Corrosion Inhibition Of 6061 Al-Alloy Using A Bio Polymer

Charitha B P[1], Padmalatha Rao[1*]
[1]Department of chemistry, Manipal Institute of Technology, Manipal, Udupi, Karnataka
*Corresponding author's email address: padmalatha.rao@manipal.edu

Abstract:

Pullulan, a biopolymer was used as an eco-friendly inhibitor to control the corrosion of 6061Al-alloy in 0.05 and 0.1 M HCl medium. The electrochemical studies like potentiodynamic polarization method, electrochemical impedance spectroscopy techniques were adopted. Evaluation of kinetic and thermodynamic parameters was done. Inhibitor adsorption on the surface of the composite was confirmed by surface morphology studies like SEM and EDX studies. Maximum inhibition efficiency of 70% was obtained at 303 K for 0.05 M HCl. Pullulan acted as mixed type of inhibitor, underwent physical adsorption and followed Freundlich adsorption isotherm.

Keywords: 6061 Al-alloy; Pullulan; Green inhibitor; PDP; EIS; SEM

1. Introduction

Aluminum is first most abundant metals found on the earth's crust. Aluminum and its alloys have low atomic weight, high strength to density ratio, high ductility and are excellent conductors of heat and electricity. Because of these properties they are used in aerospace and chemical industries. Corrosion resistance of aluminum is due to the formation of naturally formed stable oxide film [1].

When these materials come in contact with pickling agents such as HCl, H_2SO_4 dissolution of metal takes place. Heterocyclic compounds are widely used to protect the metal from undergoing dissolution [2]. But because of environmental regulation use of chemical inhibitors are restricted. Now-a-days research is more geared towards the use of environmentally benign, non-hazardous, biodegradable inhibitors. Biopolymer pullulan is expected to be cheap, easily available, nontoxic and eco-friendly green inhibitor.

2. Experimental

2.1. Materials

The material used for the study was 6061 aluminum alloy with composition (%wt) as Cu- 0.25, Mg-1.0, Cr-0.20, Si-0.60, Al-balance. The cylindrical coupon of 1cm^2 was prepared and it was mounted by using cold setting resin. The disc polishing was done in order to obtain the mirror surface. Pullulan inhibitor stock solution was prepared by dissolving 1.0 $gL^{\%1}$ of pullulan procured from Sigma Aldrich in 0.05 and 0.1 M HCl. The required concentration of solution was then prepared by dilution method.

2.2. Electrochemicalmeasurements

The electrochemical measurements such as potentiodynamic polarization (PDP) and electrochemical impedance spectroscopy (EIS) studies were carried out using electrochemical workstation, (CH600 D%series US model CH instrument with beta software). The electrochemical cell consisted of 3-electrodes; saturated calomel electrode, platinum electrode and working electrode 6061Al-alloy. The PDP studies were conducted by altering the potential of the metal from %0.25V cathodically to +0.25V anodically with respect to open circuit potential (OCP) at a scan rate of $0.001Vsec^{\%1}$.The EIS study was carried out by applying small amplitude of AC signal of 0.01V, at an OCP with a frequency ranging from 10000 Hz to0.01Hz.

2.3. Surface morphologystudies

The SEM image was taken for the corroded sample and for the sample immersed in the HCl medium containing inhibitor for 2h with the use of analytical scanning electron microscope and the elemental mapping was done for the same samples using energy dispersive X-ray analysis.

3. Results andDiscussion

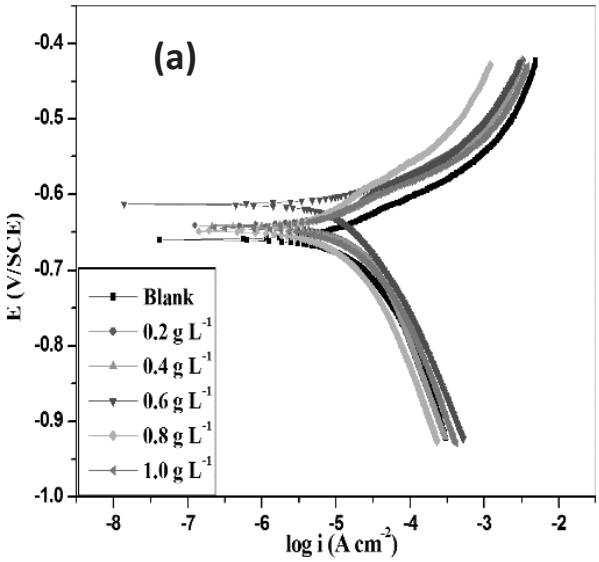
3.1. Electrochemicalmeasurements

Fig. 1 and 2 are PDP plots and Nyquist plots obtained for the corrosion control studies of 6061Al-alloy in 0.05 and 0.1 M HCl at 308K. From PDP plots parameters such as E_{corr}, i_{corr}, cathodic and anodic slopes were obtained. Thus I.E(%) was calculated using the Eq. (1)

$$I.E.(\%)= \frac{icorr—i_{corr(inh)}}{icorr} \times 100 \quad (1)$$

Nyquist plots were semicircle; they have high frequency (HF) and intermediate frequency (LF) inductive loops. The semicircle capacitive loop is an indication of charge transfer controlled corrosion process. Increase in the diameter of HF capacitive loop with increase in the concentration of pullulan proves the protection of Al-alloy from undergoing corrosion through adsorption of inhibitor molecule. For the obtained impedance values the equivalent circuit was simulated. The best fitted equivalent circuit model is R(QR(LR)) which consisted of five elements (Fig. 3) From the simulated circuit the polarization resistance R_p and C_{dl} values were obtained. Thus I.E (%) can be calculated using eq. (2). The results obtained are tabulated in Table 1 and 2.

$$I.E(\%)= \frac{RP(inh)—RP}{RP(inh)} \times 100 \quad (2)$$



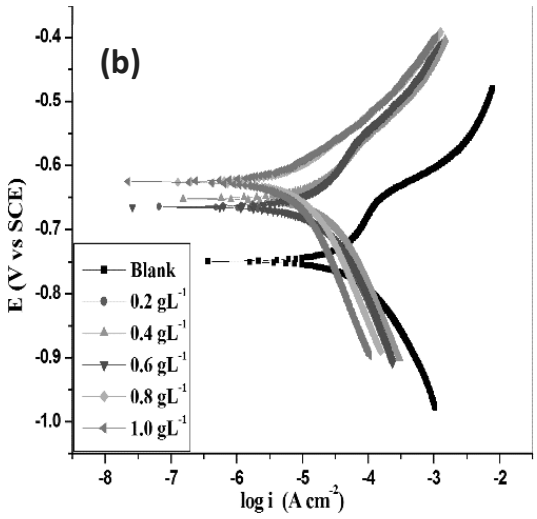


Figure 1: Potentiodynamic polarization plots in (a) 0.05 M (b) 0.1 M HCl

In PDP studies, shift in the E_{corr} was less than 85mV compared with blank. This indicated pullulan acted as mixed type of inhibitor [3]. In EIS studies increase in the R_p and decrease in the C_{dl} value is because of increase in the dielectric constant and decrease in the thickness of double layer. The maximum inhibition efficiency was found to be 69% in 0.05 M HCl at 303 K for inhibitor concentration of 1.0 gL^{-1}.

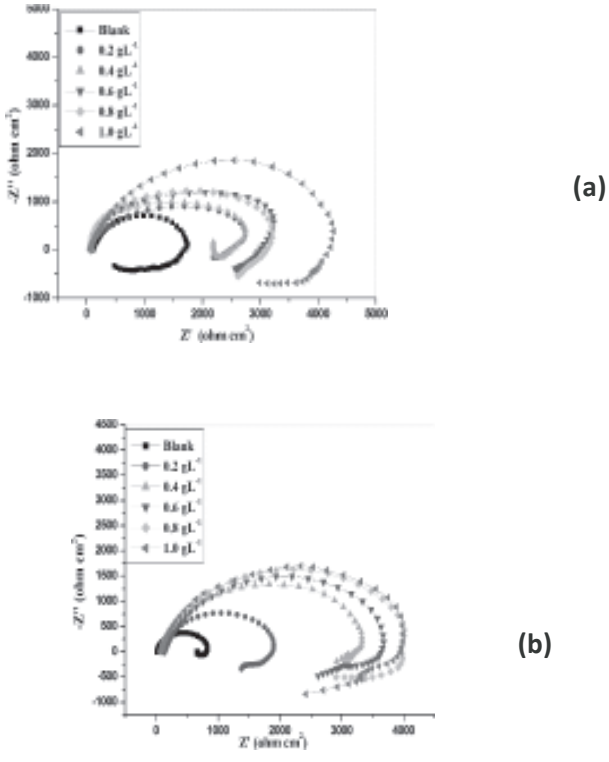


Figure 2: Nyquist plots in (a) 0.05 M (b) 0.1 M HCl

Table 1: Results of Potentiodynamic polarization plots

		0.05MHCl				0.1M HCl			
T (K)	[Pullulan] (g L^{-1})	E_{corr} (mV/ SCE)	i_{corr} (µ A cm^{-2})	-$\hat{a}_c$ ($mVdec^{-1}$)	*IE* (%)	E_{corr} (mV/ SCE)	i_{corr} (µ A cm^{-2})	-$\hat{a}_c$ ($mVdec^{-1}$)	*IE* (%)
303	Blank	%699	14.20	566	—-	%756	46.54	566	—-
	1.0	%663	4.32	561	69.5	%732	18.73	640	59.7
308	Blank	%670	18.11	612	—-	%747	52.25	612	—-
	1.0	%665	8.07	561	55.4	%709	23.90	600	54.2
313	Blank	%729	33.26	631	—-	%759	62.58	631	—-
	1.0	%694	15.41	572	53.6	%698	28.95	634	53.7
318	Blank	%741	45.29	682	—-	%779	107.9	682	—-
	1.0	%711	21.12	599	53.3	%743	56.74	693	47.4
323	Blank	%763	93.26	685	—-	%778	137.0	685	—-
	1.0	%678	49.39	640	47.0	%763	76.66	669	44.0

3.1. Evaluation of kinetic and thermodynamicparameters Experiment was performed in the temperature range of 303 to 323K and activation parameters like activation energy (E_a), activation enthalpy ($6H_a$) and activation entropy ($6S_a$) values were obtained making use of Arrhenius plots (ln(CR) vs 1/T) and transition state equations (ln(CR/T) vs 1/T) respectively. Activation energy (E_a) values increased after addition of inhibitor. This indicates the physisorption of pullulan on metal surface. Activation entropy ($6S_a$) values revealed increase in the disorderness towards the formation of activated complex [4, 5]. The results are tabulated in Table 4.

Table 4: Activation parameters

[HCl] (M)	[Pullulan] (gL^{-1})	E_a (kJ mol^{-1})	$\triangle H^{\#}$ (kJ mol^{-1})	$\triangle S^{\#}$ (J mol^{-1} K^{-1})
	Blank	75.43	72.83	-20.47
	0.2	91.05	88.46	25.50
0.05	0.4	94.88	92.28	37.02
	0.6	96.37	93.77	41.25
	0.8	100.5	97.90	53.61
	1.0	105.6	103.0	63.43
	Blank	62.44	59.84	-57.43
	0.2	73.90	71.30	-22.43
	0.4	77.89	75.29	-10.27
0.1	0.6	86.58	83.98	16.58
	0.8	89.54	86.94	25.69
	1.0	94.56	91.96	41.13

Table 2: Results of EIS studies

		0.05MHCl			0.1M HCl		
T(K)	[Pullulan] (g L^{-1})	R_p(**Ω** cm^2)	C_{dl}(ìF cm^{-2})	*IE*(%)	R_p(**Ω** cm^2)	C_{dl}(ìF cm^{-2})	*IE*(%)
303	Blank	1526	1.40	—-	698	25.6	—-
	1.0	4984	1.30	69.3	1683	14.3	58.5
308	Blank	1369	1.53	—-	515	36.3	—-
	1.0	2029	1.43	54.8	1080	20.8	52.3
313	Blank	878	1.60	—-	469	42.6	—-
	1.0	1843	1.48	52.3	1000	20.9	53.1
318	Blank	701	1.68	—-	314	56.4	—-
	1.0	1494	1.41	53.0	599	39.8	47.5
	Blank	428	1.76	—-	259	68.0	—-
323	1.0	782	1.62	45.2	403	50.7	35.7

Degree of surface coverage (8) obtained from PDP studies was applied for various adsorption isotherm, it was best fitted with Freundlich adsorption isotherm. From the intercept of the Freundlich adsorption plot 'K' adsorption/desorption equilibrium constant was calculated. Standard free energy of adsorption($6G^0$) was the nobtained by using Eq.

(3) [6].

$$K=\frac{1}{1000}\exp\left(\frac{6G^0}{RT}\,abc\right)$$

Standard enthalpy ofadsorption($6H^0_{abc}$) and Standard entropy of adsorption($6S^0_{abc}$) were calculated by plotting a graph of ($6G^0_{abc}$) against T. Results are tabulated in Table 5.

Table 5: Thermodynamic parameters

[HCl] (M)	Temp (K)	$\triangle G^o$ (kJ mol^{-1})	$\triangle H^o_{ads}$ (kJmol^{-1})	$\triangle S^o_{ads}$ (kJ mol^{-1} K^{-1})
	303	-16.44		
	308	-16.07		
0.05	313	-15.82	-32.07	-0.051
	318	-15.58		
	323	-15.39		
	303	-16.30		
	308	-16.12		
0.1	313	-15.97	-24.69	-0.027
	318	-15.87		
	323	-15.73		

The negative value of $6G^0_{ads}$ indicates the rapid binding of inhibitor molecule and feasibility of corrosion process. The values around %20kJmol$^{\%1}$ specify the physisorption of dextran on the surface of the metal [7].

3.3. Effect of acidconcentration

Concentration of acid was found to effect the inhibition efficiency of the inhibitor at all studied temperature. The studies showed decrease in inhibition efficiency with increase in concentration of acid, at all studied temperatures, both for base alloy. This is because of increase in the in H^+ ions concentration and thus the added inhibitor may be incapable to reduce the corrosion rate.

3.4 Surface morphology studies

The SEM images of 6061Al-alloy immersed in HCl and in the medium containing inhibitor are represented in the Fig. 3 (a) and (b) respectively. The rough surface indicates the pitting corrosion of the corroded sample. After the addition of pullulan the surface of the metal became smoother. This indicates the adsorption of pullulan on the metalsurface.

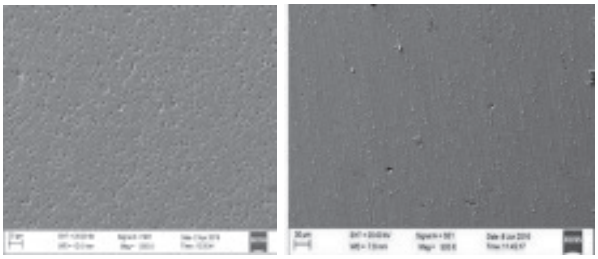


Figure 3: SEM image of (a) Corroded Al-alloy and (b) Al-alloy immersed in the medium containing inhibitor

4. Conclusions

Pullulan emerged as an effective, eco-friendly, biodegradable green inhibitor for corrosion control of aluminium alloy in acidmedium.

5. References

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