 0243 mm/y. This indicates the presence Cl^- ion corrosion on the sample by causing drastic reduction in weight of the steel sample [19-21]. Upon addition of CP inhibitor with 1ml concentration, the steel sample was protected by lowering the corrosion rate. This suggests excellent inhibition shield of CP inhibitor by displacing the water ions or molecule and Cl^- ion causing corrosion damage away from the surface of the steel sample. The protection shield of CP inhibitor was empowered by the active components present in CP inhibitor as illustrated in Table 1. Those active components acted as antioxidant and prevented the flow of oxidation corrosion reaction (metal dissolution) from attacking the surface of the steel samples. Also, Figure 1 shows that as CP inhibitor concentration level increases, decrease in corrosion rate occurred and at 5ml highest concentration of CP inhibitor, the lowest corrosion rate value was recorded as 0.0002 mm/y. This result confirms a strong film adsorption protection of CP inhibitor on the surface of the steel samples.

Furthermore, CP inhibitor performed with similar results in H_2SO_4 solution, with strong protection shield mechanism. Observation recorded that the corrosion rate values retarded as CP inhibitor concentration increases too. The corrosion rate value of sample without CP inhibitor concentration in H_2SO_4 solution occurred as 0.0453 mm/y, due to the presence of SO_4^{2-} ion [22-24]. The corrosion rate was reduced to 0.0403 mm/y after adding 5 ml CP inhibitor, this confirms excellent protection via transfer of pi electrons and functional groups present in CP inhibitor. Also, the CP inhibitor performed well with steady reduction occurrence and this justifies the active performance of CP inhibitor, as CP inhibitor increases, inhibitor efficiency (IE) increases too, as demonstrated in figure 3 and 4. This ascertain the mitigation of corrosion damage (SO_4^{2-} and Cl^- ion) on the steel sample, and the highest IE was recorded as 91% in HCl solution with the highest CP inhibitor concentration [25].

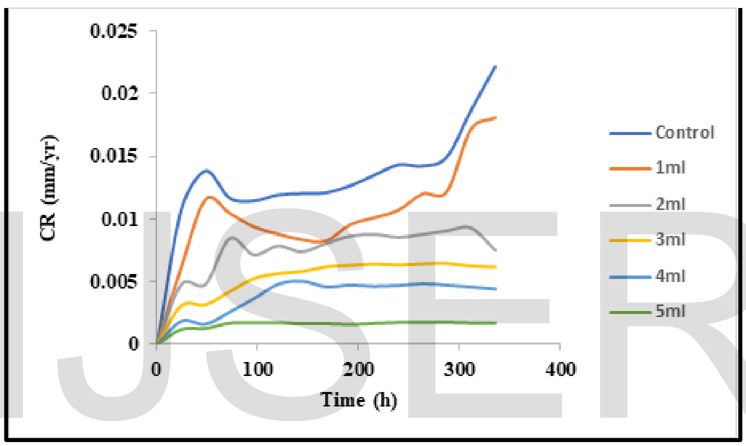

Fig1 shows corrosion rate of Ti steel in HCl solution

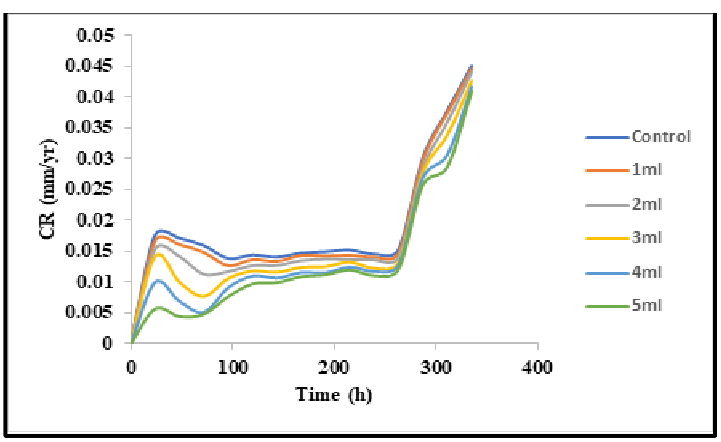

Fig 2 show corrosion rate of Ti steel in H_2SO_4 solution

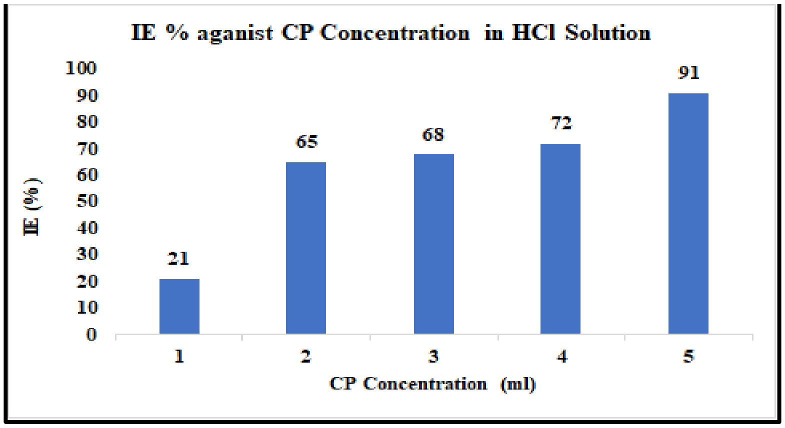

Fig 3. I.E (%) of Ti steel in HCl solution

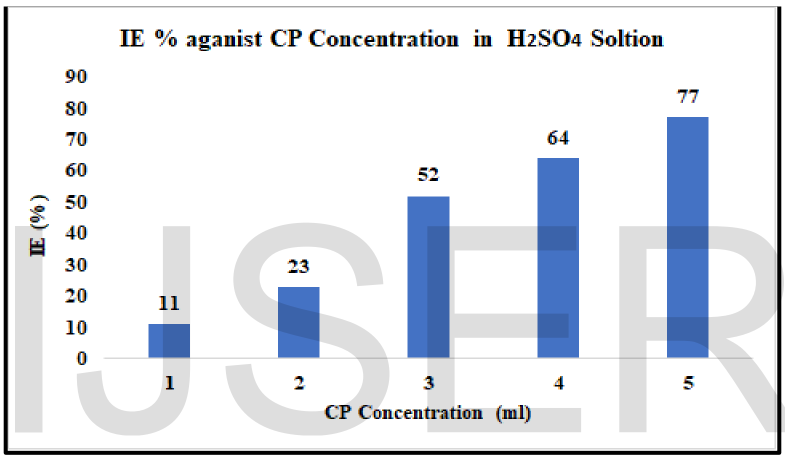

Fig 4. I.E (%) of Ti steel in H_2SO_4 solution

3.2 Open Circuit Potential

The electrochemical analysis for the potential of the steel samples plotted with Ag/AgCl reference electrode as a function of exposure time was displayed in figures 5 and 6. The results of the variation of the *Citrus* × *paradisi* inhibitor (1 ml and 5 ml) during immersion for the inhibited samples and non-inhibited sample known as control (c) in 0.25 M H_2SO_4 solution was recorded in figure 5. Observation revealed that the open circuit potential values depreciate rapidly to more negative potential, confirming hydrogen evolution interaction of the steel from H_2SO_4 corrosion damage (i.e., SO_4^{2-}). The reaction became straight line, suggesting steady state potential reaction for both 1ml and 5 ml *Citrus* × *paradisi* inhibited samples after 4000 secs till the end of the reaction [26-28]. The reaction also suggest that the inhibitor acted predominantly cathodic inhibition reaction, shielding the steel surface from the SO_4^{2-} ion attack [29-31]. Furthermore, the open circuit potential curves for 0.5 M HCl were presented in figure 6 and evidence demonstrated that, the presence of 1ml inhibitor moved the steady state potential to the positive direction. This suggest that the anodic reaction (oxidation dissolution) was preferentially affected by the inhibitor than the cathodic reaction [32-34]. However, the control steel sample (blank sample) reacted more to the cathodic region. The open circuit potential vales for the samples of the 1 and 5 ml *Citrus* × *paradisi* inhibitors was between 0.71 to 0.78 V within the completed exposure time. It was observed that the steel sample with 1ml *Citrus* × *paradisi* inhibitor concentration operate a straight-line curve, confirming steady state potential was achieved and likewise with sample 5 ml inhibitor from 3800 secs reaction to the end of the reaction [35-38].

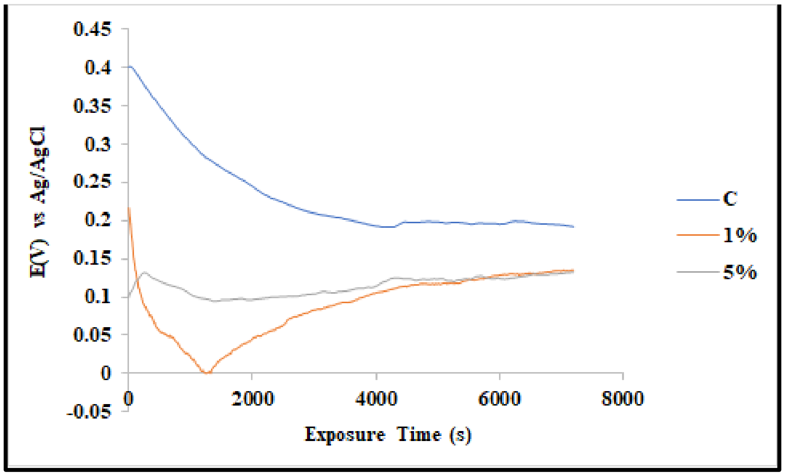

Figure 5 shows the OCP slope for in 0.25 M H_2SO_4 solution

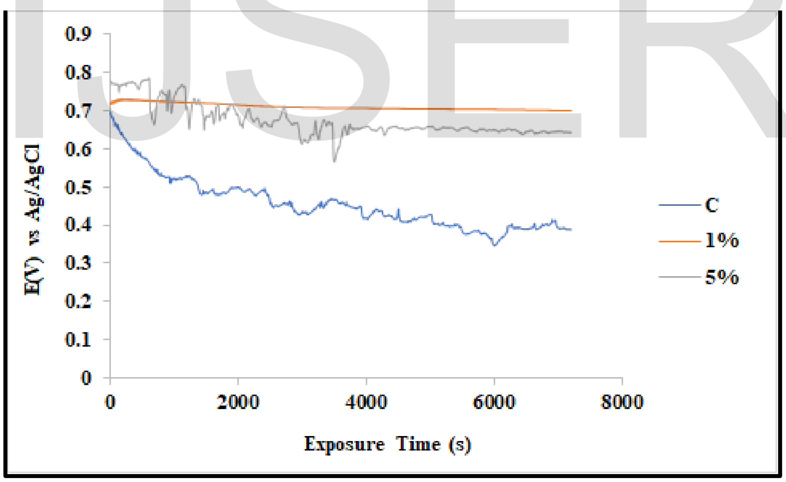

Figure 6 shows the OCP slope for in 0.5 M HCl solution

Conflict of Interest Statement

The authors declare that there is no competing financial or personal interest that could influence this research work in any form.

4. Conclusion

The adsorption study of *Citrus* × *paradisi* CP inhibitor is a useful mitigating organic compound for Ti steel in both HCl and H_2SO_4 acidic solutions. The electrochemical test of weight loss technique confirms that as *Citrus* ×

paradisi inhibitor concentrations increases, IE increases too and corrosion rate values decreases for each steel samples used. The optimum IE value was recorded as 91% in HCl solution. Also, the presence of antioxidant reactors known as active components shows that they are the main factors responsible for effective inhibitive behaviour of CP inhibitor by reducing corrosion damage on the steel samples in both acidic solutions. Furthermore, the open circuit potentials reveal that CP inhibition behaved predominantly as a mixed type inhibitor.

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