APPLICATION OF KINETICS – THERMODYNAMICS MODEL AND ADSORPTION MECHANISMS FOR INHIBITION OF ACID CORROSION ON MILD STEEL BY RED ONION PEEL EXTRACT

NURAMIRAH BINTI MANSOR

UNIVERSITI SAINS MALAYSIA

2021

APPLICATION OF KINETICS – THERMODYNAMICS MODEL AND ADSORPTION MECHANISMS FOR INHIBITION OF ACID CORROSION ON MILD STEEL BY RED ONION PEEL EXTRACT

By

NURAMIRAH BINTI MANSOR

Project report submitted in partial fulfilment of the requirements for

the degree of Bachelor of Chemical Engineering

2021

ACKNOWLEDGEMENTS

In the name of Allah, the Most Beneficent, and the Most Merciful. All praise to Allah the Almighty for giving me strength, guidance, and patience in my final year project for the completion of Degree of Bachelor of Chemical Engineering. I was able to complete my final year project entitle "Application of Kinetics – Thermodynamics Model and Adsorption Mechanisms for Inhibition of Acid Corrosion on Mild Steel by Red Onion Peel Extract" although I had undergone many obstacles and queries throughout the completion.

First and foremost, I would like to thank and express my sincere gratitude to my supervisor, Assoc. Prof. Dr. Khairiah Abd. Karim for her invaluable guidance, insightful supervision, and endless encouragement throughout this project. Without the guidance and advice from Dr., this final year project will not be done completely on time.

In the meantime, I would like to express my genuine gratitude to my beloved father and mother for their endless support and encouragement throughout the time. Thank you for always encouraged and raised to pray for my success.

Once again, I would like to thank all people, including those whom I might have missed out who helped me directly or indirectly in accomplishment of this project. Thank you.

Nuramirah binti Mansor

June 2021

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS

Symbol	Description	Unit
E_a	Activation energy	$KJ.mol^{-1}$
K_{ads}	Adsorption equilibrium constant	-
N	Avogadro's constant	mol^{-1}
C_R	Corrosion rate	-
Θ	Degree of surface coverage	-
ΔH	Enthalpy change	$KJ.mol^{-1}$
ΔS	Entropy change	$J.kmol^{-1}$
γ	Exponential factor	-
R	Gas constant	$J.mol^{-1}.K^{-1}$
ΔG_{ads}	Gibb's free energy change	$KJ.mol^{-1}$
Q_{ads}	Heat of adsorption	$KJ.mol^{-1}$
α	Lateral interaction	-
h	Planck's constant	$m^2.kg.s^{-1}$ or $J.s^{-1}$
b	Size parameter	-
T	Temperature	K

LIST OF ABBREVIATIONS

Symbol	Description
HCl	Hydrochloric acid
IE	Inhibition efficiency
ROPE	Red onion peel extract
RPM	Revolution per minute
SDGs	Sustainable development goals

PENGGUNAAN KINETIK – TERMODINAMIK MODEL DAN PENJERAPAN MEKANISME UNTUK PERENCATAN KAKISAN ASID TERHADAP KELULI LEMBUT OLEH EKSTRAK KULIT BAWANG MERAH

ABSTRAK

Kajian penggunaan kinetik–termodinamik model dan penjerapan mekanisme untuk perencatan kakisan asid terhadap keluli lembut oleh ekstrak kulit bawang merah sebagai perencat kakisan hijau telah dijalankan. Kecekapan perencatan didapati meningkat dengan kepekatan perencat yang semakin meningkat tetapi berkurangan dengan peningkatan suhu larutan asid kerana pada suhu yang tinggi keluli lembut teroksida pada kadar yang lebih tinggi dan menyebabkan perencat menyerap kembali dari permukaan keluli lembut. Nilai penjerapan haba diantara julat -39.89 hingg -41.71 $KJ.mol^{-1}$ menunjukkan bahawa tindakbalas yang berlaku adalah tindak balas luah haba. Persamaa termodinamik digunakan untuk menentukan tenaga pengaktifan (E_a), perubahan entalpi (ΔH), dan perubahan entropi (ΔS). Penjerapan garis sesuhu seperti Langmuir, Freundlich, Flory–Huggins, Frumkin, dan Temkin digunakan untuk menilai perubahan tenaga bebas Gibb (ΔG_{ads}) dari nilai pemalar keseimbangan penjerapan. Penjerapan perencat, K_{ads} di permukaan keluli lembut didapati spontan dan konsisten dengan fizikal penjerapan mekanisme kerana nilai perubahan tenaga bebas Gibb adalah negatif dan kurang daripada -20 $KJ.mol^{-1}$.

APPLICATION OF KINETICS – THERMODYNAMICS MODEL AND ADSORPTION MECHANISMS FOR INHIBITION OF ACID CORROSION ON MILD STEEL BY RED ONION PEEL EXTRACT

ABSTRACT

The study of kinetics–thermodynamics parameters and adsorption isotherms of the inhibition of corrosion mild steel in acid medium using red onion peel extract (ROPE) as green corrosion inhibitor was carried out. The inhibition efficiency was found to increase with increasing inhibitor concentration but decrease with increasing temperature of acid medium because at higher temperature the mild steel is oxidized at higher rate and causing the inhibitor to desorb back from mild steel surface. The value for heat of adsorption, Q_{ads} ranged from -39.89 to -41.71 $KJ.mol^{-1}$ indicates that the reaction is exothermic. The adsorption data fitted well to Langmuir adsorption isotherm model. Thermodynamic equations were used to determine the activation energy (E_a), enthalpy change (ΔH) and entropy change (ΔS). The adsorption isotherms such as Langmuir, Freundlich, Flory–Huggins, Temkin, and Frumkin were used to evaluate the change of Gibb's free energy from the adsorption equilibrium constant, K_{ads}, value. The adsorption of the inhibitor on surface of mild steel was found to be spontaneous and consistent with the physical adsorption mechanism as ΔG_{ads} is negative value and less than -20 $KJ.mol^{-1}$.

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Organic compounds that contain polar functional groups such as nitrogen, sulphur and oxygen in a conjugated system are effective corrosion inhibitors for steel. Plant extracts have been the popular choice for wide spectrum of inhibitors since they are environmentally acceptable, readily available, and renewable. There are several advantages of green corrosion inhibitors which are low cost of processing, biodegradability, and absence if heavy metals or toxic compound which can cause great hazard to the environment (Alaneme & Olusegun, 2012). Corrosion inhibitors have been used extensively to control corrosion of metals in various aggressive media such as acid and alkali medium. Corrosion inhibitors are substance that added in small amounts on the surfaces of metal or added to the corrosive medium, therefore reduce the tendency to be affected by corrosion.

Allium cepa L. or commonly known as onion is a type of vegetable from the Allium family that is valued not only for its taste but also as a significant source of numerous beneficial compounds. *Allium cepa* L are known to contain on analysis, vitamin C, Vitamin B_6, folic acid, and small quantities of other nutrients. Onions containing high levels of phenolic compounds, which have antioxidant properties and flavonoids are the major phenolics in onions (Liguori et al., 2017). These include quercetin and its glycosides 3, 4–diglucoside and quercetin–4–glucoside. Red onion peel extract has potential as a corrosion inhibitor since the compounds responsible for the inhibitory action is quercetin. The polyphenols like quercetin present in highest concentration in the onion peel which have a high potential to be used as corrosion inhibitors. They contain oxygen-atoms in their chain which are rich with electrons where these compounds present sites of adsorption on the surface of metal and prevent the contact between the metal and ions that can cause corrosion (Galo et al., 2020).

To conclude that the corrosion is metal deterioration and caused by the reaction of the metal with the environment. The material corrosion behaviour depends on the environment to which it is exposed (The Effects and Economic Impact of Corrosion, 2000). The main factors describing the environment are the following: physical state (gas, liquid, or solids), components and concentrations of chemical composition, and temperature. Besides, corrosion is the loss of useful qualities of metals and alloys because of a reaction with the surrounding environment. Corrosion leads to major problems in most industrial fields (Fouda et al., 2017). Rust and contaminated scales were generally removed using acid solutions in many industrial operations such as acid cleaning, acid well acidizing, and acid pickling. Furthermore, hydrochloric acid (HCl) can be created as a by–product of the desalting of crude oil and some refinery procedures.

1.2 Problem Statement

The pipeline damages could be due many reactions, however in this report will discuss more on the corrosion part. Naturally, corrosion can occur in a variety of materials, but it is most usually associated with metals. Metals corrode when the environment around them are chemically unstable. As pipeline have been used to transfer liquid, chemical, and gas for decades, the high risk of corrosion attack has gotten increasingly serious. The pipelines that are buried underground transport whether gas, crude oil, gas, or water across a variety of environment , including the seawater and soil which can lead to corrosion and eventually leakage (Saiful Azreen Bin Ismail, 2014). Use of inhibitors is one of the methods for protection against corrosion especially in acidic medium to inhibit dissolution of metals and acid consumption. Even though the inorganic inhibitors have proven to be effectives, concern about their toxicity on human health and the environment have recently increased. Besides, it is difficult to handle and dispose them. There is a growing demand to protect the environment by reducing and managing all factors that may harm and contaminate the society as well as the economy.

To minimize further losses and hazardous conditions, a study of natural corrosion inhibitor is necessary because the corrosion of pipelines will lead into leaking and rupture where it gives unsafe environment especially to humans. Corrosion inhibitors by using plant extracts are preferable because it is environmentally friendly, ecologically acceptable, low-cost, readily available, less harmful, biodegradable, and does not contain heavy metals or other toxic compounds. The extracts for the leaves, barks, seeds, fruits, and roots consists of nitrogen, sulphur, and oxygen atoms and some of it has a function as effective inhibitors of metal corrosion in aggressive environment. The kinetics–thermodynamics model and adsorption mechanism for inhibition of acid corrosion on mild steel by using red onion peel extract, ROPE as green inhibitor is studied. The role of the inhibitors in a corrosion process that has both kinetics as well as thermodynamics implications. The adsorption mechanism is analysed by using adsorption isotherms models such as Langmuir, Freundlich, Flory – Huggins, Frumkin, and Temkin. The understanding of adsorption is important for the overall adsorption mechanism pathways and effective design of adsorption systems. The Gibb's free energy is evaluated by using adsorption equilibrium constant from adsorption isotherms.

1.3 Objectives

The main objective of this study is to understand the kinetics-thermodynamics model and adsorption mechanism for inhibition of acid corrosion on mild steel by red onion peel extract, ROPE. The objectives of this study are:

i. To evaluate ROPE inhibition efficiency at different concentration of inhibitor and temperature from the secondary data gathered from research done by Chieh Choon, O (2015).
ii. To investigate different types of adsorption isotherms on the phenomenon of corrosion process.
iii. To investigate the inhibitive properties of red onion peel extract (ROPE) on mild steel in acidic medium for thermodynamics and kinetics point of view.

CHAPTER 2

LITERATURE REVIEW

2.1 Corrosion of Metal

Corrosion is a phenomenon where it is defined as the deterioration of a substance or its properties due to a reaction with the environment. One of the basic materials is metal element that cannot be separated from human life. In industrial processes, mild steel is widely used due to its excellent ductility and flexibility, thus the pipes do not crack or break when under pressure. Mild steel is carbon steel with the main content of iron (Fe) and contains a low level of carbon (C) thus making cold forming of mild steel is easier and more ductile compared to the other types of steel. It has been widely used as construction materials and in various industries, commonly used as a piping system for transportation because of its different applications and most of it has excellent mechanical properties. It is also more affordable than stainless steel or other steel, but have disadvantages such as not corrosion resistant (Muhammad Samsudin et al., 2018)

Corrosion happens when metal reacts with other substances such as oxygen, hydrogen, and an electrical current and this leads to corrosion of the materials. It happens when metals such as steel are placed under higher stress and causing the steel to crack. It has extensively been used under different conditions in chemical and allied industries for handling alkalis, acids, and salt solutions. The most corrosive medium is aqueous solution of acid which can cause metal corrosion. Acids are widely used in various industries for metal surface treatment to remove impurities. Corrosion accompanied by significant hydrogen penetration in the acid solution for some conditions. Metal corrosion is the process of degradation of metal by chemical surface reactions with aggressive components of the environment (Fouda et al., 2017).

In general, corrosion occurs when most or all the atoms on the same surface of metals oxidise and damage the entire surface. Most metals are easy to oxidize, and they tend to lose electrons to oxygen in the air or in water. The possible way for corrosion protection is by using durable material, but this is impossible because it affects the economics and costs. In these environments, the protection of mild steel often involves the addition of chemicals or chemicals that are able to reduce the corrosion rate, either by reducing the aggressiveness of the environment or by protecting the metal directly (Ali, 2016).

The Sustainable Development Goals (SDGs) also known as Global Goals are a collection of 17 interlinked global goals to achieve a better and sustainable future for all. SDGs 9: Industry, Innovation, and Infrastructure is the to build resilient infrastructure, promote inclusive, and sustainable industrialization, and foster innovation. Every thriving community relies on a well-functioning and robust infrastructure. Our industry and infrastructure must be modernised to face future challenges. To do so, we must encourage the development if breakthrough sustainable technologies and ensure that everyone has equal access to information and financial markets. This will produce wealth, create jobs, ensure that societies around the world are stable and successful. (Goal 9: Industry, Innovation and Infrastructure | The Global Goals, 2020).

2.2 Problems of Corrosion

Corrosion of mild steel is a major problem in industrial processes especially due to exposure to corrosive acids, alkalis, and salt solutions. The consequences of the corrosion process are degradation, plant shutdowns, waste of valuable resources, loss or contamination of product, reduction in efficiency, costly maintenance, expensive overdesign, and damage of equipment adjacent to that in which corrosion failure occurs. It can also endanger safety and impede technological progress. Corrosion can cause the pipeline ruptured and that spillage of oil is experienced which creates environmental pollutions, the resources are lost in cleaning up and large – scale ecological damage resulted from corrosion effect. Corrosion can cause other consequences are social where it involves the safety, health, and depletion of natural resources. For example, when it has sudden failure it can cause fire explosion, release of toxic products, and construction collapse, and pollution due to escaping product from corroded equipment or due to corrosion product itself (The Effects and Economic Impact of Corrosion, 2000).

2.3 Corrosion Mitigation

Corrosion of metals can be mitigated by using five primary methods by using inhibitors, coatings and linings, material selection, appropriate design, and cathodic protection. The common method used to prevent or minimize metal corrosion is by adding the corrosion inhibitor into the media (Ong & Karim, 2017). They protect the metals surface either by merging with them or by reacting with the impurities in the environment that may cause pollution (Popoola et al., 2013). Corrosion inhibitors are chemical substances that decrease the rate of corrosion when it presents in the corrosion system at suitable concentration without significantly changing the corrosive agent concentration. Corrosion inhibition by organic, inorganic or mixture of both inhibitors can be either chemisorption on the surface of metal or by physiosorption (Iroha et al., 2015). Corrosion inhibitor used must have antioxidant compounds where it can donate one or more electrons to the prooxidant compound and then convert it into more stable compound (Muhammad Samsudin et al., 2018) and able to slow down and eliminate the corrosive processes in the transportation, production and storage of oil and its derivatives (Ferreira et al., 2016). The corrosion inhibitors used typically organic compounds containing heteroatoms such as S, N and O and Π electrons from aromatic rings, double and triple bonds in suppressing the corrosion process. The ions or molecules adsorb on the surface of the metal, decrease the anodic and cathodic reaction, decrease the diffusion rate of reagents to the metal surface or decrease the electrical resistance of the metal surface to decrease the corrosion rate. In material selection, every metal and alloys have distinctive and inherent corrosion behaviour which will vary from the high resistance of noble metals to the low corrosion resistance of active metals. The corrosion resistance of a metal is highly dependent in the environment to which it is exposed such as the chemical composition, temperature, velocity, and others. Coating for corrosion protection can be divided in two large groups which are metallic and non – metallic: organic and inorganic. With any type of coating, the intention is the same to isolate the underlying metal from the corrosive medium. Cathodic protection inhibits the corrosion current that destroy the corrosion cell and forces the current to flow to the protected metal structure, thereby preventing corrosion or metal dissolution. Cathodic protection can be achieved in two ways depend on the surface of the protection current. Design can ensure the maximum interchangeability and standardization of parts reduces the inventory of required parts. Maintenance and repair work is imaginable, and convenient access can be provided (The Effects and Economic Impact of Corrosion, 2000).

Adsorption process connected to electrostatic attraction between inhibitor molecules. The ions that are not in direct contact with the metal surface due to the presence of interposed water molecules layer known as physical adsorption while chemical adsorption is the formation of a coordination bond with exchange of electrons from the inhibitor to the metal surface. The interaction between the lone pair of electrons of oxygen or aromatic ring and the metal surface active site causing the protective film formed on the metal surface. The action of corrosion inhibitors initiated with the adsorption of the inhibitor onto the metal surface. The adsorption of inhibitors onto the metal surface depends on electronic characteristics of the inhibitor, the surface nature, temperature and pressure of the reaction, the steric effects, multilayer adsorption and the degree of surface site activity (Abd-El-Nabey et al., 1996) . Adsorption isotherms give the information about interaction between the adsorbed molecules and their interactions with the metal surface. Corrosion inhibitors decrease the reaction rates of the metal with the media by adsorption of ions or molecules onto metal surface, increasing or decreasing the anodic or cathodic reaction, decrease the rate of diffusion for reactants to the surface of the metal, and decrease the electrical resistance of the metal surface.

2.4 Green Corrosion Inhibitor

Many industrial processes have used inorganic inhibitors for corrosion protection, but due to cost and toxicity the focus is now shifting to more environmentally friendly inhibitors. Inorganic inhibitors are toxic and harmful to the humans and the environment, thus making it difficult to handle and to dispose of them. Therefore, corrosion inhibitors by using plant extracts are preferable due to environmentally friendly, lower cost, less harmful to human health and the environment (Ong & Karim, 2017). It is also more efficient, biodegradable and does not contain heavy metals or other toxic compounds (Akinbulumo et al., 2020; Rani & Basu, 2012). *Delonix regia* extract inhibit the corrosion of aluminium in hydrochloric acid solutions, caffeic acid were studied as corrosion inhibitor for on the corrosion of mild steel in 0.1 M sulphuric acid, based on the result shows that adsorption of inhibitor on the mild steel surface was exothermic and consistent with physical adsorption mechanism and best described by the Frumkin adsorption isotherm. Okafor et al., (2010) studied the corrosion inhibition and adsorption properties of *Azadirachta indica* mature leaves extract as green inhibitor for mild steel in nitric acid and Akinbulumo et al., (2020) studied the corrosion of mild steel by *Euphorbia heterophylla L.* extract in 1.5 M of hydrochloric acid, from the result they conclude that the adsorption of *Euphorbia heterophylla L.* on mild steel is feasible, spontaneous and it occurred by physical adsorption according to Flory – Huggins isotherm model. Abeng et al., (2017) stated that adsorption of methanolic extract of *Erigeron floribundus* onto mild steel surface followed by Langmuir adsorption isotherm and Gibb's free energy value indicates that spontaneous adsorption of the extract. Table 2.1 shows several types of green corrosion inhibitors used.

Table 2.1 Green corrosion inhibitors on metals or alloys in different condition

Green corrosion inhibitors	**Metal/ alloy studied**	**Media studied**	**References**
Azadirachta Indica Extract	Mild steel	Acid media	(Okafor et al., 2010)
Caffeic acid	Mild steel	Acid media	(de Souza & Spinelli, 2009)
Delonix regia extract	Aluminium	Acid media	(Rani & Basu, 2012)
*Erigeron floribundus (*Kunth)	Mild steel	Acid media	(Abeng et al., 2017)
Ethanol extract of *Piper guinensis*	Mild steel	Acid media	(Ebenso et al., 2008)
Euphorbia heterophylla L. extract	Mild steel	Acid media	(Akinbulumo et al., 2020)
Henna extract	Carbon steel	Acid media	(Hamdy & El-Gendy, 2013)

Hibiscus sabdariffa leaves	Mild steel	Acid media	(Murthy & Vijayaragavan, 2014)
Vernonia amygdalina	Mild steel	Acid media	(Nwabanne & Okafor, 2012)

2.5 Kinetics – Thermodynamics Model

Thermodynamics parameters associated with corrosion inhibitors is the fundamental to understand the inhibition efficiency at that corrosion rate, under a corrosive prone medium at given temperature of the process. The adsorption process's spontaneity is determined by the sign of Gibb's free energy of adsorption, ΔG_{ads}. The magnitude and sign of ΔG_{ads} depend on the value of adsorption equilibrium constant, K_{ads}. When the adsorption rate exceeds the desorption rate, the ΔG_{ads} are negative, indicating spontaneous adsorption. If ΔG_{ads} less than -20 KJ/mol indicates physical adsorption while if ΔG_{ads} values greater than -40 KJ/mol indicate chemical adsorption (Akinbulumo et al., 2020). Abdul Rahiman & Sethumanickam, (2017) stated that the lower activation energy value for corrosion process in the presence of the inhibitor is attributed to its chemisorption, while higher value is associated with its physical adsorption(Abdul Rahiman & Sethumanickam, 2017). Akinbulumo et al., (2020) reported that if enthalpy change higher than 100 KJ/mol indicates chemical adsorption while enthalpy change less than 100 $KJ.mol^{-1}$ indicates physical adsorption.

2.6 Adsorption Isotherm

The organic inhibitors initiate their inhibition by inhibitor molecules adsorbing onto metal surfaces. Chemical structures of organic compounds, the distribution of charge in molecules, type of aggressive media and surface charge and nature of metal influenced the adsorption process (Zhang & Hua, 2009). Overall improvement of adsorption mechanism pathway and effective design of adsorption system can be achieved by understanding and interpreting the adsorption isotherms. The best tools to define fitting adsorption models is by using linear regression analysis because it able to quantify the adsorbates distribution, analyse the adsorption system and verify the consistency of theoretical assumptions of adsorption isotherm model (Ayawei et al., 2017). Plant extracts constituent compounds usually adsorbed on the metal surface and are described by the Langmuir model (Miralrio & Vázquez, 2020).

2.1.1 Langmuir Adsorption Isotherm

Langmuir adsorption isotherm is the most widely used model to explain the relationship between surface coverage of an adsorbed gas and gas pressure over the surface of its absorbent at constant pressure. This model was employed to determine the equilibrium of adsorption for inhibiting the inhibitor. Langmuir adsorption is designed to describe gas-solid phase adsorption and used to quantify and contrast adsorbent adsorptive capacity.

2.1.2 Freundlich Adsorption Isotherm

The Freundlich isotherm can be used to describe adsorption processes in heterogonous surfaces. The surface heterogeneity and the exponential distribution of active sites and their energy are defined by this isotherm. The linear form of the Freundlich isotherm is as shown in Table 2.2 (Ayawei et al., 2017).

2.1.3 Flory – Huggins Adsorption Isotherm

Flory – Huggins isotherm describes the adsorbate's degree of surface coverage on the adsorbent. The linear form of the Flory – Huggins equation is expressed as in Table 2.2.

This isotherms model can be used to describe the spontaneity and feasibility of an adsorption process. The adsorption equilibrium constant is used to calculate spontaneity Gibb's free energy (Ayawei et al., 2017).

2.1.4 Frumkin Adsorption Isotherm

The Frumkin isotherm used to evaluate the interactions of adsorbed molecules on the mild steel surface. The equation of Frumkin isotherm is shown in Table 2.2, where the parameter α is the interaction coefficient, it is positive for attraction and negative for repulsion and its zero indicates that no interaction between adsorbate species.

2.1.5 Temkin Adsorption Isotherm

The Temkin isotherm model considers the effects of indirect adsorbate or adsorbate interactions on the adsorption process, as well as the assumption that the heat of adsorption of all molecules in the layers decreases linearly as surface coverage increases. The Temkin isotherms are valid only for an intermediate range of ions concentration (Ayawei et al., 2017).

Table 2.2 Main adsorption isotherm models

Model	Adsorption Isotherm
Langmuir	$\frac{C_R}{\theta} = \frac{1}{K_{ads}} + C_R$
Freundlich	$log\theta = \frac{1}{n} logC_R + logK_{ads}$
Flory-Huggins	$log\frac{\theta}{C_R} = blog(1-\theta) + logK_{ads}$
Frumkin	$logC_R\left(\frac{\theta}{1-\theta}\right) = 2\alpha\theta + 2.303logK_{ads}$
Temkin	$\theta = nlnC_R + K_{ads}$

2.7 Error analysis

Microsoft Excel is a handy software that enables users to create graphs and formulas specifying calculation. By plotting the graph, the efficiency of the inhibitor can be evaluated and can conclude the best kinetic-thermodynamic model that influences the adsorption mechanism. Goodness of fit can be used to determine the kinetic model that best describes the interaction between the mild steel and ROPE. Some error function is employed to study the model fit, for example: the coefficient of correlations, sum of squared errors, Marquardt's percent standard deviation, hybrid fractional error function, etc. The coefficient of determination (R^2) refers to the variance about mean and it is used to analyze the fitting degrees of isotherms and kinetic models with experimental data. The sum square of errors is a widely used error function. There is one disadvantages of this error function which is the isotherms parameters derived using this error function will provide a better fit for experimental data obtained at higher end of liquid – phase adsorbate concentration ranges as the magnitude of the errors and thus the square of errors tends to increase, indicating a better fit for experimental data obtained at the higher end of concentration ranges.

CHAPTER 3

METHODOLOGY

3.1 Summary of experimental procedures for data collections

The experimental data used in this study was gathered from the research done by Choon Chieh, O. (2015). In brief, the materials used were red onion peel extract, mild steel coupons and chemicals used were 80% methanol solution, distilled water, 1.0 M HCl solution, acetone, and ethanol. The ROPE was extracted using ultrasound – assisted extraction using methanol as solvent. Then, the dried ROPE was cut into smaller pieces with scissors and 6.25 g of red onion peel was weighted by using the analytical balance. A weighted red onion peel was then placed with 250 mL of 80% (v/v) methanol solution in a 250 mL conical flask. The conical flask opening was covered with Parafilm to reduce methanol vaporization and placed in an ultrasonicator to ultrasonate the mixture. After 5 minutes, the conical flask was taken out from the sonicator, and it was left for stirring at 200 rpm in 10 minutes at room conditions. To optimize the extraction of inhibitors from red onion peel extract, the conical flask was placed back into the sonicator for another 5 minutes, and these two steps were repeated for six times to optimize the extraction of inhibitors from red onion peel. The sonicator temperature is regulated and controlled at below $35^{o}C$.

For the extract preparation, the red onion peel extract and methanol solution were separated by using filter paper after ultrasound–assisted extraction. Then, the extracted solution was heated using a hot – plate stirrer at temperature of $50^{o}C$ to vaporize off the methanol solvent. The remaining extract was collected and stored in a closed container. Stock solution of the extract with 50 g/L concentration was prepared. First, 2.5 g of red onion peel extract was measured using analytical balance and 50 mL of 80% (v/v) of methanol solution was mixed with red onion peel extract and stirred for 10 minutes at 250 rpm. Then, the solution is filtered using filter paper and filtrate obtained was stored and covered. The stock solution diluted into 0.5, 1.0, 1.5, and 2.0 g/L concentrations of ROPE in HCl solution. Mild steel coupons were mechanically pressed – cut into 5 cm x 3 cm dimensions with 0.1 cm thickness. Each coupon was drilled into a hole with 0.3 cm diameter. The total surface area of coupons is 31.55 cm^2. The study of mild steel corrosion rate in HCl solution through the weight loss measurement of these coupons. First, the coupons were degraded with absolute ethanol and were immersed in acetone. Then, the coupons were dried in air and weighed using analytical balance. The initial mass of coupons was recorded. The coupons were stored in the beaker that contained silica gel to avoid contamination of mild steel with air before immersion in hydrochloric acid, HCl solution. Corrosion inhibition effect of red onion peel extract on mild steel in acidic medium was investigated by determining the inhibition efficiency and corrosion rate. Corrosion rate, CR of the mild steel in HCl solution was calculated using Equation (3.1).

$$Corrosion\ Rate, CR\ (mm/y) = 87.6\left(\frac{\Delta W_t}{\rho . A_s . t}\right) \tag{3.1}$$

Where, ΔW_t is the weight loss, ρ is metal density, A_s is area of the metal surface, t is time of exposure. The corrosion rate of mild steel is expressed based on the apparent surface area. The approximated density od the mild steel is 7.85 g/cm^3.

The inhibition efficiency, IE (%) can be calculated by using Equation (3.2).

$$\%\, IE = \frac{CR_{without} - CR_{with\ I}}{CR_{without}} \times 100\% \tag{3.2}$$

The surface coverage value, Θ can be calculated using Equation (3.3).

$$\theta = \frac{CR_{without} - CR_{withI}}{CR_{without}} \tag{3.3}$$

Where $CR_{without}$ and CR_{withI} are the corrosion rates in the absence and presence of the corrosion inhibitor extract. The high corrosion rate of mild steel indicates that the inhibition efficiency of corrosion inhibitor is low, and vice versa.

3.2 Data Evaluation

Overall, this final year project focused on the application of the kinetics–thermodynamics model and adsorption mechanism for inhibition of acid corrosion on mild steel by red onion peel extract, ROPE.

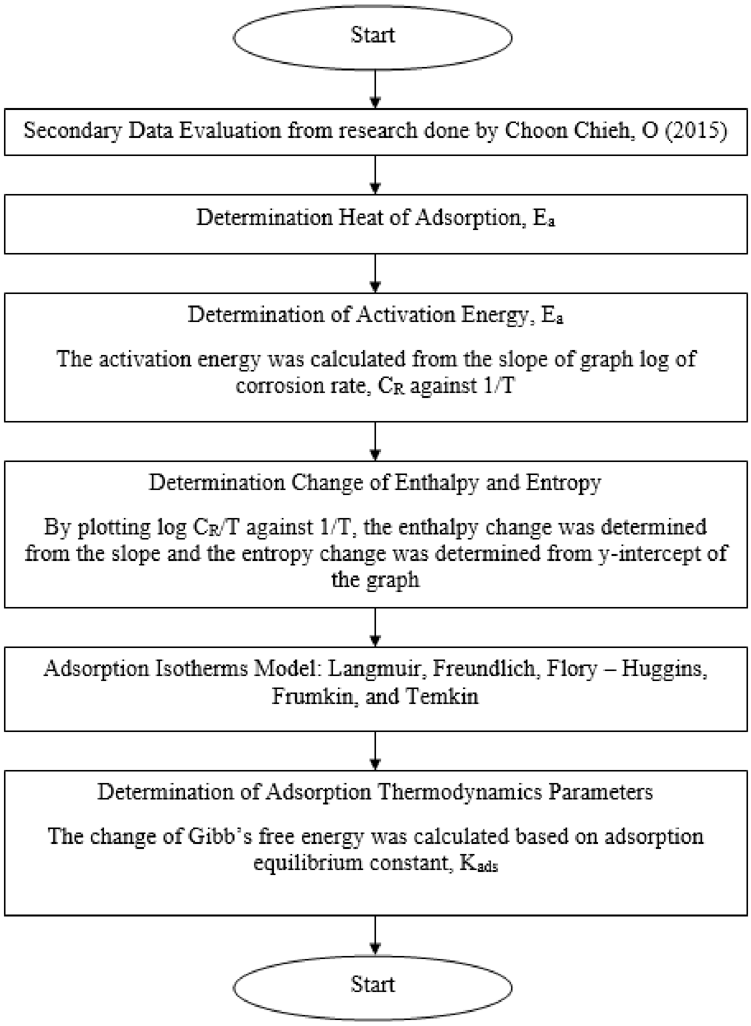

Figure 3.1 Research activity flow diagram.

The experimental data used in this study was gathered from the research done by Ong & Karim, 2017 to study the thermodynamic parameters and adsorption isotherms that are related to the corrosion process. The inhibition efficiency of ROPE at different temperature and concentration of inhibitor was studied. Figure 3.1 shows the flow diagram for research diagram. The secondary data is investigated more based on kinetics–thermodynamics model and adsorption isotherms by plotting graph. Then, determine the adsorption nature of ROPE on the surface of the mild steel.

3.3 Heat of Adsorption

The heat of adsorption Q_{ads} of inhibitor, red onion peel extract on the surface of mild steel was calculated using Equation (3.4) by using the data gathered from research done by Choon Chieh, O (2015).

$$Q_{ads} = 2.303R\left[\log\left(\frac{\theta_2}{1-\theta_2}\right) - log\left(\frac{\theta_1}{1-\theta_1}\right)\right] \times \frac{(T_1 \times T_2)}{(T_2 - T_1)}\ \frac{kJ}{mol} \tag{3.4}$$

Where *R* is the gas constant, Θ_1 and Θ_2 are the degree of surface coverage at temperatures, T_1 and T_2, respectively.

3.4 Determination of Activation Energy

Activation energy control happens when the corrosion rate is controlled by a slow electrochemical step and this slow step has a very high activation energy. The log of corrosion rate, *CR* against 1/*T* plot will give a slope where the activation energy was estimated. The Arrhenius equation is described as the relationship between the corrosion rate, *CR* and temperature, *T* as the following equations:

$$\log CR = \frac{-E_a}{2.303RT} + log\,\gamma \tag{3.5}$$

Where E_a is the activation energy, *R* is the gas constant, *T* is the temperature in Kelvin and γ is an exponential factor. By plotting graph of $\log CR$ against 1/*T*, the activation energy can be calculated from the slope, $\frac{-E_a}{2.303RT}$ of the graph by inserting the gas constant value.

3.5 Determination Change of Enthalpy and Entropy

The enthalpy and entropy change were evaluated by using Equation (3.6). The enthalpy change, ΔH was calculated from the slope, $-\frac{\Delta H}{2.303R}$ and the entropy change, ΔS was determined from the y-intercept, $\left[\log\frac{R}{Nh}+\left(\frac{\Delta S}{2.303R}\right)\right]$ from the plot of $\log\frac{C_R}{T}$ against $\frac{1}{T}$.

$$\log\frac{C_R}{T}=\frac{-\Delta H}{2.303R}\left(\frac{1}{T}\right)+\left[\log\frac{R}{Nh}+\left(\frac{\Delta S}{2.303R}\right)\right] \quad (3.6)$$

Where h is Planck's constant, N is the Avogadro's number, ΔH is the change of enthalpy and ΔS is the change of entropy. Planck's constant is the fundamental physic constant characteristics of the mathematical formulations of quantum mechanics, where it describes the behavior of the particles and waves on the atomic scales including the particle aspect of light.

3.6 Adsorption Isotherms

The study of adsorption isotherms provides a mechanism for describing how organic inhibitors adsorb on the metal surface. There are several types of adsorption isotherms models that have been studied which are Langmuir, Freundlich, Flory – Huggins, Frumkin, and Temkin. The adsorption isotherm equation is given by Akinbulumo et al., (2020); Ituen et al., (2017).

The Langmuir adsorption isotherm model:

$$\frac{C}{\theta}=\frac{1}{K_{ads}}+C \quad (3.7)$$

Where K_{ads} is adsorption equilibrium constant, C is the inhibitor concentration, θ is the degree of surface coverage of the inhibitor. By plotting a graph of $\frac{C}{\theta}$ against C, the value of K_{ads} can be determined from the y-intercept of the graph.

Freundlich adsorption isotherm model:

$$\log\theta = \frac{1}{n} logC_R + logK_{ads} \tag{3.8}$$

By plotting a graph of $\log\theta$ against $\log C$, the value of K_{ads} can be determined from the y-intercept of the graph.

Flory – Huggins adsorption isotherm model:

$$\log\left(\frac{\theta}{C_R}\right) = b\ log(1-\theta) + \log K_{ads} \tag{3.9}$$

Where b is the size parameter and is a measure of the number of adsorbed water molecules substituted by a given molecule of inhibitor. By plotting a graph of $\log\left(\frac{\theta}{C_R}\right)$ against $log(1-\theta)$, the value of K_{ads} can be determined from the y-intercept of the graph.

Frumkin adsorption isotherm model isotherm is given by Equation (3.10).

$$\log C\left(\frac{\theta}{1-\theta}\right) = 2.303\log K_{ads} + 2\alpha\theta \tag{3.10}$$

Where K_{ads} is the adsorption-desorption constant and α is the lateral interaction term describing the interaction in the adsorbed layer. By plotting a graph of $\log C\left(\frac{\theta}{1-\theta}\right)$ against $\log\theta$, the value of K_{ads} can be determined from the y-intercept of the graph.

Temkin adsorption isotherm model:

$$\theta = \ln C_R + K_{ads} \tag{3.11}$$

By plotting a graph of θ against $\ln C_R$, the value of K_{ads} can be determined from the y-intercept of the graph.

3.7 Determination of Adsorption Thermodynamics Parameters

The Gibb's free energy change of adsorption, ΔG_{ads} was calculated by using Equation (3.12) to investigate the feasibility and adsorption nature.

$$\Delta G_{ads} = -RT \ln(55.5 K_{ads}) \tag{3.12}$$

Where K_{ads} is the adsorption equilibrium constant that can be calculated from the adsorption isotherm and the value 55.5 is the molar concentration of water in solution (Akinbulumo et al., 2020).

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Experimental Data

The experimental data on corrosion inhibition of mild steel in 1.0 M HCl solution shows increment trend with the increasing concentration of the red onion peel extract. This can be explained by the adsorption of the constituent of the red onion peel extract on the mild steel surface. The inhibition efficiency and corrosion rate for 0.5 g/L, 1.0 g/L, 1.5 g/L, and 2.0 g/L red onion peel extract concentration are showed in Table 4.1.

Table 4.1 Corrosion parameters of mild steel in 1.0 M HCl without and with corrosion inhibitors at various temperatures.

Temperature, T (K)	Concentration of Inhibitor (g/L)	Corrosion Rate, CR (mm/yr)	Inhibition Efficiency (%)	Surface Coverage, Θ
303	Blank	2.3004		
	0.5	0.3030	86.83	0.8683
	1.0	0.2694	88.29	0.8829
	1.5	0.2370	89.70	0.8970
	2.0	0.2308	89.97	0.8997
313	Blank	4.4863		
	0.5	0.7451	83.39	0.8339
	1.0	0.5779	87.12	0.8712
	1.5	0.5072	88.69	0.8869
	2.0	0.4717	89.49	0.8949
323	Blank	18.0907		
	0.5	5.4697	69.77	0.6977
	1.0	4.7546	73.72	0.7372
	1.5	3.7184	79.45	0.7945

	2.0	3.5294	80.49	0.8049
333	Blank	28.2967		
	0.5	11.3915	59.74	0.5974
	1.0	9.8366	65.24	0.6524
	1.5	9.2166	67.43	0.6743
	2.0	9.0612	67.98	0.6798

The graph of inhibition efficiency against inhibitor concentration was plotted as shown in Figure 4.1.

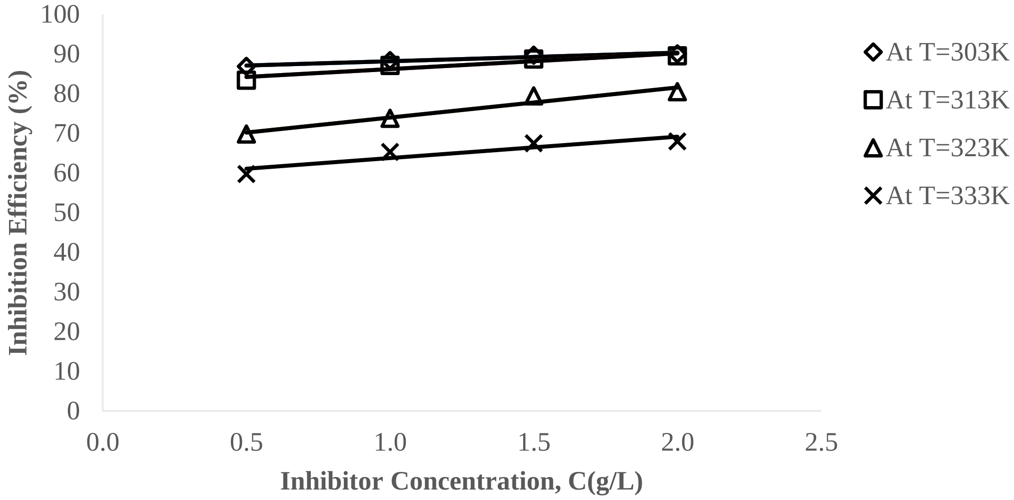

Figure 4.1 Effect of different concentrations of ROPE on its inhibition efficiency on mild steel in acid solution at different temperatures

The effect of concentration on the inhibition efficiency of red onion peel extract on mild steel in HCl solution was investigated. The results showed that the inhibitor efficiency increases with increase in the inhibitor concentration for all temperature ranges as shown in Figure 4.1. The increase in surface coverage caused by raising the inhibitor concentrations results in such behavior of red onion peel extract in 1.0 M HCl. The inhibition efficiency of inhibitor increased, thus the corrosion rate of mild steel decreased.

At higher concentration of inhibitor, more active molecules adsorbed on the surface of metals, and this will prevent the contact between corrosive medium with metal surface. The highest inhibition efficiency of 89.97, 89.49, 89.49, and 69.43 % at temperature of 303, 313, 323, and 333 K, respectively were obtained at inhibitor concentration of 2.0 g/L in acidic medium. Based on the results, the inhibitor efficiency decreases with the increasing temperature. Ebenso et al., (2011) stated that when the temperatures increase, there is reduction in surface coverage causes the desorption of inhibitor from the mild steel surface and the surface of mild steel is exposed to the acidic medium. Therefore, increase the corrosion rate of the mild steel.

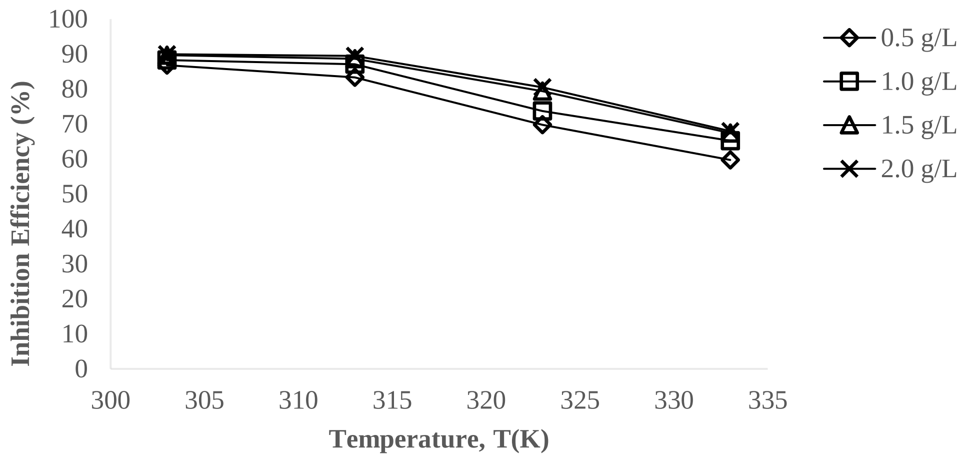

Figure 4.2 Effect of different temperatures on inhibition efficiency of different concentration of ROPE on mild steel in acid solution

The effect of temperature on the inhibition efficiency of red onion peel extract on mild steel in HCl solution was investigated by plotting the graph of inhibition efficiency against temperature. Figure 4.2 showed that the effect of increase in temperature on the inhibition efficiency of red onion peel extract. We can observe that as the reaction temperature is increased from 303 to 333K, the inhibition efficiency decreases. According to James et al., (2009) that the decreasing in temperature favors the red onion peel extract inhibition efficiency in acidic medium. At high temperature, the ability of adsorption