MINISTRY OF EDUCATION AND TRAINING

VIETNAM ACADEMY OF SCIENCE AND TECHNOLOGY

GRADUATE UNIVERSITY OF SCIENCE AND TECHNOLOGY

DAO THI BICH NGOC

RESEARCH ON CORROSION INHIBITOR SYSTEMS FROM CHLORIDE SALTS OF RARE EARTH METALS AND POLAR BETEL LEAF EXTRACT FOR CARBON STEEL IN AN ENVIRONMENT CONTAINING CARBON DIOXIDE AND CHLORIDE IONS

SUMMARY OF DISSERTATION ON SCIENCES OF MATTER

Major: Organic Chemistry

Code: 9 44 01 14

Ha Noi - 2026

The dissertation is completed at: Graduate University of Science and Technology, Vietnam Academy Science and Technology

Supervisors:

1. Supervisor 1: Assoc. Prof. Dr. Nguyen Dang Nam, Institute of Fundamental and Applied Sciences – Duy Tan University;

2. Supervisor 2: Prof. Dr. Tran Ngoc Quyen - Institute of Advanced Technology - Vietnam Academy of Science and Technology

Referee 1:

Referee 2:

The dissertation is examined by Examination Board of Graduate University of Science and Technology, Vietnam Academy of Science and Technology at ….. (date ….).

The dissertation can be found at:

1. Graduate University of Science and Technology Library

2. National Library of Vietnam

INTRODUCTION

1. Urgency of the thesis

Steel is the most widely used engineering material in modern industry, particularly in oil and gas transportation systems, pipelines, petrochemical facilities, and wastewater treatment plants, owing to its low cost and outstanding mechanical properties, including high strength, good ductility, ease of fabrication, and excellent load-bearing capacity. Despite these advantages, corrosion in environments containing chloride ions (Cl^-) and carbon dioxide (CO_2) remains a major challenge, leading to the progressive deterioration of steel infrastructure. The simultaneous presence of Cl^- and CO_2 exerts a synergistic effect that markedly accelerates corrosion, resulting in significant economic losses, increased maintenance costs, and potential safety hazards. Consequently, the development of efficient and sustainable corrosion inhibitors has become an important research priority. Based on the structure–property relationships of corrosion inhibitors, this study proposes a synergistic inhibitor system by combining surface-active natural organic compounds isolated from betel leaves with rare-earth metal salts. The synergistic interaction between these components promotes their adsorption onto the steel surface, facilitating the formation of a stable and durable protective film that effectively suppresses corrosion. Beyond improving corrosion resistance, the proposed inhibitor system provides a safer, more sustainable, and environmentally benign alternative to conventional corrosion inhibitors, which are often toxic and costly.

The integration of natural organic compounds with rare-earth metal salts represents a novel research direction in Vietnam, combining

advanced concepts from chemistry, natural product chemistry, and physical chemistry into a unified corrosion protection strategy. Beyond evaluating corrosion inhibition performance, this research seeks to elucidate the underlying protection mechanisms through advanced electrochemical techniques, including open-circuit potential (OCP), electrochemical impedance spectroscopy (EIS), potentiodynamic polarization, and the wire beam electrode (WBE) technique. Furthermore, the study addresses the growing demand for green and sustainable technologies by developing environmentally benign corrosion inhibitors that reduce reliance on toxic chemicals. Consequently, the development of a new generation of corrosion inhibitor systems for carbon steel has become increasingly important. This need is particularly urgent in Vietnam, where oil and gas transportation systems, industrial wastewater treatment facilities, and engineering infrastructures are increasingly affected by premature corrosion in Cl^- and CO_2 - containing environments, while no corrosion protection technology has yet achieved a satisfactory balance of high efficiency, cost-effectiveness, and environmental safety.

2. Research objectives of the thesis

- To develop novel, environmentally friendly corrosion inhibitors for steel in complex CO_2 and chloride-containing corrosive environments using natural compounds and rare-earth metal salts as promising corrosion-inhibiting agents;
- To investigate the process of protective layer formation over time using electrochemical techniques and surface analysis;

- To comprehensively evaluate the corrosion inhibition efficacy of the proposed/complement inhibitor systems and elucidate their inhibition mechanisms;
- To establish an interdisciplinary research framework integrating theoretical analysis, natural product chemistry, electrochemistry, and corrosion science to advance the development of corrosion inhibitor systems for CO_2 –induced corrosion.

3. The main research contents of the thesis

The dissertation includes an Introduction, Chapter 1: Research Overview, Chapter 2: Research Subjects and Methods, Chapter 3: Results and Discussion, Conclusion and Recommendations, List of Published Works, Appendix, and References. The main contents covered include:

Content 1: Literature review and evaluation of the corrosion inhibition potential of selected subjects;

Content 2: Acquisition and preparation of corrosion inhibitors

- Acquisition of rare-earth metal salts ($CeCl_3$, $LaCl_3$ and $PrCl_3$);
- Collection, taxonomic identification, and preparation of a polar extract from betel (*Piper betle* L.) leaves;

Content 3: Characterization of the betel leaf extract by determining its total polyphenol content and using Fourier-transform infrared (FTIR) spectroscopy. Isolation of hydroxychavicol from the betel leaf extract and quantification of its content by high-performance liquid chromatography (HPLC);

Content 4: Evaluation of the corrosion inhibition performance of the polar betel leaf extract, isolated organic compound-hydroxychavicol, rare-earth metal salts ($CeCl_3$, $LaCl_3$ and $PrCl_3$), and synergistic inhibitor systems consisting of rare-earth metal salts and

hydroxychavicol by using electrochemical techniques in chloride-containing, CO_2-saturated corrosive environments;

Content 5: Characterization of steel surfaces after immersion in the test solution in the absence and presence of corrosion inhibitors using surface analytical techniques;

Content 6: Investigation of the ability of the inhibitor systems to suppress localized corrosion using the wire beam electrode (WBE) technique and elucidation of the protection mechanism based on combined electrochemical and chemical interactions.

CHAPTER 1. OVERVIEW

1.1. Overview of mild steel

Mild steel, also known as low-carbon steel, typically contains 0.05–0.30 wt.% carbon and is one of the most widely used engineering materials due to its low cost and favorable combination of mechanical properties. Despite its relatively low carbon content, mild steel provides adequate tensile, compressive, and flexural strength, together with good hardness and ductility, making it suitable for a wide range of structural and engineering applications. In manufacturing and mechanical engineering, it is extensively used for fabricating components that require precise forming and welding. Its excellent formability allows easy cutting, drilling, machining, and shaping into complex geometries, making it well suited for both manual and automated manufacturing processes. The major limitation of mild steel is its poor corrosion resistance, particularly in chloride-containing and CO_2-rich environments. Nevertheless, it remains the material of choice in many industrial applications, especially in the oil and gas industry, because of its favorable balance of mechanical strength, toughness, weldability, and cost. These properties arise from its low carbon content (typically 0.05–0.25 wt.%), where interstitial carbon atoms strengthen the iron matrix while maintaining sufficient ductility and toughness. Furthermore, compared with high-alloy steels, stainless steels, and composite materials, mild steel offers a significantly lower cost, making it the most economically attractive option for large-scale industrial applications.

1.2. CO_2 corrosion in the presence of Cl^- ions

When dissolved in water, CO_2 undergoes hydration to form carbonic acid (H_2CO_3), which subsequently dissociates into HCO_3^-, CO_3^{2-}, and

H^+ ions. The resulting decrease in pH promotes the electrochemical corrosion of metals. Chloride ions (Cl^-) are particularly aggressive because they destabilize passive films, penetrate surface defects, and accelerate localized corrosion, especially pitting corrosion. Electrochemical analysis provides insight into the feasibility of corrosion reactions and the formation of corrosion products. CO_2 corrosion may occur in several forms, including uniform, pitting, atmospheric, and erosion–corrosion, depending on the material and environmental conditions. Understanding these mechanisms is essential for developing effective corrosion protection strategies.

1.3. Methods for minimizing CO_2 corrosion

Various strategies have been developed to mitigate CO_2 corrosion, including the selection of corrosion-resistant materials, environmental control (e.g., pH, temperature, pressure, flow rate, and corrosive ion concentration), protective coatings (metallic, inorganic, and organic), and corrosion inhibitors. Among these approaches, corrosion inhibitors are considered one of the most practical and cost-effective solutions because they can be introduced directly into operating systems without interrupting production or requiring structural modifications. Their effectiveness is primarily attributed to the formation of protective films through physical and/or chemical adsorption on the metal surface. When appropriately selected for the service environment, corrosion inhibitors can provide excellent corrosion protection, often achieving inhibition efficiencies exceeding 90%.

1.4. CO_2 corrosion inhibitor

CO_2 corrosion inhibitors are chemical compounds or mixtures added to CO_2-containing corrosive environments to reduce the corrosion rate

of metallic materials. Their inhibition performance primarily relies on physical and/or chemical adsorption onto the metal surface, forming a protective film that suppresses electrochemical corrosion reactions. Based on their origin, corrosion inhibitors can be classified into inorganic inhibitors, organic inhibitors, ionic liquids, and natural product-based inhibitors. Despite their different compositions, these inhibitors generally function by forming protective adsorbed films that reduce metal dissolution and hinder the access of corrosive species to the metal surface.

1.5. Overview of the betel plant

Betel (*Piper betle* L.), a climbing plant of the Piperaceae family widely cultivated in Vietnam and other Asian countries, is rich in bioactive compounds such as polyphenols, flavonoids, alkaloids, and tannins. These compounds contain functional groups (e.g., –OH, –NH, and aromatic rings) that readily adsorb onto metal surfaces through physical and chemical interactions, forming protective films against corrosion. Consequently, betel leaf extract has attracted considerable attention as an environmentally friendly corrosion inhibitor for electrochemical systems.

1.6. Overview of rare earth metal salts

Rare-earth metal salts have also emerged as promising corrosion inhibitors because of their ability to form stable hydroxide/oxide protective layers and suppress electrochemical reactions, particularly cathodic processes. In this study, $LaCl_3$, $CeCl_3$, and $PrCl_3$ were selected to evaluate their corrosion inhibition performance and to compare the influence of different rare-earth ions on the corrosion behavior of steel.

CHAPTER 2. EXPERIMENT

2.1. Research subjects

2.1.1. Sampling and identification

Betel leaves were collected in Ea Kar district, Dak Lak province, Vietnam in October 2022. The scientific name of this plant species was determined by the Southern Institute of Ecology, Ho Chi Minh City.

2.1.2. Chemicals and equipment

- Isolation of natural compounds: solvents such as n-hexane, dichloromethane, ethyl acetate, and ethanol. Equipment used in the extraction and chromatography process (Soxhle system, TLC, HPLC, column chromatography, etc.).

– Electrochemistry: Electrochemical systems (VSP), surface analysis equipment (SEM, EDS, XPS, AFM, FT-IR, …) and other chemicals and equipment.

2.1.3. Experimental design procedure

Betel (*Piper betle* L.) leaves were extracted with distilled water to obtain a polar extract. The chemical composition of the extract was preliminarily characterized by LC-QToF-MS, FTIR spectroscopy, and total polyphenol content determination. The major constituent, hydroxychavicol (DN1), was subsequently isolated by chromatographic techniques, and its chemical structure was elucidated by NMR spectroscopy in conjunction with literature data. The purity and content of DN1 in the extract were determined by high-performance liquid chromatography (HPLC).

The corrosion inhibition performance of both the polar betel leaf extract and DN1 was evaluated for mild steel in CO_2-saturated 0.01 M

NaCl solution using electrochemical techniques, including open-circuit potential (OCP), electrochemical impedance spectroscopy (EIS), and potentiodynamic polarization (PD). Steel surfaces, with and without corrosion inhibitors, were characterized by SEM, EDS, AFM, and XPS, while optical emission spectroscopy (OES) was employed to determine the elemental composition of the steel. Based on the electrochemical and surface characterization results, the corrosion and inhibition mechanisms were proposed. The same electrochemical and surface analyses were subsequently performed for the rare-earth metal salts ($LaCl_3$, $CeCl_3$, and $PrCl_3$) and the corresponding mixed inhibitor systems comprising DN1 and each rare-earth metal salt.

2.2. Experimental methods

- Determination of total polyphenol content using the Folin–Ciocalteu method.
- Isolation and structural elucidation of the major compound using thin-layer chromatography (TLC), column chromatography, and nuclear magnetic resonance (NMR) spectroscopy.
- Quantitative analysis by high-performance liquid chromatography (HPLC).
- Electrochemical techniques, including open-circuit potential (OCP), electrochemical impedance spectroscopy (EIS), potentiodynamic polarization (PD), and the wire beam electrode (WBE) technique.
- Surface characterization techniques, including scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), atomic force microscopy (AFM), and X-ray photoelectron spectroscopy (XPS).

CHAPTER 3. RESULTS AND DISCUSSION

3.1. Results of analysis and evaluation of the extract

3.1.1. Composition and properties of the extract

Characterizing the chemical composition and properties of the betel leaf extract prior to electrochemical testing is essential for understanding its corrosion inhibition mechanism. The polar extract was characterized by LC-QToF-MS, FTIR spectroscopy, and total polyphenol content determination. LC-QToF-MS analysis revealed a diverse composition ranging from highly polar polyphenols and glycosides to less polar fatty acids and their oxidized derivatives. These compounds are capable of interacting with the steel surface through coordination bonding and/or chemisorption, promoting the formation of a protective film. FTIR analysis confirmed the presence of key functional groups, including hydroxyl (–OH), carbonyl (C=O), C=C, and C–O groups, which are known to facilitate adsorption onto metal surfaces. In addition, the extract exhibited a high total polyphenol content of 162.62 ± 2.02 mg GAE/g extract, indicating its richness in phenolic compounds.

Besides, the major constituent (DN1) was successfully isolated from the polar betel leaf extract with a yield of 10.59% and a purity of 98.954%. Its structure was elucidated by NMR spectroscopy and confirmed through comparison with literature data, identifying the compound as hydroxychavicol. Owing to the presence of oxygen-containing functional groups, π-electron systems, and an aromatic benzene ring, this compound exhibits strong adsorption affinity toward metal surfaces and is therefore considered a promising

corrosion inhibitor capable of forming a protective film in corrosive environments.

3.2. Electrochemical results

The corrosion tests were conducted in a CO_2-saturated 0.01 M NaCl solution, which represents a highly aggressive industrial environment due to the combined acidifying effect of dissolved CO_2 and the strong localized corrosion induced by chloride ions (Cl^-). The corrosion and inhibition mechanisms of mild steel, in the absence and presence of the investigated inhibitors, were elucidated using electrochemical techniques, including electrochemical impedance spectroscopy (EIS), potentiodynamic polarization (PD), and the wire beam electrode (WBE) technique, together with surface characterization by SEM, EDS, AFM, and XPS. Corrosion parameters, including the corrosion potential (E_{corr}), corrosion current density (I_{corr}), corrosion rate (CR), and inhibition efficiency (η%), were determined to evaluate the performance of the investigated inhibitors. These results provide valuable insights into the corrosion protection mechanisms and support the practical application of the proposed inhibitor systems in industrial environments exposed to CO_2 and chloride ions.

3.2.1. Corrosion inhibition performance of Betel leaf extract

Electrochemical impedance spectroscopy (EIS) demonstrated the significant influence of the polar betel leaf extract on the corrosion behavior of mild steel in CO_2-saturated 0.01 M NaCl solution. The Nyquist plots exhibited capacitive semicircles whose diameters increased with inhibitor concentration, indicating enhanced corrosion protection through the formation of a protective surface film. In the absence of the inhibitor, the steel exhibited a low impedance, reflecting severe corrosion. In contrast, increasing the extract

concentration from 300 to 1800 ppm progressively increased the impedance, confirming improved corrosion resistance. The Bode plots further supported these findings by showing higher impedance moduli and phase angles in the presence of the extract. Equivalent circuit analysis revealed increased charge-transfer resistance and reduced interfacial capacitance, indicating the formation of a compact and homogeneous adsorbed film. The optimum inhibition performance was achieved at 1800 ppm extract, confirming the polar betel leaf extract as an effective corrosion inhibitor for mild steel in CO_2 and chloride-containing environments.

Table 3.1. The observed corrosion parameters were extrapolated into Tafel from the dynamic potential polarization measurements of the extract.

Concentration (ppm)	E_{corr} ($mV_{Ag/AgCl}$)	i_{corr} ($\mu A/cm^2$)	$-\beta_c$ (mV/decade)	β_a (mV/decade)	η (%)	Corrosion rate (mm/yr)
0	-689.5	127.18 ± 5.25	549	134	-	0.75
300	-680.9	87.01 ± 3.16	270	143	31.59 ± 3.76	0.51
900	-677.8	61.10 ± 0.02	187	110	51.96 ± 1.98	0.36
1800	-666.4	39.20 ± 3.67	164	96	69.18 ± 3.15	0.23

Table 3.1 shows the corrosion inhibition efficiency (η%) of the extract at different concentrations. The inhibition efficiency gradually increases as the extract concentration increases from 0 to 1800 ppm. In the presence of the extract, the inhibition efficiency improves significantly. reaching a maximum at 1800 ppm with a value of 69.18%. This increase reflects the effectiveness of the betel leaf extract in reducing the corrosion rate through adsorption on the steel surface.

3.2.2. Corrosion inhibition performance of hydroxychavicol

The electrochemical performance of hydroxychavicol (DN1) was evaluated using EIS and potentiodynamic polarization measurements. The Nyquist plots showed that the impedance increased progressively with DN1 concentration (2–12 mM), indicating enhanced corrosion protection. Although the corrosion current density and corrosion rate increased with immersion time. from 127.18 ± 5.25 μA/cm^2 and 0.75 mm/yr at 24 h to 165.44 ± 24.73 μA/cm^2 and 0.97 mm/yr at 72 h, respectively, this trend was consistent with the decrease in total system impedance over prolonged exposure. Nevertheless, the presence of DN1 significantly reduced the corrosion current density and improved the inhibition efficiency compared with the uninhibited system. Moreover, DN1 exhibited superior corrosion inhibition performance compared with the betel leaf extract.

Table 3.2. The observed corrosion parameters were extrapolated into Tafel from the dynamic potential polarization measurements of hydroxychavicol

Concentration (mM)	E_{corr} ($mV_{Ag/AgCl}$)	i_{corr} (μA/cm^2)	β_a (mV/decade)	$-\beta_c$ (mV/decade)	η (%)	Corrosion rate (mm/yr)
0	-689.5	165.44 ± 24.73	419	138	-	0.97
2	-647.9	53.15 ± 4.94	297	98	67.87 ± 5.66	0.51
6	-641.1	33.32 ± 1.26	249	66	79.86 ± 3.11	0.36
12	-625.4	18.36 ± 1.06	199	55	88.90 ± 1.78	0.23

Potentiodynamic polarization (PD) measurements showed that the corrosion current density was substantially lower in the presence of DN1 than in the uninhibited solution. As the DN1 concentration increased, the corrosion potential (E_{corr}) shifted slightly toward more positive values by less than 100 mV, indicating that DN1 acts as a mixed-type inhibitor with a predominant anodic inhibition effect. The highest inhibition efficiency, 88.90 ± 1.78%, was achieved at 12 mM

DN1. Furthermore, wire beam electrode (WBE) measurements demonstrated that DN1 effectively suppressed localized corrosion of mild steel in the CO_2-saturated chloride-containing environment.

3.2.3. Corrosion inhibition performance of rare-earth metal salts

The electrochemical behavior of the rare-earth metal salts ($REMCl_3$-$LaCl_3$, $CeCl_3$, $PrCl_3$) was evaluated using EIS, as illustrated by the Nyquist and Bode plots. The Nyquist plots exhibited concentration-dependent changes in the diameters of the capacitive semicircles, reflecting variations in the electrochemical processes at the steel/electrolyte interface in the absence and presence of $REMCl_3$. Overall, the semicircle diameter increased with increasing inhibitor concentration and reached its maximum at 2.4 mM indicating enhanced corrosion resistance. These results demonstrate that $REMCl_3$ effectively improves the corrosion protection of mild steel through the formation of a stable and protective surface film.

Bảng 3.3. The observed corrosion parameters were extrapolated into Tafel from the dynamic potential polarization measurements of $REMCl_3$

	E_{corr} ($mV_{Ag/AgCl}$)	i_{corr} ($\mu A/cm^2$)	β_a (mV/ decade)	$-\beta_c$ (mV/ decade)	η (%)	Corrosion rate (mm/yr)
0.0	-689.5	165.44 ± 24.73	419	138	-	0.97
			$LaCl_3$			
0.4	-641.8	59.13 ± 0.93	296	97	64.26 ± 5.37	0.35
1.2	-645.9	22.06 ± 0.82	255	72	86.67 ± 2.05	0.13
2.4	-614.3	6.72 ± 0.65	211	49	95.94 ± 0.72	0.04
			$CeCl_3$			
0.4	-648.5	31.79 ± 3.28	282	86	80.79 ± 3.49	0.19
1.2	-642.8	18.45 ± 0.13	202	74	88.85 ± 1.67	0.11
2.4	-635.1	10.3 ± 3.42	120	45	93.77 ± 2.26	0.06
			$PrCl_3$			
0.4	-653.5	18.62 ± 9.40	283	110	88.75 ± 5.93	0.11
1.2	-644.7	11.23 ± 1.98	207	94	93.21 ± 1.57	0.07
2.4	-637.6	6.02 ± 1.16	185	52	96.36 ± 0.89	0.04

Potentiodynamic polarization (PD) measurements showed that the presence of $REMCl_3$ significantly decreased the corrosion current density and shifted the corrosion potential toward more positive values compared with the uninhibited system. Increasing the $REMCl_3$ concentration from 0.4 to 2.4 mM enhanced the inhibition efficiency while reducing the corrosion rate. with the optimum performance achieved at 2.4 mM for all three rare-earth salts. The inhibition efficiency followed the order $CeCl_3$ < $LaCl_3$ < $PrCl_3$, indicating that $PrCl_3$ provided the highest corrosion protection. Furthermore, wire beam electrode (WBE) measurements confirmed that all $REMCl_3$ effectively suppressed localized corrosion of mild steel.

3.2.4. Corrosion inhibition performance of mixed inhibitor systems

The electrochemical performance of the mixed inhibitor systems (DN1 + $REMCl_3$), designated as (N1) DN1 + $LaCl_3$, (N2) DN1 + $CeCl_3$ (N3) DN1 + $PrCl_3$, was evaluated after 24 h of immersion in CO_2-saturated 0.01 M NaCl solution. The Nyquist plots showed substantially larger capacitive semicircles for all mixed inhibitor systems than for the uninhibited sample, indicating significantly enhanced corrosion resistance. Potentiodynamic polarization (PD) measurements further demonstrated that the inhibitor systems shifted the corrosion potential (E_{corr}) toward more positive values and markedly reduced the corrosion current density (I_{corr}), confirming improved electrochemical stability and a lower corrosion rate. The inhibition efficiency followed the order N2 < N1 < N3, with N3 exhibiting the highest corrosion protection, as shown in Table 3.4.

Table 3.4. The observed corrosion parameters were extrapolated into Tafel from the dynamic potential polarization measurements of mixed inhibitor systems

Sample	E_{corr} ($mV_{Ag/AgCl}$)	i_{corr} ($\mu A/cm^2$)	βa (mV/decade)	$-\beta c$ (mV/decade)	η (%)	Corrosion rate (mm/yr)
0	-689 ± 6	127.18 ± 5.25	549 ± 19	134 ± 10	-	0.75
N1	-634.6	8.16 ± 0.70	101	52	93.58 ± 0.61	0.51
N2	-614.1	12.73 ± 0.64	186	60	89.99 ± 0.65	0.36
N3	-608.2	4.20 ± 0.67	100	51	96.70 ± 0.54	0.23

3.3. Surface analysis results

In the absence of corrosion inhibitors, SEM images revealed severe surface degradation of mild steel, characterized by porous corrosion scales, localized pits, and an uneven surface morphology. EDS elemental mapping shows that carbon and oxygen were concentrated within the corrosion products, indicating the formation of iron corrosion compounds through electrochemical oxidation–reduction reactions. Corrosion was mainly occurred in the ferrite (α-Fe) phase, whereas the more corrosion-resistant cementite (Fe_3C) phase remained relatively intact. The porous corrosion products and localized surface damage indicate that steel corrosion in CO_2-saturated 0.01 M NaCl solution earns predominantly through a localized corrosion mechanism, facilitating the continuous penetration of aggressive chloride ions and further surface deterioration.

The addition of corrosion inhibitors significantly improved the surface morphology of mild steel. In the presence of the betel leaf extract (300 ÷ 1800 ppm), SEM images revealed the formation of a protective layer comprising large aggregated deposits that covered most of the steel surface. However, the protective film remained heterogeneous

because of the complex composition of the extract. The presence of multiple organic constituents, together with their predominantly physical and randomly oriented adsorption, led to partial desorption and the formation of a non-uniform film with structural defects, thereby reducing the corrosion protection performance. This limitation is commonly observed for plant-derived extracts, including betel leaf extract, and represents one of the major challenges to their application as corrosion inhibitors.

In the presence of hydroxychavicol (DN1, 2÷12 mM), the steel surface became considerably smoother and more uniform, with polishing scratches remaining visible, indicating effective corrosion protection. SEM images revealed the formation of a compact protective film together with localized deposits resulting from the adsorption of DN1 molecules onto the steel surface. AFM analysis further confirmed this improvement, showing a low average surface roughness of approximately 6.6 nm at 12 mM DN1. EDS analysis detected the presence of Cl, O, C, and Fe elements, while the high carbon content indicated that the protective film was primarily organic in nature. XPS analysis further confirmed the interaction between iron ions and the oxygen-containing functional groups of DN1. These results suggest that the corrosion protection mechanism involves the adsorption of hydroxyl groups and π-electron systems onto the steel surface, followed by the formation of Fe–organic complexes that suppress iron oxidation in the CO_2 and chloride-containing environment.

In the presence of rare-earth metal salts ($REMCl_3$), SEM images revealed a marked reduction in corrosion, particularly at the ferrite regions, with the degree of corrosion decreasing as the inhibitor concentration increased. This improvement is attributed to the

formation of protective rare-earth hydroxide/oxide-containing films that inhibit metal dissolution. SEM/EDS analysis showed a uniform distribution of rare-earth elements over the steel surface, indicating that REM^{3+} ions were incorporated into the protective layer and effectively suppressed electrochemical corrosion reactions. The rare-earth elements were spatially associated with oxygen-rich regions, whereas carbon was less abundant, suggesting that the protective film consisted predominantly of iron and rare-earth oxides/hydroxides rather than organic species. XPS analysis further confirmed the adsorption of $REMCl_3$ through the appearance of characteristic La 3d, Ce 3d, and Pr 3d peaks, while the high-resolution spectra revealed distinct differences between the inhibited and uninhibited steel surfaces, confirming the formation of a stable protective layer.

For the mixed inhibitor systems comprising hydroxychavicol and $REMCl_3$ (N1–N3), SEM images revealed the formation of a smooth, compact, and highly adherent protective film on the steel surface. The porous corrosion products observed on the uninhibited sample were largely eliminated, indicating that corrosion was effectively suppressed by the synergistic interaction between hydroxychavicol and the rare-earth ions. EDS analysis further supported these observations, showing a uniform distribution of Fe together with slightly increased O and C contents, consistent with the formation of a hybrid organic–inorganic protective film. This film is proposed to consist of coordination complexes between REM^{3+} ions and the functional groups of hydroxychavicol, together with iron corrosion products and rare-earth oxides/hydroxides. XPS analysis confirmed the chemical interactions between the rare-earth species and the steel surface, providing strong evidence for the formation of a stable hybrid

organic–inorganic protective layer. These results demonstrate the synergistic effect of hydroxychavicol and rare-earth metal salts in enhancing the corrosion resistance of mild steel in CO_2-saturated 0.01 M NaCl solution.

3.4. Mechanisms

3.4.1. Corrosion mechanism

In aqueous environments containing CO_2, the corrosion of mild steel proceeds through an electrochemical mechanism involving anodic iron dissolution and cathodic reduction of H^+ and HCO_3^- species generated from dissolved CO_2. Under CO_2-saturated conditions (pH ≈ 4), the Pourbaix diagram indicates that iron predominantly dissolves as Fe^{2+}, while carbonic acid mainly dissociates into bicarbonate ions. Consequently, corrosion products such as iron hydroxides, iron oxides (magnetite), and iron (II) carbonate (siderite) are formed on the steel surface. These corrosion products are generally porous and poorly adherent, making them susceptible to dissolution and detachment during exposure.

In the presence of chloride ions (Cl^-), the porous corrosion layer facilitates the penetration of aggressive species into structural defects and active sites. Owing to their moderate ionic radius and relatively low hydration energy, Cl^- ions readily shed their hydration shell, migrate toward anodic regions, and destabilize the protective corrosion products, thereby accelerating localized corrosion. The combined action of dissolved CO_2 and Cl^- significantly enhances iron dissolution and increases the overall corrosion rate. While CO_2 primarily promotes uniform corrosion, chloride ions initiate localized attack that may subsequently develop into pitting corrosion or, with continued propagation, evolve into more extensive surface corrosion.

3.4.2. Corrosion inhibition mechanisms

Upon the addition of corrosion inhibitors, the initial corrosion process still occurs at active defects on the steel surface. However, electrochemical measurements and surface characterization demonstrate the formation of a protective film that acts as a physical barrier, limiting the direct contact between the steel surface and corrosive species.

For the polar betel leaf extract, anodic dissolution of iron generates positively charged Fe^{n+} species (δ+) that promote the adsorption of negatively polarized functional groups (δ-) through electrostatic interactions. The extract contains abundant polyphenols and other polar compounds bearing hydroxyl, amine, and oxygen-containing functional groups, which adsorb onto the steel surface to form a protective layer through predominantly physical adsorption. Owing to its complex composition, however, the resulting film is relatively heterogeneous and contains structural defects, limiting its corrosion inhibition performance. Therefore, the major active constituent, hydroxychavicol (DN1), was isolated and investigated separately.

Hydroxychavicol adsorbs rapidly onto electrochemically active sites through coordination between the lone-pair electrons of the hydroxyl groups and the Fe 3d orbitals, forming stable Fe–organic complexes. This adsorption markedly increases the charge-transfer resistance during the early immersion period. Subsequently, π-electrons from the benzene ring and allyl group strengthen intermolecular interactions, promoting the formation of a compact protective film that suppresses both uniform and localized corrosion.

In contrast, rare-earth metal salts ($REMCl_3$) inhibit corrosion through a different mechanism. REM^{3+} ions undergo hydrolysis in the alkaline

microenvironment generated at cathodic sites, producing insoluble $REM(OH)_n$ precipitates that can partially transform into rare-earth oxides. These hydroxide/oxide species preferentially deposit on cathodic regions, forming a stable REM–Fe–O composite layer that blocks the diffusion of CO_2 and Cl^- and suppresses both anodic and cathodic electrochemical reactions.

When hydroxychavicol was combined with $REMCl_3$ (N1–N3), a synergistic inhibition mechanism was established. Hydroxychavicol preferentially protected anodic sites through coordination adsorption, whereas hydrolyzed rare-earth species preferentially protected cathodic regions by forming stable hydroxide/oxide deposits. The complementary actions of the organic and inorganic components produced a compact, homogeneous hybrid organic–inorganic protective film with fewer structural defects and significantly improved resistance to chloride penetration and localized corrosion. Consequently, the mixed inhibitor systems exhibited substantially higher inhibition efficiency and long-term stability than either component alone, demonstrating their strong potential as next-generation environmentally friendly corrosion inhibitors for mild steel in CO_2 and chloride-containing environments.

CONCLUSION

This thesis successfully developed a novel corrosion inhibitor system based on betel leaf (*Piper betle* L.) and rare-earth metal chlorides for mitigating the corrosion of mild steel in CO_2 and chloride-containing environments. The main findings are summarized as follows:

✓ Hydroxychavicol was successfully isolated from the polar betel leaf extract with a yield of 10.59% and a purity of 98.954%. Its chemical structure was elucidated using spectroscopic techniques and confirmed by comparison with published literature;

✓ The betel leaf extract and hydroxychavicol were evaluated as environmentally friendly corrosion inhibitors for mild steel in CO_2-saturated chloride environment. Both acted as mixed-type inhibitors with predominant anodic inhibition, achieving maximum inhibition efficiencies of 69.18% (1800 ppm extract) and 88.90% (12 mM hydroxychavicol), respectively;

✓ Rare-earth metal chlorides were investigated as individual corrosion inhibitors. All three compounds behaved as mixed-type inhibitors with a predominant anodic inhibition effect, exhibiting high inhibition efficiencies of 93.77 ± 2.26%, 95.94 ± 0.72%, and 96.36 ± 0.89% for $CeCl_3$, $LaCl_3$, and $PrCl_3$, respectively, at an optimum concentration of 2.4 Mm;

✓ A novel hybrid corrosion inhibitor system was established by combining hydroxychavicol with $LaCl_3$, $CeCl_3$, or $PrCl_3$. The mixed inhibitor systems exhibited superior corrosion protection owing to their synergistic effects, with inhibition efficiencies following the order N2 (hydroxychavicol + $CeCl_3$) < N1 (hydroxychavicol + $LaCl_3$) < N3 (hydroxychavicol + $PrCl_3$), corresponding to 89.99 ± 0.65%, 93.58 ± 0.61%, and 96.70 ± 0.54%, respectively.

NEW CONTRIBUTIONS OF THE THESIS

1. Unlike previous studies that primarily evaluated the corrosion inhibition efficacy of the total extract, this thesis successfully isolated hydroxychavicol and demonstrated its role in the corrosion inhibition mechanism. This provides an important scientific basis for shifting from evaluating the effectiveness of the extract to identifying the main active ingredient responsible for metal protection, thereby clarifying the relationship between chemical composition and the mechanism of steel surface protection.

2. The thesis develops and optimizes synergistic corrosion inhibitor systems by combining inorganic compounds with purified natural products isolated from indigenous Vietnamese plants. The proposed inhibitors effectively mitigate localized corrosion in CO2 and Cl^--containing environments relevant to the oil and gas and and pipeline transportation systems, outperforming the individual components. The study integrates chemistry, natural product chemistry, and physical chemistry in an interdisciplinary approach.

3. The investigated corrosion inhibitors and inhibitor systems exhibited high corrosion inhibition efficiencies (>90%) for steel in corrosive environments, demonstrating their strong potential as corrosion inhibitors. The thesis also provides important insights into the detailed inhibition mechanism, particularly the dual protective mechanism arising from the synergistic action of rare-earth metal ions and natural compounds isolated from plants.

LIST OF THE PUBLICATIONS RELATED TO THE DISSERTATION

1. **Thi-Bich-Ngoc Dao.** Thanh Liem Huynh. Van Kieu Nguyen. Ngoc Quyen Tran. Casen Panaitescu. Trung T. Pham. Nguyen To Hoai. Nam Nguyen Dang. "Self-forming barrier layer for carbon dioxide corrosion protection of mild steel in NaCl solution containing hydroxychavicol isolated from *Piper betle* L. Leaf." *Chemical Engineering Journal.* Volume 491(2024) 151717.
   Link: https://doi.org/10.1016/j.cej.2024.151717
2. **Thi-Bich-Ngoc Dao**. S.V. Prabhakar Vattikuti. Trung T. Pham. Casen Panaitescu. Ngoc Quyen Tran. Kim-Long Duong-Ngo. Nam Nguyen Dang. "The role of cerium chloride for protecting mild steel corrosion in chloride ions and carbon dioxide containing environment." *Surfaces and Interfaces*. Volume 67 (2025) 106564.
   Link: https://doi.org/10.1016/j.surfin.2025.106564
3. **Thi-Bich-Ngoc Dao.** Duong-Ngo Kim-Long. Thanh Liem Huynh. Thanh-Nha Tran. Trung T. Pham. Minji Kim. Nhung Thi Nguyen. Nam Nguyen Dang. "Natural formation of protective film for mild steel corrosion in sodium chloride containing saturated carbon dioxide medium using lanthanum (III) chloride." *Colloids and Surfaces A: Physicochemical and Engineering Aspects* (2025) 137208.
   Link: https://doi.org/10.1016/j.colsurfa.2025.137208
4. Dang Nam Nguyen. Lai Xuan Bach. Kim Long Duong Ngo. Cam Tu Hoang Ngoc. and **Thi-Bich-Ngoc Dao**. "Coating characterization with surface morphological techniques." In Encapsulated corrosion inhibitors for eco-benign smart coatings. CRC Press. Taylor & Francis (2024). pp. 225-267.
5. Báo cáo (Oral). "Self-forming barrier layer for carbon dioxide corrosion protection of mild steel in NaCl solution containing hydroxychavicol isolated from *Piper betle* L. Lea". hội nghị quốc tế tại Romania: "75 years of energy and performance in education and research 2023. Renewable versus fossil fuels. Global energy perspectives. November 8-10. 2023. Ploiesti. Romania".