ISSN No:-2456-2165 https://doi.org/10.38124/ijisrt/25sep757

Effect of Halide Ions Admixtures on Inhibitive Properties of *Acanthospermum hispidum* Leaf Extract on Mild Steel in HCL Solution

Egbo Uchenna Jasper[1]; Nyior. G.B.[2]; Akaaza J.N.[3]

[1;2;3]Joseph Sarwuan Tarka University, Makurdi Benue, Nigeria

Publication Date: 2025/09/22

Abstract: This study investigated the effect of halide ions admixtures on inhibitive properties of acanthospermum hispidum leaf extract on mild steel in HCL solution. *Acanthospermum hispidum*, a plant known for its abundance and dominance as a weed in local farmlands, was sourced from Imande Antsa Village near Joseph Sarwuan Tarka University, Makurdi (JOSTUM). Phytochemical analysis revealed the presence of alkaloids, flavonoids, tannins, saponins, and phenols compounds known for their corrosion-inhibiting properties. Experimental results showed that corrosion rates decreased with increasing extract concentrations, with the lowest rate of 0.052 mm/yr at 0.5 g/L and 298 K, compared to 0.1804 mm/yr for the uninhibited sample. This indicates enhanced surface adsorption at higher concentrations. The addition of halide ions, Potassium Bromide (KBr) and Potassium Iodide (KI) further improved inhibition efficiency, rising from 71.43% to 90.96%, with iodide ions showing superior performance. These findings suggest a strong synergistic effect between the plant extract and halide ions. The study concludes that the combined use of AHLE and halides is an environmentally friendly and cost-effective approach for protecting mild steel against acid-induced corrosion, making it suitable for industrial applications where sustainability and safety are essential.

Keywords: *Acanthospermum hispidum, Corrosion Inhibition, Mild Steel, Hydrochloric Acid, Plant Extract, Halide Ions.*

How to Cite: Egbo Uchenna Jasper; Nyior. G.B; Akaaza J.N. (2025) Effect of Halide Ions Admixtures on Inhibitive Properties of *Acanthospermum hispidum* Leaf Extract on Mild Steel in HCL Solution. *International Journal of Innovative Science and Research Technology*, 10(9), 1110-1122. https://doi.org/10.38124/ijisrt/25sep757

I. INTRODUCTION

Corrosion is a natural yet destructive phenomenon that poses significant threats to the longevity and performance of metallic materials across various industries. It is typically defined as the gradual deterioration of metals resulting from chemical reactions with their surrounding environment. Much like natural disasters such as earthquakes or hurricanes, corrosion inflicts substantial damage on structures and systems including vehicles, pipelines, water systems, bridges, buildings, storage tanks, and industrial facilities. Among the various metals prone to corrosion, mild steel is one of the most widely used in engineering and industrial applications due to its affordability, availability, mechanical strength, and ease of fabrication. It finds extensive application in manufacturing equipment such as reaction vessels, tanks, and containers for handling corrosive solutions including acids, bases, and salts (Bhardwaj, 2017).

Despite its versatility, the susceptibility of mild steel to corrosion poses a persistent threat to its structural integrity and functional reliability. Corrosion occurs through electrochemical redox reactions, where the metal is oxidized at anodic sites (e.g., $Fe \rightarrow Fe^{2+} + 2e^-$), and reduction occurs at cathodic sites (e.g., $2H^+ + 2e^- \rightarrow H_2$ gas). This irreversible process results in the formation of corrosion products such as oxides, which weaken the metal over time and can lead to catastrophic failures. The economic and safety implications of corrosion include increased costs for maintenance, repairs, replacements, and loss of productivity, in addition to potential environmental pollution and safety hazards (Ogunleye et al., 2019).

Among the numerous strategies developed for corrosion control, the use of corrosion inhibitors has proven to be one of the most effective and widely applied methods. A corrosion inhibitor is a chemical compound that, when added in small quantities to a corrosive environment, significantly reduces the rate of metal degradation (Miralrio and Vazquez, 2020; Yang, 2021). These inhibitors are broadly categorized as anodic (suppressing anodic metal dissolution), cathodic (slowing down cathodic reactions), or mixed-type (influencing both reactions). They may also be classified based on their chemical nature into inorganic and organic types.

Historically, inorganic inhibitors such as chromates and arsenates have been employed effectively, but due to their

ISSN No:-2456-2165 https://doi.org/10.38124/ijisrt/25sep757

toxic and non-biodegradable nature, their use is now heavily regulated. These compounds pose environmental and health risks and present challenges in terms of safe disposal and ecological impact. Organic inhibitors, especially synthetic ones like benzotriazole and pyridazine, are also effective but are often expensive and pose similar environmental concerns. This has led to a growing interest in eco-friendly alternatives known as green corrosion inhibitors (Umoren and Solomon, 2015).

Green inhibitors are derived from natural sources such as plant extracts and are increasingly being recognized as sustainable and environmentally benign alternatives to conventional inhibitors. These natural substances are rich in phytochemicals like alkaloids, tannins, flavonoids, amino acids, and steroids, which contain functional groups capable of adsorbing onto metal surfaces, thereby forming protective barriers against corrosion (Ejikeme et al., 2015; Olasehinde, 2018; Akaaza et al., 2021). Extracts from roots, bark, seeds, leaves, and fruits of various plants have been successfully tested for their corrosion inhibition potential. They offer advantages such as low cost, biodegradability, easy availability, and non-toxicity.

While green inhibitors are promising, they often exhibit limited efficiency due to their selective activity and dependence on environmental conditions. However, recent research indicates that the corrosion inhibition efficiency of green inhibitors can be significantly enhanced by combining them with halide ions (such as bromide and iodide). These halide ions assist in the adsorption of organic molecules on the metal surface, thereby improving the inhibitor's protective performance. It has been established that the halide ions facilitate adsorption of organic cations during metal corrosion by forming intermediate bridges between the metal surface and the positive end of organic inhibitor molecules. The synergistic effect of halide ions in combination with some organic compounds and naturally occurring substances have been reported by (Umoren *et al*, 2010; Umoren and Solomon,2015) Most of the studies show that halide additives synergistically increased the inhibition efficiencies of organic cation type molecules in the order Cl- < Br- < I- in different environments.

Given the urgent need for cost-effective, eco-friendly, and efficient corrosion inhibitors, the present study focuses on the use of Acanthospermum hispidum leaf extract (AHLE), in combination with halide ions (Br^- and I^-) as inhibitor for mild steel corrosion. . In this study, 0.05 M KBr and KI each were added to test media to evaluate their influence on the corrosion inhibition efficiency of AHLE extract. Experiments were conducted at temperatures of 298, 308, 318, and 328 K to assess temperature dependence. It is expected that the addition of halides of KBr and KI will enhance the performance of the AHLE due to synergism. The presence of halide ions in acidic media can enhance the inhibition efficiency of organic compounds through synergistic effects.

II. MATERIALS AND METHOD

Acanthospermum hispidum plants were collected from a farmland in Imande Antsa Village, along Joseph Sarwuan Tarka University Makurdi Road, North Bank, Makurdi, Benue State, Nigeria. The collected plant specimens were taken to the Department of Forestry, Joseph Sarwuan Tarka University, Makurdi, for proper identification. The selection of Acanthospermum hispidum was based on its abundance and dominance on farmlands in the area, where it poses a significant weed problem for farmers. Fresh leaves of the plant were harvested, thoroughly washed, and shade-dried. The dried leaves were then ground into powder and stored appropriately. To obtain the plant extract, 50 g of the powdered leaves were soaked in 500 ml of absolute ethanol for 48 hours. The mixture was subsequently filtered, and the filtrate was concentrated using a water bath at 45 °C. The resulting extract was refrigerated at 4 °C until further use. Mild steel coupons measuring 30 × 22 × 1 mm were prepared in accordance with ASTM G59 standards. The surface of each coupon was polished using emery papers of progressively finer grit sizes, followed by degreasing with acetone, drying, weighing, and storage in desiccators. The corrosive medium, 1 M hydrochloric acid (HCl), was prepared by appropriate dilution of concentrated HCl. A 2.5 g/L stock solution of the plant extract was prepared, from which various inhibitor concentrations (0.1–0.5 g/L) were obtained using standard dilution techniques. Six test solutions were formulated: five containing the respective inhibitor concentrations and one serving as a control (acid solution without inhibitor). 3 g of each of KI and KBr were added separately, to each of the 5 extract concentrations, to give 10 additional test solutions.

The concentration range of 0.1–0.5 g/L for the extract was selected based on earlier studies that demonstrated optimal corrosion inhibition performance within this range (Eddy & Ebenso, 2008; Eduok et al., 2010; Nanna et al., 2014; Akaaza et al., 2021).

Qualitative phytochemical screening of Acanthospermum hispidum leaf extract (AHLE) was conducted to identify active constituents using standard procedures as described by Vimala et al. (2012). Quantitative analysis to determine the concentrations of individual phytochemicals was also carried out following the methodology outlined by Geetha and Geetha (2014).

The corrosion rate was determined using the weight loss method, following Umoren *et al.* (2008). The difference in weight of the coupons before and after exposure to the corrosive environment was taken as weight loss (w). This was then used to calculate the corrosion rate using equation (1)

$$C.R.(mm/yr) = \frac{87.6W}{DAT} \quad (1)$$

Where:

W= weight loss in (mg),D = density of the metal, (g/cm^3),A = total surface area of the coupon (cm^2), 87.6 is the unit conversion constant, and T = time of exposure (hours).

ISSN No:-2456-2165 https://doi.org/10.38124/ijisrt/25sep757

Inhibition efficiency (I.E) is a parameter used to describe the effectiveness of an inhibitor in reducing corrosion rate of a metal exposed to corrosive environment. It is usually calculated in percentage using equation (2) (Bamaiyi and Peni, 2015).

$$I.E = \frac{CR_{0-CR_1}}{CR_0} \times 100\ \% \quad (2)$$

Where, CR_0 and CR_1 are corrosion rates in the absence and presence of inhibitor respectively. The corrosion rates and inhibition efficiencies were calculated in the presence of extract alone and in the presence of a fixed concentration of halide admixtures (KBr and KI).

The degree of surface coverage was obtained using equation (3), (Larouj *et al.*, 2017).

$$\Theta = \frac{CR_{0-CR_1}}{CR_0} \quad (3)$$

Where, Θ is the degree of surface coverage.

The effect of temperature on the corrosion behavior of mild steel in 1 M HCl, with and without various inhibitor extracts, was studied using the weight loss method at 298, 308, 318, and 328 K. Twelve pre-cleaned steel coupons were weighed and immersed (two per beaker) in 200 ml of inhibitor solutions and a control solution (acid only). The beakers were maintained at each test temperature for 3 hours using a thermostatic water bath. After immersion, coupons were cleaned, dried, reweighed, and weight loss recorded to calculate corrosion rates. Each test was repeated, and average values were taken to ensure result accuracy.

Adsorption isotherm study was conducted to determine the most suitable adsorption model for the inhibitors. Adsorption isotherms provide insight into the interaction between the inhibitor and the mild steel surface. Various models were tested to identify the best fit. These isotherms describe how substances adhere to solid surfaces from aqueous environments at constant temperature and pH (Nwabanne and Okafor, 2011).

The variation of degree of surface coverage (Θ) with inhibitor concentration specifies the adsorption isotherm that describes the system. Langmuir isotherm model was confirmed by plotting C/Θ versus concentration, according to equation (4) (Owate *et al.*, 2014).

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \quad (4)$$

Where, C = inhibitor concentration, Θ =degree of surface coverage, and $Kads$ is the adsorptive equilibrium constant.

Temkin isotherm model

$$\Theta = \frac{1}{f}\ ln\ (K_{ads}\ C) \quad (5)$$

Where, C is the concentration of inhibitor, Θ is the surface coverage, *f* is the adsorbent-adsorbates interaction and K_{ads} is the equilibrium constant.

Heat of adsorption was calculated using equation (6) based on the degree of surface coverage and temperature ranges (298 -328 K) (Nwabanne and Okafor, 2011).

$$Q_{ads} = 2.303R\left[log\left(\frac{\theta_2}{1-\theta_2}\right) - log\left(\frac{\theta_1}{1-\theta_1}\right)\right] \times \left(\frac{T_1 \times T_2}{T_2 - T_1}\right) kJ/mol \quad (6)$$

Where, R is the universal gas constant;

Θ_1, Θ_2 are the degrees of surface coverage at Temperatures T_1 (K) and T_2 respectively.

The free energy of adsorption at different temperatures was calculated using equation (7) and (8);

$$\Delta G^0 ads = -RT\ In\ 55.5K \quad (7)$$

Where, R is the universal gas constant (8.314 J/mol.K) , T is the absolute temperature in Kelvin(K), $\Delta G°_{ads}$ =Gibbs free energy of adsorption (kJ/mole) and the value 55.5 is the molar concentration of water in the solution in mol./K and K_{ads} is the film attractive power (Umoren *et al.*, 2008);

$$K_{ads} = \frac{\Theta}{C(1-\Theta)}, \quad (8)$$

Where C is the concentration of inhibitor and Θ is degree of surface coverage and K_{ads} is the film attractive power(Lg^{-1}). Therefore, $\Delta G°_{ads}$ was calculated using equation (9) by multiplying $K_{ads}$by 1000 to make it dimensionless.

$$\Delta G°_{ads} = RTln(1000K_{ads}) \quad (9)$$

Generally, values of $\Delta G°_{ads}$ less than -20 kJ/mol^{-1} is an indication of physical adsorption of the extract on the metal surface, while values above-40kJ/mol^{-1}signifies chemisorption.

The Arrhenius equation (10) was used to calculate the apparent activation energy (Ea).

$$Log\ \frac{C_{R2}}{C_{R1}} = \frac{Ea}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad (10)$$

Where: R – is the molar gas constant

C_{R1} and C_{R2} are the corrosion rates at temperatures T_1 and T_2 respectively.

ISSN No:-2456-2165 https://doi.org/10.38124/ijisrt/25sep757

III. RESULT AND DISCUSSION

➢ *Characterisation of Acanthospermum hispidum DC Leaf Extract*

Table 1 Phytochemical Constituents of *Acanthospermum hisipidum DC* Leaves Extract using Qualitative Screening

S/N	Constituents	Test carried out	Sample (AHLE)
1	Carbohydrates	Molisch test	+ Present
2	Anthraquinones	Bontragers test	_ Absent
3	Glycosides	Fehling test	+ Present
4	Cardiac glycosides	Keller-Killiani test	+ Present
5	Saponins	Frothing test	+ Present
6	Steroids and Triterpenes	Liebeman Burchard test	+ Present
7	Tannins	Ferric chloride test	+ Present
8	Flavonoids	Shinoda test	+ Present
9	Alkaloids	Dragendorff test	+ Present

- Qualitative chemical analysis was also carried out to ascertain the major constituents in the extract and the result is presented in Table 1 which shows the presence of carbohydrates,glycosides,saponins,steroids and triterpenes, tannins, flavonoids and alkaloids.
- Quantitative phytochemical analysis The quantitative phytochemical analysis (Figure 1) shows that the leaf extract of *Acanthospermum hispidum DC* contain alkaloids, flavonoids, tannins, saponins and phenols in different quantities.

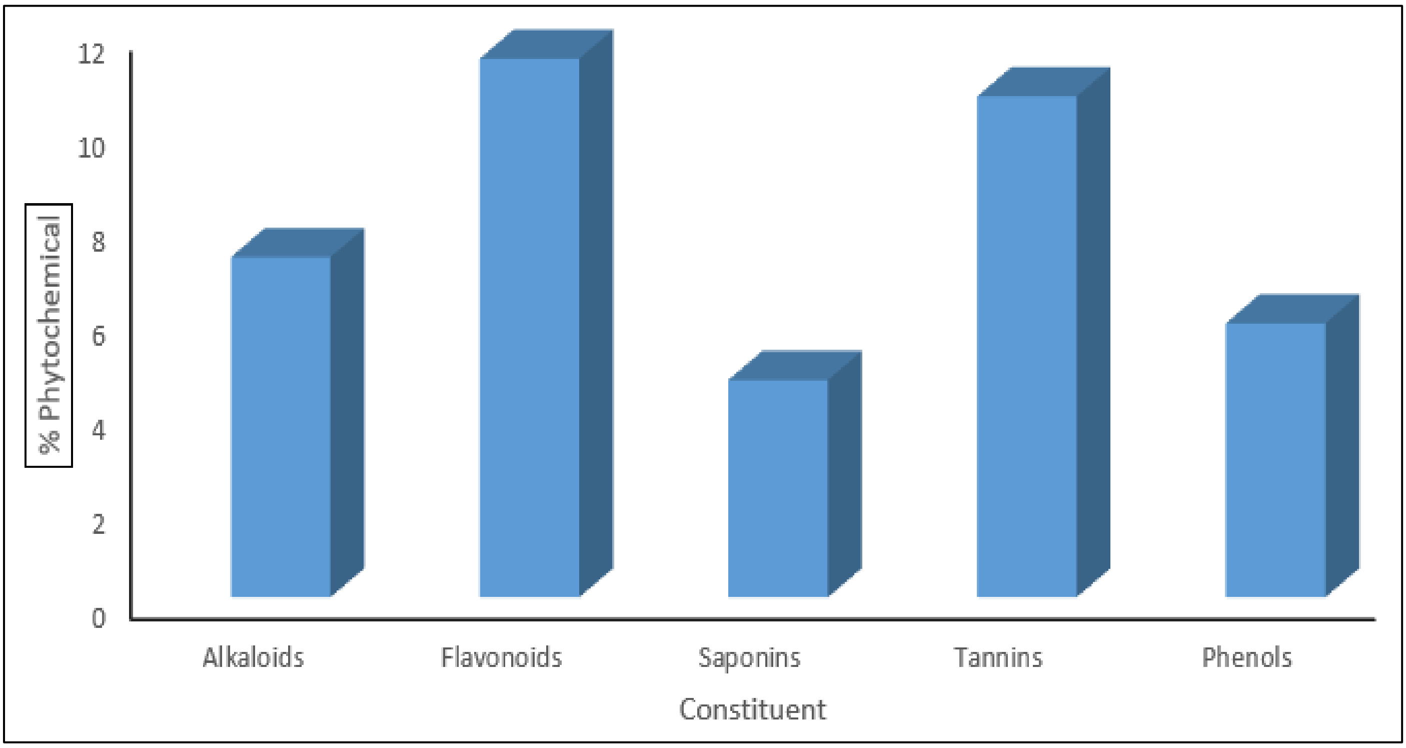


Fig 1 Percentage Composition of Phytochemical Constituents in *Acanthospermum hispidum* Leaves Extracts (AHLE).

The presence of these compounds has been reported to promote the inhibition of mild steel in aggressive acidic media (Bhardwaj, 2017; Akaaza *et al.*, 2021). The presence of these phytochemical constituents is indicative of the potentials of the extracts for use as corrosion inhibitors for mild steel corrosion in acidic medium. Figure 1 shows that the material contain more of flavonoids and tannins, followed by alkaloids.

➢ *Effect of Immersion Time/Concentration*

Figure 2 presents the effect of the variation of immersion time on the corrosion rate of the steel coupons in 1 M HCl solution at different inhibitor concentration (0.1-0.5 g/L) of AHLE. The study clearly shows that corrosion rate values increased with increase in immersion time. It was observed that the corrosion rate in the blank solution was very high but drastically reduced on addition of inhibitors. This shows the inhibitive effect of the extract that must have been adsorbed on the metal surface. However, increase in corrosion rate with time could be attributed to degradation of the protective film formed by the inhibitor due to prolonged immersion. These findings are consistent with corrosion studies from literature (Adzor *et al.*, 2014; Bam *et al.*, 2018; Olasehinde *et al.*, 2018; Olisakwe *et al.*, 2022).

ISSN No:-2456-2165 https://doi.org/10.38124/ijisrt/25sep757

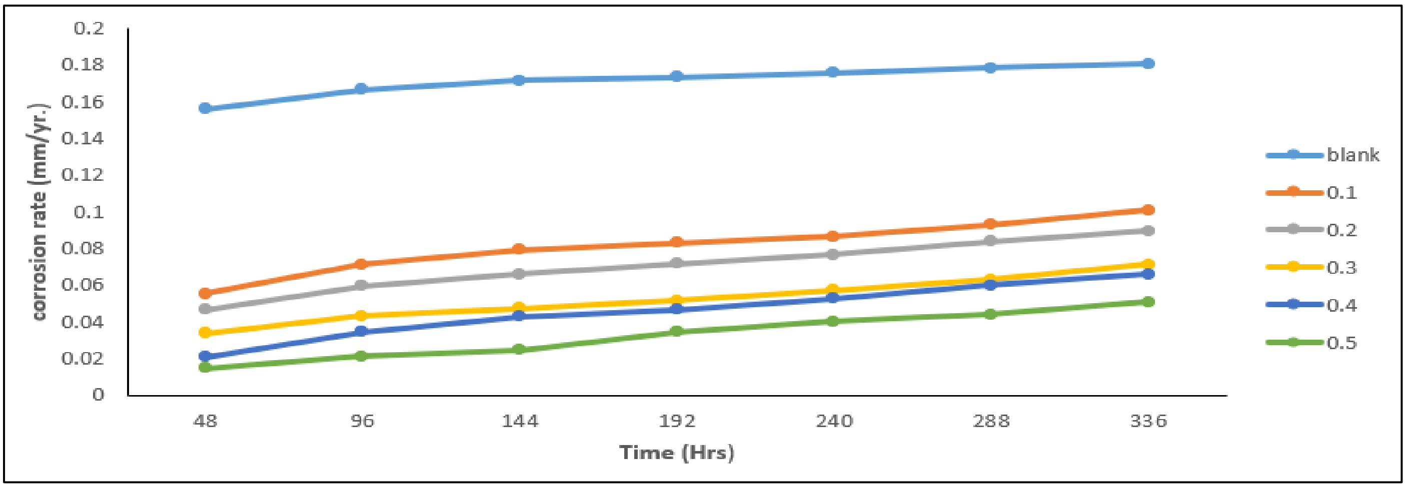


Fig 2 Variation of Corrosion Rate with Immersion Time and Inhibitor Concentration of Test Samples at Room Temperature

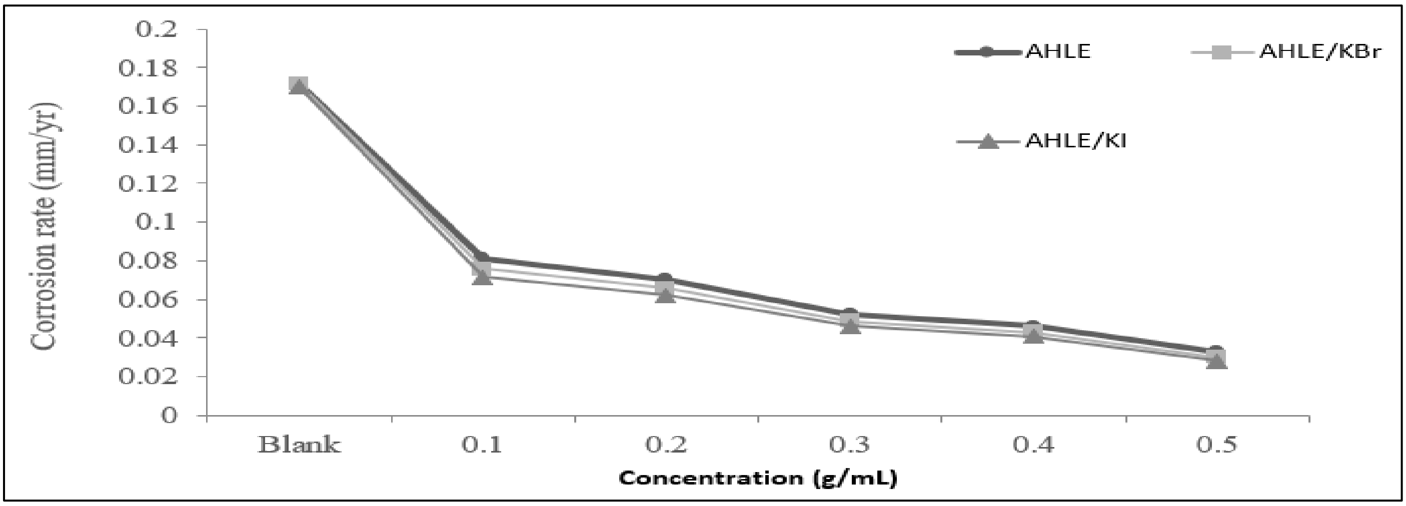


Fig 3 Variation of Corrosion Rate with Inhibitor Concentration for the Various Inhibitors used in the Study

➢ *Effect of Inhibitor Concentration on Corrosion Rate and Inhibition Efficiency*

Figures 3 shows the effect of varying inhibitor concentrations of AHLE and halide additives on the corrosion rate of mild steel coupons in 1 M HCl solution. The results clearly indicate that steel coupons immersed in a blank acidic solution exhibited the highest corrosion rates compared to those exposed to varying concentrations of the AHLE (0.1 - 0.5 g/L) with KBr and KI respectively. As the concentration of the inhibitors in the acidic medium increased, there was a significant reduction in the corrosion rates of the test coupons. This suggests that higher inhibitor concentrations facilitate greater adsorption of inhibitor molecules onto the metal surface, resulting in a lower corrosion rate. These findings are consistent with several corrosion studies in the literature (Njoku *et al.*, 2014; Adzor *et al*., 2014; Bam *et al*., 2018; Olasehinde *et al.*, 2018; Ogunleye *et al.*, 2019; Olisakwe *et al*., 2022).

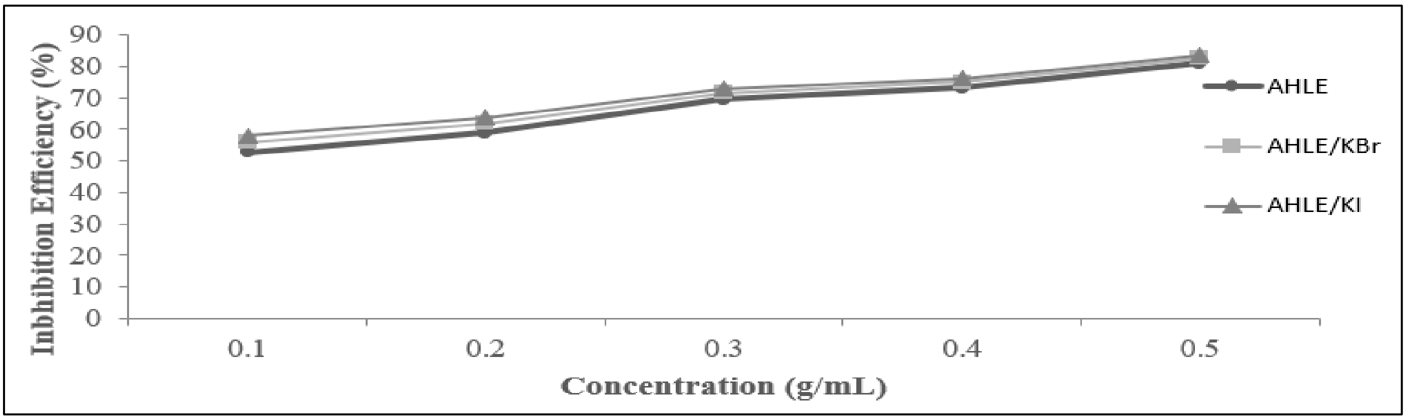


Fig 4 Variation of Inhibition Efficiency with Concentrations of Various Inhibitors at Room Temperature

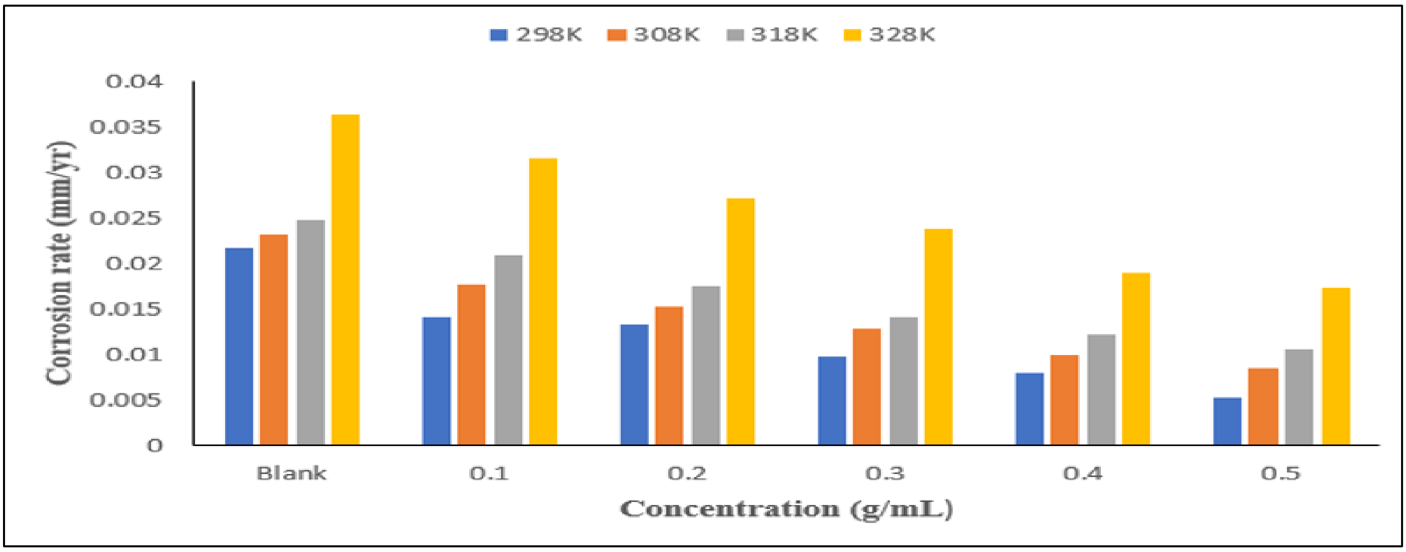
ISSN No:-2456-2165 https://doi.org/10.38124/ijisrt/25sep757

Inhibition efficiency was found to increase with increase in inhibitor concentration in the presence of the extract alone and in combination with halides as presented on Figure 4. The inhibition efficiency increased from 64.42% at 0.1 g/mL to 90.69% at 0.5 g/mL concentration for AHLE alone; in the presence of AHLE/KBr it increased from 66.91 % at 0.1g/mL to 92.05% at 0.5 g/mL concentration. Similarly, inhibition efficiency was enhanced on addition of AHLE/KI from 68 % to 93.53% at 0.1 and 0.5 g/mL respectively. This shows that the presence of the halide ions increased the inhibitor efficiency of the inhibitors. This is in agreement with the findings of (Olasehinde *et al.*, 2018 and Olisakwe *et al.*, 2022).

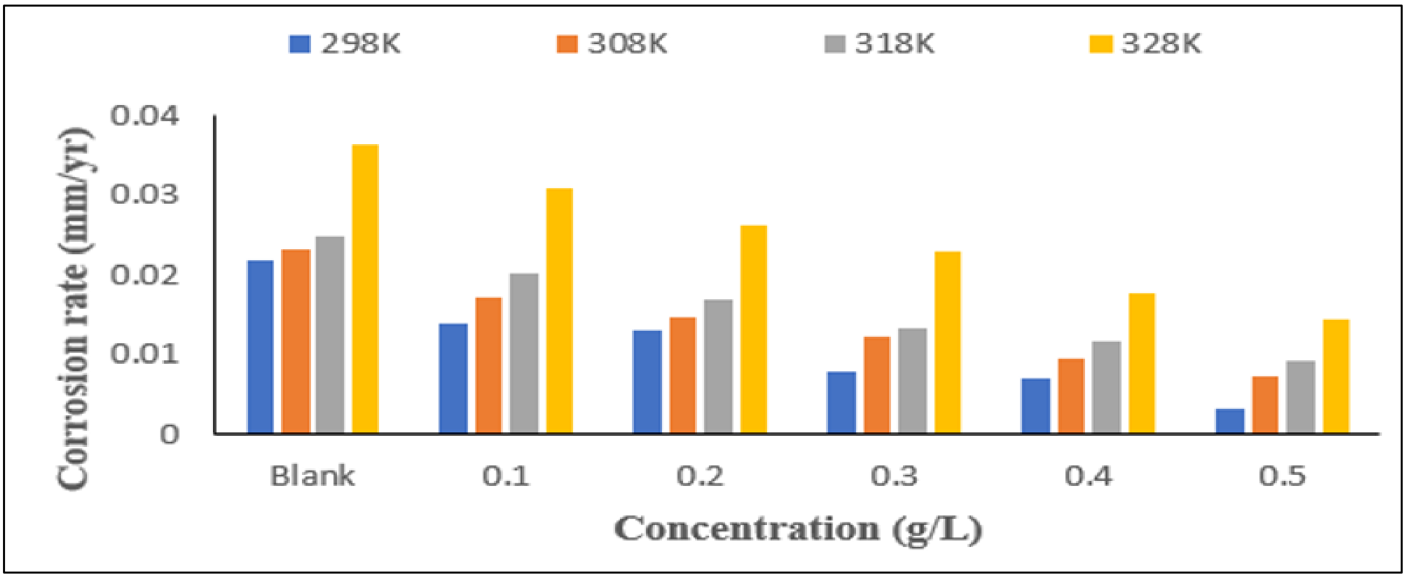
➢ *Effect of Halides*

The effect of adding halide ions on the corrosion rate and inhibition efficiency of AHLE are presented in Figures 3 and 4 respectively. It can be seen clearly that corrosion rates reduced with increase in the concentrations and are lower in the samples containing halide ions. This suggests that halide ions can interact synergistically with organic corrosion inhibitors, by adsorbing onto the metal surface, facilitating the co-adsorption of inhibitor molecules, which enhances the overall surface coverage and protective barrier. The halide ions acted as a "bridge" between the metal surface and organic inhibitors, improving the strength and uniformity of the inhibitor layer.

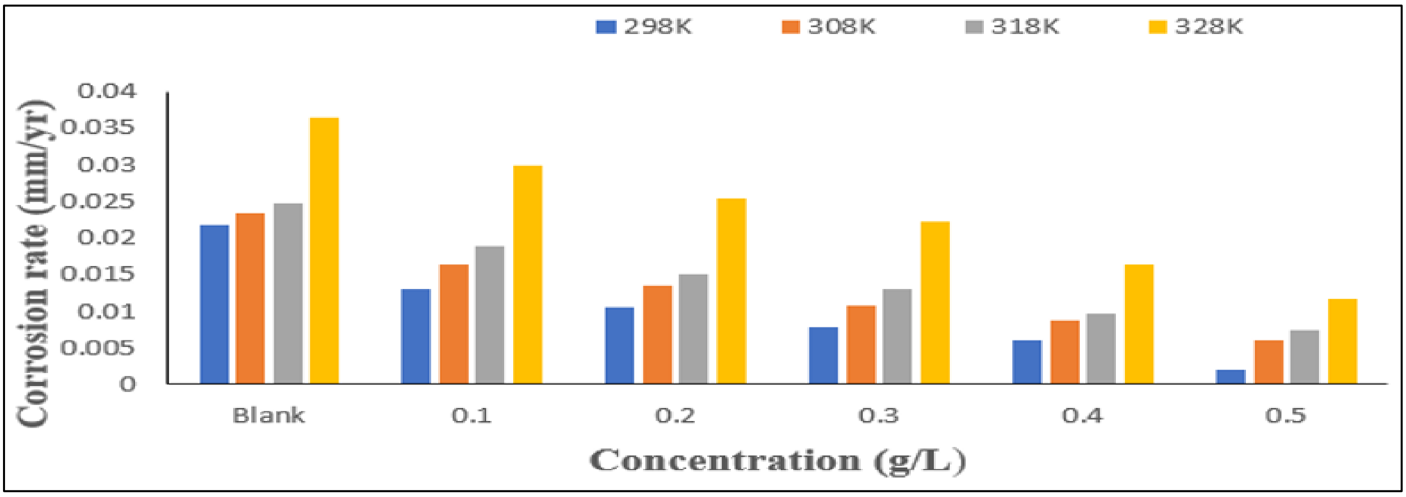
Results also show that halide ions with higher polarizability (e.g.$I > Br$) tend to adsorb more strongly onto the metal surface (Umoren and Solomon, 2010). This increases the inhibition efficiency by forming protective film as observed on Figure 4 where the inhibition efficiency for the blend of AHLE/ KI is the highest with 93.53%, followed by that of AHLE/KBr with 92.05%. This finding is in line with those of (Eduok *et al*, 2010; Njoku *et al*, 2014; Wang *et al*, 2023). The results clearly shows that there is synergism between the halide ions and the AHLE extract with the synergetic parameters of corrosion inhibitor.



(a)



(b)



(c)

Fig 5 Variation of Corrosion Rate with (a) Different Concentrations of AHLE (b) Concentrations of AHLE Containing Halide (Potassium Bromine) (c) Concentrations of AHLE Containing Halide (Potassium Iodide) at Various Immersion Temperatures after 48 hours.

- *Effect of Temperature on Corrosion Rate*

Figure 5 presents the effect of the variation of solution temperature on the corrosion rate of the steel coupons in 1 M HCl solution at different inhibitor concentrations of AHLE and the halides used. The corrosion rates reduced with increase in inhibitor concentration but increased with increasing temperature as presented in Figure 5. In the presence of 0.1g/mL AHLE only, corrosion rate increased from 0.0142 mm/yr at 298 K to 0.0316 mm/yr at 328K. In the presence of AHLE/ KBr, it increased from 0.0139 mm/yr at 298 K to 0.0309 mm/yr at 328 K; and in AHLE/KI solution, corrosion rate increased from 0.0131 mm/yr at 298 K to 0.0298 mm/yr at 328 K. The increase in corrosion rate with temperature increase may be due to enhanced chemical reaction between the metal and the acid solution. However, it can be seen that the increase was less in the inhibitors with the halide ions.

- *Effect of Temperature on Inhibition Efficiency*

The effect of elevated temperature on the inhibition efficiency of the different concentrations of AHLE and halides admixtures is presented in Figures 6-8. The inhibition efficiency was observed to reduce with increasing temperature. The inhibition efficiency values for AHLE only decreased from 71.43 % at 298 K to 52.006 % at 328 K. In the presence of the halides, inhibition efficiency decreased from 84.93% at 298 K to 60.05 % at 328 K for AHLE/ KBr and from 90.96 % at 298 K to 67.62 % at 328 K for AHLE/KI. This trend is attributed to the fact that higher temperatures accelerate the electrochemical reactions involved in corrosion (e.g., oxidation of the metal and reduction of oxygen or hydrogen). Many metals form passive films or oxide layers that protect them from corrosion but at higher temperatures, these films can degrade, crack, or dissolve, exposing the underlying metal to the corrosive environment. The results indicate that the presence of the halide ions helps in preserving the protective layer even at the higher temperature, hence improved inhibition efficiencies compared to the extract without iodide ions. These findings are consistent with several corrosion studies in the literature (Ebenso, 2003; Njoku *et al.*, 2014; Olasehinde *et al.*, 2018; Ogunleye *et al.*, 2019; Abdurrahman *et al.*, 2021).

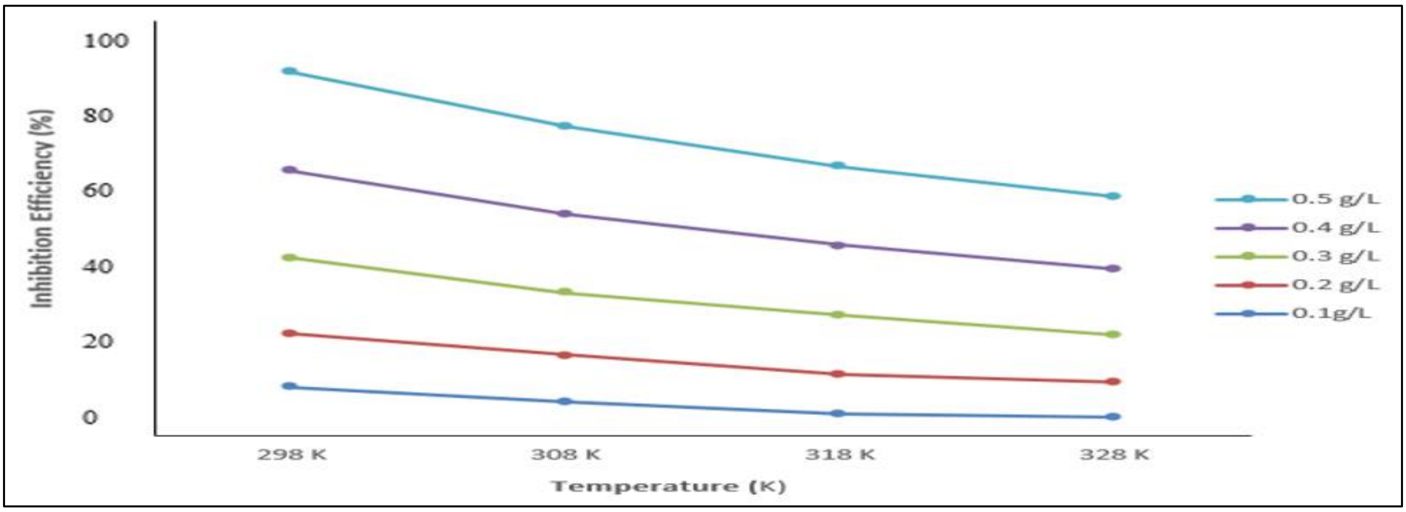


Fig 6 Variation of Inhibition Efficiency at Various Concentrations of AHLE at Different Temperatures

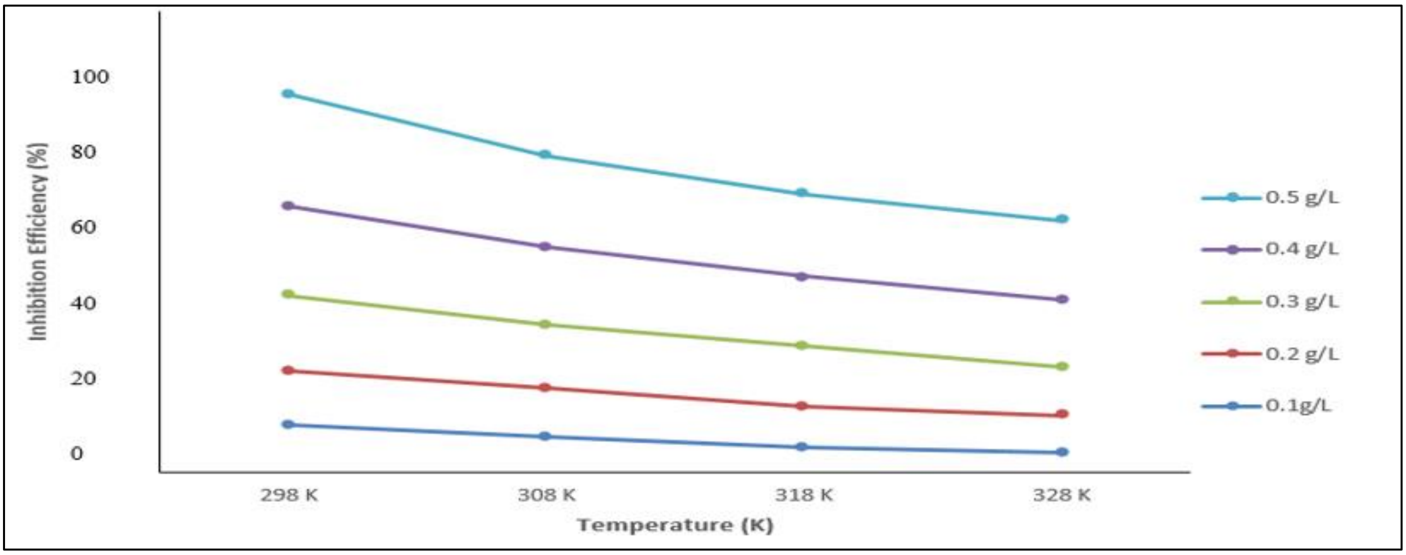


Fig 7 Variation of Inhibition Efficiency at Various Concentrations of AHLE/0.05KBr Blends at Different Temperatures

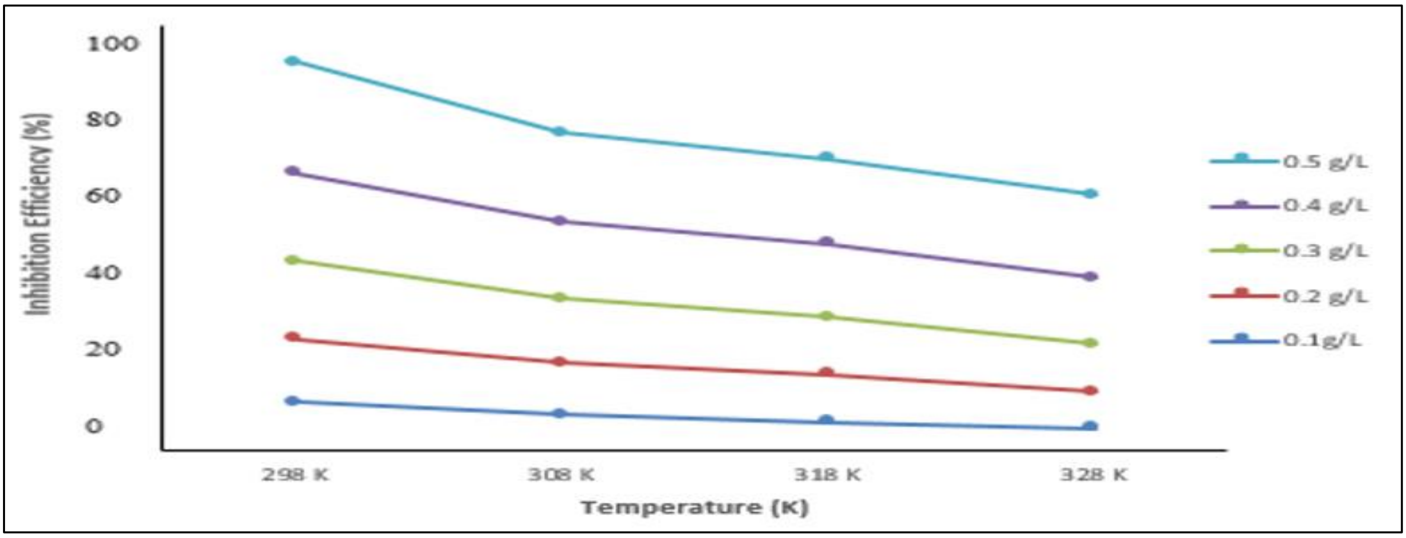


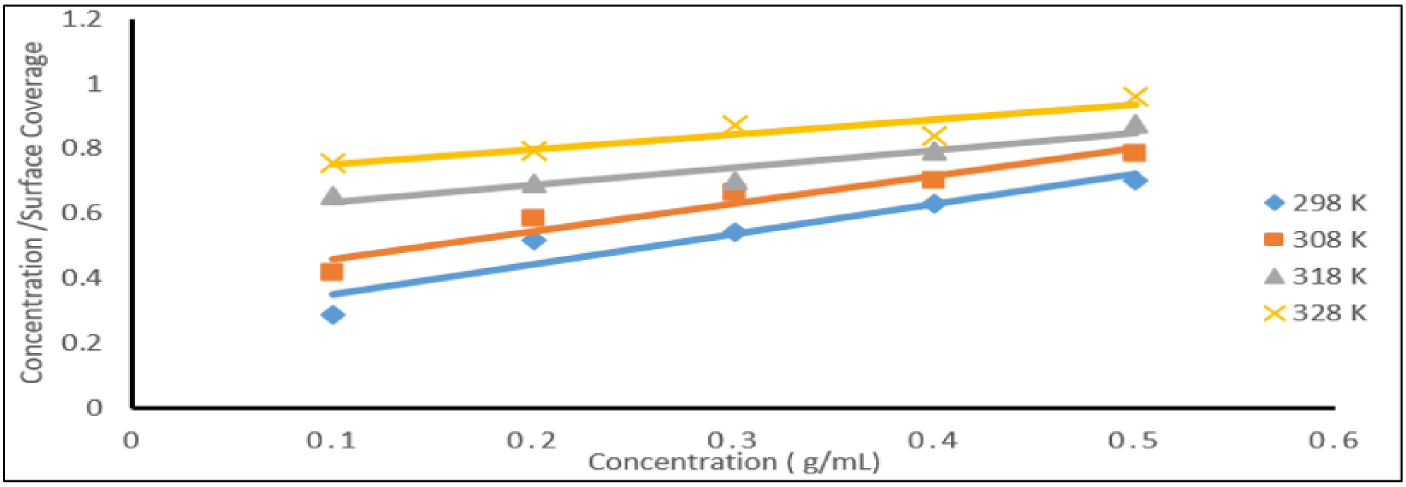
Fig 8 Variation of Inhibition Efficiency at Various Concentrations of AHLE/0.05KI Blends at Different Temperatures

Temperature-induced variations in inhibition efficiency, evident in Figures 6 - 8, reflect underlying adsorption mechanisms. In scenarios where inhibition efficiency decreases with temperature, the likely mechanism is physical adsorption (physisorption), which is known to weaken at elevated temperatures due to thermal desorption of the inhibitor molecules (Obot and Obi-Egbedi, 2010; Quraishi *et al*., 2013; Alaneme et al, 2015). Conversely, increased or stable efficiency with rising temperature implies chemical adsorption (chemisorption), where elevated thermal energy enhances electron sharing or bond formation between the inhibitor and the metal surface, as demonstrated in the works of Abiola and Oforka (2004) and Ebenso *et al.* (2010). Among the tested halides, the inhibition efficiency typically follows the order: $I^- > Br^-$. This pattern is attributed to the increasing ionic radius and polarizability down the halide group, with iodide ions showing the strongest synergistic effect (67.62 %) in promoting the adsorption of AHLE onto the metal surface (Bentiss *et al*., 2000; Ebenso and Eddy, 2008). Larger halide ions such as I^- facilitate better charge transfer and surface interaction, thereby enhancing inhibitor performance.In Figure 7, the trend of increasing inhibition efficiency with higher concentrations of AHLE is again evident and supported by adsorption isotherm models, particularly the Langmuir and Temkin models, which describe how surface saturation correlates with inhibitor dose (Umoren *et al*., 2008; Popova *et al*., 2003). As AHLE concentration increases, the availability of phytochemical constituents capable of adsorbing onto the metal surface rises, leading to the formation of a denser, more cohesive barrier layer that prevents access to corrosive media.

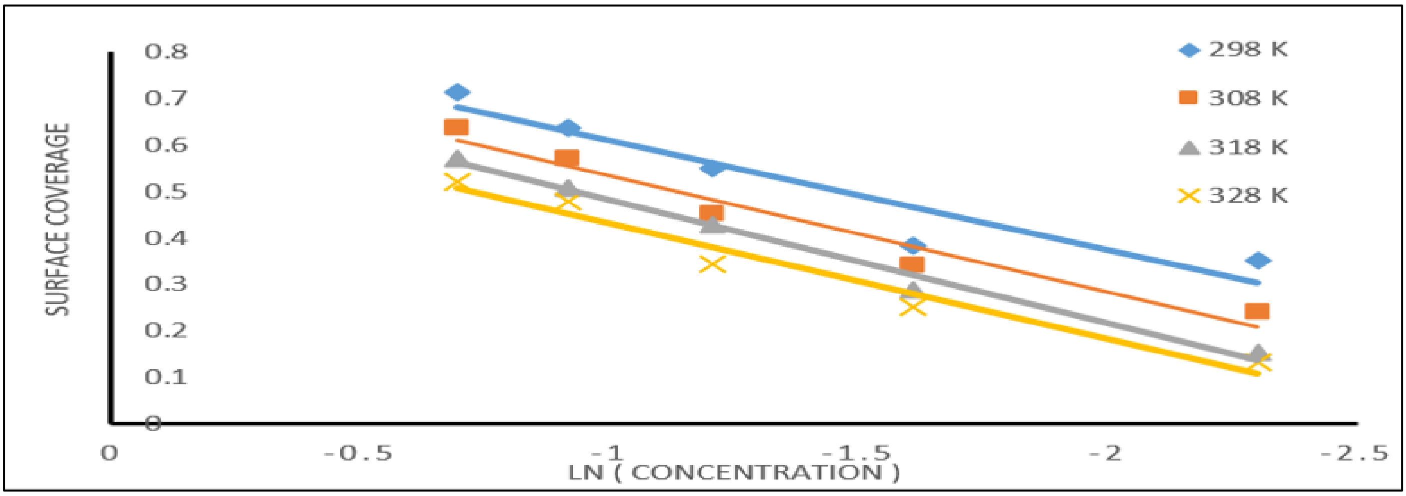
➢ *Adsorption Isotherm Considerations*

Experimental and theoretical studies have shown that the protective action of organic substances (inhibitors) during metal corrosion is based on the adsorption ability of their molecules, where the resulting adsorption film isolates the metal surface from the corrosive medium (Njoku *et al*,2014). The adsorption isotherm models considered in this study are the Langmuir and Temkin models; which were analysed based on the surface coverage and inhibitor concentrations. Langmuir isotherm plot describes the relationship between the surface coverage and inhibitor concentration of the extract used.

ISSN No:-2456-2165 https://doi.org/10.38124/ijisrt/25sep757



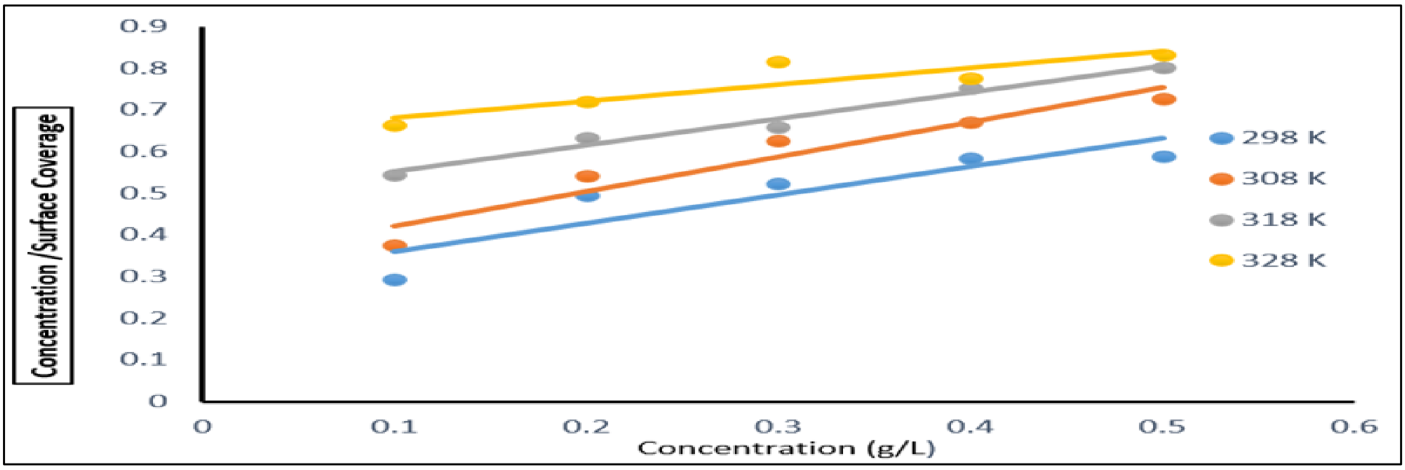
(a)



(b)

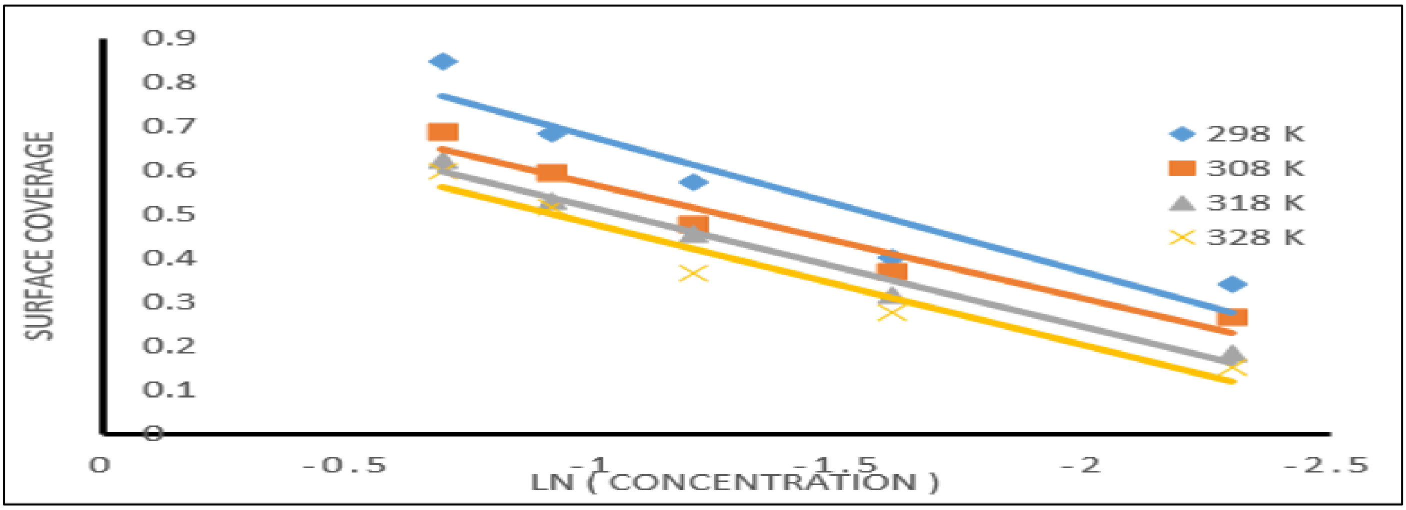
Fig 9 (a) Langmuir (b) Temkin Adsorption Isotherm in the Presence of AHLE at Various Temperatures

Langmuir isotherm plots gave straight line with good correlation of surface coverage with Ln (concentration) giving R^2 values close to unity. R^2 values ranged between 0.8410 - 0.9358 and 0.8998 - 0.9672 for Langmuir and Temkin isotherms respectively in the presence of AHLE. In the presence of AHLE/ KBr, R^2 values were between 0.7927 – 0, 9767 and 0.8853 – 0.9808, while in the presence of AHLE/KI, R^2 values were 0.8732 – 0.9846 and 0.9143 – 0.9671 for Langmuir and Temkin studies respectively. These values were obtained from isotherm plots presented in Figures 9 – 11 at various temperatures. High R^2 values close to unity shows good correlation surface coverage with Ln (concentration) and an indication that there was high adsorbent- adsorbates interaction between inhibitor molecules and the metal surface (Cookey *et al*, 2018).



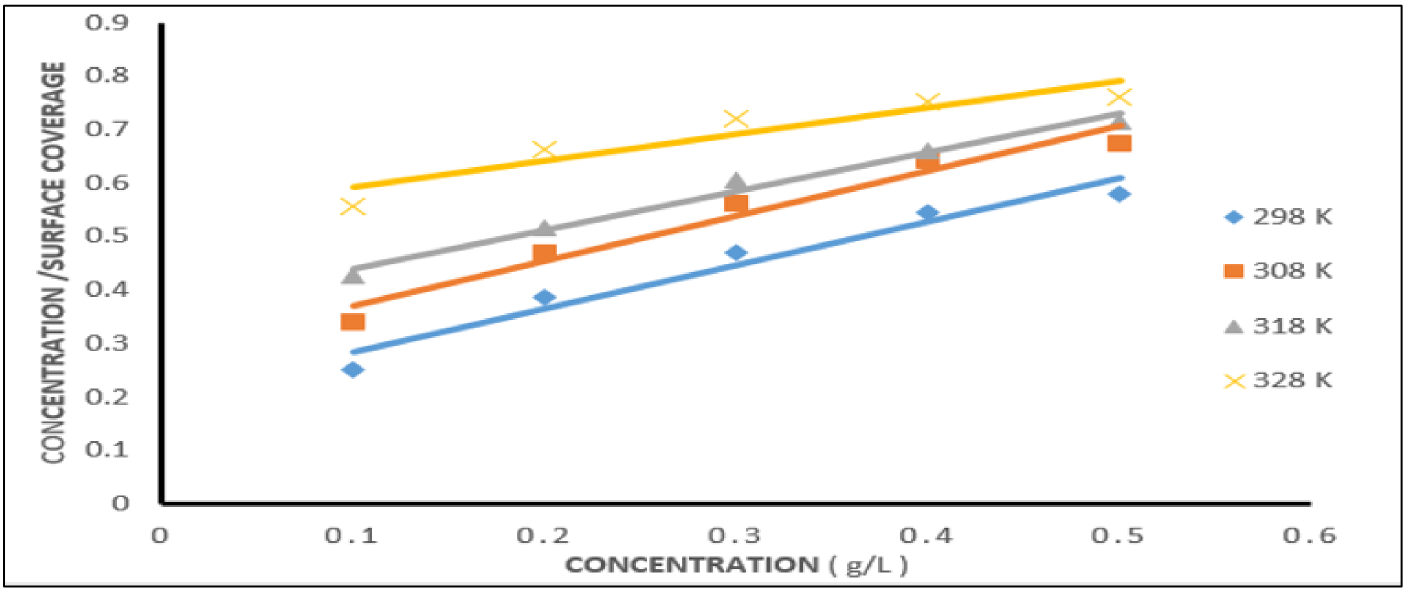
(a)

ISSN No:-2456-2165 https://doi.org/10.38124/ijisrt/25sep757

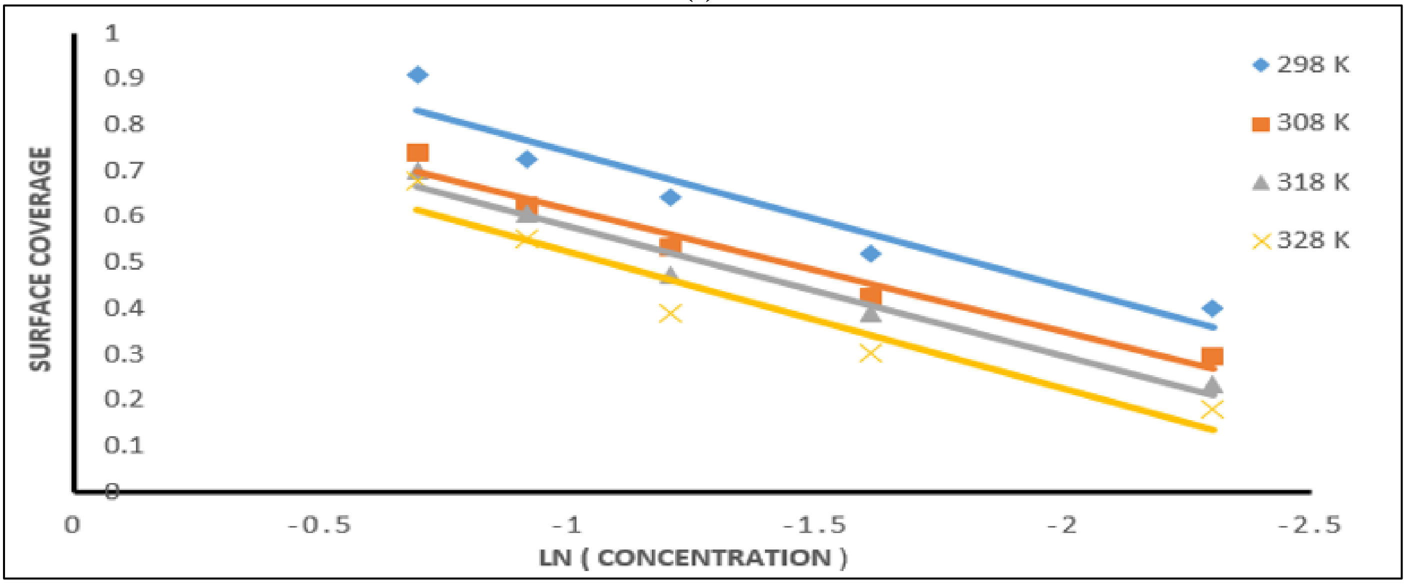


(b)

Fig 10 (a) Langmuir (b) Temkin Adsorption Isotherm in the Presence of AHLE/KBr Blend at Various Temperatures



(a)



(b)

Fig 11 (a) Langmuir (b) Temkin Adsorption Isotherm in the presence of AHLE/KI Blend at Various Temperatures

ISSN No:-2456-2165 https://doi.org/10.38124/ijisrt/25sep757

Table 2 Thermodynamic Parameters for Adsorption of Inhibitors on the Mild Steel Surface.

Inhibitor Type	Concentration (g/L)	Ea (kJ/mol)	Q_{ads}(kJ/mol)	ΔG_{ads}(kJ/mol)
AHLE	Blank	13.890	-	-
	0.1	23.358	-34.186	-14.120
	0.2	19.182	-16.687	-12.777
	0.3	24.041	-22.868	-13.441
	0.4	23.100	-17.008	-13.549
	0.5	32.209	-22.594	-13.939
AHLE/KBr	Blank	13.890	-	-
	0.1	21.645	-31.585	-13.676
	0.2	19.091	-15.259	-13.145
	0.3	29.299	-22.824	-13.333
	0.4	25.370	-17.501	-13.068
	0.5	40.106	-35.807	-12.756
AHLE/KI	Blank	13.890	-	-
	0.1	22.269	-30.025	-14.601
	0.2	23.935	-24.602	-13.929
	0.3	28.340	-27.928	-14.173
	0.4	27.078	-20.398	-14.018
	0.5	49.481	-42.603	-13.117

➢ *Thermodynamics Properties*

The values for the three thermodynamics properties evaluated in this study are presented in Table 2. It was observed that the activation energy values in the presence of inhibitors are higher than the values in the uninhibited solution (blank). The value of Ea in the blank was found to be 13.890 kJ/mol.; this increased to 32.209 kJ/mol on addition of 0.5 g/L of inhibitor concentration of AHLE. In the presence of extract combined with Potassium bromide ions Ea increased to 40.106 kJ/mol and in the presence of AHLE/KI, it further increased to 49.481 kJ/mol.at 0.5 g/L concentration. This shows that the inhibitor and halide additives considerably increased the activation energy of the corrosion process by increasing the energy barrier thereby slowing down the corrosion rate as the inhibitor got adsorbed onto the metal surface. It has also been established that activation energy value less than 80 kJ/mol is consistent with physisorption, while Ea values higher than 80 kJ/mol suggests chemisorption mechanism. Ea values obtained in this study confirm the adsorption mechanism to be physical as proposed by Nnanna *et al*, 2014; Fadare *et al*, 2016 and Cookey *et al*, 2018. The heat of adsorption values of Q_{ads} ranged from – 16.687 to – 34.186 kJ/mol in AHLE solution alone; - 15.259 to – 35.807 kJ/mol in AHLE/KBr and – 20.398 to – 42.603 kJ/mol.in AHLE/KI solutions. The calculated values were all negative implying physical adsorption mechanism and also suggests that the adsorption process is exothermic hence decrease in inhibitor efficiency with temperature increase. This observation is in agreement with the findings of (Eduok *et al* 2010; Njoku *et al*, 2014; Akaaza *et al*, 2021).

The adsorption equilibrium constant (K_{ads}) was evaluated from the relationship between surface coverage and inhibitor concentration using equation (8). The values of K_{ads} obtained shows that there was decrease in the adsorption (K_{ads}) as the temperature increased. The values of K_{ads} reduced from 4.273 to 2.12 for AHLE; from 4.497 to 1.937 for AHLE/KBr and from 6.532 to 2.121 for AHLE/KI combination. This implies that the extract and additives loses its adsorption strength onto the metal surface at higher temperatures. This could have contributed to the lowering of inhibition efficiency with temperature rise. This finding is in line with that of (Kumar and Mohana, 2014; Akaaza *et al*, 2021). The values of free energy of adsorption (ΔG_{ads}) are negative which shows the spontaneity of the adsorption process and the stability of the adsorbed layer on the mild steel surface. Since the values of ΔG_{ads} are in the range of -12 to -14 kJ/mol-1, for the studied inhibitors, it implies physisorption mechanism. Generally, negative values of ΔGads lower than -20 kJ/mol. Signifies physisorption, while values > - 40 kJ/mol. ,is an indication of chemisorption and values between – 20 and – 40 kJ/mol is attributed to mixed reaction /adsorption mechanism (.Kumar and Mohana, 2014; Akaaza *et al*, 2021).

IV. CONCLUSION AND RECOMMENDATION

➢ *Conclusions*

This study focused on the effect of halides admixture on the corrosion inhibition potential of *Acanthospermum hispidum* leaf extract (AHLE) and mild steel in HCl solution. Results revealed that *Acanthospermum hispidum* leaf extract (AHLE) contained phytochemicals such as alkaloids, flavonoids, tannins, saponins and phenols, which promote corrosion inhibition in acidic media.

- AHLE was found to be an effective green inhibitors of mild steel corrosion in 1 M HCl.
- The corrosion rates were found to decrease with increase in concentration of the extract at various temperatures. The optimum corrosion rate of 0.052 mm/yr was found at 0.5 g/L extract concentration and 298K, while that of the uninhibited was 0.1804 mm/yr.
- The addition of halide ions to *Acanthospermum hispidum* leaf extract (AHLE) enhanced the inhibition efficiency due to synergism, inhibition efficiency increased from 71.43% to 90.96% with iodide ions giving higher

efficiency than bromide ions when subjected to different temperatures.

- The synergistic effect of the halide was found to be significant (298, 308, 318, and 328 K), leading to a further reduction in corrosion rate compared to the inhibitor alone, indicating that halide ions enhanced the adsorption of the inhibitor molecules onto the metal surface.
- This study has confirmed that *Acanthospermum hispidum* performance as corrosion inhibitor improved with addition of halides (KBr and KI).

➢ *Recommendation*

Based on the results of this study, the following recommendations are made:

- The use of halides for improved performance of AHLE as green corrosion inhibitors for effective corrosion inhibition in acidic environments by 19.53% and can be used for industrial applications.
- The synergistic interaction between *Acanthospermum hispidum* leaf extract (AHLE) and halide ions gave good results and can be further explored with other eco-friendly corrosion inhibitors from plant sources.
- *Acanthospermum hispidum* leaf extract (AHLE) extract in combination with halides (KBr and KI) can be used at elevated temperatures of 328 K with 67.62 % inhibition efficiency.

REFERENCES

[1]. Abdurrahman, S. Y., Gaya, U. I., Kwalli, S. A., and Sa'idu, Y. (2021). Corrosion inhibition of mild steel in acidic medium using plant extracts: A review. Journal of Materials and Environmental Science, 12(1), 1–15.

[2]. Abiola, O. K., and Oforka, N. C. (2004). Adsorption behaviour of 2-mercaptobenzimidazole on mild steel. *Corrosion Science*, *46*(3), 389–403. https://doi.org/10.1016/S0010-938X (03)00162-5

[3]. Abiola, O. K., Otaigbe, J. O. E., and Kio, O. J. (2011). Ginger extract as corrosion inhibitor for mild steel in 1M HCl solution. *International Journal of Electrochemical Science*, *6*(1), 244–256.

[4]. Adzor, S. A., Adaga, G. T., and Gundu, D. T. (2014). Corrosion inhibitive potential of *Hibiscus sabdariffa* calyx extract for low carbon steel in 0.5M H_2SO_4 acid solution. *International Journal of Engineering Sciences and Research Technology*, *3*(8), 133–142.

[5]. Akaaza, J. N., Nyior, G. B., and Gundu, D. T. (2021). The potential of *Commelina benghalensis* L and *Acanthospermum hispidum* DC plants extract for use as green corrosion inhibitors. *Journal of Materials Science Research and Reviews*, *7*(4), 57–66.

[6]. Alaneme K.K., Daramola Y.S. Ating, E. I., Umoren, S. A., Udousoro, I. I., and Udoh, A. P. (2010). Leaves extract of *Ananas sativum* as green corrosion inhibitor for aluminum in HCl solution. *Green Chemistry Letters and Reviews*, *3*(2), 61–68. https://doi.org/10.1080/17518251003710560

[7]. Bam, S. A., Akaaza, J., and Tile, J. M. (2018). Study of corrosion inhibition of *Moringa oleifera* leaves extract blended with soluble oil on mild steel in hydrochloric acid solution. *Taraba Journal of Engineering and Technology*, *1*(1), 62–66.

[8]. Bamaiyi, B., and Peni, M. U. (2015). Effect of plant extracts on corrosion rate of mild steel in acidic medium. International Research Journal of Materials Science and Engineering, 2(1), 12–18.

[9]. Bentiss, F., Lagrenée, M., and Traisnel, M. (2000). The influence of iodide ions on the corrosion inhibition of mild steel in 1M HCl by organic compounds: Adsorption isotherm and synergistic effect. *Corrosion Science*, *42*(1), 127–146.

[10]. Bhardwaj, P. (2017). *Studies on potential green corrosion inhibitors for mild steel in different media* (PhD thesis, Faculty of Science, University of Kota). 183 pp.

[11]. Cookey, G. A., Odoemelam, S. A., and Eddy, N. O. (2018). Thermodynamic and adsorption studies of the corrosion inhibition of mild steel in acidic medium by plant extracts. Journal of Applied Sciences and Environmental Management, 22(1), 45–52.

[12]. Ebenso, E. E., Eddy, N. O., and Odiongenyi, A. O. (2003). The effect of halide ions on the corrosion inhibition of mild steel in acidic solutions using some organic compounds. *Materials Chemistry and Physics*, *79*(1), 58–70. https://doi.org/10.1016/S0254-0584 (02)00361-6

[13]. Eddy, N. O., and Ebenso, E. E. (2008). Adsorption and inhibitive properties of ethanol extracts of *Musa sapientum* peels as green corrosion inhibitor for mild steel in H_2SO_4. *African Journal of Pure and Applied Chemistry*, *2*(6), 46–54.

[14]. Eduok, U. M., Umoren, S. A., and Udoh, A. P. (2010). Synergistic inhibition effects between leaves and stem extracts of *Sida acuta* and iodide ion for mild steel corrosion in 1M H_2SO_4 solutions. *Arabian Journal of Chemistry*. 07(7): 62-75

[15]. Ejikeme, P. M., Umana, S. G., Menkiti, M. C., and Onukwuli, O. D. (2015). Inhibition of mild steel and aluminium corrosion in 1M H_2SO_4 by leaves extract of African breadfruit. *International Journal of Materials and Chemistry*, *5*(1), 14–23.

[16]. El-Etre, A. Y. (2005). Inhibition of acid corrosion of carbon steel using aqueous extract of olive leaves. *Journal of Colloid and Interface Science*, *314*(2), 578–583. https://doi.org/10.1016/j.jcis.2007.05.103

[17]. Fadare, M. O., Ogundare, F. O., and Adebayo, J. O. (2016). Corrosion inhibition and adsorption behavior of some plant extracts on mild steel in acidic medium. International Journal of Electrochemical Science, 11(5), 4564–4575.

[18]. Geetha, R., and Geetha, K. (2014). Phytochemical screening, quantitative analysis of primary and secondary metabolites of Cymbopogan citratus (DC) stapf. leaves from Kodaikanal hills, Tamil Nadu. *International Journal of PharmTech Research*, *6*(2), 521–529.

[19]. Kumar, P., and Mahama, K. N. (2014). Phytochemical screening and corrosion inhibitive behaviour of *Pterolobium hexapetalum* and *Celosia argentea* plant extracts on mild steel in industrial water medium.

[20]. Larouj, M., El Bouchti, M., and Hammouti, B. (2017). Inhibition of mild steel corrosion using natural plant extracts. *Journal of Materials and Environmental Science, 8*(12), 4385–4394.

[21]. Loto, C. A. (2011). Synergistic effects of halide ions on the corrosion inhibition of mild steel in HCl by amine and amino acids. *Corrosion Reviews, 29*(3–4), 175–188. https://doi.org/10.1515/CORRREV.2011.029

[22]. Miralrio, A., and Vázquez, A. E. (2020). Plant extracts as green corrosion inhibitors for different metal surfaces and corrosive media: A review. *Processes, 8*(942).

[23]. Njoku, V. O., Oguzie, E. E., Obi, C., and Ayuk, A. A. (2014). *Baphia nitida* leaves extract as a green corrosion inhibitor for the corrosion of mild steel in acidic media. *Advances in Chemistry.* https://doi.org/10.1155/2014/808456

[24]. Nnanna, L. A., Uchendu, K. O., Nwosu, F. O., Ihekoronye, U., and Eti, E. P. (2014). *Gmelina arborea* bark extracts as a corrosion inhibitor for mild steel in an acidic environment. *International Journal of Materials and Chemistry, 4*(2), 34–39.

[25]. Nwabanne, J. T., and Okafor, V. I. (2011). Adsorption and thermodynamics study of the inhibition of corrosion of mild steel in H2SO4 medium using Vernonia amygdalina. *Journal of Minerals and Materials Characterization and Engineering, 10*(12), 1153–1165.

[26]. Nwosu, F. O., Dosumu, O. O., and Okocha, J. O. (2014). Phytochemical composition and in vitro antimicrobial activity of aqueous and ethanolic leaf extracts of Cnidoscolus aconitifolius. *African Journal of Pharmacy and Pharmacology, 8*(19), 507–513. https://doi.org/10.5897/AJPP2014.4045

[27]. Obot, I. B., and Obi-Egbedi, N. O. (2010). An interesting and efficient green corrosion inhibitor for aluminium from extracts of *Chlomolaena odorata* L. in acidic solution. *Journal of Applied Electrochemistry, 40*(11), 1977–1983.

[28]. Ogunleye, O. O., Arinkoola, A. O., Alagbe, S. O., Agbede, O. O., Omodele, A. E., Morakinyo, A. F., and Osho, Y. A. (2019). Synthesis of green corrosion inhibitor for mild steel in acidic environment. *Indian Chemical Engineer.*

[29]. Olasehinde, E. F. (2018). A green approach to corrosion mitigation of mild steel in acid medium using *Caesapinia bonduc* seed coat extract. *FUTA Journal of Research in Sciences, 14*(1), 12–26.

[30]. Olisakwe, H. C., Ikpambese, K. K., Ipilakyaa, T. D., and Ekengwua, J. E. (2022). The inhibitive effect of *Ficus thonningii* leaves extract in 1M HCl solution as corrosion inhibitors on mild steel. *International Journal of Innovative Science and Research Technology, 7*(1), 769–778.

[31]. Owate, I. O., Nnuka, E. E., and Ezeh, N. E. (2014). Evaluation of corrosion inhibition of mild steel using green inhibitors. *International Journal of Science and Research, 3*(12), 2319–7064.

[32]. Popova, A., Christov, M., and Deligeorgiev, T. (2003). Adsorption and corrosion inhibitive properties of benzothiazole derivatives on mild steel in 1M HCl. *Corrosion Science, 45*(1), 33–58. https://doi.org/10.1016/S0010-938X(02)00096-8

[33]. Santhi, R., and Sengottuvel, R. (2016). Qualitative and quantitative phytochemical analysis of Moringa concanensis Nimmo. *International Journal of Current Microbiology and Applied Sciences, 5*(1), 633–640.

[34]. Solmaz, R., Kardas, G., and Yazici, B. (2008). The investigation of adsorption and corrosion inhibition of 2-mercaptothiazoline on mild steel in HCl medium. *Electrochimica Acta, 53*(20), 5941–5952. https://doi.org/10.1016/j.electacta.2008.03.027

[35]. Umoren, S. A., and Solomon, M. M. (2015). Effect of halide ions on the corrosion inhibition efficiency of different organic species – A review. *Journal of Industrial and Engineering Chemistry, 21*, 81–100.

[36]. Umoren, S. A., Obot, I. B., and Ebenso, E. E. (2008). Gum Arabic as a potential green corrosion inhibitor for aluminum in alkaline medium and its adsorption characteristics. *Industrial* and *Engineering Chemistry Research, 47*(21), 7875–7883.

[37]. Umoren, S.A. and Solomon M.M. (2010).Effect of halide ions additives on the corrosion inhibition of Aluminium in Hcl by Polyacrylamide. The Arabian Journal of Science and Engineering, 35(2A), 117-128.

[38]. Vimala, R., Kumar, V. R., and Sunderam, R. S. (2012). Preliminary phytochemical screening of different solvent extracts of stem bark and roots of *Ficus racemosa* (Linn.). *International Journal of Pharmacy and Pharmaceutical Sciences, 4*(2), 108–111.

[39]. Wang, H., Gao, M., Guo, Y., Yang, Y., and Hu, R. (2016). A natural extract of tobacco rob as scale and corrosion inhibitor in artificial seawater. *Desalination, 398*, 198–207.

[40]. Yang, H.-M. (2021). Role of organic and eco-friendly inhibitors on the corrosion mitigation of steel in acidic environments—A state-of-art review. *Molecules, 26*(11), 3473.