Mangrove tannins as corrosion inhibitors in acidic medium- Study of flavanoid monomers

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Abstract

Study of organic corrosion inhibitors is an interesting field of research due to its usefulness in various industries. Most of the well known efficient inhibitors in acidic media are organic compounds that contain nitrogen, sulfur, oxygen and multiple bonds in the molecules which are adsorbed on the metal surface and are used as temporary protectors or in cooling water systems.

Tannins, a class of natural, non-toxic and biodegradable organic compounds, extracted from plant sources have been proposed as a possible replacement as corrosion inhibitors in aqueous media, components of rust converters, pigments in paint coatings, corrosion inhibitors of reinforcing steel in concrete, chemical cleaning agents for removing iron-based deposits and oxygen scavengers for boiler water treatment system. Despite the long and extensive studies of various tannin extracts in metallic corrosion inhibition and protection, little is known about the corrosive efficiency of mangrove tannins.

Tannins are divided into two classes of polymers, the hydrolysable tannins and the condensed tannins. The hydrolysable tannins are gallic and/or egallic acid which easily hydrolyse in acidic media. Condensed tannins are polymeric flavanoids.

Many studies on tannins are contradictory because tannins are natural compounds and their chemical compositions vary with time and the environment. For the first time, a complete analysis of the mangrove tannins has been carried out by reversed-phased HPLC. It was established that four flavanoid monomers namely catechin, epicatechin, epigallocatechin and epicatechingallate were found to constitute mangrove tannin. The inhibitive behaviour on steel of these monomers was investigated in an aerated HCl solution via electrochemical methods. The monomers were found to be mainly cathodic inhibitors and the inhibition efficiency dependent on concentration. To explain the adsorptive behaviour of the molecules on the steel surface, a semiempirical approach involving quantum chemical calculations using HyperChem 6.0 was undertaken. The correlation between the electronic density of the molecule and the inhibiting properties is reported.

In a second study, the use of mangrove tannin, extracted from the mangrove barks as corrosion inhibitors in acidic media was investigated and its inhibitive efficiency was compared with that of commercial mimosa, quebracho and chestnut tannins. Mangrove tannin exhibited a similar inhibition behaviour to the other tannins investigated, indicating its potential in corrosion protection. The difference in the monomers present in the different tannins could account for the various inhibition behavoiur of the tannins.

Keywords: Mangrove tannin, flavanoid monomers, cathodic inhibitor, polarisation.

Introduction

At present, Malaysia is blessed with 101,877 ha of mangrove forest. Matang mangrove forest, at 40,151 ha, is the largest single mangrove forest in Peninsular Malaysia and has been acknowledged to be the best managed mangrove forest in Malaysia. Hydrolysable tannin, mainly from a chestnut tree, condensed tannin such as the mimosa tannin from the wattle tree and tannins comprising of hydrolysable and condensed tannin such as the oak tannin have long been the subject of inhibition studies[1-8]. Matamala et al. have also reported on the anticorrosive protection of tannins extracted from acacia and pine barks[9-10]. However, the corrosive efficiency of mangrove tannins has never been reported.

It is the aim of this research to determine the monomers that constitute mangrove tannins of the *Rhizophora Apiculata* species and to investigate their inhibitive behaviour on steel via electrochemical methods. To explain the adsorptive behaviour of the molecules on the steel surface, a semiempirical approach involving quantum chemical calculations using HyperChem 6.0 will be undertaken. The second study aims at investigating the use of mangrove tannin as corrosion inhibitors in acidic media and its inhibitive efficiency will be compared with that of commercial mimosa, quebracho and chestnut tannins.

Materials and methods

Phloroglucinol Degradation

Condensed tannin (0.01 g) which was extracted according to a procedure described elsewhere[11] was dissolved in 1.5 mL of the phloroglucinol solution (5 gm/mL phloroglucinol in acidic ethanol) and allowed to react at room temperature overnight. The solvent was then evaporated under nitrogen, and the residue dissolved in 0.5 mL distilled water. This solution was extracted three times with ethyl acetate (1.5 mL per extraction). The three ethyl acetate fractions were combined and evaporated under nitrogen. The residue was dissolved in 1.0 mL of 70% aqueous methanol. The procedure was repeated using the standard monomer samples.

HPLC analysis

Degradation products were analysed on a Shimadzu AD-VP, utilizing a Crestpak C18S column, at a flow-rate of 1 mL/min and detected at 280 nm using a UV detecter. The elution conditions used was solvent A, 1% aqueous acetic acid; solvent B Methanol : Solvent A, 60 : 40 (v/v); t=0, 100% solvent A; t=60 minutes, 40% solvent A, 60% solvent B; t= 65 min, 100% solvent B. The phloroglucinol and monomer standards prepared in 70% aqueous methanol were used to identify the peaks.

Electrochemical studies

Electrochemical tests were carried out in a three-electrode electrochemical cell connected to an EGG Princeton 263A and 273A potentiostats. A circular and horizontal working electrode was placed at the bottom of the cell under a Pt-disk electrode. Acquisition of data and calculation of electrochemical parameters were done by a 352 Soft Corr software. The reference electrode was a KCL-saturated calomel electrode, and all working electrode potentials are measured versus this reference electrode. The electrochemical corrosion tests were carried out using steels for automotive applications provided by Arcelor. Prior to each experiment, the electrodes were polished mechanically on a Struers Rotopol-2 polishing machine using SiC paper of 120, 400 and up to a final 1200 grit. After rinsing with distilled water, the test electrodes were cleaned with alcohol and dried in air, then immediately immersed in the aerated test solution. The following experiment sequence was used:

(i) Measurement of the corrosion potential (E_{corr}) and the polarisation resistance (Rp), performed every 1 h 30 minutes for a duration of 18 h, with a scan rate of 0.166 mV/s for a range ($E_{corr} \pm 20$ mV).

(ii) Recording the potentiodynamic curve, $i=f(E)$, from -300 to 300 mV versus E_{corr} with a sweep rate of 1 mV/s.

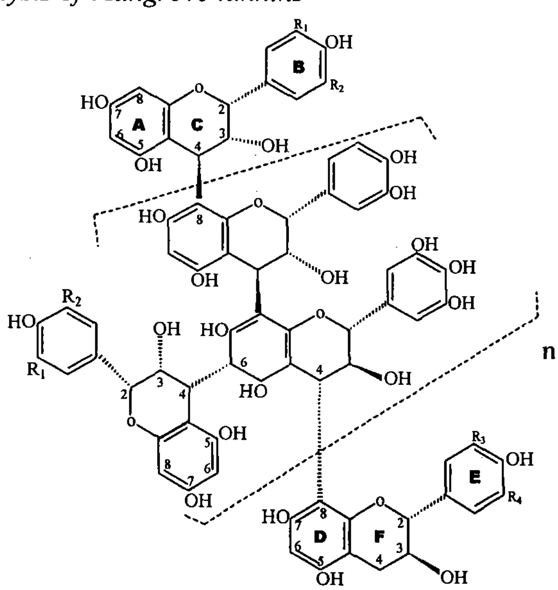
In a first study, test solutions containing the monomers ranging from 0.001 M to 0.05 M were prepared in 25% ethanolic 0.5M HCl due to the low solubility of the monomers at higher concentrations. A 25% ethanolic 0.5M HCl solution was used as the standard solution. In a second study, the test solutions containing mangrove tannin ranging from 0.1 g/L to 6.0 g/L were prepared by diluting the tannin sample in a
0.5 M HCl solution. A 3 g/L mimosa tannin, quebracho tannin and chestnut tannin were used for subsequent studies. The pH of the solutions were increased by the addition of NaOH solutions. The electrochemical tests were carried out at pH 0.02, 0.5, 2.0 and 4.0.

Molecular modelling

Quantum chemical calculations was performed using HyperChem 6.0 package. The geometry optimization of the flavanoids was obtained with PM3 semi-empirical parameterization. The potential energy minimum were obtained using the steepest descent algorithm and the iteration terminated when the RMS energy gradient reached 0.01 kcal $Å^{-1}mol^{-1}$. Single point calculation was used to determine the molecular properties of the flavanoids with minimum energy conformation.

Results and discussion

Analysis of Mangrove tannins



Extender Unit "ACB" :
Epicatechin : R_1=OH, R_2=H
Epigallocatechin : R_1=R_2=OH
Epiafzelechin : R_1=R_2=H

Terminal Unit "DFE" :
Catechin : R_3=OH, R_4=H
Gallocatechin : R_3=R_4=OH
Afzelechin : R_3=R_4=H

Fig. 1 : Structure of a condensed tannin[12]

Our previous studies[11] has shown that mangrove tannin is predominantly made up of condensed tannin. In the acid depolymerization of condensed tannin in the presence of phloroglucinol, the interflavan bonds are protonated and broken, leaving the terminal unit intact and the extender unit as a carbocation. The carbocation is then captured by the phloroglucinol either alpha or beta to the C-ring (Fig. 1) at C-4, producing a monomer-phloroglucinol adduct.

When the condensed tannin was submitted to acid degradation in the presence of phloroglucinol and ethanol the HPLC chromatogram showing well resolved peaks as shown in Fig. 2 was obtained. Comparison with the retention times and spiking the samples with monomer standards confirmed the presence of catechin, epigallocatechin, epicatechin and epicatechin gallate. At present, we are in the process of identifying the phloroglucinol adduct attributed to the extender unit.

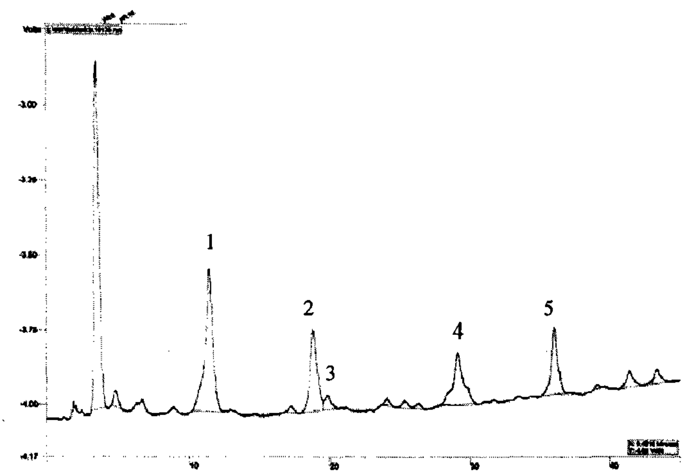


Fig. 2 : HPLC chromatogram of the condensed tannin with peaks corresponding to (1) phloroglucinol adduct (2)catechin (3)epigallocatechin (4) epicatechin and (5) epicatechin gallate

Inhibition efficiency of monomers in 0.5 M HCl

As a result of the analysis of mangrove tannin via reversed-phase HPLC, the inhibitory performance of the monomers was explored. All monomers produced some degree of inhibition for concentrations as low as 0.0025 M. In 0.5 M HCL, the inhibitory performance is greatly dependent on concentrationas the monomers gave different responses when the concentrations of the individual monomers were increased. Interestingly, for all the monomers investigated, shifts in the cathodic curves to lower density currents which subsequently gave rise to more negative E_{corr} was observed, thereby categorizing the monomers as cathodic inhibitors (Fig. 3). Consistent with the results of the potentiodynamic curves, the polarisation resistance, Rp measurements indicated similar inhibitory action of the monomers. While catechin does not show much variation in Rp values for all concentrations investigated, epicatechin (Fig. 4) and epigallocatechin gave maximum Rp at 0.005 M and epicatechingallate at 0.0025 M.

Fig. 5 represents the percentage inhibition of the monomers based on Rp measurements in 0.5 M HCl. Catechin produced percentage inhibition of between 65% - 78% for all concentrations, reaching a maximum at 0.01 M. Epicatechin on the hand has a large variation in percentage inhibition of between 30% - 78%. The lowest occurred at 0.0025 M while the highest at 0.005 M. Further increase in concentrations did not improve the inhibition percentage. The percentage inhibition for epicatechingallate decreased with increasing concentrations. Due to the scarcity of epigallocatechin, the percentage inhibition couldn't be explored further than 0.005 M. A 77% of percentage inhibition was obtained at 0.005 M.

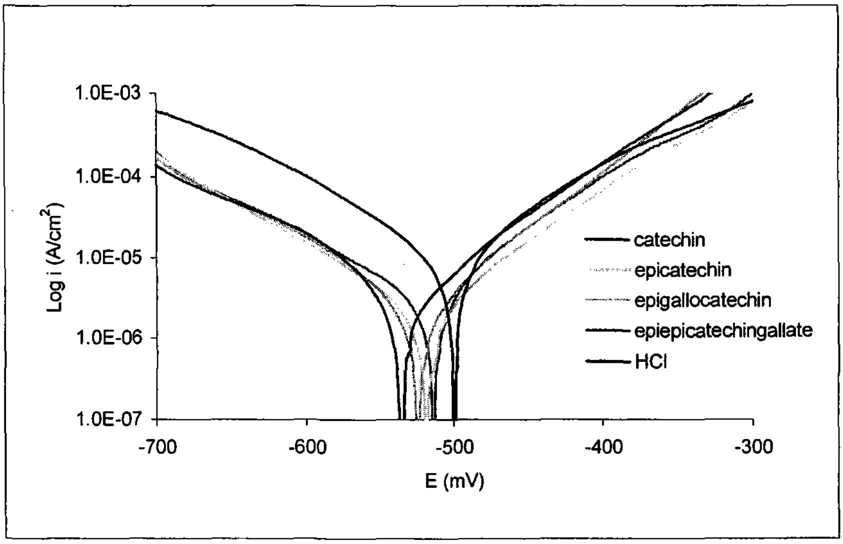


Fig. 3 : Potentiodynamic curves of steel in 0.5 M HCl solution containing 0.005 M flavanoids.

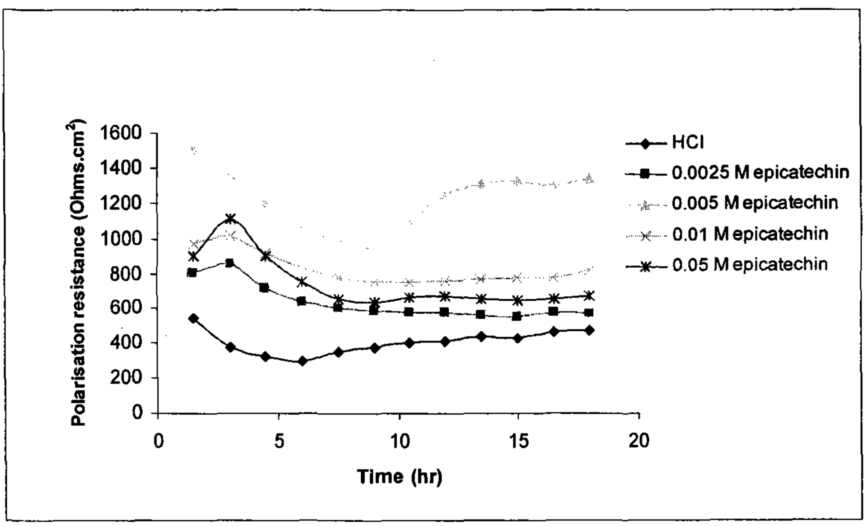


Fig. 4 : Change of polarization resistance, Rp with time of immersion in 0.5 M HCL containing various concentrations of epicatechin

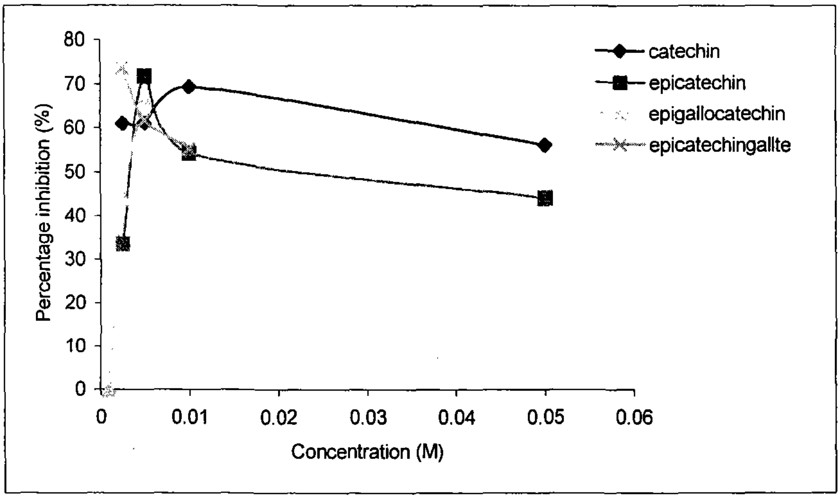


Fig. 5 : Percentage inhibition of steel corrosion at different concentrations of flavanoids based on polarisation resistance,Rp measurements in 0.5 M HCl

An example of an optimised molecular structure of a flavanoid monomer with its HOMO density is as shown in Fig. 6. The highest values of the electron density of the frontier orbital were found within the vicinity of the A aromatic ring. Adsorption could proceed via sharing of the electron donor group or aromatic π-electrons, between the flavanoid molecule and the partially filled d-orbitals of iron. From this study, it was found that adsorption could take place on either A or B aromatic ring depending on the orientation of the flavanoid monomer and the number of phenolic groups attached to the molecule. All the flavanoid molecules investigated gave rise to HOMO-LUMO energy gap of 8.92-9.12 eV, signifying soft acid-soft base interaction between iron metal and flavanoid molecule[2]. This leads to the fact that flavanoid molecules, acting as soft base inhibitors are most effective for metals corroding in acidic medium. This is indeed consistent with the results obtained via the electrochemical studies which indicated various degree of inhibition by the flavanoid monomers in acidic solution.

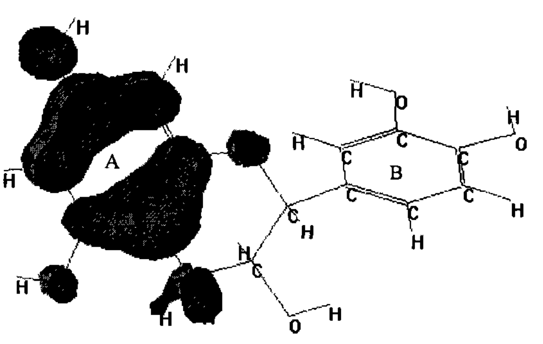


Fig. 6 : HOMO density as an isosurface for catechin monomer in its optimized conformation.

Inhibition efficiency of tannins

The effect of concentration on the inhibitory performance of mangrove tannin is as shown in Fig. 7. There was a gradual decrease of the same gradient in the cathodic curve, resulting in lower I_{corr} values, implying the increase in the degree of inhibition as the concentration of the tannin was increased. The R_p measurement indicated an increase from 126 Ωcm^2 to almost 1120 Ωcm^2, an increase of almost tenfold, when the concentration was increased from 3.0 g/L to 6.0 g/L. Inhibition was also evident at pH 0.02, 2.0 and 4.0. The potentiodynamic curves of mimosa, quebracho and chestnut tannins exhibited shifts in the cathodic slopes similar to mangrove tannin at pH 0.02, 0.5 and 2.0, indicating that all tannins act as cathodic inhibitors.

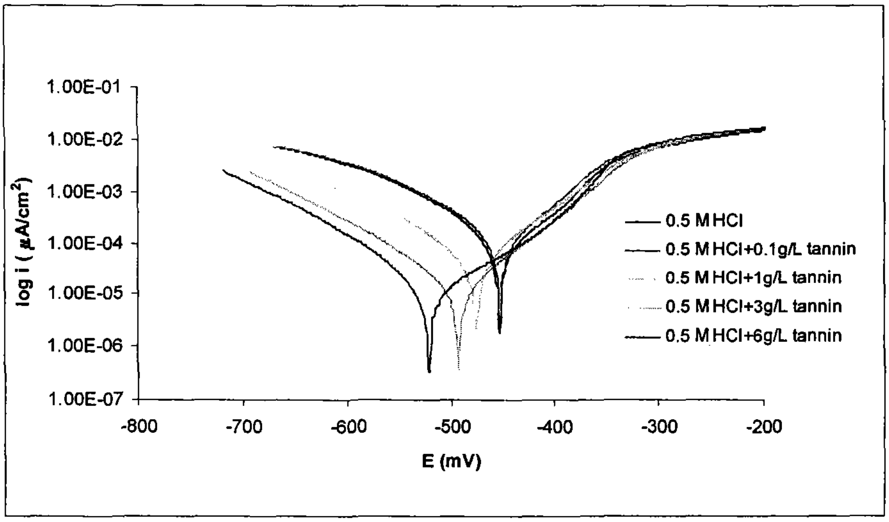


Fig. 7 : The effect of concentration of mangrove tannin on the potentiodynamic curves of steel in 0.5 M HCl

The change in Rp with respect to time of immersion at pH 4.0 is as shown in Fig. 8. While the Rp values remained constant for chestnut tannin, all other tannins showed small increments in the Rp values as the time of immersion increased. The advantage of mangrove as an inhibitor was observed when it began to produce higher Rp values than that of the HCl solution alone after 8 hours of immersion.

The percentage inhibition for all the tannins investigated at the various pH are given in Fig. 9. Regardless of whether the tannin is hydrolysable or condensed tannin, all the tannins exhibited a similar pattern of a decrease in percentage inhibition with the increase in pH with more than 80% inhibition at pH 0.02 and 0.5. Consistent with the polarization resistance measurements at pH 4.0, mangrove tannin gave a percentage inhibition of 22% as compared to other tannins.

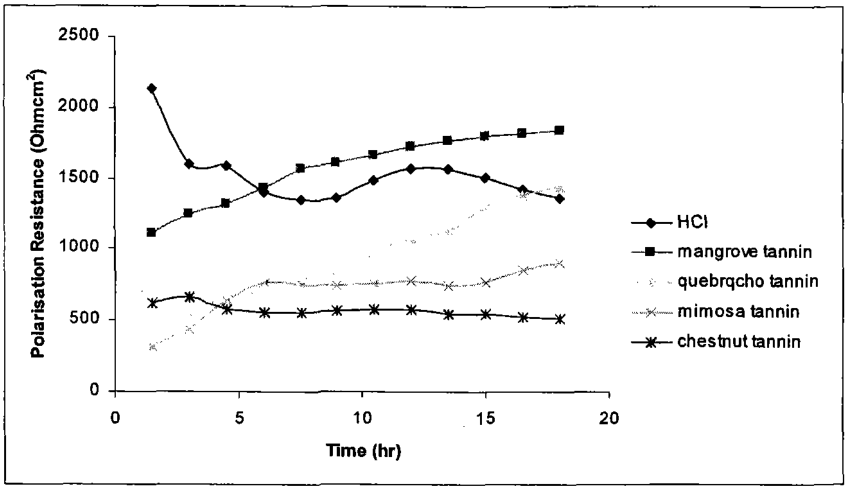


Fig. 8 : Change of polarization resistance, Rp with time of immersion in HCl solution at pH 4.0 containing 3 g/L of different tannins

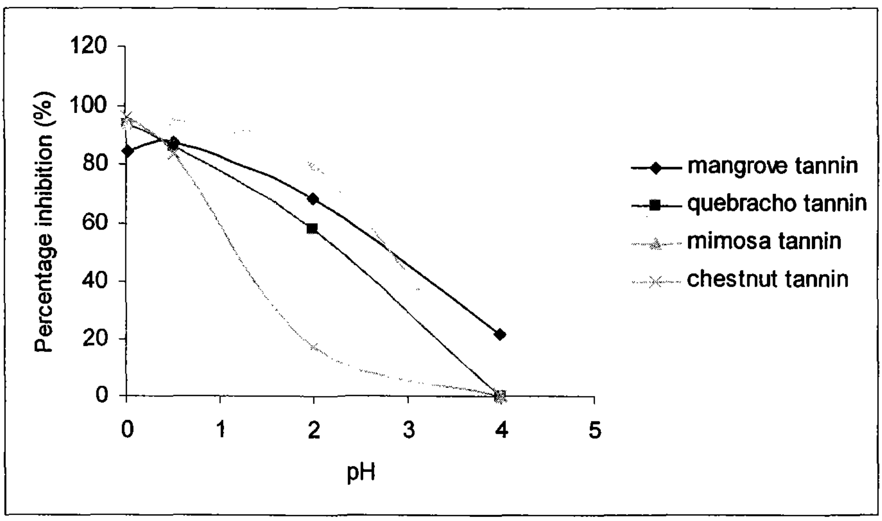


Fig. 9 : Percentage inhibition of steel corrosion with various tannins with respect to pH

Conclusion

1. Mangrove tannin constitutes predominantly of catechin, epicatechin, epigallocatechin and epicatechin gallate monomers.
2. All monomers act as cathodic inhibitors of the steel corrosion and its inhibitive performance dependent on concentration in acidic conditions.
3. Adsorption of flavanoids occurs within the vicinity of the phenolic groups on either A or B aromatic ring.
4. All tannins investigated are cathodic inhibitors and inhibition efficiency found to decrease with increasing pH.
5. The inhibitive performance of mangrove tannin is comparable with that of commercial mimosa, quebracho and chestnut tannins.

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