

**EVALUATION OF *PIPER SARMENTOSUM* (PS)
LEAVES EXTRACTS AS GREEN INHIBITOR
FOR CORROSION OF MILD STEEL IN 0.5 M HCl
SOLUTION**

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UNIVERSITI SAINS MALAYSIA

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by

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LIST OF SYMBOLS

C_{dl}	Double layer capacitance
CE	Catechin equivalent
cm	Centimetre
CPE	Constant phase element
CPE_{coat}	Coating constant phase element
CPE_{dl}	Double layer constant phase element
CR	Corrosion rate
E_a	Activation energy
E_{corr}	Corrosion potential
E_{ocp}	Open Circuit Potential
F	Faraday constant
g	Gram
I_{corr}	Corrosion current density
IE	Inhibition efficiency
m/v	Weight per volume
$mA\ cm^{-2}$	Miliampere per centimetre square
M_{ew}	Equivalent weight
mg	Milligram

min	Minutes
mL	Millilitre
mm y ⁻¹	Milimetres per year
mm	Milimetre
mpy	mils of penetration per year
mV s ⁻¹	Milivolt per second
mV	Milivolt
R	Universal gas constant
R _{coat}	Coating resistance
R _{ct}	Charge transfer resistance
R _n	Noise resistance
R _p	Polarization resistance
R _s	Solution resistance
T	Absolute temperature
v/v	Volume per volume
wt	Weight
Z	Magnitude of the impedance
Z _{CPE}	Impedance of constant phase element
β _a	Anodic Tafel constant
β _c	Cathodic Tafel constant

ΔG_{ads}	Gibbs free energy of adsorption
ΔH	Enthalpy
ΔS	Entropy
η_{c}	Anodic overpotential
η_{c}	Cathodic overpotential
θ	Phase angle
θ_{water}	Water phase angle
λ_{max}	Absorption maximum
ρ	Density
σ_{I}	Standard deviation of current noise
σ_{V}	Standard deviation of potential noise
$\Omega \text{ cm}^2$	Ohm's centimetre square
ω	Angular frequency

LIST OF ABBREVIATIONS

APTES	3-aminopropyltriethoxysilane
CAE	Catechin equivalent
DTG	Derivatized thermogravimetric
DMSO	Dimethyl sulfoxide
EDX	Energy dispersive x-ray spectroscopy
HCl	Hydrochloric acid
EIS	Electrochemical impedance spectroscopy
ENM	Electrochemical noise measurement
Flvd	Flavonoid
FTIR	Fourier transform infrared spectroscopy
GAE	Gallic acid equivalent
GCMS	Gas chromatography mass spectrometry
NMR	Nuclear magnetic resonance
PD	Potentiodynamic polarization
Phnl	Phenolic
PS	<i>Piper sarmentosum</i>
PSA	<i>Piper sarmentosum</i> ethyl acetate extract
PSE	<i>Piper sarmentosum</i> ethanol extract

PSN	<i>Piper sarmentosum</i> n-hexane extract
PSW	<i>Piper sarmentosum</i> water extract
SEM	Scanning electron microscopy
SG	Sol-gel
TEOS	Tetraethyl orthosilicate
TFC	Total flavonoid content
TGA	Thermal analysis
TPC	Total phenolic content

**PENILAIAN EKSTRAK DAUN *PIPER SARMENTOSUM* (PS) SEBAGAI
PERENCAT HIJAU BAGI KAKISAN KELULI LEMBUT DALAM
LARUTAN 0.5 M HCl**

ABSTRAK

Kajian ini tertumpu kepada penilaian ekstrak daun *Piper sarmentosum* (PS) dipencilkan menggunakan etanol (PSE), air (PSW), etil asetat (PSA) dan n-heksana (PSN) sebagai perencat kakisan bagi keluli lembut dalam larutan 0.5 M HCl. Dalam kajian ini, PSE dan PSW mengandungi kandungan TPC, TFC dan antioksidan tertinggi berbanding ekstrak yang lain. Pengukuran spektroskopi impedans elektrokimia (EIS), keketuban potensiodinamik (PD) dan pengukuran hingar elektrokimia (ENM) telah digunakan untuk menentukan sifat perencatan kakisan ekstrak. Berdasarkan data EIS, PSE and PSW memberikan kecekapan perencat tertinggi iaitu 93.24 % dan 93.00 % masing-masing pada 1000 ppm. Di samping itu, analisis PD menunjukkan bahawa PSE dan PSW bertindak sebagai perencat kakisan jenis campuran dengan kesan utama menghalang tindak balas anodik. Selain itu, mekanisme penjerapan PSE dan PSW mematuhi model isoterma Langmuir yang menerangkan proses penjerapan separuh-fizikal spontan dan/atau separa-kimia. Analisis SEM menunjukkan terdapat pemulihan morfologi permukaan kepingan keluli lembut pada kehadiran kedua-dua perencat. Kajian ini juga mengkaji ciri-ciri rintangan penglitup matriks sol-gel hibrid yang telah dihasilkan dengan menggunakan APTES dan TEOS yang didepositkan pada keluli lembut dengan menggunakan teknik celupan. Permukaan keluli lembut yang didopkan dengan penglitup sol-gel hibrid dengan perencat mendapati bahawa ia lebih bersifat hidrofobik berbanding permukaan keluli lembut (tanpa penglitup).

**EVALUATION OF *PIPER SARMENTOSUM* (PS) LEAVES EXTRACT AS
GREEN INHIBITOR FOR CORROSION OF MILD STEEL IN 0.5 M HCl
SOLUTION**

ABSTRACT

This study focused on the evaluation of *Piper sarmentosum* (PS) leaves extracts isolated using ethanol (PSE), water (PSW), ethyl acetate (PSA) and n-hexane (PSN) as corrosion inhibitors for mild steel in 0.5 M HCl solution. In this study, PSE and PSW contained the highest content of TPC, TFC and antioxidants as compared to other extracts. Electrochemical impedance spectroscopy (EIS), potentiodynamic polarization (PD) and electrochemical noise measurement (ENM) were employed to determine the corrosion inhibitive properties of the extracts. Based on EIS data, it was revealed that PSE and PSW provided the highest inhibition efficiency of 93.24% and 93.00%, respectively at 1000 ppm. Additionally, PD analysis demonstrated that PSE and PSW act as a mixed type corrosion inhibitor, predominantly mitigating the anodic reaction. Moreover, PSE and PSW adsorption mechanism obeyed Langmuir isotherm model illustrating a spontaneous semi-physisorption and/or semi-chemisorption adsorption process. SEM analysis showed the improvement of the surface morphology of mild plates in the presence of both inhibitors. The present study also investigated the coating resistance characteristics of hybrid sol-gel matrices prepared using APTES and TEOS deposited on mild steel adopting the dip-coating technique. Mild steel surfaces treated with inhibitors doped hybrid sol-gel coatings were found to be more hydrophobic compared to bare mild steel surface.

CHAPTER 1

INTRODUCTION

1.1 Background of the study

In the construction industry, the use of mild steel is widespread due to its low cost (Ansari and Quraishi, 2014). Apart from having excellent strength and hardness, this type of steel is fundamentally workable in which it can be bent, worked or welded into many shapes. However, the corrosion of mild steel has become a massive challenge for various industrial sectors, especially those that involve in acidic industrial applications such as refining crude oil, acid pickling, industrial cleaning, acid descaling, oil–well acid in oil recovery and petrochemical processes (Raja *et al.*, 2013; Hussin *et al.*, 2016). The corrosion effect on the economy is highly concerned due to the high cost involved in corrosion control, repair and maintenance (Al-Otaibi *et al.*, 2014; Hussin *et al.*, 2016; Umoren *et al.*, 2016).

The use of an inhibitor has become the most popular approach amongst the reported techniques to overcome the corrosion of mild steel. In the last decade, the corrosion of metal in the acidic media has been widely studied due to its importance in industrial application (Hussin *et al.*, 2015; Sin *et al.*, 2017; Asaad *et al.*, 2018). However, conventional corrosion inhibitors that are available in the market are synthetic organic compounds. Even though these corrosion inhibitors are effective, they are toxic and expensive. Recently, the environmental impact of conventional corrosion inhibitor has started to gain worldwide concern. Thus, many researchers have developed alternative strategies to mitigate corrosion utilising abundant plants to isolate potent corrosion inhibitors. Many plant-based natural products have unique

characteristics but are yet to be discovered as potential corrosion inhibitors. Green corrosion inhibitors extracted from plants are environmentally friendly compared to most of the chemical inhibitors which are toxic, more expensive and non-biodegradable.

Piper sarmentosum (PS) or locally known as Kaduk in Malaysia, is the abundant sources of green additive that contain active compounds. Previous studies have revealed that PS leaves contain flavonoids, phenylpropanoids, alkaloids, amides, and lignans (Sumazian *et al.*, 2010; Hussain *et al.*, 2010; Syeddan *et al.*, 2013). The flavonoid compounds can be extracted from the PS leaves to be utilised as an inhibitor since it contains OH groups and π -electrons of the aromatic rings. Theoretically, the natural and organic inhibitors contain heterocyclic compounds with polar functional groups containing N, O, or S atom and π -electrons. The electrostatic interactions between the functional groups and the surface of mild steel would result in the development of an adsorptive layer of inhibitor molecules (Migahed *et al.*, 2011).

1.2 Problem statement

Corrosion is considered as a bottleneck faced by the industries, especially in steel-related industries. In Malaysia alone, it was reported by NACE in 2015 that the cost of corrosion is approximately RM 6.7 billion. This value is significantly immense compared to RM 207.4 billion of the gross domestic product (GDP). Similarly, in the U.S and Europe, the estimated of corrosion-related damage was estimated around 3-5 % of their gross national product which involves trillions of dollars. Therefore, it is crucial to efficiently control the corrosion process which can be achieved by efficient

corrosion inhibitor. Whereas currently, there are not any inhibitor in the market that can be utilized effectively to eliminate the corrosion process at a lower cost.

In order to solve the corrosion issue, corrosion inhibitors are widely used. However, there are some environmental issues associated with the application of most of the corrosion inhibitors where they are not environmentally compliant and are toxic to the ecosystem and humans due to the compound of chromates and phosphates found in it. Due to the toxicity and health concern, the researchers are encouraged to search for corrosion inhibitors made from plant-based natural products for the environmental sustenance.

Piper sarmentosum (PS) is one of the natural products that can be used to produce green inhibitory. *Piper sarmentosum* (PS) is an herbal plant that can be easily found in Malaysia, Thailand and Indonesia. As we know, previous studies demonstrated that this plant contains various active compounds such as flavonoids, phenylpropanoids, alkaloids and amides that have been used especially in medication to treat disease, but no details studies that PS leaves as a corrosion inhibitor.

Hybrid sol-gel coatings is far easier to apply as a corrosion protective compared to others type of coatings. Even though hybrid sol-gel prepared using organic precursors to provide relatively high adhesion on metals, corrosive ions such as Cl^- and H^+ still can penetrate through the micro-pores and cracks of sol-gel coatings, leading to pitting corrosion, which is a major drawback. In order to solve this problem, eco-friendly corrosion inhibitors such as PS leaves extracts can be incorporated during the formulation of the sol-gel matrix to deliver active corrosion protection and good properties to the metal substrate. In addition, the use of organic molecules as corrosion

inhibitors is one of the most frequent, cost effective and rational approaches for corrosion protection of metals and should be proposed primarily for the industries.

1.3 Research objectives

The present study utilised *Piper sarmentosum* (PS) leaves as a raw material for the corrosion inhibition of mild steel in 0.5 M HCl solution. Therefore, the objectives of this research are:

- 1) To extract and characterize PS leaves using complementary analyses.
- 2) To study the corrosion inhibition of mild steel surface *via* electrochemical measurements and surface analyses.
- 3) To propose a suitable corrosion inhibition mechanism by manipulating the thermodynamic and adsorption isotherm data.
- 4) To study the performance of hybrid sol-gel coatings with and without the incorporation of PS leaves extracts.

1.4 Scope of studies

The present study involves the investigation of low cost, green and non-toxic compounds extracted from *Piper sarmentosum* leaves to be utilized as potential corrosion inhibitors for the corrosion protection of mild steel. The study covers the effect of inhibitor concentration and effect of temperature on corrosion while the mechanism of adsorption was studied with the use of Langmuir, Frumkin and Temkin isotherm models. Additionally, this study also focuses on the evaluation of corrosion inhibitive performance of PS leaves extracts through the incorporation into hybrid sol-

gel coatings. The effectiveness of the extracted inhibitors and the application of coatings to mitigate corrosion were investigated using electrochemical and surface analysis techniques.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction to corrosion

Corrosion is one of the most common and damaging events caused by nature. The word corrode from corrosion is originated from Latin. In Latin, the word ‘*rodere*’ means gnawing whereas ‘*corredere*’ refers to gnawing to pieces (Ghali *et al.*, 2007). According to Vema *et al.*, (2017), corrosion is the degradation of material properties that occurs when metal and its alloy interact with the environment *via* a chemical or an electromechanical reaction. The formed compound is called the corrosion product where the surface of metal becomes corroded and damaged. It is a spontaneous process in which the metals return to their stable state, i.e., ores or minerals (Umoru *et al.*, 2006). The corrosion occurs in the presence of ionic current in the solution and an electronic current in the metal where the metal ions moved into the solution at active areas (anode). Later, the process followed by the flow of electrons from the metal to an acceptor at less active areas (cathode) in which an electron acceptor such as oxygen or oxidizing agent or hydrogen ion is required (Raja and Sethuraman, 2008).

2.2 Corrosion of steel

Steel has been used since the early ages for multiple applications due to its durability, stiffness, and ability to be forged in any desired shapes. Nowadays, mild steel is dominantly used in the industrial sectors, primarily as a construction material that can be found in railways, bridges, shipbuilding, cars and road constructions. However, mild steel can severely corrode after some time. Also, the application of

metal treatment like acid pickling to remove impurities, such as stains, rust, inorganic contaminants might increase the rate of corrosion. Moreover, since this process involves exposing acid to the metal surface, it leads to the occurrence of corrosion due to the reaction with hydrogen. This problem has not only become a bottleneck to the industry players but also has become a problematic issue and a significant challenge to the researchers and corrosion engineers (Kudrashou and Nasr-El-Din, 2019).

Figure 2.1 shows the reaction between water and the mild steel surface. At the first stage of the corrosion process, Fe (iron) is oxidized to Fe^{2+} ions at the anode terminal (Equation 2.1). Then, at the cathode terminal, O_2 (oxygen) is reduced to form OH^- ions as shown in Equation 2.2 (Kruger, 2001):

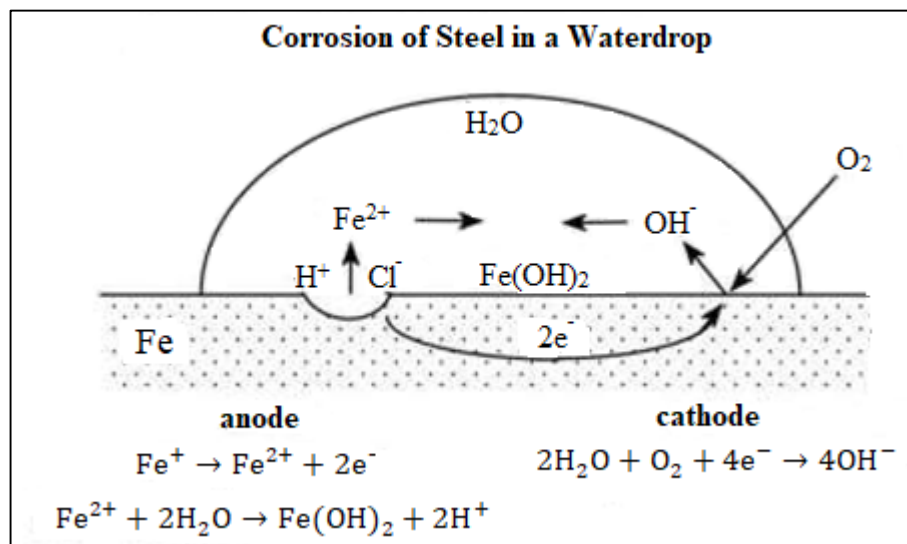


Figure 2.1: Corrosion of mild steel (Ahmad, 2006)

In acidic solution, the protonated hydrogen will be reduced to form hydrogen gas as shown in Equation 2.3 (Sheir *et al.*, 1994):



The sum of the equations 2.1 and 2.2 which involve the oxidation and reduction half-reactions, will form the insoluble iron (II) hydroxide (green rust) as shown in Equation 2.4 (Kruger, 2001):



However, due to the unstable iron (II), it would further oxidize to form a more stable iron (III) ions as depicted in Equation 2.5 (Kruger, 2001):



The iron (III) ions will then react with the hydroxide ions to produce the reddish-brown colour hydrated iron (III) oxides (rust/corroded formed) shown in Equation 2.6 (Kruger, 2001):



In the presence of an acid (hydrochloric acid, HCl), unstable ferrous chloride and hydrogen gas will be produced as shown in Equation 2.7 (Groysman, 2010):



According to Tamura (2008), FeCl_2 will be further oxidized to ferric hydroxide as shown in Equation 2.8:



Then, the iron (III) ions can be further oxidized to dehydrated oxyhydroxides, FeOOH without consuming neither acid nor base as shown in Equation 2.9 (Morgan and Stumm, 1981):



Subsequent oxidation of $\text{Fe}(\text{OH})_3$ would produce α - FeOOH (goethite), β - FeOOH (akaganite), γ - FeOOH (lepidocrocite), Fe_3O_4 (magnetite) and so forth. Therefore, a useful technique is needed to slow down and control the corrosion of mild steel.

2.3 Consequences and cost of corrosion

The corrosion has been a global problem, and its adverse effects are affecting the growth of many countries due to the high cost of corrosion control. Some industries have to spend a massive amount of money for repair and maintenance caused by corrosion (Roberge, 2008; Al-Otaibi *et al.*, 2014; Hussin *et al.*, 2016; Umoren *et al.*, 2016). Many industries are facing this problem such as construction, automotive sector, oil and gas industries, marine, electrical power plants, pulp, and paper industries and chemical processing industries (Ahmad, 2006).

According to Ahmad (2006), the corrosion can severely lead to plant shutdowns, i.e., nuclear plants, process plants, power plants and refineries which can cause complications to the industries and consumers. Moreover, it was known that corrosion could cause a loss of product and generate severe accidents and hazards due to the brittleness of the material. The corrosion in the pharmaceutical industry is also critical as the corrosion products possibly contaminate chemicals, pharmaceuticals and packaged goods.

Malaysia spends more than billions of ringgit per year for repair and maintenance due to the corrosion of metals (Hussin, 2011). Ahmad, (2006) stated that the average corrosion cost for most industrialized nations is around 3.5-4.5 % of the gross domestic product (GDP). Based on the CORROSION 2016 conference held in

Vancouver, British Columbia (B.C), it was mentioned that global savings between 15-35 % of the corrosion damage expenditure could be achieved by establishing corrosion prevention practices (Koch, 2016).

2.4 Corrosion control

As stated earlier, corrosion is the destruction of a metal surface commonly by the electrochemical or chemical reaction in the environment (Uhlig, 1985). The corrosion process is hard to control since it happens naturally when the metal is exposed to the environment (like water and oxygen). Mitigating the process of corrosion entirely is impossible. However, the corrosion can be potentially controlled and reduced by applying prevention methods. There are many ways to control and reduce corrosion in the industry namely; (i) proper material selection, (ii) proper material design, (iii) electrochemical protection (anodic or cathodic protection), (iv) control the environment (air and humidity), (v) application of coatings (vi) utilisation of corrosion inhibitors (Raja *et al.*, 2016).

Material selection is one of the methods to reduce corrosion which involves defining an appropriate material to achieve the best possible function within its actual environmental application. For instance, corrosion-resistant materials like stainless steel and nickel alloy are often used in the oil and gas industry to avoid damage caused by corrosion. The wrong choice of material may cause it to corrode quickly, thus influence the material life. Similarly, proper design can minimize corrosion by avoiding heterogeneity. Heterogeneity consists of different metals, uneven stress and temperature distribution that can speed up the corrosion (Ashby and Johnson, 2013).

Besides, corrosion can also be minimised by electrochemical protection (anodic or cathodic protection). This method is applicable for metal installed in the electrolyte medium, e.g., sea water, in which the protected metal is attached to the cathode of the electric source while a sacrificial metal (old metal) is connected to the anode. In this process, the sacrificial metal (positively charged) gets corroded thereby protecting the protected metal from corrosion. Also, corrosion can be reduced by controlling the surrounding environment where the corrosion protection of metal is intended by merely limiting the chemical interaction between the metal and surrounding gasses (Chandler, 1985). The reduction of sulphur, chloride and oxygen content in the environment can reduce the rate of corrosion.

Other common ways of avoiding corrosion are by application of coatings and inhibitors. Coatings are widely used in most metal products. Thus, hybrid sol-gel method is one of the efficient methods as a corrosion protective compared to others coatings. The coating can exist in the form of active metal (e.g., Zn), paint, oil, waxes or powders that heated to the metal surface to create a thin protective film between metal and the surrounding environment (Burn and Schuh, 1939). There are many advantages of the sol-gel method such as having high purity with large specific surface area involving simple and inexpensive equipment (Figueira *et al.*, 2015). This sol-gel process is normally used a low temperature and generally close to room temperature which is avoiding volatilization and degradation of entrapped species (Wang and Bierwagen, 2009). Thus, it can be easily to produce coatings of interest (Figueira *et al.*, 2015). In addition, sol-gel process is environmentally friendly method to prepare coatings that having microstructure and cost effective (Zheng and Li, 2010). Among all the corrosion control methods, utilisation of corrosion inhibitor is the best way to control and slow down the corrosion process because of inexpensive and easy to use.

2.5 Corrosion inhibitor

Corrosion inhibition is one of the possible ways to control the corrosion process using a corrosion inhibitor. The corrosion inhibitor is a chemical compound that is either of natural or synthetic origin and is added in a small concentration into the environment (Al-Otaibi *et al.*, 2014). The inhibitor functions to slow down the reaction and reduce the corrosion rate of metal. The corrosion inhibitor is absorbed on the surface of the corroded metal (anode), forming a protective layer which decreases the flow of ion and electron and eventually reduces the corrosion (Umoru *et al.*, 2006). According to Hussin *et al.*, (2011), the inhibitors can also reduce the corrosion rate of the metal by either inhibiting the anodic or cathodic reactions or both. The corrosion inhibitors have been used in many applications such as the cooling system, oil, and gas production units, boiler and feedwaters (Raja *et al.*, 2008).

Based on the previous studies, the corrosion inhibitors can be classified into three major categories: (i) passivators, (ii) vapor phase inhibitors and (iii) organic inhibitors (Schweitzer, 2007). The passivating inhibitor mainly contains chromates and nitrite. Chromate is known as a highly effective oxidizing anodic inhibitor used to maintain the metal surface in the passive state, prevent the breakdown and undermine the passive oxide, which leads to localized corrosion. Chromates are frequently used in the water system, while nitrites are used in the antifreeze-type cooling water systems. It will shift the corrosion potential (E_{corr}) of the metal anodically to be more passive. The passivator inhibitors are known to be excellent corrosion inhibitors due to their function as reported by Munoz *et al.*, (2007). The passivator inhibitors are also cheap and give an excellent anti-corrosive activity compared to other inhibitors. Unfortunately, this type of inhibitors are toxic and can give adverse effects to human and the environment (Halambek *et al.*, 2010; Umoren *et al.*, 2016; Muthukrishnan *et*

al., 2017). Moreover, it will cause some severe disposal issues since those wastes are not environmentally friendly.

In addition, the vapor phase inhibitor also can protect metals from atmospheric corrosion (Andreev *et al.*, 2013). It also can prevent the corrosion of ferrous and nonferrous metals (Subramanian *et al.*, 2000). Besides, the vapor phase inhibitor is an organic chemical which presents as vapor and also known as volatile corrosion inhibitor (Bavarian *et al.*, 2018). Vapor phase Corrosion Inhibitors are safe to use, do not contain harmful chemicals and they provide a low environmental impact solution for preventing corrosion in the system.

Meanwhile, the organic inhibitor can provide a protective layer in order to prevent the dissolution of the metal in the corrosive environment. Several authors have reported that organic corrosion inhibitors commonly contain polar functionalities such as N, O, or S atom and π electrons (Satapathy *et al.*, 2009). The organic corrosion inhibitors can also be the heterocyclic compounds containing the $-\text{NO}_2$, $-\text{OH}$, $-\text{OCH}_3$, $-\text{NH}_2$ and $-\text{COOH}$ polar functional groups (Vema *et al.*, 2017). Generally, the organic inhibitors are divided into two categories: (i) natural organic inhibitors and (ii) synthetic inhibitors. Due to environment and health concern, the researchers these days are interested in studying the use of plant-based natural products as green corrosion inhibitors, which substitute the toxic chromates and nitrates (Satapathy *et al.*, 2009; Lebrini *et al.*, 2011; Lecante *et al.*, 2011). Several authors have successfully utilized the natural products as organic corrosion inhibitors (Umoren *et al.*, 2016; Sin *et al.*, 2017; Saxena *et al.*, 2018; Sanaei *et al.*, 2019) as presented in Table 2.1. They have used the plant-based organic compounds that are commonly extracted from aromatic herbs, spices, and medicinal plants. Their studies have shown that natural organic

inhibitors show great potential as green corrosion inhibitors and are safe to the environment.

Table 2.1: Inhibition efficiency studies of different types of natural plants as organic corrosion inhibitors

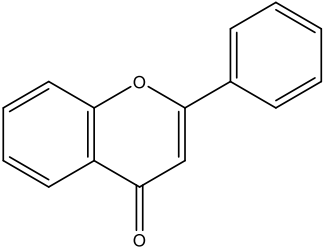
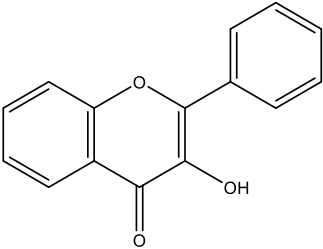
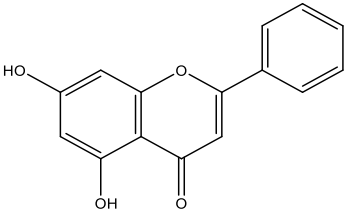
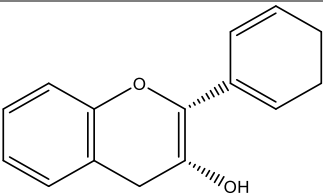
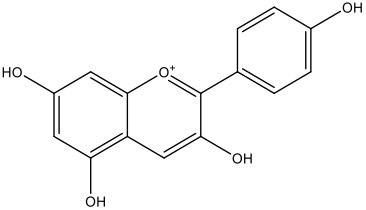
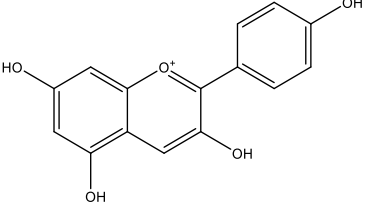
Type of natural plant	Corrosion media and metal	Properties	References
<i>Justicia gendarussa</i>	1 M HCl, mild steel	IE = 91.30 % Mixed type inhibitor	Satapathy <i>et al.</i> , (2009)
<i>Uncaria gambir</i>	1 M HCl, mild steel	IE = 78.45 % Mixed type inhibitor $\Delta G = -21.96$ kJ/mol	Hussin and Kassim (2011)
<i>Oxandra asbeckii</i>	1 M HCl, mild steel	IE = 92.00 % Mixed type inhibitor	Lebrini <i>et al.</i> , (2011)
<i>Tinospora crispa</i>	1 M HCl, mild steel	IE = 79.33 % Mixed type inhibitor $\Delta G = -21.87$ kJ/mol	Hussin <i>et al.</i> , (2011)
<i>Lansea coromandelica</i>	1 M H ₂ SO ₄ , mild steel	IE = 88.50 % Mixed type inhibitor $\Delta G = -18.5$ kJ/mol	Muthukrishnan <i>et al.</i> , (2013)
<i>Elaeis guineensis</i>	0.5 M HCl, mild steel	IE = 93.42 % Mixed type inhibitor $\Delta G = -23.01$ kJ/mol	Hussin <i>et al.</i> , (2015)
<i>Sida acuta</i>	1 M H ₂ SO ₄ , mild steel	IE = 80.00 % $\Delta G = -9.50$ kJ/mol	Umoren <i>et al.</i> , (2016)
<i>Aquilaria subintergra</i>	1 M HCl, mild steel	IE = 89.00 % Mixed type inhibitor	Sin <i>et al.</i> , (2017)
<i>Rhizophora apiculata</i>	1 M HCl, mild steel	IE = 68.10 % Mixed type inhibitor	Asaad <i>et al.</i> , (2017)
<i>Rosmarinus officinalis</i>	1 M HCl, mild steel	IE = 93.26 % Mixed type inhibitor	Loto (2018)
<i>Rollinia occidentalis</i>	1 M HCl, mild steel	IE = 85.70 % Mixed type inhibitor	Alvarez <i>et al.</i> , (2018)
<i>Asparagus racemosus</i>	0.5 M H ₂ SO ₄ , mild steel	IE = 88.85 % Mixed type inhibitor $\Delta G = -21.09$ kJ/mol	Saxena <i>et al.</i> , (2018)
<i>Rosa canina</i>	1 M HCl, mild steel	IE = 86.00 % Mixed type inhibitor	Sanaei <i>et al.</i> , (2019)

2.6 Flavonoid

Flavonoids are one of the main classes of natural products that consist of the carbon skeleton C₆-C₃-C₆. They are classified as secondary plant metabolites that comprise of a polyphenolic structure and having low molecular weight compounds that are generally found in natural plants such as fruits, greens and most of the beverages (Giada, 2013; Panche *et al.*, 2016). Moreover, the flavonoids are usually produced from the extracted plant. There are 13 subclasses of flavonoids classified by the difference in the degree of hydrogenation and hydroxylation of the three-ring systems (González, 2002). Whereas, there are 6 essential subclasses, i.e., flavonols, flavanols, flavones, flavanones, anthocyanins (or anthocyanidins) and isoflavones (Scalbert and Williamson, 2000; Narayana *et al.*, 2001). The basic structures of flavonoid subclasses and their examples are presented in Table 2.2.

Furthermore, there are many uses of flavonoid, especially for human health. According to Mustafa *et al.*, (2010), flavonoids also has been reported to have a lot of biochemical and pharmacological actions such as antioxidant, anticarcinogenic, antiviral, antimicrobial, antithrombotic and anti-inflammatory. On the other hand, flavonoids are essential constituents of the human diet and human cancer. Also, flavonoids are the most potent antioxidants found in plants due to the presence of hydroxyl groups in positions 3' and 4' of the B ring, which give high stability to the radical formed. Besides, flavonoids have shown great potential as corrosion inhibitor based on studies carried out by Chihi *et al.*, (2009), Hussin and Kassim, (2011), Barros *et al.*, (2016) and Sukul *et al.*, (2018) since they contain heteroatoms which can form strong chemical bonds with the metal surface to provide an inhibitive layer.

Table 2.2: The basic structures of flavonoid subclasses and their examples (Panche *et al.*, 2016; Giada 2013)

Flavonoid subclass	Basic structure	Examples
Flavones		Apigenin
Flavonols		Quercetin, Rutin
Flavanones		Naringenin
Flavanols		(+)-Catechin
Anthocyanins		Cyanidin
Isoflavones		Genistein

2.7 Piper sarmentosum (PS)

Piper sarmentosum (Figure 2.2) Roxb. belongs to the family *Piperaceae*. It is widely distributed in the tropical and subtropical region with more than 700 species of the world (Sumathykutty *et al.*, 1999; Chieng *et al.*, 2008; Ghazali *et al.*, 2018). PS is locally known as “kaduk” in Malaysia and commonly known as “Cha-plu” in Thailand (Zainudin *et al.*, 2013). The plant is glabrous, herbaceous shrub, growing about 7-15 cm high and grows in shaded areas. Moreover, PS plant also has an aromatic odor and a pungent taste (Rukachaisirikul *et al.*, 2004; Ridditid *et al.*, 2007; Syeddan *et al.*, 2013; Hematpoor *et al.*, 2018). According to Peungvicha *et al.*, (1998), the PS leaves are heart-shaped, simple, alternate and chordate, green in color around 5-10 cm wide, and 7-15 cm long.



Figure 2.2: *Piper sarmentosum* plant (Ugusman *et al.*, 2011)

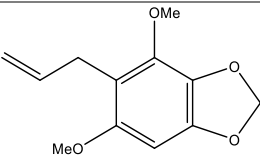
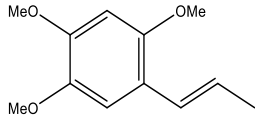
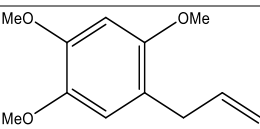
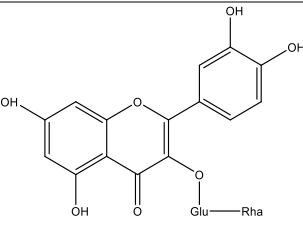
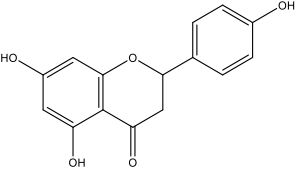
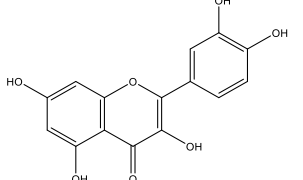
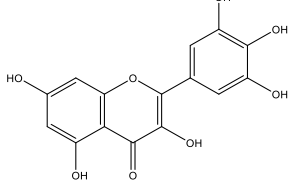
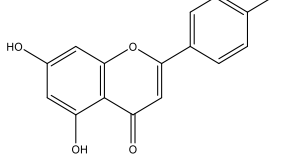
The PS plants have been used as a traditional food in Thailand and Malaysia. PS plant is not only consumed raw or cooked as main dishes but also used as a folk medicine to cure various ailments and disease (Hussain *et al.*, 2009; Syeddan *et al.*, 2013). Besides, many studies have shown that the use of the PS plant, especially leaves, roots, and fruits have high commercial and medical values to cure the diseases (Ghazali *et al.*, 2018).

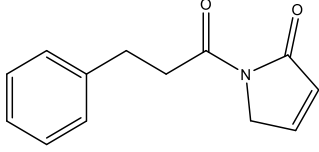
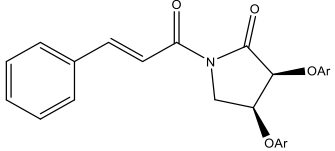
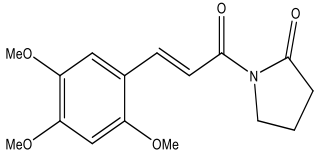
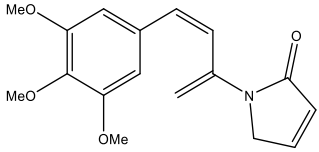
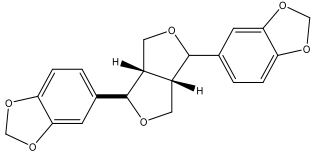
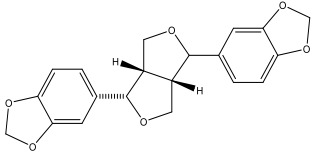
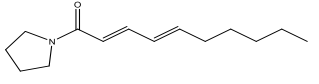
Pongmarutai (1980), have studied that the ethanolic extracts of the PS leaves have been used to cut down the blood sugar level in alloxan diabetes rabbits. Moreover, the water decoction of boiled PS leaves was used for treating sickness such as coughing, rheumatism, headache, and influenza while the roots were used as herbal remedy for toothache and fungoid dermatitis on the feet (Perry, 1980; Muhammad and Mustafa, 1994; Atiax *et al.*, 2011). According to Chaveerach *et al.*, (2006), the leaves of the PS have been used in Chinese traditional medicines system to treat fever and indigestion. In this study, the fruits and leaves of PS were used as an expectorant (Pongboonroad, 1976; Rukachaisirikul *et al.*, 2004; Sireeratawong *et al.*, 2010) while the roots were chewed may be utilized to treat asthma and cough.

Particularly in Malaysia, the plant was traditionally used to treat diabetes, hypertension and relieve joint aches (Subramanian *et al.*, 2003). According to previous studies, crushed PS leaves mixed with water was used to cure kidney difficulties in urination (Ong and Nordiana, 1999). Besides, PS was also commonly used to decrease the white discharge in the menstrual cycle of women and to treat acne, mouth odor and pain in the bones (Perry, 1981).

There are numbers of previous studies performed to identify the phytochemical groups and constituents present within all various parts of PS (e.g., leaves, roots, and fruits). The PS was found to contain flavonoids, phenylpropanoids, alkaloids, amides and lignans (Sim *et al.*, 2009; Sumazian *et al.*, 2010; Hussain *et al.*, 2010; Syeddan *et al.*, 2013). Moreover, previous studies demonstrated that PS leaves contain various compounds such as naringenin, rutin, α -asarone, γ -asarone, sarmentine, quercetin, rutin, sesamin, etc. as presented in Table 2.3 (Seyyeddan *et al.*, 2013).

Table 2.3: The phytochemical groups and their examples of various parts of PS

Part of the plant	Class of compound	Compound name	Structure	References
Leaves	Phenylpropanoid	1-allyl-2,6-dimethoxy-3,4-methylenedioxybenzene		Masuda <i>et al.</i> , (1991)
		1-allyl-2,4,5-trimethoxybenzene (α -asarone)		
		1-(1-E-propenyl)-2,4,5-trimethoxybenzene (γ -asarone)		
Flavonoid		Rutin		Miean and Mohamed (2001)
		Naringenin		Subramani <i>et al.</i> , (2003)
		Quercetin		
		Myricetin		Rukachaisirikul <i>et al.</i> , (2004)
		Apigenin		

Roots	Amide	Sarmentamide A		
		Sarmentamide B		Tuntiwach wuttikul <i>et al.</i> , (2006)
		Sarmentamide C		
	Alkaloid	Piplartine		Bokesch <i>et al.</i> , 2011
Fruits	Lignan	(+)-asarinin		
		Sesamin		Rukachaisi rikul <i>et al.</i> , (2004)
	Amide	Sarmentine		

2.7.1 Extraction techniques of *Piper sarmentosum* (PS)

Based on the previous studies, there are many extraction techniques of the *Piper sarmentosum*. Fernandez *et al.*, (2008) have studied the antimicrobial activity of the *Piper sarmentosum* (PS) plant. The *Piper sarmentosum* (PS) plant was extracted using the 70% methanol. 100 g of grounded PS plant was soaked in 500 mL and the mixtures were soaked for four days at room temperature. The mixtures were stirred every day using a sterile glass rod. After that, the extract was clarified by filtration through Whatman No. 1 filter papers and then was concentrated using an oven at 37°C for 24 hours to obtain the crude extract. Then the extract was then stored in vials at -20°C to prevent the loss of the bioactive compounds until further use.

Meanwhile, Pukclai and Kato-Noguchi, (2011) have examined the used of PS plant extracts as an allelopathic effect. 100 g of plant powder was extracted with 1 L of 80% v/v aqueous methanol for two days. Then, the extract was clarified by filtration using one layer of filter paper. After that, the residue was extracted again with 1 L of cold methanol for one day and filtered. Then, the two filterates were combined and evaporated with rotavaporator at 40°C.

In addition, Amran *et al.*, (2010) have tested the water extracts of PS leaves decreases atherosclerotic lesions in high cholesterolemic experimental rabbits. 100 g of PS leaves powder was extracted with 500 mL of water for one day and the extract was clarified by filtration using filter paper. Then, the water extract sample was then sent to the laboratory of Faculty of Pharmacy, where the freeze dried powdered extract was prepared and the powder extract was stored in dark bottles and kept in 4°C until used. The powder was mixed with 5 ml of water to dissolve it and then administered to the rabbits.

2.8 Corrosion monitoring techniques

In order to better understand the performance of organic inhibitors during the corrosion process, several corrosion measurement techniques can be applied. Electrochemical impedance (EIS), potentiodynamic polarization (PD) and electrochemical noise (ENM) are among the frequently used techniques to determine the electrochemical corrosion parameters. These corrosion measurement techniques can provide a better understanding of the corrosion inhibition phenomenon.

2.8.1 Electrochemical impedance spectroscopy (EIS)

Since the 1970s, electrochemical impedance spectroscopy (EIS) has been used by electrochemist and material scientist as a tool for studying complex system (Loveday *et al.*, 2004). Now, the EIS method is widely used as a standard diagnostic tool for the characterization of corrosion behaviour that is proven to be accurate (Roberge, 1999; Perez, 2004). This method involves the study of the variation of impedance of an electrochemical system under the application of small-amplitude alternating current (AC) perturbation (Schweitzer, 2007). EIS allows the characterization of electrodes by determination of charge transfer resistance (R_{ct}), corrosion mechanism and rate of corrosion (Bard and Faulkner, 1980; Jones, 1992; Law *et al.*, 2000).

The concept of impedance measurement shall be correlated with the basic theory of electrical resistance that is the capability of an element to resist the electrical current flow. An excellent definition of Ohm's law expresses resistance in term of a ratio between voltage (E) and current (I) as shown in Equation 2.10 (Gisela, 2016):