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Short report of corrosion inhibition of mild steel corrosion in hydrochloric acid by 4-ethyl-1-(4-oxo-4-phenylbutanoyl) thiosemicarbazide

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Abstract: The inhibitive efficacy of 4-ethyl-1-(4-oxo-4-phenylbutanoyl) thiosemicarbazide (EOPT) as a newly synthesized corrosion inhibitor on mild steel in 1 M HCl medium was investigated through gravimetric techniques. The experimental findings reveal that the inhibitive efficacy was observed to increase with increasing EOPT concentration from 100 to 500 ppm, whereas the corrosion rate decrease with increasing the concentration of the tested inhibitor. The highest inhibitive efficacy 96.1% was recognized after the addition of a 500 ppm EOPT. The inhibitive performance was described according to the adsorption of EOPT molecules on the surface of mild steel. The adsorption isotherm model obeys Langmuir adsorption isotherm through physisorption and chemisorption adsorption mechanism.

Keywords: thiosemicarbazide, EOPT, corrosion inhibitor, inhibitive efficacy, Langmuir

1 Introduction

Generally, the various usually utilized corrosion inhibitors for mild steel and metals facilities in industries were heterocyclic molecules which have in their structures heteroatoms including phosphorous, sulfur, oxygen, and nitrogen in addition to pi-bonds and aromatic rings that adsorbed onto the mild steel surface and after forming protecting layers [1-3], which are barriers to the induced solution for corrosion to attack the mild steel surface, hence decreasing corrosion [4-7]. The accepting molecule as corrosion inhibitor compound, different factors include expense, availabilities, and its impact on the environment should be taken into consideration [8-15]. The investigated inhibitor as an organic molecule having heteroatoms including oxygen, nitrogen, sulfur, and aromatic ring increase the density of electrons on the structure of inhibitor molecule. Thus, the investigated inhibitor 4-ethyl-1-(4-oxo-4-phenylbutanoyl) thiosemicarbazide (EOPT) is exhibited to act as an excellent corrosion inhibitor. The purpose of the current study is to synthesize thiosemicarbazide derivative according to the reaction of 4-oxo-4-phenylbutanohydrazide with isothiocyanatoethane

and to investigate its inhibitive performance as a corrosive inhibitor for mild steel in corrosive environment. Moreover, this investigation is continued to explain the process of adsorption EOPT molecules on the surface of mild steel and it was noticed that the EOPT molecules obey Langmuir adsorption isotherm model through both physisorption and chemisorption models.

2 Experimental Technique

2.1 Materials preparation

The mild steel sample utilized for the research were regularly split into coupons of areas 4.5 cm × 2.5 cm × 0.2 cm. Hydrochloric acid of analytical grade was diluted by double distilled water to the concentration of 1 M to be utilized as a corrosive solution. The chemical structure of the tested inhibitor is shown in Figure 1.

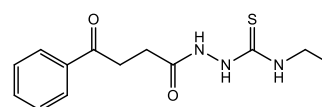


Figure 1. Structure of 4-ethyl-1-(4-oxo-4-phenylbutanoyl)

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thiosemicarbazide (EOPT).

2.2 Gravimetric analysis

All the experiments were carried out in 250 ml of 1 M HCl medium and open to the air, at 303 K with various concentrations of EOPT for 1, 5, 10, and 24 h exposure time. The coupon was polished with sandpaper, cleaned completely with doubled distilled water, acetone and finally dried in the oven. Finally, the coupons were thoroughly rinsed in distilled water, dried in the oven, and weighed accurately [16,17]. The analyses were conducted three times in an individual and the mean weight loss value was recorded [18-25]. From the gravimetric techniques, the rate of corrosion (C_R), inhibition efficiency (IE%) and Surface coverage (θ) were determined according to Equations (1), (2), and (3) respectively [26-28].

$$C_R = \frac{m_1 - m_2}{at} \quad (1)$$

$$IE(\%) = \frac{C_{Ro} - C_{Ri}}{C_{Ro}} \times 100 \quad (2)$$

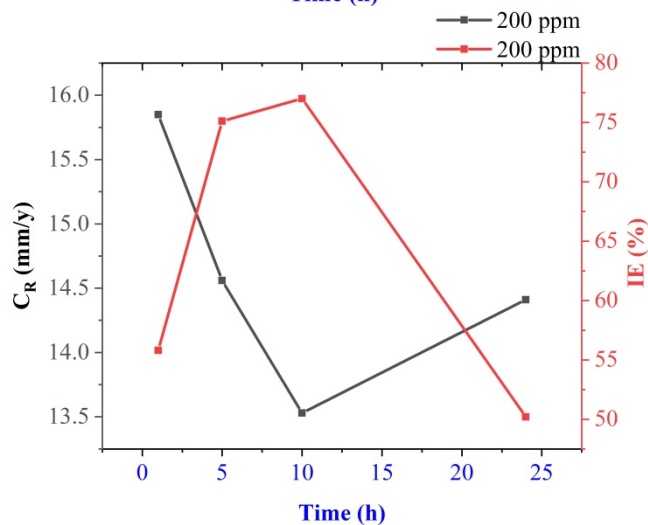
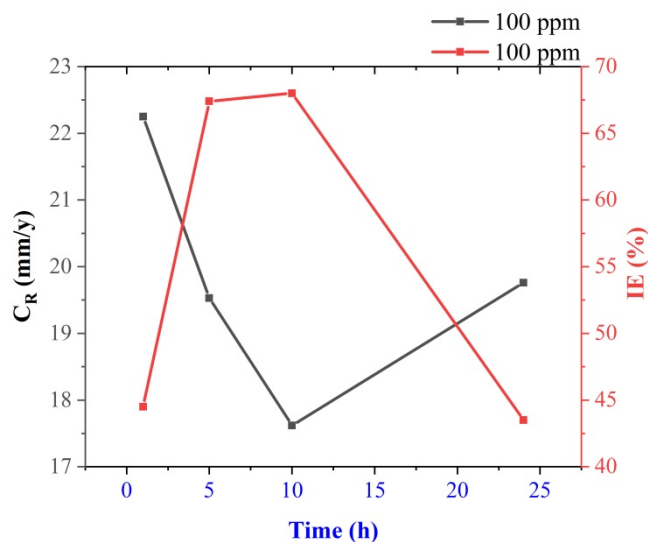
$$\theta = \frac{C_{Ro} - C_{Ri}}{C_{Ro}} \times 100 \quad (3)$$

3 Results and Discussion

3.1. Gravimetric measurements

The rate of corrosion values and inhibition efficacy were determined from gravimetric analysis at various concentrations of EOPT in 1 M corrosive solution after 1, 5, 10, and 24 hour exposure time at 303 K. The experimental results are exhibited in Figure 2. It was noted that EOPT controls or impedance the mild steel corrosion in corrosive media at different inhibitor concentrations utilized in the investigation [29,30]. It is clear from Figure 2 that the corrosion rate decreases with increasing concentration of the inhibitor while the inhibitory activity increases with increasing concentration of the inhibitor used to 500 ppm. The highest inhibitory efficacy was determined at 500 ppm EOPT concentration which was 96.1% and additional EOPT increasing concentration did not increase the inhibition efficiency. The effect of immersion time was also studied and it was found that the inhibition efficiency increases with increasing exposure period from 1 to 5 hours, but there is no significant difference from 5 to 10 hours of immersion time, but the inhibition efficiency decreases after 24 hours [31-35]. Certainly, the rate of corrosion values reduces from 19.53 mm y^{-1} to 6.74 mm y^{-1} on the increase of 100 ppm to 500 ppm of EOPT. The increased inhibitive efficacy and reduces rate of corrosion may be imputed to the increased adsorption of EOPT molecules at the surface of mild steel with increasing EOPT concentration [36-38]. The variety of inhibitive efficacy with different exposure periods from 1 h

to 24 h at various inhibitor concentrations is demonstrated in Figure 2. The inhibition efficiency increased from 67.4% to 96.1% when the exposure period increases from 1 h to 5 hours. These findings are attributed to the decreased rate of corrosion of mild steel surface with exposure period and the increase in the number of inhibitor molecules adsorbed by the surface. EOPT exhibited significant inhibitive performance for the corrosion of the surface of mild steel in hydrochloric acid media [39-42].



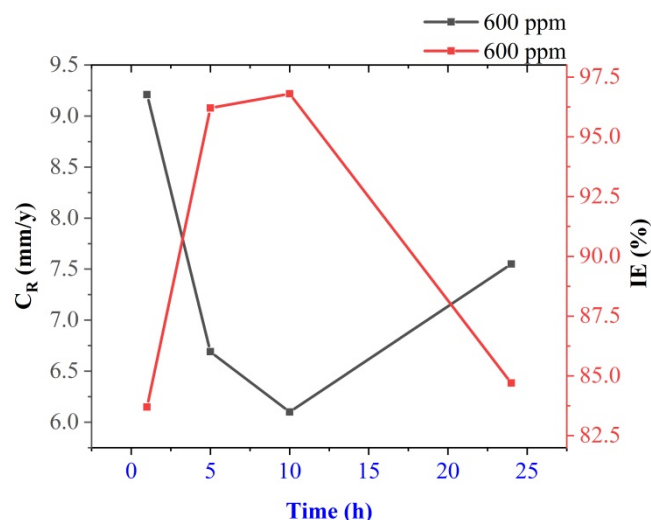
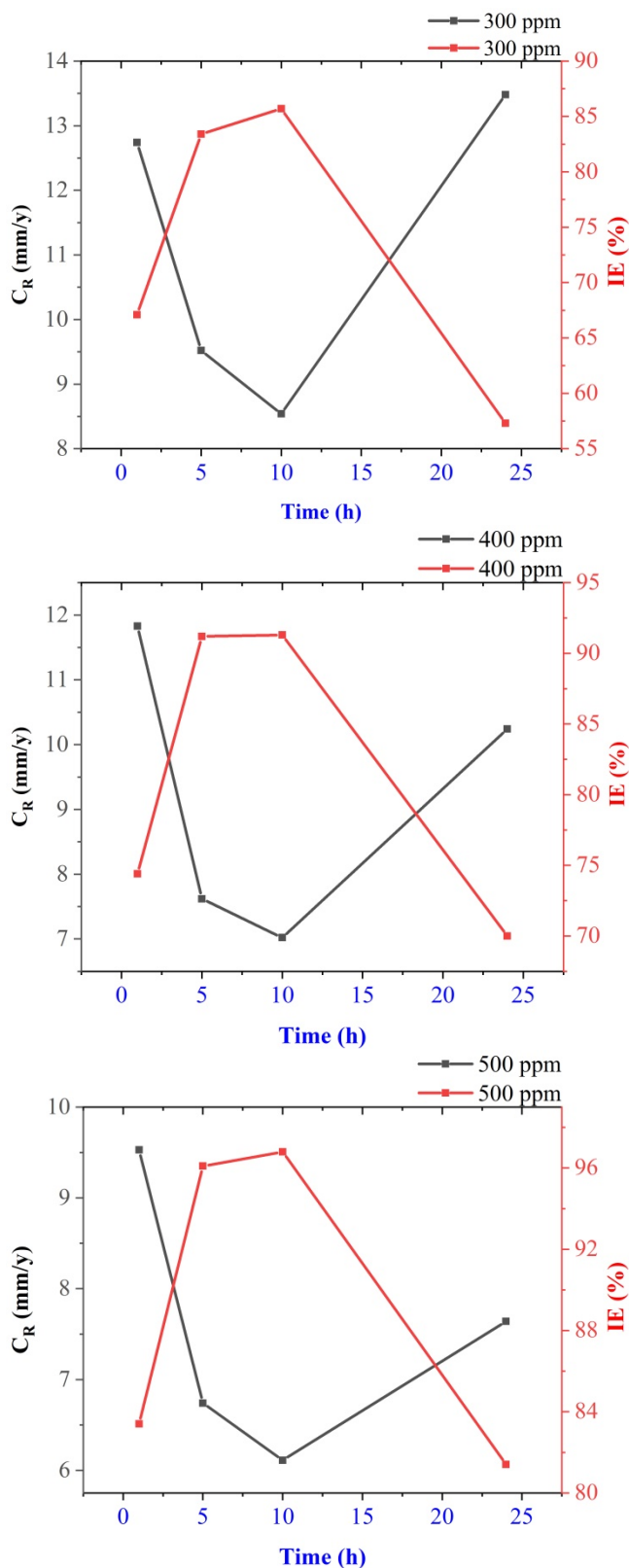


Figure 2. Difference of corrosion rate and inhibitive efficacy in 1 M HCl on the surface of mild steel with various exposure times.

3.2 Adsorption Isotherm

The investigation adsorption isotherms explain the interactions of surface steel coupons with inhibitor molecules. For this goal, the surface coverage (θ) values at various inhibitor concentrations in corrosive solution have been determined. The commonly utilized adsorption isotherms are Langmuir adsorption isotherms and Temkin adsorption isotherms. Efforts to proper datum collected from gravimetric techniques into various isotherms exhibit that the datum quite proper is Langmuir isotherm [43-45]. Langmuir hypotheses associate the adsorbate concentration (C_{inh}) to the surface coverage degree according to Equation (4) [46,47].

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \quad (4)$$

where, C_{inh} refers to the inhibitor concentration and K_{ads} represents the adsorption equilibrium constant

The R^2 which is a parameter of the linear regression that can be determined from the relation of C_{inh}/θ and C_{inh} is demonstrated in Figure 3. Figure 3 exhibits the straight line of C_{inh}/θ vs C_{inh} at 303 K. These outcomes reveal that the slope and coefficient of linear regression and are almost equal to unity, which proves that the EOPT molecules adsorbed on the metallic surface follow the Langmuir isotherm model. The plot of C_{inh}/θ vs C_{inh} exhibits variance from unity, indicating non perfect and not expected simulation from the Langmuir isotherms. It could be the issues from the interactions of the adsorbed inhibitor molecules on the metallic surface [48]. K_{ads} as adsorption constant and free adsorption energy (ΔG_{ads}^o) were determined according to equation (5);

$$\Delta G_{\text{ads}}^{\circ} = -RT \ln (55.5 K_{\text{ads}}) \quad (5)$$

where, 55.5 refers to the water concentration in molarity whereas R is the gas constant.

In general, it was reported that if the value of $\Delta G_{\text{ads}}^{\circ}$ around -20 kJ mol^{-1} then the adsorption process is harmonious with the physisorption process, whereas, if $\Delta G_{\text{ads}}^{\circ}$ is around -40 kJ mol^{-1} then the process is chemisorption [49-55]. Herein, the determined value of $\Delta G_{\text{ads}}^{\circ}$ is $-37.79 \text{ kJ mol}^{-1}$ meaning that the mechanism of adsorption of the tested inhibitor molecules on the mild steel surface in 1 M corrosive medium at 303 K, is both physisorption and chemisorption.

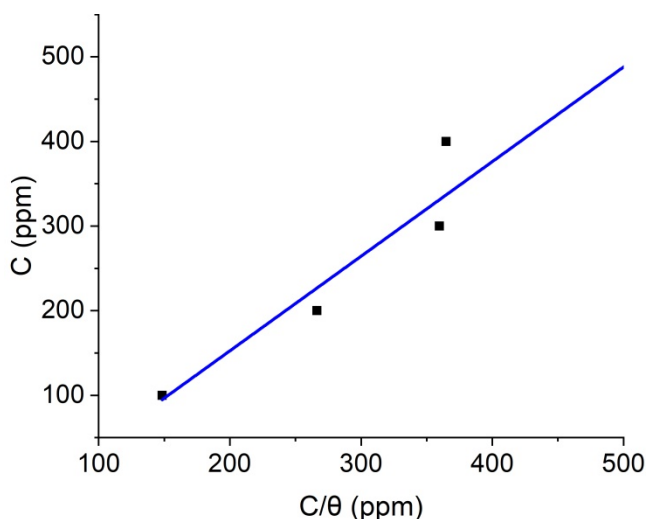


Figure 3. Langmuir isotherm plot for the adsorption of tested inhibitor molecules on the metallic coupon surface in 1 M acidic solution.

4 Conclusions

Based on the experimental findings the resulting conclusion can be expressed.

1. The experimental findings achieved point to the result that EOPT efficiently controls or retards the mild steel corrosion in 1.0 M hydrochloric acid medium.
2. The process of corrosion was controlled by the adsorption of the EOPT molecules on the metallic surface.
3. The inhibitive efficacy of the tested inhibitor increases with the increase of the EOPT concentration.
4. Adsorption of EOPT molecules on the examined metallic surface from 1.0 M hydrochloric acid solution follows the Langmuir isotherms model.

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