# Corrosion Protection of Medium Carbon Steel in Acidic Environment Using Novel Schiff Base Inhibitor



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# Corrosion Protection of Medium Carbon Steel in Acidic Environment Using Novel Schiff Base Inhibitor



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# Dedication

My heartfelt dedication during this research work goes to Almighty Supreme Allah who is my creator and a source of motivation in hurdles. I dedicate this thesis to my family; a deep debt of appreciation to my father Shabih Ul Hasan, my mother Sarah Shabih and my siblings,my friends, for their endless encourage and support. A special thanks to my supervisor for his remarkable advices and guidelines throughout my research work.

# Acknowledgements

I would like to offer uncountable praise to the holy Prophet (Peace be upon him) who is an endless model of auspicious guidance for humanity.

It is my privileged to express appreciation and gratitude to my research supervisor Dr. Muhammad Shahid and my committee members Dr. Muhammad Shoaib and Dr. Mohsin Saleem for their constant support in facilitating and managing research direction. I endorse the mindful and technical expertise of my GEC committee throughout my master's research phase.

I am also overwhelmed with uninterrupted cooperation of my family, all my friends and colleagues for giving endowing me endless love, admiration and help in completing this project.

Sincerely, Wareesha Hasan

### Abstract

The aim of this research work was to investigate the inhibition efficiency of an organic inhibitor added in different concentration under 0.1M, 0.5M and 1M HCl. Medium Carbon steel was used for the study of corrosion rate. During the experimentation, Linear Polarization Resistance and Tafel polarization tests were performed in the absence and presence of inhibitor in the electrochemical cell. Optical Microscope and SEM for surface examination were also conducted for the valuable information regarding the number of pits on the surface of medium carbon steel. The results showed that at 0.1M HCl the inhibitor performed well by lowering the corrosion current. The amount of inhibitor optimized at 0.1 M HCl was observed to be 0.6mM. The absence of inhibitor efficiency was observed at 0.5M and 1M HCl. It was concluded that organic inhibitor showed excellent behavior at lower concentration of HCl while at higher concentration the inhibitor showed no appreciable behavior in the corrosion prevention of Medium Carbon steel.

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# 1 Chapter:

# Introduction

The analysis of corrosion behavior is based on the interaction of alloys with their respective environments. A reliable guidance of corrosion testing provides technical information to the Manufacturing designers, purchasers and end user to understand inservice conditions of materials. The purpose of this study is to exercise corrosion testing on the inhibitors under corrosive media that helps to provide valuable information in the selection of materials with respect to the given environment. There are many tests performed for the corrosion evaluation like cyclic cabinet test, immersion tests and electrochemical tests. Quality control, material selection, corrosion mechanism, prediction of service life for certain environment, calculation on environmental condition, predict expected degradation mechanism. A guideline that provides directional data for the rate of corrosion. In keeping with the theme of this research, money saving corrosion protection technique is the use of inhibitors.

#### 1.1. Significance of Inhibitors Corrosion Protection Mechanism

#### 1.1.1 Classification of Corrosion Inhibitors

The corrosion inhibitors are distributed under the classification of Inorganic Inhibitor and Organic Inhibitor. The division of inhibitors as Organic and Inorganic is based on chemical nature of Inhibitors. Further division of Inorganic and Organic inhibitor as anodic, cathodic and adsorption is based on mechanism of action in the corrosive medium. [1]

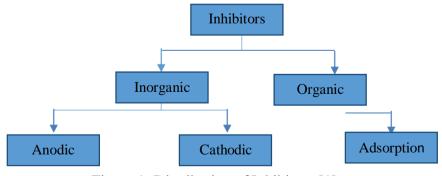


Figure 1: Distribution of Inhibitors [1]

#### **1.2.** Inorganic Inhibitors

The inorganic corrosion inhibitors are divided in to Anodic and Cathodic Inhibitors.

#### 1.2.1. Anodic Inhibitor

Anodic inhibitors commonly perceived as passivating inhibitors work by decreasing the anodic reaction of Tafel polarization curve that is by blocking the anodic reactions and supporting the natural reaction of passivation of metallic surfaces or by organizing insoluble and safe defensive film on the metallic surface by reacting with corrosion products.

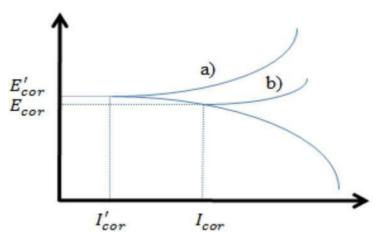


Figure 2: Tafel Polarization Curves in the Presence of Anodic Inhibitor [1]

#### 1.2.2. Cathodic Inhibitor

During the corrosion process, the cathodic Inhibitor retards the cathodic reaction on the metallic surface. The cathodic inhibitor blocks the formation of reproducible breeds, that is, the oxygen diffusion & electrons potential areas.

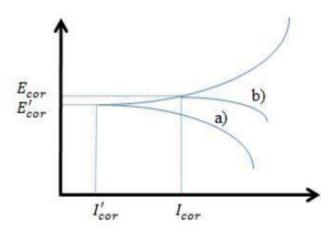


Figure 3: Tafel Polarization Curves in the Absence & Presence of Cathodic Inhibitor [1]

#### 1.2.3. Organic Inhibitors

Organic inhibitors as compounds can be utilized as Cathodic, Anodic & Mixed Inhibitors. The organic Inhibitor act through the process of assimilation the surface by forming stabilized film. The dissolution of metal in the electrolyte is ceased by formation of inhibitor"s hydrophobic film which provides barrier to corrosion process. The figure illustrates the Polarization curve of the solution with & without organic Inhibitor. It can be seen from the figure that the corrosion potential remains the same but the current decreases from Icorrto I"corr.

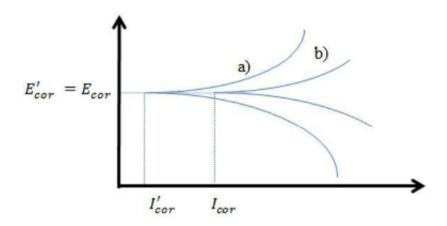


Figure 4: Tafel Polarization Curves of Organic Inhibitor [1]

The protection mechanism of organic inhibitor is shown in figure in it readily reacts with metallic surface and forms protective film. The main characteristics of organic inhibitor"s efficiency depend upon the following points below:

- 1. Chemical structure of organic molecule
- 2. Aromatic/Conjugate bond as the carbon chain length
- 3. Potentially capable of making compact &cross linked layer on metal surface
- 4. Solubility with electrolyte.

The effectiveness of these organic corrosion inhibitor depends on the presence of polar functional group with S,O or N atoms in the molecules, heterocyclic compounds and  $\pi$ -electrons. The polar functional group plays a leading role in establishing adsorption process. The active corrosion sites are blocked when O,N andS are adsorbed on these sites. The most effective and efficient organic inhibitor are

those which contain  $\pi$ -bonds [2].Schiff bases and their metal complexes render improved inhibiting performance for steels in aggressive media. The damage cause by corrosion is an afflicting problem and results in high maintenance and protection, the addition of corrosion inhibitor to prevent damages of corrosion is an applied, practical and achievable task as compared with removal. Easy synthesis are the sign of good corrosion Inhibitors and Schiff bases corrosion Inhibitors always withstand. Steels in the acidic media exhibit major dissolution problem. The acidic aqueous solution are the key issues for steels corrosion faced in many industries using specially in acid descaling and oil well acidizing [3].

A German Chemist, broadly known as Noble Prize winner Hugo Schiff in 1864, discovered the Schiff Bases. The Schiff base in terms of its structure is known as iminewhich is equivalent of Ketone or Aldehyde group.

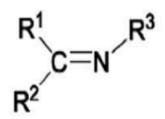


Figure 5: Schiff Bases as Corrosion Inhibitor [3]

As far as coordination chemistry is concerned, the formation of complexes of Schiff bases are most encouraging candidate of forming stable complexes with metal ions. The working principle of Schiff bases involves the donation of their lone pairs of electrons as well as any  $\pi$ -electrons to metal. The protection from dissolution is made possible by the adsorption of Schiff base on the metal surface thereby reducing corrosion. Nitrogen, Oxygen and Sulphur are the heteroatom and are proficient in forming covalent bond with metal surface. The adsorption properties of Schiff bases are influenced by following factors [3]

- 1. Character and Surface charge on the steel surface.
- 2. Type of Vigorous media.

- 3. Nature of Interactivity with steel surface.
- Existence of Heteroatoms such as Nitrogen, Oxygen, Phosphorous and Sulphur.
- 5. Presence of numerous bonds and aromatic rings.

#### 1.3. Corrosion Testing and its Objectives

It is evident that Corrosion testing and its monitoring provides desired knowledge of corrosion behavior of material in the existence and in non-appearance of Schiff base Inhibitors with respect to its application. Electrochemical method provides data- driven approach to ensure materials behavior for predicting service life in industry.

#### 1.3.1. Quality Control

In order to achieve operational excellence quality control is essential. Sound quality holds People Process and Technology. From corrosion testing the rate of corrosion is analyzed and actionable to improve future outcomes. The expectation of user has dramatically increased now a day therefore employment of inhibitors for the protection of ferrous and nonferrous alloy is fundamental to improvement of overall quality.

#### 1.3.2. Qualification Test for Newly Synthesized Inhibitors

The people from Industrial background do not give much thought to catastrophic failures caused by corrosion. Usually when investigation take place and find it is a problem it is kind of late, and the cost to correct the damage can be great. Therefore, Electrochemical techniques provide thorough inspection of inhibitors performance with respect to material before it is use in service.in our present study we are using Hydrochloric acid as a corrosive medium for Newly synthesized Schiff base performance for mild steel. Hydrochloric acid is the burdensome acid to handle from the standpoints of corrosion and materials of constructions. Extreme care is perquisite to handle the acid by itself, even in relatively dilute concentrations, or in process solutions containing considerable amounts. In industries, hydrochloric acid solutions are often used in order to exclude scale and salts from steel boilers, tanks and pipelines etc [4].

#### 1.3.3. Material Selection

Appropriate Material selection is the foundation of new developments and successful completion of targets. Corrosion testing demonstrates rate of corrosion and provides selection criteria of eligible in-service material. It is evident that zinc as well as Iron corrode in HCl but the rate of corrosion is high in the case of zinc as compared to iron. The selection criteria is based on application requirements therefore predicting corrosion of materials and identifying the mechanism of degradation with respect to requirements is important for design engineer in the selection of materials.

#### 1.3.4. Nature of Environmental condition

Corrosion testing helps in providing sound solution to material problems in various environments. The data collected by testing materials embrace economic and safety benefits. The transportation of ionic species from cathodic and anodic sides can be evaluated from corrosion monitoring nature of electrolyte and metal-electrolyte interaction can be studied with varying parameters. Several modes of corrosion can activate with one or more environment. Therefore, defining environment and its proper study help in predicting the performance of the materials.

#### 1.3.5. Prediction of Service Life

There are many situations that leads to premature failure and if we do not understand the corrosion mechanism then we would not be able to protect our structures. In dayto-day life material"s durability and long-term life prediction is getting a lot of importance.For example a corroded oil pipeline carrying an oil and it fails suddenly due to corrosion, it might catch fire and there could be explosion.

#### 1.4. Monitoring of Corrosion by Electrochemical Method

This section addresses the corrosion sensing techniques. The working principle of all the electrochemical techniques is based on Mixed Potential Theory. Mixed potential is a potential where the rates of anodic and cathodic reactions are equal. This is because these two reaction are independent of each other and that is why the rate of any of the two is reduced to control corrosion by using anodic or cathodic inhibitor. For example, incathodic protection the material to be protected is polarized cathodically in order to reduce the rate of the anodic metal.

#### 1.4.1. Dissolution Reaction.

Reaction	For Iron	For Zinc
Anodic	$e \rightarrow Fe^{2+} + 2e^{-}$	$Zn^{2+} + 2e \rightarrow H_2$
Cathodic	$2H^+ + 2e^- \rightarrow H_2$	$2H^++2e^- \rightarrow H_2$

 Table 1: Anodic and Cathodic reaction on metal Surface [5]

#### 1.4.2. Electrochemical Method

The electrochemical test take place by charge transfer between ionic reactants and a conducting material, called working electrode, acting as an electron source. Electrochemical reactions involve oxidation or reduction of the reacting elements. Oxidation is the dispatch of electrons from atoms or groups of atoms towards cathode, resulting an increment in valence, and reduction is the addition of electrons to atoms or groups of atoms, resulting in a depreciation in valence [5].

Category	Test Method	
Zero Applied Signal	<ul> <li>Open Circuit Potential Testing</li> <li>Dissimilar metal"s Corrosion Evaluation</li> <li>Electrochemical Noise Testing</li> </ul>	
minute-signal polarization	<ul> <li>Polarization resistance (linear polarization)</li> <li>Electrochemical Impedance Spectroscopy</li> </ul>	
Large-signal polarization	• Potentiostatic and galvanostatic polarization	
Scanning electrode techniques	<ul> <li>Potential &amp;Current scans Scanning techniques</li> <li>Electrochemical impedance spectroscopy scans</li> </ul>	

Table 2: Electrochemical Tests conducted for Corrosion Evaluation of Materials [5]

#### 1.4.3. Linear Polarization Resistance

The significance of conducting this testing lies not only in its data interpretation but also in its application, simplicity and reduced testing times because of its small range potential. The response of current in the result of variation in potential on the surface of the working electrode is exponential and described by Butler-Volmer equation as equation (1) [6].

$$i = i_o \left[ \exp \left( 2.3 \right) - \exp \left( 2.3 \right) \right] \quad (1)$$

Where,  $\eta = Over potential$ 

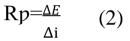
i = Electrode Current (Amperes)

 $i_0$  = Exchange Current Density (Amperes/meter square)

 $\beta_a$  = Anodic Current Density

 $\beta c$ = Cathodic Current Density

Potential range applied in linear polarization is from -20 mV to +20 mV relative to Ecorr, and measures the resulting current with a scan rate of 5mV/secs. The details collected in an LPR test is the polarization resistance Rp (shown in Fig. 6).



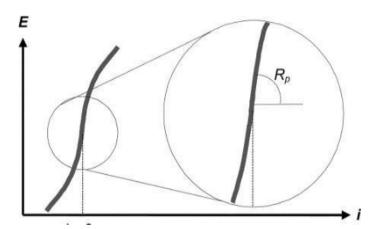


Figure 6: Representative Image shows Resistance Polarization obtained from Linear Polarization Resistance Test [6]

#### 1.4.4. Tafel Polarization

A faster Corrosion monitoring technique commonly utilized as Tafel Polarization is adopted to determine corrosion rates, corrosion current anodic and cathodic slops of corroding material. During this test, the incoming and outgoing electrons are accompanied on the working electrode immersed in corrosive electrolytic environment. Triggering corrosion of the electrode is obvious when metal is dipped in aqueous environment due to anodic and cathodic interdependent reactions [7]. The Tafel plots aids in sensing these reactions.

#### 1.5. Application

There are numerous areas of applications in which Schiff Base Inhibitors are used. The application of Schiff base inhibitors are in simulated circulating cooling water. Various amounts of gases are utilized in oil & gas sector including CO<sub>2</sub> in the presence of Chloride concentrations.to prevent corrosion in this area Schiff Base Inhibitors have been utilized. Schiff base epoxy–amine composite coatings have beenadopted to head off corrosion of mild steel. Schiff bases inhibitors are added with acids for cleaning of metallic parts like instruments, devices storage tanks and underground pipes.

Acid solutions are routinely used in the withdrawal of unwanted corrosion debris in metalworking parts, boilers and heat exchangers etc. So, the highly aggressive nature of HCl must be controlled by a suitable corrosion Inhibitor instead of using high-priced corrosion protection coatings[8-11].

- Removal of scale & salts from steel surface
- Cleaning tanks
- Industrial boilers
- Cleaning underground pipes

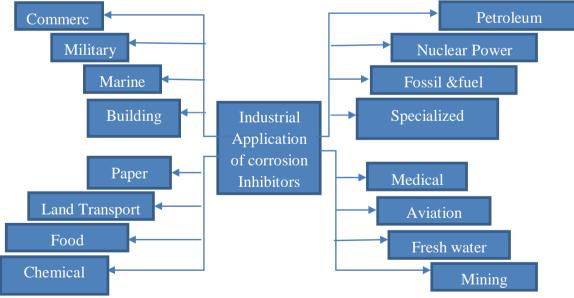


Figure 7: Area of Application for Corrosion Inhibitors [5]

#### 1.5.1. Predicted Area of Application for Novel Schiff Base Inhibitor

The area of application selected for this research work was cleaning of rusted and corroded components by utilizing HCl. It cause some surface discontinuity if inhibitor do not work well [12]. For successful application, it is necessary to have full information on the type of oxides or scales and the environment in which these are formed, in order to select the best combination of chemicals for removal of the scales The methods used to clean the rust and corroded surfaces are based on the following methods: [12]

- 1. The chemical solvent must be able to disintegrate the deposits so that these can be removed.
- 2. The chemical should be properly protected by inhibitor for the particular type of metal or equipment to be cleaned so that it does not damage the base metal.
- 3. The chemical should not be highly toxic or explosive in nature and should be cost, effective as well.

Here are some of the pictures that are showing the corroded and rusted surfaces.



Figure 8: Corroded Tank Hole



Figure 9: Water cooling towers

## 2. Chapter:

# **Literature Review**

Kumar et al. [15], circumvented the performance of novel inhibitors for low carbon steel corrosion rates in 0.5 M HCl by taking weight loss and electrochemical techniques as inhibitor"s qualification test. The test run profiles traced the act of inhibitors as mixed type. The added inhibitors reduced the corrosion rates. The cathodic and anodic branch of Tafel plots clearly experience shift as compared to uninhibited conditions. The lower branch of the Tafel plot shifted to a downswing in current densities whereas anodic metal dissolution also retarded. The surface examination of MS surface was carried out in their research, which revealed that in the absence of inhibitors the MS surface was irregular while in the presence of inhibitor the surface of the Mild Steel.

Ituen et al. [16], investigated inhibition characteristics of X 80 steel grade for oil field acidizing environment under different concentrations of inhibitors at non- identical temperatures using electrochemical techniques. The experiments were conducted in 1 M HCl with and without inhibitor. Tafel plots measurements showed decrease in I<sub>corr</sub> values. The oxidation indulged on iron was suppressed in the presence of inhibitors as depicted by the anodic curve of the Tafel plots. The surface morphological studied indicated decreased surface ambiguity in the presence of different concentrations of inhibitors in contrast to the acid solution. This behavior was appertained to the creation of film formed at metal-acid interface by inhibitor. However, the surface film was not visible in the SEM micrographs. The investigationconcluded that the blends of 3-(2-chloro-5,6-dihydrobenzo[b][1]benzazepin-11-yl)- N,N-dimethylpropan-1- amine denoted as "3CDA"should be adopted as efficient corrosion prohibition compound for deep well acidizing conditions in the oil field at temperatures not higher than 60°C.

Chitra et al. [17], investigated inhibition performance of namelyN,N'-Bis(benzylidene)-4,4"-dianiline (DAA), N,N'-Bis(benzylidene)-4-4'methylenedianiline (MDAA), N,N'-Bis(benzylidene)-4-4'-sulphonyldianiline (SDAA), N,N'-Bis(benzylidene)-4-4'-oxydianline (ODAA) by using Mild steel in 1M HCl. The Electrochemical Test were conducted for corrosion testing. It was observed that both anodic and cathodic slops were altered to appreciable extent by the addition of all the four Schiff bases inhibitors. It was articulated that among four inhibitors three of them contain mixed type character and one inhibitor possess cathodic nature. The findings of researchers also concluded that uplifting the temperature, declined the inhibitor's capability. The change in surface characteristicswere also revealed by the addition of inhibitors.

Arshad et al. [18], carried out research on the Bis-Schiff bases to understand their behavior in mild steel for acidic medium. The corrosion monitoring of three discreteBis-Schiff Bases namely 1,10 -(2,20 -dibromo-[1,10 -biphenyl]-4,40 -diyl) bis(N-phenylmethanimine) (**BNSB01**), 1,10 -(2,20 -dibromo-[1,10 - biphenyl]-4,40 - diyl)bis(N-(4-bromophenyl)methanimine) (**BNSB02**) and 4,40 -(((2,20 -dibromo-

[1,10 -biphenyl]-4,40 -diyl)bis(methanylylidene))bis(azanylylidene))diphenol (**BNSB03**)were done using Potentiodynamic Polarization. All inhibitors corroborated excellent inhibition efficiency for mild steel in 0.5 M HCl and acted as mixed type inhibitors. The concentration of inhibitors were in range containing 0.8-3.2mM. Further, the surface examination was also carried out in the assimilation of Bis-Schiff base inhibitors. The SEM images indicated the formation of inhibitor"sdefensive layer on the substrateand proved the activity of Bis-Schiff bases as distinctive compound.

Nassaret al. [19],had worked on Anticorrosion Studies of New Homo bimetallic Schiff base complexes in 0.5 M HCl. Concentration of the inhibitors ranging from (0.0001-0.0007)M. His experimental work revealed that intensifying the inhibitor's amount increased the efficiency of inhibition. The Potentiodynamic measurements were carried out in defiance of corrosion carrying different values of inhibitors. The behavior under Tafel polarization curves classified the New Homo bimetallic Schiff base complexes inhibitor as "Mixed Type".

Mir Ghasemet al. [20],Investigated the performance of Asymmetrical Schiff Base H2A3 and H2A4 as heedful inhibitors in H2SO4. The concentration were in the range of (50-400)ppm. To assess the inhibition efficiency, the Tafel polarization measurements were carried out, satisfactory results were obtained under various

concentrations of both inhibitors. Efficiencies of H2A3 and H2A4 were 95% at a concentration of 400ppm. The tafel polarization measurements indicated inhibitors as mixed anodic-cathodic type with marked delaying in material deterioration.

N.ANegm et al. [21], paid vigilance to impede corrosion through two quaternary Isoxazolium Schiff bases namely N-(4-methoxy benzylidene)-3-amino-5-methyl1,2oxazole (OA) and N-benzylidene-3-amino-5-methyl-1,2- oxazole (OB)in hydrochloric acid as an electrolyte. The outcomes indicated the substrate damage of carbon steel in acid was effectively decreased by cationic Isoxazolium Schiff base inhibitors. The improvement in the Inhibitorwas notedwith increasing concentration of the inhibitive compound. The outcomes of test indicated mixed-type inhibitors and significantly ceased the electron migration by assimilating on carbon steel surface. Impedance testing indicated the origination of capacitive twin layer at the metal surface. Readings gathered from assessment exhibited excellent inhibition performance for steel in 0.5M HCl solution.

A.Yurt et al. [22], performed inhibition activities on a chain of Schiff bases containing heteroaromatic substituents namely 2-((1E)-2-aza-2-pyrimidine-2-ylvinyl)thiophene denoted as PT, 2-((1Z)-1-aza-2-(2-pyridyl)vinyl)pyrimidine denoted as PP,2-((1E)-2aza-2-(1,3-thiazol-2-yl)vinyl)thiophene denoted TT. 2-((1Z)-1-aza-2-(2as thienyl)vinyl)benzothiazole denoted as TBT. The Schiff bases with following substituents acted as anodic inhibitor, the change in inhibition was entrenched on the category, and sort of the substituents present in the inhibitor molecule. In this research, inhibitive molecules produced a down turn in electrons activity and drifting potentials to noble direction under anodic regime. Activity of the Schiff bases declined with temperature and its decline continued escalation of corrosion process. Impedance tests manifested an uptrend in resistance during charge mobility values of inhibitor. The adsorption of Schiff bases on carbon steel in 0.1M HCl solution adopted multi-layer isotherm principle.

S.Bilgicet al. [23], researched on the effect of two inhibitive compounds, N-(1-toluidine) salicylaldimine and N-(2- hydroxyphenyl) salicylaldimine on chromiumnickel in acidic as vigorous media. The response of both the compounds were distinct in terms of interaction with metallic substrate because the compounds possesses varied structure. Molecules were anchored with solid surface through by the electron-granting atoms. The compounds employed for retardation of corrosive rebuke behaved anodically as well as cathodically. The inhibition competency of both compounds resulted in almost similar behavior ranging from (35-93) % with scanning potentials leading from negative to positive.

Emregul et al. [24], studied the inhibiting properties for steel by using Chloridesubstituted salicyaldamine Schiff bases. It was revealed that when the aggregate of the inhibitors were increased, the preferment in working contrary to corrosion was analyzed. Polarization and Impedance estimation were carried on steel in deaerated 5% HCl solution with and without inhibitive additives within the range of  $(1x10^{-4} to$  $5x10^{-3}$ ) mol/dm<sup>3</sup>. In this experimental work were salicylaldimine denoted as ",R", N-(2chlorophenyl)salicyaldimine, denoted as ..2Cl-R", N-(3as,,3Cl-R", chlorophenyl)salicyaldimine, denoted and N-(4chlorophenyl)salicyaldimine, denoted as,,4Cl-R". The compounds behaved as Anodic inhibitors. The inhibition efficiency followed by these inhibitors in terms of chloride position are 2Cl-R (containing ortho class of group) > 4Cl-R (possessing para class of group) > 3Cl-R (associated with meta class of group) > R (salicyaldimine).

Desai et al. [25], examined seven Schiff bases inhibitors for the wear protection of mild steel in HCl with concentrations of (1.0-6.0) N. Testing of VII wear retarding compounds as corrosion inhibitive substance for mild steel was carried by Galvanostatic polarization, weightloss and activation energy measurements. The inhibitors were named as Compound A (aniline, N-benzylidene), Compound B N,N'-dibenzylidene), (Ethane-1,2-diamine, Compound С [aniline, N-(pmethoxybenzylidene ) ] , Compound D [ ethylenediamine , N ,N '-di (pmethoxybenzylidene ) ], Compound E (aniline, N-salicylidene), Compound F ( ethylenediamine, N,N'-disalicylidene), Compound G ( ethylenediamine, N,N'dicinnamylidene ). All these Schiff bases were tested and it was found that all these seven compounds acted as cathodic inhibitors by being adsorbed on metal surface. All the inhibitors reduced cathodic current. They obeyed the Freundlich mathematical statement. The study on activity based energies revealed that their performance were improved by increasing temperature. From the potentiodynamic polarization measurement, all VII inhibitive substances suppressed cathodic branchof Tafel curves essential for the corrosion inhibition of the materials.

# 3. Chapter:

# **Materials and Methods**

This chapter will provide comprehensive details of methods and materials involved in the present research work.

### 3.1. Sample Preparation

AISI 1045 commonly known as Medium Carbon Steel was selected for the assimilation of characteristics in currently used inhibitive compound. The samples for the consideration were taken from a rod of diameter  $1 \text{ cm}^2$  and was cold mounted as shown in Figure-10(a). After mounting the sample; the surface was prepared using metallographic procedures. The roughness of the as polished sample was kept at  $0.8 \mu \text{m}$  according to literature as shown in Figure-10 (b).

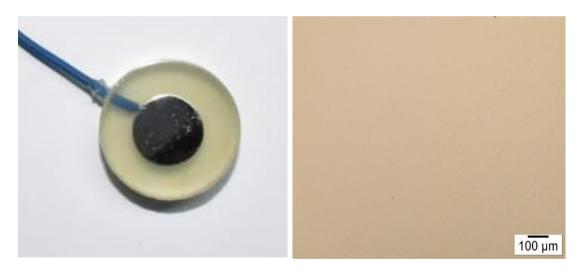


Figure 10 : (a) Working Electrode AISI 1045 after Metallography. (b) As polished Working electrode in Optical Microscope with Surface Roughness (Ra) value  $0.8\mu$ m

#### 3.1.1. Visual Inspection of Samples after Corrosion Testing in 0.1M HCl

The samples were dipped in acidic medium when inhibitive compound existed in various quantities and went under visual inspection after every corrosion testing. The condition of samples after 24 hours dipping time are shown in Figure 11.

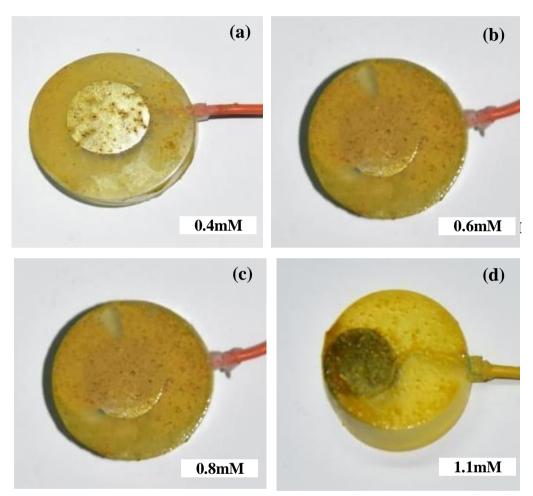


Figure 11: Samples after Corrosion Testing in 0.1M HCl with Inhibitor's concentrations (a) 0.4mM, (b) 0.6mM, (c) 0.8mM & (d) 1.1mM

#### 3.1.2. Visual Inspection of Samples after Corrosion Testing in 0.5M HCl

The samples were examined with various portions of inhibitive compound and went under visual inspection after every corrosion testing. The condition of samples after 24 hours dipping time are shown in Figure-12.

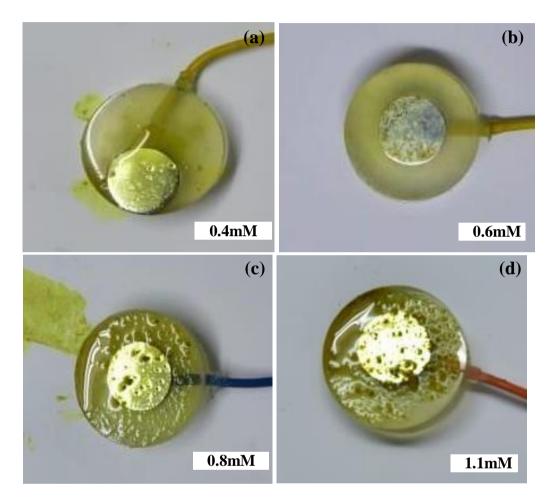


Figure 12 : Samples after Corrosion Testing in 0.5M HCl with Inhibitor's concentrations (a) 0.4mM, (b) 0.6mM, (c) 0.8mM & (d) 1.1mM

#### 3.1.3. Visual Inspection of Samples after Corrosion Testing in 1M HCl

The procedures were imitated again and went under visual inspection. The condition of samples after 24 hours dipping time are shown in Figure 13.

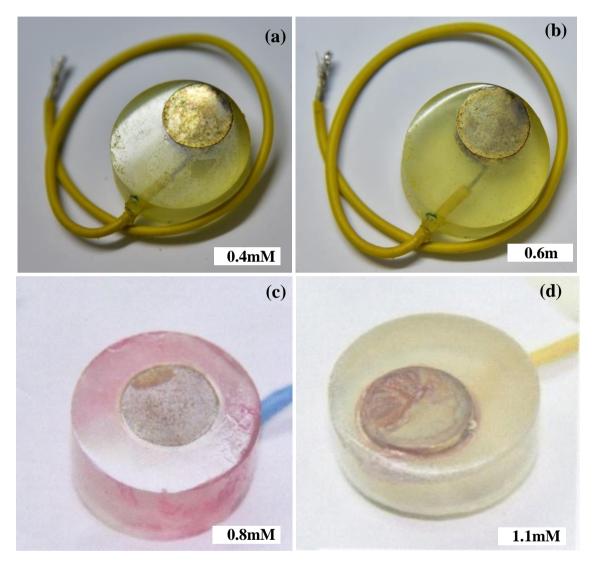


Figure 13: Samples after Corrosion Testing in 1M HCl with Inhibitor's concentrations (a) 0.4mM, (b) 0.6mM, (c) 0.8mM & (d) 1.1mM

#### 3.2. Synthesis route for Schiff Base

The synthesis of Novel Schiff Base Inhibitor took place locally in the laboratory of School of Natural Sciences at NUST.0.2g (1.305 mmol) of amine was mixed in 15mL of ethanol and similar amount 0.2g (1.305 mmol) of aldehyde also mixed by individually dissolving in 10mL solvent. The formation of Schiff base, 4-nitro-1,2-phenylenediamine involved the condensation with cinnamaldehyde in ethanol at room temperature to high temperature by refluxing at 45-50°C. Catalytic amount of glacial acetic acid was also added. Reaction continued was 12 hours. Solid product was washed with suitable solvents over filter paper to remove impurities. Impure product was cleaned again by recrystallization. Final product (named as AB22) was dried in open air. The Schematic diagram of Novel Schiff Base Inhibitor denoted as AB22 is represented Figure 14 below.

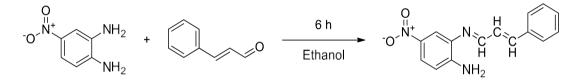


Figure 14: Schematic Synthesis of Novel Schiff Base Inhibitor (AB 22)

#### 3.3. Electrochemical measurements

Electrochemical instruments as a simplified way of characterizing Schiff base inhibitive compounds. The set consist of complementary electrode with inert nature. The purpose of this electrode is to maintain evenness of reaction commencing at reference and working electrode. The third electrode has entrenched potential and is used to maintain stable circuit in a cell.

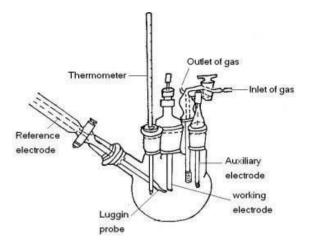


Figure 15: Schematic Diagram of Electrochemical Corrosion Testing cell [26]

#### 3.3.1. Open circuit Potential

It is the base of the electrochemical study as it indicated the establishment of equilibrium between working electrode and its electrolytic environment after a period of 10 seconds. In this work, the OCP has to define the class of inhibitive compound.

#### 3.3.2. Linear Polarization Resistance Technique

It was also conducted after establishing equilibrium open circuit potential as it is fast technique of evaluating corrosion current at the surface of working electrode over small range of potential. The slop of voltage and current was used to calculate resistance polarization value (Rp). By putting the value of Resistance Polarization in Stern-Geary Equation the value of corrosion current under different concentrations of Novel Schiff Base Inhibitor calculated. This corrosion current was then converted in to Corrosion Rate. This technique is very simple and time saving.

#### 3.3.3. Tafel Polarization Plots

The passivation characteristics of AISI 1045 was determined by polarizing the surface of the working electrode 150mV anodically and -150mV cathodically. The area exposed to the electrolyte was 1cm<sup>2</sup> in 200ml aerated environment at 25°C. The inhibition characteristics of novel Schiff base inhibitor was observed immediately after immersion in HCl. Initially no appreciable improvement in the corrosion resistance was observed immediately after adding the Inhibitor. Therefore, the working electrode remained immersed in the electrochemical cell for 24 hours for complete adherence and stability of inhibitor on the surface of the electrode.

#### 3.4. Surface examination

Examination of the steel surface analyzed before the electrochemical test. The as received condition of the Medium Carbon Steel was uniformly distributed Ferrite-Pearlite Microstructure as shown in Figure-16.

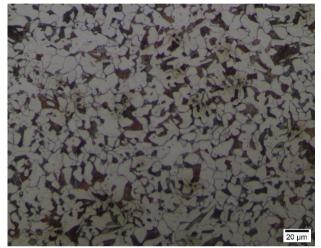


Figure 16: Microstructure of AISI 1045 with Grain size No. 9

#### 3.4.1. Surface Roughness Measurement

Surface Profilometer as shown in figure 17was used to check roughness condition of the as received steel sample after grinding and polishing. Further surface roughness Profilometer was utilized for this purpose. Every time the steel sample was washed with acetone and fine polished with 0.05µm Alumina powder to remove unwanted residues.

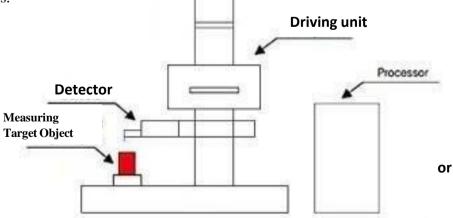


Figure 17: Surface Roughness Profilometer [27]

#### 3.4.2. Optical Microscope

The samples immediately after potentiodynamic polarization tests were examined under optical microscope to check the surface damage. The optical micrographs were taken at a magnification of 100X. The evolution of corrosion debris on the substrate overlaps the actual surface. Therefore, the samples were cleaned with ethanol in an accelerating cleaner, dried and fine polished with  $0.05\mu m$  alumina paste for clear visualization of the surface conditions after corrosion testing.



Figure 18: Optical Microscope [28]

#### 3.4.3. SEM surface analysis

The aftermath of corrosion on the surface of the sample were also examined at higher magnification 90X and 200 $\mu$ m in SEM. The same area of each sample that was observed under optical microscope was studied in SEM because of the magnification limitations of the optical Microscope.

#### 3.5. pH measurement

In the present research pH of the acidic HCl solution in 0.1M, 0.5M and 1M were investigated using the color altering pH paper. The pH value for 0.1M HCl from literature is 1[29]. The most well-known and desired methods of measuring pH are color altering pH papers and digital pH meter [30].

# 4. Chapter:

# **Results and Discussion**

#### 4.1. Electrochemical Tafel Polarization Analysis for 0.1M HCl

The testing was conducted immediately after dipping steel in Schiff base inhibitor but no progress identified. Then test was conducted again after 4 hours immersion time followed by 6 hours immersion time but no appreciable inhibition efficiency was observed. The OCP and Tafel polarization curves at 0 hour, 4 hours and 6 hours are displayed in Figure 19.

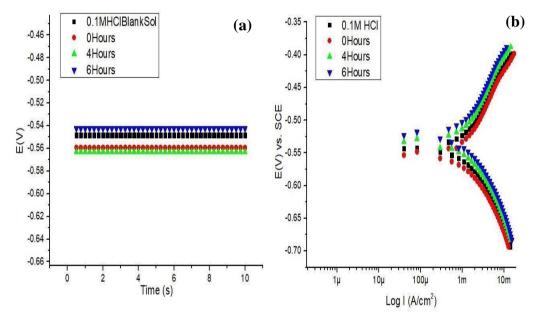


Figure 19: (a) OCP & (b) Tafel Polarization curves of Medium Carbon Steel in Absence & Presence of Schiff Base Inhibitor for 0.1M HCl

#### 4.2. Effect of Immersion Time

With the aid of literature studies about the time dependent inhibitor performance the test was conducted again after 24 hours Immersion time of sample in 0.1M HCl & Inhibition efficiency was observed in figure-20. A reasonably high Inhibition Efficiency (IE) was observed over a holding time, which confirmed the firmness of adherent inhibitor. According to literature, review the spike in the rise of inhibitive compound with immersive time is imputed to the number of Inhibitor's molecules attaching on the surface, whereby establishing an anti-corrosive shielded layer [30].

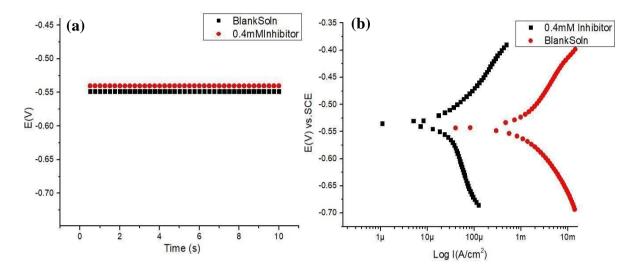


Figure 20:Effect of Immersion Time on Inhibitor's Performance. (a) OCP & (b) Tafel Polarization plots after 24 hours Immersion in 0.1M HCl

#### 4.3. OCP Analysis for 0.1M HCl

During the OCP the drift in the potential values were less than -85mV so the synthesized Inhibitive compound was classified as Mixed-Type. Slight noble turn was noted in OCP in the presence of 0.6mM Schiff Base inhibitor as shown in Table 3 and Figure 21.If the displacement in Ecorr values are more than -85mV then Inhibitors may be categorized as cathodic or anodic type and if this displacements areless than -85mV then inhibitors can be classified as mixed type Inhibitor [8].

Inhibitor (mM)	Ecorr (mV)	Shift (mV)
Blank Solution	-547	
0.4	-540	-3
0.6	-590	-47
0.8	-570	-27
1.1	-551	-8

Table 3: Representative OCP Shift Values in 0.1M HCl

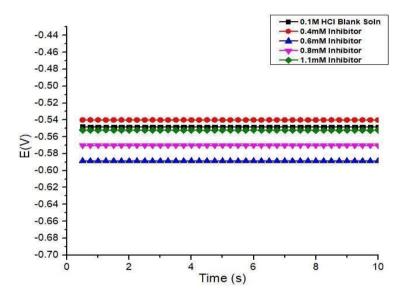


Figure 21: OCP in the Absence & Presence of Inhibitor

### 4.4. Tafel Polarization Curves in 0.1M HCl

After Open circuit potential, the Tafel polarization test was conducted. The results are summarized in the Figure 22 and Table 4. The best Inhibition efficiency was observed in 0.6mM concentration of Schiff Base Inhibitive compound. No specific trend was marked in the potential assessment of Tafel Curves with increasing concentration of Novel Schiff Base Inhibitor whereby indicating that Inhibitive compound simulated as a Mixed type Inhibitor [31].

Inhibitors Concentrations (Milli Molar)	E <sub>corr</sub> (mV)	I <sub>corr</sub> (mA/cm <sup>2</sup> )	$\beta_a$ (mV e-3)	- β <sub>c</sub> (mV e-3)	CR (mmpy)	Surface coverage ( $\Theta$ )	The inhibition efficiency (٤%)
Blank Soln	-543	9.86	109	69.6	114.35	-	-
0.4	-535	1.98	498	993	23.04	7.87	79.84
0.6	-553	0.0374	108	8.12	0.434	9.82	99.62
0.8	-541	0.0378	76.7	115	0.439	9.82	99.61
1.1	-550	0.0694	56.2	35	0.805	9.79	99.29

Table 4: Summary of Tafel Polarization Testing of AISI 1045 in 0.1M HCl

\* The corrosion rate is expressed in mmpy, millimeter per year. In metric expression one mil equals to 0.0254 mm

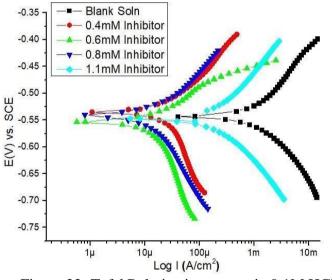


Figure 22: Tafel Polarization curves in 0.1M HCl & in

Presence of Schiff Base Inhibitor

### 4.5. Repeated Tafel Polarization Curves

The electrochemical Tafel Polarization were again repeated for the same concentrations of Schiff Base Inhibitor. The best inhibition efficiency was again observed in 0.6mM concentration of Schiff Base Inhibitor. This concentration was considered to be optimized value for the protection of Medium Carbon Steel Surface in 0.1M HCl.

Inhibitors Concentrations (mM)	E <sub>corr</sub> (mV)	Current Density (i <sub>corr</sub> /mAcm <sup>-2)</sup>	$\beta_a (mV e^{-3})$	- $\beta_c$ (mVe <sup>-3</sup> )	CR (mmpy)	Surface coverage ( $\Theta$ )	Efficiency (£%)
Blank Soln	-543	9.86	109	69.6	114	-	-
0.4	-535	1.98	498	993	23.0	7.87	79.84
0.6	-553	0.0374	108	8.12	0.43	9.82	99.62
0.8	-541	0.0378	76.7	115	0.44	9.82	99.61
1.1	-550	0.0766	128	60.3	0.87	9.78	99.22

Table 5: Repeated AISI 1045,,0.1M HCl" solution at room temperature

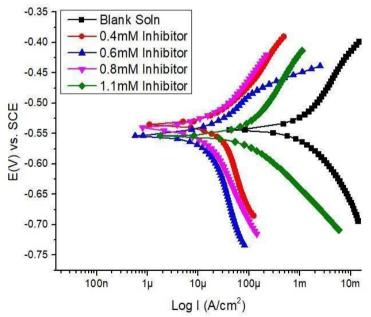


Figure 23: Repeated Tafel Polarization curves in 0.1M HCl

### 4.6. Electrochemical Polarization Resistance Analysis for 0.1M HCl

The Electrochemical Polarization Resistance test was conducted to determine realtime ongoing current density and Inhibition Efficiency of Inhibitive compound on AISI 1045. Figure 24(a) showing the slops of Resistance polarization in Schiff Base Inhibitor with distinctive quantities of Inhibitor and Figure 24(b) showing a trend of Resistance Polarization with respect to increasing Schiff Inhibitor''s concentration. Resistance to inhibit number of positive and negative ions were high when Schiff Base Inhibitor was not incorporated. That is why Resistance Polarization value was low as shown in Figure 24 and Table no. 6 below. Whereas in Schiff Base Inhibitor, resistance polarization values were high because the Inhibitive compound retarded the formation of positive and negative ions on the surface of Steel.

Inhibitors Resistance Current  $\beta_c (mVe^{-3})$ Concentrations  $\beta_a$  (mV e<sup>-3</sup>) Polarization densityicorr/ Ω (mM)mAcm<sup>-2</sup> 0.4 120 120 13.12 1.98 0.6 120 120 697 0.0374 0.8 120 120 688 0.0378 1.1 120 120 375 0.0694

Table 6: Linear Polarization Resistance in 0.1M HCl & in Presence of AISI 1045

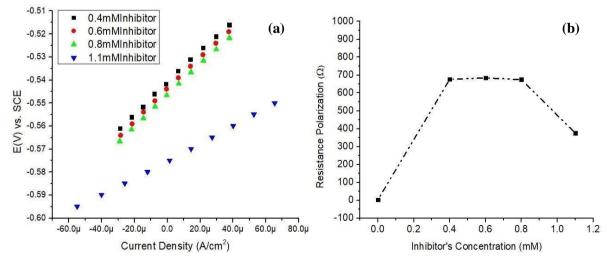


Figure 24: (a) Linear Polarization Resistance Slops in 0.1M HCl. (b) Effect of Inhibitor"s quantity on the polarization resistance of AISI 1045.

# 4.7. Prominence of Inhibitor's Concentration on I<sub>corr</sub>& Corrosion Rate in 0.1M HCl

Various quantities of Schiff base Inhibitor were introduced in 0.1M HCl and proved productive. The representative graphs correspond to depreciation in the current.

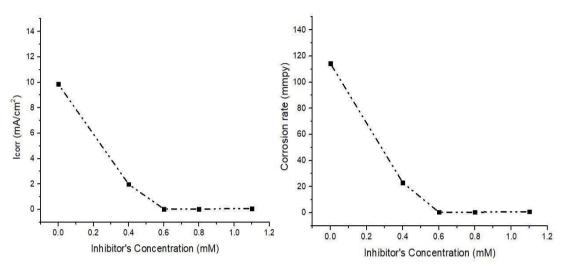


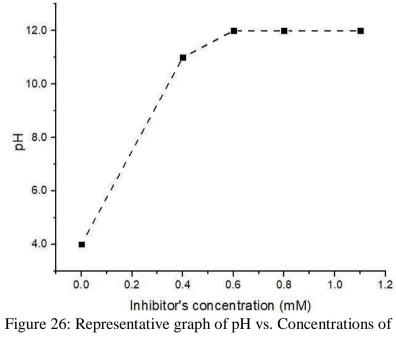
Figure 25: (a) Relationship between I<sub>corr</sub>& Inhibitor's concentrations (b) Relationship between Corrosion Rate & Inhibitor's concentrations.

## 4.8. pH Evaluation in the Presence and Absence of Inhibitor in 0.1H HCl

The pH of the electrochemical solution in 0.1M HCl was noted Inhibitor. The trend of relationship between Inhibitor & pH values is shown in the Table no. 7 and Figure 26 below.

Inhibitor (mM)	рН
0	4
0.4	11
0.6	12
0.8	12
1.1	12

Table 7: Relationship between pH & Inhibitor's Concentration for 0.1M HCl



Schiff Base Inhibitor

### 4.9. Surface Examination in 0.1M HCl

The surface Examination of steel in 0.1M HCl and in changing amounts Schiff Base Inhibitor was carried out by Surface roughness test, Optical Microscope and SEM.

#### 4.9.1. Surface Roughness of AISI 1045 in 0.1M HCl

The surface roughness test of the steel was conducted in Schiff Base Inhibitor. A spike in uplifting surface roughness was suppressed in Schiff base Inhibitor in 0.1M HCl. Results and trend of surface roughness values are shown in the table and figure respectively. A rise in roughness of the steel surface uplifts interfacial area with the corrosive environment and therefore rate of corrosion process increases [32].

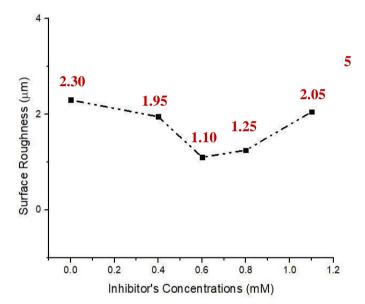


Figure 27: Surface Roughness Response in inhibitive compound in 0.1M HCl

### 4.9.2. Surface Examination in Optical Microscope in 0.1M HCl

The samples after corrosion testing as shown in the section 3.1.1 and figure 11were rinsed &cleaned for the examination of internal surface condition after 24 hours" immersion time in 0.1M HCl in Optical Microscope. Tiny pits in the vicinity of the exposed area were observed. To examine the amount of pits with respect to the Schiff Base Inhibitor"s concentration a qualitative analysis was performed using OLYSIA Phase Contrast Software"

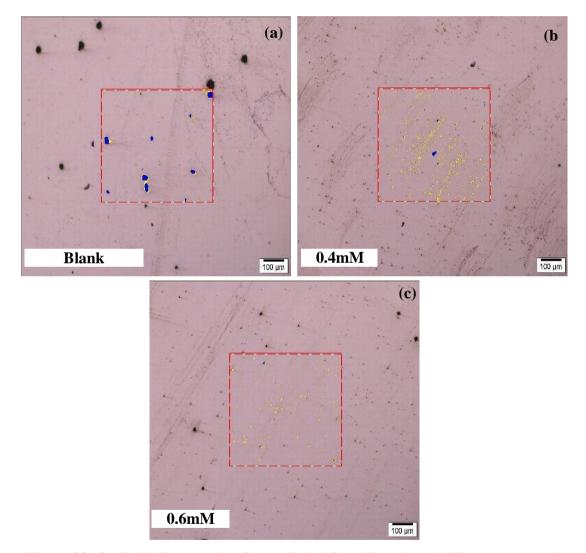


Figure 28: Optical Micrographs of As-polished Steel Samples. (a) Pits percentage in 0.1M HCl is 2.67%. (b) Pits percentage in 0.4mM Inhibitor is 1.14% & (c) Pits percentage in 0.6mM Inhibitor is 1.07%.

The surface examination of medium carbon steel in the presence of 0.8mM& 1.1mM Schiff base Inhibitor are shown in figure 29. From the Optical Micrographs it can be concluded that the pits percentage in 0.6mM Inhibitor concentration was less as compared with other three concentrations. Further, the damage on the surface of the medium carbon steel indicated that acid attacked the steel surface initially and the response of the Inhibitor was slow in forming the covalent bond. Subsequently, in 24 hours immersion, the conduct of Schiff Base Inhibitor upon rough surface resulted excellent Inhibition performance. This conclusion can be further proved from the literature study. From the literature survey it can be studied that real surface are never smooth and that roughness would affect amount of molecules adsorbed on the surface [33] .Roughness is not always beneficial. In order to bond to a rough surface, the coating material must penetrate with in the crevices of the substrate. A rough surface for bonding often shows stronger bonds because mechanical interlocking is more pronounced at rough surface [34].

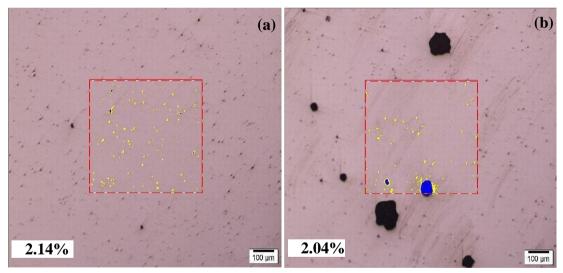


Figure 29: Optical Micrograph of as polished Steel sample in the presence of (a) 0.8mM & (b) 1.1mM Inhibitor's concentration

#### 4.9.3. Surface Examination in SEM

The SEM Analysis was carried on AISI 1045 surface exposed when varying quantities of Schiff Base Inhibitor was in cooperated in HCl. Surface of AISI 1045 was not uniform even in the presence of Inhibitor because the activity of surface protection by inhibitor started after 24 hours dipping time. The imperfection in the Surface morphology can be attributed to the corrosion products (FeO.*n*H<sub>2</sub>O and / or FeCl<sub>2</sub>.*n*H<sub>2</sub>O) [35]as shown in Figure-30.

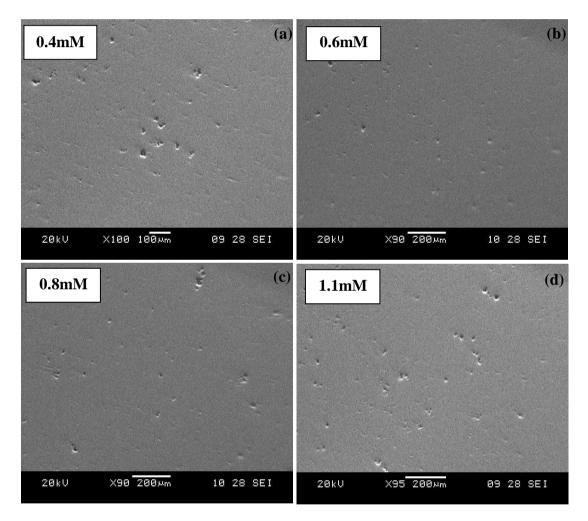


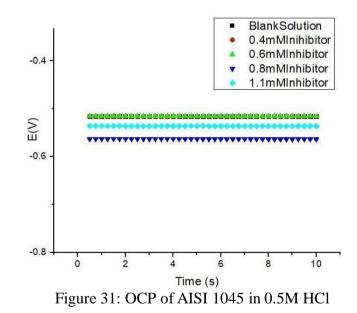
Figure 30: SEM Images of AISI 1045 after cleaning the deposits of Inhibitor and Corrosion products.

### 4.10. OCP Analysis of 0.5M HCl

To study the Inhibition efficiency in 0.5M HCl, stabilization of OCP was necessary. Slight noble shifts were observed when OCP test was conducted in the presence of 0.8mM & 1.1mM Schiff Base Inhibitor in 0.5M HCl as shown in Table 8 and Figure 31.

Inhibitor (mM)	Ecorr (mV)	Shift (mV)
Blank Solution	-517	
0.4	-517	0
0.6	-517	0
0.8	-562	-45
1.1	-536	-19

Table 8:Ecorr Shift between Uninhibited & Inhibited AISI 1045



### 4.11. Tafel Polarization Curves in 0.5M HCl

The results obtained from Tafel polarization curves showed that Schiff Base Inhibitor"s concentrations used from 0.4mM to 1.1mM were not enough to protect AISI 1045 under high concentration of 0.5M HCl. The trend of Tafel polarization curves showed that concentration higher than 1.1mM would be effective. The optimized amount of Inhibitor was not achieved under this condition.

 $\beta_a \,(mV \; e^{\text{-}3})$ densityicom The mAcm Inhibitors Current βc Surface CR inhibition (mV) Ecorr (mV Concentrations coverage efficienc (mmpy) (mM) $(\Theta)$ œ y (8%) Blank Soln -627 13 38 38 151.27 \_ \_ 0.4 -561 6.61 135 74 76.66 0.470 47 0.6 -513 124 103 77.59 0.476 47.60 6.60 360 191 0.8 -514 6.62 76.76 0.472 47.20 1.1 -540 6.60 296 229 76.59 0.476 47.61

Table 9: The Tafel plots of experiment on AISI 1045,,0.5M HCl" at atmospheric temperature

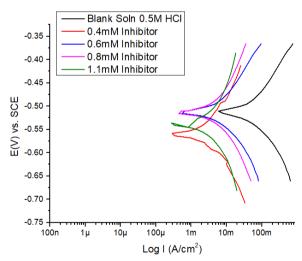


Figure 32: Tafel polarization Curves in 0.5M HCl& in various quantities of Schiff Base Inhibitor

### 4.12. Electrochemical Polarization Resistance for 0.5M HCl

The linear polarization resistance was performed to verify the results in 0.5M HCl and in the various amounts of Schiff Base inhibitor. The Linear polarization resistance (Rp) values and their slops are shown in Table 10 and Figure 33 below.

Inhibitors Concentrations (mM)	$\beta_a (mV e^{-3})$	- $\beta_c (mV e^{-3})$	Resistance Polarization Ω	Current density <i>i</i> <sub>corr</sub> /mA cm <sup>-2</sup>
0.4	120	120	3.946	6.61
0.6	120	120	3.950	6.60
0.8	120	120	3.941	6.62
1.1	120	120	3.950	6.60

Table 10: Relation between Inhibitor Concentration and Resistance Polarization

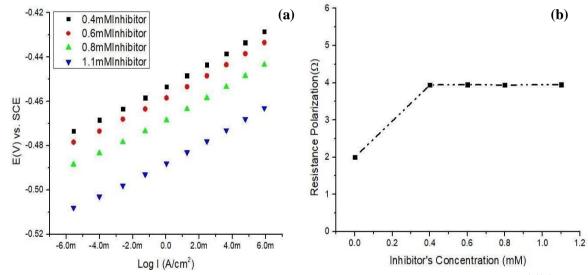


Figure 33: a) Linear Polarization Resistance Slopes in 0.5M HCl. (b) Effect of Inhibitor's concentration on the polarization resistance of AISI 1045

## 4.13. Influence of Inhibitor's Concentration on I<sub>corr</sub>& Corrosion Rate in 0.5M HCl

The Schiff Base Inhibitor added in different concentrations in 0.5M HCl Solution had proved to be efficient for keeping the corrosion current &rate of corrosion constant. The representative graphs are showing Influence of Inhibitor's concentration on refuting corrosion.

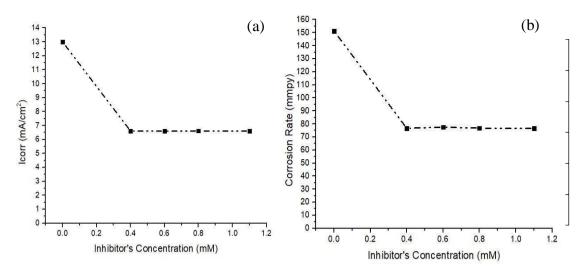


Figure 34: (a) Representative trend line shows relation between Corrosion Current Density with Inhibitor's Concentration. (b) Representative graph showing sudden dropin Corrosion Rate with steady behavior

## 4.14. pH Evaluation in the Absence & Presence of Inhibitor in 0.5M HCl

The pH of the electrochemical solution was noted in the existence of inhibitive compound. A trend of relationship between Inhibitor and pH values are shown in the Table no.11 and Figure 35 below.

Inhibitor (mM)	рН
0	1
0.4	8
0.6	8
0.8	8
1.1	8

Table 11: pH values with respect to Inhibitor"s concentrations in 0.5M HCl

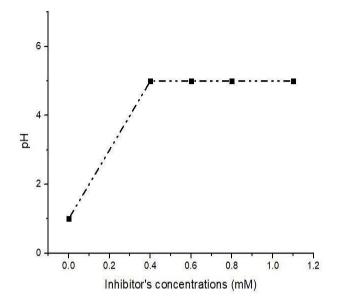


Figure 35: pH values of with increasing concentrations of Schiff Base Inhibitor remained constant in 0.5M HCl

### 4.15. Surface Examination in 0.5M HCl

The surface of the AISI 1045 was observed and examined by using surface roughness Profilometer, optical Microscope and SEM Analysis.

#### 4.15.1. Surface Roughness of AISI 1045 in 0.5M HCl

The surface roughness were observed after cleaning the residues attached on the surface. Due to high intensity of acidic medium the concentrations of inhibitors were not enough to retard the corrosion attack. Therefore, no improvement in the surface finish were observed in the availability of Inhibitor as shown in Figure 36.

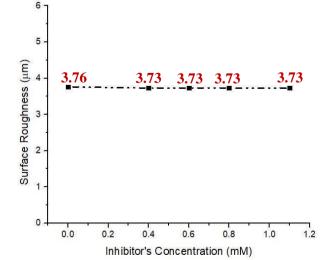


Figure 36: Surface Roughness (Ra) of AISI 1045 in 0.5M HCl & in different Concentrations of Schiff Base Inhibitor.

### 4.15.2. Surface Examination in Optical Microscope in 0.5M HCl

The samples after Electrochemical Test were cleaned to view the internal surface of the AISI 1045 in Optical Microscope. The damage due acidic attack on the surface after cleaning was advent because the amount of Inhibitors added were not enough to inhibit acid attack. No appreciable change were inspected as shown in Figure 37 & Figure 38.

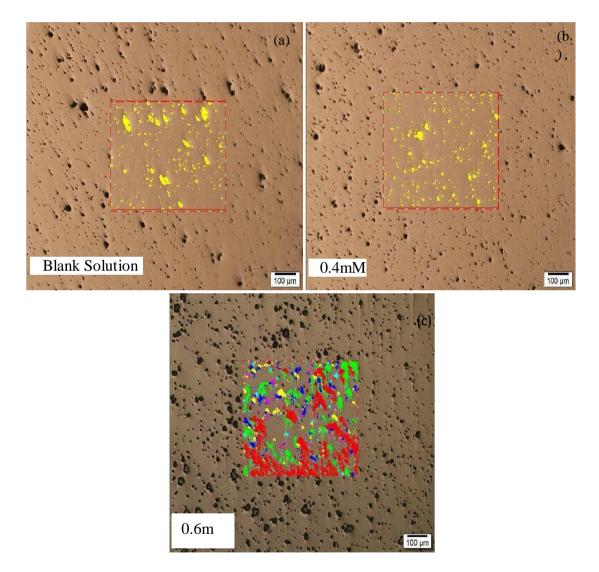


Figure 37: Optical Microscope images of AISI 1045 in 0.5M HCl followed by cleaning the corrosion deposit & Inhibitor layer.(a)Pits percentage in 0.5M HCl was 56.89% (b)Pits percentage in the presence of 0.4mM was 43.28 & (c)Pits percentage in the presence of 0.6mM was 60%

Optical Microscopy images of AISI 1045 surfaces in the presence of 0.8mM & 1.1mM concentrations of Inhibitor.

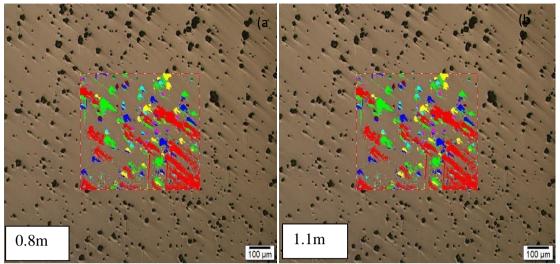
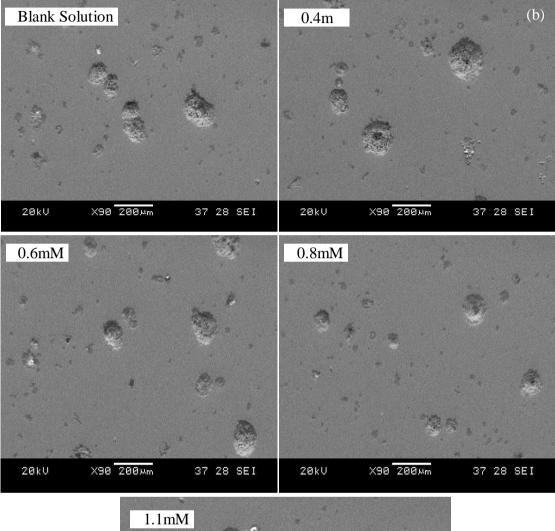


Figure 38: Optical Microscope images of AISI 1045 in 0.5M HCl & followed by cleaning the corrosion deposit & Inhibitor layer.(a) Pits percentage in was 56.89% (b) Pits percentage in the presence of 1.1mM was 43.28%

### 4.15.3. Surface Examination in SEM for 0.5M HCl

The SEM Analysis of AISI 1045 surface exposed in 0.5M HCl in varying concentrations of Schiff Base Inhibitor.



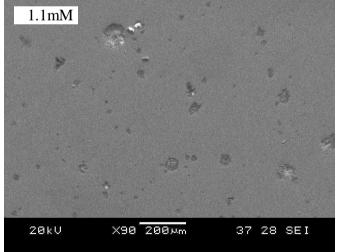


Figure 39: SEM Images of AISI 1045 after cleaning the deposits of Inhibitor and Corrosion products.

#### 4.16. OCP Analysis of 1M HCl

The corrosion testing was conducted at 1M HCl to consider of Inhibitive compound performance at higher acidic concentrations. Therefore, Open Circuit Potentials in varying amounts Inhibitor were inspected. No  $E_{corr}$  shifts were analyzed when Inhibitive compound was incorporated in 1M HCl. The results showed that Inhibitor did not worked in 1M HCl.

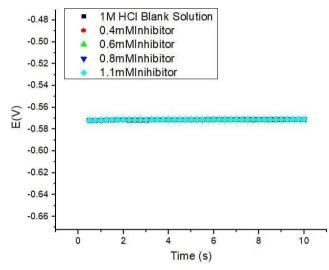


Figure 40: Open Circuit Potentials in the 0.5M HCl & in existence of Schiff Base Inhibitor

### 4.17. Tafel Polarization Curves in 1M HCl

Followed by the Open Circuit Potentials, the Tafel Polarization curves were performed in 1M HCl. From the results it can be concluded that locally synthesized Schiff Base Inhibitor completely failed at concentration of 1M HCl.

Inhibitors Concentrations (mM)	Ecorr (mV)	Current densityicorr/m Acm-2	βa (mV e-3)	- βc (mV e-3)	CR (mmpy)	Surface coverage (Θ)	Inhibition efficiency (E%)
Blank Soln	-568	13.18	876.70	554	152.88	-	-
0.4	-568	13.18	876.70	554	152.88	-	-
0.6	-568	13.18	876.70	554	152.88	-	-
0.8	-568	13.18	876.70	554	152.88	-	-
1.1	-568	13.18	876.70	554	152.88	-	-

Table 12: The Tafel plots of experiment on AISI 1045,,1M HCl" solution in 1M HCl

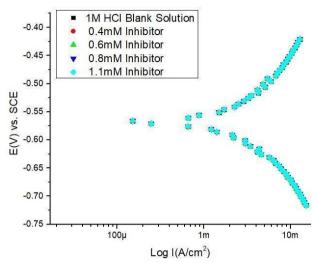


Figure 41: Tafel Polarization curves in 1M HCl & in participation of varying concentrations of Schiff Base Inhibitor.

#### 4.18. Electrochemical Polarization Resistance for 1M HCl

The electrochemical linear polarization test were performed to confirm the results of tafel polarization curves. From the result it was concluded that no response of Schiff Base Inhibitor was observed in 1M HCl. Therefore, locally synthesized Schiff base Inhibitor should not be applicable for the protection of AISI 1045 in 1M HCl.

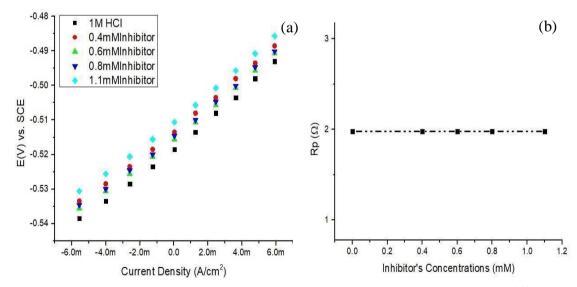


Figure 42: (a) Linear Polarization Resistance Slops in 1M HCl. (b) Impacts of Inhibitor"s quantity on the resistance of substrate charges at AISI 1045 in 1M HCl

# Conclusion

- The locally synthesized Novel Schiff base Inhibitor works effectively in lower concentration of HCl i.e. 0.1M.
- The optimized concentration of Schiff base inhibitor was found to be 0.6mM in 0.1M HCl.
- Corrosion rates in varying quantities of Schiff Base Inhibitor in 0.1M HCl were from 0.434 mmpy to 2.304 mmpy. The decrease in the rate of corrosion has affected the substrate roughness by reducing its surface roughness values from 2.30µm to 1.10µm.
- The corrosion rate in the presence of Schiff Base Inhibitor in 0.5M HCl was depreciated from 151.27mmpy to 76.59mmpy. In addition, the corrosion rate in 1M HCl remained unchanged when Inhibitor was incorporated. Therefore, response of inhibitor at higher concentrations of HCl was not satisfactory.
- The presence of Inhibitor showed appreciable shift towards the basic values in the pH of the electrolytic solution of 0.1M HCl.

### References

- Camila G. Dariva and Alexandre F. Galio Corrosion Inhibitors Principles, Mechanisms and Applications, InTech (pp.365-380), (2014)
- [2] I. Mohamed Mustafa et al, Micro review Schiff bases and their metal complexes as corrosion inhibitors for steel alloys in acidic media, an Indian Journal OCAIJ, 9(12),(pp.493-499),2013.
- [3] Katarzyna BRODOWSKA, Elżbieta ŁODYGA-CHRUŚCIŃSK; A Schiff bases interesting range of applications in various fields of science; CHEMIK 68, 2, (pp.129–134), (2014)
- [4] K.F. Khaled Evaluation of electrochemical frequency modulation as a new technique for monitoring corrosion and corrosion inhibition of carbon steel in perchloric acid using hydrazine carbodithioic acid derivatives Journal of Applied Electrochemistry, 2009.
- [5] Stephen D. Cramer and Bernard S. Covino Jr., Corrosion: Environments and Industries ASM Volume 13, ASM International, (2005).
- [6] Jones, D. A., Principles and Prevention of Corrosion, second edition, Prentice Hall, Upper Saddle River, 572 pp., NJ, Vol.3 No.5, 1995.
- [7] Zaki Ahmad Principles of Corrosion Engineering and Corrosion Control Butterworth Heinemann, Butterworth-Heinemann/IChemE Series, First Edition, (2006)
- [8] Bentiss F, Bouanis M, Mernari B, Traisnel M, Vezin H, Lagrenée M. Understanding the adsorption of 4H-1, 2, 4-triazole derivatives on mild steel surface in molar hydrochloric acid. Appl Surf Sci; 253, (pp. 3696-704),(2007)
- [9] Amin MA, Abd El-Rehim SS, El-Sherbini EEF, Bayyomi RS. The inhibition of low carbon steel corrosion in hydrochloric acid solutions by succinic acid: Part I. Weight loss, polarization, EIS, PZC, EDX and SEM studies. Electrochim Acta,52: (pp.3588-600),(2007)

- [10] Tazouti A, Galai M, Touir R, et al. Experimental and theoretical studies for mild steel corrosion inhibition in 1.0 M HCl by three new quinoxalinone derivatives. J Mol Liq 2016; 221: 815-32.
- [11] Alaoui K, El Kacimi Y, Galai M, et al. Poly (1-phenylethene): As a Novel Corrosion Inhibitor for Carbon Steel/Hydrochloric Acid Interface. Anal Bioanal Electrochem 2016; 8: 830-47
- [12] H. S. Gadiyar, Chintamani Das and K. B. Gaonkar ;"CHEMICAL CLEANING, DECONTAMINATION AND CORROSION"- an evaluation' Report BARC-E/011, 1991.
- [13] https://www.process-cooling.com/articles/89875-cleaning-scale-from-coolingtower-systems (Accessed on January 15,2022)
- [14] https://jooinn.com/img/get
- [15] Pradeep Kumar et al., Corrosion inhibition efficiency and adsorption characteristics of some Schiff bases at mild steel/hydrochloric acid interface, , Journal of the Taiwan Institute of Chemical Engineers, Volume 45, Issue 3,(pp. 1031–1042), (2014)
- [16] Ituen, E. B et al., Inhibition of X80 steel corrosion in oilfield acidizing environment using 3-(2-chloro-5,6-dihydrobenzo[b][1]benzazepin-11-yl)-N,Ndimethylpropan-1-amine and its blends. Journal of King Saud University -Science, 31(1), (2019). (pp. 127–135).
- [17] Chitra, S., Parameswari, K., & Selvaraj, A.. Dianiline schiff bases as inhibitors of mild steel corrosion in acid media. International Journal of Electrochemical Science,5(11), 1675–1697. (2010)
- [18] Mohammad Ifzan Arshad, et al.,Bis-Schiff bases of 2,2'-dibromobenzidine as efficient corrosion inhibitors for mild steel in acidic medium, RSC Advances, 10,pp.4499–451, (2020).
- [19] Nassar, A. M., Hassan, A. M., Shoaib, M. A., & El kmash, A. N. Synthesis, Characterization and Anticorrosion Studies of New Homobimetallic Co(II),

Ni(II), Cu(II), and Zn(II) Schiff Base Complexes. Journal of Bio- and Tribo-Corrosion, pp. 1–16,(2015).

- [20] Hosseini, M et al., Asymmetrical Schiff bases as inhibitors of mild steel corrosion in sulphuric acid media. Materials Chemistry and Physics, 78(3), pp. 800–808 (2003).
- [21] N. ANegm, F. M.Ghuiba&, S. M Tawfik, Novel Isoxazolium cationic Schiff base compounds as corrosion inhibitors for carbon steel in hydrochloric acid, Journal of Corrosion Science,53(11), pp.3566–3575.(2011).
- [22] Yurt, A., Balaban, A., Kandemir, S., Bereket, G., &Erk, B., Investigation on some Schiff bases as HCl corrosion inhibitors for carbon steel. Journal of Materials Chemistry and Physics 85, pp.420–426. (2004).
- [23] Bilgiç, S. et al., Investigation of some Schiff bases as corrosion inhibitors for austenitic chromium-nickel steel in H2SO4. Journal of Applied Electrochemistry, 31, 79–83,(2001).
- [24] Kaan C. Emregul et al., An investigation of chloride-substituted Schiff bases as corrosion inhibitors for steel, Journal of Corrosion Science, 45, pp.2803–2817, (2003).
- [25] M.N. Desai et al., Schiff bases as corrosion inhibitors for mild steel in hydrochloric acid solutions, Journal of Corrosion Science, 26(10),pp.827–837, (1986).
- [26] Ehteram A. Noor et al., Corrosion Behavior of Mild Steel in Hydrochloric Acid Solutions, International Journal of Electrochemical Science, 3 ,pp.806 – 818, (2008).
- [27] <u>https://www.keyence.com/ss/products/microscope/roughness/equipment/line\_01.</u> jsp. (Accessed on January 20, 2022)
- [28] https://variscancoast.co.uk/under-the-microscope. (Accessed on January 20, 2022)

- [29] Therald Moeller at el., Acids and Bases, Chemistry with Inorganic Qualitative Analysis, Academic Press,pp.480-520, (1980)
- [30] Saman Zehra, Mobin Aslam, et al. Phenylalanine methyl ester hydrochloride as a green corrosion inhibitor for mild steel in hydrochloric acid solution and the effect of surfactant additive. RSC Adv., 6, 5890; (2016)
- [31] M.A. Hegazy et al., A novel Schiff base-based cationic Gemini surfactants: Synthesis and effect on corrosion inhibition of carbon steel in hydrochloric acid solution; Corrosion Science 51, (pp. 2610–2618), (2009)
- [32] Barmatov Evgenyaet al., Effect of surface roughness on corrosion behavior of low carbon steel in inhibited 4 M hydrochloric acid under laminar and turbulent flow conditions; Vol 103;pp. 196-205; (2016)
- [33] S. Brunauer, P.H. Emmett and E. Teller, Adsorption of the gases in Multi molecular layers, Journal of the American Chemical Society, 60,309; (1938)
- [34] https://www.3m.com/3M/en\_US/bonding-and-assembly-us/resources/science-ofadhesion/influence-surface-roughness/. (Accessed on January 20, 2022)
- [35] Priyanka Basera, at el., Potential of dynamic bacterial communities in the biocorrosion process: a proof study with surface morphology of metal coupons, Royal Society of Chemistry,9,pp.17040-17050, (2019)