EXTRACTION OF FLAVONOIDS FROM BUTTERFLY PEA (*CLITORIA TERNATEA*) FLOWER AND THEIR INHIBITIVE EFFECT FOR CORROSION UNDER CO_2 IN LOW-CARBON STEEL

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2024

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by

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Thesis submitted in fulfilment of the requirements
for the degree of
Master of Science

September 2024

ACKNOWLEDGEMENT

In the name of Allah, the most beneficent and merciful, I offer this project as I thank Him for giving me strength, effort, time and opportunity to surmount all the challenges that I went through in accomplishing my research project. I wholeheartedly would like to thank and express my sincere indebtedness to my supervisor, Assoc. Prof. Dr. Mohd. Hazwan Hussin, for providing me with the opportunity to do research and providing invaluable guidance throughout this research. I would also like to express my profound thanks to my co-supervisor, Dr. Pandian Bothi Raja.

I would like to sincerely acknowledge Universiti Sains Malaysia for the financial support offered through USM Research University Incentive (RUI) grant, 203/PKIMIA/6712021. My sincere gratitude to all technicians of the School of Chemical Sciences, and Centre for Global Archeological Research for providing good facilities and assistance during the testing of samples. I am glad to express my appreciation to my fellow lab mates in School of Chemical Sciences USM, Dr. Tuan Sherwyn Hamidon, Ms. Najhan, Ms. Farah, Ms. Liyana, Ms. Fatin, Dr. Hidayah, Dr. Hanis, and Mr. Rushan for the unfailing support through the process of research and writing this thesis. I have no valuable words to express my thanks, but my heart is still full of the favours received from every person.

I am incredibly grateful to my parents, Azahar Bin Hashim and Zarina Binti Shintamadar for their invaluable love, prayers, and sacrifices for educating me and preparing me for my future and their guidance to complete this thesis. Special thanks go to my husband; Muhammad Safiq, my little family, and my best friend for their tremendous support, moral boost and continuous encouragement throughout my years of study and through the process of researching and writing this thesis. Thank you.

TABLE OF CONTENTS

CHAPTER 4 RESULTS AND DISCUSSION 50

APPENDICES

LIST OF PUBLICATIONS

LIST OF TABLES

LIST OF FIGURES

Page

LIST OF SYMBOLS

°C	Degree Celsius
K	Kelvin
T	Absolute temperature
T	Time
Ω	Ohm
R	Universal gas constant
cm	centimeter
mm	millimeter
R_n	Noise resistance
R_{ct}	Charge transfer resistance
R_s	Solution resistance
i_{corr}	Corrosion density
IE	Inhibition efficiency
M_{ew}	Molecular equivalent weight
Z	Magnitude of impedance
Z_{CPE}	Impedance of constant phase element
ΔG_{ads}	Standard Gibbs free energy of adsorption
β_a	Anodic Tafel constant
β_c	Anodic Tafel constant
θ	Phase angle
λ_{max}	Absorption maximum
μ	micro
σ_I	Standard deviation of current noise
σ_V	Standard deviation of potential noise

Ω	angular frequency
wt. %	weight percent
min	minutes
mpy	mils per year
g	gram
w	weight
V	Volume
kV	kilo Volt
h	hour
ρ	density
ppm	parts per million

LIST OF ABBREVIATIONS

AC	Alternating current
ASTM	American Society for Testing and Materials
ATR	Attenuated total reflection
CE	Counter electrode
CPE	Constant phase element
CO_2	Carbon dioxide
CT	*Clitoria ternatea*
CTCH	*Clitorria ternatea* chloroform extract
CTEA	*Clitoria ternatea* ethyl acetate extract
CTET	*Clitoria ternatea* ethanol extract
CTW	*Clitoria ternatea* water extract
DC	Direct current
DSC	Differential scanning calorimetry
DTG	Differential thermogravimetric
EDX	Energy dispersive X-ray
EIS	Electrochemical impedance spectroscopy
ENM	Electrochemical noise measurement
FESEM	Field emission scanning electron microscope
FT-IR	Fourier transform infrared
HPLC	High-performance liquid chromatography
LC-MS	Liquid chromatography-mass spectrometry
NaCl	Sodium chloride
NMR	Nuclear magnetic resonance
PD	Potentiodynamic polarization

RE	Reference electrode
H_2CO_3	Carbonic acid
H_2SO_4	Sulphuric acid
SEM	Scanning electron microscope
TGA	Thermogravimetric
UV-Vis	Ultraviolet-visible
WE	Working electrode
ZRA	Zero resistance ammeter

PENGEKSTRAKAN FLAVONOID DARIPADA BUNGA TELANG (*CLITORIA TERNATEA*) DAN KESAN PERENCATAN BAGI KAKISAN KELULI RENDAH KARBON DI BAWAH CO_2

ABSTRAK

Kajian ini menekankan pengekstrakan flavonoid iaitu quercetin dan kaempferol daripada bunga telang biru (*Clitoria ternatea*) yang mengandungi sifat antioksidan yang sangat kuat. Ekstrak disediakan menggunakan pelarut dengan kekutuban yang berbeza, iaitu kloroform (CTCH), etanol (CTET), etil asetat (CTEA), dan air (CTW). Kajian fitokimia bagi semua ekstrak telah dinilai untuk menyaring kandungan fenolik, kandungan flavonoid, ujian penurunan kuasa, dan kandungan tanin sebagai sumber potensi sifat antioksidan bunga. Semua ekstrak kemudiannya dicirikan menggunakan analisis pelengkap, termasuk Spektroskopi Inframerah Transformasi Fourier (FTIR), analisis Termogravimetrik (TGA), Kalorimetri pengimbasan pembezaan (DSC), analisis resonans magnetik nuclear (termasuk ^{1}H dan ^{13}C NMR). Menurut analisis Kromatografi Cecair Berprestasi Tinggi (HPLC) dan Kromatografi Cecair-spektrometri Jisim (LC-MS), sebatian yang terdapat dalam ekstrak CT telah dikenal pasti secara kualitatif dan kuantitatif. Pengukuran elektrokimia, termasuk Spektroskopi Impedans Elektrokimia (EIS), Polarisasi Potensiodinamik (PD), dan Pengukuran Hingar Elektrokimia (ENM) mendedahkan prestasi antikarat keluli lembut di bawah atmosfera CO_2. Prestasi keluli lembut untuk mengelakkan kakisan dalam medium NaCl 3.5% yang mengandungi ekstrak CTW dan CTET pada kepekatan dan suhu yang berbeza telah dipastikan melalui pengukuran elektrokimia. Kedua-dua ekstrak merekodkan kecekapan perencatan (IE%) yang tinggi berdasarkan analisis EIS ($CTW_{IE\%}$: 89.91 % > $CTET_{IE\%}$: 85.33 %), menunjukkan proses penjerapan berkesan molekul perencat CT pada permukaan keluli lembut. Lengkung polarisasi menggambarkan tingkah laku perlindungan kakisan jenis campuran perencat CT. Analisis EDX mengesahkan bahawa ekstrak CT 1000 ppm mempunyai kandungan besi tertinggi (90.79 wt.%), menunjukkan bahawa ia paling kurang terdedah kepada kakisan. Penjerapan perencat CT pada permukaan keluli lembut mematuhi isoterma penjerapan Langmuir, mendedahkan proses penjerapan berlaku terutamanya melalui penjerapan fizikal. Simulasi pemodelan molekul mendedahkan jurang tenaga yang sempit antara keadaan tenaga HOMO dan LUMO bagi molekul flavonoid, seterusnya mengesahkan keupayaan mereka untuk memindahkan dan menerima elektron daripada orbital kosong atom Fe. Adalah jelas bahawa CTW adalah unggul dari segi perencatan kakisan keluli lembut dalam larutan NaCl 3.5% tepu CO_2 berbanding ekstrak CTET, menunjukkan prestasi perencatan kakisan yang sangat baik terhadap media tinggi CO_2.

EXTRACTION OF FLAVONOIDS FROM BUTTERFLY PEA (*CLITORIA TERNATEA*) FLOWER AND THEIR INHIBITIVE EFFECT FOR CORROSION UNDER CO_2 IN LOW-CARBON STEEL

ABSTRACT

The present study emphasizes the extraction of flavonoids which are quercetin and kaempferol from Butterfly blue pea (*Clitoria ternatea*) flower containing very strong antioxidant properties. The extracts were prepared using solvents with different polarities, namely chloroform (CTCH), ethanol (CTET), ethyl acetate (CTEA), and water (CTW). The phytochemical studies for all extracts were evaluated to screen the phenolic content, flavonoid content, reducing power assay, and tannin content as a potential source of antioxidant properties of the flower. All the extracts were then characterized using complementary analyses, including Fourier-transform infrared spectroscopy (FT-IR), Thermogravimetric analysis (TGA), Differential scanning calorimetry (DSC), Nuclear magnetic resonance (NMR) analysis (including ^{1}H and ^{13}C NMR). According to High-performance liquid chromatography (HPLC) and Liquid chromatography-mass spectrometry (LC-MS) analysis, the compounds found in CT extracts were identified both qualitatively and quantitatively. Electrochemical measurements, including Electrochemical impedance spectroscopy (EIS), Potentiodynamic polarization (PD), and Electrochemical noise measurement (ENM) revealed the anticorrosion performance of mild steel under a CO_2 atmosphere. The performances of mild steel to prevent corrosion in 3.5% NaCl medium containing CTW and CTET extracts at different concentrations and temperatures were ascertained through electrochemical measurements. Both extracts recorded high inhibition efficiency (IE%) values based on EIS analysis ($CTW_{IE\%}$: 89.91 % > $CTET_{IE\%}$: 85.33

%), implying effective adsorption of CT inhibitor molecules on mild steel surface. Polarization curves illustrated a mixed-type corrosion protection behaviour of CT inhibitors. The EDX analysis confirmed that the 1000 ppm CT extracts had the highest iron content (90.79 wt.%), indicating that they were the least prone to corrosion. Adsorption of CT inhibitors on mild steel surface obeyed the Langmuir adsorption isotherm, revealing the adsorption process occurred mainly *via* physisorption. Molecular modelling simulation revealed a narrow energy gap between HOMO and LUMO energy states of flavonoid molecules, further affirming their capability to transfer and accept electrons from vacant orbitals of Fe atoms. It was apparent that CTW was superior in terms of corrosion inhibition of mild steel in CO_2-saturated 3.5% NaCl solution compared to CTET extract, indicating its excellent corrosion inhibition performance against CO_2-enriched media.

CHAPTER 1

INTRODUCTION

1.1 Background of study

The dependence on the oil and gas sector is growing as a result of the rising demand for fossil fuels and the dearth of clean energy technologies (Si et al., 2023). The most widely used materials in oil and gas production and transmission infrastructure are carbon and low alloy steels, regardless of their susceptibility to CO_2 corrosion. This is because of their availability, strength, affordability, mechanical qualities, ease of use in construction, and economic effectiveness through corrosion inhibition (Jalab et al., 2023; Wang et al., 2011). When CO_2 dissolves in water and hydrates in the form of carbonic acid (H_2CO_3), it facilitates electrochemical interactions between surface of mild steel and the contacting aqueous phase, which results in the disintegration of iron and retards the pipe surface as well as the internal walls (Gupta et al., 2022; Usman et al., 2017).

An estimate of US 2.5 trillion, or 3.4% of GDP, is the cost of corrosion worldwide (Koch, 2017). This phenomenon is estimated to cost billions of dollars annually, especially in the oil and gas sector. According to a study finding by the Pipeline and Hazardous Materials Safety Administration (PHMSA), the direct costs of corrosion in the oil and gas pipeline industry in the United States were projected to be between $7-8 billion annually. This covers expenses related to environmental damage and clean-up as well as maintenance, repair, and replacement of corroded equipment (Koch et al., 2002). For this reason, there is a growing interest in addressing pipeline corrosion, to lower maintenance costs and avoiding production shutdown besides any wretched accidental failure.

These days, the usage of inhibitors is more prominent to prolong the metal life span due to their impressive efficacy and cost-effectiveness for controlling metal corrosion (Yüce, 2020). As mentioned by Gupta et al. (2022), these inhibitors provide a protective coating that prevents corrosion on the metal by being adsorbed on the metal surface (*via* physisorption and chemisorption). In the past, numerous synthetic corrosion inhibitors such as inorganic salts, azoles and polymeric inhibitors have been used to inhibit the corrosion of carbon mild steel (Aaziz & Abdallah, 2023; Talebian et al., 2019). However, these inhibitors are pricey but effective, and few of them are harmful to the environment. Therefore, it is vital to explore possibilities to produce environmentally friendly, inexpensive, and green corrosion inhibitors as a viable alternative to inorganic and synthetic organic inhibitors. Natural plant extracts have recently been suggested as a renewable, non-toxic, and eco-friendly CO_2 corrosion inhibitor. However, this research remains very scarce due to the lack of knowledge on the roles and electronic transfer/interaction mechanism of organic inhibitors during the anti-corrosion process.

Clitoria ternatea Linn Fabaceae popularly identified as ‘butterfly pea or blue pea’ is a flower that has great antioxidant properties and commonly used to treat various ailments traditionally owing to flavonoids group present including anthocyanins, alkaloid, steroid and tannin (Jamil et al., 2018). This herbaceous plant has been identified as a fast-growing legume and can be easily found in Southeast Asia. Quercetin and kaempferol derivatives are the major bioflavonoid compound that belong to the class called flavonols were found in CT flower during extraction that contribute to their significant antioxidant properties, further affirming their potential as a green alternatives to various inorganic and organic inhibitors exploited in industrial and chemical treatments (Indrianingsih et al., 2021; Makasana et al., 2017). Kumar et al. (2013) revealed that *Clitoria ternatea* (CT) flower extracts possess the potential to be used as corrosion inhibitors in saline solution.

1.2 Problem statement

Corrosion persists as a major global issue that has affected many industries. The corrosion of carbon mild steel is accentuated by dissolved acidic gases such as CO_2 (causing sweet corrosion) and H_2S (causing sour corrosion). This has been identified as a severe danger, limiting the use of carbon mild steel, as the corroded steel loses its structural stability in different forms (pitting, pores, erosion, etc.) (Solovyeva et al., 2023). In 1970s, sweet corrosion is responsible for 28% of corrosion-related failures. Today, it is responsible for almost 60% of such cases (Cao et al., 2017). In 2021, the World Bank predicted 96.1 trillion US dollars of global GDP, reflecting that the cost of corrosion was projected to roughly 6 trillion US dollars (Iannuzzi & Frankel, 2022).

Corrosion inhibitors have become prevalent in a variety of industries, from construction materials to surface treatments for cultural assets, to suppress or at least mitigate the corrosion process of metals. These inhibitors including azoles (thiazole, pyrazole, oxazole, imidazole, and isoxazole) have been studied in a variety of metals and alloys for a long time. Besides, the used of inorganic inhibitors such as of cadmium, phosphates, nitrates, arsenates, chromates, and dichromates are also common to combat corrosion (Aaziz & Abdallah, 2023; Al-Amiery et al., 2023;

Yuchun et al., 2002). Although they have demonstrated encouraging inhibitory efficiency, inorganic inhibitors are intolerable because they pose long-term risks to social health, and some of them are only effective at higher concentrations. This has prompted the hunt for environmentally benign or non-toxic corrosion inhibitors that can safeguard metallic buildings to the greatest extent possible while having the least negative effects on people and the environment. Non-toxic or green corrosion inhibitors are favoured because they offer a combination of environmental friendliness, safety, effectiveness, and regulatory compliance, making them a more sustainable choice for mitigating mild steel corrosion. These bio-based corrosion inhibitors were mostly designed not just recorded lower environmental footprint, but also to be highly effective where they can form protective layers on the metal surface, preventing the corrosive agents from reaching the steel and thereby extending the lifespan of the material. Although some green inhibitors may have a higher initial cost, their long-term benefits, including reduced environmental clean-up costs and lower health-related expenses, can make them cost-effective over time.

Adsorption is the process of adhesion of atoms, molecules, or ions to a substance's surface. Adsorbents attract adsorbate species, which preferentially concentrate near the adsorbent surface due to unsaturated surface forces. Adsorption of corrosion inhibitors may be seen as a substitution process, replacing water in the aqueous phase. Initially limited by high cost, toxicity, and regeneration difficulties, research has led to the development of low-cost, renewable, and environmentally friendly materials like plant biomasses for corrosion inhibition, water treatment, decontamination, and remediation processes.

Plant extracts have recently been recognised as an environmentally friendly and renewable source for a wide range of corrosion inhibitors, but the availability of plant source is always a problem. Butterfly pea (*Clitoria ternatea*) plant has been identified as a fast-growing legume and can be easily found in Southeast Asia. It can also easily be planted since it has high growth rate and easy to maintain. Besides, this herbaceous flower is a renewable source with rich antioxidant properties as it contains polyphenols (Singh et al., 2022). Previous work also has revealed that Butterfly pea flower contains majorly flavonoids such as quercetin and can act as an excellent antioxidant and corrosion inhibitor (Ghuzali et al., 2021).

1.3 Research objectives

Clitoria ternatea (CT) flower was used as the raw material. The aims of this research study are:

1) To isolate flavonoids from CT flower petals using different solvents (water, ethanol, ethyl acetate, chloroform) and perform characterization using complementary physicochemical and phytochemical analyses.

2) To investigate the corrosion inhibition performance of mild steel employing CT extracts enriched in CO_2-saturated 3.5 wt.% NaCl (with and without inhibitors) adopting electrochemical techniques.

3) To propose a mechanism of corrosion inhibition process of CT extracts on the mild steel surface in 3.5 wt.% NaCl medium by performing molecular modelling simulation.

4) To investigate thermodynamics of adsorption, adsorption isotherm modelling, and molecular modelling through quantum calculations.

1.4 Scope of study

This theoretical-experimental work initially devotes on extracting flavonoids from CT flower petals using a maceration technique employing solvents with distinct polarity (water, ethanol, ethyl acetate, and chloroform). All the extracts were then characterized using complementary analyses including FTIR, TGA, DSC, ^{1}H and ^{13}C NMR and were subjected to phytochemical analyses to screen the phenolic content, flavonoid content, reducing power assay and tannin content as potential source of antioxidant properties of the flower. High-performance liquid chromatography (HPLC) was conducted to separate and identify flavonols compounds of plant pigments including quercetin and kaempferol. Special attention will then be focused on electrochemical analysis through electrochemical impedance spectroscopy (EIS) and potentiodynamic polarisation (PD) analysis to determine the corrosion inhibition performance of this herbaceous plant. The carbon mild steel was exposed to 3.5% NaCl medium throughout the corrosion study. The molecular modelling simulation was performed to investigate the properties of the additives (hydrophilicity, electronegativity, and reduction power) and inhibition mechanism (physisorption/chemisorption, and electron transfer). It is expected that the roles of those natural additives in inhibiting the steel corrosion will be revealed. Besides exploring the antioxidant profile and nutritional value of the flower extracts, the incorporation of CT extracts as potent corrosion inhibitors for the corrosion mitigation of mild steel substrates in 3.5% NaCl medium under CO_2 environment was uncovered, in which to the best of our knowledge is yet to be discovered.

CHAPTER 2

LITERATURE REVIEW

2.1 Brief overview of corrosion

Corrosion remains a major repercussion as it causes a steel-destructive phenomenon that results from chemical and/ or electrochemical interactions with aqueous environments. It occurs at the interface between metal and electrolyte, producing an electrical charge transfer or ion diffusion process (Liu et al., 2009). Metals or alloys that are subjected to conditions that trigger or initiate the process of corrosion are vulnerable to this damaging corrosion attack. This process is typically irreversible that occurs on the outer layer of the metal surface in an electrochemical reaction involves two half-reactions occurring simultaneously. Oxidant reduction and metal coupon oxidation. In the oil field, common types of corrosion are of great importance: sweet and sour corrosion, oxygen corrosion, galvanic corrosion, erosion corrosion, crevice corrosion, and stress corrosion cracking (Popoola et al., 2013). When water is introduced into the system and wets the metal surface, corrosion occurs. This process is composed of three components that consist of an electrochemical cell: an anode, a cathode, and an electrolyte (Figure 2.1). The oxidization of metal takes place at the anode, where it dissolves and produces positively charged metal ions. Concurrently, electrons transfer from the anode to the cathode, and the cathode functions as an electron acceptor without being consumed.

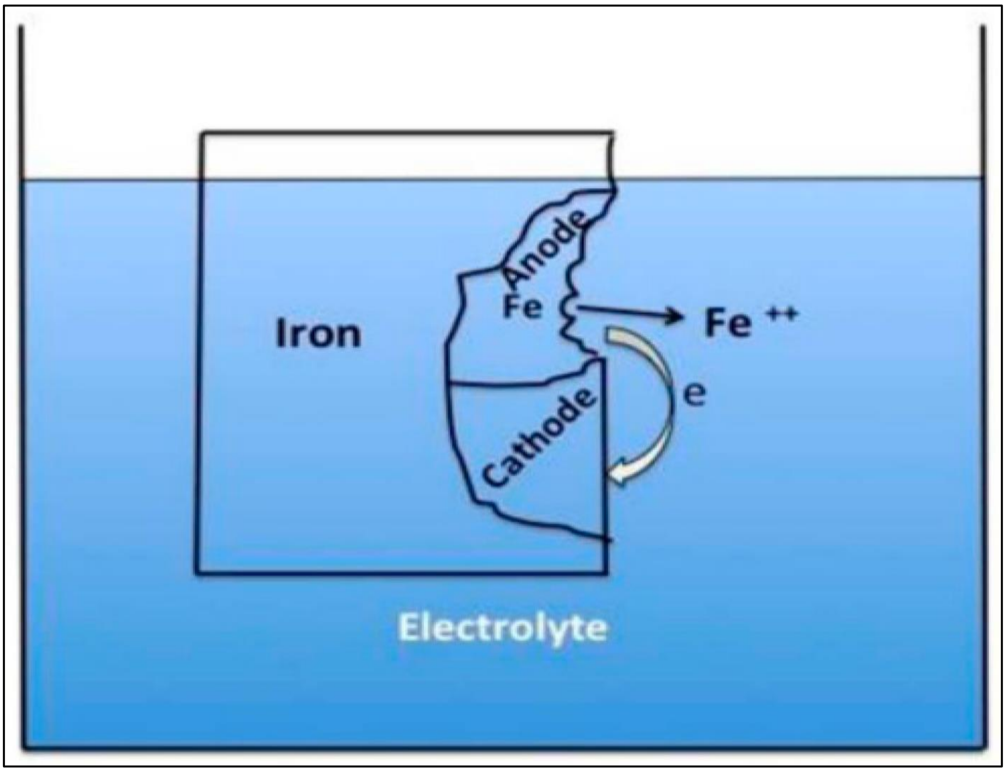

Figure 2.1: Schematic diagram of local corrosion on steel surface (Solovyeva et al., 2023).

Corrosion has long been recognized as one of the costliest obstacles that has affects all kinds of industries and government agencies. The natural degradation of metal properties is brought about by reactions between the metal and its surroundings, which interact chemically, biologically, and electrochemically (Ferraa et al., 2023; Fontana & Greene, 1967). Carbon mild steel is widely utilized as a primary construction material in several industries such as the oil and gas refineries, petrochemical plants, automotive, and power sectors solely due to its superior mechanical and chemical properties (Aljibori et al., 2023; Haddadi et al., 2019). Although mild steel has various advantages, notably low cost, good ductility, malleability, and adjustable surface hardness, its poor resistance to corrosion in aggressive environments remains an expensive, difficult, and problematic issue (Ansari & Quraishi, 2014; Haldhar et al., 2018; Prabakaran et al., 2016). For example, metal exposure to saline solutions in oil and gas industries and seawater processes can cause severe corrosion problems since chloride ions (Cl^-) are present, making prompt intervention crucial (Heakal et al., 2018; Wang et al., 2015).

2.2 CO_2 corrosion

The sweet corrosion is a form of corrosion which is particularly prevalent in environments where CO_2 is present in the absence of significant amounts of hydrogen sulphide (H_2S), often leading to severe deterioration of carbon steel and other alloys. One of the main reasons for oil and gas pipeline failures is CO_2 corrosion, which can happen at any point in the production process, from downhole equipment to surface facilities and processing plants (Okafor et al., 2009). These failures in the reservoir brine are primarily caused by dissolved acidic gases such as CO_2 (which causes sweet corrosion) and H_2S (which causes sour corrosion), and corrosion triggered by dissolved oxygen in the water (Al-Janabi, 2020; Kermani et al.; Solovyeva et al., 2023). The most widely used materials in oil and gas production and transmission infrastructure are carbon and low-alloy steels, regardless of their susceptibility to CO_2 corrosion. This is because of their availability, strength, affordability, mechanical qualities, ease of use in construction, and economic effectiveness through corrosion inhibition (Jalab et al., 2023; Wang et al., 2011). These metal pipes and other components are frequently exposed to chemicals in the oilfield environment, which can lead to corrosion. This is particularly true when the chemicals and metals are combined to form a solution, such as downhole fluids. In addition, uniform or localized corrosion and environmental cracking are the primary issues for downhole tubulars that are associated with corrosion problems. Figure 2.2 exhibits the internal corrosion of a crude oil pipeline caused by the presence of salt water and CO_2 in the pipeline's stream (Askari et al., 2019). Since carbonate scales are formed as an obvious corrosion on the surface, it can be noticed that the corrosion mechanism is only metal loss. Mesa attacks and pitting corrosion are the two types of localized corrosion that can occur. The different types of corrosion that occur results from dissolved CO_2 that vary greatly based on variations in specific environmental parameters (temperature, pH, CO_2 partial pressure, etc.) (Abbasov et al., 2013).

Figure 2.2: Internal corrosion of a crude oil pipeline (Askari et al., 2019).

The chemical and presumably electrochemical reactions involved in the mechanism of sweet corrosion has been investigated by many researchers, including Lopes et al. (2023) and Popoola et al. (2013). The corrosion mechanism for steel in CO_2 solutions was postulated by De Waard and Milliams (1975), involving direct reduction of carbonic acid as the main cathodic mechanism. Figure 2.3 illustrates the corrosion mechanism of carbon mild steel in CO_2 environment (sweet corrosion). Naturally, dry CO_2 gas itself is not corrosive. However, when CO_2 is dissolved in water, it can initiate an electrochemical reaction between steel and the contacting phase. Carbon dioxide will dissolve in the aqueous phase and form carbonic acid (H_2CO_3) which is corrosive to carbon mild steel.

$CO_{2(g)} \leftrightarrow CO_{2(aq)}$ (Eq. 2.1)

$CO_{2(aq)} + H_2O \leftrightarrow H_2CO_{3(aq)}$ (Eq. 2.2)

The weak carbonic acid is then dissociating in two steps:

$H_2CO_{3(aq)} \leftrightarrow H^+_{(aq)} + HCO^-_{3(aq)}$ (Eq. 2.3)

$HCO^-_{3(aq)} \leftrightarrow H^+_{(aq)} + CO^{2-}_{3(aq)}$ (Eq. 2.4)

Water can also dissociate, as expressed in Equation 2.5:

$H_2O_{(l)} \leftrightarrow H^+_{(aq)} + OH^-_{(aq)}$ (Eq. 2.5)

The electrochemical reactions of CO_2 corrosion occur at the steel surface and are classified as heterogeneous reactions. Iron dissolution, which is the primary anodic reaction (Equation 2.6), is followed by the cathodic reactions (Equations 2.7 to 2.10), which include the direct reduction of other weak acids in the system, such as H_2CO_3, HCO_3^-, and H^+ and H_2O (Kahyarian & Nesic, 2020).

$Fe_{(s)} \rightarrow Fe^{2+} + 2e^-$ (Eq. 2.6)

$2H^+ + 2e^- \rightarrow H_{2(g)}$ (Eq. 2.7)

$2H_2CO_3 + 2e^- \rightarrow 2HCO_3^- + H_{2(g)}$ (Eq. 2.8)

$2HCO_3^- + 2e^- \rightarrow 2CO_3^{2-} + H_{2(g)}$ (Eq. 2.9)

$2H_2O + 2e^- \rightarrow 2OH^- + H_{2(g)}$ (Eq. 2.10)

And overall reaction of CO_2 reaction as follows:

$Fe_{(s)} + H_2CO_3 \rightarrow FeCO_{3(s)}(\text{iron carbonate}) + H_{2(g)}$ (Eq. 2.11)

CO_2 corrosion is the outcome of several chemical and electrochemical processes. The primary corrosion product in a CO_2 environment is iron carbonate, or $FeCO_3$, which when the limit of its solubility is reached, it can form a protective film on the mild steel surface against corrosion (Guo, 2017).

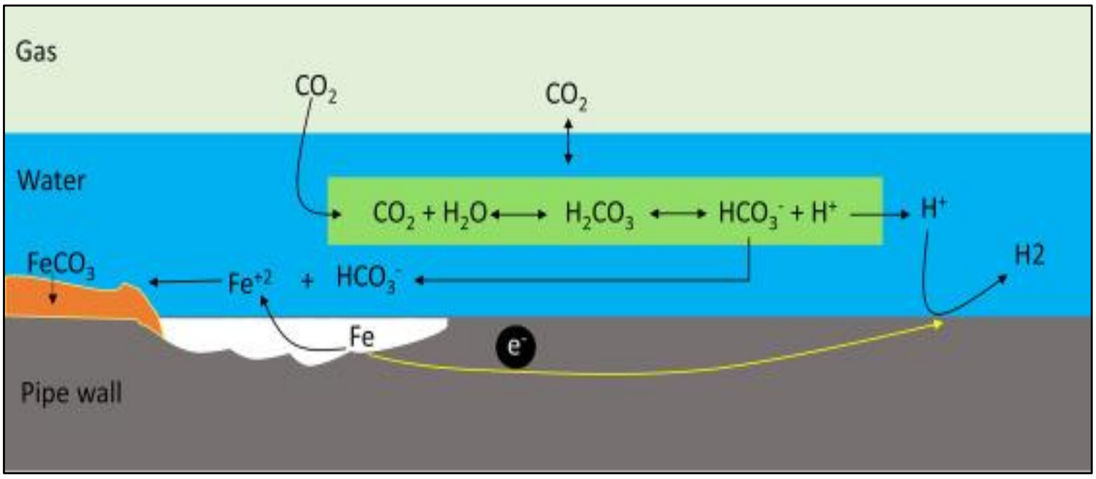

Figure 2.3: Sweet corrosion mechanism in the pipeline system (Hussein, 2022).

2.3 Current advancements on CO_2 corrosion inhibition

The current advancements in CO_2 corrosion research reflect significant progress in understanding the mechanisms, developing corrosion-resistant materials, and implementing effective mitigation strategies. The search for effective CO_2 corrosion inhibitors is crucial for extending the lifespan of industrial equipment and reducing maintenance costs. For instance, the use of amines, such as alkanolamines, have been effective in mitigating CO_2 corrosion. Recent research by Sahu et al. (2023) demonstrated that the incorporation of nitrogen-containing heterocyclic compounds, like imidazoles, significantly enhanced the protective film formation on carbon steel surfaces, thereby improving corrosion resistance. These compounds interact with the metal surface through chelation, forming stable complexes that inhibit corrosion. Besides, the use of polymers including polyamines and polyelectrolytes, has shown promising results in recent studies. A notable study by Ahmad et al. (2024) investigated the use of a novel polyamide copolymer which exhibited superior performance in high CO_2 environments. The copolymer's ability to form a protective barrier on the metal surface was attributed to its high molecular weight and specific functional groups. With growing environmental concerns, there is a trend towards developing more eco-friendly inhibitors. Recent studies have focused on biodegradable and less toxic compounds. For example, Hanafi et al. (2024) developed a new class of bio-based inhibitors derived from plant extracts, which showed convincing results in reducing CO_2 corrosion while being environmentally benign. Advancements in characterization and testing methods have also contributed to the progress in CO_2 corrosion inhibitor development. Techniques such as Atomic Force Microscopy (AFM), Scanning Electron Microscopy (SEM), and Electrochemical Impedance Spectroscopy (EIS) have provided deeper insights into the effectiveness of inhibitors and the mechanisms of corrosion. In the work of Martinez et al. (2024) utilized these advanced methods to evaluate the protective films formed by new inhibitor systems, leading to more precise optimization of inhibitor formulations. As research progresses, it is expected that new inhibitors and improved formulations will further mitigate CO_2 corrosion, contributing to the durability and efficiency of industrial infrastructure.

2.4 Corrosion consequences

In today's world, corrosion is ubiquitous and leads to serious problem in plaguing various industries. Research from all around the world revealed that rust caused a number of oil pipelines to burst, resulting in oil spill and subsequent degradation of the environment (Prasad et al., 2020). This has been linked to widespread harm to ecosystems, costly oil clean-up, and resource depletion. Failures occur when structures or components can no longer bear the stress imposed on them. Failures are typically caused by localized concentrations of stress and can arise from a variety of causes, including corrosive attacks like pitting and structural defects like holes, notches, and small-diameter transitional curves, as well as cavities in the microstructure of materials. About 60% of oil field installation failures are known to be attributable to CO_2 corrosion, primarily as a result of the low corrosion resistance of commonly used steels, including carbon steel, and inaccurate corrosion prediction (Lopes et al., 2023). Corrosion is projected to cost the globe over US $2.5 trillion a year, or roughly 3.4% of GDP (gross domestic product) (Koch, 2017). In numerous industrial mishaps, corrosion has resulted in losses estimated at around billions of dollars. According to estimates, the overall yearly cost of corrosion in the oil and gas production sector is $1.372 billion. This amount is divided into three categories: $589 million for surface pipeline and facility costs, $463 million for downhole tube expenses, and an additional $320 million for corrosion-related capital expenditures (Koch, 2017; Popoola et al., 2013). There are numerous devastating incidents brought on by corrosion failure had been documented in the past.

In May 2015, an oil spill incident occurred in Santa Barbara, California. A spill of 540 m^3 of crude oil took place on one of the US coasts with the greatest biological diversity. There was crack propagation in the lowest quadrant of the pipeline, whose thickness had decreased by 45% as a result of corrosion. Unfortunately, a significant environmental calamity was caused by the oil spill. Another incident was reported on November 17th, 2014, in Newbury, England, where a railroad traffic light that was falling over two tracks was struck by a train moving at 180 km h^{-1}. The wall of the hollow pylon almost completely collapsed due to corrosion (Petrović, 2016). In a case study reported by Hanafiah et al. (2015) in Malaysia, the Human Health and Safety Loss

(HHSL) in both rural and urban locations in light of pipeline failure caused by corrosion were investigated. They concluded that both locations had the potential for pipeline failure due to corrosion. In another study reported by Azam and co-workers (2020), the corrosion behaviour of API-5L-X42 pipeline steel was examined using electrochemical testing in the natural seawater (which acts as the electrolyte) surrounding the Peninsular Malaysia. They found that the majority of the corrosion product formed on the exposed surface experienced uniform and localized/ pitting corrosion. On top of that, they inferred that the seawaters in the Strait of Melaka contributed to a higher corrosion rate and potential compared to the seawaters in South China. Sweet corrosion can be effectively mitigated by corrosion inhibitors and corrosion-resistant alloys (CRAs) (Tamalmani & Husin, 2020). However, the use of inhibitors has long been regarded as the first line of defence against corrosion in the oil extraction and processing sectors.

2.5 Classification of corrosion inhibitors

Carbon mild steel is intended to be protected from corrosion using a range of methods, such as coating application, inhibitor use, and cathodic/ anodic protection application. The most practical and convenient way to prolong the life of metal among the various corrosion prevention techniques is to utilize inhibitors due to their impressive efficacy and cost-effectiveness (Bashir et al., 2018; Shadi et al., 2023; Yüce, 2020). According to Al-Amiery et al. (2023), a corrosion inhibitor is known as a chemical compound or mixture of compounds that is added to corrosive medium in modest doses to slow down and minimize the rate of corrosion. Corrosion inhibitors can either retard the cathodic or anodic reaction of the corrosion process or both. However, in order to achieve an optimal level of inhibition, the inhibitors need to be added above a specified minimum concentration (ranging from ten ppm to several thousand ppm) (Vaszilcsin et al., 2023).

It has been postulated that adsorption serves as an underlying mechanism for inhibiting corrosion on metal surfaces *via* physisorption or chemisorption, and it further improves the inhibition efficacy. There are two ways involving the separation process for the inhibition mechanism of the inhibitor molecules: (i) by adsorbing on the metal surface and creating a compact protective thin layer; and (ii) by precipitating on the metal surface and acting on the aggressive medium to create protective precipitates and inhibit the growth of aggressive agents (El-Sayed et al., 2010).

There exist two primary types of corrosion inhibitors: inorganic and organic (Abdallah et al., 2006; Desai et al., 2023). In the past, the use of various inorganic and organic inhibitors, such as cathodic, film, anodic (passivating), and volatile inhibitors, has been favourable especially in oil and gas field operations where they have reduced installation failure and consequently increased revenue (Onuegbu et al., 2020). The inorganic inhibitors include chromate, dichromate, phosphate, nitrite, and nitrate (Al-Amiery et al., 2023; Chauhan et al., 2022; Sastri, 2012; Yuchun et al., 2002). Flavonoids, tannins, organic amino acids and alkaloids are examples of organic inhibitors (Rani & Basu, 2012). Nevertheless, the organic inhibitors have one or more polar groups, which are made up of π electrons and the atoms O, N, P, and S. These heteroatoms compounds that adhere to the metallic surface, further obstructing the active sites and creating a physical barrier, which reduces the transport of corrosive species to the metal surface (Hosseini et al., 2022; Wang et al., 2011). Organic inhibitors are more effective than inorganic inhibitors in preventing corrosion and most of the well-known inhibitors for mild steel corrosion are organic chemicals. Besides, other type of inhibitors includes volatile inhibitors, passivating (anodic) inhibitors, cathodic inhibitors, and precipitation inhibitors. The inhibitors are prevalent in a wide range of applications, such as cooling water systems, pickling and washing solutions, crude oils and liquid fuels, and processing liquids from the food and pharmaceutical sectors, etc (Vaszilcsin et al., 2023).

Nowadays, a large number of research studies are devoted to the development of metal corrosion inhibitors that promise high levels of efficiency, up to 99%. Corrosion inhibitors such as imidazoline, inorganic salts and polymeric inhibitors have been used to inhibit the CO_2 corrosion of mild steel. However, research on synthetic corrosion inhibitors has ceased due to their high cost, toxicity, and lack of biodegradability. Hence, the attention of many researchers has been drawn to explore ‘green’ and eco-benign corrosion inhibitors as an alternative to toxic and hazardous inhibitors. These inhibitors are based on plant extracts and oils that are rich in active molecules and can be derived from a variety of plant parts, including seeds, leaves, flowers, fruits, peels, bark, stems, roots, and even entire plants. Since they produce their own food by absorbing carbon dioxide and releasing oxygen through the process of photosynthesis, plants contribute positively to the climate. Besides, they are also biodegradable, using the plant extract as an inhibitor also benefits the environment. Table 2.1 lists some of the literature on the utilization of organic corrosion inhibitors on metallic surfaces in different corrosion environments.

Table 2.1: Literature on the utilization of organic corrosion inhibitors on metallic surfaces in different corrosion environments.

Metallic substrate	Corrosion inhibitor	Environment	IE%	References
AP15 L X 60 Steel	Tannic acid and KI	CO_2-saturated 3.5% NaCl solution	90	(Usman et al., 2017)
Mild steel	*Clitoria ternatea* flower extract	Acid medium 0.5 M H_2SO_4	88	(Kumar et al., 2013)
Mild steel	*Calotropis procera* leaves extract	CO_2-saturated 3.5% NaCl solution	80	(Ibrahim et al., 2016)
N80 steel	*Ginkgo biloba* fruit extracts	CO_2-saturated 3.5% NaCl solution	92	(Singh et al., 2014)
Mild steel	Sunflower (*Helianthus annuus*)	1 M HCI	83	(Khoshsang & Ghaffarinejad, 2022)
Mild steel	*Eucallyptus* leaves extract	NaCl	90	(Bahlakeh et al., 2019)
API5L- Steel	*Dimorcapus* longan peel extract	CO_2-saturated 3.5% NaCl solution	50	(Priyotomo et al., 2018)
A106 Carbon steel	*Jatropha curcas* oil	CO_2-saturated 3.5% NaCl solution	82	(Mohadyaldinn et al., 2017)
API5L - X65	*Sida acuta* extract	CO_2-saturated 3.5% NaCl solution	90	(Aribo et al., 2017)
API5L - Grade B	Licorice extract	CO_2-saturated 3.5% NaCl solution	82	(Bajelani & Fattah, 2016)
Mild steel	*Clitoria ternatea* flower extract	CO_2-saturated 3.5% NaCl solution	90	This work

2.6 *Clitoria ternatea*

Clitoria ternatea, commonly named Asian pigeon wings, blue bellvine, Butterfly pea or blue pea and traditionally known as ‘bunga telang’, is a perennial twine herbaceous plant originating from Fabaceae family (Figure 2.4) (Das et al., 2020; Tuan Putra et al., 2021). This ornamental flower native to Malaysia and is now widely distributed around the world, including in Indonesia, India, Sri Lanka, Central America, Africa, and Phillipines (Lakshan et al., 2019; Morris, 2009). The deep and vivid blue colour of CT is attributed to anthocyanin compounds present (Nair et al., 2015). Plant species such as CT have been recognised as a major source of antioxidants due to their diverse phytochemical content.

Figure 2.4: Digital photograph of *Clitoria ternatea* flower.

This flower consists of large and small nodules with an oval to irregular shape and a diameter ranging from 0.5 to 1.5 cm. The thickness of the cortex varies between 0.05 and 0.1 cm. Additionally, the stem of this species does not exhibit any variations, rather they were all creeping over each other in the competition of sunlight. The stem's length of five metres matched the description given by Backer and Bakhuizen van den Brink Jr (1963), who stated that stem lengths varied from one to five metres. In traditional medicine, this telang plant is considered to be an extremely unique herbal plant. It is said that every component has the ability to strengthen and heal organs, from the root to the bloom. Due to its numerous health benefits, this legume has been used in drinks, as an organic food colouring, medicine, and decorative planting (Jeyaraj et al., 2022; Oguis et al., 2019; Sofiah et al., 2021; Thanh et al., 2020). Not only is this plant utilized as a colouring agent, but it's also commonly used as a nootropic, anti-stress, anti-inflammatory, antidepressant, analgesic, anti-diabetic and memory booster (Haditio et al., 2021; Morris, 2009; Mukherjee et al., 2008).

Plants generate a broad family of polyphenolic substances called flavonoids, which include anthocyanins, neo-flavonoids, isoflavones, flavanonols, flavonols, flavanones, chalcones and flavones (Karak, 2019). Previous research on *Clitora ternatea* legume found that the flower composed of high phenolic compounds, namely saponin, tannin, flavonoids such as quercetin and kaempferol, anthocyanin glycosides, and alkaloids as well as ternatin anthocyanins (A1-A3, B1-B4, C1-C4, and D1-D3) (Kumar et al., 2013; Lakshan et al., 2019; Lijon et al., 2017). Flavonoids are heterocyclic compounds that contain oxygen and are made up of a heterocyclic ring (ring C) joined to two phenyl rings (rings A and B) as displayed in Figure 2.5. The structure of this fragment allows for the distinction of many types of flavonoids (Dmitrienko et al., 2012). According to Karak (2019), the carbon of the C ring, to which the B ring is linked, can be used to distinguish between different subgroups of flavonoids. The list consists of the following seven: chalcones, flavones, isoflavones, flavanols, anthocyanins, flavonols, and flavanones (Chen et al., 2023).

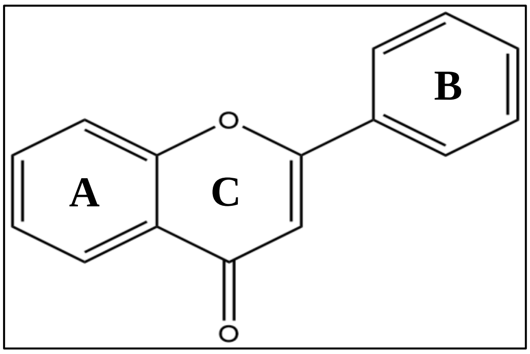

Figure 2.5: Basic monomeric structure of flavonoid.

2.6.1 Quercetin

Flavonols are flavonoids with the presence of ketone group. They occur abundantly in a variety of fruits and vegetables. The most studied flavonols are kaempferol, quercetin, myricetin and fisetin (Panche et al., 2016). The majority of flavonoids are flavonols, with quercetin being the most prevalent type. Research revealed that quercetin-rich foods include apples, raw onions, fruit pomace and berries (Ali et al., 2022; Srinivas et al., 2010). The word quercetin is derived from the Latin ‘quercetum’, which means oak forest or quercus oak with three rings and five hydroxyl groups. The molecular structure of quercetin ($C_{15}H_{10}O_7$) can be observed in Figure 2.6.

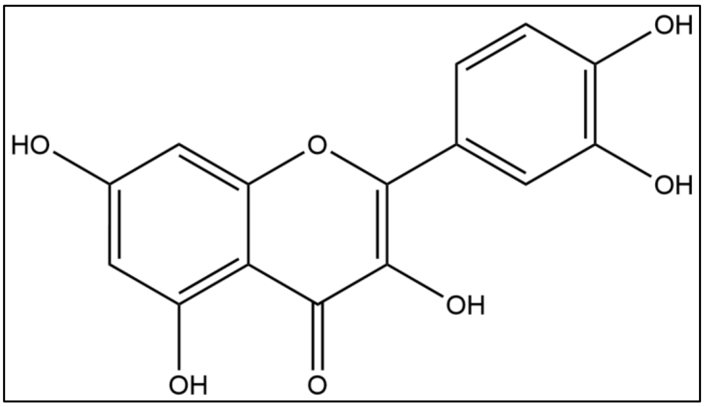

Figure 2.6: Molecular structure of quercetin [2-(3,4-dihydroxyphenyl)-3,5,7-trihydroxychromen-4-one].

Quercetin comes in three different forms: monohydrate, dihydrate, and anhydrous. When attempting to crystallize the hydrated forms from aqueous solvents, it can be challenging due to their limited solubility in water (Vasisht et al., 2016). As delineated by Dehghani et al. (2020), quercetin as a naturally occurring flavonoid group of polyphenols, possessed a strong anti-corrosion capacity in a variety of corrosive conditions since the structure of quercetin is rich in oxygen, making it possible to form chemical bonds with metal cations.

2.6.2 Kaempferol

At present, kaempferol ($C_{15}H_{10}O_6$) is of interest due to its anticancer, anti-inflammatory, anti-ulcer, and anti-oxidant, as well as its ability to block HIV protease (Chen & Chen, 2013). Many fruits, vegetables, and drinks, including broccoli, French beans, onions, black tea, and apples, have been found to contain kaempferol or its derivatives (M Calderon-Montano et al., 2011; Miean & Mohamed, 2001). Although the 3-hydroxyflavone backbones of quercetin and kaempferol are similar, quercetin has an extra hydroxyl group on the B ring (Figure 2.7). As a result, due to the absence of one hydroxyl group, kaempferol is less reactive and more chemically stable than quercetin (Dabeek & Marra, 2019).

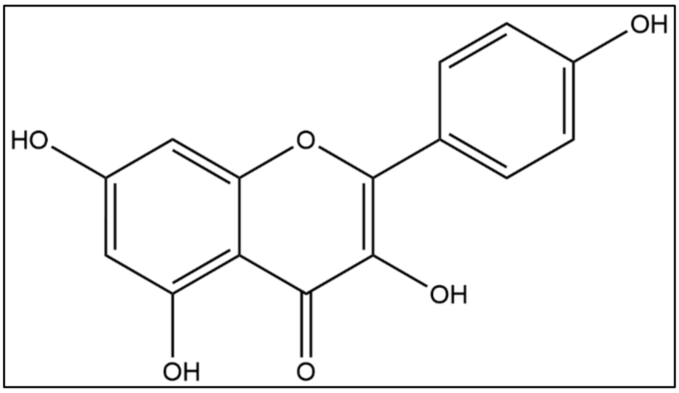

Figure 2.7: Molecular structure of kaempferol [3,5,7-trihydroxy-2-(40hydroxyphenyl) chromen-4-one].

2.7 *Clitoria ternatea* as a corrosion inhibitor

Clitoria ternatea flower has been employed as a bio-benign corrosion inhibitor to mitigate the corrosion of mild steel. As reported by Kumar et al. (2013), the corrosion inhibitory action of CT flower extracts was determined in 0.5 M H_2SO_4 on metal surface. The corrosion inhibition performance of the extract was investigated using the weight loss method, potentiodynamic polarization, and EIS measurements. It was discovered that the addition of 25 ppm of TBAB (Tetrabutylammonium bromide) solution to 100 ppm of plant extracts reduced the corrosion rate and increased the inhibition efficiency to 88.42 %. Sheydaei et al. (2023) worked with a sol-gel-based hybrid silanol coating incorporated with nanoparticles consisting of CT extracts and sodium montmorillonite. The EIS results showed that the coating resistance of the sample containing 3 wt.% CT-MMT was 86 %. In a separate study, Ghuzali et al. (2021) evaluated the corrosion mitigation capability of sol-gel coating doped with CT extracts on the surface of mild steel. The maximum inhibition efficiency of 89.6% was reported for coated mild steel doped with a concentration of 75 ppm extracts of CT. It was also observed that the corrosion current density decreased when the CT inhibitor concentration was increased up to 75 ppm due to the adsorption mechanism of inhibitor molecules on the surface of mild steel. These organic compounds can adsorb on the steel surface and hinder corrosion because they contain many heteroatoms (such as N, O, and S) as well as double and triple bonds which make them an excellent alternative corrosion mitigators particularly in the oil and gas industry. However, many of these studies fail to include detailed descriptions of the mechanisms of CO_2 corrosion inhibition and do not provide explicit explanations of how inhibitors interact with metal surfaces to prevent corrosion. Most of the studies on CO_2 corrosion inhibition often lack detailed insights into the underlying mechanisms of inhibitor action, focusing primarily on performance metrics rather than the fundamental interactions between inhibitors and metal surfaces.

2.8 Corrosion monitoring techniques

The effectiveness of bio-based corrosion inhibitors can be ascertained by applying a variety of corrosion monitoring techniques. These approaches have emerged as the preferred technique to better understand the corrosion mechanism since they are reasonably quick and very accurate. Standard methods for evaluating the features of electrochemical corrosion include potentiodynamic polarization (PD) and electrochemical impedance analysis (EIS). Electrochemical noise measurement (ENM) has also been applied to measure naturally occurring fluctuations of current and potential, and it is preferable to use these techniques in conjunction with other electrochemical techniques. The application of these techniques will yield instantaneous corrosion rate, thus determining the phenomenon of corrosion inhibition.

2.8.1 Electrochemical impedance spectroscopy (EIS)

Electrochemical impedance spectroscopy (EIS) is a novel electrochemical technique that has flourished in recent years. Its sensitive and adaptable nature makes it useful for a wide range of applications, including examining the mechanisms underlying electrochemical kinetic reactions, quantifying the dielectric and transport characteristics of materials, examining the characteristics of porous electrodes, and examining passive surfaces (Meddings et al., 2020). Since the 18th century, this technique has been a popular theoretical approach for studying the electrical properties of conducting materials, corrosion studies, and corrosion control (Hernández et al., 2020). It is