Gallic Acid as Corrosion Inhibitor for Aluminum 6061 in Alkali Solutions

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Abstract

The research aims to study the corrosion of aluminum alloy (6061) in 0.6 mol. dm^{-3} NaCl solution in base medium (pH = 12) was examined with out and with Gallic acid as environmentally – friendly corrosion inhibitor at temperature range (298-313) K. The inhibitive action of gallic acid on corrosion of aluminum alloy (6061) in KOH solution was examined through electrochemical polarization method using potentiostatic technique and surface analysis by optical microscopy, Polarization measurements indicate that the examined compound act as a mixed type inhibitor. Results appeared that the inhibition occurs through adsorption of the inhibitor molecules on the metal surface and it was obeyed Langmuir adsorption isotherm. Some thermodynamic parameters activation energy (E_a) and ($\Delta G_{ads.}$) were calculated to elaborate the mechanism of inhibition. The surface characteristic of the inhibited and uninhibited metal samples was examined by optical microscopy.

Keywords: Aluminum, Corrosion inhibition, Gallic acid, Adsorption Mechanism, thermodynamic parameters.

1.Introduction

Corrosion is a destructive phenomenon (chemical or electrochemical), which can attack any material or alloy due to interactions with the surrounding medium that leads to a deterioration of metal physical and chemical properties. according to this definition term corrosion can include all materials, metals and non-metals [1, 2]. It is a continues problem and often difficult to complete deletion, so prevention is more practical [3]. But practically term corrosion is used with metals exclusively.

Aluminum was used widely in many sections such as chemical plant, manufacturing lines, and marine industries. The advantage is the use of aluminum is due to their excellent corrosion resistance property and it has excellent formability, low density, high thermal and electrical conductivity, and thus it becomes a seniority in materials selections in most industries [4, 5]. As well-known aluminum compounds have been used for centuries, the production of aluminum metal begun 170 years ago [6].

Aluminum has an attractive appearance and good resistance to corrosion when exposed to atmosphere or various aqueous environments because its ability to form a highly compact passive oxide layer [7-9]. These properties made aluminum one of the most attractive materials for industrial applications like automobiles, aviation, aerospace, food handling, containers, electronic devices, buildings, marine, etc[10]. Although the oxide film formed on aluminium relies for its corrosion immunity, this film is amphoteric so it dissolves in case of exposes to high concentrations of bases or acids especially in present of chloride [11]. Among the most common protection method is inhibitors (organic and inorganic) [12-15], when the inhibitor added to corrosive sample in a small quantity reduce the corrosion are commonly used to reduce corrosion. The present work is another attempt to obtain environmentally and cheap inhibitor for aluminum in basic medium containing (3.5% w/w) NaCl, where gallic acid is tested.

Gallic acid is an organic acid, also known as 3, 4, 5-trihydroxybenzoic acid, , a type of phenolic acid, Gallic acid is a colorless or slightly yellow crystalline compound obtained from nutgalls., found in plants free and as part of hydrolyzable tannins[15]. Gallic acid occurring mostly in certain red fruits, black radish, and onions [16] Due to the OH− groups in the ortho position on the aromaticrings, gallic acids are able to form chelates with copper and other metallic cations (e.g., iron) [17,18].

2.Materials and Method

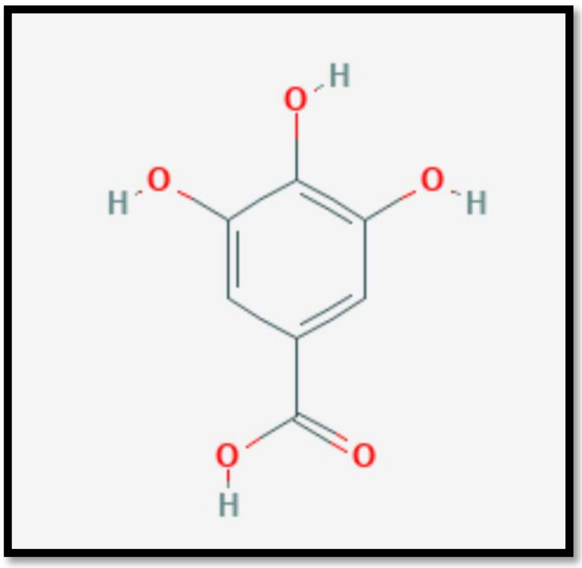
The experiments were performed with aluminum alloy 6061 of following composition as shown in **Table1** of 2mm thickness which was mechanically press-cut into circular form 2cm diameter.

Table 1. The chemical composition of aluminum 6061.

Aluminum alloy	Si	Fe	Cu	Mn	Mg	Cr	Ni	Zn	V
6061	0.66	0.35	0.33	0.004	1.04	0.21	-	0.09	0.008

Chemicals used in this work include:

a. Sodium chloride, was used for preparation of the aggressive solution of $0.6 mol\ dm^{-3}$.
b. Potassium hydroxide.
c. Gallic acid tested as inhibitor (>98% purity). Its structure is shown below.



Structure of gallic acid

2.1. Solution

The solution used was made of A.R. Sodium chloride to prepare $0.6 mol\ dm^{-3}$concentration in $\mathrm{pH} = 12$. Doubled distilled water was used for the preparation. For each experiment a freshly solution was made. Three concentrations of the inhibitor (Gallic acid) were used $(3 \times 10^{-5}, 6 \times 10^{-5}$ and $9\ \times 10^{-5})\mathrm{mol.\,dm^{-3}}$.

3. Results and Discussion

3.1 Tafel Polarization Measurements

Tafel polarization technique was used to study the corrosion of aluminium alloy 6061 in 0.6 mol. dm^{-3} Sodium chloride solution in basic medium at four temperatures over rang (298-313). **Figure 1.** shows potentiostatic polarization curves. Corrosion parameters $(\mathrm{i_{corr}})$, $\mathrm{E_{corr}}$, $(\mathrm{b_a})$ and $(\mathrm{b_c})$ are obtained from the Tafel polarization curves and tabulated in **Table 2.**

The results show the increase in the corrosion current density $(\mathrm{i_{corr}})$with temperature rising. From negative shift of $\mathrm{E_{corr}}$ with temperature rising can be concluded that anodic process is much more affected than cathodic, this observation is in accordance with other published results[1,3] which proposed the dependence of $(\mathrm{i_{corr}})$ and $(\mathrm{E_{corr}})$ on solution parameters.

The electrochemical cathodic and anodic reactions of aluminum alloy 6061, in basic solution can be described as follows [19].

$$Al + 3OH^{-} \rightarrow Al(OH)_3 + 3e^{-} \qquad (1)$$

$$Al(OH)_3 + OH^{-} \rightarrow Al(OH)_4{}^{-} \qquad (2)$$

$$Al + 4OH^{-} \rightarrow Al(OH)_4{}^{-} + 3e^{-} \qquad (3)$$

Table 2. Data of polarization curve for corrosion of aluminum alloy 6061 in PH=12over temperature range (298-313) K. with presence of $(0.6\mathrm{mol.\,dm^{-3}})$NaCl.

PH	T/K	Corrosion		b		Weight loss/g.m-².d-¹	Penetration loss/mm.year⁻¹
		Ecorr/mV-	icorr /µA.cm-²	-b/mV-decade-¹	+b/mV-decade-¹		
12	298	1361.3	127.51	116.5	248.95	1.03×10^{-1}	1.39
	303	1362	200	92.3	241.9	1.62×10^{-1}	2.18
	308	1373	290.21	78	263	2.3×10^{-1}	3.16
	313	1380	343.94	82	451.9	2.77×10^{-1}	3.74

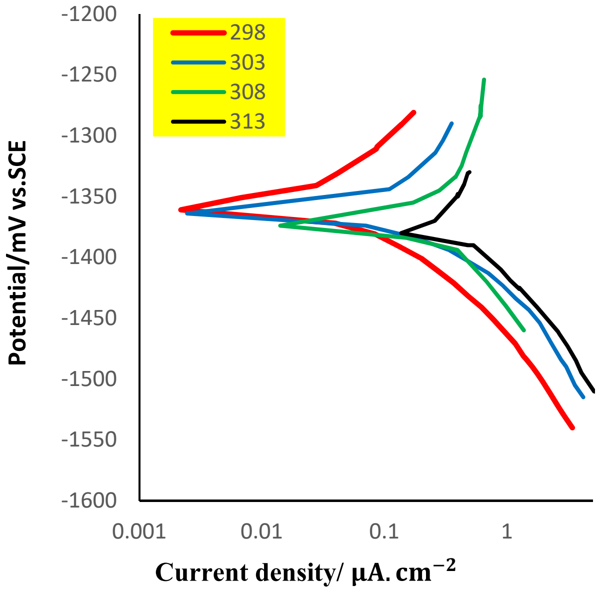


Figure 1. Polarization curves of aluminum alloy 6061 in KOH with 0.6 mol.dm^{-3} NaCl solution .

3.2 Effect of Temperature

The effect of temperature on the corrosion rate of aluminum alloy (6061) expressed by i_{corr},was studied by measuring the corrosion at the temperature range of (293-308) K which followed Arrhenius equation [20].

$$rate\ (r) \equiv i_{corr} = A\ exp\left(-\frac{E_a}{RT}\right) \qquad (4)$$

$$ln\ i_{corr} \equiv \ln A - \frac{E_a}{RT} \qquad (5)$$

WhereE_a and A are respectively the activation energy and pre-exponential factor of corrosion reaction. A typical linear plot relating values of $\ln i_{corr}$ to the reciprocal of temperature $\left(\frac{1}{T}\right)$. The values of E_a could be derived from the slope of the line, and when the linear plot was extrapolated to $\ln i_{corr}$ value at $\left(\frac{1}{T}\right) = 0$, the value of A could be obtained. **Table 3.** represents the values of $\Delta S^*, E_a$ and the pre-exponential factor (A) for aluminum sample in $(pH = 12)$. (ΔS^*) was computed using equation (6)

$$A = \frac{kT}{h} \exp \frac{\Delta S^*}{R} \qquad (6)$$

Where(h) is Plank constant, (k) is boltzman constant, (R) is the universal gas constant and (T) the asbsolute temperature of the solution [21]. The values of (ΔS^*) were calculated and listed in **Table 3**. The negative values of (ΔS^*) reflect that the activated complex in r.d.s represents association rather than dissociation, this means that the activated molecules.

Figure 2. Shows the typical polarization curves of aluminums alloy 6061 in 0.6mol dm^{-3} NaCl solution containing three different concentrations of gallic acid as a green inhibitor over the temperature range (298-313)K. **Table 4** presents the polarization data (E_{cor} and i_{corr}) which shows that there is adecrease in corrosion current densities of aluminium alloy(6061)due the addition of gallic acid. The inhibition effect of gallic acid increases as the concentration of the inhibitor increases in the range $(3 \times 10^{-5} - 9 \times 10^{-5})$mol dm^{-3} at all temperatures ofstudy as shown in **Table 5.** The values of inhibition efficiencies (IE%) :

$$\text{IE\%} \equiv \frac{i^0_{corr} - i_{corr}}{i^0_{corr}} \times 100\% \qquad (7)$$

Where i^0_{corr} and i_{corr} are corrosion current densities in absence and presence of the inhibitor respectively.

Table 3. Activation energy (E_a),pre-exponential factor (A) and entropy of activation (ΔS^*) for the corrosion of Aluminum alloy 6061 in the pH = 12 in 0.6mol. dm^{-3} NaCL solution Gallic.

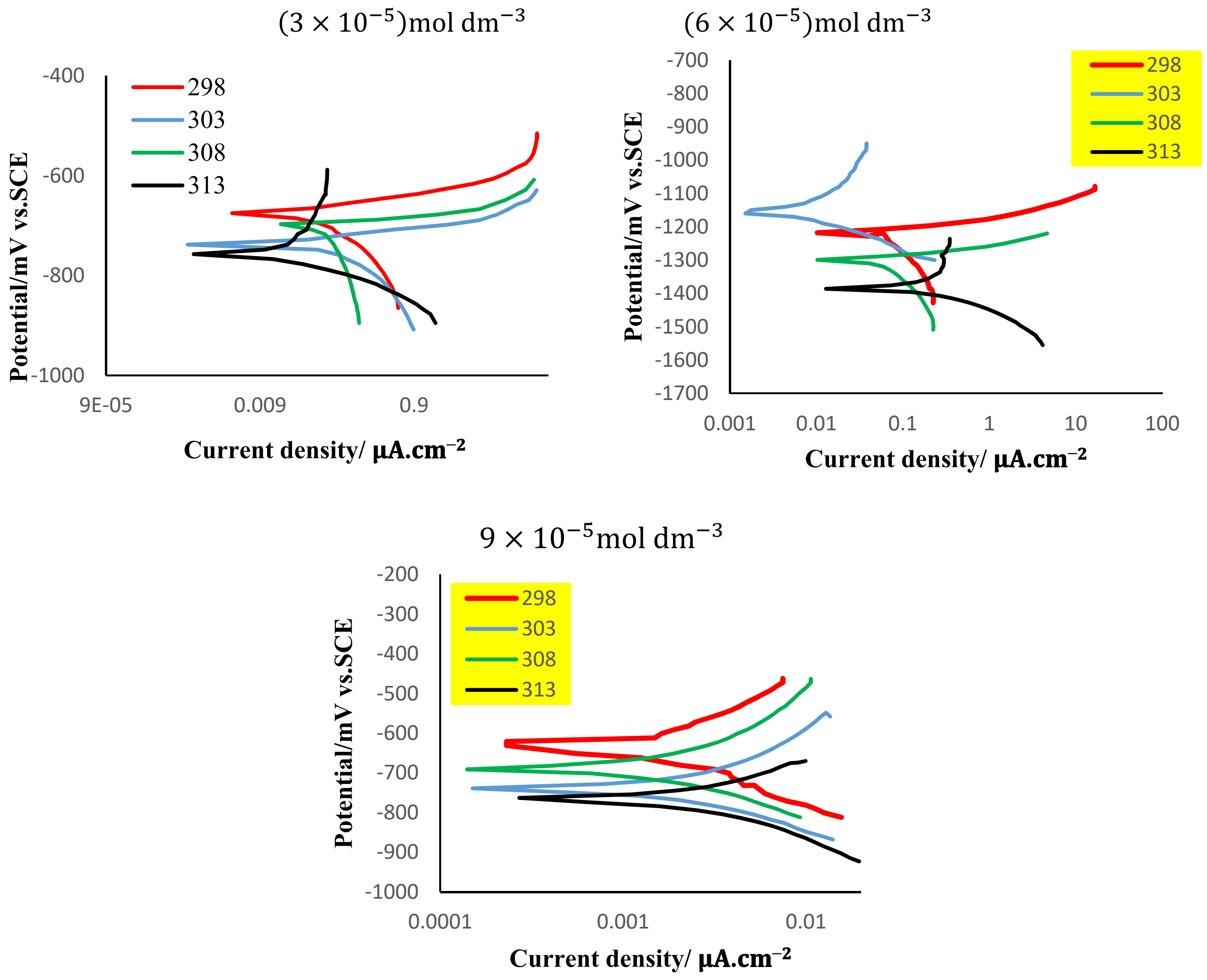
Conc. of Gallic acid $mol.dm^{-3}$	$E_a/kJ.mol^{-1}$	$-\Delta S^* J.K^{-1}.mol^{-1}$	**A/molecule** $m^{-2}.S^{-1}$
Blank	50.99	36.746	7.0103× 10 $-^{34}$
3×10^{-5}	94	89	300.06×10^{39}
6×10^{-5}	97.8	95.7	600.602×10^{39}
9×10^{-5}	99.7	100	1000.13×10^{39}

Table 4. Values of (E_{corr}, i_{corr}) with different concentrations of Gallic acid at temperature range (298-313) K in pH = 12

T/K	**Inhibitor conc. $mol.dm^{-3}$**	$-E_{corr}/mv$	$i_{corr}/\mu A.cm^{-2}$
298	0		
	3×10^{-5}	1163	9.71
	6×10^{-5}	1176.2	5.84
	9×10^{-5}	1067	4.55
303	0		
	3×10^{-5}	1292.3	21.51
	6×10^{-5}	1318.9	13.79
	9×10^{-5}	1281.7	11.12
308	0		
	3×10^{-5}	1295	56.96
	6×10^{-5}	1348.8	42
	9×10^{-5}	1374.2	40.83
313	0		
	3×10^{-5}	667.1	96.05
	6×10^{-5}	1388.2	94.35
	9×10^{-5}	652.4	81.41

Table 5. Values of inhibitor efficiencies (IE%) calculated from i_{corr}. For Aluminum alloy 6061 in pH = 12.

Conc. of Gallic acid	**T/K**	**IE% from i_{corr}.**
3×10^{-5}	298	92
	303	89
	308	80
	313	72
6×10^{-5}	298	95
	303	93
	308	85.5
	313	73
9×10^{-5}	298	96
	303	94
	308	86
	313	76


$(3 \times 10^{-5})\text{mol dm}^{-3}$

$(6 \times 10^{-5})\text{mol dm}^{-3}$

$9 \times 10^{-5}\text{mol dm}^{-3}$

Figure 2.The typical polarization curves of aluminum alloy 6061 in solution containing of Gallic acid as inhibitor (a= 3×10^{-5}, b = 6×10^{-5}, c =9×10^{-5} mol.dm^{-3}) over the temperature rang (298-313)K. PH=12 with (0.6 mol.dm^{-3}) NaCl.

3.3 Adsorption Isotherm

In order to understand the electrochemical process of adsorption of inhibitor molecules on the metal surface, it is necessary to study the adsorption isotherms. The adsorption isotherm fitted the experimental data for adsorption of gallic acid molecules on aluminum 6061 surface is due to Langmuir isotherm **Figure 3**. which is given by the following equation [22].

$$\frac{C_{gal.}}{\theta} = \frac{1}{k_{ad}} + C_{gal.} \qquad (8)$$

Where k_{ads} is the equilibrium constant for the adsorption , and C_{gal} gallic acid concentration. K_{ads} were calculated from the intercepts of the straight lies on the $C_{gal.}/\theta$ axis **Figure 3**.(k_{ads}) relate to the standard free energy of adsorption ΔG^0_{ads}according to the equation.

$$\Delta G^0_{ads} = -RTln(55.5\ k_{ads}) \qquad (9)$$

Where 55.5 is concentration of water in solution.

The standard free energy of adsorption was calculated. Generally, the standard free energy of adsorption values $-20kJ.mol^{-1}$ or less negative are associated with an electrostatic interaction between charged metal surface or more negative involves charge sharing or transfer from the inhibitor molecules to the metal surface to form a coordinate covalent bond. So it can be concluded that adsorption of gallic on to aluminum 6061 surface takes place through physical adsorption [22].

From **Table 6.** it was clearly seen that gallic acid decrease the corrosion rate of aluminums in KOH solution E_{corr} shifts to little more negative values in the presence of gallic acid. This result indicates that the inhibitors have been adsorbed to both cathodic and anodic areas. That mean acid gallic a is mixed type inhibitor. The same results have been reported by other authors [23, 24].

On basis of Van't Hoff relation, the values of standard enthalpy of adsorption can be calculated:

$$\ln K_{ads} = -\frac{\Delta H^0_{ads}}{RT} + constant \qquad (10)$$

The slope of straight line of the plot of $\ln k_{ads}$ vs. $1/T$ is $-\frac{\Delta H^0_{ads}}{R}$ as show in **Figure 4.** and **Table7.** Generally, endothermic adsorption process is suggesting chemisorption while exothermic process attributed to either physisorption or chemisorption. Negative sign of ΔH^0_{ads} shows that adsorption of tannin molecules is exothermic process [25].

Table 6. Corrosion parameter, surface coverage and corrosion inhibition efficiency for Aluminum (6061) in $0.6mol.dm^{-3}$ NaCL solution in pH = 12 with different concentrations of Gallic at various temperature.

T/K	conc.Gal.. $mol.dm^{-3}$	$-E_{corr}/mv$	$i_{corr}/\mu A.cm^{-2}$	θ	IE%
298	0	1361.3	127.51		
	3×10^{-5}	1163	9.71	0.92	92
	6×10^{-5}	1176.2	5.84	0.95	95
	9×10^{-5}	1067	4.55	0.96	96
303	0	1362	200		
	3×10^{-5}	1292.3	21.51	0.89	89
	6×10^{-5}	1318.9	13.79	0.93	93
	9×10^{-5}	1281.7	11.12	0.94	94
308	0	1373	290.21		
	3×10^{-5}	1295	56.96	0.80	80
	6×10^{-5}	1348.8	42	0.855	85.5
	9×10^{-5}	1374.2	40.83	0.86	86
313	0	1380	343.94		
	3×10^{-5}	667.1	96.05	0.72	72
	6×10^{-5}	1388.2	94.35	0.73	73
	9×10^{-5}	652.4	81.41	0.76	76

Table 7. Thermodynamic parameters for adsorption of gallic acid on aluminum inKOH+NaCl.

T/K	$k_{ads}\ mol^{-1}$	$-\Delta G^0_{ads} kJ.mol^{-1}$	$\Delta H^0_{ads} kJ.mol^{-1}$	$-\Delta S^0_{ads}\ J.mol^{-1}.K^{-1}$
298	0.937	9.791	-48.56	-0.1301
303	0.612	8.882		-0.1309
308	0.389	7.882		-0.1321
313	0.303	7.345		-0.1317

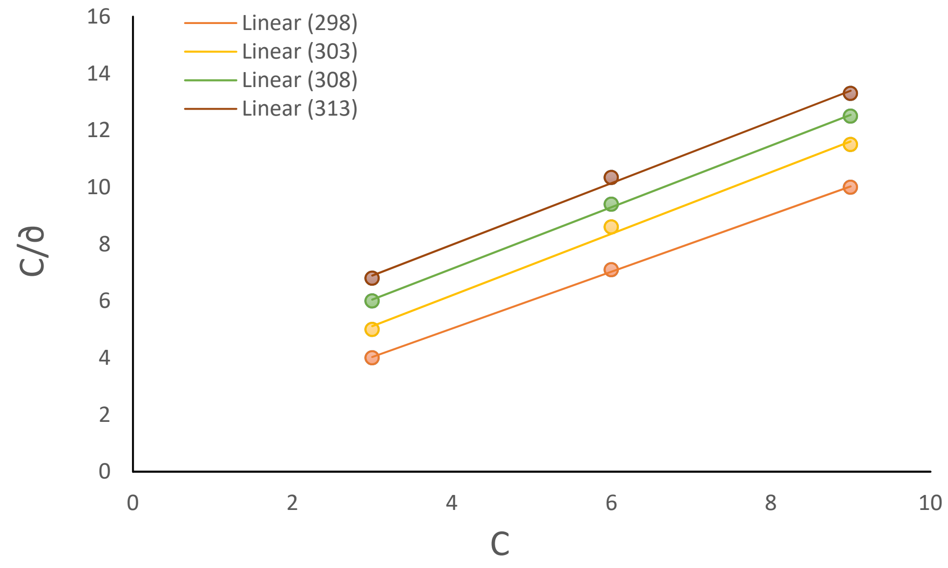


Figure 3. Langmuir adsorption plots of gallic acid on the Al Alloy (6061) in 0.6 mol.dm^{-3} NaCl solution at various temperatures.

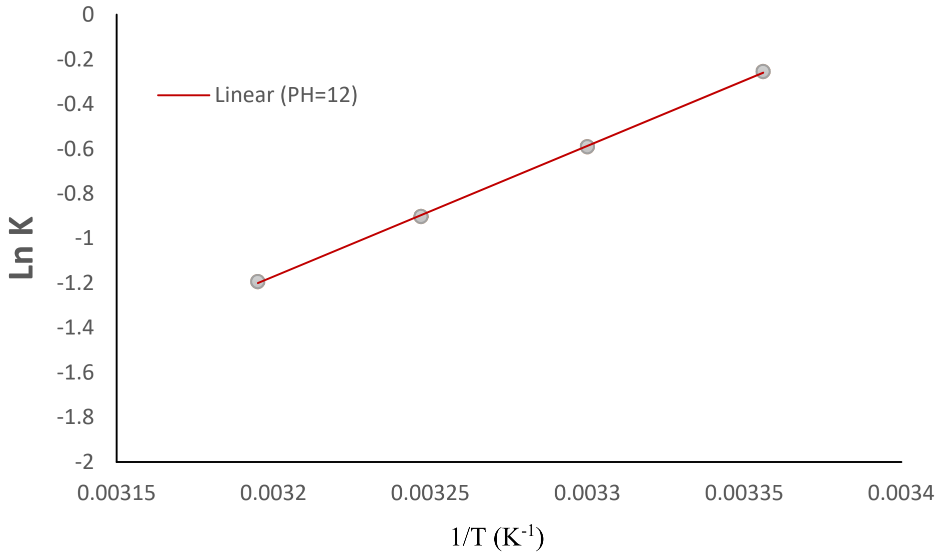
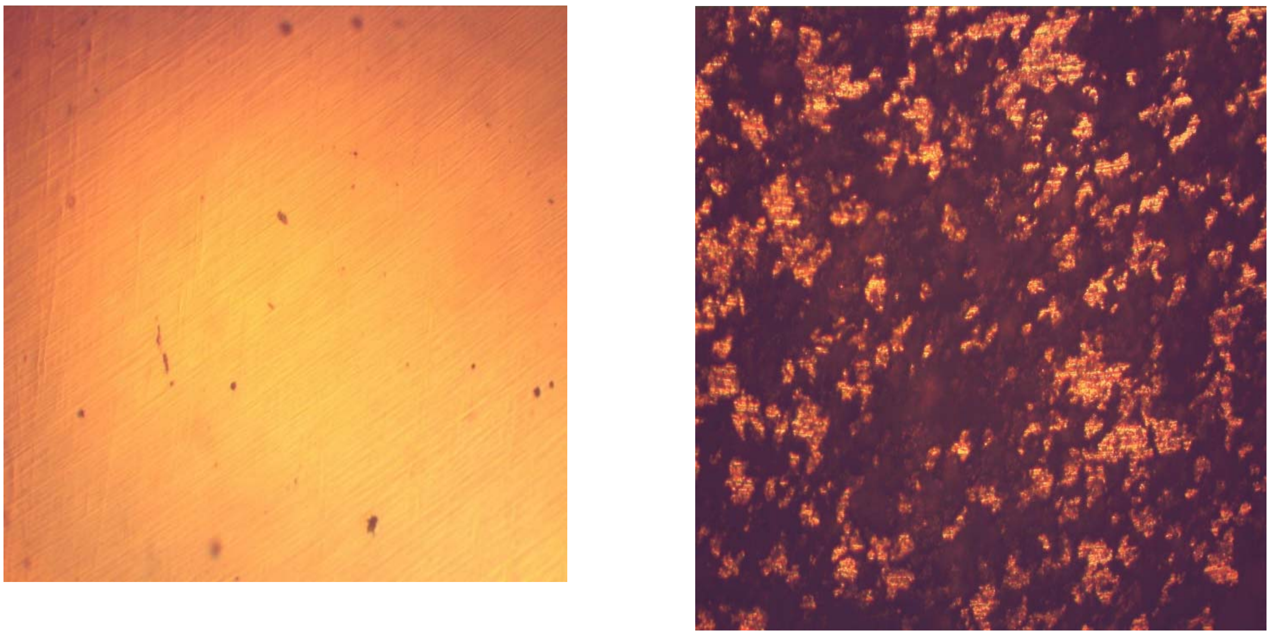


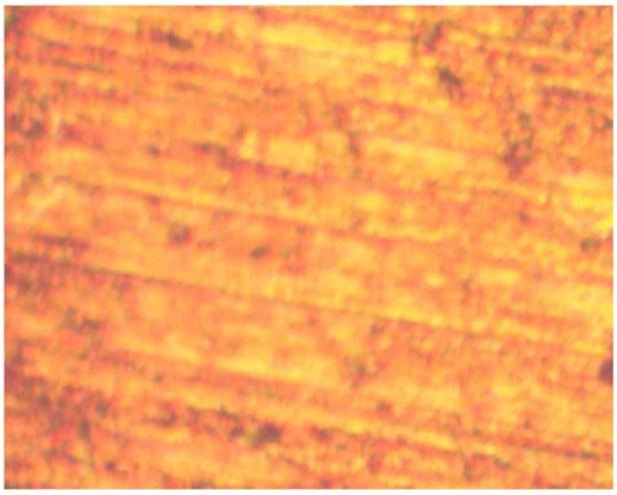
Figure 4. Van't Hoff plot for aluminum alloy 6061 at pH=12 in $(0.6\ mol.dm^{-3}\ )$NaCl containing Gallic.

3.4 Optical Microscopy Observation:

To study the effect of gallic acid on the surface morphology of aluminum alloy 6061, surface out examined by optical microscope technique. **Figure 5**. **Figure 5**-a polished aluminium alloy 6061 surface ,b) 6061 surface immersed in KOH+ NaCl the specimen surface was strongly damaged, c) in presence of gallic acid $(9 \times 10^{-5}$ mol. dm^{-3}) shows that there was much less damage on the surface compared to the surface treated with uninhibited potassium hydroxid solution.



a. (6061) b. immersed in(KOH+NaCl)



c.immersed in (KOH+ NaCl) + Gallic acid

Figure 5. Typical microstructure of Aluminum alloy(6061) in the corroded medium at pH = 12 , magnification power 400×.

4. Conclusion

Results indicate that gallic acid is a good inhibitor for corrosion of aluminum alloy6061 in in3.5% NaCl solution at pH=12. The corrosion process is inhibited by adsorption of gallic acid on the aluminum surface obeys Langmuir isotherm. Inhibition efficiency increases with increasing the concentration of inhibitors as well as with decreasing temperature that suggested physical adsorption. The presence of gallic acid increased the corrosion activation energy in alkaline medium and the adsorption heat gave negative value.

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