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**STUDY ON THE CHEMICAL CONSTITUENTS AND CORROSION
INHIBITION APPLICATION FOR CARBON STEEL OF
EXTRACTS FROM BARRINGTONIA ACUTANGULA
(LECYTHIDACEAE)**

SUMMARY OF MATERIALS SCIENCE DOCTORAL THESIS

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INTRODUCTION

1. Scientific rationale of the dissertation

Metal corrosion is a critical issue in numerous industries such as petroleum, chemical manufacturing, construction, and transportation. The corrosion of carbon steel and its alloys not only results in substantial economic losses but also compromises operational efficiency, equipment lifespan, and even human health and safety. Currently, synthetic corrosion inhibitors such as chromates, phosphonates, and imidazolines are widely used. However, these compounds pose significant drawbacks like environmental toxicity, health hazards, and the high cost of waste treatment. Against this backdrop, corrosion inhibitors derived from nature are gaining increased attention owing to their high inhibition efficiency, environmental friendliness, safety for users, and biodegradability. Organic compounds of plant such as alkaloids, flavonoids, terpenoids, and tannins,...can adsorb onto metal surfaces *via* various mechanisms to form protective films that shield steel from corrosive agents. Additionally, plant materials are abundant, renewable, and economically accessible, making them attractive for sustainable industrial applications. Thus, the development of plant-based corrosion inhibitors not only contributes to metal protection but also aligns with the goals of green chemistry and sustainable development by gradually replacing hazardous synthetic chemicals, utilizing locally available resources, lowering production costs, and reducing environmental waste. In this study, *Barringtonia acutangula*, a plant species commonly cultivated in Vietnam, presents a promising yet underexplored source of bioactive compounds. Especially, a comprehensive and application-focused studies on different parts of this plant remain limited. There is no scientific work has been conducted on the flowers of *B. acutangula*, and the few existing studies on its leaves are incomplete. Moreover, its potential as a corrosion inhibitor

has not yet been investigated in the corrosion science literature. This opens up a promising new research direction for exploring the chemical constituents of *B. acutangula* and applying the findings to elucidate the corrosion inhibition mechanisms. In this dissertation, both the flowers and leaves of *B. acutangula* are investigated as plant materials. Their chemical compositions are elucidated, and their corrosion inhibition performance on carbon steel in 1 M HCl is evaluated. Additionally, molecular simulations and adsorption isotherm modeling are employed to reinforce the mechanistic understanding of the organic film formation on the steel surface. Hydrochloric acid (1 M, pH = 0) is selected as the corrosive medium due to its high aggressiveness, which enables clear observation of inhibition performance. HCl is widely used in industrial operations across various sectors. The 1 M concentration ensures a sufficiently rapid yet controllable corrosion rate, suitable for electrochemical analyses such as EIS, PDP, and LPR. Moreover, 1 M HCl is frequently used in corrosion studies, allowing for comparison with previous work and facilitating future practical applications. Based on these considerations, the PhD candidate selected the research topic: "Study on the chemical constituents and corrosion inhibition application for carbon steel of extracts from *Barringtonia acutangula* (Lecythidaceae) “

2. Research objectives of the dissertation

Evaluation of the corrosion inhibition efficiency for carbon steel in HCl 1 M solution using aqueous extracts prepared from the flowers and leaves of *B. acutangula*, through the preparation and screening of a promising inhibitor, accurate identification of chemical constituents, advanced electrochemical techniques, and surface analyses. The inhibition mechanism was elucidated via theoretical simulations based on the clarified organic components and supported by adsorption isotherm models.

3. Main Research Contents of the Dissertation

- Content 1: Collection of plant materials, botanical identification, and preparation of extract from the flowers and leaves of *B. acutangula*;
- Content 2: Evaluation of the suitability of the aqueous extracts as corrosion inhibitors through quantification of flavonoids, polyphenols, and terpenoids, along with LC-MS and FT-IR analysis;
- Content 3: Investigation of the chemical composition and elucidation of the organic structures present in the aqueous and ethyl acetate extracts of the flowers, and the aqueous extract of the leaves of *B. acutangula*;
- Content 4: Assessment of the corrosion inhibition efficiency of the aqueous extracts from flowers and leaves on carbon steel in 1 M HCl solution ($\text{pH} = 0$) using electrochemical methods;
- Content 5: Surface analysis of carbon steel specimens after immersion in 1 M HCl solution, with and without the presence of the inhibitor, using advanced surface characterization techniques;
- Content 6: Quantification of isolated compounds from the aqueous flower extract using HPLC, combined with molecular dynamics (MD) simulation and adsorption isotherm models to reinforce the proposed corrosion protection mechanism for carbon steel.

Chapter 1. RESEARCH BACKGROUND

1.1. Overview of Carbon Steel

Carbon steel is an alloy primarily composed of iron and carbon (ranging from 0.02% to 2.14%), in which carbon plays a critical role in determining the hardness, strength, and wear resistance of material. In addition, carbon steel may contain minor amounts of other elements such as manganese, silicon, sulfur, and phosphorus, which can significantly influence its mechanical properties and machinability. Based on carbon content, carbon steels are generally classified into three categories: low, medium, and high carbon steels. The properties of carbon steel can be tailored through various heat treatment processes such as quenching, tempering, or annealing to optimize its hardness, strength, and toughness.

Carbon steel is widely used in various industries such as petroleum, chemical processing, wastewater treatment, and mechanical engineering due to its outstanding advantages, including low cost, ease of fabrication, high load-bearing capacity, and excellent tensile strength. However, its major drawback is its poor corrosion resistance, particularly in environments containing chloride ions or dilute acids. In the case of high-carbon steel, increased hardness often comes at the expense of brittleness, making it more susceptible to fracture under impact, and its mechanical stability also decreases at elevated temperatures. Therefore, protective measures such as surface coatings, the use of corrosion inhibitors, or alloying with elements like chromium and nickel are commonly employed to enhance the durability of material under harsh service conditions. Despite these limitations, carbon steel continues to play a pivotal role in industrial applications owing to its versatility, high performance, and cost-effectiveness.

1.2. Electrochemical corrosion

Electrochemical corrosion is the degradation of metals in an electrolyte environment, driven by simultaneous oxidation and reduction reactions occurring at the anode and cathode, respectively. These are inherently electrochemical processes involving the transfer of electrons. Four essential components are required for this process: an anode, a cathode, an electrolyte, and an electronic pathway. Corrosion proceeds when metal atoms at the anode are oxidized, releasing metal ions into the solution, while reduction reactions at the cathode, typically the reduction of H^+ ions or O_2 . In some cases, corrosion products such as oxides or hydroxides may form, leading to the development of a passive film that slows down corrosion rate. Electrochemical corrosion can manifest in various forms, including uniform corrosion, pitting corrosion, crevice corrosion, galvanic corrosion, erosion corrosion, stress corrosion cracking, intergranular corrosion, and filiform corrosion. Each type has a distinct mechanism and is influenced by both the properties of the metal and the environmental conditions. A thorough understanding of these mechanisms is essential for selecting appropriate control strategies and protective measures in industrial systems.

1.3. Methods of electrochemical corrosion protection

Electrochemical corrosion protection methods include: cathodic protection (using sacrificial anodes or impressed current to maintain the metal in a cathodic state); protective coatings (organic, inorganic, or self-healing coatings designed to act as barriers against corrosive agents); environmental control (adjusting pH, removing oxygen, and reducing corrosive ion concentrations); proper design and maintenance (selecting corrosion-resistant materials, avoiding geometries prone to corrosion, and conducting regular inspections); and the use of corrosion inhibitors (anodic,

cathodic, or mixed-type) to slow down the electrochemical reactions responsible for corrosion

1.4. Corrosion inhibitors

Corrosion inhibitors are compounds capable of slowing down the corrosion process of metals by adsorbing onto the metal surface, forming a protective film, or interfering with electrochemical reactions. They can be classified into several categories: inorganic inhibitors (chromates, phosphates,...), organic inhibitors (containing functional groups such as amino, carboxyl, or phosphonate,...adsorbing via physical or chemical interactions), hybrid inorganic-organic inhibitors (combining rare earth metals with organic ligands), and naturally derived inhibitors (flavonoids, alkaloids,...). Their mechanisms of action typically involve surface adsorption, formation of a protective film, and inhibition of electrochemical reactions, thereby reducing metal dissolution and preventing aggressive species from reaching the metal surface.

1.5. Overview of *Barringtonia acutangula*

Barringtonia acutangula, , is a woody plant species belonging to the family Lecythidaceae, predominantly distributed in South and Southeast Asia, including Vietnam. It is widely cultivated for ornamental purposes and has been recognized for its pharmacological potential, including anti-inflammatory, antibacterial, antioxidant, and enzyme inhibitory activities. Various parts of the plant such as the bark, leaves, flowers, and seeds,...are rich in bioactive organic compounds, notably flavonoids, saponins, triterpenoids, and polyphenols. However, the detailed chemical composition and potential applications of the flowers and leaves, particularly in materials science and metal corrosion inhibition, remain underexplored, offering promising opportunities for future research and technological development.

Chapter 2. RESEARCH SUBJECTS AND METHODS

2.1. Research materials

2.1.1. Sample collection and identification

Leaf and flower samples of *B. acutangula* (L.) Gaertn. were collected in October 2021 from Long Phuoc Ward, Thu Duc City, Ho Chi Minh City, Vietnam. The scientific name of the plant was verified by Dr. Dang Van Son, Institute of Science and Technology of Vietnam.

2.1.2. Chemicals and instruments

Solvents including n-hexane, dichloromethane, ethyl acetate, ethanol, and HCl. Equipment employed during extraction and chromatography procedures (Soxhlet system, TLC, HPLC, column chromatography), electrochemical measurements (VSP), surface characterization (SEM, EDX, XPS, OES, FT-IR,...) along with other supporting chemical reagents and instruments.

2.1.3. Experimental Design

The research process is displayed in Figure 2.1. Five extracts with increasing polarity (n-hexane, dichloromethane, ethyl acetate, ethanol, and aqueous) were obtained from the leaves and flowers of *B. acutangula* using Soxhlet extraction and a rotary evaporator system.

The aqueous extract was subjected to preliminary characterization to assess its potential as a corrosion inhibitor, employing total content determination of polyphenols, terpenoids, and flavonoids, as well as LC-MS and FT-IR analyses. Chemical constituents in the aqueous extracts of both flowers and leaves, as well as in the ethyl acetate extract of the flowers, were isolated *via* chromatographic methods. Their structures were elucidated using nuclear magnetic resonance (NMR) spectroscopy in combination with

literature references. Selected compounds were quantitatively determined in the extracts by HPLC. The corrosion inhibition performance of aqueous extracts from both leaves and flowers against carbon steel in 1 M HCl solution was evaluated using electrochemical techniques such as OCP, EIS, LPR, and PD. Additionally, surface morphology and composition of the steel samples before and after exposure to the inhibitor were analyzed by SEM, EDX, AFM, and XPS. The elemental composition of the experimental steel was determined *via* OES. Based on the electrochemical data and surface analysis, the corrosion and inhibition mechanisms were proposed. Molecular modeling calculations based on isolated pure compounds, combined with adsorption isotherm analysis, were employed to reinforce the proposed inhibition mechanisms.

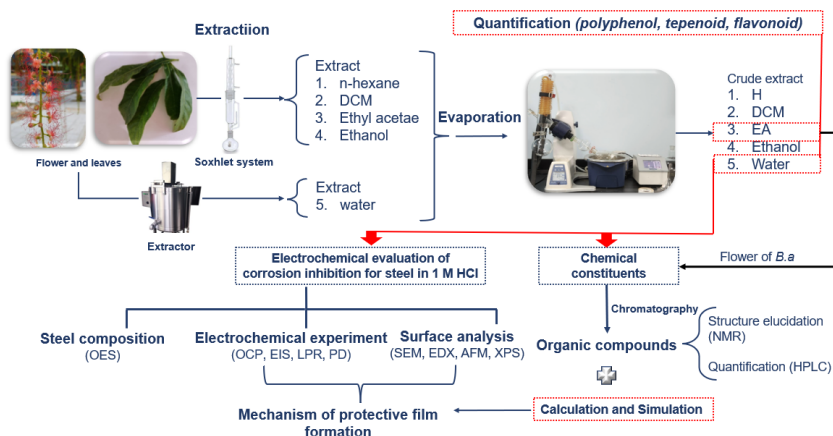


Figure 2.1. Experimental design of the study.

2.2. Experimental Methods

The experimental methods employed in this study include: qualitative analyses such as the determination of total polyphenol content using the Folin-Ciocalteu method, total terpenoid content *via* the vanillin assay, and total flavonoid content based on a colorimetric reaction with

aluminum chloride (AlCl_3); methods for compound isolation and structural elucidation involving thin-layer chromatography (TLC), column chromatography, and nuclear magnetic resonance (NMR) spectroscopy; quantitative analysis performed using high-performance liquid chromatography (HPLC); electrochemical techniques including open-circuit potential (OCP), electrochemical impedance spectroscopy (EIS), linear polarization resistance (LPR), and potentiodynamic polarization (PD); surface characterization methods including scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), and X-ray fluorescence spectroscopy (XRF); and theoretical approaches including quantum chemical calculations and molecular dynamics simulations. In addition, the adsorption behavior of the inhibitor molecules on the metal surface was analyzed through adsorption isotherm models, including Langmuir, Flory–Huggins, El-Awady, and Freundlich isotherms.

Chapter 3. RESULTS AND DISCUSSION

3.1. Evaluation of extract composition and properties

3.1.1. Chemical composition and characteristics of the aqueous extract

In the investigation of natural corrosion inhibitors for metals, the assessment of the composition and physicochemical properties of the aqueous extract prior to conducting electrochemical experiments plays an important role. The chemical constituents present in the aqueous extract largely determine the inhibition mechanism by influencing the adsorption behavior on the metal surface and affecting redox reactions occurring in the corrosive environment..

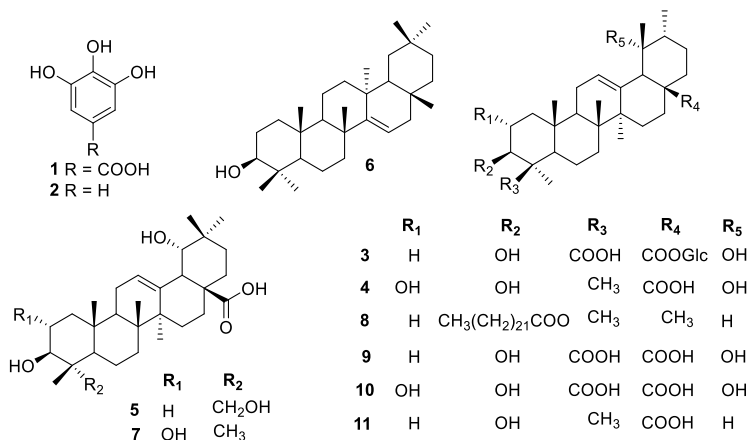


Figure 3.1. Chemical structures of eleven compounds isolated from the flowers and leaves of *B. acutangula*.

FT-IR results revealed that the aqueous extracts of *B. acutangula* flowers and leaves contain key functional groups such as hydroxyl (-OH), carbonyl (-C=O), carbon-carbon double bonds (-C=C-), and ether linkages (-C-O-), indicating their potential to adsorb onto metal surfaces and form

protective films. Quantitative analysis of the total constituents showed that the aqueous leaf extract exhibited significantly higher levels of flavonoids and polyphenols than the flower extract. Specifically, the total flavonoid content in the leaf extract reached 852.25 ± 38.89 mg/g, approximately 2.8 times higher than that of the flower extract, while the total polyphenol content was measured at 261.13 ± 12.34 mg GAE/g. These components suggest strong antioxidant activity and the ability to facilitate the formation of a protective layer on the metal surface. LC-MS analysis identified several organic compounds with potential corrosion-inhibiting properties. The aqueous flower extract contained Gamabufotalin, Bufotalin, and Vobassan-17-oic acid, whereas the aqueous leaf extract contained Beclomethasone, Cortisone, Rescinnamine, and Pregn-4-ene-3,20-dione. Additionally, auto-chromatography-MS detected various polyphenolic compounds such as brevifolin carboxylate, galloyl glucose, quinic acid, and gallic acid in both types of aqueous extracts, thereby enhancing antioxidant activity and metal protection.

Comprehensive chemical profiling was conducted on the aqueous extracts of both flowers and leaves, and major constituents in the ethyl acetate extract of *B. acutangula* flowers were also characterized. A total of eleven compounds were isolated and structurally elucidated based on spectroscopic methods (NMR) in conjunction with comparison to existing literature. Specifically, gallic acid (1), pyrogallol (2), and ilexaponin A1 (3) were isolated from the aqueous flower extract; gallic acid (1), arjunic acid (4), ilexosapogenin A (5), taraxerol (6), tormentic acid (7), and Urs-12-en-3-ol, 3-docosanoate (8) were identified in the aqueous leaf extract; while ilexgenin A (9), $2\alpha,3\beta,19\alpha$ -trihydroxy-urs-12-ene-23,28-dioic acid (10), and ursolic acid (11) were obtained from the ethyl acetate extract of the flowers

(Figure 3.1). To date, all eleven isolated compounds are reported here for the first time as constituents identified from *B. acutangula*.

3.1.2. Simulation Analysis

In this study, simulation methods (DP4+ and MD) were employed to investigate in detail the corrosion inhibition potential of isolated compounds from the aqueous extracts of *B. acutangula* leaves and flowers on carbon steel surfaces. Compounds such as gallic acid (GA) and ilexaponin A1 (ISA1) were specifically evaluated through Boltzmann distribution analysis and binding energy calculations, as presented in Table 3.1.

Table 3.1. Binding energy calculations for the adsorption of gallic acid (GA) and ilexaponin A1 (ISA1) on the Fe(110) surface.

	E_{all}	$E_{sub+sol}$	$E_{inh+sol}$	E_{sol}	E_b	E_b
	(kcal/mol)	(kcal/mol)	(kcal/mol)	(kcal/mol)	(kcal/mol)	(eV)
GA (1)	-89667,79	-89511,24	-7728,96	-7669,41	-97,00	-4,21
ISA1 (2)	-89215,09	-88928,65	-7704,84	-7672,45	-254,06	-11,02

Table 3.2. Binding energy calculations for the adsorption of arjunic acid (AJA), tormentic acid (TMA), ilexosapogenin A (ILSG), 3 β -docosanoyloxy-urs-12-ene (DUE), and taraxerol (TX) on the Fe(110) surface.

	E_{all}	$E_{sub+sol}$	$E_{inh+sol}$	E_{sol}	E_b	E_b
	(kcal/mol)	(kcal/mol)	(kcal/mol)	(kcal/mol)	(kcal/mol)	(eV)
AJA (4)	-	-	-	-	-	-
ILSG(5)	-90008,81	-89874,61	-7843,82	-7822,88	-113,26	-2,91
TX (6)	-	-	-	-	-	-
TMA (7)	-89854,99	-89812,69	-7710,00	-7672,40	-4,69	-0,2
DUE (8)	-	-	-	-	-	-

The simulation results indicated that ISA1 exhibited a stronger adsorption affinity to the carbon steel surface compared to GA, which facilitate the formation of a more stable protective film. The calculated binding energies of GA and ISA1 confirmed their effectiveness as corrosion inhibitors. Additionally, the simulations revealed that gallic acid, when interacting with terpenoid compounds present in the aqueous leaf extract, plays a pivotal role in enhancing corrosion inhibition efficiency. However, these compound including AJA, TMA, and DUE exhibited negligible corrosion inhibition effects (Table 3.2). Overall, the simulation outcomes affirm that the synergistic interaction between organic constituents, particularly gallic acid and ilexaponin A1 is a key factor in forming an effective protective film on the steel surface, thereby improving corrosion resistance in 1 M HCl acidic medium.

3.2. Electrochemical analysis results

3.2.1. Corrosion inhibition efficiency of flower extract (BAFE)

The EIS results revealed the influence of the corrosion inhibitor BAFE on the total impedance of carbon steel in 1 M HCl solution. The Nyquist plots exhibited, in the absence of BAFE, the steel exhibited very low impedance, indicating severe corrosion. In contrast, upon the addition of BAFE at concentrations ranging from 500 to 4000 ppm, the impedance increased progressively with concentration, indicating the formation of a protective layer on the steel surface. However, at 4000 ppm, the stability of the protective film tended to decline, likely due to aggregation and rapid precipitation phenomena. The Bode plots provided additional insight into impedance magnitude and phase angle across the frequency spectrum, further confirming the corrosion-inhibitive capability of BAFE. Equivalent circuit analysis of resistance and capacitance elements revealed that at 3000 ppm, the extract achieved optimal inhibition performance, attributed to the

formation of a uniform adsorbed film that effectively suppressed corrosion current density. These findings confirm that BAFE is an effective corrosion inhibitor for carbon steel in acidic environments, with the optimal concentration at 3000 ppm.

Table 3.3. Corrosion parameters obtained by Tafel extrapolation from potentiodynamic polarization measurements.

Conc (ppm)	E_{corr} (mV _{Ag/AgCl})	i_{corr} ($\mu\text{A}/\text{cm}^2$)	β_a (mV/decade)	$-\beta_c$ (mV/decade)	η (%)
0	-420 ± 8	$2377,34 \pm 271,51$	189 ± 15	218 ± 7	-
500	-504 ± 16	$203,51 \pm 51,28$	185 ± 14	114 ± 5	$90,91 \pm 3,25$
1000	-485 ± 36	$137,61 \pm 31,91$	174 ± 17	109 ± 7	$93,80 \pm 2,03$
2000	-481 ± 36	$127,16 \pm 33,61$	127 ± 15	90 ± 7	$94,21 \pm 2,06$
3000	-503 ± 18	$88,66 \pm 18,52$	119 ± 16	84 ± 8	$96,00 \pm 1,20$
4000	-494 ± 21	$112,80 \pm 21,12$	175 ± 19	109 ± 6	$94,90 \pm 1,40$

Table 3.4 presents the corrosion inhibition efficiency (% η) of BAFE at various concentrations, determined using EIS, LPR, PD, and weight loss (WL) methods. In all applied methods, BAFE consistently exhibited a similar trend in inhibition performance. The inhibition efficiency increased progressively as BAFE concentration rose from 0 ppm to 3000 ppm. At 0 ppm, no inhibition effect was observed ($\eta = 0\%$). However, upon the addition of BAFE, the efficiency improved markedly, reaching its maximum at 3000 ppm with values of 94.55% (EIS), 91.88% (LPR), 94.89% (PD), and 96.86% (WL). This increase reflects the effectiveness of BAFE in reducing the corrosion rate through an adsorption-based mechanism on the steel surface. At 4000 ppm, the efficiency tended to slightly decline, for example, EIS values decreased from 94.55% to 93.93% indicating that the optimal concentration of BAFE is 3000 ppm. This observation is consistent with the trend of increasing polarization resistance (R_p) and decreasing corrosion

current density (i_{corr}) with increasing inhibitor concentration, particularly evident in EIS and PD analyses. In the case of BAFE, the inhibition efficiency derived from R_p values did not differ significantly from that based on i_{corr} , suggesting that the presence of BAFE in 1 M HCl ($\text{pH} \approx 0$) does not alter the acidity of the medium. Consequently, the inhibition mechanism of BAFE primarily relies on surface adsorption and the formation of a thin protective film that hinders charge transfer at the carbon steel/electrolyte interface.

Table 3.4. Corrosion inhibition efficiency of BAFE evaluated using different methods.

Conc ppm	EIS		LPR		PD		WL	
	R_p	η (%)	R_p	η (%)	i_{corr} ($\mu\text{A}/\text{cm}^2$)	η (%)	m_{TB} (g)	η (%)
0	15,54	0	20,3	0	2377,34	0	0,2273	0
500	130,49	88,09	104,25	80,53	203,51	90,91	0,0194	91,44
1000	195,47	92,05	186,5	89,12	137,61	93,80	0,0148	93,49
2000	243,88	93,63	208,0	90,24	127,16	94,21	0,0107	95,31
3000	284,87	94,55	250,0	91,88	88,66	96,00	0,0098	95,70
4000	256,06	93,93	236,5	91,42	112,80	94,90	0,0107	95,29

3.2.2. Corrosion inhibition efficiency of leaf extract (BALE)

The electrochemical analysis of BALE is presented through Nyquist and Bode plots. The Nyquist diagrams showed that the overall impedance of the system increased as the concentration of BALE increased from 500 to 3000 ppm, followed by a slight decrease at 4000 ppm. This trend reflects the corrosion inhibition capability of BALE, with the optimal concentration identified at 3000 ppm. Notably, at 3000 and 4000 ppm, the presence of two capacitive semicircles during the first 4 hours, which later merged into one,

indicated the progressive formation of a protective film on the steel surface. The Bode plots confirmed the trend of increasing low-frequency impedance, with phase angles approaching 90° , suggesting the formation of a stable and adherent protective layer on the steel surface. Potentiodynamic polarization measurements revealed that BALE functions as a mixed-type inhibitor with a predominant effect on the cathodic reaction. The corrosion current density decreased sharply with increasing BALE concentration, reaching a maximum inhibition efficiency of 96.56% at 3000 ppm. Tafel extrapolation showed a significant decrease in i_{corr} even at 500 ppm, from 3335.7 to 374.93 $\mu\text{A}/\text{cm}^2$ and inhibition efficiencies exceeding 90% were achieved at concentrations above 1000 ppm. Although the maximum inhibition was observed at 3000 ppm, a slight decline at 4000 ppm was noted.

Table 3.5. Corrosion parameters obtained by Tafel extrapolation from potentiodynamic polarization measurements.

Conc (ppm)	E_{corr} (mV _{Ag/AgCl})	i_{corr} ($\mu\text{A}/\text{cm}^2$)	β_a (mV/decade)	$-\beta_c$ (mV/decade)	η (%)
0	$-425 \pm 3,3$	$3335,7 \pm 10,4$	$174 \pm 23,1$	$205,4 \pm 7,3$	-
500	$-498 \pm 0,5$	$274,58 \pm 10,71$	$161,0 \pm 2,0$	$96,50 \pm 3,5$	$87,92 \pm 0,32$
1000	$-507 \pm 11,5$	$223,09 \pm 11,69$	$136,0 \pm 4,0$	$92,5 \pm 1,5$	$89,69 \pm 0,61$
2000	$-504 \pm 3,5$	$217,29 \pm 13,64$	$123,5 \pm 1,5$	$87,5 \pm 1,5$	$91,61 \pm 0,06$
3000	$-514 \pm 6,7$	$107,9 \pm 3,8$	$113,0 \pm 9,5$	$89,7 \pm 10,3$	$96,56 \pm 0,12$
4000	$-497 \pm 6,5$	$156,36 \pm 7,87$	$144,5 \pm 10,5$	$92 \pm 2,0$	$92,91 \pm 0,125$

The results obtained from EIS, LPR, PD, and weight loss measurements all exhibited consistent trends, further confirming the surface protection capability of BALE on carbon steel. As the concentration increased from 500 to 3000 ppm, the inhibition efficiency improved across all methods. However, a slight decline or plateau was observed at 4000 ppm.

These findings suggest that 3000 ppm represents the optimal concentration, providing high inhibition efficiency without unnecessary excess of inhibitor. The corrosion and protection mechanisms of BALE will be discussed in greater detail in the following sections.

Table 3.6. Corrosion inhibition efficiency of BALE evaluated using different methods.

Conc ppm	EIS		LPR		PD		WL	
	R _p	η (%)	R _p	η (%)	i _{corr} (μA/cm ²)	η (%)	m _{TB} (g)	η (%)
0	10,93	0	12,8	0	3335,7	0	0.2554	0
500	81,41	81,41	76,9	83,36	274,58	87,92	0.0154	93,18
1000	113,43	90,36	79,9	83,99	223,09	89,69	0.0094	95,84
2000	142,30	92,32	106,2	87,95	217,29	91,61	0.0079	96,51
3000	142,71	92,34	143,0	91,05	107,9	96,56	0.0071	96,86
4000	123,68	91,16	125,5	89,80	156,36	92,91	0.0088	96,10

3.3. Surface analysis results

3.3.1. Surface characterization of steel after treatment with aqueous flower extract of *B. acutangula*

The surface morphology of carbon steel after 24 hours of immersion in 1 M HCl solution containing the corrosion inhibitor derived (BAFE) were examined using SEM, AFM, EDS, and XPS techniques. SEM images revealed severe surface degradation in the absence of BAFE, while protective surface layers were observed at BAFE concentrations ranging from 500 to 4000 ppm, characterized by aggregated particle deposition. The density and size of these surface particles increased with BAFE concentration, reaching a maximum at 3000 ppm and slightly decreasing at 4000 ppm, this is consistent with EIS results, which showed a decline in

impedance at higher concentrations. EDS analysis confirmed the presence of Cl, O, C, and Fe on the steel surface. The elevated carbon content indicated that the protective layer was predominantly composed of organic compounds from the inhibitor. AFM analysis demonstrated the formation of a protective film with a root mean square (Rms) roughness of 10.30 nm, indicating a substantial reduction in surface corrosion. XPS spectra identified key corrosion products such as Fe_2O_3 and FeOOH , and confirmed interactions between Fe ions and oxygen-containing functional groups (e.g., $-\text{OH}$, $-\text{COOH}$, and $-\text{C}=\text{O}$) present in the organic compounds of BAFE. The corrosion inhibition mechanism of BAFE involves the adsorption of these functional groups onto the steel surface, forming coordination complexes with Fe ions that hinder iron oxidation in the highly acidic environment. The combined XPS and EDS data support this proposed mechanism, demonstrating the formation of a stable protective film that effectively reduces corrosion in 1 M HCl solution.

3.3.2. Surface characterization of steel after treatment with aqueous leaf extract of *B. acutangula*

AFM analysis of carbon steel immersed in 1 M HCl solution containing 3000 ppm of BALE demonstrated the effective formation of a protective organic layer, with a surface roughness (Rms) of 14.3 nm. SEM images showed that in the absence of the inhibitor, the steel surface was severely corroded. Upon the addition of BALE at concentrations ranging from 500 to 2000 ppm, corrosion was significantly reduced. At 3000 ppm, the steel surface appeared smoother and was uniformly covered by protective particles. However, at 4000 ppm, the deposited particles became smaller and unevenly distributed, which explains the slightly reduced inhibition efficiency observed at this concentration. EDS spectra indicated that at 3000 ppm BALE, characteristic peaks of Si, P, and Cl were suppressed, suggesting

the formation of an organic coating that effectively covered the steel surface. The protective film was composed of oxygen-rich organic compounds containing functional groups such as -OH, -COOH, and -COOR. XPS analysis confirmed the presence of C, Cl, Fe and O on the inhibited steel surface, with Fe predominantly existing in oxidized forms such as Fe^{3+} (Fe_2O_3 , Fe_3O_4 , FeOOH). The C 1s and O 1s spectra showed characteristic peaks corresponding to functional groups including -C-O, -COO-, and -C=O, which are indicative of a protective organic layer that inhibits metal dissolution. The Cl 2p spectrum confirmed the presence of chloride ions on the steel surface, while P and N elements were not detected. Overall, the results obtained from AFM, SEM, EDS, and XPS analyses consistently demonstrated the formation of an organic protective film on the steel surface, in agreement with previous electrochemical findings.

3.4. Corrosion and Inhibition Mechanisms

3.4.1. Comparative inhibition performance of aqueous flower and leaf extracts of *B. acutangula*

OES analysis (Table 3.7) revealed that the steel sample used in the experiment with *B. acutangula* flower extract exhibited a higher carbon content (0.0430% compared to 0.0350%), other minor elements have differences but not too significant. To ensure a fair comparison, the potentiodynamic polarization (PD) experiment for the flower extract at 3000 ppm was repeated using the same steel type as that used with the leaf extract. The results showed a corrosion inhibition efficiency of 97.08% for the flower extract, slightly higher than the 96.56% obtained for the leaf extract. This marginal difference reflects the similar chemical composition of the two extracts, both of which contain aromatic ring-based compounds and terpenoids.

Table 3.7. Corrosion parameters obtained by Tafel extrapolation from potentiodynamic polarization measurements using the optimal concentration of 3000 ppm of the aqueous flower and leaf extracts of *Barringtonia acutangula*.

Conc ppm		E_{corr} (mV _{Ag/AgCl})	i_{corr} ($\mu\text{A}/\text{cm}^2$)	β_a (mV/decade)	$-\beta_c$ (mV/decade)	η (%)
3000	L1	-517	108,11	102	69	96,57
	L2	-501	115,45	132	95	96,32
	Lá	L3	-525	100,26	105	96,78
	Tb	-514,4 ± 6,7	107,9 ± 3,8	113,0 ± 9,5	89,7 ± 10,3	96,56 ± 0,12
3000	L1	-509	98,21	72	49	97,06
	L2	-498	93,01	88	63	97,21
	Hoa	L3	-497	101,39	149	96,96
	Tb	-501,3 ± 3,8	97,5 ± 2,3	103 ± 23,0	72,3 ± 16,3	97,08 ± 0,07

3.4.2. Adsorption isotherms applied in the corrosion inhibition study of aqueous flower extract of *B. acutangula*

The corrosion inhibition behavior of aqueous *Barringtonia acutangula* flower extract (BAFE) on carbon steel in 1 M HCl was evaluated through adsorption isotherms and electrochemical analysis. Langmuir, Flory–Huggins, El-Awady, and Freundlich models were applied, with Langmuir showing the best fit ($R^2 = 0.9994\text{--}0.99991$), indicating monolayer chemisorption. Calculated ΔG_{ads}^0 values (-58.15 to -62.27 kJ/mol) confirmed spontaneous, strong adsorption. Increasing temperature reduced adsorption affinity (lower K_{ads}), and Flory–Huggins and El-Awady models suggested possible multi-site and polymolecular adsorption at elevated temperatures. Polarization results revealed that BAFE effectively reduced corrosion rates, with maximum inhibition (at 3000 ppm) declining slightly at

4000 ppm and high temperatures. Thermodynamic studies using Arrhenius and transition state theory showed increased activation energy (E_a) and enthalpy (ΔH), while entropy (ΔS) remained negative but less so in the presence of BAFE, indicating the formation of a more ordered, protective adsorbed layer.

3.4.3. Corrosion and Inhibition Mechanism

The corrosion inhibition mechanisms of the aqueous flower and leaf extracts of *Barringtonia acutangula* (BAFE and BALE, respectively) are largely similar, both functioning primarily through the formation of an adsorbed organic film on the steel surface. In 1 M HCl solution, carbon steel undergoes electrochemical corrosion, especially at defect sites, due to localized potential differences. In the absence of inhibitors, the corrosion process proceeds aggressively, as evidenced by high corrosion current densities and SEM images revealing severe surface rust formation. Upon addition of the plant extracts, active organic molecules rapidly adsorb onto the steel surface, particularly at anodic sites, facilitated by polar functional groups such as $-\text{OH}$, $-\text{COOH}$, and $-\text{C}=\text{O}$. This adsorbed organic film reduces the contact between the metal surface and aggressive Cl^- ions, thereby impeding charge transfer and ion diffusion processes, ultimately decreasing the corrosion rate. At the optimal concentration of 3000 ppm, the inhibition efficiencies reached 97.08% (flower extract) and 96.56% (leaf extract), with significantly increased impedance values and substantial reductions in corrosion current density. EDS and XPS analyses confirmed the accumulation of carbon and oxygen elements on the inhibited steel surface, providing direct evidence for the formation of an adsorbed organic layer. Due to the presence of functional groups capable of electronic interactions with Fe^{n+} ions, the major compounds in both extracts undergo chemisorption, forming a stable protective film. Molecular dynamics (MD)

simulations and adsorption energy (E_b) calculations demonstrated that gallic acid and ilex saponin A1 possess superior adsorption behavior and corrosion protection capability. In contrast, although certain triterpenoids from the leaf extract exhibited theoretical potential, they showed limited adsorption stability. The synergistic interaction between simple aromatic compounds and triterpenoids plays a critical role in the overall inhibition performance. The slight decline in efficiency at 4000 ppm is attributed to saturation effects and decreased molecular adsorption at excessively high concentrations. Integration of experimental data with simulation results indicates that the flower extract offers superior inhibition performance, owing to its content of high-binding-energy compounds and optimal molecular adsorption configurations.

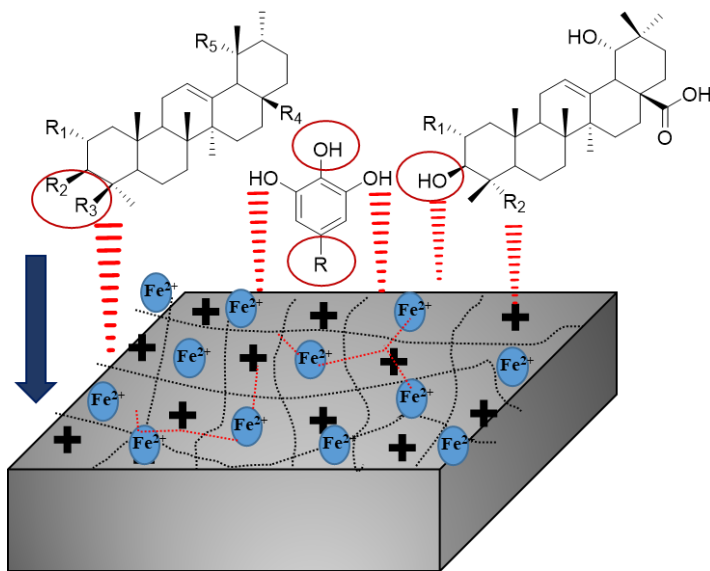


Figure 3.2. Mechanism of protective film formation on the steel surface.

CONCLUSIONS AND RECOMMENDATION

CONCLUSION

Aqueous flower and leaf extracts of *Barringtonia acutangula* were chemically characterized and evaluated for their corrosion inhibition performance on carbon steel in 1 M HCl. This study is among the first to integrate advanced spectroscopy, electrochemical techniques, and molecular simulations to elucidate inhibition mechanisms. Eleven compounds were isolated, including newly reported constituents, with ilexaponin A1 showing superior theoretical inhibition efficiency ($E_b = -11.02$ eV) due to its extensive surface interaction and multiple polar groups. Both extracts acted as mixed-type inhibitors with predominant cathodic behavior, achieving optimal efficiencies at 3000 ppm: 96.00% (flower) and 96.56% (leaf). Electrochemical results were consistent with surface analyses (SEM, XPS, EDS, AFM), confirming the formation of a stable protective film. Adsorption followed chemisorption-dominated monolayer behavior, supported by isotherm modeling. Thermodynamic parameters indicated that the inhibitor reduced system disorder through protective film formation, with optimal surface coverage observed at 3000 ppm.

RECOMMENDATIONS

Other parts of *B. acutangula*, such as seeds, stems, bark, and roots, warrant further investigation as potential sources of corrosion inhibitors. Future research should focus on both crude extracts and isolated active compounds, with corrosion performance evaluated under diverse and industrially relevant conditions to enhance practical applicability.

NOVEL CONTRIBUTIONS OF THE DISSERTATION

This dissertation represents one of the pioneering studies on demonstrating the presence and functional role of key bioactive constituents

in the extracts using advanced, high-precision analytical techniques, thereby contributing to resolving ongoing debates within the field of corrosion science.

Notably, this study is among the few to concurrently integrate both experimental investigations and computational simulations, combined with physicochemical modeling, to elucidate the adsorption mechanisms and surface protection behavior. The methodologies employed include state-of-the-art, highly sensitive techniques, which significantly enhance the accuracy and academic value of the results.

Both flower and leaf extracts of *B. acutangula* exhibited excellent corrosion inhibition efficiency (> 96%) at the optimal concentration of 3000 ppm, attributed to the formation of a stable organic adsorption film on the carbon steel surface. From a scientific perspective, these findings provide robust foundational data supporting the development of natural product-based corrosion inhibitors. Practically, the extracts of *B. acutangula* demonstrate strong application potential in acid-utilizing industries such as petrochemicals and metallurgy, while also promoting the sustainable exploitation of local biological resources in alignment with circular economy principles and long-term environmental sustainability.

LIST OF PUBLICATIONS

1. **Thanh-Nha Tran**, Nguyen Si Hoai Vu, Thien Tri Tran, Deok Su Jo, Thanh Liem Huynh, Thi-Thao-Van Nguyen, Casen Panaitescu, Hoa Thi Thu Nguyen, Van-Kieu Nguyen, Nam Dang Nguyen*. “*Precise major compounds in Barringtonia Acutangula flower – water extract for mitigating carbon steel corrosion*”. Journal of the Taiwan Institute of Chemical Engineers. 155(2024), 105251. <https://doi.org/10.1016/j.jtice.2023.105251>
2. **Thanh-Nha Tran**, Thien Tri Tran, Deok Su Jo, Phan-Si-Nguyen Dong, Van-Kieu Nguyen, Thanh Liem Huynh, Nam Nguyen Dang*. “*Self-formation of protective layer on carbon steel surface in 1 M HCl solution containing Barringtonia acutangula leaf extract*”. Journal of Industrial and Engineering Chemistry 135 (2024) 175-187. <https://doi.org/10.1016/j.jiec.2024.01.030>
3. Ngoc-Van-Trang Dao, Minh-Khanh Nguyen, Phan-Si-Nguyen Dong, Hoang-Vinh-Truong Phan, Vu-Duy Nguyen, Thi-Kim-Dung Leg, Le-Thuy-Thuy-Trang Hoang, Dinh-Tri Mai, Warinthorn Chavasiri, Van-Kieu Nguyend, **Thanh-Nha Tran***, Vo-Thi-Minh Thao*. “*Effect of different solvents on bioactive phenolics and antioxidant, antimicrobial, and α -glucosidase inhibition activities of Barringtonia acutangula Gaertn. flower extracts*”. Natural Product Research (2025) 1-10. <https://doi.org/10.1080/14786419.2025.2486322>
4. Oral presentation at an international conference in Romania: “75 Years of Energy and Performance in Education and Research 2023, Renewable Versus Fossil Fuels. Global Energy Perspectives,

November 8-10, 2023. Ploiesti, Rumania” with the title of the presentation “*Precise major compounds in Barringtonia acutangula flower – water extract for mitigating carbon steel corrosion*”.