WINGED BEANS EXTRACT-DOPED-HYBRID COMPOSITE SOL-GEL COATING FOR CORROSION RESISTANCE OF CARBON STEEL IN 0.5 M HYDROCHLORIC ACID

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by

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LIST OF SYMBOLS

η	Overpotential
$\boldsymbol{\theta}$	Phase angle
$\boldsymbol{\theta}_{water}$	Water phase angle
λ_{max}	Absorption maximum
σ_i	Standard deviation of current noise
σ_v	Standard deviation of potential noise
Ω cm^2	Ohm`s centimetre square
ω	Angular frequency
β_a	Anodic Tafel constant
β_c	Cathodic Tafel constant
C_{dl}	Double layer capacitance
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
F	Faraday constant
g	gram
h	hour
i_{corr}	corrosion current density
IE	Inhibition efficiency

$mA\ cm^{-2}$	Milliampere per centimetre square
mg	Milligram
min	minute
mL	Millilitre
mpy	Mils of penetration per year
mmpy	Millimetres per year
mV	Millivolt
$mV\ s^{-1}$	Millivolt per second
R	Universal gas constant
R_{ct}	Charge transfer resistance
R_p	Polarization resistance
R_s	Solution resistance
R_{coat}	Coating resistance
Rn	Noise resistance
T	Absolute temperature
v/v	Volume per volume
Z	Magnitude of impedance
ΔG_{ads}	Gibbs free energy of adsorption
ΔH	Enthalpy
ΔS	Entropy

LIST OF ABBREVIATIONS

DTG	Derivative thermogravimetric
EDX	Energy dispersive x-ray
EIS	Electrochemical impedance spectroscopy
ENM	Electrochemical noise measurement
FRAP	Ferric reducing antioxidant power
FTIR	Fourier transform infrared
GAE	Gallic acid equivalent
HCl	Hydrochloric acid
HPLC	High-performance liquid chromatography
NMR	Nuclear magnetic resonance
PD	Potentiodynamic polarization
PDMS	Polydimethylsiloxane
TEOS	Tetraethyl orthosilicate
TFC	Total flavonoid content
TGA	Thermogravimetric analysis
TPC	Total phenolic content
WB	Winged bean
WBE	Winged bean ethanol
WBH	Winged bean n-hexane
WBM	Winged bean methanol
WBW	Winged bean water

PENGLITUP KOMPOSIT SOL-GEL EKSTRAK KACANG KELISA-DIDOP-HIBRID BAGI KELULI KARBON UNTUK RINTANGAN KAKISAN DALAM 0.5 M ASID HIDROKLORIK

ABSTRAK

Kajian ini memfokuskan pada pengekstrakan kacang kelisa (WB) dengan pelarut yang berbeza sifat polar bagi penghasilan perencat kakisan bagi mengurangkan kakisan keluli bertetulang dalam medium 0.5 M HCl. Didapati bahawa ekstrak air kacang kelisa (WBW) mempunyai hasil peratusan tertinggi, diikuti oleh ekstrak etanol (WBE), metanol (WBM), dan ekstrak heksana (WBH). Pencirian analisis pelengkap menunjukkan nilai TPC, TFC dan FRAP dalam tren seperti WBW (TPC: 117.40; TFC: 54.65) > WBE (TPC: 98.52; TFC: 52.67) > WBM (TPC: 82.64; TFC: 37.29) > WBH (TPC: 23.80; TFC: 17.59). Siri pemeriksaan fitokimia dan analisis HPLC secara kualitatif menunjukkan kehadiran sebatian fenolik seperti asid galik dan asid ferulik yang kemudiannya dinilai. FTIR spektrum ekstrak WB menemukan kumpulan berfungsi yang mencirikan sifat perencat kakisan yang baik. Tindakan perencatan ekstrak WB yang dikaji menggunakan spektroskopi impedans elektrokimia (EIS), kekutuban potensiodinamik (PD), dan teknik pengukuran hingar elektrokimia (ENM) mendedahkan bahawa kecekapan penghambatan WBW dan WBE (IE) dari ketiga-tiga teknik pada kepekatan 1000 ppm melebihi 80 %. Secara keseluruhan data yang diperoleh menunjukkan mekanisma isoterma penjerapan Langmuir serta penjerapan fizikal dengan $\Delta G_{ads} \leq -20$ kJ mol^{-1}, yang paling tepat bagi menggambarkan sifat perencat kedua-dua ekstrak WB. Aplikasi selanjutnya adalah dengan menggunakan ekstrak WB sebagai bahan tambahan dalam lapisan sol-gel menemukan pembentukan Fe-Si-O melalui pencirian FTIR-ATR dan analysis SEM-EDX dengan hidrofobik

yang baik dengan sudut pembasahan > 100 °. Data yang diperoleh menyokong potensi WB sebagai bahan yang berguna bagi aplikasi bahan terutama dalam perlindungan logam.

WINGED BEANS EXTRACT-DOPED-HYBRID COMPOSITE SOL-GEL COATING FOR CORROSION RESISTANCE OF CARBON STEEL IN 0.5 M HYDROCHLORIC ACID

ABSTRACT

The present work focuses on the extraction of winged bean (WB) with different polarity of solvent for the application of corrosion inhibitor to reduce the corrosivity of carbon steel in 0.5 M HCl medium. It was revealed that winged bean water extract (WBW) had the highest percentage yield, followed by winged bean ethanol (WBE), methanol (WBM), and hexane (WBH) extract. Further characterization using complementary analyses disclosed the values of TPC, TFC and FRAP in trend such WBW (TPC: 117.40; TFC: 54.65) > WBE (TPC: 98.52; TFC: 52.67) > WBM (TPC: 82.64; TFC: 37.29) > WBH (TPC: 23.80; TFC: 17.59). A series of phytochemical screening and HPLC analysis qualitatively show the presence of phenolic compounds like gallic acid and ferulic acid which then quantified. FTIR spectra of WB extract discovered the presence of functional groups that characterize good corrosion inhibitors. The inhibition action of WB extracts studied using electrochemical impedance spectroscopy (EIS), potentiodynamic polarization (PD), and electrochemical noise measurement (ENM) techniques revealed that WBW and WBE inhibition efficiencies (IE) from the three different techniques at 1000 ppm were beyond 80%. Overall data obtained suggested the Langmuir adsorption isotherm and physisorption mechanism with $\Delta G_{ads} \leq -20$ kJ mol^{-1}, best described the inhibitory process of both WB extracts. Further application of WB extracts as additive in sol-gel coating results in the formation of Fe-Si-O from the characterization through FTIR-ATR and SEM-EDX with good hydrophobicity with wetting angle of > 100°. The data

obtained support WB potential to be useful for material application especially in metal protection.

CHAPTER 1

INTRODUCTION

1.1 Background of the study

Carbon steel including alloy steel is widely happened to be in the foundation of buildings and bridges, daily appliances and tools, rails, pipelines and many more. Carbon steel always high in demand due to their versatility. High carbon steel is known for its strength in both tension and compression. Meanwhile low carbon steel offers more malleable and ductile characteristics. The various types of carbon steel are applicable to a wide range of industries and sectors.

Nevertheless, exposure of carbon steel to extreme conditions such as in an acidic environment or even in alkaline conditions could trigger corrosive attack. Corrosion of carbon steel and other embedded metals (Surahyo, 2019) potentially causing structural deterioration. The exposure of materials to acidic conditions is more prevalent and frequent in the petroleum and gas industry than in alkaline environments (M. A. M. El-Haddad et al., 2019). To add, hydrochloric acid is a common mineral acid stapled with various applications such as well acidization, acid pickling, chemical cleaning in industries, water treatment and petrochemical processes.

Metal surfaces can contain impurities that may affect usage of the product or further processing like plating with metal or painting. Strong acids, such as hydrochloric acid and sulfuric acid are commonly applied to clean impurities on metals. slight is a metal surface treatment used to remove impurities, such as stains, inorganic contaminants, and rust or scale from metals and alloys. Carbon steels, including alloys are often pickled in hydrochloric or sulfuric acid. The acids used often regard as pickle liquor used to remove the surface impurities to descale or clean steel surfaces. Technical quality HCl at typically 18% concentration is the most commonly used pickling agent for the pickling of carbon steel grades.

Corrosion inhibitors are often an option as one of the efficient techniques used to suppress and control corrosion. Normally, inhibitors are directly added to the metal material in a corrosive environment where it will form a hindrance that suppresses the corrosion process and thus lower the corrosion rate (Pratikno et al., 2018). Nevertheless, due to environmental toxicity, the widespread use of commercial corrosion inhibitors to reduce corrosion is being curtailed (Tamalmani & Husin, 2020). Corrosion inhibitors are reported to contain harmful chemicals and some have a high concentration of heavy metals, which are threats to human health, toxic to plants and animals (Tchounwou et al., 2012). In consequence, the emergence of "green" chemistry has led to the use of safer sources focusing on natural products where most of their extracts containing the necessary elements, which proven through studies to be a potent corrosion inhibitor.

Furthermore, numerous researchers have shown success in using naturally occurring chemicals to offer corrosion inhibitors in both acidic and alkaline environments (Miralrio & Espinoza Vázquez, 2020). Simultaneously, there is a growing interest in sol-gel protective coatings since they are an environmentally friendly method that has superior chemical stability, oxidation control, and better corrosion resistance for metal substrates (Figueira et al., 2015; Wang & Bierwagen, 2009). Additionally, sol-gel technology allows for a variety of techniques to create functional coatings with varying qualities. In recent years, sol-gel coatings doped with inhibitors show an encouraging performance as an effort on battling corrosion (Rani

& Basu, 2012). Inhibitors must be infused into the coating film in order for the corrosion process to be slowed by a self-healing action (Montemor et al., 2006; Shi et al., 2010; Zheludkevich et al., 2005).

Psophocarpus tetragonolobus, commonly known as the winged bean, popular as one of the protein-rich antioxidant legumes, can be seen as a potential green corrosion inhibitor. Literature confirmed the presence of flavonoids like catechin, epicatechin, quercetin and myricetin (Mustafa et al., 2010). Meanwhile, another study supports the findings with extra reveals of gallic acid, protocatechuic acid, chlorogenic acid, caffeic acid, ferulic acid, rutin and kaempferol, which can also be found in winged bean tubers (Mohanty et al., 2013). Theoretically, phenolic acids and flavonoids in plants contain functional groups that can generate electrostatic interactions with the surface of the metal substrate, consequently lead to the formation of an adsorptive layer of inhibitor molecules (Migahed et al., 2011).

1.2 Problem statement

Corrosion is a naturally occurring process in which metals and alloys attempt to revert to more stable thermodynamics as a result of reactions with the environment, which is often difficult to eradicate. Corrosion processes develop quickly once the protective barrier is disrupted. Consequently, this condition triggers the occurrence of a series of reactions capable of altering both the composition and properties of the metal surface and the surrounding environment. Inevitably, economics are affected as a consequence in terms of repair, replacement, product losses, safety, and pollution.

Corrosion inhibitor is one of the most preferred techniques used to combat corrosion. Although corrosion inhibitors assist in decreasing or preventing the reaction of the metal with the inconducive media, the usage of inorganic inhibitors, which are said to be cost-effective, such as chromate and phosphate, are toxic to humans and other living organisms. Recently, the application of sol-gel is gaining attention as its preparation can be controlled by varying parameters that influence the processes and the properties of the final coatings. However, applying a sol-gel coating solely made up of inorganic precursors deals with few problems such as micropores, low thickness and cracking due to brittleness. Thus, researchers were triggered to study more on sol-gel coatings doped with inhibitors in order to handle the existing drawbacks of sol-gel application.

Meanwhile, winged bean is an easy plantation known to be rich in bioactive compounds that are potent as corrosion inhibitors, and this species is yet to have any physical application. A few studies have focused on the physicochemical analysis, antioxidant compound and properties, and winged bean as chymotrypsin inhibitor. However, it still does not discover to be used as a corrosion inhibitor.

1.3 Research objectives

This present study proposed hybrid (TEOS/PDMS) composite sol-gel coating doped with Winged bean to enhance coating application for corrosion protection. As a result, the following are the objectives of this study:

1) To extract and characterize winged beans with different solvent polarities and perform physical and chemical characterization via complementary analyses (FTIR, NMR, HPLC and phytochemical analyses).

2) To study the inhibitive properties of winged bean extract on the corrosion of carbon steel using electrochemical measurement.

3) To produce a TEOS-PDMS hybrid sol-gel matrix with the addition of WB extract as a corrosion inhibitor and evaluate coating performance via electrochemical measurement and surface analysis.

4) To propose an effective corrosion inhibition mechanism by interpreting thermodynamic, evaluating adsorption isotherm data and performing quantum chemical calculations.

1.4 Scope of study

The present study focuses on the investigation of extractive compounds from winged beans using varying solar polarity (methanol, ethanol, water and hexane) to be utilized as a potential green corrosion inhibitor for the corrosion protection of carbon steel. Carbon steel was subjected to 0.5 M HCl electrolyte throughout this study. The effect of various concentrations of winged bean extract being incorporated within the sol-gel matrix, and the effect of temperature will be studied prior to optimization. As an addition, this study will include thermodynamics and adsorption isotherm modelling such as Langmuir, Frumkin and Temkin in order to provide a suitable corrosion inhibition mechanism. Furthermore, the effectiveness of winged bean extract as a corrosion inhibitor and incorporating it into a TEOS-PDMS hybrid sol-gel matrix will be meticulously examined through electrochemical and surface analyses to comply with a novel approach towards providing superior corrosion protection for carbon steel with a wide range of applications.

CHAPTER 2

LITERATURE REVIEW

2.1 Winged bean (WB)

The winged bean (*Psophocarpus tetragonolobus*) (Figure2.1) is a tropical legume of Fabaceae that grows up to nearly 4 metres with creeping stems and leaves. They are blessed with pinnate or palmate to trifoliate leaves. Bean pods are on average, 7 inches long and have four angles. The flowers are large and range in colour from pale blue to vivid blue. Oil (up to 17%), protein, vitamin E, and calcium are abundant in winged beans. According to studies, *P. tetragonolobus* is rich in proteins, has a high carbohydrate content, with the addition of a significant fat and fibre content (Parca et al., 2018).

Figure 2. 1: Winged bean plant (Zona, 2021)

WB has antibacterial, anti-inflammatory, anti-nociceptive, antioxidant, platelet aggregation inhibitory, and hepatoprotective effects, according to studies (Bassal et al., 2020; Kumar et al., 2017). Six Malaysian medicinal plants namely *Carica papaya, Musa acuminata, Oenanthe javanica, Piper sarmentosum, Sauropus androgynus,* including *Psophocarpus tetragonolobus* (WB), have been studied for their anti-inflammatory, antioxidant, and anti-nociceptive activities. The study found that all plants analysed had strong nitric oxide inhibitory activity without inducing cytotoxicity in the cells studied. They were all high in antioxidant activity, which was attributed to phenolic compounds (Lee et al., 2011).

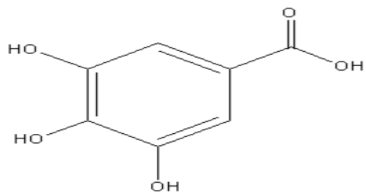
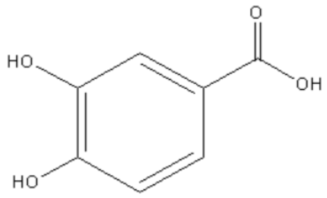
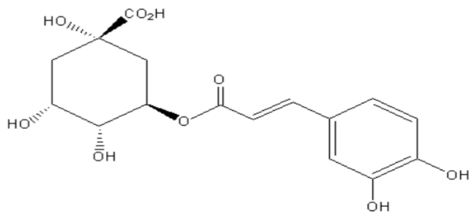
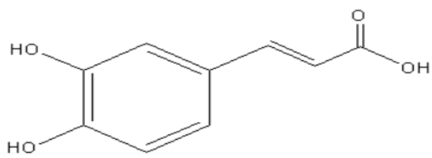
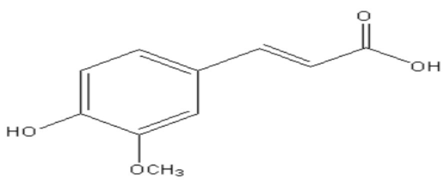
2.2 Phytochemicals

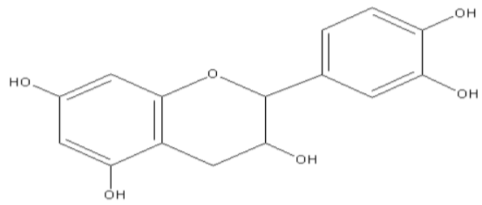
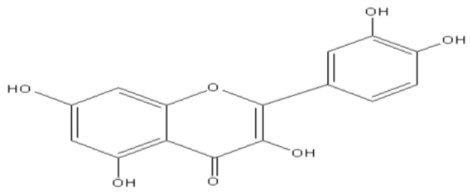
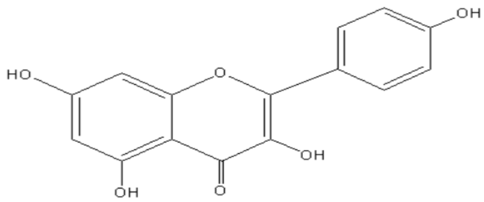
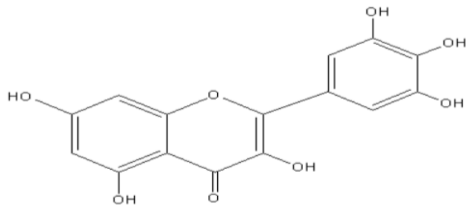
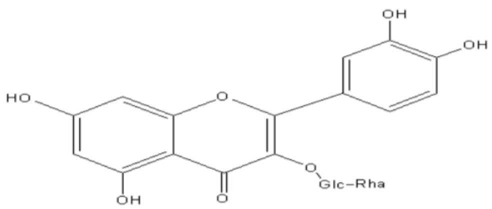
In general, phytochemicals are compounds that are produced by plants. The popular groups of phytochemicals include flavonoids, phenolic acids, carotenoids, carbohydrates, lipids, terpenoids, alkaloids and other nitrogen-containing metabolites. Phytochemicals help in plant growth and provide resistance against fungi, bacteria and virus infections, and also serve as nutrient sources for insects and other animals. The study of phytochemicals requires the essential initial process of extracting and isolating compounds from the origin plant, followed by structural defining and relevant laboratory testing. Plant extracts and traditional herbs have grown popular as a sustainable, widely available, and renewable source for a variety of applications.

Plant-derived natural products comprise various organic chemicals, including phenolics, flavonoids, alkaloids, tannins, pigments, and amino acids, the preponderance of which are known to have inhibitory properties (Espinoza-Vázquez et al., 2020). Organic chemicals containing nitrogen, oxygen, phosphorus, and sulphur make up the majority of excellent acid inhibitors (Al-Qudah, 2011). In a previous study, it was found that flavonoid extracted from Molokhia is one of the possible candidates of the active compound(s) that effective in stopping or slowing corrosion (ElShami et al., 2020). In the presence of acids, phytochemicals found in plant extracts have been shown to participate in physisorption, chemisorption, and retrodonation with steel surfaces, acting as corrosion inhibitors. The appropriate mechanism of inhibition, however, is dependent on the presence of such phytochemicals in plant extracts.

Previous literature done on winged beans confirmed the presence of flavonoids like catechin, epicatechin, quercetin and myricetin (Mustafa et al., 2010). Meanwhile, another study supports the findings with extra reveals of gallic acid, protocatechuic acid, chlorogenic acid, caffeic acid, ferulic acid, rutin and kaempferol, which can also be found in winged bean tubers (Mohanty et al., 2013). The chemical structures of the phenolic compounds present in WB were tabulated as in Table 2.1.

Table 2. 1: The polyphenolic compounds contain in WB (Vermerris & Nicholson, 2007)

Compound name	Class of compound	Structure
Gallic acid	Phenolic acid	
Protocatechuic acid	Phenolic acid	
Chlorogenic acid	Phenolic acid	
Caffeic acid	Phenolic acid	
Ferulic acid	Phenolic acid	

Catechin	Flavonoid-flavanol	
Quercetin	Flavonoid-flavonol	
Kaempferol	Flavonoid- flavonol	
Myricetin	Flavonoid-flavonol	
Rutin	Flavonoid-flavone	

2.3 Corrosion

Corrosion is defined as the destructive attack on a metallic material via chemical or electrochemical reactions within an undesirable environment that results in deterioration of the metal itself and its properties (Das et al., 2020; Husaini, 2021). In general, a material's corrosion behaviour is determined by the environment to which it is exposed, whereas an environment's corrosivity is determined by the material exposed to that environment (Wei et al., 2020).

The corrosion cell comprises four requirements or conditions: an anodic reaction, a cathodic reaction, a metallic pathway of contact between anodic and cathodic sites, and the presence of an electrolyte (Refait et al., 2020). The electrochemical process of corrosion (Figure 2.2) is usually caused by the functioning of related electrochemical half-cell reactions rather than a direct chemical reaction of a metal with its environment (McCafferty, 2010). In the anodic reaction, oxidation takes place where the metal is dissolved (Equation 2.1) and transferred to the solution as ions which cause loss of metals (Espallargas et al., 2015; Gunavathy & Murugavel, 2012). The electrons released by this reaction are conducted through the metal to the cathodic site (Equation 2.2), where they are consumed in the cathodic reaction (Refait et al., 2020). This explains how the cathodic reaction is linked to the anodic reaction and how limiting the cathodic reaction will also hamper the anodic response. The reduction reaction occurs at the cathode due to the increase in electrons at the cathodic site once electrons being consumed by the reaction, thus decreasing the oxidation number.

$$Fe\ (s) \longrightarrow Fe^{2+}\ (aq) + 2e^- \tag{2.1}$$

$$O_2\ (g) + 2H_2O\ (l) + 4e^- \longrightarrow 4OH^-\ (aq) \tag{2.2}$$

Simultaneously, the hydrogen gas produced as in acidic solution the protonated hydrogen tends to be reduced (Equation 2.3).

$$2H^+\ (aq) + 2\ e^- \longrightarrow H_2 \tag{2.3}$$

The oxidation and reduction half-reaction at anodic and cathodic site results in Equation 2.4,

$$2Fe\ (s) + O_2\ (g) + 2H_2O\ (l) \longrightarrow 2Fe(OH)_2\ (s) \tag{2.4}$$

where the iron(II) ions then combine with hydroxide ions to form iron(II) hydroxide (green rust) as in Equation 2.5:

$$Fe^{2+}\ (aq) + 2OH^-\ (aq) \longrightarrow Fe(OH)_2\ (s) \tag{2.5}$$

Cathodic reactions can generate corrosion as a result of secondary effects caused by the reaction's products formed at the cathodic site. The continuance of these processes commence rust formation as the iron(II) hydroxide is then further oxidised by oxygen to form hydrated iron(III) oxide ($Fe_2O_3.xH_2O$) that appeared in brown shades of typical rust.

The corrosion rate is controlled mainly by the net balance among all of these components of the corrosion cell (Roberge, 2019). In another context, there are also another two parameters that contribute to corrosion events which are the change in Gibbs free energy and Pilling-Bedworth ratio.

Corrosion of metallic materials can be divided into three main groups: wet corrosion that involves water as the corrosive environment, dry corrosion that has dry gas as the corrosive environment, and corrosion that occurs in other fluids such as fused salts and molten salts (McCafferty, 2010). Corrosion is classified primarily by one of three factors: the nature of the corrodent, the mechanism of corrosion, and the appearance of the corroded metal which is particularly useful where analysis is done through visual observation on the surface morphology to identify forms of corrosion that occurred (Shreir, 2013). Further corrosion classification divides corrosion into eight forms: general corrosion, crevice corrosion, pitting corrosion, stress corrosion cracking, galvanic corrosion, selective leaching, and erosion-corrosion.

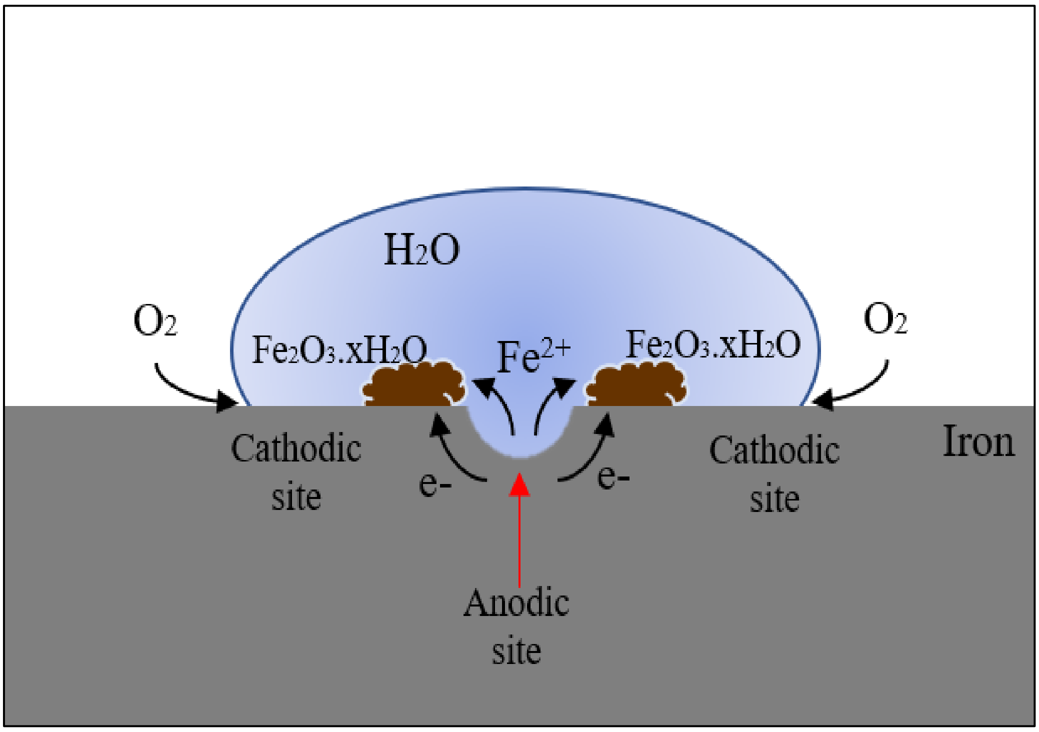


Figure 2. 2: Mechanism of rusting (Salunkhe & Rane, 2016)

2.3.1 Corrosion of carbon steel

Carbon steel that has been widely used in many sectors mostly in civil engineering applications as they provide great strength, wear resistance and toughness. Carbon steel been used in storage tanks and pipes in many industries where exposure to acid is a great concern. The contact of carbon steel with concentrated acid generates an immediate acid attack with the formation of hydrogen gas and ferrous ions, which, in turn, form a protective layer like $FeCl_2$ on the metallic surface. This could lead to a serious problem that will affect many aspects such as economic, safety and environment. Localized damage should be avoided because it can result in severe secondary damage to the structure's vital facilities (Sangho et al., 2021). In most circumstances, the corrosion of the reinforcing steel is mainly due to chloride attack through an exposed channel such as cracks (Figure 2.3), which leads to pitting, producing a great threat to the service life of carbon steel structure compared to uniform corrosion induced by carbonation exposure. This is owing to the degradation effect of corrosion pits (Shi et al., 2021).

Figure 2. 3: Corrosion of carbon steel pipe (Kehr, 2018)

2.4 Preventing corrosion

Preventing corrosion may require the extra cost of utilising expensive materials or techniques and also may come from the loss or destruction of the products themselves. Generally, selection of materials, application of coatings, the addition of inhibitors, cathodic protection, and proper design are the five basic approaches to corrosion control. As the corrosion resistance of a metal is highly dependent on the environment to which it is exposed, selection of material ranging from a noble metal which often offers high resistance to the low corrosion resistance of active material is crucial. Another way that can help combat corrosion is by applying coating available as metallic and nonmetallic (organic and inorganic) with the primary intention of isolating the underlying metal from the corrosive media. The use of corrosion inhibitors involves using chemical species with corrosion inhibitive potential such as chromates, silicates, and organic amines.

On the other hand, cathodic protection helps to decrease the current that causes damage in a corrosion cell by forcing it to flow to the metal structure that has to be protected. Corrosion or metal disintegration is thus avoided. Many corrosion problems can be avoided by using rational design principles, which as well slash the time and expense of corrosion maintenance and repair. Design must take into the measure of eliminating dead space and crevices.

2.4.1 Corrosion inhibitors

Corrosion inhibitors have received a lot of attention since they provide a straightforward solution for protecting metals from corrosion in an aqueous environment. A corrosion inhibitor is a chemical compound that, when applied to the environment in which a metal is exposed, reduces, slows, or prevents the metal from corroding (Palanisamy, 2019). They operate as a barrier to corrosion by producing an adsorbed layer or by retarding the cathodic, anodic, or both processes. Corrosion inhibitors are responsible for any corrosion retardation process of the metal that produced by the addition of a chemical substance to the system. Inhibitors are frequently simple to apply and have the advantage of not affecting or creating major process disturbance. Corrosion inhibitors are one of the most effective means of preventing corrosion (Palanisamy, 2019).

2.4.1(a) Type of corrosion inhibitor

Generally, corrosion inhibitor can be either inorganic and organic inhibitor. Inorganic inhibitor further classified into cathodic and anodic inhibitor. Cathodic inhibitors are corrosion inhibitors that induce a delay in the cathodic reaction. Likewise, anodic inhibitors retard the anodic process. Meanwhile, organic inhibitor takes in mixed type inhibitor whose affect both the cathodic and the anodic reactions. These inhibitors, which are primarily adsorption-based, are referred to as adsorption inhibitors. Recent approaches make use of organic compounds derived from expired pharmaceutical medications, mushroom extracts, and plant extracts, with plant extracts being the significant group (M. N. El-Haddad et al., 2019; Espinoza-Vázquez et al., 2020; Miralrio & Espinoza Vázquez, 2020).

2.4.1(b) Plant based corrosion inhibitor

A number of green organic compounds have shown the ability to act as corrosion inhibitors and have proven to be effective in preserving metal surfaces. As a result, these substances have begun to take the role of old hazardous corrosion inhibitors. Plant extracts are gaining popularity as a sustainable, widely available, cost-effective, and environmentally benign alternative to harmful chemical corrosion inhibitors. These extracts are another intriguing alternative since they provide a first step toward identifying the class of natural components that aid to slow down the corrosion process. The advantage is that extracting any plant is considered a simple job, allowing for greater efficiency in both extraction and exploration with these chemicals. In addition, plant extracts reduce corrosion mainly through physisorption, chemisorption, and retrodonation. Table 2.2 summarise few studies using plant extracts used as corrosion inhibitors. Most of the inhibitors made from plant extract are able to provide more than 80% protection on metals against corrosion. In short, plants do fulfil the characteristics of potent corrosion inhibitors.

Table 2. 2: Corrosion inhibition efficiency studies on plant as green corrosion inhibitors

Plant	Corrosion media	Inhibitor efficiency	Reference
Dioscorea septemloba	1 M HCl	72.00%	(Emori et al., 2020)
Ficus racemose	1 N H_2SO_4	90.50%	(Bagga et al., 2016)
Ammi visnaga	1 M HCl	84.00%	(Zaher et al., 2020)
Ananas comosus	1 M HCl	97.60%	(Mobin et al., 2019)
Euphorbia heterophylla linneo	1.5 M HCl	69.00%	(Akinbulumo et al., 2020)
Chamaerops humilis	1 M HCl	88.00%	(Fekkar et al., 2020)
Tinospora crispa	1 M HCl	80.00%	(Hussin et al., 2016)
Ginkgo	1 M HCl	90.00%	(Qiang et al., 2018)
Zingiber officinale	1 M HCl	92.50%	(Gadow & Motawea, 2017)
Myristica fragrans	0.5 M H_2SO_4	87.80%	(Haldhar et al., 2018)
Eucalyptus globulus	0.5 M H_2SO_4	93.09%	(Haldhar & Prasad, 2020)
Rhizophora apiculata	1 M H_2SO_4	66.80%	(Gambier et al., 2018)

2.4.2 Sol-gel coatings

The sol gel method is an environmentally safe surface protection approach that has shown promise in replacing toxic pre-treatments and conventional coatings that have commonly been employed to increase metal corrosion resistance. Chemical stability, oxidation control, and the capacity to improve corrosion resistance for metal substrates have all been demonstrated with sol-gel protective coatings. Sol-gel allows inorganic and organic materials to be combined in a single phase, leading to the development of organic–inorganic hybrid (OIH) coatings for various uses, including corrosion prevention.

Multicomponent compounds with at least one organic and inorganic component in the sub-micrometric or nanometric size range are known as OIH materials (Mishra, 2018). This entails the introduction of molecular precursors that allow the organic component to be formed. Within the OIH network, the creation of reactive functional groups can be employed to anchor molecular recognition groups and allow entrapping greater concentrations of species (Figueira, 2020). The creation of OIH sol–gel coatings based on siloxanes for corrosion mitigation has been extensively investigated in recent years, revealing that siloxanes are helpful in preventing corrosion on a variety of metallic substrates. Simple OIH coatings enhanced the adhesion of organic based coatings to the substrate (Figueira, 2020). Despite this, they simply serve as a physical barrier.

Additional functionalities, such as corrosion inhibitors, must be added to the OIH network to achieve anticorrosive performance (Lakshmi et al., 2017; Yasakau et al., 2017). Hybrid sol-gel doped with green (plant-based) inhibitors has been reported to generate films with improved barrier characteristics such as a more uniform coating layer. These green inhibitors are eco-friendly, inexpensive, and simple to make. Table

2.3 summarises the literature of integrating green plant extract inhibitors into the hybrid sol-gel coating.

Table 2. 3 Previous study on sol-gel doped green inhibitors on a metal substrate

Precursors	Green inhibitors	Media/substrate	References
PVTMS	Henna leaves extract	SBF / stainless steel 316L	(Motalebi et al., 2012)
MTES, γ-GPS, TEOS, epoxy resin	*Mentha longifolia* extract	0.1M NaCl / mild steel	(Nikpour et al., 2018)
TMSM, PMMA	Henna leaves extract	0.1 M HCl/ Carbon steel	(Khoshkhou et al., 2018)
TEOS, TEMS	Nettle leaves extract	3.5wt% NaCl / mild steel	(Izadi et al., 2017)
APTES, TEOS	tea leaves caffeine extract	3.5wt% NaCl / mild steel	(Hamidon & Hussin, 2020)
TEOS	Mangrove bark tannins	3.5wt% NaCl / aluminium A6061	(Hamidon et al., 2019)
TEOS, TMSM	Rosemary	3.5% NaCl/ Stainless steel 304L	(Nasr-Esfahani et al., 2014)
TEOS	Castor and Linseed oil	3.5wt% NaOH, 3.5wt% HCl / mild steel	(Akram et al., 2017)
GPTMS, TEOS, AHMT	*Davidia involucrata* leaf extract	0.5 M H_2SO4 / Copper	(Balaji et al., 2021)
GPTMS, TEOS, MTEOS	*Bamboosa vulgaris*	1 M HCl / mild steel	(Emran et al., 2018)
PAS epoxy coating	*Mangifera indica* leaves	3.5wt% NaCl / carbon steel	(Karattu Veedu et al., 2019)

2.5 Electrochemical corrosion monitoring techniques

Corrosion monitoring techniques are commonly used to inspect and predict the extent of corrosion damage in metal structures. The information presented has aided in the development and implementation of effective strategies for reducing corrosion-related losses. Electrochemical methods have been widely employed for corrosion monitoring because they are responsive to the surface condition of engineering structures.

2.5.1 Electrochemical impedance spectroscopy (EIS)

Electrochemical impedance spectroscopy (EIS) is a multifrequency AC electrochemical measurement technique generally applied to estimate the corrosion rates of metals covered with an electrolyte layer. EIS is capable of characterising changes that occurred on a surface under certain system variables and offer a great assist in developing system parameters in order to achieve the coveted effect on a surface. In essence, EIS uses Faraday's Law to define a chemical process employing electrical measurements. It measures the metal/solution interface's electrical resistance (impedance) over a wide frequency range (1 mHz to 10 kHz). Resistance R, from the AC theory, is given by Ohm's law as:

$$E = IR \tag{2.6}$$

Since AC current and voltage are vector quantities, resistance, R was expressed as vector quantities of the impedance, Z which contain frequency-dependent of real (Z') and imaginary (Z'') representing capacitance and inductance, respectively. Thus, the expression is such Equation 2.7:

$$Z = \frac{E}{I} \tag{2.7}$$

Since,

$$Z_{total} = Z' + Z'' \tag{2.8}$$

then (referring Figure 2.5),

$$tan\theta = \frac{-Z"}{Z'} \quad (2.9)$$

Where Ө is the phase angle.

The EIS data allows for the determination of polarization resistance, a low-frequency region, a high-frequency region of solution resistance, and double-layer capacitance. Electrochemical Impedance Spectroscopy (EIS) applies a low amplitude of alternating current (AC) to the corrosion system under investigation in a specific frequency domain. EIS data is typically obtained using a potentiostat or galvanostat device and then fitted to an equivalent electrical circuit model (Figure 2.4) for interpretation and analysis, with the objective of getting a significant physical interpretation (Hernández et al., 2020). The double-layer capacitance (C_{dl}) expressed as Equation 2.10:

$$\text{Cdl} = \frac{1}{\omega Rp} \quad (2.10)$$

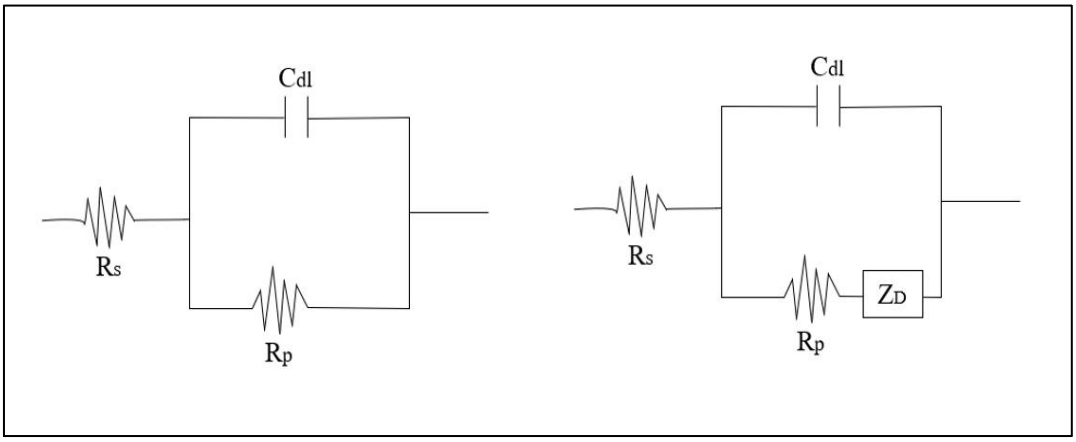


Figure 2. 4: Typical electrochemical equivalent circuits used in corrosion studies (Perez, 2004)

The complex response of the system, which reveals the internal dynamics as the consequence of the capacitance effect at the metal/electrolyte interface, is usually displayed in Nyquist (Figure 2.5) and Bode format (Figure 2.6).

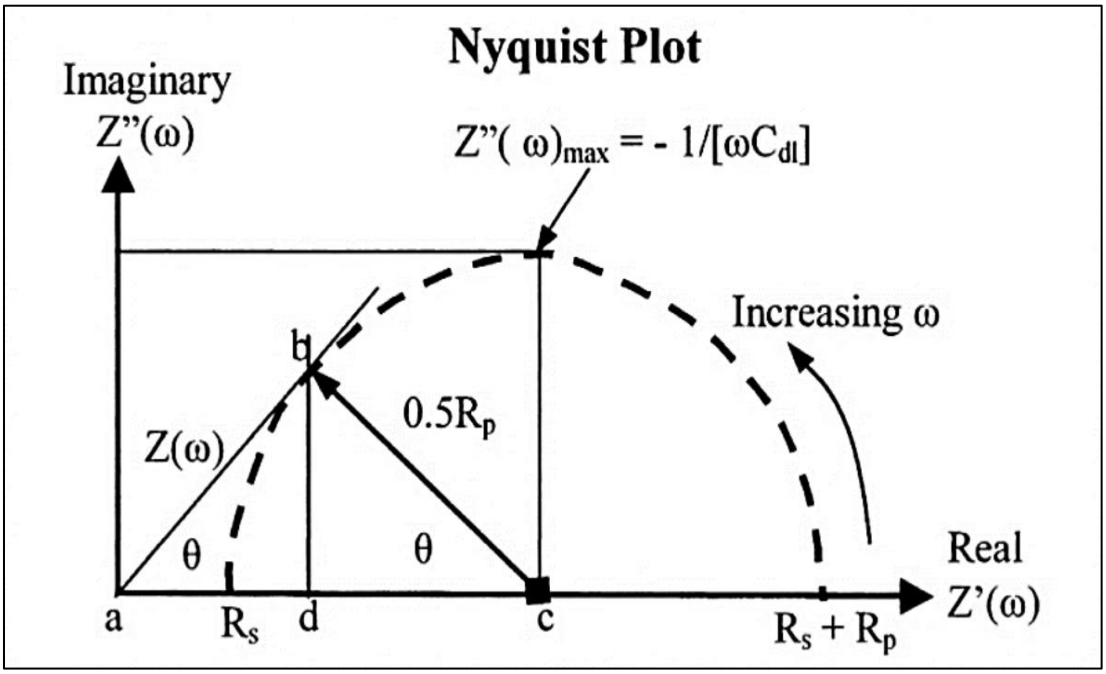


Figure 2. 5: Nyquist plot for steel in acid medium (Perez, 2004)

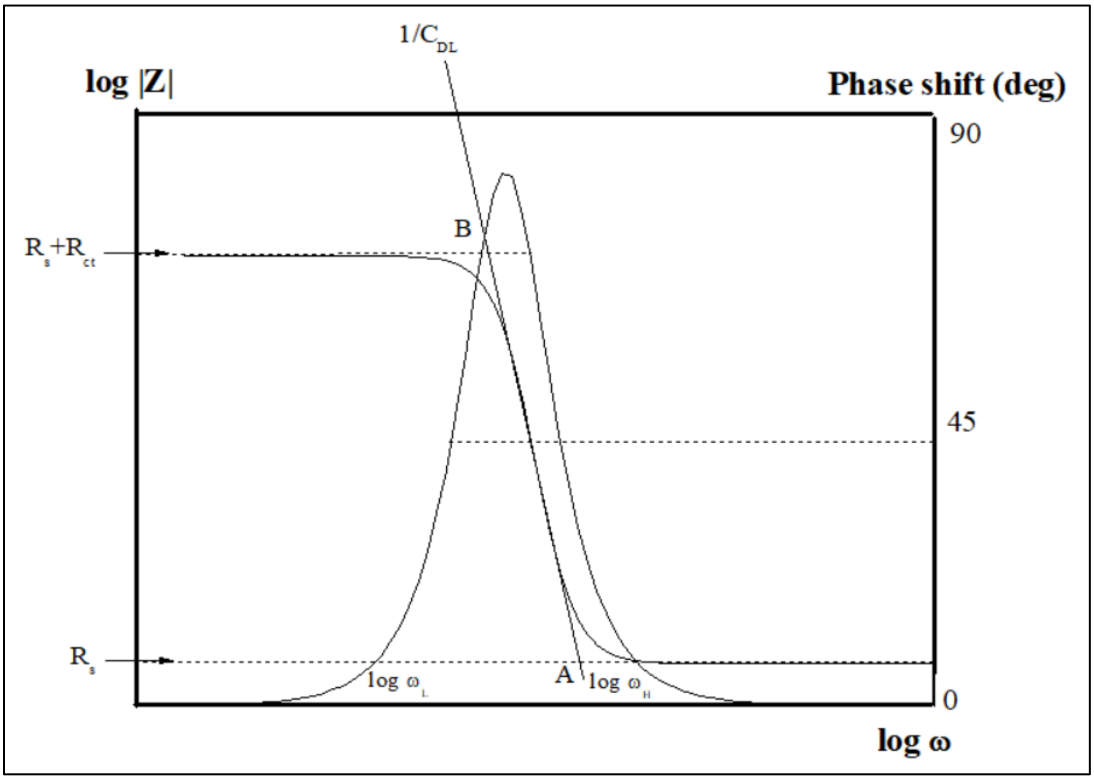


Figure 2. 6: Bode plot for steel in acid medium (Berradja, 2019)