The inhibition of mild steel corrosion in 0.5 M H$_2$SO$_4$ solution by N-phenethylhydrazinecarbothioamide (N-PHC)

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Abstract. A new corrosion inhibitor namely N-phenethylhydrazinecarbothioamide (N-PHC) was synthesized through the reaction of hydrazine hydrate and (2-isothiocyanatoethyl)benzene. N-PHC has been characterized by spectroscopically techniques and CHN micro-elemental analysis. The inhibitive activity of N-PHC on mild steel corrosion in 0.5 M sulphuric acid solution was examined by the weight loss techniques. The findings exhibited that the inhibition efficiency increased with an increase in the concentration of N-PHC and decreased with an increase in temperature. The inhibition efficiency reached 94.7% with 250 ppm at 303 K. The inhibitive mechanism involved chemical adsorption and the adsorption of the N-PHC molecules through active sites on the surface of mild steel to control or retard corrosion. The adsorption isotherm obeyed the Langmuir isotherm.

Keyword: phenethylhydrazinecarbothioamide, corrosion, weight loss, N-PHC, Langmuir adsorption isotherm

1. Introduction
Metal corrosion is a global and scientific issue, as it affects the industries in general and chemical and oil processes in particular [1,2]. The considerable applications of corrosive solutions such as sulfuric acid in industries have led to the need to obtain information about the impedance and control on the mild steel corrosion to the attack of corrosive solutions [3-5]. In general, corrosive solutions are utilized in industrial processes such as polishing, cleaning, and pickling. Due to the etching of the acids, inhibitors are used to decrease the metals dissolution rate. Organic compounds which have heteroatoms such as phosphorous, sulfur, oxygen and nitrogen were reported as superior inhibitors [6-10].

Further studying and complement to our previous research [11-16] related to the synthesis of new corrosion inhibitor, in the present study, weight loss techniques were used to examine the inhibition of mild steel corrosion by N-phenethylhydrazinecarbothioamide (N-PHC) (see Figure 1) with respect to concentration of inhibitor, immersion time and temperature on the inhibitory performance in 0.5 M sulfuric acid solution. Another section of the paper. Figure 1, represents the structure of the corrosion inhibitor.
2. Experimental and Materials

2.1. Synthesis of N-PHC

An ethanolic solution of equimolar quantities of (2-isothiocyanatoethyl)benzene and hydrazine hydrate was stirred for 30 minutes at room temperature. The pall solution was then cooled in an ice bath. The filtered and precipitate was cold ethanol and allowed to dry. White powder (yield = 67%). H NMR: δ ppm (DMSO-d6) 2.15 (1H, dd, NH), 2.79 (2H, s, CH2), 3.02 (2H, s, CH2), 7.21 (1H, t, CHaromatic), 7.25 (1H, dd, CHaromatic), 7.3 (1H, dd, CHaromatic). Anal. Calc. for C9H13N3S (%): C, 55.35; H, 6.71; N, 21.52. Found (%): C, 55.65; H, 6.51; N, 21.04.

2.2. Mild steel coupons

Mild steel coupons have the composition (0.210 wt.% carbon, 0.050 wt.% manganese, 0.380 wt.% silicon, 0.010 wt.% aluminum, 0.050 wt.% sulfur, 0.090 wt.% phosphorus, and the remainder was iron. The size for mild steel coupons utilized for the gravimetrical analysis was 4.5 × 2.0 × 0.1 cm³. The mild steel coupons were washed with double distilled water then acetone and dried [17, 18].

2.3. H2SO4 solution

The sulfuric acid solution at the concentration of 0.5 M, was prepared by adding concentrated sulfuric acid to distilled water.

2.4. Weight loss techniques

Weight loss methods of the mild steel coupons were performed at various temperatures (303-333 K) in a 0.5 M H2SO4 solution. The mild steel coupons were immersed in a corrosive solution with different concentrations of N-PHC for various immersion time (1, 5, 10 and 24 h). After exposure time the mild steel coupons were washed, dried, and weighed. The experiments were performed three times and the average was used in the calculations [19,20]. The results of weight loss measurements were used to determined corrosion rate \( C_R \) (g m\(^{-2}\) h\(^{-1}\)) according to equation 1.

\[
C_R = \frac{\Delta W}{s \times t}
\]  

(1)

Where \( \Delta W \) is mild steel coupon weight loss (mg); s, is the area of examined coupon (cm²), t is the exposure time (h).

Surface coverage \( \theta \) and inhibition efficiency \( \eta \) were evaluated [21] using equations 2 and 3.

\[
\theta = \frac{C_{R0} - C_{Ri}}{C_{R0}}
\]  

(2)
\[
\eta = \frac{C_{R0} - C_{Ri}}{C_{R0}} \times 100 \quad (3)
\]

Where \(C_{R0}\) is the corrosion rate without N-PHC, \(C_{Ri}\) is the corrosion in the presence of N-PHC.

3. Results and discussion

3.1. Effect of N-PHC concentration and immersion time- Weight loss measurements

The inhibition efficiency of various concentrations of N-PHC on the corrosion of mild steel coupons in the corrosive environment was studied through gravimetric techniques for different immersion time (1, 5, 10, and 24 h) at 303 K. Figure 2 demonstrates the N-PHC concentration effect on corrosion rates inhibition efficiencies. It is obvious from Figure 2, that the corrosion rate decrease an increase in the concentration of N-PHC. On the other hand, the inhibition efficiency increased with increasing concentration of N-PHC and decreased with increasing immersion time. The inhibition efficiency decreased after exposure for 24 h. The corrosion rate was 2.45 g m\(^{-2}\) h\(^{-1}\), and the inhibition efficiency was 94.7% at the concentration of N-PHC was 250 ppm. The significant efficiency of N-PHC as corrosion inhibitor for the tested mild steel coupons was imputed to the molecular structure of N-PHC which has three nitrogen atoms on one sulphur atom in addition to the aromatic ring. These heteroatoms represent polar sites which represent the adsorption centers [22,23]. The N-PHC adsorbed on the mild steel coupon surface and form a protective film, that reducing the corrosion rate and increasing the inhibition efficiency in the 0.5 M H\(_2\)SO\(_4\).
Figure 2. Corrosion rates and inhibition efficiencies at various concentrations of N-PHC in 0.5 M sulfuric acid environment at 303 K.

3.2. Effect of Temperature and immersion time- Weight loss measurements

Figure 3 shows the corrosion rate and inhibition efficiency of tested coupons with various concentrations of N-PHC in the solution of sulfuric acid at various Temperatures 303–333 K range for 5 h as exposure time. From Figure 3, it is obvious that the inhibition efficiency decreased with increasing temperature, which may be due to the equilibrium adsorption and desorption between the N-PHC molecules and the mild steel surface [24]. When the temperature rise, the equilibrium direction heading to the desorption which means low inhibition efficiency decreased from 94.7% to 63.83% at the maximum used concentration. These findings proposed that the adsorption of N-PHC molecules on the coupon surface may be generally chemical adsorption.
3.3. Adsorption isotherm and thermodynamic calculations

N-PHC molecules control the corrosion of mild steel coupon surface through adsorption at the mild steel coupon/acidic environment interface, while the significant interaction parameters between N-PHC molecules and the mild steel coupon surface can be evaluated from the adsorption isotherm.

Langmuir adsorption isotherm, determine the relationship of surface coverage ($\theta$) and N-PHC concentration (C) through equation 4.

$$ \frac{C}{\theta} = \frac{1}{K_{ads}} + C $$

(4)

where C: is the N-PHC concentration, $K_{ads}$ is the equilibrium constant between adsorption–desorption.

From Figure 4, the correlation coefficient of this plot was near to 1, which indicates that the adsorption of N-PHC molecules on the coupon surface in acidic environment obeys the Langmuir adsorption isotherm.
Figure 4. Langmuir adsorption isotherm plots for the investigated coupons at 303 and 333 K.

Conclusion

Organic compound namely N-phenethylhydrazinecarbothioamide (N-PHC) was successfully synthesized and fully characterized; it was acted as a significant corrosion inhibitor for mild steel in 0.5 M H₂SO₄ environment. Inhibitive performance evaluated from weight loss techniques. The adsorption of the N-PHC of mild steel coupons in 0.5 M H₂SO₄ follow the Langmuir adsorption isotherm and the molecules form a protective film on coupon surface.

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