PIPER BETLE LEAVES EXTRACT AS A GREEN CORROSION INHIBITOR FOR ALUMINIUM IN ACIDIC MEDIUM: CHARACTERIZATION AND EVALUATION OF ANTIOXIDANT, PHENOLIC AND FLAVONOID CONTENT

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by

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TABLE OF CONTENTS

LIST OF TABLES

CHAPTER 2

CHAPTER 3

CHAPTER 4

APPENDIX

LIST OF FIGURES

CHAPTER 2

CHAPTER 3

CHAPTER 4

APPENDIX

LIST OF EQUATIONS

LIST OF ABBREVIATIONS

FTIR	Fourier-Transform Infrared Radiation
SEM	Scanning Electron Microscopy
PBLE	Piper Betle leaves extract
HCl	Hydrochloric acid
TPC	Total Phenolic Content
TFC	Total Flavonoid Content
Al	Aluminium
IE	Inhibition Efficiency

LIST OF SYMBOLS

Symbols	Description	Unit
C_{inh}	Concentration of inhibitor (PBLE)	$\frac{mg}{L}$
W_I	Initial weight of Al plate	g
W_F	Final weight of Al plate	g
C_R	Corrosion rate	$\frac{g}{m^2.hr}$
θ	Surface coverage	-
ΔW	Difference between initial and final weight	g
t	Immersion period	hour
C_{GA}	Concentration of gallic acid	$\frac{mg}{L}$
C_Q	Concentration of quercetin	$\frac{mg}{L}$
R^2	Correlation coefficient	-
A	Surface area of Al	m^2
K_{ads}	Adsorption constant	-
$\Delta G^{\circ}{}_{ads}$	Adsorption free energy	$\frac{kJ}{mol}$
IE	Inhibition efficiency	%
R	Universal gas constant	-

PENGGUNAAN DAUN SIRIH SEBAGAI PERENCAT KAKISAN HIJAU UNTUK ALUMINIUM DALAM LARUTAN 1.0M ASID HIDROKLORIK: CIRI-CIRI DAN PENILAIAN KANDUNGAN ANTIOKSIDA, FENOLIK DAN FLAVONOID

ABSTRAK

Aluminium (Al) adalah salah satu logam yang paling banyak diaplikasikan dalam pelbagai industri seperti kimia, mekanikal, aeroangkasa dan sebagainya. Walau bagaimanapun, kakisan berlaku dalam Al disebabkan oleh persekitaran yang agresif seperti medium berasid atau beralkali yang tinggi kekal sebagai fenomena yang tidak dapat dielakkan. Terdapat banyak kaedah yang diterokai dan dilaksanakan untuk mengelakkan kakisan Al dalam media yang agresif. Penggunaan produk semula jadi seperti ekstrak tumbuhan sebagai perencat kakisan adalah salah satu kaedah yang paling lestari dan mesra alam untuk mencegah kakisan di Al. Dalam penyelidikan ini, ekstrak daun sirih (PBLE) dipilih sebagai perencat kakisan hijau bagi Al dalam larutan asid hidroklorik (HCl). Daun sirih diekstrak dengan menggunakan air ultratulen yang mempunyai ciri-ciri seperti harga yang rendah, mesra alam dan keterlarutan yang baik berbanding dengan pelarut lain. Kaedah pengekstrakan ini sangat mudah dan kosnya adalah rendah. Sifat perencatan bagi ekstrak daun sirih pada permukaan Al dalam larutan asid hidroklorik ditentukan dengan pengukuran gravimetrik. Parameter bagi kepekatan PBLE dan tempoh rendaman Al dalam larutan HCl dengan ketiadaan dan kehadiran PBLE telah dianalisis dalam penyelidikan ini. Julat kepekatan PBLE yang digunakan dalam penyelidikan ini adalah dari 50 mg/L hingga 1000 mg/L manakala julat tempoh rendaman Al tanpa kehadiran dan kehadiran PBLE adalah dari 1 jam hingga 24 jam. Kecekapan perencatan maksimum bagi ekstrak daun sirih ialah 94.41%

pada permukaan Al dalam larutan asid hidroklorik yang mengandungi kepekatan perencat 1000 mg/L selama satu jam pada suhu bilik. Pengukuran gravimetrik mendedahkan bahawa kecekapan perencatan meningkat apabila kepekatan perencat meningkat manakala kecekapan perencatan berkurangan apabila tempoh rendaman Al meningkat. Sinaran inframerah transformasi fourier (FTIR) mengesahkan bahawa kewujudan kumpulan hidroksil (-OH) dan polifenol dalam molekul ekstrak daun sirih menghalang proses kakisan pada permukaan Al dalam medium berasid. Sebaliknya, analisis bagi pengimbasan mikroskop elektron (SEM) menunjukkan molekul exkstrak daun sirih membentuk penghalang atau lapisan pada permukaan Al untuk menghalang kakisan dalam larutan berasid. Jumlah kandungan fenolik (TPC) dan flavonoid (TFC) dalam ekstrak daun sirih ialah 64.87 mg/g asid gallik dan 120.39 mg/g kuersetin masing-masing menunjukkan bahawa molekul ekstrak daun sirih mengandungi sifat antioksida yang lebih tinggi yang boleh menghentikan tindak balas kakisan pada permukaan Al dalam persekitaran berasid. Di samping itu, perencatan berlaku melalui penjerapan molekul ekstrak daun sirih pada permukaan Al yang mematuhi model isoterma Langmuir. Nilai tenaga bebas penjerapan yang dikira (ΔG°_{ads}) menunjukkan proses penjerapan molekul ekstrak daun sirih pada permukaan Al adalah spontan melalui fisisorpsi. Dengan ini, ia boleh disimpulkan bahawa ekstrak daun sirih boleh digunakan sebagai perencat kakisan hijau yang berkesan pada Al dalam larutan asid hidroklorik (HCl).

***PIPER BETLE* LEAVES EXTRACT AS A GREEN CORROSION INHIBITOR FOR ALUMINIUM IN ACIDIC MEDIUM: CHARACTERIZATION AND EVALUATION OF ANTIOXIDANT, PHENOLIC AND FLAVONOID CONTENT**

ABSTRACT

The aluminium (Al) is one of the most utilized metals in various industries such as chemical, mechanical, aerospace and among others. However, the corrosion occurs in the Al due to aggressive environment such as highly acidic or alkaline medium remain as unavoidable phenomena. There are numerous methods are explored and implemented to avoid the corrosion of Al in the aggressive medium. The usage of natural products like plant extract as a corrosion inhibitor is the most sustainable and eco-friendly method to prevent the corrosion in the Al. In this research, the *Piper Betle* leaves extract (PBLE) was chosen as a green corrosion inhibitor for Al in hydrochloric acid (HCl) solution. The *Piper Betle* leaves were extracted by using ultrapure water which was affordable, environmentally friendly and high solubility compared to other solvents. This extraction method was simple and low cost. The inhibitive properties of PBLE on Al surface in 1.0M HCl solution was determined by gravimetric measurement which was known as weight loss method. The concentration of PBLE and immersion duration of Al in HCl solution with absence and presence of PBLE parameters were analyzed in this research. The range of PBLE concentrations utilized in this research was from 50 mg/L to 1000 mg/L while the range of immersion period of Al in absence and presence of PBLE was from 1 hour to 24 hours. The maximum inhibition efficiency of PBLE was 94.41% on Al surface in 1.0M HCl solution containing inhibitor concentration of 1000 mg/L at room temperature for 1 hour. The gravimetric analysis showed

that the inhibition efficiency gradually increases with increasing inhibitor concentrations while it decreases with increasing Al immersion duration. The Fourier-Transform Infrared Radiation (FTIR) characterization confirmed that the existence of hydroxyl (-OH), carboxylic acid and polyphenol groups in PBLE molecule prevent the corrosion process on Al surface in acidic medium. On the other hand, the Scanning Electron Microscopy (SEM) analysis showed the PBLE molecules formed a barrier or layer on Al surface to inhibit the corrosion in the acidic solution. The total phenolic content (TPC) and flavonoid content (TFC) of PBLE were 64.87 mg/g of gallic acid and 120.39 mg/g of quercetin, respectively, indicated that the PBLE molecules contain higher antioxidant properties which can terminate the corrosion reaction on Al surface in acidic environment. In addition, the inhibition occurred via adsorption of PBLE molecules on the Al surface obeyed Langmuir isotherm model. The calculated adsorption free energy (ΔG°_{ads}) value which was -17.09 kJ/mol showed the adsorption process of PBLE molecules on the Al surface was spontaneous via physisorption. Thus, it can be concluded that the PBLE can be served as an effective green corrosion inhibitor on Al in HCl solution.

CHAPTER 1

INTRODUCTION

1.1 Research Background

Corrosion was one of the unavoidable aspects in our daily life which always gets special attention for prevention due to its technical, aesthetical and economic importance. It can be found in the soil, water, air and any other environment we come into contact with. Corrosion, often known as rust which was an unfavourable phenomenon that degrades the lustre and attractiveness of materials as well as shortening their lifespan. Most of the corrosion occurred on the surface of metals and alloys. Although there were various types of metals and alloys in the world, Aluminium (Al) was also one of the metals that is mostly involved in the corrosion process. Al was one of the metals that was being used widely all over the world, mostly in chemical production industries. Al may be present in ionic form in most animal, plant tissues and in natural waters all over the world (Xhanari et al., 2017).

In the earth's crust, it was the third most popular element representing approximately 8% of total mineral components (Verstraeten, Aimo and Oteiza, 2008). The availability aspect was proven when Al was the second most abundant metal in the world after iron, with a specific weight of 2.7 g/cm^3 (Raghavendra, 2020). Al was the most often employed metal in transmission system and nonferrous metal processing because of its superior electrical and thermal conductivity, good working and forming qualities, low density, lightweight, ease of recycling, high mechanical strength, and ductility. (Umoren et al., 2012). Besides that, its high strength weight ratio as well as low cost, make it an extremely attractive metal in various fields such as packaging, transportation, construction materials, electrical engineering, aerospace, and domestic appliances due to its excess availability and noble properties. Besides utilization in industrial applications, Al was a basic metal that was widely utilized in a variety of human activities too (Raghavendra, 2020).

The most corrosion cases occurred in chemical industries due the high amount usage of concentrated chemicals. Hence, the corrosion on Al was caused by a variety of factors including surface impurities, pressure, temperature, and solution interaction (Hossain, Asaduzzaman Chowdhury and Kchaou, 2020). Al was not resistant to corrosion by itself. When the oxide layer formed on the surface of Al, it became extremely resistant to corrosive attack in a variety of mediums. Therefore, exposure of acidic medium caused the oxide layer destroyed and revealed the Al components to the corrosive environment's attack (Xhanari et al., 2017). Hence, it showed significant challenges to both large and small enterprises since corrosion was unavoidable. Since corrosion can occur easily in the presence of stated factors, the industries would face a lot of drawbacks in various aspects which will result in loss.

The major aspects that consider the drawbacks of corrosion were economic, material and safety as well as health and safety (Goni and Mazumder, 2022). The impact of corrosion on the equipment and its surroundings must be given a lot of consideration while an industry was developing. Corrosion was regarded as one of the most difficult concerns affecting most industrialized countries. From the aspect of material and energy, corrosion of equipments, pipes, machine metal components and other structures can result in huge material and economic losses for a country (Goni and Mazumder, 2022). Besides that, corrosion failure can affect the safety of running equipment in the industries. Furthermore, corrosion's consequences extended beyond metals to include water, energy and the production phase of metal frames. According to Goni. and Mazumder, one tonne of Al rusted every 1.5 minutes when acidic medium solution flowed through the surface of Al but at the same time the energy required to produce one tonne of Al was equivalent to the energy consumed by an ordinary household over three months (Goni and Mazumder, 2022).

Economic losses due to the corrosion process can be classified into two categories which are direct losses and indirect losses. Replacement and maintenance of the corroded equipments, pipes and other structures as well as implementation of preventive methods to reduce the corrosion process will contribute to the direct losses. On the other hand, indirect losses include plant closures, medium loss through damaged pipelines, reduced efficiency in energy conversion systems brought on by corrosion processes, and contamination of solution with corrosive particles that might affect the final product. From the aspect of health and safety, corrosion may impact negatively on human life and safety in ways that are unimaginable. Corroded equipments, pipes and structures might be dangerous to the employees who were working near the working area if any leaking, accidents and explosions. Hence, health and safety of employees was also one of the aspects that should be considered if corrosion occurs in the industries.

Therefore, corrosion had become a global issue due to the rapid advancement of industrial technology. Corrosion caused significant damage to assets and economic loss to the industries that utilize equipments and pipelines which were mostly using metals especially Al. Every year, one-third of Al was lost to corrosion, resulting in a global economic loss (Pikaar et al., 2014). Hence, numerous researchers have developed a variety of corrosion prevention technologies to prevent this loss. Therefore, different corrosion control techniques can be employed to protect the Al from corrosion. By adopting the corrosion control techniques, the corrosion of Al can be reduced rather than preventing it

(Mercer, 1973). There were several effective anticorrosion techniques, including modifying the metal, adjusting the design, changing the corrosive environment, modifying the potential of the metal environment, employing inhibitors, and adjusting the surface (Palanisamy, 2019). These techniques can be applied singly or collectively.

Among the proposed techniques, corrosion inhibitors were one of the best anti corrosion techniques to avoid metal surface damage or degradation. Besides that, corrosion inhibitors were effective in closed systems and in some cases even under ambient conditions (Xhanari et al., 2017). However, in terms of both financial viability and protective efficacy, corrosion inhibitors were one of the most effective methods, which has recently led to an increase in inhibitor demand. Environmental safety and the health of living organisms had become more valued in the perspective of worldwide interest in sustainable greenness. The corrosion resistance of Al was owing to the formation of an invisible adhering protective coating on its surface. The process of Al disintegration was prevented in such accessible settings by the natural invisible protective layer, which was stable in a pH range of 3 to 8, in a variety of sectors (Raghavendra, 2020). A chemical substance known as a corrosion inhibitor is added to corrosive media at incredibly small amounts (typically less than 1% by weight) (Xhanari et al., 2017). These chemicals adsorb on the metal surface and avoid corrosion process.

1.2 Problem Statement

Most of the industries in Malaysia and all over the world have witnessed corrosion as a serious drawback since it can affect the entire production process and as well as the purity of products. The corrosion mainly occurs when the aggressive medium or solution is flowed during the process of production and maintenance period. To prevent corrosion, inhibitors are utilized in the industries. Therefore, organic inhibitors are used as industrial corrosion inhibitors which can form the protective layer between metal surface and corrosive medium to prevent corrosion. Besides that, the inorganic inhibitors which can withstand high temperature and are cost effective compared to organic inhibitors, can reduce the corrosion by mixing with acid solutions to scrape all the unprotected metal surface on cathode's cell. Although both organic and inorganic inhibitors can minimize the corrosion, both prevention methods pose serious shortcomings to the environment. These methods discharge contaminated corrosion inhibitors to the water bodies which have serious environmental impacts towards the ecosystem (Tamalmani and Husin, 2020).

Hence, the green and environmentally friendly inhibitors are becoming more prominent. Therefore, the plant extract is suitable to use as a green corrosion inhibitor for Al in acidic medium because it is nontoxic in nature and has higher demand compared to commercial inhibitors. Besides that, the plant extracts are considered green and sustainable materials because of their natural and biological qualities, and they can prevent metals and alloys from corroding.

Therefore, in this research, the *Piper Betle* plant, known as betel plant was chosen as a green corrosion inhibitor for Al plate in acidic medium. This plant was primarily found in the central and eastern peninsular Malaysia after being widely distributed over East Africa and the tropical regions of Asia (Pin et al. 2010; Jaganath 2000). The leaves part of the *Piper Betle* plant was utilized as a corrosion inhibitor. The leaf, more than any other part of the plant, was regarded for its amounts of phytochemicals (active components) created by synthesis that function in a similar way to commercial inhibitors (Tamalmani and Husin, 2020). From the literature, the plant contains a high polyphenol bioactive compound that is suitable to be used as a corrosion inhibitor for Al in acidic medium. As a result, a study found that the PBLE contained considerable amounts of bioactive substances like polyphenols, alkaloids, steroids, saponins, and tannins (Das et al., 2019). Although the *Piper Betle* leaves were widely and abundantly existed in Malaysia as well as contains polyphenols, there was limited research topics about betel leaves used as corrosion inhibitors. Besides that, the *Piper Betle* Leaves Extract (PBLE) has never been tested as a corrosion inhibitor on Al in acidic environment. Hence, from this research, the PBLE was tested on Al plate in acidic medium to determine the effectiveness on prevention of corrosion.

1.3 Sustainability

This research can achieve the sustainable development goal which is industries, innovation and infrastructure. This objective primarily focused on infrastructure and innovation, associated with integrated and sustainable industrialization, which had the potential to provide competitive and dynamic economic forces that generate employment and incomes. They were essential for introducing and promoting new technologies, for facilitating international trade, and for enabling resource efficiency. Based on in this research, the innovation of implementing green corrosion inhibitor instead of organic and inorganic inhibitor has contributed the industries to obey the sustainable goals by protecting the environment. By employing the green corrosion inhibitor in metals or alloys in acidic or alkali medium, the release of toxic to the environment can be avoided. Therefore, the green corrosion inhibitor is one of the innovations for the industries to prevent the corrosion of metals or alloys in acid or alkaline medium. Thus, the specific equipment can be maintained from corrosion attack as well as contribute to higher production and economics since the green corrosion inhibitor was known as eco-friendly and sustainability products.

1.4 Research Objective

The objectives of this research paper are:

1. To identify the functional groups of PBLE using Fourier- Transform Infrared Radiations (FTIR) and observe the morphology surface of Al in absence and presence of PBLE via Scanning Electron Microscopy (SEM).
2. To study the effects of different PBLE concentration and various immersion period on the percentage of inhibition efficiency in Al.
3. To investigate the adsorption mechanism and isotherm of corrosion inhibition by PBLE on Al in HCl solution.
4. To evaluate the total phenolic and flavonoid contents in PBLE and determine the antioxidant capacity of PBLE.

CHAPTER 2

LITERATURE REVIEW

2.1 Overview of corrosion

Corrosion was the most common way for metals to corrode. Corrosion was a universal phenomenon that is both omnipresent and omnipotent (Raghavendra, 2020). It was described as the degradation or breakdown of metals and alloys in the presence of an environment by chemical or electrochemical mechanisms from a chemical perspective (Bentiss et al., 1999). Corrosive or aggressive medium referred to the environment in which the metal corrodes. Basically, the aggressive medium referred to either acid or alkaline medium. All other metals corrode and convert into materials similar to the mineral ores from which they were obtained, excluding gold and platinum (Yurt et al., 2004). The corrosion products are referred to as chemical compounds that contain metal in its oxidized state.

2.2 Corrosion of metals

It was easy to consider that a variety of metals are utilized to manufacture the many types of chemical process equipment. It was challenging to identify the best corrosion-resistant materials for each type of equipment in order to minimize the overall cost of the chemical process equipment. This was due to the massive and frequently troubling variety of metals and alloys that were accessible to the chemical process sector. Almost all metals were oxidized when they are first formed, and it took a lot of energy to convert oxides into metals. Unfortunately, metals and their alloys had stronger corrosion resistance and hence returned more quickly to their stable oxide form. In reality, metal alloys had a greater tendency for corrosion than their constituent metals individually. Most of the metals such as steel, iron, copper, aluminium, magnesium, zinc and alloys can be corroded easily due to certain factors such as surface impurities, pressure, temperature, and solution activity (Hossain et al., 2020).

Numerous types of corrosion existed, including uniform or general corrosion, galvanic corrosion, pitting corrosion, intergranular corrosion, selective leaching, erosion corrosion, stress corrosion, corrosion fatigue, and fretting corrosion (Palanisamy, 2019). It was separated into two primary groups, intrinsic and extrinsic, as shown in Figure 2.1, to help corrosion and design engineers understand each other better. The intrinsic corrosion referred the corrosion was independent of design configuration while the extrinsic corrosion was the corrosion that depends on design configuration.

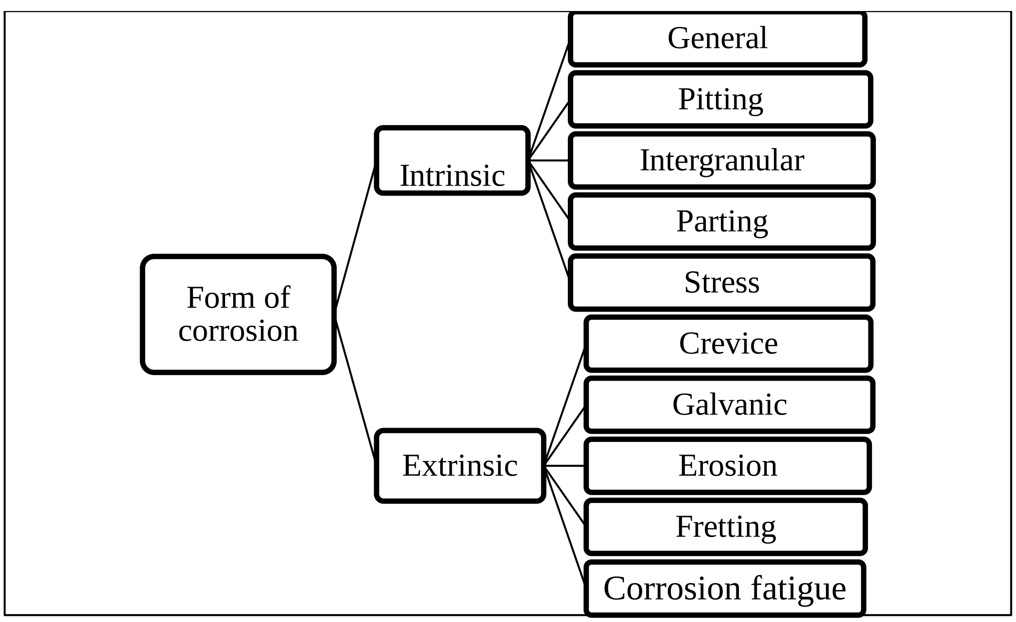

Figure 2. 1 Form of corrosions

2.3 Corrosion of Al in acidic medium

As mentioned earlier, Al was the most chosen material for equipment designation due to its properties. Even though Al possessed features that make it a good material for designing equipment, when an aggressive media passed through the surface of Al, it had low mechanical strength, fatigue strength, thermal stability, and corrosion resistance. (Trung et al., 2021). This was due to the fact that while Al was not naturally resistant to corrosion, it can become quite resistant to corrosive attacks in a variety of environments when an oxide layer formed on the surface (Xhanari et al., 2017). The oxide layer was destroyed and exposed Al components to the corrosive environment such as acidic, alkaline, or chloride-containing medias (Xhanari et al., 2017). Therefore, the corrosion resistance of Al in aggressively acidic environments needed to be improved in order to expand the range of industrial uses.

A common inorganic chemical used to clean rust and dust in many different industries was hydrochloric acid (HCl). De-scaling, ore fabrication, boiler cleaning, oil well acidification, pickling, chemical and electrochemical as well as Al etching were the main uses for hydrochloric acid solutions (Tan et al., 2021). Besides hydrochloric acid, nitric and sulfuric acids were common inorganic pickling solutions. Hydrochloric acid was the most well-known industrial acid and superior than the other acids in the pickling process because it reduced pickling time and improved surface quality (El-Hajjaji et al., 2019, Fatima et al., 2019). When utilizing a hydrochloric acid pickling solution to pickle metal surfaces, the metal substrate will eventually corrode to different degrees. This was because the solution of hydrochloric acid is highly concentrated and extremely corrosive (Raghavendra, 2020). In various industries, the HCl solution dissolved in the oxide layer and produces Al degradation, which eventually deteriorated the structure of Al. When Al was in contact with an acidic environment, it went through a sequence of electrochemical processes (Raghavendra, 2020).

$$Al_2O_3 + 3H_2O \rightarrow 2Al(OH)_3$$

$$Al(OH)_3 + H^+ \rightarrow Al(OH)^{+2} + H_2O$$

$$Al(OH)^{+2} + 2H^+ \rightarrow Al^{3+} + 2H_2O$$

The overall reaction:

$$Al_2O_3 + 6H^+ \rightarrow 2Al^{3+} + 3H_2O$$

Hence, Al^{3+} exists as Al$[(H_2O)_6]^{3+}$ in acid solution.

The growth of the protective layer may be inhibited when Al comes into direct interaction with the HCl solution, leading to pit formation. This process accelerated and increased the damage to Al's surface. Besides pitting corrosion, galvanic corrosion also will occur since the acidic medium flowed through the surface of Al (Trung et al., 2021). This was due to the potential difference that arose when two metals that were not identical were exposed in a corrosive fluid. The difference in potential between the metals caused an electron flow. The breakdown of Al in a HCl environment not only weakens the structure of the metal as well as resulted in financial impacts. As a result, Al corrosion in HCl solutions frequently resulted in significant financial losses and physical injury. Hence, one of the most frequent techniques was to apply a little amount of corrosion inhibitor to reduce the damaging effects of acid-induced corrosion.

2.4 Corrosion Inhibitor

To prevent metal degradation and reduce acid consumption, inhibitors are utilized. Corrosion inhibitors are widely employed due to their economical cost, wide application, and significant effects (Tan et al., 2021). From Figure 2.2, it showed that the inhibitors appear in both organic and inorganic forms (Javidparvar et al., 2019). When present at the right proportions, organic and inorganic substances can affect the overall surface of a corroding material, resulting up a considerable class of corrosion inhibitors. To prevent corrosion attack, the corrosion inhibitor was adsorbed on the whole metal surface of the corroding metal.

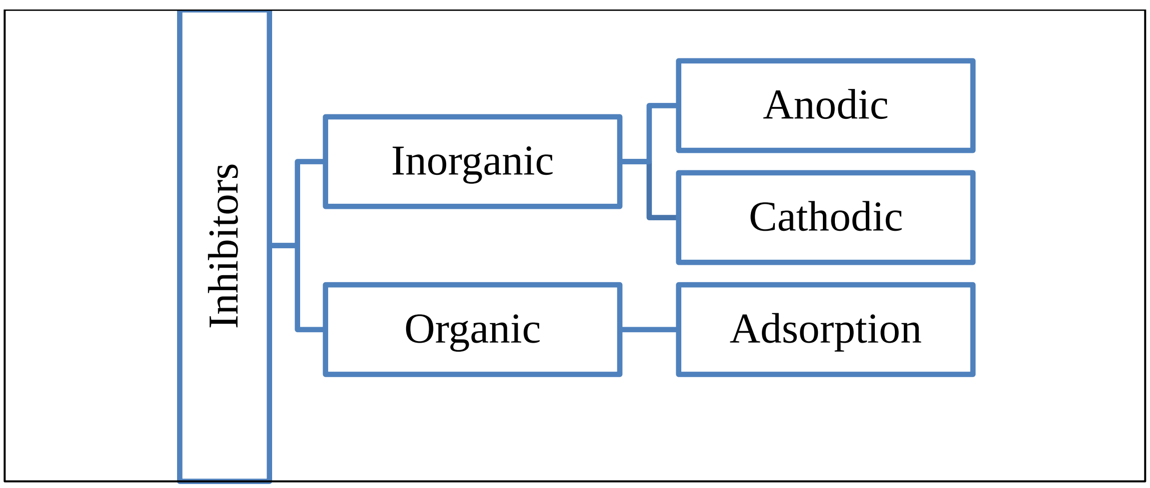

Figure 2. 2 Types of inhibitors

Therefore, the inhibitors can be splited into two groups which were those that produce a protective layer coating on anodes or cathodes because of an interaction between the metal and the corrosive medium (Palanisamy, 2019). These inhibitors, which function in neutral or alkaline solutions, are known as anodic inhibitors and cathodic inhibitors. Anodic inhibitors, often referred to as passivation inhibitors, prevent the anode reaction from occurring and promote the natural passivation of metal surfaces. They also produced a layer that was adsorbed on the metal. (Camila and Alexandre, 2014). A compact and impermeable coating was typically formed when the inhibitors interacted with the corrosion product that was first produced on the metal surface. The metallic ions, Me^{n+} formed on the anode through anodic inhibitor reaction and yielded insoluble hydroxides that are adsorbed on the metal surface as an impenetrable coating that was resistant to metallic ions (Camila and Alexandre, 2014). OH^{-} ions were produced when inhibitors are hydrolyzed. The Figure 2.3 showed the mechanism and effect of anodic inhibitor (Camila and Alexandre, 2014).

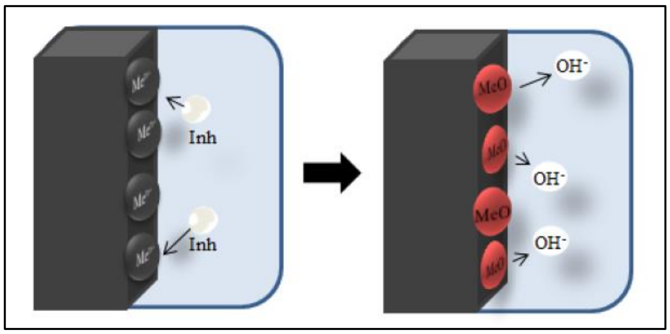

Figure 2. 3 Mechanism of anodic inhibitor (Camila and Alexandre, 2014)

The main passivation potential shifted to a noble sense when the cathodic current density at that potential surpassed the critical anodic current density, which passivated the metal when the inhibitor concentrations were at high level (Camila and Alexandre, 2014). To provide the required anodic inhibitor impact, the inhibitor concentrations in the solutions must be high enough. The formation of layer protection was affected by the insufficient inhibitor concentrations because the layer did not completely cover the metal, allowing exposed parts that lead to localized corrosion. Examples of anodic inorganic inhibitors were nitrates, molybdates, sodium chromates, phosphates, hydroxides, and silicates. (Camila and Alexandre, 2014).

Cathodic corrosion inhibitors prevented the metal from undergoing a cathodic reaction during the corrosion process (Camila and Alexandre, 2014). These inhibitors' metal ions had the ability to cause a cathodic reaction in the presence of alkalinity, producing complex compounds that formed only on cathodic sites. Limit the dispersion of active species in these sections of the metal by covering it with a dense and adhering material. As a result, reducible species like oxygen diffusion and electrons that interfaced in these locations have increased surface resistance and diffusion limitation (Camila and Alexandre, 2014). High cathodic inhibition was caused by these inhibitors. The cathodic inhibitors created an insoluble precipitate barrier that protects the metal. The following Figure 2.4 showed the mechanism and effect on the surface of metal by using cathodic inhibitors.

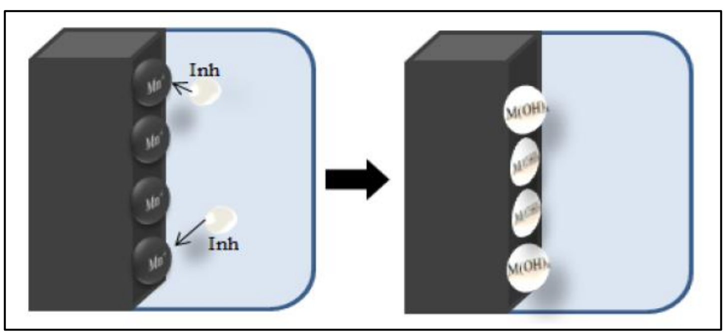

Figure 2. 4 Mechanism and effect of cathodic inhibitor (Camila and Alexandre, 2014)

The cathodic inhibitors created an insoluble precipitate barrier that covers the metal. As a result, even if the metal was entirely immersed, it was limited in its contact with the environment, preventing corrosion (Camila and Alexandre, 2014). Cathodic inhibitors were therefore more secure than anodic inhibitors since they were concentration independent

(Camila and Alexandre, 2014). Inorganic cathodic inhibitors included magnesium, zinc, and nickel ions, which reacted with the hydroxyl (OH^-) in water to generate insoluble hydroxides $Mg(OH)^2$, $Zn(OH)^2$, $Ni(OH)^2$ that were adsorpted on the metal surface's cathodic site, protecting it (Camila and Alexandre, 2014). Additional examples of substances that undergo the same reaction pathway including polyphosphates, phosphonates, tannins, lignins, and calcium salts.

The interaction of surface charges with ionic or molecule dipole charges caused another category of inhibitors that can be deposited directly on the metal surface (Palanisamy, 2019). Mostly, the organic inhibitors binded to the metal's surface. Organic compounds employed as inhibitors can act as cathodic, anodic, or combination cathodic and anodic inhibitors, but they virtually invariably acted on surface adsorption process known as layer formation. (Camila and Alexandre, 2014). Compound with high inhibitory efficiency and minimal environmental impact were spontaneously produced when molecules with a strong attraction for metal surfaces were involved. These inhibitors prevented the metal from degrading in the electrolyte by forming a protective hydrophobic barrier and adsorbing molecules to the metal surface. They must dissolve or disintegrate in the medium around the metal (Camila and Alexandre, 2014). This classification of inhibitors was based on the pH of the fluid in which they function. To be truly effective, inhibitors must be present in a limited quantity (Palanisamy, 2019). The Figure 2.5 below showed the mechanism of organic inhibitor in preventing corrosion on metal surface.

The performance of organic inhibitors can be improved in the presence of particular halogen ions. Halogen ions were also intended to somewhat prevent corrosion in acidic solutions. The order of corrosion inhibition performance was as follows: I- > Br- > Cl-

(Palanisamy, 2019). In addition, substances both organic and inorganic with P, S, N, O, and double bonds among their constituents are referred to be inhibitors (Raghavendra, 2020). These were the essential adsorption sites, which suggested that these acceptors elements attach to the surface of Al and produce a dense, durable coating that prevents Al from deteriorating (Raghavendra, 2020).

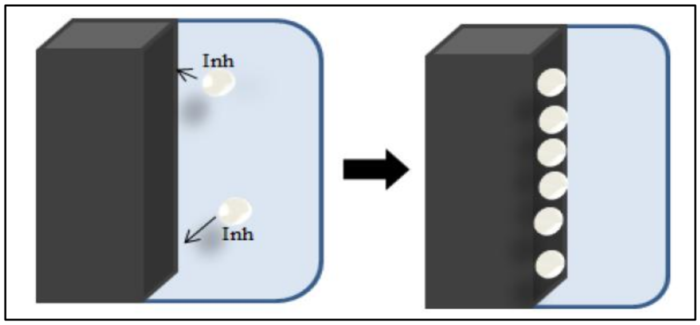

Figure 2. 5 The mechanism of organic inhibitor on metal surface (Camila and Alexandre, 2014)

Compared to organic corrosion inhibitors, inorganic corrosion inhibitors were more costly and had a higher concentration. Additionally, it had a more detrimental effect on the environment, which limited their use. In contrast, organic corrosion inhibitors have been used in more industrial applications than inorganic corrosion inhibitors. The main problems to using organic compounds as corrosion inhibitors were their expensive and toxicity, despite the fact that most of them had strong inhibition activity (Tan et al., 2021). For instance, many synthetic corrosion inhibitors might contribute to eutrophication in water bodies due to traits like limited biodegradation and organic corrosion inhibitors that contain phosphorus. On the other hand, the organic corrosion inhibitors had a difficult time adsorbing on metal surfaces due to their limited solubility, resulting in unnecessary economic waste.

2.5 Plant extract as potential green corrosion inhibitor

As a result of changes in environmental legislation, the majority of corrosion inhibitor research in recent years has focused on the creation of "environmentally friendly" substances. This term described formulations that were efficient, cost-effective, and low in environmental consequences as well as being non-toxic to humans and animals. Therefore, research on green corrosion inhibitors had become an attractive pathway for resolving corrosion on metals, particularly Al (Othman, Yahya and Ismail, 2019). This was because the natural product extracts can meet the required criteria. It was also important to note that the majority of natural resource were plentiful in nature and simple to access, which ultimately lowered the cost of extracts. The Paris Commission's legislative body (PARCOM) has established the following requirements for green metal corrosion inhibitors (Umoren et al., 2019):

1. It must not accumulate biologically
2. It must decompose naturally
3. It must be marine toxicity-free or extremely low.

There were numerous natural sources that include the green corrosion inhibitors. Additionally, they contained significant amounts of polar atoms and the electron-rich interactions that were common in organic compounds. The mechanisms of the corrosion and inhibition processes must be fully discussed in order to comprehend how the green corrosion inhibitors perform. The molecules of green corrosion inhibitors were adsorbed onto the metal surface as well as created a protective barrier in the inhibition process. The Figure 2.6 showed the protective layer that formed on steel when using green corrosion inhibitor. They might transfer an electron to the metal atoms' open d-orbitals as part of that process, creating coordinate bonds (Hossain, Asaduzzaman Chowdhury and Kchaou, 2020).

Contrarily, during corrosion, metal ions are transported into the solution at the anode and transfer electrons from the metal to the cathode, as described in Figure 2.6 (Hossain, Asaduzzaman Chowdhury and Kchaou, 2020). The cathodic process required electron acceptors such as oxygen, oxidizing agents, or hydrogen ions. Therefore, corrosion can be reduced by preventing or delaying anodic or cathodic processes. Thus, inhibitors were deposited on the metal surface and create a protective barrier. They then combine with anodic, cathodic, or both reactions to minimize corrosive oxidation, reduction, or both reactions. In our case, the suitable green corrosion inhibitor should be identified which is most effective on Al in acidic medium.

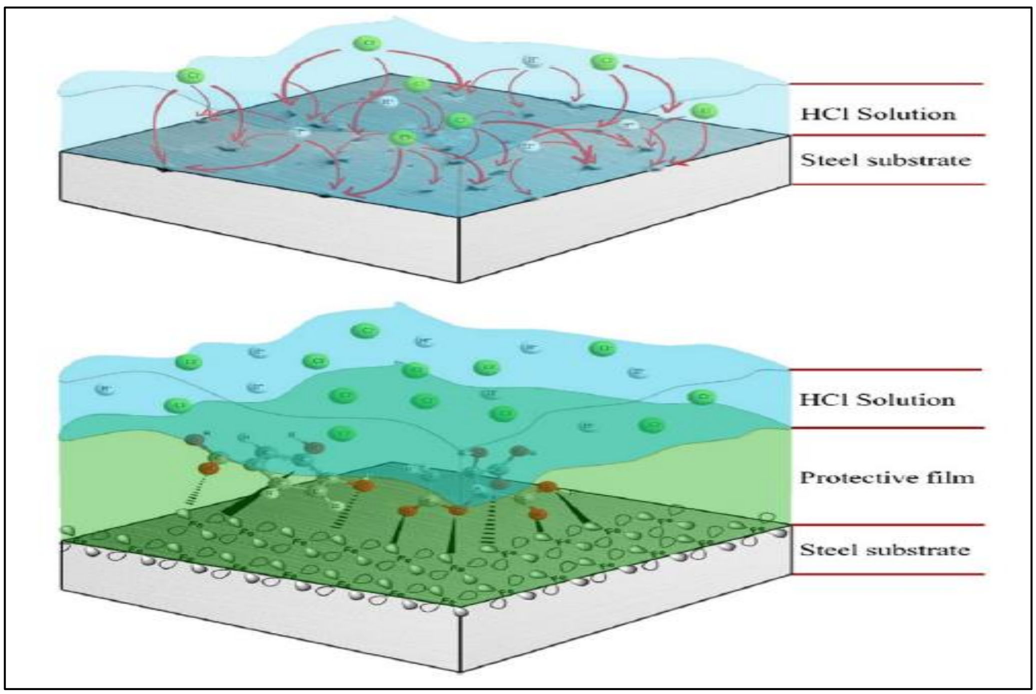

Figure 2. 6 Formation of protective layer on steel surface when adding green corrosion inhibitor

The majority of research investigations have been conducted on plant extracts, despite the fact that green corrosion inhibitors can be found in a variety of natural sources. This was revealed by a distribution of research work published in the last two decades. From Figure 2.7, it clearly showed that about 68% of research studies on plant extracts have been performed compared to other natural products (Xhanari et al., 2017). Due to their large diversity of organic chemicals, which include polyphenols, terpenes, carboxylic acids, and alkaloids as primary ingredients, plant extracts can meet the requirements of the green corrosion inhibitor. The most of these compounds also contained P, N, S, and O atoms, as well as a number of bonds that serve as bonding centers for the adsorption on the surface of Al (Xhanari et al., 2017)

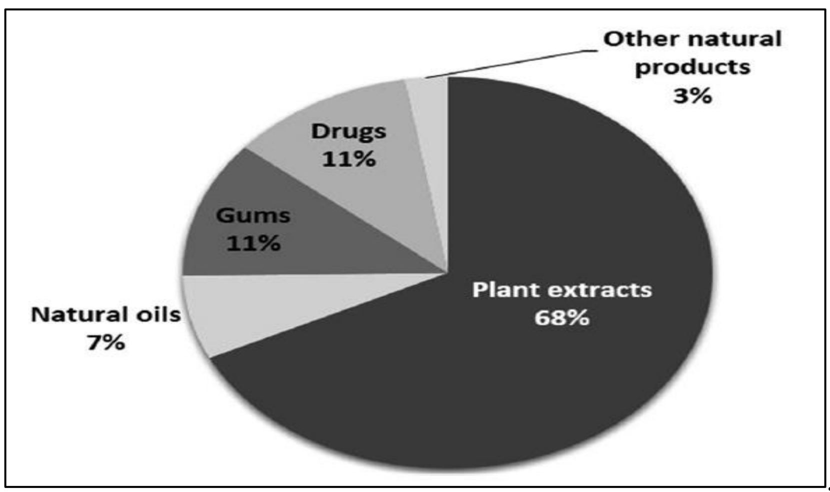

Figure 2. 7 Distribution of the research work performed on natural products as corrosion inhibitors for Al

As very powerful reactive oxygen scavengers, several of these compounds had the potential to prevent microbial growth. Moreover, the polyphenol-based extracts appeared to fulfill the most of the requirements for a composite anti-corrosion product, as well as being less toxic compared to other plant extracts (Xhanari et al., 2017). The plant extracts can be obtained from any part of the plant such as leaves, branch, stem and root. Table 2.1 showed the summary of the green corrosion inhibitors from plants that have been used to prevent corrosion from the surface of Al. To achieve objective of this study, the suitable plant should be selected based on its availability and abundance in Malaysia which can be utilized as a corrosion inhibitor on Al plate in acidic medium.

Table 2. 1 Green corrosion inhibitors that used to prevent corrosion on Al

Green Corrosion Inhibitor	**Extraction Solvent**	**Medium**	**IE (%)**	**Reference**
Rosemary leaf extract (0.1 - 0.5g/L)	Ethanol	Biodiesel	62.7 - 97.3	(Deyab, 2016)
Coffee husk extract (100 – 500 ppm)	Methanol	0.5M HCl	48.9 – 92.7	(Chaubey et al., 2021)
Olive seed extract (1 – 10%vol)	Water	1.0M HCl	48.56 – 98.86	(Khadijah M. Emran, 2015)
Aloe leaf extract (4 – 60%vol)	Water	0.5M HCl	15 – 88.42	(Mehdipour, Ramezanzadeh and Arman, 2015)
Coconut coir dust extract (0.1 – 0.5 g/L)	Acetone	1.0M HCl	18.6 - 80	(Umoren et al., 2012)

2.6 *Piper betle* leaves as a potential for green corrosion inhibitor

The *Piper Betle* was a member of the *Piperaceae* family and shown in Figure 2.8, which has long been considered as one of the beneficial plants with great medicinal potential and a wide range of pharmacological activity. Figure 2.9 illustrated the wide distribution of the *Piper Betle,* a historically and commercially significant plant, throughout India, Sri Lanka, Malaysia, Indonesia, Thailand, China, and the Philippines as well as other subtropical nations. Thus, the leaves of this plant were deep green, heart-shaped, smooth, shiny, and long stalked, with a pointy apex.

Piper Betle leaf had a strong aromatic smell and has been used in traditional Indian ayurveda herbal medicines for a long time. It also has been considered as a chewing gum along with areca nut, clove, and cardamom since ancient times. Besides that, it has been used as a source of medicine to cure a variety of illnesses, including conjunctivitis, boils and abscesses, cuts and injuries (Peter, 2004; Guha, 2006). It also worked as a breath refresher, a digestive and pancreatic lipase stimulator, and a joint pain reliever (Pradhan.D, 2013). Even though all the betel leaf's beneficial properties are recognized, the biochemicals that cause them are still unknown.

Because of this, research on the *Piper Betle* leaf extract has mainly concentrated on pharmaceutical applications, with special attention paid to constituent content such as eugenol, chavicol (phenylpropene derivative), vitamins, thiamin, riboflavin, and niacin as well as bioactive compounds such as phenolic, tanin, ester, sugar, flavonoid, essential oil, carotene, and others. (Umar et.al, 2018). Some of these substances may have a strong antiseptic impact on microorganisms including *Coccus*, *Streptococci*, and the bacteria

Bacillus subtilis and *Escherichia coli,* enabling their use as medications for dysentery and malaria.

Figure 2. 8 The *Piper Betle* Leaves

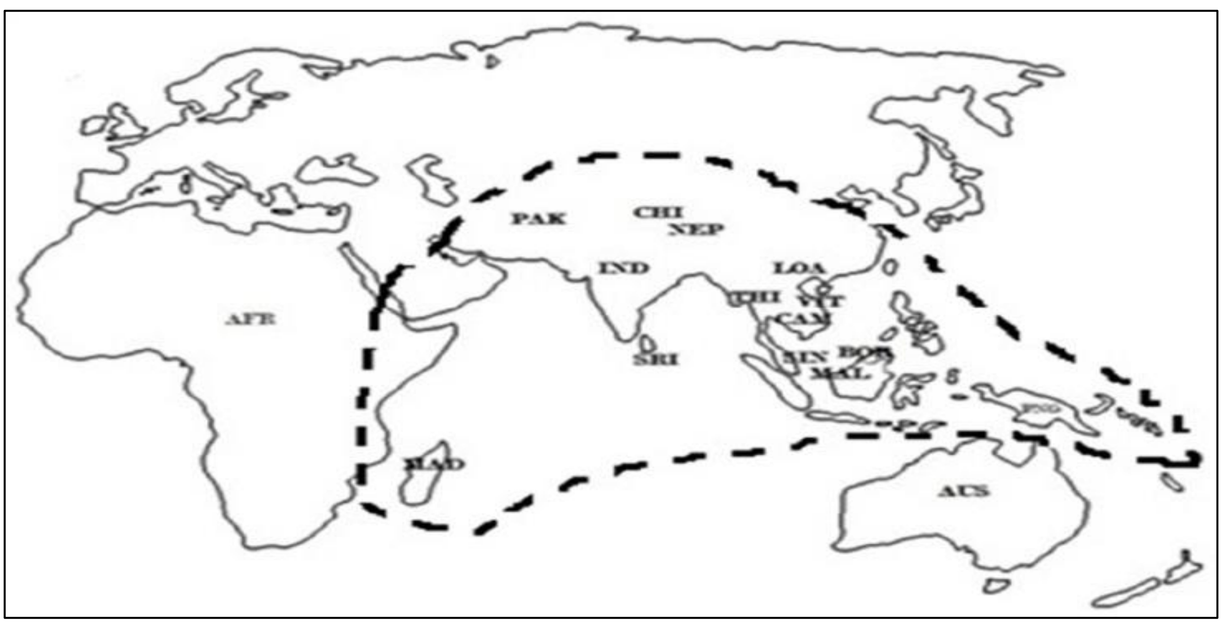

Figure 2. 9 The region with dotted line shows major areas consumption of *Piper Betle* leaves (Pradhan.D, 2013)

As a result, it had significantly aided uses for anti-inflammatory, antioxidant, anti-bacterial, anti-fungal, and anticorrosion (Desai and Parikh, 2015; Tan et al., 2021). Besides that, anti-platelet, anti-allergic, antidiabetic, anti-ulcer, antifertility, analgesic wound healing, and immunomodulatory properties were also found in the leaves of this plant (Trung et al., 2021). Since the most of research on *Piper Betle* leaf focused on either identifying phytoconstituents or reviewing pharmacological actions, hence only a few studies examining the relationship regarding biological activity and extracted chemicals (Ramji, Ramji, Iyer and Chandrasekaran, 2002). Moreover, bioactive substances such as polyphenols, alkaloids, steroids, saponins, and tannins are abundant in *Piper Betle* leaf extract (Shetty and Vijayalaxmi 2012).

From that research results, it shows that using *Piper Betle* leaves as corrosion inhibitors, have various pharmacological activities including the development of anti-ulcer agents, hepatoprotective agents, and antiseptic agents. Its various components, which were mainly composed of nitrogen, oxygen, sulfur, and carboxylic acids, have shown promising properties for their various industrial applications. Therefore, surface analysis and electrochemical techniques might be used to characterize these advantageous qualities, which could build a strong protective film on an Al surface as an environmentally friendly corrosion inhibitor (Trung et al., 2021). Depending on the extraction technique used, the antioxidant activity, total phenolic, and total flavonoid content of *Piper Betle* leaves may vary.

2.7 Extraction techniques of *Piper Betle* leaves

Beside choosing *Piper Betle* plant as a green corrosion inhibitor, extraction techniques also were a vital aspect to obtain the plant extracts. This was because the extraction technique employed to analyze the target content of plant species WAs affected by the chemical composition of the compound, sample particle size, and the existence of interfering compounds (Xhanari et al., 2017). The extraction method needed to be properly selected in conjunction with the study's goal. The extraction method employed ultimately affects the efficiency, productivity, and purity of plant extracts depending on the concentration of the component of interest and the level of purity required (Xhanari et al., 2017). The results showed that the method of extraction significantly affects the amount and type of phytoconstituents found in the leaf extract (Das et al. 2010). Each extraction process had its own set of operating parameters that influence the plant extract's concentration and antioxidant activity, and these factors must be optimized (Xhanari et al., 2017). Therefore, the primary variables that affected extraction kinetics were the sample's number of repetitive extractions, temperature, solvent-to-feed ratio, and extraction duration.

The extraction time and temperature parameters were directly proportional to the solubility parameter. Another element that affects extraction kinetics was material pretreatment, which had an impact on sample matrix, water content, particle size, and dispersion. There were many different ways to extract plant material, including traditional and contemporary procedures. Traditional liquid-liquid and solid-liquid extraction techniques were still commonly employed because of their ease of use, effectiveness, and wide range of applications. Although there were several conventional extraction methods, the most common were maceration, percolation, and soxhlet. These methods typically