

# Condensed Tannins from Mangrove and Grape Pomace as Renewable Corrosion Inhibitors and Wood Adhesive

François Gambier<sup>1,2</sup>, Affaizza Mohd Shah<sup>2</sup>, Hazwan Hussin M<sup>2</sup>, Mohamad Nasir Mohamad Ibrahim<sup>2</sup>, Afidah Abdul Rahim<sup>2</sup> and Nicolas Brosse<sup>2\*</sup>

<sup>1</sup>Laboratoire d'Études et de Recherche sur le Matériau Bois (LERMAB), Faculté des Sciences et Techniques, Université de Lorraine, France

<sup>2</sup>Lignocellulosic Research Group, School of Chemical Sciences, Universiti Sains Malaysia, Penang, Malaysia

## Abstract

The potential of tannins extracted from mangrove bark was tested as inhibitors of copper corrosion and tannins from grape pomace and mangrove bark were used as wood adhesives. Anticorrosion properties were assessed through electrochemical properties, adsorption isotherms and surface observations. Adhesives were prepared and integrated into wood particleboards. The tannins extracted from mangrove barks acted predominantly as cathodic inhibitors and acted as efficient corrosion inhibitors. Particleboards produced from these tannins did not meet the European standard specifications for interior grade wood particleboard. Mangrove tannins can be used as corrosion inhibitors. Grape pomace and mangrove tannins are utilizable as adhesives for wood panels, although some formulation improvements are needed to satisfy the standards.

**Keywords:** Tannins; Grape pomace; Mangrove bark; Tannins based adhesive; Corrosion inhibitor

## Introduction

The utilization of agricultural and forest industries' co-products for the production of renewable energy and materials has been a topic of considerable interest for many years both in the western and developing countries. In Peninsular Malaysia, about 92,300 ha are reserved as forest and another 15,400 ha are commercialized planted mangroves. According to Clough [1], Perak is the biggest state planted with mangrove. There are two types of *Rhizophoraceae* species in Perak mangrove forest reserves, namely *Rhizophora apiculata* Blume and *Rhizophora mucronata*, however only *Rhizophora apiculata* Blume is allowed to be harvested for charcoal production. In the charcoal-making process, the bark of mangrove (*Rhizophora apiculata* Blume) are waste products that will be burned off. Studies have shown that the high content of raw tannins up to 29% (w/w) could be extracted from the mangrove bark based on the 3-day solid-liquid extraction with 70% (v/v) aqueous acetone [2]. Mangrove bark are a good source of tannins as they are low in cost and abundantly available. The extraction of tannins from the mangrove bark involves simple and inexpensive methods, thus they are of great commercial value.

Grape (*Vitis vinifera*) is one of the world's largest fruit crops and this production generates a substantial volume of solid organic by-product. In France, about 700,000 to 1,000,000 tons of dry grape pomace are produced each year [3] and only small amounts of these by-products are up-graded or recycled. The remaining solid residue (grape pomace which mainly consists of grape skins) retains high levels of condensed tannins because of their low extraction during winemaking. The successful tannin extraction from grape pomace is previously described and characterized [4,5].

Tannins are a class of non-toxic biodegradable organic compounds. Mangrove tannins (MT) and grape pomace tannins (GT) are both of the condensed type that are also known as proanthocyanidins (PAs), consisting of mainly polymers of flavonoids [4-6]. Recent development of the industrial uses of tannins as corrosion inhibitors in the formulations of pigments in paint coatings [7-10], flocculants [11,12], depressants [13], viscosity modifier agent, chemical cleaning agents for removing iron-based deposits [14] and oxygen scavengers for the boiler-water treatment system reflects their importance as industrial raw materials relative to the synthetic phenols. A review presenting

some important patents in the development of vegetal tannins in the corrosion protection of iron and steel has also been published [15]. Wood adhesives from condensed tannins have been developed and used industrially for many years [16-18]. It is demonstrated that tannins are both chemically and economically interesting for the preparation of green resins destined for the production of particleboards and that they could be successfully used as substitutes of phenol in the production of phenol-formaldehyde resins. Condensed tannins used in the previously described studies are generally extracted from the bark of various trees like mimosa, pine or quebracho. However, the ability of green adhesives to make significant impact as a substitute for polymeric materials depends on the availability of low-price tannin fractions in large quantities, displaying a good chemical reactivity towards cross-linking agents.

Several investigations have been reported on the use of plant extracts containing alkaloids, polyphenolic compounds as well as carbohydrates as inhibitors [15,19]. It has been reported that most of the effective inhibitors possess an active functional group such as nitro (-NO<sub>2</sub>) or hydroxyl (-OH) groups as in tannins. Tannins extracted from the mangrove (*Rhizophora Apiculata* Blume) bark are phenolic compounds with high molecular masses. Afidah et al. [20], previously identified mangrove tannins as condensed tannins. Mangrove tannins have been found to contain high proportions of procyanidins to prodelphinidins with the predominant interflavanoid linkages of C4-C8, and flavanoid units with *cis*-configuration at C2 and C3 formed the bulk of the oligomers and that mangrove tannin oligomers have complex structures with high degree of polymerisation from the trimers to decamers that corresponded to the molecular weight up to 3,000 Da. The multiple groups of hydroxyphenolics enable the formation of

**\*Corresponding author:** Nicolas Brosse, Lignocellulosic Research Group, School of Chemical Sciences, Universiti Sains Malaysia, Penang, Malaysia, Tel: +33372745626; Fax: +33383684004; E-mail: [nicolas.brosse@univ-lorraine.fr](mailto:nicolas.brosse@univ-lorraine.fr)

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tannin complexes with protein, metal ions and other macromolecules. In previous studies, we demonstrated that mangrove tannins (MT) are excellent inhibitors for mild steel corrosion [21]. Due to the vicinity of hydroxyl groups on the aromatic rings, tannins are able to form chelates with metallic cations and it is very important for anti-corrosion activities, because "site-specific scavenging" may occur [22]. Hence, the tannin extracts are expected to have excellent abilities for inhibitory action through the oxygen active centres [23]. The extraction of grape pomace tannins (GT) is possible using a water medium. The tannins fraction reactivity was evaluated towards formaldehyde [4,5]. Despite their low phenolic contents, these extracts displayed promising properties for future applications.

The goal of the present paper is to demonstrate how phenolic-based compounds extracted from natural co-products may be converted into high value-added products as an alternative to products derived from oil; we described the extraction of condensed tannins from grape pomace and mangrove trees bark. The extracts have been used to evaluate their potential as (1) copper corrosion inhibitors in acidic solution and (2) wood adhesives. We verified the possible use of a mixture of these tannin extracts for the production of green wood particleboards.

## Experimental

### Tannins extraction

White grape pomace was obtained from a French distillery located in the Champagne area. The extraction of tannins from grape pomace was carried out according to previous studies [4,5] with slight changes. The utilization of harsh conditions for the extraction of tannins from grape pomace can be rationalised by the fact that the easily hydrolysable fraction of condensed tannins was extracted during the vinification process [5]. Grinded pomace was immersed in 80°C water containing 2.5% of Na<sub>2</sub>CO<sub>3</sub> and 2.5% of Na<sub>2</sub>SO<sub>3</sub> (m/m based on the weight of dried pomace) for 4 h. After filtration, the resulting aqueous fraction was spray-dried and the extract obtained was used for analysis.

Mangrove (Bakau minyak: *Rhizophora apiculata*) bark was obtained as a waste from the Larut Matang, Taiping, a Malaysian charcoal manufacturer. The bark was dried and grinded to 250 mesh followed by further drying until a constant weight was obtained. The extraction of tannin from the mangrove bark was carried out in the laboratory by total immersion of the finely ground bark in aqueous acetone (acetone/water 70/30 v/v) for 72 h at 30°C. The acetone was removed under pressure and the resulting aqueous fraction was freeze dried. The extraction processes were carried out in triplicate and the extract obtained was used for further analysis.

### Characterization of tannins

The total phenol contents were measured by the Folin-Ciocalteu method, based on a colorimetric oxidation/reduction reaction of phenols [24]. The total polyphenol content was expressed as gallic acid equivalent. The proanthocyanidin contents were calculated from the absorbance at 550 nm of polyphenolic solutions obtained after HCl-BuOH treatment at 95°C for 50 min [24] and cyanidin-3-O-glucoside was used as reference. The Stiasny number reaction was used to determine the reactivity of tannins towards formaldehyde. According to Yazaki and Collins [25] about 0.2 g (oven-dry mass) of tannins sample, 5 ml of 37% aqueous formaldehyde and 5 ml of 10 M hydrochloric acid solution (HCl) were mixed together and heated under reflux for 30 min. At the end of this reaction, the mixture was filtered through a sintered glass filter (filter no. 3) while it was still hot. The precipitate

was dried to constant weight in an oven at 105°C. The Stiasny number was determined as a percentage of the weight of the precipitate to the weight of the starting sample. The gel time of tannin was referred to the working time of tannin towards formaldehyde from a colloidal solution to become a solid or semi-solid jelly or gel. A Polytech "H" gel timer from Polymer Technologies PTE. LTD. (Singapore) was used. About 80 g of a 40% (w/w) of dried tannins solution, 5% of powdered paraformaldehyde on a dry and solid tannins matter content basis were added to a cup and placed in the heater (already set at 100°C) at normal atmospheric pressure. The time taken to reach the gel point was recorded during constant stirring with the aid of a wire. The test was duplicated and the average value was reported. The pH of the mixture was measured using a microprocessor pH meter. 33% of sodium hydroxide solution (NaOH) was used to adjust different pHs of the mixture.

### Electrochemical measurements

A conventional three-electrode cell, employing a copper disc (99.9% pure) as working electrode (WE), platinum as counter electrode, and saturated calomel electrode as reference electrode (SCE) were used for measurements. The WE was polished using different grades of abrasive paper ranging from P400 to P1000, washed with distilled water, degreased with acetone and finally thoroughly rinsed with distilled water before immersing into the test solution in an exposed area of 3.142 cm<sup>2</sup>. The measurements were performed in 1.0 M and 0.5 M H<sub>2</sub>SO<sub>4</sub> solutions with and without the addition of different inhibitor concentrations in an aerated environment. The polarisation curves were recorded by using Voltalab 21 model PGP201 potentiostat-galvanostat, equipped with a VoltaMaster 4 software for data analysis. The working electrode was immersed into the test solution for 15 min to establish a steady state open circuit potential ( $E_{ocp}$ ). The potentiodynamic polarisation experiments were conducted at a scan rate of 1 mV s<sup>-1</sup> in the potential range  $\pm 300$  mV relative to the open circuit potential and they were carried out in duplicate. The corrosion inhibition efficiency, *IE*, at different concentrations of the tannins in acidic solutions was calculated from the corresponding electrochemical polarisation measurements according to:

$$E = \left( 1 - \frac{i_{corr_i}}{i_{corr_o}} \right) \times 100 \quad (1)$$

where  $i_{corr_i}$  and  $i_{corr_o}$  are the corrosion current density with and without inhibitor, in the solution.

### Weight loss method

The copper specimens of size 10 mm × 10 mm × 0.3 mm for weight loss measurements were polished using different grades of abrasive paper from P400 up to P1000. The experiment was carried out in a test tube containing 10 mL test solution. A clean weighed specimen was completely immersed in the solution. After 72 h of immersion in 1.0 M and 0.5 M H<sub>2</sub>SO<sub>4</sub> solutions with and without the addition of MT at different concentrations, the specimen was withdrawn, rinsed with distilled water, washed with acetone, dried and weighed. Three measurements were performed in each case. The percentage inhibition efficiency, *IE*% was calculated by applying the following equation:

$$E = \left( 1 - \frac{W_i}{W_o} \right) \times 100 \quad (2)$$

where,  $W_o$  is the weight loss for the blank and  $W_i$  is the weight loss in the presence of inhibitor. While the corrosion rate, CR was calculated by using the following equation:

$$mpy = \frac{534W}{DAT} \quad (3)$$

where, mpy is corrosion rate in mils per year, W is weight loss (g), D is metal density, A is the exposed copper specimen area (cm<sup>2</sup>) and T is time (h).

### Scanning Electron Microscopy (SEM) analysis

Surface analysis was conducted on the copper substrate from the electrochemical experiments. After the electrochemical measurements, copper substrates in 1.0 M and 0.5 M H<sub>2</sub>SO<sub>4</sub> in the presence and absence of MT were removed, slowly rinsed with distilled water and dried. The analysis was performed using SEM LEO SUPRA 50VP.

### Preparation of resin formulation

The phenol formaldehyde resin was prepared as described by Lei et al. [26]. A 500 mL, flat-bottom flask equipped with a condenser, thermometer, and magnetic stirrer bar was charged with 94 parts by mass of phenol, a 40 part (20/80) methanol/water solution, and 55 parts by mass of 96% paraformaldehyde. After stirring was conducted for 30 min at 40°C, the temperature was slowly increased to reflux (94°C), over a period of 30 min. A total of 20 parts by mass of 33% sodium hydroxide solution was added in 4 equal parts at 15 min intervals. The mixture was refluxed for 60 min and then cooled in an ice bath.

The dried tannins were solubilized in water to obtain a 40% solution and then adjusted to pH 10 with a 33% sodium hydroxide solution.

### Thermomechanical analysis

Modulus of elasticity (MOE) of tannin formulations were studied using a thermomechanical analyzer (Mettler Toledo TMA/SDTA840). 30 mg of the adhesive formulation was coated between two plies of beech wood (5 mm × 18 mm), which were tested by three-point bending TMA mode. The test was conducted at a heating rate of 10°C min<sup>-1</sup> from 25 to 250°C.

### Particleboard manufacture and testing

Single layer laboratory particleboards of 350 mm × 350 mm × 14 mm dimension were prepared using particles of beech (*Fagus sylvatica*) and Norway spruce (*Picea abies*) at 35 kg cm<sup>-2</sup> maximum pressure, 195°C press temperature and 7.5 min press time. 10% (w/w based on dry particles) of adhesive resin solid was loaded. The resins were composed of 50% phenol formaldehyde and 50% tannin formaldehyde resins (on a dry matter). One board was pressed for each formulation. The dry internal bond (IB) strength of the particleboards was tested on thirteen samples, according to a relevant international standard European Norm EN 312, wood particleboard specifications.

## Results

### Characterization of tannins

Total polyphenol contents, proanthocyanidin content, Stiasny numbers and gel times of MT and GT are given in Table 1. The values of total polyphenols, proanthocyanidin and Stiasny numbers are an indication of the tannin purity of the Gt and MT extracts. Gel times are a quantification of the extracts reactivity with formaldehyde.

### Electrochemical measurements

Figure 1a and 1b show the anodic and cathodic polarization curves of copper in 1.0 M and 0.5 M H<sub>2</sub>SO<sub>4</sub> solutions containing different concentrations of MT, respectively. The electrochemical parameters of the curves, namely the corrosion potential ( $E_{corr}$ ), corrosion current density ( $i_{corr}$ ), cathodic Tafel slope ( $\beta_c$ ), anodic Tafel slope ( $\beta_a$ ) and percentage inhibition efficiency ( $IE$ ) are listed in Table 2. It can be observed that the inhibition efficiencies increased as the inhibitor concentration increased to reach a maximum value of 69.4% with the addition of 3 g L<sup>-1</sup> MT in 1.0 M H<sub>2</sub>SO<sub>4</sub>. Meanwhile in 0.5 M H<sub>2</sub>SO<sub>4</sub>, 46.8% of IE was obtained with the addition of 3 g L<sup>-1</sup> MT.

### Weight loss method

From the weight loss measurements, the corrosion rates of copper were calculated by considering the total area of sample and immersion times, which is expressed in mils per year (mpy). The data are shown in

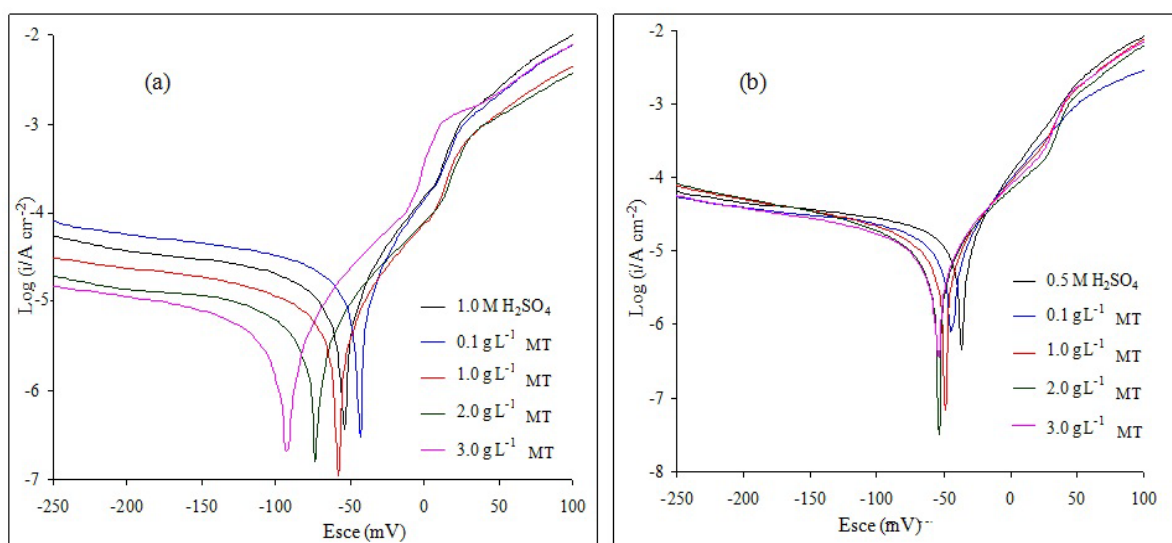


Figure 1: Potentiodynamic polarization curves of copper in (a) 1.0 M H<sub>2</sub>SO<sub>4</sub> solution and (b) 0.5 M H<sub>2</sub>SO<sub>4</sub> without and with the addition of different concentrations of mangrove tannins (MT).

	Total Phenol <sup>a</sup>	Proanthocyanidin <sup>b</sup>	Stiasny number (%)	Gel time <sup>c</sup> (s)
MT	2.2 ± 0.1	139.7 ± 1.8	76.9 ± 1.0	155
GT	1.5 ± 0.1	46.8 ± 1.6	42.4 ± 0.9	938

<sup>a</sup> mg gallic acid equivalent g<sub>dry matter</sub><sup>-1</sup>

<sup>b</sup> mg cyanidin-3-O-glucoside g<sub>dry matter</sub><sup>-1</sup>

<sup>c</sup> 40% of tannin extract, in water with 5% paraformaldehyde at pH 10

**Table 1:** Phenolic contents, Stiasny numbers and gel times of Mangrove Tannins (MT) and Grape pomace Tannins (GT).

Concentration	Parameters				
	$E_{corr}$ (mV) <sup>a</sup>	$\beta_a$ (mV dec <sup>-1</sup> ) <sup>b</sup>	$\beta_c$ (mV dec <sup>-1</sup> ) <sup>c</sup>	$i_{corr}$ ( $\mu$ A cm <sup>-2</sup> ) <sup>d</sup>	IE (%)
1.0 M H <sub>2</sub> SO <sub>4</sub>	-54.2	43.8	-135.4	9.7	-
0.1 g L <sup>-1</sup> MT	-42.7	47.7	-141.9	14.4	-36.4
1.0 g L <sup>-1</sup> MT	-58.3	56.2	-148.0	6.4	46.4
2.0 g L <sup>-1</sup> MT	-72.9	57.3	-150.0	4.5	62.5
3.0 g L <sup>-1</sup> MT	-92.7	51.0	-142.7	3.3	69.4
0.5 M H <sub>2</sub> SO <sub>4</sub>	-36.5	34.4	-155.2	13.6	-
0.1 g L <sup>-1</sup> MT	-43.6	42.6	-157.4	11.1	18.4
1.0 g L <sup>-1</sup> MT	-48.2	48.2	-166.1	10.0	26.5
2.0 g L <sup>-1</sup> MT	-46.9	49.0	-130.2	8.0	41.2
3.0 g L <sup>-1</sup> MT	-53.1	48.9	-121.9	7.3	46.3

<sup>a</sup>  $E_{corr}$ : corrosion potential

<sup>b</sup>  $\beta_a$ : anodic slope

<sup>c</sup>  $\beta_c$ : cathodic slope

<sup>d</sup>  $i_{corr}$ : corrosion current density

**Table 2:** Corrosion parameters and Inhibition Efficiency (IE) for copper in 1.0 M and 0.5 M H<sub>2</sub>SO<sub>4</sub> solutions, in the presence of different concentrations of Mangrove Tannins (MT) at 303 K.

Concentration (g L <sup>-1</sup> )	CR <sub>corr</sub> (mpy) ± 0.5	IE (%)
1.0 M H <sub>2</sub> SO <sub>4</sub>	6.6	-
0.1 g L <sup>-1</sup> MT	4.1	37.1
1.0 g L <sup>-1</sup> MT	3.2	51.8
2.0 g L <sup>-1</sup> MT	2.9	59.4
3.0 g L <sup>-1</sup> MT	2.2	66.5
0.5 M H <sub>2</sub> SO <sub>4</sub>	2.4	-
0.1 g L <sup>-1</sup> MT	1.9	20.3
1.0 g L <sup>-1</sup> MT	1.8	24.1
2.0 g L <sup>-1</sup> MT	1.6	32.3
3.0 g L <sup>-1</sup> MT	1.3	44.3

**Table 3:** Corrosion Rate (CR<sub>corr</sub>) and Inhibition Efficiency (IE) of copper in the acidic solution containing different concentrations of Mangrove Tannins (MT) obtained from the weight loss method at 303 K.

Table 3. The IE calculated reached maximum values of 66.5% at 3 g L<sup>-1</sup> MT in 1.0 M H<sub>2</sub>SO<sub>4</sub>, while in 0.5 M H<sub>2</sub>SO<sub>4</sub> MT gave maximum IE values of 44.3% also at 3 g L<sup>-1</sup> MT.

### Scanning Electron Microscopy (SEM) analysis

In order to have a better understanding of the corrosion phenomena on the copper surface, SEM analysis was carried out. The SEM images were obtained after the copper surface was polarized in both acidic solutions before and after the addition of MT. Figure 2a and 2b show the surface morphology of the copper substrate with and without the addition of MT in 1.0 M H<sub>2</sub>SO<sub>4</sub> solution. The morphology of the copper surface in 0.5 M H<sub>2</sub>SO<sub>4</sub> in the absence and presence of MT is shown in Figure 3a and 3b.

### Particleboard manufacture and testing

Finally, MT and GT were tested for application to wood panels

such as the particleboard. In this study, we also consider a mixture of 50% MT + 50% GT. The internal bond (IB) strengths of the panels which are a direct measure of the performance of the adhesive are given in Table 4.

## Discussion

### Characterization of tannins

It has already been demonstrated that the harsh conditions used for the extraction of GT lead to extracts of low purity, with high sugar contents [4]. The MT exhibits a much higher purity in polyphenols and a higher reactivity toward formaldehyde compared to GT. Nevertheless, despite a high proanthocyanidin content, MT with a gel time above 150 s at pH 10 can be classified as slow reacting tannins, such as quebracho extracts.

### Electrochemical measurements

The mechanism of the anodic dissolution of copper in acidic solution is as follows [27]:



The cathodic corrosion reaction in an aerated acidic solution is:



It is clearly observed from the potentiodynamic experiments data that the presence of MT, in both solutions, decreased the  $i_{corr}$  values with the increase of MT concentrations, thus the inhibition efficiencies increased (Table 2). From Figure 1a and 1b, the presence of MT clearly showed the shift of the corrosion potential value ( $E_{corr}$ )

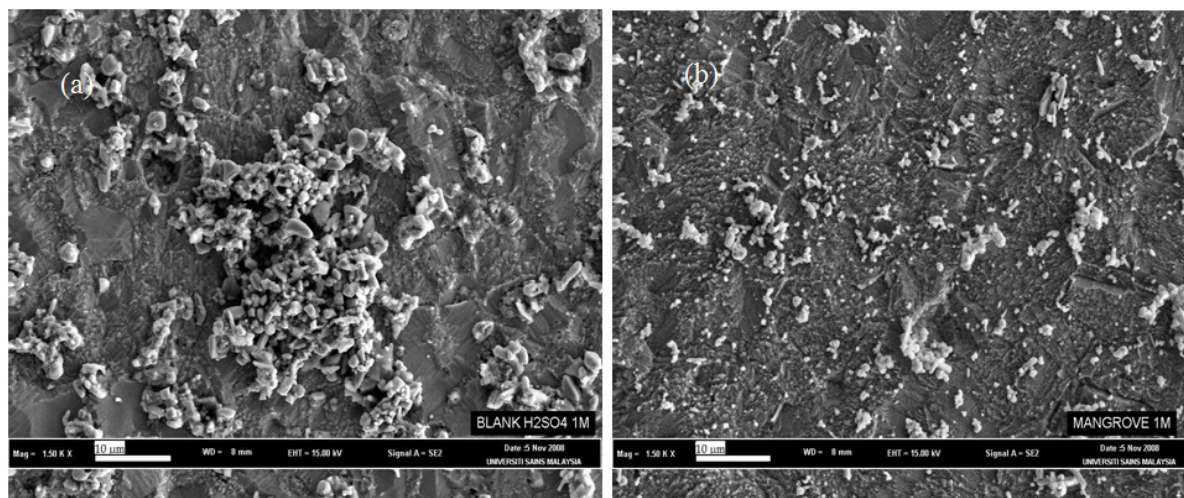


Figure 2: SEM micrographs of copper surface in 1.0 M H<sub>2</sub>SO<sub>4</sub> (a) without tannins and (b) in the presence of mangrove tannins (MT).

towards the negative direction due to the strong influence of MT on the predominant decrease in the reduction of dissolved oxygen and hydrogen evolution reactions (cathodic reactions), as compared to the anodic dissolution of copper [28]. The effect is more observable in 1.0 M H<sub>2</sub>SO<sub>4</sub>. In addition, from Table 2, the cathodic Tafel slope ( $\beta_c$ ) and anodic Tafel slope ( $\beta_a$ ) are observed to have changed with the addition of MT, which indicates the influence of MT on the cathodic and anodic reactions, with the cathodic curves being more affected. Thus the MT acts as relatively mixed type inhibitors for copper in 1.0 and 0.5 M H<sub>2</sub>SO<sub>4</sub> with a predominantly prevailing cathodic action. Since the change in values of  $\beta_c$  is greater than that of  $\beta_a$  as compared to the blank upon the addition of MT, this also indicated that the corrosion process is controlled by the cathodic reaction [28]. The transfer of oxygen from the bulk solution to the copper/solution interface will strongly affect the rate of the oxygen reduction, according to the reaction of equation (6) it can be inferred that the molecules on the adsorbed layer behaved as a cathodic inhibitor to copper corrosion by retarding the transfer of oxygen to the cathodic sites of the copper surface. In the anodic curves, a dual-current plateau appeared in the presence of MT at higher concentrations (from approximately -15 to 40 mV), signifying a protective film formation on the copper surface.

### Weight loss method

In the Table 3, MT shows similar inhibitive behaviour when compared to the potentiodynamic measurement in both acidic media. The data further revealed that the corrosion rate decreased with the increase in concentration. From the weight loss and potentiodynamic measurements the better inhibitive performance was observed in MT in 1.0 M H<sub>2</sub>SO<sub>4</sub> compared to 0.5 M H<sub>2</sub>SO<sub>4</sub>. A report [29] suggests that the increase of sulphate ion concentrations consequently increase the tendencies of the inhibitors to adsorb onto the metal surface. MT contains the hydroxyl functional group (-OH) in its molecule. In acid solution, the hydroxyl group may be protonated and the molecule exists as a polycation. However, in H<sub>2</sub>SO<sub>4</sub> solution, copper is believed to be positively charged and sulphate as a hydrated ion is being weakly adsorbed on the surface, creating oriented dipoles, thereby giving rise to the negatively charged copper surface and consequently increased the adsorption of the organic cations on the dipoles [30]. The formation of positively charged protonated species facilitates the adsorption of the compound on the metal surface through the electrostatic interaction

between the MT molecule and the copper surface. This phenomenon can therefore be used to explain the higher inhibition efficiency of MT in 1.0 M H<sub>2</sub>SO<sub>4</sub> compared to 0.5 M H<sub>2</sub>SO<sub>4</sub> solutions.

### Adsorption isotherm

The increase in the inhibition efficiencies of copper in 1.0 M and 0.5 M H<sub>2</sub>SO<sub>4</sub> solution, with increasing MT concentrations can be explained by the adsorption isotherm. The adsorption of organic inhibitors on the metal surface could change the corrosion resistant properties of the metal. The studies on the adsorptive behavior of the corrosion inhibitor is important as they can provide the information of the interaction between the inhibitor and the metal surface.

In order to clarify the nature and the strength of adsorption, the experimental results from the potentiodynamic and weight loss measurements were fitted to several adsorption isotherms (Frumkin, Temkin and Langmuir). In 1.0 M and 0.5 M H<sub>2</sub>SO<sub>4</sub> solution, the adsorption behavior of MT on the copper surface was found to fit the Langmuir adsorption isotherm best (Figure 4 and Table 5) as compared to other adsorption isotherms (data not shown) according to the following equation:

$$\frac{\theta}{1-\theta} = KC \quad (7)$$

where  $K$  is the equilibrium constant,  $C$  the MT concentration and  $\theta$  is the degree of surface coverage. The surface coverage ( $\theta$ ) can be calculated from corrosion inhibition efficiency. The free energy of adsorption  $\Delta G_{ads}$  can be calculated from the equation:

$$\Delta G_{ads} = -RT \ln(55.5K_{ads}) \quad (8)$$

where  $R$  is the universal gas constant and  $T$  is the absolute temperature. Table 5 shows linear relationship for Equation 7 with correlation coefficient ( $R^2$ ) in the range of 0.887 to 0.989 for the addition of MT in sulfuric acid. Using Equation 8, the values of  $\Delta G_{ads}$  calculated are in the range of -9.77 kJ mol<sup>-1</sup> to -18.79 kJ mol<sup>-1</sup> (Table 3). The negative values indicate that the adsorption process takes place spontaneously. It is accepted that values of  $\Delta G_{ads}$  of the order -20 kJ mol<sup>-1</sup> or more signify an electrostatic interaction between the charged inhibitor molecules and the charged metal surface (physical adsorption); those of the order -40 kJ mol<sup>-1</sup> or less involves charge sharing or a transfer from the inhibitor molecules to the metal surface to form a co-ordinate covalent bond (chemical adsorption) [31,32]. The

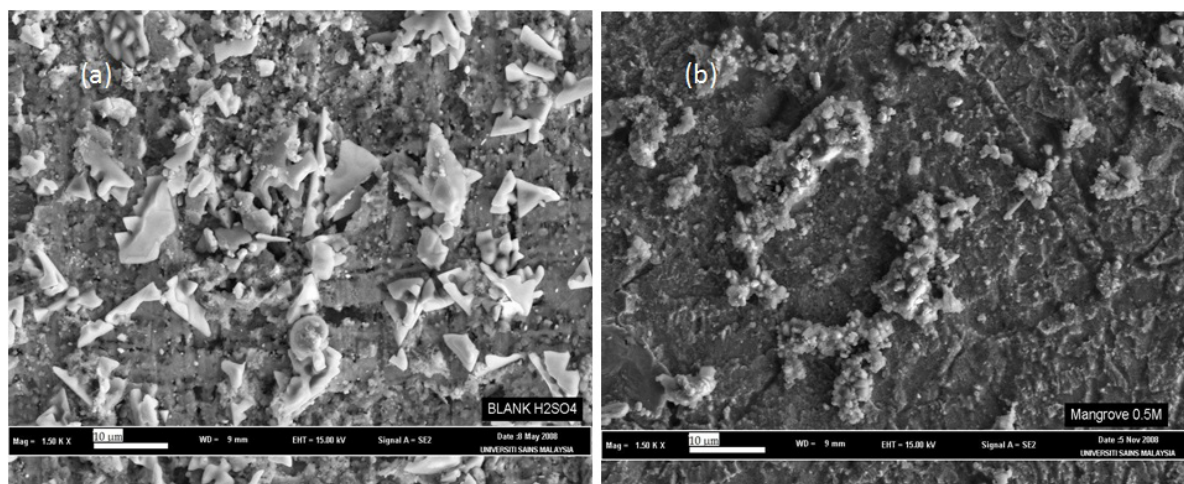


Figure 3: SEM micrographs of copper surface in 0.5 M H<sub>2</sub>SO<sub>4</sub> (a) without tannins and (b) in the presence of mangrove tannins (MT).

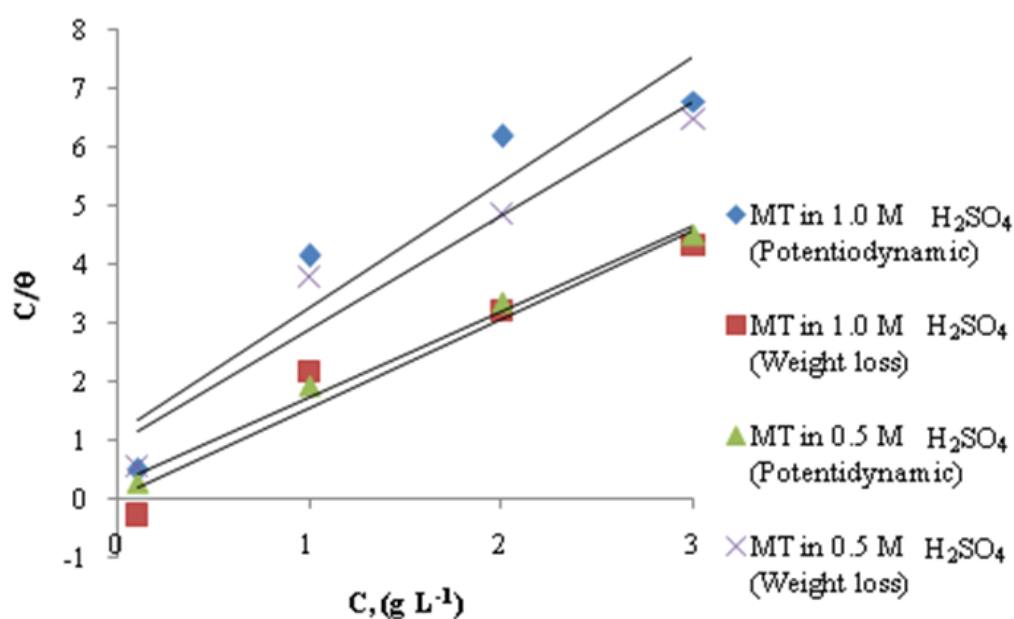


Figure 4: Langmuir adsorption plots of the mangrove tannins (MT) on copper in 1.0 M and 0.5 M H<sub>2</sub>SO<sub>4</sub>.

$\Delta G_{ads}$  values obtained in our study are closer to  $-20 \text{ kJ mol}^{-1}$  indicating that the adsorption mechanism of the MT on copper in 1.0 M and 0.5 M H<sub>2</sub>SO<sub>4</sub> is typically physisorption.

### SEM analysis

From Figures 3a and 4a, it is clearly observed that the surfaces are very rough, severely damaged with several cracks in the absence of MT due to copper dissolution in H<sub>2</sub>SO<sub>4</sub>. Upon addition of MT, the transformation of morphology was observed (Figures 3b and 4b). The surface was transformed to become smoother with more uniform deposits although not totally homogeneous. The partial transformation of the copper surface in the presence of MT could be due to the adsorption of the tannin molecules on the metal surface forming copper-tannate complexes, thus retards further corrosion process of copper.

### Wood particle boards

It can be seen from Table 4 that both the MT-based formulation and GT-based formulation did not satisfy the relevant European standard specification for interior-grade type wood particleboard (IB<0.35 MPa). These results confirm the slow reactivity of MT and GT toward cross linking reactions established through the gel time experiments (Table 1). Surprisingly, the grape pomace extract gave a higher TMA performance (MOE=3,175 MPa) than the mangrove tannins (MOE=907 MPa) but yielded a panel with poorer properties (IB=0.191 MPa and 0.279 MPa respectively). We have no explanation to rationalize this observation, but the difference in the chemical composition of the two formulations could induce a difference of viscosity and of interaction with wood particles in the panels. A diisocyanate cross-linking agent (e.g., pMDI) could be used to increase the performance of the adhesives. In fact, we have previously described

	MOE <sup>a</sup> at 195°C (MPa) 3 Specimens	Density (kg m <sup>-3</sup> ) 13 Specimens	IB <sup>b</sup> (MPa) 13 Specimens
GT	3175 ± 431	741 ± 37	0.19 ± 0.09
MT	907 ± 65	711 ± 38	0.28 ± 0.12
50% GT+50% MT	2041 ± 712	719 ± 40	0.20 ± 0.08

<sup>a</sup> Modulus of elasticity determined by thermomechanical analysis experiments

<sup>b</sup> Internal bond strength of the particle boards

**Table 4:** Adhesive formulation compositions, thermomechanical analysis and particle board testing.

Method	Fitting equations	Correlation coefficient (R <sup>2</sup> )	ΔG <sub>ads</sub> (kJ mol <sup>-1</sup> )
MT in 1.0 M H <sub>2</sub> SO <sub>4</sub> (potentiodynamic)	$C_{inh}/\theta = 0.032 + 1.52 C_{inh}$	0.942	-18.79
MT in 1.0 M H <sub>2</sub> SO <sub>4</sub> (weight loss)	$C_{inh}/\theta = 0.298 + 1.456 C_{inh}$	0.989	-13.17
MT in 0.5 M H <sub>2</sub> SO <sub>4</sub> (potentiodynamic)	$C_{inh}/\theta = 0.962 + 1.934 C_{inh}$	0.934	-10.22
MT in 0.5 M H <sub>2</sub> SO <sub>4</sub> (weight loss)	$C_{inh}/\theta = 1.145 + 2.134 C_{inh}$	0.887	-9.77

**Table 5:** Langmuir isotherm parameters for the inhibitors.

that the strength of a grape pomace adhesive-based is enhanced by the addition of diisocyanate, reacting with the hydroxyl groups of carbohydrates present in the extract [5].

## Conclusion

The extraction of tannins from agricultural (grape pomace) and forest (mangrove tree bark) residues has been developed using simple and inexpensive methods. It is demonstrated that, despite a high purity in polyphenols, mangrove tannins exhibit a low reactivity toward cross linking reactions. The corrosion inhibition studies have revealed that mangrove tannins exhibit potential corrosion inhibition properties. Mangrove tannin behaves predominantly as cathodic inhibitors in 1.0 M and 0.5 M H<sub>2</sub>SO<sub>4</sub>. The inhibition efficiency obtained via electrochemical measurements is in good agreement with that obtained by using the weight loss method. The adsorption of the MT on copper in sulfuric acid fits the Langmuir adsorption isotherm best, and the adsorption of MT on copper is typically physisorption. Mangrove and pomace tannins-based wood adhesive formulations have been prepared and wood particle boards were successfully produced, but they do not satisfy the relevant standard specification for interior-grade type wood particleboard. As an addition, the formulations of a cross linking agent should be used to increase the performance of these adhesives.

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