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## Inhibitive Behaviour of Corrosion of Aluminium Alloy in NaCl by Mangrove Tannin

(Kelakuan Perencatan Kakisan Aloi Aluminium  
di dalam NaCl oleh Tanin Bakau)

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### ABSTRACT

*Anticorrosion potential of mangrove tannins on aluminium alloys AA6061 in NaCl solution has been studied using potentiodynamic polarisation method and scanning electron microscopy (SEM). The study was carried out in different pH of corrosive medium in the absence and presence of various concentrations of tannin. The corrosion inhibition behaviour of the mangrove tannin on AA6061 aluminium alloy corrosion was found to be dependant on the pH of NaCl solution. Our results showed that the inhibition efficiency increased with increasing tannins concentration in chloride solution at pH 6. Treatment of aluminium alloy 6061 with all concentrations of mangrove tannins reduced the current density, thus decreased the corrosion rate. Tannins behaved as mixed inhibitors at pH 6 and reduction in current density predominantly affected in cathodic reaction. Meanwhile, at pH 12, addition of tannins shifted the corrosion potential to more cathodic potentials and a passivating effect was observed in anodic potentials. SEM studies have shown that the addition of tannins in chloride solution at pH 12 reduced the surface degradation and the formation of pits.*

*Keywords: Corrosion; inhibition efficiency; potentiodynamic polarisation; tannin*

### ABSTRAK

*Potensi tanin bakau sebagai antikakisan bagi aloi aluminium AA6061 di dalam larutan NaCl telah dikaji menggunakan teknik piawaian, iaitu kaedah pengutuban potensi dinamik dan mikroskopi elektron imbasan (SEM). Kajian telah dijalankan di dalam larutan NaCl pada pH berbeza dengan kehadiran pelbagai kepekatan ekstrak tanin. Kelakuan perencatan kakisan bagi aloi aluminium didapati bergantung pada pH larutan NaCl. Keputusan menunjukkan kecekapan perencatan kakisan meningkat dengan peningkatan kepekatan tanin di dalam NaCl pada pH 6. Perawatan aloi aluminium dengan semua kepekatan tanin bakau telah mengurangkan ketumpatan arus yang seterusnya merendahkan kadar kakisan. Tanin bertindak sebagai perencat jenis campuran di dalam NaCl pada pH 6 dan penurunan ketumpatan arus kakisan didominasi oleh tindakbalas katodik. Sementara itu, pada pH 12, penambahan tanin telah menganjak keupayaan kakisan kepada keupayaan yang lebih katodik dan kesan pempasifan telah diperhatikan pada keupayaan anodik. Kajian SEM menunjukkan penambahan tanin di dalam larutan NaCl pada pH 12 telah mengurangkan degradasi permukaan aloi aluminium dan pembentukan liang.*

*Kata kunci: Kakisan; kecekapan perencatan; pengutuban potensi dinamik; tanin*

### INTRODUCTION

The study of organic corrosion inhibitors is an interesting field of research due to its usefulness in various industries. The environmental requirements that are currently imposed on the development of cleaner chemical inhibitors represent a strong motivation for the study of inhibition by natural products. Many years ago, tannins were used as corrosion inhibitors because of their ability to act as corrosion protectors. Tannins from mimosa, quebracho, chestnut and pine bark have been used in the formulation of corrosion inhibitors such as in paints, adhesives, coating primers and other coating substances. Tannin consists of flavan-3-ol units linked together through C4-C6 or C4-C8 bonds (Hernes et al. 2001). The most widely studied condensed tannins are based on flavan-3-ols (-)-epicatechin

and (+)-catechin (Martinez et al. 2005; Mendoza-Wilson & Glossman-Mitnik 2006; Wang & Zhang 2005). Tannin in mimosa and mangrove have polymeric structures that provide antioxidant properties and excellent sites for complexation with other metals and biopolymers (Afidah & Jain 2008; Martinez 2002).

In our earlier studies, tannins from the bark of Mangrove *Rhizophora apiculata* have been found to have an ability to reduce corrosion rate of mild steel (Afidah et al. 2008) and copper (Affaizza et al. 2011) in acidic medium. Aluminium alloy 6061 with the main composition of magnesium and silicon is widely used in the construction of aircraft structures and marine transportation. However, long exposures of Al surfaces in corrosive media may lead to the generation of oxide films such  $Al_2O_3$ ,  $Al(OH)_3$

and AIO(OH) phases (Mishra & Balasubramaniam 2007). Our present work is to investigate the ability of mangrove tannins to minimize the corrosion rate of Al alloys in NaCl solutions at pH 6 and pH 12.

#### MATERIALS AND METHODS

Mangrove bark was obtained from Larut Matang Forest, Perak Malaysia. The bark were dried and ground to ~250 mesh followed by further drying. Tannins from mangrove bark were extracted by total immersion of finely ground bark in 70% aqueous acetone for 72 hr at room temperature.

For the polarisation measurements, a three electrode system was used. Al alloy 6061 was used as a working electrode, while platinum and saturated calomel electrodes (SCE) were used as the counter and reference electrodes, respectively. An open circuit potential was measured for 30 min prior to each measurement. The working electrode was wet-polished, degreased with acetone, rinsed with distilled water and dried before treatment. The specimens were then placed in an electrochemical cell containing 0.5 M NaCl at pH 6 and pH 12 in the absence and presence of various concentrations of mangrove tannins (MT) solution (1-3 g L<sup>-1</sup>). The potentiodynamic polarisation experiment was performed in the applied potential range from -1000 to -100 mV with a scan rate of 0.5 mV s<sup>-1</sup> by using a potentiostat-galvanostat model PGP201, equipped with VoltaMaster 4 software. The inhibition efficiency was calculated using the following equation:

$$\%IE = 1 - \frac{I_{corr(i)}}{I_{corr(o)}} \times 100 \quad (1)$$

where,  $I_{corr(i)}$  is the corrosion current density with tannin,  $I_{corr(o)}$  is the corrosion current density without tannin. The surface morphology study was carried out via scanning electron microscopy, SEM LEO SUPRA 50VP.

#### RESULTS AND DISCUSSION

Various kinetic parameters, namely corrosion current density,  $I_{corr}$ , corrosion potential,  $E_{corr}$ , corrosion rate,

$W_{corr}$  and the percentage of inhibition efficiency, % IE are given in Table 1. The polarisation results are presented as potentiodynamic polarisation curves (Figures 1 and 2). From the results, at pH 6 the addition of MT decreased the  $I_{corr}$  values and consequently increased the % IE values. At 3 g L<sup>-1</sup> of MT at pH 6, the highest inhibition efficiency of 78 % was achieved with the lowest  $W_{corr}$  values. However, the inhibition efficiency at pH 12 shows negative value for all concentrations of MT. The corrosion current density,  $I_{corr}$  and corrosion rate,  $W_{corr}$  also increase significantly.

In neutral or basic solution, a cathodic reaction that is frequently encountered in metallic corrosion is oxygen reduction. Oxygen reduction is very common, since any aqueous solution in contact with air is capable of reducing this reaction:



At pH 6, in the presence of MT, the values of  $E_{corr}$  remained almost unchanged. The reduction in cathodic current density clearly can be observed for all MT concentrations at pH 6. (Figure 1, Table 1). The predominant action in the cathodic redox reaction implies the inhibitors are adsorbed on the metal surface at the cathodic sites and hence inhibition occurs (Benabdellah et al. 2007). From our results, due to the reduction in current density, MT are adsorbed and inhibited the cathodic redox reaction, namely the oxygen reduction that is normally under diffusion control. MT probably reacted with the hydroxyl ion to precipitate insoluble compounds on the cathodic sites, thus blanketing the cathode from the electrolyte and preventing access of oxygen to the sites (Trethewey & Chamberlain 1990).

The reduction in current density at anodic curve occurs at specific applied anodic potentials, approximately in a range of -700 to -600 mV. The addition of 2 and 3 g L<sup>-1</sup> MT at pH 6 resulted in reductions in current density within the range of -708 to -645 mV. While at 1 g L<sup>-1</sup>, a drop in current density was observed at a range of -704 to -575 mV. Addition of MT was found to accelerate the dissolution process after the potential of -645 mV. A limiting diffusion current appears on both anodic and cathodic polarisation

TABLE 1. Kinetic parameters of Al alloy corrosion in 0.5 M NaCl at pH 6 and pH 12 in the absence and presence of MT

Test Solution (g L <sup>-1</sup> MT)	Corrosion potential, $E_{corr}$ (mV)	Current density, $I_{corr}$ (mA cm <sup>-2</sup> )	Corrosion rate, $W_{cor}$ (mm Y <sup>-1</sup> )	Inhibition Efficiency, (% IE)
pH 6				
0.5 M NaCl	-711	0.0063	$6.83 \times 10^{-5}$	-
1	-697	0.0036	$3.92 \times 10^{-5}$	43
2	-708	0.0020	$2.18 \times 10^{-5}$	68
3	-704	0.0014	$1.52 \times 10^{-5}$	78
pH 12				
0.5 M NaCl	-1392.2	0.2407	2.720	-
1	-1428.5	0.4696	5.307	-95
2	-1413.6	0.4726	5.340	-96
3	-1437.0	0.3650	4.125	-52

curves at higher overvoltage, showing that at higher current densities, the transport of ions towards the electrode surface becomes the rate-determining step (concentration polarisation), thus the electroactive species cannot reach the electrode surface at a sufficient rapid rate (Branzoi et al. 2002). The onset of pitting is not visible on the curve since the pitting potentials,  $E_{\text{pit}}$  coincided with the corrosion potentials,  $E_{\text{corr}}$  (Figure 1). It is expected that Al alloys suffer pitting attack immediately after their immersion in the aggressive media at the open circuit potential (Pardo et al. 2008; Zaid et al. 2008). According to the Pourbaix diagram, Al alloys are passive (protected by its oxide film) in the pH range of 4-8.5 and thus the passive layer was able to protect the corrosion of metals. In our study (at pH 6), no passive region was observed in the Tafel curve, suggesting that the corrosion inhibition in NaCl at pH 6 is due to the interaction of MT molecules at the interface of the electrode/bulk solution; either by an accumulation of MT molecules at the interface of the electrode/bulk solution or adsorption on the Al alloy surface.

In contrast, at pH 12 in the presence of MT, the values of  $E_{\text{corr}}$  were shifted to more negative potentials. Reduction in current density in the cathodic branch was not observed for all concentrations of MT (Figure 2). From the Pourbaix diagram for Al, beyond the limits of the passive range (at pH of 4-8.5), Al corrodes in aqueous solutions because the oxides are soluble in many acids and bases. This may result in the non-inhibiting effect by MT in NaCl at pH 12. However, in the anodic branch, a passivating plateau was observed before the onset of pitting at -500 mV. Within the plateau region of -1300 to -500 mV, 2 and 3 g L<sup>-1</sup> MT gave almost the same trend of current density as MT-free solution. Meanwhile, the addition of 1 g L<sup>-1</sup> MT gave higher current density than the MT-free solution. Onset of pitting began approximately at -500 mV, which then promoted the dissolution of the Al alloy by the breakdown of the passive layer. Pitting potential remained unchanged with the addition of MT. At the transpassive region (-500 to -100 mV), the rate of Al alloy dissolution in the presence of MT is lower than that of MT-free solution.

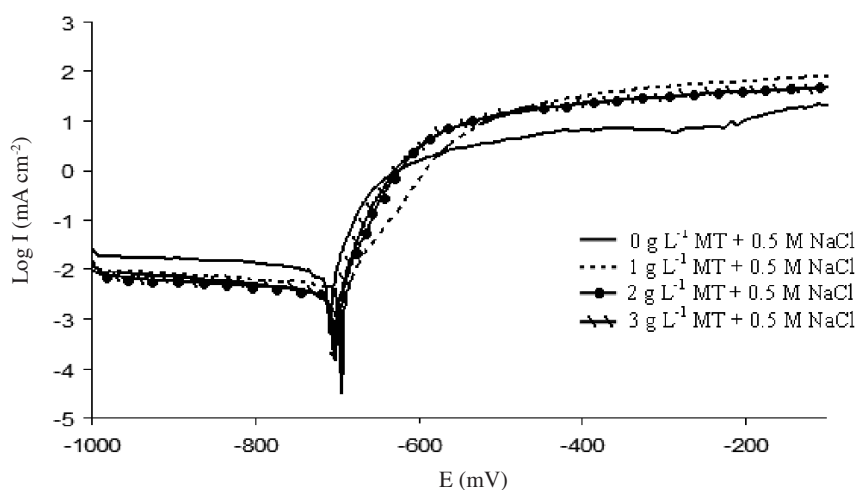


FIGURE 1. The potentiodynamic polarisation curves of Al alloy containing various concentration of MT in 0.5 M NaCl at pH 6

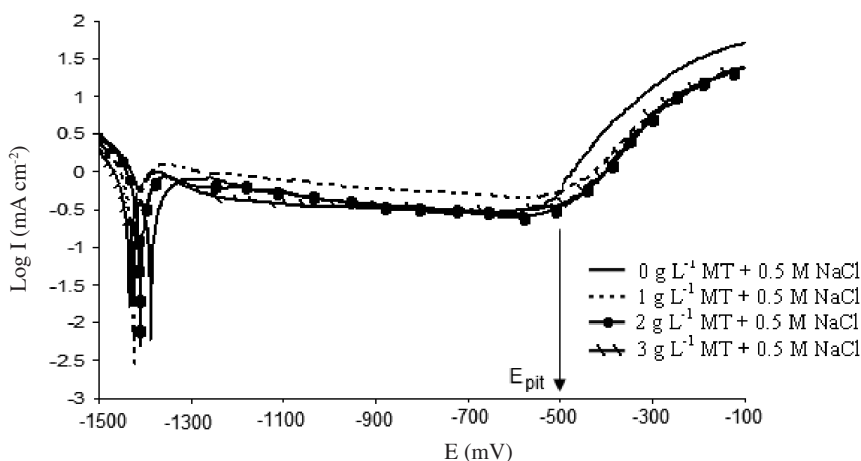


FIGURE 2. The potentiodynamic polarisation curves of Al alloy containing various concentration of MT in 0.5 M NaCl at pH 12

Figure 3 shows the results of the surface morphology via the SEM analysis. At both pH values, pits were formed on the surface even in the presence of MT solution. Formation of pits promoted by the existence of chloride ions in the solution was also contributed by the presence of intermetallics components (Hosni et al. 2008; Na & Pyun 2008) which consist of different metals and composition. Our result showed that at pH 6, the surface morphology after the treatment in MT solution gave the same results as in MT-free solution (Figure 3a). This is probably due to the continuous polarisation of the surface, which may cause the aggressive dissolution of the Al alloy, thus promoting the corrosion. As shown in the Tafel curve (Figure 1), dissolution of Al alloy was promoted at the more positive potential, -600 mV and above. Therefore, in our case, the morphology observed via the SEM analysis could not represent the inhibition effect at pH 6 after polarisation measurements. It was noted that, an inhibition and the reduction in current density was only observed at the potential of -700 to -600 mV prior to the final potential measurement (-100 mV). At pH 12, large and irregular sized pits were observed in MT free-solution (Figure 3c). The presence of MT at chloride pH 12 seems

to reduce the formation of pits as well as degradation of corroded areas (Figure 3d). This phenomenon is due to either the protection from the strong passive layer formed on the Al alloy surface or the adsorption of MT molecules on the strong passive layer.

## CONCLUSION

Mangrove tannins are predominantly cathodic inhibitors for Al alloys in 0.5 M NaCl at pH 6. The inhibition efficiency increased with increasing MT concentration. The corrosion inhibition and the reduction in current density only occurred at specific anodic potential ranges. At pH 6, the corrosion inhibition may be accomplished by the adsorption of MT on Al alloys surface. This phenomenon is also resulted from the accumulation of MT molecules at the interface of Al alloy/bulk solution. At pH 12, there was no inhibition and the corrosion rate increase with the increase in MT concentrations. Nevertheless, the protection from a strong passive layer formed on the Al alloys surface could be the reason for the minimizations of pits formation.

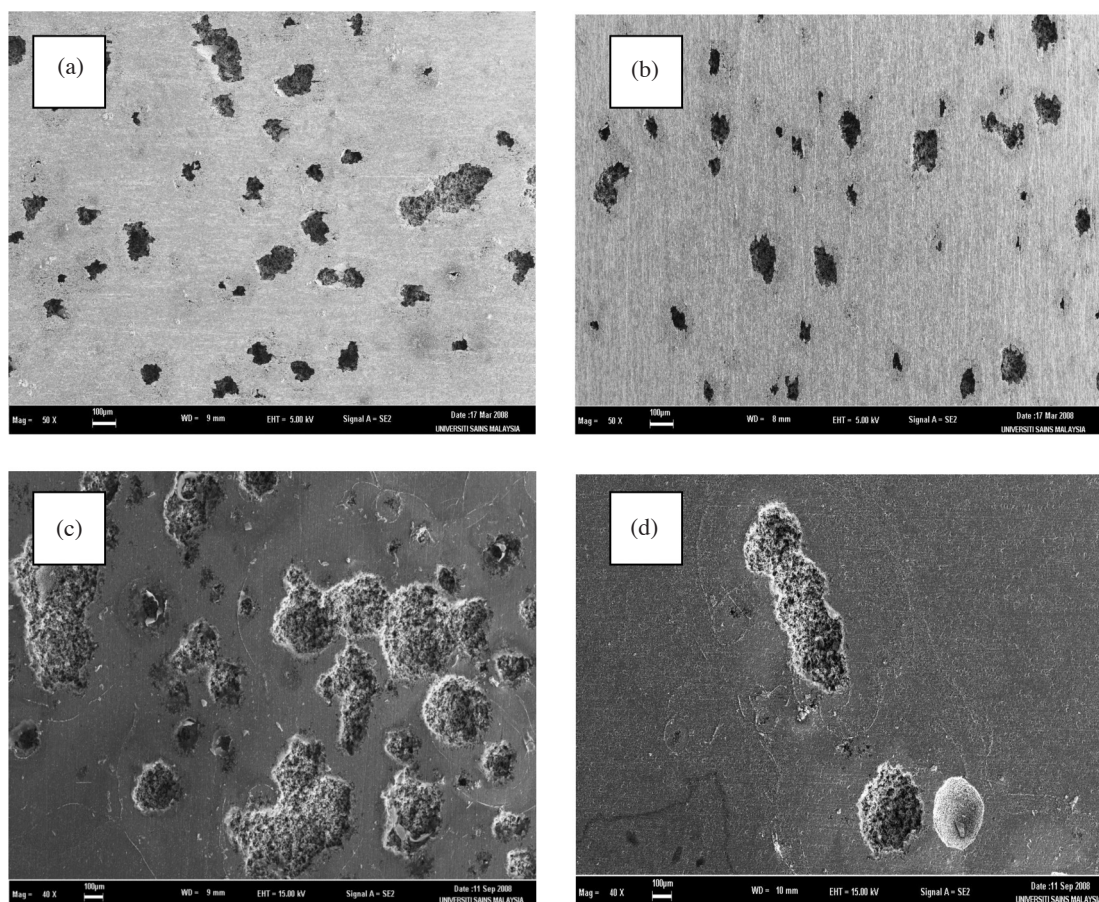


FIGURE 3. SEM micrograph of Al alloys in (a) 0.5 M NaCl pH 6 (b) 0.5 M NaCl pH 6 + 3 g L<sup>-1</sup> MT (c) 0.5 M NaCl pH 12 and (d) 0.5 M NaCl pH 12 + 3 g L<sup>-1</sup> MT

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