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Investigation of the inhibition effect of benzaldehyde on the corrosion of aluminium in nitric acid solution

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Abstract: The effect of benzaldehyde as an inhibitor on the corrosion of aluminum in a nitric acid solution was studied using the weight loss method. The experiment varied the inhibitor concentration and temperature. The results demonstrated that benzaldehyde effectively inhibited the corrosion of aluminum in nitric acid. As the inhibitor concentration increased, the corrosion rate of aluminum in 1.4 M HNO_3 decreased. Inhibition efficiency increased with higher inhibitor concentration but decreased as temperature rose. The highest inhibition efficiency observed was 85.47%. The activation energy for the blank acid solution was found to be 15.12 kJ mol^{-1}, which increased to 31.25 kJ mol^{-1} in the presence of 0.1 M inhibitor. Thermodynamic parameters such as enthalpy change (ΔH), entropy change (ΔS), and Gibbs free energy of adsorption (ΔG_{ads}) were calculated and discussed. Adsorption studies indicated that the Langmuir adsorption isotherm best described the inhibitor molecule's adsorption on the aluminum surface.

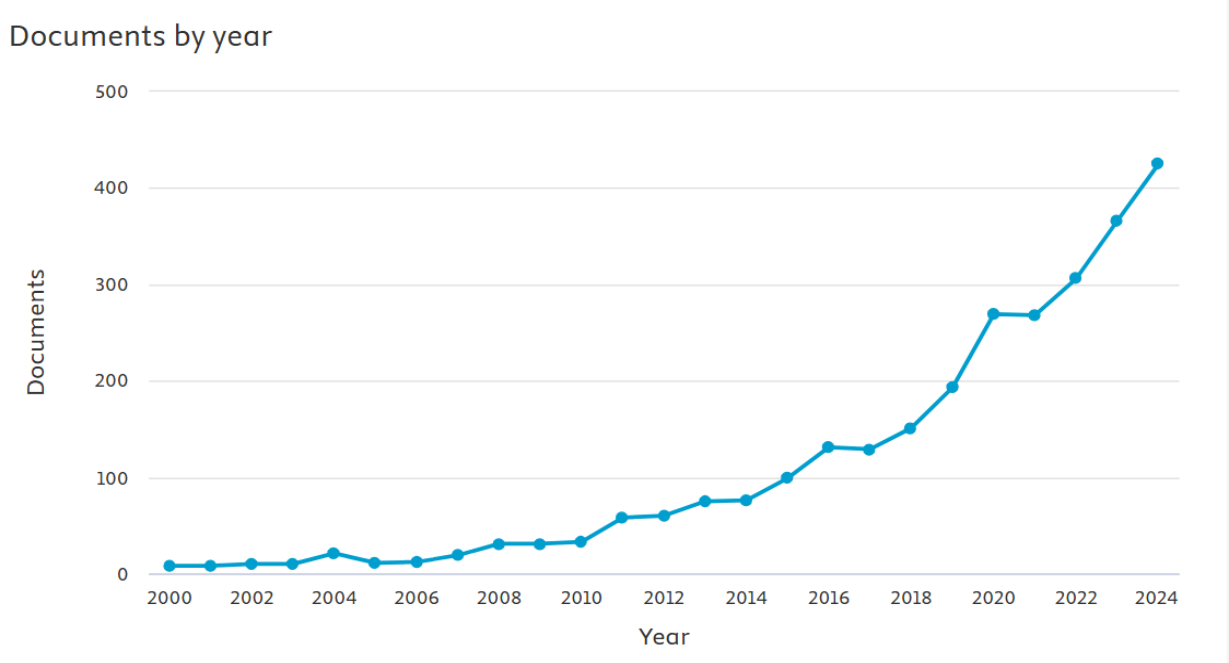
1. Introduction

The corrosion of aluminum in acidic environments is a significant concern in various industrial applications, particularly in the fields of aerospace, automotive, and construction, where aluminum alloys are widely used due to their light weight and excellent mechanical properties (Aadil *et al.*, 2025; Lamghfri *et al.*, 2025; Bazzi *et al.*, 2003;). However, these properties are compromised when aluminum comes into contact with aggressive acidic solutions, such as nitric acid, which induces a rapid degradation of the material. The search for efficient corrosion inhibitors has become critical in preventing such damage and extending the service life of aluminum components in these environments (Husaini and Ibrahim, 2019). Nitric acid is considered as highly corrosive of metallic materials

(aluminium, steels, copper, zinc…) because of the high soluble of nitrate compounds (Roscher *et al.*, 2024; Fouda *et al.*, 2023; Barouni *et al.*, 2014; Hammouti *et al.*, 2010; Zarrouk *et al.*, 2010 & 2011; Mihit *et al.*, 2006). Corrosion inhibitors function by adsorbing onto the surface of metal substrates, thereby forming a protective layer that hinders the electrochemical reactions responsible for corrosion. Among various organic compounds, aldehydes have garnered attention due to their potential as effective corrosion inhibitors. Benzaldehyde, a simple aromatic aldehyde, has been shown to possess significant corrosion inhibition properties due to its ability to interact with metal surfaces and form stable complexes, which could reduce the aggressive effects of corrosive environments like nitric acid (Husaini *et al.*, 2018).

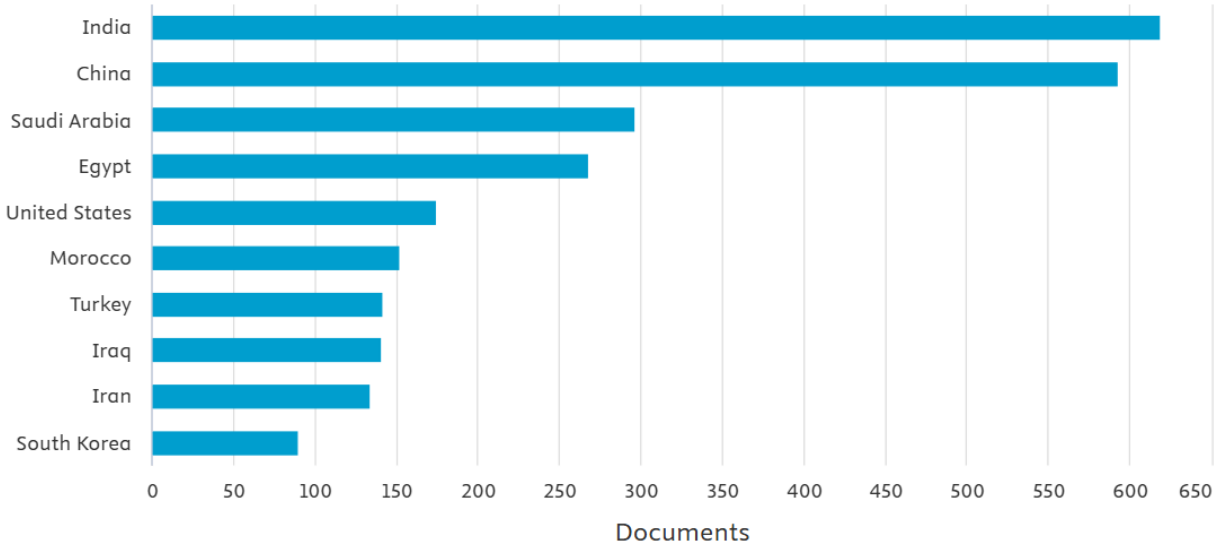
Recent studies have demonstrated that benzaldehyde exhibits notable inhibition effects on various metals, including steel, copper, and aluminum, in different acidic solutions. The inhibition mechanism is primarily attributed to the adsorption of benzaldehyde molecules onto the metal surface, which blocks active sites and prevents further corrosion (Rahman *et al.*, 2023; Ali *et al.*, 2022). The effectiveness of benzaldehyde as a corrosion inhibitor depends on several factors, such as the concentration of the inhibitor, temperature, and the nature of the acidic solution (Liu *et al.*, 2023). Furthermore, the environmental impact and toxicity of synthetic corrosion inhibitors have led to increased interest in green inhibitors (El Azzouzi *et al.*, 2022). Benzaldehyde, being relatively less toxic and environmentally friendly, is considered promising alternative to conventional inhibitors, which are often based on hazardous chemicals (Sharma *et al.*, 2021). In this context, the present investigation aims to explore the corrosion inhibition effects of benzaldehyde on aluminum in nitric acid solution, providing insights into its potential application as an eco-friendly corrosion inhibitor in industrial settings.

Search on Scopus « Corrosion & Benzaldehyde » gave more than 3000 documents. Then, a bibliometric analysis can be conducted to show the evolution against the period from 2000 to 2024, the most published authors and the major countries as well as collaboration between the authors to form clusters (Salim *et al.*, 2022; N'diyae *et al.*, 2022; Hassan *et al.*, 2024; Aichouch *et al.*, 2025). VOS viewer tool can elucidate this opportinity via the nods corresponding (Zhao *et al.*, 2021; Hammouti *et al.*, 2025). **Scheme 1** described the net increase in publication from 2010 to present.

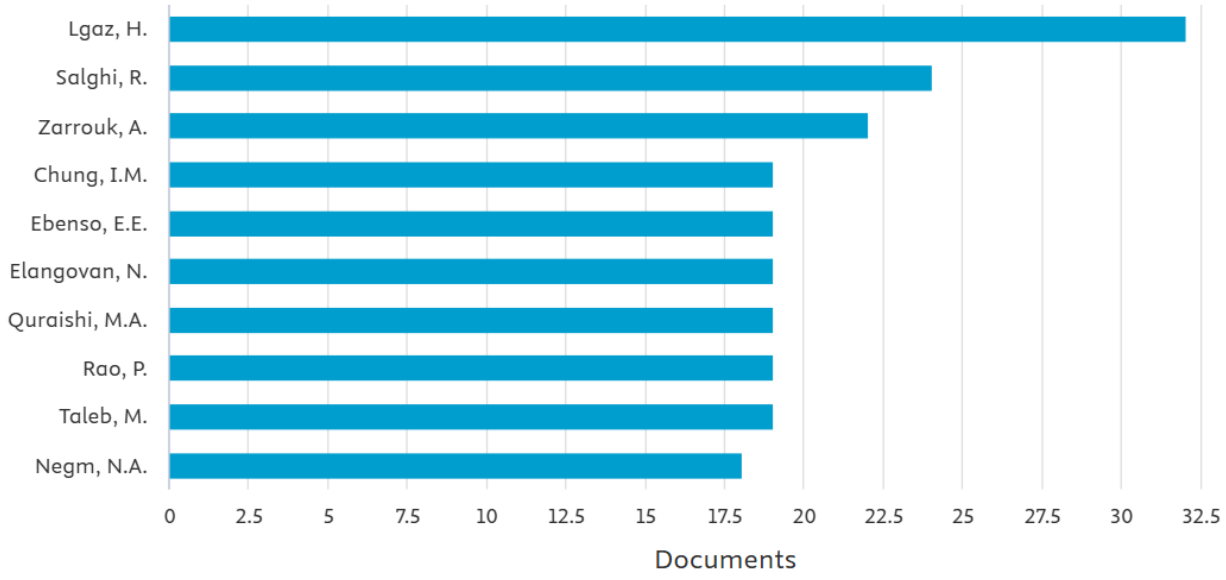


Scheme 1. Remarkable increase of publication on benzaldehyde as Corrosion last years.

The quantitative analysis of countries indicates which countries contribute the most to any specific research area. The ten most active countries in the field are shown in the **Scheme 2.** India and China are the most active countries publishing around 600 articles. The Top ten productive authors (>18 articles) are collected in **Scheme 3**. The most productive author in the field is Lgaz from the South Korea with 32 articles, more than 12000 in total citations, and an H-index of 60. The second and third authors are Salghi and Zarrouk, with publication numbers of 24 and 22.

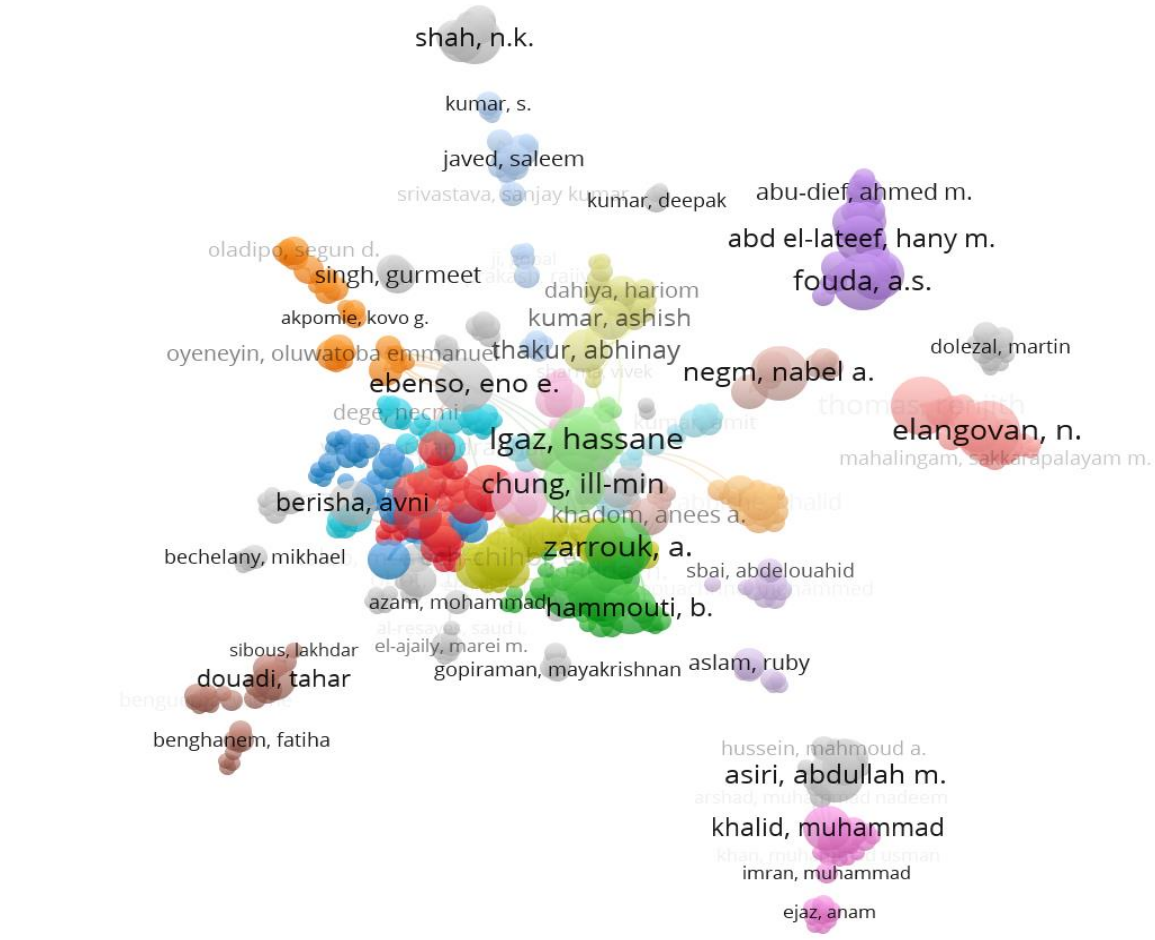


Scheme 2. Most ten Countries affiliated tot he corresponding publications

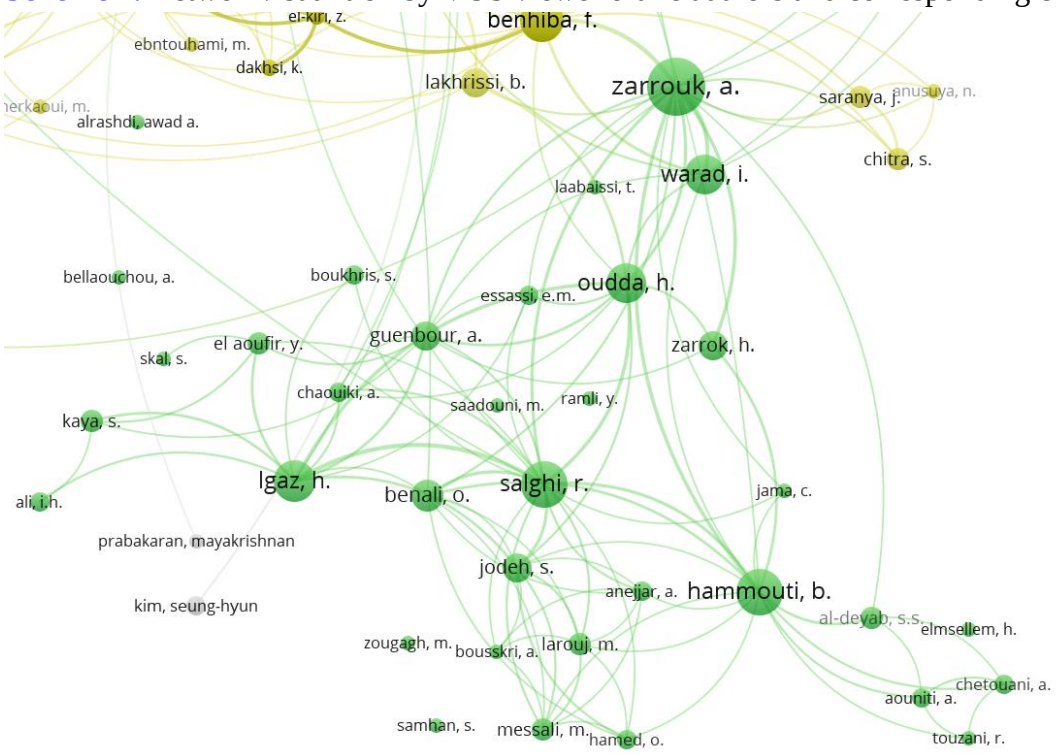


Scheme 3. Major ten published authors

VOS viewer allows to analyze the groupment of authors called research clusters (**Scheme 4).** The circle (node) size means contribution frequencies, while the line thickness indicates a closer collaboration relationship. The different colors represent clusters generated by various groups of countries. For example, the most published author Lgaz and also Chung are shown by a Green color indication from the same country (South Korea). The Moroccan reserachers (Salghi, Zarrouk, Taleb…) are shown at dark green nods (**Scheme 5**).



Scheme 4. Netwok visualition by VOS viewer oft he authors and corresponding clusters



Scheme 5. Moroccan cluster of Salghi, Zarrouk… Green nods

The objectives of this study include evaluating the inhibition efficiency of benzaldehyde on aluminum corrosion in nitric acid, determining the adsorption characteristics of benzaldehyde on the aluminum surface, and understanding the mechanism behind its inhibitory action. The results of this study are expected to contribute to the development of more sustainable and efficient corrosion protection strategies for aluminum in acidic environments.

2. Methodology

2.1 Sample Preparation

The method employed by Husaini *et al.* (2019a) will be followed in this study, where aluminum sheets with a purity of 99.95%, supplied by the Metal Focus Fabrication Technology Incubation Centre in Kano State, Nigeria, were examined. The aluminum sheets, each 0.1 cm thick, were mechanically cut into 3 × 2 cm coupons. These coupons were then polished using emery paper of grades 600, 800, and 1000, degreased with absolute ethanol, dried with acetone, and stored in desiccators to keep them free from moisture before use.

2.2 Preparation of Solutions

A stock solution of analytical-grade nitric acid (68%, 1.51 g/L) was prepared using double-distilled water. To obtain the required concentration of 1.4 M, the acid solution was diluted accordingly. The inhibitor used in the study was benzaldehyde (95%, 1.04 g/cm³), with concentrations ranging from 0.02 to 0.1 M. These inhibitor concentrations were diluted in the prepared acid solutions to create test solutions for the weight loss experiments (Husaini *et al.*, 2023).

2.3 Weight loss Measurement

In the weight loss experiment, a pre-weighed aluminum coupon was fully immersed in 50 cm³ of the test solution at specified concentrations of the corrosive substance, both with and without the inhibitor. The beaker was covered with aluminum foil to prevent contamination from particles and to reduce the evaporation of the corrosive media at elevated temperatures. The beaker was then placed in a water bath set to the desired temperature. At intervals of 1, 2, and 3 hours, the coupon was removed, washed with a brush under tap water, rinsed with distilled water, followed by acetone, air-dried, weighed, and recorded. This procedure was repeated with different inhibitor concentrations (0.02, 0.04, 0.06, 0.08, and 0.1 M) and temperatures (308, 313, and 318 K). The weight loss was determined by calculating the change in weight. Using the experimental data, the weight loss (g), corrosion rates (g cm^{-2} h^{-1}), degree of surface coverage (Θ), and inhibition efficiency (% IE) of the inhibitor were calculated using the respective equations (Husaini, 2023).

$$\Delta w = \boldsymbol{W_1} - \boldsymbol{W_2} \quad \text{Eqn. 1}$$

$$C_R \text{ (g cm}^{-2}\text{ h}^{-1}) = \frac{\boldsymbol{W_1} - \boldsymbol{W_2}}{\boldsymbol{At}} \quad \text{Eqn. 2}$$

$$\Theta = \frac{\boldsymbol{W_i} - \boldsymbol{W_f}}{\boldsymbol{W_i}} \quad \text{Eqn. 3}$$

$$\eta = \left(\frac{\boldsymbol{W_i} - \boldsymbol{W_f}}{\boldsymbol{W_i}}\right) \times 100 \quad \text{Eqn. 4}$$

Here, $\boldsymbol{W_1}$ and $\boldsymbol{W_2}$ represent the weight losses of the aluminum coupons before and after treatment. W_i and W_f are the weights of the coupon without and with the inhibitor, respectively. Θ denotes the degree of surface coverage of the inhibitor, η is the inhibition efficiency, A is the area of the coupon (in cm²), and t is the immersion time (in hours).

2.4 Scanning Electron Microscope (SEM) Analysis

The surface morphologies of the aluminium coupons, both before and after inhibition, were examined using the PRO: X: Phenonm World 800-07334 model, manufactured by Phenom World in Eindhoven, Netherlands. Scanned images were captured of an unreacted aluminium coupon, an aluminium coupon immersed in acid without inhibitor, and an aluminium coupon immersed in acid with inhibitor at 308 K for 3 hours. The images were taken at an accelerating voltage of 15.00 kV and a magnification of x500 (Husaini, 2021).

3.0 Results and discussion

3.1 Effect of inhibitor concentrations on corrosion rate

The results presented in the figure 1 illustrate the impact of inhibitor concentrations on the corrosion rate of aluminum in 1.4 M HNO_3. The corrosion rate in the uninhibited system was found to be higher compared to the inhibited systems. The corrosion rate was monitored by varying the reaction medium temperature from 308 to 318 K. The data indicate that the corrosion rate of aluminum in 1.4 M HNO_3 decreases as the inhibitor concentration increases at all studied temperatures. This is expected, as higher inhibitor concentrations lead to greater adsorption of inhibitor molecules onto the aluminum surface, forming a barrier that reduces charge and mass transfer. As a result, the interaction between the metal and the corrosive environment is minimized, which in turn reduces the corrosion rate. A similar finding was reported by Husaini *et al.* (2019b) in their study on the inhibitive effect of glutaraldehyde on aluminum corrosion in hydrochloric acid, where the corrosion rate decreased with increasing inhibitor concentration.

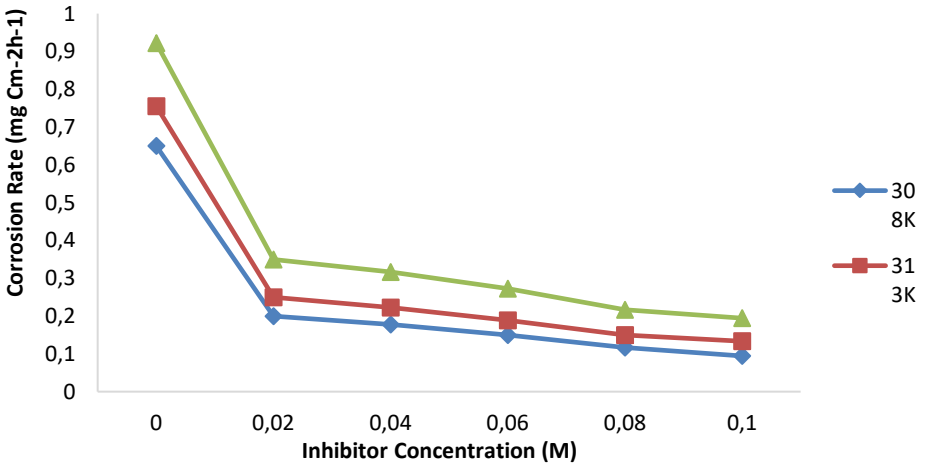


Figure 1. Corrosion Rate against Inhibitor Concentration

3.2 Effect of Inhibitor Concentrations on Inhibition Efficiency

The result presented in **Figure 2** show that the inhibition efficiency increases as the inhibitor concentration rises, which is attributed to a greater fraction of the aluminum surface being covered by the inhibitor molecules at higher concentrations, leading to more extensive surface coverage (Husaini and Ibrahim, 2020). This trend illustrates a progressive increase in inhibition efficiency with higher inhibitor concentrations. A similar study by Ladha et al. (2013) investigated cumin (Cuminum cyminum) extract as an eco-friendly corrosion inhibitor for pure aluminum in an acidic medium. Their results showed that aluminum's inhibition efficiency increased from 79.30% to 90.20% with inhibitor concentrations of 0.04% and 0.13%, respectively.

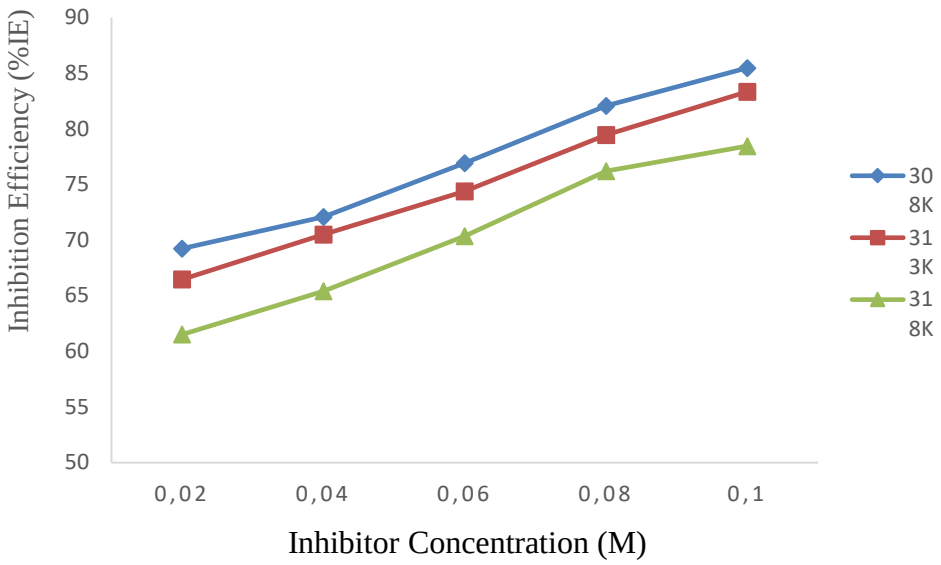


Figure 2. Inhibition Efficiency against Inhibitor Concentration

3.3 Effect of Temperature on Corrosion Rate of Aluminum

The influence of temperature on the corrosion rate of aluminum in both blank acid and acid with varying inhibitor concentrations was examined within the temperature range of 308 K to 318 K, as shown in **Figure 3.** The results indicate that the corrosion rate of aluminum in both the blank and inhibited acid solutions increases with rising temperature. This is expected, as higher temperatures lead to an increase in the average kinetic energy of the reacting molecules, thereby accelerating the corrosion rate (Husaini *et al.,* 2020). The rise in corrosion rate with temperature at a given inhibitor concentration can be attributed to the desorption of inhibitor molecules from the metal surface. The reduced corrosion rate in the inhibitor-containing solution is due to the inhibitor's ability to decrease the corrosion rate of aluminum. A similar study by Udom *et al.* (2017) who investigated the effect of Acanthus montanus leaf extract on aluminum corrosion in hydrochloric acid, with results showing an increase in the corrosion rate from 7.27 to 17.67 mg cm^{-2} day^{-1} at temperatures of 303 K and 333 K.

3.4 Effect of temperature on inhibition efficiency

The impact of temperature on the inhibition efficiency of the inhibitor on aluminum is presented in **Figure 4**. As shown, the inhibition efficiency decreases as the temperature increases from 308 K to 318 K. This reduction in efficiency is believed to be due to the desorption of inhibitor molecules from the aluminum surface as the temperature rises, which destabilizes the inhibitor molecule and weakens the effectiveness of physical adsorption (Husaini *et al.,* 2020b). A similar study by Namrata *et al.* (2015) examined the corrosion inhibition of aluminum alloy in alkaline media using Neolamarkia cadamba bark extract as a green inhibitor. Their results showed a decrease in inhibition efficiency from 87.1% to 78.5% as the temperature increased from 303 K to 333 K.

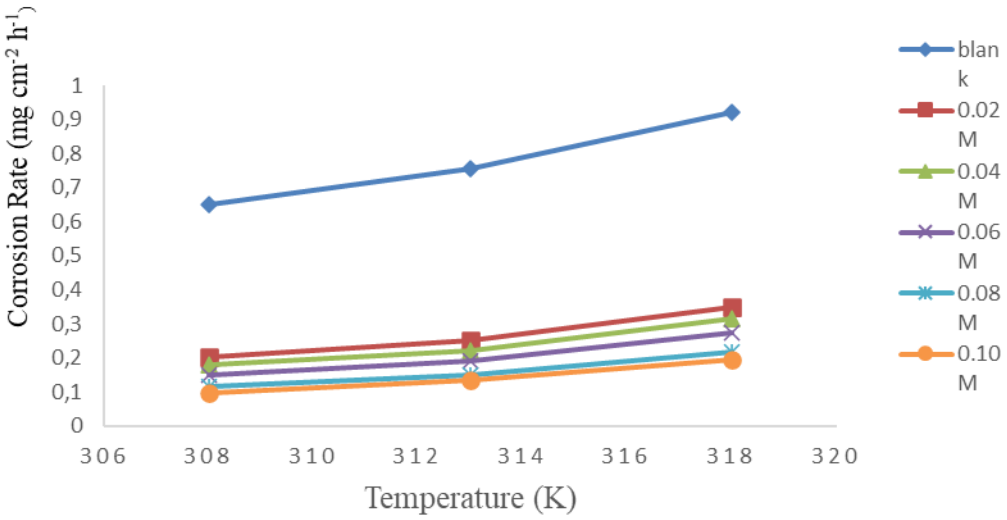


Figure 3. Corrosion Rate against Temperature

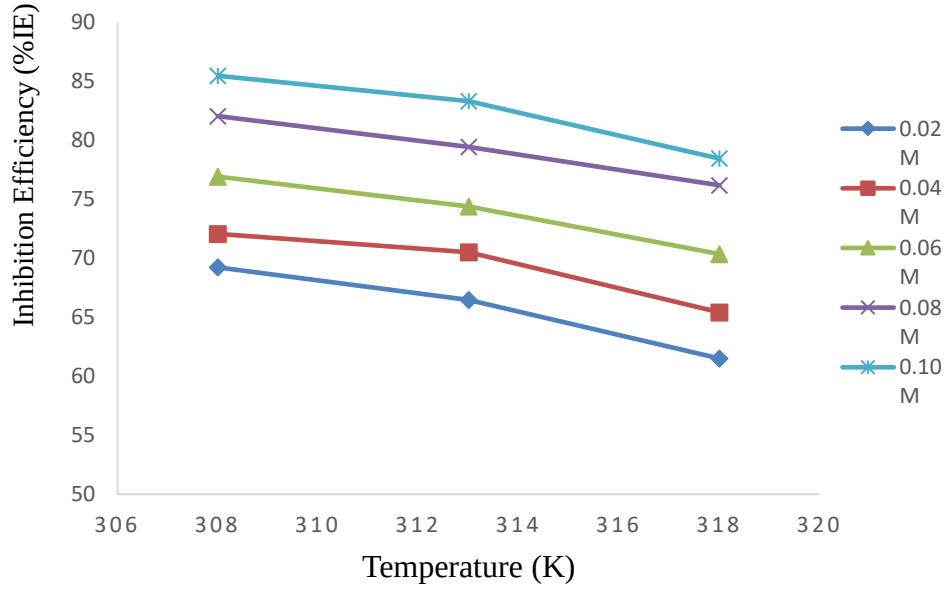


Figure 4. Inhibition Efficiency against Temperature

3.5 Kinetic Study

3.5.1 Activation Energy (E_a)

The apparent activation energy (E_a) for the corrosion process in the absence and presence of the inhibitor was evaluated from Arrhenius eqn 5;

$$\ln(C_R) = \mathbf{lnB} - \frac{\mathbf{E_a}}{\mathbf{RT}} \qquad \text{Eqn. 5}$$

B represents a constant, R is the universal gas constant, and T is the absolute temperature. The graph of ln(CR) versus the reciprocal of absolute temperature (1/T) produced a straight line with a slope of $-\mathbf{E_a}/R$, which was used to calculate the activation energy ($\mathbf{E_a}$) for the corrosion process. Table 1 displays the calculated $\mathbf{E_a}$ values for aluminum corrosion both with and without an inhibitor. The activation energy was determined to be 15.12 kJ/mol in the uninhibited acid solution, which increased to 31.25 kJ/mol when the highest inhibitor concentration (0.1 M) was used. This indicates the formation of a physical barrier by the adsorbed organic molecules. The increase in activation energy with higher inhibitor concentration further supports the notion that inhibition efficiency improves as the inhibitor

concentration rises. When $\mathbf{E_a}$ > 80 kJ/mol, chemical adsorption occurs, while $\mathbf{E_a}$ < 80 kJ/mol suggests physical adsorption (Husaini *et al.*, 2020c). Since the $\mathbf{E_a}$ values in this study were below 80 kJ/mol, physical adsorption was proposed as the mechanism. The observed increase in activation energy in the presence of the inhibitor is attributed to the significant rise in inhibitor adsorption on the aluminum surface. This trend aligns with findings reported by Patel *et al.* (2012).

3.5.2 Rate Constant (k)

Corrosion is a heterogeneous process consisting of cathodic and anodic reactions, which may occur at the same or different rates. Based on this, a kinetic analysis of the data is required. In this study, the initial weight of aluminum at time t is denoted as W_i, the weight loss as ΔW, the weight change as (W_i - ΔW), and the first-order rate constant as k_1. The combination of these factors leads to Equation. 6:

$$\ln (W_i - \Delta W) = -k_1 t + \ln \Delta W \qquad \text{Eqn. 6}$$

From this Equation, plotting ln (W_i - ΔW) against time t at 308 K yields a linear relationship, confirming that the corrosion of aluminum in HNO_3 with the presence of an inhibitor follows first-order kinetics. The rate constant for the first-order reaction was determined from the slope of the plot, and the results are presented in Table 2. The rate constant (k_1) for the corrosion of aluminum in the blank acid solution was found to be higher than in the inhibited acid solution, thereby confirming the inhibitory effect of the inhibitor in the HNO_3 solution.

3.5.3 Half-Life ($t_{1/2}$)

The half-life ($t_{1/2}$) for the whole process was calculated from Equation. 7;

$$t_{1/2} = \frac{0.693}{k} \qquad \text{Eqn. 7}$$

The half-life ($t_{1/2}$) values shown in Table 2 increase from the blank acid solution to the inhibited solution. The higher half-life values in the presence of the inhibitor, compared to the blank acid solution, support the previous findings that the corrosion rate decreases when an inhibitor is present (Husaini 2020a).

Table 1. Kinetic Parameters for Aluminium Corrosion with and without various inhibitor concentrations

Inhibitor Concentration (M)	Activation Energy (kJ mol^{-1})	Rate Const. (k $\times 10^{-3}$) ($hour^{-1}$)	Half-life (hours)
Blank	15.12	3.92	176.61
0.02	24.18	1.20	576.35
0.04	24.95	1.06	648.53
0.06	25.75	0.90	768.82
0.08	26.77	0.70	988.78
0.10	31.25	0.56	1221.68

3.6 Thermodynamic Study

3.6.1 Enthalpy change (ΔH) and Entropy change (ΔS)

Enthalpy change (ΔH) and entropy change (ΔS) are additional thermodynamic parameters of the activation process, which were determined by analyzing the effect of temperature on the corrosion rate of aluminum in nitric acid using the transition state Equation:

$$\ln\left(\frac{C_R}{T}\right) = \ln\left(\frac{R}{Nh}\right) + \left(\frac{\Delta S_a}{R}\right) - \left(\frac{\Delta H_a}{RT}\right) \qquad \text{Eqn. 8}$$

The corrosion rate (CR) at temperature T is related to the molar gas constant (R), Avogadro's constant (N), and Planck's constant (h). A plot of ln(CR/T) versus 1/T produced a straight-line graph, with a slope of $-\Delta H_a/R$ and an intercept of $\ln(R/Nh) + \Delta S_a/R$. From this graph, the values of ΔH and ΔS were determined from the slope and intercept, respectively.

The results in Table 2 indicate that all ΔH values are positive. This positive sign of the enthalpies reflects the endothermic nature of the aluminum dissolution process (Husaini *et al.*, 2023a, b, and c). Additionally, the negative ΔS values suggest that the activation complex in the rate-determining step involves an association, rather than dissociation, process. A similar result was reported by Olasehinde *et al.* (2017) in their study of the inhibitive properties of *Alchornea laxiflora* leaves on the corrosion of mild steel in HCl, where the ΔH values were positive and the ΔS values negative.

Table 3. Enthalpy and Entropy change of the reaction process with various concentrations of the inhibitor

Inhibitor Concentration (M)	ΔH (kJ mol^{-1})	- ΔS (kJ $mol^{-1}k^{-1}$)
Blank	13.74	262.35
0.02	22.80	243.30
0.04	23.57	241.85
0.06	24.36	240.74
0.08	25.36	239.54
0.10	29.87	226.86

3.6.2 Free Energy of Adsorption (ΔG_{ads})

The free energy of adsorption (ΔG_{ads}) values was determined using Eqn. 9;

$$\Delta G_{ads} = - RT \ln (55.5 \times K_{ads}) \quad \text{Eqn. 9}$$

The calculated ΔG_{ads} values are shown in Table 3. The results reveal that ΔG_{ads} values are negative in all cases, indicating the spontaneity and feasibility of the reaction, as well as the strong adsorption of the inhibitor on the aluminum surface. In this study, ΔG_{ads} values ranged from -22.1 to -22.26 kJ/mol, suggesting that the inhibitor adsorption on the metal surface follows a physical adsorption mechanism (Yunusa *et al.*, 2021; Husaini *et al.*, 2023d). This is consistent with the findings of Husaini *et al.* (2020d), who stated that ΔG_{ads} values around -20 kJ/mol indicate electrostatic interactions between charged molecules and a charged metal, which is characteristic of physisorption. In contrast, values around -40 kJ/mol are indicative of charge sharing or transfer from the inhibitor molecule to the metal surface, forming a coordinate bond associated with chemisorption (Husaini et al., 2024a, b). This result aligns with the study by Ebenso *et al.* (2008).

3.7 Adsorption Isotherm

The adsorption isotherm provides essential information about the interaction between an inhibitor and a metal surface. The surface coverage (Θ) indicates the formation of a chemical bond between the metal atoms and the inhibitor molecules. The Langmuir adsorption isotherm is considered the ideal model for both physical and chemical adsorption on a smooth surface. It assumes monolayer adsorption on a surface with a finite number of identical sites (Rabiu *et al.*, 2023; Husaini *et al.*, 2023e and f). The Langmuir adsorption isotherm is expressed by the following Equation:

$$\frac{C_{ads}}{\theta} = \frac{1}{K_{ads}} + C_{ads} \quad \text{Eqn. 10}$$

Where C_{ads} is the inhibitor concentration, K_{ads} is the adsorption equilibrium constant, and Θ represents the degree of surface coverage by the inhibitor (Obot *et al.*, 2020; Husaini, 2020b). A plot of C_{ads}/Θ versus C_{ads} produces a straight line with an intercept equal to $1/K_{ads}$. The results

demonstrate that the slopes and the correlation coefficient (R^2) values are close to unity, suggesting that the adsorption of the inhibitor on the aluminum surface follows the Langmuir adsorption isotherm. The values of R^2 and K_{ads} are provided in Table 3.

Table 3: Adsorption parameters deduced from Langmuir adsorption isotherm

Temperature (K)	R^2	K_{ads}	ΔG (kJ mol^{-1})
308	0.9952	101.01	-22.10
313	0.9950	95.23	-22.31
318	0.9953	81.96	-22.26

3.8 Scanning Electron Microscope (SEM) Result

Figure 5a displays a micrograph of aluminum that has not been exposed to corrosive environment media. In **Figure 5b,** the aluminum immersed in corrosive environment appears rough and severely damaged due to the corrosive effects of the acid. **Figure 5c** shows that the presence of inhibitor prevented the acid attack on the aluminum surface. This suggests that benzaldehyde effectively reduces the extent of corrosion on aluminum in nitric acid solution by forming a protective layer on the surface, which was absent when the aluminum interacted directly with the acid. These results suggest that benzaldehyde is a promising corrosion inhibitor for aluminum in acidic environments.

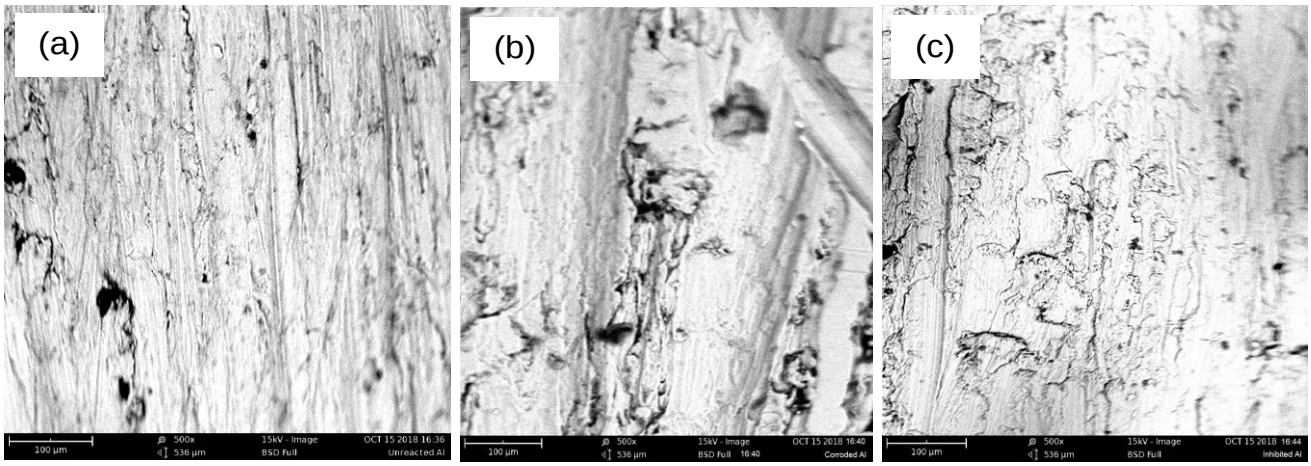


Figure 5. Micrograph of (a) Unreacted Aluminum (b) Corroded Aluminum (c) Inhibited Aluminum

Conclusion

Based on the results of this study, it was concluded that benzaldehyde effectively inhibits the corrosion of aluminum in nitric acid at temperatures of 308, 313, and 318 K. The inhibition efficiency increases with the concentration of the inhibitor but decreases with rising temperature. The corrosion rate increases in both inhibited and uninhibited solutions, but it decreases more significantly in the presence of the inhibitor. Thermodynamic parameters indicate that the adsorption of the inhibitor on the aluminum surface is spontaneous and follows a physical adsorption (physisorption) mechanism. The FT-IR analysis of the corrosion products reveals the presence of functional groups from the inhibitor, suggesting the formation of a thin layer of inhibitor molecules on the aluminum surface. The adsorption of the inhibitor at various concentrations on the aluminum surface adheres to the Langmuir adsorption isotherm.

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Disclosure statement: *Conflict of Interest:* The authors declare that there are no conflicts of interest.
Compliance with Ethical Standards: This article does not contain any studies involving human or animal subjects.

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