ELECTROCHEMICAL AND THERMODYNAMIC EVALUATIONS OF *SPONDIAS MOMBIN* LEAVES EXTRACT AS GREEN INHIBITOR FOR MILD STEEL CORROSION IN ACIDIC MEDIUM

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ABSTRACT

Acid corrosion of steel-based structural equipment is a serious challenge for the chemical industry, especially, during descaling practices. Adding efficient corrosion inhibitors into the acid solution can significantly mitigate against this phenomenon. Currently, greener corrosion inhibitors, such as extracts of plant parts, have gained outstanding attention because they impact minimally when discharged into the environment. In this work, electrochemical and thermodynamic methods were employed to investigate the inhibitive efficiency of the water and ethanol extracts of Spondias mombin leaves against the corrosion of typical industrial steel (C1020) in 1.0M HCl. Both extracts protect the steel surface by blocking anodic and cathodic reactions on the steel surface, and lowering the capacitive behavior of the steel-acid interface. The extracts adsorb according to the models of Langmuir and Freundlich isotherms. The ethanol extract performs better (with an efficiency 96–98 %) than the water extract (efficiency 36–38 %), and exhibits more negative ΔG (-28.00 KJ/mol.) which is synonymous with more feasible and spontaneous adsorption.

Keywords: *Electrochemical, Thermodynamics, Corrosion inhibition, Green product, Spondias mombin extracts.*

1. INTRODUCTION

Carbon steel constitutes the most abundantly used alloy for fabricating major equipment in the chemical process industry due to its natural abundance, cheapness and strength (Palaniappan et al., 2020; Verma et al., 2019). Over time, inorganic scales would percolate on the surface of the steel-based equipment; interfering with production and diminishing the structural integrity of the equipment. Acid-cleaning, with dilute mineral acids like hydrochloric acid (HCl), is a common industrial practice that dislodges these scales and restores the efficiency of the equipment. However, the acid solution eventually impacts severe corrosion attack on the steel surface during acid-cleaning. Globally, the financial and material losses associated with this acid corrosion is enormous (Alrefaee et al., 2020; Marzorati et al., 2019; Verma et al., 2019). One of the most conventional ways to mitigate against this corrosion is to add effective corrosion inhibitors into the acid-cleaning solution.

Most chemical process industries usually add toxic chemicals to acid-cleaning solutions (Alrefaee et al., 2020; Muthukumarasamy et al., 2020; Fouda et al., 2019; Ishak et al., 2019), but these chemicals impact dangerously on the environment (Alrefaee et al., 2020; Belakhdar et al., 2020; Berrissoul et al., 2020; Chen et al., 2020; Asfia et al., 2020; Bidi et al., 2020). Identifying greener alternatives, with high inhibition efficiency, is important for the chemical industry since they would be excellent replacements for the toxic chemicals. The extracts of plant parts are remarkable in this regard (Ahanotu et al., 2020, Akinbulumo et al., 2020). They are naturally abundant, cheap and environmentally safe. They also contain phytochemicals which offer enormous active sites for interaction with metal atoms (Alrefaee et al., 2020; Chaudhary and Tak 2022). Several research works exist on the use of plant extracts as corrosion inhibitors for steel in acidic solutions (Marzorati et al., 2019; Verma et al., 2019; Ishak et al., 2019; Chen et al., 2020; Asfia et al., 2020; Alrefaee et al., 2020; Ahanotu et al., 2020). However, majority of reported works used only single (and toxic) solvents for their extraction. We have a concept that the amount/characteristics of phytoconstituents extracted from a plant part would influence its corrosion inhibition efficiency, and depends on the extracting solvent. Knowledge of this will guide the industry on the most preferable solvent for extraction.

It is important, also, that these solvents (like water and ethanol) also exhibit green properties in case of eventual discharge to environment.

This work reports a study conducted to investigate the capability of water and ethanol extracts of *spondias mombin* leaves to ameliorate the acid corrosion of carbon steel C1020. Potentiodynamic polarization (PDP) and electrochemical impedance spectroscopy (EIS) were utilized as electrochemical methods to understand the effect of extracts on the kinetics and mechanism of the steel corrosion in 1 M HCl solution. Thermodynamic assessment was performed based on adsorption isotherm and ΔG calculations.

2. MATERIALS AND METHODS

2.1 Materials

The materials used include fresh samples of *spondias mombin* leaves, sterile plastic bags, industrial blender, solvents: acetone, distilled water and ethanol (98 %), rotary evaporator, steel coupons and polishing papers, acid/extract concentrations tested: 1 M HCl /100, 200, 300, and 500 ppm.

2.2 Methods

2.2.1. Sample preparation

Coupons with surface area of 1.0 x 1.0 cm^2 were used for electrochemical measurement. Prior to use, they were abraded mechanically using abrasive polishing papers (successively) with 400 and 600 grit sizes, rinsed with distilled water and acetone, and dried using a Buchler Torramet specimen dryer. Analytical grade HCl (36 wt. %) was dissolved in distilled water to prepare the corrodent (1 M HCl). Fresh samples of *spondias mombin* leaves were obtained from the campus of Edo State University Uzairue and was validated accordingly in Biological Science Department, Edo State University Uzairue, Nigeria. The leaves were thoroughly washed with distilled water, dried at room temperature for fourteen days and then ground to powdered form using an industrial blender. The extraction was performed by soaking the powder for 72 h in ethanol and water as solvent in the ratio of 1:10 (plant powder (g): solvent volume (mL)). Thereafter, the mixture was filtered and the filtrate was concentrated using a rotary evaporator. The powder residue was also air-dried until a constant mass was obtained. The difference in powder mass before and after extraction was utilized to calculate the amount of plant phytochemical extracted by each solvent.

2.2.2 Electrochemical and thermodynamic investigations

The electrochemical experiments were conducted on a Gamry Potentiostart/Galvanostat/ZRA Reference 600 work station following the method reported previously by Ahanotu et al. 2020. The setup comprises a three-electrode system where an epoxy-encapsulated C1020 steel functioned as the working electrode, the auxiliary electrode was a graphite rod, and the reference electrode was a Ag/AgCl electrode. The electrochemical experiments were performed after monitoring the variation of open circuit potential (OCP) for an hour. The electrochemical impedance spectroscopy (EIS) measurements were performed, at OCP, within the frequency range of $10^5\ Hz\ to\ 10^{-3}\ Hz$ with $\pm 10\ mV$ amplitude signal. The signal amplitude perturbation was $\pm 10\ mV$. On the other hand, the potentiodynamic polarization (PDP) measurements were conducted by polarizing the working electrode within $\pm 0.25\ V$ versus OCP using a scan rate of 0.166 mVs^{-1}. The analysis of EIS data was done using Echem analyst while EC-lab software was used for PDP data analysis. The experiments were conducted in triplicates to achieve reproducibility. The inhibition efficiency (from EIS and PDP results) was calculated according to Solomon et al., 2018 and Fang et al., 2019, based on Equations (1) and (2), where R_{ct} is the resistance to charge transfer and i_{corr} is the corrosion current density.

$$\%\, IE_{EIS} = 1 - \frac{R_{\text{ct(without}\,inhibitor)}}{R_{\text{f(with}\,inhibitor)} + R_{\text{ct(with}\,inhibitor)}} \times 100\% \quad (1)$$

$$\%\, IE_{PDP} = 1 - \frac{i_{corr(with\,inhibitor)}}{i_{corr(without\,inhibitor)}} \times 100\% \quad (2)$$

Different adsorption isotherm models were adopted to investigate the thermodynamic interactions and properties of the inhibitor. From the investigated isotherm models, the Gibbs free energy was evaluated to understand the spontaneity and feasibility of inhibitor protection.

3. RESULTS AND DISCUSSION

3.1. Electrochemical studies

3.1.1 Electrochemical impedance spectroscopy (EIS)

The analysis of the EIS is presented in the form of a Nyquist, Absolute impedance and Phase angle plots as shown in Figure 1. The addition of different concentrations of the *spondias mombin* leave extracts caused the size of the Nyquist arcs to expand significantly in comparison to the size displayed by the uninhibited solution (blank solution). This is shown in Figure 1(a). This enlargement of the Nyquist arc size depicts lower rate of corrosion and increase in corrosion resistance. It can be seen that, at 500 ppm, the ethanol extract (with charge transfer resistance, R_{ct}, of 2004.10 Ω cm^2) shows larger sizes than the water extract (with charge transfer resistance, R_{ct}, of 121.00 Ω cm^2), which confirm that the ethanol extract exhibits greater protection of the steel surface than the water extract.

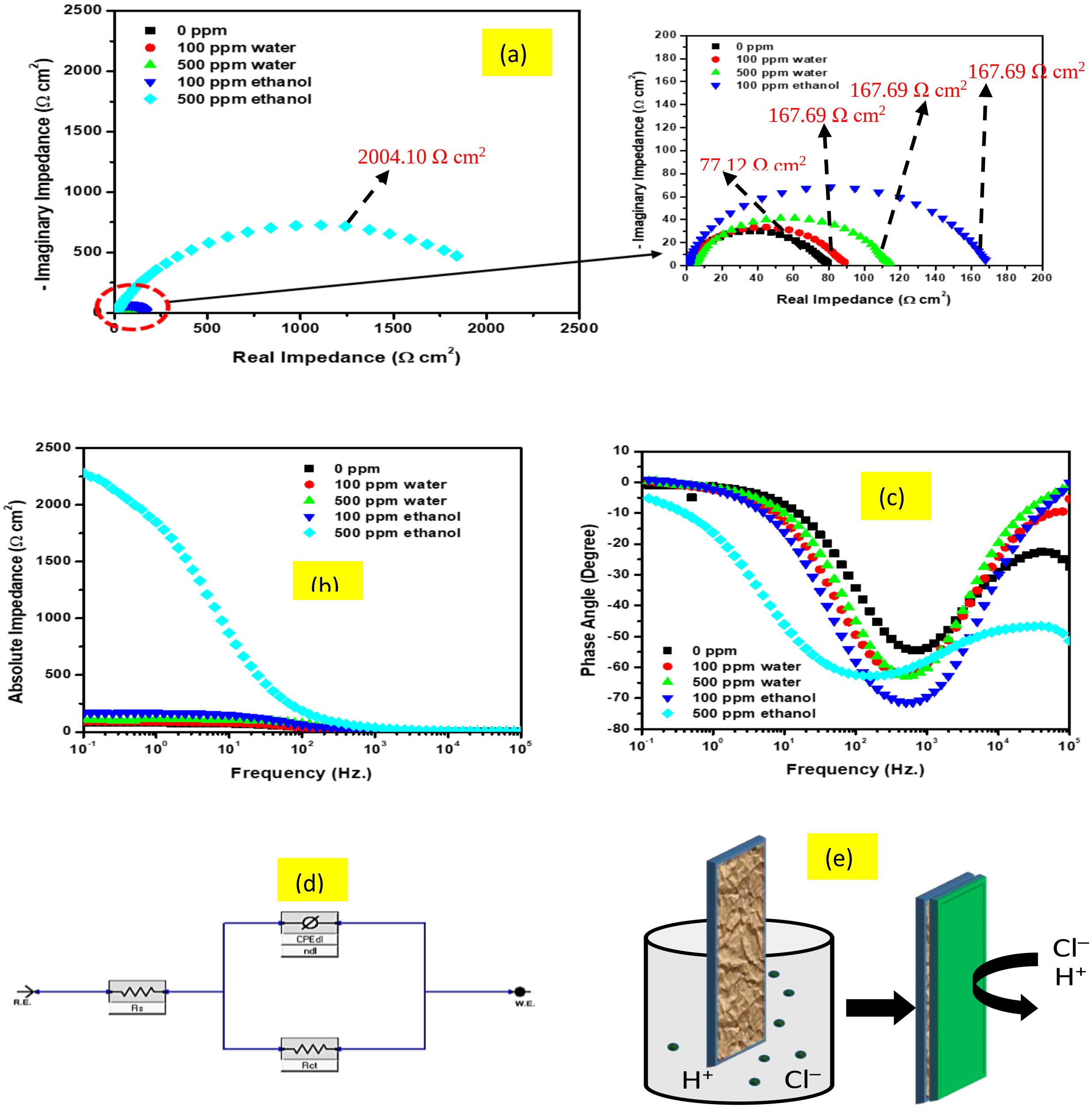

Figure 1: EIS analysis shown as (a) Nyquist (R_{ct} values in red font) (b) absolute impedance and (c) phase angle plots, along with (d) electrical equivalent circuit model and (e) schematic illustration of inhibition mechanism.

The Nyquist trend is also supported by the absolute impedance plots in Figure 1(b) whereby the addition of inhibitor extracts continuously increases the value of impedance at low frequency, compared with the blank solution. Also, the phase angle plots of Figure 1(c) reveal higher peaks in the presence of inhibitor extract. Higher peaks depict greater corrosion resistance. Consequently, the impedance behavior of the inhibited and uninhibited steel is modeled using the one-time electrical equivalent circuit in Figure 1(d). The model depicts that the extracts effectively modify the electric double layer at the steel-solution interface, by repelling water and chloride ions from the acid away from the steel surface, as depicted in Figure 1(e).

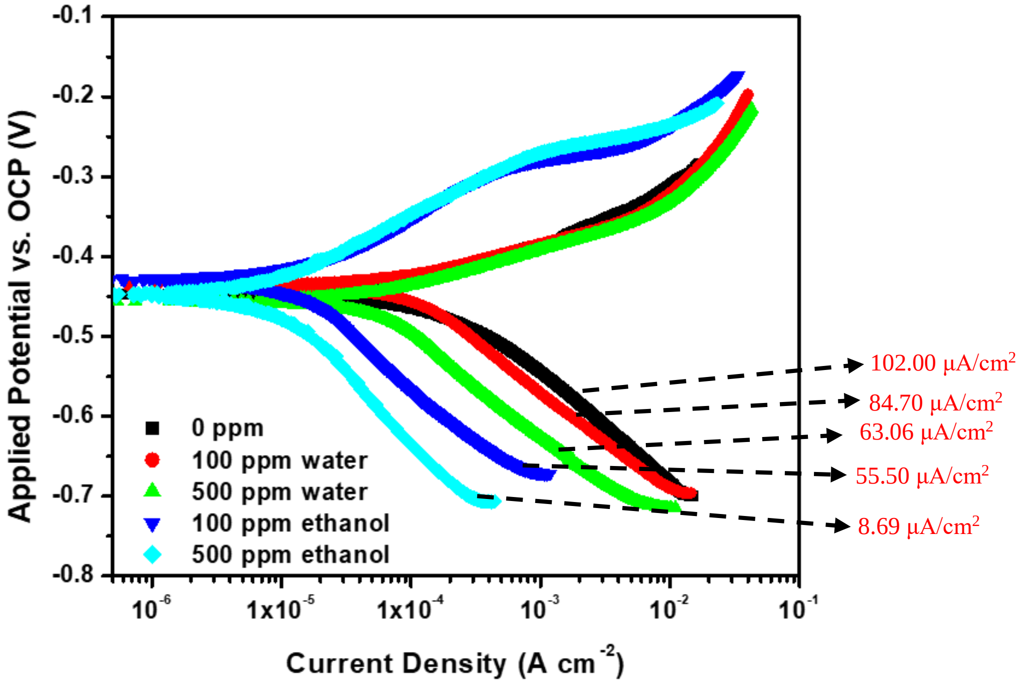

Figure 2: PDP analysis of C1020 steel in 1 M HCl containing water and ethanol extracts of *Spondias mombin* leaves at 25 °C (corrosion current, i_{corr}, values given in red font).

3.1.2 Potentiodynamic polarization (PDP)

The influence of the extracts on the anodic and cathodic reactions on the steel surface during the corrosion in the acid solution was investigated using the PDP technique. In the present study, the predominant anodic reaction is the oxidation of Fe to Fe^{2+} while that of the cathodic reaction is the reduction of H^+ to H_2(g). Figure 2 shows the result of the polarization of the steel samples in the acid solution without and with concentrations of 100 and 500 ppm of the different extracts. The influence of both extracts on the corrosion potentials of the steel was observed to be minimal. This implies that the extracts had minimal influence on the thermodynamic propensity of the steel to corrode in the acid solution. However, the extracts significantly shifted both anodic and cathodic current to lower values. The implication is that the extracts exhibited mixed-type inhibitions since they were able to lower both anodic and cathodic reactions.

3.2. Adsorption Isotherm Analysis

The electrochemical results confirm that the ethanol extract of *Spondias mombin* leave performed better than the water extract. This could be attributed to the fact the ethanol, being a more vigorous solvent, could extract more phytoconstituents from the leaves, compared with the less aggressive solvent (water). It has also been well documented that the plant constituents protect corroding metal surfaces by adsorbing on active sites to block the electrochemical reactions. Adsorption isotherms are usually employed to decipher the predominant adsorption mechanism by corrosion inhibitors. In this work, we have tested the extract adsorption using the Langmuir, Freundlich and Temkin isotherms (Equations (3)–(5), respectively), by focusing on the ethanol extract. The results are presented in Figure 3.

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \quad (3)$$

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

$$\theta = -\frac{1}{2\alpha}\ln C - \frac{1}{2\alpha}K_{ads} \quad (5)$$

The most appropriate model is usually identified by the isotherm with the highest correlation coefficient (R^2). Figure 3 shows that the Freundlich isotherm (0.9975) exhibited the highest value of R^2. This indicates that the extract components adsorbed as single layer on roughened steel surface during the corrosion inhibition (Akinbulumo et al., 2020; Chaudhary and Tak 2022).

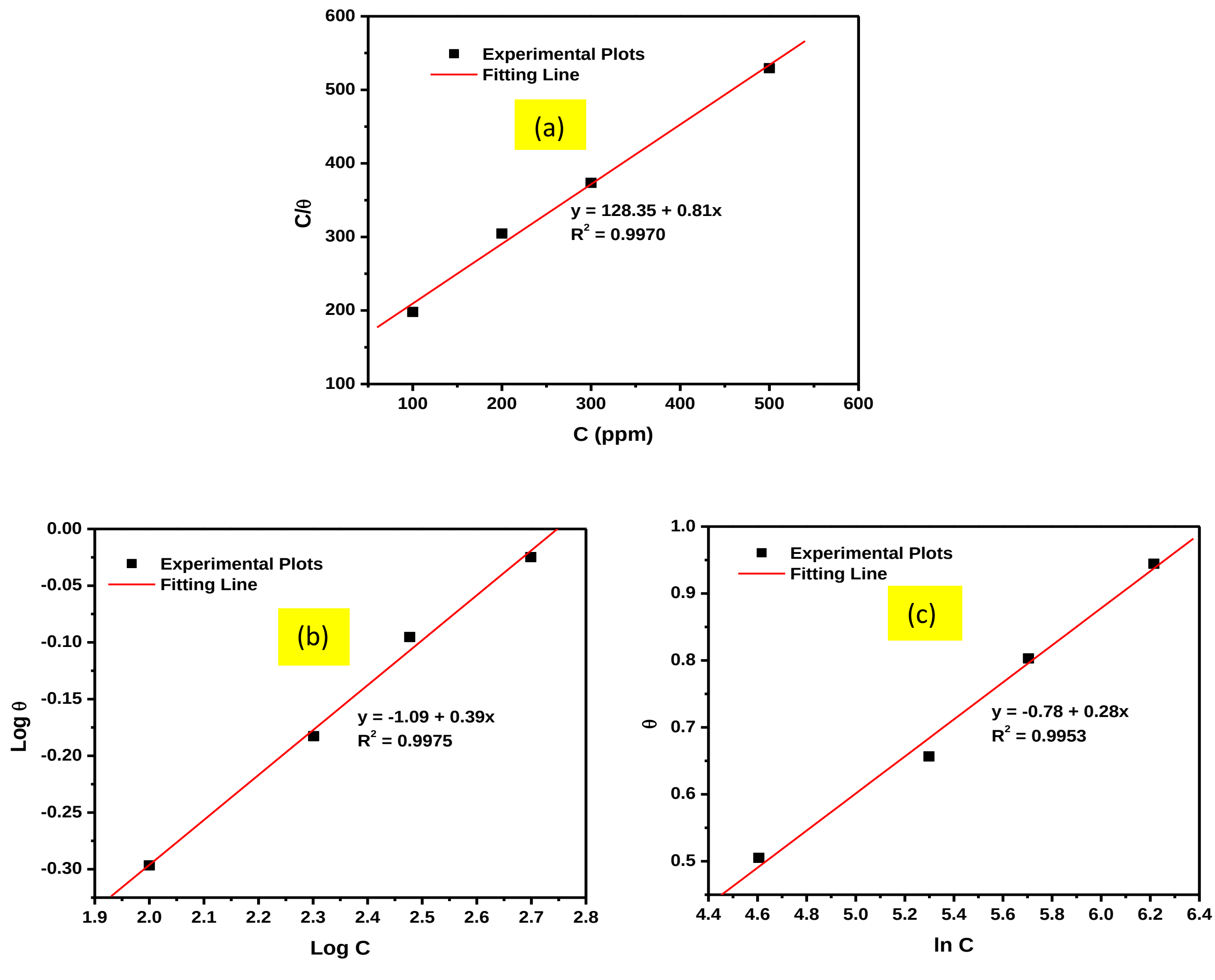

Figure 3: (a) Langmuir (b) Freundlich and (c) Temkin and isotherm plots for C1020 steel in 1 M HCl containing different concentrations of water extract of *Spondias mombin* leaves at 25 °C.

The adsorption constant, K_{ads}, can be extrapolated from the intercept of the Freundlich plot, according the Equation (4), can be introduced into the following $\Delta G_{ads} = -RT(10^6 K_{ads})$ to calculate the thermodynamic Gibbs free energy change which describes the feasibility and spontaneity of inhibitor adsorption. The adsorption equilibrium constant was calculated as 0.081 ppm mol.$^{-1}$ and, from this value, the Gibbs' free energy was deduced as –28.00 KJ mol.$^{-1}$. The negative value confirms that the extract adsorption was spontaneous and feasible.

4. CONCLUSIONS

This study examines current developments in the use of plant extracts as corrosion inhibitors based on the use of *Spondias mombin* leave extracts. Several plant extracts have been evaluated as inhibitors against metallic corrosion due to their environmentally friendly behavior and excellent inhibitory efficiency. The adsorption of the *Spondias mombin* leave extracts on the mild carbon steel was via Langmuir and Freundlich isotherm indicating the components adsorbed as single layer on much roughened steel surface during the corrosion process. The water extract had dominant effect on the anodic corrosion reactions while the ethanol extract had major effect on the cathodic corrosion reactions. The electrochemical analysis revealed lower rate of corrosion and increase in corrosion resistance of the extracts.

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