Electrochemical study of the corrosion inhibition effect of 3-cyanophenyl compound on 420 martensitic stainless steel in strong acid media

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Abstract. The corrosion inhibition performance of 3-cyanophenyl organic compound on heat treated 420 martensitic stainless steel in 6 M H₂SO₄ was evaluated through potentiodynamic polarization test, ATR-FTIR spectroscopy and adsorption isotherm studies. Results obtained proves the compound to be effective with highest inhibition performance value of 99.4%. The inhibition property was determined to be mixed type inhibition with significant anodic inhibition tendencies. Adsorption of the compound onto the steel was through chemisorption mechanism in agreement with the Langmuir and Freundlich isotherms models at correlation coefficients of 1 and 0.7570. The transmittance of detected functional groups of 3-cyanophenyl diminished at distensible wavelengths because of excellent surface coverage and adsorption of the compound onto the steel.

1. Introduction
Stainless steels are metallic alloys with high corrosion resistance in comparison to carbon steels due to varying weight content of chromium, nickel etc. alloyed with the iron substrate metal. 420 martensitic steel, an alteration of 410 steel, has slightly greater volumetric composition of carbon which enhances the hardness, strength and wear resistance of the steel. They basically derive their corrosion resistance from the presence of a passive protective film formed on their surfaces. Destruction of the film leads to localized corrosion deterioration and failures. Acids are extensively applied in numerous industrial technological processes leading to corrosion. Corrosion is a major problem in the petrochemical industries resulting in high maintenance cost [1-2]. Research on 420 steel concludes the overwhelming effect quenching on their corrosion resistance by as much as 60% [3]. Further increase in the versatility and application of 420 steels requires the use of chemical compounds (inhibitors) capable of inhibiting its corrosion in corrosive environments. Most corrosion inhibitors act through adsorption, retarding the cathodic, anodic or both electrochemical corrosion reactions. Most promising inhibitors are organic compounds that contain heteroatoms which chemically adsorbed onto metallic surfaces [4, 5]. Research on organic derivatives of 3-cyanophenyl has proven their corrosion inhibition effectiveness however in low molar concentrations of acid media [6-8]. This research evaluates the corrosion inhibiting action of 3-cyanophenyl on 420 martensitic stainless in 6M H₂SO₄ acid solution.

2. Material and methods
420 stainless steel (420SS) procured from the open market has the following percentage content of alloying elements after analysis; shown in Table 1. The steel samples are of cylindrical dimension with an unconcealed area of 0.79 cm² after embedding in resin mounts. 420SS samples were cut and sectioned before being abraded with silicon carbide papers (80, 320, 600, 800 and 1000 grits). They
were washed with distilled water and acetone for electrochemical tests. 420SS samples were heat heated in a muffle furnace to 1000°C before quenching in distilled water. The furnace temperature was controlled at an accuracy ± 10°C coupled with thermocouple (K-Type). 3-cyanophenyl (3CL) shown in Fig. 1 was procured from BOC Sciences, USA is achromatic organic liquid with a sweet almond odour. It has a density of 103.12 g/mol and a chemical formula of C7H5N. 3CL was prepared in quantitative concentrations of 9.25 x 10^3, 1.85 x 10^2, 2.77 x 10^2, 3.70 x 10^2 and 4.62 x 10^2 in 400mL of 6 M H2SO4 acid prepared from standard grade (98% purity) with distilled water. Electrochemical evaluation through polarization was performed out at 34°C with a triple electrode cell system, consisting of 200 mL of the electrolyte and 420SS electrodes connected to Digi-Ivy 2311 potentiostat. Graphical plots were produced at a scan rate of 0.0015 V/s from -1.5 V and +1.5 V. The acid inhibitor solution, before and after polarization tests were subjected to infrared ray beams using Bruker Alpha FTIR spectrometer from 375 to 7500 cm^-1 wavelength and 0.9 cm^-1 resolution. Graphical plots of ATF-FTIR absorption including of spectra peaks were evaluated and correlated with theoretical ATF-FTIR absorption Table for identification of functional groups involved in the corrosion inhibition of 420SS.

### Table 1. Percentage content of alloying elements in 420SS

| Element | C  | Mn | P  | S  | Si | Cr | Ni | Mb | N  | Fe |
|---------|----|----|----|----|----|----|----|----|----|----|
| % Composition | 0.28 | 0.8 | 0.04 | 0.02 | 0.8 | 14 | 0.4 | -  | -  | 79.15 |

![benzonitrile](image)

**Figure 1.** Molecular structure of benzonitrile

### 3. Results and discussion

#### 3.1 Potentiodynamic polarization studies

The results of the polarization test are given in Table 2. 420SS at 0% 3CL concentration exhibited a corrosion rate value of 3.30 mm/y, analogous to corrosion current density of 3.04 x 10^-4 Acm^-2. This value is significantly higher than the corrosion rates of 420SS at 0.13% - 0.63% 3CL due to the activity of SO_4^{2-} ions in the aqueous media. The strong ionization potential of 6M H2SO4 in H2O at 0% 3CL causes the release two protons which aggressively reacts with and deteriorates 420SS surface. This also shows 3CL alters the mechanism of electrochemical reactions responsible for 420SS corrosion through adsorption, surface coverage, and suppression of the reduction reactions. Addition of 3CL (0.13% - 0.63% 3CL) to the acid solution significantly altered the corrosion resistance properties of 420SS as shown from the changes in corrosion potential values from -0.306 V at 0% 3CL to -0.274 V at 0.13% 3CL due to anodic inhibition through surface coverage and precipitation of 3CL on reactive sites on the steel surface. The visible change in anodic Tafel slope values after 0% 3CL is due to changes in the electrode substrate, rate controlling step and influence of potential controlled conditions. This is consistent with the earlier observation of the corrosion potential values. The maximum change in corrosion potential with respect to the value at 0% 3CL is less than 85 mV as a result 3CL is a mixed type inhibitor with dominant anodic inhibiting properties.
Table 2. Results of 420SS potentiodynamic polarization behaviour in 6 M \( \text{H}_2\text{SO}_4 \) solution at 0% - 0.63% 3CL concentration

| Sample | 3CL Conc. (%) | 3CL Conc. (M) | 420SS Corrosion Rate (mm/y) | 3CL Inhibition Efficiency (%) | Corrosion Current (A) | Corrosion Current Density (A/cm²) | Corrosion Potential (V) | Polarization Resistance, \( R_p \) (Ω) | Cathodic Tafel Slope, \( B_c \) (V/dec) | Anodic Tafel Slope, \( B_a \) (V/dec) |
|--------|---------------|---------------|----------------------------|-------------------------------|----------------------|-------------------------------|------------------------|--------------------------|-------------------------------|-------------------------------|
| A      | 0             | 0             | 0                          | 2.40E-04                      | -0.316              | 107.10                        | -10.30                 | 8.06                     |                               |                               |
| B      | 0.13          | 0.5E-03       | 0.19                       | 9.94                         | 1.31E-05             | 1.71E-05                     | 9.22                   | 90.97                    |                               |                               |
| C      | 0.23          | 1.8E-02       | 0.19                       | 9.39                         | 1.74E-05             | 9.27                         | 107.00                 | 9.97                     |                               |                               |
| D      | 0.38          | 2.77E-02      | 0.21                       | 9.73                         | 1.57E-05             | 9.28                         | 107.00                 | 9.97                     |                               |                               |
| E      | 0.50          | 3.70E-02      | 0.33                       | 9.83                         | 2.40E-05             | 9.35                         | 107.00                 | 9.97                     |                               |                               |
| F      | 0.63          | 4.62E-02      | 0.22                       | 9.99                         | 2.02E-05             | 9.48                         | 121.00                 | 9.68                     |                               |                               |

3.2 Mechanism of Inhibition

3CL consist of a 5-membered 1, 3-thiazole ring fused to a benzene ring. The presence of heteroatoms of N and S, and π-electrons on the thiazole rings of 3CL strongly influences its adsorption and mode of interaction with 420SS surface, and the resulting formation of metallic complexes. The lone pair of electrons in the heteroatoms within 3CL molecules facilitates transfer of electrons from 3CL to the metal. The S atom enables the formation of dπ-dπ bond resulting from the overlapping of 3d-electrons, while the double bonds in 3CL molecule reverse release of metal d-electron to the π-orbital.

The wide variation in corrosion rate values of 420SS before and after 3CL inhibition shows that 420SS strongly oxidizes in 6M \( \text{H}_2\text{SO}_4 \) solution releasing metallic cations. This behaviour results in vacant ‘d’ orbital of the iron substrate metal leading to the formation of co-ordination bond between Fe–N–S, hence adsorption. Electrostatic attraction occurs between 3CL inhibitor and 420SS; the positively charged 420SS surface electrostatically attracts \( \text{SO}_4^{2-} \) ions, which preadsorbed onto steel surface. The excess negative charge draws cationic 3CL molecules forming a protective \( (\text{FeSO}_4^{2-}\cdot3\text{CL-H})_{\text{ad}} \) layer. 3CL cations are also attracted to cathodic sites on 420SS surface, competing with H ions for reduction, hence stifling the hydrogen evolution reaction.

3.3 AT-FTRIR Spectroscopy analysis

Functional groups within 3CL molecules i.e. atoms and bonds responsible for electrostatic attraction, molecular adsorption and invariably corrosion inhibition of 420SS surface were identified by AT-FTRIR spectroscopy and correlated with the ATR-FTRIR Theoretical Table [9, 10]. Fig. 2 shows the spectra plots of the 6 M \( \text{H}_2\text{SO}_4/3\text{CL} \) solutions before and after 420SS corrosion. The transmittance of the spectra plot of 6 M \( \text{H}_2\text{SO}_4/3\text{CL} \) before corrosion decreased significantly after the corrosion test by comparison with the transmittance of the spectra plot of 6 M \( \text{H}_2\text{SO}_4/3\text{CL} \) after corrosion at wavelengths between of 526 - 673 cm\(^{-1}\), 826 - 1030 cm\(^{-1}\), 1360 - 1433 cm\(^{-1}\), 1529 - 1597 cm\(^{-1}\), 1776 - 2822 cm\(^{-1}\) and 3004 - 3489 cm\(^{-1}\) due to corrosion inhibition resulting from adsorption of specific 3CL functional groups. The identified moieties are alkynes, aromatics, primary, secondary amines, carboxylic acids, alkenes, alkanes, nitro compounds, aldehydes, alkynes (terminal), amides and alcohols, phenols which all consists of bonds such as –C(triple bond)C–H: C–H "oop", N–H wag, O–H bend, =C–H bend, C–H rock, C–C stretch (in–ring), N–O asymmetric stretch, N–H bend, H–C=O: C–H stretch, =C–H stretch, C–H stretch, –C(triple bond)C–H: C–H stretch, N–H stretch, O–H stretch and H–bonded. The decrease in transmittance at the specific wavelength range confirmed the surface coverage effect and adsorption of 3CL compound on 420SS resulting on MCS surface.
3.4 Adsorption Isotherm

3CL adsorption on 420SS surface was further determined and studied through adsorption models. Studies show 3CL agrees with the Langmuir and Freundlich isotherm at correlation coefficients of 1 and 0.7570 respectively. Langmuir isotherm plot of $\frac{C_{BEZT}}{\theta}$ versus $C_{3CL}$ [Fig. 3(a)], calculated from equation 1 assumes that; (i) The molecular interactions at the metal- solution interface is constant, (ii) Gibbs free energy results (equation 3) is non-dependent on the extent of molecular protection and (iii) The effect of interaction of adsorbates on the value of Gibbs free energy is negligible [11]. The Frumkin plot of $\log \frac{\theta}{1-\theta}$ versus $\theta$ [Fig. 3(b)], determined from equation 2 proposes complete adsorbate covering at peak 3CL concentrations for a non-disparate alloy surface coupled with negligible effect of lateral interaction.

$$\theta = \frac{K_{ads}C_{3CL}}{1 + K_{ads}C_{3CL}}$$

(1)

$$\log [C_{3CL} * (\frac{\theta}{1 - \theta})] = 2.303 \log K_{ads} + 2a\theta$$

(2)

3.5 Thermodynamics of the corrosion inhibition

Data for Gibbs free energy ($\Delta G_{ads}$) for the molecular interaction are shown in Table 3 and were calculated from the mathematical relationship below.

$$\Delta G_{ads} = - 2.303RT \log [55.5K_{ads}]$$

(3)
55.5 is a constant for standard water concentration in the acid media, \( R \) represents the universal gas constant, \( T \) stands for the absolute temperature and \( K_{\text{ads}} \) is the equilibrium constant of adsorption. \( K_{\text{ads}} \) is related to surface coverage (\( \theta \)) from the Langmuir equation (equation 1). The surface properties and non-homogeneous nature of 420SS strongly influences the \( \Delta G_{\text{ads}} \) values of 3CL adsorption with respect to the extent of 3CL coverage value. Negative values of \( \Delta G_{\text{ads}} \) signifies the spontaneous behaviour of the adsorption species on the metal surface. The highest \( \Delta G_{\text{ads}} \) value obtained for 3CL adsorption on 420SS is -42.22 KJmol\(^{-1}\) at 2.5% 3CL, while the lowest value in both acids are -38.89 KJmol\(^{-1}\) at 1.5% 3CL and -41.53 KJmol\(^{-1}\) at 6.5% 3CL. This observation is consistent with chemisorption adsorption mechanism [12, 13].

### Table 3. Result for Gibbs free energy (\( \Delta G_{\text{ads}} \)), surface coverage (\( \theta \)) and equilibrium constant of adsorption (\( K_{\text{ads}} \)) for 3CL adsorption on 420SS in 6M H\(_2\)SO\(_4\)

| 420SS Samples | 3CL Concentration (M) | Surface Coverage (\( \theta \)) | Equilibrium Constant of adsorption (\( K_{\text{ads}} \)) | Gibbs Free Energy, \( \Delta G_{\text{ads}} \) (KJmol\(^{-1}\)) |
|---------------|-----------------------|-------------------------------|---------------------------------------------|---------------------------------------------|
| A             | 0                     | 0                             | 0                                           | 0                                           |
| B             | 9.25E-03              | 0.994                         | 17838.8                                    | -34.21                                      |
| C             | 1.85E-02              | 0.994                         | 8768.9                                     | -32.45                                      |
| D             | 2.77E-02              | 0.993                         | 5276.3                                     | -31.19                                      |
| E             | 3.70E-02              | 0.989                         | 2498.3                                     | -29.34                                      |
| F             | 4.62E-02              | 0.993                         | 3013.8                                     | -29.80                                      |

### 4. Conclusion

3-cyanophenyl compound effectively suppressed the degradation and surface deterioration of 420 martensitic steel in 6M H\(_2\)SO\(_4\) solution. The compound acted through surface coverage and chemisorption adsorption molecular interaction with respect to the Langmuir and Freundlich isotherm model. The inhibition property of 3-cyanophenyl was calculated to be mixed type with dominant anodic inhibition effect.

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