New Aminocoumain as Corrosion Inhibitor

Yasameen K. Al-Majedy
Department of Applied Science, Branch of Chemistry, University of Technology (UOT), Baghdad-Iraq.
Corresponding author: yasmin.chem79@gmail.com.

Abstract
New green organic molecules as corrosion inhibitor namely, 2-amino-4-(4-nitrophenyl)-3-cyano-4, 5-dihydropyrano (3,2-c) coumarin (AND) was synthesized starting from 4-hydroxycoumarin, malonitraile and 4-nitrobenzaldehyde and tested on mild steel (MS) in 1 M HCl media by a weight loss method and identification of the surface technique employee scanning/electron/microscope (SEM) studies. The AND as an inhibitor compound have been elucidate spectroscopically (FT-IR, 1HNMR and 13CNMR) The weight loss investigation demonstrated that inhibition performances have been improved via concentration raising of inhibitor. To support our results scanning electron microscopy was employed to clarify the surface of the MS with and without AND in 1.0 M HCl media. The inhibition performance rate was 96% at the maximum utilized concentration of AND. [DOI: 10.22401/JNUS.21.2.08]

Keywords: 4-hydroxycoumarin; 4-nitrobenzaldehyde; malonitraile; SEM.

1. Introduction
Mild steel has been utilized as some auxiliary materials for reactors of vessels, tanks, and pipeline, so forth that were known to consume perpetually in contact with different solutions. From the view purpose of country's economy and monetary ramifications of consumption peril, it is important to embrace fitting means and approaches to decrease the misfortunes because of erosion. In acidic/basic fluid conditions, its corrosion and counteractive action are all around considered, however in non-aqueous solvents restricted reports are accessible [1-4]. The inhibitory activity practiced by organic compounds on disintegration of materials species are typically identified with adsorption cooperation among inhibitors and surface of MS [5-7]. The planarity (p) and lone pairs of electrons present on N, and O atoms are important structural features that control the adsorption of these molecules onto the surface of the metal. The reason for this work was to confirm the already settled outcomes on the consumption restraint impact of heterocyclic compound on mild steel in acidic media [8-9]. Numerous specialists have revealed that the restraint impact depends for the most part on many physic/chemical with electronic characteristics of the natural inhibitors identified with functional groups, steric/impacts, electronic thickness of contributor iotas and orbital significant for electrons giver [10-12]. We focused on the synthesis of new heterocyclic compound as novel natural consumption inhibitor. We report the amalgamation of AND, and concoction structure illustration utilizing spectroscopic strategies (i.e., IR and NMR). Late investigations have demonstrated that natural compound containing polar functional groups are very productive in limiting the impact of erosion not withstanding heterocyclic compound having polar gatherings and π-electrons. The atomic outline of the AND particle is comprises of NH$_2$, NO$_2$, keto and π-electrons, which could successfully contributes toward reducing of MS consumption in HCl solution. Suggested structure for combined consumption inhibitor is appeared in Fig.(1).
2. Experimental

2.1 Synthesis and elucidation of AND

The inhibitor AND has been prepared through the reaction of benzaldehyde (2.5 mmol), malononitrile (3.75 mmol), and 10 mL of water. The reaction mixture has been stirred. TBAB (tetrabutyl ammonium bromide 10 mol %) have been adding to reaction media stirring and 4-hydroxycoumarin (2.5 mmol) was added. For 3 hrs. the solution has been reflux and the disappearance of reactants was figured according to TLC technique. the mixture left to cool at 25°C then filtered and crystallized with ethanolic alcohol (hot) to get the target compound [13], yield 75%, M.P (212-214°C).

2.2 Gravimetric Approaches

2.2.1 MS specimens.

MS specimens got by the Metal Samples Company were employed all through this investigation. The composition (wt %) of the mild steel was as follows: Fe, 99.21; C, 0.21; 0.38; 0.09; 0.05; 0.05; and 0.01 for Fe, Si, P, S, Mn, Al respectively. The measurements were conducted in aerated, non-stirred 1.0 M HCl solutions containing different concentrations of AND compound.

2.2.2 Technique of Weight Loss

Copouns in duplicate were suspended in 200 mL of the examine media, with & without the AND corrosion Inhibitor of different concentration (0×10⁻² mM, 5×10⁻² mM, 10×10⁻² mM, 15×10⁻² mM, 20×10⁻² mM, 25×10⁻² mM and 50×10⁻² mM), for 1, 2, 3, 4, 5, 10, 24, 48 and 72 hrs. at room temperature, [14] Specimens weights for before/after immersed was computed. Inhibition efficiency of the mild steel was determined using the average of the duplicate value using the equation:

\[
\text{Inhibition Efficiency (IE %)} = \left(1 - \frac{W_2}{W_1}\right) \times 100
\]

Where, \(W_1\) and \(W_2\) are weight loss of MS without and with the AND.

3. Results and Discussion

3.1 Identification of AND

The investigated compound of coumarin derivative have been proved regarding to spectroscopically techniques namely FTIR and NMR. According to spectrum of the FTIR the inhibitor demonstrated the bands at 2195.1 cm⁻¹ for C≡N and 3482.0-3429.8 cm⁻¹ for NH₂, 1605-1594.7 cm⁻¹ for N-N str. 1430 cm⁻¹ for C-N str., 1717 cm⁻¹ for C=O str. and 1370-1456 cm⁻¹ for C-O str.
Fig.(2): FTIR spectra of AND.

Fig.(3): $^1$HNMR spectrum of AND.

Fig.(4): $^{13}$C NMR spectrum of AND.
$^{1}H$-NMR (CDCl$_3$): refers to the presence of (s, NH$_2$ group) at δ 8.49 ppm. The compound showed prominent singlet at δ 8.14, s, 1H and 4.25, s, 1H for (CH) groups and (δ 7.4-7.75),m,4H for aromatic ring. $^{13}C$-NMR (CDCl$_3$): 166.9, 162.4, 152.3, 144.3, 125.4, 127.9, 129.1, 115.2, 114.6, 60.5, 35.9. Regarding to FTIR, $^{1}HNMR$ with $^{13}C$NMR spectra, the results confirm the structure of AND.

3.2 Technique of Weight Loss
3.2.1. Concentration Effect
The inhibition efficiency (IE) esteems computed from weight reduction estimations for MS in the corrosive mixture that contain different concentrations of AND at encompassing temperature are appeared in Fig.(5), that the AND diminished the corrosion of MS in corrosive media especially. The IE% expanded with a rise in concentration of AND [15] and reached maximum IE at 50x10$^{-2}$ mM concentration of AND. The raising in IE% with raise in concentrations were prompsed of the raise in the extent of performance of AND protection. The inhibition efficiency of inhibitor for the corrosion of steel was obtained by using the following equation:

$$IE(%) = 1 - \frac{W_{corr}}{W^{\circ}corr}$$

$W_{corr}$ and $W^{\circ}corr$ are the corrosion rate of steel samples with and without the inhibitor, respectively.

**Fig.(5): Different concentrations of AND vis different immersion periods time for Inhibition Efficiency (IE %) of mild steel.**

3.3. Scanning Electron Microscopy (SEM) Analysis
SEM instrument examine is done at the UKM Electron Microscopy Unit. SEM analysis was performed to investigate the surface morphology of the mild steel after immersion in 1.0 M HCl in the absence and the presence of AND, Fig.(6) Damaged surface was observed in the absence of AND due to high dissolution rate of iron at such pH however a thin and uniform layer on the metal surface is observed in the presence of AND, the cracks in the film is due to the dehydration of surface since the surface was dried prior the SEM imaging. This is evidence that AND can be absorbed on the mild steel surface and insulates the surface from the acidic medium [16].
4. Conclusions

Results of this investigations revealed that the prepared coumarin derivative namely AND worked as an excellent corrosion inhibitor in corrosive media for surface MS in solution of HCl with concentration subordinate mode. Inhibition performance of AND as an inhibitor most extreme hindrance proficiency was up to 96% at 0.5 mM AND concentration. AND is shows as a productive natural inhibitor having great inhibitive characteristics because of quality of atoms namely nitrogen with oxygen. SEM estimations bolstered development of a defensive layers through AND on the MS surface. The anti-corrosion investigation for AND showed the protection of surface of MS in corrosive solution.

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