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Mangrove (*Rhizophora apiculata*) tannins as a potential corrosion inhibitor for aluminium in acidic medium

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Abstract

Utilisation of a green corrosion inhibitor formulated from natural, biodegradable and non-toxic organic compounds in industries has been extensively explored by a great number of researchers. Investigation of tannins extracted from Mangrove *Rhizophora Apiculata sp.* as a corrosion inhibitor for aluminium alloy has been carried out in acidic medium. Tannins at 1-3 g L^{-1} were used in the electrochemical measurements. Results showed a good inhibitive action of tannins in all acidic medium. Localised corrosion on the metal surface in the different corrosive medium reduced after the addition of tannins as shown from SEM analysis. Weight loss analysis was conducted at ambient temperature and the inhibition efficiency was found to increase with increasing concentrations of tannins. Determination of the type of adsorption isotherm corresponds to the Langmuir adsorption. The inhibitive efficiency of mangrove tannins was also compared with that of commercial mimosa tannins. Mangrove tannins exhibited similar inhibitive behaviour to mimosa tannins. Theoretical studies of the adsorption behaviour of catechin, a monomer of mangrove tannins, and the orientation of adsorption between aluminium atom and the active sites of the monomer was investigated using quantum chemical calculations. Correlations between the inhibition efficiency and the mode of adsorption are in good agreement with experimental data.

Keywords: Mangrove tannins, potentiodynamic, aluminium alloy, acidic

Introduction

Aluminium alloy has an impressive economic and industrial importance due to its low cost, light, high thermal and electrical conductivity. In industries, pickling of aluminium for its chemical or electrochemical etching usually are performed in acidic medium [1,2]. Aluminium alloy 6061 is widely used in the construction of aircraft structures and marine transportation. A good mechanical characteristic of this alloy is due to its heat treatable and weldable property. Nevertheless, long exposures of aluminium surfaces in corrosive media may lead to the generation of oxide films such Al_2O_3, $Al(OH)_3$ and $AlO(OH)$ phases [3]. Minimization of corrosion attack on the metal surface requires an effective corrosion inhibitor. Chromates that have been widely used in the formulation of corrosion inhibitors are highly toxic and health hazardous. Nowadays, new environmentally friendly corrosion inhibitors are necessary in order to overcome such problems. Recently, a number of inhibitors have been studied towards the corrosion of pure aluminium and aluminium alloys against corrosive action in aqueous solution. Ashassi *et al.* [4] has studied on the inhibition effect of some amino acids in a mixture of 1 M HCl + 1 M H_2SO_4 solution. El-Eltre *et al.* has found Opuntia [5] and vanillin [6] extract are good inhibitors in 2 M HCl and 5 M HCl, respectively. Foad *et al.* [7] have investigated ethoxylated fatty acids as inhibitors in 1 M HCl. Three inhibitors, namely sulfonic acid, sodium cumene sulfonate and sodium alkyl sulfate have also been evaluated as corrosion inhibitors in 2 M HCl by Maayta [1]. Monomers of tannins have been found to be able to act as an alternative corrosion inhibitors in acidic medium for steel [8,9]. The environmental requirements that are currently imposed on the development of cleaner chemical inhibitors represent a strong motivation for the study of inhibition by tannins. In our study, an investigation on tannins extracted from the bark of Mangrove *Rhizophora Apiculata sp.* as a corrosion inhibitor for aluminium alloy 6061, has been carried out in acidic medium. Potentiodynamic polarization and weight loss methods have been used to evaluate the potential of tannins as corrosion inhibitors.

Experimental method

In this work, electrochemical experiments were conducted on aluminium alloy 6061 (Si 11.61%, Mg 3.61%, Fe 0.24%, Ag 0.47% and Al remainder). The specimen was polished with four grades abrasive paper 600, 800, 1000 and 1200. The plates were degreased with acetone and rinsed with distilled water. The specimens were placed in an electrochemical cell containing 0.5 M HCl and 0.25 M H_2SO_4 solutions. The potentiodynamic polarization experiment was performed in the applied potential range from -1000 to -100 mV with a scan rate of 0.5 mV s^{-1} by using a PGP201 potentiostat-galvanostat, equipped with VoltaMaster 4 software. Platinum and saturated calomel electrodes (SCE) were used as the counter and reference electrodes, respectively. Tannin solutions ranging from 1-3 gL^{-1} in 0.5 M HCl and 0.25 M H_2SO_4 were used as test samples. Open circuit potential was carried out for 30 min prior each measurement.

Weight loss measurements were performed for 24 hours in 0.5 M HCl and 0.25 M H_2SO_4 with various concentrations of tannins. Aluminium plates (3 cm x 1.5 cm x 0.1mm) were cleaned washed, dried at room temperature and weighted before and after treating with tannins. Mangrove barks were obtained from Larut Matang Forest, Perak Malaysia. The mangrove tannins were extracted using 70 % acetone for 72 hour at room temperature (30 °C). Commercial mimosa tannins were obtained from SILVACHIMICA, Italy.

Theoretical calculations were accomplished using semi empirical Parameterization 3 (PM3) method performed using GAUSSIAN 03W computational packages. The structure of (+) – catechin was optimized without any constraints and the geometrical parameters are found to be comparable to that of the results by Mendoza-Wilson & Glossman-Mitnik [10]. The introduction of Al atom to catechin was investigated at various sites using different initial Al-O-C-C dihedral angles.

Results and discussion

a) Inhibition of corrosion by Mangrove and Mimosa tannins in 0.5 M HCl

Fig.1 represents the potentiodynamic polarisation curves of aluminium alloy containing various concentrations of mangrove and mimosa tannins in 0.5 M HCl. From the results, mangrove tannins performed as a mixed inhibitor due to the dual action of both anodic and cathodic inhibitive actions. In contrast, mimosa tannins behaved as a cathodic inhibitor in 0.5 M HCl. High inhibition efficiency for both tannins in HCl resulted in decreasing the corrosion rate.

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A maximum inhibition efficiency of 78 % and 95 % was achieved for mangrove tannins and mimosa tannins, respectively.

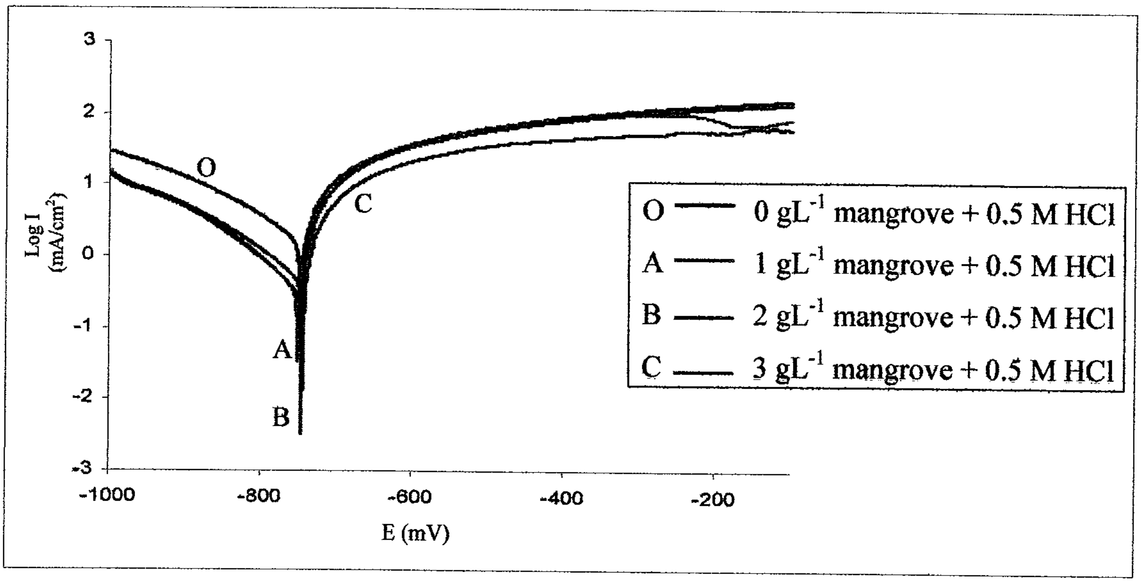

Fig.1: The potentiodynamic curves of Al containing various concentration of mangrove tannin in 0.5 M HCl

From the weight loss method, the inhibition efficiency of tannins evaluated increased with increasing concentrations of tannins (Table 1). Both tannins are inhibitors of aluminium alloy with the percentage inhibition of mimosa tannins being greater than mangrove tannins. The adsorption and the coverage of inhibitors on the aluminium surface increased with the increase in concentration. Thus the aluminium alloy surface is efficiently separated from the aggressive anions of the acid [4,5].

Table 1: Inhibition efficiency of corrosion inhibition of aluminium alloy by mangrove and mimosa tannin in 0.5 M HCl calculated from weight loss analysis

Conc. inhibitor gL^{-1}	Inhibition efficiency (%)	
	Mangrove	Mimosa
0	-	-
1.0	10	61
1.5	16	67
2.0	26	69
2.5	33	71
3.0	54	77

Homogeneous corrosion occurs on the surface of the plate immersed in HCl as viewed in Fig 2(a). Dissolution of aluminium alloy surfaces occurs mainly due to the presences of aggressive chloride ions in acidic medium [11]. The morphology of the plate's surface seems to have changed upon treatment with mangrove tannins (Fig. 2(b). The molecules of tannins were possibly adsorbed on the aluminium alloy surface, thus preventing the metal from dissolution.

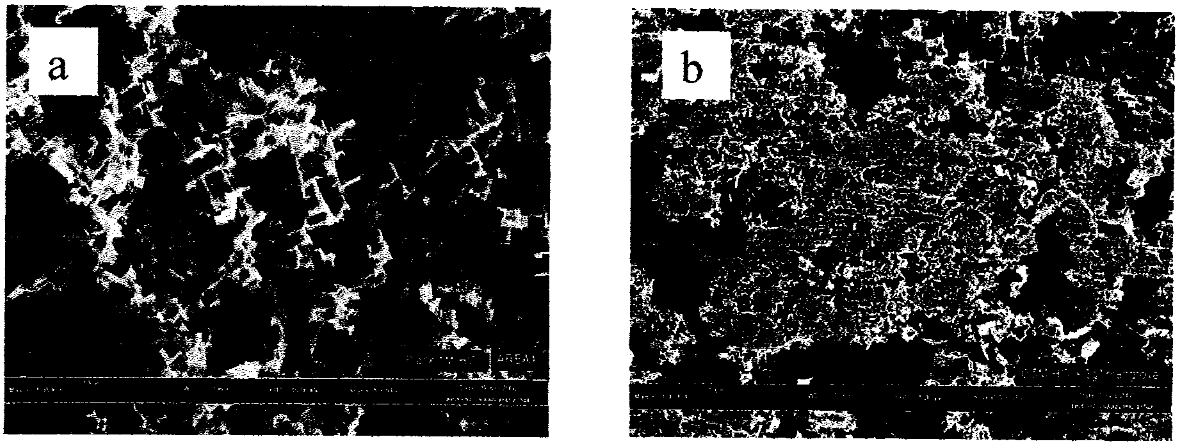

Fig.2: SEM micrograph of (a) blank 0.5 M HCl, (b) 0.5 M HCl + 3 gL^{-1} mangrove tannin

b) <u>Inhibition of corrosion by Mangrove and Mimosa tannins in 0.25 M H_2SO_4</u>

Potentiodynamic polarization performed in 0.25 M H_2SO_4 similarly shows that mangrove tannins are anodic inhibitors in H_2SO_4 medium (Fig. 3). E_{corr} also shifted to more positive values. A passive region was observed in the anodic curves indicating the possibility of the formation of a passive layer on the aluminium alloy surface. In contrast, mimosa tannins are cathodic inhibitors in 0.25 M H_2SO_4. A maximum inhibition efficiency of 78 % and 89 % was achieved for mangrove tannins and mimosa tannins, respectively.

Inhibition efficiency evaluated from weight loss measurements in 0.25 M H_2SO_4 shows that the efficiency of both tannins increased with the increment in contentration. The percentage inhibition was less than that was observed from the electrochemical measurement.

Surface analysis on treated aluminium alloy surfaces in the presence of mangrove tannins shows a reduction in corrosion. A difference in the distribution of pits formed on surfaces before and after treatment can be observed. The roughness of the surface was also reduced following treatment with tannins.

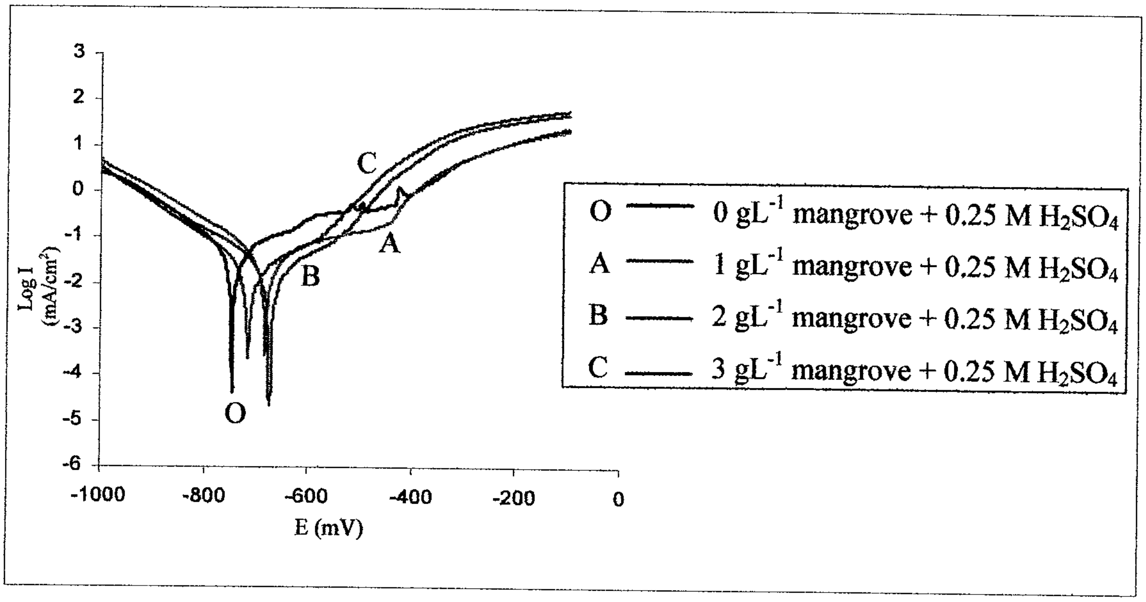

Fig.3: The potentiodynamic curves of Al containing various concentration of mangrove tannin in 0.25 M H_2SO_4

c) Adsorption Isotherm

In this study, experimental data obtained from the weight loss method have been applied to several adsorption isotherm equations. The experimental results in both acids fit well with the Langmuir isotherm. A plot of log ($\theta/1-\theta$) vs log C gave a straight line, where θ represents the surface coverage and C is the concentration of mangrove tannins (Fig. 4).

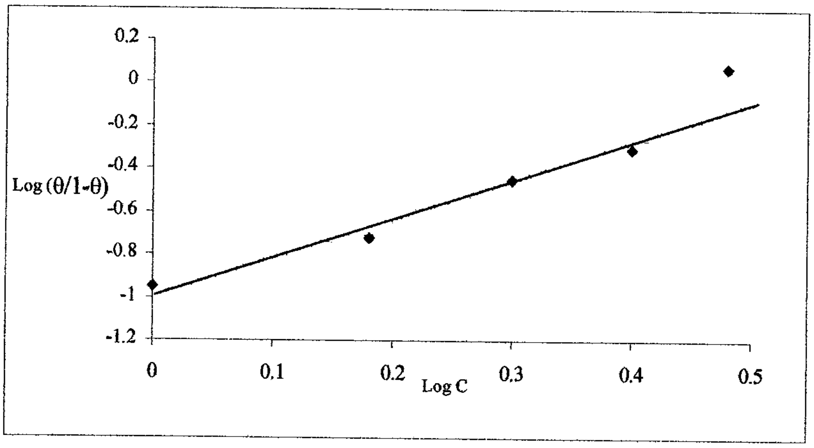

Fig. 4: Adsorption isotherm of the correlation between the surface coverage and mangrove concentration

The increase in inhibition efficiency with the increase in concentration indicates that more inhibitors molecules are adsorbed on the metal surfaces as the concentration of mangrove tannins increases, thus providing wider surface coverage and these compounds are acting as adsorption inhibitors [11]. Corrosion inhibition depends on the surface conditions and the mode of adsorption of inhibitors [12]. It is suggested that chemisorption is the adsorption mode, involving charge sharing or charge transfer from the tannin molecules to the metal surface.

d) Computational studies of the adsorption behaviour

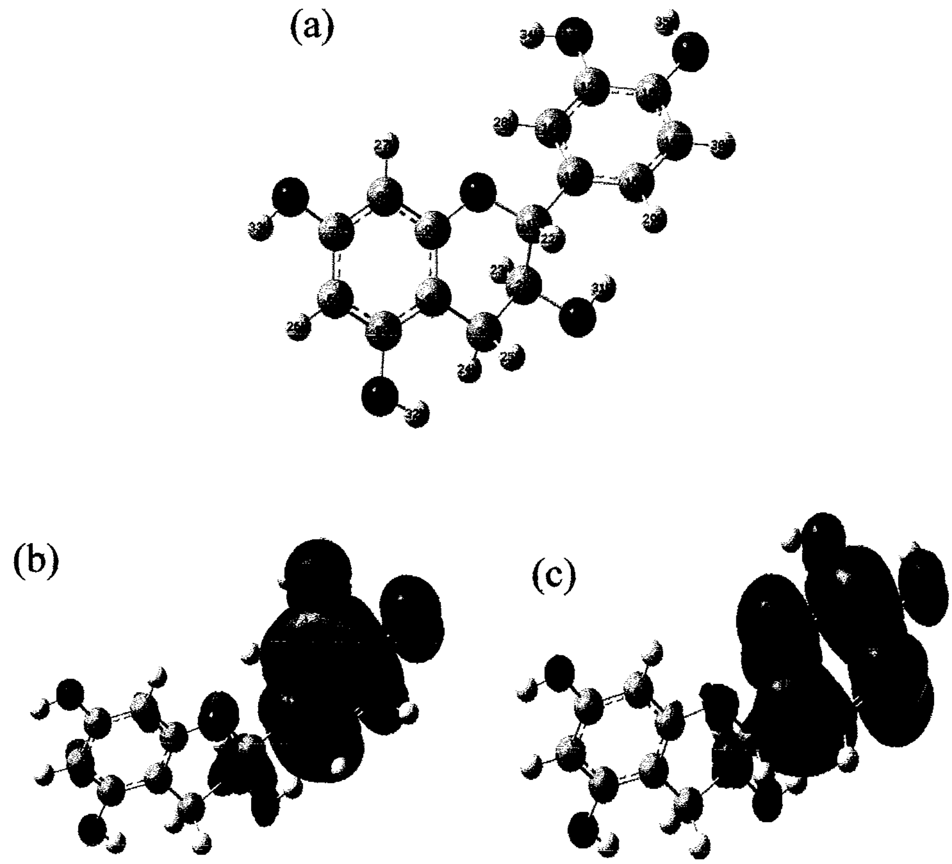

Fig. 5: (a) Optimized structure of (+)-catechin and its charge distribution (b) HOMO (c) LUMO

The optimized structure of (+)-catechin is shown in Fig. 5. HOMO and LUMO energies of the tannin monomer were calculated to be -0.311eV and -0.166 eV respectively, giving the energy gap of 0.145 eV. The results show that the electron density is more concentrated on the B ring. Based on the HOMO and LUMO electron density distribution, B ring which consists of two

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hydroxyl groups is the most probable site for adsorption. The introduction of Al atom to (+)-catechin molecule results in changes in geometrical parameters of the (+)-catechin molecule, which corresponds to the interaction between the Al atom and the hydroxyl groups in the catechol group. The calculated bond distance of Al and O_{21}, $r_{Al\text{-}O}$ is 1.742 Å and this is characterized by the sharing of electrons pair between the atoms. The results show that adsorption of catechin to Al atom prefers the orientation parallel to the B ring at O^{-}_{21}. This is in accordance with the lowest total energy values calculated on the geometry of (+)-catechin + Al atom at various binding sites. To further investigate this possibility, our future work will involve the use of cluster model to better describe the surface of aluminium and its adsorption behaviour with (+)-catechin.

Conclusion

Potentiodynamic polarization and weight loss measurements showed that tannins extracted from mangrove bark are good corrosion inhibitors of aluminium alloy and its inhibition efficiency is comparable to that of commercial mimosa tannins. The adsorption reaction follows the Langmuir isotherm. The active site for adsorption was found to be at the catechol group in B ring of the (+)-catechin molecule. The results indicate that the possible orientation of adsorption of (+)-catechin on Al surface would be parallel to the B ring.

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