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Plants Polyphenols: An Alternative Source for Green Corrosion Inhibitor

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Abstract. Corrosion inhibitors are chemical compounds when added in a small concentration to the corrosive environment will significantly reduced the corrosion rate of metals or its alloys. The environmental toxicity of organic and synthetic corrosion inhibitors has prompted the search for green corrosion inhibitors as they are biodegradable, do not contain heavy metals or other toxic compounds. As in addition to being environmental friendly and ecologically acceptable, plant products are inexpensive, readily available and renewable. Although substantial research has been devoted to corrosion inhibition by plant extracts, reports on the detailed mechanisms of the inhibition process and identification of the active ingredient are still scarce. Most plant extracts constitute of oxygen and nitrogen containing compounds. Most of the oxygen-containing constituents of the extracts is a hydroxy aromatic compound such as polyphenolic compound. It is postulated that a number of OH groups around the molecule lure them to form strong links with hydrogen and form complexes with metals. The complexes caused blockages of micro anodes and/or micro cathodes and hence retard the subsequent dissolution of the metal. Another suggestion was through and adsorption of polyphenols to the metals due to the presence of donor-acceptor interactions between the π-electrons of aromatic ring and vacant *d* orbital of surface metal atoms. The present paper will highlight some of Malaysian plant extracts which are potential to be used as corrosion inhibitors for mild steel in acidic media.

Keywords: Plant polyphenols, total phenolic content, corrosion, inhibitor, adsorption

Introduction

Corrosion may be defined as deterioration of metal and its alloys due to the chemical or electrochemical reaction with its environment. Corrosion is a natural process where the metal returned to its natural state as their oxides or salts. Thus, corrosion of metal is unavoidable but a controllable process. The use of inhibitor for controlling metal corrosion is one of the most practical and an acceptable practice. However, owing to the increasing ecological awareness as well as strict environmental regulation have led to the search for green corrosion inhibitors as they are biodegradable, do not contain heavy metals and ecological acceptable.

There have been an increased of researches devoted to use plant extracts as corrosion inhibitor for sustainable development (Abdel-Gaber *et al.*, 2006; Raja & Sethuraman, 2008; Abdullah, 2011). Plant extract contained rich source of natural occurring chemical compounds that are environmentally acceptable, inexpensive, readily available and renewable resources of materials. Extracts of plant materials contain a wide variety of organic compounds such as polyphenols, terpenes, carboxylic acids and alkaloids. Most of them contain heteroatoms such as P, N, S, O and multiple bonds in their molecules which may be adsorbed, coordinated or formed complexes with metal atom or their ions. Polyphenols are recognized as one of the largest and most widespread class of plant constituents occurring throughout the plant kingdom, and are also found in substantial levels in commonly consumed fruits, vegetables and beverages. Polyphenols have recently aroused considerable interest because of their potential beneficial biochemical and antioxidant effects on human health. Commonly referred to as antioxidants, they may prevent various diseases associated with oxidative stress, such as cancers, cardiovascular diseases, inflammation and others (Harborne & Williams, 2000).

Polyphenols containing multiple phenolic functionalities with diverse chemical structures and properties. Lately, polyphenols especially tannin in plant extracts have been reported to account for inhibition of acid corrosion of metals (Rahim *et al.*, 2007; Saratha & Meenakshi, 2010; Tan & Kassim, 2011; Hussin & Kassim, 2011). Thus, the objective of the present work is to study the correlation between polyphenols profile (based on the total phenolic contents) of some plant extracts (*Uncaria gambir, Rizophora apiculata* and *Tinospora crispa*) towards the inhibitive action on corrosion of mild steel in 1.0 M HCl solution.

Materials and Methods

Extraction of polyphenols

All the plant samples were cleaned, dried and ground into powder (250 mesh) followed by further drying to constant weight. The 250-mesh samples powder was defatted using Soxhlet extraction with n-hexane for a period of 24 h with the rate of 2-cycles per hour before extraction. Approximately 2 g of defatted samples powder was were extracted with 50% aqueous ethanol (1:10 m/v), incubated for 2 h at 200 rpm under maceration and at room temperature. The ethanol was removed under pressure and the resulting aqueous fraction was freeze-dried.

Determination of total phenolic content

The total phenolic content (TPC) was determined by Folin–Ciocalteu assay described by Kim *et al.* 2003 with some modifications. An amount of 5.0 mL of Folin reagent (10% v/v) was added to a 10.0 mL volumetric flask containing 0.5 mL aliquot of appropriately diluted extracts or standard solutions of gallic acid. After 5 min, 4.0 mL of 1 M Na_2CO_3 was added and the solution was diluted to 10.0 mL and mix thoroughly. After incubation for 90 min at room temperature, the absorbance versus blank was measured at λ =750 nm. The total phenolic content was expressed as gallic acid equivalents (mg of GAE/g sample) through the calibration curve of gallic acid. All samples were analyzed in three replications.

Corrosion studies

Mild steel (MS) specimen having the composition (wt%) of 0.08 C, 0.01 Si, 1.26 Mn, 0.02 P and remaining Fe was used. MS specimens were mechanically abraded with 180, 600, 1000 and 2000 grades of emery papers, degreased with acetone and rinsed with distilled water before each electrochemical test. The specimens were fitted into sample holder leaving an exposed area of 0.785 cm^2.

Polarization measurements were carried out with Voltalab 21 electrochemical analyzer model PGP201 at room temperature using MS specimens as working electrode. The saturated calomel electrode and the platinum electrodes were used as reference and counter electrodes, respectively. Polarization studies were recorded by scanning for a range of ±250 mV versus open circuit potential (OCP) with the scan rate of 1 mV s^{-1}. Inhibition efficiency (η%) was calculated from the corrosion current density values by,

$$\eta\% = \left(\frac{I_{\text{corr(uninh)}} - I_{\text{corr(inh)}}}{I_{\text{corr(uninh)}}}\right) \times 100 \qquad (1)$$

where, $I_{corr(inh)}$ and $I_{corr(uninh)}$ are the corrosion current densities of mild steel in the presence and absence of inhibitor, respectively.

Electrochemical impedance spectroscopy (EIS) experiments were conducted using computer controlled Gamry Instruments model Reference 600 with Echem Analyst v5.60 software for curve fitting. AC impedance measurements were carried out at corrosion potential, with the frequency ranging from 0.01 Hz to 10 kHz at an amplitude of 10 mV. η% were calculated from R_{ct} (charge transfer resistance) values by,

$$\eta\% = \left(\frac{R_{\text{ct(inh)}} - R_{\text{ct(uninh)}}}{R_{\text{ct(inh)}}}\right) \times 100 \qquad (2)$$

where $R_{ct(uninh)}$ and $R_{ct(inh)}$ are charge transfer resistance of mild steel in the absence and presence of inhibitor, respectively.

Results and Discussion

Total phenolic content

TPC of the extracts are presented in Table 1. The TPC of extracts ranged from 65.0 to 92.0 mg of GAE/g sample with the *R. apiculata* extract gave highest yield of phenolic content among the extracts.

Table 1. Total phenolic content of plant extracts.

Plant extracts	Total phenolic content (mg GAE/g sample)
Uncaria gambir (gambir powder)	81.35
Tinospora crispa (stem)	67.05
Rhizophora apiculata (bark)	92.30

Corrosion inhibition of the extracts

The potentiodynamic polarization curves of MS in 1.0 M HCl in the absence and presence of different concentrations of extracts are shown in Figure 1. The calculated inhibition efficiency (η%) based on I_{corr} from the Tafel curves by using equation (1) are given in Table 2. The inhibitory performance of all the extracts was concentration dependent with the increase in concentration of extract, more polyphenol molecules are being adsorbed on to the surface of MS, enhancing more uniform surface coverage, which decreases the corrosion current density and consequently reduced the corrosion rate. The polarization curves shows that these inhibitors have an effect on both, the cathodic and anodic slopes, and reduced both cathodic and anodic current density. This indicates the extracts inhibited the cathodic process of hydrogen evolution as well as anodic dissolution of iron, which suggest that the extracts were powerfully inhibits the overall corrosion reaction of MS. Further inspection of Figure 1 also reveals that E_{corr} values do not show any significant change (less than 150 mV) in the presence of various concentrations of the inhibitors suggesting that inhibitor are a mixed type which influenced both metal dissolution and hydrogen evolution.

It is clear that from Table 1 and Table 2, a close correlation between the TPC of the extracts with the η% of MS in 1.0 HCl. The higher the TPC of the extract, the higer of its η%. As can be seen from Table 2, at 1000 ppm concentration the *R.apiculata* which having TPC of 92.36 mg GAE/g showed higher inhibition efficiency (83.5%) as compared to *T. cripsa* (72.5%) due to less TPC (67.05 mg GAE/g).

Table 2. Effects of different concentrations of plant extracts on the corrosion inhibition efficiecy of MS in 1.0 M HCl.

Concentration of extract (ppm)	Inhibition efficiency (η%)		
	U.gambir	*T. cripsa*	*R. apiculata*
50	20.0	16.5	36.5
100	45.5	39.0	54.0
500	68.0	61.0	72.0
1000	78.5	72.5	83.5

The corrosion behaviour of MS in 1.0 M HCl solution in the absence and presence of inhibitor was also investigated by the EIS method at room temperature (30°C). The R_{ct} values for respective extracts were calculated from the difference in impedance from Nyquist plot (Figure 2). It can be seen that the R_{ct} values were also concentration dependent and gave higher values for the extract with higher TPC for the same concentration. Using R_{ct} values and equation (2) the inhibition efficiency (η%) of each extract can be calculated, and the results were in good agreement with those calculated based on potentiodynamic polarization as shown in Table 2.

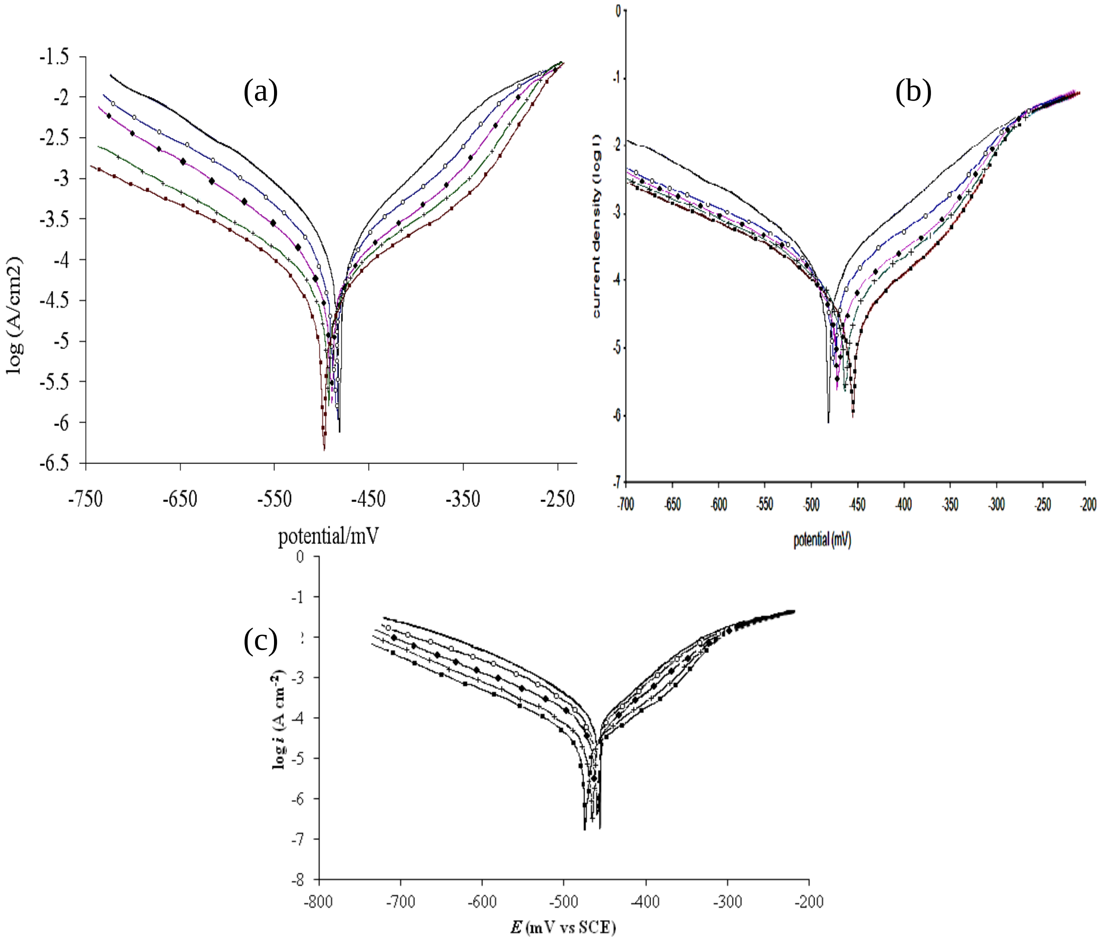
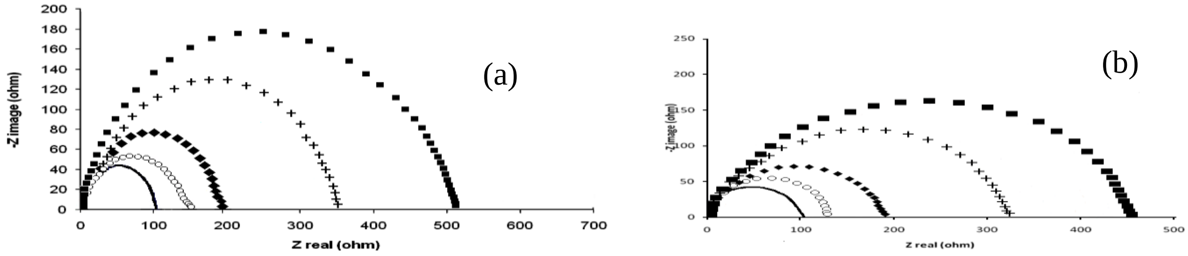


Figure 1. Polarization curves for MS in 1.0 M HCl in the absence and presence of different concentrations of extracts of (a) *Uncaria gambir* (b) *Tinospora cripsa* and (c) *Rhizophora apiculata*. Concentrations: ——— 1.0 M HCl; -○-○-○ 50 ppm; ◆-◆-◆ 100 ppm; +++ 500 ppm and ■-■-■ 1000 ppm.

It is worth noting that the presence of inhibitor does not alter the profile of impedance diagrams which are almost semi-circular (Figure 2), indicating that a charge transfer process mainly controls the corrosion of MS. Deviations of perfect circular shape are often interpreted due the inhomogeneity of the electrode surface arising from surface roughness or interfacial phenomena. Since the impedance diagrams (Nyquist plots) as shown in Figure 2 were well fitted with simple Randle circuit (Figure 2d), suggesting that the inhibition process is through an adsorption mechanism.



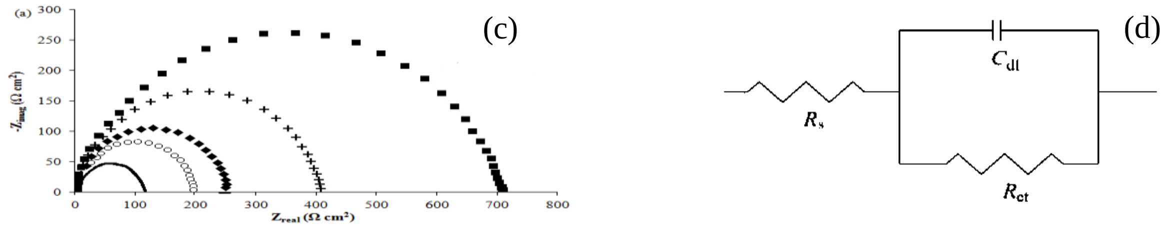


Figure 1. EIS diagrams for MS in 1.0 M HCl in the absence and presence of different concentrations of extracts of (a) *Uncaria gambir* (b) *Tinospora cripsa* and (c) *Rhizophora apiculata*. Concentrations: ——— 1.0 M HCl; -○-○-○ 50 ppm; ◆ ◆ ◆ 100 ppm; +++ 500 ppm and ■-■-■ 1000 ppm. (d) Randle circuit diagram of corrosion mechanism.

Conclusions

Plant extracts were found to be effective green inhibitors of mild steel in 1.0 M HCl. A good correlation was obtained between corrosion inhibition efficiency of the plant extracts with their total phenolic contents. The higher the total phenolic contents, the better inhibition efficiency of the extracts. Therefore, the total phenolic contents may act as a guide for screening plant extracts for its inhibitive properties. The phenomenon of physical adsorption is proposed from the EIS measurement.

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