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Performance and Corrosion Inhibitive Mechanism of *Prosopis Africana* Pod Extracts on Mild Steel in Acidic Medium

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Abstract

This study investigates the influence of *Prosopis Africana* pod extract (PAPE) on corrosion behavior of mild steel in 1.0 M HCl. The *Prosopis African Seed Extract* (PASE) was previously characterized as a green corrosion inhibitor without considering its pod, which often constitutes environmental pollution. The PAPE solution was administered in varying concentrations of 0.0 g/ml to 10.0 g/ml as a green inhibitor of mild steel in 1M Hydrochloric (HCl) medium at room temperature using gravimetric, gasometric and electrochemical (Tafel Polarization) techniques. The volume of hydrogen evolution determined with gasometric process decreases as the concentration of the extract increases. The gravimetric technique recorded the highest inhibition efficiency (IE%) of 97.14% with a 1.0g/l concentration of PAPE. The electrochemical measurements of the corrosion current density (I_{Corr}) decreased as the concentration of PAPE increased, with a maximum IE% of 80.59% (PAPE) at 1.0g/l recorded. Generally, IE% increases with the concentration of the extract. The decrease in the corrosion rate is caused by the intensified obstructive mechanism in the coupon surfaces instigated by the pod extract's adsorption. Hence, the extract from *Prosopis Africana* Pod is equally suitable as a green inhibitor for corrosion.

Keywords: Steel, *Prosopis Africana*, Gravimetric, Tafel polarization, Inhibiting efficiency

Received: 10th January, 2022

Accepted: 30th March, 2022

1. Introduction

Carbon steel is reactive in a corrosive environment and it is the subject of several studies due to its low-cost, wide range of mechanical properties and industrial applications especially in steel structures (Shuaib-Babata *et al.*, 2018). Despite all these properties, the consequences of this reaction that affect the safe, reliable and effective operation of equipment or structures is often more serious than the simple loss of a mass of metal in the presence of air, water, and other media. However, the use of inhibitors to control its corrosion processes has been found effective (Argyropoulos *et al.*, 2021; Inamuddin *et al.*, 2021; Shuaib-Babata *et al.*, 2019; Shuaib-Babata *et al.*, 2018; Odewunmi *et al.*, 2015). Organic inhibitors have effectively isolated the metal from corrosion agents (Argyropoulos *et al.*, 2021; Geethamani, 2019; Brycki *et al.*, 2018; Rani and Basu, 2012) since the inorganic compounds

endanger the ecosystem (Ahmed *et al.*, 2020; Finšgar and Jackson, 2014; Tanwer and Shukla, 2022). One of the challenges of this type of inhibitor has been to develop a scalable particular approach to identify sustainable bio-material that portend excellent inhibition, which can be minimized by the introduction of coating or conditioning of the corrosive environment (Yang, 2021; Inamuddin *et al.*, 2021; Brycki *et al.*, 2018; Odusote *et al.*, 2016; Rani and Basu, 2012).

The effectiveness of an inhibitor is determined not only by the properties of the environment in which it operates, but also by the nature of the metal surface and area, the electrochemical potential at the interface, their charge density, mode of adsorption, and formation of metallic complexes. The sustainable green technique that prevents this electrochemical reaction is to isolate the metal with a surface film that dissolves significantly when exposed to high concentrations

of acids or bases (Eliaz, 2019; Shahmoradi *et al.*, 2021). Inhibitors typically react to the area of exposure of the metal surfaces in one of three ways. It generates a passive film, a barrier film of adsorbed inhibitor that may be merely a monolayer or less, or a thick barrier layer of reaction products or inhibitors (Inamuddin *et al.*, 2021; Branford and Bringas, 1993).

Prosopis Africana is a forest species used to combat the sustainable environment in sub-Sahara Africa due to increasingly difficult climate change. The potential of *Prosopis Africana* as a green inhibitor revealed its suitability, but the study was limited to the use of its seed extract *Prosopis Africana* (PASE) as a corrosion inhibitor of low carbon steel in an acidic medium (Shuaib-Babata *et al.*, 2019). Similarly, the stem bark, leaf and seed have been deployed to combat some medical and microorganism challenges (Ezike *et al.*, 2010; Ugwu *et al.*, 2018), however, the pods seem to portend agro-waste management challenges. The concern of this investigation is to further reduce the nuisance created by this plant for a sustainable environment by broadening the use of the *Prosopis Africana* as a green inhibitor. This present study explores the potential suitability of *Prosopis Africana* pod extract (PAPE) as a green corrosion inhibitor for mild steel in 1M HCl medium at room temperature and its efficiency using three different characteristic techniques. This would eventually assist in mitigating the adverse effects of pollution caused by irrational dumping of the *Prosopis Africana* pod into the environment, which is prevalent practice in rural areas and in some

Nigerian academic campuses where *Prosopis Africana* plants are common.

2. Materials and methods

2.1 Steel sample preparation

Mild steel was sourced within a major commercial steel market in Ilorin, Nigeria and its elemental compositional analysis was performed with Optical Emission Spectroscopic (OES) analysis (Spectromaxx LMF06, Agilent Scientific Instruments) at Midwal Engineering Materials Testing Laboratory, Lagos, Nigeria. The mild steel sample was cut into pieces measuring 2.5 x 2.9 x 0.1 cm, polished using emery paper of different grades, degreased in ethanol, dried in acetone and then stored in a desiccator following the guidelines in ASTM G1-30 and G4 and as an earlier practice by Shuaib-Babata *et al.* (2019).

2.2 Preparation of the *Prosopis Africana* pod extract

The agro-waste samples of *Prosopis Africana* were sourced from the main campus of the University of Ilorin, Ilorin Nigeria. Fig. 1 depicts the process where the *Prosopis Africana* pod was crushed to remove seeds from the pod. Subsequently, the pod was dried for seven (7) days and pulverized into fine powder. Extraction was carried out on Soxhlet apparatus with n-hexane as a solvent at Chemistry Lab, University of Ilorin, Nigeria. The extract was concentrated by evaporation. The stock solution was prepared from this extract and used throughout the investigations.



Fig. 1: *Prosopis Africana* pod oil extraction process

2.3 Preparation of medium solution

Based on Equation (1), the 1.0 molarity of the HCl acid (sp.gr.1.18) was prepared in the corrosion Laboratory.

$$\text{Molarity} = \frac{\text{Specific gravity of HCl} \times \text{Percentage of Purity}}{\text{Molecular Weight of HCl}} \quad (1)$$

2.4 Gravimetric analysis

The test specimens were pre-weighed and kept in a desiccator, which was later retrieved and completely soaked in a 200 ml solution of 1.0 M HCl with a various concentration of PAPE before the setup was sealed from the atmosphere. The exposure time of the test coupon in the acidic

medium was within twenty-four (24) to two thousand, one hundred and sixty (2160) hours following ASTM G1 and ASTM NACE/ASTM G31 standards. Fig. 2 shows the experiment set-up and some of the coupons in the analysis. The test specimens (coupons) were retrieved from the medium of exposure, cleaned with distilled water, and ethanol was used to rinse them. The acetone solvent was used to dry and remove the organic residues. The coupons were then reweighed on the weighing balance (HX 302, Mettler Toledo) of $\pm 0.01\text{g}$ accuracy). Equations (2) and (3) were respectively used to calculate the corrosion rate and inhibiting efficiency (IE %) of PAPE based on the weight loss measurement.

$$\text{Corrosionrate}(\text{mpy}) = \frac{kW}{ATD} \quad (2)$$

where (W) is the measured weight loss, (A) is surface area of steel in cm^2 , k is a constant = 3.45×10^6 mils per year (mpy), (D) is the steel density in (g/cm^3) and the exposure time (T) in hours were the parameters used in Equation (2).

$$I.E(\%) = \frac{CR_{Blank} - CR_{Inh}}{CR_{Blank}} \times 100 \quad (3)$$

The corrosion rate without the inhibitor is denoted with CR_{Blank} , while the rate with the presence of inhibitor is CR_{Inh} .



Fig. 2: (a) Weight loss set-up and (b) some of the cleansed specimens after corrosion test

2.5 Hydrogen evolution (gasometric) measurement

The gasometric was set up to monitor hydrogen evolution. The 200 ml of hydrochloric acid (1 M) was put into a two goose-neck flask. The preliminary amount of air in the 50 ml burette was measured. The test sample was measured and dipped into HCl solution and prompt sealing of flask with a cork to guarantee that no gases could escape. The volume of hydrogen gas produced by the corrosion reaction was estimated by measuring the change in the water level in the burette every 10 minutes for roughly 300 minutes. Other concentrations of PAPE of 0.2, 0.4, 0.6, 0.8 and 1.0 g/l were verified using the same process. Equation 4 was used to calculate the inhibition efficiency using gasometric measurements.

$$IE_{He} = 1 - \frac{CR_{Inh}}{CR_{abs}} \times 100\% \quad (4)$$

2.6 Tafel polarization procedures

The mild steel coupon for this process was cut into 1.0 x 1.0 cm dimensions using a guillotine machine. A flexible cable was connected to the specimen with the use of aluminium foil which held it together on a cup mould. An accelerator was added to the mixture of Polyester resin and hardener in the mould. The properly stirred solution was poured into the mould containing the specimens and allowed to solidify for 15-20 minutes. After solidification, the specimens were removed from the mould. The coupon was further polished using different grades of emery papers, to obtain a shiny reflective surface (like a mirror) before it was now exposed into the environment. Figure 3 shows the electrochemical measurement setup and stages in the preparation of specimen samples for Tafel polarization techniques.

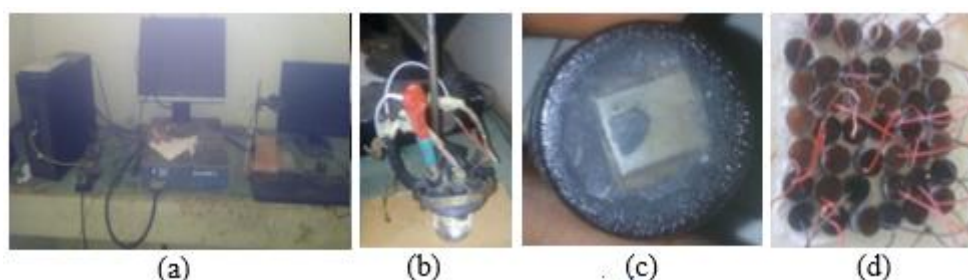


Fig. 3: (a) Electrochemical measurement analysis setup, (b) Connection of electrodes inside the medium, (c) mounted Tafel sample before polishing (d) Tafel samples ready for test

3. Results and discussion

3.1 Mild steel composition

The elemental constituents of the mild steel sample used in the preparation of the test coupons

are as presented in Table 1. The results revealed that the steel is a low carbon steel within the range of 0.01 – 0.3 wt.% carbon (Manglik, 2021; Mahmoud, 2013).

Table 1: Mild steel chemical compositions

Element	C	Mn	Si	Cr	Ni	Al	P	Sn	Fe
(wt%)	0.0112	0.102	0.0052	0.0342	0.0015	0.0134	0.0222	0.0053	99.700

3.2 Phytochemical analysis

The phytochemical screening of the *Prosopis Africana* pod analysis reveals that the extract contains saponin, alkaloids, tannin, phenol, steroids, flavonoid, and glycosides, which are among the active ingredients extracted from the pod as depicted in Table 2. It can be deduced that Saponin, Alkaloids and Tannin are the most abundant constituents and are the most powerful component in the pod for inhibiting corrosion, which is consistent with previous findings (Odewunmi *et al.*, 2015; Odusote *et al.*, 2016; Shuaib-Babata *et al.*, 2019).

Table 2: Qualitative and Quantitative Analyses of PAPE

Constituent (mg/100g)	PAPE
Saponin	108.71
Alkaloids	101.61
Tannin	83.81
Phenol	9.99
Steroids	7.80
Flavonoid	2.10
glycosides	1.06

3.3 Weight loss (gravimetric) technique

The differences in the weight loss recorded in the steel coupon with various concentrations of PAPE in 1M HCl at varying times of immersion are depicted in Fig. 4. It can be deduced from the graph that an increase in the concentration of inhibitor leads to a decrease in weight loss with a significant reduction for a longer duration of exposure. For instance, the weight loss was 0.07 g and 1.89 g after 168 hours of the dip with 1.0g/l concentration and without inhibitor (i.e., 0.0g/l), respectively. Furthermore, during the exposure to an acidic medium for 2160 hours, the weight loss was 0.32g and 2.93 g, respectively. The reduction could be adjudged to adsorption of the inhibitor to the metal surface with similar observations in Odusote *et al.* (2016) and Shuaib-Babata *et al.* (2019). This indicates that PAPE is effectively inhibited at all doses. More so, after 2160 hours of observation, as presented in Figure 4, the rate of weight loss is reduced as the concentration increases. This automatically implies that better inhibiting efficiency will be a higher inhibitor concentration, according to the results obtained by Petchiammal *et al.* (2012).

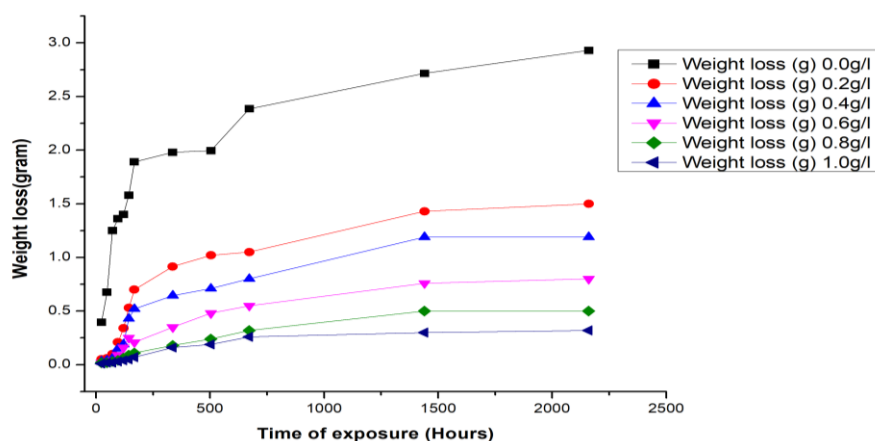


Fig. 4: Weight loss against time of mild steel in 1M HCl with PAPE inhibitor and without PAPE (0.0g/l) after 2160 hours of exposure

The disparity of corrosion rates of PAPE within the time of dip is illustrated in Fig. 5. The results indicate the corrosion rate of mild steel coupon decreases with an increase in the PAPE concentration. More so, the rate of corrosion also reduces with the increase in time of exposure. Sequentially, the increase in the proportion of

PAPE as an inhibitor will enhance the absorption rate of the inhibitor elements on the surface of mild steel that leading to a reduction in corrosion (El Ibrahim *et al.*, 2020; Olusegun *et al.*, 2018; Alaneme *et al.*, 2015; Arukalam *et al.*, 2015; Eddy *et al.*, 2015; Chakravarthy and Mohana, 2014; Oguize *et al.*, 2015).

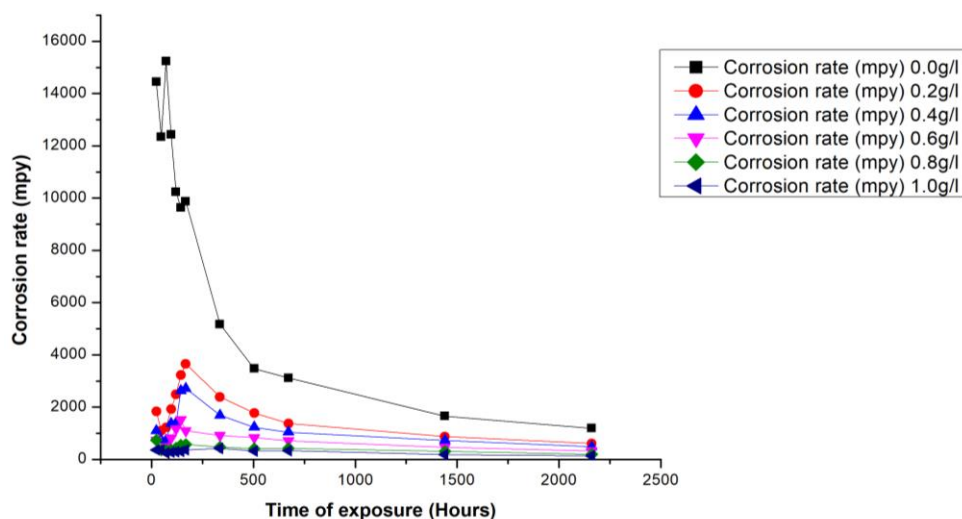


Fig. 5: Corrosion rate (mpy) against time (hours) of mild steel in 1M HCl with and without (0.0g/l) PAPE as inhibitor after 2160 hours of exposure

The Inhibition Efficiency against the time curve at a varying concentration of PAPE in 1M HCL is presented in Fig. 6. The result indicates that the inhibiting efficiency increase with the increasing concentration of the extract, but it is not consistent with an increase in time. At 1.0g/l PAPE concentration, the optimum inhibitory effectiveness of 97.79% was obtained. The specimens in HCl

media containing PAPE, on the other hand, were intact after 2160 hours of exposure. The efficiency might be attributed to the transition of the metal contact from an active to a passive state, which give rise to creation of a protective layer over the samples surface and edge(Shuaib-Babata *et al.*, 2019).

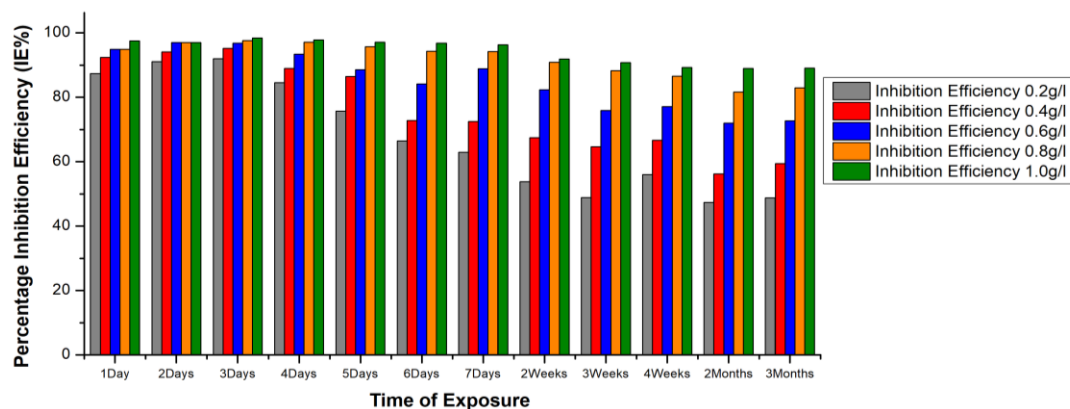


Fig. 6: Inhibition efficiency of *Prosopis Africana* pod extract (PAPE) on the corrosion of mild steel in 1M HCl solutions

3.4 Gasometric test

The amounts of hydrogen gas evolved in the existence and nonexistence of PAPE was analysed. Fig. 7 shows the manner in which the volume of hydrogen gas developed increases over time but reduces when the concentration of PAPE extract increases. Similar trends were observed in the green inhibitive potential as the concentration increases (Nya *et al.*, 2018; Odusote *et al.*, 2016; Abeng *et al.*, 2013). Furthermore, variation of

inhibition efficiency against time is illustrated in Fig. 8. The figure shows that when the concentration of the inhibitor extracts increases, the inhibition efficiency increases. This shows that the metal's breakdown rate was slowed, resulting in a decrease in H^+ . In 1.0 g/l and blank solutions, the lowest and largest volumes of hydrogen evolved 5.20 ml and 27.00 ml respectively were found. This could be due to the extract inhibitor's creation of a passive layer on the metal's surface.

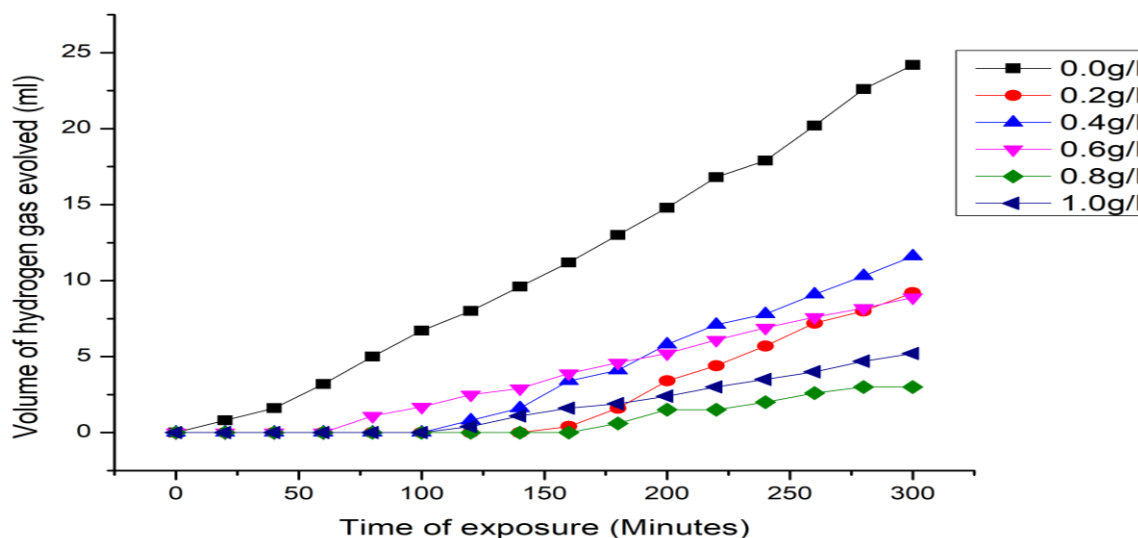


Fig. 7: Evolution rate of hydrogen gas in the acidic medium with PAPE concentrate

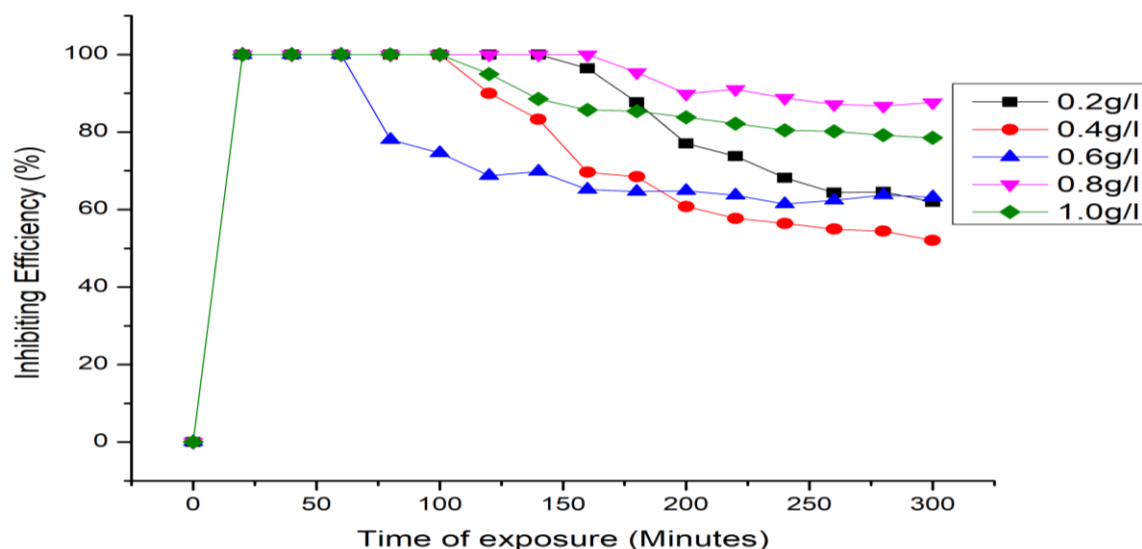


Fig. 8: Variation of inhibition efficiency vs. time of exposure of PAPE concentrations

3.5 Tafel polarization

The Tafel polarization curves obtained for mild steel without PAPE and with PAPE at different concentrations is shown in Fig. 7. Table 3 reveals the important polarization parameters such as

corrosion potential (E_{corr}), Cathodic (β_c) and anodic (β_a) Tafel slopes, corrosion density (I_{corr}), and surface coverage (θ) for mild steel corrosion with and without inhibitor.

Table 3: Tafel polarization parameters for corrosion of test coupon with and without PAPE varying concentration

Extracts	Conc. (g/l)	I_{corr} (μA)	E_{corr} (mV)	β_c (mV)	β_a (mV)	CR (mmpy)	IE%	θ
Blank	0.0	1274	-439.179	117.366	205.646	14.794		
PAPE	0.6	743.062	-421.034	84.021	111.158	8.6222	41.67488	0.416749
	0.8	576.027	-441.088	498.129	5456	6.684	54.78595	0.547859
	1.0	247.281	-430.312	87.365	68.548	2.8694	80.59019	0.805902

Furthermore, the PAPE Tafel polarization analysis indicates the corrosion potentials (E_{corr}) shifted toward the negative potentials for the test coupons in the PAPE inhibitor. However, the corrosion current density (I_{corr}) values decrease as the concentration of the extracts increased while the estimated (IE) of the inhibitor increases. The highest (IE) of 80.59 % was achieved at 1.0 g/l concentration. The difference in Tafel slopes of cathodic (β_c) and anodic (β_a) interactions with and

without the PAPE is seen in Figure 9. This demonstrates that perhaps the inhibitor influences both the reaction at the anode and cathode. In the HCl solution, some of the components present in the studied extracts may be protonated and these protonated species may adsorb directly on the cathodic sites of the mild steel surface. According to Odusote *et al.* (2016), the inhibitive mechanism is activated by basically obstructing the available cathodic and anodic sites on the metal surface.

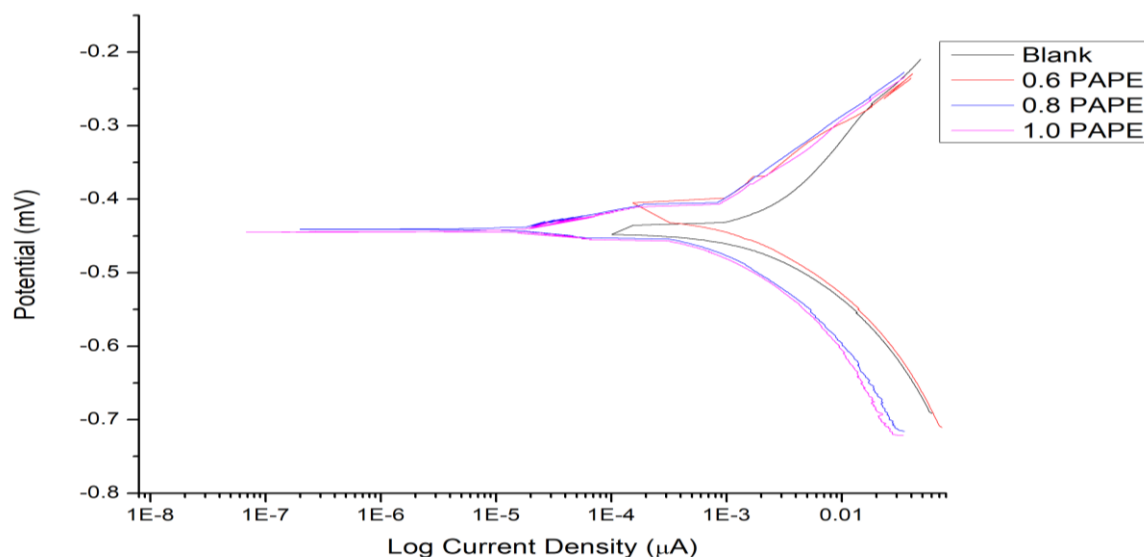


Fig. 9: Polarization curves of mild steel in 1M HCl with and without PAPE Inhibitor

4. Conclusion

In the study of corrosion inhibition of mild steel in hydrochloric acid solution by the PAPE using the techniques highlighted, the following are concluded:

- The mild steel corrosion inhibition rate in HCl solution increases with an increase in the concentration of PAPE giving rise to inhibiting efficiency extract.
- The green inhibitor (*Prosopis African* pod: PAPE) displayed its best inhibiting efficiency (IE) of 97.14% at a 1.0 g/l concentration continuously for 2160 hours of dip in 1M HCl media for mild steel in gravimetric technique.
- Extracts of *Prosopis Africana* pods act as varied-typed inhibitors which influence the reaction of cathodic hydrogen evolution as well as the anodic dissolution of the steel coupon as displayed in the Tafel polarization tests. The percentage of inhibiting efficiency is increased based on the green inhibiting concentrate; therefore, with 1.0 g/l extract concentrate provided a superlative inhibiting efficiency of about 80.59%.
- The PAPE extract could contribute to the evolving sustainable green inhibitor of mild steel in acidic environment.

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