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Electrochemical effect of 1, 4-diaminobenzene on the corrosion inhibition of mild steel in dilute acid media

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ABSTRACT

1,4-Diaminobenzene was studied for its electrochemical influence on the corrosion behaviour of mild steel in dilute H_2SO_4 and HCl acid at ambient temperature with the application of weight loss technique, open circuit potential measurement and potentiodynamic polarization test. Results show the inhibition efficiency of the organic derivative varied with concentration with maximum inhibition efficiency of 70% and 78.2% at 0.093M inhibitor concentration in H_2SO_4 acid and a maximum inhibition efficiency of 81.1% and 94.3% at 0.069M inhibitor concentration in HCl acid from weight loss and polarization tests proving to be more effective in HCl. Potential measurement results varied, with passivity potentials being maintained at specific concentrations. SEM observations showed a significant morphological appearance with contrasts micrographs from uninhibited samples. X-ray diffractometry confirmed the absence of reaction products and phase complexes associated with corrosion. Statistical analysis showed relevance and statistical significance of concentration and exposure time on the inhibition performance of 1, 4-diaminobenzene.

Keywords: corrosion; diaminobenzene; steel; inhibition; acid; sulphuric; hydrochloric

INTRODUCTION

Corrosion of mild steels in aqueous environments is a worldwide engineering problem ranging from corrosion of steel structures in oil production and refining processes to metal extraction, chemical processing plants, marine applications, the automobile industries etc. as it is the preferred material of construction due to its low cost and easy availability. The corrosion phenomenon that takes place on mild steel is complex and miscellaneous due to differential anodic and cathodic surface reaction sites on the steel surface. Use of chemical compounds known as inhibitors is one of the most economical techniques for mitigation against mild steel corrosion. The inhibitors interact with reactive sites, influencing the electrochemical reactions or obstructing the electrolytic transport of corrosive ions from the solution to the metal/solution interface [1]. A significant number of high performance inhibitors applied in industry are of organic origin consisting mainly of oxygen, sulfur, nitrogen atoms, and multiple bonds in their molecules that facilitate adsorption on the metal surface [2-6]. Their corrosion inhibition efficiency is directly related to their adsorption characteristics due to the presence of valence electrons, heteroatoms and the degree of solubility and dispersion [7, 8]. These enhance greater adsorption of the inhibitor molecules onto the surface of the steel. Notable work has been done on the use of organic molecules for corrosion inhibition of metals

in interaction with aggressive aqueous solutions [9-16]. To further establish and encourage the use of organic inhibiting compound for corrosion control due to their ecological advantages this research aims to assess the electrochemical behaviour of 1,4-diaminobenzene (PPD) an aromatic amine derivative on the corrosion inhibition of mild steel in dilute sulphuric and hydrochloric acid. PPD is used as a precursor to aramid plastics and fibers such as kevlar. It is easily oxidized thus it is used as antiozonants in the productions of rubber products. The aquatic LD₅₀ of PPD is 0.028 mg/L, its exposure in the diet of rats and mice showed no clinical signs of toxicity [17-19]. The Log P value of PPD is -0.3 [20]. It is used as a common hair dye. The carcinogenicity of 1,4-diaminobenzene to humans has established as not classifiable [21, 22]

MATERIALS AND METHODS

Material

The mild steel used for this work was obtained from Steel Works, Owode, Nigeria and analyzed at the Applied Microscopy and Triboelectrochemical Research Laboratory, Department of Chemical and Metallurgical Engineering, Tshwane University of Technology, South Africa. The mild steel has the nominal per cent (%) composition: 0.401% C, 0.169% Si, 0.440% Mn, 0.005% P, 0.012% S, 0.080% Cu, 0.008% Ni, 0.025% Al, and the rest being Fe.

Inhibitor

1, 4-diaminobenzene (PPD, *p*-phenylenediamine as a common name) a whitish pink solid granules is the compound used for corrosion inhibition. The molecular formula is C₆H₄(NH₂)₂, while the molar mass is 108.1 g mol⁻¹. The chemical structure of PPD is shown in Fig. 1.

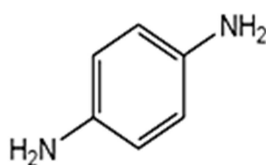


Figure 1 Chemical structure of 1, 4-diaminobenzene (PPD)

PPD was prepared in molar concentrations of 0.023M, 0.045M, 0.069M, 0.093M, 0.116M and 0.139M per 200 ml of the acid media respectively.

Test Media

0.5 M sulfuric acid and 0.5 M hydrochloric acid with 3.5% recrystallized sodium chloride of Analar grade were used as the corrosion test media.

Preparation of Test Specimens

A cylindrical mild steel rod with a diameter of 14.5 mm was carefully machined and cut into a number of test specimens of average dimensions in length of 6 mm. A 3 mm hole was drilled at the centre for suspension. The steel specimens were then thoroughly rinsed with distilled water and cleansed with acetone for weight loss analysis. The potentiodynamic polarization technique involved grinding the two surface ends of each specimen with silicon carbide abrasive papers of 80, 120, 220, 800 and 1000 grits before being polished with 6.0 μm to 1.0 μm diamond paste, washed with distilled water, rinsed with acetone, dried and stored in a desiccator before the test.

Weight-loss Experiments

Weighted test species were fully and separately immersed in 200 ml of the test media at specific concentrations of the PPD for 360 h at ambient temperature of 25°C. Each of the test specimens was taken out every 72 h, washed with distilled water, rinsed with acetone, dried and re-weighed. Plots of weight-loss (mg) and corrosion rate (mm/y) versus exposure time (h) (Figs. 2, 3, 6 & 7) for the two test media and those of percentage inhibition efficiency (%IE) (calculated) versus exposure time (h) and percentage PPD concentration (Fig. 4, 5, 8 & 9) were made from Tables 1 & 2.

The corrosion rate (*R*) calculation is from this equation 1:

$$R = \left[\frac{87.6W}{DAT} \right] \quad (1)$$

Where W is the weight loss in milligrams, D is the density in g/cm^3 , A is the area in cm^2 , and T is the time of exposure in h. The %IE was calculated from the relationship in equation 2.

$$\%IE = \left[\frac{W_1 - W_2}{W_1} \right] \times 100 \quad (2)$$

W_1 and W_2 are the corrosion rates in the absence and presence of predetermined concentrations of PPD. The %IE was calculated for all the inhibitors every 72 h during the course of the experiment, while the surface coverage is calculated from the relationship:

$$\theta = \left[1 - \frac{W_2}{W_1} \right] \quad (3)$$

Where θ is the substance amount of adsorbate adsorbed per gram (or kg) of the adsorbent. W_1 and W_2 are the weight loss of mild steel coupon in free and inhibited acid chloride solutions respectively.

Open Circuit Potential Measurement (OCP)

A two-electrode electrochemical cell with a silver/silver chloride was used as reference electrode. The measurements of the OCP were obtained with Autolab PGSTAT 30 ECO CHIMIE potentiostat. Resin mounted test electrodes/specimens with exposed surface of 165 mm^2 were fully and separately immersed in 200 ml of the test media (acid chloride) at specific concentrations of PPD for a total of 288 hours. The potential of each of the test electrodes was measured every 48 hours. Plots of potential (mV) versus immersion time (h) (Fig. 10 & 11) for the two test media were made from the tabulated values in Table 3 & 4.

Potentiodynamic Polarization

Potentiodynamic polarization measurements were carried out using, a cylindrical coupon embedded in resin plastic mounts with exposed surface of 165 mm^2 . The electrode was polished with different grades of silicon carbide paper, polished to $6 \mu\text{m}$, rinsed by distilled water and dried with acetone. The studies were performed at ambient temperature with Autolab PGSTAT 30 ECO CHIMIE potentiostat and electrode cell containing 200 ml of electrolyte, with and without the inhibitor. A graphite rod was used as the auxiliary electrode and silver chloride electrode (SCE) was used as the reference electrode. The potentiodynamic studies were then made from -1.5V *versus* OCP to +1.5 V *versus* OCP at a scan rate of 0.00166 V/s and the corrosion currents were registered. The corrosion current (i_{cr}), corrosion current density (I_{cr}) and corrosion potential (E_{cr}) were determined from the Tafel plots of potential *versus* $\log I$. The corrosion rate (R), the degree of surface coverage (θ) and the percentage inhibition efficiency (%IE) were calculated as follows

$$R = \frac{0.00327 \times j_{cr} \times E_q}{D} \quad (4)$$

Where j_{cr} is the current density in $\mu\text{A/cm}^2$, D is the density in g/cm^3 ; E_q is the specimen equivalent weight in grams. The percentage inhibition efficiency (%IE) was calculated from corrosion rate values using the equation.

$$\%IE = 1 - \frac{R_2}{R_1} \times 100 \quad (5)$$

R_1 and R_2 are the corrosion rates in absence and presence of PPD respectively.

Scanning Electron Microscopy Characterization

The surface morphology of the uninhibited and inhibited steel specimens were investigated after weight-loss analysis in 0.5 M H_2SO_4 and 0.5 M HCl solutions using Jeol JSM - 7600F UHR Analytical FEG SEM, a state-of-the-art Ultra-High Resolution Analytical Thermal Field Emission Gun Scanning Electron Microscope which successfully combines ultra-high resolution imaging with optimized analytical functionality. SEM micrographs images were taken and recorded.

X-Ray Diffraction Analysis

X-ray diffraction (XRD) patterns of the film formed on the metal surface with and without PPD addition were analyzed using a Bruker AXS D2 phaser desktop powder diffractometer with monochromatic Cu-K α radiation produced at 30 kV and 10 mA, with a step size of 0.03° 2 θ . The measurement program is the general scan xcelerator.

Statistical Analysis

Two-factor single level statistical analysis using ANOVA test (*F*-test) was performed so as to investigate the significant effect of inhibitor concentration and exposure time on the inhibition efficiency values of the PPD in the acid media.

RESULTS AND DISCUSSION**Weight-loss measurements**

Weight-loss of the steel at various time intervals, in the absence and presence of PPD concentrations in 0.5 M H₂SO₄ and 0.5 M HCl acid at 25°C was studied. The values of weight-loss (*W*), corrosion rate (*R*) and the percentage inhibition efficiency (%*IE*) are presented in Table 1 & 2. Fig. 2, 3, 4, 6, 7 & 8 shows the variation of weight-loss, corrosion rate and percentage inhibition efficiency versus exposure time at specific PPD concentration while Fig. 5 & 9 shows the variation of %*IE* with inhibitor concentration. In Fig. 5 there is a progressive increase in %*IE* values from 0.023M PPD till 0.093M PPD, after which the %*IE* decline sharply due to desorption and lateral repulsion of the inhibitor molecules from the steel surface. The inhibitor is unable to form a compact protective barrier necessary for inhibition but simply dissipates into the solution. At 0.023M PPD the %*IE* is far below acceptable minimal performance for inhibitors. The effectiveness of PPD in this solution is significant between (0.046M – 0.093M) with a maximum %*IE* of 70% at 0.093M PPD. The %*IE* values in Fig.6 showed a compound whose inhibition efficiency performance is well above average at 0.069M PPD (81%), before and after which there is a progressive increase and decline of %*IE* values far below the minimal acceptable value for effective inhibition. This shows PPD to be specific in action; its %*IE* is highly dependent on its concentration

The mode of inhibition is by adsorption to the steel surface, due to the formation of a compact protective barrier through electrostatic attraction and the cationic charge of the protonated PPD molecule in solution which seems to affect the cathodic sites of the specimen and also the anodic sites by virtue of donation of the electron-pair on the nitrogen atom of the unprotonated molecule [23]. The presence of PPD in acidic solution inhibits the hydrogen evolution, oxygen reduction and the anodic dissolution processes. This is understood to be mixed inhibition reaction and control over the redox process. The strong adherence of PPD on the steel is due to donor acceptor interactions between the pi-electrons of the nitrogen atoms and the vacant d-orbital of steel surface atoms, or interaction of PPD with already adsorbed corrosive ions [24]. The inhibiting efficiency of PPD as shown in the figures is the relative reduction in corrosion rate which is quantitatively related to the amount of adsorbed PPD on the metal surface. Corrosion reactions are inhibited from occurring over the active sites of the metal surface covered by PPD molecules, whereas the corrosion reaction occurs normally on the surface at inhibitors free area.

Table 1 Data obtained from weight loss measurements for mild steel in 0.5 M H₂SO₄ in presence of specific concentrations of the PPD at 432 h

Sample	Inhibitor Concentration (%)	Weight Loss (mg)	Corrosion Rate (mm/y)	Inhibition Efficiency (%)
A	0	1.863	10.527	0
B	0.25	1.73	10.1436	7.1
C	0.5	0.657	3.8479	64.7
D	0.75	0.609	3.106	67.3
E	1	0.559	2.8799	70.0
F	1.25	2.13	11.8387	-14.3
G	1.5	1.927	10.9834	-3.4

Table 2 Data obtained from weight loss measurements for mild steel in 0.5 M HCl in presence of specific concentrations of the PPD at 432 h

Sample	Inhibitor Concentration (%)	Weight Loss (mg)	Corrosion Rate (mm/y)	Inhibition Efficiency (%)
A	0	2.146	14.751	0
B	0.25	1.167	7.32	37.7
C	0.5	0.362	1.89	81.1
D	0.75	1.851	8.84	18.2
E	1	0.952	6.29	43.6
F	1.25	1.086	7.23	40.0
G	1.5	1.198	7.9976	35.3

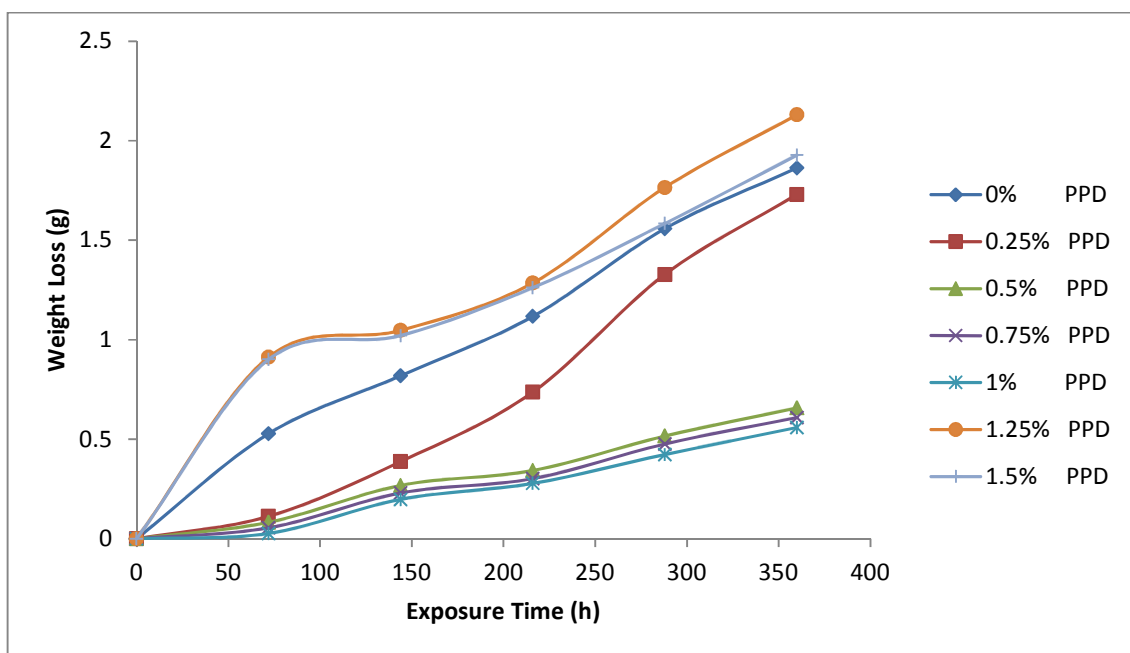


Figure 2 Variation of weight-loss with exposure time for samples (A – G) in 0.5 M H₂SO₄

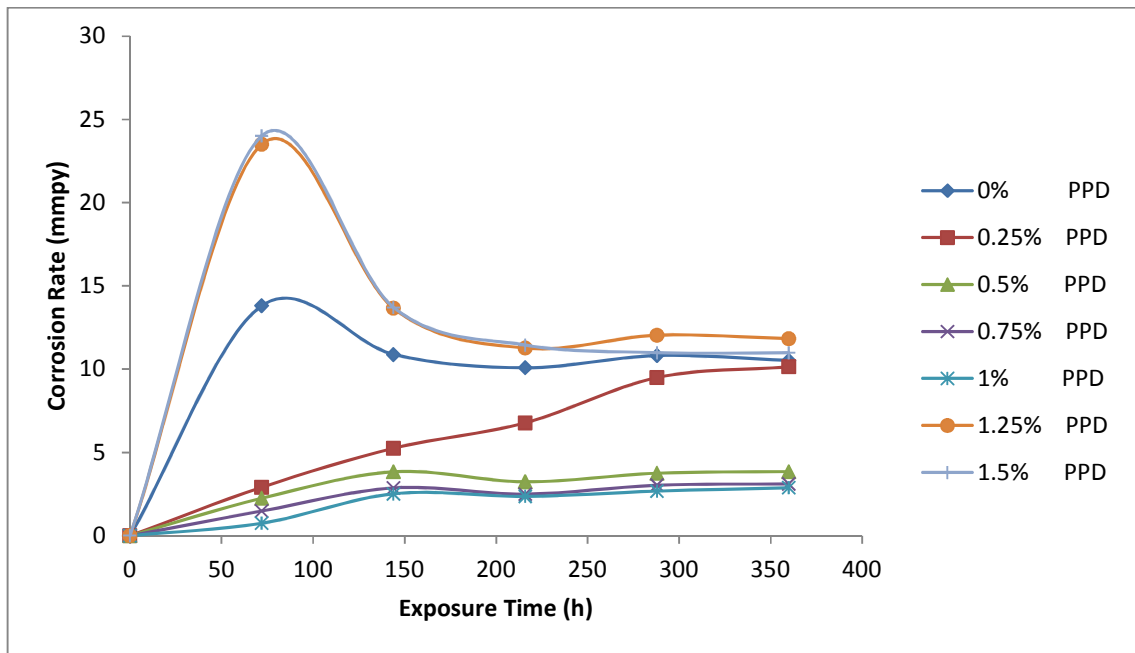


Figure 3 Effect of percentage concentration of PPD on the corrosion rate of mild steel in 0.5 M H₂SO₄

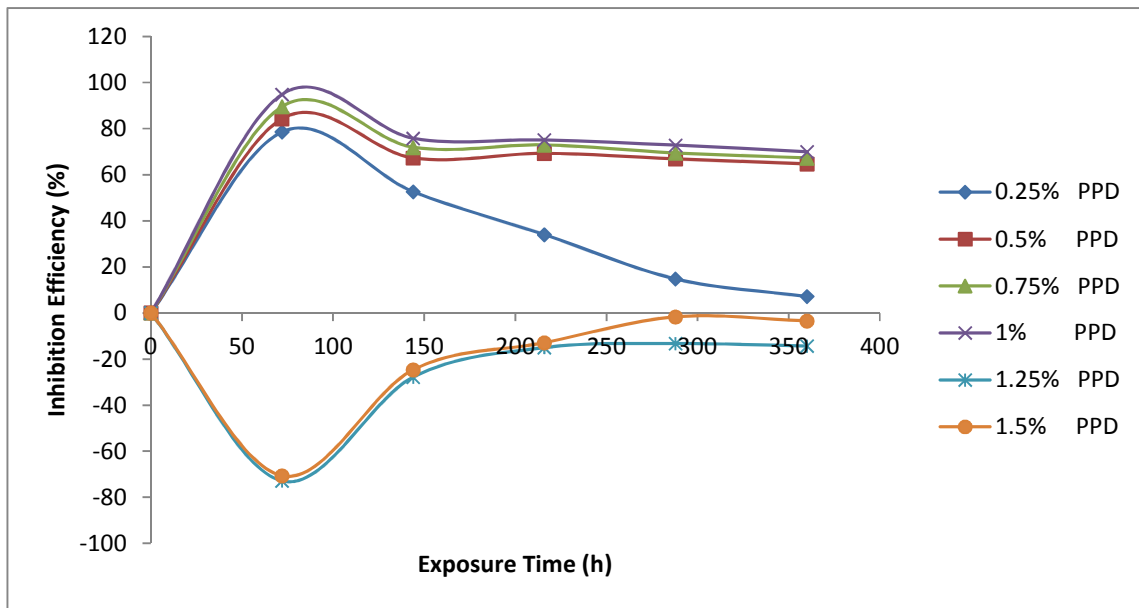


Figure 4 Plot of inhibition efficiencies of sample (A-G) in 0.5 M H₂SO₄ during the exposure period

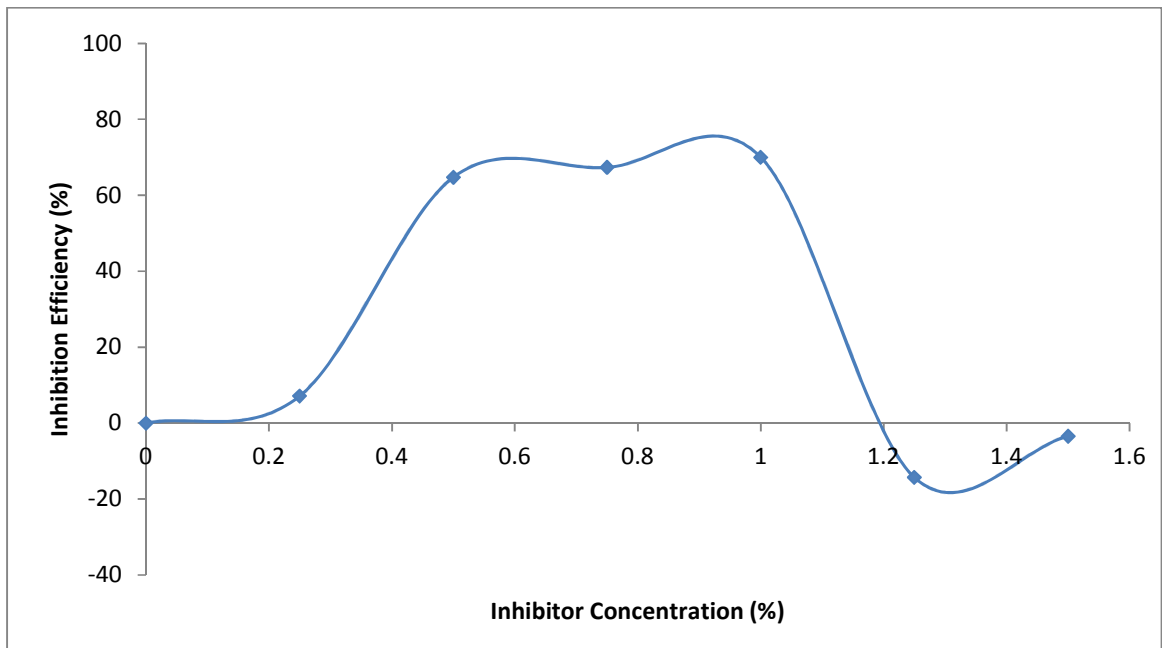


Figure 5 Variation of percentage inhibition efficiency of PPD with inhibitor concentration in 0.5 M H₂SO₄

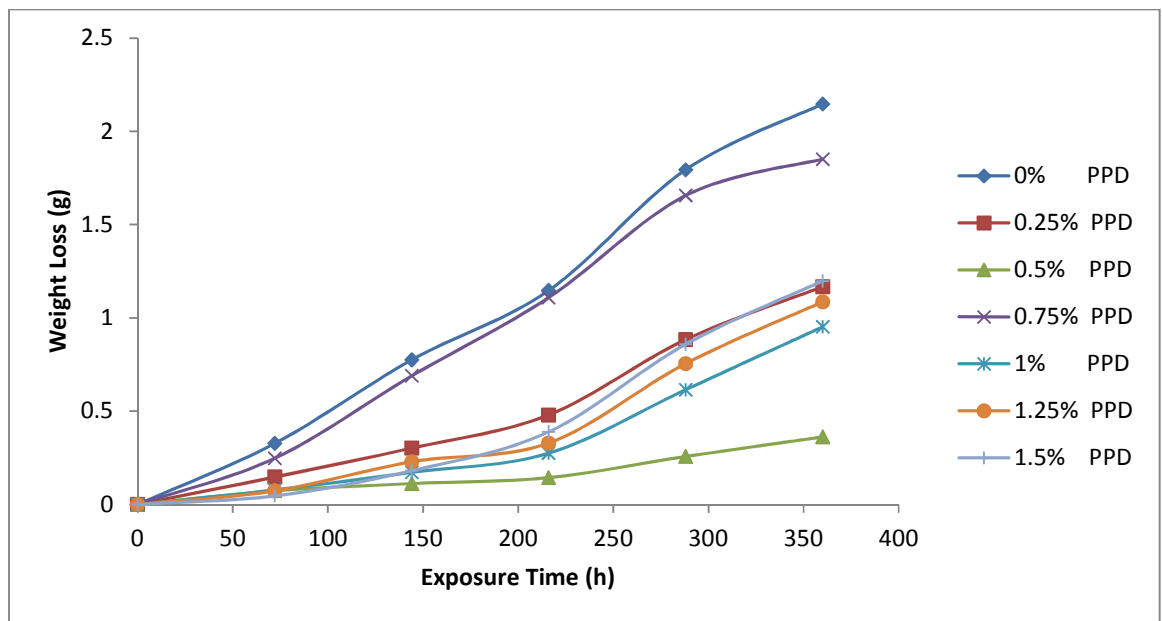


Figure 6 Variation of weight-loss with exposure time for samples (A – G) in 0.5M HCl

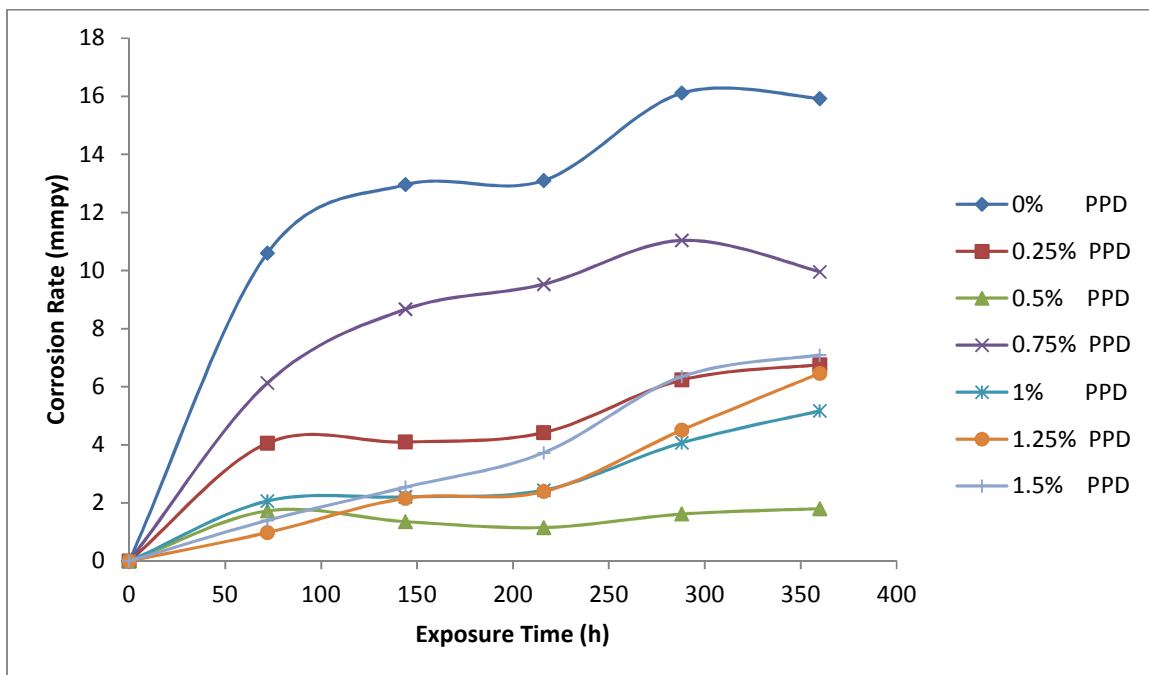


Figure 7 Effect of percentage concentration of PPD on the corrosion rate of mild steel in 0.5M HCl

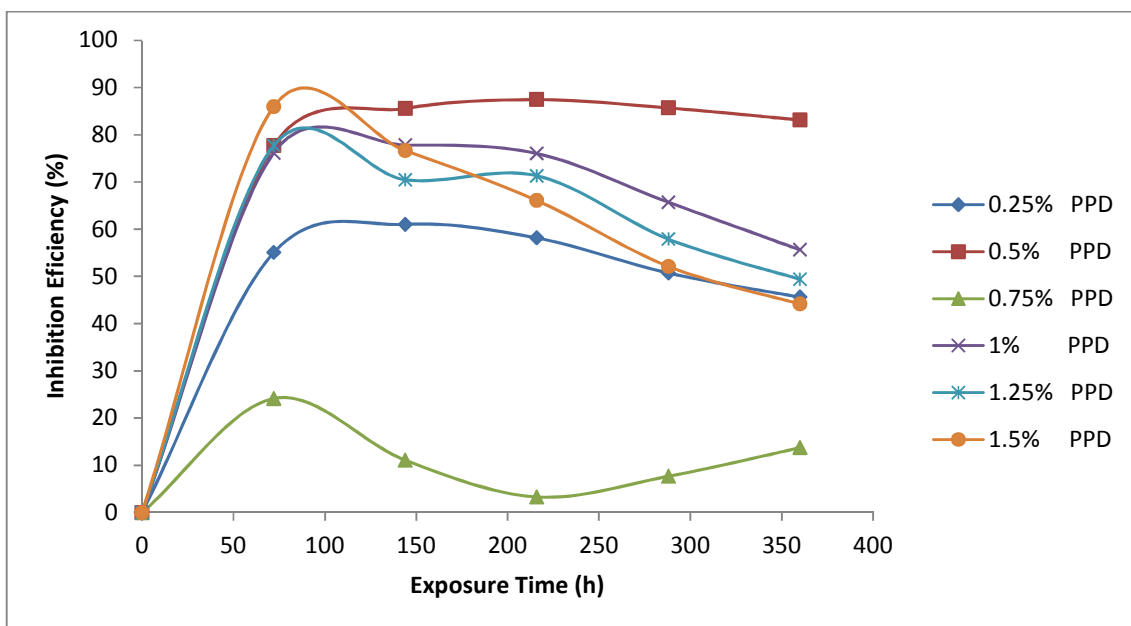


Figure 8 Plot of inhibition efficiencies of sample (A-G) versus exposure time in 0.5 M HCl during the exposure period

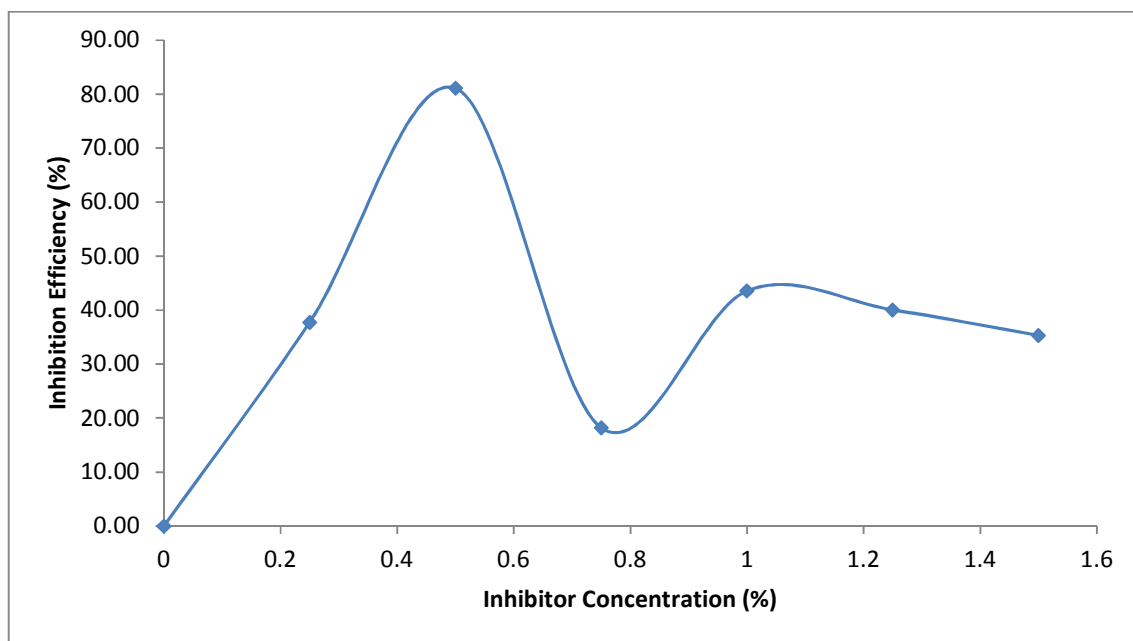


Figure 9 Variation of Inhibition efficiency of PPD versus PPD concentrations from weight loss analysis in 0.5 M HCl

Open Circuit Potential Measurement

The open-circuit potential value of the steel electrodes was monitored for 288 hours in the acid solutions as shown in Table 3 & 4. Fig. 10 & 11 shows the variation of open-circuit potentials with time in 0.5 M H₂SO₄ and 0.5 M HCl chloride solutions respectively in the absence and presence of specific concentrations of PPD inhibiting compound. At 0% PPD concentration in both solutions, rapid corrosion takes place on the steel electrode as observed from the potential readings (Table 3 & 4). The potential values at this concentration progressed significantly towards negative potentials, due to anodic dissolution. Observation of Table 3 (0.023M PPD) showed potential value far below passivity potential. Active corrosion is taking place at this potential which corresponds with the value from weight-loss analysis. The potential value from 0.046M PPD – 0.093M PPD showed drastic transition to noble values within the domain of passivity due to strong adsorption of PPD cations on the steel through physiochemical mechanism. Lateral attraction is also likely to play a major role in the formation of a protective film necessary to prevent attack of corrosive species. Beyond 0.093M PPD active corrosion resumes to weak adherence of the inhibitor molecules onto the steel and also laterals repulsion between the molecules which causes a collapse of the protective film thus exposing the steel to corrosion.

The potential values in HCl solution (Fig.11) show a sharp contrast from Fig.10 due to differential electrochemical mechanism of inhibition of PPD in the solution. With the exception of 0.046M PPD every other concentration recorded values negative potential values well with the domain of active corrosion. The potential value at 0.046M PPD is with the values that results in the passivation of the steel surface i.e. the formation of a protective film responsible for corrosion inhibition which is well sustained throughout the immersion period. The potential values for PPD inhibitor is highly dependent on the influence of PPD on the electrochemical reaction responsible for the corrosion of mild steel and the secondary products formed. The values obtained are not linearly proportional to the inhibitor concentration but dependent on the intermolecular interactions of PPD molecules, reaction of the molecules with the corrosive species and the reaction precipitates capable of forming a protective barrier only at specific concentrations. The negative potentials obtained in HCl is probably due to the formation of ammonium chloride which itself is acidic. When PPD protonates in solution it acquires a positive charge wherewith it combines with the excess chloride ions in solution to produce ammonium chloride one of the byproducts of the electrochemical process. This weakens the inhibitive tendencies of PPD, hence the poor %IE for weight-loss analysis.

Table 3 Data obtained from potential measurements for mild steel in 0.5 M H₂SO₄ in presence of specific concentrations of the PPD

PPD Concentration (%) \ Exposure Time (h)	0%	0.25%	0.5%	0.75%	1%	1.25%	1.5%
0	-415	-417	-323	-331	-321	-437	-427
48	-414	-420	-346	-325	-313	-464	-442
96	-414	-418	-336	-320	-311	-498	-482
144	-410	-410	-318	-321	-315	-491	-460
192	-433	-424	-324	-318	-306	-503	-480
240	-427	-421	-321	-311	-294	-480	-471
288	-417	-417	-315	-307	-297	-463	-470

Table 4 Data obtained from potential measurements for mild steel in 0.5 M HCl in presence of specific concentrations of the PPD

PPD Concentration (%) \ Exposure Time	0%	0.25%	0.5%	0.75%	1%	1.25%	1.5%
0	-470	-430	-304	-448	-328	-354	-342
48	-472	-475	-286	-475	-338	-354	-355
96	-468	-471	-289	-454	-338	-354	-388
144	-447	-504	-303	-442	-356	-353	-391
192	-445	-495	-310	-457	-368	-372	-399
240	-459	-490	-312	-469	-378	-373	-352
288	-478	-491	-298	-483	-374	-382	-355

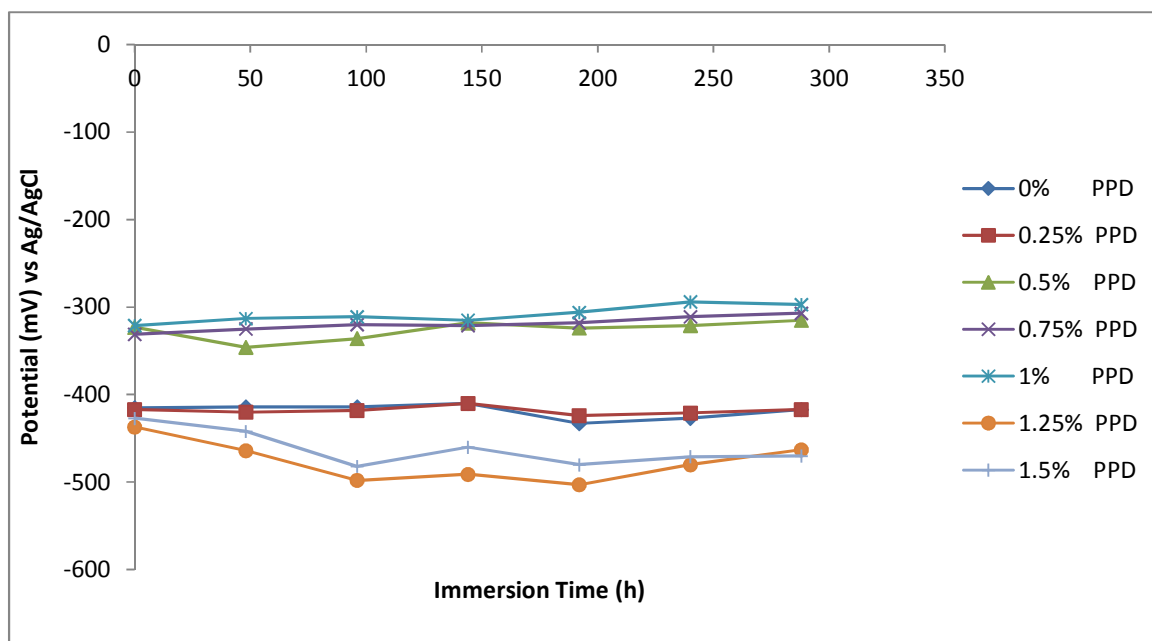


Figure 10 Variation of potential measurements with immersion time for PPD concentrations in 0.5 M H₂SO₄

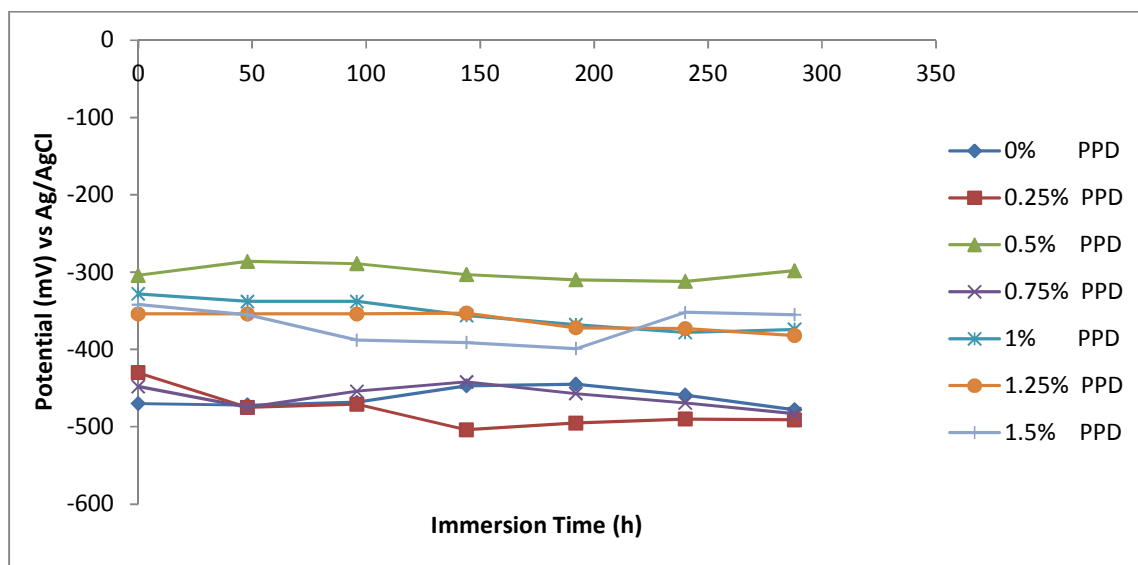


Figure 11 Variation of potential measurements with immersion time for PPD concentrations in 0.5 M HCl

Potentiodynamic Polarization studies

Potentiostatic potential was cursorily examined from -1.5V to $+1.5\text{V}$ vs. Ag/AgCl at a scan rate of 0.00166 mV s^{-1} . The effect of the addition of PPD on the polarization curves of Mild steel in $0.5\text{ M H}_2\text{SO}_4$ and 0.5 M HCl solutions was studied at ambient temperature. Fig. 12 shows the polarization curves of the steel in absence and presence of PPD at specific concentrations in $0.5\text{ M H}_2\text{SO}_4$ while Fig. 13 shows the polarization curves in 0.5 M HCl . As earlier observed from weight loss analysis, the effect of PPD varies non-linearly with the value of its concentrations at specific range of values in both solutions as shown in Fig. 14 & 15. The inhibition effect of PPD in $0.5\text{ M H}_2\text{SO}_4$ at 0.023M is negligible due to the aggressive action of the corrosive anions, however from 0.046M PPD to 0.093M PPD the %IE varies from 66.6% to 78.2% after which there is a sharp decline indicating desorption of the inhibitor molecules from the steel surface. The protective film breaks down, thus it's unable to prevent the electrolytic transport of the corrosive anions.

In 0.5 M HCl increase in PPD concentration results in a sharp increase in inhibition efficiency ($0.023\text{M} - 0.046\text{M}$ PPD) after which the %IE values declined progressively. The only appreciable value in HCl is at 0.046M PPD due to lateral attraction between the inhibitor molecules and the ability of PPD to bond with the steel surface through adsorption, thus protecting the steel. The values in both solutions correspond with the results obtained from weight-loss analysis. the availability of more PPD molecules to counteract the actions of the corrosive species, block the active sites and form a compact protective barrier on the alloy surface in the solutions till 0.069M PPD after which the %IE values declined sharply.

Results obtained shows that PPD influences the electrochemical process only at specific concentrations as observed in the %IE values. Generally, all scans in Fig. 12 exhibited slightly similar behavior (with few exceptions) over the potential domain examined. The corrosion rate reduced drastically rate with differential changes in the electrochemical parameters. In addition small changes in the anodic Tafel constants in the presence of PPD signify that anodic dissolution reactions are only slightly influenced. The cathodic Tafel constant shows differing values due to the film forming characteristics of PPD which in effect suppresses hydrogen evolution reactions. The inhibitive action of the inhibitor is related to its adsorption and formation of a barrier film on the electrode surface. The electrochemical variables such as, corrosion potential (E_{cr}), corrosion current (i_{cr}) corrosion current density (j_{cr}), cathodic Tafel constant (bc), anodic Tafel slope (ba), surface coverage θ and percentage inhibition efficiency (%IE) were calculated and given in Table 5 & 6. The corrosion current density (I_{cr}) and corrosion potential (E_{cr}) were ascertained from the intersection of the extrapolated anodic and cathodic Tafel lines, %IE was calculated from equation 5.

Table 5 Data obtained from polarization resistance measurements for mild steel in 0.5 M H₂SO₄ in presence of PPD

Sample	Inhibitor Concentration (%)	Corrosion Rate (mm/yr)	% IE	Polarization Resistance (Ω)	E _{cr, Obs} (V)	i _{cr} (A)	I _{cr} (A/cm ²)	bc (V/dec)	ba (V/dec)
A	0	6.30	0	16.17	-0.418	9.00E-04	5.45E-04	0.046	0.123
B	0.25	6.08	3.6	34.32	-0.418	8.62E-04	5.22E-04	0.129	0.144
C	0.5	2.11	66.6	110.03	-0.408	3.00E-04	1.82E-04	0.126	0.191
D	0.75	2.34	62.8	106.28	-0.408	3.32E-04	2.01E-04	0.139	0.195
E	1	1.38	78.2	142.77	-0.441	1.96E-04	1.19E-04	0.093	0.209
F	1.25	6.38	-1.3	37.48	-0.430	9.05E-04	5.48E-04	0.101	0.343
G	1.5	5.7	9.5	58.03	-0.420	8.10E-04	4.91E-04	0.172	0.291

Table 6 Data obtained from polarization resistance measurements for mild steel in 0.5M HCl in presence of specific concentrations of the PPD

Sample	Inhibitor Concentration (%)	Corrosion Rate (mm/yr)	% IE	Polarization Resistance (Ω)	E _{cr, Cal} (V)	i _{cr} (A)	I _{cr} (A/cm ²)	bc (V/dec)	ba (V/dec)
A	0	9.38	0	39.41	-0.384	1.33E-03	8.07E-04	0.179	0.370
B	0.25	5.25	44.0	28.70	-0.420	7.45E-04	4.52E-04	0.107	0.091
C	0.5	0.53	94.3	135.16	-0.485	7.47E-05	4.53E-05	0.069	0.035
D	0.75	7.10	24.2	28.37	-0.478	1.01E-03	6.13E-04	0.222	0.094
E	1	4.89	47.8	33.66	-0.486	6.94E-04	4.21E-04	0.064	0.335
F	1.25	4.97	47.0	44.36	-0.485	7.05E-04	4.27E-04	0.102	0.244
G	1.5	6.22	33.6	31.39	-0.511	8.83E-04	5.35E-04	0.127	0.128

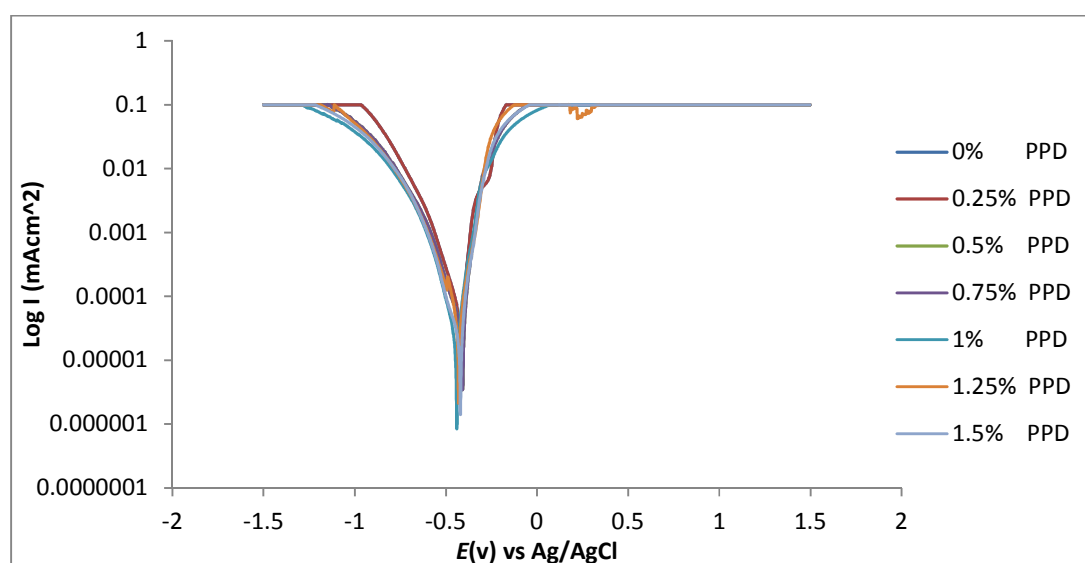


Figure 12 Comparison plot of polarization scans for mild steel in 0.5 M H₂SO₄ + 3.5% NaCl solution in the absence and presence of specific concentrations of PPD

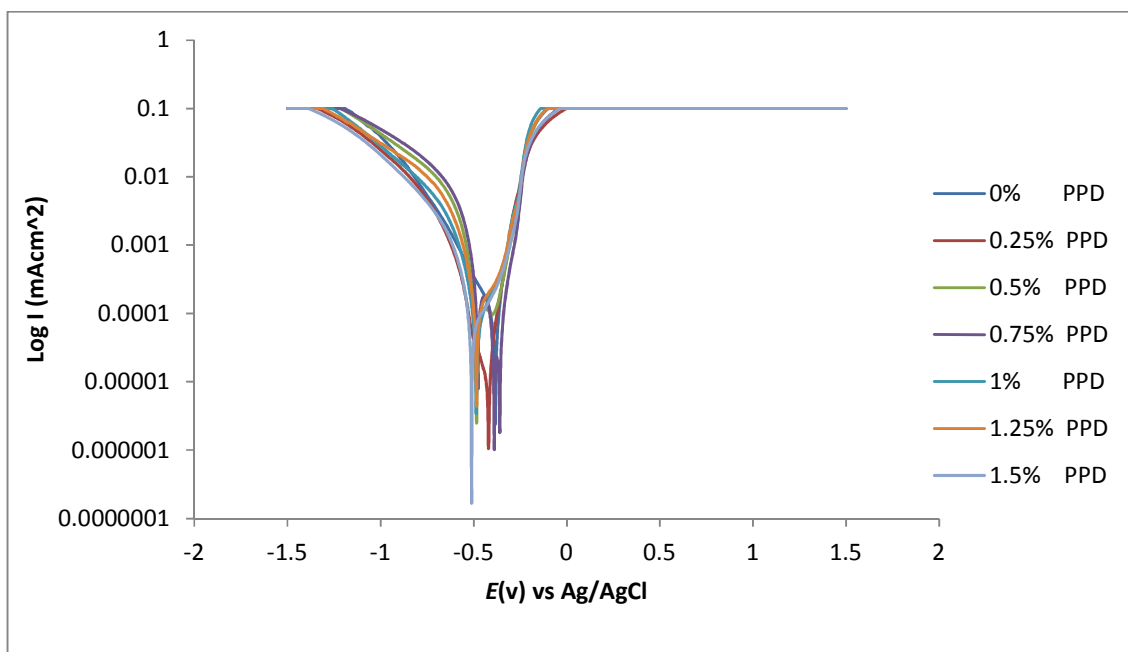


Figure 13 Comparison plot of cathodic and anodic polarization scans for mild steel in 0.5 M HCl + 3.5% NaCl solution in the absence and presence of (0% - 15%) PPD

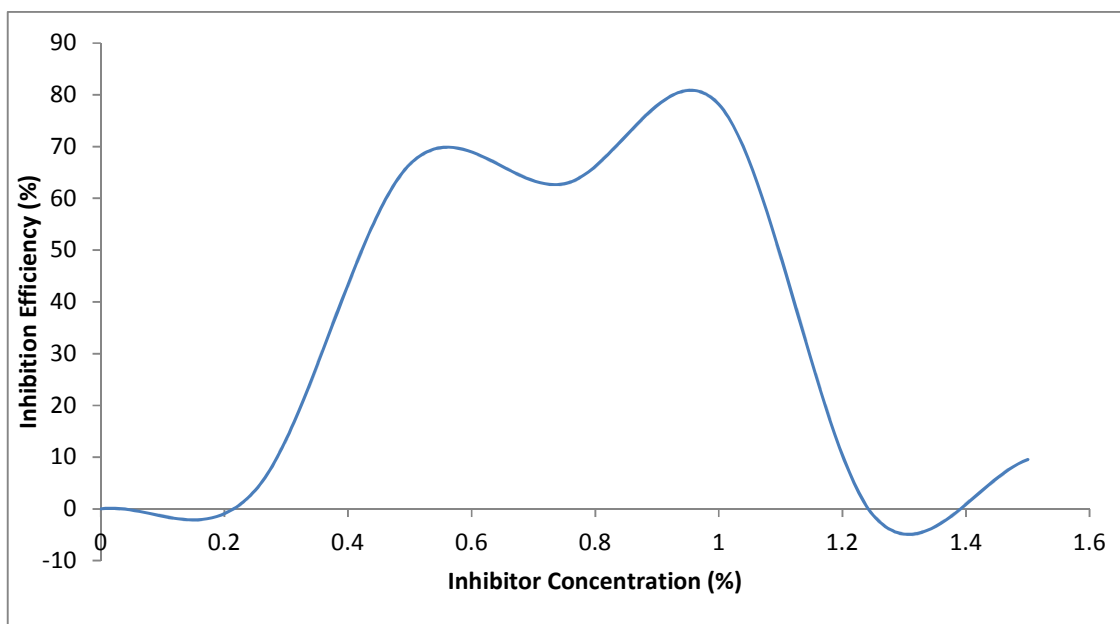


Figure 14 Relationship between %IE and inhibitor concentration for polarization test in 0.5 M H₂SO₄

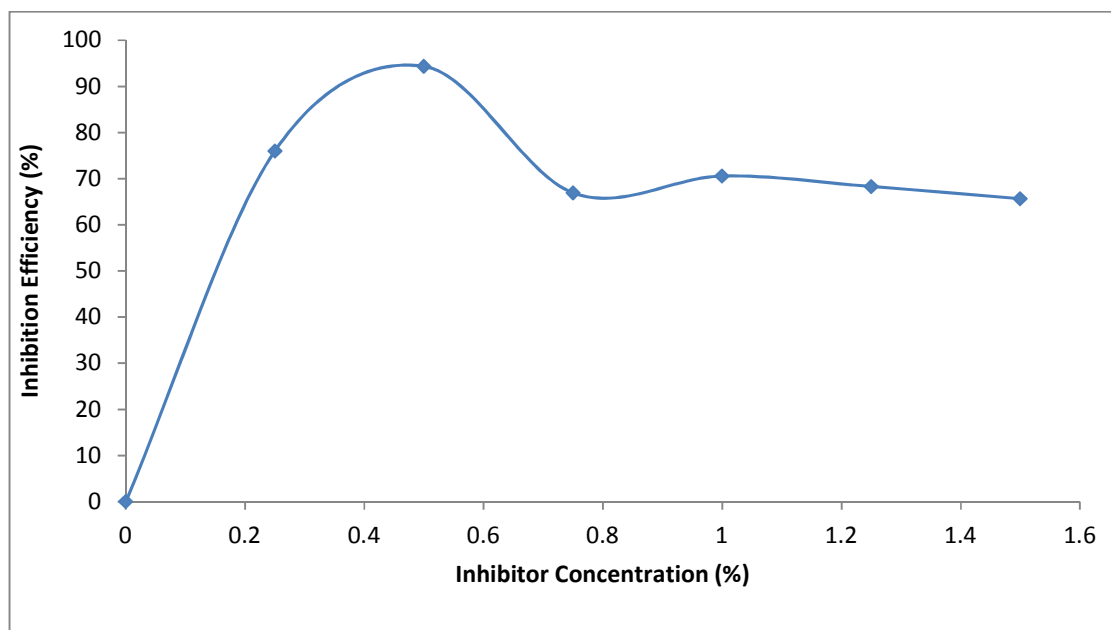


Figure 15 Relationship between %IE and inhibitor concentration for polarization test in 0.5 M HCl

PPD showed mixed inhibiting tendencies in H_2SO_4 depending on its concentration from observation of the corrosion potential values (E_{cr} , Table 5). At concentrations of high %IE (0.046M – 0.093M PPD), the cations react with the cathodic and anodic sites suppressing hydrogen evolution and anodic dissolution reactions through surface kinetics. The current density values declined sharply at these concentrations indicating passivation due to corrosion inhibition of the steel after which there is a sharp increase in current density due to increase in corrosion activity on the steel. The Tafel constant of the redox process varied differentially i.e. PPD has minimal overall influence on the overall electrochemical process. It must be noted that the polarization resistance corresponds with the %IE values; at high %IE the polarization resistance increases before declining after 0.093M PPD. The surface coverage and adsorption characteristic of PPD is responsible for the anodic inhibition of the redox process. The inhibitor was first adsorbed onto the metal surface and impedes the passage of metal ions from the metal/solution interphase into the solution as a result of the compact barrier formed on the metal surface.

At the initial stage of polarization, the corrosion current densities decreased slowly and anodic polarization was enhanced predominantly with the polarization potential shifting to less negative potentials, which implies that the rate of adsorption is much higher than the desorption rate of PPD molecules on the steel surface, and the adsorption process dominates the anodic reaction. The slight shift of the corrosion potential toward positive values, i.e. the decrease of anode current relative to cathode current, indicates the predominant inhibition of oxidation reactions. The cathodic reaction of the redox process involves the electrochemical reduction of water molecules and hydrogen atoms. Adsorption of the inhibitor molecules displaces the water molecules thereby it stifles the reaction of surface water molecules and rate of hydrogen evolution, thus affecting the cathodic reactions process.

The inhibitor molecules are adsorbed via their functional groups and hetero-atoms onto the steel surface forming a protective layer. These groups are electroactive and interact with the metals surface to form covalent bonds through physiochemical mechanism. A compound can be classified as an anodic or a cathodic-type inhibitor if the displacement in E_{corr} value is larger than 85 mV. If displacement is less than 85 mV, the inhibitor can be seen as mixed type [25, 26]. The maximum displacement of E_{corr} values in H_2SO_4 is 23 mV in the cathodic direction and 10 mV in the anodic direction, thus in H_2SO_4 PPD can be classified as mixed. In HCl the maximum displacement is 127 mV in the negative direction, thus its overwhelming cathodic. Cathodic inhibition occurs either by slowing the cathodic reaction itself and selectively precipitating on cathodic areas to limit the diffusion of reducing species to the surface whereby PPD form an invisible film along the cathode surface. This polarizes the metal by restricting the access of dissolved oxygen to the metal substrate. The film also acts to block hydrogen evolution sites and prevent the resultant depolarizing effect. This film specifically forms on cathodic reaction sites of the steel to increase the

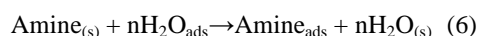
surface deterrence and limit the transport of reducible ions. This inhibits the ionic combination and diffusion of hydrogen atoms while at the same time preventing oxygen induced cathodic depolarization.

The cathodic corrosion current density varied differentially at all PPD concentrations with the exception of 0.046M PPD where the current density was significantly lower compared to other values. The addition of PPD does change the cathodic reduction mechanism and the decreases of H^+ ions on surface of mild steel takes place mainly through a charge transfer mechanism and covering of monolayer of PPD molecules on the cathodic sites. This proves that PPD blocks the surface active sites and decrease the area available for hydrogen evolution and metal dissolution reactions. The relative inhibition efficiencies of PPD can be summarized under the following assumptions that: (i) the inhibition is due to surface coverage of the metal surface by the PPD molecules; (ii) strong adherence of the molecules on the metal surface is as a result of the coordination of pi-electron with the metal atom; (iii) the stability of the precipitate is somewhat related to the molecule's being planar [27].

Mechanism of inhibition

PPD inhibits metal dissolution by forming a hydrophobic protective barrier on the metal surface due to selective adsorption. This suppresses the cathodic processes and less significantly the anodic process [28]. The inhibitive efficiency of PPD is not proportional to the fraction of the surface coverage as observed from the results in Table 4 & 5 but tends to be highly effective at specific PPD concentrations. The effective performance of the adsorbed inhibitor species in retarding the corrosion reactions is greater at low surface coverage due to weak lateral repulsion at these concentrations. This weakens molecular adsorption leading desorption of the inhibiting species from sample F to G. The adsorption of PPD is due to electrostatic attraction between the positive charge on the adsorbed PPD cationic species and the negative charge on the metal at the metal/solution interface. The attraction results in electron transfer through the functional groups on the inhibitor molecule to form coordinate bonds with the metal in solution [29]. This is possible by the by the presence of relatively loosely bound electrons in the amine functional group and vacant low energy electron orbitals of the metal electrode.

The non-linear relationship between %IE efficiency and surface coverage of PPD is most probably as a result of strong lateral repulsion between PPD cationic molecules at higher concentrations [30]. The lateral repulsion decreases Van der Waals attractive force between adjacent molecules leading to weaker adsorption and possibly desorption [31]. This occurs between PPD molecules containing dipoles responsible for the weak adsorption at these concentrations. The protective film at low PPD concentration modifies the metal surface through decrease of the number of metal atoms released into the solution i.e. products of the corrosion reactions through suppression of the redox process especially cathodic reactions as earlier described. Adsorption of PPD molecules involves the removal of pre-adsorbed molecules of water from the surface [32]. The amines functional group of PPD may be adsorbed over the metal surface in the form of neutral molecules as



and dual electron transfer between the metal and the nitrogen atom of the PPD molecule. The positively charged amine ion is electrostatically pulled to the negatively charged cathode site of the metal, enhancing their rate of diffusion. The adsorption of the cations is facilitated in the presence of corrosive anions as a result of their initial adsorption unto the metal surface; their presence creates negative charges which attracts the cations of PPD. The PPD molecules are covalently bond onto the metal forming a compact protective barrier against further corrosion [33-36].

Scanning Electron Microscopy

The SEM images of the Mild steel surfaces before and after immersion in 0.5 M H_2SO_4 and 0.5M HCl solutions and after 360 h immersion with and without PPD additions are shown in Fig. 16(a–e), respectively. Fig. 16(a & b) shows the steel sample before immersion, the lined and jagged surfaces are due to cutting and machining during sample preparation. Fig. 16(b & d) shows the steel surfaces after 360 hours of immersion in 0.5M HCl and 0.5M H_2SO_4 without PPD, while Fig. 16(d & f) shows the steel surface in the acid media with PPD. In the absence of PPD, a very rough, pitted and totally uneven surface is observed in Fig. 16(b & d); large number of macro pits and badly corroded topography of the steel coupons are visible due to the action of corrosive species. The surface morphology in Fig. 16b consists of chlorides deposited on the surface during the electrochemical process. The positive charge on the steel surface is counterbalanced by the negative charged on the chloride and sulphate ions. This result in the diffusion of Fe^{2+} into the electrolyte and produces the observed uniform and intergranular corrosion with large

macro pits. Fig. 16d is basically due to the action of sulphate ions and to lesser extent chloride ions when compared to Fig. 16b

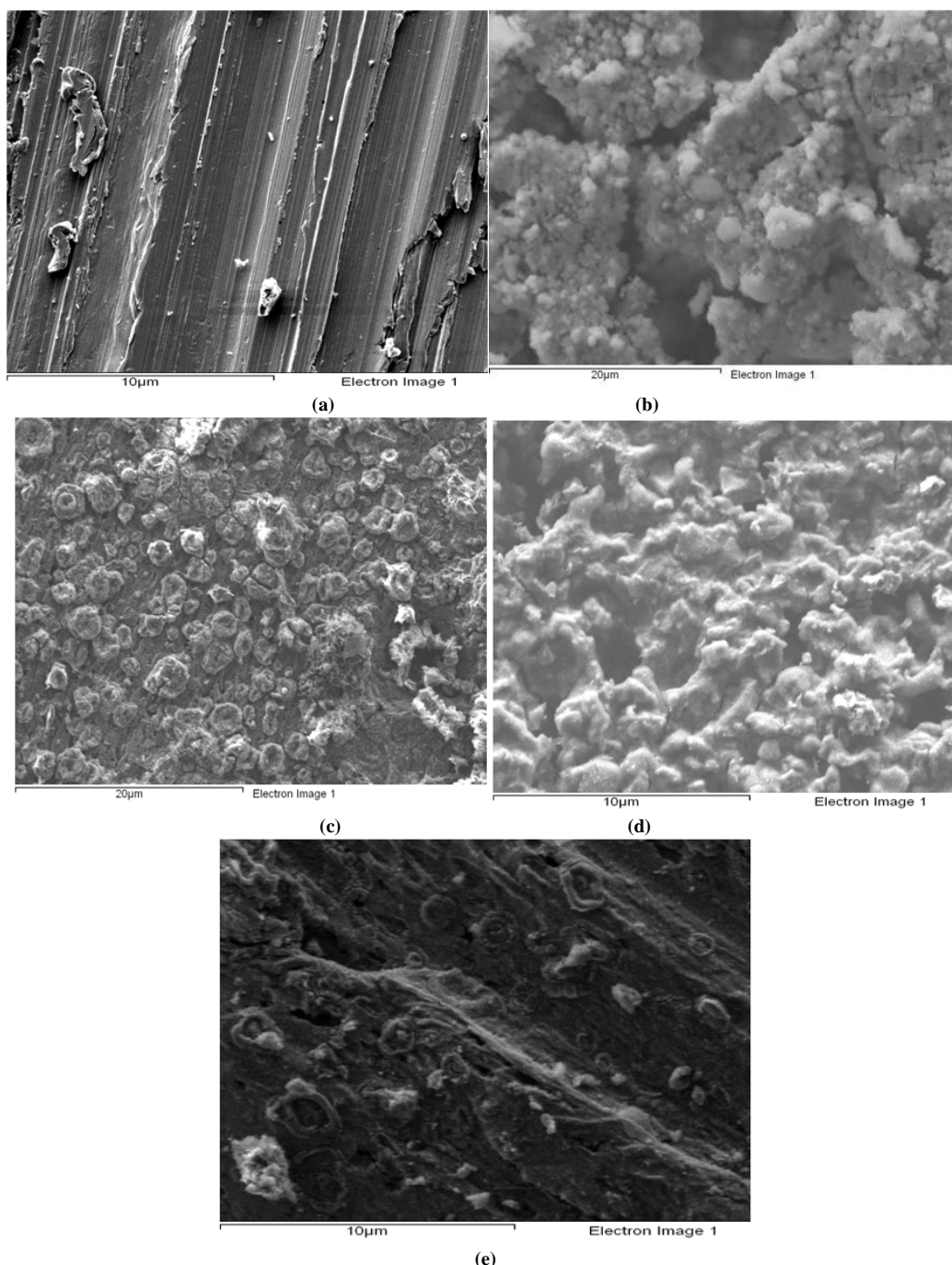
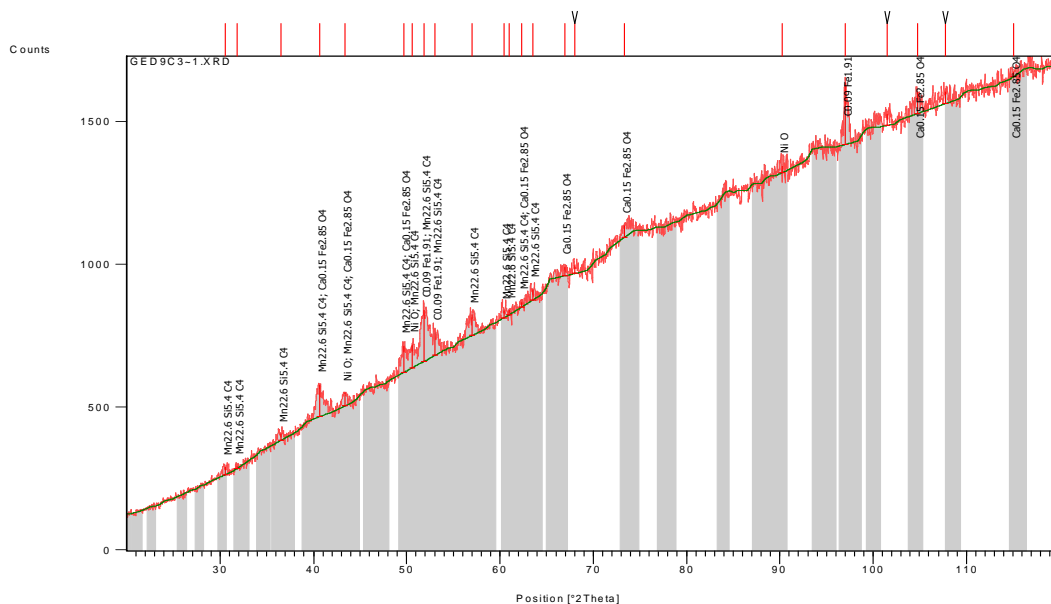


Figure 16 SEM micrographs of: a) Mild steel, b) Mild steel in 0.5 M HCl, c) Mild steel in 0.5 M HCl with PPD, d) Mild steel in 0.5 M PPD, e) Mild steel in 0.5M H₂SO₄ with PPD

The SEM image of the steel sample with PPD addition Fig. 16 (c & e) differs significantly different from the control specimens in sulphuric and hydrochloric acid. The surface is covered with chemically adsorbed protective coating on the steel. The adsorption of the negatively charged chloride and sulphate ions on the steel surface facilitates cation adsorption through electrostatic attraction onto the steel surface. Fig. 16(c & e) shows a specimen where the

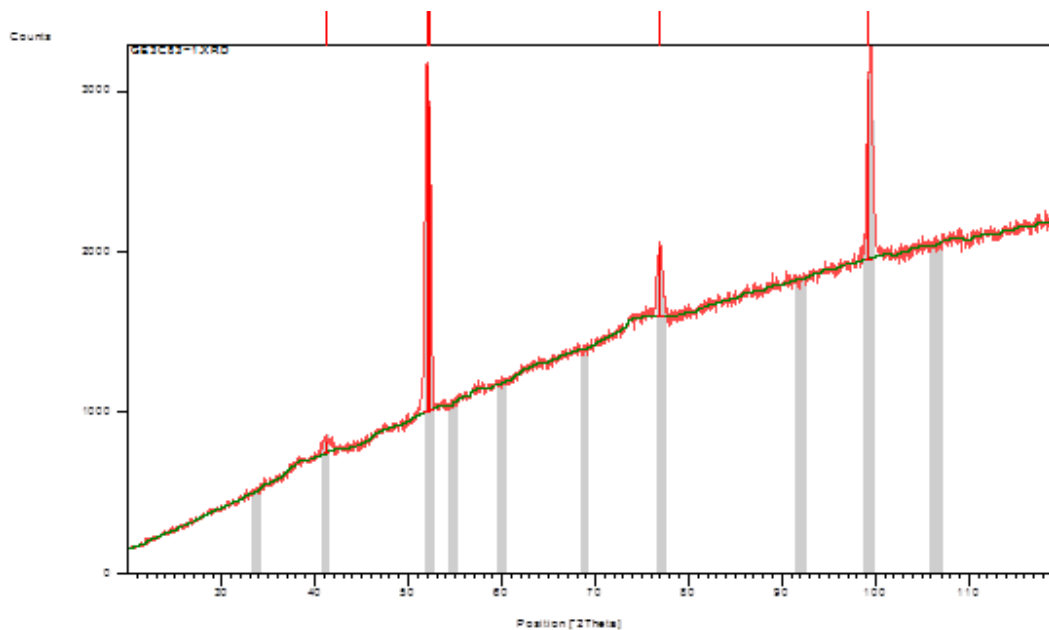


(b)

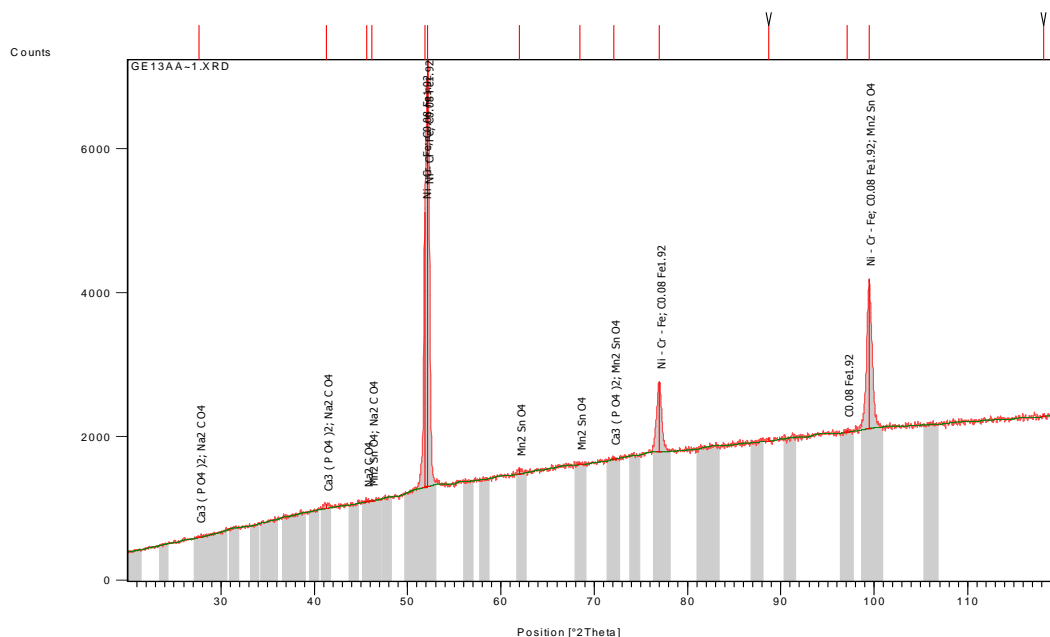
Figure 17 Identified Patterns List for XRD analysis of Mild steel (a) in 0.5 M H₂SO₄ without PPD (b) in 0.5 M HCl without PPD

Table 8 Identified Patterns List for XRD analysis of Mild steel in 0.5 M HCl without PPD

Visible	Ref. Code	Score	Compound Name	Displacement [°2Th.]	Scale Factor	Chemical Formula
*	01-078-0429	45	Nickel Oxide	-0.28	0.224	Ni O
*	00-044-1292	36	Martensite	0.446	0.395	C0.09 Fe1.91
*	00-029-0887	31	Manganese Silicon Carbide	-0.065	0.422	Mn22.6 Si5.4 C ₄
*	00-046-0291	21	Calcium Iron Oxide	0.038	0.31	Ca0.15 Fe2.85 O ₄



(a)



(b)

Figure 18 Identified Patterns List for XRD analysis of Mild steel (a) in 0.5 M H₂SO₄ with PPD (b) in 0.5 M HCl with PPD
 Table 9 Identified Patterns List for XRD analysis of Mild steel in 0.5 M H₂SO₄ with PPD

Visible	Ref. Code	Score	Compound Name	Displacement [°2Th.]	Scale Factor	Chemical Formula
*	00-034-0396	84	434-L steel	0.051	0.944	Fe - Cr
*	00-018-1897	0	Sodium acetylene diolate	-1.185	0.107	C ₂ Na ₂ O ₂

Table 10 Identified Patterns List for XRD analysis of Mild steel in 0.5 M HCl with PPD

Visible	Ref. Code	Score	Compound Name	Displacement [°2Th.]	Scale Factor	Chemical Formula
*	00-035-1375	68	Chromium Iron Nickel	-0.193	0.998	Ni - Cr - Fe
*	00-044-1291	37	Martensite	-0.029	0.159	C _{0.08} Fe1.92
*	00-003-0681	28	Calcium Phosphate	1.14	0.007	Ca ₃ (P O ₄) ₂
*	00-023-0406	24	Manganese Tin Oxide	-0.78	0.007	Mn ₂ SnO ₄
*	00-052-1105	20	Sodium Percarbonate	-0.127	0.007	Na ₂ CO ₄

Thermodynamics of the corrosion process

The values of the apparent free energy change i.e. Gibbs free energy (ΔG_{ads}) for the adsorption process can be evaluated from the equilibrium constant of adsorption using the following equation as shown in Table 5.

$$\Delta G_{ads} = - 2.303RT \log [55.5 K_{ads}] \tag{7}$$

Where 55.5 is the molar concentration of water in the solution, R is the universal gas constant, T is the absolute temperature and K_{ads} is the equilibrium constant of adsorption. K_{ads} is related to surface coverage (θ) by the following equation.

$$K_{ads} C = \left[\frac{\theta}{1-\theta} \right] \tag{8}$$

Table 11 Data obtained for the values of Gibbs free energy, Surface coverage and equilibrium constant of adsorption at varying concentrations of PPD in 0.5 M H₂SO₄ for Mild Steel

Samples	Surface Coverage (θ)	Equilibrium Constant of Adsorption (K_{ads})	Free energy of Adsorption (ΔG_{ads}) (kJ/mol)
B	0.0714	3342.55	-30.06
C	0.6473	39904.71	-36.22
D	0.6731	29842.22	-35.47
E	0.7000	25083.19	-35.02
F	-0.1433	-1080.62	27.26
G	-0.0344	-238.94	23.50

Table 12 Data obtained for the values of Gibbs free energy, Surface coverage and equilibrium constant of adsorption at varying concentrations of PPD in 0.5 M HCl for Mild Steel

Samples	Surface Coverage (θ)	Equilibrium Constant of Adsorption (K_{ads})	Free energy of Adsorption (ΔG_{ads}) (kJ/mol)
B	0.3774	26355.77	-35.18
C	0.8109	93208.93	-26.90
D	0.1820	3224.73	-20.30
E	0.5644	13934.08	-33.60
F	0.5996	12908.51	-33.41
G	0.6469	13178.08	-33.46

Values of ΔG_{ads} around -20 kJ/mol are consistent with physisorption; those around -40 kJ/mol or higher involve charge sharing to form a coordinate type of bond chemisorption. The value of ΔG_{ads} in H₂SO₄ and HCl for mild steel under the action of PPD organic compounds as shown in Tables 11 and Tables 12 reveals the strong adsorption of PPD onto the steel surface. The negative values of ΔG_{ads} showed that the adsorption of inhibitor molecules on the metal surface is spontaneous. The values of ΔG_{ads} for PPD on mild steel in H₂SO₄ (Table 11) ranged from -30.06 kJ mol⁻¹ to -35.02 kJ mol⁻¹ for samples B to E after which there are no molecular interaction between PPD compound and steel surface for samples F and G, while the values of PPD on mild steel in HCl (Table 12) ranged between -35.18 kJ mol⁻¹ and -33.46 kJ mol⁻¹ for samples B to G. These values are consistent with physiochemical interaction and adsorption onto the steel surface.

The value of ΔG_{ads} obtained shows that the molecules chemisorb on the steel producing a bond resistant to penetration and competitive adsorption from the corrosive species. The negative values of ΔG_{ads} showed that the adsorption of inhibitor molecules on the metal surface is spontaneous [38, 39]. The intermolecular bonding is sufficiently strong to prevent displacement of adsorbed inhibitor molecules along the surface. The precipitates formed are stable in the acid solution throughout the exposure period.

Statistical Analysis

Two-factor single level experimental ANOVA test (*F* - test) was used to analyse the separate and combined effects of the percentage concentrations of PPD and exposure time on the inhibition efficiency of PPD in the corrosion of inhibition of mild steels in 0.5 M H₂SO₄ and 0.5 M HCl solutions and to investigate the statistical significance of the effects. The *F*-test was used to examine the amount of variation within each of the samples relative to the amount of variation between the samples.

The Sum of squares among columns (exposure time) was obtained from the following equations.

$$SS_c = \frac{\sum T_c^2}{nr} - \frac{T^2}{N} \quad (9)$$

Sum of Squares among rows (inhibitor concentration)

$$SS_r = \frac{\sum T_r^2}{nc} - \frac{T^2}{N} \quad (10)$$

Total Sum of Squares

$$SS_{Total} = \sum x^2 - \frac{T^2}{N} \quad (11)$$

The results using the ANOVA test is tabulated (Table 13 & 14) as shown.

Table 13 Analysis of variance (ANOVA) for inhibition efficiency of PPD inhibitor in 0.5 M H₂SO₄ (at 95% confidence level)

Source of Variation	Sum of Squares	Degree of Freedom	Mean Square	Mean Square Ratio	Min. MSR at 95% confidence	
					Significance F	F%
Inhibitor concentration	60059.19	5	12011.84	1186.01	2.71	97.1
Exposure Time	97.03	4	24.26	2.40	2.87	0
Residual	202.56	20	10.13			
Total	60358.78	29				

Table 14 Analysis of variance (ANOVA) for inhibition efficiency of PPD inhibitor in 0.5 M HCl (at 95% confidence level)

Source of Variation	Sum of Squares	Degree of Freedom	Mean Square	Mean Square Ratio	Min. MSR at 95% confidence	
					Significance F	F%
Inhibitor concentration	15268.79	5	3053.76	301.52	2.71	87.8
Exposure Time	1282.39	4	320.60	31.65	2.87	6.63
Residual	202.56	20	10.13			
Total	16753.74	29				

The analysis in 0.5 M H₂SO₄ was evaluated for a confidence level of 95% i.e. a significance level of $\alpha = 0.05$. The ANOVA results reveal that only one of the experimental sources of variation (inhibitor concentration) is statistically significant on the inhibition efficiency values of PPD with F - values of 1186.01. This is far greater than significance factor at $\alpha = 0.05$ (level of significance or probability). The F - values of exposure time is less than the significant value factor hence it is statistically irrelevant. The statistical influence of the inhibitor concentration is 97.1%, while the influence of the exposure time 0% hence negligible. The inhibitor concentration is the only significant model terms influencing inhibition efficiency of PPD on the corrosion of the steel specimen. On this basis only percentage concentration of PPD significantly affects the inhibition efficiency of PPD in the acid media.

The ANOVA results for the influence of the independent variables (inhibitor concentration and exposure time) in 0.5 M HCl reveal slightly different results. Both the inhibitor concentration and exposure time are statistically relevant with F - values of 301.52 and 31.65 which are greater than the significance factor at $\alpha = 0.05$. The statistical influence of the inhibitor concentration is 88.8% while the exposure time is 6.63% depicting the overwhelming influence of inhibitor concentration on the values of inhibition efficiency from the experiments in comparison to the exposure time which is very small; however both are influential on the performance of PPD in 0.5 M HCl solution.

CONCLUSION

1, 4-diaminobenzene (PPD) performed effectively at specific concentrations in the acid media. The kinetics of the electrochemical reactions was significantly influenced by PPD resulting in complete protection of the metal's surface. It showed mixed inhibiting characteristics in H₂SO₄ acid and cathodic inhibition in HCl acid at optimal concentration from observation of the corrosion potential values, however the performance of the inhibitor was more effective in HCl than H₂SO₄ acid. ANOVA results reveal that only the inhibitor concentration is statistically significant at 97.1% on the inhibition efficiency values in sulphuric acid while in HCl acid both the inhibitor concentration and exposure time are statistically relevant with values of 88.8% and 6.63%. The scanning electron microscopy characterization showed surfaces which has been electrochemically altered due to the inhibitive action of PPD molecules on the steel surface. X-ray diffractometry indicates the absence of phase compounds and corrosion products from H₂SO₄ acid solution, however analysis of the surface of the steel from HCl acid with PPD addition reveals trace amounts of iron oxides probably due to limited diffusion of chloride anions resulting in lower inhibition efficiency compared to the values in H₂SO₄ acid.

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