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Proceeding Paper

Effective Corrosion Inhibition of Mild Steel in an Acidic Environment Using an Aqueous Extract of Macadamia Nut Green Peel Biowaste †

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Abstract: Improving the corrosion resistance of mild steel in an acidic aqueous environment is an important industrial consideration due to the use of acids for descaling and cleaning. The application of corrosion inhibitors is one of the most effective and economical means of protecting metals against corrosion. Plant-derived compounds have recently gained attention due to their low cost, non-toxic, and environmentally friendly properties. Biowastes are recognized as a potential cheap source of green corrosion inhibitors, and their use can help to lower the costs associated with corrosion inhibitors. Green peel biowaste (GPBW) generated from macadamia nut processing is typically dumped into the environment, posing a disposal concern. The use of the waste as a potential source of organic compounds with green chemistry attributes for mild steel corrosion inhibition in an acidic solution was proposed in this study. The gasometric and optical methods were used to carry out the investigations. Results showed that mild steel corrosion rates decreased as extract concentrations increased. As a result, mild steel corrosion inhibition increased with increasing inhibitor concentration and reached a peak value of 81% at 0.5 g/L extract concentration. The optical images showed that the inhibitor molecules adsorbed on the metal surface to form a protective film that isolated the mild steel from the corrosive solution. The adsorption of inhibitor molecules on the mild steel surface followed the Langmuir adsorption isotherm, indicating the formation of a monolayer film with a homogeneous distribution of adsorbed molecules. A Gibbs free energy (G°ads) of 24 kJ/mol indicated the inhibition process was mainly characterized by physical adsorption. The results of this study suggest that aqueous GPBW extract could serve as an inexpensive, non-toxic, and renewable corrosion inhibitor of mild steel in acidic solutions.

Keywords: corrosion inhibition; macadamia green peels; biowastes; green chemistry; mild steel; acidic solution

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1. Introduction

Mild steel corrosion is an inevitable process, particularly in the oil and gas industries, due to repetitive exposure to corrosive acidic environments during industrial cleaning, acid pickling, and acid descaling procedures. These procedures are performed at regular intervals to improve the efficiency of industrial processes. Consequently, corrosion control is commonly applied to extend the lifetime of mild steel materials in these acidic environments. Some common methods employed to control mild steel corrosion include the use of corrosion-resistive materials, corrosion inhibitors, and protective coatings. Among these, corrosion inhibitors are the most effective, practical, and economical method of metal corrosion control. Synthetic corrosion inhibitors such as chromates and phosphates deliver a satisfactory performance. However, these chemicals can cause toxic and harmful effects on the environment and organisms [1]. Therefore, the search for corrosion inhibitors with environmentally friendly properties is important.

Plant extracts are a good source of organic chemicals that are inexpensive, mostly nontoxic, and renewable. The organic compounds can adsorb on a metal surface through electron-rich sites, such as nitrogen, sulfur, or oxygen heteroatoms, to form a corrosion-resistive film. Thus, extracts containing compounds such as tannins, terpenes, alcohols, polyphenols, carboxylic acids, and alkaloids display corrosion inhibition properties [2]. Similar compounds can be found in plant biowastes, which are often discharged into the environment. Recently, there has been increased interest in using biomass waste extracts as a potential source of compounds with green chemistry credentials [3]. The increased production of crops due to population growth demonstrates that there are significant amounts of biomass wastes produced from the agricultural sector [4]. Organic compounds derived from biomass wastes serve as a potentially inexpensive and readily available resource. The use of biowaste compounds for corrosion control is associated with increased farm income, reduced environmental pollution, and lower inhibitor prices [5].

The processing of *Macadamia tetraphylla* nuts produces a significant amount of green peel biowastes (GPBW). The wastes are discarded into the environment, and some are burned, resulting in the loss of significant chemical resources and environmental impacts through groundwater pollution and emissions of greenhouse gases (CO_2, CH_4, N_2O) [6,7]. Macadamia nut green peels contain organic compounds, such as lignin, cellulose, hemicellulose, flavonoids, tannins, and proanthocyanidins, that can act as effective metal corrosion inhibitors [8]. However, the efficacy of GPBW-sourced compounds in metal corrosion inhibition has not yet been reported. The current study was an attempt of using the GPBW aqueous extract for mild steel corrosion protection in an acidic solution.

2. Materials and Methods

2.1. Materials

2.1.1. Inhibitor Preparation

The GPBW aqueous extract was prepared as previously reported [9]. In a nutshell, the green skins of *Macadamia tetraphylla* fruits were peeled, dried in the sun, and then processed into a powder using a blender. The resultant powder (20 g) was refluxed in 200 mL of distilled water for 240 min and then cooled to room temperature. To eliminate any remaining undissolved solids, the mixture was filtered, and the filtrate was then dried for 24 h at 318 K to produce a solid product. A stock solution formed by dissolving the solid sample (5.0 g) in 2 M HCl (50 mL) was used to make working solutions with various inhibitor concentrations ranging from 0 to 0.5 g/L.

2.1.2. Preparation of Specimens

Rectangular mild steel specimens with a surface area of 0.184 cm^2 were prepared from the metal material with the composition previously reported [10]. Specimens were mechanically abraded using sandpapers of different grit sizes, washed with distilled water to remove solid particles adsorbed on surfaces, and rinsed in acetone for degreasing before use for corrosion studies.

2.2. Methods

Gasometric Method

Corrosion tests were performed using the gasometric technique as previously described [9]. Briefly, the mild steel specimens were immersed in 10 mL of 2 M HCl contained in a test tube. The volume of sodium chloride solution (red colored with methyl red) displaced with the hydrogen gas in a burette was recorded at a regular time interval of two minutes for one hour. Experiments were repeated using different concentrations (0–0.5 g/L) of the GPBW extract. The hydrogen evolution rate was used to determine the corrosion rate (CR) using Equation (1). The performance of the inhibitor was evaluated using the inhibition efficiency (IE) calculated from corrosion rates (Equation (2)).

$$CR = \frac{V_t - V_i}{T_t - T_i} \times \frac{1}{A} \quad (1)$$

where A is mild steel surface area (cm^2), V_t is the volume of hydrogen evolved in the absence of inhibitor at time T_t, and V_i is the volume of hydrogen evolved in the presence of inhibitor at time T_i

$$IE(\%) = \left(\frac{CR_{un} - CR_i}{CR_{un}}\right) \times 100 \quad (2)$$

where CR_{un} is the corrosion rate in the absence of the inhibitor and CR_i is the corrosion rate in the presence of the inhibitor.

3. Results

3.1. Influence of Inhibitor Concentration

A protective coating that separates a metal surface from a corrosive solution leads to corrosion inhibition. The effectiveness of a corrosion-resistant layer on the metal surface is influenced by the inhibitor concentration. Thus, the influence of inhibitor concentration on mild steel corrosion was investigated. The results (Figure 1 and Table 1) demonstrated the mild steel corrosion rate (CR) declined as the amount of the inhibitor increased. As a result, the corrosion inhibition efficiency (IE) increased as inhibitor concentrations increased. The adsorption of hydrophobic organic molecules on the metal surface may have caused the observed decrease in CR and rise in IE. The adsorption of hydrophobic molecules on the mild steel surface may have caused the observed decrease in CR and rise in IE. The organic layer created by molecules that have been adsorbed limits oxygen diffusion and access to the metal surface, which slows the rate of corrosion. The results indicated that the GPBW extract contains chemical compounds with effective anti-corrosion properties.

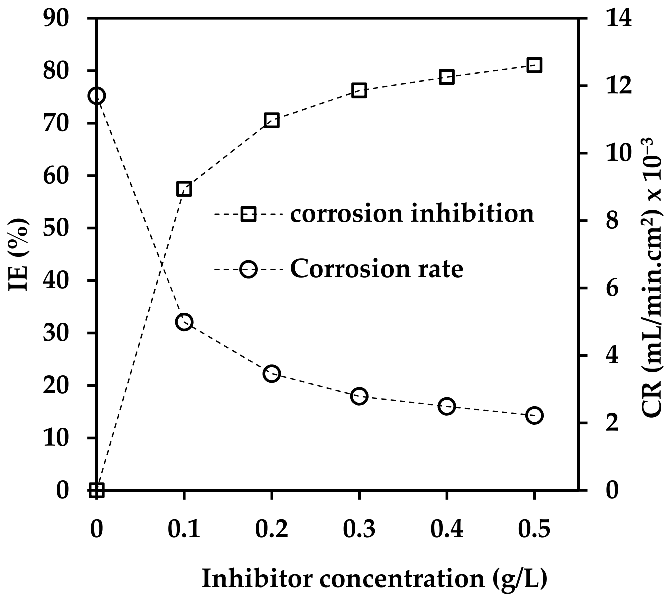

Figure 1. Influence of the amount of GPBW extract on IE and CR of mild steel corrosion in 2 M HCl at 28 °C.

Table 1. Influence of the amount of aqueous GPBW extract on mild steel corrosion inhibition in 2 M HCl at 28 °C.

Concentration (g/L)	CR (mL/min. cm^2) × 10^{-3}	IE (%)	θ
0	11.7	0	0
0.1	4.99	57	0.57
0.2	3.46	71	0.71
0.3	2.79	76	0.76
0.4	2.49	79	0.79
0.5	2.22	81	0.81

3.2. Temperature Effect on Inhibition Performance of GPBW Extract

The influence of temperature on the performance of the inhibitor was also investigated. Figure 2 shows that IE declined with increasing solution temperature. The observation possibly signifies that the inhibitor molecules and the mild steel surface were in a state of adsorption–desorption equilibrium. As a consequence, the equilibrium shifted towards desorption as the temperature increased, diminishing the surface area of the mild steel covered by inhibitor molecules. Thus, a decline in IE with increasing temperature suggests the existence of weak forces of attraction (physical interactions) between organic molecules contained in the inhibitor and the metal surface [3].

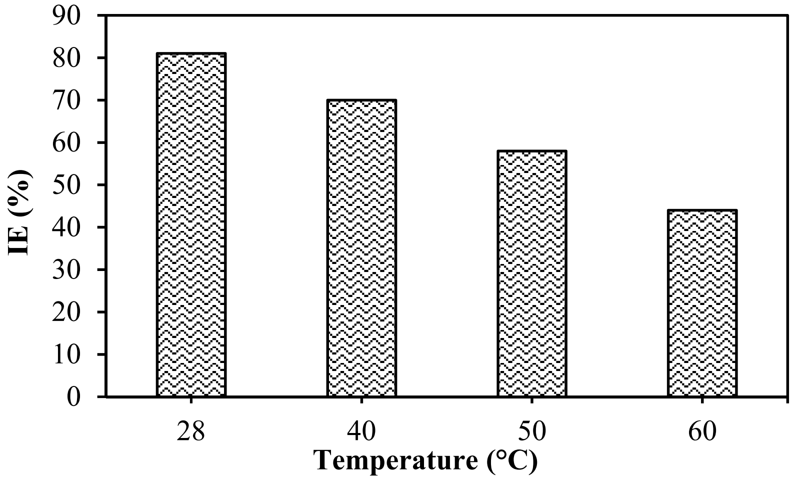

Figure 2. Influence of temperature on mild steel corrosion inhibition using aqueous GPBW extract of concentration 0.5 g/L in 2 M HCl at 28 °C.

3.3. Adsorption Isotherms

The performance of a corrosion inhibitor results from the adsorption of lipophilic organic molecules onto a metal surface to form a layer that inhibits contact between the metal surface and corrosive solutions. The adsorption process involves the substitution between organic and water molecules at the metal-solution interface (Equation (3)).

$$Org_{(soln)} + nH_2O_{(ads)} \leftrightarrow Org_{(ads)} + nH_2O_{(soln)} \quad (3)$$

where n is the number of water molecules displaced by organic molecules, and $Org_{(soln)}$ and $Org_{(ads)}$ are inhibitor molecules in solution and adsorbed on the metal surface, respectively.

At equilibrium, it is possible to examine the nature of metal-inhibitor interactions by using different adsorption isotherm plots. The degree of surface coverage (θ) can be plotted as a function of inhibitor concentration. The experimental data in this study were tested using Langmuir, Freundlich, Frumkin, Temkin, and Flory–Huggins adsorption isotherms. The results (Table 2) showed that the adsorption of the extract on the mild steel surface was adequately described by all the tested adsorption isotherms as indicated by high correlation coefficient values (R^2 > 0.96) for all the plots. However, the best fit ($R^2 \approx 1$) was obtained for the plot of the Langmuir adsorption isotherm (Figure 3) as described by Equation (4). This indicates that extract molecules were likely adsorbed on the metal surface to form a monolayer film with a homogenous distribution [11].

$$\frac{C}{\theta} = C + \frac{1}{K_{ads}} \quad (4)$$

where C is the inhibitor concentration (g/L) and K_{ads} is the adsorption–desorption equilibrium constant.

Table 2. Adsorption isotherms of macadamia biowaste aqueous extract of concentration 0.5 g/L in 2 M HCl at 28 °C.

Adsorption Isotherm	Relationship Plots	R^2
Langmuir	C/θ versus C	0.9991
Freundlich	log θ versus log C	0.9633
Frumkin	In (θ/C (1 − θ)) versus θ	0.9742
Temkin	θ versus log C	0.9791
Flory-Huggins	log θ/C versus (1 − θ)	0.9596

Where θ—surface coverage, C—inhibitor concentration and R = linear correlation coefficient.

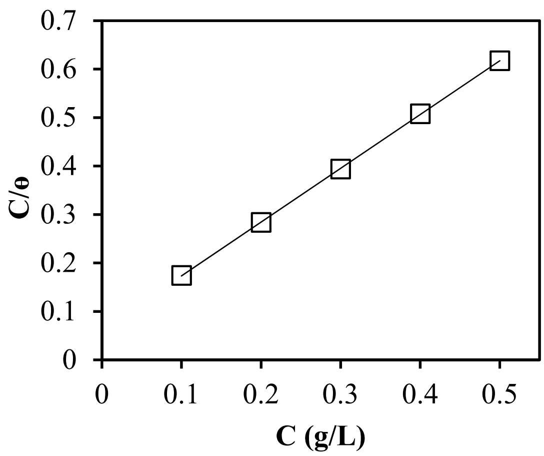

Figure 3. Langmuir adsorption isotherm for the adsorption of GPBW in 2 M HCl on mild steel at 28 °C.

The equilibrium adsorption constant (K_{ads}) relates to the standard free energy of the adsorption process (Equation (5)). The value of the calculated standard free energy (ΔG°_{ads}) is negative (Table 3), which is a likely indicator of the spontaneous adsorption of inhibitor molecules on the metal surface [3]. Free energy values lesser than or close to 20 kJ/mol usually indicate physical adsorption, whereas values greater than 40 kJ/mol indicate chemical adsorption. In the current study, the free energy value of 24 kJ/mol indicates the adsorption of compounds from the extract involved physical interactions.

$$\Delta G_{ads} = -RT\ \mathrm{In}(K_{ads} \times A) \quad (5)$$

where R = gas constant (8.314 J/K mol), T = temperature (298 K) and A = water density (1000 g/L).

Table 3. Thermodynamics parameters for aqueous GPBW (0.5 g/L) on mild steel in 2 M HCl at 28 °C.

Inhibitor	Slope	K_{ads} (L/g)	R^2	ΔG°_{ads} (kJ/mol)
GPBW	1.110	16.103	0.999	−23.99

3.4. Optical Surface Examination

After 10 days of immersion at 28 °C, the mild steel surfaces exposed to a 2 M HCl acidic solution in both the absence and presence of the inhibitor (0.5 g/L) were examined using optical microscopy. The results showed that the mild steel surface exhibited a rough surface morphology with reasonably uniform corrosion and minimal selectivity in the absence of the inhibitor (Figure 4b). However, the surface was noticeably smoother and showed fewer corrosion signs when the inhibitor was present (Figure 4c). Our inference that a protective layer formed on the surface of the mild steel is supported by the smoothness observed in the presence of the inhibitor. Consequently, based on the results of the surface analysis, GPBW can serve as a potential green chemistry corrosion inhibitor of mild steel and other related metal materials in an acidic solution.

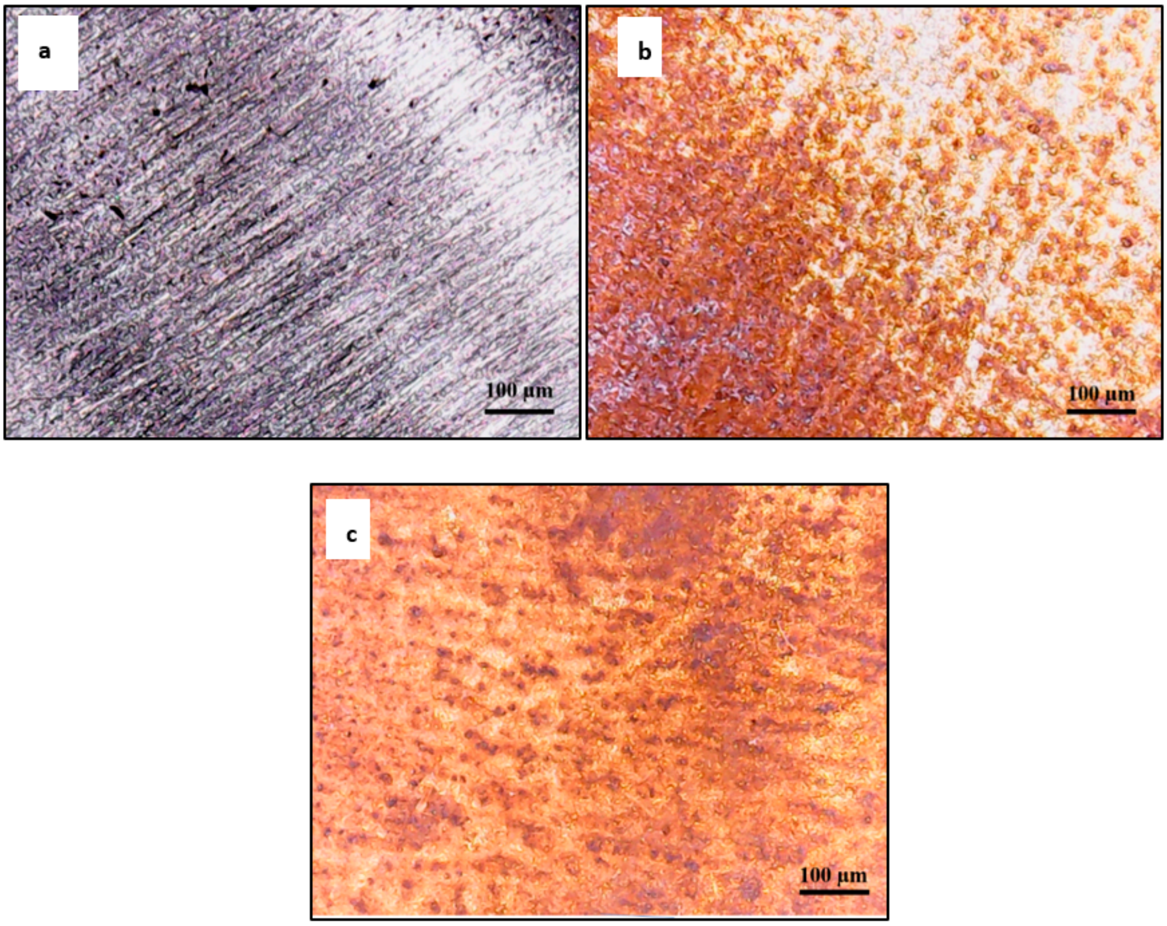

Figure 4. Mild steel surface images of (**a**) polished unexposed mild steel; (**b**) exposed mild steel in 2 M HCl, and (**c**) exposed mild steel in 2 M HCl containing 0.5 g/L of the extract after 10 days of immersion at 28 °C.

4. Conclusions

Green peel biowaste from the macadamia nut processing industry was successfully explored as a source of organic molecules effective for inhibiting the corrosion of mild steel in a 2 M HCl acidic solution. The formation of an anti-corrosion coating on the metal surfaces was indicated by the decrease in corrosion rate in the presence of the GPBW extract. The adsorption of organic molecules on the mild steel surfaces followed the Langmuir isotherm which suggests the formation of a homogenous monolayer film. The adsorption was a spontaneous process characterized by physical interactions. A surface morphology examination also indicated the formation of a protective film on the metal surface. The results from the current study strongly indicate the green chemistry credentials of macadamia green peel biowaste as a source of effective, nontoxic, and renewable metal corrosion inhibitors.

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