ALKALOID EXTRACT OF *ALNUS NEPALENSIS* BARK AS GREEN INHIBITOR FOR MILD STEEL CORROSION IN 1 M H_2SO_4 SOLUTION

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BOARD OF EXAMINER AND CERTIFICATE OF APPROVAL

This dissertation entitled, "**Alkaloid Extract of *Alnus nepalensis* bark as Green Inhibitor for Mild Steel Corrosion in 1 M H_2SO_4 solution''** by **Ms. Kamala Dhakal** under the supervision of Asst. Prof. Hari Bhakta Oli, Department of Chemistry, Amrit Campus, Tribhuvan University, Kathmandu, Nepal, and under co-supervision of Asst. Prof. Dr. Deval Prasad Bhattarai, Department of Chemistry, Amrit Campus, Tribhuvan University, Kahtmandu, Nepal, hereby submitted has been approved for partial fulfillment of the requirement for completion of her Master of Science (M.Sc.) Degree in Chemistry. This dissertation has not been submitted in any other university or institution previously for the award of a degree.

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LETTER OF RECOMMENDATION

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DECLARATION

I, Kamala Dhakal, hereby declare that the work entitled "**Alkaloid Extract of *Alnus nepalensis* bark as Green Inhibitor for Mild Steel Corrosion in 1 M H_2SO_4 solution**" submitted to Institute of Science and Technology Tribhuvan University as partial fulfillment for the requirements of Master of Science Degree in Chemistry has been done by myself and has not been submitted earlier in part or full in this or any other form to any other university/institute, here or elsewhere for the award of any degree. All sources of information have been specifically acknowledged by reference to the authors or institutions.

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ABSTRACT

Extraction of alkaloids from *Alnus nepalensis* bark has been successfully carried out, and used as green inhibitor for mild steel corrosion exposed to 1 M H_2SO_4 solutoin. Corrosion inhibition has been monitored by weight loss measurement and electrochemical methods (open circuit potential method and potentiodynamic polarization method). Alkaloids have been tested by two qualitative chemical analysis: Mayers test and FTIR spectroscpic test. Weight loss measurement was employed to study the inhibitor concentration and immersion time effect. Similarly, temperature effect on inhibition efficiency was also carried out by this method. The corrosion inhibition efficiency with concentration at the various time showed that the maximum efficiency occurs at 3 h for 1000 ppm solution is 71.94 % at 25 °C. These results concluded that the inhibition efficiency was incresed with inhibitor concentration.

Potentiodynamic polarization for 3 h immersed samples in the presence and absence of inhibitors has been carried out. The maximum efficiency of immersed sample is 90.00 % for 1000 ppm solution. The corrosion potential density was decreased with increase in concentration. The OCP measurement revealed that alkaloids acted as a mixed type of inhibitor. The adsorption isotherm and theromdynamic parameters are calculated and energy of activation (Ea) is found to be 74.48 kJ/mol. The positive value of enthalpy indicated that the reaction involves is endothermic in nature.

Keywords: *Green inhibitor, Mild steel, Polarization, Alnus nepalensis,* thermodynamic *parameters, Weight loss.*

LIST OF ABBREVIATIONS

θ	Fraction of Surface Coverage
C_{inh}	Corrosion Inhibitors
CR	Corrosion Rate
E_a	Activation Energy
E_{corr}	Corrosion potential
FTIR	Fourier Transform Infrared Spectroscopy
I_{corr}	Corrosion current
MS	Mild Steel
mV	Milivolt
mV/s	Milivolt per second
OCP	Open Circuit Potential
Ppm	Parts per million
SCE	Saturated Calomel Electrode
UV	UltraViolet

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CHAPTER 1
INTRODUCTION

1.1. Background

Mild steel is well known ferrous alloy having a composition (0.15-0.30% C, 0.4% Si, 0.7-0.9% Mn, 0.04% S, 0.04% P, and rest of Fe) is an excellent material used in structural and construction applications. Extravagance use of mild steel as construction materials is because of its outstanding mechanical properties, ease of fabrication, excellent weldability, and low purchasing cost [1, 2]. However, it has low corrosion resistance especially in acidic environments [3]. Mild steel suffers from corrosion which is an unwanted natural phenomenon and whose avoidance process is very complicated for industry and requires bearing the huge cost for industry to overcome this effect [4]. It is estimated that the global cost of corrosion is equivalent to 3-4% of their gross domestic product [5-7]. Karki *et.al* estimated that about 4.3% of GDP has been expected to be loss due to corrosion in the context of Nepal [8].

Corrosion is an electrochemical phenomenon where anodic and cathodic reactions take place. In an anodic reaction, the dissolution of metal/alloy takes place with the liberation of electrons, and in a cathodic reaction, the reduction of the ions takes place. The most frequently occurring reaction in the mild steel dissolution process in an acidic medium can be represented as:

a. Oxidation of mild steel

   $M \rightarrow M^{n+} + ne^-$

b. Oxygen reduction in acidic solution

   $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$

c. Hydrogen evolution from acidic solution

   $2H^+ + 2e^- \rightarrow H_2$

Where M is Fe for mild steel, n is the integer that represents the number of electrons involved in the reaction [10].

The overall reaction is

$Fe + nH^+ \rightarrow Fe^{n+} + H_2$

The major economic and social consequences of corrosion include the replacement of corroded equipment and materials, shut down of electrical, chemical, and nuclear plants, contamination and loss of valuable products,

serious damage to the liability of products, and safety and health of the public.

1.2. Corrosion Protection Methods

Corrosion is a natural and spontaneous process which cannot be completely protected by any means but can be minimized by using effective methods and strategies. There are primary ways to control corrosion.

1.2.1. Design of structures

Corrosion inhibition by proper design is the first strategy for effective corrosion control of materials, metals/alloys, composites, equipment, and infrastructure [11]. Corrosion prevention and control must be an integral part of the total design process and not something added as an afterthought since one can avoid the area where the corrosive medium becomes more corrosive (like dead spaces or crevices) in the design process. In this way, the application of rational design principles eliminates many corrosion problems and greatly reduces the time and cost associated with corrosion maintenance and repair [11, 12].

1.2.2. Material Selection

Once a proper design has been implemented, corrosion control by proper materials selection is the next stage for corrosion control. There are various metals and alloys to select, each having inherent and unique corrosion behavior that can range from the high resistance of noble metals (gold and platinum) to the low corrosion resistance of active metals. The corrosion resistance of metal also strongly depends on the environment to which it is exposed, like chemical composition, temperature, velocity, and so forth [11].

1.2.3. Protective coatings

A third general group of methods to control corrosion is to cover the metal surface with a protective coating, which separates the metal from the environment. These coatings can be of several types: metallic, inorganic, or organic and they can be applied in different ways such as dipping, spraying, electrolytic deposition, etc. [12].

1.2.4. Cathodic Protection

The mechanism of corrosion involves metal dissolution due to an electrochemical phenomenon. Thus, corrosion is associated with current flow over finite distances from the corroding metal. By supplying external electric current to the corroding metal, corrosion can be reduced essentially to zero. A metal surface that is cathodically protected can be maintained in a corrosive environment without deterioration for an indefinite time [9].

1.2.5. Inhibitors

An inhibitor is a chemical substance which when added in small concentration to an environment, effectively decreases the corrosion rate. Corrosion inhibitors are most used in the industrial sector due to their low cost and easy practice [13].

1.3. Corrosion inhibitors

Different acids of high concentration are extensively employed in various industrial processes such as acid pickling, descaling, cleaning of boiler, acidization of oil well, and petrochemical process which result in corrosion of metal [36]. To protect the metals from an aggressive environment, many organic compounds have been studied and employed as corrosion inhibitors [14].

Corrosion inhibitors are either synthetic or natural chemicals that, when added to an aggressive environment effectively decreases the corrosion rate. Corrosion inhibitors are needed to reduce the corrosion rates of metallic, alloy materials in the different mediums [6]. Interest in synthetic compounds is diminishing due to toxic effects on humans, animals, and aquatic life while natural products have been prompted as an alternative to replace inorganic and organic inhibitors. Researchers on corrosion inhibition are concentrating on natural products as inhibitors mainly due to their low cost and eco-friendliness [1].

The general classification of inhibitors based on their work is listed here.

1.3.1. Anodic inhibitors

Anodic inhibitors are also called passivating inhibitors. They are usually used in near-neutral solutions where sparingly soluble corrosion products such as oxides,

hydroxide, or salts are formed. They facilitate the formation of passivating films that inhibit the anodic metal dissolution reaction. Chromates, nitrite, phosphates, molybdates are some examples of anodic inhibitors [13].

1.3.2. Cathodic inhibitors

The class of inhibitors which decreases the rate of cathodic reaction in a metal or alloy surface is called cathodic inhibitors. Oxygen reduction and hydrogen reduction are the two mechanisms of cathodic inhibitors. Polyphosphates, zinc salts are examples of cathodic inhibitors [13].

1.3.3. Organic Inhibitors

The most common types of organic inhibitors are long-chain (C_{18}) hydrocarbons and heteroelements containing compounds. They are neither anodic nor cathodic but inhibit both the anodic and cathodic areas to varying degrees depending on the type of inhibition. Amine, amine salts, esters, imidazolines, mercaptanes, amines, and ammonia derivatives, green inhibitors are examples of organic inhibitors [13].

1.3.3.1. Green corrosion inhibitors

Organic chemicals operating as corrosion inhibitors in the petroleum and concrete industry was a major problem related to their toxicity. Corrosion scientists are not very satisfied with chemical inhibitors as they are generally not readily available, expensive, water-insoluble, and pollute the environment in their synthesis and application processes. The search for eco-friendly inhibitors is the major pivot for the use of natural products as environmentally friendly inhibitors [15]. Interest in synthetic compounds is diminishing due to toxic effects on humans, animals, and aquatic life while natural products have been prompted as an alternative to replace inorganic and organic inhibitors.

Extracts of the natural products contain various chemical compositions which are biodegradable and do not contain heavy metals or other toxic compounds [16]. The inhibition performances of plant extract are due to presence of organic compounds such as alkaloids, flavonoids, polyphenol, tannins, nitrogen bases, phenolics, carbohydrates, protein as well as hydrolysis products, etc [17, 18]. These

metabolites usually bear polar functional group-containing nitrogen, sulfur, or oxygen as heteroatoms, as well as triple or double conjugate bonds which act as major absorption centers on the surface of the metal. The lone pairs of electrons in heteroatoms or π-electrons in conjugate bonds are responsible for the formation of layer over steel materials [18, 19].

1.4. *Alnus nepalensis* (Uttis) as Green Corrosion Inhibitor

Alnus nepalensis known as uttis in Nepali and Nepalese Alder in English is a large alder tree found throughout Nepal in subtropical highlands of the Himalayas [20]. The systematic classification of the plant is given below.

Kingdom: Plantae
Division: Tracheophyta
Class: Magnoliopsida
Order: Fagales
Family: Betulaceae
Genus: *Alnus*
Species: *nepalensis*

Figure 1: *Alnus nepalensis tree and powder of the tree bark*

A bark of *Alnus nepalensis* is used to treat diarrhoea, bacillary dysentery, and anti-inflammatory diseases. It contains various phytochemicals such as flavonoids, alkaloids, phenolic compounds, amino acids, etc. The members of the genus Alnus are well known for their traditional uses in the treatment of various diseases like cancer, hepatitis, inflammation of the uterus, uterine cancer, dysentery, stomachache, diarrhoea, fever, etc. [21].

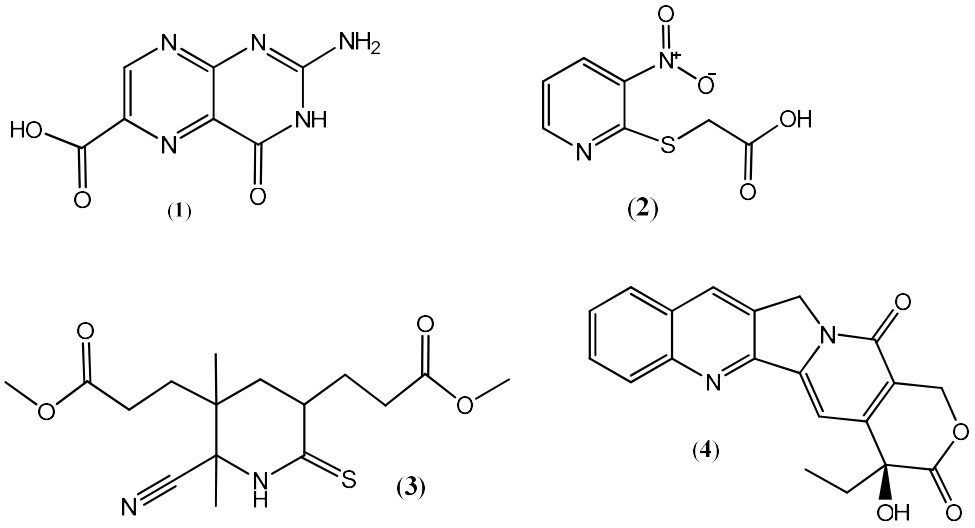
Chemical constituents present in *Alnus nepalensis* are 1,7-bis-(3,4-dihydroxyphenyl)-hexane-3-one-5-O-β-D xylopyranoside {oregonin}, taraxerone, taraxerol, betulin, beutilic acid, lupeol and β-sitosterol [22]. 2-Amino-4-oxo-3,4-dihydro-pteridine-6-carboxylic acid (**1**), (3-nitorpyridin-2-ylsulfanyl)-acetic acid (**2**) and (6-cyano-5-methoxycarbonylmethyl-5,6-dimethyl-2-thioxo-piperidin-3-yl)-

propionic acid methyl ester (**3**), camptothecin (**4**), are reported as alkaloids present in the *Alnus nepalensis* bark [32,33].

The lone pair of electrons and π- electrons present in these structures is responsible for the formation of a protective layer on the metal surface and hence can protect the metal from an aggressive environment. Therefore, in this study, it is used as a green inhibitor and studied its inhibition efficiency.

1.5. Introduction of Alkaloid

Alkaloids are cyclic organic compounds containing nitrogen in the ring structure. It is one of the most diverse groups of secondary metabolites found in living organisms. They are naturally occurring chemical compounds that have basic properties connected with heterocyclic tertiary nitrogen. Most alkaloids are biosynthetically derived from amino acids such as phenylalanine, tyrosine, tryptophan, ornithine, and lysine. In addition to carbon, hydrogen, and nitrogen, alkaloids may also contain oxygen, sulfur, and more rarely, other elements such as chlorine, bromine, and phosphorus [19]. In their pure form, most alkaloids are colorless, non-volatile, crystalline solids and tend to have a bitter taste. There are various types of alkaloids like ruspestine, lycoctonine, pyrrolizidine, purines, polyamine, peptides, indole, piperidine, pyrrolidine, alkamides, and flavoalkaloids. As already stated, the structure of alkaloids in the *Alnus nepalensis* bark extract are given in the scheme 1-4 below.



Scheme 1: *Alkaloids found in Alnus nepalensis species.*

1.6. Role of Alkaloid

Various types of alkaloids can be extracted from different plants which makes this very interesting due to the presence of heteroatoms. These heteroatoms, nitrogen, and oxygen commonly associated with double bonds promote the adsorption between metals and inhibitors. That's why alkaloid plant extracts can reveal the fascinating features about inhibiting corrosion and alkaloids were found to prevent metal corrosion by adsorption of their molecules on metals surface to form a protective layer [1]. Heteroelements such as S, N, and O present in the structure given above, are responsible for adsorption on the metal surface to form a protective layer. The working mechanism of the inhibitor molecule can be explained as in figure 2.

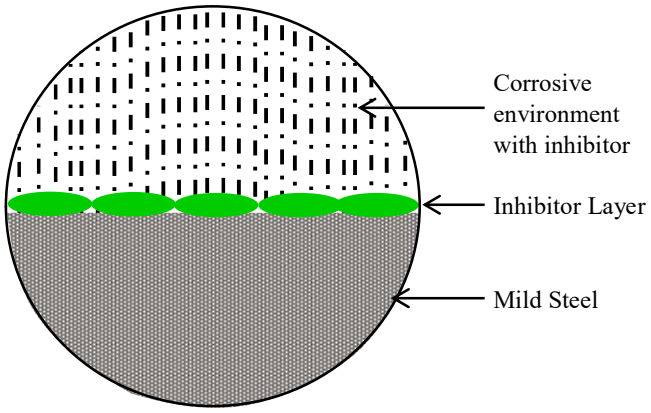


Figure 2: *Formation of inhibition layer on the surface of a metal*

1.7. Corrosion Monitoring Methods

Corrosion Monitoring is the process where changes in a material such as loss of weight, the alteration of physical, chemical, electrical, magnetic, or mechanical properties, and the loss of integrity of components, etc are monitored quantitatively in a given period [30]. Corrosion monitoring methods use the properties of a metal, environment, and border of metal-environment as these are the main factors that influence corrosion. Various data and information can be acquired from corrosion monitoring techniques which can be utilized to assist in providing adequate control of corrosion.

There are mainly two types of corrosion monitoring techniques: direct corrosion monitoring and indirect corrosion monitoring techniques. These two are further classified into more titles based on the principle behind them [13]. In this experiment,

the weight loss measurement method, open circuit potential measurement, and potentiodynamic polarization methods are used.

1.7.1. Weight Loss Method

This is the simplest and best-known method for corrosion monitoring. In this method, a small sample specimen is exposed to a corrosive environment for a specific period and subsequently removed from it for the weight loss measurement. Similar experiment is repeated for next specimen to the environment in presence of inhibitor in similar conditions to calculate the inhibition efficiency. The corrosion rate is calculated by using the following formula [18];

$$\text{Corrosion rate (mm/y)} = \frac{K \times \Delta W}{A \times T \times D} \quad \ldots (1)$$

Where, K = constant = 87600

ΔW = weight loss in gram

A = Total surface area of mild steel in cm^2

T = Immersion time in hour

D = Density of mild steel in g/cm^3

$$\text{Inhibition efficiency (IE\%)} = \frac{W_a - W_p}{W_a} \times 100 \quad \ldots (2)$$

Where, Wa and Wp are the weight loss values in the absence and presence of inhibitors respectively.

The degree of surface coverage was calculated from the weight loss measurement using a formula,

$$\text{Surface coverage } (\theta) = \frac{W_a - W_p}{W_a} \quad \ldots (3)$$

1.7.2. Potentiodynamic Polarization Method

The potentiodynamic polarization measurement is made to evaluate the corrosion current, corrosion potential, and Tafel slope. Potentiodynamic polarization involves the characterization of a sample by its current-potential relationship. A three-electrode corrosion system is used to polarize the electrode of interest. The current response is measured as the potential which is shifted away from the corrosion potential. If the applied potential from external source is more

positive than the corrosion potential then it is known as anodic polarization. As the anodic polarization increases, the cathodic current becomes negligible concerning the anodic current. Conversely, on the cathodic polarization of the sample, the cathodic current predominates and the anodic current becomes negligible [23]. The advantage of this method is reflected in the possibility of localized corrosion detection, easy and quick determination of the corrosion rate, efficiency of the corrosion protection, etc. The corrosion inhibition efficiency was calculated using the given formula [1];

$$\text{Corrosion Inhibition Efficiency (\%)} = \frac{I_{corr} - I^{*}_{corr}}{I_{corr}} \times 100 \qquad \ldots (4)$$

Where, I_{corr} = corrosion current in absence of inhibitor

I^{*}_{corr} =corrosion current in the presence of inhibitor.

The linear Tafel segment of the anodic and cathodic curves was extrapolated to corrosion potential to obtain corrosion current densities.

1.7.3. Tafel Extrapolation Method

Tafel extrapolation is one of the faster experimental techniques widely utilized to measure corrosion rates, compared with the classical weight-loss estimation. This method is based on the mixed potential theory. Both the anodic and cathodic reactions are the component of a mixed electrode involved in the corrosion process and the intersecting point of anodic and cathodic reactions corresponds to corrosion-current density (I_{corr}) and corrosion potential (E_{corr}). Plotting the logarithms of current density (log i) vs potential and extrapolating the current densities in the two Tafel regions gives the E_{corr} and I_{corr}, the corrosion rate can be calculated [9].

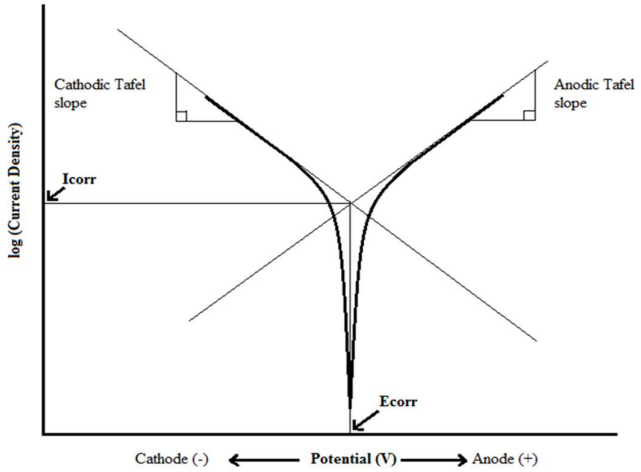


***Figure 3**: Schematic diagram of Tafel plot*

1.10. Objectives

1.10.1. General Objectives

The general objective of the work is to extract the alkaloids from *Alnus nepalensis* bark and to study its corrosion inhibition efficiency on mild steel in an acidic medium.

1.10.2. Specific Objectives

The specific objectives of the work are as follows:

- Preparation of the methanol extract of *Alnus nepalensis* bark.
- Separation of alkaloids from the phytochemicals of the plants.
- Use the crude alkaloids extract as an inhibitor in acid solution.
- Study the inhibition efficiency and thermodynamic parameters of alkaloid inhibitors.

1.11. Literature Review

Various scientific corrosion literatures have descriptions and lists of numerous plants that exhibit inhibitive properties for mild steel in acidic solutions.

Ashassi-Sorkhabi, et. al., 2016, investigated the inhibition effect of Pomegranate peel extract on the corrosion of mild steel in hydrochloric acid (HCl) solution by using polarization, mass loss, and electrochemical impendence techniques. The

inhibition action was attributed to the adsorption of the chemical compounds present in the extract solution, on a mild steel surface [24].

Alaneme, 2016, studied the corrosion inhibition characteristics of *Hunteria umbellata* seed husk extracts on mild steel immersed in 1M HCl and H_2SO_4 solutions by using Mass loss, Atomic absorption spectroscopy (AAS), Fourier transform infrared spectroscopy (FTIR), and Scanning electron microscopy (SEM). Specifically, the inhibition efficiency of the extracts was observed to be generally very high but more effective in 1 M HCl and H_2SO_4 solution. Langmuir adsorption isotherm best fits the data obtained suggesting physical adsorption as the adsorption mechanism between the extract and the mild steel substrate [25].

Aloysius, et. al., 2017, studied the corrosion inhibition of thiamine hydrochloride (vitamin B1) and biotin (vitamin B7) on corrosion of mild steel in 240 ppm chloride ions solution using weight-loss method, potentiodynamic polarization curve, and electrochemical impedance spectroscopy. Experimental results show that both thiamine and biotin act as good corrosion inhibitors [28].

Karki, et. al., 2018, studied the corrosion inhibition of methanol extract of *Artemisia vulgaris* on the corrosion of mild steel in 1M H_2SO_4 has been investigated using weight loss measurements. The inhibition efficiency increases with an increase in concentration and decreases with an increase in temperature beyond 308 K. Adsorption of the extract on metal follows Langmuir adsorption isotherm, the activation and free energies for the inhibitor reactions support the mechanism of physical adsorption [38].

Adams, 2019, studied the effect of bark extract of *Polythialongifolia* on the corrosion of mild steel in 1 M H_2SO_4 solution by using the weight loss technique. The study gives an account of the efficiency of inhibition increased with increasing the concentration of extract but decreased with increasing temperature and the inhibitor follows Langmuir and Tempkin's adsorption isotherm [4].

Thapa, et. al., 2019, studied the inhibitive action of the bark extract of *Euphorbia royleana* in 1 M HCl using weight-loss method and potential measurement. The results show that the corrosion rate decreases with the time of immersion and inhibition efficiency increase with the concentration of extract. A potential measurement study shows that the bark extracts act as a mixed type of inhibitor [18].

Santana, 2020, tested the aqueous extracts of castor beans as a natural inhibitor of the corrosion of mild steel in 1 M HCl using gravimetric tests, potentiodynamic polarization curves, electrochemical impedance measurements, surface analysis by scanning electron microscopy (SEM) and chemical characterization by Fourier transform Infrared Spectroscopy (FTIR). The extracts from castor beans acted as a good corrosion inhibitor and the macromolecules present in high molecular weight fractions have fundamental participation in this process [14].

Karki, et. al., 2020, researched the inhibitor properties of stem extract of *Berberis aristata* in 1 M H_2SO_4 by using gravimetric and electrochemical measurements. The thermodynamics parameters (ΔG and E_a) showed that chemisorption dominated the behaviour of the extract. Electrochemical measurements indicated a mixed type of inhibitor, and the extract suppressed the corrosion rate by blocking the active surface of the metal surface [19].

The inhibition action was attributed to the adsorption of the chemical compounds present in the extract solution on the mild steel surface. Still, investigations and research works are going on for greenery inhibitor alternatives.

1.12. Research Gap

Degradation of any material can cause a shutdown of the entire system with the subsequent loss of productivity, system reputation, money, and costly in terms of environmental damage and human safety. The chemical, petrochemical, construction, manufacturing and transportation industries are the largest contributors to corrosion losses. Corrosion results in tremendous loss and slows down the economic growth of all countries. It is generally believed that the cost of corrosions

is about 3-4% of the Gross National Product (GNP) of most industrialized countries of the world [39]. There is about 4.3% of GDP loss due to corrosion in our country Nepal [8], among which 30-35% can be saved through corrosion protection methods. It causes direct and indirect losses in the economic system. And that's why corrosion is known as one of the most serious problems in our society. So, we should study and implement corrosion monitoring and control techniques. In recent years, plenty of plant sources have been studied as corrosion inhibitors for MS corrosion in acidic medium, and the inhibitive ability of their extracts is satisfactory to excellent. The type of phytochemical is mainly showing inhibitive activity is to be identified. There is a very high possibility of indigenous plants in our country and such plant extracts can work as efficient inhibitors.

CHAPTER 2

MATERIALS AND METHODS

2.1. Collection of Plant and Preparation of powder

Plant material was selected with the help of the literature survey and professors of chemistry who suggested studying on bark extract of *Alnus nepalensis* (Uttis). The bark of *Alnus nepalensis* was collected from Belkotgadi (latitude: 27°83'21", longitude: 85°15'93", and altitude: 1050 m), Nuwakot, Bagmati Province, Nepal. The collected sample was shade dried, and dry bark was ground into the fine powder with the help of a grinding machine.

Figure 4: *Google map of plant collected area*

2.2. Extraction of Alkaloid

The powdered plant sample was soaked in hexane for 24 h to remove unsaturated organic compounds and fats and filtered. Residue is then subjected to 700 mL of methanol for 120 hours followed by filtration. The process was repeated until the colorless effluent was obtained. The filtrate was taken into a large vessel and acidified by using 5% tartaric acid. The pH of the acidified solution was maintained >10 by adding ammonia solution in order to deprotonating 1°, 2°, 3° alkaloids. Alkaloids were separated from this alkaline solution with chloroform using separating funnel. The chloroform layer containing

alkaloids was collected in a beaker. Initially it was concentrated using IKA RV 10 digital rotatory evaporator and then further dried on a water bath to get a solid residue as *Alnus nepalensis* alkaloid. The dry alkaloid was stored in the vessel in moisture-free desiccator.

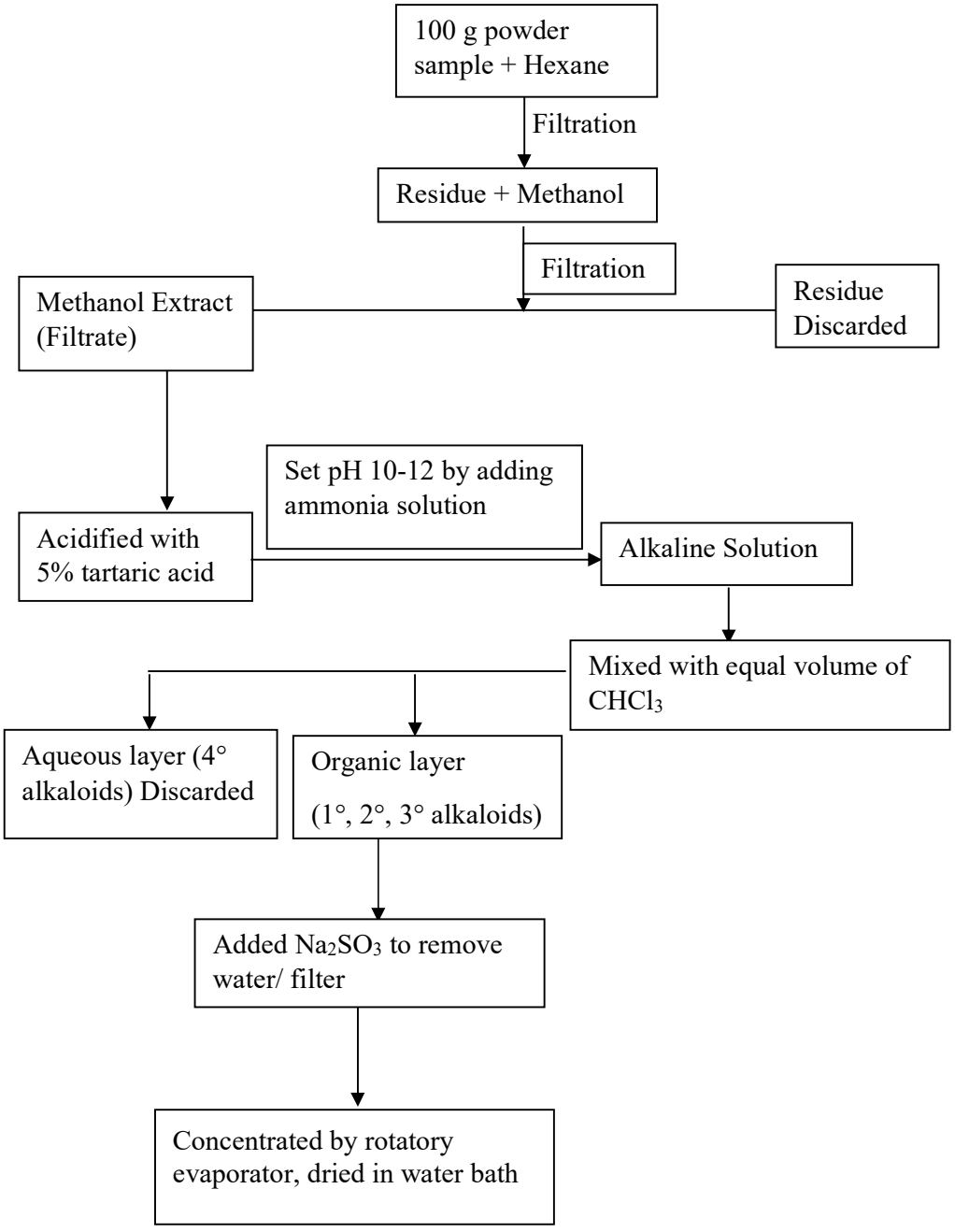


Figure 5: *Schematic diagram showing the extraction of alkaloids.*

2.3. Preparation of mild steel sample

The mild steel sample coupons of equal dimension (4cm×4cm×0.15cm) were

collected from Banasthali, Kathmandu. Each coupon was polished using different grade silicon carbide papers (100, 200, 400, 600, 800, 1000, 1200) and then washed with hexane. Coupons are then sonicated in ethanol for 30 minutes and then dried before each weight loss and electrochemical experiment.

2.4. Preparation of inhibitor solution

The stock solution of the inhibitor was prepared by dissolving 1 g of alkaloid in 100 mL of 1M H_2SO_4. The mixture was filtered to remove the undissolved part and the filtrate was transferred to a 1000 mL volumetric flask and 1 M H_2SO_4 was added up to mark. This results in the formation of 1000 ppm of stock solution. These concentrations (200, 400, 600, and 800 ppm) of inhibitor solutions were prepared by serial dilution.

2.5. Preparation of Corrosive Environment

A corrosive environment was prepared by taking 55.1 mL of sulphuric acid (sp. gravity 1.835, 97% purity) in a 1000 mL volumetric flask containing distilled water. Further addition of distilled water up to mark results the formation of 1M sulphuric acid solution. This solution is taken as corrosive media and used while analyzing the weight loss and polarization measurement.

2.6. Test for Alkaloids

a) Mayer's Test:

A small amount of extract was treated with Mayer's reagent with $HgCl_2$ (0.567 g) dissolved in distilled water and then K_2HgI_4 (potassium mercuric iodide) was added. An orange precipitate of potassium-alkaloid indicates the presence of alkaloids.

b) Dragondroff's Test:

A small amount of extract was treated with Dragendorff's reagent (Solution A: 3 g of Bismuth nitrate was taken and then dissolved in 4 N H_2SO_4 (8 mL). Solution B: 12 g of KI was dissolved in 18 mL distilled water. Solution A and solution B was mixed in a 50 mL volumetric flask with distilled water) the appearance of an orange-red precipitate of potassium- alkaloid indicates the presence of alkaloids.

c) Wagner's Test:

In this test, 2 g of iodine was mixed with 6 g of KI in 100 mL of distilled water and the extract was added. Reddish-brown precipitate of potassium-alkaloid indicates the presence of alkaloids.

2.7. Weight Loss Measurement

In the weight loss measurement, the effect of immersion time, the effect of inhibitor concentration on corrosive media, and the effect of temperature were studied. Before studying each effect, the dimension of coupons was measured by using the digital Vernier calliper and weighed by using an electronic balance (PH2204C). The weight of coupons was noted and then dipped in 100 mL of corrosive media and inhibitor solutions of different concentrations separately. After 30 minutes of immersion, coupons were taken out from the solution, washed with distilled water, and dried. The weight of dry coupons was measured. The difference in weight of the coupon before and after immersion was used to calculate the corrosion rate. A similar process was repeated for a different interval of time (1, 3, 6, 18, and 24 hrs.). Similarly, the inhibitor concentration effect was studied by immersing corrosion-free coupons in acid and inhibitor solutions of different concentrations (200, 400, 600, 800, and 1000 ppm) separately for 6 hours at room temperature. To study the temperature effect, the coupons were immersed in acid and 200, 600, and 1000 ppm inhibitor solution separately for 1 hour at various temperatures (25, 35, 45, and 55 °C).

From the weight loss data, the corrosion rate (mm/y), inhibitor efficiency (IE%), and surface coverage (Ɵ) is calculated using the formula in equation (1), (2), and (3) respectively.

2.8. Electrochemical Measurements

2.8.1. Open Circuit potential measurement

The open-circuit potential (OCP) is important to explain the mode of inhibition by the inhibitor solution. The measurement of OCP was conducted for a better understanding of the corrosion behavior of the mild steel sheet in 1M H_2SO_4 solution at room temperature in the absence and presence of alkaloid as a corrosion inhibitor. The measurement was carried out using Hokuto Denko potentiostat

(HA151, Japan) in central Department of Chemistry, Tribhuvan University, Nepal. Measurement was carried out in a three-electrode system for which the mild steel coupon was used as a working electrode, graphite as a counter electrode, and a saturated calomel electrode was used as a reference electrode. The OCP was measured in different concentrations of inhibitor solutions for 30 minutes, for 3 hours immersed samples.

2.8.2. Potentiodynamic Polarization

The polarization measurement method was used to evaluate the corrosion current, the corrosion potential, and Tafel slopes. Potentiodynamic polarization measurements were carried out using Hokuto Denko potentiostat (HA-151) in central Department of Chemistry, Tribhuvan University, Nepal. A three-electrode cell the system was used for the polarization. Experiment was carried out in the same electrolytic cell used to determine OCP. The working electrode i.e., the mild steel specimen whose small area was exposed in extract solution as compared to that of the counter electrode to exert uniform potential on the working electrode. A salt bridge was made to connect the working electrode to the SCE. A time interval of 30 minutes before polarization was given for each experiment to attain the steady-state OCP. Then the sample was subjected to cathodic and anodic polarization in the potential window -0.85 (V) to -0.1 (V) i.e., ±350mV from OCP. Polarization measurement was carried out for steel samples in different concentrations of inhibitors as well as in acid solution in 3 h immersed conditions.

From the polarization curves, Tafel slope, corrosion potential, and corrosion current were calculated. The corrosion inhibition efficiency was calculated using the formula in equation (4). The linear Tafel segment of the anodic and cathodic curves was extrapolated to corrosion potential to obtain corrosion current densities.

2.9. UV-Visible Spectroscopic Analysis

The spectroscopic characterization of *alnus nepalensis* alkalloid was performed using a labtronics, LT-2802 double beam ultraviolet-visible (UV-Vis) spectrometer at department of chemistry, Amrit Campus, Kathmandu to identify the unsaturation and electron rich centers in the alkaloids [26]. While recording spectra, aqueous and methanol solution of the alkaloid were used.

2.10. FTIR Analysis

FTIR spectroscopic analysis is a powerful tool that can be used to identify the type of bonding particularly the functional group present in the organic compounds. In this experiment, the FTIR spectra of the alkaloid sample were collected using (PerkinElmer Spectrum IR Version 10.6.2) FTIR spectrometer in Amrit Campus, Kathmandu. FTIR spectra give an idea of the functional groups, π-bond conjugate system, aromatic and aliphatic structures present in the alkaloid samples.

CHAPTER 3

RESULTS AND DISCUSSION

The corrosion inhibitory behavior of the alkaloid was studied by the weight-loss method, open circuit potential, and potentiodynamic polarization. For the characterization of alkaloids, qualitative chemical test, UV spectroscopic and FTIR spectroscopic measurements were performed.

3.1. Test of Alkaloids

A qualitative test for the confirmation of alkaloids extracted from *Alnus nepalensis* was performed. Different tests as tabulated in table 1 confirm the presence of alkaloids.

Table 1: *Phytochemical screening of the extract solution*

S.N.	Experiment	Result	Inference
1.	Mayer 's Test	The appearance of orange precipitate.	+ve
2.	Dragendroff ’s Test	The appearance of orange-red color.	+ve
3.	Wagner 's Test	Appearance of reddish-brown precipitate.	+ve

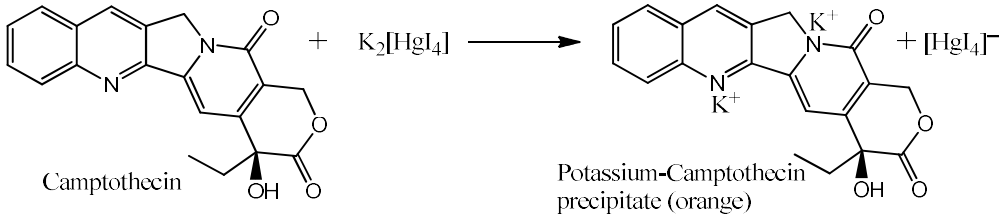
Reactions involved in phytochemical screening of alkaloids are as follows [27]:

- **Mayer’s test**

Mayer's reagent is potassium mercuric iodide (K_2HgI_4), which when added to the alkaloid solution, an orange precipitate of potassium-alkaloid was obtained indicates the presence of alkaloids. The possible reaction involves is given with the reference of camptothecin as below.

$HgCl_2 + 2KI = HgI_2 + KCl$

$HgI_2 + 2KI = K_2[HgI_4]$

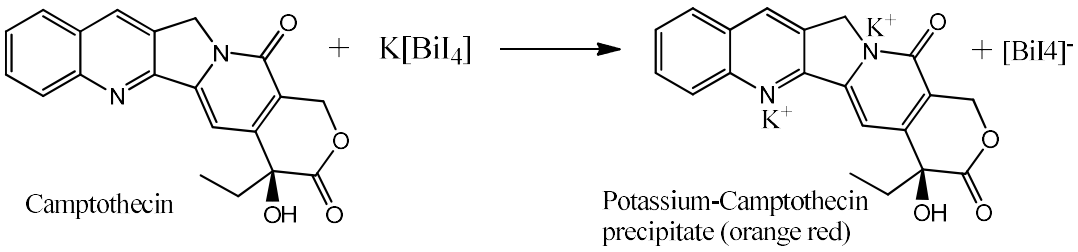


- **Dragendroff's test**

Potassium bismuth iodide is the Dragendroff's reagent. When it is treated with alkaloids, the orange red precipitate of potassium-alkaloid is obtained which indicates the presence of alkaloid. The possible reaction involves is given with the reference of camptothecin as below.

$Bi(NO_3)_3 + 3KI = BiI_3$ (Brown) $+ 3KNO_3$

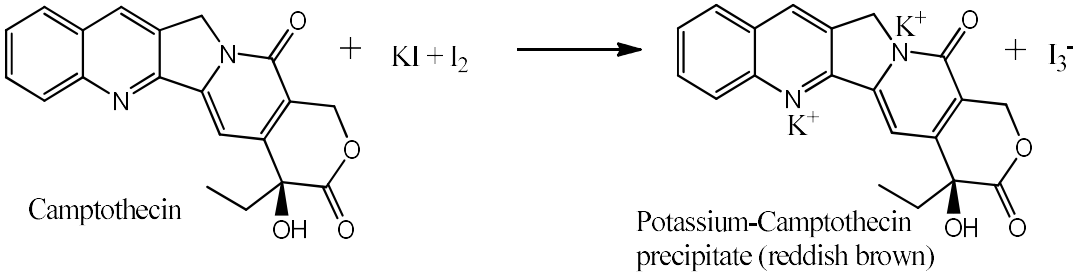
$BiI_3 + KI = K[BiI_4]$



- **Wagner's test**

Iodine when dissolved in potassium iodide solution then the solution contains potassium and tri-iodide ions. These ions, when treated with alkaloids the reddish-brown precipitate of potassium alkaloid is obtained which indicates the presence of alkaloids. The possible reaction involves is given with the reference of camptothecin as below.

$I_2 + I^- = I_3^-$



3.2. UV Spectroscopic Measurements

The UV measurement is carried out for identification of unsaturation or presence of lone pair of electrons in the organic compounds. The UV spectra of alkaloid have been recorded using a labtronics, LT-2802 double beam ultraviolet-visible (UV-Vis) spectrometer in Amrit Campus, Kathmandu. In the spectra, the sharp peak at 337 nm and 427 nm indicates the presence of lone pair of electrons and the unsaturation in the

compound. The sharp peak at 337 nm is due to n-π* transition whereas the sharp peak at 427 is due to π-π* transition of the alkaloids [31]. If camptothecin is taken as reference then these two sharp peaks indicates the presence of aromatic ring containing N as heteroelement and the polyphenolic group in the structure.

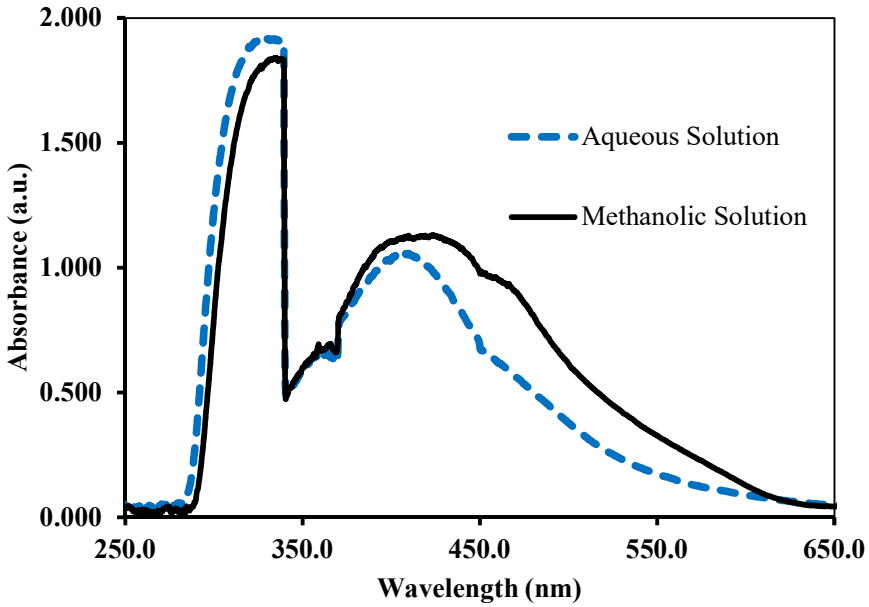


Figure 6: *UV-Visible spectrum of methanol extract of A. nepalensis*

3.3. FTIR Spectroscopic Measurements

FTIR spectroscopic analysis is a powerful tool that can be used to identify the type of bonding, π-bond conjugate system, aromatic and aliphatic structures, and particularly the functional group present in the organic compounds. FTIR spectrum of alkaloid extract of *A. nepalensis* was recorded by PerkinElmer Spectrum IR Version 10.6.2 FTIR spectrometer, as shown in figure 7. The spectrum of FTIR provides information about the molecular structure and confirmation of organic molecules as well as different functional groups present in the sample. It is useful to identify the carbon-heteroatom bond from their stretching frequency in the FTIR spectrum.

The peak around 3350 cm^{-1} is due to N-H stretching vibrations, sharp peak at 2900 cm^{-1} due to C-H stretching of aromatic ring, peak around 1232 cm^{-1} and 1024 cm^{-1} is due to C-N stretching of amines, and peak around 712 cm^{-1} is due to N-H bending vibration of primary and secondary amine [31].

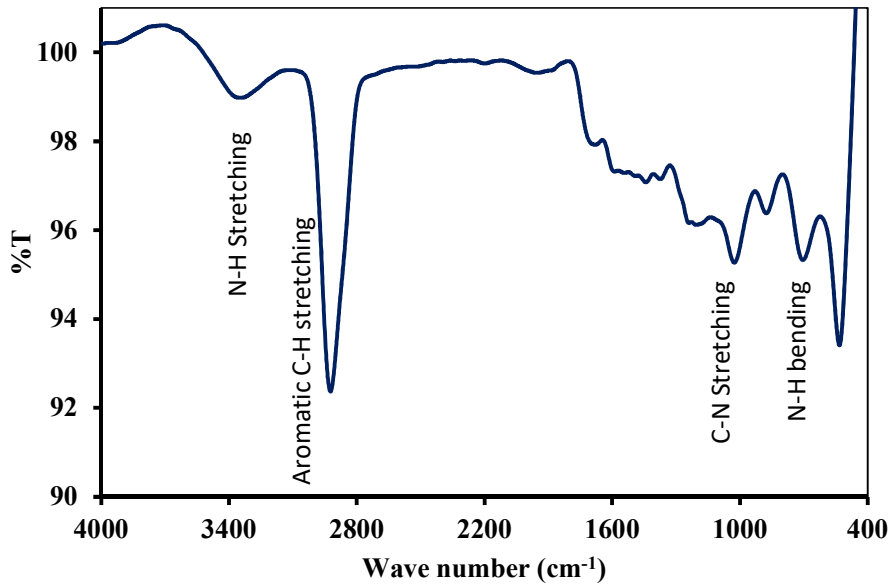


Figure 7: *FTIR spectrum of alkaloid extract of A. nepalensis*

3.4. Weight Loss Measurements

3.4.1. Variation of weight loss with immersion time

The results of the weight loss experiment for MS immersed in 1 M H_2SO_4 with and without inhibitor were shown in Figure 8. The weight loss measurement showed that the presence of an alkaloid inhibitor reduces the weight loss of metal in the acidic inhibitor medium as compared to that in 1M H_2SO_4 solution. Experiments were performed in different time intervals i.e., 0.5, 1, 3, 6, 18, and 24 h in 1 M H_2SO_4 in the presence and absence of inhibitor.

The weight loss of MS coupons in gram per unit area has been determined and tabulated in the table 2. The loss in weight of MS in acid only is very high in comparison to inhibitor solutions. Even though there is weight loss in presence of inhibitor solution but the weight loss is very small than that of acid only. This decrease in weight loss is due to inhibition by inhibitor. Weight loss of MS for half an hour immersion time is very small but the corresponding inhibition efficiency is not so high. This is because at very beginning there is no complete coverage of MS surface by inhibitor molecules. On increasing immersion time, the weight loss in all the cases increases but the corresponding inhibition efficiency increased indicating the inhibition effect of the inhibitor molecule. Even though, the weight loss

gradually increases on increasing immersion time, but the corresponding inhibition efficiency decrease after 6 h immersion time. The decrease in inhibition efficiency for prolonged immersion is due to the desorption phenomenon of inhibitor molecules. For 24 h immersion time the weight loss of MS is highest for all the cases. This is may be due to desorption of inhibitor molecule of the due to presence of defects on the inhibitor layer which allowed the aggressive environment to be in contact with MS surface.

Table 2: *Variation of weight loss (g/cm^2) with different immersion time at different concentrations of inhibitors*

Time (h)	Acid	200 ppm	400 ppm	600 ppm	800 ppm	1000 ppm
0.5	0.000694	0.000518	0.000427	0.000349	0.000314	0.000233
1	0.002443	0.001811	0.001547	0.001191	0.001027	0.000767
3	0.011702	0.008293	0.007473	0.005736	0.00499	0.003284
6	0.023252	0.016566	0.014181	0.012493	0.009482	0.008063
18	0.061981	0.048643	0.04169	0.036487	0.034344	0.027791
24	0.073173	0.059112	0.050419	0.043272	0.04234	0.036187

From the figure 8, it is clear that, on increasing the time, the weight loss of metal increase in both but the ratio of weight loss reduces in inhibitor as compared to 1M H_2SO_4. This is because the inhibitors get adsorbed on the MS surface forming an adsorptive layer on it. This adsorptive layer acted as a barrier for acid. There is a slight increase in weight loss observed even in presence of inhibitors. This may be due to desorption phenomena and may be due to the large size and orientation of inhibitor molecules. On exposing MS sample for a longer time, desorption of molecule from MS surface takes place and hence increase in weight loss. As in Figure 8, the weight loss of the MS coupons is highest in acid solution and lowest weight loss of the MS samples in presence of 1000 ppm inhibitor solution.

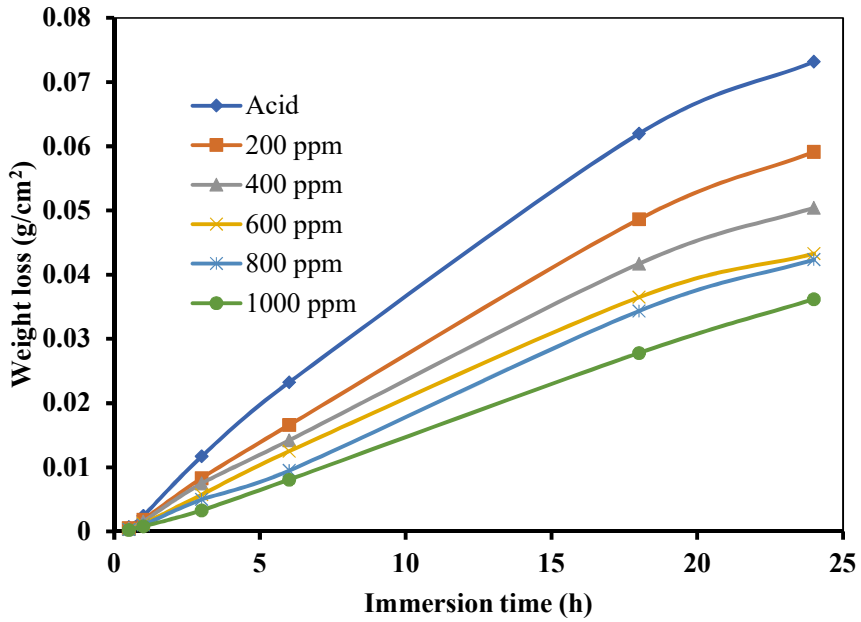
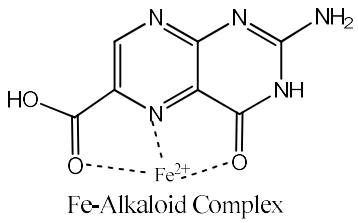


***Figure 8**: Variation of weight loss with immersion time for the corrosion of mild steel in the solution of 1M H_2SO_4 and solution of different inhibitor concentrations at room temperature.*

The inhibition efficiency of the inhibitor molecules of different concentrations in 1 M H_2SO_4 for MS samples is shown in Figure 9. It is clear from the figure that the inhibition of the inhibitor is very good at 1-6 h immersion time. The inhibition efficiency of the 1000 ppm solution is the highest. The maximum inhibition efficiency is found to be 71.94 % of 1000 ppm solution at 3 h immersion time. The inhibition efficiency increases up to 3 hours of immersion. However, with a prolonged immersion period there is a decrease in efficiency after 3 hours. This decrease in efficiency can be attributed to the dynamic desorption/absorption of inhibitor constituents at the metal/solution interface.

It seems that IE of the inhibitor is less than 80% (i.e. maximum 66.38%) in short time of exposure. It means metal ions are dissolved in acid solution. These dissolved metal ions undergo chelation with inhibitor molecules forming chelate complex. With increase in time, the availability of inhibitor molecules decreases resulting in the decrease in IE.



Scheme 2: *Fe-Alkaloid Complex*

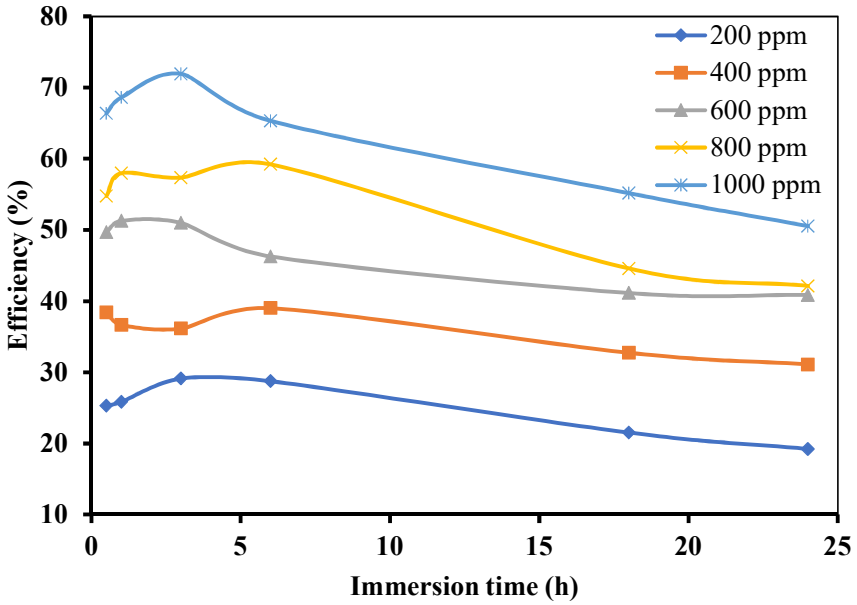


Figure 9: *Variation of inhibition efficiency of different inhibitor solutions in 1M H_2SO_4 solution vs time for the corrosion of mild steel at various times.*

3.4.2. Variation of weight loss with temperature

The effect of temperature on the inhibition process was studied using the inhibitor solution of three different concentrations (200, 600, 1000 ppm). The weight loss measurement in these three different inhibitor solutions in different temperatures was measured as taking reference of acid solution. For this measurement, the MS coupons were immersed in these solutions for one hour at different temperatures (25, 35, 45, and 55 °C). Observed data are tabulated in table 3.

***Table 3**: Weight loss (g/cm²) of MS immersed in different concentration of inhibitor at different temperatures*

Temperature °C	Acid	200 ppm	600 ppm	1000 ppm
25	0.002041	0.001375	0.000986	0.00063
35	0.006583	0.004498	0.002378	0.001429
45	0.012974	0.008968	0.007411	0.003636
55	0.021196	0.016969	0.013403	0.009688

The weight loss of MS is maximum in acid solution and minimum at 1000 ppm inhibitor solution. The weight loss of MS in inhibitor solutions gradually increased on increasing temperature. This increasing in weight loss may have two reasons: may be due to desorption of the inhibitor molecules from MS surface, and may be due to the structural deformation of the inhibitor molecules [34]. The increasing in weight loss leads the decreasing in inhibition efficiency of the inhibitor.

The graph obtained by plotting weight loss per unit area in unit time shows that there is small weight loss at low temperature but on increasing temperature the weight loss increases as in figure 10.

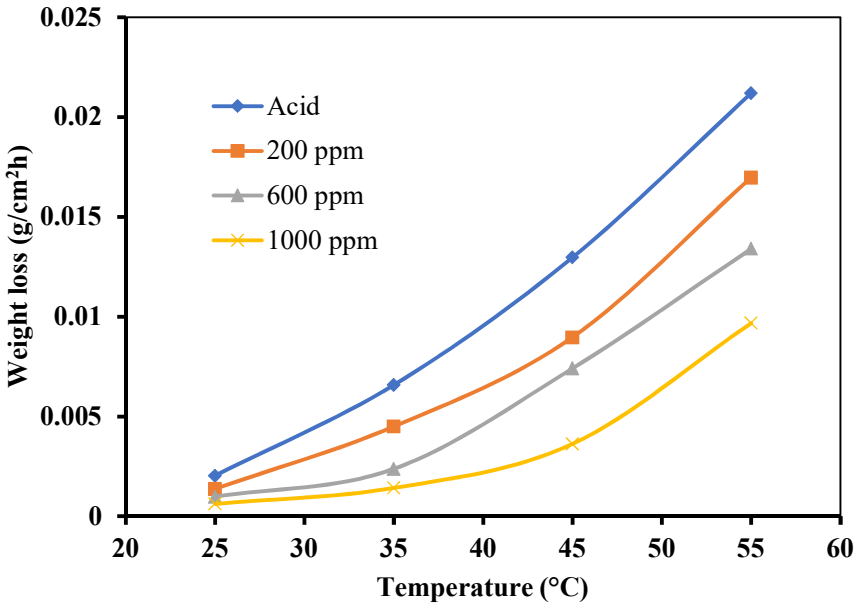


***Figure 10:** Variation of weight loss of mild steel coupons in 1 M H_2SO_4 and 200, 600, and 1000 ppm inhibitor at different temperatures.*

3.4.3. Effect of Temperature on Inhibition Efficiency

The effect of temperature on the corrosion inhibition with and without inhibitors was studied with different temperatures at constant 1 h immersion time. Thus obtained data are tabulated in table 4. Form table it is clear that the inhibition efficiency of 200 ppm inhibitor solution has almost negligible inhibition efficiency at every temperature and one more interesting fact that there is almost no effect to temperature up to 45 °C. For 600 ppm inhibitor solution, on increasing temperature the inhibition efficiency is increased which declines after 35 °C forming a hump structure. This indicates that the effective temperature for formation of inhibitor layer and inhibition is 35 °C after which the molecular desorption from MS surface may take place. For 1000 ppm inhibitor solution, the inhibition efficiency is almost good and linear up to 45 °C after which it declines. After these results it can be concluded that the structural deformation of molecules may occur than that of desorption of molecule from MS surface. This deformation leads the decreasing in inhibition efficiency of inhibitor for MS in acidic medium. Results show the less thermal stability of inhibitor at high temperature.

Table 4: *Inhibition efficiency (%) of the inhibitor of different concentration on MS at different temperatures*

Temperature (°C)	200 ppm	600 ppm	1000 ppm
25	32.64108	51.70345	69.11226
35	31.67159	63.88393	78.2978
45	30.88314	42.87825	71.97346
55	19.94206	36.76527	54.29104

Figure 11 shows the variation of inhibition efficiency with temperature. It is clear from the figure that the 200 ppm inhibitor solution is almost inefficient at every temperature. And the 600 ppm inhibitor solution showed good inhibition at 35 °C. Inhibition efficiency of 1000 ppm inhibitor solution was observed highest at 35 °C temperature.

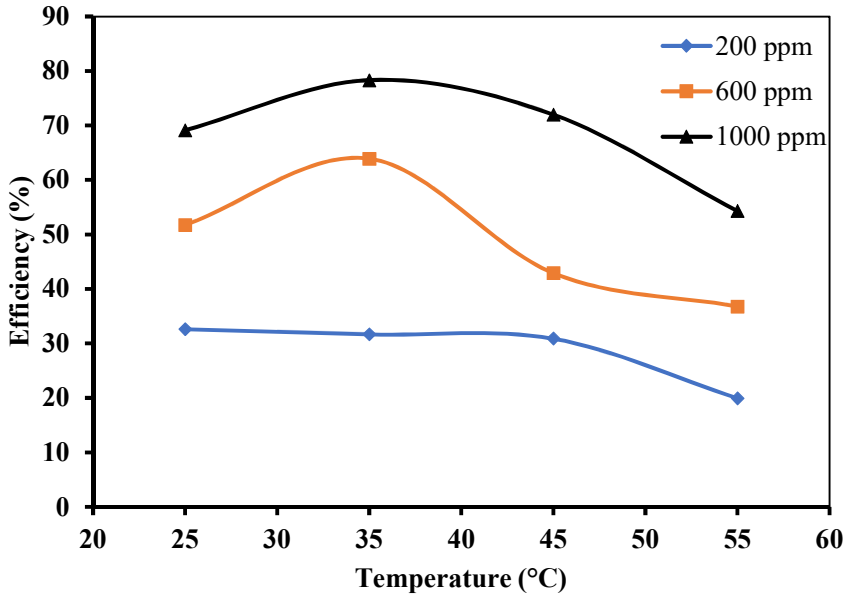


Figure 11: *Variation of inhibition efficiency with temperature on the mild steel in presence of 200, 600, and 1000 ppm inhibitor in 1 M H_2SO_4 solution.*

3.4.4. Weight loss of MS in different concentrations of alkaloid

When MS coupons are dipped in the acid solution then the acid reacts with the MS surface resulting in the formation of corrosion products. After the formation of the corrosion product, the weight of MS has decreased. The decrease in the weight of MS coupons is related to the nature of the MS surface, temperature, and concentration of the solution. The loss in weight of MS is very high in absence of an inhibitor. Besides inhibitor the loss in weight of MS gradually decreases with an increase in the concentration of inhibitor as shown in Figure 12. It may be due to the adsorption of inhibitor molecules on the metal surface. The minimum weight loss was observed in the 1000 ppm solution at 3 hours of immersion.

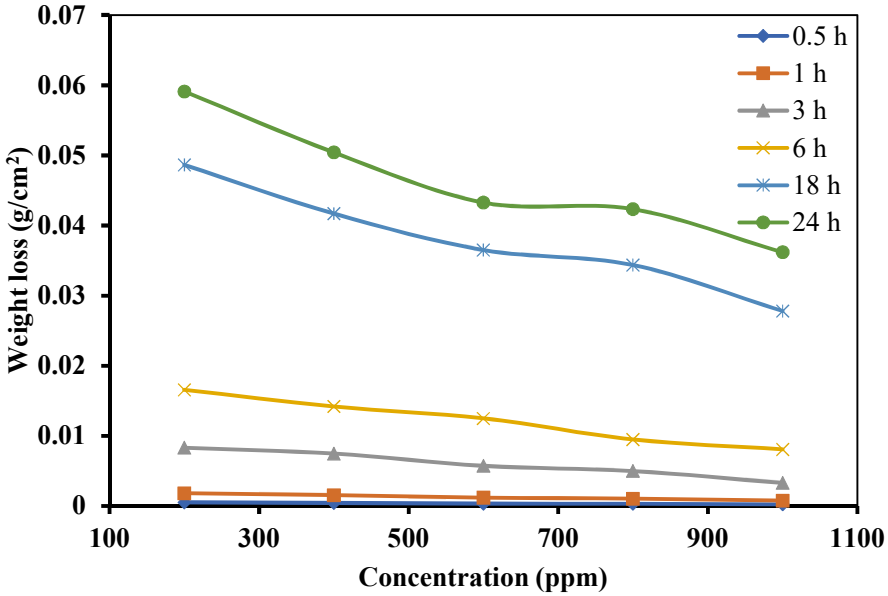


Figure 12: *Variation of weight loss versus concentration of extract on mild steel in 1 M H_2SO_4 solution at various times.*

3.4.5. Inhibition efficiency by different concentrations of alkaloid

The inhibition efficiency of the inhibitor highly depends on the inhibitor concentration. In this experiment, the inhibition efficiency of 200 ppm inhibitor solution is almost negligible at every immersion time. This indicates that the inhibitor concentration is not sufficient to cover the MS surface and hence inhibition is significantly less. On increasing the concentration, inhibition is in increasing order, which indicates the increase in surface coverage of the MS by inhibitor molecules. The optimum concentration for highest inhibition is 1000 ppm inhibitor solution. It showed highest inhibition efficiency at 3 h immersion time.

Table 5: *Inhibition efficiency (%) of different concentration of inhibitor at different immersion time*

Time (h)	200 ppm	400 ppm	600 ppm	800 ppm	1000 ppm
0.5	25.27	38.41	49.68	54.78	66.38
1	25.86	36.67	51.28	57.96	68.61
3	29.14	36.14	50.98	57.35	71.94
6	28.76	39.01	46.27	59.22	65.32
18	21.52	32.74	41.13	44.59	55.16
24	19.22	31.10	40.86	42.14	50.55

The inhibition efficiency of the inhibitor of different concentration has been tabulated in table 5. The inhibition efficiency of 200 and 400 ppm inhibitor concentration are almost negligible (less than 30% and 40% respectively) and can be explained in the way that these concentrations are not sufficient to cover the more surface of MS. Similarly, the 600 and 800 ppm inhibitor concentration moderately inhibit the MS surface from aggressive environment. However, the inhibition by 1000 ppm inhibitor solution is more than 60% up to 6 h immersion time. This indicates that the 1000 ppm inhibitor solution can act as good inhibitor up to 6 h immersion time, but beyond this the inhibition is not less than 50% which is also quite acceptable.

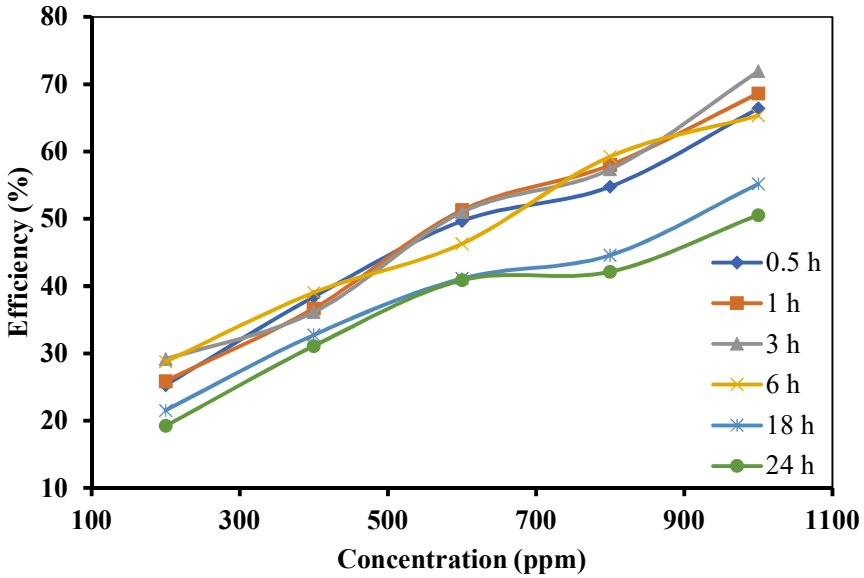


Figure 13: *Inhibition efficiency at different concentration of inhibitor on mild steel in 1 M H_2SO_4 solution at various times.*

3.5. Adsorption Isotherm

This is a well-known fact that when solid substances are immersed in solutions, molecules from the solution get adsorbed on the solid surface. Likewise, here MS coupons are immersed in acid as well as inhibitor solution. When MS is immersed only in acid solution then the acid molecules get adsorbed and a vigorous reaction occurs causing deterioration of MS coupon. Similarly, in the presence of a mixture of acid and inhibitor solution, at first, inhibitor molecules get adsorbed on the MS

surface results in a decrease in the deterioration of MS. For a clear explanation of this adsorption process, it is better to know the adsorption isotherm. For a better understanding of the adsorption isotherm and the type of adsorption between MS surface and inhibitor molecule, it is better to check adsorption isotherms. Adsorption isotherm gives the basic information on the interaction between the inhibitor and MS surface. At first, water molecules are adsorbed on the MS surface in an aqueous solution. These adsorbed molecules are then replaced by inhibitor molecules. So, the adsorption of inhibitor molecules from an aqueous solution is a quasi-substitution process.

In order to identify the adsorption isotherm, Langmuir, Freundlich and Tempkin adsorption isotherms were determined. Though this may not be enough and the mixture of alkaloids may not follow this trend but for the reference camptothecin (**4**) molecule is taken in order to calculate the molar concentration of inhibitor solution. Langmuir's adsorption isotherm equation can be applied to find whether the adsorption process is monolayer or multilayer [34, 35]. The linear relation between the fraction of covered surface (θ) and molar concentration (C) should be known to find the adsorption isotherm. If the slope of the curve obtained by plotting $\frac{C}{\theta}$ vs C in equation (5) is unity then it indicates the monolayer adsorption,

$$\frac{C}{\theta} = \frac{1}{K} + C \quad \ldots (5)$$

As we plot $\frac{C}{\theta}$ vs C, a straight line with R^2 value equal 0.8578 is obtained as in table 6. This value is highly deviated from unity indicating the adsorption of inhibitor molecules on MS surface does not obey Langmuir adsorption isotherm. This indicates that adsorption may be mono- or multilayer but the complete monolayer has not been formed before multilayer formation. The value of slope and R^2 strongly deviated from unity so that the adsorption process in this corrosion inhibition process cannot be explained by this Langmuir isotherm [34, 35].

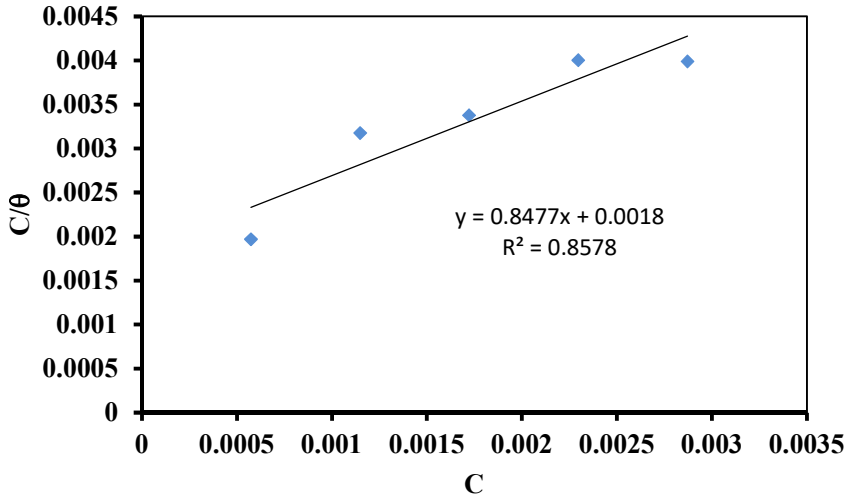


Figure 14: *Langmuir adsorption isotherm plot for MS in 1 M H_2SO_4 with different concentration of inhibitor.*

For the explanation of corrosion inhibition mechanism and the nature of interaction taking place in the adsorbed layer Temkin adsorption isotherm in equation (6) has been checked. A plot of θ against ln C with slope 0.2553 and R^2 value 0.9076 is obtained as in table 6.

$$\theta = -\frac{1}{2a}\ln C - \frac{1}{2a}\ln K \quad \ldots (6)$$

From the slope of the straight line in figure 15, the molecular interaction parameter (a) is calculated and found to be negative 1.96 indicating there is strong attraction taking place in the adsorbed layer [35]. The value of K from intercept is calculated and fond negative 1.73 indicating inhibitor molecules are strongly absorbed on the MS surface.

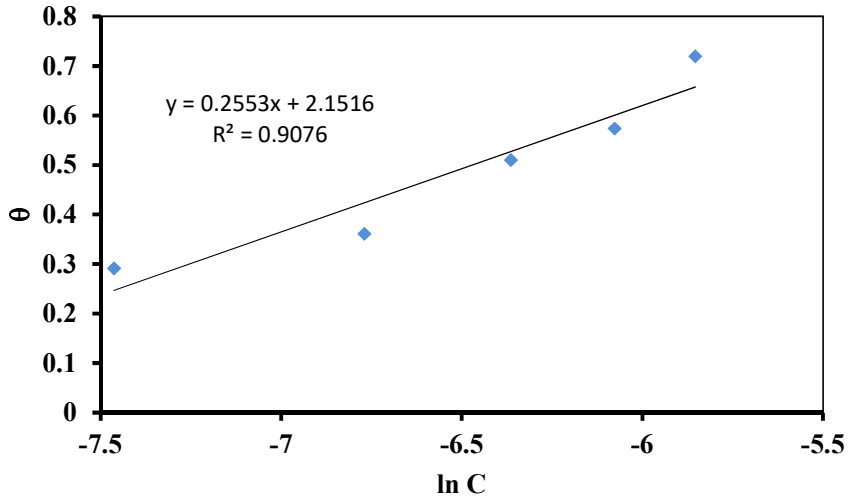


Figure 15: *Temkin adsorption isotherm plot for MS in 1 M H_2SO_4 with different concentration of inhibitor.*

In order to find how easily the adsorption of inhibitor molecules on the MS surface Freundlich adsorption isotherm has been checked. From the linear form of Freundlich adsorption isotherm equation (7), a curve between ln θ vs ln C is plotted as in figure 16. The R^2 value of the straight line is 0.9588, with slope value (1/n) equal to 0.5582 which is in between 0<1/n<1 indicating the adsorption process is easy [35].

$$\ln\theta = lnK + \frac{1}{n}\ln C \qquad \ldots (7)$$

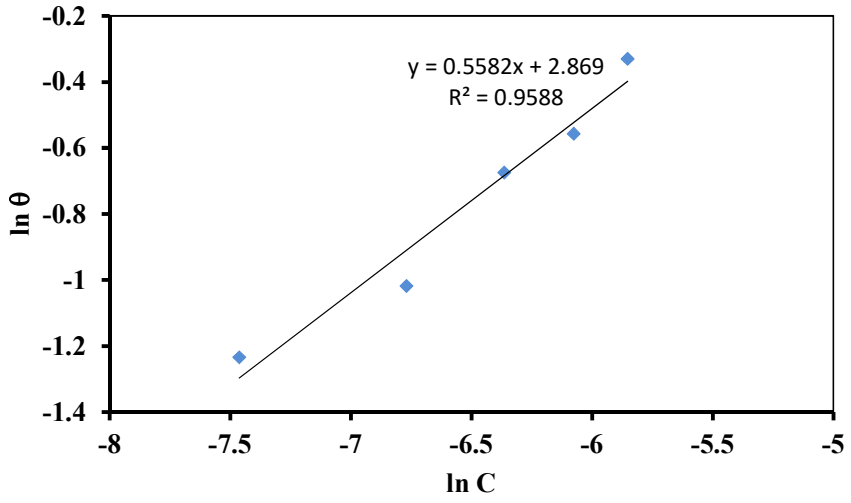


Figure 16: *Freundlich adsorption isotherm plot for MS in 1 M H_2SO_4 solution.*

The values of slope and intercept have their usual significances which have been explained above. The R^2 value gives the correlation between the measured values and hence helps to check the linearity range in order to check whether the measured values are acceptable. There are three different R^2 values listed in table 6 for three different isotherms. Among them the R^2 value for Langmuir isotherm is highly deviated whereas for Temkin it is more nearer to unity and for Freundlich isotherm it is quite acceptable and equal to 0.9588. Since, these data are not fitted for Langmuir adsorption isotherm so that the Gibb's free energy has not been calculated.

Table 6: *Different parameters obtained from three different adsorption isotherms*

Isotherm	Plotting	Slope	Intercept	R^2
Langmuir	C/θ vs C	0.8477	0.0018	0.8578
Temkin	θ vs ln C	0.2553	2.1516	0.9076
Freundlich	ln θ vs ln C	0.5582	2.869	0.9588

3.6. Activation energy and thermodynamic parameters

The activation energy of the reaction in the presence and absence of inhibitor in an electrochemical cell can be explained by rearranging the Arrhenius equation. The activation energy of the reaction is related to corrosion rate as,

$$\log(CR) = \log(A) - \frac{E_a}{2.303RT} \quad \ldots (8)$$

Where A is the Arrhenius pre- exponential constant, T is the absolute temperature. Equation (8) reveals that the activation energy of the reaction is equal to the slope of the Arrhenius plot i.e. a plot obtained between logarithms of corrosion rate with $\frac{1}{2.303RT}$ along axes.

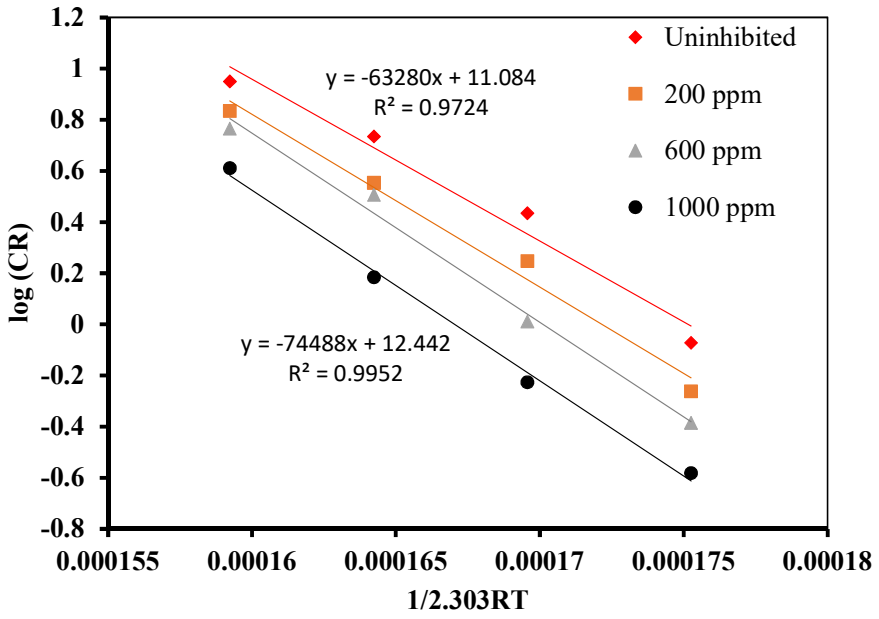


Figure 17: *Arrhenius plot for MS in 1M H_2SO_4 with and without inhibitor*

Arrhenius plot (Figure 17) shows that energy of activation of the reaction between MS and acid in absence of inhibitor is 63.20 kJ/mol. On addition of 200, 600 and 1000 ppm inhibitor the activation energy increases to 67.53, 73.96 and 74.48 kJ/mol respectively as shown in table 7. This increase in activation energy reveals that with the addition of inhibitor, inhibitor molecules suppress the reaction rate between acid and MS resulting in the decrease in corrosion rate. These calculated values are intermediate value between physical (less than or equal to 20 kJ/mol) and chemical interactions (more than 80 kJ/mol). Therefore, adsorption of alkaloids on MS surface in 1M H_2SO_4 solution involves mixed type of adsorption with domination of chemisorption. [36].

Enthalpy and entropy of the system can be calculated by using transition state equation, an alternative form of Arrhenius equation,

$$\log(\frac{CR}{T}) = \log(\frac{R}{hN}) + \frac{\Delta S^\circ}{2.303R} - \frac{\Delta H^\circ}{2.303RT} \qquad \ldots (9)$$

Where, h is plank's constant, 6.6261×10^{-34} Js, and N is the Avogadro's number, 6.0225×10^{23} mol^{-1}.

Enthalpy of activation (ΔH^o) is obtained as slope of a straight line by plotting

$\log\left(\frac{C.R.}{T}\right)$ vs. $\frac{1}{2.303RT}$ in the equation and the entropy of activation (ΔS^{o}) can be calculated from its intercept.

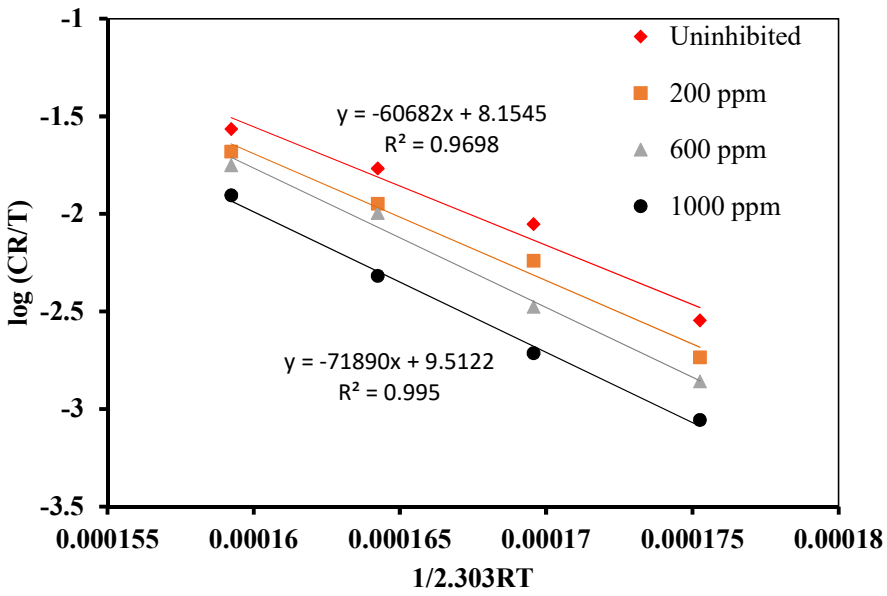


Figure 18: *Transition state plot for MS in 1M H_2SO_4 with and without inhibitor.*

From the transition state plot (Figure 18), the enthalpy of the system in the absence and presence of inhibitor is estimated as in table 7. The positive value of ΔH* for adsorption of inhibitor on MS surface indicates that the adsorption is endothermic process. The gradual increase in the value of ΔH° from 60.68 to 71.89 kJ/mol including 64.93 and 71.36 kJ/mol for acid only, and different concentration of inhibitor solution indicates a decrease in the corrosion rate controlled by kinetic parameters of activation. The Ea value higher than that of ΔH° indicates the involvement of a gaseous reaction i.e. cathodic hydrogen evolution reaction, results the decrease in total reaction volume. The values of Ea and ΔH° also confirm the adsorption of alkaloid is by both physical and chemical interactions [35, 36].

Calculated values of E_a, ΔH°, and ΔS° for acid without and with inhibitor are tabulated in Table 6. The activation energy of the system has increased with the addition of inhibitors of three different concentrations. An increase in activation energy reduces the reaction rate resulting in the suppression in corrosion rate. On increase in E_a with the addition of inhibitor shows the strong adsorption of inhibitor molecules on the metal surface with complete or nearly complete coverage so that

acid molecules have the least or almost no chance to react with metal.

Table 7: *Activation parameters of the MS dissolution in 1 M H_2SO_4 without and with inhibitor.*

Electrolyte	A (g/cm^2)	E_a (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol/K)
1M H_2SO_4	11.084	63.20	60.68	-41.3827
1M H_2SO_4 + 200 ppm Inhibitor	11.625	67.53	64.93	-31.0165
1M H_2SO_4 + 600 ppm Inhibitor	12.58	73.96	71.36	-12.7271
1M H_2SO_4 + 1000 ppm Inhibitor	12.442	74.48	71.89	-15.3866

Similarly, the entropy of these systems has been calculated from the intercept of the transition state plot. A significant negative value of ΔS° in 1M H_2SO_4 indicates the decrease in disordering from solution to activated complex formation phase on MS surface, also labeled as the association step in the rate determining step. On addition of inhibitor ΔS° value increases as negative 31.02, 12.72 and 15.38 J/mol/K for 200, 600 and 1000 ppm inhibitor solutions respectively. This implies that the randomness increased on the transition state due to replacement of water molecules by alkaloid molecules [36].

The slope of the straight lines is gradually changed indicating that the inhibition is due to physical adsorption process and there is no change in mechanism of corrosion inhibition. The detailed process of physical adsorption is explained under mechanism of inhibition title.

3.7. Electrochemical Methods

3.7.1. Open Circuit Potential (OCP) measurement

The variation of open circuit potential (OCP) of mild steel in 1 M H_2SO_4 was studied by monitoring changes in corrosion potential with time. The OCP changes of MS immersed in inhibitor of different concentrations (200, 400, 600, 800, 1000 ppm) and acid solutions for 30 minutes at room temperatures. Three-electrode system was used to measure the change in OCP with time. OCP measured in acid solution and in presence of inhibitor solutions of different concentration is as in Figure 19. It

reveals that there is slightly shifting of potential towards increase in OCP towards positive potential in presence of inhibitor but less than 50 mV. This indicates that it might act as mixed type of inhibitor. The positive shifting of potential from OCP indicates the formation of protective layer by inhibitor molecules in acid solution on the MS surface that limits the interaction of aggressive ions with MS surface [37].

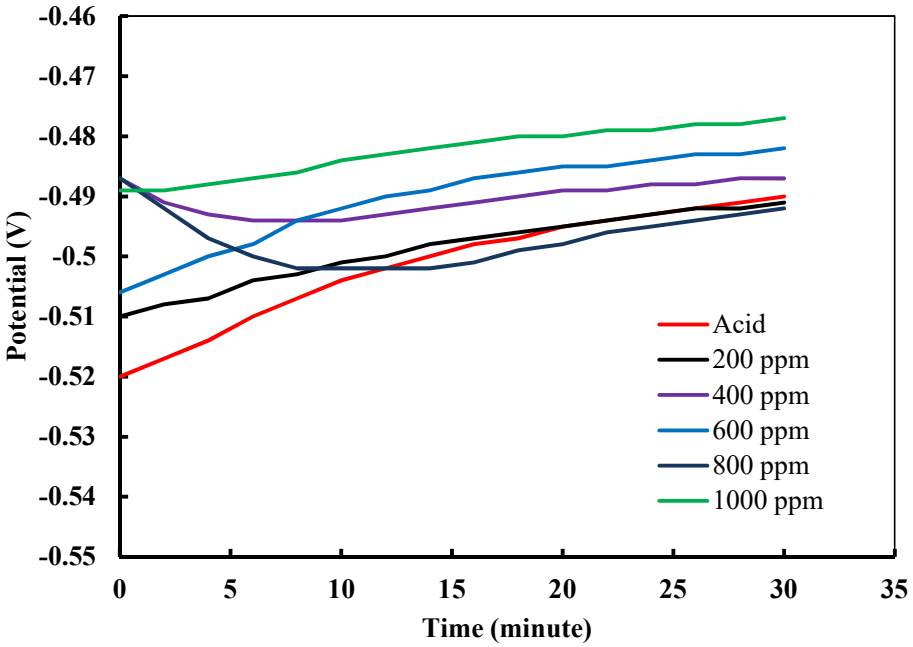


Figure 19: *Variation of OCP with the time of immersion of mild steel in different concentrations inhibitor in 1M H_2SO_4 when measured after 3 h immersion.*

3.7.2. Polarization of 3 hr. immersed MS sample in 1M H_2SO_4 and different concentrations of alkaloids solution

Figure 20 demonstrates the effect of inhibitor concentration (200, 400, 600, 800, and 1000 ppm) in 1 M H_2SO_4 solution on the polarization. The slight shifting of potential (<85 mV) on both anodic and cathodic directions indicates the mixed types of behavior of the inhibitors. After polarization of 3 h immersed sample, it is found that the anodic slope is higher than the cathodic slope for the same concentration of acid and inhibitor solution. This seems that the oxidation in anode and reduction in cathode with different rates. But, in an actual way, the dissolution of mild steel i.e. iron oxidation to ferric ion release two electrons while reduction of hydrogen ion to hydrogen accepts one electron at the same time. This results in the difference in anodic and cathodic slope. Starting from acid solution to acidic 1000 ppm inhibitor

solution, the current density gradually decreases. The decrease in current density implies that the inhibitor molecules highly resists and minimizes the corrosion reaction.

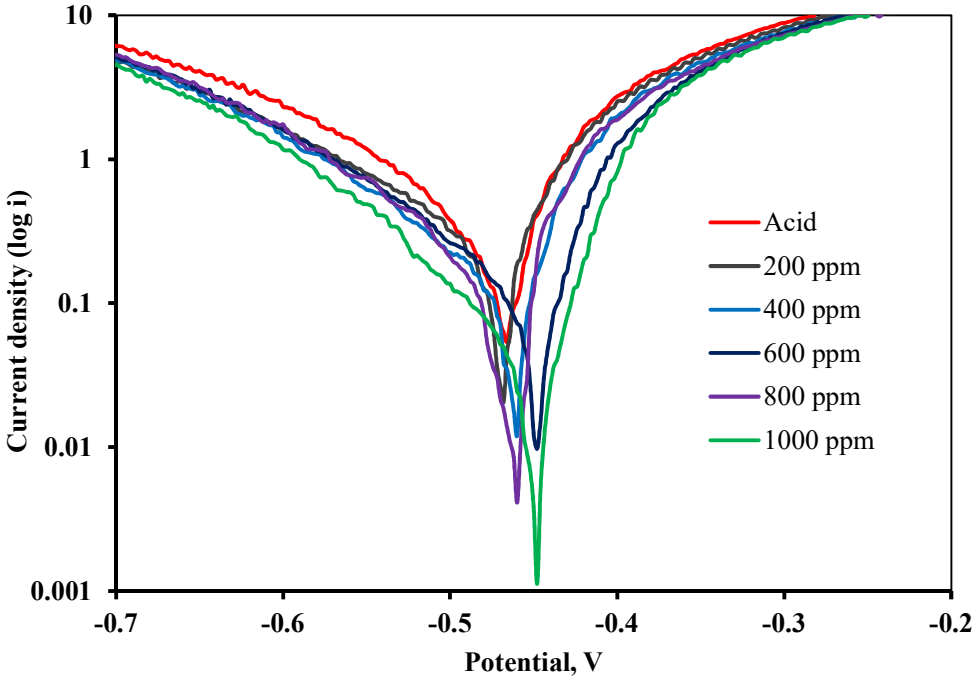


Figure 20: *Potentiodynamic polarization curves for mild steel in 1M H_2SO_4 containing different concentrations of alkaloids in 3 h immersed condition.*

The polarization curve also indicates that there is a decrease in current density on the addition of inhibitor. In the presence of an inhibitor, the MS surface is covered with inhibitor molecules so that the active site of MS is small. The reaction at this small the area produces a small current density. This also indicates that the alkaloids used in the experiment are working as a good inhibitor. The inhibition efficiency, cathodic and anodic slope, corrosion potential and corrosion current densities of the alkaloid are also tabulated in Table 8. The current density in acid only solution is 0.12 A/cm^2 and the corrosion potential is 0.466 V. On addition of different inhibitor concentration and polarization, the decrease in current density is achieved. The minimum current density is at 1000 ppm inhibitor solution and is equal to 0.012A/cm^2 with corrosion potential 0.448V. This decrease in current density is due to the adsorption of inhibitor molecule on the MS surface to form a protective barrier and reducing active sites.

Table 8: *Table showing the anodic slope, cathodic slope and inhibition efficiency for 3 hours immersed sample.*

Medium	E_{corr}	i_{corr}	Anodic Slope	Cathodic Slope	Inhibition Efficiency (%)
Acid	0.466	0.12	28.6	12.6	-
200	0.468	0.064	25.3	9.3	46.67
400	0.46	0.042	26.3	7.1	65
600	0.448	0.034	24.3	6.4	71.67
800	0.46	0.026	29.8	7.6	78.33
1000	0.448	0.012	5.5	2.9	90

The inhibition of alkaloids increases by increasing the concentration of the inhibitor. This polarization experiment was carried out at a laboratory temperature 23 °C. The efficiency of the inhibitor is found higher in polarization measurement than that of weight loss measurement method. The lower the value of efficiency in weight loss measurement method may be due to possible sources of errors.

3.8. Inhibition efficiency of alkaloid for 3 hours immersed condition

For 3 hours immersed sample and all the concentration of inhibitor polarization was carried out. The inhibition efficiency of the alkaloid is calculated from the polarization method. The inhibition efficiency of 200 ppm alkaloid solution is almost negligible whereas the inhibition by 400 ppm inhibitor solution is of acceptable range. From this drastic change in the inhibition efficiency it can be generalized that more than 400 ppm inhibitor concentration may be the effective concentration. To attain steady state equilibrium between adsorbed and free inhibitor molecules, the inhibitor concentration plays important role. After 400 ppm inhibitor concentration the inhibition gradually increases up to 1000 ppm concentration and inhibition reaches to 90 %. This is because, higher the concentration of inhibitor, inhibitor molecules can have sufficient concentration to get adsorbed and attain an equilibrium state [37]. This adsorbed layer protects the MS from an aggressive environment and reduces the corrosion rate. The detail efficiency variation is shown in Figure 21.

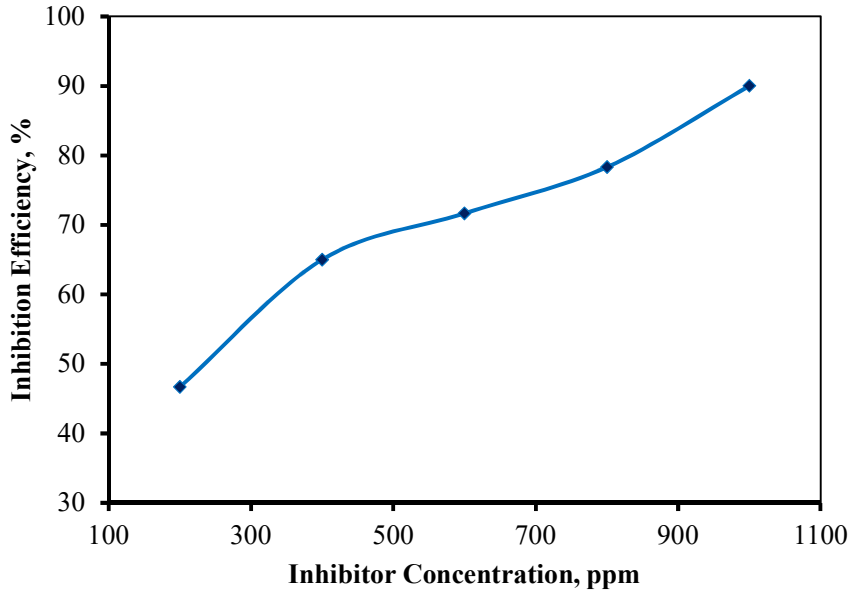


Figure 21: *Inhibition efficiency of inhibitor obtained from the polarization of 3 hours immersed MS sample in 1 M H_2SO_4 in presence and absence of inhibitor.*

3.9 Mechanism of Corrosion Inhibition

Energy of activation (67.53 kJ/mol in 200ppm, 73.96 kJ/mol in 600 ppm, and 74.48 kJ/mol in 1000 ppm inhibitor solution) reveals that there is mixed type; physical adsorption followed by chemical adsorption between MS and alkaloid molecules. Corrosion inhibition by alkaloid molecules is due to adsorption of inhibitor molecules on the MS surface by the replacement of water molecules, called quasi-substitution process.

$$Org(sol) + xH_2O(ads) === Org(ads) + H_2O(sol)$$

Where, Org(sol) and Org(ads) represents the solvated and adsorbed organic (alkaloid) molecules respectively. Similarly, $H_2O(ads)$ represents the adsorbed water molecules on MS surface, and x represents the size ratio i.e. number of water molecules that are replaced by one organic molecule [36].

OCP gives the information where there is positively or negatively charged MS surface. The OCP of MS is recorded around 0.49V, which is positive than PZC value. It implies that the surface of metal is positively charged in inhibitor solution [1]). In positively charged surface, there could be interaction of SO_4^{2-} ions. And the surface becomes negatively charged. Alkaloids contain mainly nitrogen as heteroelement in the ring, which when dissolved in acidic solution gets protonated. The protonated alkaloid molecules interact with sulfate ions by electrostatic force of attraction. The protonated alkaloids return to its neutral form after releasing H_2 molecules [36, 37].

Then, electron pair of HOMO with high electron density of alkaloids especially the lone pair of nitrogen is shared with vacant d-orbital of iron forming co-ordinate covalent bond, which bring the accumulation of extra negative charge on metal surface. To relive the charge, electrons are returned to LUMO with high orbital density especially to antibonding π* orbital of organic molecule to form feedback bond. This retrodonation strengthen the bond and inhibitors are adsorbed chemically.

The steps of corrosion inhibition mechanism and the schematic diagram with reference to camptothecin molecule are shown in figure 22:

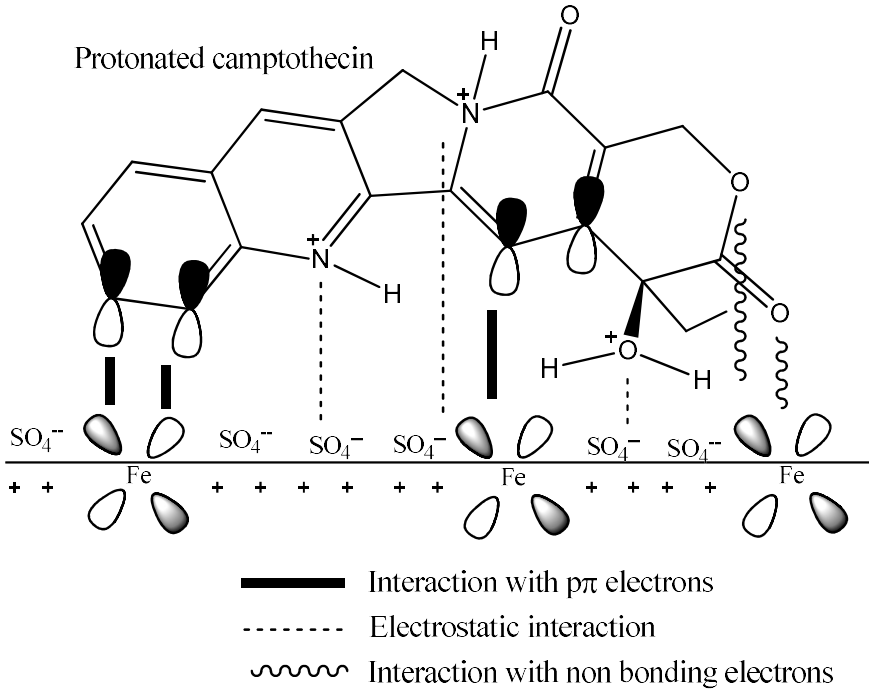


Figure 22: *Schematic diagram for different mode of adsorption of alkaloids on MS.*

CHAPTER 4

CONCLUSION

In this study, corrosion of mild steel in 1M H_2SO_4 in the presence and absence of inhibitor made of alkaloid extract from the bark of *Alnus nepalensis* was carried out. Then the inhibition efficiency of the inhibitor was measured through weight-loss method and electrochemical polarization method. A comparative study of corrosion at different periods and concentrations was done. Alkaloids are successfully extracted by solvent extraction method and characterized by chemical and spectroscopic method. From the data and results obtained, the following statements can be inferred;

- The weight loss of mild steel increased with time in both the presence and absence of inhibitor in 1M H_2SO_4 which in turn increases the corrosion rate. However, the extent of weight loss is greatly reduced in presence of inhibitors.
- The weight loss of mild steel decreased with an increase in the concentration of the inhibitor in 1M H_2SO_4 and so does the corrosion rate.
- The inhibition efficiency of the inhibitor seemed to increase with time of immersion up to 3 hours.
- The inhibition efficiency of the inhibitor also increased as its concentration increased in 1M H_2SO_4.
- Potentiodynamic polarization analysis showed that the *Alnus nepalensis* extract act as a mixed type of inhibitor for corrosion of steel in acidic solution.
- The inhibitor showed maximum inhibition efficiency at 90.00 % for mild steel immersed in 1000 ppm concentration in 1M H_2SO_4 for 3 hrs.
- FTIR result confirmed the presence of N-H and C-N group of alkaloids. The calculated thermodynamic parameters revels that adsorption process endothermic and is physical dominated chemical.

Thus, it can be concluded that the bark of *Alnus nepalensis* contains an alkaloid which when extracted and used as a green corrosion inhibitor gives efficient corrosion control to mild steel in 1M H_2SO_4 for at least up to 3 hours.

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