

**SYNTHESIS AND CHARACTERIZATION OF
CARBOXYLIC – BASED POLYMERS AND THEIR
EFFICIENCY AS CORROSION INHIBITORS**

BY

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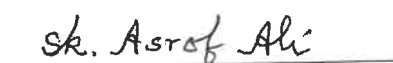
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Dedication

I humbly dedicate this work to Allah, and to my beloved family whose patience and support during this challenging time mean the world to me.

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LIST OF ABBREVIATIONS

I_{corr}^B	: Blank solution current density
I_{corr}^I	: Inhibited solution current density
R_p^I	: Inhibited solution polarization resistance
R_p^B	: Blank solution polarization resistance
$^1\text{H NMR}$	: Proton nuclear magnetic resonance spectroscopy
1M HCl-3.5% NaCl	: 1 Molar hydrochloric acid-3.5% sodium chloride
304 SS	: 304 Stainless steels
ACs	: Activated carbon
AFM	: Atomic force microscope
CA-CQDs	: Citric acid- carbon dots
CQDs	: Cardon dots
CI	: Corrosion inhibitor
CMC	: Carboxymethyl cellulose
CND	: Carbon nanodots
CPE	: Constant phase element
CQDs	: Carbon dots
CR	: Corrosion rate
DFT	: Density functional theory
E_{corr}	: Corrosion potential
EIS	: Electrochemical impedance spectroscopy
FMO	: Frontier molecular orbitals
FTIR	: Fourier transform infrared spectroscopy
GA	: Gum Arabic
GDP	: Gross domestic product
GQDs	: Graphene quantum dots
HCl	: Hydrochloric acid

HEC	: hydroxyethyl cellulose
HOMO	: Highest occupied molecular orbital
IE %	: Inhibition efficiency
IL	: Ionic liquid
IL-CQDs	: Ionic liquid-carbon dots
K_{ads}	: Equilibrium constant
KJ/mol	: Kilojoule per mole
LPR	: Linear polarization resistance
LUMO	: Lowest unoccupied molecular orbital
N, S-CQDs	: Nitrogen, Sulphur carbon dots
NaCl	: Sodium Chloride
N-ACs	: Nitrogen doped Activated carbon
N-CQDs	: Nitrogen doped carbon dots
OCP	: Open circuit potential
P3OT	: Poly (3-octylthiophene)
PAS	: Poly aspartic acid
PAS/N-CQDs	: Poly aspartic acid modified nitrogen doped carbon dot
PAS-Na	: Sodium poly aspartate
PDP	: Potentiodynamic polarization
PL	: Photoluminescence
Ppm:	: Part per million
PSAM	: Poly aspartic acid-co-melamine
PSI	: Poly succinimide
PVA	: poly vinyl alcohol
R_{ct}	: Film resistance
R_f	: Charge transfer resistance
R_s	: Solution resistance
SEM	: Scanning electron microscopy
TCQDs	: Carbon dot modified Poly (tartaric acid-diethylene)
TDA	: Poly (tartaric acid-diethylene)
TEM	: Transmission electron microscopy

TGA	: Thermo-gravimetric analysis
UV-VIS	: Ultraviolet-Visible spectroscopy
W_i	: Inhibited solution weight loss
W_o	: Blank's weight loss
XRD	: X-ray diffraction
ΔG_{ads}°	: Gibb's free energy of adsorption

ABSTRACT

Full Name : ZAHRADEEN MUHAMMAD

Thesis Title : SYNTHESIS AND CHARACTERIZATION OF CARBOXYLIC-BASED POLYMERS AND THEIR EFFICIENCY AS CORROSION INHIBITORS

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Corrosion significantly impacts safety, environmental degradation and economy as well. It impacts numerous areas such industries, transportation, automobile and infrastructure. Corrosion inhibitors are substances that are added in minute quantities within the corrosive medium to mitigate corrosion without significantly reacting with the components. Consequently, developing an efficient, eco-friendly, cost effective, compactible inhibitor to prevent corrosion is crucial. This research focus on synthesizing carbon dots modified with copolymer effective inhibitor for corrosion on different media. We reported the synthesis of a nitrogen doped carbon dots and a bare carbon dot. In the first study doped carbon dots were modified with poly aspartic acid(PAS/N-CQDs) to enhance the inhibitive efficacy of poly aspartic acid. PAS/N-ACs was synthesized by ring-opening poly succinimide (PSI) with nitrogen-doped carbon quantum dots (N-CQDs) synthesized through a one-step hydrothermal process from waste banana peels and ethylene-diamine. Several analyses such UV-Vis, PL emission, XRD, TEM and TGA studies were applied to evaluate the chemical composition and surface characteristics of the synthesized N-CQDs,

while FTIR and ^1H NMR were employed to characterize the poly-aspartic acid and the modified polymer. Electrochemical and traditional weight loss methods were employed to determine the efficacy of the inhibitor on C1018 steel in a 1M hydrochloric acid - 3.5% sodium chloride corrosive medium. All analyses confirm the inhibitor's effective protective behavior. The findings indicated that the highest inhibitory efficacy of 94.4% was attained at 30 ppm. Furthermore, the inhibition mechanism was examined using the isothermal adsorption model, which revealed the inhibitor obeyed Langmuir isotherm with a physicochemical adsorption taking place. SEM confirmed the protective layer creation on the C1018 surface.

The second study employed weight loss, linear polarization resistance (LPR), potentiodynamic polarization (PDP), and electrochemical impedance spectroscopy (EIS) to assess the effectiveness of a melamine grafted poly aspartic acid copolymer (PSAM) in inhibiting the corrosion of carbon steel C1018 in a 1M Hydrochloric acid - 3.5% sodium chloride environment (1M HCl – 3.5% NaCl). The grafted polymer was analyzed using a Fourier transform infrared (FTIR) spectroscopy, as well as proton nuclear magnetic resonance (^1H NMR) technique. Various concentrations of the inhibitor were examined. DFT calculations using the B3LYP functional in Gaussian 09 with the 6-31G+(d,p) basis set were performed to calculate the electronic properties, frontier molecular orbitals, and reactivity parameters of PSAM. The inhibitor effectiveness rose with concentration rise, attaining a maximum of over 93% at 200 ppm. The PDP measurement suggests that PSAM acts as an inhibitor with a mixed-type inhibitor behavior. The Scanning electron microscopy (SEM) image reveals the inhibitor effectiveness in inhibiting C1018 in the tested medium. The DFT calculation shows that PSAM has an excellent inhibition efficiency.

Moreover, A poly (tartaric acid–diamine) (TDA) copolymer was produced and evaluated as a corrosion inhibitor in the last study. The synthesized copolymer was validated by Fourier transform infrared spectroscopy, and ^1H nuclear magnetic resonance. TDA thermal degradation was analyzed by employing thermogravimetric analysis (TGA), indicating that TDA exhibits exceptional stability. Electrochemical and conventional weight reduction techniques were u employed to assess TDA effectiveness on 304 stainless steels (sample) in a 3.5% sodium chloride corrosive environment. All analyses validate the inhibitor's efficacious protective function. The findings demonstrated that an optimum inhibitory efficacy of 91% was attained at 90 ppm, with the inhibitor functioning as a mixed-type inhibitor. Isothermal adsorption model was utilized to analyze the mechanism of inhibition, which demonstrated that the inhibitor adhered to the Langmuir isotherm, showing a physicochemical adsorption process. Scanning Electron Microscopy (SEM) validated a protective layer of protection created on the sample surface.

ملخص الرسالة

الاسم الكامل : زهر الدين محمد

عنوان الرسالة : تخليق وتوصيف البوليمرات القائمة على الحمض الكربوكسيلي وكفاءتها كمثبطات للتآكل

المجال الرئيسي : الكيمياء

تاريخ الحصول على الدرجة : مايو 2025

يؤثر التآكل بشكل كبير على السلامة وتدهور البيئة والاقتصاد كذلك. كما يؤثر على العديد من المجالات مثل الصناعة، والنقل وصناعة السيارات، والبنية التحتية. مثبطات التآكل هي مواد تُضاف بكميات ضئيلة إلى الوسط التآكلي لتقليل التآكل دون أن تتفاعل بشكل كبير مع المكونات. لذلك، فإن تطوير مثبط فعال وصديق للبيئة ومنخفض التكلفة ومتوافق لمنع التآكل أمر بالغ الأهمية. يركز هذا البحث على تخليق نقاط كربونية معدلة ببوليمر كمثبط فعال للتآكل في أوساط مختلفة. قمنا بتخليق نقاط كربونية مشوبة بالنيتروجين ونقاط كربونية نقية. في الدراسة الأولى، تم تعديل النقاط الكربونية المشوبة مع حمض البوليمر الأسبارتيكي عن طريق فتح الحلقة لبولي PAS/N-ACs لتعزيز كفاءة تثبيط حمض البوليمر الأسبارتيكي. تم تخليق (PAS/N-CQDs) التي تم تحضيرها من خلال عملية مائية (N-CQDs) باستخدام النقاط الكربونية المشوبة بالنيتروجين (PSI) السكسينيميد حرارية من خطوة واحدة باستخدام قشور الموز المهملة والإيثيلين ديامين والأشعة، (PL) وانبعاث الضوء الضوئي، (UV-Vis) تم إجراء العديد من التحليلات مثل الامتصاص فوق البنفسجي المرئي لتقييم التركيب الكيميائي (TGA) والتحليل الحراري الوزني، (TEM) والمجهر الإلكتروني النافذ، (XRD) السينية للحيود والرنين المغناطيسي (FTIR) وخصائص السطح للنقاط الكربونية المحضرة، بينما تم استخدام مطيافية الأشعة تحت الحمراء لتوصيف حمض البوليمر الأسبارتيكي والبوليمر المعدل ($^1\text{H NMR}$) النووي للبروتون في وسط تآكلي يحتوي C1018 تم استخدام الطرق الكهروكيميائية وطريقة فقدان الوزن التقليدية لتحديد كفاءة المثبط على الفولاذ على 1 مولار حمض الهيدروكلوريك و3.5% كلوريد الصوديوم. أكدت جميع التحليلات السلوك الوقائي الفعال للمثبط. وأشارت النتائج إلى تحقيق أعلى كفاءة تثبيط بلغت 94.4% عند تركيز 30 جزء في المليون.

كما تم فحص آلية التثبيت باستخدام نموذج الامتزاز الحراري، الذي أظهر أن المثبط يتبع متساوي الامتزاز من نوع لانجموير مع C1018 تكوين طبقة حماية على سطح الفولاذ (SEM) حدوث امتزاز فيزيائي وكيميائي. وأكد المجهر الإلكتروني الماسح (PDP) والاستقطاب الجهد الديناميكي (LPR) في الدراسة الثانية، تم استخدام طرق فقدان الوزن، ومقاومة الاستقطاب الخطي كمثبط لتآكل (PSAM) لتقييم فعالية كوبوليمر حمض الأسبارتيك المطعم بالميلامين (EIS) ومطيافية الإعاقة الكهروكيميائية M HCl – في وسط يحتوي على 1 مولار حمض الهيدروكلوريك و 3.5% كلوريد الصوديوم (1 C1018 الفولاذ الكربوني 3.5% NaCl).

وكذلك تقنية الرنين المغناطيسي النووي للبروتون (FTIR) تم تحليل البوليمر المطعم باستخدام مطيافية الأشعة تحت الحمراء. وتم اختبار عدة تراكيز من المثبط. (^1H NMR). مع مجموعة Gaussian 09 في برنامج B3LYP باستخدام وظيفة (DFT) تم إجراء حسابات نظرية الدالة الوظيفية للكثافة PSAM لحساب الخصائص الإلكترونية والمدارات الجزيئية الأمامية ومعلومات التفاعلية للـ G+(d,p) الأساس 31-6. أظهرت النتائج أن كفاءة التثبيت تزداد مع زيادة التركيز، محققة أعلى كفاءة بلغت أكثر من 93% عند 200 جزء في المليون يعمل كمثبط من النوع المختلط. كما كشفت صور المجهر PSAM إلى أن (PDP) وأشارت قياسات الاستقطاب الديناميكي PSAM أن DFT في الوسط المختبر. وأظهرت حسابات C1018 عن فعالية المثبط في حماية الفولاذ (SEM) الإلكتروني الماسح. يتمتع بكفاءة تثبيت ممتازة.

وتم تقييمه كمثبط للتآكل في الدراسة الأخيرة (TDA) علاوة على ذلك، تم إنتاج كوبوليمر بولي (حمض الطرطريك-ديامين) (^1H NMR) والرنين المغناطيسي النووي للبروتون (FTIR) تم توثيق تخليق الكوبوليمر بواسطة مطيافية الأشعة تحت الحمراء. يتمتع بثبات حراري استثنائي TDA مما أظهر أن (TGA) الحراري باستخدام التحليل الحراري الوزني TDA تم تحليل تحلل على الفولاذ المقاوم للصدأ 304 في وسط TDA تم استخدام الطرق الكهروكيميائية وطريقة فقدان الوزن التقليدية لتقييم فعالية. تأكلي يحتوي على 3.5% كلوريد الصوديوم. أكدت جميع التحليلات الدور الوقائي الفعال للمثبط وأظهرت النتائج أن أعلى كفاءة تثبيت بلغت 91% تم تحقيقها عند تركيز 90 جزء في المليون، مع عمل المثبط كمثبط من النوع المختلط.

تم استخدام نموذج الامتزاز الحراري لتحليل آلية التثبيت، حيث أظهرت النتائج أن المثبط يتبع متساوي الامتزاز من نوع لانجموير. تكوين طبقة واقية على سطح العينة (SEM) مما يشير إلى حدوث امتزاز فيزيائي وكيميائي. كما أكد المجهر الإلكتروني الماسح

CHAPTER 1

INTRODUCTION

1.1 Background

Corrosion is an unwanted natural phenomenon that degrades the mechanical characteristics and appearance of metals, hence reducing their lifespan. It significantly impacts the safety, environmental degradation as well as economy. Corrosion impacts numerous areas, including infrastructure, transportation, industries, autos, and pipelines [1]. Various types of media, such as acidic, alkaline, and saline, influence the corrosion process to varying degrees; predominantly, acidic media significantly increase the corrosion rate. Consequently, it is essential to regulate this deterioration process using suitable anti-corrosive substances in minimal doses [2]. When selecting a corrosion inhibitor, it is essential to evaluate economic feasibility, inhibitor efficiency, toxicity, dangers, and their environmental impact and effects on inhabitants [3][4][5]. Traditional inorganic or organic compounds utilized as inhibitors must be substituted with biodegradable, economical, and environmentally benign alternatives concerning the third issue [6]. Polymers are seen as promising inhibitors because of their favorable effects on the environment and economy, exhibiting better control corrosion inhibition efficiency when compared to organic molecules [7]. The polymers offer two benefits: (i) numerous molecules of water on the metal surface can be displaced easily with a single polymeric chain, rendering the process favorable, (ii) a lower rate of deposition occurs due to multiple binding sites presence. Polymers, their composites, and blends containing functional groups such as $-OH$, $-NH_2$, and $-COOH-S$, etc, have great water solubility and are documented as corrosion protectors in diverse harsh environments via the complexation of polymers with metal ions, resulting

in several uses [8][9]. Polymer complexes and their composites enhance the metal surface area, creating a protective layer that shields the interface from deterioration. These inhibitors function through molecular adsorption method, whereby the substance mitigates corrosion by regulating both reactions (anodic and cathodic) [10][11][12]. Hydrogen gas evolution diminishes as the protonated species adsorbs onto the surface cathodic sites, resulting in a reduced corrosion rate [13]. Recently, scientists have conducted investigations on the inhibitory efficacy of various polymers, their composites, and combinations in various mediums, showing improved efficiency [14]. Their investigation utilized both natural and synthesized polymers, revealing that macromolecular mass, chemical composition, and distinctive inhibitor structure account for the modes and methods of corrosion protection. Natural polymers possess functional groups, such as amino and hydroxyl groups, that facilitate chelation with the metal ion, their lone electron pairs effectively engaged in coordination bonding during the metal/solution interaction [15][16][17].

Carbon steel is an economically viable alloy characterized by its ease of production and strength. Carbon steel is utilized as the primary material for pipelines, oil tanks, etc, in the oil and gas sectors. This material is corrosion susceptible when subjected to an aggressive environment, compromising the industrial production system continuity [18]. Carbon steel deterioration generates iron oxide at areas with weak adhesion on the metal surface. Subsequently, it readily disintegrates into a solution-phase, resulting in the depletion of conducting metal. Corrosion control methods include selecting appropriate alloys, modifying the corrosive medium, applying protective coatings, painting, anodic and cathodic protection. Another method to reduce degradation due to corrosion is the

incorporation of inhibitors. An inhibitor is any substance that diminishes the rate of corrosion on the affected material by adsorbing onto its surface [19][20]. These substances form a thin protective coating on the surface. Employing inhibitors is an efficient and pragmatic approach for safeguarding metals from corrosion in acidic and saline environments[20]. The protection of several metals, including carbon steel, mild steel, copper, and aluminum, by inhibitors addition has been documented [21]. Nevertheless, some organic and inorganic inhibitors are environmentally toxic, carcinogenic to human, hence jeopardizing the life of living organisms. Due to the ineffectiveness of these inhibitors, extensive research has sought to produce eco-friendly alternatives derived from organic or natural sources [22].

Carbon is a prevalent element in nature, it is regarded as possessing weak fluorescence with little solubility in water. Numerous carbon allotropes exist, including graphite, diamond, amorphous carbon, fullerene, among others. Recently, studies concentrated on utilizing carbon dots as a type of carbon-based fluorescent nanomaterial, owing to their distinctive characteristics, including excellent water solubility, little cytotoxicity, and remarkable luminosity. Another characteristic of carbon dots (CQDs) is their excellent biocompatibility [23]. The features are frequently utilized for applications in bioimaging, biosensing, biomedicine, optoelectronic devices, drug delivery, and various other domains. The four main categories of carbon dots are graphene quantum dots (GQDs), carbon nanodots (CNDs), polymer carbon dots (CPDs), and carbon quantum dots (CQDs), all measuring less than 10 nm in size. These materials can be manufactured using straightforward processes from diverse natural sources containing long carbon chains,

hence ensuring the safety of living creatures. The precursors are typically natural sources, cost-effective, and renewable [24].

Simultaneously, the doping of heteroatoms significantly enhances the distinctive qualities of activated carbon, including the emission spectrum range, fluorescence characteristics, corrosion inhibition, and additional attributes. Numerous researchers have reported that carbon dots containing solutions significantly diminishes the corrosion rate on the surface of metal [24]. This phenomenon is ascribed to the hydrophilic functional groups of the activated carbon, which attract molecules of water and sequester oxygen from the metal surface. Subsequently, oxygen molecules adsorbed on the carbon dots surface are directly transformed into water molecules by four-electron routes, so inhibiting the corrosion process [25].

1.2 Statement of the Problem

Corrosion remains a significant challenge in our daily life, leading to a substantial economic loss, structural failures, safety hazards, as well as environmental degradation. Corrosion impacts numerous areas, including infrastructure, transportation, industries, autos, and pipelines. Traditional corrosion inhibitors, including organic and inorganic compounds often have environmental risks due to their high toxicity and limited biodegradability. As a result, the need for a sustainable, cost-effective, eco-friendly, and high-performance corrosion inhibitor that can effectively protect metal surfaces with no to minimal environmental impact arises.

1.3 Objectives of the Study

This work aims at the synthesis of quantum dots modified with copolymers. The specific objectives are:

- I. To synthesize poly aspartic acid using thermal condensation process.
- II. To modify the synthesized poly aspartic acid for inhibition enhancement as a coating and inhibitor.
- III. To characterize the prepared materials by Fourier Transform Infrared Spectroscopy (FT-IR), Proton Nuclear Magnetic resonance spectroscopy (H-NMR), Scanning Electron Microscopy (SEM), Thermo-gravimetric Analysis (TGA), Transmission electron microscopy (TEM), Ultraviolet-Visible spectroscopy (UV-Vis), X-ray diffraction (XRD).
- IV. To evaluate the prepared materials for their efficiency as inhibitors in corrosion inhibition.

1.4 Significance of the Study

The importance of carbon-dots composite is due to their high solubility in water tunable surface chemistry, biodegradability, cost-effective and tunable surface chemistry. This modifications in turn facilitate the required doping with polymers for efficient corrosion inhibition.

1.5 Scheme of the Research Work

To facilitate reading and understanding, the thesis report is organized and structured into the following five chapters:

- **Chapter 1:** describes the problem of corrosion, the need for the carbon-based inhibitors, highlight of the objectives, problem statement, significance of the study and the research scheme.
- **Chapter 2:** provides an overview of the current literature on corrosion inhibitors using polymers and carbon dot composite.
- **Chapter 3:** inhibition effect of nitrogen-doped carbon dots on the corrosion of low-grade carbon steel in a salty acidic environment
- **Chapter 4:** corrosion inhibition of poly-aspartic acid-co-melamine against low-grade carbon steel (C1018) in 1m HCl-3.5% NaCl medium, an experimental and theoretical study.
- **Chapter 5:** investigating the corrosion resistance of 304 stainless steels using a carbon dot modified polymer in a 3.5% NaCl medium.
- **Chapter 6:** A summary of the study's findings is presented.

CHAPTER 2

LITERATURE REVIEW

2.1 Corrosion Inhibitors (CIs)

CIs are substances that are introduced in minimal amounts (ranging from 1ppm to 15,000 ppm) within an aggressive medium to mitigate corrosion without significantly reacting with ambient components [26][27][28]. Corrosion inhibitors are crucial in the oil extraction, processing, and chemical industries. They are categorized into organic and inorganic types [29] [30]. Inorganic types exhibit either anodic or cathodic effects, while the organic inhibitors exhibit both cathodic-anodic mixed action and adsorption action. Inorganic inhibitors perform superiorly across a broader temperature range for extended durations compared to organic corrosion inhibitors. Organic corrosion inhibitors, albeit more costly than inorganic ones, demonstrate reduced toxicity. Organic inhibitors adsorb onto surface of the metals via heteroatoms like oxygen, nitrogen, phosphorus, and sulfur [31] [32].

2.1.1 Inorganic Inhibitors

Anodic inhibitors: sometimes referred to as passivators, obstruct the anode reaction and facilitate the passivation of metal. They react with the corrosion product, creating an insoluble coating on the metal surface. Examples include silicates, chromates, nitrates, phosphates, and hydroxides [33][34].

Cathodic inhibitors: Cathodic inhibitors impede the cathodic reaction of the metal during corrosion. Alkalinity causes metal ions to participate in a cathodic reaction, resulting in the

formation of compounds that precipitate on cathodic sites. examples of some inorganic cathodic inhibitors that are applied to the cathodic site to safeguard the metal are magnesium hydroxide and zinc hydroxide. Calcium salts and phosphonates may also be mentioned [35].

2.1.2 Organic Inhibitors

The chemicals utilized as organic inhibitors may function as either cathodic, anodic, or both [36]. They can additionally create a film by the process of surface adsorption. Examples include benzotriazole, benzothiazole, mercaptobenzothiazole (MBT), amines, urea, heterocyclic nitrogen and sulfur-containing chemicals, as well as caffeine, ascorbic acid, succinic acid, and extracts from other natural resources [37][38]. Dicyclohexylammonium benzoate, diisopropylammonium nitrite, and ethanolamine carbonate are volatile vapor-phase corrosion inhibitors [33].

2.2 Polymers for Corrosion Inhibition

Polymers used as inhibitors are primarily categorized according to their origin [39]. Polymers encompassing natural and biopolymers, such as chitosan, starch, gum Arabic, cellulose, are classified as natural polymers. Synthetic polymers are classified into three subclasses: thermoplastics (e.g. polyethene.), elastomers (e.g. nitrile rubber), and thermosets (e.g., melamine) [39] [4]. These polymers effectively substitute the inorganic and organic inhibitors because of their rigorous environmental requirements and cost, which diminishes their popularity and usage., in addition to serving as corrosion inhibitors, polymers and polymer-composite have several uses such as cosmetics, food processing, medicine, etc [40][41][42].

2.2.1 Corrosion Inhibition Using Natural Occurring Polymers

Polymers occurring naturally have demonstrated promise efficacy as inhibitors in various mediums. The inhibitory impact of pectin polymer on aluminum in an acidic environment was examined and documented. The inhibitory efficacy initially rose with concentration linearly and thereafter exponentially until it reaches a plateau, as shown by the result. The temperature significantly influenced the inhibitory efficiency, exhibiting a drastic reduction from 91% at 10°C to 31% at 40°C using the same dosage. Carboxymethyl cellulose (CMC) inhibition efficacy was examined on a mild steel in H₂SO₄ solution at varying temperatures of 30 to 60 °C range by Solomon *et al.*, [43]. Thermometric, hydrogen evolution and weight loss methods were used to examine the efficacy. The results shows that the inhibitory efficacy rise with higher CMC content but reduced with rising temperature, suggesting a physical adsorption process. CMC adsorption onto the mild steel surface followed Langmuir and Dubinin-Radushkevich isotherm models. Nevertheless, the authors compared the CMC inhibition efficacy derived from their study with that reported by Bayol *et al.*, [44]. In Hydrochloric acid solutions, discovering that the CMC efficiency in Bayol *et al.*'s research was superior. This corroborates the assertion that organic compounds demonstrate a greater inhibitory efficiency in chloride-containing solutions compared to sulfate-containing ones [45]. Arukalam and his co-workers [46] compared the influence of hydroxyethyl cellulose (HEC) on mild steel and aluminum corrosion in a 0.5 M Hydrochloric acid medium under atmospheric conditions, utilizing the weight reduction method. It was found that HEC is more effective for mild steel compared to aluminum in the tested medium. Bentrach *et al.*, [47] investigated the corrosion-inhibiting efficacy of Gum Arabic (GA) on API 5L X42 pipeline steel in a 1 molar Hydrochloric acid solution,

utilizing electrochemical methods. The findings indicate that a protection of about 92% at 2 g/L was achieved. The GA's adsorption on the steel surface was determined as Langmuir adsorption isotherm and entails physical adsorption. The Gum Arabic was identified as a mixed-type inhibitor.

2.2.2 Corrosion Inhibition with Synthetic Polymers

Synthetic polymers have garnered significant attention as inhibitors of metal corrosion just as the naturally occurring ones. A meticulous examination of their structures disclosed polar functional groups presence, which is a requisite for an organic compound to be classified as an inhibitor for corrosion [45]. Two unique classes of intriguing polyurea derivatives, denoted as 6(a-c) and 7(a-c), was synthesized via a polycondensation approach, involving the reaction between bis(2-aminothiazol-4-ylbenzylidene) cycloalkanone and diisocyanate compounds in pyridine. The synthesized polymers inhibition properties on steel in a 0.5 molar sulfuric acid solution at 40°C were evaluated [48]. Polyurea designated 6a exhibits nearly constant inhibition efficiency across all selected concentrations, except for 1 and 2 ppm, while the remaining derivatives inhibits corrosion in the tested medium at low concentrations with improvement at elevated concentrations [48]. Three distinct polyvinyl alcohol (PVA) with different molecular weights (14,000, 72,000, and 125,000 g/mol) were tested as inhibitors in hydrochloric acid solution via the electrochemical analysis at room temperature [49]. PVA was found to inhibit mild steel corrosion in the hydrochloric acid medium, with the inhibition efficiency degree contingent upon the polymer molecular weight and concentration. PVA was identified as a mixed-type inhibitor and adsorbs on the mild steel surface through physical adsorption process. Langmuir adsorption isotherm was found as the adsorption model.

Leon-Silva *et al.*, [50] synthesized poly(3-octylthiophene) (P3OT) through the direct oxidation of the 3-octylthiophene monomer using ferric chloride (FeCl_3) as the oxidizing agent. The thermal annealing impact of P3OT on stainless steel (304SS) corrosion inhibition in sodium chloride solution was examined. P3OT films were placed onto the 304 stainless steel electrodes using the drop-casting process, and the 304SS coated with P3OT films underwent thermal annealing for 30 hours at several temperatures. the coated stainless steel corrosion inhibition resistance was assessed via the electrochemical methods. The results showed that thermal annealing at higher temperatures enhanced the corrosion resistance of the steel in the solution. Morphological analysis indicates that upon heating the films, there was increase in grain size and the surface became denser, enhancing the film resistance property.

2.3 Polymer Nanocomposites for Corrosion Inhibition

Nanostructured materials have emerged as a contemporary advancement in fields ranging from automotive engineering to bioengineering, offering a diverse range of unique properties attributable to their elevated surface-volume ratio, significant grain boundary volume and optimal grain size [51]. Polymeric nanocomposites demonstrate interfacial interactions between the reinforcing and matrix constituents in corrosion analysis [52]. Nanoparticles thin film coating serve as essential protective layers by integrating with organic compounds, including polyurethane, polyamide, epoxies, among others [53]. They are accountable for impeding the transition of corrosive substances in many situations, including hydroxyl ions, water, contaminants, oxygen, chloride ions. Furthermore, they exhibit a propensity to interact with the metal surface. Polymeric nanocomposites create a physical barriers and layers of inhibitor between the aggressive medium and metal surfaces.

Polymer nanocomposites are extensively utilized for corrosion inhibition and can markedly reduce the rate of corrosion on surface of the metal [6][54]. A variety of metals or metal oxides were used into the epoxy coating as fillers to improve their inhibition efficiency. A prevalent technique for enhancing the barrier and anticorrosive efficacy of epoxy coatings involves the incorporation of metallic nanoparticles such as zinc, titanium, and aluminum [55].

2.4 Mechanism of Inhibition by Polymers

An inhibitor degree of efficiency relies on its capacity to adsorb and create a layer on the coupon matrix. The inhibition process commences by replacing the hydrated water with the inhibitor molecules, resulting in the inhibitor adsorption onto the metal matrix. Nonetheless, this process is affected by some attributes such the charge and nature of the metal, inhibitor chemical structure, and characteristics of the medium. The heteroatoms in the polymers functions as the center of interaction between the metal matrix and the inhibitor. According to Khairou and El-Sayed [56] heteroatoms presence within inhibitor form bridges between the inhibitor and surface of the metal, hence reducing corrosion rate. Furthermore, the heteroatom(s) lone pairs of electrons may augment the positively charged metal surface and the inhibitor's interaction [57][58][59]. Physical and chemical adsorptions are the adsorption types associated with polymers. Physical adsorption is characterized by the electrostatic interaction between charged surface and the molecules, whereas chemical adsorption entails charge transfer or share from the inhibitor to the metal matrix, resulting in the formation of a coordinating bond [39]. Umoren and colleagues [60] elucidate that molecules of inhibitor occur as protonated species in equilibrium with their relating species. They adsorb onto the positively charged metal surface by displacing water

molecules and facilitating electron sharing between the free electrons of the heteroatoms and the unoccupied metal orbitals [60].

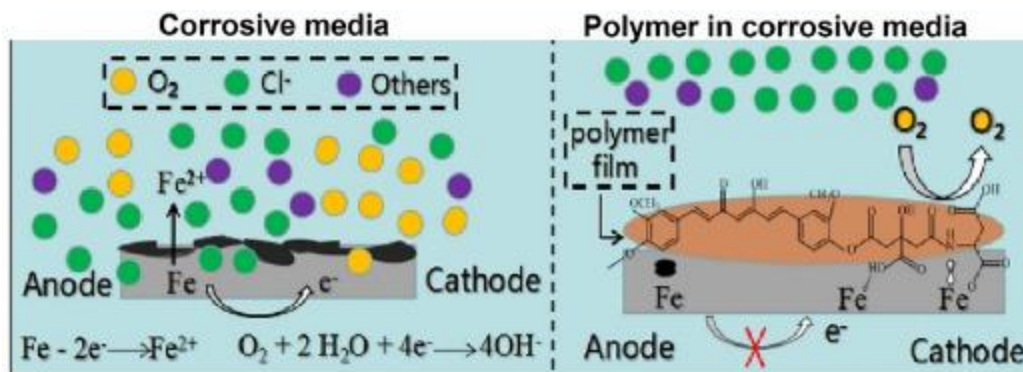


Figure 2.1 Inhibition mechanism of polymers in corrosive medium.

2.5 Carbon Dots: Basics and Anticorrosive Applications

Carbon dots are a novel carbon-based nanomaterial having a dimension below 10 nanometers [61][62] [63]. Carbon dots (CQDs) are emerging entities within the carbon family, garnering considerable attention due to their diverse attributes, which encompass exceptionally tunable photoluminescence (PL), biocompatible, less toxic, enhanced adsorption capacity, cost-effectiveness, environmental sustainability, highly soluble in water, and remarkable stability. Carbon dots are widely utilized in numerous applications (industrial and biological), including catalysis, biomedicine, sensors, energy storage, optoelectronics, and, more recently, as inhibitors to corrosion [64][65][66]. Currently, applications of current allotropes of carbon are significantly constrained due to the challenges and high costs associated with their synthesis and purification. fullerenes, graphene, and carbon nanotubes are less soluble in polar solvents, which substantially restricts their applicability [67][68]. Unlikely, Carbon dots demonstrate exceptional

solubility and anticorrosive properties. Carbon dots are manufactured using several processes documented in the literature, with their characterization mostly conducted via diverse spectral studies, including transmission electron microscopy, ultraviolet-Visible spectroscopy, Raman spectroscopy, Fourier transform infrared spectroscopy, X-ray diffraction, energy dispersive X-ray spectroscopy, X-ray photoelectron spectroscopy techniques [69] [70] [71] especially their inhibition properties, can be altered effectively by heteroatoms(Nitrogen ,Sulfur, and phosphorus) doping. Literature indicates that Carbon dots (CQDs), both doped and undoped, have widely been utilized as inhibitors in various corrosive mediums. Due to their nanometric characteristics, Carbon dots exhibit superior surface coverage and anticorrosive properties [72] [73] [74].

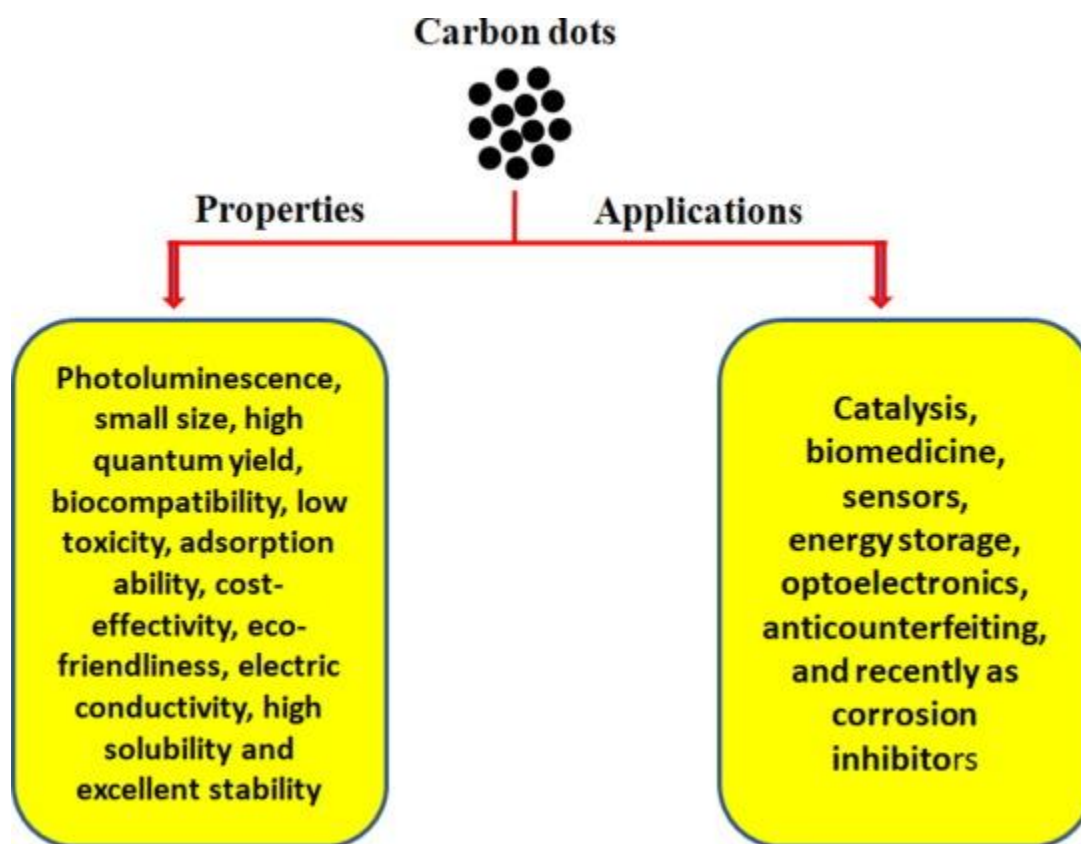


Figure 2. 2 Carbon dots properties and application.

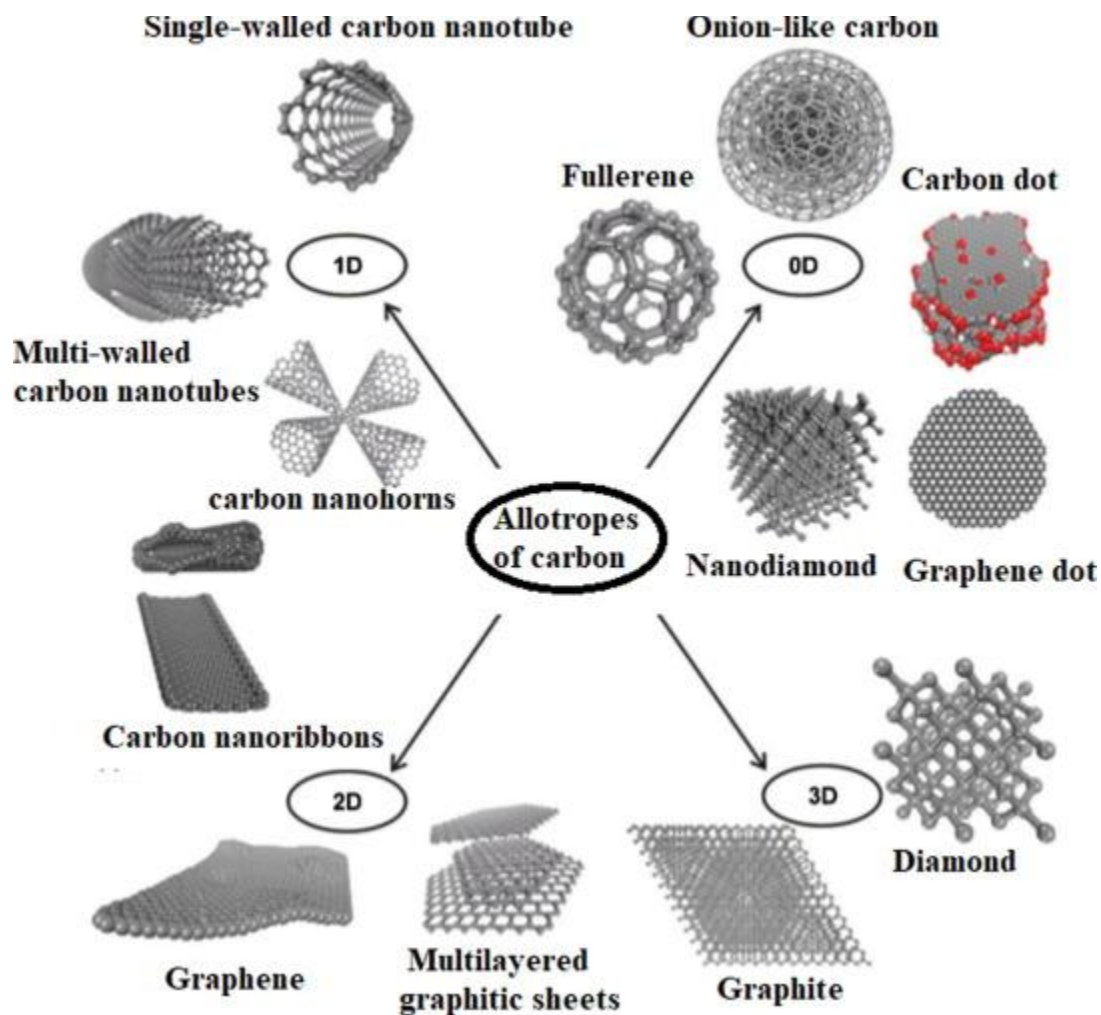


Figure 2. 3 Different carbon allotropes.

Like conventional heterocyclic corrosion inhibitors, Carbon dots also achieve efficacy by adsorption and a protective layer formation. The heteroatoms of doped are anticipated to function as adsorption active sites due to their electron-rich nature [75] [76]. Consequently, doped carbon dots are believed to function as a better inhibitor than undoped carbon dots. This doping facilitates the solubilization of carbon dots in polar electrolytes. It can be inferred that upon adsorption, carbon dots obstruct the active sites on the surface of the

metal that facilitate corrosion. The corrosion inhibition adsorption mechanism by carbon dots can be demonstrated through electrochemical methods and surface analysis techniques [77][78]. Common techniques applied to determine the anticorrosive properties of carbon dots include scanning electron microscopy, transmission electron microscopy, ultraviolet-Visible spectroscopy, Raman spectroscopy, Fourier transform infrared spectroscopy, X-ray diffraction, energy dispersive X-ray spectroscopy, X-ray photoelectron spectroscopy. Clearly, both technologies allow for the observation of alterations in surface shape and variations in surface elements composition [79].

2.5.1 Nitrogen-Doped Carbon as Sustainable Corrosion Inhibitors

Nitrogen-doped ACs and Nitrogen, Sulphur-CQDs are the most often employed heteroatom-doped carbon dots for corrosion prevention. N-CQDs utilized for corrosion inhibition are predominantly produced via hydrothermal or solvothermal techniques employing various precursors, and chemicals like citric acid, L-histidine [80], thiourea [81], serine [82], tryptophan [83], ethylene diamine [84], aminoguanidine hydrochloride[85], sulfamic acid[86], among others. Conversely, N, S-CQDs synthesis necessitates an extra sulfur source, such as methionine [87], or cysteine [88][89]. The synthesized N-CQDs and N, S-CDs are primarily characterized utilizing transmission electron microscopy, ultraviolet-Visible spectroscopy, [90].Zhu et al [91]. synthesized N-CQDs utilizing folic acid and o-phenylenediamine and evaluated their inhibition efficiency through different electrochemical analysis and surface morphology. Potentiodynamic polarization analysis reveals that N-CQDs influence both reaction rates (cathodic and anodic), although E_{corr} values were not altered substantially. A partial capacitive reactance

semicircular arc is observable on the Nyquist plot. As the N-CQDs quantity increases, the arc's radius as well as its height increases. N-CQDs incorporation increased the impedance and inhibition property without affecting the reaction. Moreover, a singular charge transfer time constant was determined according to the Bode plot. N-CQDs inhibitor adsorption on the Q235 surface accounts for these results by obstructing electron transfer and increasing capacitive reactance [91]. In a separate work, Ye and co-workers [92] examined the efficacy of a synthesized functionalized carbon dots, imidazole and citric acid-carbon dots (CA-CQDs) against corrosion on Q235 carbon steel in 1M HCl medium via electrochemical analysis and surface morphology. According to the electrochemical analysis conducted at 200pm for all the three inhibitors, the functionalized CQDs has the highest inhibition efficacy followed by imidazole and lastly CA-CQDs. A rise in concentration for all the inhibitors resulted in enlargement of the Nyquist curves, indicating an enhancement in the mechanism of charge transfer. The inhibitor presence in the tested medium reduces the current density by inhibiting the Tafel processes. The enlargement of Nyquist curves results from the development of a coating by the inhibitors at the surface, which improves charge transfer barrier. The reduction in current density signifies that these inhibitors adsorb on the surface and obstruct active sites. There was no alteration in the E_{corr} value, demonstrating their function as mixed-type inhibitors. The elevated Bode phase angle value of inhibited when compared to the blank resulted from the smoothing of the inhibited surface by the adsorption of the inhibitors. Finally, SEM and AFM investigations were used to analyze the adsorption of the inhibitors on the steel surface [92].

2.6 Mechanism of Carbon Inhibition and Adsorption

ACs significantly affected both the cathodic and anodic electrochemical processes as shown by electrochemical analysis. ACs primarily function as mixed-type inhibitors, significantly obstructing both cathodic hydrogen oxidation and anodic iron reduction in acidic and saline environments [93]. The ACs create a thin protective layer on the metal surface, which effectively shields it from corrosive damage [94]. **Fig.2.4** illustrates the visual depiction of the inhibitory mechanisms of N-ACs on the surface of steel in an acidic environment (0.5 molar sulfuric acid). Hydrogen and sulfate ions primarily contribute to corrosion on the surface. At the cathodic location, hydrogen gas was formed from hydrogen oxidation, while sulfate ions oxidize iron to produce iron sulfate salts. Both hydrogen gas evolution and steel corrosion are contingent upon the sulfuric acid concentration and temperature, indicating that an increase in either parameter results in an elevated corrosion rate [95]. In contrast, the reactions processes were significantly diminished in N-ACs presence. The N-ACs possessed various functional groups, which readily engaged in chemical interactions with the surface via coordination bonds formation [96]. Furthermore, the hydrogen ions protonate certain N-ACs heteroatoms, resulting in the formation of the protonated variant of N-ACs, which engaged in electrostatic interactions with the metal surface [97]. The adsorption process is physical adsorption, which could enhance the inhibitory efficacy of N-ACs. The inhibitory mechanism is contingent upon the charge distribution and molecular architecture of the N-ACs [98].

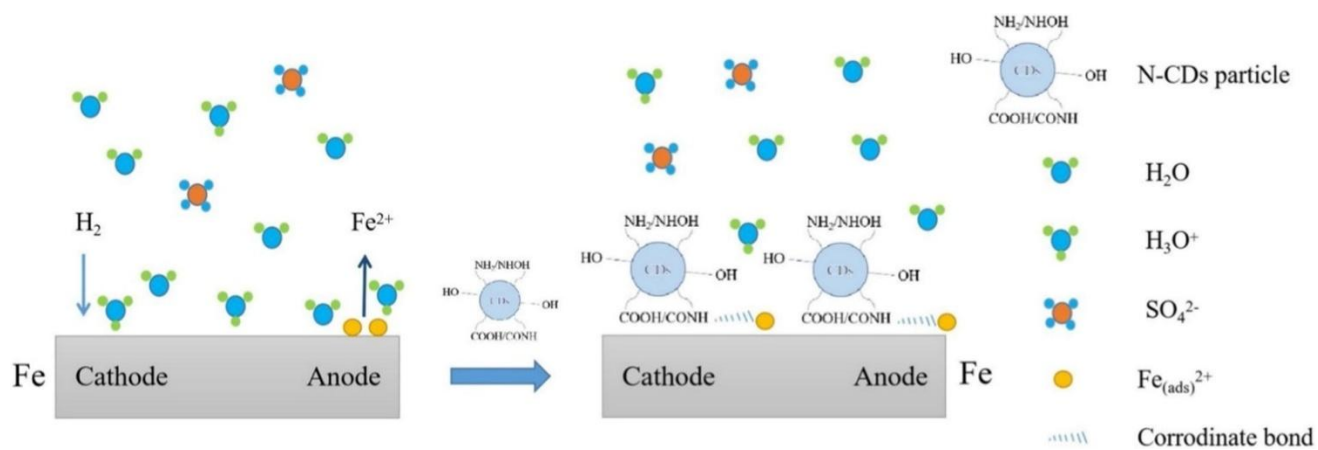


Figure 2. 4 Inhibition mechanism of polymers in corrosive medium.

CHAPTER 3

INHIBITION EFFECT OF NITROGEN-DOPED CARBON ON THE CORROSION OF LOW-GRADE CARBON STEEL IN A SALTY ACIDIC ENVIRONMENT

3.1. Introduction

Corrosion in alloys and metals is an electrochemical phenomenon wherein the surfaces of metals deteriorate by interaction with environmental elements [99]. Annually, GDP loss due to corrosion for developed as well as developing countries is about 3.4% of their GDP. China, Japan, and South Africa incur losses of around 310, 9.2, and 9.6 billion dollars, respectively according to a report. Such losses accounted for 3.34% of China's GDP, and 2% of Japan's GDP, [100] [101][102]. Both personal safety and economic loss are impacted significantly by corrosion. Consequently, it is crucial to use as well as enhance innovative technologies to safeguard metallic materials against deterioration [103]. One of the most efficacious technologies for safeguarding metallic materials from corrosion is the use of inhibitors, which are small amounts of external substances added to harsh environments to protect metallic surfaces from deterioration. Initially, inorganic salts, like chromates, zinc, silicates, borates, nitrates, and phosphates were first widely used to safeguard the metals surfaces from deterioration [19]. They interact with metal surface cations, leading to the deposition of a crystalline layer that shields the metal against further corrosion. However, inorganic corrosion inhibitors, such as nitrates and chromates pose environmental and health risks because of their toxicity and non-biodegradability, can precipitate and cause fouling, are p^H -sensitive, may trap corrosive species leading to under-deposit corrosion, and can be incompatible with other chemical additives. Organic inhibitors are primarily

composed of acyclic and cyclic carbon-containing compounds, including heterocyclic ones with atoms like phosphorus, sulfur, nitrogen, and oxygen. These compounds, particularly those with functional groups such as amine and carboxyl are highly effective because of their chemical reactivity and structural orientation. The electron-rich centers in organic molecules, such as alkenes, aromatic rings, and alkyls interact with metal cations to create nucleophilic linkages that are stable. The inhibitor's effectiveness depends on its adsorption onto the metal surface, influenced by its structure and chemical properties [104][105][106]. Organic compounds having functional groups (amine, carboxyl, epoxy, etc.) are employed as corrosion inhibitors [19]. These functional structures contain diverse heteroatoms, including S, N, P & O, among several electron-rich bonds (alkenes, aromatic rings, and alkyls). The engagement of the organic molecules (electron-rich centers) with metal cations establishes a stable bond that functions as a nucleophile [107][6].

Corrosion inhibitors typically engage with the surfaces of the metal, forming a barrier on them. The focus of researchers has been on producing corrosion inhibitors that are economically viable, environmentally benign, and exhibit minimal toxicity. Consequently, the efforts on carbon-bonding compounds have gained more concentration. Among them, carbon quantum dots (CQDs) have been employed as corrosion inhibitors owing to their affordability, rigidity, diverse uses, non-toxicity, and environmental friendliness [108]. Numerous CQD-based materials, including nitrogen-doped [109], ionic liquid [110], polymer-based [111], and SN-co doped CQDs [112], have recently been used as inhibitors. Carbon dots are classified as a recent category of zero-dimensional carbon-based nanomaterials, having dimensions between 2 and 10 nanometers. There is a significant interest in carbon dots (CQDs) due to their diverse industrial and biological uses [113].

Carbon dots possess distinct characteristics such as low toxicity, significant biocompatibility, high photoluminescence, chemical inertness, enhanced adsorption capacity, cost-effectiveness, environmental sustainability, high solubility, and good stability, among others. Multiple techniques, such as laser ablation processes, ultrasonic microwave irradiation, and hydrothermal, among others, have been established for carbon dots preparation [114]. Food waste, ammonium citrates, amino acids, citric acid, and other natural substances have been utilized for the fabrication of carbon dots [115]. These precursors are typically abundant in nature, cost-effective, and renewable, and the synthesis processes are environmentally sustainable. Simultaneously, carbon dots (CQDs) surface chemistry can be effectively altered through doping with sulfur, nitrogen, oxygen, and phosphorus heteroatoms, leading to adjustable physicochemical features [116]. ACs can adsorb onto the metal surface forming a layer that prevents corrosion, just like traditional heterocyclic corrosion inhibitors. Furthermore, increased inhibitor penetration on the metal surface enhances corrosion resistance [117]. Consequently, ACs benefit from their extensive surface covering and the significant availability of coordinated chemical moieties attributed to their nanometric characteristics. Numerous studies have indicated that solutions containing ACs can significantly diminish the corrosion rates of copper, steel, and aluminum in different mediums [23][90] [118][66]. Shuyun and co-workers documented nitrogen-doped ACs for inhibition efficiency against carbon steel corrosion in an acid. They utilized methodologies such as XRD, TEM, FTIR spectroscopy, and electrochemical techniques to assess N-CQDs as a carbon steel effective inhibitor. The PDP analysis indicated a 97.8% inhibition efficacy at 30 ppm N-CDs. Furthermore, their study indicated that the β_a and β_c values diminished progressively as the inhibitor concentration

increased [119]. Yang et al. produced CDs derived from citric acid and imidazole (IM-CDs) and studied their inhibitory efficacy on Q235 steel in a saline environment (3.5 weight percent sodium chloride). At the cathodic region, the hydrogen charge was impeded by CDs presence. Hydrogen evolution reaction over potential was elevated, while there was a decrease in acid corrosion cathodic process [120]. The examined inhibitor significantly changed the cathodic electrochemical reactions, as evidenced by the electrochemical data, which demonstrated a possible positive shift in the inhibited solution relative to the blank. The electrochemical results demonstrate that more inhibitors and longer immersion time result in improved efficacy. The CQDs' physicochemical adsorption mechanism in the saline media was shown by the Gibbs free energy calculations [120].

Here, N-ACs were synthesized via the hydrothermal technique. N-ACs possess a surface abundant in amino groups compared to undoped CQDs. The N-ACs were integrated into poly-succinimide (PSI) ring-opening reaction, resulting in the effective synthesis of the PAS/N-CQDs. PSI has been extensively utilized for the synthesis of poly aspartic acid (PAS) modifications due to its mild reaction condition. The N-ACs were analyzed using TEM, TGA, UV-Vis, and XRD. While the PSI and PAS were analyzed using FT-IR and ^1H NMR. Weight loss, EIS, LPR, and PDP were used to determine the inhibition efficacy. The immersed steel surface morphology was determined by SEM.

3.2. Experimental

3.2.1. Reagents

Banana peel waste, Ethylenediamine (Sigma-Aldrich, 99%). L-Aspartic Acid (Sigma-Aldrich, 98%), *o*-phosphoric acid (Supelco, 85%), Methanol (Honeywell, 99.8%), Acetone

(Honeywell, 99.5%), HCl (Fischer Scientific, 37^W/_v %), NaCl (Fischer Scientific), carbon steel (C1018). Distilled water was obtained from the Thermo-scientific Distillation Apparatus (Model A1015-B-61). Analytical reagent grades were employed and used directly as received.

3.2.2. ACs and N-ACs Synthesis

N-ACs and ACs were produced by hydrothermal process, as seen in **Fig 3.1**. At 80 degrees Celsius, the banana peels were dried throughout the night to remove the moisture and subsequently pulverized into a powder. The refined powdered sample serves as carbon source. The best optimal fluorescence properties of N-ACs were ascertained when ethylenediamine was employed as a nitrogen source during synthesis. The technique entailed combining 0.06 g of the produced carbon precursor and 0.5 mL of ethylenediamine into 60 mL of water and, thereafter, undergoing a hydrothermal procedure in a Teflon-lined autoclave. A brown solution was obtained which was subsequently filtered by 0.22 micrometer syringe filter for residue elimination. The same method was employed for the synthesis of bare ACs, excluding the incorporation of any nitrogen source (**Fig.3.1**).

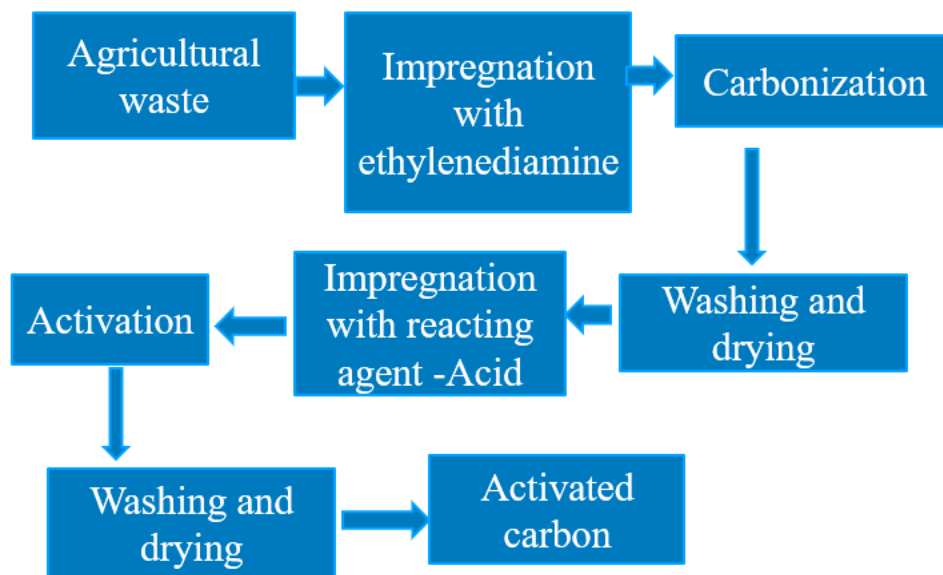


Figure 3. 1 N-ACs synthesis design.

3.2.3. Synthesis of Poly-Succinimide

About 85% o-phosphoric acid (1 g, 8.67 mmol) and aspartic acid (10 g, 0.0752 mol) were combined at an ambient temperature for 15 minutes. The mixture was kept in 150-mL round-bottom flask fitted with a thermometer, condenser, magnetic stirrer, and nitrogen inlet, and subsequently heated to 200 °C for 8 hours. The product was rinsed with 200 mL of water until neutral, thereafter treated with 200 mL of methanol, and dried at 85 °C to obtain poly succinimide. PSI underwent hydrolysis as detailed below: 3 g of PSI, 1.4 g of sodium hydroxide (stoichiometrically equivalent to succinimide residues), and 20 milliliters of water were added in a beaker under chilling conditions. Following one hour of agitation, the mixture was combined with 300 mL of methanol, and the resultant

precipitate was subjected to filtration and dried at 40 °C to get sodium poly-aspartate (PAS-Na). (**Fig. 3.2**).

3.2.4. PAS/N-ACs Synthesis

A total of 0.6 grams of PSI was dispersed in 10 milliliters of DI water under continuous stirring, forming a suspension. Next, N-ACs were incorporated into the mixture, followed by the rapid addition of 5 milliliters of 1 M sodium hydroxide solution. The resulting blend was maintained at 60 degrees Celsius under constant agitation for 24 hours. After completion of the reaction, hydrochloric acid was used to adjust the pH to neutrality. The product was then precipitated by adding anhydrous ethanol and left undisturbed for 12 hours. The obtained precipitate was dried at 60°C, yielding the solid PAS/N-ACs composite (**Fig. 3**). PAS was synthesized with a comparable technique, excluding the incorporation of N-ACs (see **Fig 3.3**).

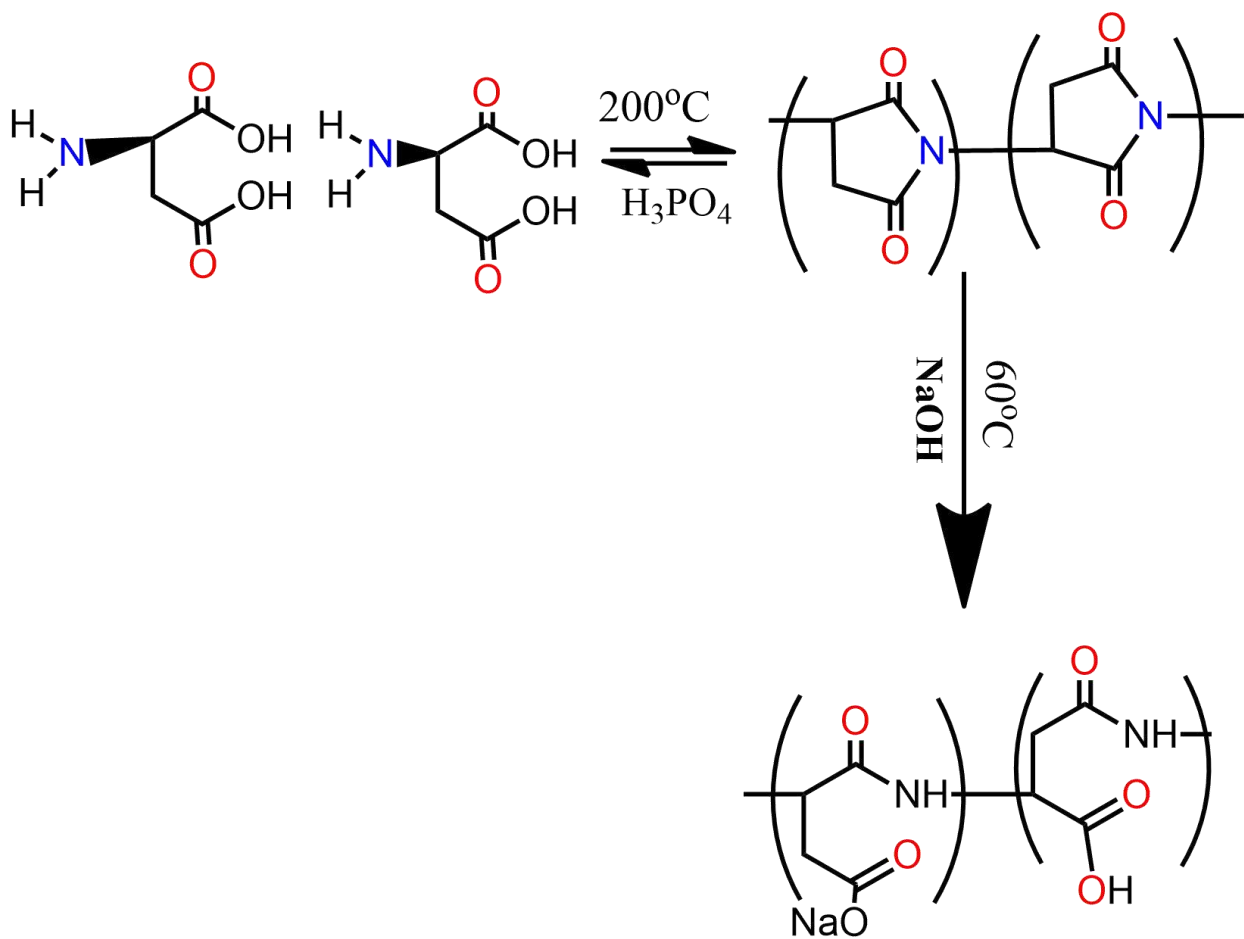
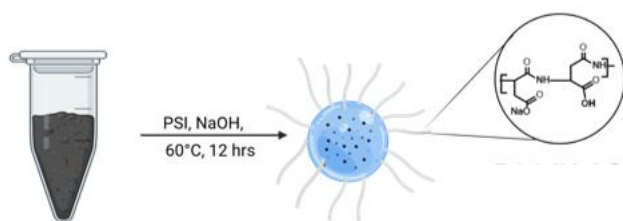


Figure 3. 2 PAS synthesis scheme



PAS/N-AC synthesis

Figure 3. 3 PAS/N-ACs inhibitor synthesis design.

3.2.5. N-ACs Characterization

JEM-2100F transmission electron microscope was employed to obtain the bare and doped carbon dots morphology in an aqueous solution. Photoluminescence (PL) spectra were recorded using a Hamamatsu compact Fluorescence C16361 spectrophotometer, while UV–visible (UV–vis) spectra were determined by Genesys 10S UV-VIS spectrophotometer. To investigate the phase composition of the carbon dots, X-ray powder diffraction analysis was carried out by Bruker-D8 diffractometer. The thermal stability was assessed utilizing a STA 429 thermal analyzer manufactured by Netzsch-Geratebau. The polymers were subjected to heating at 700 °C at a consistent rate of 10 °C/min in an air atmosphere.

3.2.6. PAS/N-ACs and PAS Characterization

PSI, PAS, and PAS/N-ACs were characterized using FTIR and ^1H NMR techniques. The Attenuated Total Reflectance (ATR) - Fourier Transform Infrared (FTIR) spectrometer (model: Smart iTR NICOLET iS10) was utilized to collect FTIR spectra of the PSI, PAS, and PAS/N-ACs. The spectra were obtained at 4 cm^{-1} resolution and covered a range of frequencies from $400 - 4000\text{ cm}^{-1}$. PSI and PAS ^1H NMR were collected using the Bruker AVANCE IIIHD 400 MHz NMR spectrometer in deuterated dimethyl sulfoxide and deuterium oxide respectively.

3.2.7. Testing Preparation

The specimen (C1018 Carbon steel) for the gravimetric test was shaped into 2.5cm x 2.5cm x 0.3cm dimensions, providing 15.5 cm² as a total surface area. In contrast, the specimen for the electrochemical analysis was shaped into a cube with 1.0 cm on all sides, embedded in an epoxy/hardener mix. The preparation involved sanding the specimens with silicon carbide sheets from grit 120 to 800. After cleaning with the use of distilled water and acetone, the product was dried. 2000 mL of 3.5% sodium chloride solution was prepared in distilled water. Subsequently, the prepared NaCl solution was used to dilute the necessary amount of HCl (37%) to obtain the corrosive medium. Various amounts of the inhibitor were prepared using 1M HCl-3.5% NaCl solution for further testing.

3.2.8. Weight Loss Measurements

The weight loss analysis, known for its directness and accuracy, was utilized to evaluate the corrosion-inhibiting efficacy of PAS and PAS/N-ACs. This test involved weighing square stainless-steel specimens. Both before and following dipping them in a 100-milliliter volume of a 1M HCl-3.5% NaCl solution having a varied inhibitor concentration, kept at constant temperatures for 24 hours. The rate of corrosion was calculated using equation (1) [121], whereas equation (2) determined the inhibition efficacy (% IE).

$$CR = \frac{W * 8.79 * 10^4}{D * A * T} \quad (1).$$

Where the variable W represents the mean weight reduction in grams.

A = surface area measured in square centimeters.

T = represents the immersion time (hours).

D = coupon's density (7.87 g/cm³).

$$\%IE_{wl} = \left(\frac{W_0 - W_i}{W_0} \right) \times 100 \quad (2).$$

Where W₀ is blank's weight loss, W_i is weight loss of inhibited solution.

3.2.9. Electrochemical Measurements

For electrochemical analysis, Potentiostat/Galvanostat/ZRA Gamry Reference 3000 was employed. The arrangement included a cold-mounted specimen functioning as working electrode, while graphite rod serving as the counter electrode, and the Ag/AgCl electrode as a reference electrode. The object being studied was inserted in the media for 1h at open circuit potential (OCP) to stabilize. Techniques used included electrochemical impedance spectroscopy (EIS) from 10 millihertz to 100 kilohertz with 10 millivolts amplitude. Linear polarization resistance (LPR) was measured at 0.1250 mV/s around ± 10 mV of OCP, and potentiodynamic polarization (PDP) at 0.25 mV/s within ± 250 mV of OCP. The resulting curves were analyzed using a Gamry Echem analyst.

Regarding EIS, %IE was obtained using equation (3) [122] :

$$\%IE_{(EIS)} = \left(1 - \frac{R_p^B}{R_p^I} \right) \times 100 \quad (3).$$

where R_p is the sum of R_f and R_{ct}, with R_pⁱ and R_p^B denoting the inhibited and uninhibited solutions polarization resistance respectively.

Regarding constant phase element (CPE), the CPE impedance was calculated using equation (4) [123].

$$Z_{CPE} = Y_o^{-1} (j\omega)^{-n} \quad (4).$$

Where Y_o = CPE magnitude, i = square root of -1, n is phase shift, and j is the angular frequency.

Regarding LPR, the %IE was determined using equation (5) [124]:

$$\%IE_{(LPR)} = \left(1 - \frac{R_p^B}{R_p^I} \right) \times 100 \quad (5).$$

Where R_p^B indicates the polarization resistance of the blank, while R_p^I signifies the inhibited solution polarization resistance.

To compute the inhibition efficiency regarding PDP, equation (6) was used [125].

$$\%IE_{(PDP)} = \left(1 - \frac{I_{corr}^i}{I_{corr}^B} \right) \times 100 \quad (6).$$

Where I_{CORR}^I and I_{CORR}^B represent corrosion the inhibited and uninhibited solution current density respectively.

3.2.10 Surface Morphology Examination

The carbon steel surface roughness and morphology were analyzed using SEM for both protected and unprotected. The SEM micrographs were obtained using a JEOL JSM-6610LV scanning electron microscope.

3.3. Results and Discussion

3.3.1 XRD Diffraction and TGA Analysis

X-ray diffraction (XRD) was employed to collect diffraction patterns of basic and amino-functionalized ACs, **Fig. 3.4**. The observed peaks at approximately $2\theta \approx 28^\circ$ are indicative of the (002) lattice planes characteristic of carbon-based structures, indicative of graphitic carbon characteristics [126]. This fact is equally pertinent to the very chaotic structure of carbon.

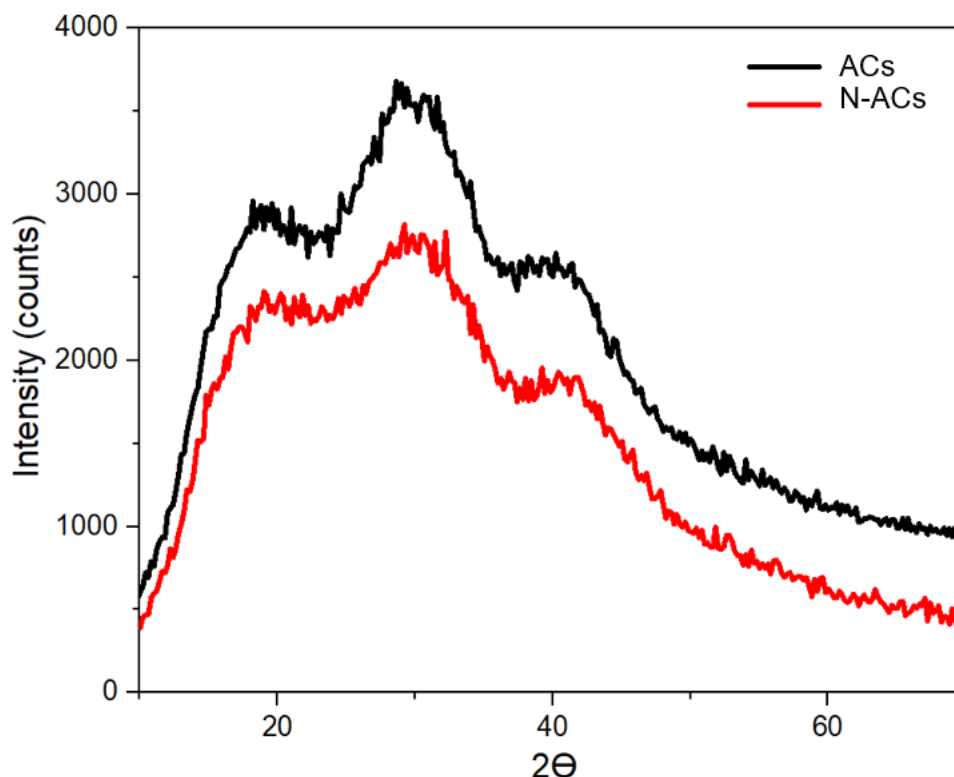


Figure 3. 4 X-ray diffraction pattern of ACs and N-ACs.

Conversely, both bare and doped ACs thermal stabilities were assessed using a thermogravimetric analysis (TGA). **Fig. 3.5** displays ACs and N-ACs stability curve. The removal of water molecules and other loosely bound species on the surface of the CQDs is responsible for the initial 15% weight loss at temperatures as high as 200 °C. ACs are stable at this temperature, as evidenced by the small weight loss. The weight decreases that occur between 200 and 500 °C are also a sign of the loss of oxygenated functional groups. The weight loss of 56.5% at about 300–400 °C is ascribed to the species that are firmly attached to ACs, hence validating the ACs' surface modification [127]. The degradation of unreacted acid and amine functionalities in the ACs is the subject of this observation. At temperatures exceeding 750 °C, the trajectory toward the total disintegration of ACs is evident in TGA.

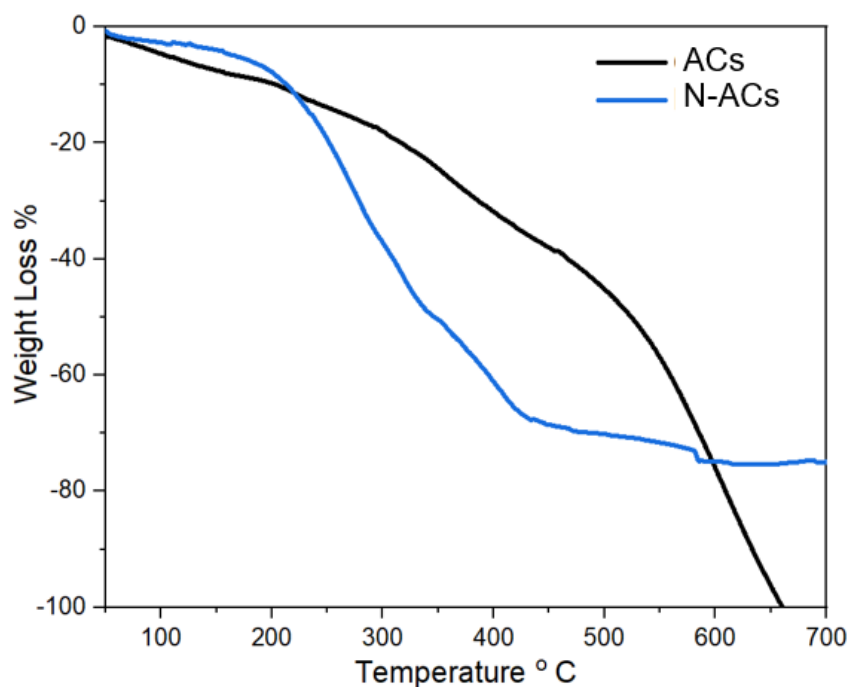


Figure 3. 5 The degradation decomposition of ACs and N-ACs

3.3.2 PSI, PAS, and PAS/N-ACs FTIR Characterization

Fig. 3.6 displays PSI FTIR spectrum, CN stretching of CONH was detected at 1190 cm^{-1} . The 1745 cm^{-1} band is assigned to $\text{C}=\text{O}$, whereas the band at 1790 cm^{-1} corresponds to the nearby carbonyl coupling effect, signifying the imide group with the five-membered ring. 2980 and 3500 cm^{-1} bands correspond to amide CH and NH stretching, respectively. The PAS spectrum displays typical absorption lines at 3300 cm^{-1} for NH and 1680 cm^{-1} for CO.[128] CN and NH stretching are represented by the bands at 1390 cm^{-1} and 1600 cm^{-1} , respectively. The absence of 1790 cm^{-1} band (cyclic imide band) in the PAS spectrum, shows imide absence and the PAS effective synthesis [129].

PAS/N-ACs FT-IR spectrum exhibits an absorption band at 3233 cm^{-1} ascribed to NH amide group stretching, while bands at 1604 and 1404 cm^{-1} for CO and CN. This implies that N-ACs take part in PSI's ring-opening reaction to generate PAS/N-ACs [130].

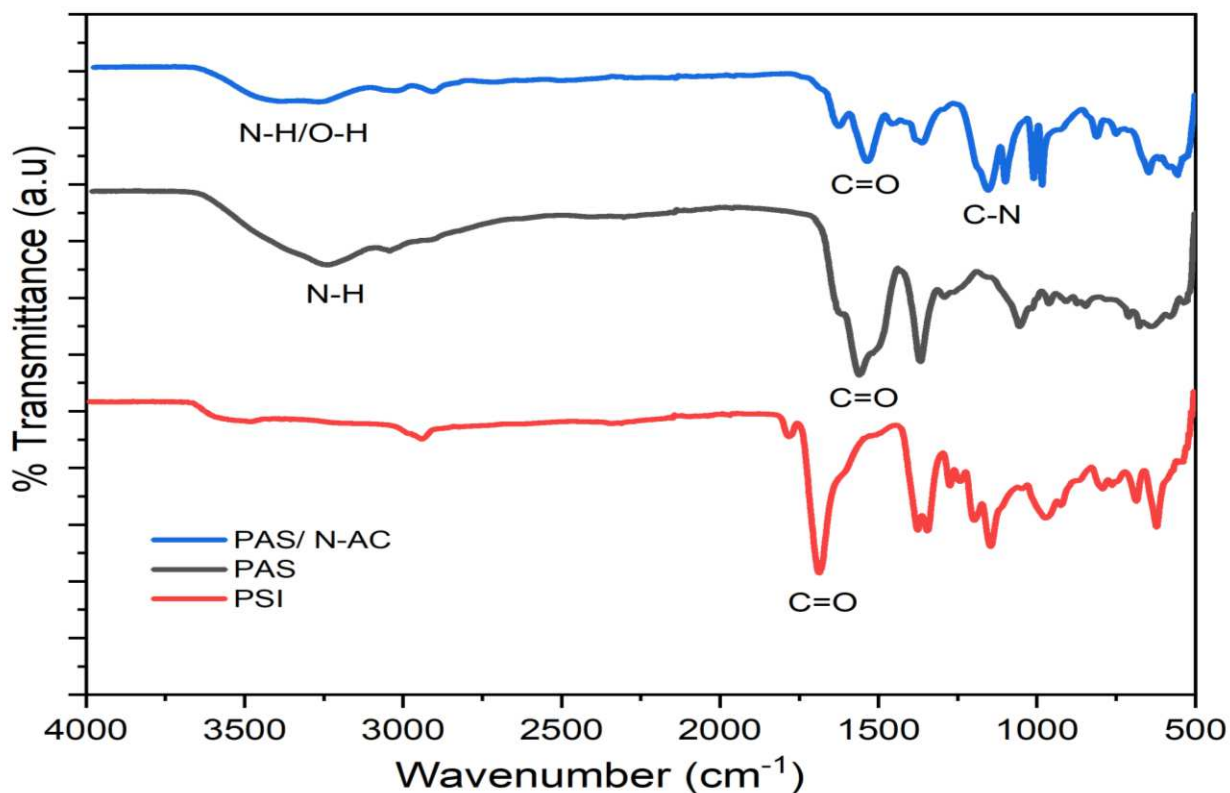


Figure 3. 6 FT-IR spectrum of synthesized PSI, PAS, and PAS/N-ACs.

PSI proton-nuclear magnetic resonance (NMR) investigation was conducted in DMSO- d_6 solvent. The signal within 5 ppm range is attributed to the methine protons, whereas the other two peaks around 3.4 and 2.5 ppm attributed to the inequivalent methylene protons of PSI in the ^1H NMR spectrum (**Fig. 3.7**). The NMR of PAS was thoroughly examined in a Deuterium D_2O solvent. (**Fig. 3.8**) illustrates the PAS ^1H NMR spectra. The spectrum shows two resonances for the methine proton at 4.3 and 4.5 ppm. The methylene protons were detected at 2.7–3.1 parts per million.

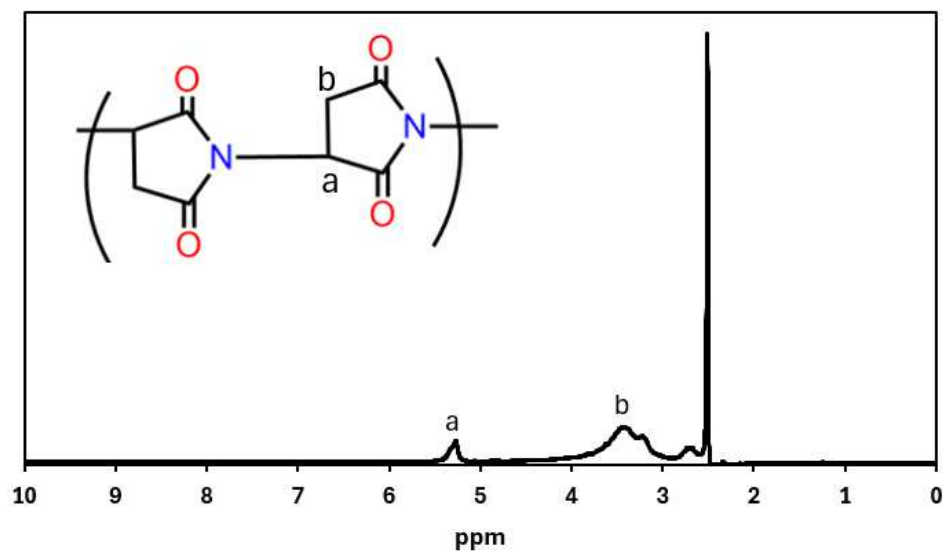


Figure 3. 7 The ^1H NMR spectrum PSI.

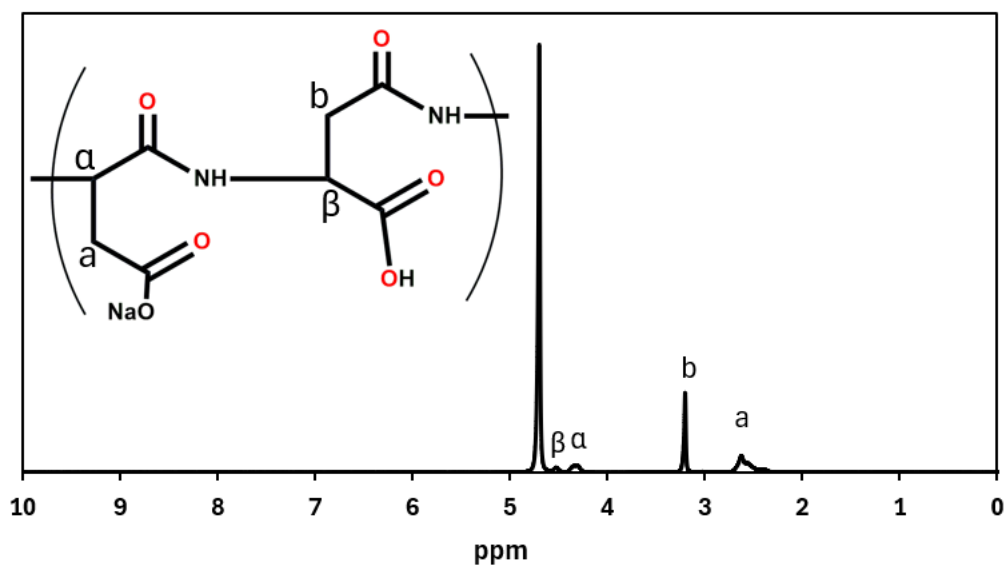


Figure 3. 8 The ^1H NMR spectrum PAS.

3.3.3 Weight Loss Experiment

The uninhibited and PAS-inhibited solutions' weight reduction measurement parameters at 25 ± 1 °C are shown in Table 1, whereas Table 2 displays the uninhibited and PAS/N-ACs inhibited solutions weight loss data at 25 ± 1 °C, 40 °C, and 60 °C.

Table 3.1 Parameters for weight reduction measurement of uninhibited and PAS-inhibited solutions at a temperature of 25 ± 1 °C (ambient).

PAS Concentration	Weight loss (g)	Corrosion rate (mm/year)	% IE
Blank	0.396	10.79	-
5 ppm	0.225	6.14	43
10 ppm	0.2064	5.63	47.8
20 ppm	0.1895	5.17	52.0
30 ppm	0.173	4.72	56.2
40 ppm	0.1822	4.97	53.9

Table 3. 2 Parameters for measuring weight reduction in blank and PAS/N-ACs inhibited media at temperatures of 25 ± 1 (ambient), 40°C , & 60°C .

Temperature	PAS/N-ACS Concentration	Weight loss (g)	Corrosion rate (mm/year)	% IE
$25 \pm 1^\circ\text{C}$	Blank	0.396	10.79	-
	5 ppm	0.0429	1.17	89.1
	10 ppm	0.0341	0.93	91.3
	20 ppm	0.0315	0.86	92.0
	30 ppm	0.0220	0.60	94.4
40°C	Blank	1.3343	36.4	—
	30 ppm	0.1375	3.75	89.3
60°C	Blank	2.1234	56.59	—
	30 ppm	0.3266	8.91	84.6

The coupon reduction weight was assessed to determine the inhibition efficacy of PAS in a 1M HCl-3.5% sodium chloride solution. **Table 3.1** illustrates the rate of corrosion and %IE at different amounts of PAS for carbon steel in the medium, derived from weight loss measurements. The inhibition initially escalated and subsequently diminished with rising PAS levels. The highest inhibition was recorded at 30 ppm PAS, reaching 56.2%. The outcome may be elucidated by organic ions' influence on corrosion. A protective layer is

created by PAS on the surface of carbon steel to mitigate corrosion, however, organic ions from PAS significantly contribute to the acceleration of corrosion. Consequently, corrosion inhibition diminished with elevated concentrations of PAS owing to the rising levels of organic ions. PAS at 30 ppm was chosen for further studies because of its superior corrosion inhibition.

Furthermore, the inhibitory efficacy of the PAS/N-ACs was assessed using various ratios of PSI:N-ACs. All analyses were conducted at 25 °C for 24 hours. The varying ratios of PSI:N-ACs demonstrated a notable inhibition efficiency improvement relative to the bare PAS, as illustrated in **Fig. 3.9**. The PAS/N-ACs synthesized from 0.6-gram Poly succinimide and 0.01-gram N-ACs exhibited a marginal enhancement in inhibitory performance relative to PAS, but 0.06-gram N-ACs demonstrated a superior improvement compared to the former. When the ratio is modified to 0.6 grams Poly succinimide and 0.1-gram N-ACs, the PAS/N-ACs exhibit a significant improvement in inhibitory efficiency, reaching about 94 percent at 30 ppm concentration. Additional increments in the Poly succinimide fractions lead to diminished efficacy of corrosion inhibition in the resultant PAS/N-ACs. Consequently, the PAS/N-ACs employed in the succeeding experiments are all synthesized from 0.6-gram of PSI and 0.1-gram of N-ACs.

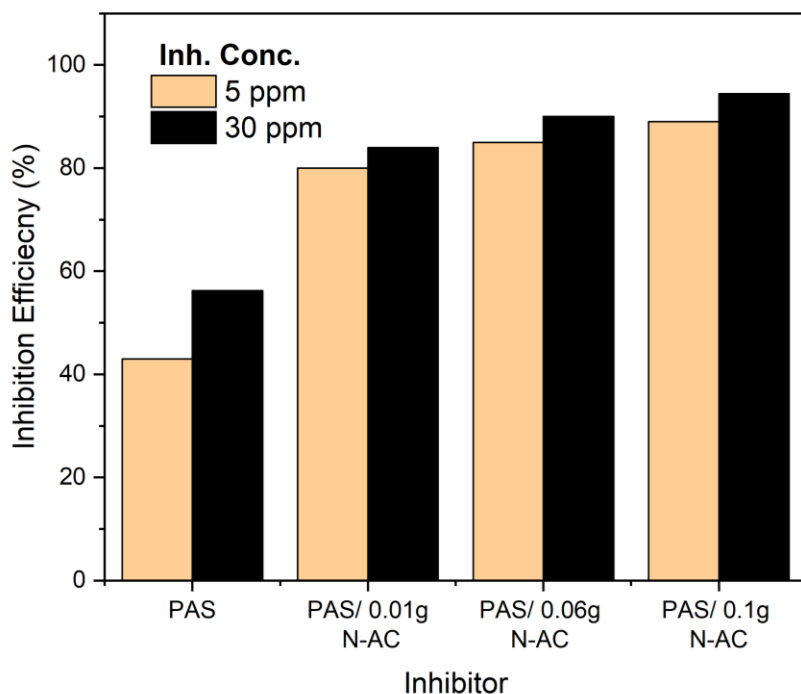


Figure 3. 9 Chart showing the inhibition efficiency with varying ratios of N-ACs.

The grafting of PAS onto N-ACs improves the modified PAS adsorption onto the surface of the metal, as indicated by the reduced PAS/N-ACs rate of corrosion as compared to the unmodified PAS solution. The rate of corrosion values for PAS/N-ACs inhibited media was lower compared to that of the uninhibited solution, and these rates decreased with increasing concentrations of PAS/N-ACs. The reduced corrosion rate for the PAS/N-ACs inhibited solution is ascribed to the adsorption of PAS/N-ACs adsorption on the steel surface, creating a protective layer protect the steel. Additionally, heteroatoms are anticipated to serve as active sites in the adsorption process due to their electron-rich nature. Consequently, PAS/N-ACs functioned as more effective corrosion inhibitors than PAS. The enhancement in inhibitory efficiency with elevated PAS/N-ACs concentration results from a greater number of adsorbed PAS/N-ACs molecules. The peak inhibitory

efficiency percentage (94.4%) was observed at 30 ppm PAS/N-ACs at 25 ± 1 °C. A subsequent weight reduction method was conducted for the blank and 30 ppm PAS/N-ACs at 40 and 60 °C to evaluate the impact of temperature on the efficacy of PAS/N-ACs. The rates of metal corrosion often rise with elevated environmental temperatures, this results from the corrosive chemicals increased mean kinetic energy. The inhibitory efficacy of PAS/N-ACs diminished from 89.3% at 40 °C to 84.6% at 60 °C, **Table 3.2**. Notwithstanding a reduced efficacy at 60 °C, the corrosion rate measured was 8.91 mm/yr at this temperature.

3.3.4 LPR Technique

LPR is a quick method mostly employed to gain a deeper understanding of material corrosion rates. From the OCP, 10 mV polarization is used to enable a direct relationship between current and potential, rendering it non-destructive. The parameters derived from the LPR approach are presented in **Table 3.3** There is no discernible trend in the inhibited solutions' E_{corr} values, which exhibited a greater tendency toward negative values relative to the blank solution. The rate of corrosion markedly diminishes in the inhibitors' presence, and this reduction is proportional to the rising concentration of the inhibitors. A much greater polarization resistance was obtained for the PAS/N-ACs inhibited solutions compared to the uninhibited ones. This signifies an increased resistance to corrosion when utilizing the PAS/N-ACs inhibitor.

Table 3. 3 LPR parameters for uninhibited and PAS/N-ACs inhibited solutions at ambient temperature.

PAS/N-ACs Concentration	E_{corr} (mV vs Ag/AgCl)	I_{corr} ($\mu\text{A}/\text{cm}^2$)	Polarization Resistance (Ω)	Corrosion rate (mm/year)	%IE
Blank	-443	2388	10.91	27.72	-
5 ppm	-449	308.4	84.47	3.580	87.08
10 ppm	-435	258.7	100.7	3.003	89.1
20 ppm	-454	242.6	107.4	2.817	90
30 ppm	-469	162.5	160.3	1.886	93.1

Enhanced inhibitory efficiency was noted with rising PAS/N-ACs concentration, attributable to the increased quantity of adsorbed PAS/N-ACs molecules on the steel surface as concentration increased. This is congruent with the weight reduction and EIS measurement results obtained.

3.3.5 Potentiodynamic Polarization (PDP)

PDP, as compared to the linear polarization resistance technique, utilizes a greater OCP polarization, spanning 200 to 400 mV, rendering it a destructive technique. Nonetheless, it

offers greater information than LPR's. While PDP approach analyzes the cathodic and anodic inhibitors' effect. **Fig. 3.10** illustrates the PDP graphs for the blank, PAS/N-ACs solutions. The classification of an inhibitor as mixed, cathodic, or anodic is based on the potential deviation extent from the OCP. A displacement of 85 mV or greater towards the cathodic or anodic arm, is categorized as anodic or cathodic, while a displacement below 85 mV on either the cathodic or anodic arm is classified as mixed type [131]. PAS/N-ACs functioned as mixed-type inhibitors, which affect the cathodic hydrogen gas evolution and the anodic metal dissolution, with cathodic type preferred. The cathodic arm is where PAS/N-ACs solutions' current densities are most impacted. **Table 3.4** displays the corrosion rate, corrosion potential, cathodic current density, anodic current density, cathodic Tafel constant, and anodic Tafel constant values.

Table 3. 4 Parameters for potentiodynamic polarization measurements of the blank and PAS/N-ACs solutions at ambient temperature.

PAS/N-ACs Conc (ppm)	β_a (mV/dec)	β_c (mV/dec)	E_{corr} (mV vs Ag/AgCl)	I_{corr} ($\mu A/cm^2$)	Corrosion rate (mm/year)	%IE
Blank	47.6	192	-467	1060	12.27	-
5 ppm	176.1	112.1	-458	120	1.392	88.6
10 ppm	76.63	63.68	-459.3	101.8	1.182	90.3
20 ppm	37.43	32.46	-464.1	94.44	1.096	91.06
30 ppm	52.55	44.17	-456	63.75	0.740	93.9

A discernible pattern in E_{corr} value across the inhibitor concentration was not observed, indicating mixed-type. The inhibited media exhibited significantly lower I_{corr} values

compared to the blank media; the diminished I_{corr} value, with adding PAS/N-ACs, results from the inhibitor adsorption on the steel surface, forming a protective layer that stops the corrosive components to reach the steel. As seen from **Table 3.4**, concentration increase led to enhanced inhibitory efficiency, with PAS/N-ACs reaching a peak efficiency of 93.9% at 30 ppm concentration, consistent with the other methodologies. The incorporation of N-ACs markedly enhanced the corrosion inhibition efficacy of the PAS.

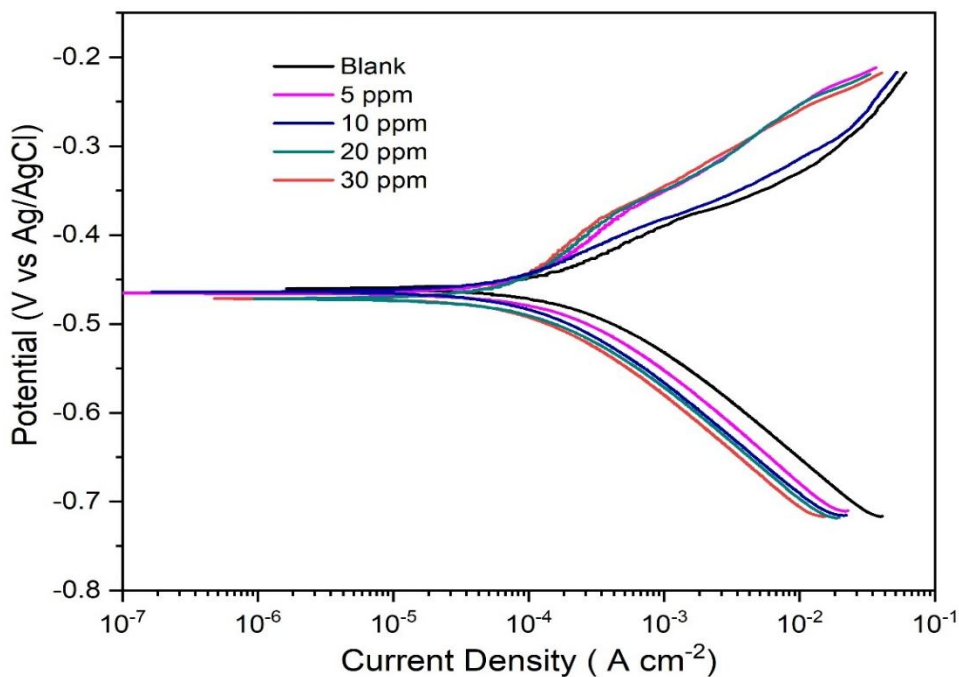


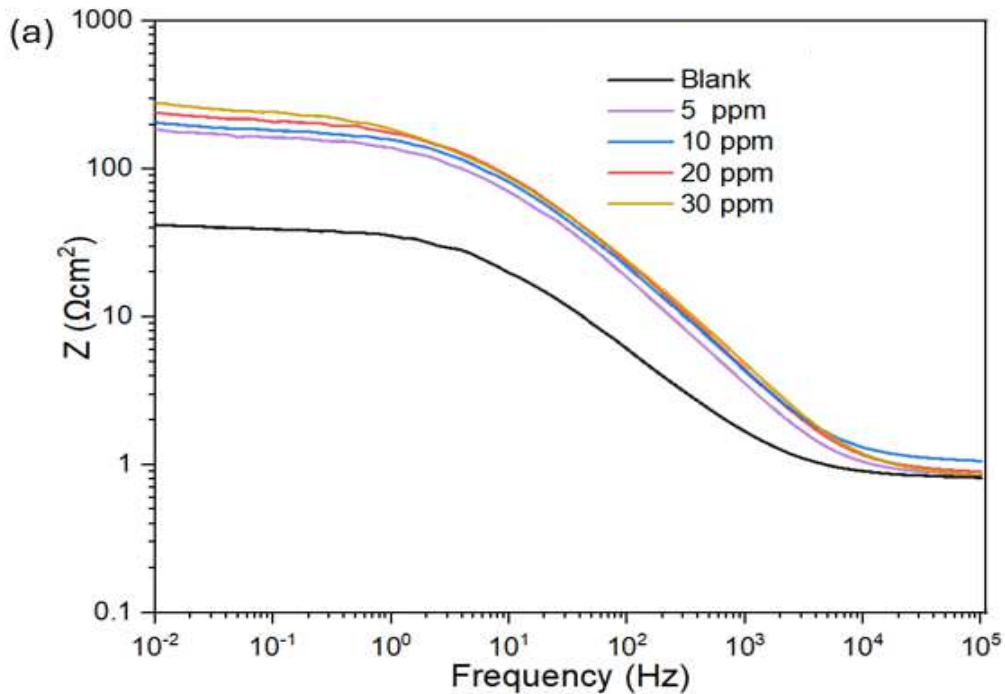
Figure 3. 10 Equivalent circuit model employed for fitting the impedance curves.

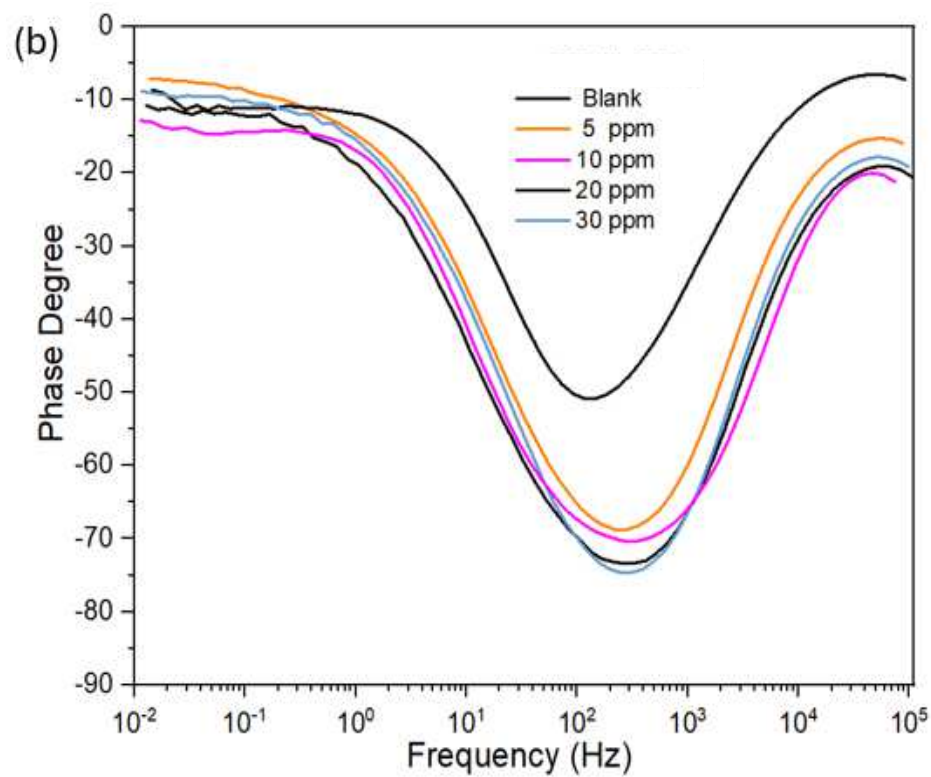
3.3.6 EIS Analysis

Fig. 3.11 presents the Nyquist and Bode data for the analyzed steel, both in the absence and presence of PAS/N-ACs at varying concentrations. As more PAS/N-ACs were added, the capacitive reactance arc diameter in the Nyquist data increased, suggesting the degree of steel corrosion in these solutions had decreased [132][133]. The capacitive reactance arc diameter was found to correlate with the inhibitor concentration. As the concentration

of inhibitor rose, the the capacitive reactance arc diameter exhibited an upward trend (**Fig. 3.11 (c)**). This occurred because the steel surface might be coated with additional PAS/N-ACs inhibitors [134]. The adsorption film grew more concentrated as the concentrations of PAS/N-ACs rose. Simultaneously, two capacitive reactance arcs were observed in all Nyquist plots, corresponding to the charge transfer and relaxation processes.

The Bode phase graphs for all test solutions displayed two peaks (**Fig 3.11 (b)**). The two distinct peaks identified in the solutions correspond to a dual time constant, and the Bode phase graphs for the prevented solutions exhibit a wider diameter than that of the blank. The diameter of the inhibited solutions rises with higher concentrations of inhibitors, according to the Nyquist plots.





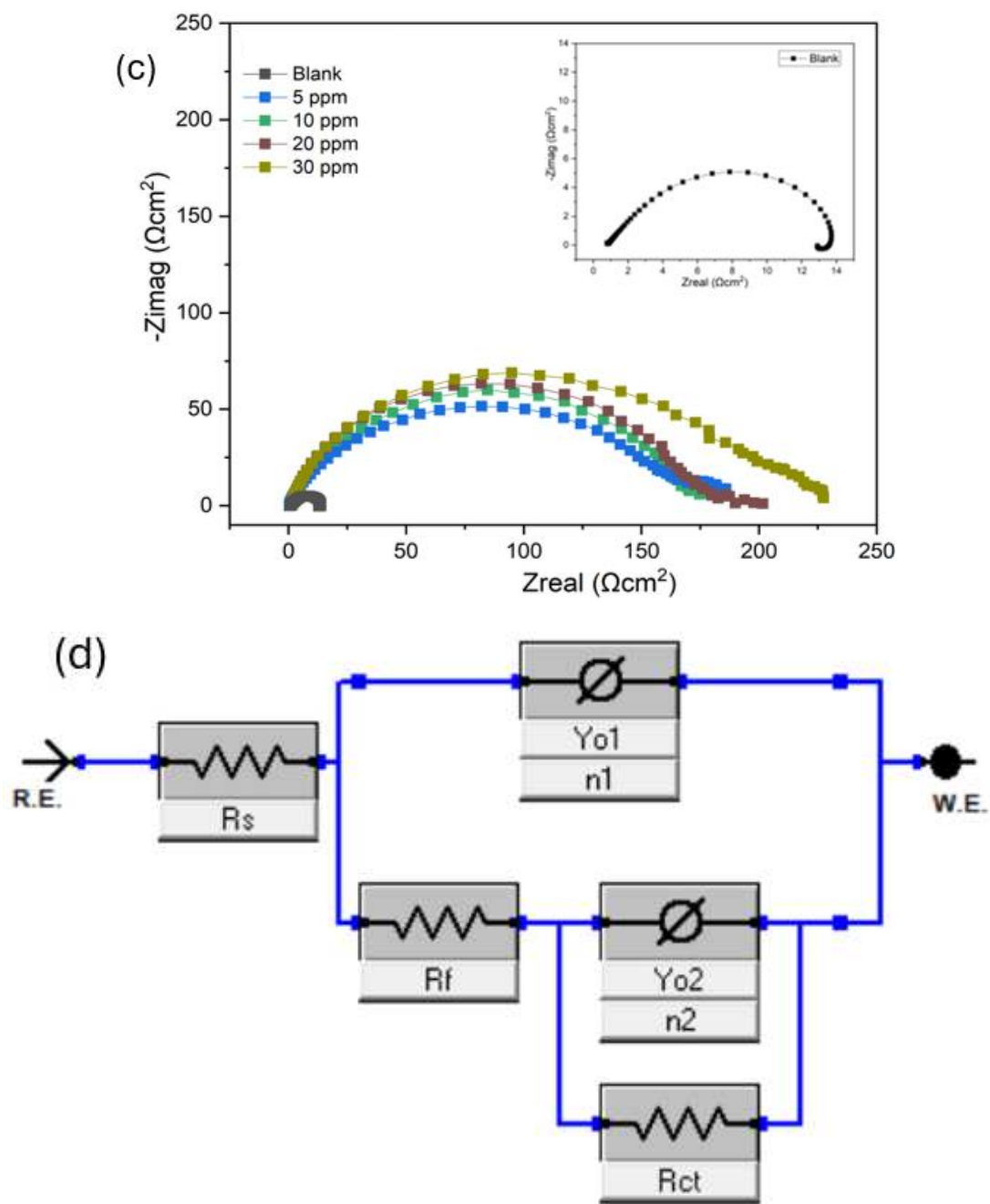


Figure 3. 11 Bode modulus (a) Bode phase of (b) Nyquist plot of blank and various PAS/N-ACs concentrations (c) equivalent circuit model employed for fitting the impedance curves.

In the Bode modulus graphs (**Fig. 3.11 (a)**), the uninhibited solution's linear segments at intermediate frequencies are less noticeable than those of the inhibited media. Additionally, the linearity increases as the inhibitor's concentration does, indicating enhanced inhibitory efficacy with increased concentration.

Table 3. 5 Parameters for Electrochemical impedance spectroscopy measurements of the blank and PAS/ N-ACs solutions at ambient temperature.

PAS/N-ACs Concentration	R_s (Ωcm^2)	CPE_f		R_f (Ωcm^2)	CPE_{dl}		R_{ct}	R_p	$\chi^2 \times 10^{-3}$	%IE
		Y ₀₁	n1		Y ₀₂	n2				
Blank	1.743	1.140	0.887	10.83	0.198	0.796	2.014	12.8	0.666	
5 ppm	1.016	0.577	0.256	58.39	0.329	0.860	50.4	108.79	821.3	88.2
10 ppm	1.039	0.475	0.133	44.83	0.406	0.791	91.8	136.7	782.4	90.3
20 ppm	1.105	0.310	0.557	42.24	0.521	0.767	109.3	151.54	819.4	91.5
30 ppm	1.003	0.207	0.812	51.91	0.824	0.546	143.0	174.91	973.3	93.4

To improve understanding of the corrosion process, the corrosion test's equivalent circuit model is displayed in **Fig. 3.11 (d)**, and the fitting parameters are compiled in **Table 3.5**. R_s is the solution resistance, R_f is the charge transfer resistance, R_{ct} is film resistance and CPE is the constant phase angle element [135] [136][137]. Comparable values of R_s were seen across various concentrations of PAS/N-ACs solutions, as shown in **Table 3.5**. When inhibitors were added, the R_f and R_{ct} values increased, indicating that the steel surface had an effective adsorption layer. Both values were simultaneously raised gradually as the inhibitor's concentration rose. In comparison, 30 ppm of the PAS/N-ACs exhibited the

greatest degree of increase. Furthermore, the trend of CPE_{dl} exhibited an inverse relationship with the R_{ct} value as the inhibitor amount rose. The corrosive solution on the steel surface was progressively substituted with inhibitors. R_{ct} and R_{ct0} represent the charge transfer resistances in the absence and presence of the inhibitor solution, respectively. The calculated η values of steel in different inhibitor solutions exhibited significant variation. Nonetheless, the η values of carbon steel in PAS/N-ACs solutions significantly improved with the increase in inhibitor concentration. At concentrations of PAS/N-ACs of 20 & 30 ppm, the η values attained 91.5% & 93.4%, respectively. Simultaneously, the efficacy of PAS/N-ACs surpassed with an increase in concentration, indicating that the protective capability of PAS was enhanced by the incorporation of N-ACs.

3.3.7 Adsorption Study Analysis

The mechanism of inhibition can be evaluated using the adsorption isotherm. Out of all the adsorption isotherms that were investigated, the Langmuir adsorption isotherm provided the best fit. Equation (7) [51] below represents the adsorption isotherm.

$$\frac{C}{\theta} = \frac{1}{K_{ad}} + \frac{a_L}{k_L} C \quad (7).$$

Where k_L and a_L are the constants of the Langmuir's isotherm, while the K_{ads} represents the adsorption equilibrium constant, and C is the inhibitor concentration. **Fig. 3.12** illustrates the correlation between C and C/θ values.

Table 3. 6 Adsorption study parameters of PAS and PAS/N-ACs.

Compound	Technique	ΔG_{ads}^o (kJmol ⁻¹)	k_{ads} (Lmg ⁻¹)	Slope	R ²
PAS/N-ACs	Weight Loss	-33.06	2.1240	1.0492	0.9997
	PDP	-32.50	1.675	1.062	0.9995
PAS	Weight Loss	-28.25	0.2548	1.6723	0.9979

The PAS/N-ACs inhibitor's calculated linear regression coefficients yielded R² values of around 0.9995 for PDP and 0.9997 for weight loss respectively, indicating a nearly perfect linear association. The R² value approaching 1 signifies that the inhibitor's adsorption process aligns with the Langmuir adsorption isotherm. A high K_{ads} signifies robust adsorption activity [138]. The corrosion-protecting efficacy of the inhibitor can be assessed using K_{ads}. The K_{ads} values for PAS/N-ACs were around 2.1240 and 1.675 L/mg, respectively. The order of K_{ads} for the two inhibitors was PAS/N-ACs > PAS. The steel in the PAS/N-ACs solution exhibited the highest K_{ads} value, indicating the most robust adsorption capacity of the inhibitor at the steel/solution interface. **See Table 3.6.**

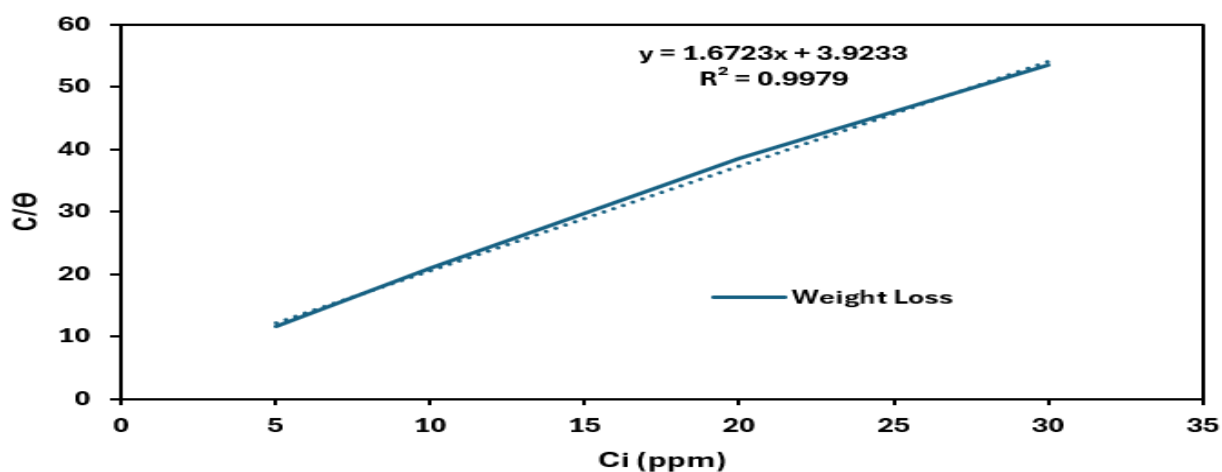
K_{ad} is associated with Gibb's free energy of adsorption ΔG_{ads}^o as demonstrated in equation (8) [139].

$$\Delta G_{ads}^o = -RT\ln(1 \times 10^6 K_{ads}) \quad (8).$$

Here, R denotes the molar gas constant, while T represents the absolute temperature (298K).

A physisorption adsorption mechanism is said to be physisorption adsorption if its ΔG_{ads}^o values ≤ -20 kJ/mol. It is suggested that this is characterized by electrostatic interactions between charged inhibitor molecules and charged metal surfaces. The transfer of lone pairs of electrons from the inhibitor molecules into the metal's unoccupied d-orbital, on the other hand, is what makes a mechanism of chemisorption adsorption. This is shown for ΔG_{ads}^o values ≥ -40 kJ/mol. The range of ΔG_{ads}^o values between -20 and 40 kJ/mol indicates a mixed-type adsorption mechanism that combines chemisorption & physisorption [140].

The studied compounds exhibit ΔG_{ads}^o values of -28.25 kJ/mol for PAS for weight loss, and -33.06 and -32.5 kJ/mol for PAS/N-ACs for the weight reduction and PDP experimental results, respectively. Consequently, the molecule can be described as adsorbed onto the steel surface of the steel through both mechanisms: physisorption and chemisorption. It is hypothesized that PAS/N-ACs contribute lone pairs of electrons to the metal's unoccupied d-orbitals while interacting with the charged steel surface to adsorb onto the carbon steel surface. A negative ΔG_{ads}^o value indicates a spontaneous and stable adsorption process.



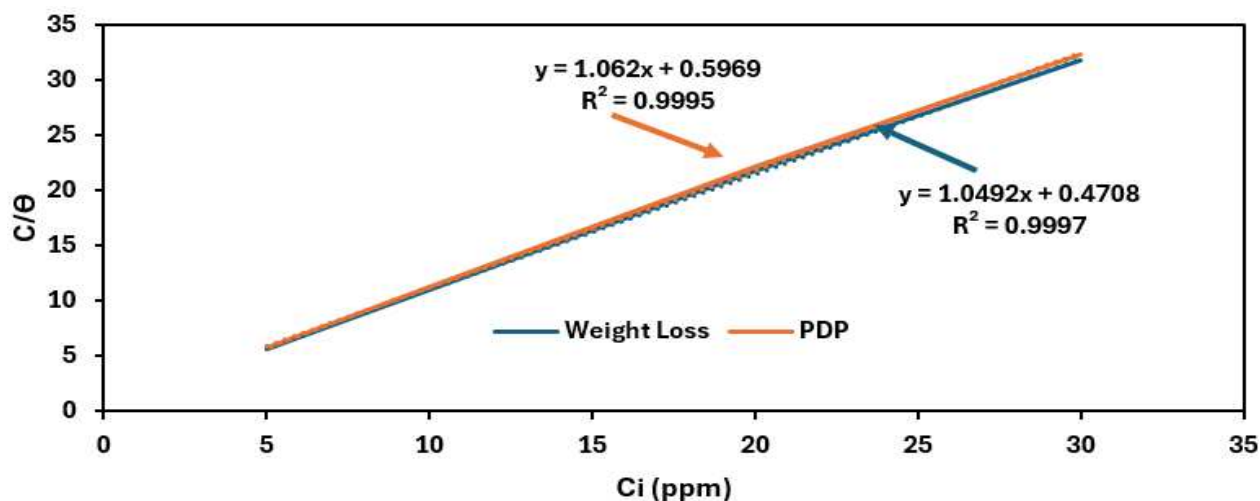


Figure 3. 12 Adsorption study of PAS in weight Loss technique (a) and PAS/N-ACs(b) in Weight Loss and PDP technique.

3.3.8 Inhibition Mechanism

The protective mechanisms of the steel under examination in various test media are depicted in **Fig. 3.14**. The essential nature of the adsorption layer on the steel surface in both PAS and PAS/N-ACs solutions is described by a physicochemical adsorption behavior, according to the analysis of Langmuir adsorption isotherms ($-40 \text{ kJ/mol} < \Delta G_{ads}^0 < -20 \text{ kJ/mol}$). The aggregation action of aromatic heterocycles on the steel surface was attributed to physical adsorption in the case of PAS. The heteroatom of nitrogen was responsible for chemical adsorption because, because of its lone pair of electrons, it could easily occupy the empty d-orbitals around the iron atoms, creating a coordinate connection between the heteroatom and steel (**Fig 3.14**). However, because of the restricted distribution and localized deposition of PAS, only a small portion of the steel surface was exposed to the corrosive medium (**Fig 3.13a**). The adsorption behavior of the PAS/N-ACs inhibitor was of a mixed type, with the steel/solution interface exhibiting the strongest

contact, as indicated by the highest K_{ads} value. The produced PAS/N-ACs inhibitor may uniformly adsorb onto the steel surface, thus establishing a robust physicochemical interaction. Subsequently, the direct interaction between the corrosive liquid and the steel surface was mitigated by the establishment of an adsorption coating (**Fig 3.13b**). To sum up, the PAS/N-ACs inhibitor maximizes the protection of carbon steel by combining the beneficial properties of both PAS and nitrogen-doped carbon dots.

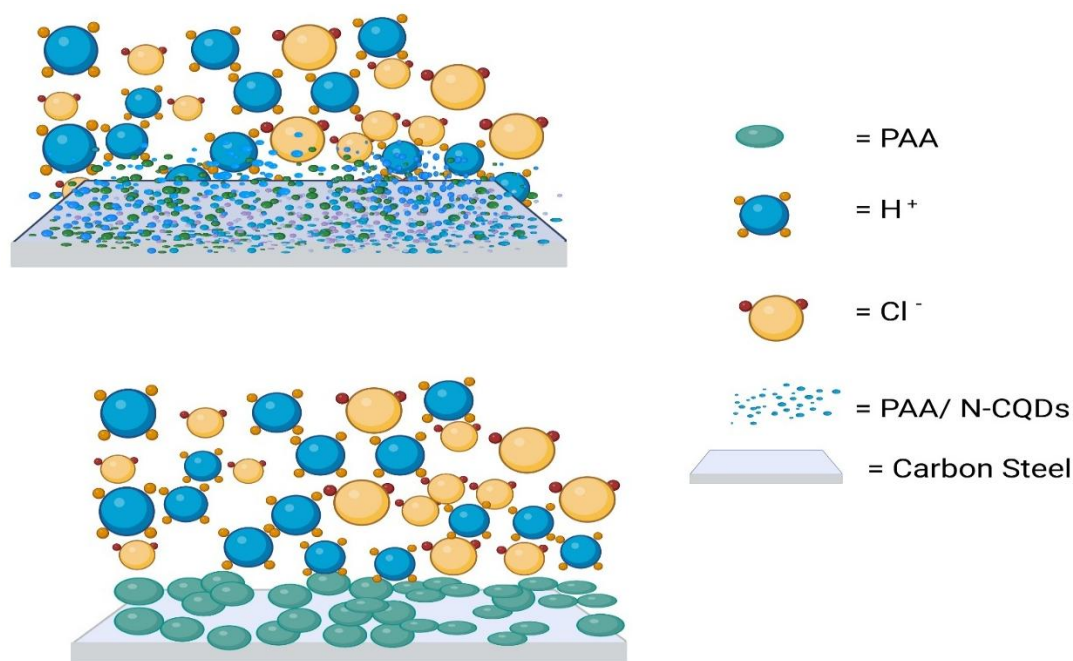


Figure 3. 13 PAS/N-ACs (a) and PAS (b) adsorption layer.

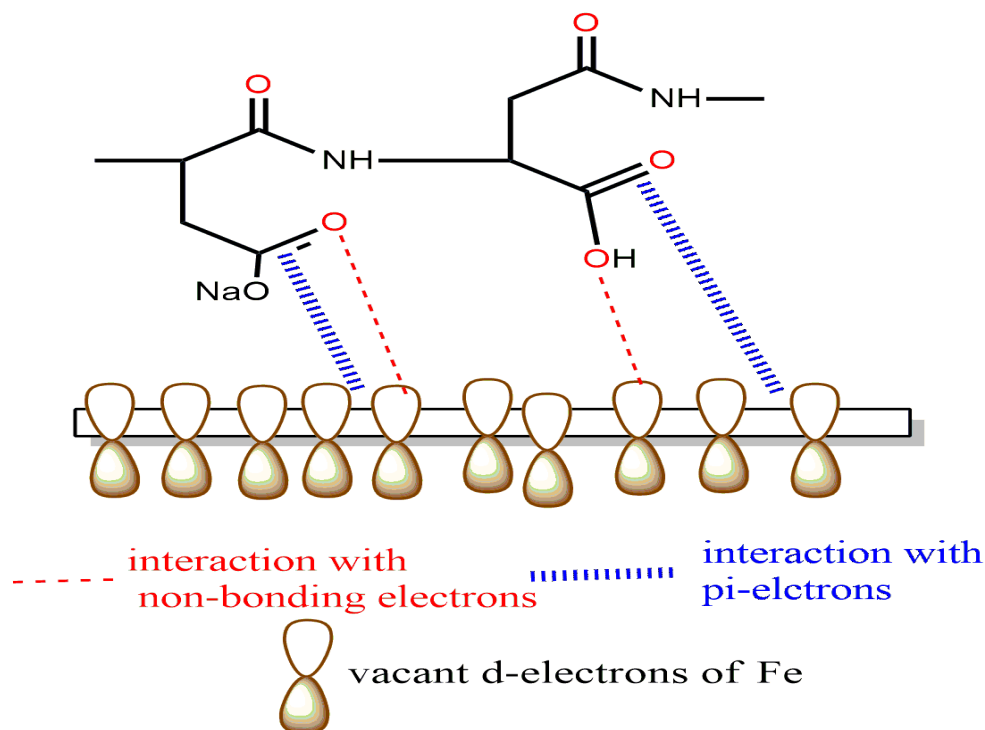


Figure 3. 14 The inhibition schematic diagram of PA for carbon steel in the corrosive medium.

3.3.9 SEM Analysis

Scanning electron microscopy images of carbon steel taken before and after a 24-hour immersion in a 1M HCl-3.5% NaCl solution, both with and without 30 ppm of PAS/N-ACs, are displayed in **Fig. 3.15**. The freshly ground steel surface is quite flat, with minor polishing markings visible, **Fig. 3.15(a)**. Without inhibitors, the image of the steel surface, **Fig. 3.15(b)**, showed extensive corrosion, as seen by the substantial cracks. However, the steel surface's corrosion damage was greatly reduced after submersion in the inhibited solution **Fig. 3.15 (c)**, with fewer corrosion artifacts than the damaged specimen in the uninhibited solution. This results from the inhibitors' facilitation of a protective layer formation.

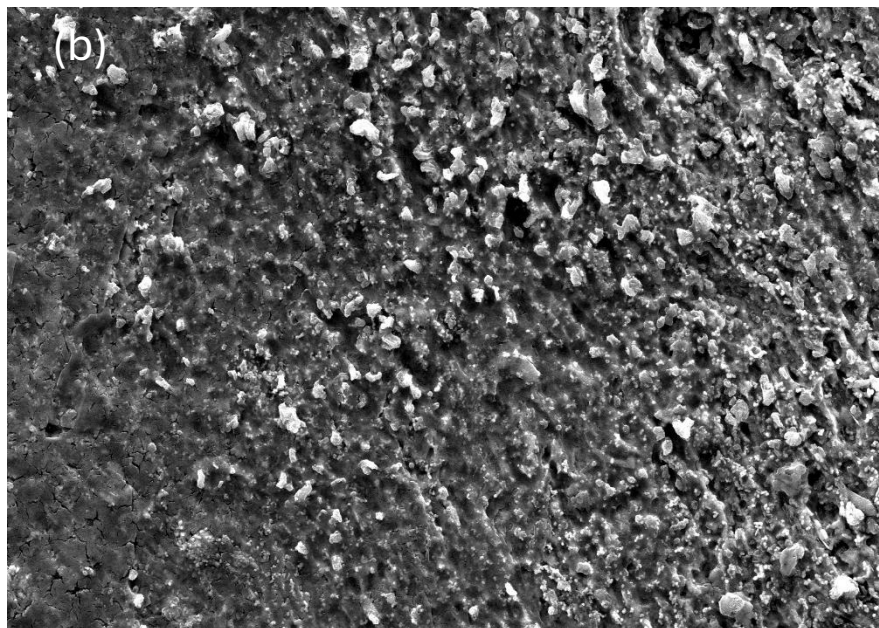
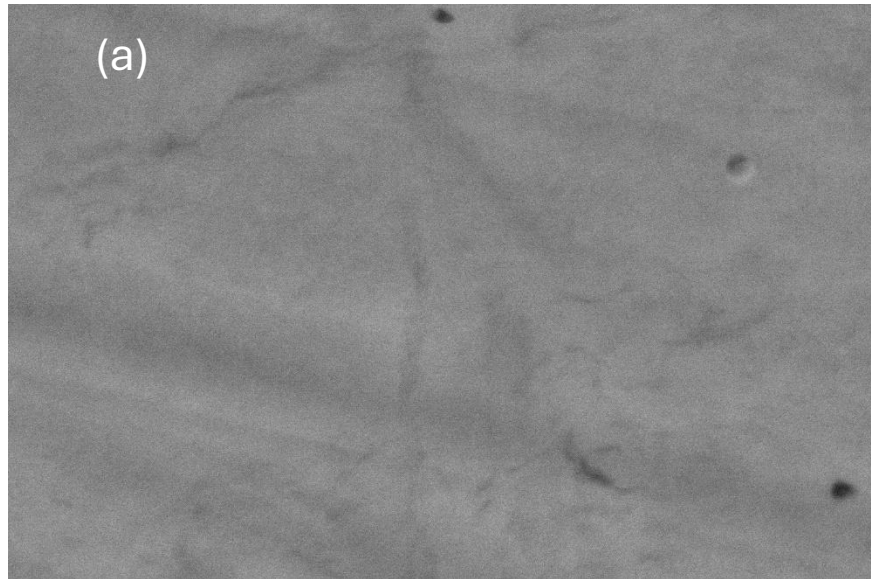




Figure 3. 15 SEM images of the bare carbon steel (a) after 24h immersion in 1m HCl-3.5% NaCl solutions in the absence (b) and presence of 30 ppm PAS/N-ACs (c)

CHAPTER 4

CORROSION INHIBITION OF POLY-ASPARTIC ACID-CO-MELAMINE AGAINST LOW-GRADE CARBON STEEL (C1018) IN 1M HCL-3.5% NACL MEDIUM, AN EXPERIMENTAL AND THEORETICAL STUDY

4.1. Introduction

Corrosion is a process where metals gradually deteriorate when exposed to environments like air, moisture, or soil [141]. This exposure triggers chemical and electrochemical reactions that transform the original metal into more stable compounds [142][143]. According to International Union of Pure and Applied Chemistry, corrosion can be defined as an irreversible interaction between a substance and its surrounding, leading to the consumption or dissolution of the substance by a component in the surrounding [144][145][146]. Corrosion creates environmental, economic, conservation, as well as safety risks in engineering fields [147]. Corrosion impacts the global GDP by 3-4% annually. The implementation of corrosion protection methods has the potential to cut annual costs by up to 35%, reducing the previously estimated \$875 billion expenditure. Preventing corrosion is crucial not only to limit financial losses but also to tackle environmental and safety risks [148][149] [150] [151][152]. Residual corrosion products pose a threat of contaminating transported cargo, whether in gas or liquid form, highlighting the importance of effective corrosion management [153][154]. To manage corrosion, industries rely on four primary methods namely cathodic protection, inhibitors dosage, utilization of corrosion-resistant materials, and organic coatings. Among these, inhibitors addition stands out as the most practical, economical, and effective approach for safeguarding industrial facilities and operations, providing a reliable layer of protection in

harsh environments. Inhibitors are specialized compounds that, even when used in minimal quantities, effectively reduce the rate of corrosion in hostile conditions [20][19][103][155][156]. They serve as a crucial line of defense, mitigating material degradation and extending the lifespan of equipment and infrastructure in various industries. They mitigate corrosion by creating a protective barrier, forming an adsorbed layer on the surface, or interfering with the reactions to slow down the degradation process [157][158][159]. Corrosion inhibitors (CIs) are primarily composed of organic compounds featuring multiple bonds, heteroatoms such as oxygen and nitrogen, and heterocyclic or aromatic rings in their molecular structure [26][160]. These functional sites facilitate adsorption onto metal surfaces and enable interaction with vacant metal orbitals, leading to the formation of a thin protective layer through coordinated covalent bonding [26].

Carbon steel is among the materials used globally, serving industries like pharmaceuticals, medicine, power generation, oil refining, electroplating, automotive, and aerospace industries. In 2019 alone, global production of crude steel reached approximately 1,391 million tons, underscoring carbon steel's critical role in society. Nevertheless, carbon steel is highly prone to corrosion under different environments, as well as atmospheric exposure. Recent years have seen significant research focused on steel corrosion prevention, highlighting its electrochemical nature where initial electron and Fe^{2+} formation at the anode leads to complex reactions resulting in rust formation [161]. Numerous studies on steel corrosion prevention have emerged in the past years [162]. These generated electrons transverse the steel, which reacts with water and oxygen forming hydroxyl ion or with proton for hydrogen production. The Fe^{2+} then dissolves, later reacting with hydroxyl ions to create $\text{Fe}(\text{OH})_2$, which upon oxidation by air, form the typical red rust, indicating

hydrated ferric oxide [163]. Organic inhibitors are extensively utilized in a variety of aggressive environments encompassing both low and high molecular weight compounds, to protect steel from corrosion [37]. However, their application is limited to nonpolar electrolytes due to their low solubility [164]. Among the promising candidates for eco-friendly corrosion inhibitors are those that are naturally occurring and biodegradable. Amino acids, with their intrinsic metal-binding capabilities and favorable environmental profiles, have garnered attention for their corrosion inhibitive properties [2][165]. Aspartic acid, a non-essential amino acid, is noted for its dual functionality derived from its amine and carboxyl groups, which facilitate strong adsorption onto metal surfaces through chemisorption and physisorption mechanisms [166][167][168][169]. Melamine, a triazine derivative, is renowned for its thermal stability and strong adherence to surfaces [170], which can synergistically enhance corrosion resistance when used in conjunction with amino acids. The integration of melamine into amino acid-based corrosion inhibitors could potentially create a layer on the surfaces, mitigating the corrosive effects of chloride ions. A study carried out by Ayman El-Faham and colleagues [171] examined the corrosion prevention properties on three derivatives of melamine on steel in an acidic medium. All the derivatives displayed exceptional corrosion inhibition efficacy as demonstrated by the result. Liao and co-workers [172] examined the efficacy of 5 similar derivatives of melamine in preventing corrosion on mild steel in a hydrochloric medium. Two derivatives possessing a greater number of substituents and longer chains exhibited superior protection efficiency, whereas the remaining three inhibitors showed low protection efficiencies.

This study focuses on the synthesis and evaluation of PSAM as carbon steel (C1018) corrosion inhibitor in a simulated seawater solution containing 1 molar hydrochloric acid.

The inhibitory efficacy was analyzed via gravimetric measurement and electrochemical analysis. FTIR and ^1H NMR were utilized for PSAM structural characterization. Additionally, SEM was employed to examine the morphological images between PSAM-inhibited and blank steel surfaces in the corrosive environment. To gain further insight into PSAM's electronic properties, frontier molecular orbitals, and reactivity parameters, density functional theory (DFT) calculations were performed.

4.2. Experimental

4.2.1. Chemicals and Material

Melamine (Sigma Aldrich, 99%), L-aspartic acid (Sigma-Aldrich, 98%), *o*-phosphoric acid (Supelco, 85%), methanol (Honeywell, 99.8%), acetone (Honeywell, 99.5%), HCl (Fischer Scientific, 37^W/_v %), NaCl (Fischer Scientific), carbon steel (C1018). Distilled water was obtained from Thermo-scientific Distillation Apparatus (Model A1015-B-61). Analytical reagent grades were employed and used directly as received.

4.2.2. Synthesis of PSAM

Aspartic acid (10 g, 0.0752 mol) was mixed with 85% *o*-phosphoric acid (1 g, 8.67 millimole) at ambient temperature for a period 15 minutes. The resulting mixture was transferred to a 150-millilitre flask connected to thermometer, condenser, nitrogen inlet, and magnetic stirrer, then heated to 200°C for 8 hours. The obtained product was thoroughly washed with 200 mL of water until neutral, followed by 200 milliliters of methanol, and subsequently dried at 85°C under lower pressure to produce poly succinimide (PSI). PSI hydrolysis was carried out by dissolving 3 grams of PSI in a solution containing 1.4 grams of sodium hydroxide (stoichiometric to succinimide

residues) and 20 mL of deionized water under cooling conditions. After one hour stirring, the mixture was added to 300 mL of methanol, leading to the precipitation of the product. The precipitate was filtered and dried at 40°C, yielding sodium poly(aspartate) (PAS-Na). Finally, 1.1575 grams of melamine was added to PAS-Na, and the mixture was stirred for 1 hour before being separated by centrifugation. Deionized water was used to wash the obtained solid thrice, dried, and preserved. PSAM synthesis scheme is shown in **Fig. 4.1**.

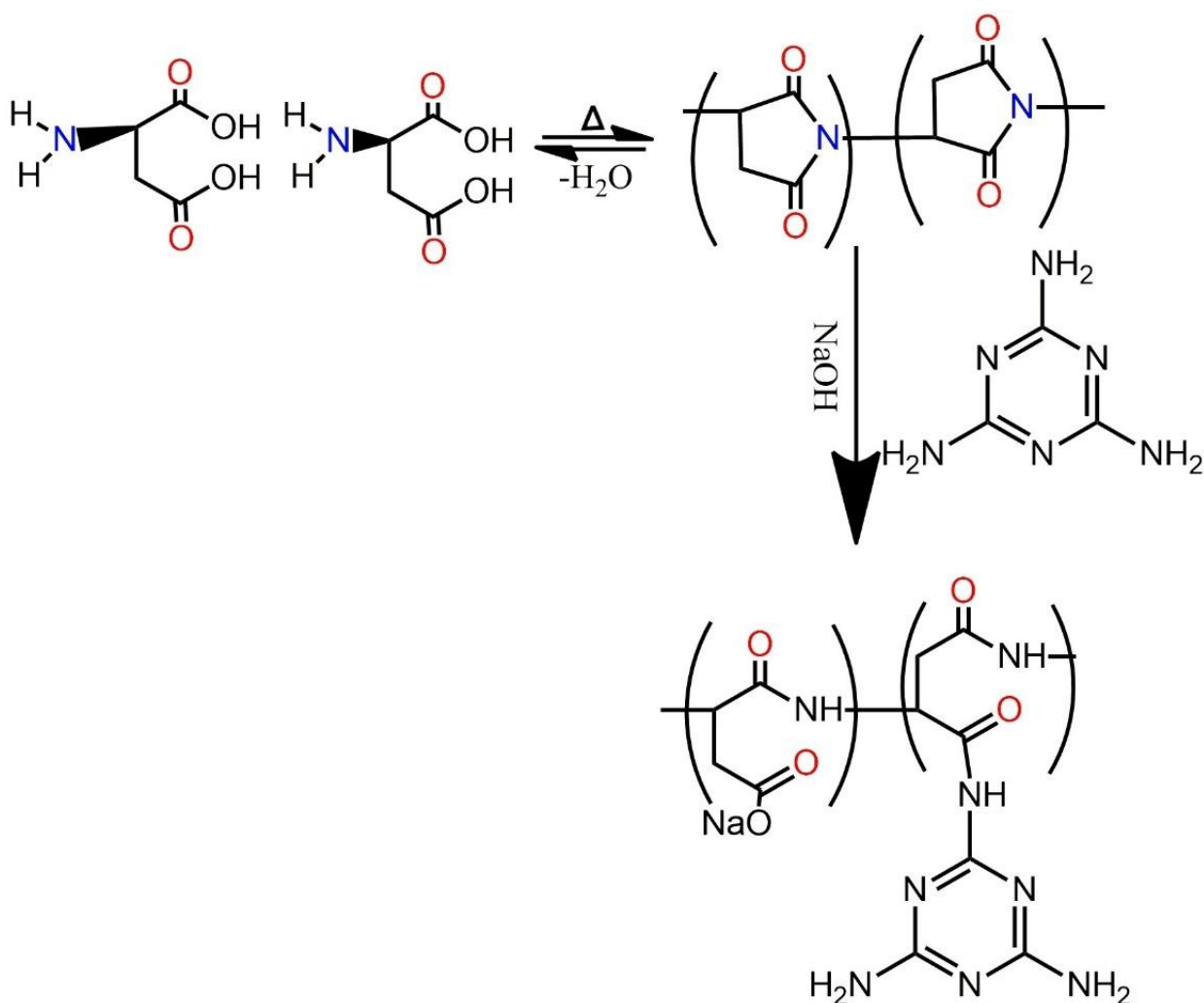


Figure 4.1: Schematic of PSAM synthesis.

4.2.3. Characterization of PSAM

PSAM was characterized using ^1H NMR and FTIR spectroscopy. FTIR spectra were obtained using an Attenuated Total Reflectance (ATR) setup on a Smart iTR NICOLET iS10 spectrometer. A frequency range of $400 - 4000\text{ cm}^{-1}$ with a resolution of 4 cm^{-1} was used to analyze the functional groups present in PSAM. PSAM ^1H NMR was collected using the Bruker AVANCE IIIHD 400 MHz NMR spectrometer in deuterated dimethyl sulfoxide.

4.2.4. Testing Preparation

The specimen (C1018 Carbon steel) for the gravimetric test was shaped into $2.5\text{cm} \times 2.5\text{cm} \times 0.3\text{cm}$ dimensions, providing 15.5cm^2 as a total surface area. In contrast, the specimen for the electrochemical analysis was shaped into a cube with 1.0 cm in all sides, embedded in an epoxy/hardener mix. The preparation involved sanding the specimens with silicon carbide sheets from grit 120 to 800. After cleaning with the use of distilled water and acetone, the product was dried. Various amounts of PSAM (150, 200 and 250 ppm) were prepared in the corrosive medium (1M HCl-3.5% NaCl solution) for testing. The corrosive medium was prepared by dissolving $\&\%$ NaCl in 2000 mL of distilled water. This NaCl solution was then used to dilute 37% HCl to achieve the desired corrosive environment (1M HCl-3.5% NaCl solution).

4.2.5. Weight Loss Measurements

The gravimetric measurement also known as weight loss analysis, known for its directness and accuracy, was utilized to evaluate the corrosion inhibiting efficacy of PSAM. This test

involved weighing square stainless-steel specimens Both prior to and following dipping them in a 100-milliliter volume of a 1M HCl-3.5% NaCl solution with varying PSAM concentrations, kept at constant temperatures for 24 hours.

4.2.6 Electrochemical Measurements

Electrochemical measurements were conducted using a three-electrode glass cell with a Gamry Reference 3000 Potentiostat/Galvanostat/ZRA linked to a personal computer via a USB electrochemical interface and were executed at ambient temperature. A steel specimen served as the working electrode, a graphite rod as the auxiliary electrode, and a Ag/AgCl electrode as the reference electrode. The open circuit potential (OCP) was determined by submerging the working electrode in a 3.5% NaCl test solution for 3600 seconds. EIS measurements were conducted at corrosion potentials (OCP) over the frequency range of 10 millihertz to 100 kilohertz, utilizing a waveform amplitude of 10 mV. For PDP studies, the potential was scanned from -250 to +250 millivolt at a scan rate of 0.25 mV s⁻¹ scan rate. LPR was measured at 0.12 millivolt per second scan rate within a potential range of -10 mV to +10mV. All data pertaining to electrochemical measurements were examined with the Gamry Echem program.

4.2.7. Surface Morphology Examination

The surface roughness and morphological features of C1018, both in PSAM presence and absence were examined using SEM. SEM micrographs were captured using a JEOL JSM-6610LV scanning electron microscope to assess surface modifications induced by corrosion and inhibitor protection.

4.2.8. Density Functional Theory (DFT)

The B3LYP functional was used to assess the electronic properties of PSAM. The calculations were performed with Gaussian 09 software, employing the 6-31G+(d,p) basis set [173]. the inhibitor's electronic properties, which play a vital role in determining its effectiveness, were analyzed [174][175]. Reactivity parameters were computed from the frontier molecular orbitals (FMOs) energies using Equations (9-15). These parameters are essential for understanding the inhibitor's potential performance.

$$\Delta E = E_{\text{HOMO}} - E_{\text{LUMO}} \quad (9).$$

$$\text{IP} = -E_{\text{HOMO}} \quad (10).$$

$$\text{EA} = -E_{\text{LUMO}} \quad (11).$$

$$\eta = \frac{1}{2} (E_{\text{HOMO}} - E_{\text{LUMO}}) \quad (12).$$

$$\sigma = \frac{1}{\eta} \quad (13).$$

$$\chi = -\frac{1}{2} (E_{\text{HOMO}} + E_{\text{LUMO}}) \quad (14).$$

$$\Delta N = \frac{\chi_{\text{Fe-Xinh}}}{2(\eta_{\text{Fe}} - \eta_{\text{Inh}})} \quad (15).$$

4.3. Results & Discussion

4.3.1. PSAM Characterization

The FTIR spectrum (**Fig. 4.2**) of the grafted copolymer reveals an absorption peak in the range of 3000-3400 cm⁻¹, corresponding to N-H stretching, which confirms the presence

of amine groups. A peak around 2850 cm^{-1} is observed for C-H stretching, while the absorption band at $1599\text{--}1689\text{ cm}^{-1}$ is attributed to C=O stretching vibrations. Additionally, the distinct peak at 1630 cm^{-1} confirms the presence of a C=N bond from the triazine ring. These characteristic spectral features validate the successful synthesis of the PSAM-grafted copolymer.

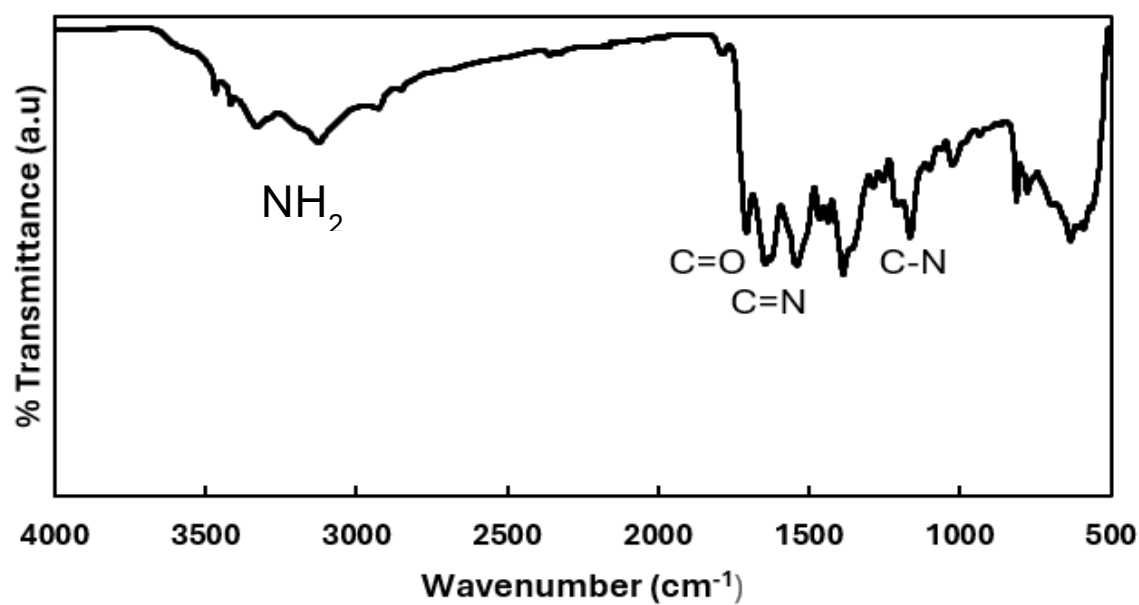


Figure 4.2: PSAM FTIR spectrum.

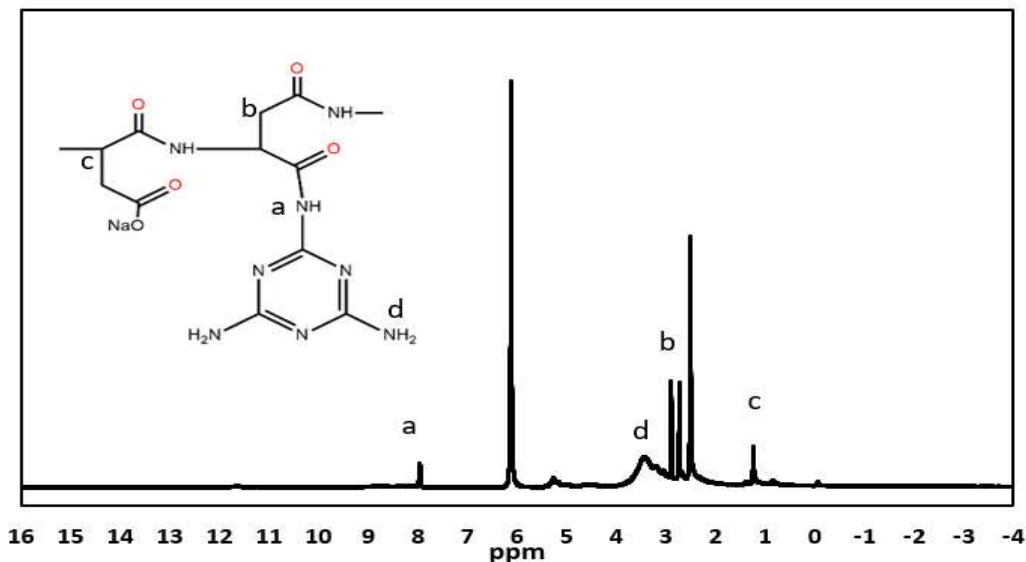


Figure 4.3: ^1H NMR spectrum of PSAM.

The ^1H NMR of PSAM in DMSO (**Fig. 4.3**) displays characteristics signals at 1.2, 2.4, 3.5 and 8 ppm. The signals at 1.2 ppm correspond to CH_2 protons, The peak at 8 ppm is attributed to the amide bond, further supporting the successful synthesis of PSAM. These findings, along with the FTIR analysis, confirm that the desired grafted copolymer has been successfully synthesized.

4.3.2. Weight Loss Tests

Table 1 lists the gravimetric measurement result for the inhibited and blank solutions at $25 \pm 1^\circ\text{C}$. Equation (16). was used to determine the corrosion rate [176] [177][178].

$$CR = \frac{W \cdot 8.79 \cdot 10^4}{D \cdot A \cdot T} \quad (16).$$

Where The variable W represents the average weight reduction in grams.

A = surface area measured in square centimeters.

T = represents the immersion time (hours).

D= Coupon's density (7.87 g/cm³).

The inhibition efficacy percentage was determined with Equation (17).

$$\%IE_{wl} = \left(\frac{W_0 - W_i}{W_0} \right) \times 100 \quad (17).$$

Where inhibited solution weight loss is denoted by W_i , while blank weight loss is represented by W_0 .

The solution containing PSAM exhibited a slower corrosion rate compared to the uninhibited solution. The rate of corrosion decreased from 10.79 mm/yr in PSAM absence to 1.415 mm/yr at 150 ppm, achieving a lowest of 0.785 mm/yr at 200 ppm, with an inhibition efficiency of 93%. The rate of corrosion decreased as the PSAM concentration rose from 150 to 200 ppm but slightly increased at higher concentrations (**Table 4.1**). The corrosion rate reduction with PSAM is related to the inhibitor binding to the surface of the metal and forming a protective layer, preventing the dissolution of steel in the corrosive medium. The inhibition efficiency improved from 87% at 150 ppm to 93% at 200 ppm, which was the most effective concentration. At 250 ppm, the inhibition efficiency decreased due to saturation, where the adsorbed inhibitor molecules interacted with un-adsorbed ones, leading to the desorption of the inhibitor and negatively impacting the effectiveness. The rate of corrosion in the PSAM solutions (**Table 4.1**) remained significantly lower as to the blank.

Table 4. 1: Blank and PSAM solutions weight loss measurement analysis at ambient temperature.

PSAM Conc (ppm)	Weight loss (g)	Corrosion rate(mm/yr)	% I.E
Blank	0.396	10.79	-
150	0.0457	1.415	87
200	0.025	0.785	93
250	0.031	0.964	91.0

4.3.3. Electrochemical Impedance Spectroscopy

Fig. 4.4 shows three distinct solution plots. Both the Nyquist plots for the PSAM and uninhibited mediums exhibit two semicircular capacitance loops, each corresponding to a double time constant observed in the bode plots. At lower frequencies, the time constant ($R_f//CPE_f$) is attributed to the porous PSAM film, while the ($R_{ct}//CPE_{dl}$) time constant at higher frequencies reflects the double layer formation at the metal/electrolyte interface. All the inhibited solutions impedance plots resemble the uninhibited, which shows the inhibitor diminishes the corrosion without affecting the fundamental mechanism. Imperfection is a common characteristic of solid electrodes, resulting from surface inhomogeneity, roughness, and irregularities in the electrode surface. The Nyquist plots diameter (**Fig. 4.4**) of the PSAM solutions exceeded that of the uninhibited solution, increasing with higher inhibitor concentrations, peaking at 200 ppm, and subsequently declining at elevated concentration, consistent with the weight loss measurements.

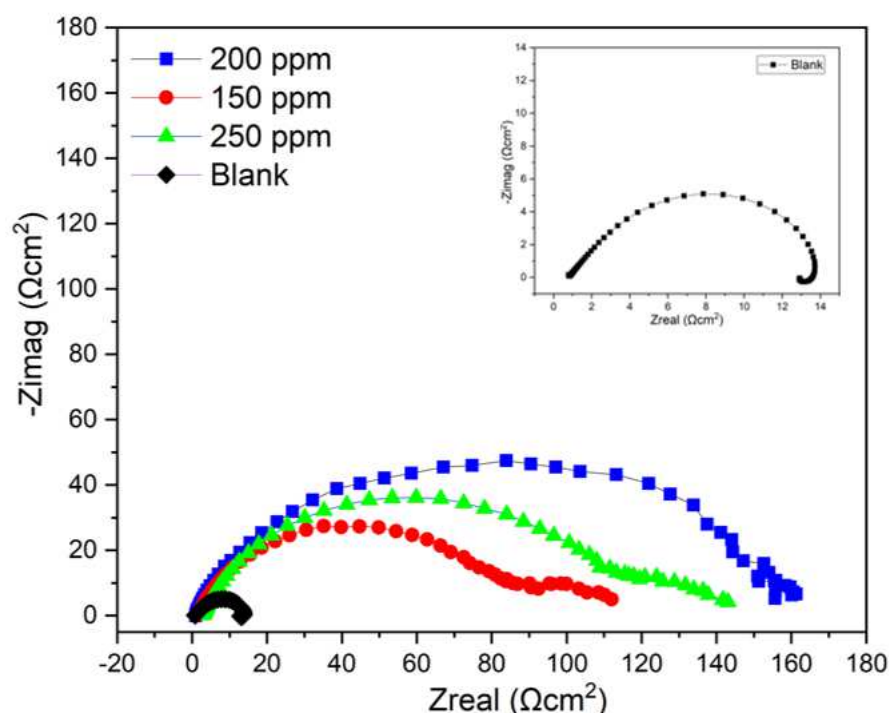


Figure 4.4: Nyquist plot of uninhibited and various PSAM concentrations.

The improved corrosion resistance of the protected steel is attributed to PSAM adsorption onto the surface creating a protective film which prevents the steel from aggressive agents. As the inhibitor concentration rise, a greater interaction between PSAM and the metal is observed. This results in enhanced PSAM adsorbing on the surface, effectively blocking charge transfer pathway while reducing the corrosion rate.

The Bode phase diagrams exhibited two separate peaks **Fig. 4.5(a)**. The two-time constants are represented by the two peaks, with the uninhibited solution diameter exceeding that of the controlled. Like the Nyquist phenomenon, the inhibited solution breadth expands with increasing PSAM concentration. Uninhibited solution Bode modulus plots exhibit less noticeable linear segments at middle frequencies compared to the PSAM solutions **Fig**

4.5(b). The linearity improves as the concentration increases, indicating that concentration amplifies inhibitory efficacy.

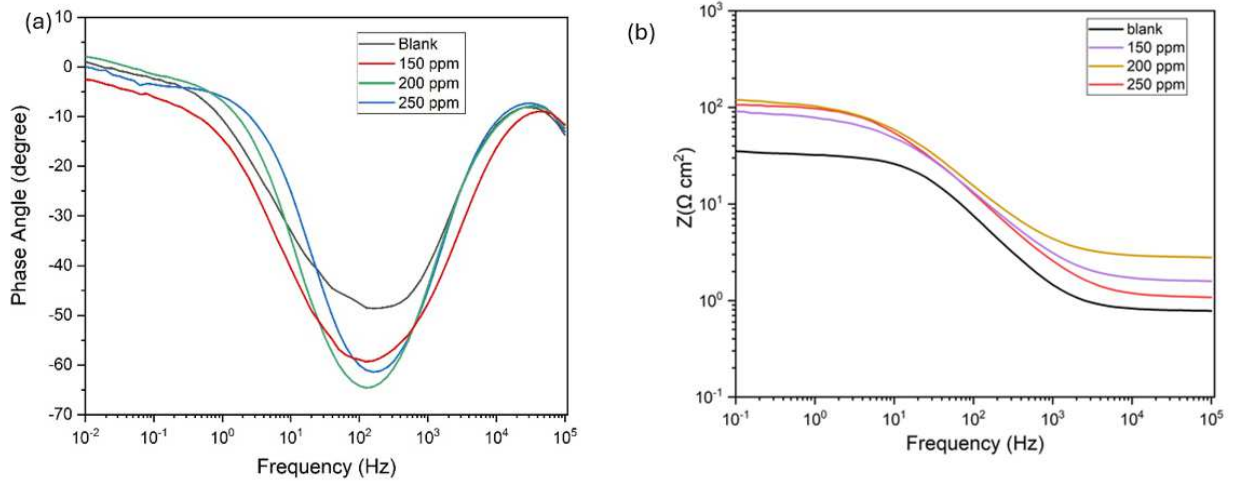


Figure 4.5: Bode phase plots of blank and various PSAM concentrations (a) Blank and various PSAM concentrations Bode modulus plots (b).

The equivalent circuit model used for PSAM solutions impedance curves is illustrated in **Fig. 4.6**. it consists of several key components: charge transfer resistance (R_{ct}), solution resistance (R_s), film resistance (R_f), first phase shift (n_1), second phase shift (n_2), the double layer constant phase element (CPE_{dl}) and film constant phase element (CPE_f). These elements collectively represent the electrical characteristics of the system, allowing for a more accurate analysis of the PSAM solution's behavior.

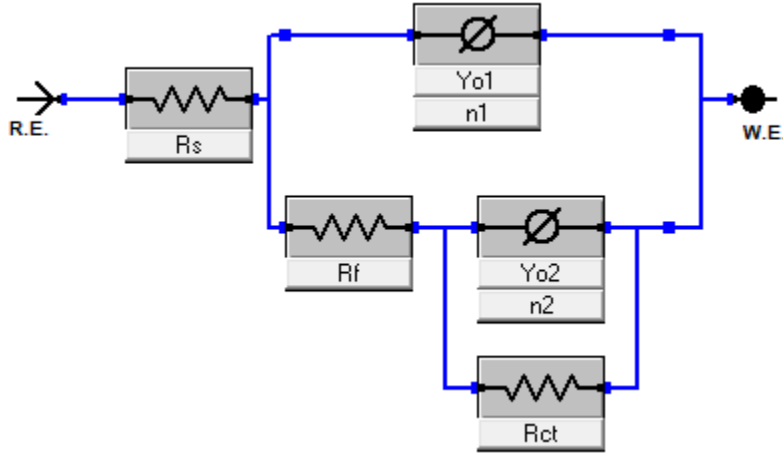


Figure 4.6: Equivalent circuit model employed for fitting the impedance curves.

The impedance of the CPE was calculated using Equation (18) [123][44].

$$Z_{CPE} = Y_0^{-1} (j\omega)^{-n} \quad (18).$$

Where Y_0 represents the magnitude of the constant phase element (CPE), i is the imaginary unit (i.e., $\sqrt{-1}$), n denotes the phase shift, and j corresponds to the angular frequency.

The surface-adsorbed inhibitor layer exhibits behavior more characteristic of a constant phase element (CPE) rather than an ideal capacitor, justifying the use of a CPE model for improved accuracy and fit. The charge transfer resistance (R_{ct}) values in PSAM solutions were higher than those in the blank solution, indicating that the inhibited systems provide greater resistance to charge transfer. This suggests that the PSAM inhibitor layer effectively protects the steel surface from the aggressive medium, thereby hindering both mass and charge transfer. Additionally, the film resistance (R_f) in the PSAM solution exceeded that of the blank, suggesting the formation of a less conductive protective film compared to the highly porous and conductive corrosion layer observed in the uninhibited system. In both inhibited and uninhibited solutions, the phase shift (n) values were close to one, confirming

a predominantly capacitive interaction at the carbon steel/solution interface and supporting the application of the CPE model. Additionally, the Y_0 value provides insights into the characteristics of the surface coating. A lower Y_0 value indicates a more compact corrosion layer or an effective adsorbed inhibitor film. The lower Y_0 values observed in the inhibited solutions suggest that the formed inhibitor film is denser than the formed corrosion layer. **Table 4.2** displays the outcomes of fitting the curve. The inhibition efficacy was determined with Equation (19) [179][180].

$$\%IE_{(EIS)} = \left(1 - \frac{R_p^B}{R_p^I}\right) \times 100 \quad (19).$$

Where R_p is the sum of R_f and R_{ct} , with R_p^I and R_p^B denoting the inhibited and uninhibited solutions polarization resistance respectively.

Table 4.2: Blank and PSAM solutions EIS measurement analysis at ambient temperature.

PSAM Conc (ppm)	R_s (Ωcm^2)	CPE_f		R_f (Ωcm^2)	CPE_{dl}		R_{ct}	R_p	$\chi^2 \times 10^{-3}$	%IE
		Y_01	$n1$		Y_02	$n2$				
Blank	1.743	1.140	0.887	10.83	0.198	0.796	2.014	12.8	0.666	

150	0.817	0.102	0.616	84.67	0.913	0.207	2.162	86.8	0.856	85.2
200	1.024	0.231	0.825	22.24	0.931	0.377	125.9	148	1.281	91.3
250	0.934	0.495	0.596	22.12	0.292	0.892	84.88	107	0.785	88.0

4.3.4. Linear Polarization Resistance (LPR)

This method is simple for evaluating the rate of material corrosion. This method involves applying a 10mV offset from OCP to create a slight, non-intrusive polarization. It elucidates current as well as potential connections. The rate of corrosion drops dramatically in PSAM presence, as evidenced by weight measurement and EIS test. The rate diminishes as the concentration of PSAM increases, reaching its lowest point at 200 ppm, with an efficiency of 89.6 % which is the maximum efficiency concentration. for both the weight measurement and the EIS studies. **Table 4.3** outlines the LPR findings. The inhibitory efficacy was estimated employing Equation (20) [181].

$$\%IE_{(LPR)} = \left(1 - \frac{R_p^B}{R_p^I}\right) \times 100$$

(20).

Where R_p^B denotes the blank polarization resistance, while R_p^I signifies the inhibited solution polarization resistance.

Furthermore, the polarization resistance in PSAM solution is greater as to the blank solution, indicating PSAM presence enhances the steel corrosion resistance. This suggests that the inhibitor effectively diminishes the electrochemical activity, thereby improving the steel's overall corrosion resistance.

Table 4.3: Blank and PSAM solutions LPR measurement analysis at ambient temperature.

PSAM (ppm)	Conc	E_{corr} (mV vs Ag/AgCl)	I_{corr} ($\mu\text{A}/\text{cm}^2$)	Polarization Resistance (Ω)	Corrosion rate (mm/year)	%IE
Blank		-443.4	2388	10.91	27.72	-
150		-468.9	93.12	279.8	4.255	84.6
200		-466.1	248	105	2.879	89.6
250		-452	266.2	97.88	3.090	88.8

4.3.5. Potentiodynamic Polarization (PDP)

The PDP method employs a broader polarization range (200–400 mV from OCP) than the LPR technique, making it a more destructive method that provides a wider scope of information. It is primarily used to assess the effects of inhibitors on both the cathodic production of H_2 gas and the anodic oxidation of metals. **Fig.4.7** displays the PDP curves for both uninhibited and controlled solutions. An inhibitor is classified as anodic or cathodic when it causes a polarization shift of 85 mV or more on the respective side; shifts below 85 mV indicate a mixed-type inhibitor [182]. PSAM primarily acts as a mixed-type inhibitor. **Table 4.4** summarizes the parameters derived from the PDP curves fitting, while the inhibition efficiency was calculated utilizing Equation (21) [135].

$$\%IE_{(PDP)} = \left(1 - \frac{I_{corr}^I}{I_{corr}^B}\right) \times 100 \quad (21).$$

Where I_{CORR}^I and I_{CORR}^B represent corrosion current densities of the inhibited and uninhibited solution respectively.

Table 4.4: Blank and PSAM solutions PDP measurement analysis at ambient temperature.

PSAM Conc (ppm)	β_a (mV/dec)	β_c (mV/dec)	E_{corr} (mV vs Ag/AgCl)	I_{corr} ($\mu A/cm^2$)	Corrosion rate (mm/year)	%IE
Blank	47.6	192	-452	1060	12.27	-
150	42.84	57.00	-466	168.4	1.97	85
200	49.47	56.83	-463	102.5	1.19	90
250	52.77	68.83	-467	128.6	1.493	88

The corrosion potential (E_{corr}) values didn't show a clear pattern across different inhibitor concentrations, suggesting a mixed-type inhibition behavior. However, lower current density (I_{corr}) values were seen in the protected solutions as to the blank solution. I_{corr} reduction is attributed to PSAM adsorption onto the surface of the metal, creating a protective layer that restricts the access of the aggressive medium, thereby lowering the corrosion rate. The PDP results align with findings from weight loss measurements, EIS, and LPR, showing an increase in inhibition efficiency from 150 to 200 ppm, followed by a slight decline at 250 ppm.

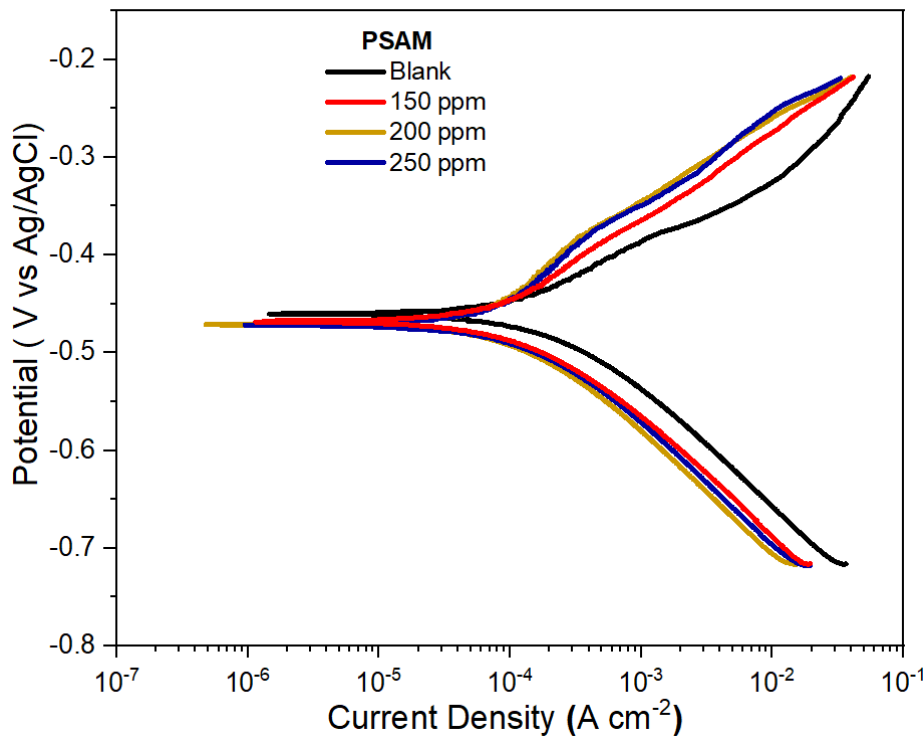


Figure 4.7: PDP plots for blank and PSAM inhibited solutions.

4.3.6. Adsorption Analysis

Inhibitor compounds protect surfaces of metals from deterioration by surface adsorption and forming a protective layer that are either chemically or physically adsorbed, or by utilizing a mix of both approaches. This procedure establishes protective barriers. The Langmuir adsorption isotherm, which asserts homogeneous monolayer adsorption, was identified as the most accurate model. Langmuir's theory stated that a linear plot of C/θ against C will have an intercept of $1/K_{ad}$ and a slope of a_L/k_L [183][184]. The plots, derived from weight loss and PDP measurements, are presented in **Fig. 4.8**, with values specified in **Table 4.5**.

Table 4.5: Adsorption study parameters of PSAM.

Compound	Technique	ΔG_{ads}^o (kJmol ⁻¹)	K_{ad} (Lmg ⁻¹)	Slope	R ²
PSAM	Weight Loss	-27.5	0.0620	1.0231	0.9908
	PDP	-26.5	0.04429	1.0233	0.9929

$$\frac{c}{\theta} = \frac{1}{K_{ad}} + \frac{a_L}{k_L} C \quad (22).$$

Where k_L and a_L are the constants of the Langmuir's isotherm, while the adsorption equilibrium constant (K_{ads}) represents the inhibitor molecules and metal surface interaction strength, while C denotes the inhibitor concentration. The degree of surface coverage (θ) is determined by dividing the percentage inhibition efficiency by 100. K_L signifies the maximum adsorbable concentration of the inhibitor, whereas a_L reflects the inhibitor's affinity for the metal surface.

K_{ad} is associated with Gibb's free energy of adsorption ΔG_{ad}^o as demonstrated in equation (23) [185].

$$\Delta G_{ad}^o = -RT \ln(1 \times 10^6 K_{ad}) \quad (23).$$

Where R is the molar gas constant & T is the temperature (Kelvin).

Physisorption takes place when ΔG_{ad}^o is equal to or less than -20 kJ/mol, while chemisorption is dominant when ΔG_{ad}^o is equal to or greater than -40 kJ/mol. For values ΔG_{ad}^o within -20 and -40 kJ/mol, a chemically enhanced physisorption adsorption

mechanism is proposed [181]. The analysis of weight loss and PDP data showed ΔG_{ad}^o values of -27.5 and -26.5 kJ/mol. This implies that PSAM is absorbed via a physisorption mechanism that is chemically enhanced, i.e. chemical and physical adsorption. The negative of ΔG_{ad}^o value signifies a spontaneous and stable process of adsorption.

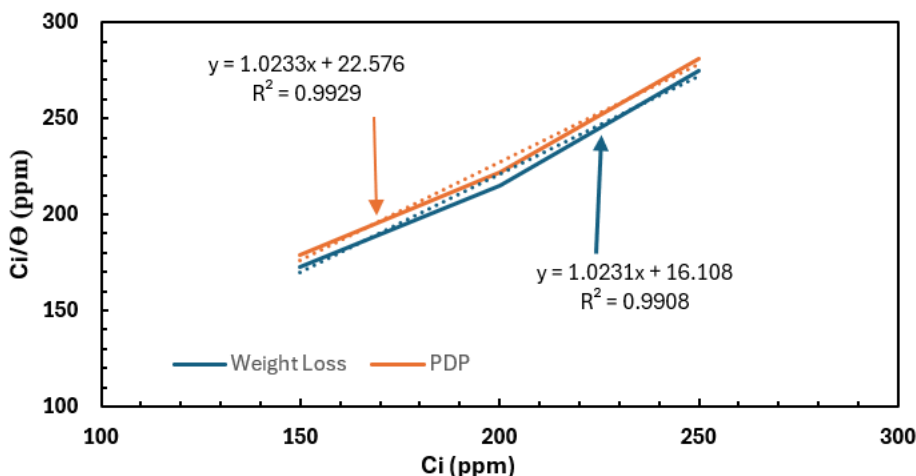


Figure 4.8: Adsorption study of PSAM in weight loss and PDP technique.

4.3.7. Density Functional Theory Calculations

Fig. 4.9 illustrates the PSAM frontier orbitals and optimized structure. Theoretical parameters obtained from the computations are shown in **Table 4. 6**. The HOMO and LUMO areas are concentrated around the carboxyl group, amine group and the aromatic ring moieties, respectively as illustrated in **Fig 4.9**. PSAM orbitals (HOMO and LUMO) engage with the surface of the metal by donation and acceptance of electron. Consequently, the carboxyl group, amine group, and aromatic ring moieties are essential for the efficacy of PSAM in reducing corrosion. For an enhanced efficacy, ΔE is preferred to have a low value [186]; nevertheless, PSAM, with a HOMO-LUMO energy gap of 5.032 eV (see **Fig**

4.10.), suggests a comparatively facile electrons transfer from PSAM to the C1018 surface. With a strong correlation between the ionization energy (IE) and E_{HOMO} [187]. An ionization energy (IE) of 6.713 eV indicates that PSAM can be easily ionized, facilitating electron donation to the C1018 surface. Similarly, the low electronegativity (χ) of -4.198 eV suggests a strong tendency for PSAM to donate electrons, thereby enhancing surface coverage, considering that the initial IE of iron is approximately 8 eV. The determination of hardness (η) and softness (σ) values is essential, as they reflect the effectiveness of anticorrosion chemicals. The hardness value (η), defined as $\eta = (I - A)/2$, serves as an indicator of a compound's stability, with higher η values signifying greater stability. Additionally, electrons fraction transferred (ΔN) provides insight into electron migration. A negative ΔN ($\Delta N < 0$) indicates electron migration from the surface of the metal to PSAM, whereas a positive ΔN ($\Delta N > 0$) suggests electron transfer from the inhibitor to the surface of the metal [188]. The latter condition ($\Delta N > 0$) represents the optimal PSAM and the C1018 surface interaction. The electrophilicity (ω) parameter have a vital role in assessing the efficacy of an inhibitor, as it reflects the molecule's tendency to accept electrons from the metal surface via backdonation or retro-donation [189]. A high electrophilicity value of 8.809 eV indicates that PSAM exhibits strong interaction with the surface of the metal through backdonation. The dipole moment (μ) shows the overall molecule polarity, describing the distribution of positive and negative charges. A dipole moment increase enhances the inhibitor adsorption onto the surface of the steel due to strengthened intramolecular interactions [174]. PSAM demonstrates a notable dipole moment of 4.197 eV, signifying its strong adsorption capability on the C1018.

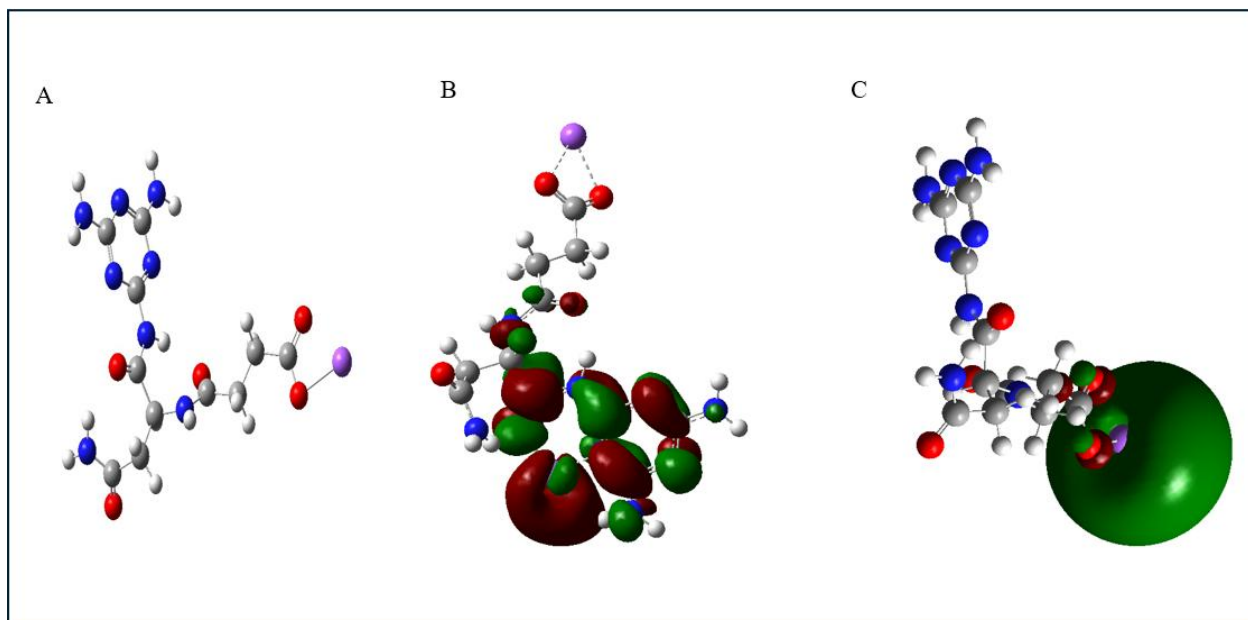


Figure 4.9: Optimized (a), HOMO (b), and LUMO (c) PSAM structures.

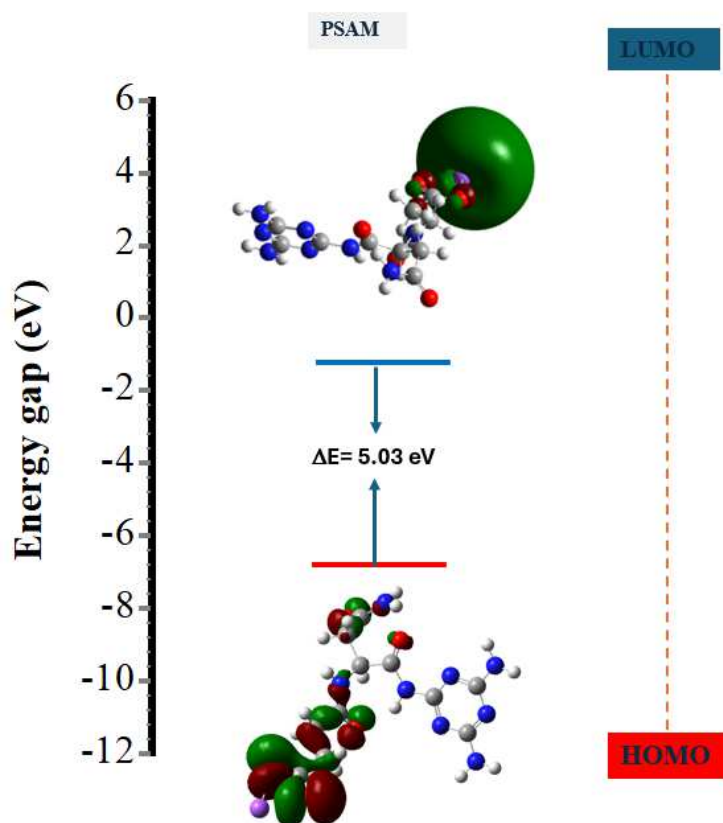


Figure 4.10: HOMO-LUMO energy plot of PSAM.

Table 4.6: Predicted values of molecular descriptors at the B3LYP/6-31G+(d,p)

Compo und	HO- MO	LU- MO	ΔE	IE	EA	η	σ	χ	ΔN	μ	ω
PSAM	6.71	1.68	5.03	6.71	1.68	2.51	0.39	4.19	2.12	4.19	8.80

4.3.8. Surface Analysis

Fig.4.11. shows surface morphology images using SEM of a steel surface submerged in an uninhibited and PSAM-inhibited solution respectively. From the image, the blank solution's steel surface is rough, and cracks dispersed extensively. PSAM controlled steel has a smoother surface. Protective inhibitor molecules form a barrier on the steel surface, preventing aggressive ions from causing corrosion and resulting in a considerably smoother surface than that of blank.

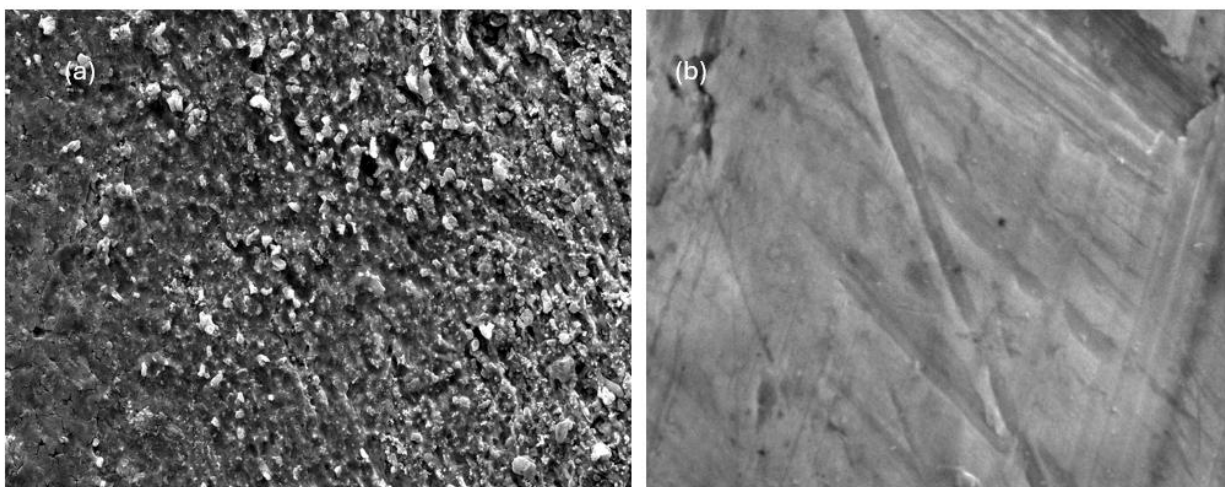


Figure 4.11: SEM images of the carbon steel surface after 24h immersion in 1M HCl-3.5% NaCl solutions in blank (a) 200 ppm PSAM (b)

4.3.9. Mechanism of Inhibition

Inhibitor molecules typically physisorbed, chemisorb, or a mix of the two to attach to the metal surface. One important method is retro-donation, in which iron atoms' d-electrons are moved to the inhibitor's anti-bonding orbitals, thereby enhancing adhesion (**Fig. 4.12**). PSAM is more protonated than poly-aspartic acid (PAS) due to its imine group ($>\text{CH}=\text{N}$), which improves its adsorption onto steel. This adsorption is driven by two main interactions: the donation of lone pair electrons from heteroatoms (N and O) and the interaction of free π -electrons from its aromatic structure and unsaturated $\text{C}=\text{N}$ bonds with the empty d-orbitals of iron, leading to the formation of coordinate bonds. As suggested from the potentio-dynamic polarization and adsorption analysis, PSAM adsorbs onto the steel surface via a mixed mechanism that combines both chemisorption and physisorption.

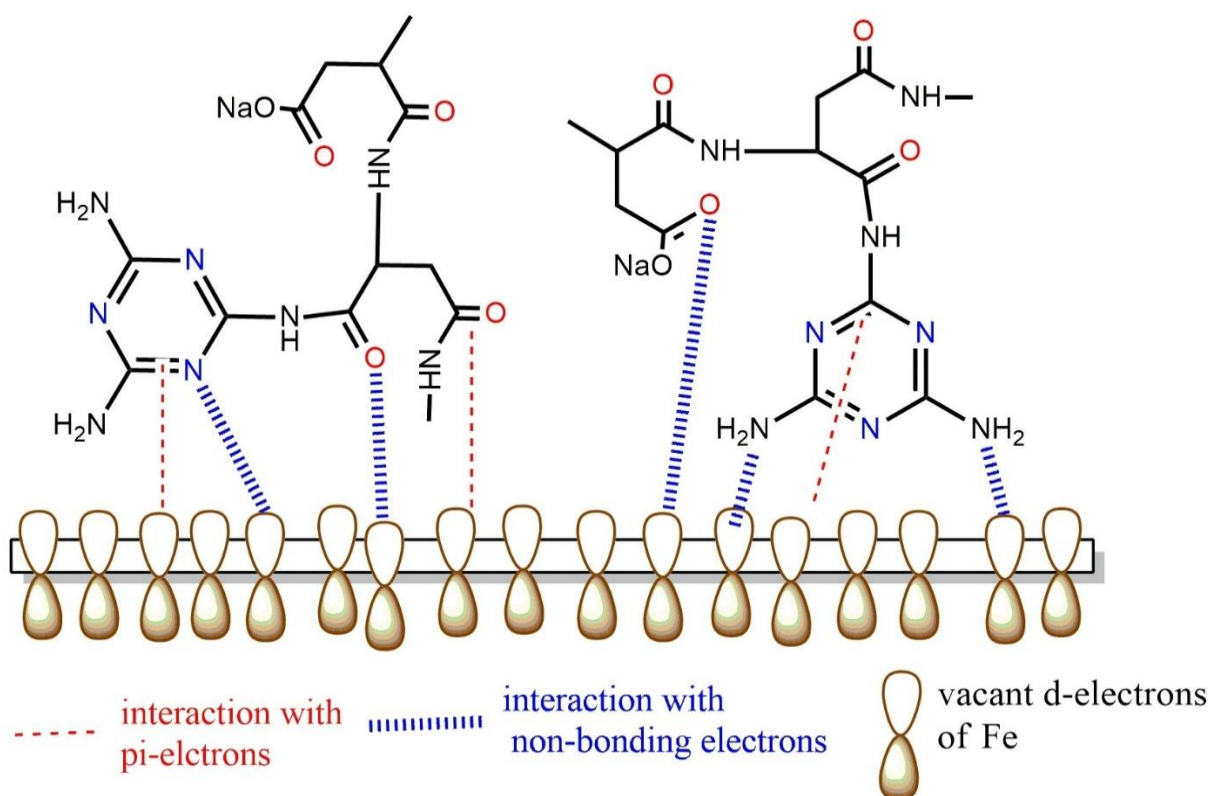


Figure 4.12: Plausible mechanisms of inhibition by PSAM.

CHAPTER 5

INVESTIGATING THE CORROSION RESISTANCE OF 304 STAINLESS STEELS USING A CARBON DOT MODIFIED POLYMER IN A 3.5% NACL MEDIUM.

5.1 Introduction

Corrosion is an unwanted phenomenon that degrades the mechanical characteristics and appearance of metals, hence reducing its lifespan [190]. It significantly impacts the safety, environmental degradation as well as economy [191]. Corrosion impacts numerous areas, including infrastructure, transportation, industries, autos, and pipelines [192][193][1][194]. Various types of media, such as acidic, alkaline, and saline, influence the corrosion process to varying degrees; predominantly, acidic media significantly increase the corrosion rate [195][39]. Consequently, it is essential to regulate this deterioration process using suitable anti-corrosive substances in minimal doses [2]. When selecting a corrosion inhibitor, it is essential to evaluate economic feasibility, inhibitor efficiency, toxicity, dangers, and their environmental impact and effects on inhabitants [3][4][5].

Traditional inorganic or organic compounds utilized as inhibitors must be substituted with biodegradable, economical, and environmentally benign alternatives concerning the third issue [6]. Polymers are seen as promising inhibitors due to favorable effects on the economy and environment, exhibiting better inhibition efficiency when compared to organic molecules [196] [7][45]. They offer two benefits: (i) numerous molecules of water on the metal surface can be displaced easily with a single polymeric chain, rendering the process favorable, (ii) a lower rate of deposition occurs due to multiple binding sites presence. Polymers, their composites, and blends containing functional groups such as –OH, –NH₂, and –COOH-S, etc, have great water solubility and are documented as corrosion protectors in diverse harsh environments via polymers complexation with metal ions, resulting in several uses [8][9]. Polymer complexes and their composites enhance the metal surface area, creating a layer of protection that shields the interface from deterioration. These inhibitors function through molecular adsorption method, whereby the substance mitigates deterioration by regulating both reactions (anodic and cathodic) [10][11][12]. Hydrogen gas evolution diminishes as the protonated species adsorbs onto the cathodic sites of the surface, resulting in a reduced corrosion rate [13]. Recently, scientists have conducted investigations on the inhibitory efficacy of various polymers, their composites, and combinations in various mediums, showing improved efficiency [14]. Their investigation utilized both natural and synthesized polymers, revealing that macromolecular mass, chemical composition, and distinctive inhibitor structure account for the modes and methods of corrosion protection.

Steel deterioration generates iron oxide at areas with weak adhesion on the metal surface. Subsequently, it readily disintegrates into a solution-phase, resulting in the depletion of

conducting metal [197]. Corrosion control methods include selecting appropriate alloys, modifying the corrosive medium, applying protective coatings, painting, anodic and cathodic protection. Another method to reduce degradation is inhibitors incorporation. An inhibitor is any substance that diminishes the rate of corrosion on the affected material by adsorbing onto its surface [19]. These substances create a thin protective coating on the surface. Employing inhibitors is an efficient and pragmatic approach for safeguarding metals from corrosion in acidic and saline environments [20]. The protection of several metals, including carbon steel, mild steel, copper, and aluminum, by inhibitors addition has been documented [21]. Recently, studies concentrated on utilizing carbon dots as a type of carbon-based fluorescent nanomaterial, owing to their distinctive characteristics, including excellent water solubility, little cytotoxicity, and remarkable luminosity. Another characteristic of carbon dots is their excellent biocompatibility [23]. The features are frequently utilized for applications in bioimaging, biosensing, biomedicine, optoelectronic devices, drug delivery, and various other domains. The four main categories of carbon dots are graphene quantum dots (GQDs), carbon nanodots (CNDs), polymer carbon dots (CPDs), and carbon quantum dots (CQDs), all measuring less than 10 nm in size. These materials can be manufactured using straightforward processes from diverse natural sources containing long carbon chains, hence ensuring the safety of living creatures. The precursors are typically natural sources, cost-effective, and renewable [24].

Simultaneously, the doping of heteroatoms significantly enhances the distinctive qualities of carbon dots, including the emission spectrum range, fluorescence characteristics, corrosion inhibition, and additional attributes. Numerous researchers have reported that carbon dots containing solutions significantly diminishes the metal corrosion rate [24].

This phenomenon is ascribed because of carbon dots hydrophilic functional groups, which attract molecules of water and sequester oxygen from the metal surface. Subsequently, oxygen molecules adsorbed on the carbon dots surface are directly transformed into water molecules by four-electron routes, so inhibiting corrosion [25]. Zhu et al [91] synthesized N-CQDs utilizing folic acid and o-phenylenediamine and evaluated their inhibition efficiency through different electrochemical analysis and surface morphology. Potentiodynamic polarization (PDP) analysis reveals that N-CQDs influence both reaction rates (cathodic and anodic), although E_{corr} values were not altered substantially. A partial capacitive reactance semicircular arc is observable on the Nyquist plot. As the N-CQDs quantity increases, the arc's radius as well as its height increases. N-CQDs incorporation increased the inhibition property without affecting the charge transfer mechanism. Moreover, a singular charge transfer time constant was determined. The N-CQDs adsorption on the Q235 surface leads to obstructing electron transfer and increasing capacitive reactance [91]. In a separate work, Ye and co-workers [92] examined the efficacy of a synthesized functionalized carbon dots, imidazole and citric acid-carbon dots (CA-CQDs) against corrosion on Q235 steel in 1M hydrochloric acid medium via surface morphology and electrochemical study. According to the electrochemical analysis conducted at 200pm for all the three inhibitors, the functionalized CQDs has the highest inhibition efficacy followed by imidazole and lastly CA-CQDs. A rise in concentration for all the inhibitors resulted in enlargement of the Nyquist curves, indicating an enhancement the charge transfer mechanism. The inhibitors presence in the tested medium resulted in a current density reduction by inhibiting the Tafel processes. The enlargement of Nyquist curves results from the development of a protective coating by the inhibitors at the surface

of metal, which improves the charge transfer barrier. The current density reduction signifies that these inhibitors adsorb on the surface and obstruct active sites. There was no alteration in the E_{corr} value, demonstrating their function as mixed-type inhibitors. The elevated Bode phase angle value of inhibited when compared to the blank resulted from the smoothing of the inhibited surface by the inhibitors adsorption. Finally, SEM and AFM investigations were utilized to analyze the inhibitors adsorption on the surface [92].

in this study, CQDs was synthesized using a hydrothermal method. A polymer was synthesized via condensation polymerization between tartaric acid and ethylenediamine. The CQDs were integrated in the synthesized polymer by surface modification, resulting in the effective synthesis of a polymer carbon dot composite (TCQDs). The modified polymer was analyzed using FT-IR and 1H NMR. Weight loss, EIS, LPR, and PDP were applied to determine its inhibition efficacy. Surface morphology was determined using scanning electron microscopy.

5.2 Experimental

5.2.1 Chemicals and material

Tartaric acid, ethylene-diamine, sulfuric acid (Supelco, 85%), ethanol (Honeywell, 99.8%), Dimethylformamide, NaCl (Fischer Scientific), stainless steel (304). Distilled water was obtained from Thermo-scientific Distillation Apparatus (Model A1015-B-61). Analytical reagent grades were employed and used directly as received.

5.2.2 TCQDs synthesis.

The copolymer (TDA) was prepared by step-growth polymerization and condensation polymerization (**Fig.5.1**). 150 milliliters dry round bottom flask was equipped with a magnetic stirrer, a dean stark apparatus, and dropping funnel was used. 1:1.5 M of tartaric acid and ethylene diamine was added to 35 milliliters of DMF and magnetically stirred. Concentrated acid was added a catalyst, the solution was heated to 200 °C [198]. The reaction was kept for 24 hours, after cooling to room temperature, absolute ethanol was added for product precipitation. A rotary evaporator was used for solvent removal, the obtained product was purified after solvent evaporation and vacuum dried for 24 hours.

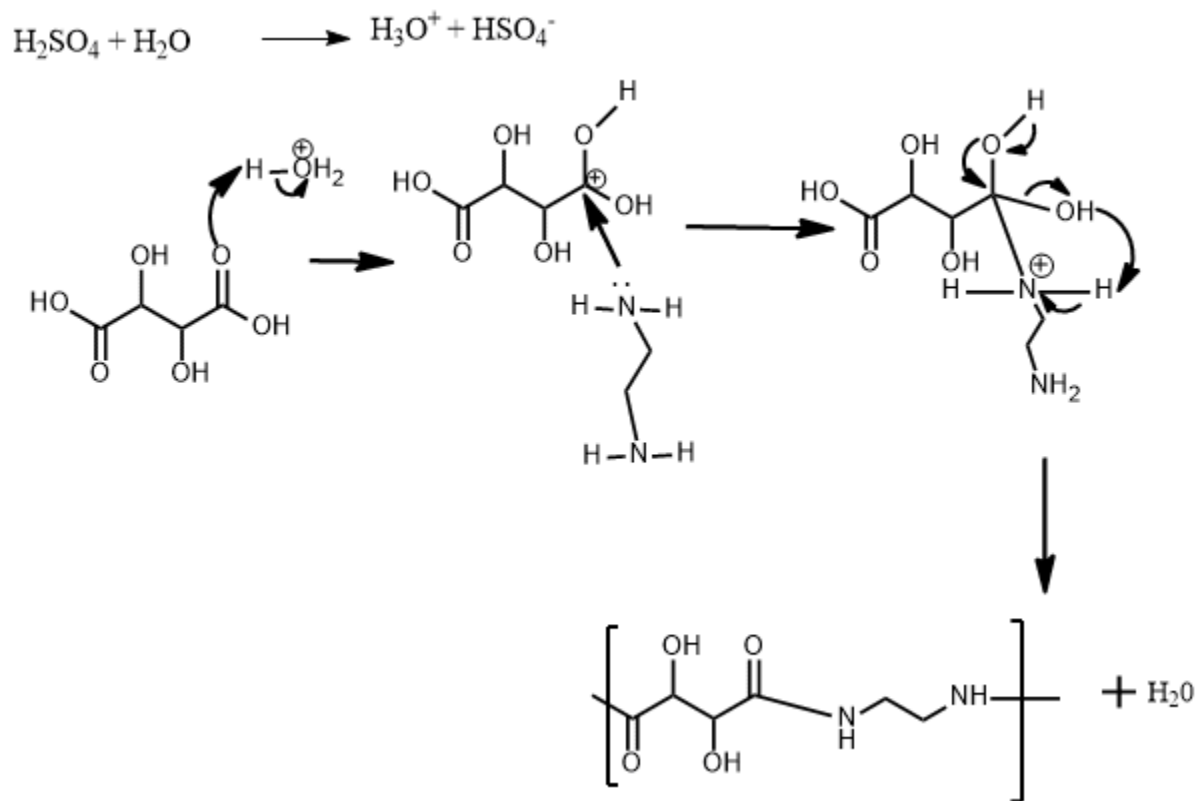


Figure 5.1: TDA synthesis scheme

Carbon quantum dots (CQDs) were synthesized utilizing a straightforward hydrothermal technique, as seen in (Fig. 5.2). The banana peels were dehydrated overnight at 80 degrees Celsius and then ground into a powder. Refined banana powder (0.3 g) was added to 60 milliliters of water and thereafter subjected to a hydrothermal process in a Teflon-lined autoclave at 185 °C for 24 hours [199][200]. A yellow solution was obtained and subsequently filtered through a 0.22-micrometer syringe filter to remove residues.

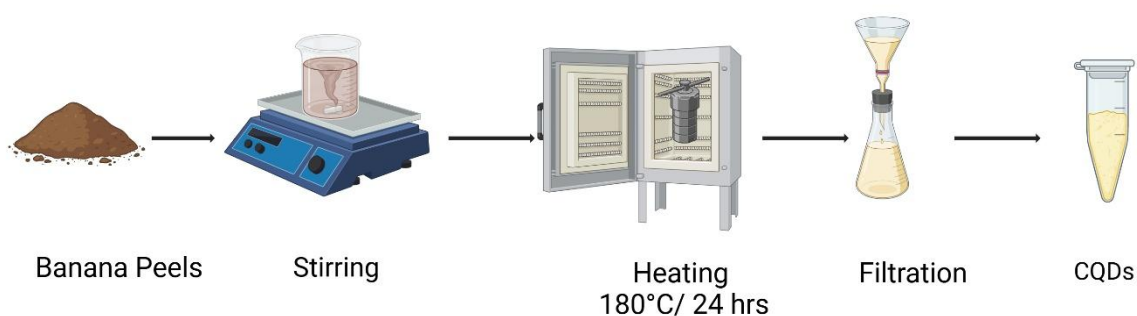


Figure 5.2: CQDs synthesis design

The synthesis of TCQDs proceeded as outlined below. 0.05 g of CQDs powder was dissolved in 20 milliliters of deionized water, and the solution was adjusted to a pH of 4. EDC (0.5 grams) and NHS (0.5 grams) were introduced to activate the CQDs carboxyl groups on the surface for one hour [201][202]. An excessive quantity of TDA was included into the prior solution. The reaction is permitted to continue for three days at 80 °C. The synthesized polymer carbon dot was purified using a microporous filter (0.22 micrometer) and a dialysis bag (1000 Da) for 48 hours to exclude molecular contaminants such as EDC and NHS. The prepared TCQDs were acquired and subsequently utilized in the subsequent tests.

5.2.3 TCQDS Characterization

^1H NMR and FTIR technique were used to characterize TCQDs. The ^1H NMR was collected using the Bruker AVANCE IIIHD 400 MHz NMR spectrometer in deuterated oxide. The Attenuated Total Reflectance (ATR) - Fourier Transform Infrared (FTIR) spectrometer (Smart iTR NICOLET iS10) was used to collect TCQDs FTIR spectra. The spectrum obtained at a resolution of 4 cm^{-1} resolution with frequency range of $400\text{--}4000\text{ cm}^{-1}$.

5.2.4 Electrodes and solutions

The investigations utilized stainless steel (304) with the following composition: 2.00% Manganese, 0.030% Sulfur, 18.00% Chromium, 0.08% Carbon, 8.00% Nickel, 0.100% Nitrogen, 0.75% Silicon, 0.045% Phosphorus and the remainder iron. The steel (sample) was cut into rectangular shapes with 1 cm^2 area, which were soldered for electrical connectivity using copper wire. The steel was subsequently affixed to the epoxy resin, providing a single exposed surface to the aggressive environment. The steels were mechanically polished with different emery paper grades (120-1000) and subsequently rinsed with alcohol and acetone for a duration of fifteen minutes to eliminate all residues. The corrosive medium was formulated using analytical grade sodium chloride and distilled water. TCQDs concentrations were measured in grams per liter for studies.

5.2.5 Weight Loss Measurements

The weight loss technique, known for its directness and accuracy, was utilized to evaluate the corrosion inhibiting efficacy of TCQDS. This test involved weighing square stainless-

steel specimens Both prior to and following dipping them in a 100-milliliter volume of a 3.5% sodium chloride solution with varying inhibitor concentrations, kept at room temperature for 15 days.

Equation (24) was used to determine the corrosion rate [176].

$$CR = \frac{W * 8.79 * 10^4}{D * A * T} \quad (24).$$

Where The variable W represents the average reduction of weight in grams.

A = surface area measured in square centimeters.

T = represents the immersion time (hours).

D= Coupon's density (7.87 g/cm³).

The percentage inhibition efficacy was calculated with equation. (25) [104].

$$\%IE_{wl} = \left(\frac{W_o - W_i}{W_o} \right) \times 100 \quad (25).$$

Here W_o is blank weight loss, W_i refers to inhibited solution weight loss.

5.2.6 Electrochemical measurements

A standard three-electrode glass cell connected to a Gamry Reference 3000 Potentiostat/Galvanostat/ZRA linked to a computer. The electrochemical interface was executed at ambient temperature was used for the electrochemical analysis. A steel specimen served as the working electrode, a graphite rod as the auxiliary electrode, and a

silver/silver chloride electrode as the reference electrode. The open circuit potential (OCP) was determined by submerging the sample in the solution for 3600 seconds. The object being studied was inserted in the medium for an hour at OCP to stabilize. Techniques used included electrochemical impedance spectroscopy (EIS) From 10 millihertz to 100 kilohertz with an amplitude of 10 millivolts., linear polarization resistance (LPR) measured at 0.1250 mV/s around ± 10 mV of OCP, and PDP at ± 0.25 mV/s within ± 250 mV of OCP. The resulting curves were analyzed using Gamry Echem analyst.

Regarding EIS, %IE was obtained using equation (26)[122] :

$$\%IE_{(EIS)} = \left(1 - \frac{R_p^B}{R_p^I}\right) \times 100 \quad (26).$$

Here R_p refers to sum of R_f and R_{ct} , with R_p^I and R_p^B denoting the inhibited and uninhibited solutions polarization resistance respectively.

Regarding constant phase element (CPE), the CPE impedance was calculated utilizing equation (27) [123].

$$Z_{CPE} = Y_o^{-1} (j\omega)^{-n} \quad (27).$$

Where Y_o = CPE magnitude, i = square root of -1, n is phase shift, and j is the angular frequency.

Regarding LPR, the %IE was determined using equation (28) [124]:

$$\%IE_{(LPR)} = \left(1 - \frac{R_p^B}{R_p^I}\right) \times 100 \quad (28).$$

Where R_p^B indicates the polarization resistance of the blank polarization resistance, while R_p^I signifies the TCQDs solution polarization resistance.

To compute the inhibition efficiency regarding PDP, equation (29) was used [125].

$$\%IE_{(PDP)} = \left(1 - \frac{I_{corr}^i}{I_{corr}^B}\right) \times 100 \quad (29).$$

Where I_{CORR}^I and I_{CORR}^B represent corrosion current densities of the TCQDs and blank solution.

5.2.7 Surface analysis

The steel's surface roughness and morphology were analyzed using SEM, both protected and unprotected. JEOL JSM-6610LV scanning electron microscope was utilized for obtaining the SEM images.

5.3 Result & Discussion

5.3.1 TCQDs Characterization

TDA proton-nuclear magnetic resonance (NMR) investigation was conducted in Deuterium D₂O solvent. The signal within 2.5 ppm range is attributed to the methine protons, whereas the other peak around 1.5 ppm correspond to the methylene protons of the amine in the ¹H NMR spectrum (**Fig.5.3**).

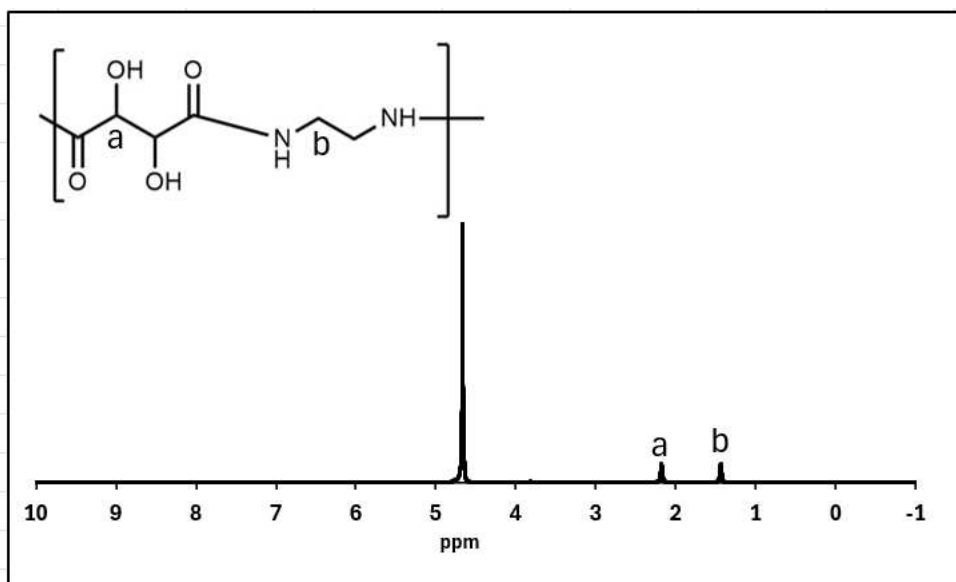


Figure 5.3: ^1H NMR spectrum TDA

Fig.5.4 displays TDA and TCQDs FTIR spectrum, CN stretching of CONH was observed at 12000 cm^{-1} . 1760 cm^{-1} peak corresponds to CO. 3500 and 2980 cm^{-1} peaks correspond to amide NH and CH stretching, respectively [203].

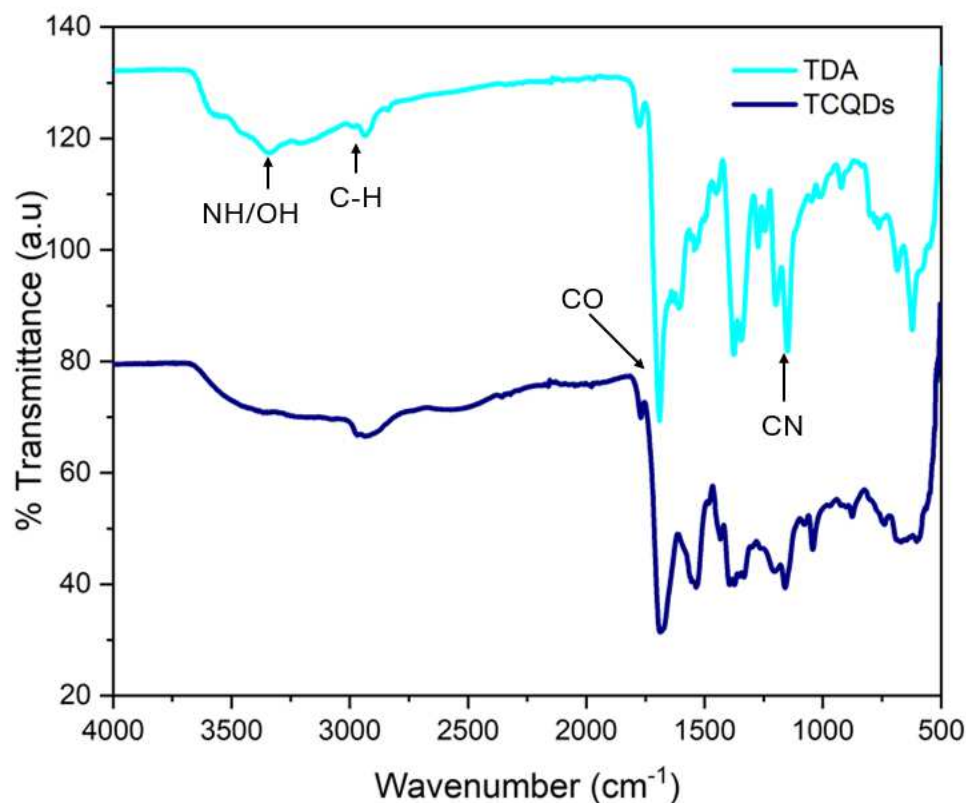


Figure 5.4: FT-IR spectrum of synthesized TCQDs, TDA.

5.3.2 TGA

TDA decomposition behavior in a nitrogen atmosphere was analyzed employing TGA(**Fig.5.5**). TDA thermal degradation can be divided into three stages. The initial stage, occurring between 25 and approximately 150°C, is attributed to the adsorbed volatile substances and moisture decomposition. Next stage, commencing above 200°C and concluding around 350°C, is associated with the carboxylic groups on the backbone of the polymer. The last stage, occurring above 300°C, pertains to the decomposition of the polymer backbone [204][205].

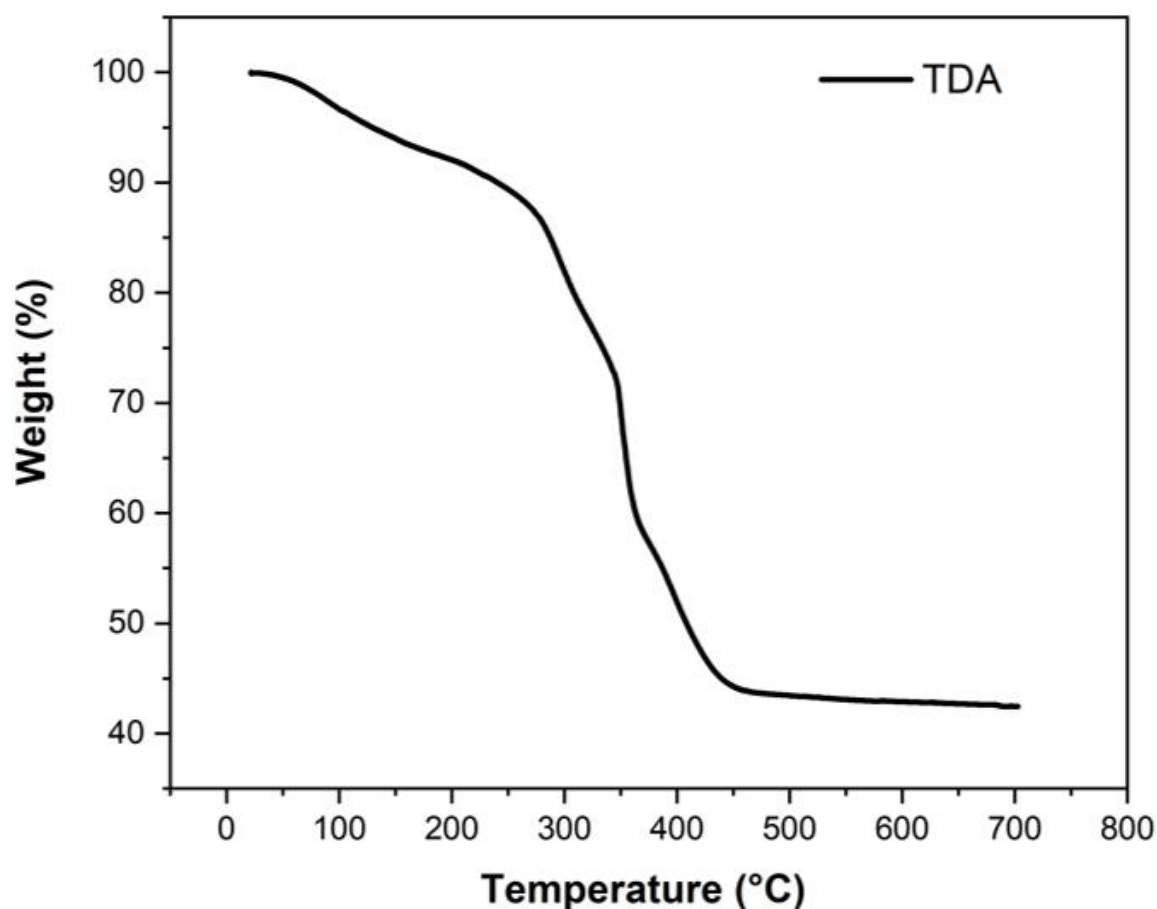


Figure 5.5: TGA of copolymer TDA

5.3.3 Gravimetric measurement

The gravimetric measurement result for TCQDs and blank solutions room temperature is listed below. The solution containing TCQDs experienced corrosion at a slower rate compared to the uninhibited solution (**Fig.5.6**). The rate of corrosion reduces with TCQDS concentration rise. The rate of corrosion diminished from 1.4706 for the blank to 0.1562 at 90 ppm, reaching a minimum of 0.1562 at 90 ppm with an efficiency of 89 %. The reduced corrosion rate when TCQDS is present is due to the inhibitor binding onto the matrix of

the metal and creating a protection layer. This protects iron dissolution in corrosive medium. The effect of TCQDS was investigated by altering its concentration in a corrosive setting. The inhibition efficacy improved from 83 % at 50ppm to 89 % at 90 ppm, which was the most effective. The rate of corrosion in TCQDs -inhibited solutions (**Table 5.1**) remained significantly lower as to the blank.

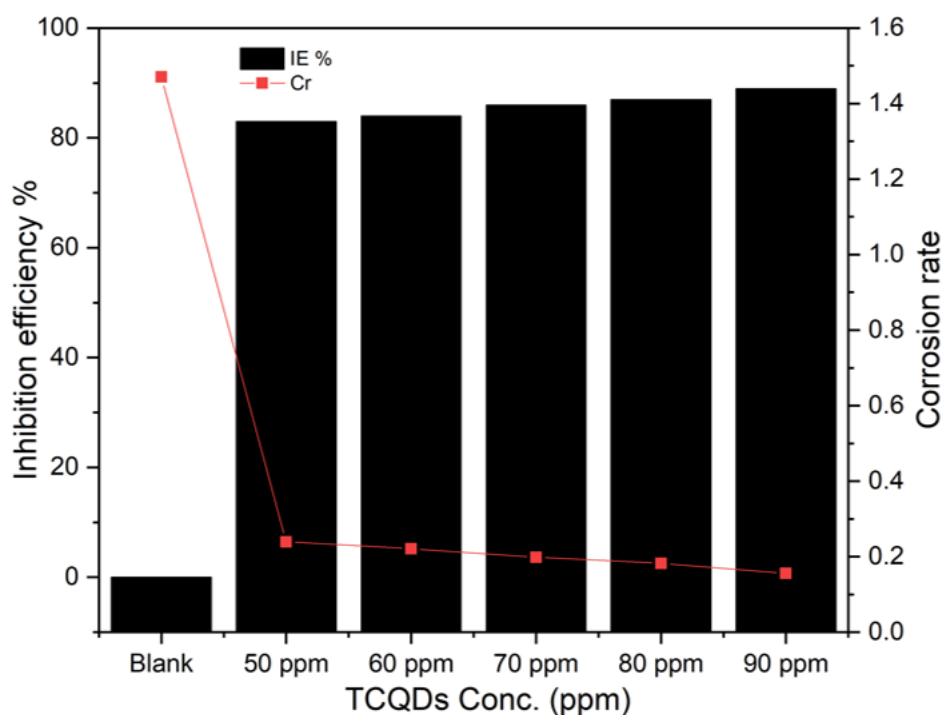


Figure 5.6: Chart showing inhibition efficiency and rate of corrosion with varying TCQDs amount

Table 5.1: Parameters for weight loss analysis of blank and TCQDs solutions at ambient temperature.

TCQDs Conc. (ppm)	Weight loss (g)	Corrosion rate(mm/yr)	% IE
Blank	1.3410	1.4706	-
50	0.2181	0.2392	83
60	0.2017	0.2212	84
70	0.1810	0.1985	86
80	0.1662	0.1823	87
90	0.1424	0.1562	89

5.3.4 OCP

The equilibrium potential in an open circuit, defined by absence of electrical interruption, is typically known as the open circuit potential (OCP). OCP is an electrode surface's nobility measurement. **Fig.5.7** shows the OCP variation for the tested sample in relation to the reference electrode in 3.5% sodium chloride solutions, both in TCQDs presence and absence at room temperature. The uninhibited solution demonstrates a more negative open circuit potential, because soluble corrosive chemicals formation and passive coating absence on the surface of the sample. TCQDs presence improves the sample's positive potential by surface adsorption, hence reducing the corrosion process. The sample's potential gets progressively more positive with increasing concentration. This finding suggests that a rise in inhibitor concentration is associated with an improvement in the inhibitor corrosion prevention effectiveness.

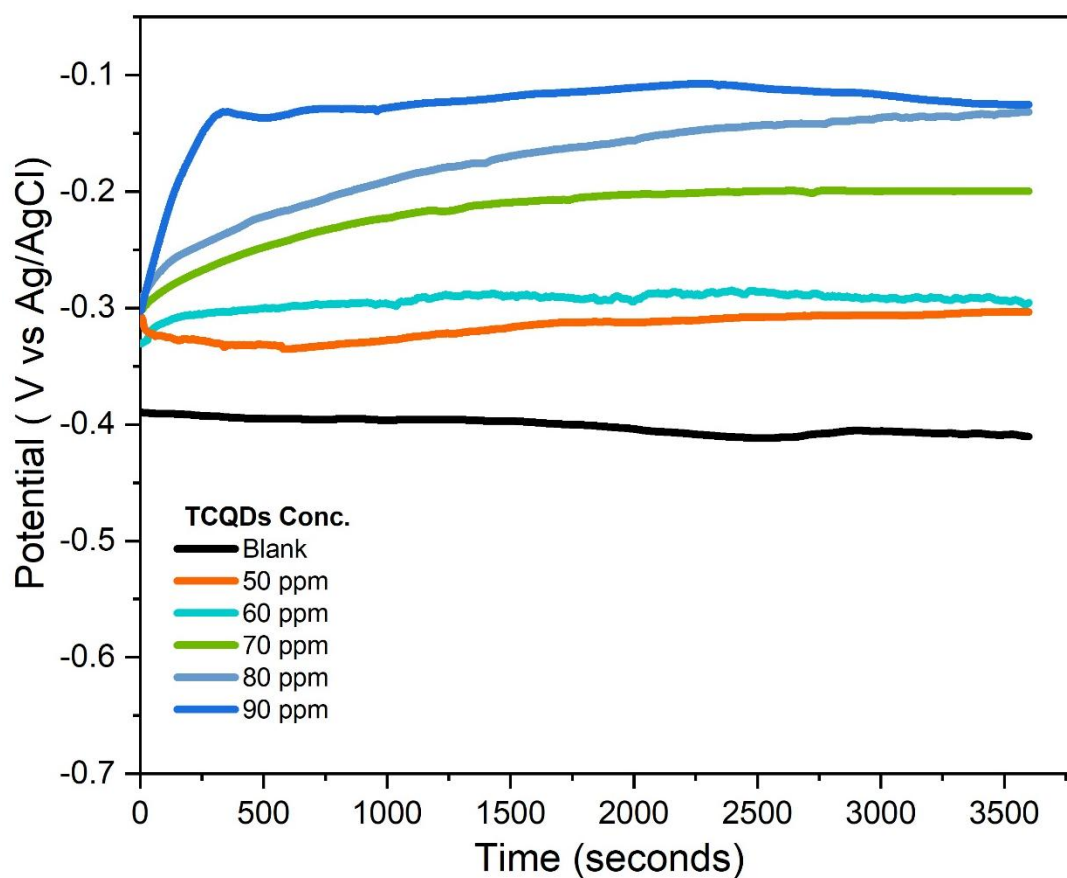


Figure 5.7: Time dependence of OCP time dependence for different concentrations of TCQDs.

5.3.5 LPR Technique

LPR is a quick analysis primarily utilized to attain a comprehensive grasp of material corrosion rates. A 10mV polarization from the OCP facilitates a potential and current correlation, making it non-invasive. The LPR methodology obtained parameters are displayed in **Table 5.2**. The E_{corr} readings for the TCQDs solutions lack a recognizable trend and show a larger inclination towards negative values as to blank. TCQDs solution rate of corrosion diminishes significantly, and this reduction is directly proportional to the

increasing TCQDs concentration. A greater polarization resistance was seen in the TCQDs-solutions as to the uninhibited. This shows an enhancement in the corrosion resistance to corrosion with TCQDs inhibitor.

Table 5.2: Parameters for LPR parameters of the blank and TCQDs solutions.

TCQDs Conc (ppm)	E_{corr} (mV vs Ag/AgCl)	I_{corr} ($\mu\text{A}/\text{cm}^2$)	Polarization Resistance (Ω)	Corrosion rate (mm/year)	%IE
Blank	-291.1	1.064	24.49	12.35	-
50	-289.7	0.189	137.4	2.201	82.1
60	-211.7	0.177	146.6	2.063	83.2
70	-264.2	0.163	159.1	1.901	84.6
80	-233.9	0.141	183.6	1.647	86.6
90	-255.4	0.119	217	1.391	88.7

Enhanced inhibitory efficiency was noted with rising inhibitor concentration, attributable to the increased quantity of adsorbed molecules of TCQDs on the sample surface of the sample. This is congruent with the EIS and weight reduction measurements results obtained.

5.3.6 PDP

The PDP technique, in contrast to the linear polarization resistance approach, employs a wider open circuit potential (OCP) that spans between 200 and 400 mV, making it an invasive technique. Nevertheless, it provides more information than the LPRs. The PDP methodology examines the effects of inhibitors on the cathodic H₂ generation and the anodic dissolution of iron. **Fig.5.8** shows the TCQD solutions and blank PDP graphs. The categorization of an inhibitor as mixed, cathodic, or anodic depends on the degree of potential divergence from the open circuit potential (OCP) [184]. A shift of 85 millivolts or more towards the anodic or cathodic side is classed as cathodic or anodic, whereas a shift below 85 millivolts on either arm is designated as mixed type [182][185]. TCQDs acted as mixed-type inhibitors, influencing both the cathodic evolution of H₂ gas and the anodic Fe dissolution. The current densities of TCQDs solutions are mostly influenced by the cathodic arm, as seen in (**Fig.5.8**). Following the completion of the Tafel fit, the parameters of anodic current density, cathodic current density, anodic Tafel constant, cathodic Tafel constant (β_c), corrosion rate, and corrosion potential are displayed in **Table 5.3**.

Table 5. 3: Parameters for PDP measurements of the blank and TCQDs solutions.

TCQDs			E_{corr} (mV vs Ag/AgCl)	I_{corr} ($\mu\text{A}/\text{cm}^2$)	Corrosion	
Conc (ppm)	β_a (mV/dec)	β_c (mV/dec)			rate (mm/year)	%IE
Blank	21.3	32.4	-316	3.00	34.83	-
50	316	114	-239	0.534	6.20	82.3
60	376.3	60.7	-248	0.489	5.67	83.7
70	326	82.2	-255	0.415	4.79	86.2
80	397	143	-248	0.331	3.84	88.9
90	316	184	-245	0.260	2.964	91.4

The corrosion potential (E_{corr}) data exhibited no discernible trend across varying inhibitor doses, indicating a mixed-type inhibitory behavior. Nevertheless, diminished current density (I_{corr}) values were noted in the shielded solutions relative to the blank. I_{corr} decrease resulted from TCQDs adsorption onto the metal surface. The adsorbed inhibitor generates a layer of protection that restricts the hostile medium's access to the sample surface, hence lowering the rate of corrosion. The PDP aligned with weight reduction, EIS, and LPR, with inhibition efficiency rising from 50 to 90 ppm.

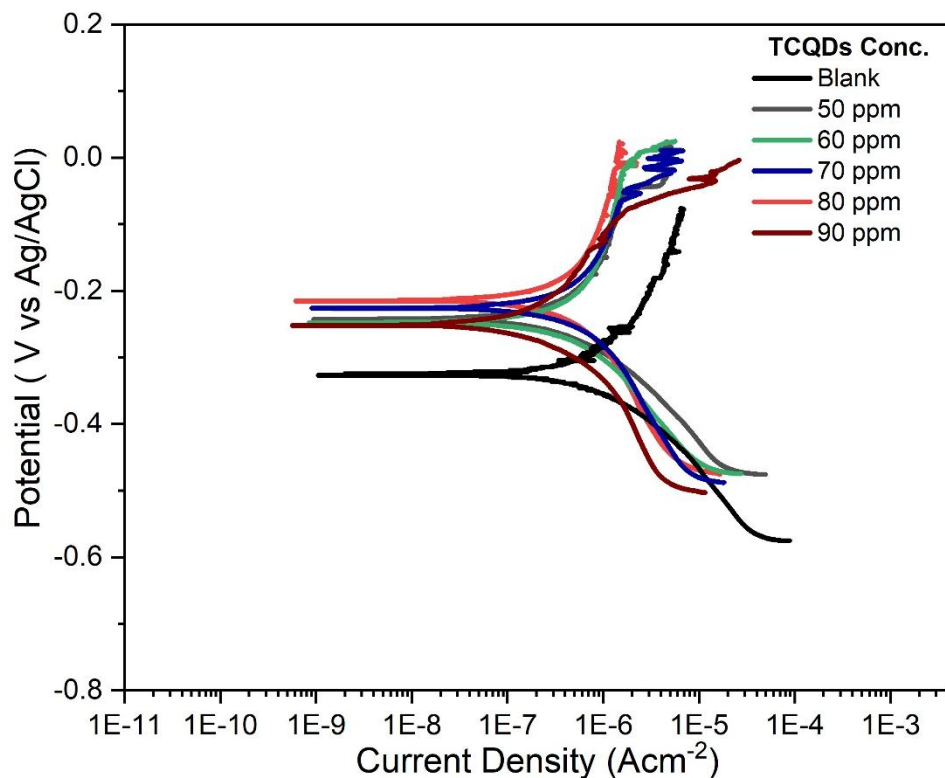


Figure 5.8: PDP plots recorded blank and TCQDs solutions.

5.3.7 EIS Analysis

The Nyquist and Bode data for the sample at TCQDs present at different concentrations and blank, are shown in **Table 5.4** and **Fig.5.9,5.10**. The Nyquist capacitive reactance arc diameter is expanded with the incremental TCQDs addition, showing a corrosion rate decline. TCQDs concentration and the capacitive reactance arc diameter relationship was established. With increasing TCQDs concentration, the capacitive reactance arc diameter demonstrated an increased trend (**Fig.5.9**). This transpired due to the potential coating of the sample surface with further TCQD concentration. The adsorption layer became increasingly concentrated as the concentrations of TCQDs elevated. one capacitive

reactance arc was concurrently detected in all Nyquist plots, representing the charge transfer resistance.

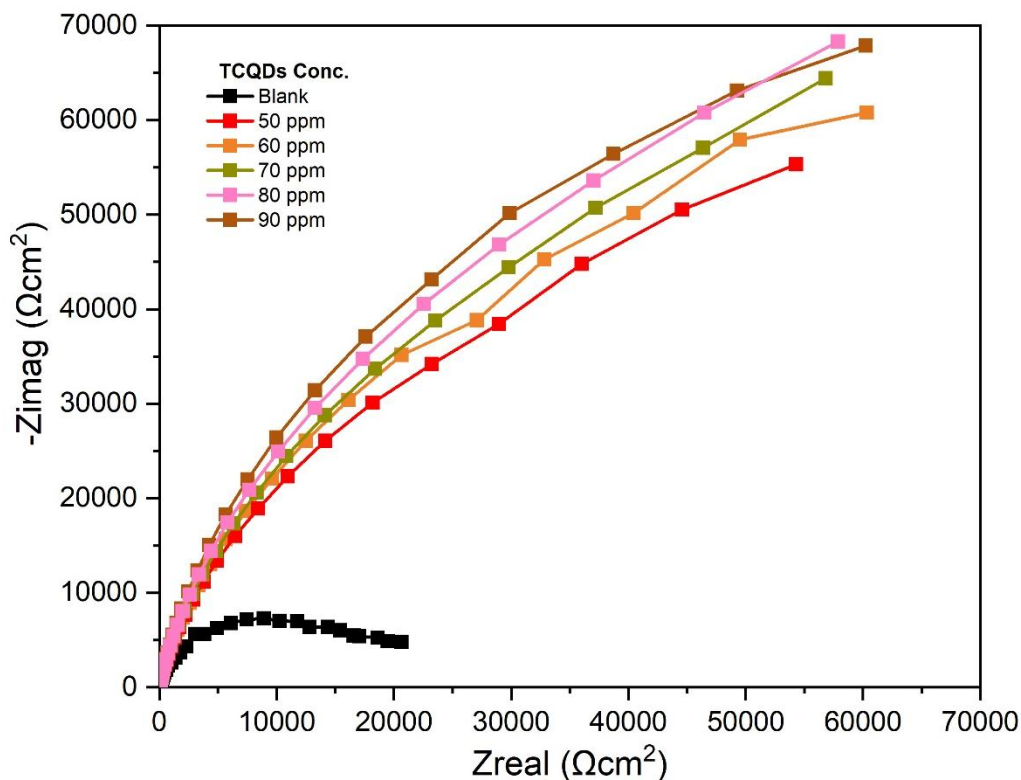


Figure 5.9: Nyquist plot of uninhibited and various TCQDs concentrations.

All test solutions exhibited one peak in their Bode phase graphs (**Fig.5.10**). A distinct peak observed in the solutions correlates with a singular time constant, whereas the TCQDs solutions bode phase display a greater diameter compared to the blank. TCQDs solutions diameter increases with higher quantities of TCQDs, as indicated by the Nyquist plots.

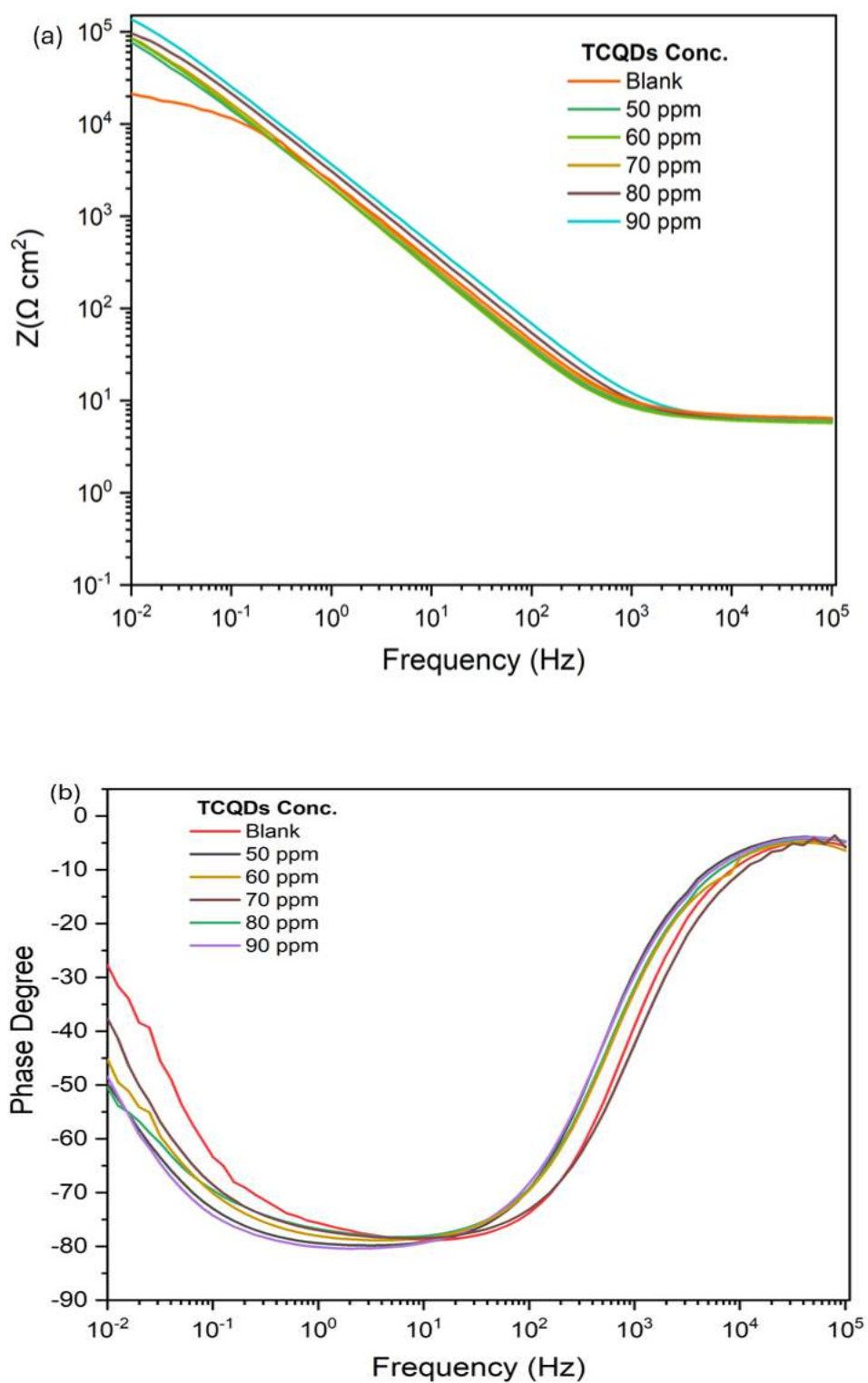


Figure 5.10: Bode plots of uninhibited and various TCQDs concentrations.

Table 5.4: Parameters for Electrochemical impedance spectroscopy measurements of the blank and TCDQs solutions at ambient temperature.

TCQDs (ppm)	Conc	$R_s (\Omega\text{cm}^2)$	CPE _f		R_{ct} (Ωcm^2)	$\chi^2 \times 10^{-3}$	%IE
			Y ₀₁	n1			
Blank		6.614	84.36	0.867	19.4	7.098	-
50		5.969	102.7	0.872	115.1	8.456	83.4
60		6.320	103.9	0.866	133.7	5.106	85.4
70		6.295	88.95	0.879	144.0	7.694	86.5
80		6.554	96.18	0.892	168.4	6.474	88.4
90		6.034	88.53	0.863	194.1	8.498	90

The EIS spectra were analyzed by equivalent circuit model fitting, which consists of R_s in series with the parallel combination of CPE and R_{ct} , as illustrated in **Fig. 5.11**. Here, R_s represents the solution resistance, identified at the high-frequency intercept, while R_{ct} denotes the charge transfer resistance at the low-frequency intercept, as indicated on the real axis of the Nyquist plots. The constant phase element (CPE) is utilized instead of a pure capacitor to account for changes in ideal dielectric behavior associated with electrode surface inhomogeneity.

Both R_f and R_{ct} values increased following the introduction of inhibitors, indicating that the sample was effectively coated by an adsorption layer. Concurrently, both values were incrementally elevated with the concentration of TCQDs. In contrast, 90 ppm of the

TCQDs had the highest level of enhancement. Moreover, the trend of CPE_{dl} demonstrated an inverse correlation with the R_{ct} value as the inhibitor concentration raised. The corrosive solution on the steel surface was gradually replaced with inhibitors. The thickness of the electric double layer increased, whilst the exposed area of the electrode decreased with rising inhibitor concentration. These modifications would result in a decrease in CPE_{dl} value. The computed η values in TCQDs solutions markedly enhanced with the elevation of inhibitor concentration. At TCQD concentrations of 80 and 90 ppm, the η values reached 87.9% and 90%.

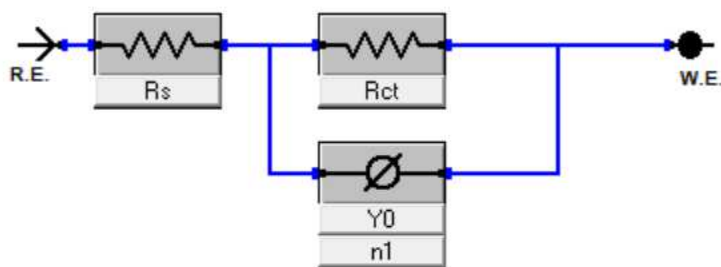


Figure 5.11: Equivalent circuit model employed for fitting the impedance curves.

5.3.8 Adsorption Analysis

Inhibitor molecules safeguard metal surfaces from corrosion by establishing layers that are either chemically or physically adsorbed, or by employing a combination of both methods. This protocol implements protective barriers. The Langmuir adsorption isotherm, which posits homogenous monolayer adsorption, was recognized as the most precise model. Langmuir's theory posits that a linear graph of C/θ vs C will exhibit an intercept of $1/K_{ad}$ and a slope of $a-L/K-L$ [206]. The graphs, based on weight loss and PDP measurements, are illustrated in **Fig 5.12**, with values detailed in **Table 5.5**.

Table 5.5: Adsorption study parameters of TCQDs.

Compound	Technique	ΔG_{ads}^o (kJmol ⁻¹)	k_{ads} (Lmg ⁻¹)	Slope	R ²
TCQDs	Weight loss	31.0197	9.625	1.0229	0.999
	PDP	36.3053	13.446	0.9982	0.9982

$$\frac{c}{\theta} = \frac{1}{K_{ad}} + \frac{a_L}{k_L} C$$

(30)

Where k_L and a_L are the constants of the Langmuir's isotherm, while the K_{ad} refers to adsorption equilibrium constant, and C represents TCQDs concentration.

The surface coverage degree, represented by θ , is determined by dividing the percentage of inhibition efficiency by 100. K_L denotes the maximum adsorbable concentration of the inhibitor, whereas a_L signifies the inhibitor's affinity for surface of the metal.

K_{ad} is associated with adsorption Gibb's free energy ΔG_{ad}^o as demonstrated in equation (31) [137].

$$\Delta G_{ad}^o = -RT \ln(1 \times 10^6 K_{ad}) \quad (31).$$

Where T represents temperature (Kelvin) and R represents molar gas constant.

Physisorption occurs when ΔG_{ad} is lower than or equal to -20 kJ/mol, while chemisorption is prevalent above -40 kJ/mol. A chemically enhanced physisorption adsorption process is proposed for values of ΔG_{ad} between -20 and -40 kJ/mol. The weight loss and PDP data revealed ΔG_{ad} values of -31.0 and -36.3 kJ/mol. This indicates that TCQDS is absorbed through a physisorption mechanism that is chemically augmented, encompassing both chemical and physical adsorption. The ΔG_{ad} negative values signify that a spontaneous and stable adsorption took place.

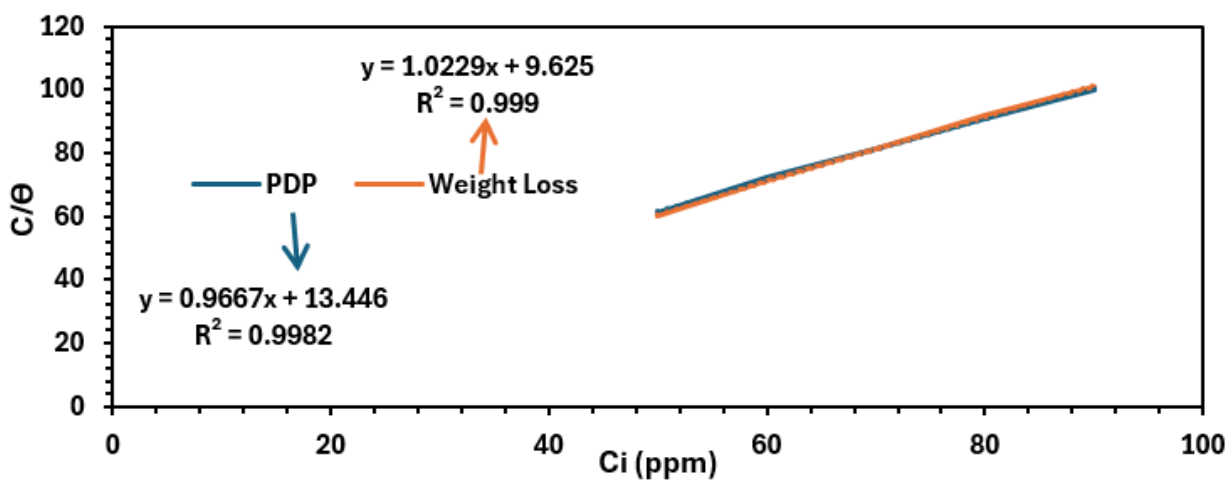


Figure 5.12: Adsorption study of TCQDS in Weight Loss and PDP technique.

5.3.9 Surface Analysis

Fig.5.13 shows surface morphology images using scanning electron microscope (SEM) of a steel surface submerged in an uninhibited solution and an inhibited solution. From the image, the blank solution's steel surface is rough, containing many cracks dispersed extensively. Protected steel has a smoother surface with less or minimal cracks. Protective

inhibitor molecules shield the steel surface from chloride ion corrosion, leading to a much smoother surface.

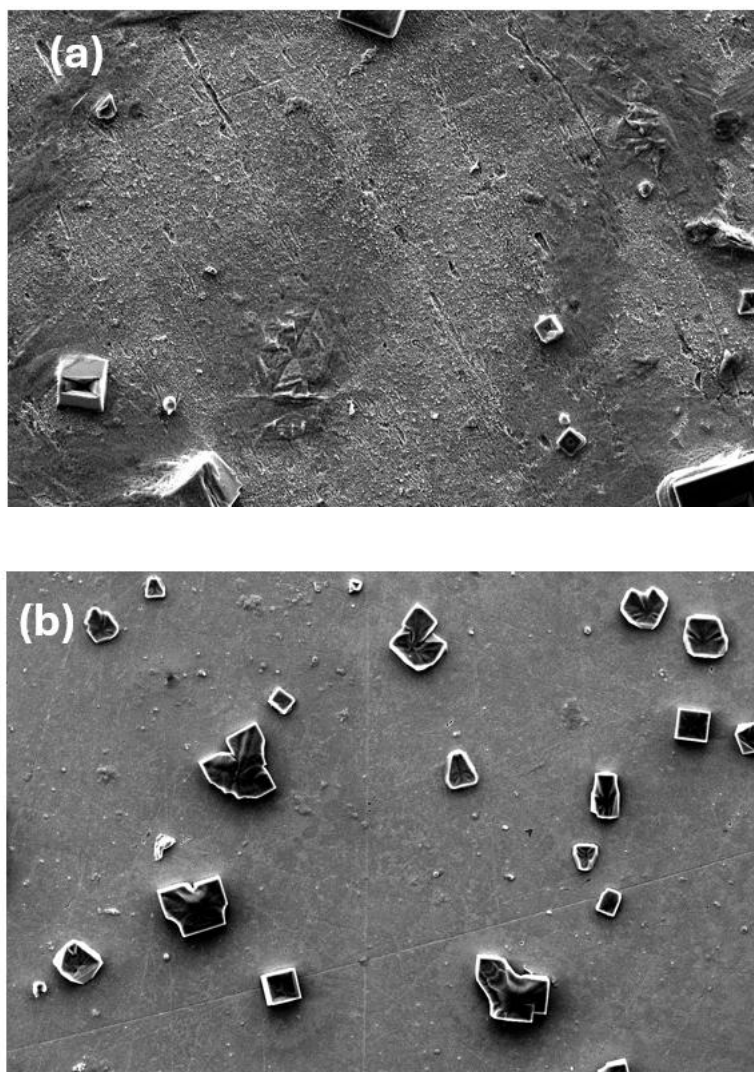


Figure 5. 13: SEM images after 15 days immersion in 3.5% NaCl solutions in the absence
(a) 90 ppm TCQDS (b)

5.3.10 Mechanism of Inhibition

Inhibitor molecules adhere to metal surfaces through multiple ways, including physisorption, chemisorption, or a mixture of both processes. A particular attachment approach entails a retro-donation process. In this mechanism, d-electrons from the surface iron atoms are transferred to the anti-bonding molecular orbitals of the inhibitor molecules. The transfer of electrons promotes the binding of inhibitor molecules to the metal surface, so enhancing their protective efficacy. Look to **Fig 5.14**. The TCQDs inhibitor is more protonated due to the presence of CQDs, which enhances the modified polymers' capacity for surface adsorption on steel. TCQDs adsorption on the sample surface is affected by the lone pairs of electrons on the donor heteroatoms (N and O) of the inhibitor molecules and CQDs (**Fig.5.14**). Conversely, the free π -electrons from TCQDs structures and unsaturated carbon dot molecules can engage with the vacant d-orbitals of iron atoms to establish coordinate bonds. The potentiodynamic polarization curve and adsorption studies indicate that TCQDs adsorption onto the sample surface entails both chemisorption and physisorption methods (**Fig.5.15**).

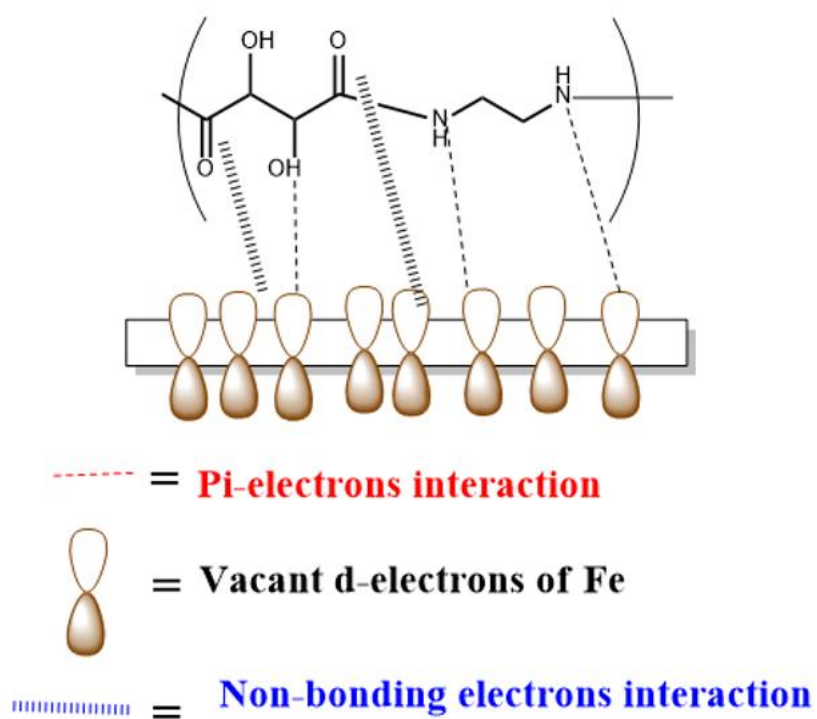


Figure 5.14: Inhibition mechanism of TDA

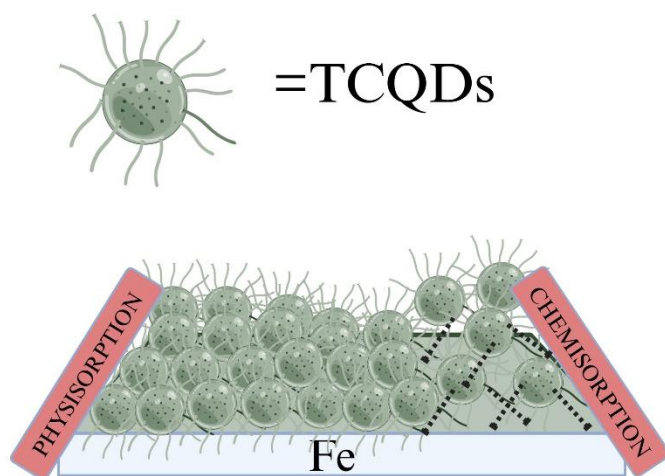


Figure 5. 15: TCQDs adsorption on the steel surface.

CHAPTER 6

CONCLUSION

To achieve highly efficient inhibitors for corrosion, this study focuses on synthesizing carbon dots, co-polymers and modification of the polymer with carbon dots as inhibitors. Nitrogen doped-Carbon dots and bare carbon dots were synthesized via a single step procedure from banana peels. The synthesized carbon dots were characterized using XRD, UV-VIS, TEM, PL emission, TGA. The structure of the synthesized copolymers (PAS, TDA and PSAM) were confirmed using FT-IR and NMR characterization. N-ACs were used to modify PAS (PAS/N-ACs), while CQDs were used to modify TDA (TCQDs). The inhibitory characteristics were evaluated in 1M HCl-3.5% NaCl and stimulated saline medium. The TGA results indicate both the carbon dots are thermally stable, which is beneficial when evaluating at high temperatures. Weight loss, electrochemical and surface morphology were used to evaluate the inhibition efficacy. PSAM and PAS/N-ACs were evaluated in 1M HCl-3.5% NaCl using weight loss and electrochemical analysis (EIS, LPR and PDP). The findings indicated that the highest inhibitory efficacy of 94.4% was attained at 30 ppm for PAS/N-ACs while the maximum efficiency for PSAM is 93% at 200ppm. According to the PDP results, both PAS/N-ACs and PSAM act as a mixed-type inhibitor, with their adsorption onto the steel surface occurring through both physisorption and chemisorption. Physisorption takes place when the protonated inhibitor molecule, particularly the amino group, interacts with the steel surface, involving some degree of retro-donation. Chemisorption, on the other hand, occurs when oxygen and nitrogen heteroatoms donate electron pairs to the d-orbitals of iron, forming a stable bond. These combined interactions enable the inhibitors to form a protective layer on the steel surface,

effectively preventing exposure to the aggressive medium, as evidenced by surface morphology analysis.

Moreover, the inhibitory efficacy of TCQDs was evaluated in a stimulated saline environment. The efficacy of TCQDs has been assessed to mitigate corrosion of 304 stainless steel in a stimulated sea water solution. TCQDs functioned as a mixed-type inhibitor. The inhibitory efficacy escalates with TCQDs concentration increment, achieving its peak at 90 ppm, with an efficiency of 89% for weight loss and 91% for PDP. The inhibitory mechanism of TCQDs relies on the establishment of an efficient protective layer on the surface of 304 steel within the corrosive solution, as verified by SEM Kinetic and thermodynamic investigations (i.e., K_{ads} and ΔG_{ads}) indicate that the Langmuir adsorption isotherm applies to TCQDs. The adsorption mechanism is governed by physical and chemical processes, as demonstrated by the ΔG_{ads} values.

In conclusion, all the synthesized inhibitors showed an effective inhibition efficacy in different media, with all the inhibitors acting as a mixed type.

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VITAE

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EDUCATION

MSc Chemistry

King Fahd University of Petroleum & Minerals (KFUPM), Dhahran, Saudi Arabia

January 2023 – Present

GPA: 3.821 / 4.00 (Distinction)

Relevant Courses: Advanced Analytical Chemistry (A+), Physical Chemistry (A+), Chemometrics (A), Electrochemical Corrosion (A)

BSc Industrial Chemistry

Kaduna State University (KASU), Kaduna, Nigeria

July 2016 – November 2021

Final Grade: 4.84 / 5.00 (First Class)

Relevant Courses: Analytical Chemistry (A), Organic Chemistry (A), Organic Spectroscopy (A)

RESEARCH EXPERIENCE

Advanced Materials and Corrosion Lab, KFUPM, Saudi Arabia

Project 1: Synthesis and characterization of a biodegradable polymer-carbon composite for enhanced corrosion protection (July/2024 – January/2025)

- Synthesized eco-friendly polymers and modified activated carbon from banana peels achieving 85% waste utilization
- Characterized materials using TEM, XRD, FTIR, TGA, ¹H-NMR
- Analyzed surface morphology and elemental composition through SEM-EDX.
- Investigated nanoscale surface features and roughness profiles using atomic force microscopy (AFM) to support coating performance evaluation.

- Conducted DFT calculations to analyze electronic properties and correlate with experimental results
- Evaluated corrosion inhibition on C1018 carbon steel using electrochemical techniques (EIS, LPR, PDP, OCP, EFM)

Project 2: Nitrogen-enriched polymeric inhibitor for HCl-NaCl corrosive environments (December 2023 – May2024)

- Synthesized and functionalized poly aspartic acid-co-melamine using green chemistry protocols
- Evaluated corrosion inhibition via gravimetric and electrochemical method (EIS, LPR, PDP, OCP, EFM) and surface analysis
- Performed theoretical DFT modeling to predict adsorption mechanisms and inhibition efficiency

Materials Synthesis Lab, Kaduna State University, Nigeria

Project: Corrosion inhibition of Carbon metal using Schiff base (May 2021 – September 2021)

- Synthesized and characterized Schiff bases using FTIR, UV-VIS, ¹H-NMR.
- Assessed inhibition efficiency via gravimetric and SEM techniques
- Identified structure-activity relationships influencing inhibition performance
- Optimized synthesis conditions to improve yield from 55% to 78%

PUBLICATIONS

- Lawal, M. A., Musa, A., **Muhammad, Z.**, Haruna, K., & Saleh, T. A. (2025). Assessment of inhibition performance of expired chloroquine phosphate on 304 L stainless steel corrosion in hydrochloric acid solution: An experimental and computational study. *Sustainable Chemistry for the Environment*, 10, 100251. <https://doi.org/10.1016/J.SCENV.2025.100251>
- Haruna, K., Musa, A., Lawal, M. A., **Muhammad, Z.**, & Saleh, T. A. (2025). Experimental and DFT study of the corrosion inhibition potential of expired diclofenac potassium on stainless steel in hydrochloric acid solution. *Environmental Surfaces and Interfaces*. <https://doi.org/10.1016/J.ESI.2025.04.001>
- A.I., Lawal, **Z., Muhammad**, Obunadike C.V., Yakubu Y.Y., Ogunsanmi A.O., Olabode O.O., Ayodele C.O., and Komolafe F.E. (2022). “Photocatalytic Degradation of Phenol in Wastewater: A Mini Review.” *International Journal of Research and Innovation in Applied Science* 07(09):59–64. doi: 10.51584/IJRIAS.2022.7906.
- Chizoba, V. O., Yussif, Y. Y., **Zahradeen, M.**, et al. (2022). *Effect of Pesticide Residue in Food Crops on Man, and the Environment*. *World News of Natural Sciences*, 44, 192-214

Manuscripts Under Review:

- **Zahradeen M.**, Saleh A.T., Kabiru H. Hybrid polymeric-carbon composite inhibitor for corrosion inhibition in desalination plant. (under review)
- **Zahradeen M.**, Saleh A.T., Kabiru H. Corrosion inhibition of Poly-aspartic acid-co-melamine against low-grade carbon steel (C1018) in 1M HCl-3.5% NaCl medium, an experimental and theoretical study. (under review)

TEACHING & WORK EXPERIENCE**Teaching Assistant – CHM 311 (Term 242)**

KFUPM, Saudi Arabia (January 2025 – Present)

- Design and grade assignments and quizzes for a class of 40 students
- Conduct weekly review sessions focusing on problem-solving strategies

Teaching Assistant – CHM 572 (Term 241)

KFUPM, Saudi Arabia (July 2024 – December 2024)

- Supported graduate-level chemistry course through grading, technical assistance, and discussion facilitation
- Assisted 18 graduate students with advanced analytical techniques and equipment operation

Teaching Assistant – CHM 101 (Term 232)

KFUPM, Saudi Arabia (January 2024 – June 2024)

- Graded assignments and quizzes for a class of 30 students
- Conducted revision classes that improved exam scores by an average of 12%
- Proctored exams and assisted in quiz preparation

Graduate Assistant – CHM 101 Lab Instructor (Term-222, 231)

KFUPM, Saudi Arabia (January 2023 – December 2023)

- Led laboratory sessions for 14 students per term, achieving 100% safety compliance
- Provided instruction in safety protocols, data analysis, and experimental execution
- Designed and graded lab quizzes and reports, contributing to 15% improvement in overall class performance
- Received average student evaluation score of 4.7/5.0

Laboratory Assistant

Federal Polytechnic, Kaduna, Nigeria (10/2021 – 12/2022)

- Supervised and assisted with laboratory experiments, equipment maintenance, and standard analytical procedures

Internship - Laboratory Unit

Kaduna State Water Corporation (05/2019 – 11/2019)

- Conducted water quality analyses using AAS, UV-VIS, and titration methods
- Participated in public health awareness campaigns reaching over 500 community members

- Implemented improved sample collection protocols that reduced contamination rates by 30%
- Contributed to monthly water quality reports for regulatory compliance

PROFESSIONAL MEMBERSHIP

Member, American Chemical Society (ACS)

Member, The Electrochemical Society (ECS)

Member, Polymer Institute of Nigeria (PIN)

Member, Chemical Society of Nigeria (CSN)

Member, Association of Material Protection & Performance (AMPP)

Member, Institute of Corrosion

CONFERENCES AND POSTERS

- **Poster Presentation:** "Biodegradable Polymer-Carbon Composites for Corrosion Protection," 2nd Chemistry Poster Presentation, KFUPM, Saudi Arabia (February 2025)
- **Seminar:** "Ionic Liquids as Sustainable Corrosion Inhibitors," Department of Chemistry, KFUPM (November 2023)
- **Poster Presentation:** "Corrosion Inhibition of Zinc with Novel Schiff Bases," Undergraduate Research Symposium, Kaduna State University (August 2021)
- **Oral Presentation:** "Green Approaches to Corrosion Prevention," 3rd Annual Conference, SCSN NW Chapter, Sokoto State University (May 2021)
- **Workshop:** "Non-biodegradable Polymers and Their Environmental Effects," Polymer Institute of Nigeria (March 2021)

LEADERSHIP AND SERVICE

President, SCSN KASU Chapter (2019 – 2021)

- Organized and coordinated orientation seminars for newly admitted students
- Developed and maintained an administrative structure to ensure effective management of the student body
- Represented students in faculty and school meetings, actively promoting student interests

Group Leader, Final Year Project (2020 – 2021)

Covid-19 Enforcement Team Member, KASU (2020 – 2021)

- Participated in campus safety monitoring and protocol enforcement
- Assisted in developing safety guidelines for laboratory operations
- Conducted awareness sessions on laboratory safety during the pandemic

Tutor & Coordinator, Community Service Project (2020 – Present)

- Tutored and guided 50 high school students for University Entrance Examinations
- Supported 24 students in successfully gaining admission into 4 Nigerian universities
- Organized weekly group study sessions with measurable improvement in practice test scores

Chairman, Academic Committee, SCSN KASU Chapter (2019 – 2021)

- Organized and coordinated academic tutorials (chemical thermodynamic, chemical kinetics, polymer technology, material science etc.) for students which lead to significant improvement in their grades.
- Assisted in simplifying complex courses during tutorial classes for easy understanding and assimilation.

AWARDS

- Best Graduating Student, Dept. of Pure and Applied Chemistry, KASU (2021)
- Overall Best Student of the Year, SCSN KASU Chapter (2021)
- Best Teacher of the Year, Katari Schools (2022)