

**ELECTROCHEMICAL METHODS FOR REAL
CORROSION INHIBITOR DETECTION IN OIL AND
GAS INDUSTRY**

BY

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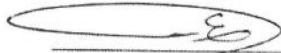
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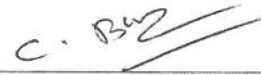
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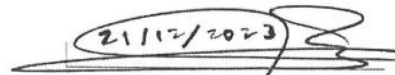
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[In honor of my parents, whose love and sacrifices have been the cornerstone of my educational pursuits.]

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LIST OF ABBREVIATIONS

CI s	:	Corrosion Inhibitors
CV	:	Cyclic Voltammetry
SWV	:	Square Wave Voltammetry
LOD	:	Limit of Detection
LOQ	:	Limit of Quantitation

ABSTRACT

Full Name : [Muhammad Shuaibu Ahmad]
Thesis Title : [Electrochemical Methods for Real Corrosion Inhibitor Detection in Oil and Gas Industry]
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[An electrochemical technique for detecting corrosion inhibitors using platinum electrode materials has been investigated as a sensitive method for detecting corrosion inhibitors (CIs) both in aqueous and buffered medium. The platinum electrode was chosen due to its exceptional sensitivity and selectivity in detecting corrosion inhibitor standards, especially in deionized water. The method showed robust performance under optimized conditions, with limits of detection (LOD) of 0.051% and 0.074% and limits of quantitation (LOQ) of 0.156% and 0.224%, for standard X and Y respectively. However, prolonged use led to a significant drop in signal due to electrode fouling.

To expand the scope of electrochemical detection, the study explored the use of a buffered medium with a supporting electrolyte and 1M phosphate buffer. Under optimized conditions, the method achieved a detection limit of 0.060% and a LOQ of 0.182% for standard X. The platinum electrode, combined with optimized measurement conditions, provides a robust platform for sensitive and selective corrosion inhibitor detection. The electrochemical detection method developed holds potential applications in corrosion monitoring and control across various environmental settings. The study's findings pave the way for further advancements in electrochemical detection methodologies, emphasizing both efficacy and practical applicability.]

ملخص الرسالة

الاسم الكامل: محمد شعيبو أحمد

عنوان الرسالة: الطرق الكهروكيميائية للكشف عن مثبطات التآكل الحقيقية في صناعة النفط والغاز

التخصص: كيمياء

تاريخ الدرجة العلمية: ديسمبر ٢٠٢٣

تم التحقيق في تقنية كهروكيميائية للكشف عن مثبطات التآكل باستخدام مواد قطب البلاتين كطريقة حساسة للتآكل. تم اختيار قطب البلاتين نظرا لحساسيته الاستثنائية وانتقائيته في الكشف عن معايير مثبطات التآكل ، خاصة في الماء بنسبة 0.051% و (LOD) منزوع الأيونات. أظهرت الطريقة أداء قويا في ظل ظروف محسنة ، مع حدود الكشف على التوالي ، ومع ذلك ، أدى Y و X بنسبة 0.156% و 0.224% ، للمعيار (LOQ) وحدود الكمية 0.074% . الاستخدام المطول إلى انخفاض كبير في الإشارة بسبب تلوث القطب الكهربائي.

لتوسيع نطاق الكشف الكهروكيميائي ، استكشفت الدراسة استخدام وسيط مخزن مع إلكتروليت داعم ومخزن فوسفات يوفر X بنسبة 0.182% لمعيار LOQ في ظل الظروف المحسنة ، حققت الطريقة حد الكشف بنسبة 0.060% و 1M. قطب البلاتين ، جنبا إلى جنب مع ظروف القياس المحسنة ، منصة قوية للكشف عن مثبطات التآكل الحساسة والانتقائية. تحمل طريقة الكشف الكهروكيميائية المطورة تطبيقات محتملة في مراقبة التآكل والتحكم فيه عبر بيانات بيئية مختلفة. تمهد نتائج الدراسة الطريق لمزيد من التقدم في منهجيات الكشف الكهروكيميائي ، مع التركيز على كل من الفعالية والتطبيق العملي.

CHAPTER 1

INTRODUCTION

Corrosion is the process of material deterioration caused by its interaction with the surrounding environment, which is a natural risks connected to facilities for the production and transportation of oil and gas [1]. The occurrence of this corrosion can be observed in various complex conditions within the industry, including pipeline, processing, and production systems, as it can be stimulated by almost any aqueous environment [2]. This susceptibility to corrosion presents a widespread challenge in this sector, leading to the degradation of metal components and giving rise to problems such as leaks and increased maintenance expenses.

The mechanism of corrosion is fundamentally an electrochemical process, wherein metals interact with their surroundings to form oxides and other compounds. This process can be described from Fig 1.1 where the electrochemical reactions that interconnect half-cell reactions of oxidation and reduction denoted as anodic and cathodic processes, where shown correspondingly [3]. During the anodic reactions, known as oxidation reactions, metal ions and free electrons are generated, which are subsequently consumed in the reduction reaction, also known as the cathodic reactions [4]. This electrochemical process is based on three essential components: the anode (where metal corrosion occurs), the electrolyte, which is a corrosive substance which helps move electrons from the anode's

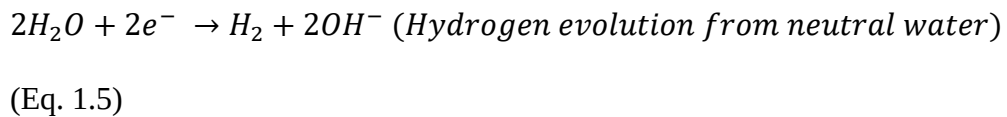
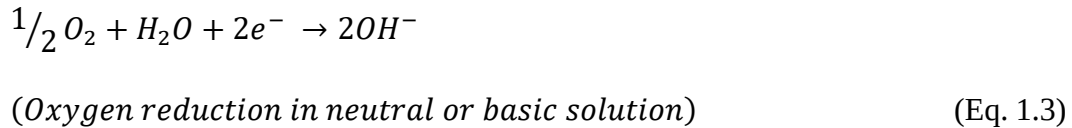
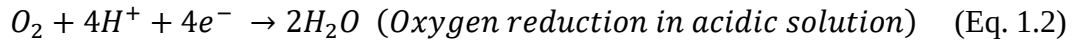
surface to the cathode, and the cathode, which is an electrical conductor resistant to corrosion[3].

Moreover, the electrochemical reaction entails the involvement of chemical entities, which can be either neutral molecules or ions, as well as electrons. In terms of anode and cathode, an anode refers to an electrode that facilitates oxidation, with the current flowing outward from the positive electrode towards into the electrolyte. Alternatively, the negative electrode serves as an electrode that facilitates reduction, with the electric current entering the cathode from the electrolyte [4]. In a more general scenario, the metal undergoes oxidation, identical to the anodic process that follows.



where n is the metal's valence, or the number of electrons released during the reaction.

There are four typical cathode reactions that occur when electrons are released from metal atoms at the anode site [5]:



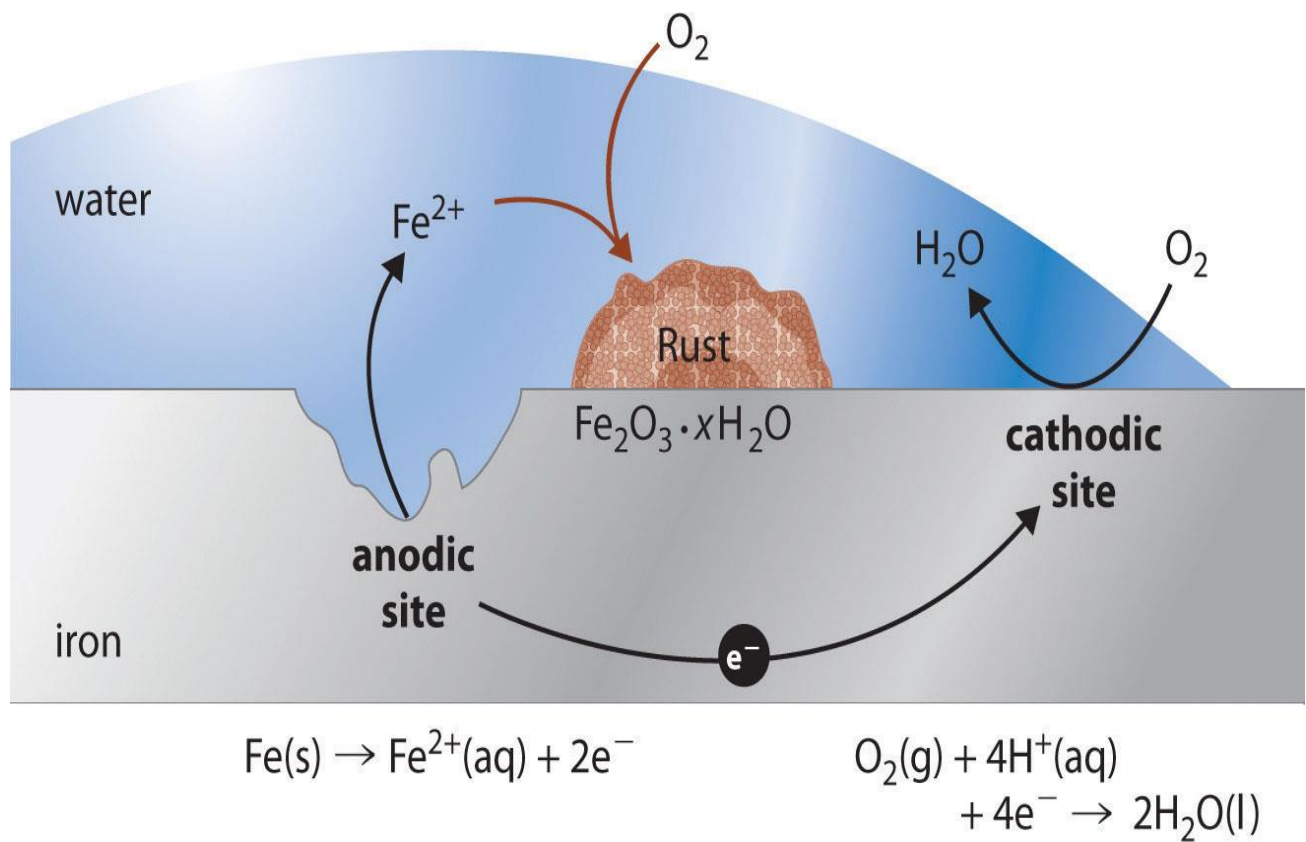


Fig.1.1 The process of corrosion [6]

In the petroleum and natural gas sectors, it is known from observations made by these industries that crude oil and natural gas encompass many high-impurity materials that possess inherent corrosive properties. The corrosiveness of these fluids is contingent upon several factors, including bacteria, pH, temperature, pressure, solids, and acid gases. Specifically, hydrogen sulfide (H_2S), carbon dioxide (CO_2), and free water have been identified as highly corrosive media within this context [7,8]. These components are recognized as significant contributors to corrosion within the sector. Moreover, there are

several ways that corrosion can appear in this field. For instance, iron can dissolve in water and form an acidic oxide.[9].

1.1 Types of Corrosion

It is difficult to consistently classify the different types of corrosion that are found in the petroleum and natural gas industries. The categorization of corrosion could be established on the visible manifestation of the resultant harm, the fundamental process of attack, the particular industry sector, and the preventive measures employed [7]. Within the realm of petroleum and natural gas industries, the most common types of corrosion found are sour corrosion, sweet corrosion, , galvanic corrosion, oxygen corrosion, microbiologically induced corrosion, crevice, stress corrosion cracking and erosion corrosion [10].

1.1.1 CO₂ Corrosion (Sweet Corrosion)

The oil and gas industry has long been aware of the issue of sweet corrosion, commonly referred to as CO₂ corrosion [11]. CO₂ is a primary agent responsible for corrosion in production and transportation facilities [12]. The temperatures that these systems usually operate are not corrosive for dry CO₂ gas. But when it dissolves in an aqueous solution, this may lead the metal and the surrounding aqueous solution to electrochemically react, which can have corrosive effects [7]. Although recent studies have shown that a significant portion of structural failures in this industry can be attributed to sweet corrosion, accounting for roughly sixty percent of all corrosion-related breakdowns, primarily as a result of insufficient knowledge and predictive capacity, as well as the limited resistance exhibited by carbon and low alloy steels towards this particular form of corrosive attack[13]. The mechanisms underlying carbon dioxide corrosion are intricate. When CO₂

gas first dissolves in water, bicarbonate, carbonic acid, and hydrogen ions are produced. These substances possess the ability to move in the direction of metallic surfaces and participate in the reduction process. Bicarbonate reactions can result in corrosion rates that are higher than anticipated based only on acidity. The rate of iron ion production controls corrosion at temperatures below 60 °C and pH values below 4, resulting in an iron carbonate layer covering the surface [14].

Numerous theories have been put forth to explain the process of CO₂ corrosion, and they are all centered around the presence of carbonic acid, or the bicarbonate ion that develops when CO₂ dissolves in water. The best-known process was described as follows and was put forth by de Waard et al [15]



With the steel reacting on the anodic site



Where the cathodic processes encompass the generation of hydrogen gas via the reduction of hydrogen ions.



FeCO₃ is formed by combining all of the previous equations. $CO_2 + H_2O + Fe \rightarrow$



One major and urgent problem in the field of oil and gas pipeline integrity is the localized corrosion caused by CO₂ induced corrosion. This form of corrosion can manifest in three distinct modes, specifically characterized as pitting corrosion, flow-induced localized corrosion and mesa attack [14] as shown in Fig. 1.2 and 1.3.



Fig. 1.2 Pitting Corrosion[14]

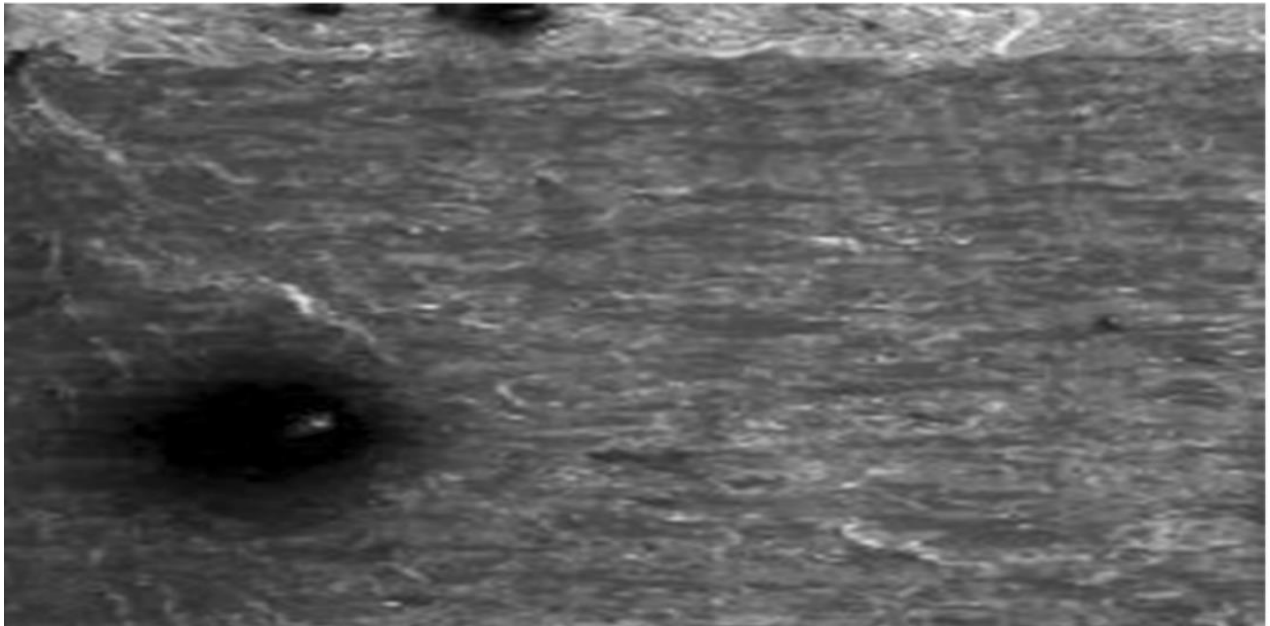


Fig. 1.3 Mesa attack[14].

A significant outcome of this situation involves the occurrence of localized corrosion on the inner surfaces of steel pipelines, which can ultimately result in pipeline breaches, leading to the release of combustible and potentially dangerous pipeline contents. [16].

1.1.2 H₂S Corrosion (Sour Corrosion)

For many years, the oil and gas industry has been plagued by a different kind of corrosion that is called sour corrosion. It first came to light in the 1940s in oil wells in Texas and Louisiana [17, 18]. Sour corrosion refers to the deterioration of metal resulting from contact with moisture and hydrogen sulfide (H₂S), and it poses the greatest threat to drill pipes [7]. The corrosion processes that involve steel, water, and hydrogen sulfide are extremely intricate. When H₂S dissolves in water, a weak acid is formed. This acid then partially decomposes to produce ions of bisulfate and hydrogen [19]. Hydrogen and iron sulfides (FeS_x) are the products of corrosion that are produced. According to recent research, mackinawite which are products of corrosion are formed when sour corrosion progresses, and the formation and transition of these products are highly dependent on temperature, acid gas concentration, exposure duration, and other factors [20].

The different types of sour corrosion include pitting, uniform, and stepwise cracking. Depending on the CO₂/H₂S ratio in the fluid inside the pipe, these corrosion mechanisms can be categorized [14]:

- CO₂/H₂S < 20: H₂S corrosion is dominant.
- 20 ≤ CO₂/H₂S ≤ 500: H₂S and CO₂ combined corrosion
- CO₂/H₂S > 500: CO₂ corrosion is dominant.

The same variables that impact sweet corrosion rate also affect the rate of sour corrosion, including pH, temperature, partial pressure, flow rate, and others. [21]–[23]. Fig. 1.4A and 1.4B shows some examples of corrosion caused by H_2S .





Fig. 1.4A & 1.4B Corrosion caused by H_2S [24].

1.1.3 Galvanic Corrosion

Galvanic corrosion is a form of corrosion that arises when two metallic substances with dissimilar electrochemical potentials make contact and are subjected to an electrolytic atmosphere. In this circumstance, the metal with the lesser or more adverse potential takes on the role of the anode and experiences corrosion. [3]. Due to the crystalline nature of metals, multiple cells are established, leading to intergranular corrosion. The level of

severity of the issue reaches its peak when the ratio of the cathode area to the anode area is considerable [15]. Even though galvanic corrosion frequently has a uniform morphology, situations where it is restricted to a small area are the most harmful. This particular type of localized corrosion is greatly aided by a large cathodic area in contact with a small anodic area [24]. A diagrammatic depiction of the galvanic corrosion process is shown in Fig.1.5.

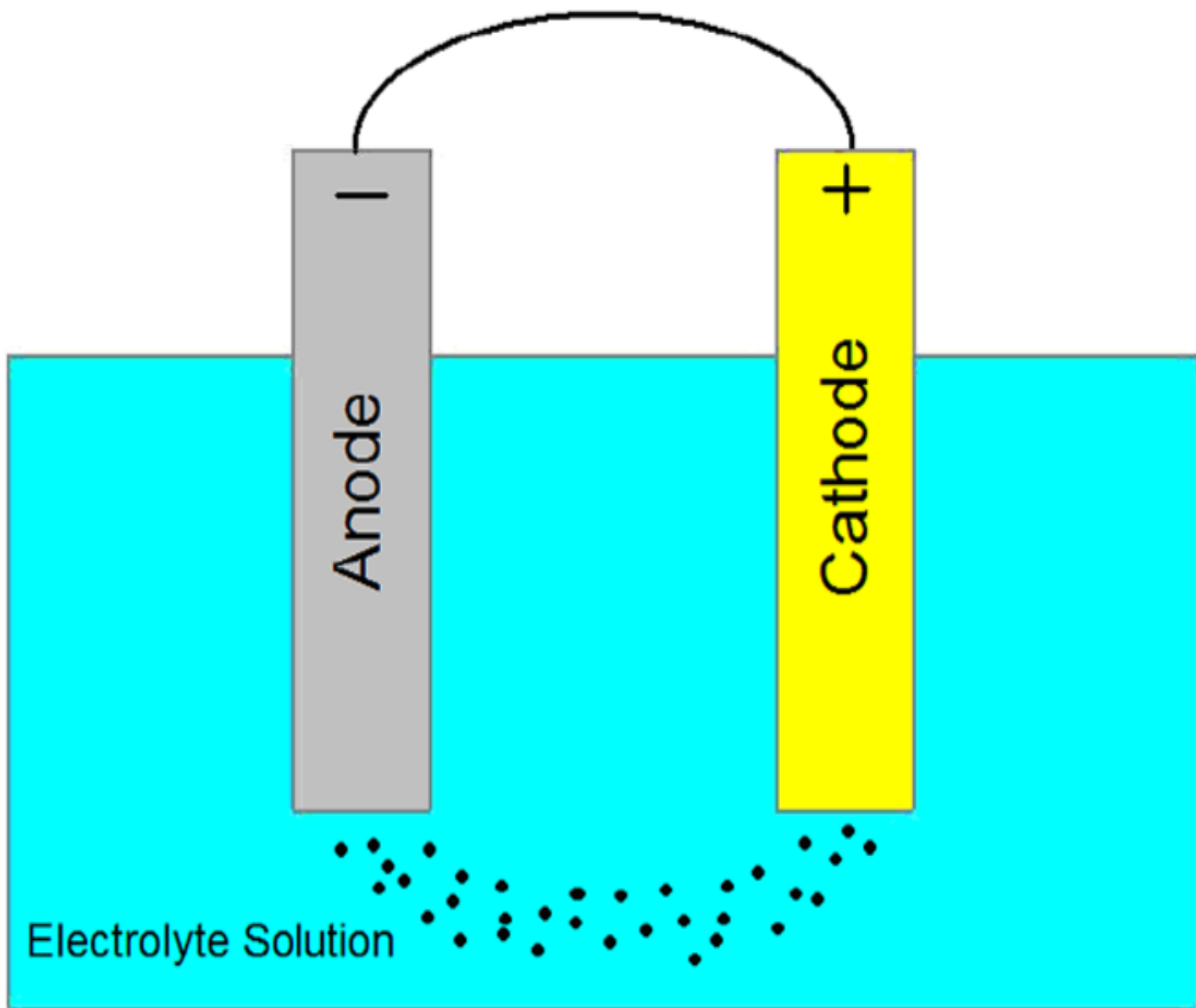


Fig. 1.5 The process of galvanic corrosion [7].

1.1.4 Crevice Corrosion

A localized type of attack known as "crevice corrosion" usually happens in small spaces with little oxygen flow with the presence of electrolyte solution that is stagnant. It may cause flanges, subpar welds, and metal-metal and metal-non-metal junctions to deteriorate, including those in bolted and lock tight joints. [25]. Fig. 1.6A and 1.6B shows metal components under crevice corrosion.



Fig. 1.6A & 1.6B Metal Crevice corrosion[26]

Chloride salts, contaminants, and moisture from the surroundings are amassed in the crevice. This leads to anodic dissolution and the deterioration of the passive film by making

the internal environment of the crevice more acidic, enriched in chlorides, and depleted of oxygen [26].

1.1.5 Erosion Corrosion

Numerous materials are subjected to corrosive fluids, frequently containing solid materials like sand, in the oil and gas sector. The combination of a corrosive surrounding, high fluid velocity, and entrained solids typically results in the loss of material from the surfaces in contact with the flowing hydrocarbon fluid [27]. The corrosive products that form as an oxide film on the pipeline's surface during the erosion-corrosion process are influenced by the solid erosion process's mechanical action [28]. The erosion corrosion mechanism serves to amplify the pace of the corrosion reaction through the perpetual elimination of the passive layer [7].

1.2 Corrosion Mitigation

This uncontrollable chemical process that gives rise to the different kinds of corrosion discussed above in the petroleum and natural gas industry ultimately leads to the oxidation or degradation of the metal or metal alloy [29]. Corrosion issues in the social and industrial sectors are a significant cause of damage. According to the National Association of Corrosion Engineers (NACE), the yearly economic loss caused by metal component corrosion is estimated to be around US\$2.5 trillion, or 3.5% of global GDP [30]. It is imperative to prevent corrosion on metallic equipment by using mitigating techniques like coatings or corrosion inhibitor injections [31]. However, combating corrosion to enhance the lifespan of equipment and plants remains a challenging task for many plant

operators[32].

Throughout the oil and gas well's life cycle, integrity and safety are the two main factors that must be preserved at all times in order to address these problems. Different corrosion mitigation techniques have varying cost implications [33]. Despite the importance of these mitigation methods, the appropriate corrosion mitigation plan should be carefully selected, considering a wide range of influencing factors, including the well's rate of corrosion, the existence and level of sour hydrocarbon, and changes in operating conditions like temperature and pressure [33].

Numerous methods for controlling corrosion have been documented, such as using corrosion-resistant alloys, cathodic protection, internal linings or metal coatings, and chemical treatments like applying corrosion inhibitors [31], [33].

1.2.1 Corrosion Resistance Alloys

According to NACE International Publication 1F192 (2013 Edition), corrosion-resistant alloys (CRA) are alloys that have an intrinsically low corrosion rate in the working environment of interest, usually much lower than carbon and low-alloy steels (e.g., 1 to 2 orders of magnitude less). Their range of application is often limited by their susceptibility to environmental assisted cracking or localized corrosion, such as pitting and crevice corrosion [34].

1.2.2 Metal Coating

Applying a thin layer of a material to the surface of metal can slow down the rate of corrosion. This process is known as metal coating. The coating acts as a barrier between the metal surface and the adverse environment, regulating electrochemistry to prevent corrosion [35]. Its applications include resistance to heat and fire, erosion, pitting, general wear, cavitation, and resistance to scratches and abrasions [36]. Different categories of metal coatings are shown in Fig. 1.7.

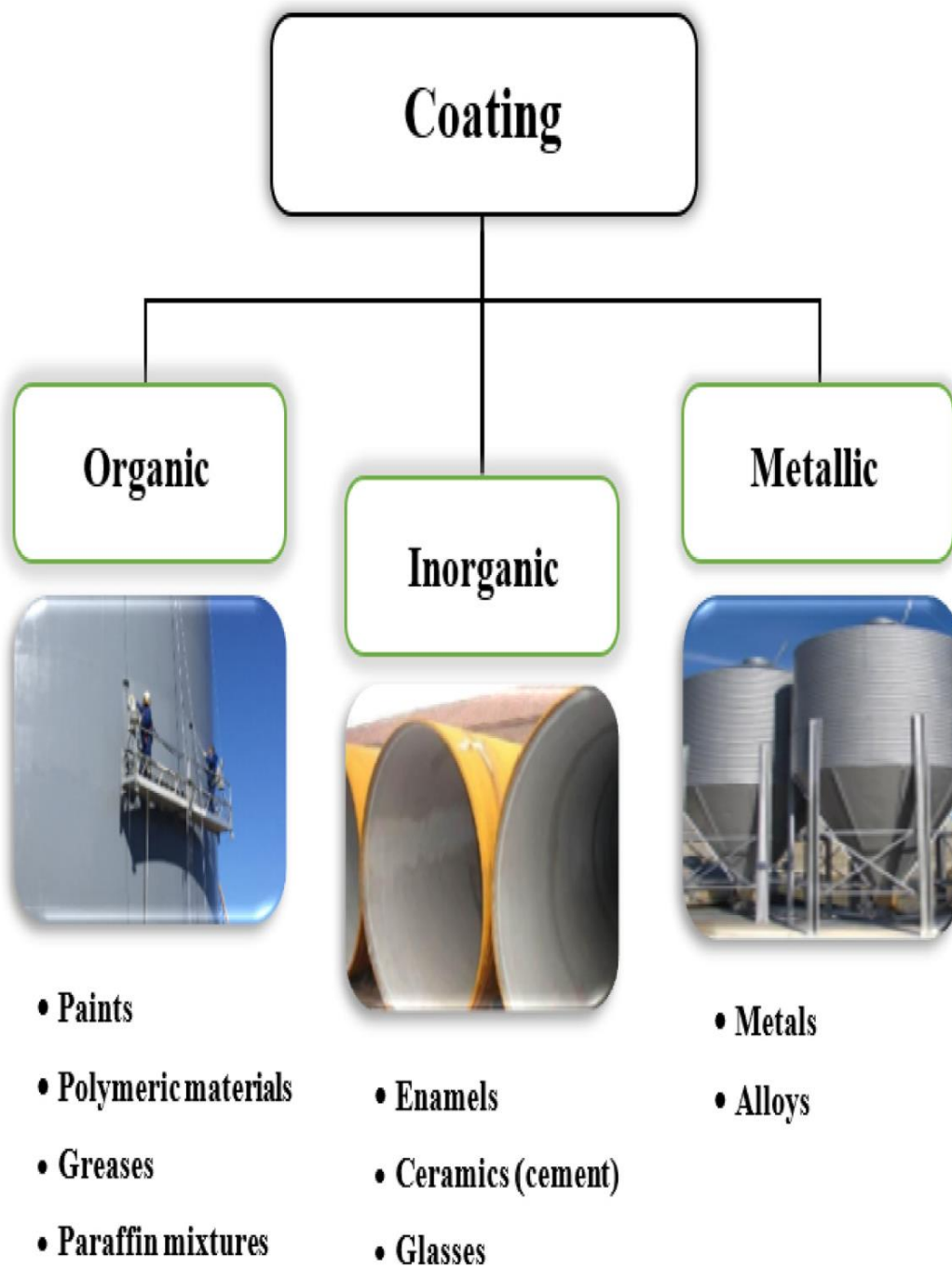


Fig. 1.7 Different types of coating used in refineries[31].

1.2.3 Corrosion Inhibitors

The lack of an affordable means of inspection and maintenance makes internal corrosion among the most dangerous forms of corrosion that can happen in refineries. One practically feasible method of preventing expensive alloy upgrades and commonly employed in the petroleum industry to manage internal corrosion is the use of substances known as corrosion inhibitors, which can prevent or reduce corrosion[31,38] Since the 1930s, corrosion-inhibiting substances have been widely used in oil and gas wells [33]. When these substances are applied in small amounts to a corrosive medium, it decreases the rate of corrosion by creating a film that shields the exposed metal surface from the corrosive agent [37]. Nowadays, corrosion inhibitors are widely recognized as the most widely used technique for preventing corrosion, especially in wells with carbon steel components [33].

These corrosion inhibitors are frequently applied to metal parts in the oil and gas facilities and distribution lines to reduce the effects of corrosion and protect them. When a metal alloy or metal is left exposed to the environment, corrosion happens. The majority of corrosion inhibitors (CIs) used are primarily inorganic and organic composites, where organic inhibitors control corrosion by using adsorption method whereas inorganic inhibitors do so by reacting with the cathodic or anodic elements of the process[39]. The formulation of these corrosion inhibitors includes two or more of the following ingredients: quaternary amines, amides, imidazolines, phosphate esters, and surfactants[40]. In addition, there are several inhibitor formulations with a small number of base compounds that are available. For instance, the primary ingredients used to create some of these inhibitors are fatty acids and various compounds that contain nitrogen. Nonetheless, the

most widely used organic inhibitors are fatty imidazolines, which are produced from fatty acids and polyethylene amines.

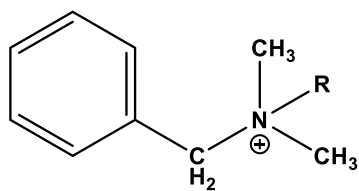
The imidazoline compounds can be solubilized in solutions that are based on either hydrocarbons or a mixture of water and alcohol. The reactions of salting with acetic acid or quaternizing with alkyl chloride are commonly observed [41]. It has also been reported that in the petroleum and gas production business, quaternary ammonium compounds (quats) serve as surfactants, corrosion inhibitors, and biocides, making them of special relevance[40]. Also, it has been conclusively shown that a lot of inhibitors contain a combination of surfactants, amides, phosphate ester compounds, quaternary ammonium compounds, and imidazolines[33]. The potency of the inhibition is contingent upon the chemical composition of the inhibitor.

In general, inhibitors that are effective tend to be organic compounds containing functional groups with high electronegativity and an abundance of π -electrons density in either triple or conjugated double bonds. As per observation, the presence of aromatic or heteroatom rings like those found in phosphorus, sulfur, oxygen and nitrogen can enhance the inhibition effect on the product. This phenomenon arises as a result of their capacity to serve as locations for the process of adsorption, indicating that the inhibition occurs through a superficial adsorption mechanism[42]. The structures of some typical corrosion inhibitors components are shown in Fig. 1.8. Moreover, the levels of these inhibitors need to be monitored routinely to ensure the safety of the metal structures. These corrosion inhibitors are essential for the prevention of corrosion in the petroleum and natural gas industries. They serve to prevent the equipment and infrastructure from deteriorating, which could cause spills, leaks, and other environmental catastrophes.

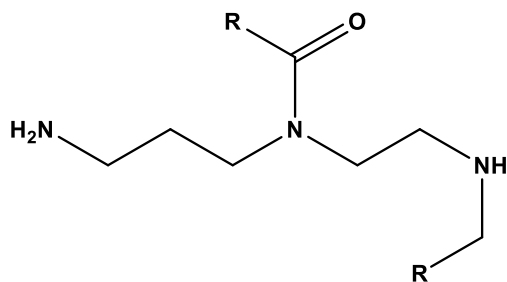
The quantification of corrosion inhibitors is crucial to make sure that the right amount is being utilized, since an excessive amount may be expensive and wasteful while an inadequate amount can cause equipment damage and accelerated corrosion rates[43]. Different methods have been employed to monitor the amount of corrosion inhibitors, however most of corrosion the CIs used in the oilfield sector are complex combinations containing complex formulation of active ingredients and surfactants, making it challenging to determine their concentrations in oilfield waters therefore a technique for accurately evaluating real-time and on-site data must therefore be developed. The majority of labs employ titration and UV-Visible spectroscopy techniques, which require basic and affordable equipment[40]. However, these techniques are not precise and cannot provide real time data. Additionally these methods can be time-consuming, requiring multiple steps and careful handling of samples [44], they often require sample preparation, such as extraction or derivatization, which adds complexity to the analysis process[45]. Furthermore these methods are typically performed in a laboratory setting, making them less suitable for on-site or field analysis[46] and they may have limited sensitivity, making it challenging to detect low concentrations of corrosion inhibitors[47]. It was also observed that these methods can be affected by interference from other substances present in the sample, leading to inaccurate results[48]. Another drawback of these methods is sometimes the use of hazardous reagents, posing safety concerns for operators and the environment.

More complex procedures such as chromatographic and spectroscopic techniques have been documented, these methods aid in monitoring the concentration of corrosion inhibitors but several of them are complex and demand expensive instruments and skilled users for their operation[49]. As a result, electrochemical methods can be used to monitor

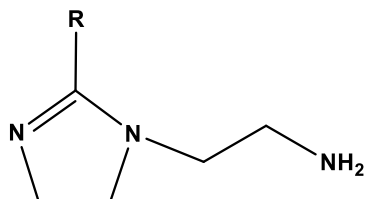
corrosion inhibitors on-site, ensuring adequate industrial equipment maintenance and averting unforeseen breakdowns. Electroanalytical techniques can be viewed as alternative methods for corrosion inhibitor monitoring owing to their speed of analysis, portability, cost-effectiveness, and simplicity. Moreover, these electroanalytical techniques can be used without pretreatments of the sample[50].



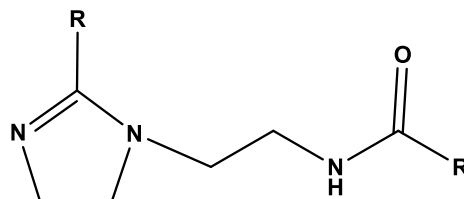
[CoCo "Quat" where $R = C_8-C_{18}$]



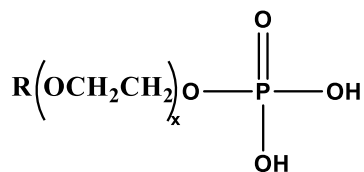
[Diamide, where $R = \text{predominantly } C_{18}$]



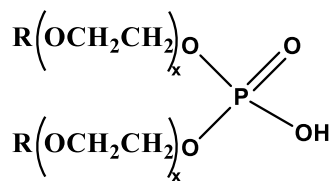
[Amidoimidazoline, where
 $R = \text{predominantly } C_{18}$]



[Imidazoline, where $R = \text{predominantly } C_{18}$]



[(Mono)- Phosphate Ester, where
 $R = \text{alkyl group}$]



[(Di)- Phosphate Ester, where $R = \text{alkyl group}$]

Fig. 1.8 Structure of some common CIs[40]

CHAPTER 2

LITERATURE REVIEW

The current development of electrochemical methods has been prompted by the need for reliable and rapid detection of low-concentration analytes at the point of need. These methods are cost-effective and user-friendly, making them a valuable analytical tool for various applications[51]. Moreover, these methods possess distinct benefits such as portability and affordability, allowing their utilization in non-laboratory settings as a means to address the limitations of conventional analytical techniques[52]. Furthermore, they provide a high degree of selectivity and sensitivity, they are compatible with emerging microfabrication technologies and have the innate ability to be smaller and disposable, they also have little operational complexity, and are robust with the use of little energy [53]. However, there are a number of drawbacks that need to be resolved if these sensors are to function better. One of the main limitations of electrochemical sensors is electrode fouling which presents a major obstacle to achieving reproducibility and greater sensitivity in detection, and maintaining continuous operation. The fouling of the electrode surface can be affected by a range of variables such as the concentration of the analyte, the pH of the solution, and the specific surfactant agents used[54].

Recent studies have established the development of numerous electrochemical techniques with low detection limit for the detection of both organic and inorganic corrosion inhibitors. These sensors are capable of concurrently detecting several corrosion inhibitors, which offer complete corrosion protection for the petroleum and natural gas industries.

These detection techniques utilize different electrode materials such as platinum, gold, and carbon with high selectivity and sensitivity to detect these corrosion inhibitor compounds with real time monitoring capabilities. For instance, Alhanasios et al.[55] devised an indirect electroanalytical sensing approach that makes use of screen-printed graphite macroelectrodes to measure the important corrosion inhibitors cyclohexylamine and morpholine compounds. It is not possible to use carbon and noble metal-based macroelectrodes for the direct electrochemical detection of morpholine and cyclohexylamine in aqueous solutions. However, the authors propose a new electrochemical sensing process that utilizes screen-printed graphite macroelectrodes and an EC type mechanism with two mediators, namely N,N'-I(1,4-phenylene) dibenzenesulfonamide and N-(4-amino-2-methyl-phenyl)-benzenesulfonamide. These mediators undergo electrochemical oxidation and then react chemically with the target analytes to produce reaction products. Both morpholine and cyclohexylamine can now be quantified using these products' electrochemical measurements, which yield an indirect electroanalytical signal.

Additionally, the authors claim that this is the first time such an indirect approach has been proposed for the detection of these analytes, which resolves the issue of electrochemical detection of these two analytes in aqueous solutions with the use of carbon and noble metal based macroelectrodes. Furthermore, it is demonstrated that the use of cyclic voltammetry in conjunction with this indirect sensing approach permits the electroanalytical detection of morpholine and cyclohexylamine within the range of 1 to 10 mgL⁻¹ in pH 10 carbonate buffer. In addition, the corrosion inhibitors can be measured remotely or on-site with this indirect electroanalytical approach that uses screen-printed sensors. This method yields a

sensitive and quick determination of these two neutralizing amines. Nevertheless, this paper fails to provide a comparison of the developed indirect electroanalytical protocol with existing analytical protocols for the detection of compounds. Also, the study does not investigate the potential interference, limitations and challenges of other compounds or substances that may be present in real water samples on the electrochemical detection of cyclohexylamine and morpholine.

In another research, Rocha et al.[50], reported on a novel electroanalytical technique that utilized square wave voltammetry and a cathodically prepared boron-doped diamond (BDDE) electrode to detect morpholine, a corrosion inhibitor. Moreover, on optimizing the conditions for square wave voltammetry, a broad linear working range, an acceptable detection limit, and simplicity in morpholine determination was achieved. This approach gave LOD and LOQ of 2.1 and 6.9 mgL⁻¹, respectively, with a linear range from 5.0 to 100.0 mgL⁻¹. In addition, the accuracy values for intraday and interday measurements of this method were 0.92 to 3.19% and 0.41 to 5.86%, respectively. It is noteworthy that on verifying the accuracy of the method, synthetic boiler water samples containing interfering compounds were analyzed which yields high recovery values from 90.9 to 109.4%. However, the paper fails to specify information on the stability of the boron-doped diamond electrode during long-term use or multiple analyses.

Oliveira et al., [56] also proposed an electrochemical technique for morpholine determination that uses flow injection analysis and amperometric detection utilizing screen-printed carbon electrodes. This allows for the monitoring of the residual amount of inhibitors, which regulate internal corrosion in petroleum pipelines as well as the quality of commercial morpholine-based inhibitors. This method exhibits a strong

linear correlation coefficient ($r = 0.9941$) with low LOD and LOQ of 10 mg L^{-1} and 30 mg L^{-1} respectively, and a linear response over a concentration range of $20\text{-}120 \text{ mg L}^{-1}$. Additionally, the method was precise, linear, and homoscedastic, with a recovery rate of $100 \pm 6\%$ for the amperometric method and $99 \pm 2\%$ for the real condensate sample. In addition, it's noteworthy that the amperometric method's lack of a significant matrix effect indicates that the sensitivity of the method developed is not affected by other components in the sample. Overall, the proposed method offers a simple and low-cost alternative to ion chromatography techniques for analyzing morpholine-based commercial inhibitors in oil industry pipelines. Also, the method's utilization of screen-printed carbon electrodes minimizes the adsorption effect by reducing the duration of contact between the sample and the electrode. However, the authors fail to compare the proposed amperometric method with other commonly used analytical techniques for morpholine determination.

Furthermore, Squissato and co-workers [57] worked on the development of a portable electrochemical system that uses a portable batch-injection cell and disposable screen-printed graphitic electrodes (SPGEs) to continuously monitor corrosion inhibitors in a variety of matrices, including seawater, ethanol, and mineral oil. The authors made a pioneering contribution by introducing the first electrochemical methodology for the determination of 2,5-dimercapto-1,3,5thiadiazole (DMCT). This innovative approach is particularly significant as it can be applied to diverse sample types, including fuel ethanol, seawater, and mineral oil, where DMCT and other additives may be present. Additionally, the SPGEs reported solves the problem of non-compatibility with organic solvent thus its organic-resistant and may be utilized continuously for more than 200 injections.

In addition, the proposed method showed fast response rates (180 h^{-1} injections) and precise responses with a detection limit of $0.3\text{ }\mu\text{mol L}^{-1}$ and also its accuracy was confirmed through recovery tests and comparison with spectrophotometric methods and for the analysis of every sample, the results were statistically consistent with the spectrophotometry method. Additionally, this suggested electrochemical approach demonstrated good linearity, low standard deviations, and the ability to track the levels of DMCT in solutions used to inhibit corrosion. Overall, the suggested approach provides quick and accurate response with a low detection limit and high accuracy that has been verified by recovery testing and comparing approaches. Notably, this newly developed technique has important implications for the prevention and management of corrosion in several sectors.

2.1 Research Objectives

One of the biggest challenges facing the oil and gas sectors today is the precise and real time quantification of corrosion inhibitors. Traditional methods, such UV-Vis spectroscopy and titration, are limited in their capacity to offer real-time data and precise results. Moreover, more complex techniques such as chromatographic methods, among others, developed to solve previous challenges are expensive and require highly skilled users for their operation. Therefore, electroanalytical techniques can be viewed as a promising alternative method to solve this challenge. However, electrode fouling is one of the significant challenges associated with electroanalytical techniques, resulting in a decrease in sensitivity and the ability to operate continuously. The development of a new

and robust electrochemical technique is thus vital if we are to overcome these difficulties and enable the accurate real-time quantification of corrosion inhibitors.

The main objective of this research is to design an electrochemical method for the for real time corrosion inhibitor detection in the oil and gas industry in order to address the shortcomings of present approaches. This research proposal aims to provide a more accurate and reliable method for the detection of corrosion inhibitors by addressing the issues of imprecise data, a lack of real-time measurements, and electrode fouling. This will improve decision-making, lower costs, and improve safety and environmental protection. The future goals and/ or benefits of this research activity are as follows.

1. To develop a simple and sensitive electrochemical method capable of real time detection and quantification of corrosion inhibitors employing one or possibly more electrochemical techniques such as;
 - Cyclic Voltammetry
 - Square Wave Voltammetry
2. To optimize measurement parameters for achieving a higher limit of detection, while enabling analyte detection without the need for buffer and supporting electrolyte, thus reducing method costs, and improving environmental protection.
3. To modify/functionalize a suitable working electrode with nanoparticles or any suitable materials towards eliminating the problem of electrode fouling to achieve higher sensitivity and maintaining continuous usage.

The proposed research study will focus on the detection of commercial corrosion inhibitors using a 3-electrodes electrochemical system.

CHAPTER 3

EXPERIMENTAL

3.1 Reagents and Samples

Corrosion inhibitor standards were purchased commercially. In this experiment, all chemical and solvent used were of high purity and analytical grade. Among these chemicals are;

NaOH (BDH, Radnor PA, USA), Na₂SO₄ (Sigma Aldrich, MA, U.S.A), KCl (BDH, Radnor PA, USA), KHCO₃ (Sigma Aldrich, MA, U.S.A), HCl (Fluka, MA, U.S.A), Phosphate Buffer (1 M Sigma Aldrich, MA, U.S.A), Potassium Ferrocyanide, and washing acetone. Highly pure deionized water (VWR deionizer) was used to prepare all aqueous solutions. Stock solutions of corrosion inhibitor standards were prepared with highly pure deionized water (resistivity 18.2 MΩ cm) obtained from VWR deionizer. The stock solution was appropriately diluted to prepare additional working solutions. All working, reference and counter electrodes were purchased commercially.

3.2 Instrumentation

All electrochemical experiments were carried out using CHI440C Potentiostat coupled with a computer as shown in Fig. 3.1. CHI440c electrochemical software was used to control the instrument. Platinum wire was utilized as the counter electrode and an Ag/AgCl electrode as the reference electrode, respectively. Different electrode

materials ranging from Glassy carbon, Platinum electrode, Silver foam, Nickel foam, Graphite sheet, Graphite pencil electrode, Fabric electrode, Titanium electrode, and Steel mesh coated with PANI were used as the working electrodes as depicted in Fig 3.2.

3.3 Solution Preparation

20% of each commercial corrosion inhibitor sample was prepared from 100% standard solution by appropriate dilution with deionized water. 1 M of electrolyte solution was prepared by dissolving the required mass of each reagent; (NaOH, Na₂SO₄, KCl, KHCO₃) in 1L volumetric flask.

3.4 Electrochemical Measurements

The working electrodes were voltametrically scanned in the range of 0.0 and +0.5V in 0.5mM potassium ferrocyanide solution to check their electrochemical profile and compare it with previously reported work using similar electrodes before making any electrochemical measurements. Then each of these working electrodes were utilized to develop a method of determining CIs using different electrochemical techniques optimizing various parameters such as supporting electrolyte, pH, and potential windows. In addition, all electrochemical measurements were carried out in a static setting under room temperature.

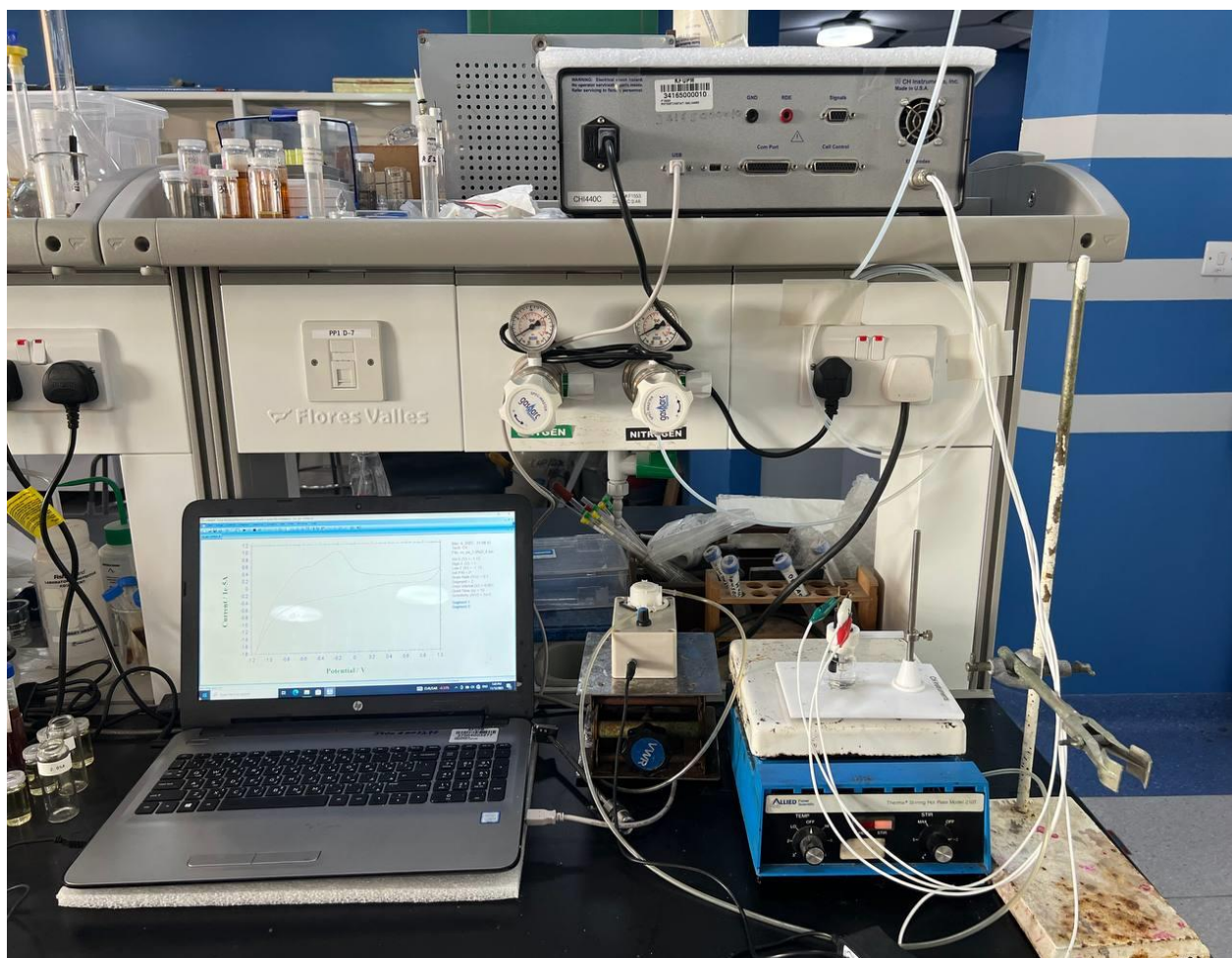


Fig. 3.1 Electrochemical working station.

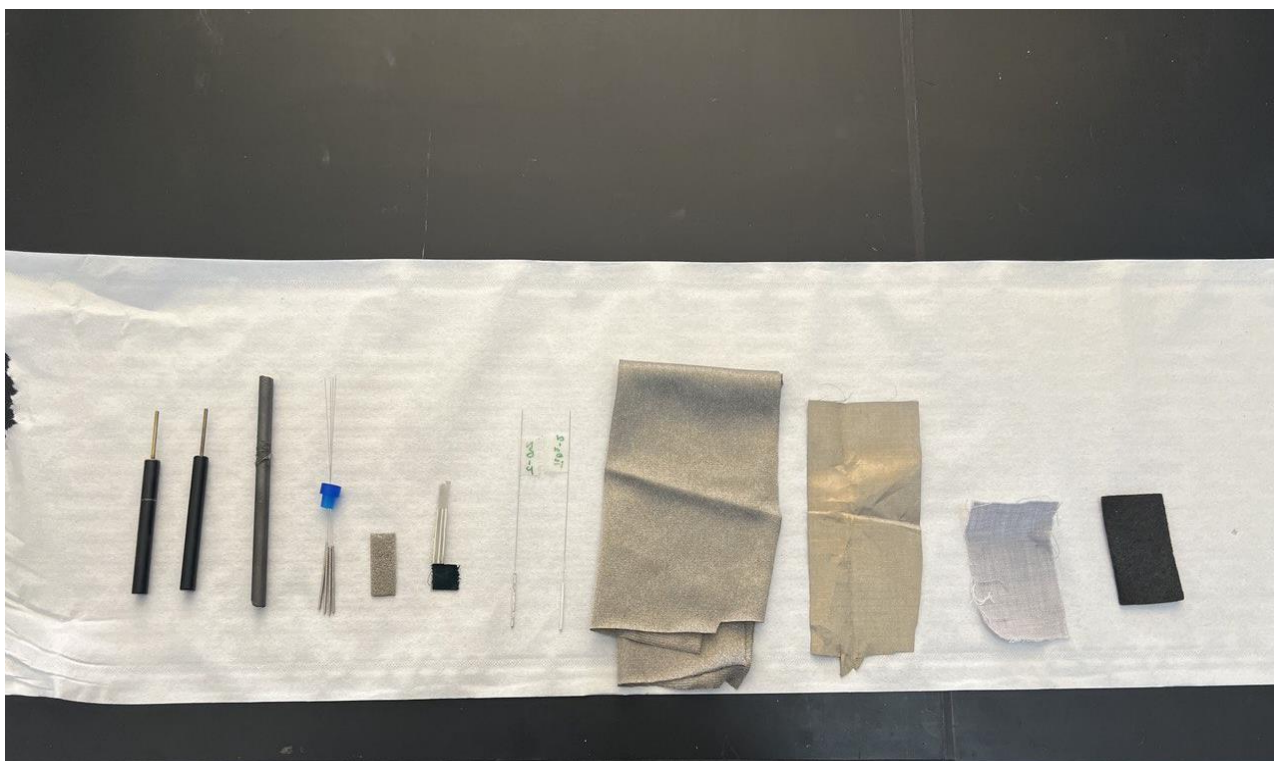


Fig. 3.2. Examples of Working Electrodes (from left; Glassy Carbon, Platinum, Graphite Pencil, Titanium, Nickel Foam, Coated Titanium, Silver Foam, Fabric Electrode, Graphite Sheet)

CHAPTER 4

RESULTS AND CONCLUSION

4.1 Electrochemical Characterizations

The electrochemical characteristics of the various working electrodes utilized in this work were investigated using cyclic voltammetry. where 0.5mM potassium ferrocyanide $K[Fe(CN)_6].3H_2O$ and 0.5M KCl were used as the electroactive species and supporting electrolyte, respectively. The cyclic voltammograms obtained for glassy carbon and platinum electrodes, as well as nickel sheet, exhibited a clear oxidation and reduction peaks as shown in Fig. 4.1. These distinctive peaks indicate the occurrence of electrochemical processes on these electrodes. The presence of both oxidation and reduction peaks suggests a reversible electrochemical reaction since the difference between the anodic and cathodic peak potential is greater than 59mV.

Contrastingly, fabric electrodes and graphite electrodes did not manifest any detectable electrochemical behavior. The cyclic voltammograms for these electrodes did not exhibit oxidation or reduction peaks similar to the voltammograms of the electroactive species reported in the literature. It has been observed that the surface of the fabric electrode becomes electroactive only after several run of about 20 cycles. The surface of the electrode might become electroactive only after pretreatment with the electrolyte solution.

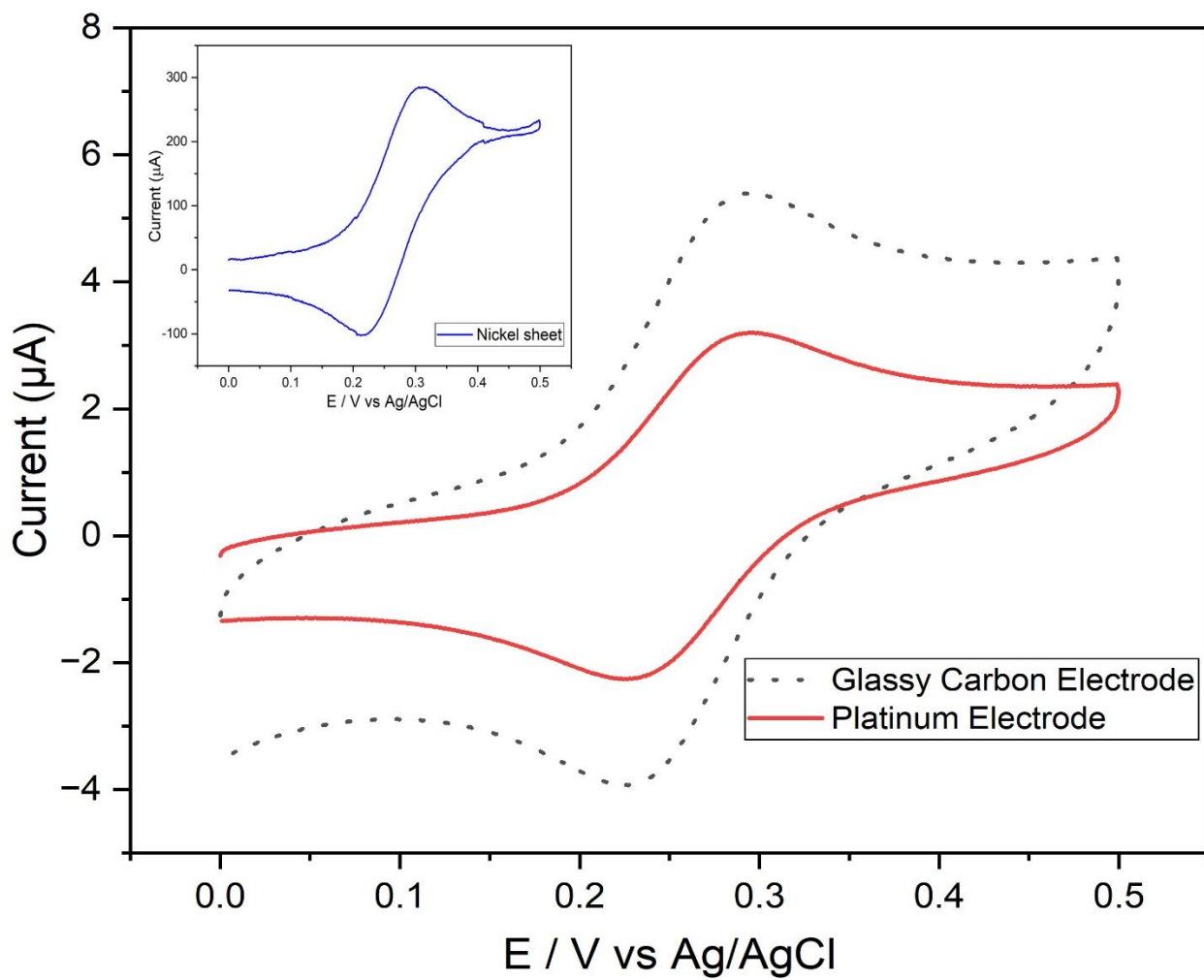


Fig. 4.1 CV of 0.5mM $K_4Fe(CN)_6$ solution in 0.5M KCl at a scan rate of 100mVs^{-1} at glassy carbon and platinum electrode respectively.

4.2 Voltametric Determination of Corrosion Inhibitors

The electrochemical determination of corrosion inhibitors using a platinum electrode was undertaken due to its widespread commercial availability, sensitivity, and stability.

Notably, this electrode exhibited the capability to detect these analytes even in water alone, eliminating the necessity for additional use of chemicals such as buffers and supporting electrolytes.

Extending the application of the platinum electrode beyond aqueous medium, the study also utilized square wave voltammetry to detect corrosion inhibitors in buffered solutions, specifically 1 M KHCO_3 and 1 M phosphate buffer (pH 7.5). This expansion of applicability broadens the range of conditions under which corrosion inhibitors can be studied, adding versatility to the experimental approach.

Various parameters, including the potential window, pH, supporting electrolyte, and scan rate, were systematically investigated to obtain maximum enhancement for a higher sensitivity and low detection limit.

4.2.1 Optimization of Working Potential

The working potential of the working electrode is a crucial parameter while carrying out electrochemical measurement. The selection of the working electrode is subject to modification from one experiment to another, thereby allowing for the manipulation of potential windows or the manipulation of surface adsorption of the species under investigation[58]. Moreover, the potential of the working electrode is varied to promote surface adsorption for enhancing detection because it allows for the modulation of surface

interactions and the induction of partial desorption of adsorbed molecules. By biasing the electrode to more negative potentials, an increased adsorption barrier can be achieved, leading to enhanced adsorption of molecules[59]. For instance, in the study of picolinic acid, isonicotinic acid, and nicotinic acid on a silver electrode, it was found that the adsorption behavior changed with varying potential values[60].

In this study, the process of optimization was conducted in a solution containing 1.0% of a corrosion inhibitor. The working potential was systematically varied over a range from -2.0V to 2.0V. The resulting cyclic voltammograms are depicted in Figure 4.2 and it is evident from the figure that the highest peak current was achieved within the potential range of -2.0V to 1.0V. Therefore, this particular working potential was employed for the purpose of the current study.

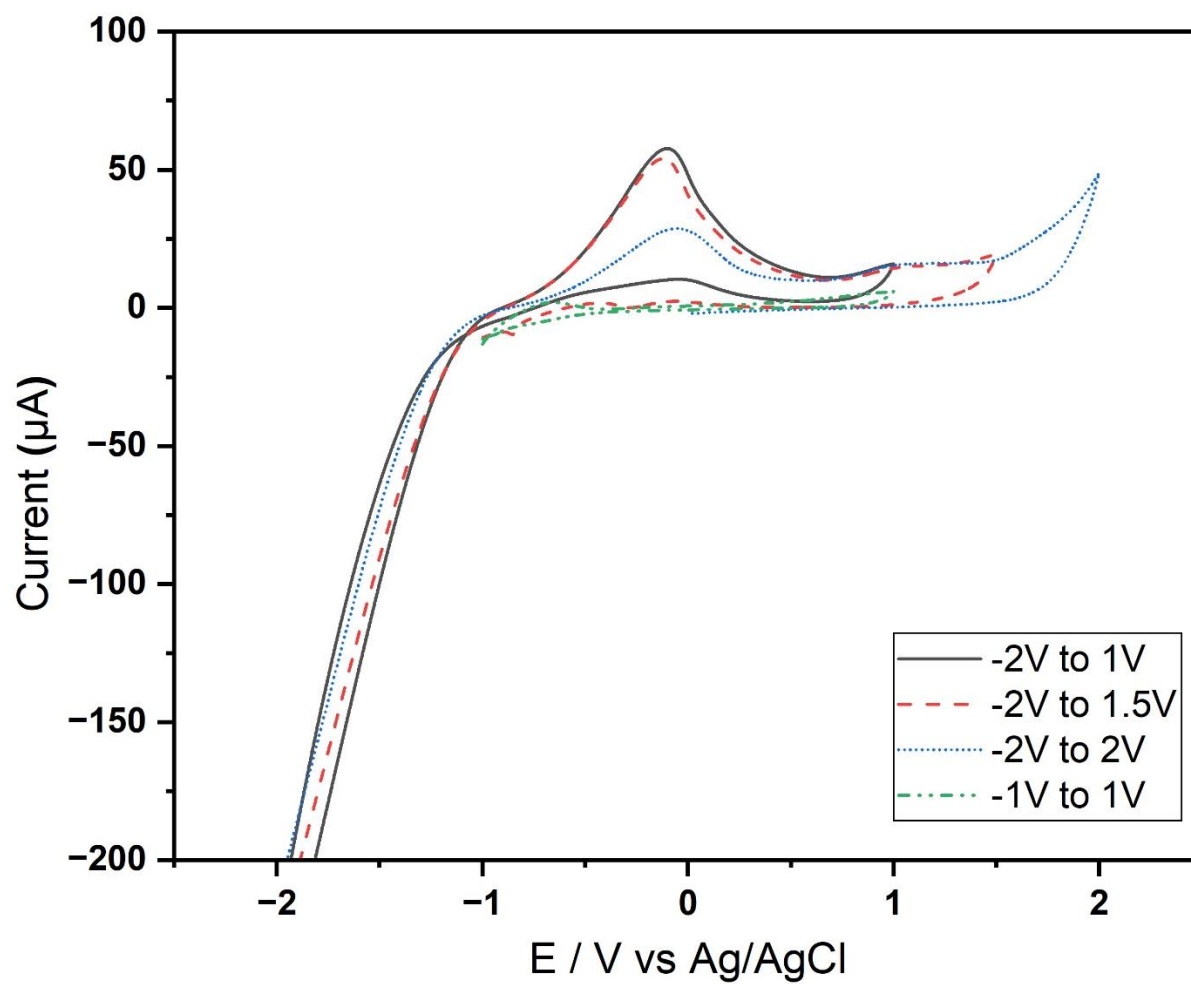


Fig. 4.2 CV of 1.0% Corrosion Inhibitor standard in deionized water using a platinum electrode under varying working potential from -2.0 V to +2 V.

4.2.2 Optimization of Scan Rate

In the electrochemical measurements conducted to detect various compounds, the optimization of the scan rate is a crucial parameter due to its substantial impact on both the sensitivity and selectivity of the measurements. The speed at which the potential change during a measurement is known as the scan rate. One important piece of knowledge about the electrochemical mechanism is the connection between peak current and scan rate[61]. In this experiment, the scan rate on platinum electrode in 1% corrosion inhibitor standard was investigated from 50 – 350mVS⁻¹ as shown in Fig. 4.3. This relationship between the peak current and the square root of the scan rate applies to both irreversible and reversible systems. The plot of peak current against the square root of scan rate reveals an approximately linear relationship with R² of 0.970 which indicates that the process is controlled by diffusion.

In the context of this experiment, the scan rate of 100 mVS⁻¹ was chosen for the electrochemical detection of corrosion inhibitor, yet as the scan rate increases, current also increases, accompanied with a slight shift of potential, while a negative reduction peak was observed at scan rates higher than 100 mVS⁻¹. So, a compromise has to be made in order to obtain a well-defined peak. As a result, 100 mVS⁻¹ was selected for this study.

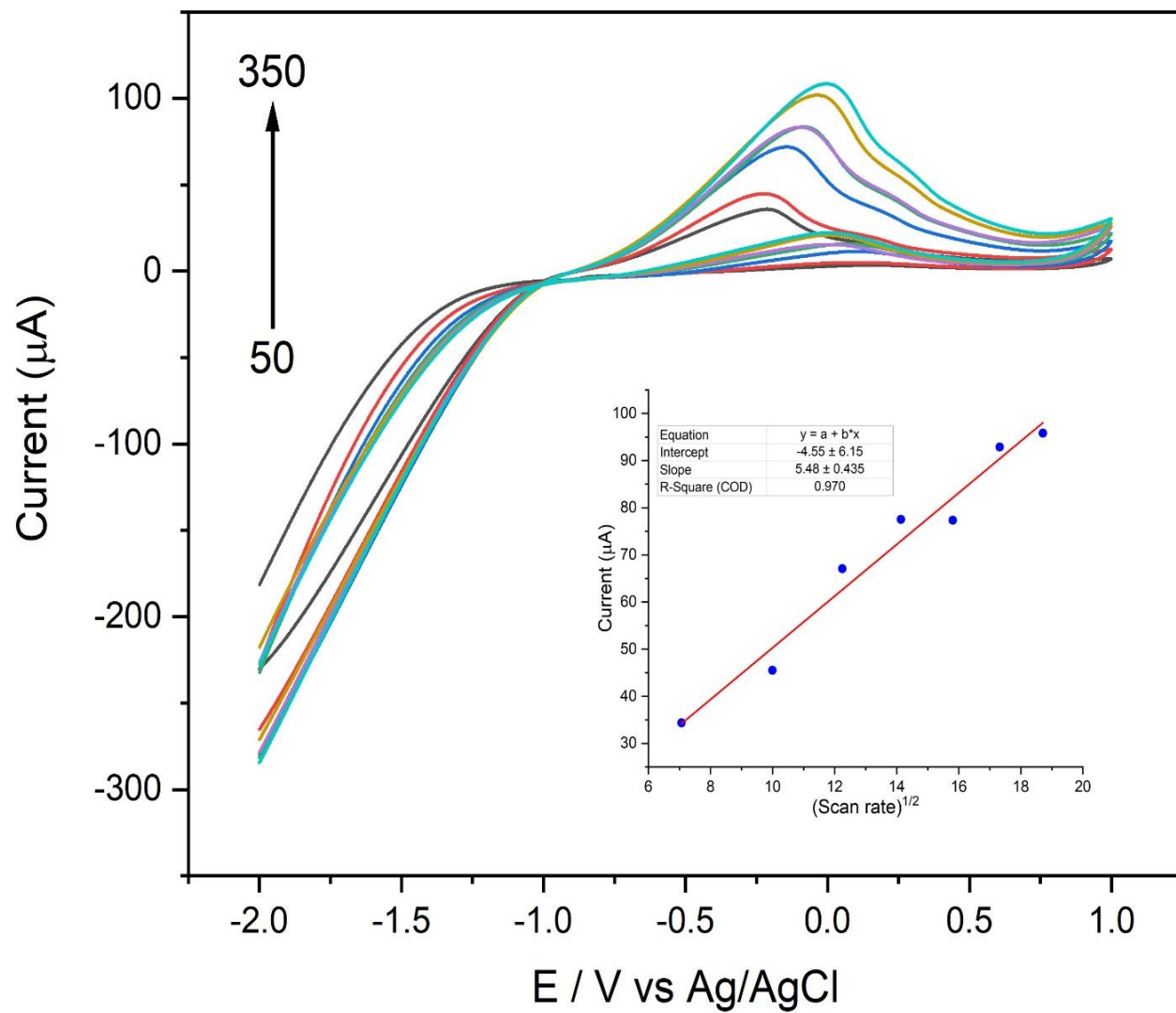


Fig. 4.3 Effect of Scan Rate on the Peak current in the presence of 1.0% Corrosion Inhibitor (X). Inset: Plot of Peak Current vs Square Root of Scan Rate.

4.2.3 Construction of Calibration Curve

Calibration curves were constructed for cyclic voltametric detection of two corrosion inhibitors standards (X and Y) in deionized water using optimized measurement parameters of working potential window (-2V to +1V) and scan rate of 100mVs⁻¹ with platinum electrode over concentration ranges of (0.05%- 1.5%). The results of this method (Fig. 4.4 and Fig. 4.5) show a linear relationship between the voltametric current and the concentration of corrosion inhibitor at the platinum electrode with R² equals 0.999 and 0.997 for standard X and Y, respectively. The Limit of Detection (LOD) and Limit of Quantification (LOQ) for both corrosion inhibitor standards were calculated using the relation $LOD = 3.3 \frac{\delta}{S}$ and $LOQ = 10 \frac{\delta}{S}$ respectively and their results are summarized in Table 4.2

Table 4.1 R² value, LOD and LOQ values for CI standard detection at platinum electrode.

Standard	R ²	LOD (%)	LOQ (%)
X	0.999	0.051	0.156
Y	0.997	0.074	0.224

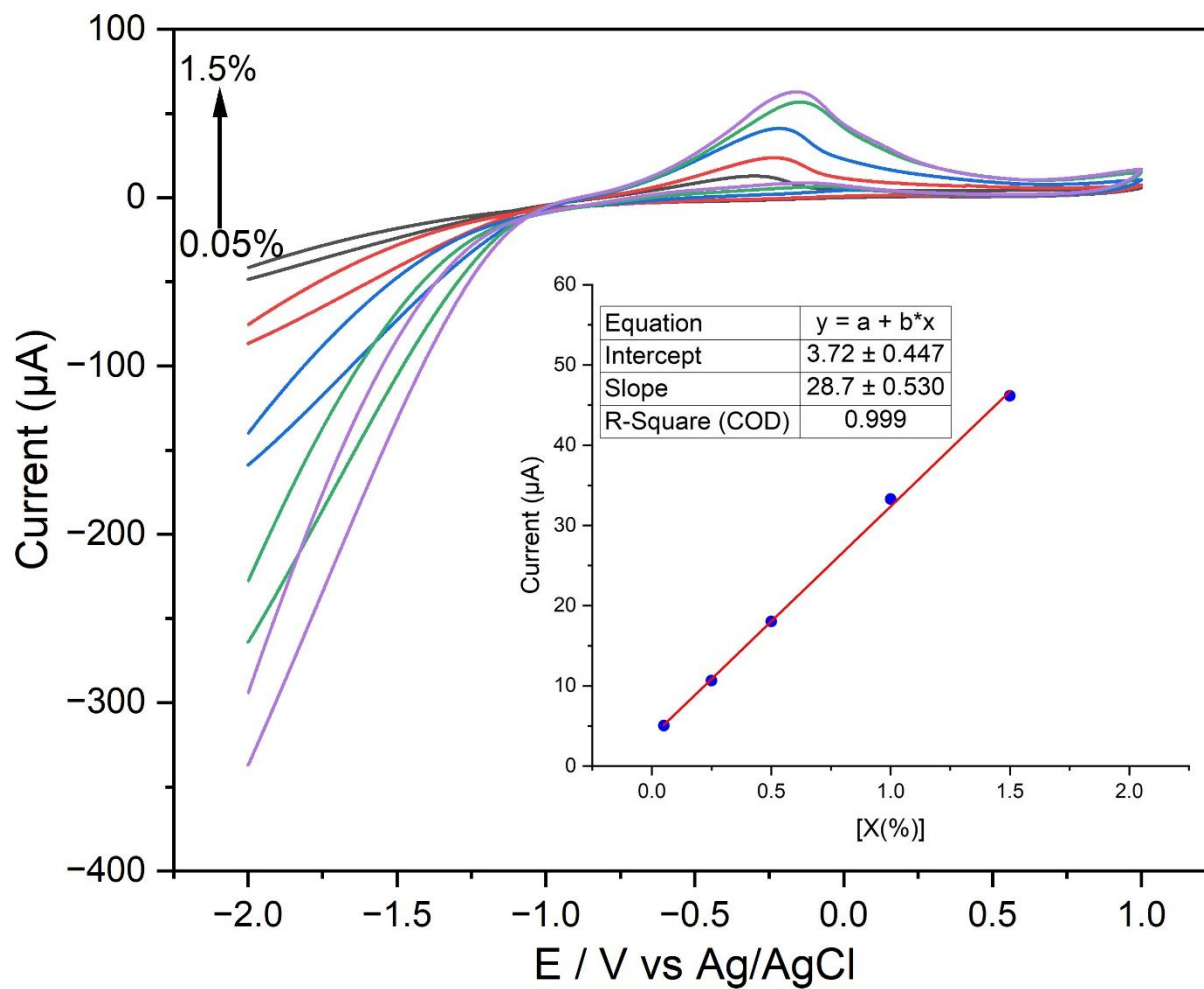


Fig. 4.4 CV of Corrosion Inhibitor standard (X) in Deionized water with platinum electrode. Inset: Calibration Plot of Corrosion Inhibitor standard (X).

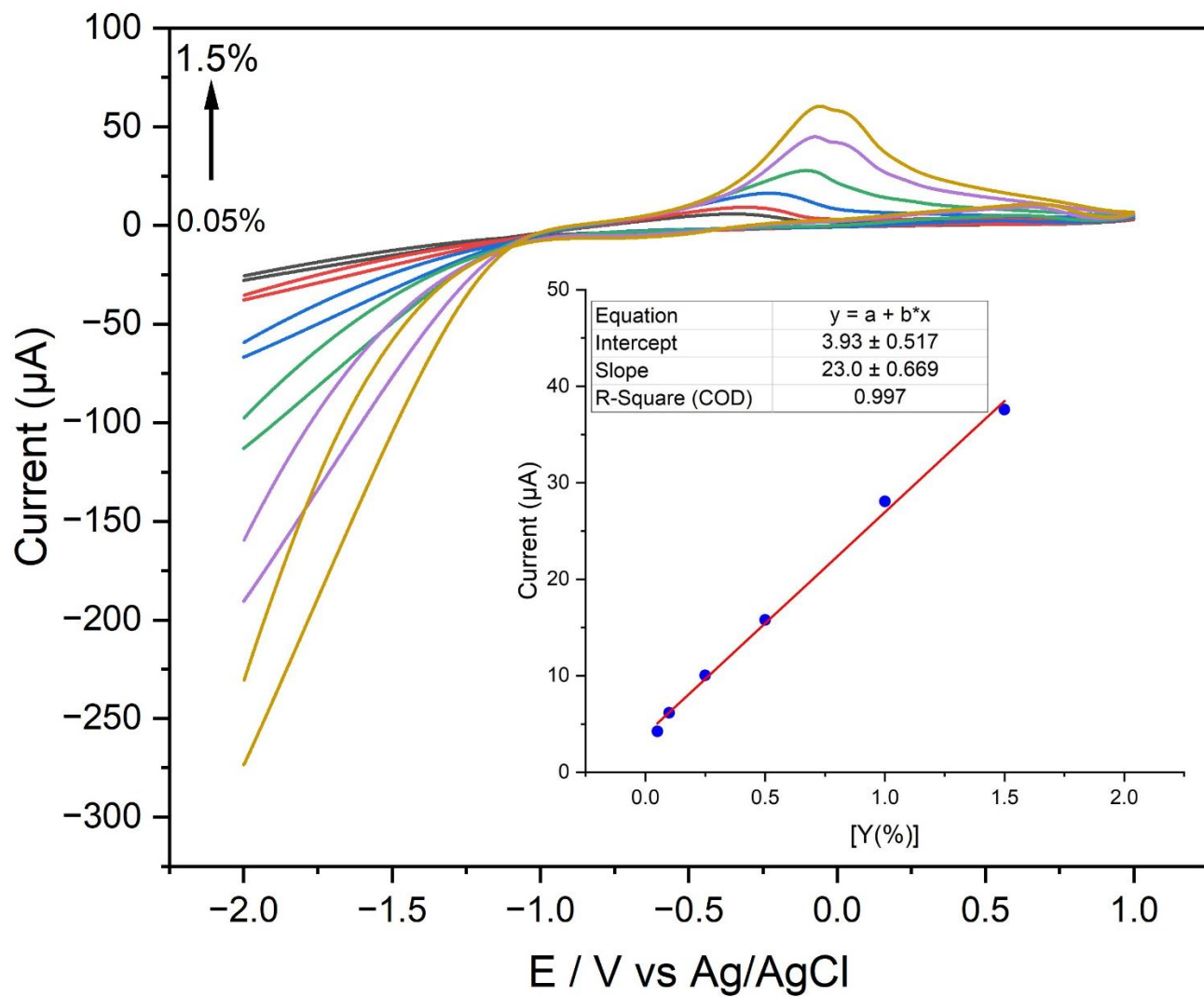


Fig. 4.5 CV of Corrosion Inhibitor standard (Y) in Deionized water using platinum electrode. Inset: Calibration Plot of Corrosion Inhibitor standard (Y).

Following the construction of the calibration curve for corrosion inhibitor standards, the research extended to the analysis of real field samples treated with corrosion inhibitor standard X sourced from industrial facilities in various regions. Utilizing the developed calibration curve for standard X, the concentrations of residual corrosion inhibitors in these field samples were determined and are graphically represented in Table. 4.2

Table 4.2 Concentration profile of corrosion inhibitors in real field samples.

Samples	Conc (%)
A	0.29
B	2.35
C	2.35

Furthermore, electrochemical performance of the platinum electrode was also evaluated through multiple cycles (5 cycles) using a 1% corrosion inhibitor standard (X) in deionized water. Fig. 4.6 shows the observed changes in voltammetric current during these successive cycles. Notably, the voltammetric current exhibited a slight decrease from the first to the second run, followed by a more pronounced decrease down to the fifth cycle. Concurrently, a slight shift in potential was observed. The drop in voltammetric current over successive cycles, as illustrated in Figure 4.6, suggests a phenomenon known as electrode fouling. Electrode fouling refers to the accumulation of analytes present in the corrosion inhibitor (CI) standard on the electrode's surface during electrochemical

processes. This accumulation adversely affects the sensitivity and overall performance of the electrode.

The initial decrease in current from the first to the second cycle indicates a gradual onset of electrode fouling, when analytes began to adhere to the electrode surface. Subsequently, the significant drop in voltammetric current observed in later cycles points to a more pronounced fouling effect, likely due to the continued buildup of analytes on the electrode.

The slight shift in potential accompanying these current reductions further supports the hypothesis of electrode fouling. The accumulation of analytes on the electrode surface can alter the electrochemical environment, resulting in a shift in potential. The challenge of electrode fouling can be effectively addressed through the process of surface functionalization or modification of the working electrode. This solution enhances the overall performance of the electrode, enabling its continuous and prolonged usage.

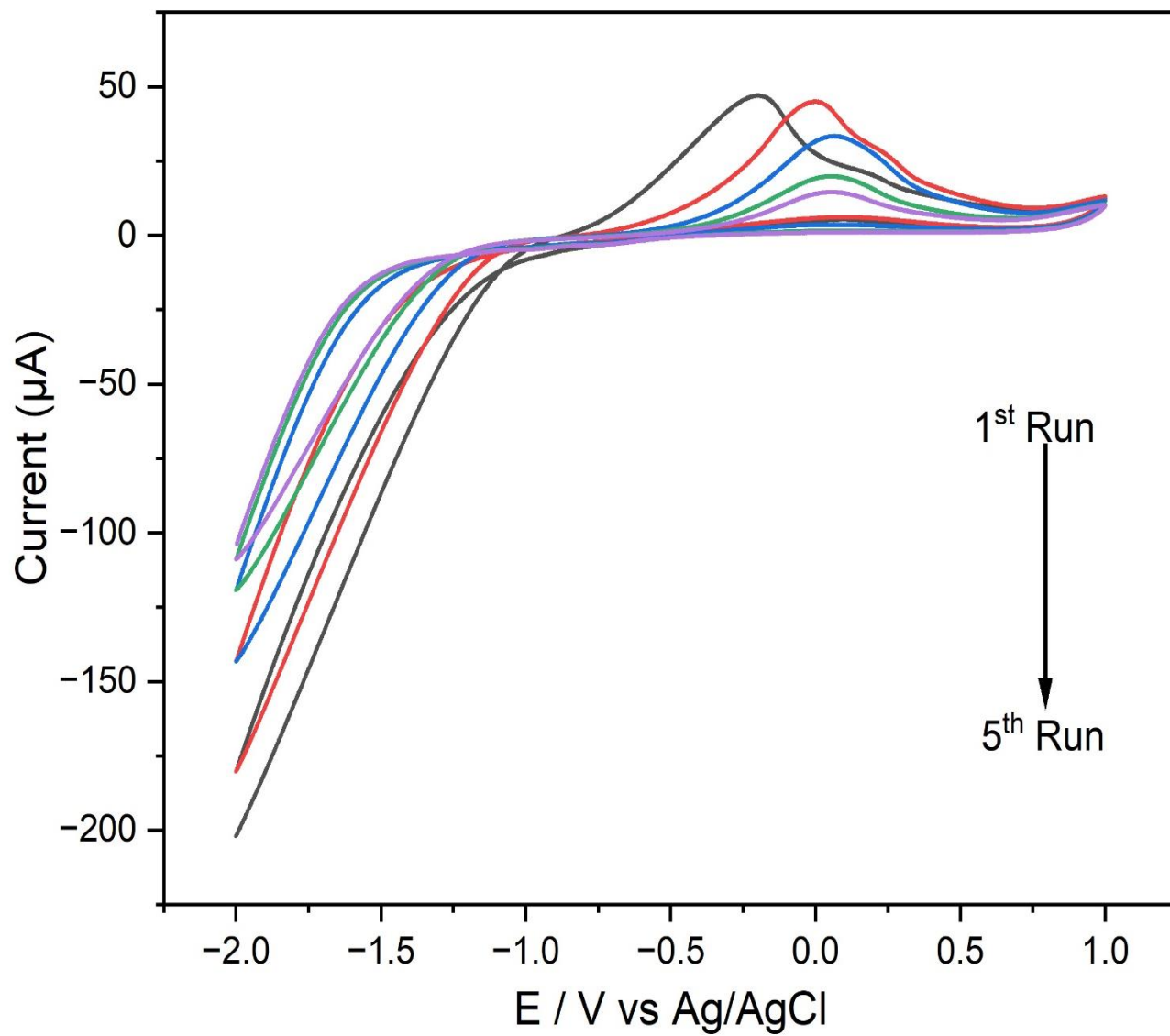


Fig. 4.6 CV of corrosion inhibitor standard (X) in deionized water using platinum electrode (run in five cycles).

CHAPTER 5

RESULT AND DISCUSSION

5.1 Detection of Corrosion Inhibitor in Buffered Medium

In this study, the electrochemical detection of the corrosion inhibitor (CI) was explored through square wave voltammetry (SWV) analysis. SWV typically uses faster scan rates compared to CV due to the rapid switching between potentials in SWV, allowing for faster data acquisition. This can result in improved temporal resolution and the ability to detect compounds more quickly. The investigation incorporated the addition of pH buffers and supporting electrolytes to elucidate their effects on the detection sensitivity. To achieve a comprehensive understanding, different supporting electrolytes and pH conditions were systematically varied. By systematically altering these parameters, we sought to elucidate the optimal conditions for maximizing the sensitivity of CI detection.

5.1.1 Effect of Supporting Electrolyte

A series of electrolyte solutions was tested in a blank solution in order to obtain an electrolyte solution that does not give a background signal with 1 M phosphate buffer. This electrolyte solutions include 1 M Na_2SO_4 , 1 M NaCl , 1 M KCl , 1 M KHCO_3 . The objective was to identify a supporting electrolyte that exhibited no oxidation or reduction peaks in the blank measurement, signifying minimal interference in subsequent detection processes.

Notably, the electrolyte solution that emerged as the optimal choice for subsequent studies was found to be 1 M KHCO_3 in 1 M phosphate buffer as shown in Fig 5.1

This selection was based on its ability of ensuring a clean voltamogram without introducing any discernible background signal. The absence of interference from oxidation or reduction peaks in the chosen electrolyte solution enhances the reliability and accuracy of the detection process.

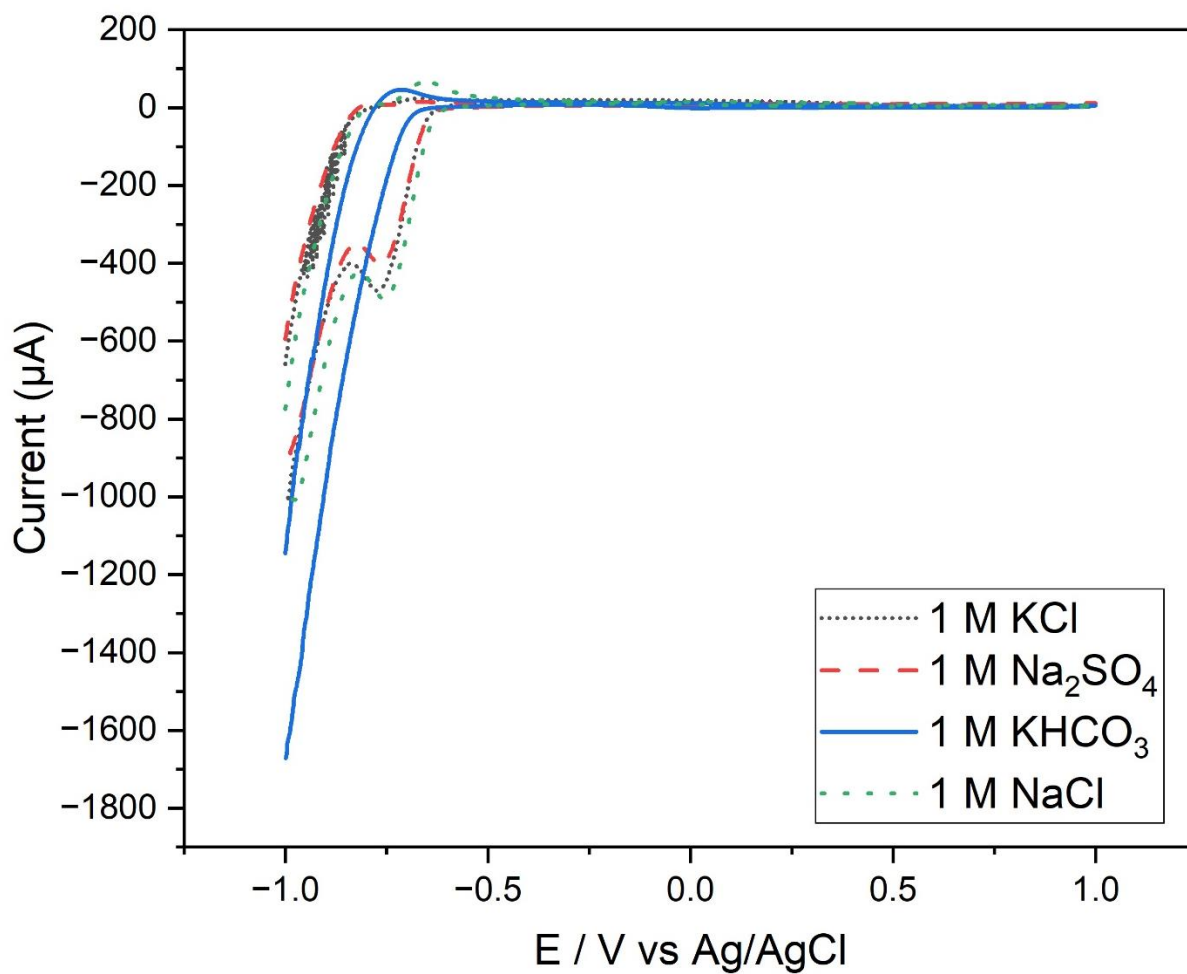


Fig. 5.1 CV of various electrolyte solution in 1 M phosphate buffer solution at platinum electrode.

5.1.2 Effect of pH

The peak current for the electrochemical detection of CIs in buffered medium was found to be strongly pH dependent. Square wave voltammograms were recorded in 1 M phosphate buffer at various pH levels. This is achieved by using H_2SO_4 and NaOH to adjust the solution until the desired value was reached, the pH was adjusted between 1 and 14. The pH of the electrolyte has a significant impact on how the platinum electrode in this investigation behaves electro-analytically.

Under an extreme acidic condition of pH 1, a relatively low peak current was observed for 0.5% CI standard (X). Subsequently, a sharp decline in peak current was noted at higher pH values of 3 and 5. However, at pH 7, a distinct peak with well-defined characteristics emerged, accompanied by a slight positive shift in potential. This was followed by another abrupt decrease in current at higher pH values ranging from 10 to 12, with a concurrent shift in potential to more negative values. Notably, at pH 14, no peak current was observed, as shown in Figure 5.2

The observed displacement of oxidation peaks towards more negative potentials with increasing pH levels suggests a more facile oxidation process under alkaline conditions[62]. This pH-dependent behavior aligns with the understanding that the electroanalytical behavior of the platinum electrode is strongly influenced by the concentration of hydrogen ions in the medium. The continuous shift in peak potential (E_p) across the varied pH values further corroborates this dependence, indicating the consumption of hydrogen ions within the electrochemical system. The pH dependence of the peak potential E_p was discovered, with a continuous shift being observed across the

range of pH values. This behavior is a common feature in electrochemical systems where the consumption of hydrogen ions occurs [63]. Given the pH-dependent nature of the electrochemical response, the selection of an optimum pH for subsequent studies becomes crucial. In this context, pH 7 emerged as the chosen condition for further investigations.

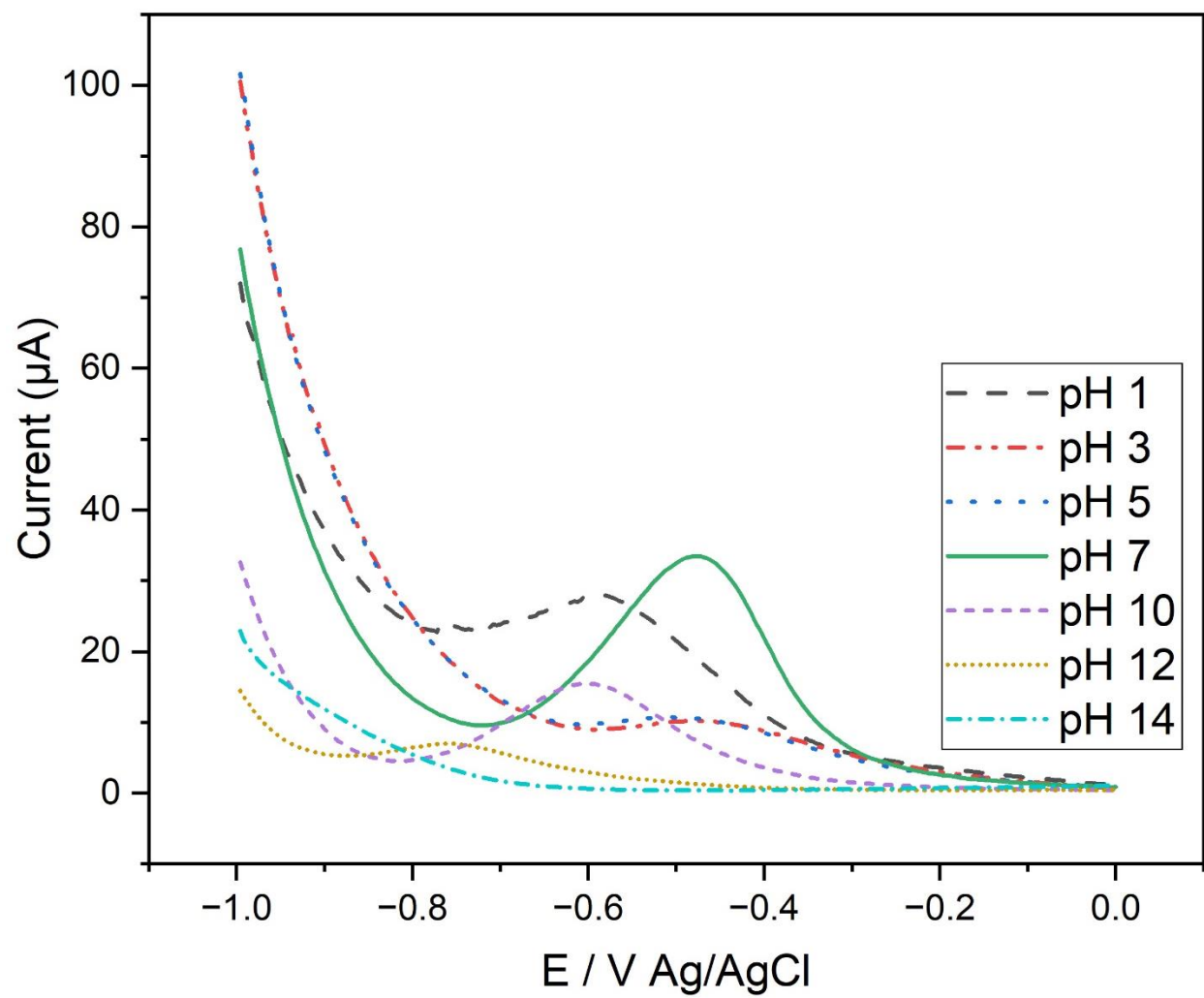


Fig. 5.2 SWV of 0.5% CI (X) in 1 M phosphate buffer and 1 M KHCO_3 ; pH 1-14.

5.2 Construction of Calibration for CI (X) Detection in Buffered Medium.

Calibration curves were meticulously established using square wave voltammetry to detect corrosion inhibitor standards (X) in a buffered medium, employing a platinum electrode. The concentration ranges investigated spanned from 0.05% to 0.5%. This research reveals a linear relationship between the peak current and the concentration of standard X. The obtained correlation is highly significant, as evidenced by the R^2 value of 0.992, indicating a strong and positive correlation between the two variables as depicted in Fig. 5.3. This linear relationship suggests that the electrochemical response is proportional to the concentration of the corrosion inhibitor standard X, which is crucial for accurate quantification. Additionally, the method demonstrates exceptional sensitivity, as indicated by the low limits of detection (LOD) and quantitation (LOQ) values of 0.060 and 0.182, respectively. The low LOD and LOQ values signify the capability of this technique to reliably detect and quantify low concentrations of the corrosion inhibitor standard X.

However, it was observed that, there is a sudden drop of current for corrosion inhibitor concentration beyond 0.5% when SWV was employed, this clearly implies that the working electrode in use cannot detect the CI beyond this concentration due to saturation. This saturation is as a result of high concentrations of analytes on the electrode surface. When the electrode is fully covered or saturated with the analyte, it can hinder the ability to detect additional molecules, resulting in a decreased response.

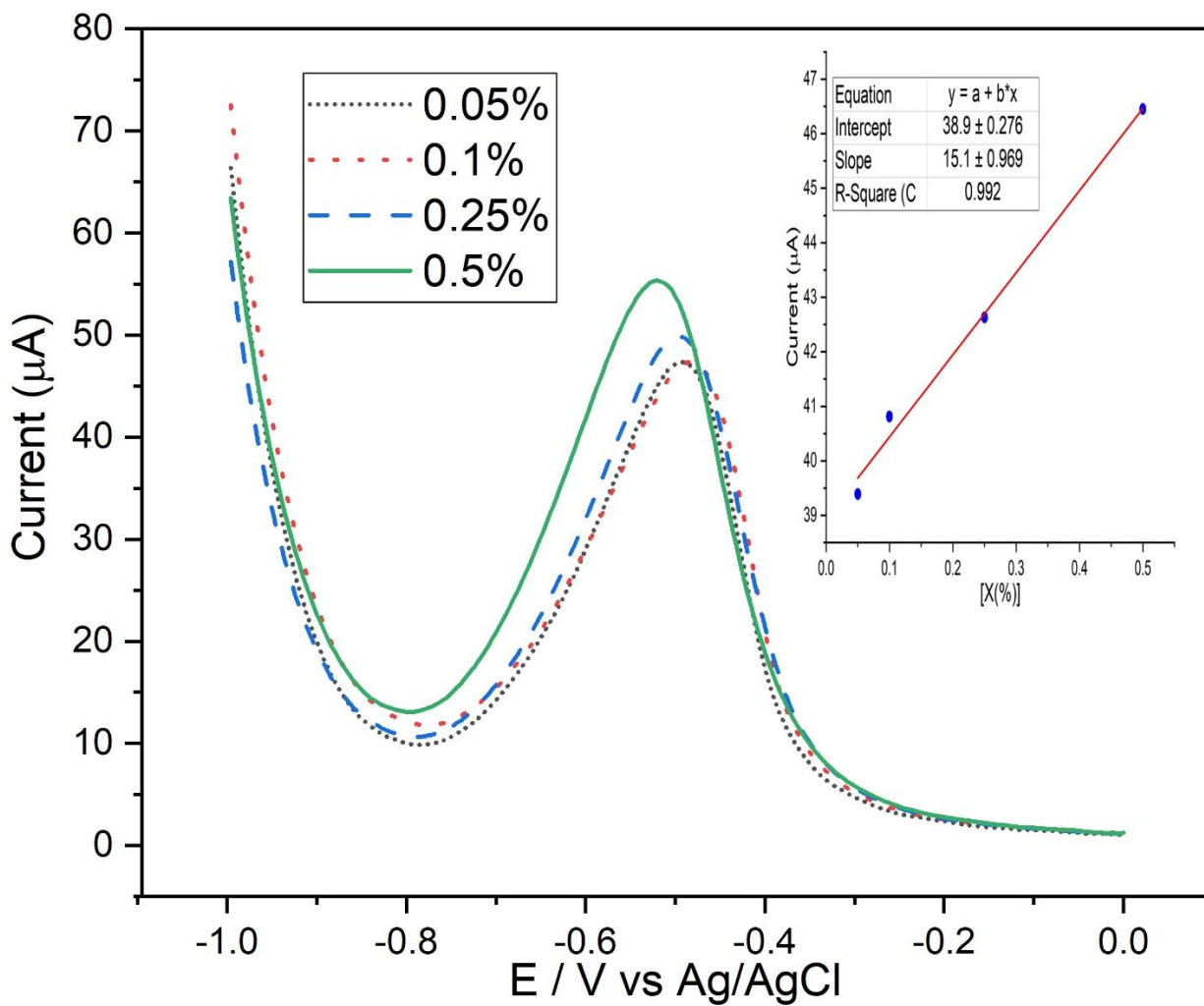


Fig. 5.3 SWV of Corrosion Inhibitor standard (X) in 1 M KHCO₃ and 1 M phosphate buffer at platinum electrode. Inset: Calibration Plot of Corrosion Inhibitor standard (X).

CHAPTER 6

CONCLUSION AND RECOMMENDATIONS

6.1 Conclusion

In the pursuit of an effective and sensitive method for the detection of corrosion inhibitors, this research comprehensively explored various electrode materials. Among the screened electrodes, the platinum electrode emerged as the optimal choice, demonstrating exceptional sensitivity and selectivity in detecting corrosion inhibitor standards. Notably, the platinum electrode exhibited its superior capabilities exclusively in deionized water, highlighting its unique suitability for corrosion inhibitor detection in specific environmental conditions.

Through systematic screening of measurement parameters, such as scan rate and potential range, the screening of these parameters revealed that the maximum enhancement for detection processes could be achieved under the optimized conditions of a potential window ranging from -2 to 1 V and a scan rate of 100 mV/s. Under these optimized conditions, the developed method showcased its ability in detecting two corrosion inhibitor standards, X and Y. The method exhibited a commendable limit of detection (LOD) of 0.051% and 0.074% for standards X and Y, respectively. Furthermore, the limit of quantitation (LOQ) for standard X and Y was determined to be 0.156% and 0.224%, underscoring the precision and sensitivity of the developed electrochemical detection

method. However, when 1% of standard X was run in 5 consecutive cycles on a single electrode, there is a significant drop in signal, which is due to electrode fouling.

Expanding the scope of electrochemical detection, the study further explored the use of a buffered medium with a supporting electrolyte and 1 M phosphate buffer. Under the optimized conditions of pH 7 and 1 M phosphate buffer, employing square wave voltammetry, the method demonstrated its versatility by achieving a detection limit of 0.060% and a limit of quantitation of 0.182% for standard X.

In conclusion, the platinum electrode, coupled with the meticulously optimized measurement conditions, serves as a robust platform for the sensitive and selective detection of corrosion inhibitors. The developed electrochemical detection method, with its favorable LOD and LOQ values, presents a valuable tool for the precise quantification of corrosion inhibitors, offering potential applications in corrosion monitoring and control in diverse environmental settings.

6.2 Recommendations

- I. **Optimization of Square Wave Voltammetry Parameters:** Further investigation is recommended to optimize the square wave voltammetry parameters, such as amplitude and frequency. Systematic exploration of these parameters can enhance the sensitivity and precision of corrosion inhibitor detection, providing a more comprehensive understanding of their impact on the electrochemical response.
- II. **Selection of Suitable Coating for Working Electrode:** The issue of electrode fouling can be addressed by exploring and selecting an appropriate coating for the working electrode. Coatings that offer enhanced stability and resistance to fouling could contribute to prolonged electrode lifespan and improved reliability in corrosion inhibitor detection.
- III. **Design and Implementation of Onsite Flow System:** Consideration should be given to the design and implementation of a flow system that enables the onsite and real-time detection of corrosion inhibitors. Integrating a continuous flow system can facilitate automated measurements, allowing for continuous monitoring in practical applications.
- IV. **Exploration of Dual-Mode Electrochemical and Spectroscopic Measurements:** For method validation and increased analytical insight, the possibility of using an electrochemical cell designed to accommodate both electrochemical and spectroscopic measurements should be explored. This dual-mode approach would allow for the simultaneous acquisition of electrochemical and spectroscopic

signals, providing complementary information and enhancing the overall method robustness.

- V. **Real-Time Monitoring Strategies:** Develop real-time monitoring strategies within the flow system to enable instantaneous feedback and intervention. This could involve the integration of smart sensors or automated control mechanisms that respond to fluctuations in corrosion inhibitor concentrations, ensuring timely and accurate detection. Implementing these recommendations will contribute to the refinement and advancement of the electrochemical detection method for corrosion inhibitors, offering practical solutions for real-time monitoring and validation through dual-mode measurements.

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Research Interest

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Publications

- Hemin-modified multi-walled carbon nanotube incorporated PVDF membranes: computational and experimental studies on oil-water emulsions separations - (<https://doi.org/10.3390/molecules28010391>)
- Analytical detection methods for measuring residual corrosion inhibitors in oil and gas and other industrial facilities - (submitted and under review)