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Azadirachta Indica's adsorptive behavior on mild steel in a sulfuric acid medium

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Abstract
This research investigated the corrosion of mild steel by exploring the anti-corrosion potentials of Azadirachta Indica leaf extract in 1.5 M of H_2SO_4 acid medium. Assessment was made using weight loss, fourier transform infrared spectroscopy, optical microscopy, and potentiodynamic polarization method. Measurements revealed that on the first four days, samples with 4g/l, 5g/l, and 6g/l extract showed the best inhibitory efficiency of 72.03%, 71.89%, and 71.33%, respectively. While in general, inhibition efficiency was found to decrease as exposure time increases. The computed ΔG_{ads} values for the extract ranged from -6.993 to -9.675 kJ mol^{-1}, while the adsorption isotherm data fitted well into the Temkin isotherm, confirming a physisorption interaction between the extract molecules and the surface of the mild steel coupons. Going by the results obtained, the extract can be applied against corrosion attack on mild steel and other metals in acidic media.

Keywords: Adsorption, concentration, inhibition efficiency, organic extract, weight loss.

1. Introduction

Among all the classes of engineering material, it is a common knowledge that metals are the least resistant to corrosion. This is because despite the fact that ceramics are considered as an important class of material with great attractive features like corrosion resistant, yet they are not as easy to design with when compared to metals since they have no ductility, low tolerance for stress concentrations (i.e., cracks or holes), but ductile metals accommodate stress concentrations by deforming in a way which redistributes the load more evenly; and by so doing, they can be used under static loads no matter how little the yield strength of the material (Ashby, 1999). In as much as good designs exploits the superior properties of metals, time to time investigation of the corrosion rate of metals is paramount.

Mild steel is less expensive than other forms of steel and metals, this led to its applicability as a structural material. Also known as simple carbon steel, mild steel has numerous applications due to its unique characteristics (Kumar et al., 2016). But because of its low corrosion resistance in a neutral and acidic environment, it is regarded a considerable difficulty. Severe corrosion attacks are known to happen in the acidic environment (Kanayo, Joseph, & Tomi, 2015; Nwigwe et al., 2019; Tanwer, & Shukla, 2022). Corrosion is associated with loss of metal caused by corrosive substances (Salman et al., 2019). Therefore, corrosion prevention in mild steel is important both conceptually and practically (Melchers, 2019), since corrosion results to safety problems as well as huge financial loss (Verma, Ebenso, & Quraishi, 2021). Because it is impossible to completely eradicate corrosion, corrosion

science and engineering must focus on regulating instead of preventing it (Oyedeko, Lasisi, & Akinyanju, 2022). The use of corrosion inhibitors is an appealing method of fighting corrosion (Okiongbo, & Ogobiri, 2013). Corrosion inhibitors are chemicals that, when used in small amounts in a corrosive medium, reduce the rate of corrosion by providing a barrier through creating an adsorbed film or by slowing the cathodic and/or anodic reaction (Sastri, 2011; Bilgiç, 2022).

Due to the toxicity and/or high cost of several chemical inhibitors now in use, it is vital to create environmentally friendly and low-cost alternatives (Miralrio, & Vázquez, 2020; Nwigwe, Mbam, & Umunakwe, 2019). Several authors have examined and documented the ability of extracts of several plants, such as Azadirachta indica, carica papaya, ceratonia silique, vernonia amygdalina, thymus algeriensis, eruca sativa, beta vulgaris, jatropha curcas, camellia sinensis, aquilaria crassna, justicia secunda, spirulina platensis, elaeis guineensis, xanthan gum, gingko biloba, chamaerops humilis, rhizophora apiculate, allium cepa, citrus aurantium and others, to minimize metal dissolution in various strong acids for use as green inhibitors (Oyedeko, Lasisi, & Akinyanju, 2022), (Nwigwe, Mbam, & Umunakwe, 2019; Kamal, & Sethuraman, 2012; Asaad et al., 2013; Mobin, & Rizvi, 2016; Singh et al., 2015; Fekkar et al., 2020; Asaad et al., 2017; Aiboudi et al., 2019; Hassan, Khadom, & Kurshed, 2016; Helen et al., 2014; Peter, & Sharma, 2017; Abro, Abro, & Assad, 2020; Ghazi, Siniti, & Elattari, 2022; Khadraoui et al., 2015; Alrafai, 2022; Joycee et al., 2022; Ajayi, Odusote, & Yahya, 2014; Loto, & Loto, 2016; Iroha, & Maduelosi, 2021). The extract of these plants, as well as the efficiency of their corrosion inhibition properties, varies greatly depending on the plant's part and geographical area.

The leaves of Azadirachta indica extract has not been adequately explored to combat the corrosion of mild steel in acidic environments. Different techniques such as potentiodynamic polarization, optical microscopy, fourier transform infrared spectroscopy, and weight loss were used for the experiment and to analyze results. It is believed that the results will be relevance to corrosion experts and other professionals in this field.

2.0 Experimental

2.1 Materials

The mild steel sheet used for this study was of the composition (wt %) C (0.15), Mn (0.6), P (0.36), and Si (0.03) and Fe (balance). The sheet was marked and press cut with hand sharer to produce many coupons with same dimension of 2cm × 2cm × 2mm. Before the corrosion test, the coupons were immersion into undiluted sulfuric acid for pickling so as to remove the black oxide that formed on the surface of the sheet due to long exposure to the atmosphere. This was done to properly expose the main coupons bodies for direct corrosion attack. Pickling is preferred to ordinary polishing using emery papers to ensure equal removal of the oxide surface layer and it is faster. Hence, samples were pickled for 10 minutes in sulfuric acid, removed and placed into distilled water, followed by degreasing with absolute ethanol and dried using acetone. All of the chemicals used were of Analar grade and double-distilled water was used for 1.5 M of H_2HO_4 preparation.

2.2 Preparation of the leaf extract

Leaves of Azadirachta indica used for this study were collected as required from plants from the city around the Alex Ekwueme Federal University, Ndufu-Alike, Ikwo, Nigeria. These were dried under the Varanda using room temperature and the scorching heat from the sun, crushed into powder form using laboratory mortar and pestle. 500g of the power was soaked in a 2 litre solution of ethanol for five days, the resultant solution was filtered with Whatman Grade 1 filter paper with 10mm hole size. The filtrate was concentrated into a thick syrup using a Thermostatic Water Bath (model No: Dk-420, S.N: 31660). The thick syrup was spread in a laboratory pan and allowed for 48 hours to dry through the evaporation of the excess ethanol and stored. From the stock solution, 2, 3, 4, 5 and 6g concentrations were measured and dissolved into five different 200ml of 1.5 M of H_2HO_4 test solution, excluding the control that was not with the extract.

Table 1: Phytochemical components of Azadirachta indica leaf extract (Madaki, Kabiru, & Mailafiya, 2016):

Phytochemical	Result
Cardiac glycosides	+
Saponins	+
Steroids	+
Flavonoids	+
Alkaloids	+
Tannins	+
Phenols	+
Terpenes	+
Anthraquinones	-
Carbohydrates	-
Reducing sugar	+

Absent -, present +

3.0 Results and Discussions

3.1. Weight loss measurements

Immersed samples were first allowed for two days to enable the inhibitor to get properly absorbed on the coupons. And after that, coupons were subsequently removed at every 2 days interval due to the high acidity nature of the medium, as it was observed that longer exposure time may not be favourable to the unprotected (control) samples. At every removal, coupons were placed into distilled water, followed by degreasing with ethanol and dried using acetone before their weight loss were taken.

3.2 Calculation of the corrosion rate by weight loss

By weight loss technique, the corrosion rates of mild carbon steel coupons were calculated using the formula (Ovri, Okeahialam, & Onyemaobi, 2013),

$$CR = \frac{534W}{DAT} \qquad (1)$$

where, CR = corrosion rate in mile per year (mpy), W = weight loss in grams (g), D = density of steel (7.87 g/cm^3), A = the total surface area (cm^2), and T = exposure time in hours (hrs). Inhibition efficiency is calculated as represented in equation (2) below.

$$Inhibition\ efficiency = \left[\frac{CR_{0g/l} - CR_{inh}}{CR_{0g/l}}\right] \times 100\ \% \qquad (2)$$

where $CR_{0g/l}$ and CR_{inh} are the corrosion rate in the absence and presence of the plant extract. The results as calculated are shown in table 2.

The dimensions of the coupons used which are rectangular in shape is as given below.
Length = L = 20 mm = 2 cm
Breath = B = 20 mm = 2 cm
Thickness = T = 2 mm = 0.2 cm
D_h = diameter of holes = 5 mm = 0.05 cm
The total surface area, A, of the rectangular steel coupons used in this investigation was calculated using the following relationship (Ovri, Okeahialam, & Onyemaobi, 2013),

$$A = 2\left([LB + BT + LT] - 2\left(\pi\left({D_h}^2\right)/4\right)\right) \qquad (3)$$

Therefore, A = 2(2 × 2 + 2 × 0.2 + 2 × 0.2) – 2(3.142 × (0.5)^2/4) = 9.6 – 2(0.07) = 9.207 cm^2

Table 2: Acidic (1.5 M of H_2SO_4) medium

0g/l concentration of extract							2g/l concentration of extract					
Time (days)	Initial weight (g)	Final weight (g)	Weight loss (g)	Corrosion rate (mpy)			Time (days)	Initial weight (g)	Final weight (g)	Weight loss (g)	Corrosion rate (mpy)	Inhibitor Efficiency (%)
4	4.384	2.516	1.868	0.1434			4	4.283	3.674	0.609	0.0467	67.43
6	4.202	2.076	2.126	0.1088			6	4.658	3.733	0.925	0.0473	56.52
8	4.353	2.243	2.110	0.0809			8	4.774	3.651	1.123	0.0431	46.72
10	4.539	2.245	2.294	0.0704			10	4.480	3.091	1.389	0.0426	39.48
12	4.333	2.299	2.034	0.0520			12	4.479	3.019	1.460	0.0373	28.26
14	4.787	2.554	2.233	0.0489			14	4.450	2.975	1.475	0.0323	33.94
3g/l concentration of extract							4g/l concentration of extract					
Time (days)	Initial weight (g)	Final weight (g)	Weight loss (g)	Corrosion rate (mpy)	Inhibitor Efficiency (%)		Time (days)	Initial weight (g)	Final weight (g)	Weight loss (g)	Corrosion rate (mpy)	Inhibitor Efficiency (%)
4	4.247	3.636	0.611	0.0469	67.29		4	4.087	3.564	0.523	0.0401	72.03
6	4.705	3.771	0.934	0.0478	56.06		6	4.541	3.605	0.936	0.0479	55.97
8	4.611	3.378	1.233	0.0473	41.53		8	4.566	3.370	1.196	0.0459	43.26
10	4.825	3.469	1.356	0.0416	40.90		10	4.599	3.279	1.320	0.0405	42.47
12	4.318	2.809	1.509	0.0386	25.76		12	4.247	2.836	1.411	0.0361	30.57
14	4.534	3.035	1.499	0.0328	32.92		14	4.750	2.925	1.825	0.0400	18.20
5g/l concentration of extract							6g/l concentration of extract					
Time (days)	Initial weight (g)	Final weight (g)	Weight loss (g)	Corrosion rate (mpy)	Inhibitor Efficiency (%)		Time (days)	Initial weight (g)	Final weight (g)	Weight loss (g)	Corrosion rate (mpy)	Inhibitor Efficiency (%)
4	4.176	3.650	0.526	0.0403	71.89		4	4.105	3.569	0.536	0.0411	71.33
6	4.694	3.773	0.921	0.0471	56.70		6	4.225	3.473	0.752	0.0384	64.70
8	4.352	3.331	1.021	0.0391	51.66		8	4.440	3.455	0.985	0.0378	53.27
10	4.981	3.564	1.417	0.0435	38.21		10	4.626	3.378	1.248	0.0383	45.59
12	4.333	2.976	1.357	0.0347	33.26		12	4.286	3.004	1.282	0.0328	36.92
14	4.543	3.057	1.486	0.0325	33.53		14	4.777	2.954	1.823	0.0399	18.40

The results on table 2 shows that the samples in all experienced varying amounts of weight loss in all the concentrations they were subjected to. But the presence of uniform corrosion attack dominated in each coupon's surface, though the 0g/l specimens suffered minor pitting corrosion which is believed to be due to lack of inhibitor with appreciable uniform corrosion. The uniform attack was fairly and evenly distributed over the surface area of the coupons, which resulted to an almost even reduction in thickness. Usually, homogeneous materials like the kind used in this investigation that shows little or no reasonable likelihood for passivation in their current environment are pruned to suffer this kind of corrosion attack. And among the methods known for combating uniform corrosion attack is the use of inhibitors (Fontana, 1987; Bardal, 2004). 0g/l specimens suffered the highest weight loss which is responsible for the highest corrosion rate it also recorded. Samples in 4g/l, 5g/l and 6g/l concentrations indicated the best inhibition efficiencies (72.03%, 71.89%, and 71.33%) on their first 4 days respectively. In general, inhibition efficiency was observed to be decreasing with increase in exposure time. The least inhibition efficiencies of 18.20% and 18.40% were recorded by 4g/l and 6g/l concentrations of extract on their last day, respectively.

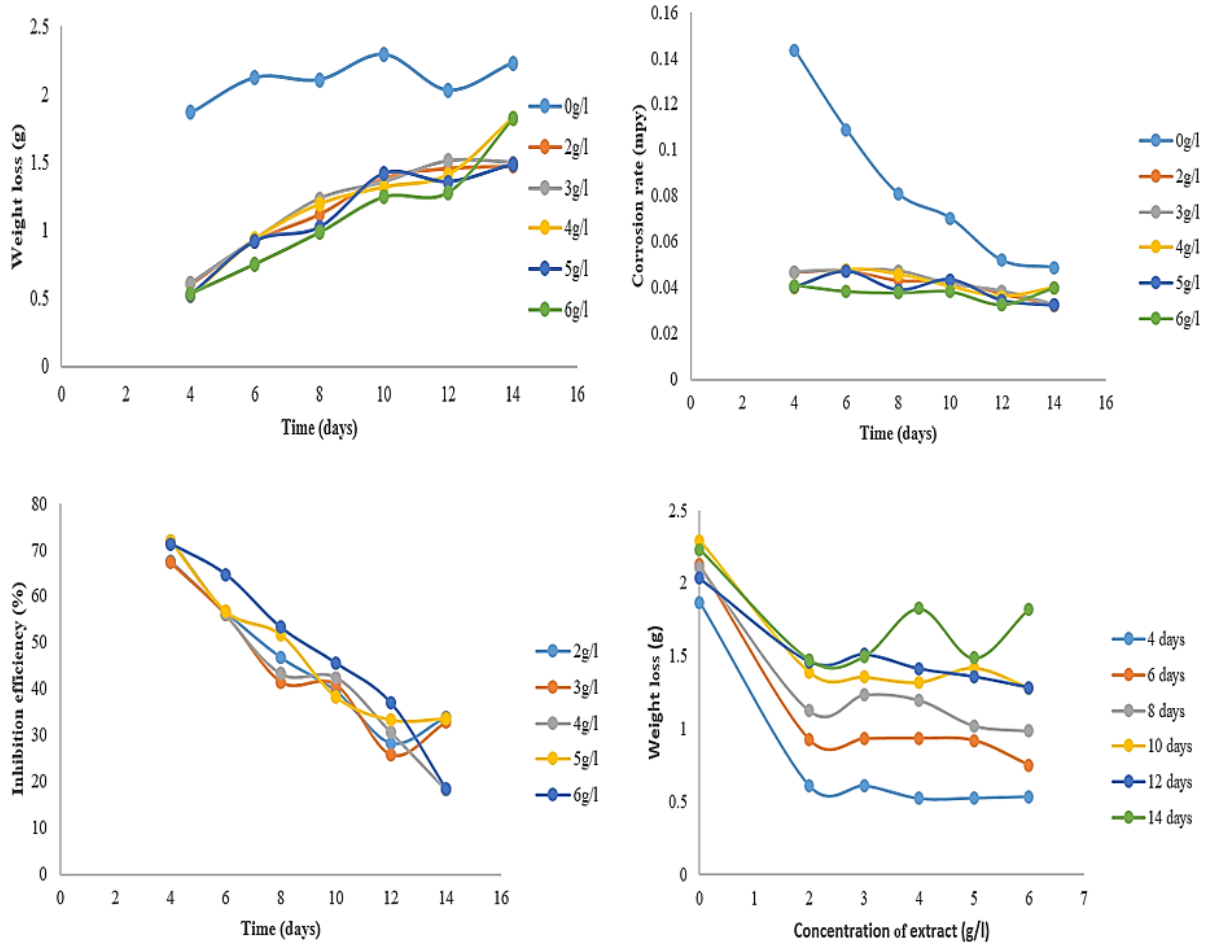

Figure 1: Plots of different variables of mild steel surface exposed to 1.5M of H_2SO_4 medium without/with Azadirachta indica extract

Figure 1 is the plots of weight loss, corrosion rate, inhibition efficiency and concentration of extract for 0g/l to 6g/l extract concentrations. The weight loss increases with increase in time, while the corrosion rate and the inhibition efficiency both decreases with increase on time of exposure for the different concentrations of extract used. "The behavior is attributed to a higher adsorption level of active inhibitor molecules from the extracts on the metal surface forming a thin film on metal surface to prevent further attack from the corrosive environment" (Oyedeko, Lasisi, & Akinyanju, 2022).

3.3 Fourier transform infra-red (FTIR) analysis

The Fourier Transform Infrared (FTIR) was done with Cary 630 FTIR machine, a product of Agilent Technologies at the Chemical Engineering laboratory, Alex-Ekwueme Federal University, Ndufu-Alike, Ikwo, Ebonyi state, Nigeria. The test was able to evaluate the nature of the film formed on the surface of the metal. The figure 2 shows the FTIR spectra of the Azadirachta indica extract on the coupons in the as-received form, blank and different inhibition concentrations respectively. To have a better understanding of the probable interactions between the adsorbed inhibitor and the mild steel surface in the sulfuric medium, FTIR measurements were performed. However, the effectiveness of an inhibition is determined by the inhibitor's molecular structure (Hassan, Khadom, & Kurshed, 2016). Since the stock solution was extracted using ethanol, it justifies the presence of ethanol band in the spectra. However, the properties of ethanol are responsible for the stretching vibrations of the hydroxyl group (-OH) which are seen at the peaks of every stretching vibration at 3906.3 cm^{-1}, 3855.9 cm^{-1}, 3891.3 cm^{-1}, 3837.3 cm^{-1}, and 3872.7.21 cm^{-1} for sample B to F respectively as inhibited. Figure 2 shows the presence of cardiac glycosides, saponins, steroids, flavonoids, alkaloids, tannins, phenolic compounds, terpenes, anthraquinones, carbohydrates and reducing sugar in all the samples with extract.

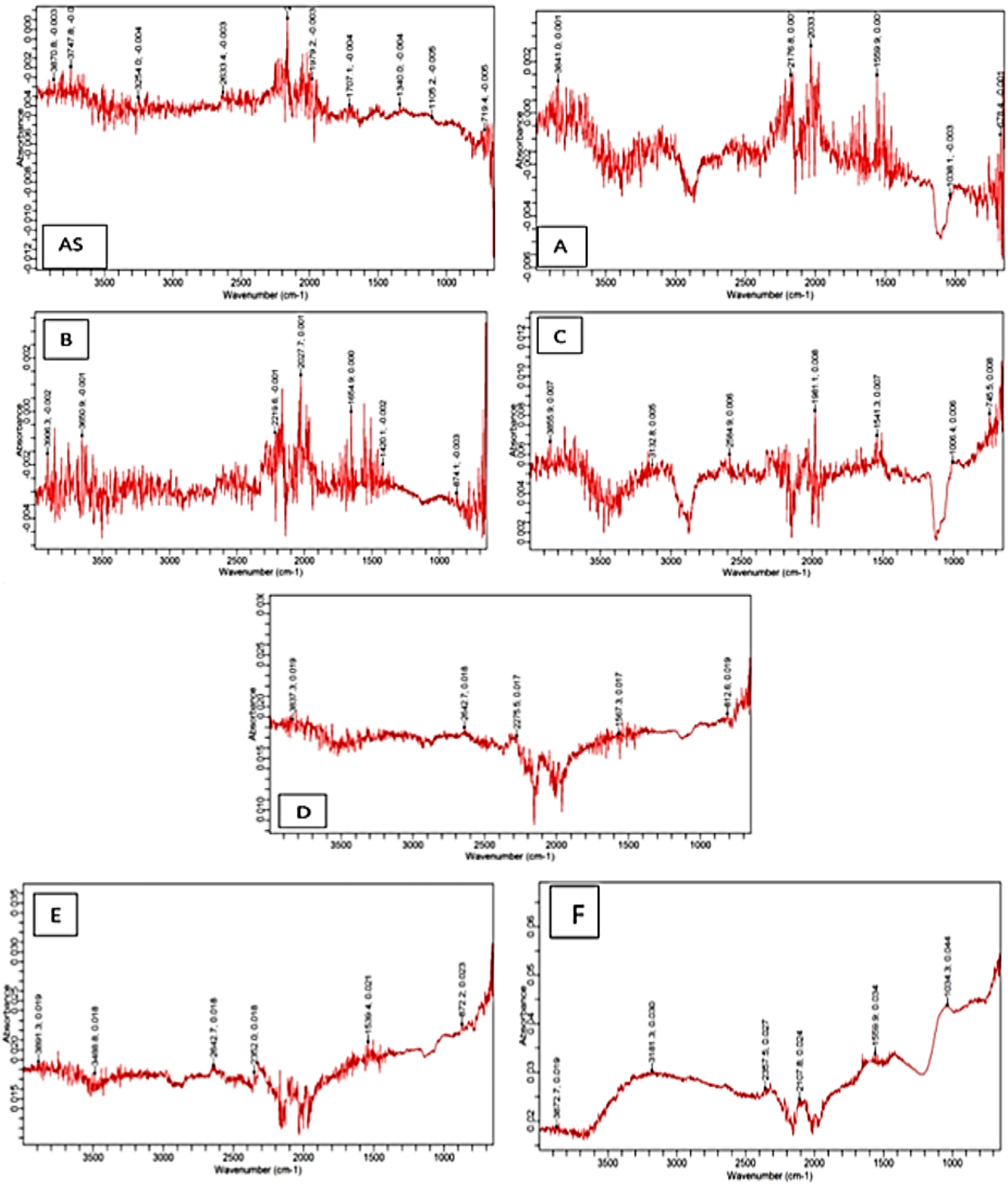

Figure 2: Mild steel FT-IR spectra, (AS) for As-received, (A) after 12 days immersion in 1.5 M of H_2HO_4 test solution with 0g/l (blank), (B) after 12 days immersion with 2g/l plant extract, (C), after 12 days immersion with 3g/l plant extract, (D) after 12 days immersion with 4 g/l plant extract, (E) after 12 days immersion with 5g/l plant extract, and (F) after 12 days immersion with 6g/l plant extract concentration in 1.5 M of H_2HO_4 test solution

However, it is considered that the presence of tannins in the extract is one of the major factors accountable for the inhibitory property of the extract (Oyedeko, Lasisi, & Akinyanju, 2022; Hassan, Khadom, & Kurshed, 2016). While the peak vibrations of sample AS and A without extract are seen at location 3870.8 cm^{-1} and 3841.0 cm^{-1} respectively. In summary, the peaks are in the range of 4000 – 650 cm^{-1} signifying the presence of different functional groups. For instance, sample B which has its peaks at 3906.3, 2219.6, 1654.9 and 874.1 (cm^{-1}) represents -OH stretching, -C=O stretching, -C-O stretching and -C-O stretching respectively.

3.4 Preparation of coupons for optical metallography

Coupons were prepared and analyzed at the Materials and Metallurgy laboratory, Federal University of Technology, Owerri, Imo state, Nigeria. The instrument used for the investigation of the microstructures of the coupons was Keyence Digital Microscope, model VH-Z450 with high magnification lens. A sample from the as-received was mounted and ground with different grades of emery paper sizes in the order of 220, 400, and 600-grits under running water till a smooth surface was obtained, and thereafter, they were polished with cloth covered with a solution of silicon carbide until a mirror-like smooth surface was obtained. Finally, etching was done with 2% nitric acid and after which the surfaces were immediately observed with the metallurgical microscope. While the immersed samples were simply viewed without mounting and etching so as not to remove the thin film protective effect formed on the surface of specimens by the extract.

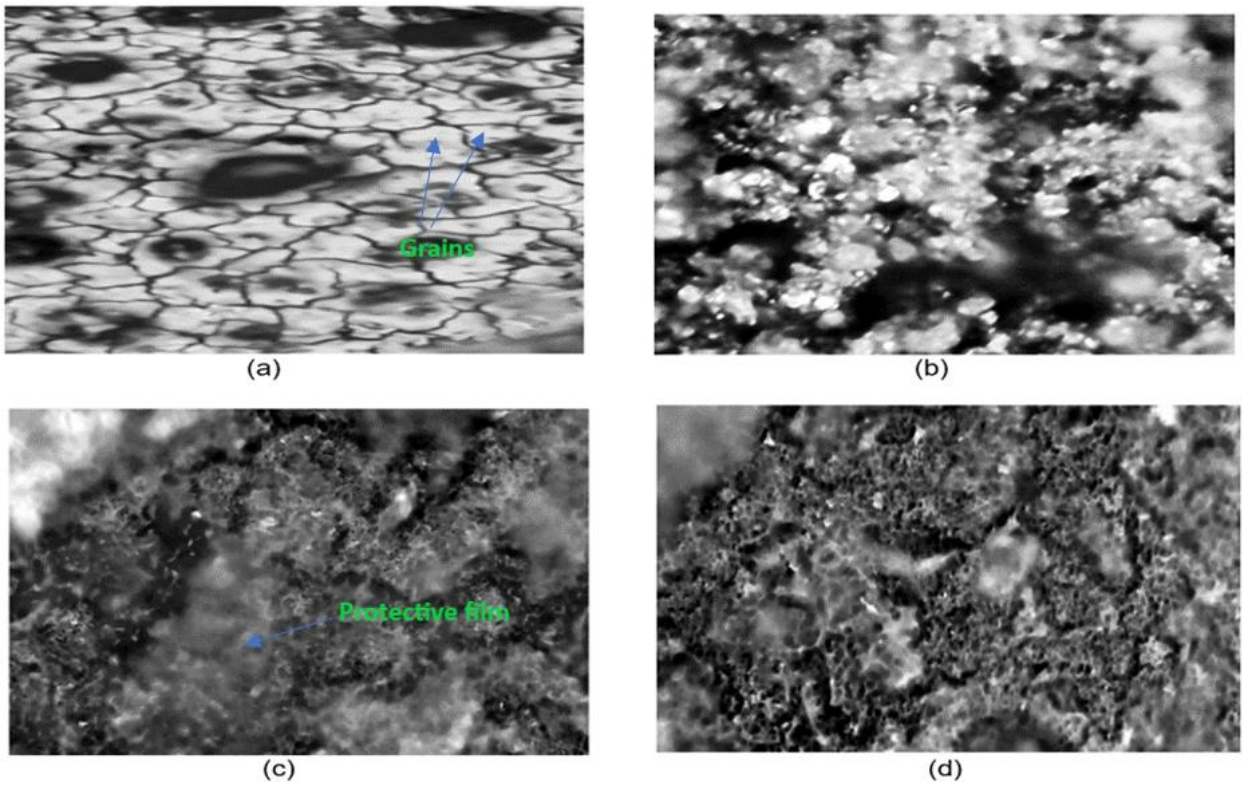

Figure 3: Optical micrographs of samples, (a) for as-received, (b) 0g/l (blank) after 12 days immersion in 1.5 M of H_2HO_4 test solution, (c) after 12 days immersion with 5g/l plant extract, and (d) after 12 days immersion with 6g/l plant extract in 1.5 M of H_2HO_4 test solution

The micrograph on figure 3 (a) for as-received sample displays clearly the grains and their boundaries since the sample was not immersed, that of (b) which was the control sample has no inhibitor and only the grains could be seen, while that of (c) and (d) with inhibitors has areas exposed and areas covered by a shadow-like images which is believed to be the protective film form by the extract to protect the surface of the mild steel from corrosion attack.

3.5 Applicability of the adsorption isotherms

Adsorption on the metal surface is generally agreed to be the vital process in the action of inhibitors in acid solution. This assumes that corrosion attacks are prevented from occurring on the area of the metal surface covered by adsorbed inhibitor species, whilst they occur normally on the inhibitor-free area (Yaro, Khadom, & Wael, (2013). Adsorption isotherms are very useful for determining the nature of the relationship and/or interaction between inhibitor molecules and metal substrate surfaces (Mistry, & Jauhari, 2014; Alaneme, Olusegun, & Adelowo, 2016). Langmuir, Frumkin, Temkin, and Flory-Huggins are some of the most commonly utilized adsorption isotherms (Iroha, & Maduelosi, 2021).

Table 4: Adsorption parameters

Weight loss values							**2g/l concentration of extract**					
Time (days)	**0g/l Weight loss (g)**	**2g/l Weight loss (g)**	**3g/l Weight loss (g)**	**4g/l Weight loss (g)**	**5g/l Weight loss (g)**	**6g/l Weight loss (g)**	θ	$\left[\frac{\theta}{1-\theta}\right]$	$\left[\frac{C_{inh}}{\theta}\right]$	$\left[\frac{\theta}{C_{inh}}\right]$	$[1-\theta]$	$C_{inh}\left[\frac{\theta}{1-\theta}\right]$
4	1.868	0.609	0.611	0.523	0.526	0.536	0.673	2.058	2.971	0.336	0.327	4.116
6	2.126	0.925	0.934	0.936	0.921	0.752	0.564	1.293	3.546	0.282	0.436	2.586
8	2.110	1.123	1.233	1.196	1.021	0.985	0.467	0.876	4.282	0.233	0.533	1.752
10	2.294	1.389	1.356	1.320	1.417	1.248	0.394	0.650	5.076	0.197	0.606	1.3
12	2.034	1.460	1.509	1.411	1.357	1.282	0.282	0.392	7.092	0.141	0.718	0.784
14	2.233	1.475	1.499	1.825	1.486	1.823	0.513	1.053	3.898	0.256	0.487	2.106
3g/l concentration of extract							**4g/l concentration of extract**					
Time (days)	θ	$\left[\frac{\theta}{1-\theta}\right]$	$\left[\frac{C_{inh}}{\theta}\right]$	$\left[\frac{\theta}{C_{inh}}\right]$	$[1-\theta]$	$C_{inh}\left[\frac{\theta}{1-\theta}\right]$	θ	$\left[\frac{\theta}{1-\theta}\right]$	$\left[\frac{C_{inh}}{\theta}\right]$	$\left[\frac{\theta}{C_{inh}}\right]$	$[1-\theta]$	$C_{inh}\left[\frac{\theta}{1-\theta}\right]$
4	0.672	2.048	4.464	0.224	0.328	6.144	0.720	2.571	5.555	0.180	0.28	10.284
6	0.560	1.272	5.357	0.186	0.44	3.816	0.559	1.267	7.155	0.139	0.441	5.068
8	0.415	0.709	7.228	0.138	0.585	2.127	0.433	0.763	9.237	0.108	0.567	3.052
10	0.408	0.689	7.352	0.136	0.592	2.067	0.424	0.736	9.433	0.106	0.576	2.944
12	0.258	0.347	11.627	0.086	0.742	1.041	0.306	0.440	13.071	0.076	0.694	1.76
14	0.328	0.488	9.146	0.109	0.672	1.464	0.182	0.222	21.978	0.045	0.818	0.888
5g/l concentration of extract							**6g/l concentration of extract**					
Time (days)	θ	$\left[\frac{\theta}{1-\theta}\right]$	$\left[\frac{C_{inh}}{\theta}\right]$	$\left[\frac{\theta}{C_{inh}}\right]$	$[1-\theta]$	$C_{inh}\left[\frac{\theta}{1-\theta}\right]$	θ	$\left[\frac{\theta}{1-\theta}\right]$	$\left[\frac{C_{inh}}{\theta}\right]$	$\left[\frac{\theta}{C_{inh}}\right]$	$[1-\theta]$	$C_{inh}\left[\frac{\theta}{1-\theta}\right]$
4	0.718	2.546	6.963	0.149	0.282	12.73	0.713	2.484	8.415	0.118	0.287	14.904
6	0.566	1.304	8.833	0.113	0.434	6.52	0.646	1.824	9.287	0.107	0.354	10.944
8	0.516	1.066	9.689	0.103	0.484	5.33	0.533	1.141	11.257	0.088	0.467	6.846
10	0.382	0.618	13.089	0.076	0.618	3.09	0.455	0.834	13.186	0.075	0.545	5.004
12	0.332	0.497	15.06	0.066	0.668	2.485	0.369	0.584	16.26	0.061	0.631	3.504
14	0.334	0.501	14.97	0.066	0.666	2.505	0.183	0.223	32.786	0.030	0.817	1.338

The degree of surface coverage (θ) at different concentrations of the extract in 1.5 M of H_2HO_4 medium from the gravimetric techniques was used to evaluate the best isotherm that fits into the experimental data obtained using the equation below:

$$\theta = \left[\frac{W_{0g/l} - W_{inh}}{W_{0g/l}}\right] \quad (4)$$

where $W_{0g/l}$ and W_{inh} are the weight loss values in the presence and the absence of inhibitor, respectively. At any given time, the inhibitor molecules cover a fraction (θ) of the metal surface, and the uncovered fraction (1- θ) reacts with acid medium as it would in the absence of the inhibitor [41].

$$\frac{C_{inh}}{\theta} = \frac{1}{K} + C_{inh} \qquad (Langmuir\ isotherm) \quad (5)$$

$$exp(-2a\theta) = KC_{inh} \qquad (Temkin\ isotherm) \quad (6)$$

where θ is the degree of surface coverage of the inhibitor, C_{inh} is the concentration of the extract, and K is the adsorption equilibrium constant. For Langmuir isotherm, the plots of C_{inh}/θ against C_{inh} are shown in figure 4 (a)

below with the intercepts of the plots equated to $1/K$. The linear plots obtained, could not show good regression coefficients (R^2), this suggests that the inhibitor's adsorption does not follows Langmuir adsorption isotherm. In Temkin expression, a is an interaction parameter that is related to the molecules of the extract that is been adsorbed on the surface of the coupons (also known as molecular interaction parameter). K is the intercept parameter. The plots of θ against C_{inh} has the best fitted straight lines since it is evident that all the linear correlation coefficients are almost equal to unity, with the slope values also very close to 1, indicating the extract adsorption on the mild steel surface obeys Temkin adsorption isotherm.

The values for equilibrium constant of adsorption (K) for Langmuir and Temkin isotherms were used to calculate the ΔG_{ads} for concentrations 2g/l, 3g/l, 4g/l, 5g/l and 6g/l, respectively. The equilibrium constant of adsorption (K) is related to the standard free energy of adsorption (ΔG_{ads}) as given below (Vimala, Leema, & Raja, 2011):

$$\Delta G_{ads} = -2.303RT\ log\ (55.5K) \quad (7)$$

Where R is the gas constant (8.314 J. $K^{-1}mol^{-1}$), T is absolute temperature (K), and 55.5 is the water concentration in solution expressed in mol L^{-1}.

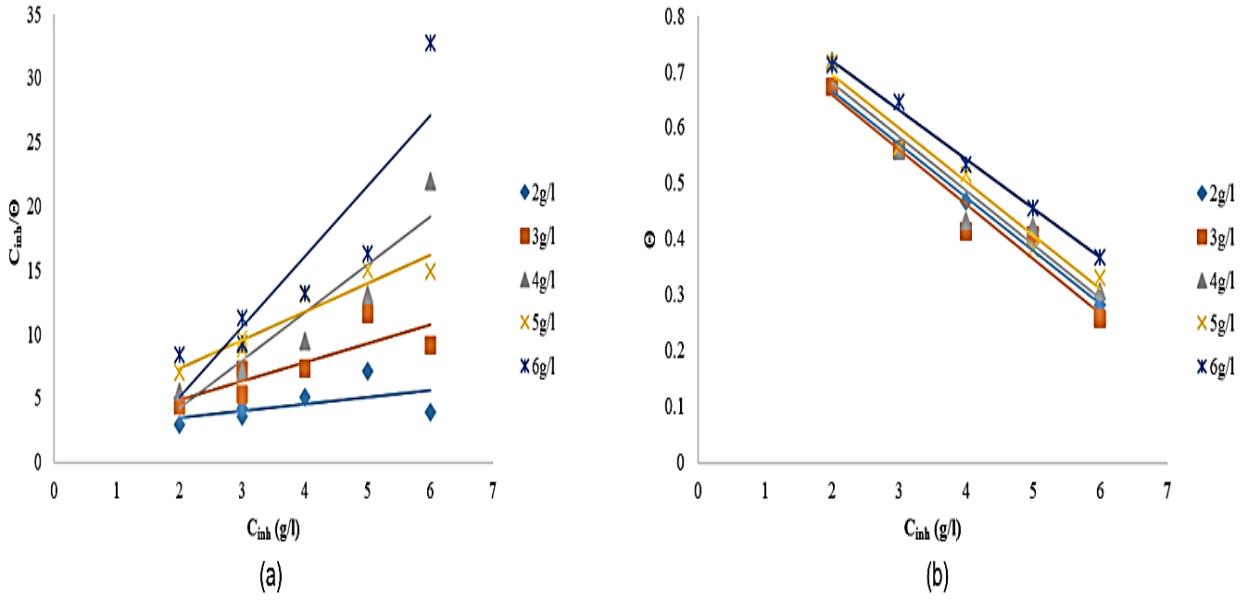

Figure 4: Adsorption isotherm plots of (a) Langmuir, and (b) Temkin for mild steel in the presence of azadirachta indica extract in sulfuric acid medium.

Table 4: Azadirachta indica extract adsorption thermodynamic parameters onto mild steel in 1.5 M of H_2SO_4, at 25 ^{0}C (298 K) room temperature, from Langmuir and Temkin adsorption isotherms

Adsorption isotherm	Concentration of extract (g/l)	Slope	Intercept	Regression	ΔG_{ads} (KJmol^{-1})
Langmuir	2	0.516	2.497	0.27	-7.682
	3	1.470	1.890	0.696	-8.374
	4	3.747	3.293	0.870	-6.993
	5	2.214	2.946	0.912	-7.272
	6	5.506	5.917	0.799	-5.547
Temkin	2	-0.095	0.885	0.996	-9.649
	3	-0.098	0.854	0.956	-9.561
	4	-0.096	0.873	0.935	-9.616
	5	-0.095	0.885	0.969	-9.649
	6	-0.087	0.894	0.995	-9.675

The calculated values of standard free energy of adsorption process (ΔG_{ads}) as shown on Table 4 were all negative for both Langmuir and Temkin Isotherms as applied. Therefore, the negative values of ΔG_{ads} shows that the adsorption of the extract on the mild steel surfaces was spontaneously. Values of standard free energy values less than −20 kJ mol^{-1} confirms physisorption process, which is associated with charge interaction between the charged molecules of the extract and charged molecules from the mild steel surface, while those from negative –40 kJ mol^{-1} or more are indicative of chemisorption process, which implies sharing of electrons from the extract molecules and those from the mild steel surface to form a chemical bond between them. Hence, in this presence study with Azadirachta indica leaf extract, the ΔG_{ads} values for the inhibitor as found between the range of −6.993 to −9.675 kJ mol^{-1}, indicates that the method of adsorption of extract on the mild steel surface is by physical adsorption (physisorption) process (Ayuba, & Abdullateef, 2012; Fathabadi et al., 2021).

3.6. Potentiodynamic Measurement

The anodic potentiodynamic polarization technique was done following the same procedure as detailed in article (Nwigwe et al., 2012).

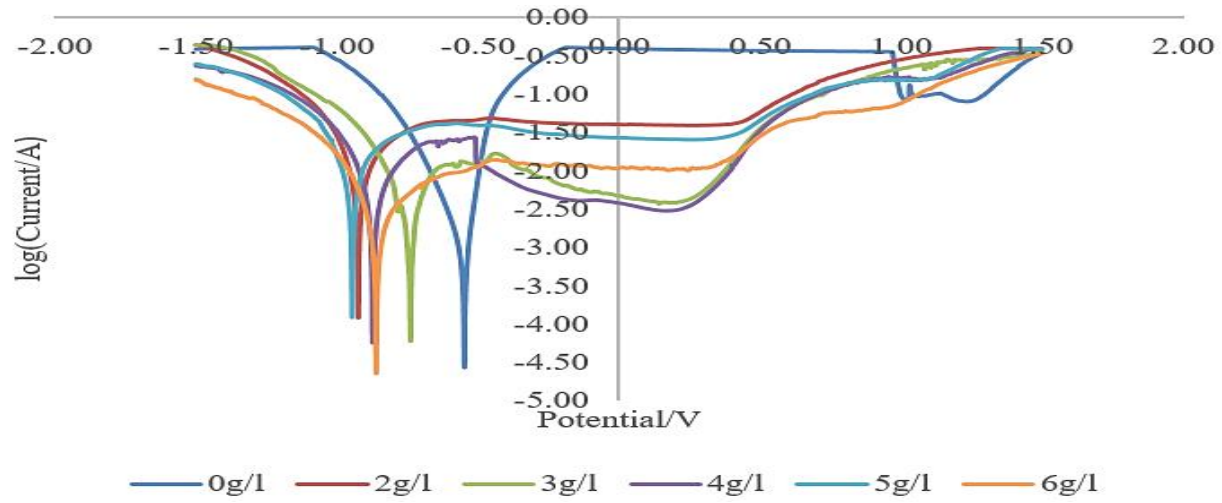

Figure 5. The Tafel plots of corrosion potentials verses corrosion currents as obtained from potentiodynamic polarization test of coupons in 1.5 M of H_2HO_4

The polarization curves for the mild steel coupons gave corrosion rates of 9.871e^{+002}, 5.883e^{+003}, 1.820e^{+003}, 2.358e^{+003}, 5.748e^{+003}, and 3.684e^{+003} in miles per year (mil/yr.), respectively for the different concentration of inhibitor between 0 to 6g/l in that ascending order in the 1.5 M of H_2HO_4 at room temperature as can been seen on figure 4 above.

3.7. The proposed corrosion inhibition mechanism

The inorganic inhibitor as used was able to control mild steel corrosion by physisorption and chemisorption process. This two corrosion inhibition mechanisms were predicted or arrived at based on the possible corrosion reactions of the mild steel in the 1.5 M of H_2HO_4 medium. The corrosion inhibition mechanism was a result of the inhibitive properties of the neem extract which contains some phytochemicals, whose molecules are capable of adsorbing themselves on a mild steel surface to form a thin layer which reduces the contact of the mild steel with the corrosive agents in the 1.5 M of H_2HO_4 solution.

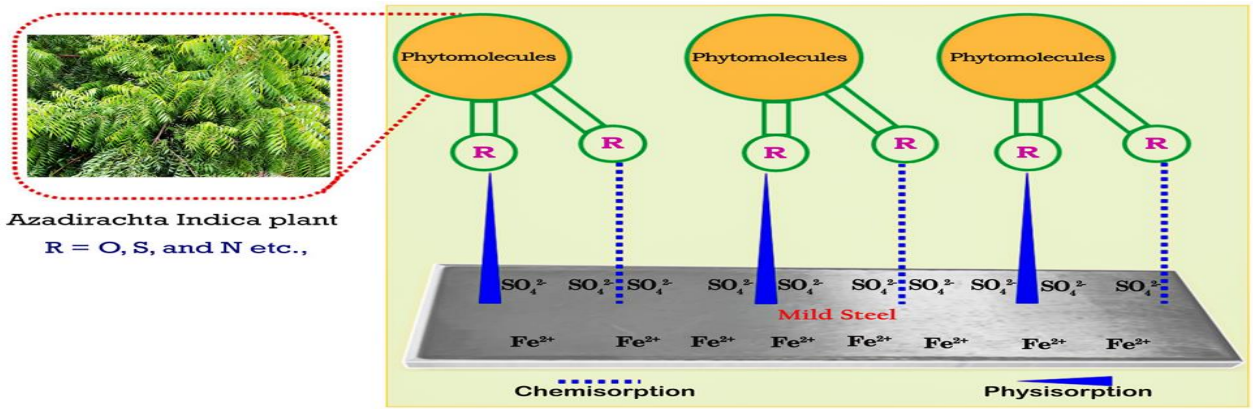

Figure 6: The schematic representation of the proposed corrosion inhibition mechanism.

4.0 Conclusions

Extract from Azadirachta indica leaves has been effectively tested in this study as a potent corrosion inhibitor. It was determined that:

1. The Azadirachta indica leaf extract was able to inhibit the corrosion of mild steel in sulfuric solution to significant extent. The inhibition efficiencies of the extract increased with increase in concentration of the extract and decreased with increase in exposure time.
2. The corrosion inhibition could be rightly attributed to physical adsorption of the phytochemical constituents of the plant extract onto the surface of the immersed mild steel coupons.
3. The adsorption isotherm data fitted well into the Temkin isotherm which is suggestive of physical adsorption interaction between the extract molecules and the surface of the mild steel samples, since the calculated ΔG_{ads} values for the inhibitor were between the range of −6.993 to −9.675 kJ mol^{-1}.
4. Going by the results obtained through the polarization curves, corrosion rate of the mild steel sample in the 1.5 M of H_2HO_4 at 0g/l concentration was the highest followed by that 2g/l, while that of 3g/l concentration gave the best corrosion resistance.

The results obtained, shows that the extract can be usefully applied by researchers in corrosion field against corrosion attack on metallic materials. Finally, it is recommended that more research be done using this extract as a corrosion inhibitor for mild steel in different acidic settings.

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Conflict of Interest

The authors declare that there are no conflicts of interest.

References

Ashby, M. F. 1999. Materials selection in mechanical design. Oxford: Butterworth-Heinemann Publishing Ltd.

Kumar, D. et al. 2016. 4 (N, N-dimethylamino) benzaldehyde nicotinic hydrazone as corrosion inhibitor for mild steel in 1 M HCl solution: An experimental and theoretical study. J Mol Liq., 216, pp.738–746. doi: 10.1016/j.molliq.2016.02.012.

Kanayo, K., Joseph, S., & Tomi, O. 2015. Corrosion inhibition and adsorption mechanism studies of Hunteria umbellata seed husk extracts on mild steel immersed in acidic solutions. ALEXANDRIA Eng J., xxx, pp. 1–9. doi: 10.1016/j.aej.2015.10.009.

Nwigwe, U. et al. 2019. The inhibition of Carica papaya leaves extract on the corrosion of cold worked and annealed mild steel in HCl and NaOH solutions using a weight loss technique. Eng Appl Sci Research, 46, pp. 114–119. doi: 10.14456/easr.2019.14.

Tanwer, S. & Shukla, S. 2022. Corrosion Inhibition Activity of Cefixime on Mild Steel Surface in Aqueous Sulphuric Acid. Prog Color Color Coat., 15, pp. 243–255.

Salman, T. et al. 2019. Novel ecofriendly corrosion inhibition of mild steel in strong acid environment: Adsorption studies and thermal effects. Int J Corros Scale Inhib., 8(4), pp. 1123–1137. doi: 10.17675/2305-6894-2019-8-4-19.

Melchers, R. 2019. Predicting long-term corrosion of metal alloys in physical infrastructure. Npj Materials Degradation, 3(1), pp. 1–7. doi.org/10.1038/s41529-018-0066-x.

Verma, C., Ebenso, E., & Quraishi, M. 2021. Recent developments in sustainable corrosion inhibitors: design, performance and industrial scale applications. Mater Adv., 2, pp. 3806–3850. doi: 10.1039/d0ma00681e.

Oyedeko, K., Lasisi, M., & Akinyanju, A. 2022. Study of Blend of Extracts from Bitter Leaf (Vernonia Amygdalina) Leaves and Banana (Musa Acuminata) Stem as Corrosion Inhibitor of Mild steel in Acidic Medium. Eur J Eng Technol Res., 7(1), pp. 1–9.

Okiongbo, K. & Ogobiri, G. 2013. Predicting Soil Corrosivity along a Pipeline Route in the Niger Delta Basin Using Geoelectrical Method: Implications for Corrosion Control. Sci Res., 5, pp. 237–244.

Sastri, V. 2011. Green corrosion inhibitors. New Jersey: John Wiley & Sons, Inc.

Bilgiç, S. 2022. Plant extracts as corrosion inhibitors for mild steel in H2SO4 and H3PO4 media – Review II. Int J Corros Scale Inhib., 11(1), pp. 1–42. doi: 10.17675/2305-6894-2022-11-1-1.

Miralrio, A., & Vázquez, A. 2020. Plant extracts as green corrosion inhibitors for different metal surfaces and corrosive media: A review. Processes., 8(8), pp. 1-27. doi.org/10.3390/PR8080942.

Nwigwe, U., Mbam, S., & Umunakwe, R. 2019. Evaluation of Carica papaya leaf extract as a bio-corrosion inhibitor for mild steel applications in a marine environment. Mater Res Express., 6(10), pp. 1-13. doi: 10.1088/2053-1591/ab3ff6.

Kamal, C., & Sethuraman, M. 2012. Spirulina platensis – A novel green inhibitor for acid corrosion of mild steel. Arab. J. Chem., 5(2), pp. 55–161. doi: 10.1016/j.arabjc.2010.08.006.

Asaad, M. et al. 2013. Elaeis guineensis leaves extracts as eco-friendly corrosion inhibitor for mild steel in hydrochloric acid. J Teknol., 2, pp. 19–25.

Mobin, M., & Rizvi, M. 2016. Inhibitory effect of xanthan gum and synergistic surfactant additives for mild steel corrosion in 1M HCl. Carbohydr Polym., 136, pp. 384–393. doi: 10.1016/j.carbpol.2015.09.027.

Singh, A. et al. 2015. Gingko biloba fruit extract as an eco-friendly corrosion inhibitor for J55 steel in CO2 saturated 3.5% NaCl solution. J Ind Eng Chem., 24, pp. 219–228. doi: 10.1016/j.jiec.2014.09.034.

Fekkar G. et al. 2020. Eco-friendly chamaerops humilis l. Fruit extract corrosion inhibitor for mild steel in 1 M HCl. International Journal of Corrosion and Scale Inhibition, 9(2), pp. 446–459. doi.org/10.17675/2305-6894-2020-9-2-4.

Asaad M. et al. 2017. Rhizophora Apiculata as Eco-Friendly Inhibitor Against Mild Steel Corrosion in 1M HCl. Surf Rev Lett., 24(8), pp. 1–11. doi: 10.1142/S0218625X18500130.

Aiboudi M. et al. 2019. Eco-friendly Allium cepa L. seeds extracts as corrosion inhibitor for mild steel in 1 M HCl solutions. J. Mater. Environ. Sci., 10(4), pp. 339–346.

Hassan, K., Khadom, A., & Kurshed, N. 2016. Citrus aurantium leaves extracts as a sustainable corrosion inhibitor of mild steel in sulfuric acid. South African J Chem Eng., 22, pp.1–5. doi: 10.1016/j.sajce.2016.07.002.

Helen, L. et al. 2014. Aquilaria Crassna Leaves Extracts – a Green Corrosion Inhibitor for Mild Steel in 1 M HCl Medium. Int. J. Electrochem. Sci., 9, pp. 830–846.

Peter, A., & Sharma, S. 2017. Use of Azadirachta indica (AZI) as green corrosion inhibitor against mild steel in acidic medium: anti-corrosive efficacy and adsorptive behavior. Int J Corros Scale Inhib., 6(2), pp. 112–131. doi: 10.17675/2305-6894-2017-6-2-2.

Abro, I., Abro, M., & Assad, M. 2020. Investigation and evaluation of neem leaves extract as a green inhibitor for corrosion behavior of mild steel: An experimental study. J Mech Eng Sci., 0(0), pp. 1–10. doi: 10.1177/0954406220937723.

Peter, A., & Sharma, S. 2017. Use of Azadirachta indica (AZI) as green corrosion inhibitor against mild steel in acidic medium: Anti-corrosive efficacy and adsorptive behaviour. International Journal of Corrosion and Scale Inhibition., 6(2), pp. 112–131. doi.org/10.17675/2305-6894-2017-6-2-2.

Ghazi. I., Siniti, M., & Elattari, R. 2022. Corrosion Inhibition of Carob Pod Pulp (Ceratonia siliqua L .) on Carbon Steel Surface C38 in Hydrochloric Acid. J Bio-Tribo-Corrosion., 8(31), pp. 1–23. doi: 10.1007/s40735-022-00630-y.

Khadraoui, A. et al. 2015. Thymus algeriensis extract as a new eco-friendly corrosion inhibitor for 2024 aluminium alloy in 1 M HCl medium. Journal of Molecular Liquids., 214, pp. 293–297. doi.org/10.1016/j.molliq.2015.12.064.

Alrafai, H. 2022. Corrosion inhibition properties of the oil extracted from the leaves of Eruca sativa for carbon steel in acidic medium. Int J Electrochem Sci., 17, pp. 1–12. doi: 10.20964/2022.02.24.

Joycee, S. et al. 2022. Corrosion mitigation by an eco-friendly inhibitor: Beta vulgaris (beetroot) extract on mild steel in simulated oil well water medium. Int J Corros Scale Inhib., 11(1), pp. 82–101. doi: 10.17675/2305-6894-2022-11-1-4.

Ajayi, O., Odusote, J., & Yahya, R. 2014. Inhibition of mild steel corrosion using Jatropha Curcas leaf extract. J. Electrochemical Sci Eng., 4(2), pp. 67–74. doi: 10.5599/jese.2014.0046.

Loto, C., & Loto, R. 2016. Inhibition effect of garlic extracts on the corrosion of alpha brass in nitric acid. Der Pharma Chem., 8(2); pp. 162–171.

Iroha, N., & Maduelosi, N. 2021. 'Corrosion Inhibitive Action and Adsorption Behaviour of Justicia Secunda Leaves Extract as an Eco-friendly Inhibitor for Aluminium in Acidic Media', Biointerface Res Appl Chem., 11(5), pp. 13019–13030.

Madaki, F., Kabiru, A., & Mailafiya, S. 2016. Phytochemical and Proximate Analyses of Methanol Leaf Extract of Neem Azadirachta indica. European J Med Plants., 15(2), pp. 1–6. doi: 10.9734/EJMP/2016/25191.

Ovri, J., Okeahialam, S., & Onyemaobi, O. 2013. Microbial corrosion of mild and medium carbon steels. J Eng Sci Technol., 8(5), pp. 639–653.

Fontana, G. 1987. Corrosion engineering. Singapore: McGraw-Hill Book Company.

Bardal, E. 2004. Different Forms of Corrosion Classified on the Basis of Appearence, Corrosion and Protection, Engineering Materials and Processes. London: Springer.

Yaro, A., Khadom, A., & Wael, R. 2013. Apricot juice as green corrosion inhibitor of mild steel in phosphoric acid. Alexandria Eng J., 52(1), pp. 129–135. doi: 10.1016/j.aej.2012.11.001.

Mistry, B., & Jauhari, S. 2014. Corrosion Inhibition of Mild Steel in 1N HCl Solution by Mercapto-Quinoline Schiff Base. Chem Eng Commun., 201, pp. 961–981. doi: 10.1080/00986445.2013.785946.

Alaneme, K., Olusegun, S., & Adelowo, O. 2016. Corrosion inhibition and adsorption mechanism studies of Hunteria umbellata seed husk extracts on mild steel immersed in acidic solutions. Alexandria Eng J., 55(1), pp. 673–681. doi: 10.1016/j.aej.2015.10.009.

Vimala, J., Leema, A., & Raja, S. 2011. Cassia auriculata extract as corrosion inhibitor for mild steel in acid medium. Int J ChemTech Res., 3(4), pp. 1791–1801.

Nwabanne, J., & Okafor, V. 2012. Adsorption and Thermodynamics Study of the Inhibition of Corrosion of Mild Steel in H_2SO_4 Medium Using Vernonia amygdalina. J Miner Mater Charact Eng., 11, pp. 885–890.

Ayuba, A, & Abdullateef, A. 2012. Investigating the corrosion inhibition potentials of strichnos spinosa l. extract on aluminium in 0.3M hydrochloric acid solution. J Appl Sci Envir Stud., 4(1), pp. 336–348.

Fathabadi, H. et al. 2021. Corrosion Inhibition of Mild Steel with Tolyltriazole. Mater Res., 24(4), pp. 1–16.

Nwigwe, U. et al. 2012. Effects of Different Holding Time and Quenchants on the Hardness and Corrosion rate of Medium Carbon Steel. J Mater Environ Sci., 12(7), pp. 962–973.