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Citrus sinensis peel extract as corrosion inhibitor for mild steel in hydrochloric acid solution

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Abstract

This study investigated the corrosion inhibition properties of *Citrus sinensis* (CS) as a green inhibitor for mild steel in1 M HCl solution at different concentrations (100 mM, 150 mM and 200 mM). The corrosion behaviour of mild steel in the presence of absence of CS was evaluated using weight loss measurement, and scanning electron microscopy (SEM). Results of weight loss measurement showed that the corrosion rate of mild steel in 1 M HCl solution was significantly reduced with increasing concentrations of CS, inhibition efficiency reaching up to 98 %. SEM analysis revealed that the surface of mild steel in the presence of CS was covered a thin and homogenous protective film, while the surface of mild steel without CS was corroded and rough. An isothermal analysis was also carried out and the results indicated that the adsorption of CS on the mild steel surface followed the Freundlich isotherm equation. The value of n was found to be greater than 1, indicating that the adsorption of CS on the mild steel surface was favourable and increased with the inhibitor concentration. The value of the adsorption coefficient (K_f) was found to be highest at 200 mM of CS, indicating a high adsorption capacity and strength of the CS on the mild steel surface

Keywords: Corrosion; Corrosion inhibitor; Mild steel; *Citrus sinensis*

1. Introduction

Mild steel is a versatile metal that is extensively used in various industries, including metallurgy, food processing, electricity, chemicals, and construction. This is due to its exceptional properties such as high mechanical strength, resiliency, and toughness. However, mild steel is also known to be susceptible to corrosion, which poses a significant challenge in terms of durability and longevity. Therefore, finding sustainable solutions to the problem of mild steel corrosion is of paramount importance [1].

One of the most effective ways of controlling mild steel corrosion is through the use of corrosion inhibitors. These are chemical substances that are introduced in small quantities to the metal surface or corrosive environment, and they slow down the corrosion rate of the metal. There are majorly two classes of inorganic inhibitors – organic and inorganic [2].

Recent studies have shave shown that the use of organic corrosion inhibitors is an environmentally friendly and sustainable approach to combatting metal corrosion [3]. These inhibitors work by forming adsorption layers on the metal surface, which blocks the active sites of the anode and cathode, thereby protecting the metal from dissolution. The adsorption of these inhibitors is made possible by the presence of heteroatoms such as O, H, N, and S [4].

Organic corrosion inhibitors can be obtained from the waste parts of certain plants, including orange and they contain phytochemicals such as alkalioids, steroids, tannins, and flavonoids. Natural products/organic compounds such as

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lignin, tannin, cinchona alkaloids, pomegranate alkaloids have been investigated [5, 6].Inorganic complexes and their derivatives such as salts of zinc, copper, nickel, arsenic, and additional metals, with the arsenic compounds being the one commonly used. Various inorganic complexes, and their derivatives –aromatic thiosemicarbazones, methyl and phenyl thiosemicarbazones, pyridoxal, 4-ethyl semithiocarbazide, pyridoxal-(4-methyl semicarbazone) and its zinc (II) complex, acetamide and thiourea, 2- acetyl pyridine-(4-penylthiosemicarbazone),2-acetylpyridine-(-) and 2-acetylpyridine–(4-phenyl isoethylthiosemicarbazone) have been investigated and reported as corrosion inhibitors by different researchers [7, 8, 9].

The use of citrus peels as inhibits in corrosive media of mild steel has been extensively studied by researchers. For instance, [10] obtained 90.3 % inhibitor efficiency from the use of citrus peels inhibitor concentration of 900 ppm for mild steel in 1 M HCl medium, by considering both the experimental and theoretical approaches.

The aim of this research therefore, is to establish the corrosion inhibition performance of *Citrus sinensis* as inhibitor and to establish the appropriate adsorption isotherms for the corrosion inhibitor process of mild steel in 0.1 M HCl. The knowledge acquired from this research will be beneficial in finding a sustainable solution to the problem of mild steel corrosion, and the use of extract of *Citrus sinensis* peels as an inhibitor will contribute to a cleaner and greener environment.

2. Material and methods

2.1. Preparation of mild steel

The mild steel coupon used for this research was obtained from Yongxing Steel Co.Ltd, Benin City in Nigeria. The mild steel coupon was cut into 3 cm square and a hole was drilled in the middle. A thread was then tied in a whole for easy suspension in a media. The mild steel samples were polished to a mirror-like nature with emery paper to remove dirt and rust and then cleaned in acetone. It was further dried and weighed. The weight of each sample was recorded and labeled.

2.2. Preparation of *Citrus sinensis* peels extract

Oranges were purchased from uselu market, Benin City in Nigeria. The oranges were washed under running water. The peel was sun dried for two weeks and ground into fine powder. The orange peels powder (30 g) was heated in distilled water (500 ml) for 30 minutes in a round bottom flask using a foil paper and left for 24 hours. The extract was separated into beakers, each containing the extract (100 mM, 150 mM and 200 mM) which served as the inhibitor concentrations for this study.

2.3. Gravimetric method

Weight loss technique was employed in the experiment as follows. Each coupon was weighed using Analytical weighing balance and recorded as weight W_1. The coupon was suspended in a 500 mL beaker using a thread. A 150 mL of 1 M HCl was introduced into reaction beakers. The experimental set-up was kept in the laboratory away from direct sunlight, while the time of exposure for each coupon was carefully noted. Each coupon was retrieved from the test medium in intervals of 24 hours. The corroded coupons were washed in 20 % NaOH in 100 g/L zinc dust to stop the corrosion reaction and dried using acetone. The coupons were reweighed and the final weights, W_1 recorded. Weight losses, $\Delta W = W_0 - W_1$ were calculated. The inhibition efficiency % IE and surface coverage θ was determined by using the following equations: where W_1 and W_0 are the weight loss value in presence and absence of inhibitor, respectively. The experiment was repeated using concentrations of 100mM, 150mM and 200mM of the plant extract in the 1 M HCl medium, a varying time of between 24 hours for five days.

$$\Theta = \frac{W_o - W_1}{W_0} \text{.............}(1)$$

$$\%IE = \frac{W_o - W_1}{W_0} \text{ X } 100 \ldots\ldots (2)$$

The corrosion rate (CR) is expressed as an increase in corrosion depth per unit time in (mg cm^{-2} h^{-1}). The corrosion rate equation is given as:

$$CR = \frac{\Delta w}{At} \ldots\ldots\ldots\ldots (3)$$

Where Δw = weight loss of coupon, t = immersion time, and A=area of coupon.

2.4. Isotherm analysis

2.4.1. Freundlich isotherm

The Freundlich isotherm is useful for describing equilibrium data and adsorption characteristics for a heterogeneous surface. It is applicable to both monolayer (chemisorption) and multilayer adsorption (physisorption). The linear form of the equation is expressed as:

$$\log \Theta = \log k_{ads} + \frac{1}{n}\log C_e \; \ldots\ldots\ldots \; (4)$$

Where K_{ads} (mg/g)/(mg/L)^n and n (dimensionless) are Freundlich isotherm constants related adsorption capacity and adsorption intensity respectively, Θ = % IE/100 (mg/g) is the amount of adsorbate uptake

2.4.2. Langmuir isotherm

The Langmuir theoretical equation was developed by assuming the following: (i) a fixed number of accessible sites are available on the adsorbent surface, and all sites have the same energy; (ii) adsorption is reversible; (iii) once an adsorbate occupies a site, no further adsorption can occur on that site; and (iv) no interaction occurs between adsorbed species. The linear form of the isotherm is described as:

$$\frac{C_e}{\Theta} = \frac{1}{K_{ads}} + Ce \ldots\ldots\ldots (5)$$

Where K_{ads} (mg/L) is the Langmuir constant related to affinity between and adsorbent and adsorbate, Θ= % IE/100 the maximum saturated monolayer adsorption capacity of an adsorbent

3. Results and discussion

3.1. Effects of inhibitor concentration of extract on inhibition efficiency

Figure 1 shows that inhibition efficiency (IE %) increases with increase in the concentration of the extract. Similar observation was reported by [11]. In this study, the inhibition efficiency using 100 mg/L increased from 82 to 85 % while the inhibition efficiency using 150 mg/L increased from 82 to 86 %. For 200 mg/L, the inhibition efficiency increased from 88 to 91 %. In Figure 2, it was observed that corrosion rate decreased with increasing concentration of extract of *Citrus sinensis*. This observation is consistent with the findings by [12] and further indicative that the extract is effective in inhibiting corrosion.

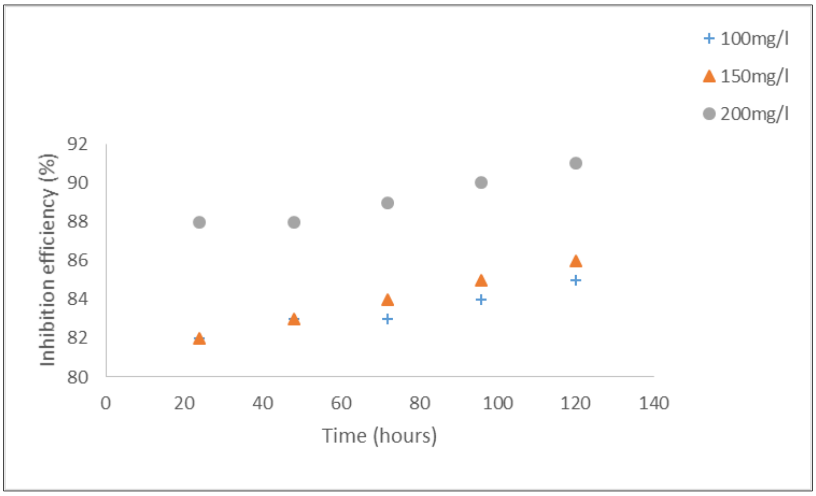


Figure 1 Variation of inhibition efficiency with time at different concentration

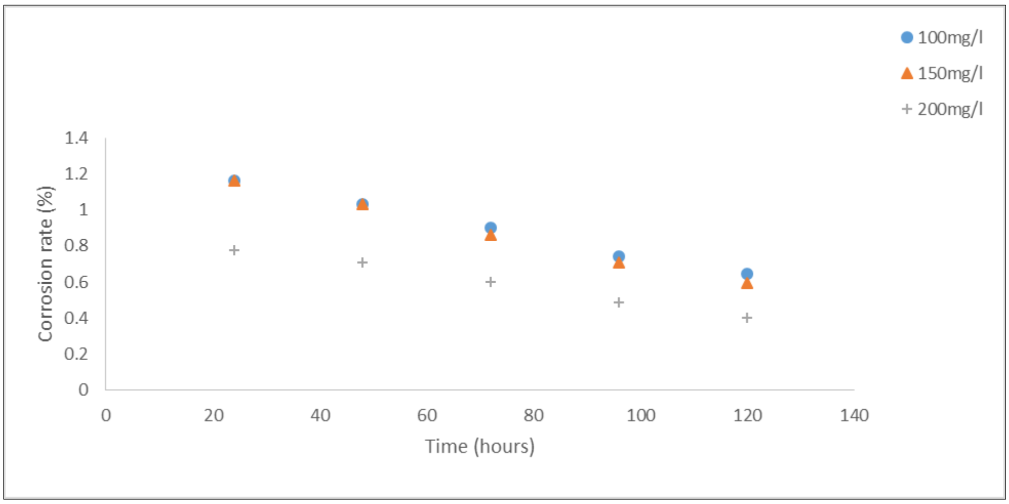
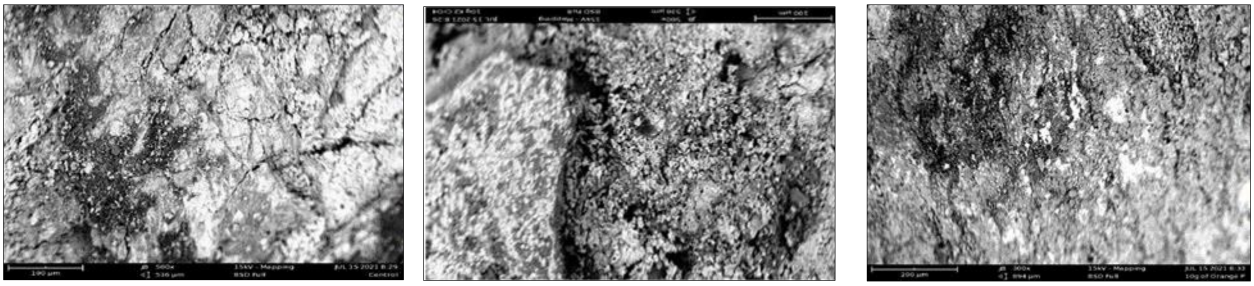


Figure 2 Variation of corrosion rate with time at different concentration



A B C

Figure 3 SEM analysis of steel surface with (A) and (B) without extract (C) extract *Citrus sinensis*

Fig 3 reveals the SEM analysis of steel at various conditions. With the extract *Citrus sinensis*, morphology of the steel is smoother compared surfaces without extract. More visible cracks were observed on the surface without extract, indicating that the extract is a potential corrosion inhibitor.

Table 1 Isothermal analysis

Langmuir		**Freundlich**	
R^2	K_{ads}	R^2	K_{ads}
0.8575	0.00373	0.8603	>10000

The fitness of the isotherm equation (Equation 4 and 5) in the prediction of the adsorption behavior of the inhibitor was justified by the approximate values of one (1) obtained for each of the coefficient of determination (R^2), as shown in Table 1. In this case, Freundlich isotherm was found to better describe the adsorption behaviour due to higher value of correlation coefficient. This imply that the inhibitor adsorbs on the metal surface in a non-uniform multilayter process and the adsorption is favourable and increases with the inhibitor concentration.

4. Conclusion

In conclusion, the study investigated the corrosion inhibition properties of *Citrus sinensis* (CS) as a green inhibitor for mild steel in a 1 M HCl solution at various concentrations (100 mM, 150 mM, and 200 mM). The results demonstrated the effectiveness of CS in reducing the corrosion rate of mild steel, with inhibition efficiency reaching up to 98 %. Weight loss measurement and SEM analysis provided valuable insights into the corrosion behavior and surface characteristics of mild steel in the presence and absence of CS. Overall, this study emphasizes the promising corrosion inhibition properties of *Citrus sinensis* as a green inhibitor for mild steel in acidic environments. CS effectively reduced the corrosion rate, formed a protective film, and exhibited favorable adsorption characteristics. These attributes make CS a potentially eco-friendly option for corrosion protection in mild steel applications. Future research can delve into understanding the underlying mechanism of CS inhibition, evaluating its long-term stability, and assessing its performance under diverse environmental conditions.

Compliance with ethical standards

Acknowledgments

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Disclosure of conflict of interest

We declare that we have no conflict of interest.

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