

Inhibitive Action of Glutathione Reduced on the Deterioration of AA6061 in 0.5M HCl

Nagalaxmi^a, P. Shetty^{a,*}, P.P. Kumari^a

^aDepartment of Chemistry, Manipal Institute of Technology, Manipal Academy of Higher Education (A Deemed University), Manipal-576104, Karnataka, India.

Keywords:

AA6061
Glutathione reduced
Acid corrosion
Weight loss
Potentiodynamic polarization

* Corresponding author:

Prakash Shetty 
E-mail: prakash.shetty@manipal.edu

Received: 31 October 2019

Revised: 9 December 2019

Accepted: 20 February 2020

ABSTRACT

Corrosion inhibitive action of glutathione reduced (Gth), an eco-friendly inhibitor of aluminium alloy 6061 (AA6061) was investigated in a 0.5 M HCl medium. Experiments were conducted using weight loss and potentiodynamic polarization (PDP) methods. The inhibition efficiency of Gth increases with increasing its concentration and decreases with increasing temperature. Gth demonstrated reasonably good inhibition performance (87 % at 0.7 mM at 303 K) by acting as a mixed inhibitor. The measurement of activation and thermodynamic parameters regulating the inhibition behavior of Gth shows the mixed adsorption of Gth on the alloy surface, which follows the Langmuir isotherm model. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) was used to conduct the surface morphological examination of corroded and inhibited alloy specimens.

© 2020 Published by Faculty of Engineering

1. INTRODUCTION

The process of material deterioration (such as that of metals, alloys, composites) that occurs due to their association with the environment is commonly referred to as corrosion. In reality, metallic corrosion is the conversion of pure metal to its compound form. As a result, the desired lifetime of the metal / alloy is shortened. Therefore, there is a need to protect metallic structures and components that are exposed to corrosion in different environments. As per the report published in the year 2016, the estimated cost of corrosion is almost equal to 3.4 % of global GDP and this will increase over the years. In this connection, an annual savings of 375 to

875 billion USD can be achieved by implementing appropriate control practices against corrosion. Adequate consideration should, therefore, be given over the years to the prevention of corrosion, which would help to conserve the world's material resources [1].

Commercial aluminium alloys of the 6xxx series consist mainly of Al, Mg, and Si as the main alloy components. AA6061 is commonly used in aircraft, aerospace, automotive and marine industries mainly due to its high tensile strength and thermal resistance and corrosion resistance properties [2,3]. The corrosion resistance of Al and its alloys is attributed to their ability to form a natural surface oxide film due to passivation

[4,5]. In aggressive chloride/acid media, a breakdown of the passive layer and pit formation can occur due to localized corrosion [6,7]. Al and its alloys (including AA6061) can be better protected by the use of chemical inhibitors from the corrosive attack of the aggressive acid media [8-11]. In many industries, hydrochloric acid is widely used as a pickling agent for Al, and its alloys. In such pickling processes, it is absolutely necessary to control the degradation of the metal. Among the various available corrosion control techniques, the use of inhibitors is the simplest and most cost-effective method.

Research on eco-friendly corrosion inhibitors has become increasingly important in recent years. Compounds with high safety efficiency at low risk of environmental pollution are most favoured. Amino acids and their derivatives are being studied as eco-friendly inhibitors for corrosion of different metals and alloys [12-15]. An amino acid derivative, glutathione reduced (Gth) is basically a tripeptide with the chemical structure as shown in Fig. 1.

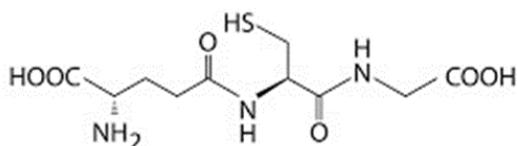


Fig. 1. The molecular structure of glutathione reduced.

It contains multiple heteroatoms (S, O, and N) and polar groups. It is therefore required to demonstrate reasonably good inhibition behaviour as a corrosion inhibitor. Gth showed a good inhibition efficiency towards copper in the hydrochloric acid medium [16]. This paper describes the finding of Gth as an eco-friendly corrosion inhibitor of AA6061 in 0.5 M HCl medium. Potentiodynamic polarization and weight loss methods were used in this study. Inhibition occurs by adsorption of Gth on alloy surfaces as revealed by SEM and AFM analysis.

2. EXPERIMENTAL PROCEDURE

2.1 Materials

The elemental composition of the AA6061 sample investigated in the present work is as mentioned in Table 1. The rectangular coupons of the sample with 1cm × 2 cm × 0.5 cm

dimensions were used to carry out weight loss tests. A cylindrical AA6061 coupon was embedded in an acrylic resin material having one end exposed (surface area, 1.0 cm²). Initially, the specimen was abraded by emery papers of varied grades (200-800) and then in a disc polisher, finally washed thoroughly with deionized water. A corrosive medium of hydrochloric acid (0.5M) was prepared from an analytical grade (37 %) sample. Glutathione reduced (Analytical grade, Merck) was used as an inhibitor and its aqueous solutions of the appropriate concentration were prepared.

Table 1. The composition of AA6061 specimen material.

Element	Si	Cu	Mg	Cr	Al
Wt. (%)	0.51	0.18	0.82	0.04	98.45

2.2 Weight loss technique

Accurately weighed test specimens were immersed in 100 ml of 0.5 M HCl in the absence and presence of varying concentrations of Gth at 303K for 12h without any stirring. The temperature was accurately maintained within ±1 °C using a calibrated thermostat. After exposure, the specimens were removed from the test solution, washed thoroughly with distilled water and subsequently with ethanol, and finally dried at room condition. The dried coupons were weighed and the corresponding weight loss was calculated. The same tests were performed at 24, 36 and 48 h immersion time. Each experiment was repeated three times and the mean value was used for further calculations.

2.3 PDP technique

Corrosion studies were performed with the help of a CH-instrument (604D-series, US model). A cell system with a counter electrode of Pt, a reference electrode of saturated calomel, and a working electrode of AA6061specimen were used. A freshly abraded specimen of AA6061 with an exposed surface area of 1.0 cm² was immersed in 0.5 M HCl at varying temperatures (303, 313 and 323 K). The temperature was precisely maintained within ±1 °C using a calibrated thermostat. Initially, the cell system was dipped in the acid medium for 30 min at OCP (open circuit potential). Then, the PDP studies were performed by polarizing AA6061

specimen electrode from +250 mV to -250 mV potential with reference to OCP at 0.01Vs⁻¹ scan rate. From Tafel curves, E_{corr} (corrosion potential), i_{corr} (current density) and the slope corresponding to the linear portion of anodic (β_a) and cathodic (β_c) curves were recorded.

2.4 Surface characterization

The surface morphological studies were performed on a freshly abraded specimen of AA6061, specimens immersed separately in 0.5M HCl without and with 0.7mM Gth for 12h. The SEM pictures of alloy specimens were recorded using EVO 18-5-57 model analytical scanning electron microscope and AFM images using the IB342 Innova model atomic force microscope.

3. RESULTS AND DISCUSSION

3.1 Weight loss measurements

By measuring weight loss, inhibition efficiency (IE) can be calculated from the relationship [17]:

$$IE(\%) = \frac{w_0 - w}{w_0} \times 100 \quad (1)$$

In the above equation, W_0 and W represent the observed weight loss of AA6061 specimen immersed in the acid medium without and with Gth respectively.

The results of the weight loss method are shown in Table 2. From Fig. 2, it is evident that IE increases with an increase in Gth concentration but decreases with an increase in immersion time. The weight loss measured decreases with an increase in the concentration of Gth, which leads to a decrease in the corrosion rate of AA6061. The IE of Gth, therefore, increases with an increase in its concentration. The increase in IE of Gth can be attributed to the increase in surface coverage due to its adsorption at the alloy/acid solution interface [18]. This indicates that an increase in the concentration of Gth increases the number of molecules adsorbed on the surface of the alloy and reduces the surface area available for direct acid attack on the surface of the alloy. However, the weight loss achieved remains almost constant beyond the optimum concentration of Gth (0.7 mM). The highest IE of 87.8 % was evinced at 0.7 mM of Gth.

Table 2. The results of weight loss method at a varying concentration of Gth and 303 K.

Immersion time (h)	[Gth] (mM)	Wt. loss (mg cm ⁻²)	IE (%)
12	0	30.20 ± 0.04	-
	0.06	7.42 ± 0.07	75.4
	0.08	6.50 ± 0.05	78.4
	0.3	5.62 ± 0.03	81.4
	0.5	4.66 ± 0.02	84.5
	0.7	3.66 ± 0.03	87.8
24	0	38.42 ± 0.05	-
	0.06	10.56 ± 0.06	72.5
	0.08	8.22 ± 0.03	78.6
	0.3	7.84 ± 0.05	79.6
	0.5	6.82 ± 0.04	82.2
	0.7	5.78 ± 0.02	85.0
36	0	45.68 ± 0.03	-
	0.06	13.01 ± 0.08	71.5
	0.08	10.86 ± 0.04	76.2
	0.3	9.00 ± 0.02	80.3
	0.5	7.48 ± 0.03	83.6
	0.7	6.80 ± 0.01	85.1
48	0	51.84 ± 0.05	-
	0.06	14.88 ± 0.09	71.3
	0.08	13.02 ± 0.04	74.9
	0.3	12.06 ± 0.03	76.7
	0.5	11.12 ± 0.02	78.5
	0.7	8.30 ± 0.03	84.0

It is evident from the results that the IE of Gth decreases marginally by increasing the immersion time of alloy specimens from 12 to 48 h.

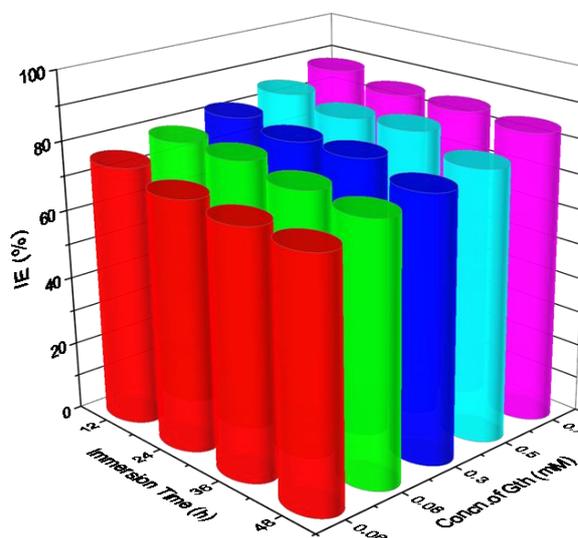


Fig. 2. The graph indicating the influence of concentration of Gth and the immersion time of specimen on the IE of Gth at 303K.

3.2 PDP measurements

Inhibition activity of Gth on AA6061 corrosion was analysed using the PDP technique. The corrosive action of 0.5M HCl medium without

and with the presence of Gth on AA6061 at 303K was graphically represented as Tafel polarization curves (Fig. 3). The corrosion rate (CR) of AA6061, surface coverage (θ) and inhibition efficiency (IE) of Gth, were computed from the following relations [19, 20]:

$$CR(mmpy) = \frac{3270 \times M \times i_{corr}}{\rho \times z} \quad (2)$$

In the above relation, 3270 is the unit conversion constant, i_{corr} equal to corrosion current density in Acm^2 , ρ is the density, M is the atomic mass of Al, and Z is the number of electron transfer occurs per metal atom.

$$\theta = \frac{i_{corr} - i_{corr(inh)}}{i_{corr}} \quad (3)$$

In the above equation, i_{corr} equal to corrosion current density in the blank medium, whereas $i_{corr(inh)}$ that in the inhibited medium.

$$IE(\%) = \theta \times 100 \quad (4)$$

Electrochemical parameters such as E_{corr} , i_{corr} , CR, IE, β_a , β_c are shown in Table 3. The i_{corr} and CR values are reduced when the additive concentration of Gth increases. It can be possible by the adsorption of Gth, which protects the alloy surface from more corrosion [9]. The inhibition activity of Gth increased with an increase in its additive concentration, while it decreased slightly with an increase in temperature.

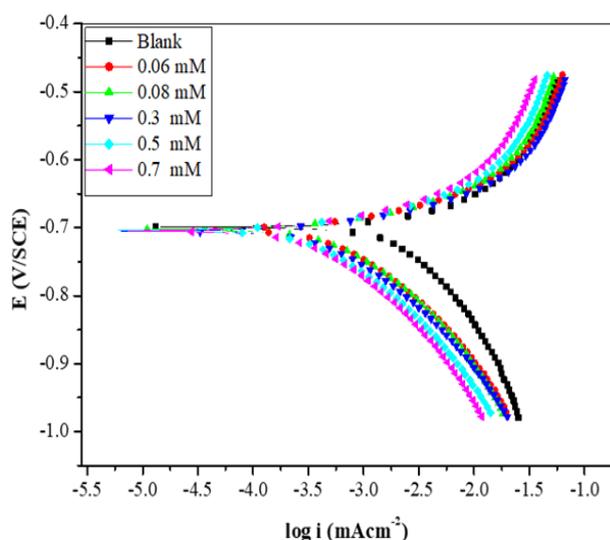


Fig. 3. Tafel plot for AA6061 in 0.5M HCl without and with Gth at 303K.

The maximum IE of 86 % was reached by adding 0.7 mM Gth at 303K. Generally, if the observed

change in E_{corr} value in the inhibited medium exceeds ± 85 mV compared to that in the uninhibited medium, then the added inhibitor can be classified as belongs to cathodic or anodic type [21]. In the present case, the highest change in the E_{corr} value found in the inhibited medium is around -20 mV, which means that Gth has a mixed inhibitor behaviour. Table 3 shows that the value of β_c does not change significantly with an increase in the additive concentration of Gth.

Table 3. PDP results for AA6061 in 0.5 M HCl without and with Gth at varied temperatures.

T (K)	[Gth] (mM)	E_{corr} (mV)	$-\beta_c$ (mV dec ⁻¹)	β_a (mV dec ⁻¹)	i_{corr} (mA cm ⁻²)	CR (mmpy)	IE (%)
303	0	-729	558.2	568.1	4.650	50.64	0
	0.06	-723	738.0	797.3	1.210	13.18	73.9
	0.08	-724	736.9	751.0	1.073	11.71	76.8
	0.3	-728	763.8	816.9	0.803	8.76	82.7
	0.5	-722	753.6	787.1	0.712	7.76	84.6
	0.7	-728	731.0	775.5	0.652	7.10	85.9
313	0	-739	532.3	513.9	8.165	90.98	0
	0.06	-733	664.0	612.9	2.251	24.52	72.4
	0.08	-732	652.5	701.0	2.023	22.27	75.2
	0.3	-733	731.0	690.3	1.430	15.58	82.4
	0.5	-735	751.3	720.7	1.443	15.73	82.8
	0.7	-734	754.4	741.2	1.191	12.97	85.4
323	0	-749	374.3	497.4	12.17	132.8	0
	0.06	-740	673.4	568.9	3.273	35.66	69.1
	0.08	-741	670.8	538.7	3.227	35.15	73.2
	0.3	-742	674.3	589.3	2.959	32.23	75.7
	0.5	-742	647.1	565.7	2.679	29.18	78.0
	0.7	-740	700.3	608.8	2.180	23.75	82.1

It means that the added Gth raises the energy barrier for the proton discharge reaction and therefore regulates the kinetics of the cathodic reaction. Similarly, the anodic slope (β_a) does not vary significantly when the additive concentration of Gth is increased. This shows that the added Gth regulates the metal dissolution reaction by blocking the anodic reactive sites without altering the inhibition mechanism [22,23].

3.3 Influence of temperature

The data relating to the effect of the temperature increase on the IE of Gth are recorded in Table 3 and are also graphically represented in Fig. 4.

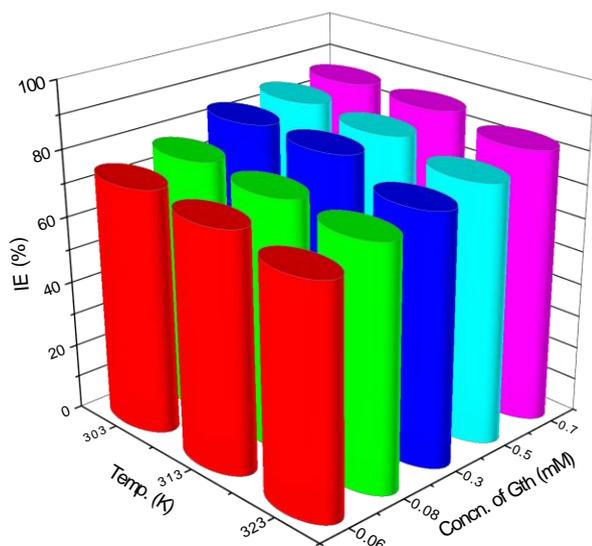


Fig. 4. The effect of temperature on the IE of Gth.

In the absence of Gth, the corrosion rate was found to increase sharply with an increase in the temperature of the acid medium (Table 3). Generally, the rate of a chemical reaction including electrochemical reaction increases with an increase in temperature due to the increase in the activation energy of the reacting species. It is clear from the findings (Fig. 4) that there is a slight decrease in IE of Gth with a temperature increase from 303 to 323K. This can be attributed to the weaker adsorption of Gth at higher temperatures due to the shorter time gap between its adsorption and desorption. This may lead to the desorption of some of the adsorbed Gth molecules from the alloy surface at higher temperatures. As a result, a larger surface area of the alloy is exposed to the acid medium, which may result in an increase in CR of the alloy and a decrease in IE of Gth. The observed decrease in IE with temperature increase indicates that Gth molecules are adsorbed on the surface of the alloy through physisorption [24]. The effect of the temperature on the deterioration of AA6061 is useful in the measurement of the activation parameters such as the activation energy (E_a), enthalpy change (ΔH_a), and entropy change (ΔS_a).

The Arrhenius equation was used in computing E_a values [25].

$$\ln(CR) = B - \frac{E_a}{RT} \quad (5)$$

In the above relation, CR refers to the corrosion rate, B represents Arrhenius constant, R is the gas constant, and T refers to temperature.

Arrhenius plot of $\ln(CR)$ vs. $1/T$ presented in Fig. 5 displays the straight-line graphics. The E_a value was derived from the slope equal to $-E_a/R$. The findings presented in Table 4 indicate that the E_a values obtained in the inhibited medium are higher than in the blank medium. This resulted in a decrease in CR of AA6061 due to the adsorption of Gth. The observed rise in E_a value correlates with an increase in Gth concentration suggesting the physisorption of Gth [9]. The activation parameters (ΔH_a and ΔS_a) for the deterioration of AA6061 are computed from the transition state relation [26], which is represented as,

$$CR = \frac{RT}{Nh} \exp\left(\frac{\Delta S_a}{R}\right) \exp\left(-\frac{\Delta H_a}{RT}\right) \quad (6)$$

In the above relation, h represents Planks constant, N refers to Avogadro's number.

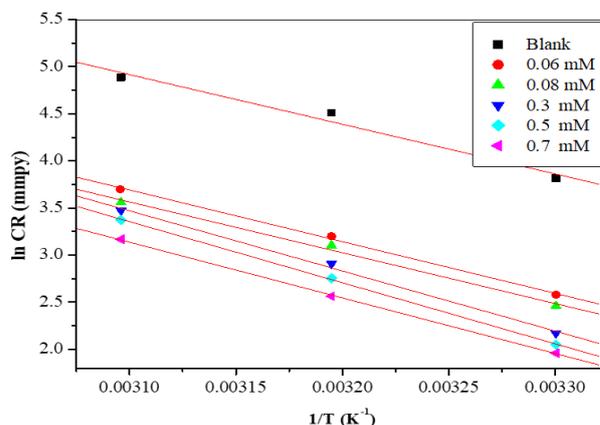


Fig. 5. Arrhenius plot for AA6061 in 0.5M HCl without and with Gth.

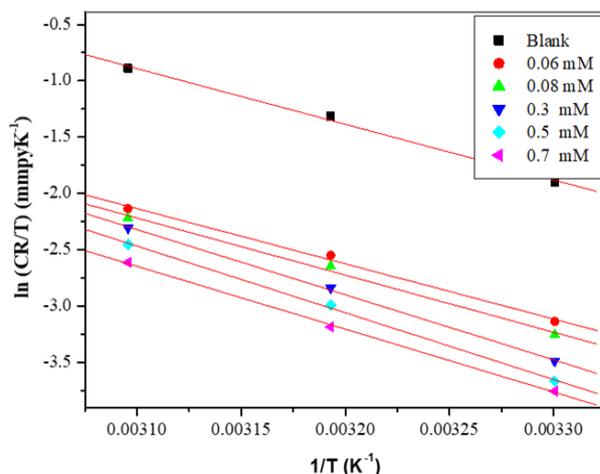


Fig. 6. Plot of $\ln(CR/T)$ vs. $1/T$ for AA6061 in 0.5M HCl without and with Gth.

The graph of $\ln(CR/T)$ vs. $1/T$ for AA6061 in 0.5 M HCl without and with the presence of Gth gave

straight lines (Fig. 6). The ΔH_a values are obtained from the slope equal to $-\Delta H_a/R$ while ΔS_a values from the intercept equal to $[\ln(R/Nh) + \Delta S_a/R]$. The positive value of ΔH_a indicates (Table 4) that the inhibition reaction is an endothermic process. The ΔH_a values obtained are almost equal to the corresponding E_a values for the deterioration of alloy, which indicates the possible physisorption of Gth. The large negative values of ΔS_a reveals that the inhibition proceeds with an increase in ordering [27].

Table 4. Activation results for AA6061 in 0.5 M HCl without and with Gth.

[Gth] (mM)	E_a (kJmol ⁻¹)	ΔH_a (kJmol ⁻¹)	ΔS_a (Jmol ⁻¹ K ⁻¹)
0	43.83	41.09	-77.55
0.06	45.59	40.72	-89.02
0.08	44.79	42.12	-85.37
0.3	53.04	48.05	-67.84
0.5	53.90	49.21	-65.45
0.7	49.09	46.36	-75.80

3.4 Adsorption behaviour of Gth

The type of interactions between the inhibitor molecule and the alloy can be best studied by applying the findings to different models of adsorption, namely Langmuir, Temkin Frumkin, and Freundlich. The type of adsorption model followed becomes important in understanding the potential mechanism for inhibition. The best fittings of the data were obtained with the Langmuir isotherm model according to the relationship [28]:

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \quad (7)$$

Where $C_{inh} = [Gth]$, whereas K_{ads} refers to the equilibrium constant for adsorption.

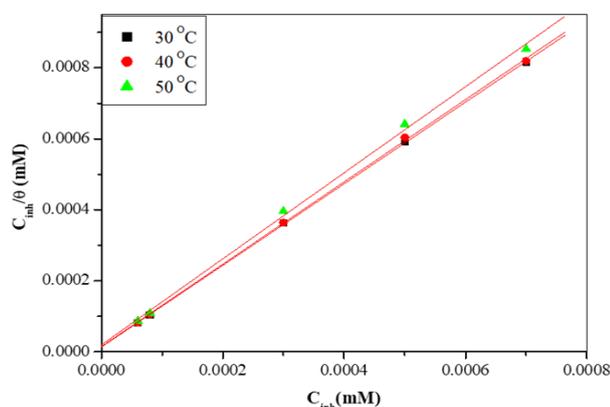


Fig. 7. Langmuir isotherm model for the adsorption of Gth on AA6061 in 0.5M HCl.

The graph, C_{inh}/θ vs. C_{inh} , gave straight lines (Fig. 7) with both the slopes and linear coefficient values (R^2) almost equal to one (Table 5), which implies that adsorption of Gth follows the Langmuir isotherm model [29-31]. The K_{ads} value is computed from the intercept, which is equal to $1/K_{ads}$.

The equilibrium constant (K_{ads}) is related to the standard free energy change (ΔG°_{ads}) for adsorption as per the equation: [32]

$$K_{ads} = \frac{1}{55.5} \exp\left(\frac{-\Delta G^{\circ}_{ads}}{RT}\right) \quad (8)$$

In the above relation, R refers to gas constant and the concentration of water is 55.5 mol L⁻¹.

A straight-line graph is obtained by plotting ΔG°_{ads} vs. T (Fig. 8). The standard value of the entropy change (ΔS°_{ads}) is given by the slope and the enthalpy change (ΔH°_{ads}) is obtained by the point of intercept according to the relationship:

$$\Delta G^{\circ}_{ads} = \Delta H^{\circ}_{ads} - T\Delta S^{\circ}_{ads} \quad (9)$$

The values obtained for ΔG°_{ads} , ΔS°_{ads} and ΔH°_{ads} are recorded in Table 5.

Table 5. Thermodynamic results for the adsorption behaviour of Gth.

T (K)	K_{ads} (10 ³ M ⁻¹)	Slope	R^2	ΔG°_{ads} (kJ mol ⁻¹)	ΔH°_{ads} (kJ mol ⁻¹)	ΔS°_{ads} (Jmol ⁻¹ K ⁻¹)
303	71.50	1.14	0.9999	-38.27	-14.06	-80.07
313	65.20	1.15	0.9998	-39.29		
323	50.40	1.22	0.9992	-39.86		

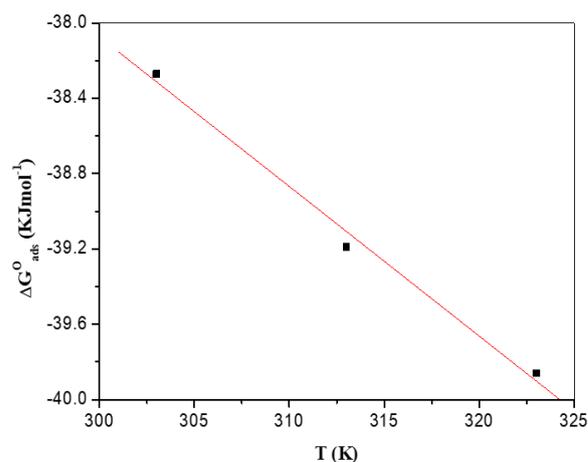


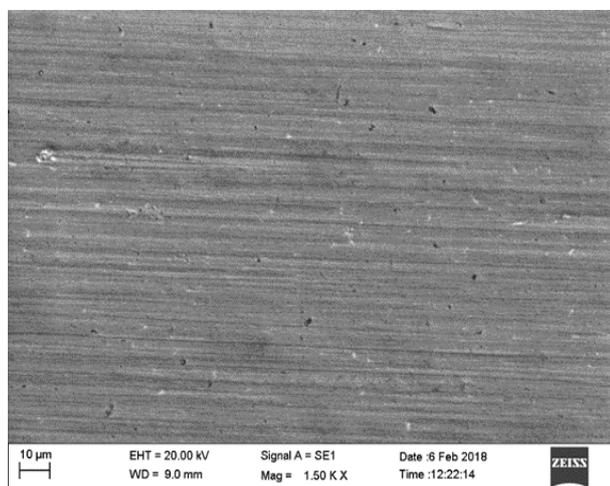
Fig. 8. Plot of ΔG°_{ads} vs. T for the adsorption of Gth on AA6061 in 0.5 M HCl.

Large values of K_{ads} , as well as a negative sign of ΔG°_{ads} , indicate that inhibitor film formed on

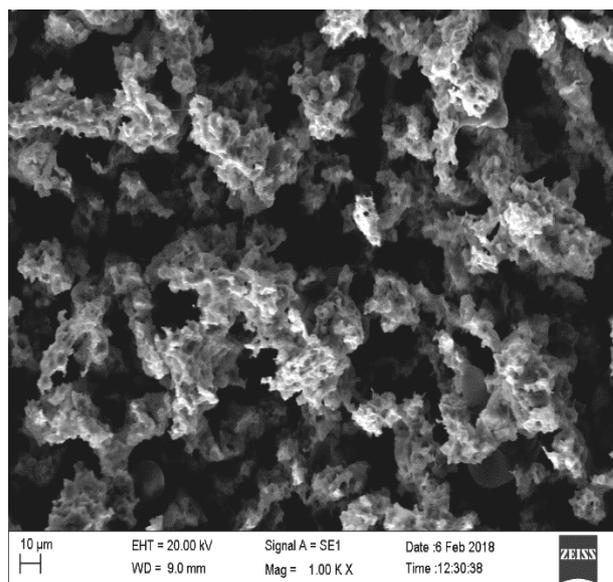
AA6061 is reasonably stable. Generally, ΔG°_{ads} values around -20 kJmol^{-1} or more positive mean physisorption, while that around -40 kJmol^{-1} or more negative mean chemisorption of inhibitor molecules [33, 34]. The ΔG°_{ads} values obtained for Gth are between -20 and -40 kJmol^{-1} , suggesting the mixed adsorption of Gth on AA6061. The negative value of ΔH°_{ads} indicates the exothermic character of the adsorption process. This indicates the possible reduction in IE of Gth with an increase in temperature (Table 3) which also supports its mixed adsorption activity mainly by physisorption. According to the literature, the ΔH°_{ads} value for physisorption is lower than $-41.86 \text{ kJmol}^{-1}$, whereas it is -100 kJmol^{-1} for chemisorption [35]. The obtained value of ΔH°_{ads} (Table 5) in the present case is $-14.06 \text{ kJmol}^{-1}$. It shows the physisorption of Gth on the surface of the alloy. The high negative value of ΔS°_{ads} shows that inhibition results in a decrease in disorder [35].

3.5 SEM Analysis

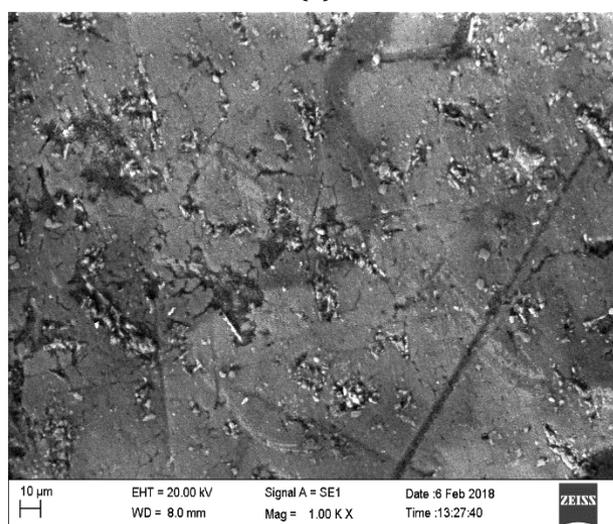
The SEM image of freshly abraded AA6061 specimen (Fig. 9a) depicts a smooth surface texture with few scratches that may be formed during polishing. Fig. 9b represents the SEM image of the corroded alloy specimen with a completely damaged surface containing more pits/cracks created by the corrosive action of the acid medium. The rough surface with pits and cracks indicate the micro galvanic corrosion of the alloy sample. However, in the presence of Gth, the extent of damage to the alloy surface is significantly reduced with lower pits on the surface (Fig. 9c). This improvement in surface morphology is due to the formation of a protective film of Gth on the alloy surface that is responsible for inhibition.



(a)



(b)



(c)

Fig. 9. SEM images of AA6061 specimen (a) freshly abraded, immersed in 0.5 M HCl (b) without and (c) with 0.7 mM Gth for 12 h.

3.6 AFM Analysis

Three-dimensional AFM images of AA6061 specimens - fresh abraded, immersed in 0.5M HCl without and with 0.7mM Gth are recorded as shown in Figs. 10a-10c respectively. The measured values of average surface roughness (R_a) and root mean square roughness (R_q) of the corroded and inhibited specimen are shown in Table 6. It is clear that the measured R_a and R_q values of the inhibited alloy specimen are drastically reduced compared to that for an uninhibited sample but almost closer to that for the fresh specimen. The possible adsorption of Gth is clearly indicated by a drastic decrease in the surface roughness values in the case of the

inhibited specimen compared to the corroded specimen. This controls the deterioration of AA6051 in HCl media.

Table 6. The surface roughness results for AA6061 specimens.

Samples	R _a (nm)	R _q (nm)
AA6061	27.5	41.0
AA6061 in 0.5M HCl	1073.0	1366.0
AA6061 in (0.5M HCl + 0.7 mM Gth)	51.4	69.1

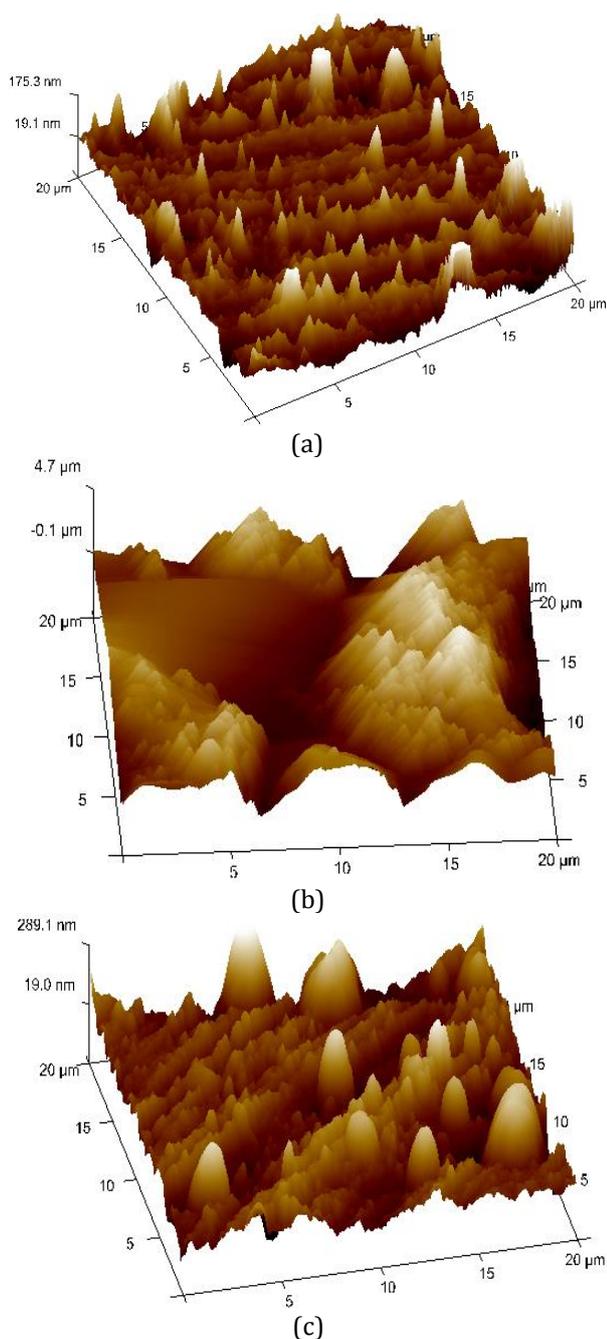
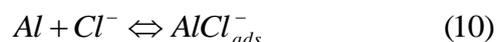


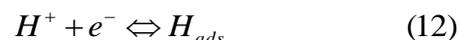
Fig. 10. Atomic force micrographs of AA6061 specimens (a) freshly abraded, immersed in 0.5M HCl, (b) without and (c) with 0.7mM Gth for 12h.

3.7 Corrosion of AA6061 and its inhibition mechanism

According to the literature [36], the deterioration of Al in the hydrochloric acid medium follows a general mechanism. On this basis, the anodic reaction involves the following steps:

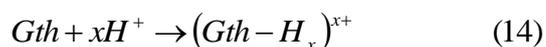


The reaction at cathode involves the evaluation of hydrogen gas as per the following steps:



On this basis, an effective inhibition mechanism for AA6061 corrosion in the HCl medium can be predicted. Organic inhibitors normally adsorb on the surface layer surrounding the alloy. The inhibition mechanism involved is regulated by factors such as the structure of the inhibitor and its molecular charge distribution, the nature of the metal and its surface charge. Organic inhibitors can adsorb via physisorption, chemisorption or both. Electrostatic attraction of the charged inhibitor species (like protonated species) to the oppositely charged alloy surface will lead to physisorption. Whereas, chemisorption can occur by sharing of lone pair of electrons in hetero-atoms, and/or π -electrons of multiple bonds or aromatic ring in an inhibitor with empty metal atom d-orbitals [37,38].

The possible inhibition mechanism for inhibiting the deterioration of AA6061 by adsorption of Gth can be demonstrated as follows. Based on the values of ΔG_{ads}^0 (as explained in section 3.4 Adsorption behaviour of Gth) it can be inferred that Gth follows a mixed adsorption process. In an acidic environment, aluminium alloy surface can be positively charged because the pH_{zc} value for aluminium (i.e., pH at zero charge potential) is 9.1 [39]. As a result, the chloride ions are first adsorbed by the electrostatic force of attraction at the alloy/HCl solution interface. Hence, the alloy surface can acquire a negative charge (Fig. 11). Similar to amino acids and their derivatives, Gth can also be protonated in an acidic medium [8,12]. The protonation of Gth in the acidic medium may be represented as follows:



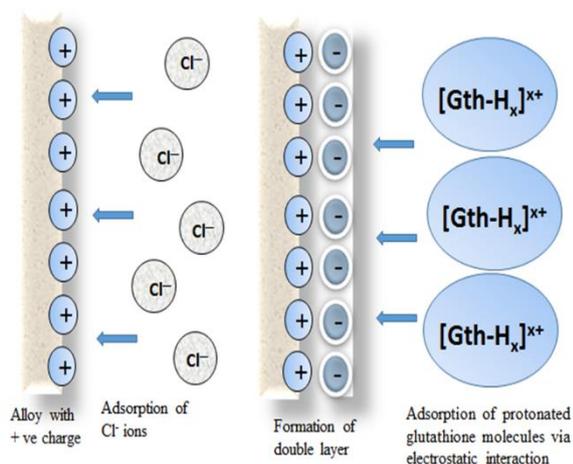


Fig. 11. The physisorption of Gth.

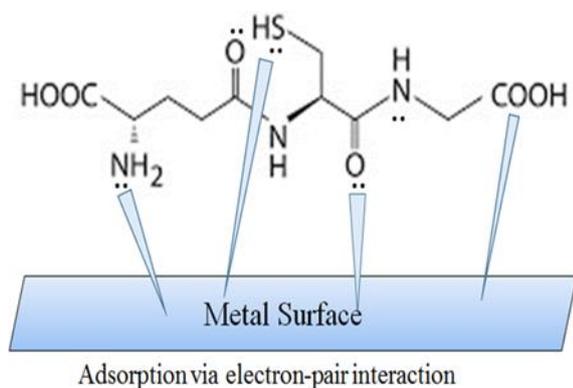


Fig. 12. The chemisorption of Gth.

The protonated inhibitor, $[Gth-H_x]^{x+}$ can easily be attracted to the negatively charged alloy surface. As a result, the protonated inhibitor, $[Gth-H_x]^{x+}$ can electrostatically adsorb on the alloy surface leading to physisorption [32] as shown in Fig. 11. The chemisorption of Gth can arise as a result of the sharing of lone pair electrons on N, S, O atoms and π -electrons of carbonyl groups in Gth with the empty d-orbitals of aluminium leading to coordination bond [10] as depicted in Fig.12.

4. CONCLUSION

The following conclusions are drawn from electrochemical and surface morphological studies of inhibition behaviour of Glutathione reduced on AA6061 corrosion in 0.5M HCl.

- Glutathione reduced has been shown to be a reasonably good eco-friendly inhibitor of AA6061 corrosion in 0.5M HCl.
- Glutathione reduced showed mixed inhibitor behaviour and improved its protective power

by increasing its additive concentration and lowering the temperature.

- Inhibition accompanied by mixed adsorption and followed the Langmuir isotherm model.
- Adsorption of Gth on the alloy was demonstrated by SEM and AFM tests.
- Corrosion inhibition results obtained by weight loss and PDP method are very well matched.

Acknowledgment

The authors are grateful to the Manipal Institute of Technology, Manipal Academy of Higher Education, Manipal for its laboratory facilities.

REFERENCES

- [1] G. Koch, J. Vamey, N. Thompson, O. Moghissi, M. Gould, J. Payer, *International measures of prevention, application, and economics of corrosion technologies (IMPACT) study*, NACE International, Houston, TX, 2016.
- [2] J.R. Davis, *ASM Specialty Handbook: Aluminium and aluminium alloys*, ASM International, Metals Park, OH, 1993.
- [3] X. Yaqing, X. Shuisheng, L. Jingan, W. Tao, *Practical directory of aluminium alloys technology*, Metallurgical Industry Press, Beijing, 2005.
- [4] J.O'M. Bockris, Lj.V. Minevski, *On the mechanism of the passivity of aluminium and aluminium alloys*, Journal of Electroanalytical Chemistry, vol. 349, iss. 1-2, pp. 375-414, 1993, doi: [10.1016/0022-0728\(93\)80186-L](https://doi.org/10.1016/0022-0728(93)80186-L)
- [5] J.H.W. de Wit, H.J.W. Lenderink, *Electrochemical impedance spectroscopy as a tool to obtain mechanistic information on the passive behaviour of aluminium*, Electrochimica Acta, vol. 41, iss. 7-8, pp. 1111-1119, 1996, doi: [10.1016/0013-4686\(95\)00462-9](https://doi.org/10.1016/0013-4686(95)00462-9)
- [6] M. Whelan, K. Barton, J. Cassidy, J. Colreavy, B. Duffy, *Corrosion inhibitors for anodised aluminium*, Surface and Coatings Technology, vol. 227, pp. 75-83, 2013, doi: [10.1016/j.surfcoat.2013.02.029](https://doi.org/10.1016/j.surfcoat.2013.02.029)
- [7] N. Murer, R.G. Buchheit, *Stochastic modeling of pitting corrosion in aluminium alloys*, Corrosion Science, vol. 69, pp. 139-148, 2013, doi: [10.1016/j.corsci.2012.11.034](https://doi.org/10.1016/j.corsci.2012.11.034)
- [8] G. Bereket, A. Yurt, *The inhibition effect of amino acids and hydroxyl carboxylic acids on pitting*

- corrosion of aluminium alloy 7075, Corrosion Science, vol. 43, iss. 6, pp. 1179-1195, 2001, doi: [10.1016/S0010-938X\(00\)00135-9](https://doi.org/10.1016/S0010-938X(00)00135-9)
- [9] K.F. Khaled, M.M. Al-Qahtani, *The inhibitive effect of some tetrazole derivatives towards Al corrosion in acid solution: Chemical, electrochemical and theoretical studies*, Materials Chemistry and Physics, vol. 113, iss. 1, pp. 150-158, 2009, doi: [10.1016/j.matchemphys.2008.07.060](https://doi.org/10.1016/j.matchemphys.2008.07.060)
- [10] S.P. Fakrudeen, H.C. Ananda Murthy, V. Bheema Raju, *Corrosion inhibition of AA6061 and AA6063 alloy in hydrochloric acid media by Schiff base compounds*, Journal of Chilean Chemical Society, vol. 57, no. 4, pp. 1364-1371, 2012, doi: [10.4067/S0717-97072012000400007](https://doi.org/10.4067/S0717-97072012000400007)
- [11] K. Raviprabha, R.S. Bhat, *Inhibition effects of ethyl-2-amino-4-methyl-1,3-thiazole-5-carboxylate on the corrosion of AA6061 alloy in hydrochloric acid media*, Journal of Failure Analysis and Prevention, vol. 19, pp. 1464-1474, 2019, doi: [10.1007/s11668-019-00744-5](https://doi.org/10.1007/s11668-019-00744-5)
- [12] A. Yurt, G. Bereket, C. Ogretir, *Quantum chemical studies on inhibition effect of amino acids and hydroxy carboxylic acids on pitting corrosion of aluminium alloy 7075 in NaCl solution*, Journal of Molecular Structure: THEOCHEM, vol. 725, iss. 1-3, pp. 215-221, 2005, doi: [10.1016/j.theochem.2005.01.048](https://doi.org/10.1016/j.theochem.2005.01.048)
- [13] O. Olivares, N.V. Likhanova, B. Gomez, J. Navarrete, M.E. Llanos-Serrano, E. Arce, J.M. Hallen, *Electrochemical and XPS studies of decylamides of α -amino acids adsorption on carbon steel in acidic environment*, Applied Surface Science, vol. 252, iss. 8, pp. 2894-2909, 2006, doi: [10.1016/j.apsusc.2005.04.040](https://doi.org/10.1016/j.apsusc.2005.04.040)
- [14] V. Prathipa, A. Sahaya Raja, *A Review on the assessment of amino acids used as corrosion inhibitor of metals and alloys*, Journal of Chemical, Biological and Physical Sciences, vol. 5, no. 2, pp. 1585-1619, 2015.
- [15] L. Hamadi, S. Mansouri, K. Oulmi, A. Kareche, *The use of amino acids as corrosion inhibitors for metals: A review*, Egyptian Journal of Petroleum, vol. 27, iss. 4, pp. 1157-1165, 2018, doi: [10.1016/j.ejpe.2018.04.004](https://doi.org/10.1016/j.ejpe.2018.04.004)
- [16] D.-Q. Zhang, Q.-R. Cai, X.-M. He, L.-X. Gao, G.S. Kim, *The corrosion inhibition of copper in hydrochloric acid solutions by a tripeptide compound*, Corrosion Science, vol. 51, pp. 2349-2354, 2009, doi: [10.1016/j.corsci.2009.06.015](https://doi.org/10.1016/j.corsci.2009.06.015)
- [17] J.I. Bhat, V.D.P. Alva, *A study of aluminium corrosion inhibition in acid medium by an antiemetic drug*, Transactions of the Indian Institute of Metals, vol. 64, pp. 377-384, 2011, doi: [10.1007/s12666-011-0102-9](https://doi.org/10.1007/s12666-011-0102-9)
- [18] P.O. Ameh, N.O. Eddy, *Commiphora pedunculata gum as a green inhibitor for the corrosion of aluminium alloy in 0.1 M HCl*, Research on Chemical Intermediates, vol. 40, pp. 2641-2649, 2014, doi: [10.1007/s11164-013-1117-0](https://doi.org/10.1007/s11164-013-1117-0)
- [19] F. Mansfeld, M.W. Kendig, W.J. Lorenz, *Corrosion Inhibition in Neutral, Aerated Media*, Journal of the Electrochemical Society, vol. 132, no. 2, pp. 290-296, 1985, doi: [10.1149/1.2113820](https://doi.org/10.1149/1.2113820)
- [20] M.G. Fontana, *Corrosion Engineering*, Singapore: McGraw-Hill, 1987.
- [21] W.-h. Li, Q. He, S.-t. Zhang, C.-h. Pei, B.-t. Hou, *Some new triazole derivatives as inhibitors for mild steel corrosion in acidic medium*, Journal of Applied Electrochemistry, vol. 38, pp. 289-295, 2008, doi: [10.1007/s10800-007-9437-7](https://doi.org/10.1007/s10800-007-9437-7)
- [22] G. Moretti, G. Quartarone, A. Tassan, A. Zingales, *5-amino-and 5-chloro-indole as mild steel corrosion inhibitors in 1N sulphuric acid*, Electrochimica Acta, vol. 41, iss. 13, pp. 1971-1980, 1996, doi: [10.1016/0013-4686\(95\)00485-8](https://doi.org/10.1016/0013-4686(95)00485-8)
- [23] I. Ahamed, M.A. Quraishi, *Bis (benzimidazol-2-yl) disulphide: An efficient water soluble inhibitor for corrosion of mild steel in acid media*, Corrosion Science, vol. 51, iss. 9, pp. 2006-2013, 2009, doi: [10.1016/j.corsci.2009.05.026](https://doi.org/10.1016/j.corsci.2009.05.026)
- [24] S.S. Abd El Rehim, H.H. Hassan, M.A. Amin, *The corrosion inhibition study of sodium dodecyl benzene sulphonate to aluminium and its alloys in 1.0 M HCl solution*, Materials Chemistry and Physics, vol. 78, iss. 2, pp. 337-348, 2002, doi: [10.1016/S0254-0584\(01\)00602-2](https://doi.org/10.1016/S0254-0584(01)00602-2)
- [25] M. Schorr, J. Yahalom, *The significance of the energy of activation for the dissolution reaction of metal in acids*, Corrosion Science, vol. 12, iss. 11, pp. 867-868, 1972, doi: [10.1016/S0010-938X\(72\)80015-5](https://doi.org/10.1016/S0010-938X(72)80015-5)
- [26] S.S. Abdel Rehim, M.A.M. Ibrahim, K.F. Khaled, *4-Aminoantipyrine as an inhibitor of mild steel corrosion in HCl solution*, Journal of Applied Electrochemistry, vol. 29, pp. 593-599, 1999, doi: [10.1023/A:1003450818083](https://doi.org/10.1023/A:1003450818083)
- [27] E.E. Oguzie, V.O. Njoku, C.K. Enenebeaku, C.O. Akalezi, C. Obi, *Effect of hexamethyl pararos aniline chloride (crystal violet) on mild steel corrosion in acidic media*, Corrosion Science, vol. 50, iss. 12, pp. 3480-3486, 2008, doi: [10.1016/j.corsci.2008.09.017](https://doi.org/10.1016/j.corsci.2008.09.017)
- [28] E. Bayol, K. Kayakırlmaz, M. Erbil, *The inhibitive effect of hexamethylene tetramine on the acid corrosion of steel*, Material Chemistry and Physics, vol. 104, iss. 1, pp. 74-82, 2007, doi: [10.1016/j.matchemphys.2007.02.073](https://doi.org/10.1016/j.matchemphys.2007.02.073)
- [29] R. Rosliza, W.B. Wan Nik, *Improvement of corrosion resistance of AA6061 alloy by tapioca*

- starch in seawater*, Current Applied Physics, vol. 10, iss. 1, pp. 221-229, 2010, doi: [10.1016/j.cap.2009.05.027](https://doi.org/10.1016/j.cap.2009.05.027)
- [30] R. Rosliza, W.B. Wan Nik, S. Izman, Y. Prawoto, *Anti-corrosive properties of natural honey on Al-Mg-Si alloy in seawater*, Current Applied Physics, vol. 10, iss. 3, pp. 923-929, 2010, doi: [10.1016/j.cap.2009.11.074](https://doi.org/10.1016/j.cap.2009.11.074)
- [31] R. Rosliza, A. Noraaini, W.B. Wan Nik, *Study on the effect of vanillin on the corrosion inhibition of aluminium alloy*, Journal of Applied Electrochemistry, vol. 49, pp. 833-840, 2010, doi: [10.1007/s10800-009-0066-1](https://doi.org/10.1007/s10800-009-0066-1)
- [32] L. Tang, X. Li, L. Li, G. Mu, G. Liu, *Interfacial behavior of 4-(2-pyridylazo) resorcin between steel and hydrochloric acid*, Surface and Coatings Technology, vol. 201, iss. 1-2, pp. 384-388, 2006, doi: [10.1016/j.surfcoat.2005.11.132](https://doi.org/10.1016/j.surfcoat.2005.11.132)
- [33] I. Ahamad, R. Prasad, M.A. Quraishi, *Thermodynamic, electrochemical and quantum chemical investigation of some Schiff bases as corrosion inhibitors for mild steel in hydrochloric acid solutions*, Corrosion Science, vol. 52, iss. 3, pp. 933-942, 2010, doi: [10.1016/j.corsci.2009.11.016](https://doi.org/10.1016/j.corsci.2009.11.016)
- [34] M.A. Amin, M.A. Ahmed, H.A. Arida, T. Arslan, M. Saracoglu, F. Kandemirli, *Monitoring corrosion and corrosion control of iron in HCl by non-ionic surfactants of the TRITON-X series-Part II. Temperature effect, activation energies and thermodynamics of adsorption*, Corrosion Science, vol. 53, iss. 2, pp. 540-548, 2011, doi: [10.1016/j.corsci.2010.09.019](https://doi.org/10.1016/j.corsci.2010.09.019)
- [35] P. Kumari, P. Shetty, A.S. Rao, D. Sunil, *Corrosion inhibition and adsorption behaviour of (2E)-2-(3-hydroxy benzylidene)hydrazinecarbothiamide on mild steel in 1M HCl*, Revue Roumaine de Chime, vol. 59, no. 5, pp. 323-333, 2014.
- [36] A.A. El-Awady, B.A. Abd-El-Nabey, S.G. Aziz, *Thermodynamic and kinetic factors in chloride ion pitting and nitrogen donor ligand inhibition of aluminium metal corrosion in aggressive acid media*, Journal of Chemical Society Faraday Transactions, vol. 89, iss. 5, pp. 795-802, 1993, doi: [10.1039/FT9938900795](https://doi.org/10.1039/FT9938900795)
- [37] I.L. Rozenfeld, *Corrosion Inhibitors*, New York: McGraw-Hill Inc., 1981.
- [38] F. Mansfield, *Corrosion Mechanisms*, New York: Marcel-Dekker, 1987.
- [39] G. Bereket, A. Pinarbasi, *Electrochemical thermodynamic and kinetic studies of the behaviour of aluminium in hydrochloric acid containing various benzotriazole derivatives*, Corrosion Engineering, Science and Technology, vol. 39, iss. 4, pp. 308-312, 2004, doi: [10.1179/174327804X13136](https://doi.org/10.1179/174327804X13136)