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Original Article

Corrosion inhibition effect of benzaldehyde (Methoxybenzene) for Aluminium in sulphuric acid solution

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ABSTRACT

Corrosion inhibitory effect of benzaldehyde (methoxybenzene) on aluminium in sulphuric acid media was studied by weight loss measurement and characterization was carried by FTIR analysis. From the results it was found that increase in inhibitor concentration lead to the increase in inhibition efficiency and decreases when the temperature increased. Plots of ln (wi - Δw) against time gave a linear graphs which confirmed a first order reaction mechanism for aluminium in inhibited and uninhibited acid solution. The activation energy value of uninhibited acid solution was found to be 36.39 kJ/mol which increased to 62.32 kJ/mol when 0.1 M concentration of the inhibitor was added. There was a decreased in the values of the rate constant from uninhibited to inhibited acid solution while those of half-life increased from uninhibited to inhibited acid. The obtained values of entropy change (ΔS), enthalpy change (ΔH) and Gibbs free energy of adsorption (ΔG_{ads}) were also evaluated and discussed. The activation energy values and that of Gibbs free energy of adsorption support the physisorption mechanism between the molecules of the inhibitor and Aluminium surface.

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1. Introduction

Corrosion is termed as the destructive attack of materials due to chemical and electrochemical reaction with its surrounding medium. Degradation by physical causes is describe as erosion wear or galling, but not called corrosion. At some instant chemical attack go with physical deterioration base on the following terms; corrosive wear, fretting corrosion and corrosion – erosion. Nonmetallic materials are excluded from this definition of corrosion. Nonmetallic substances like plastic may crack and swell, wood can decay and split, cement may leach away and granite may erode, but in aqueous solution corrosion of metal is limited to chemical attack of metals. Medium that corrodes a metal can be anything, the common ones are water, air and soil but everything that come from juice of tomato and majority of the environment are corrosive. The word corrosion is a natural process for metallic substances that make them to react with their surrounding medium and give out more stable compound [1]. Aluminum is one of the commonly used metals. Its lightness coupled with its conductivity, strength, barrier properties and its good corrosion resistance has been its most useful application and reasons for the continual growth in its usage. Untreated aluminium shows a good corrosion resistance in different medium. This occurred as a result of thin layer formation which usually prevents further oxidation. However, low or high pH values (acidic or basic condition) lead to the dissolving of oxide layer and consequent rapid corrosion of aluminum. Inorganic acids and strong alkaline solutions are very corrosive for aluminum. Therefore, the protection of the corrosion of aluminium in acidic environment is very useful [2-4]. One of the most common method to protect metallic substances in acidic medium from corrosion is the use of organic compounds that contain functional groups, pi electrons and

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heteroatoms (P, S, N, & O) in their structures. Inhibition efficiency of these heteroatoms is primarily dictated by the ability of electron transfer to or from metal surface and generally follows the order of phosphorus> sulphur> nitrogen> oxygen. Approximately 80% of inhibitors are made up of organic compounds known as mixed inhibitors. Efficiency of the inhibitor is strongly influenced by the ability to form a thin oxide layer on metal surface through electrostatic attraction ultimately to form lasting adsorbed layer of the inhibitor molecules that reduces the corrosion rate by slowing down the reaction taking place at cathodic, anodic or both cathodic and anodic sites [5]. Adsorption capability is based on the inhibitor structure, charge on surface of the metal and the type of electrolyte. This current research studied benzaldehyde effect as inhibitor for aluminium corrosion in sulphuric acid medium by the use of weight loss method and used of Fourier transform infrared spectroscopy upon characterization.

2. Material and Methods

2.1 Preparation of Specimen

The Aluminium specimen with a chemical composition of 99.500 % Al, 0.0024 % Sn, 0.0007 % Pb, 0.3202 % Fe, 0.0030 % Mn, 0.0015 % Cu, 0.0018 % Mg, 0.0074 % Ti 0.0045 % Ni, 0.0041 Cr, 0.0060 % Zn and 0.0085 % Si was used in the current study. The metal specimen, was press cut in to 3 x 2 x 0.1cm dimensions. The metal specimen was polished by emery paper of different grade. It was degreased by using ethanol, acetone was used to dry it and it was kept in a desiccator for experimentation.

2.2 *Preparation of Solutions*

The corrosive environment was sulphuric acid with percentage purity (95 %) and density (1.84 g/L). The volume 7.85 ml of the stock solution was diluted with distilled water to the mark 100 ml conical flask to prepare 1.4 M H_2SO_4 solution. Benzaldehyde (methoxybenzene) with percentage purity (95 %) and density (1.04 g/L) was used as inhibitor. The concentrations of the inhibitor used for the study were 0.02, 0.04, 0.06, 0.08 and 0.1 M. Each of these concentrations was diluted in the prepared desired concentrations of acid for use as test solutions in weight loss experiment.

2.3 Weight loss measurement

In the weight loss experiment, the prepared aluminium specimen was each suspended completely in sulphuric acid solution in the absence and presence of different inhibitor concentrations (0.02, 0.04, 0.06, 0.08 and 0.10 M) by using glass hooks at a temperature of 308, 313 & 318 K, using 3 hours immersion time. The volume of solution kept 100 ml, the aluminium specimen was washed using distilled water upon retrieval after 3 hours which was then dried well and reweighed.

2.4 Fourier Transform Infrared Spectroscopic Analysis

FT-IR analysis for fresh inhibitor and that obtained from product of aluminium corrosion immersed in H_2SO_4 solution in the presence of inhibitor were performed using Agilent Technology, FTIR (Cary 630). The aluminium specimens were scanned through 650 – 4000 cm^{-1} wave number during the analysis.

3. Results and Discussion

3.1. Weight loss experiments

Weight loss and rate of aluminium corrosion in sulphuric acid solution without and with various concentration of the inhibitor for 3 hours immersion time were evaluated using the weight loss data from the equation given below;

$$\text{Loss of weight } (W_L) = W_1 - W_2 \qquad (1)$$

Where W_1 and W_2 are the weight of specimen before and after immersion

$$\text{Corrosion Rate } (mg/cm^2h^{-1}) = \frac{\text{loss of weight}}{\text{Area} \times \text{Time}} \qquad (2)$$

The surface coverage (Ɵ) and inhibition efficiency (I.E) for different concentration of the inhibitor in acid solution have been evaluated from weight loss experiments using the equations below:

$$\text{Surface coverage} = 1 - \frac{W_i}{W_u} \qquad (3)$$

$$\text{Inhibition Efficiency} = \left(1 - \frac{W_i}{W_u}\right) \times 100 \qquad (4)$$

From the above equations W_u and W_i stand for the weight of the specimen in absence and presence of the inhibitor.

3.2 Inhibitor concentration effect on corrosion rate and inhibition efficiency

Figure 1 shows result for the effect of inhibitor concentration on the aluminium corrosion in sulphuric acid solution. The result shows that increase in concentration of the inhibitor decreases the corrosion rate. Corrosion rate values with various inhibitor concentration were found to be lower than corrosion rate value in the absence of inhibitor. This shows that the ability of the protection increases with increase in concentration of the inhibitor. This phenomenon might be due to the fact that the surface covered by the molecules of the inhibitor increases when the inhibitor concentration increase. Similar work was reported by Husaini *et al.* [6].

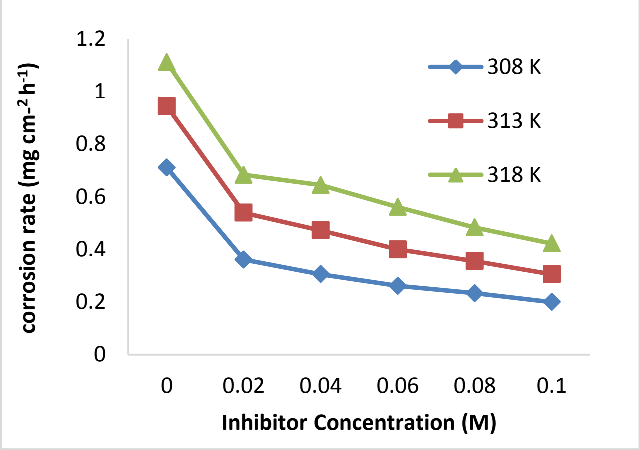

Fig 1. Variation of Corrosion Rate with Inhibitor Concentration for Al Corrosion in H_2SO_4

Figure 2 shows the result for the effect of inhibition efficiency against the concentration of the inhibitor. From the result it can be seen that inhibition efficiency increases when the concentration of the inhibitor increase. The highest inhibitor concentration produced the highest inhibition efficiency. Increase in the efficiency of the inhibitor when the concentration of the inhibitor increase is as a result of the increase in the surface of the aluminium covered by inhibitor molecules that adsorbed at higher concentration providing wider surface coverage. Similar result was reported by Husaini *et al.* [7].

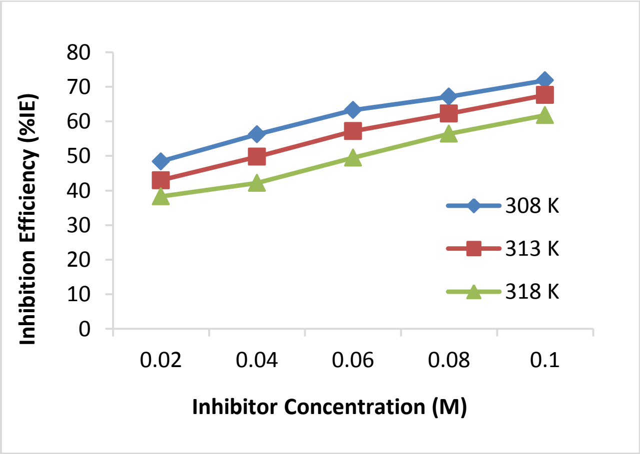

Fig 2. Variation of Inhibition Efficiency with Inhibitor Concentration for Al Corrosion in H_2SO_4

3.3 Effect of Temperature on Corrosion Rate and Inhibition Efficiency

Effect of temperature on the rate of corrosion of aluminium in inhibited and uninhibited acid was studied at temperature range of 308, 313 and 318 K as presented in figure 3. Corrosion rate of aluminium in inhibited and uninhibited acid was found to increase with rise in temperature. This is acceptable because increase in temperature lead to increase in the rate of chemical reaction due to the increase in kinetic energy of the molecules undergoing the reaction. Similar result was reported by Husaini *et al.* [7].

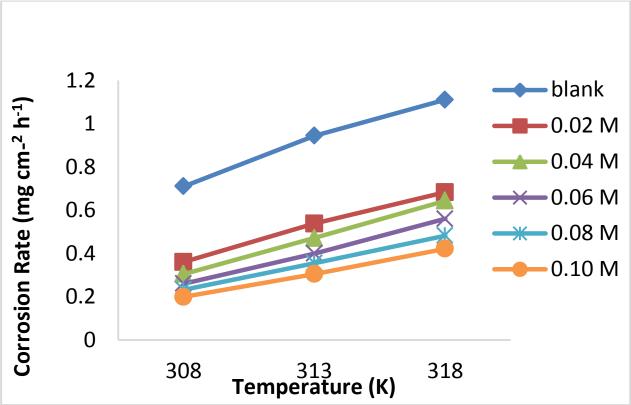

Fig 3. Variation of Corrosion Rate with Temperature for Al Corrosion in H_2SO_4

The result for the effect of temperature on the inhibition efficiency at various concentration of the inhibitor is shown in figure 4. It can be seen that from the result increase in temperature result in the decrease in the efficiency of the inhibitor. It is suggested that the surface coverage variation might be due to the desorption of inhibitor molecule on the aluminium surface as a result of the increase in temperature which result in destabilizing the inhibitor molecule on the metal surface and this lead to the decrease in the efficiency of physical adsorption [8]. Similar result was reported by Husaini *et al.* [9].

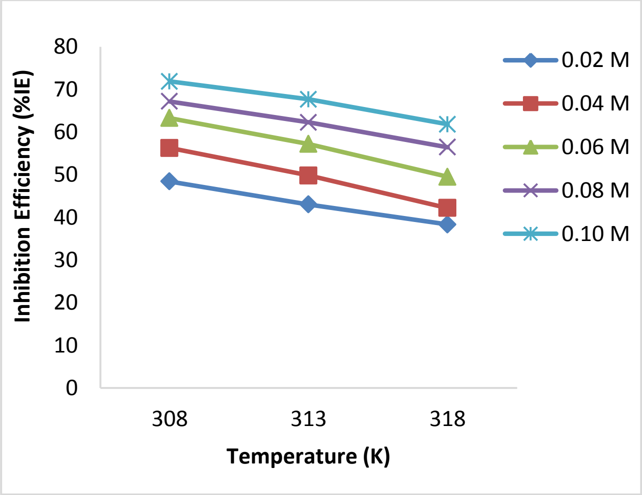

Fig 4. Variation of Inhibition Efficiency with Temperature for Al Corrosion in H_2SO_4

3.4 Kinetic Study

3.4.1 Activation Energy (Ea)

The apparent energy of activation (E_a) for the process of corrosion was evaluated by using Arrhenius equation given below;

$$\ln (C_R) = \ln A - \frac{E_a}{RT} \quad (5)$$

Where A is a constant, R served as the universal gas constant, and T served as the absolute temperature [10]. The graph of ln C_R against 1/T produced a linear plot (Figure 5) with slope = $-E_a/R$ from which the energy of activation values for the entire corrosion process were calculated. The obtained activation energy values for the corrosion of aluminium in the presence and absence of inhibitor were presented in table 1. Activation energy in uninhibited acid solution was 36.39 kJ/mol which increased to 62.32 kJ/mol in the presence of 0.1 M concentration of the inhibitor. Increase in the values of energy of activation with increasing inhibitor concentration is another evidence to the fact that increase in concentration of the inhibitor result in the increase in inhibition efficiency [11]. Addition of inhibitor causes the increase in activation energy due to the increase in appreciable adsorption of the inhibitor molecule on the surface of aluminium. Chemical adsorption mechanism (chemisorption) occurred if the activation energy value is greater than 80 kJ/mol whereas values of activation energy below 80 kJ/mol infers physical adsorption (physisorption) mechanism. The present study is consistent with the mechanism of physical adsorption as the energy of activation values were all below 80 kJ/mol.

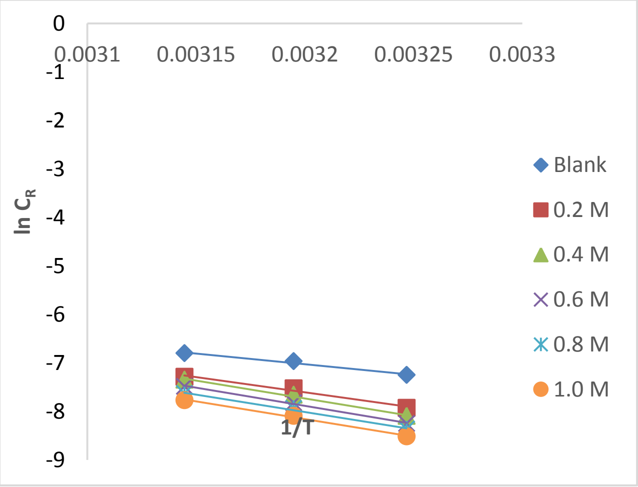

Fig 5. Arrhenius Plot in absence and at Various Inhibitor Concentration

3.4.2 Rate Constant (k)

Corrosion is heterogeneous process that made up of cathodic and anodic reactions with different or equal rate. This made the kinetic analysis of the data necessary. In the current study the initial weight of aluminum at a given time t is Wi, the weight loss is ΔW and (Wi - ΔW) stand for the weight change at a given time t and k stand for first order rate constant.

$$\ln (Wi - \Delta W) = -k_1 t + \ln \Delta W \quad (6)$$

A first order reaction was confirmed from linear variation for the plot of ln (Wi - ΔW) against time (Figure 6), with respect to the aluminium corrosion in H_2SO_4 and with the addition of inhibitor. Table 1 shows the rate constant of first order kinetic obtained from equation 6. Rate constant values for aluminium corrosion in the presence of various inhibitor concentration were lower than the rate constant in the absence of inhibitor and this confirmed the inhibition action of the inhibitor in sulphuric acid solution [12]

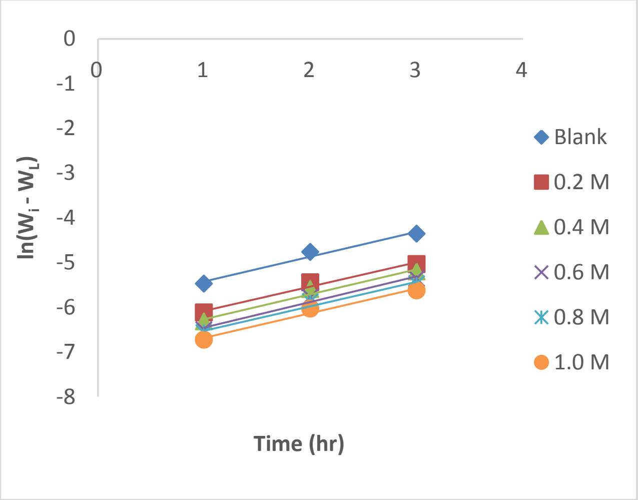

Fig 6. Plot of ln (W_i-W_L) Against Time for Blank and at Various Inhibitor Concentration

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

The equation 7 was used to calculate half-life ($t_{1/2}$) of the entire process

$$t_{1/2} = \frac{0.693}{k} \quad (7)$$

The half-life ($t_{1/2}$) values presented in Table 1 decreased from inhibited acid solution to uninhibited acid solution. The lower half-life value in uninhibited acid solution in comparison to the inhibited acid support the results reported earlier that rate of corrosion decreases in the presence of inhibitor.

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

Inhibitor Concentration (M)	Activation Energy (kJ mol^{-1})	Rate Const. (k $\times 10^{-3}$) ($hour^{-1}$)	Half-life (hours)
Blank	36.39	4.29	161.35
0.02	52.00	2.17	318.75
0.04	59.34	1.83	376.89
0.06	60.81	1.57	441.22
0.08	60.88	1.40	493.87
0.10	62.32	1.20	576.35

3.5 *Thermodynamic Study*

3.5.1 *Enthalpy change (ΔH) and Entropy change (ΔS)*

Other thermodynamic activation parameters are enthalpy change(ΔH) and entropy change (ΔS) which are associated with effect of temperature on the rate of aluminium corrosion without and with various inhibitor concentration and their values were obtained from equation 8;

$$\ln\left(\frac{C_R}{T}\right) = \ln\left(\frac{R}{Nh}\right) + \left(\frac{\Delta S}{R}\right) - \left(\frac{\Delta S}{RT}\right) \qquad (8)$$

From the above equation, the corrosion rate is C_R at temperature T, the universal gas constant is R, the Avogadro's constant is N and the Planck's constant is h. The slope of the straight line graph = $-\Delta H/R$ and and intercept = $\ln(R/Nh) + \Delta S/R$ were all resulted from the plot of ln (C_R/T) against 1/T. The calculated enthalpy (ΔH) and entropy (ΔS) values are shown in Table 2. It can be seen that ΔH values are all positive which indicate the endothermic nature of the process. From the negative values of entropy (ΔS) it can be said that in the rate determining step the activation complex represents an association not dissociation [13].

Table 2. Enthalpy and Entropy change of the corrosion process without and with various concentrations of the inhibitor

Inhibitor Concentration (M)	**ΔH (kJ mol^{-1})**	**- ΔS (kJ mol^{-1}k^{-1})**
blank	33.78	195.58
0.02	49.40	150.48
0.04	56.74	120.30
0.06	58.21	115.61
0.08	58.28	130.34
0.10	59.72	126.64

3.5.2 *Free Energy of Adsorption (ΔG_{ads},)*

Gibbs free energy of adsorption (ΔG_{ads}) and adsorption equilibrium constant are related according to the equation given below;

$$\Delta G_{ads} = - RT \ln (55.5 \times K_{ads}) \qquad (9)$$

Where 55.5 is the amount of H_2O in mol dm^{-3}, T is the temperature, R is the universal gas constant and K_{ads} is the adsorption equilibrium constant [14].

Table 3 shows the values of ΔG_{ads} evaluated from equation 9. It can be seen that from the result the values of ΔG_{ads} are all negative and this indicate the spontaneous behaviour of the entire process. Values of ΔG_{ads} in the current research ranged from -20.30 to -20.47 kJ mol^{-1} and this is in accordance with physical adsorption (physisorption) mechanism since the ΔG_{ads} values are close/around -20 kJmol^{-1}. It was reported in the literature that ΔG_{ads} values around/close to -20 kJmol^{-1} are in accordance with physical adsorption (physisorption) mechanism [15]. Similar result of negative ΔG_{ads} values was also reported by Husaini *et al*, [16].

3.6 *Adsorption Isotherm*

Adsorption isotherm is used to provide the important information between the adsorbate (inhibitor) and adsorbent (metal surface). There is the formation of bond between the inhibitor molecule and metal atom as suggested by the degree of surface coverage. The experimental result obtained was tested on different adsorption isotherm model. But the finding shows that the best fit isotherm was Langmuir adsorption isotherm that explained the characteristics of the inhibitor adsorption on the aluminium surface. The perfect adsorption model for chemical and physical adsorption on a smooth surface is Langmuir adsorption isotherm. . It assumed monolayer adsorption on the surface of the adsorbent that contain finite identical sites number [17]. The equation given below is the linear representation of Langmuir adsorption isotherm;

$$\frac{C_{inb}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \qquad (10)$$

From the above equation C_{inh} served as the inhibitor concentration, K_{ads} served as the constant of equilibrium adsorption and the degree of surface coverage is represented by θ. intercept of $1/K_{ads}$ was obtained from the linear plot of C/θ against C (Figure 7) [18].

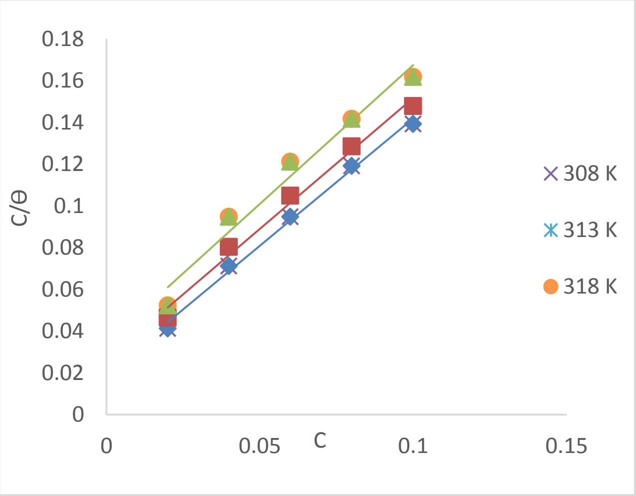

Fig 7. Langmuir Adsorption Isotherm Plot at Different Temperature

The values of correlation coefficient obtained are close to unity showing the inhibitor adsorption on the surface of aluminium is in accordance with Langmuir adsorption isotherm. The correlation coefficient (R^2) and equilibrium constant of adsorption (K_{ads}) values are all presented in table 3.

Table 3: Adsorption Parameters Obtained from Langmuir Adsorption Isotherm for Corrosion of Aluminium in H_2SO_4

Temperature (K)	**R^2**	**K_{ads}**	**ΔG (kJ mol^{-1})**
308	0.995	50.00	-20.30
313	0.998	45.45	-20.38
318	0.997	41.67	-20.47

3.7 *Role of Benzaldehyde as Corrosion Inhibitor*

Benzaldehyde undergoes protonation in acid medium and the protonated benzaldehyde molecule gets adsorbed to the anodic side of aluminium via the pre-adsorbed SO_4^{-2} ions. Due to the small degree of hydration the sulphate ion get adsorbed first on the surface of positively charge aluminium. Excess negative charge was created due to the adsorption of sulphate ion. The negative charge goes toward the side solution of the aluminium and the higher adsorption of cationic form inhibitors was favored. The positively charged benzaldehyde molecule and negative charge of aluminium surface formed a protective adsorbed layer. The protonated molecule of benzaldehyde also get adsorbed on aluminium cationic sites in competition with ions of hydrogen that become hydrogen gas [19].

3.8 *Infrared Spectroscopic Analysis Results*

FTIR result of benzaldehyde inhibitor and that of the corrosion product are shown in Figures 8 and 9. Figure 8 is the result for the FT-IR analysis of the benzaldehyde inhibitor which shows the presence of C=O stretch of carbonyl group at 1640 cm^{-1}, aldehyde C-H stretch at 2745 cm^{-1} and aromatic C-H stretch at 3073 cm^{-1}. Figure 9 shows the result for the FT-IR analysis of the corrosion product, the presence of C=O stretch of carbonyl group, aldehyde C-H stretch and aromatic C-H stretch in the FT-IR result of the corrosion product indicated that the thin layer of the inhibitor molecules has been formed on the aluminium surface.

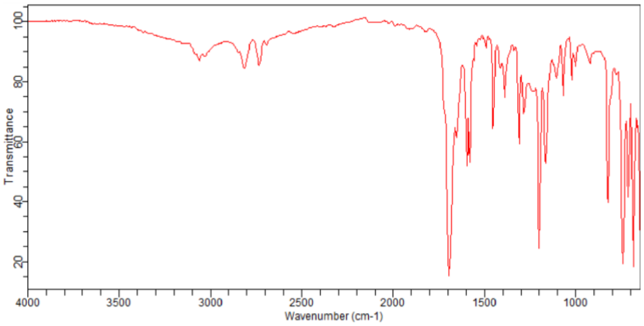

Fig 8. FT-IR Spectrum of Benzaldehyde

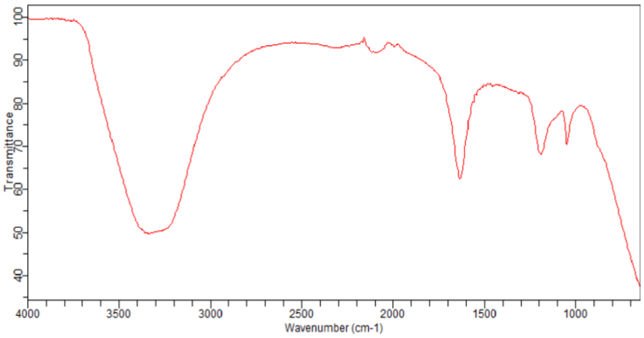

Fig 9. FT-IR Spectrum of the Corrosion Product

4. Conclusion

The weight loss method used for this study confirm that benzaldehyde protected the aluminium from corrosion in the solution of sulphuric acid. Increase in inhibitor concentration lead to decrease in corrosion rate and the corrosion rate increases when the temperature rise. The entire process was endothermic due to the positive values of enthalpy. The appearance of the functional group molecule of inhibitor in the result of fourier transform infrared analysis of the corrosion product proved the thin layer formation of the molecule of inhibitor on the surface of aluminium. Inhibitor adsorption on the aluminium surface is in accordance with Langmuir adsorption isotherm. Inhibitor molecules were spontaneously adsorbed on the surface of aluminium from the negative values of Gibbs free energy of adsorption and was in accordance with physisorption (physical adsorption mechanism).

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