STUDY ON THE EFFECTS OF *Vitex negundo* AND *Catharanthus roseus* LEAVES EXTRACT AS A GREEN INHIBITOR FOR CORROSION CONTROL OF MILD STEEL IN BIOETHANOL AND ITS BLEND

An *M. Sc. Dissertation*

Submitted to:

The Central Department of Chemistry, Tribhuvan University, Kirtipur, Kathmandu,

for Partial Fulfillment of the Requirements for the Degree of Master of Science in Chemistry

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February, 2021

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LETTER OF ACCEPTANCE

This dissertation work entitled *"Study on the effects of Vitex negundo and Catharanthus roseus leaves extract as a green inhibitor for corrosion control of mild steel in bioethanol and its blend"* submitted by Mr. Ramesh Regmi (Symbol No.: 769/073; T. U. Regd. No.: 5-2-37-1455-2011) has been accepted as partial fulfillment of the requirements for the Degree of Masters of Science in Chemistry.

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FOREWORD

This dissertation work entitled *"Study on the effects of Vitex negundo and Catharanthus roseus leaves extract as a green inhibitor for corrosion control of mild steel in bioethanol and its blend"* submitted by Mr. Ramesh Regmi (Symbol No.: 769/073; T. U. Regd. No.:5-2-37-1459-2011) for the degree of Master of Science in Chemistry of Tribhuvan University was carried out under my supervision in the academic year 2019/020 (2076/77). During the research period, Mr. Regmi had performed the dissertation work sincerely and satisfactorily.

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DECLARATION

I, *Ramesh Regmi*, hereby declare that the present dissertation work is done originally and has not been submitted elsewhere for any degree. Any literature, data, or work done by others and cited in this dissertation has been given due acknowledgments and listed in the reference section.

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ACKNOWLEDGEMENTS

I express my sincere gratitude to my respected supervisor Professor Dr. Jagadeesh Bhattarai and co-supervisor Associate Professor Dr. Susan Joshi of Central Department of Chemistry, Tribhuvan University, for their valuable guidance, support, and suggestion throughout this dissertation work.

I am indebted to the Head of the central department of chemistry Professor Dr. Ram Chandra Basnyat, for providing me the necessary research facilities to conduct this dissertation work. I would like to thank the University Grants Commission, Nepal (UGC-Nepal) for providing me the Master's Research Support Grants-MRS-75/76-S&T-32 to conduct this dissertation work.

I would like to express my sincere thanks to all faculty members, laboratory technicians, and administrative staff of the department, for providing a friendly environment during this dissertation work. My sincere thanks also go to the Department of Plant Resources, Thapathali for providing the facility of five-digit electronic balance.

I am grateful to my seniors; Mr. Prakash Katuwal, Mr. Kumar Amgain, Mr. Bhesh Nath Subedi, Mr. Nav Raj Phulara, and my colleagues; Mr. Nirmal Acharya, Mr. Madan Somai, and other friends for their help and co-operation during this dissertation work.

Finally, I am deeply obliged to my family members and relatives for their support, and encouragement to complete this research work.

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February 2021

ABBREVIATIONS

ASTM	American Society for Testing and Materials
CI	Compression Ignition
CR	Corrosion Rate
E0	Commercial Petrol
E100	Pure Bioethanol
E15	15 % Bioethanol Blend with 85 % Petrol
FFVs	Flexible Fuel Vehicles
GDP	Gross Domestic Product
IE	Inhibition Efficiency
IUPAC	International Union of Pure and Applied Chemistry
MBT	Mercaptobenzothiazole
MIC	Microbiologically Induced Corrosion
mm/y	Millimeter Per Year
mV	Millivolt
OCP	Open Circuit Potential
ppm	Parts Per Million
SCC	Stress Cracking Corrosion
SCE	Saturated Calomel Electrode
SFGS	Simulated Fuel- Grade Ethanol
SI	Spark Ignition
SiC	Silicon Carbide
SRB	Sulfate Reducing Bacteria
SSCC	Sulfide Stress Cracking Corrosion

SYMBOLS

ϕ_{corr}	Corrosion Potential
i_{corr}	Corrosion Current Density
θ	Degree of Surface Coverage

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ABSTRACT

The study of the effect of Nepal origin *Vitex negundo* and *Catharanthus roseus* plant extracts on the corrosion behavior of mild steel in pure bioethanol (E100) and its 15 % blend (E15) with 85 % commercially available Euro-4 grade petrol (E0) was carried out using corrosion tests, corrosion inhibition efficiency and mechanism at 25 ± 2 °C in airtight condition. Fourier transform infrared (FTIR) spectra were used to characterize the used E100, E15 blend, and commercially available Euro-4 grade petrol (E0). Among E100, E15, and E0 fuels, the E100 has the highest corrosion susceptibility to the mild steel; mostly due to the water-absorbing ability of E100 and E15. However, the corrosion resistance property of the mild steel was found to be increased with increasing concentrations from 500 to 2000 ppm of both *Vitex negundo* and *Catharanthus roseus* methanol extracts as green-based corrosion inhibitors in both the E100 and E15 blend. Additions of *Vitex negundo* extract seem to be more effective than that of *Catharanthus roseus* extract to increase the corrosion-resistant properties of the mild steel both in pure E100 and E15 blend.

The % corrosion inhibition efficiency was steeply increased with the additions of 500-1000 ppm of both plants extract and it attained an almost steady-state with the additions between 1000 and 2000 ppm of both plants. Maximum inhibition efficiencies of about 89 % and 75 % were obtained at 2000 ppm *V. negundo* and *C. roseus* extract, respectively, for the mild steel in E100, and it was about 86 % and 72 % in the E15 blend at 25 ± 2 °C in airtight condition. Especially, the corrosion-resistant properties of the mild steel in E100 and E15 blend with 1500 ppm and 2000 ppm *V. negundo* plant extract were found to be higher even than the corrosion-resistant properties in E0 after 1008-1344 hrs or more exposure times. Such high corrosion inhibition mechanism on the surface of the mild steel sheet by green-based corrosion inhibitors of *V. negundo* and *C. roseus* plant extracts in E100 and E15 biofuels was obeyed both the Langmuir and Temkin adsorption isotherms. Consequently, it can be said summarized that leaf extract of both plants act as good green-based inhibitors to minimize/control the electrochemical corrosion of the mild steel in E100 and E15 at room temperature.

Keywords: Biofuels, *Catharanthus roseus*, Corrosion inhibitor, Mild steel, *Vitex negundo*

Chapter- 1

INTRODUCTION

1.1 General Introduction of Corrosion

Metallic materials (i.e., metals or/and alloys) have been excessively used since human civilization and their uses increase continuously. However, the degradation of such materials is one of the great problems. Corrosion is defined as the deterioration of a substance and its properties due to interaction between its substance and its environment and is an endless process that cannot be eradicated but can be controlled by using suitable methods. It is mainly due to the spontaneous instability of metallic substances result from the charge transfer reactions at electrified interfaces between the metallic substances and their environment (Bockris & Reddy, 2001). Moreover, corrosion is simply defined as the destructive attack of metallic materials by electrochemical or/and chemical reactions with their environment leading to their degradation (Revie & Uhlig, 2008).

In the 1990s, the International Union of Pure and Applied Chemistry (IUPAC) recommended the definition for corrosion term as an irreversible interfacial reaction of materials (metallic, ceramic, or polymer) with their environment which results in the consumption of engineering materials (Heusler *et al.*, 1989). This is a very broad definition used for the corrosion term that incorporates not only the corrosion of metallic substances but almost all materials including polymers and ceramics used for engineering purposes. However, the IUPAC recommended corrosion definition is not widely accepted by corrosionists and material scientists. In recent years, the term corrosion defines as "an undesirable deterioration of metallic materials (metals or/and alloys) by electrochemical or/and chemical reactions with their corrosive environment that adversely affects those properties of metals or/and alloys that are to be preserved" (Bhattarai, 2010a).

The tendency of a metal to corrode depends on the grain structure of the metal, its composition as formed during alloying, or the temperature for deformation of a single metal surface developed during fabrication. Given that the environment plays an important part in corrosion, corrosion mechanisms can be as varied as the environments to which a substance is exposed and thus may be complex to understand. Factors that cause corrosion include reactivity of metal, presence of impurities, presence of air, moisture, gases like sulfur dioxide and carbon dioxide, so on. Corrosion prevention and retardation are aimed at addressing these factors. The corrosion scientists are concerned with the study of corrosion mechanism through which a better understanding of the corrosion processes can be obtained and hence it becomes easy to apply an appropriate corrosion control technique (Bockris & Reddy, 2001; Revie & Uhlig, 2008).

Because of its association with very high economic and safety losses, corrosion is an important issue that must be addressed by scientists and engineers working in the field of corrosion discipline and engineering throughout the world. Corrosion can occur in different types of atmospheres, soils, electrolyte solutions, melted ionic environments, and environments polluted by micro-organisms (Panayotova *et al.*, 2008; Davis, 2001). Corrosion is a major scientific, industrial, and technological problem whose effect is shown in many sectors. The understanding of the surface phenomenon is very important to find out the remedies of corrosion problems, those are generally costly. It is reported that the industrial importance of corrosion study is mostly of three folds (Revie & Uhlig, 2008). The first one is the economic factor that includes the cost of replacing the corroded materials, cost of the shutdown, cost of production and corrosion-resistant materials, efficiency loss, and cost of the system so on. The second importance of the corrosion study is to improve the safety of 3 different operating systems and the third one is the conservation of precious metallic materials from our nature. The corrosion scientists and engineers help to conserve the wealth of the precious metallic materials resources by designing and re-building corroded materials. Some important reasons behind studying corrosion science in the world are as follows:

- Engineer’s knowledge is generally incomplete without an understanding of the corrosion phenomenon and hence it is said that the airplane, ships, automobiles, and other transport carriers are designed by knowing the corrosion behavior of the materials used in these systems.

- The designing of artificial implants for the human body requires a complete understanding of corrosion science and engineering, because all the surgical implants must be very corrosion-resistant in human fluids and so on.

- Several engineering disasters can be prevented by applying appropriate knowledge for the corrosion protection world widely.

1.2 Corrosion and its Impacts

Corrosion science is one of the multidisciplinary subjects, probably unique in crossing the borders of almost all the sciences and technologies. The lack of corrosion properties of the engineering materials will be a cause of wastage of much money, labor as well as deterioration in the quality of such materials in a short time (Revie & Uhlig, 2008). Hence, it is said that the works of engineering and technology become unreliable without the testimony of corrosion properties of the engineering metallic materials in different aggressive environments.

A study revealed that the total annual estimated direct corrosion cost was US$ 276 billion that is equivalent to approximately 3.1 % of the USA gross domestic products, GDP (FHWA-RD-01-156, 2015). Studies in other countries have shown that the cost of corrosion losses is about 3-4 % of their GDP and it is considered that about 20-35 % of this GDP loss can be reduced by applying appropriate corrosion control methods (DNV, 2015). The study was focused on four major industries, i.e., energy (oil and gas, coal and nuclear), transportation (rail and marine), utilities (power and water/wastewater), and infrastructure (bridges and highways), and it was reported that the chemical, petrochemical, transportation industries and so on are the largest contributors of the corrosion losses (DNV, 2015).

1.3 Electrochemical Corrosion Mechanism and Theories

The corrosion mechanism of any types of metallic materials in aggressive environments can describe based on the three electrochemical theories as (i) local cell or heterogeneous, (ii) homogeneous, and (iii) mixed-potential theories. According to the local cell theory, A corroding metallic material has both anodic and cathodic sites where the respective anodic and cathodic reaction occurs. Hence the anodic and cathodic reactions produce the anodic current and cathodic current, respectively, which are equal but opposite in sign (Revie & Uhlig, 2008). The separate cathodic and anodic sites are formed due to heterogeneity or impurity in the metallic materials and these sites are usually distinct in space according to the local or heterogeneous theory of corrosion. The corrosive environment acted as the electrolyte for the corrosion cell. According to this theory corrosion phenomena is possible only in heterogeneous metallic substances, and this theory could not explain the occurrence of corrosion in ultra-pure metals. Therefore, later the homogeneous theory was proposed to explain the corrosion mechanism of such ultra-pure metals (Bockris & Reddy, 2001). The only sufficient and necessary condition is the occurrence of both the anodic and cathodic reactions on the surface of corroding materials. This happens only when the corrosion potential or open circuit potential of the corrosion cell is more positive than the equilibrium potential of the anodic reaction and more negative than the equilibrium potential of the cathodic reaction in the corrosive environment as explained with the help of the Evans diagram (Bhattarai, 2010a). Thus, the homogeneous theory of corrosion suggests that even an ultrapure metal tends to corrode in a corrosive environment irrespective of heterogeneity in the corroding materials. It becomes unstable due to the different electrodic reactions occurring simultaneously and in opposite directions randomly at the corroded surface.

In recent years, both the heterogeneous and homogeneous theories of corrosion are combined to form a third type of electrochemical theory of corrosion that explains corrosion phenomenon more conveniently with the advantage to predict the corrosion kinetics, known as mixed-potential theory (Ohtsuka, 2007). The mixed-potential theory of corrosion is becoming a versatile tool to have a better understanding of the corrosion mechanism of metallic substances. The mixed-potential theory is mainly based on two hypotheses (Bhattarai, 2010a; Revie & Uhlig, 2008), as given below

- An electrochemical reaction is divided into two or more partial half-reactions and
- The total rate of oxidation reactions must be equal to the total rate of reduction reactions.

It is often considered that reaction of several redox pairs is involved in the corrosion process and the resulting open circuit potential or corrosion potential across the interface of a corrosion cell in a corrosive environment is called the mixed-potential. From the second hypothesis of mixed-potential theory, the mixed-potential is determined by the balance of both the anodic current and cathodic current that originates in different redox reaction across the interface resulting in net-zero current which is called corrosion current density (i_{corr}) and the corresponding open circuit potential is called corrosion potential (ϕ_{corr}), as shown in Fig. 1 (Bhattarai, 2010a).

Moreover, the mixed or corrosion potential lies in between the equilibrium potential of the anodic reaction and the equilibrium potential of the cathodic reaction when the metallic material is exposed to the de-aerated acidic condition as shown in Fig. 1 (Bhattarai, 2010a). According to the mixed-potential theory of corrosion, both anodic dissolution and cathodic reactions occur simultaneously on the surface of the metallic substance with the same rates at the open circuit corrosion potential when a metallic substance is immersed in an electrolytic solution (Hashimoto, 1993), that is;

$$i_a = i_c \text{ (at } i_{corr.}) \qquad (1)$$

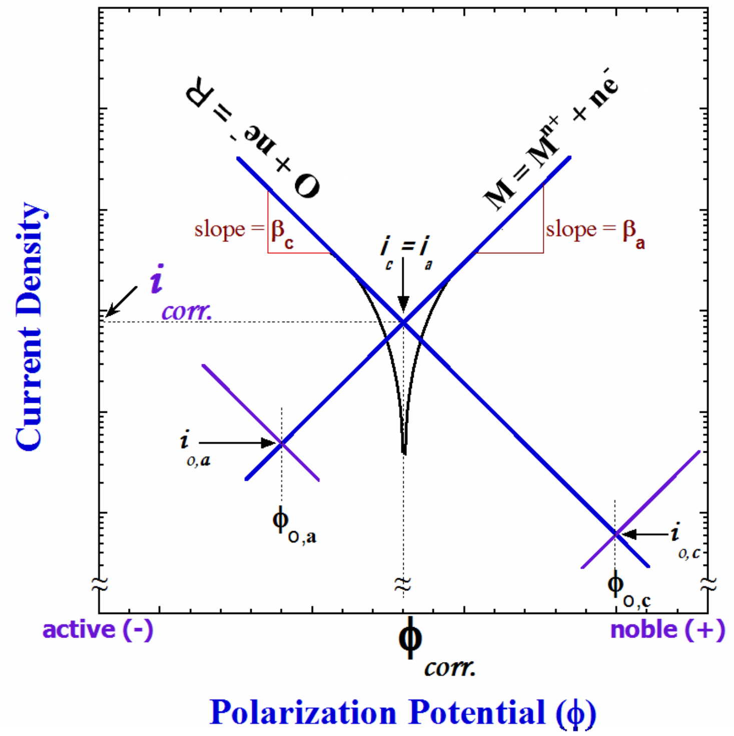


Figure 1: Evans diagram showing ϕ_{corr} and i_{corr} (Bhattarai, 2010a)

1.4 Types of Corrosion

Different types of corrosion depend on the appearance of the corroded metallic surfaces and corrosive environments. Furthermore, the types of corrosion based on the appearance of the corroded substances are also classified into uniform or general, and the localized corrosion is described briefly below.

1.4.1 Based on Appearance of Corroded Metals Surface

Uniform corrosion: This type of corrosion mainly destroys uniformly the whole surfaces of the metallic substances when exposes to the corrosive environment and hence it makes the corroded surface thin.

Galvanic corrosion: Galvanic corrosion is a localized type of corrosion that occurs with an electrolyte when two metals having different values of electrical potentials. In this type of corrosion, metallic materials are destroyed due to the formation of the galvanic cell. More noble potential acts as the cathode, while the metal with less noble potential acts as the anode in such type of localized galvanic corrosion.

Pitting corrosion: The pitting corrosion occurs because of random attacks on parts of the metal’s surface to form pits. The pit acts as the anode while the remaining less corroded part of the metal acts as the cathode.

Stress corrosion: The cracking form of corrosion that arises due to stress in an aggressive environment is called stress corrosion. This is also localized corrosion, which mainly occurs in the mechanically weak points of substances.

Inter-granular corrosion: It occurs on or near the grain boundaries of a metal. It is a localized form of corrosion that is caused by the segregation of impurities at the grain boundaries or by enrichment or depletion of one of the alloying elements in the grain boundary areas. In general, the grain boundary region acts as an anodic for the rest of the grain matrix and hence more rapidly observed the inter-granular corrosion, which causes loss of the metallic substance strength.

Crevice corrosion: crevice corrosion occurs in confirmed spaces where access to fluid from the environment is limited such as gaps and contact areas between parts, under gaskets or seals, inside cracks and seams, and spaces filled with deposits.

Bio-corrosion: The deterioration of the metallic materials caused by the activity of micro-organism is termed bio-corrosion or microbiologically induced corrosion (MIC). Bacteria, fungi, and other micro-organisms corrode the metallic materials which are to be preserved. Some sulfate-reducing bacteria (SRB) produce hydrogen sulfide under anaerobic conditions, which results from a serious case of sulfide stress cracking corrosion (SSCC).

1.4.2 Types of Corrosion Based on Corrosive Environments

Soil corrosion: The degradation of the buried metallic materials due to different soil parameters is called soil corrosion (Dahal *et al.*, 2021; Bhattarai, 2013). The soil parameters such as resistivity/conductivity, pH, chloride, sulfate and sulfide ion content, organic matter, moisture, oxidation, and reduction potential so on influenced the corrosion of the buried metallic materials mostly in the disturbed soil (Poudel *et al.*, 2020; Dahal *et al.*, 2018; Bhattarai *et al.*, 2016; Regmi *et al.*, 2015; Bhandari *et al.*, 2013).

Concrete corrosion: Concrete is a complex composite material and the most widely produced material in the world. It has a very high compressive strength while its tensile strength is very low, and hence it is common practice to reinforce steels/stainless steels in concrete structures to improve their tensile mechanical properties (Angst, 2018). Therefore, the mechanical and other deterioration properties of the reinforcing concrete structures such as bridges, buildings, highways, tunnels, offshore oil platforms dam walls depend on the corrosion behavior of the reinforced-steels materials. The deterioration of the reinforced-steels that are exposed to concrete structures is called concrete corrosion. It involves chemical, physicochemical, electrochemical, and biological processes. The concrete corrosion is mainly caused by saltwater or acidic groundwater, ingress of carbon dioxide, sulfates, chlorides, nitrates, fluorides, sulfides, microbes in sewer pipes, and industrial waste like slag and corrosive gases so on (Phulara & Bhattarai, 2019; Perez, 2004).

Atmospheric corrosion: Metallic materials are corroded when they are exposed to atmospheric air and its pollutants; the process is known as atmospheric corrosion. It is an electrochemical process that depends upon the presence of environmental pollutants as electrolytes in the wet atmosphere. Atmospheric corrosion takes place under humid conditions and a small amount of water is one of the necessary conditions for the occurrence of atmospheric corrosion. The factors for atmospheric corrosion are dust content, gases in the atmosphere, and moisture (Bhattarai, 2010a; Revie & Uhlig, 2008).

Aqueous corrosion: The metallic materials tend to corrode in presence of large or small amounts of water containing aggressive environments due to the thermodynamic instability is called aqueous corrosion. The corrosion rate of the metallic materials in the corrosive aqueous environment depends upon the ion concentration, electrolytic activity, bacteria, and other impurities so on (Bhattarai, 2021, 2020, 2014, 2010b; Jha & Bhattarai, 2008; Bhattarai *et al.*, 1998a, 1998b, 1998c, 1997, 1995). It is meaningful to mention here that the corrosion damages by fissile fuels or biofuels to the metallic materials are mostly due to the presence of even small amounts of moisture with other gaseous contaminants. The details about the biofuel corrosion to the metallic materials are discussed in subsequent sections.

1.5 Advantages of Biofuels over Fossil Fuels

For many decades, fossil fuels like petroleum products are the major non-renewable sources of energy used in the world. It was reported that about 90 % of petroleum products are used as energy sources for transportation, heating, cooling, electricity generation, and feedstock in chemical industries (Hoekman *et al*., 2012). Fossil fuels are limited as energy demands are increasing and hence researchers have directed their works towards alternative renewable energy sources like biomass, hydropower, solar, wind, and so on. Nowadays, scientists are focusing to develop biofuels obtained from biomass.

Biofuels are increasingly used in the ground transportation sector and several countries have introduced policies to support the production and use of the biofuels like bioethanol and biodiesel. The green nature of the biofuels allows their applications not only in ground transportation but also in marine vessels and airplanes. Continued depletion of petroleum reserves coupled with environmental factors makes renewable energy resources more attractive. The most feasible way to meet this growing demand is by utilizing alternative renewable biofuels. Among various renewable fuels, bioethanol and biodiesel are the most attractive.

Bioethanol is a type of biofuel and it can be mixed more significantly with petrol and diesel fuels without the need to modify the existing engines. It can run at a much higher exhaust gas recirculation rate and with higher compression ratios in spark ignition (SI) engines and has a higher-octane rating than most petroleum products and creates very few particulates. It serves as an oxygenation additive when blended with gasoline and helps to increase the octane number of the fuel while simultaneously reduce carbon monoxide (CO) emissions and air pollution (Anderson *et al.*, 2012) and hence bioethanol is called one of the environmentally friendly renewable energy sources. Octane is the measure of a fuel’s ability to resist “knocking”, which a driver may detect as a pinging noise coming from the engine. Knocking is the burning of the fuel in the engine's combustion chamber. The higher the fuel's octane number, the better the fuel and the more resistant it will be for knocking.

1.6 Corrosive Nature of Bioethanol and Its Blends

However, bioethanol is a more corrosive medium than petroleum products to the metallic components like CI and SI engines, and other vehicle and oil storage parts. It was reported that the corrosion of bioethanol for an aluminum alloy (A348) was increased with increasing the concentrations of the bioethanol in its blends with petrol at 100 °C but did not show a significant effect at 80 °C or below (Park *et al.*, 2011). Therefore, such corrosive behavior of the fuel system metallic components can be controlled by adding green corrosion inhibitors obtained from different plant extract in the bioethanol. The green corrosion inhibitors can be used as fuel additives that inhibit or suppress the corrosive properties of biofuels like bioethanol, biodiesel, and their blends with fossil fuels.

Metallic materials such as steel, cast-iron, aluminum, copper, brass, and so on are commonly used as structural materials for vehicle engines and fuel storage systems. For instance, steel is used for making major components, including connecting rods, timing gear, and piston pins. Aluminum and its alloys are used for making engine blocks, cylinder heads, oil sumps, driveshafts, rocker arms, and so on. Copper is used for making windings for alternators, starters, or ignition coils owing to its good conductive properties. Brass is used for tubes in fuel distribution systems, tubing for coolers, electrical connections. Moreover, each of the selected metals and alloys has different corrosion resistance (different electrochemical potential) properties, which adds to the comprehensiveness of evaluation of the corrosive behavior of fossil and biofuels. If all types of fuels contain corrosiveness factors, such as sulfur compounds, organic acids, and water-soluble inorganic acids and bases, in the presence of water and oxygen, each of the above-mentioned metals and alloys plates will be affected by electrochemical corrosion, although the process will be running at different rates.

1.7 Use of Green Inhibitors for Biofuel Corrosion

The corrosion control of the materials by fossil and biofuels using different organic and inorganic compounds as inhibitors are constantly studied by corrosion scientists. The use of corrosion inhibitors is one of the best-known methods to control corrosion and is mostly used in the industry due to its low cost and easy practice method (Bardford, 2001). An efficient inhibitor is compatible with the environment and is economical for application (Dariva & Galio, 2014). Nowadays, the corrosion control method of metallic materials using various types of eco-friendly green corrosion inhibitors is becoming a fundamental research concern of corrosion scientists and engineers (Bhattarai *et al.*, 2017; Bardford, 2001).

Based on the latest information US$ 3.7 billion is spent per year to mitigate corrosion by the oil and gas industries (Miksic*et al.*, 2009). Mostly the synthetic organic compounds (Fazal *et al.*, 2011; Finsgar & Milosev, 2010; Yildirim & Cetin, 2008) are widely practiced to use in different fossil and biofuels to reduce their corrosiveness to various metallic materials used in transportation engine parts and fuel storage systems. Surfactants are most likely corrosion inhibitors employed in the petroleum industry to protect iron and steel equipment used in the production, transport, and refining of hydrocarbon fuels (Noor El-Din *et al.*, 2016). Further study on the effectiveness of plant extracts as a corrosion inhibitor added to biodiesel and its blends are needed.

The increasing industrialization and motorization of the world have led to a steep rise in the demand for petroleum-based fuels which are obtained from limited natural reserves. These finite reserves are highly concentrated in certain regions of the world. Therefore, those countries not having or limited these resources, Nepal for example, are necessary to look for alternative renewable biofuels, which can be produced from biomasses/wastages available within the country. In such circumstances, different types of biofuels might have been a high possibility for a complete or partial replacement of natural petroleum products in the future, because they have very close properties to that of the petroleum products and are environmentally ecofriendly (Haseeb *et al.*, 2011; Torsner, 2010). They provide an improvement of exhaust gas emissions from the internal combustion engine of transport vehicles without any significant sacrifices in terms of energy conversion efficiency. An interesting finding of biofuel uses over the conventional fuel in aircraft is recently reported to minimize the emission of soot benefitting human health and the environment (Kumal *et al.*, 2020).

Different biofuels such as bioethanol, biodiesel, and their blends have been used as fuel by mixing with fossil fuels since the invention of the automobile as petroleum-based fuels are limited and hazardous to the environment. The first use of bioethanol in a four-cycle internal combustion power engine was reported by Nicolaus Otto in 1826 (Bevill, 2008). At the beginning of World War II, both allies and Germans have utilized biofuels in their vehicles due to the extreme shortage of petroleum products as an energy source. The vehicles were then powered using bioethanol blends with alcohol (Abede, 2008). It was reported that bioethanol produced from different biomasses such as sugar, starch, and renewable lingo-cellulosic resources not only improved the energy availability but, also decrease the emission of greenhouse gases and air pollutants (Prasad *et al.*, 2007). Currently, major automotive companies in the developed countries have developed flexible-fuel vehicles (FFVs), whose fuel system and engine are designed to run with bioethanol and its blend even up to E100 fuel (Yacobucci & Schnepf, 2008). The components of FFVs are made from those materials which are compatible with ethanol such as, stainless steel or polymer.

The bioethanol blended fuel is generally used in ordinary vehicles in most countries of the world including Nepal, where the fuel storage systems and engines are composed of light metals, particularly made by steel, copper, aluminum, and their alloys. The global bioethanol industry has witnessed high growth primarily because of the mandatory usage of bioethanol fuel blends, especially in vehicles in many countries that are looking for an alternative fuel source with fewer greenhouse gases (GHG) emissions. Moreover, researchers found that the tested exhausts from a flex-fuel gasoline vehicle using different ethanol-gasoline blends did not induce adverse cell responses in such exposure (Bisiga *et al.*, 2016). It was reported that the eco-friendly bioethanol contained 34.7 % oxygen whereas it was absent in petroleum products and hence it was reported that the combustion efficiency of the bioethanol is about 15 % higher than that of the petroleum products (Masum *et al.*, 2013).

There are insufficient numbers of reports providing test data on the corrosiveness of bioethanol blended fuel. It was reported that different engine components were susceptible to corrosion upon exposure to bioethanol. Since bioethanol absorbs water, which accelerates the corrosion of metals and alloys used in transport engines. Also, the structural composition of bioethanol-gasoline blends can change during the liquid phase and this change is dependent on the fluid temperature, atmospheric pressure, the number of polar components in the gasoline as well as aromatic substances. It was reported that the stress cracking corrosion by bioethanol was increased with increasing its water content and pH value decreased (Kane *et al.,* 2004). Similarly, the study revealed that localized type of pitting corrosion on aluminum alloy in bioethanol blend of E10 at 100 °C (Yoo *et al.,* 2011), and it was recommended the upper bioethanol blend limit was E10 in fuels for ordinary motor vehicles. Aluminum alloy was found to be more corrosive in E20 than in E5 as well as E10 (Aperador *et al.,* 2013). Therefore, the durability and safety of fuel system components using ethanol-blended gasoline fuel should be predicted by an investigation into the corrosion characteristics of steel along with the variables of modified fuel conditions. It was proved that mixing of 15 % bioethanol to gasoline increased significantly the corrosion rate of steel and copper as much as 6.5 and 7.5 times, respectively, compared to the bioethanol-free gasoline (Jafari *et al.,* 2010). Chloride, water content, pH, dissolved oxygen so on affect the SCC susceptibility of carbon steel in 19 simulated fuel-grade ethanol (SFGE) (Lou *et al.,* 2009). It was also reported that the corrosion rate of the carbon steel pipelines, car storage, and fuel tanks was soared by ethanol blend.it was also found that the Corrosion rate of metals in bioethanol blends with biodiesel and petro-diesel BDE was in the order: aluminum < mild steel < copper at both room and 60 °C temperatures and It were reported that the corrosion rate of aluminum metal in bioethanol blend of E50 was reported to be 0.216 mpy, which was lower than the corrosion rate of copper (0.441 mpy) and mild steel (0.487 mpy) in bioethanol (Thangavelu *et al.,* 2016). Similarly, the previous study shows that bio-ethanol blended gasoline of 10 % ethanol volume (E10) reduces the cost by approximately 3 % and is already in use around the world. The USA spent billions of dollars to combat corrosion in the oil and gas industry (Miskic, 2009).

Due to global warming and environmental issue researchers are focus on the use of different plant extracts to prevent corrosion of different metallic materials. However, only a few research works have been done to mitigate corrosion of different metals and alloy by using such plant extracts mixing with bio-ethanol, bio-diesel, and their respective blends. It was proved that *Gongronemena latifolium* extract acted as an efficient corrosion inhibitor in 1 M HCl (Akalezi *et al.,* 2016). Similarly, it was reported that the green inhibitor of *Elaeocarpus ganitrus* and *Aegle marmelos* plant extract acts as a mixed type of green inhibitor for mild steel corrosion in bio-ethanol and its blend (Katuwal *et al.,* 2020, 2018). Similarly, it was reported that the *Ascorbyl palmitate* plant extract acts as a good corrosion inhibitor for carbon steel corrosion control in bioethanol blended gasoline (Deyab, 2014).

1.8 Justification of the Study

The question that why or under what conditions petroleum products, bioethanol and their blends used in Nepal are aggressive to the CI and SI engines, and other accessory parts of vehicles including fuel storages that are mostly fabricated by using the mild steel, is a very crucial point for corrosion scientists and technologists. However, there are many works on the corrosion control of different metals and alloys particularly in biodiesel, bioethanol, and their blends, still very few research works are done to control the corrosion of these metallic materials using the green corrosion inhibitors. Therefore, it is very interesting to study the effect of different green inhibitors obtained from different plant extract to control the corrosion rate of mild steel in bioethanol and its blends with petrol.

1.9 Motivation of the Study

The present study gives ample information about the corrosivity of biofuels and petroleum fuel to different metallic materials such as mild steel, cast iron mainly used in automobile engine parts and fuel storage systems. So that corrosion scientists, technologists, and researchers can develop an idea and knowledge to select an appropriate, efficient biofuel used in vehicles and other machinery parts. The outcome data of this work are diagnostic and predictive values for the corrosion control of the vehicles and other machinery parts in different petroleum products and biofuels. The outcomes of this work help to solve the questions that which corrosion control methods are relevant to control such corrosion failures of systems for transportation and storage liquid fuels. The present study will also provide solutions to such questions to the related authorities and locals. The result of this work also helps to solve the question of which green corrosion inhibitors are efficient and beneficial to improve the corrosion resistance property of the CI engines and other machinery parts of the vehicles that are exposed to petrol, bioethanol, and its blends.

Vitex negundo (English: Chaster tree & Nepali: SIMALI) belonging to the Verbenaceae family, is a small plant distributed throughout the lower part of Himalayan regions of Nepal and is used as animal fodder to Ayurvedic medicine in Nepal (Kunwar *et al.*, 2010). As reported previously that the methanol extract of the Nepalese origin *V. negundo* leaf contained eight major compounds of negundoside, agnuside, vitegnoside, 7,8 dimethyl herbacetin 3-rhamnoside; 5,3'-dihydroxy-7,8,4'-trimethoxy flavanone; 5-hydroxy-3,6,7,3',4'-pentamethoxy flavones; 5,7 dihydroxy- 6,4' dimethoxy flavonone and 5 hydroxy-7,4' dimethoxy flavones (Gautam *et al*., 2008). Moreover, the methanol extracts of *V. negundo* leaves collected from different parts of the world had yielded polar organic phytoconstituents like phenols, alkaloids, steroids, glycosides, flavonoids, and so on (Chen *et al*., 2014; Patel & Deshpande, 2013; Zheng *et al*., 2010).

On the other hand, *Catharanthus roseus* (Periwinkle in English and SADABAHAR in Nepali) belonging Apocynaceae family are perennial herbal or undershrub that grows up to one meter tall in subtropical areas. Its extract is rich in organic phytochemicals such as alkaloids, polyphenolic compounds, and flavonoids. It produces over 100 alkaloids and significant amounts of bioactive compounds, which are used as a folk medicine (Moon *et al*., 2018). *C. roseus* produces vinblastine (branded named as velban) and vincristine which extracted from the *C. roseus* generally utilized in treating Hodgkin’s disease, testicular tumors, breast carcinoma, choriocarcinoma, Kaposi sarcoma acute lymphocytic leukemia, lymphosarcoma, lympho-granulomatosis, and in solid infant tumors so on (Ghozali *et al*., 2015). It contains several functional entities such as fused heterocycles, hydroxyl, and Scarbonyl groups which enhanced the corrosion inhibition action for mild steel in NaCl (Palaniappan *et al*., 2020) and HCl (Shahba *et al*., 2016) media.

However, it has not yet reported one of the promising aspects of these two plant extracts as a corrosion inhibitor in bioethanol and its blends to minimize their corrosive nature to different metallic materials which are widely used in the transportation means and the petroleum storage and transportation systems, although these plant extracts had used as green inhibitors for corrosion controlling of metals and alloys in corrosive environments other than bioethanol and its blends (Rana *et al*., 2017; Sirajunnisa *et al*., 2014; Bhardwaj *et al*., 2018; Bhattarai *et al*., 2018). For example, the corrosion inhibitive performance of *V. negundo* leaf extract in nitric acid for copper metal (Hussin *et al*., 2016) and in alkaline solution for aluminum metal (Sirajunnisa *et al*., 2014) was investigated. The phytochemicals of *C. roseus* extract were tested as a good corrosion inhibitor for mild steel in aqueous 3.5 % NaCl (Zheng *et al*., 2010) and 1 M HCl (Shahba *et al*., 2016) solutions. In such circumstances, this research work aimed to carry out the research works on the effects of methanol extracts of *Vitex negundo*, and *Catharanthus roseus* plants on the mild steel corrosion control in bioethanol and its blend.

1.10 Objectives of the study

1.10.1 Main Objectives

The main objective of the present work is to investigate the effects of plant extracts of *Vitex negundo* and *Catharanthus roseu*s in pure bioethanol (E100) and its 15 % blend (E15) with 85 % Euro-4 grade gasoline (E100) upon exposure to the mild steel in these biofuels at room temperature (i.e., 25 ± 2 °C) in airtight condition using corrosion tests, inhibition mechanism, and electrochemical corrosion potential measurements with following special objectives.

1.10.2 Specific Objectives

1. To estimate the corrosion rate of mild steel in bioethanol, petrol, and their blends at room temperature in airtight conditions.

2. To study the effects of green extracts as green corrosion inhibitors extracted from *Vitex negundo* and *Catharanthus roseus* plant leaves to control the corrosion behavior of mild steel in pure bioethanol and its 15 % blend at room temperature in airtight condition.

3. To study the corrosion inhibition mechanism of mild steel in bioethanol and its 15 % blend with 85 % petrol using both adsorption isotherms models of Langmuir and Temkin.

Chapter– 2

EXPERIMENTAL METHODS

2.1 Preparation of Sample Specimen

The sample specimens of the commercial mild steel sheet were cut in dimensions of size 2.4 cm × 2.4 cm ×0.5 cm for corrosion test, inhibition mechanism, and electrochemical tests. Each sample coupon was mechanically polished by SiC paper having 200-1500 grit numbers using ethanol till the surface exhibits mirror-like reflection and then they were rinsed with acetone and air-dried to obtained fruitful results. Thus, the prepared sample coupon was stored in a desiccator to prevent moisture. After each corrosion test in bioethanol and its blends, corrosion products formed on the surface of test coupons were removed by using filter paper, rinsing with acetone, and dried. Finally, the weight of the exposed sample was taken using a microbalance of five digits (SHIMADZU, AUW220D) available at the Department of Plant Research, Thapathali, Kathmandu.

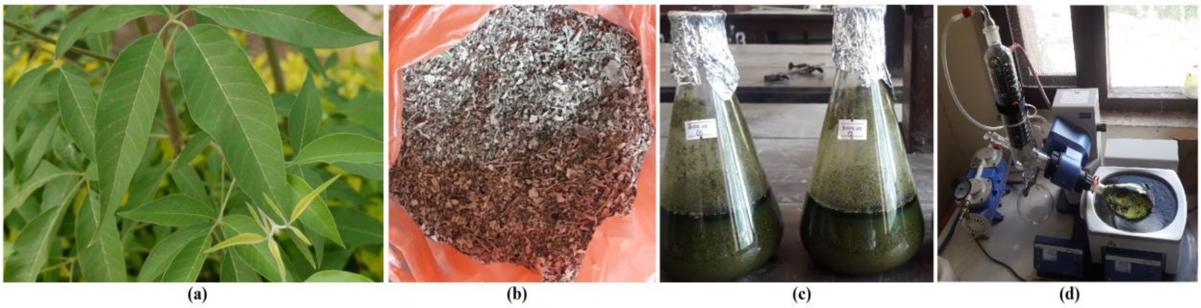
2.2 Preparation of Plant Extracts as Green-Based Inhibitor

The plant leaves of both *Vitex negundo* (Fig. 2) and *Catharanthus roseus* (Fig. 3) plants were collected and then they were cleaned by distilled water and dried in shade for three weeks to make fine powder separately using grinders, as shown in Fig. 4(b). The phytochemicals present in the powdered leaves were extracted by cold percolation method using methanol as a solvent, as depicted in Fig. 4(c).

About 100 grams of each plant's leaves powder were kept separately in clean and dry conical flasks and then about 400 ml of methanol was added to each conical flask and kept for 10 days with subsequent shaking. Then, the mixture was decanted and filtered with the help of a cotton plug, and thus, obtained filtrate was concentrated with the help of rota evaporator by distillation process at about 40 °C temperature, as shown in Fig. 4(d). The concentrated filtrates were kept in a beaker wrapping with aluminum foil containing a small pore to facilitate the evaporation of the solvent. After complete evaporation of the solvent, semi-solid methanolic extracts were obtained which were used in the present study. Moreover, different chemical tests were done to identify the major phytoconstituents present in both the methanol plant extracts.

Figure 2: A Catharanthus roseus plant

Figure 3: A Vitex negundo plant



(a) (b) (c) (d)

Figure 4: Plant extract preparation using rotatory evaporator

2.3 Preparation of Electrolytic Solution

Commercially available pure bioethanol (E100) and Euro-4 grades petrol (E0) and 15 % bioethanol blend with 85 % Euro-4 petrol (E15) were used as electrolytic solutions for corrosion and electrochemical tests. The different concentrations of 500, 1000, 1500, and 2000 ppm of methanol fraction of both *Vitex negundo* and *Catharanthus roseus* plant leaves extracts were prepared in pure bioethanol (E100) and its 15 % blend (E15) used to measure corrosion rate and electrochemical measurements.

2.4 Estimation of Corrosion Rate

Mild steel cut into a rectangular shape with dimension (2.4 cm × 2.4 cm × 0.5 cm) was used in weight loss measurements and electrochemical measurement. Each sample specimen of mild steel sheet was first mechanically abraded with various grades of SiC paper (100 to 1500) and washed with ethanol and then sonication for 10 minutes. After the sonication of samples, the specimen was dried by air-blowing. The clean and dried specimens were weighed before and after the immersion in the electrolytic solution. The reading was noted in the different intervals of the hour (360-3672 hrs.) by using five digits balance. Tests were conducted with different concentrations of green inhibitors. After immersion, the specimens were carefully washed with acetone, dried, and finally reweighted. Triplicate experiments were performed in each case and the mean values were reported. The corrosion rate was estimated by the following equation (7) (Pokharel *et al.*, 2019).

$$\text{Corrosion Rate (mm.y}^{-1}\text{)} = \frac{dw \times 8760 \times 10}{d \times A \times t} \tag{7}$$

Where Δw is the weight loss of the mild steel specimen in gram, d is the density of the mild steel specimen in g/cm^3, A is an area of mild steel specimen in cm3 and t is immersion time in an hour.

2.5 Corrosion Efficiency and Mechanism

The inhibitor efficiency based on the corrosion rate ($IE_{CR,\%}$) and the degree of surface coverage of the inhibitor molecule (θ) was estimated using equations (8) and (9), respectively (Subedi *et al.*, 2020).

$$IE_{CR,\%} = \frac{CR_{(O)} - CR_{(inhib)}}{CR_{(O)}} \times 100 \tag{8}$$

$$\theta = \frac{CR_{(o)} - CR_{(inhib)}}{CR_{(o)}} \tag{9}$$

Where, $CR_{(O)}$) and $CR_{(inhib)}$.) are the corrosion rates in the absence and presence of *Vitex negundo* and *Catharanthus roseus* plant extracts, respectively.

The corrosion inhibition mechanism was studied using different adsorption models. For example, Langmuir adsorption isothermal, as expressed in equation (10) can be used (Langmuir, 1916; Langmuir, 1917).

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \tag{10}$$

Where, C is the concentration of *Vitex negundo* and *Catharanthus roseus* plant extract; K_{ads} is the adsorptive equilibrium constant and θ is the surface coverage as given by equation (9).

Temkin adsorption isotherm was also applied for both green corrosion inhibitors of *Vitex negundo* and *Catharanthus roseus* plant extracts. Temkin isotherm is the early model describing the adsorption of hydrogen into a platinum electrode with biofuel solutions. This isotherm model contains a factor that explicitly taking into account adsorbent-adsorbate interactions. By ignoring the extremely low and large value of concentrations, the model assumes that the heat of adsorption (the function of temperature) of all molecules in the layer would decreases linearly rather than logarithmic with coverage (Tempkin & Pyzhev, 1940; Ahorai *et al.*, 1977; Foo *et al.*, 2010). The model is given by the following equation (Tempkin & Pyzhev, 1940).

$$q_e = \frac{RT}{b_t}\ln(A_{TC_e}) \qquad (11)$$

Where, q_e = adsorbed quantity (mg/g), C_e = Concentration of adsorbed species (g/L), A_T = Temkin isotherm equilibrium binding constant (L/g), B_T = Temkin isotherm constant, R = Universal gas constant (8.314 J/mol/K), T = Temperature at 298 K.

The Temkin model is linearly represented as the equation (12) and generally applied in the form.

$$q_e = \mathrm{B} \ln A_T - B \ln C_O \qquad (12)$$

Where, $B = \frac{RT}{b_T}$ and it is related to the heat of adsorption (J/mole). For a monolayer adsorption [52],

$$q_{e=\theta} \qquad (13)$$

Thus, the above equation (12) can be written as given below as given in equation (14)

$$\theta = 2.303 \times B \log A_T + 2.303 \times B \log C_e \qquad (14)$$

2.6 Characterization of E100 and E15 Blend using FTIR Spectra

FTIR analysis of pure bioethanol (E100), 2000 ppm of both *Vitex negundo* and *Catharanthus roseus* plant extract E100 pure Euro-4 grade petrol (E0), and 15 % bioethanol blend (E15) with 85 % Euro-4 grade petrol was carried out using IR Prestige-21 Spectrometer (Shimadzu Co., Japan) of the smart attenuated total reflection accessory to collect data in the Department of Plant Resources, Thapathali, Kathmandu.

Chapter– 3

RESULTS AND DISCUSSION

3.1 Phytochemical Screening of *Vitex negundo* and *Catharanthus roseus*

The details about the experimental procedures for each of the main phytoconstituents of the plant extract were carried out as described in Appendix 1 (Bandiola, 2018; Thilagavathi *et al.*, 2015). The major chemical constituents present in the methanolic extract of the leaf part of both the *Vitex negundo* and *Catharanthus roseus* plants are summarized, as summarized in Table 1. The table showed that the leaves of plants contain mainly alkaloids, polyphenols, flavonoids, glycosides may help to resist corrosion of the mild steel when exposed to different biofuels.

Table 1: Phytochemical Test

Phytochemicals	**Test Performed**	*V. negundo*	*C. roseus*
Phenolic compounds	Lead acetate test	+ve	+ve
Alkaloids	Dragendroff test	+ve	+ve
Carbohydrates	Molish test	+ve	-ve
Terpenoids	Salkowski test	-ve	-ve
Steroids	Libermann-Buchard test	-ve	+ve
Saponins	Foam test	+ve	+ve
Flavonoids	Alkaline reagent test	+ve	+ve
Glycosides	Legal test	+ve	+ve
Tannins	Ferric chloride test	+ve	+ve

+ve *indicate positive test &* -ve *indicate negative test*

3.2 Corrosion Test

3.2.1 Corrosion Rate in Bio-ethanol, Petrol and Their Blends

The corrosion rate of the mild steel was estimated in E100, E15, and E0 after immersion for different time intervals between 360 to 2330 hours in an airtight bottle at room temperature (25 ± 2 °C) using immersion tests and the results are shown in Fig. 5. It observed that the corrosion rate of the mild steel is decreased with increasing the immersion time up to about 1500 hours and it becomes almost steady-state after immersion for about 1500 hours up to 2330 hours in all three types of fuels. These results illustrated that the corrosion rate of the E0 was nearly one order of magnitude lower than those in the E100 and E15 blend. The corrosion resistance property of the mild steel is in the order: E100 < E15 < E0. With increasing the bioethanol concentration in petrol, the corrosion rate of mild steel is increased. The result indicated that pure bioethanol has the highest corrosion susceptibility to the mild steel among three types of fuels, because conductivity and ability of the bioethanol blend to absorb water increases with increasing the bioethanol content in gasoline (Matejovsky *et al.*, 2017), and hence the resulting biofuel becomes more corrosive.

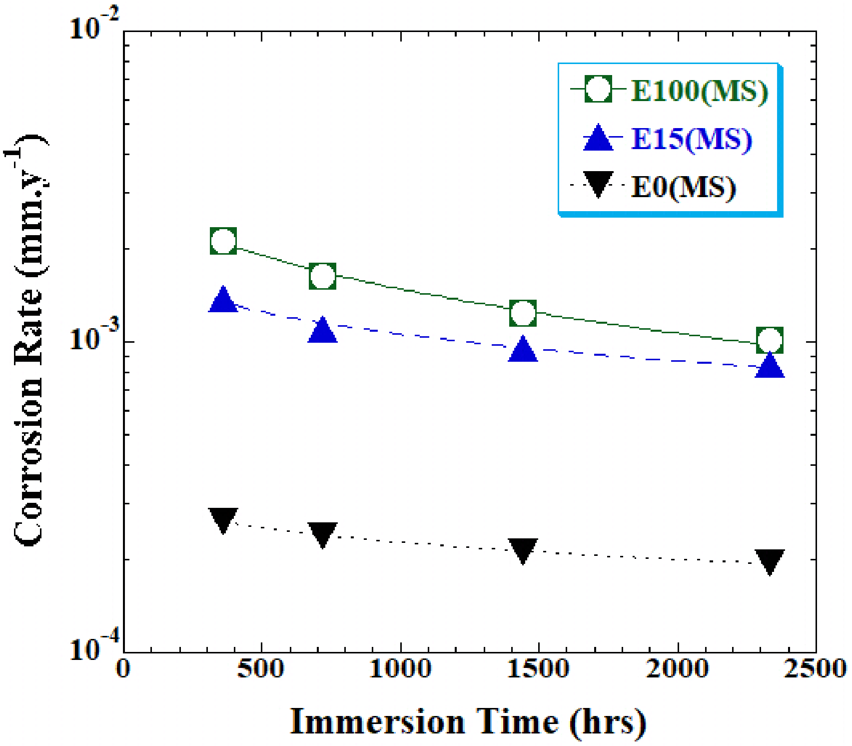


Figure 5: Changes in the corrosion rate of mild steel in E00, E15, Euro-4 grade petrol at 25 ± 2 °C in airtight condition, as a function of immersion time

Similar behavior of the corrosive degradation of stainless steel in bioethanol and its blends was reported that was lower than pure biodiesel and was higher than petro-diesel (Wan *et al.*, 2020). In another study, the increase of water concentration in fuel-grade ethanol prompted the pitting corrosion loss of different types of carbon steel (Lou & Singh, 2010). Results showed that the water in the ethanol strongly influenced the surface film stability and interface electrochemistry in ethanolic environments. Moreover, the corrosion resistance properties of the mild steel in both biofuel and petrol fuels are found to agree with the previously reported results (Katuwal *et al.*, 2020). In this context, further research was carried out to decrease the corrosion rate of the mild steel in both the E100 and E15 biofuels with the additions of 500, 1000, 1500, and 2000 ppm of methanol extracts extracted from the leaves of two Nepal origin plants of *V. negundo* and *C. roseus* as a green-based corrosion inhibitor, expecting to minimize such high corrosivity of E100 and its E15 blend to the mild steel and bring close to that of the petrol (E0) at the minimum or less.

3.2.2 Effects of Plant Extracts as Corrosion Inhibitor

The effect of *V. negundo* and *C. roseus* plant extracts on the corrosion rate of the mild steel after immersion for different time intervals between 350 to 2330 hours in E100 and E15 at room temperature (25 ± 2 °C) in an airtight bottle was estimated using weight loss method and the results are depicted in Figs 7 and 8. The figures show that the corrosion rate of the mild steel is decreased with increasing the concentrations of both the plant extracts of *V. negundo* in both E100 and E15 blend at room temperature in airtight condition which is also lower corrosion rate even lower than in E0, as shown in Figs 6 and 7 also.

The decreasing trend of the corrosion rate of the mild steel in E100 with the additions of 500 to 2000 ppm *V. negundo* is more pronounced than the additions of 500 to 2000 ppm *C. roseus* plant extract. Similarly, the corrosion rate of the mild steel is also decreased with increasing the concentration of the plant extract of *C. roseus* in both E100 and E15 biofuels at room temperature in airtight conditions, as shown in Figs 6 and 7, respectively. However, the corrosion rate of the mild steel in E100 and E15 with additions of 500-2000 ppm of *C. roseus* plant extract did not lower than in E0, although they enhanced remarkably the corrosion resistance property in both the biofuels. These results revealed that leaf extract of each two plants acts as good green-based inhibitors to minimize/control the electrochemical corrosion of the mild steel in E100 and E15 at room temperature.

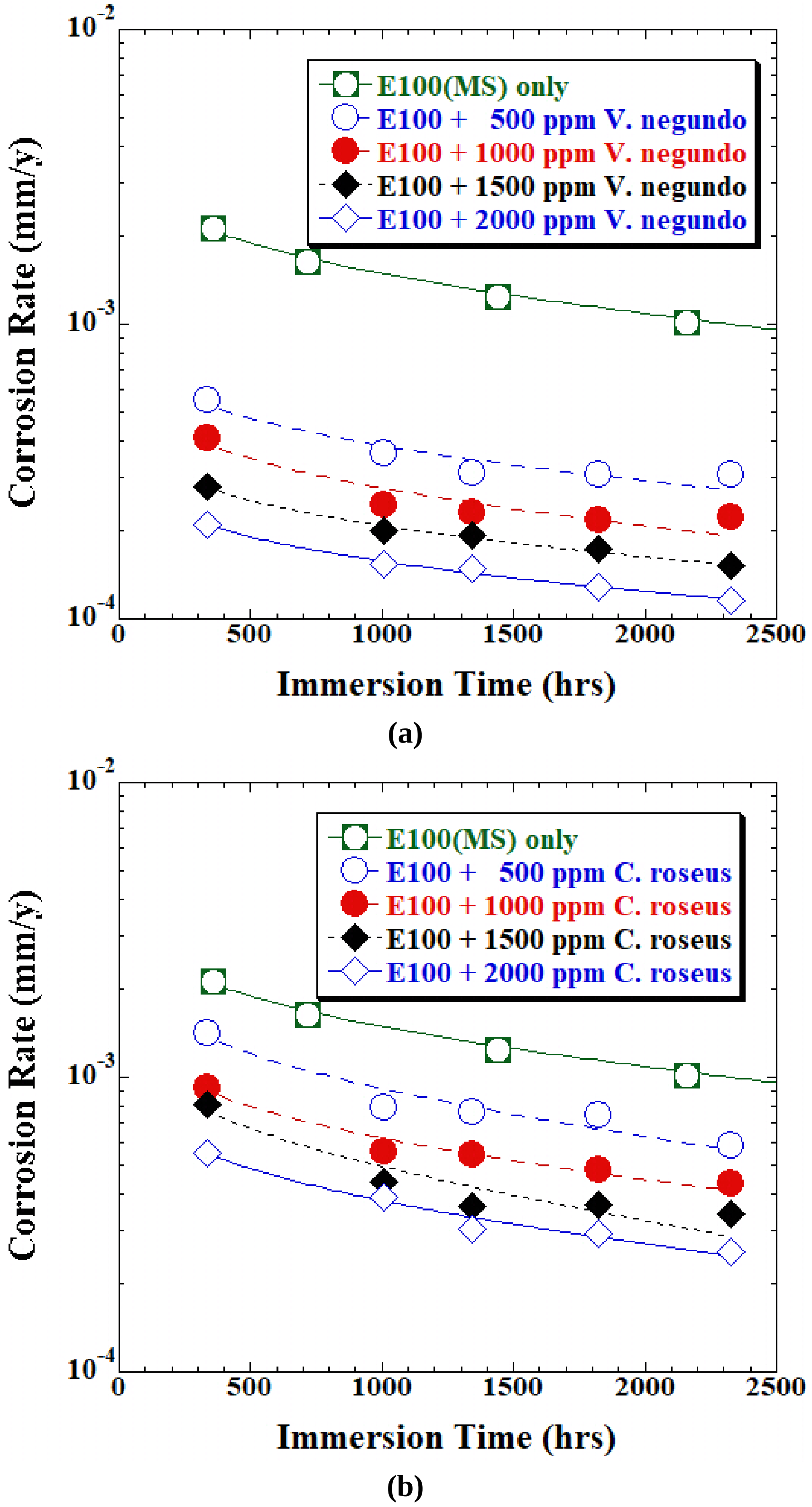
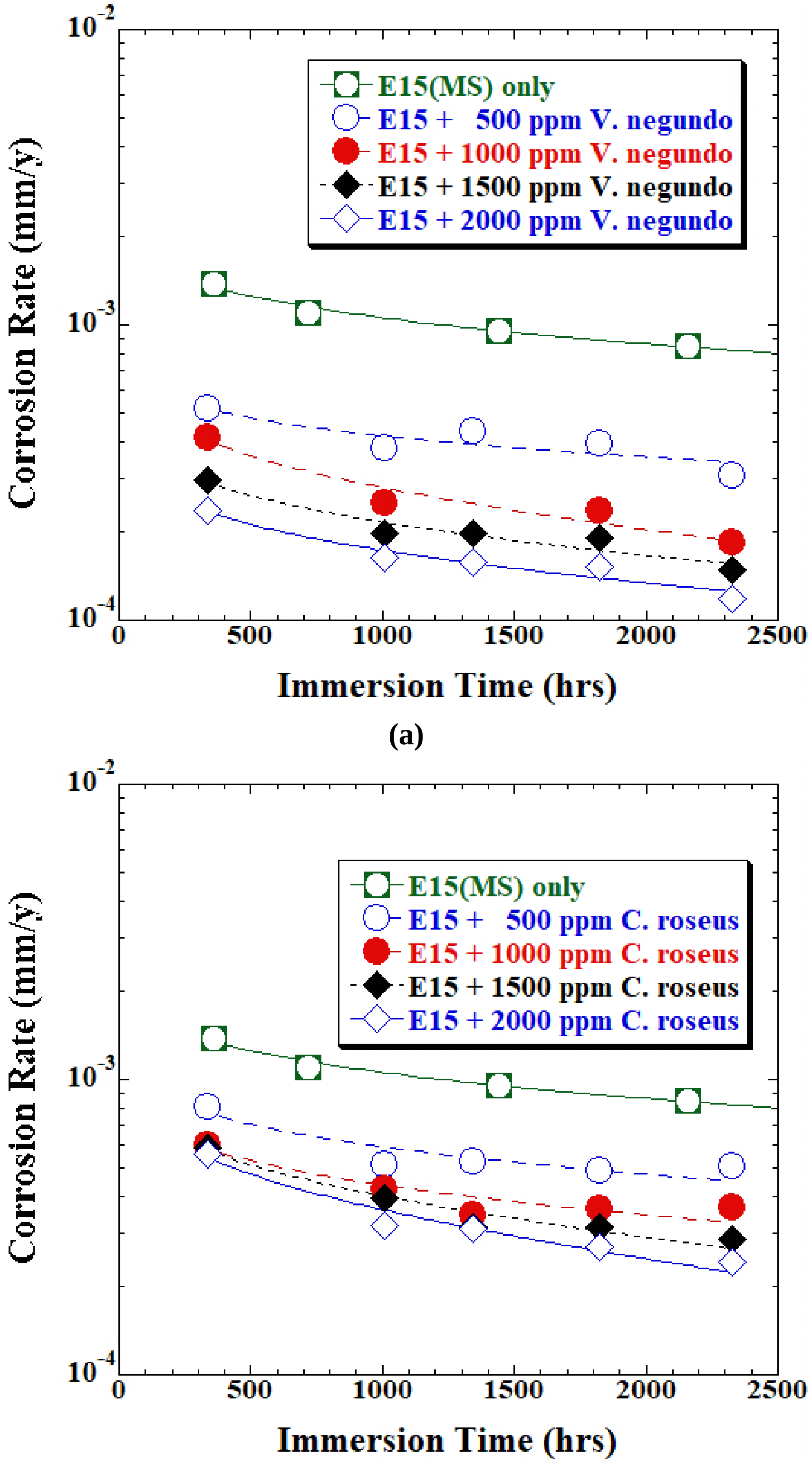


Figure 6: Changes in the corrosion rate of the mild steel in E100 with absence and presence of different concentrations of (a) V. negundo and (b) C. roseus plants extract at 25 ± 2 °C in airtight condition, as a function of immersion of time



(a)

(b)

Figure 7: Changes in the corrosion rate of the mild steel in E15 with absence and presence of different concentrations of (a) V. negundo and (b) C. roseus plants extract at 25 ± 2 °C in airtight condition, as a function of immersion of time

3.3 Corrosion Inhibition Efficiency and Mechanism

The changes in corrosion inhibition efficiency of mild steel in different concentrations of *V. negundo* and *C. roseus* plants leaves extracts both in E100 and E15 5 at 25 ± 2 °C in airtight condition was studied and results are depicted in Fig. 8.

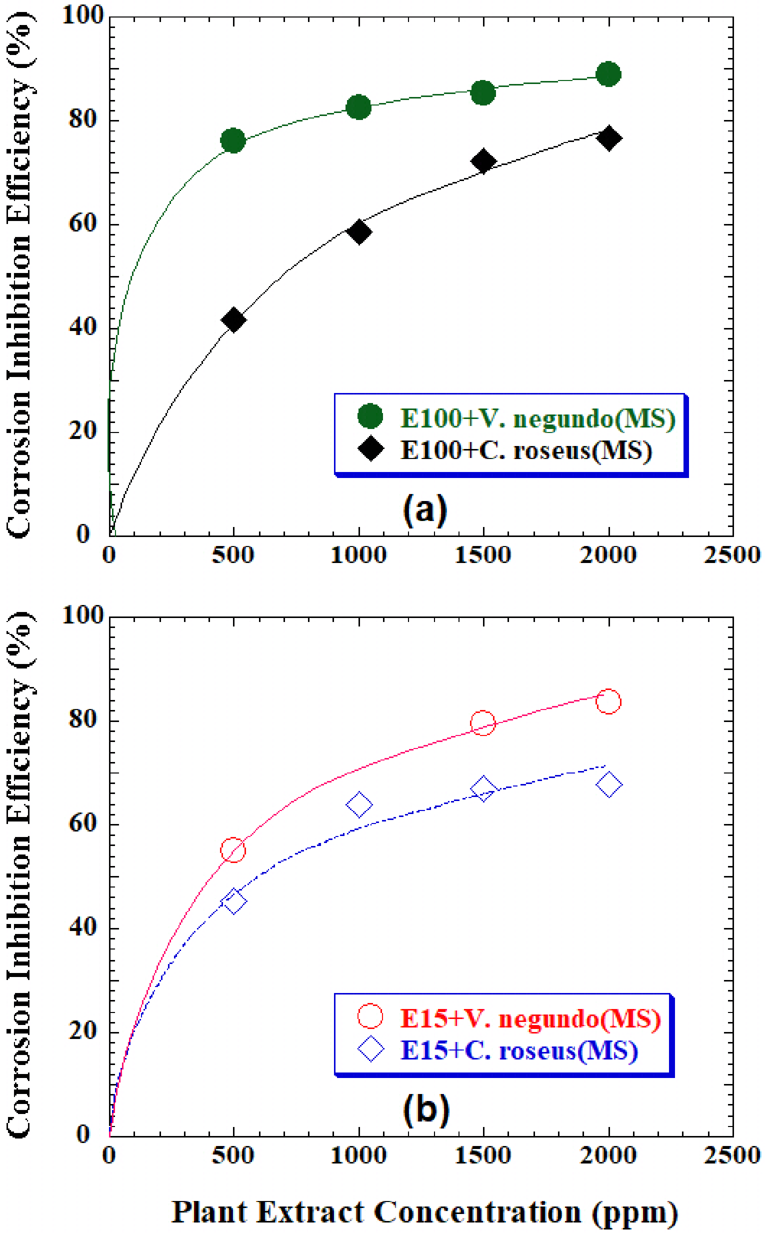


Figure 8: Changes in the corrosion inhibitor efficiency for the mild steel after immersion for 2330 hours in (a) E100 and (b) E15 at 25 ± 2 °C in airtight condition, as a function of V. negundo and C. roseus plant extract concentrations

In most cases, the corrosion inhibition efficiency of both plants leaves extracts increases at a steep angle with increasing concentration from 500 ppm and 1000 ppm, and the maximum inhibition efficiencies of about 89 % and 75 % were obtained at 2000 ppm *V. negundo* and *C. roseus* extract, respectively, for the mild steel in E100 at 25 ± 2 °C in airtight condition. Meanwhile, it was about 86 % and 72 % in the E15 blend, as shown in Figs 8(a) and 8(b), respectively. These results revealed that 2000 ppm of both plant extracts can be used as a green corrosion inhibitor to decrease the corrosion rate of the mild steel only 72 to 89 %, although the inhibition efficiency of the plant extract of *V. negundo* is found remarkably higher than that of the plant extract of *C. roseus* in both the E100 and E15 biofuels, as shown in Fig. 8.

Consequently, the corrosion inhibition efficiency of the methanol extracts of these two plant species in E100 and E15 for the mild steel is arranged in order as; $IE_{(E100+V.negundo)} \geq IE_{(E15+V.negundo)} > IE_{(E100+C.roseus)} \geq IE_{(E15+C.roseus)}$. Therefore, it can be reasoned out from these results that the methanol fraction of *V. negundo* plant extract seems to be the most efficient additives in both E100 and E15 for controlling their corrosive nature to mild steel. These results agree with the results of corrosion tests, as depicted above in Figs 7 and 8 as well as summarized in Table 2. It is noteworthy to mention herein that the corrosion-resistant properties of the mild steel in E100 and E15 blend with 1500 ppm and 2000 ppm *V. negundo* plant extract are found to be higher even than the corrosion-resistant properties in E0 after 1008-1344 hrs or more times exposure, as shown in bolded values in Table 2.

The most effective corrosion inhibition efficiency of both the *V. negundo* and *C. roseus* extracts in bioethanol and its blend is most probably due to the presence of ample amounts of heteroatoms and aromatic ring compounds as the major phytoconstituents in these two plants. For example, abundant amounts of eight major ring compounds of flavonoids reported in methanol extract of Nepal origin *V. negundo* leaf were reported by Gautam *et al.* (2008). Similarly, the main alkaloids in *C. roseus* plant are reported as; vincristine, vindolicine, anhydrovinblastine, ajmalicine, tabersonine, catharanthine, vindoline, vinblastine, and ajmalicine so on, which are aromatic ring compounds (Barrales-Cureño *et al.*, 2019).

Table 2: Estimated corrosion rate of mild steel in E100 and E15 blend with and without V. negundo and C. roseus plants extract concentrations at different exposure times.

Extract concentration (ppm)	Time (hrs)	CR$_{E100}$ (mm/y)	CR$_{E15}$ (mm/y)	CR$_{E0}$ (mm/y)	
without plant extract	360	0.00213	0.00137	0.00027	
	720	0.00163	0.00110	0.00024	
	1440	0.00123	0.00095	0.00021	
	2330	0.00101	0.00085	**0.00019**	
		V. negundo		*C. roseus*	
		CR$_{E100}$ (mm/y)	CR$_{E15}$ (mm/y)	CR$_{E100}$ (mm/y)	CR$_{E15}$ (mm/y)
500	336	0.00055	0.00052	0.00142	0.00081
	1008	0.00036	0.00038	0.00079	0.00051
	1344	0.00031	0.00043	0.00076	0.00053
	1824	0.00031	0.00040	0.00074	0.00049
	2330	0.00031	0.00031	0.00059	0.00051
1000	336	0.00041	0.00042	0.00092	0.00060
	1008	0.00024	0.00025	0.00056	0.00042
	1344	0.00023	nd	0.00054	0.00035
	1824	0.00022	0.00024	0.00049	0.00036
	2330	0.00022	0.00018	0.00044	0.00037
1500	336	0.00028	0.00030	0.00081	0.00059
	1008	0.00020	0.00020	0.00044	0.00040
	1344	**0.00019**	0.00020	0.00036	0.00032
	1824	**0.00017**	**0.00019**	0.00037	0.00032
	2330	**0.00015**	**0.00015**	0.00034	0.00029
2000	336	0.00021	0.00024	0.00056	0.00056
	1008	**0.00015**	**0.00016**	0.00039	0.00032
	1344	**0.00015**	**0.00016**	0.00031	0.00031
	1824	**0.00013**	**0.00015**	0.00029	0.00027
	2330	**0.00012**	**0.00012**	0.00026	0.00024

nd = not determined; CR = corrosion rate; E100 = bioethanol; E15 = 15 % bioethanol blend

For the efficacious use of corrosion inhibitors, it is mandatory to know the action mechanism of materials in the given environment and various factors such as environment properties, inhibitory properties, the potential presence of anticorrosion agents, and others must be considered while choosing such corrosion inhibitor. Among different adsorption isotherm models, Langmuir and Temkin are used to describe the molecular interaction between the green corrosion inhibitor molecules of plant extract and the active surface sites of the mild steel to explain its inhibition mechanism in pure bioethanol and its 15 % blend with 85 % petrol.

The Langmuir isotherm is one of the simplest models and assumes that all adsorption sites are equivalent and the particle binding occurs independently from nearby sites being occupied or not (Langmuir, 1916, 1917). It also shows the relationship between the ratio of inhibitor concentration to surface coverage (C/θ) and the inhibitor concentration (C) as given above in equation (10). While, the applicability of Temkin adsorption isotherm verified a monolayer adsorption of the green inhibitors on a uniform mild steel surface with interaction between the adsorbed species of the corrosion inhibitors (Tempkin & Pyzhev, 1940; Aharoni & Ungarish, 1977; Foo *et al*., 2010; Maron & Prutton, 1951). Figures 9 and 10 show the relationship between the C/θ and C, and between the surface coverage (θ) and log(C), respectively, for the mild steel in both the E100 and E15 at 25 ± 2 °C in airtight condition.

The linear correlation coefficient (R^2) was used to choose the isotherm that best fit experimental data because it was found almost equal to unity in all eight straight lines, as shown in Figs 9 and 10. The results illustrated that the adsorption process obeyed both the Langmuir and Temkin adsorption isotherm models to study the corrosion inhibition mechanism on the surface of the mild steel by the methanol extracts obtained from plants *V. negundo* and *C. roseus* leaves in E100 and E15 biofuels at 25 ± 2 °C in airtight condition.

Furthermore, the favorability of the Langmuir adsorption isotherm process was confirmed from the calculation of a dimensionless separation factor (R_L) (Dabrowski, 2001), which was found between 1 and 0. Hence, the corrosion controlling mechanism of the mild steel in both biofuels of E100 and E15 with different amounts of both plant extracts can be explained by the formation of a stable and diffusion barrier metal-oxide layer formed on the surface of the mild steel samples at 25 ± 2 °C in airtight condition. On the other hand, the applicability of Temkin adsorption isotherm verified a monolayer adsorption of the green-based inhibitors on the uniform surface of mild steel (Rana *et al*., 2018; Tempkin & Pyzhev, 1940). These results indicated that the adsorption process obeyed both the Langmuir and Temkin adsorption isotherms to study the corrosion inhibition mechanism on the surface of the mild steel sheet by green-based corrosion inhibitors of *V. negundo* and *C. roseus* plant extracts in E100 and E15 biofuels.

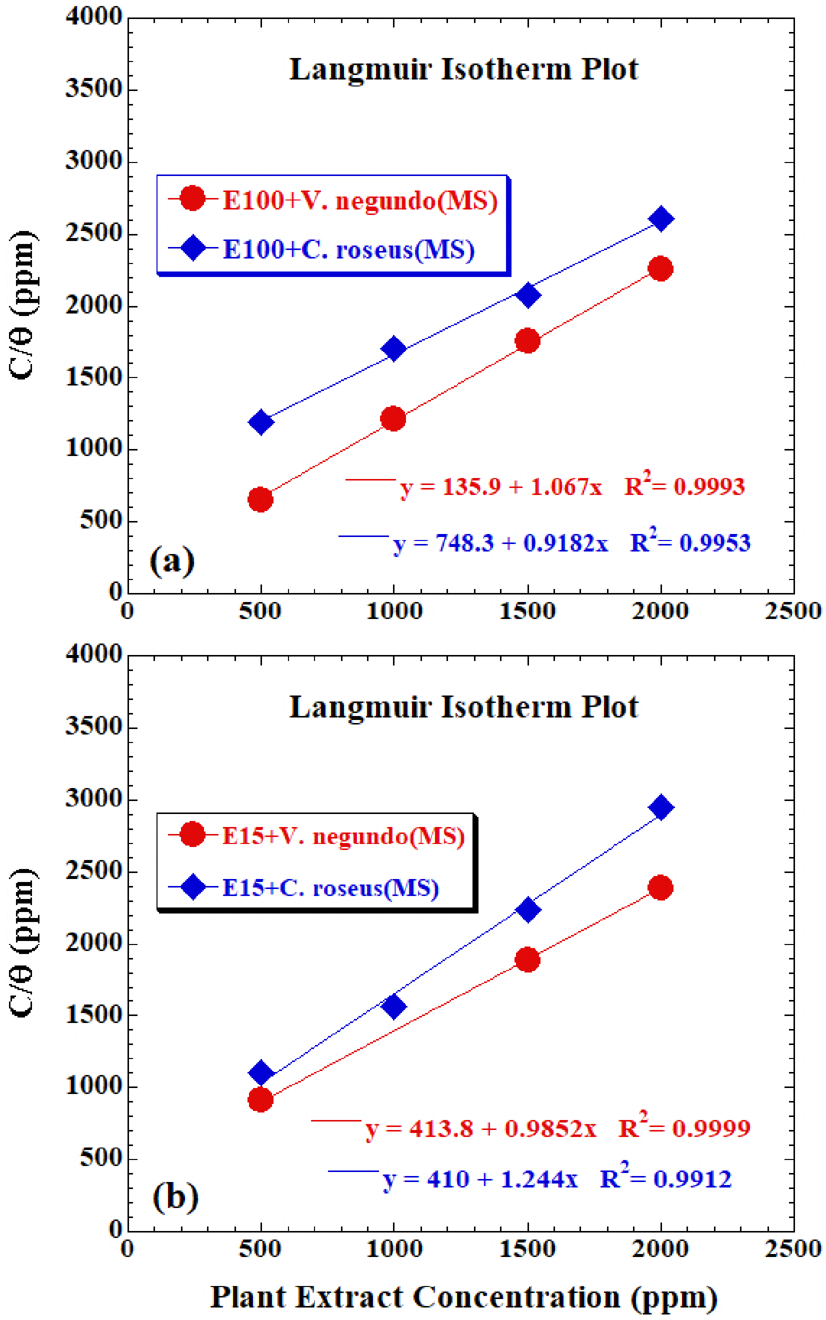


Figure 9: Langmuir's adsorption plots for the mild steel after immersion for 2330 hours in E100 and E15 with additions of different concentrations of (a) V. negundo and (b) C. roseus plant extracts at 25 ± 2 °C in airtight condition

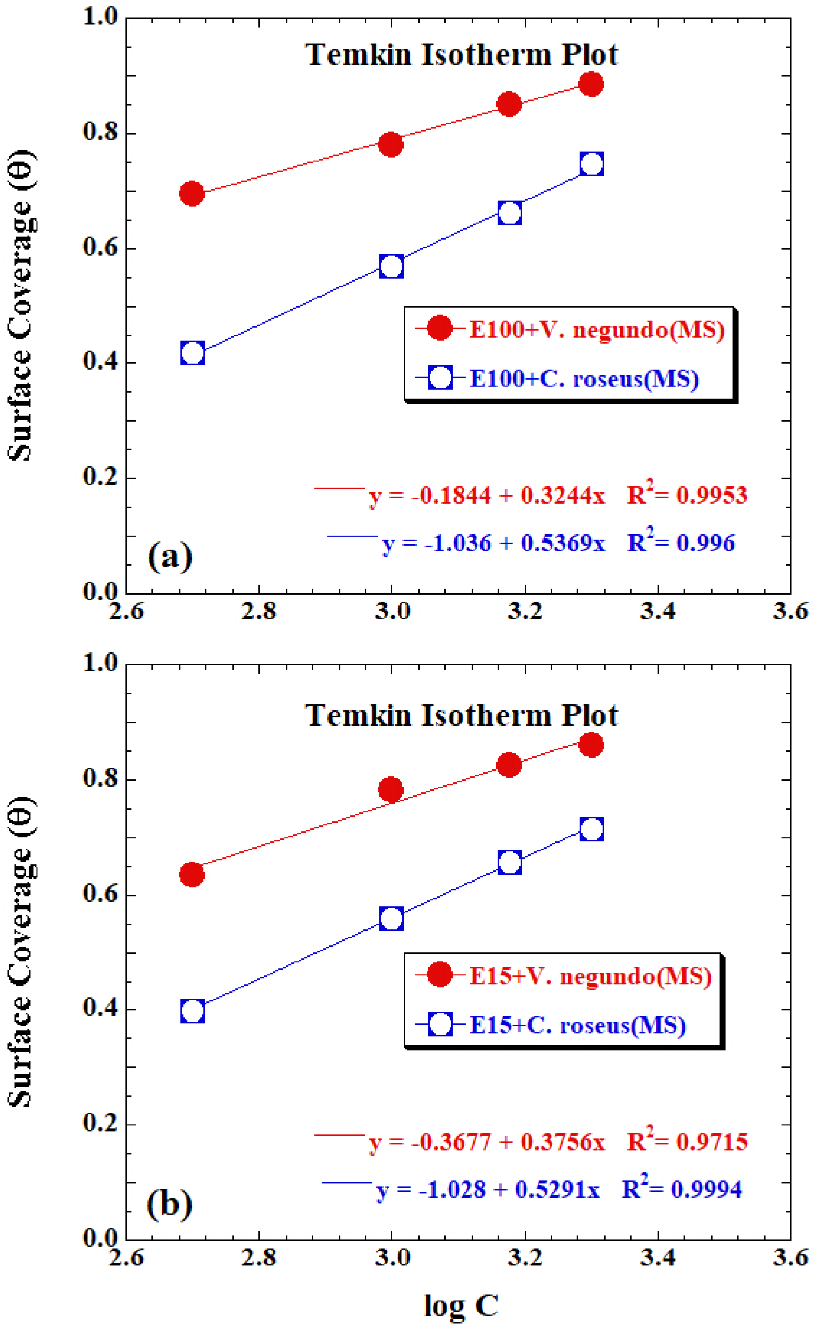


Figure 10: Temkin's adsorption plot for the mild steel after immersion for 2330 hours in (a) E100 and (b) E15 with additions of different concentrations of V. negundo and C. roseus plant extracts at 25 ± 2 °C in airtight condition

Oxygen-, nitrogen-, sulfur- and phosphorus-based organic compounds constituted in these plant extracts are thus adsorbed on the surfaces of the mild steel which prevent their corrosion by forming barrier layers (Popoola, 2019), because such constituents of plants have shielding effect and corrosion-inhibiting potentials for material attack. Their increasing order of corrosion inhibition efficiency has been stated to be oxygen < nitrogen

< sulfur < phosphorus (Patni *et al.*, 2013). It is substantive to cite here that amine-based inhibitors were reported the formation of corrosion protective layers onto the metal surface by adsorption phenomena occur either through a metal–nitrogen bonding via π electrons by chemisorption or with a protonated amine by the formation of a hydrogen bond to the metal surface (Li *et al.*, 1997).

3.4 FTIR Spectroscopic Analysis of Bioethanol and its Blend

Most biofuels exhibit oxygen-containing compounds, which is one of the significant differences with their counterpart fossil fuels (i.e., petrol and petro-diesel so on). The latter type of fuel consists of hydrocarbons with no oxygen incorporated. Consequently, the FTIR spectral patterns change significantly and may pose a challenge to established analytical tools to characterize these biofuels and their bends. A review of bioethanol characterization using infrared (IR) spectroscopic technique was applied by different researchers (Zhuang *et al.*, 2020; Fonseca *et al.*, 2020; Bañuelos *et al.*, 2018; Conklin *et al.*, 2014). Among the carbon-carbon (C-C), carbon-oxygen (C-O), oxygen-hydrogen (O-H), and carbon-hydrogen (C-H) bond present in ethanol, the C-C bond has absorptions which occur over a wide range of wavenumbers in the fingerprint region that makes it very difficult to decide on an infrared spectrum analysis. However, the carbon-oxygen single bond also has an absorption in the fingerprint region, varying between 1000 and 1300 cm^{-1} depending on the molecule and hence it is very wary about choosing it from IR spectra of bioethanol. Contrarily, the O-H bond in liquid bioethanol absorbs at a higher wavenumber somewhere between 3100-3500 cm^{-1}.

The FTIR spectra were used to identify the functional group and the bands corresponding to various stretching and bending vibrations in three types of fuels of bioethanol (E100), 15 % bioethanol blend (E15), and commercially available Euro-4 grade petrol (E0), as shown in Fig. 11. A broad absorbance peak for the OH stretching band is observed at about 3330 cm^{-1} for the pure bioethanol (E100). Besides, the vibrational modes of the bioethanol (E100) are identified at 2970 cm^{-1} and 2885 cm^{-1} wavenumbers. Also, characteristic doublet absorbance peaks for symmetric and asymmetric CO stretches are appeared at about 1044 cm^{-1} and 1086 cm^{-1}, respectively, for the E100 biofuel, as shown in Fig. 11(a). These FTIR analysis results agree with the previously reported FTIR absorption peak values for pure ethanol (https://www.chemguide.co.uk/analysis/ir/interpret.html).

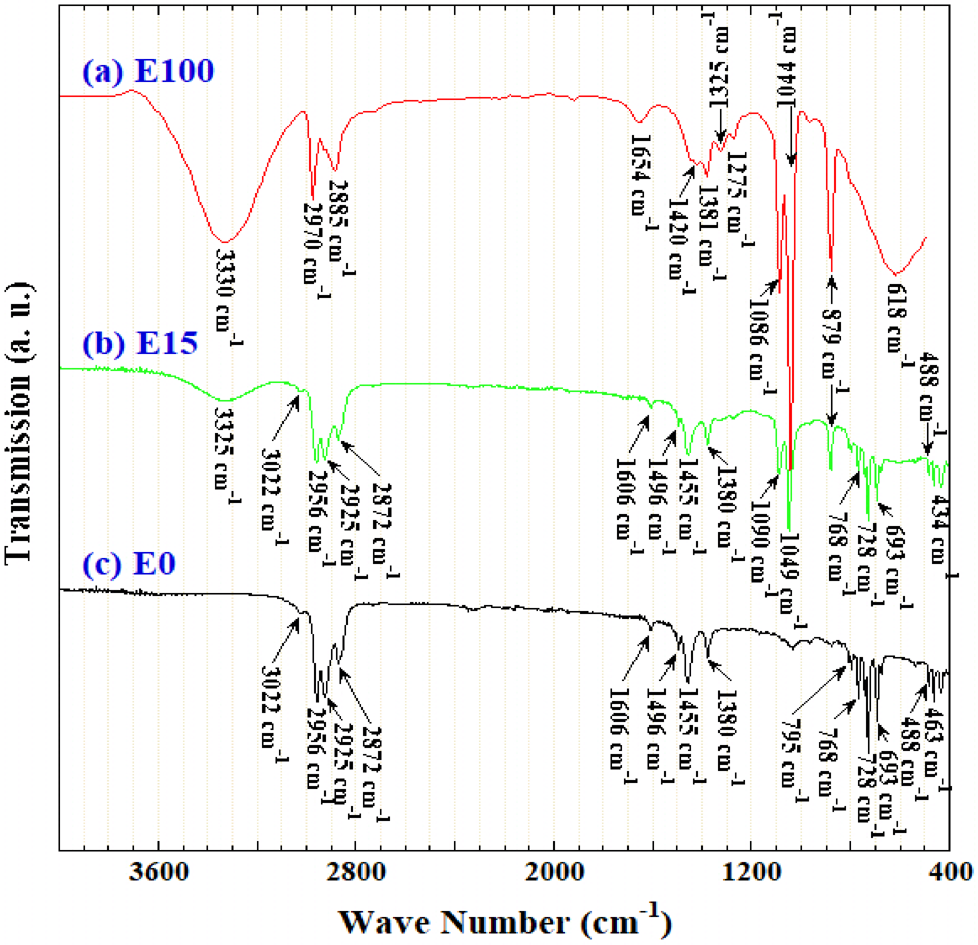


Figure 11: FTIR spectra of pure bioethanol (E100), 15 % bioethanol blend with petrol (E10) and pure petrol (E0)

Interestingly, both peaks of the E100 sample at 1044 and 1086 cm^{-1} wavenumbers are shifted slightly to higher peak values (i.e., at 1049 and 1090 cm^{-1}) with decreasing the concentration of E100 in 15 % bioethanol blend (E15) and finally disappeared both peaks in the FTIR spectra of pure petrol, as shown in Figs 11(b) and 11(c). These observations are consistent with the result reported by Coldea *et al.* (2013) from the FTIR spectra of pure ethanol. Besides, such peak value shifting indicates a strengthening of the C−O bond, which is most likely caused by a weakening of the intermolecular hydrogen bonds between bioethanol molecules (Corsetti *et al.*, 2015). However, such blue shifting affects around 880 cm^{-1} due to the C−O stretching mode (Larkin, 2011) in the E15 sample is negligible compared with the pure bioethanol. Such anomaly effects shown by pure bioethanol and its 15 % blend with 85 % petrol are mostly due to the weakening of the intermolecular interactions between the bioethanol molecules. Van der Waals forces are dominant in the mixtures with high gasoline content while in bioethanol hydrogen bonding is the predominant interaction mechanism (Corsetti *et al*., 2015).

However, no such a broad peak in OH stretching region between 3100 and 3500 cm^{-1} and doublet peaks in the CO stretching region between 1044 and 1086 cm^{-1} are recorded for the petrol (E0) sample, as shown in Fig. 11(c), while the pure bioethanol (E100) exhibits distinct FTIR peaks in both these wavenumber regions, as shown in Fig. 11(a). Overlapping bands for the E100 and E0 fuels are observed in the C−H stretching and bending regions at 3000-2850 cm^{-1} and 1600-1200 cm^{-1}, respectively, as shown in Fig. 11(b). These observed transmission peaks agree with the previously reported FTIR peaks for C–H stretching vibration corresponding to $–CH_2$ and $–CH_3$ groups of bioethanol (Irshad *et al*., 2018). The predominant peaks of the hydrocarbons in the petrol (E0) are found at 2956 cm^{-1}, 2925 cm^{-1} (asymmetric C−H stretching vibrations), and 2872 cm^{-1} (symmetric C−H stretching vibrations), as depicted in Fig. 11(c).

The FTIR absorption peaks of E0 crosses the peaks of E15 in the isosbestic points at 2966, 2896, 2876, and 2846 cm^{-1}. Moreover, these FTIR absorption peaks located between 2960 and 2840 cm^{-1} are more dominated for E0 than E15 bioethanol blend containing 85 % petrol, as shown in Figs 11(b) and 11(c). Therefore, the integrated absorbance in this entire C−H stretching region is found to be decreased with increasing the percentage of bioethanol. The FTIR peaks for pure bioethanol (E100) at 2970 cm^{-1} and 2885 cm^{-1} are seen in Fig. 11(a), but both peaks are not observed for the E0, as shown in Fig. 11(c) and even in the E15 blend, as shown in Fig. 12(b). Considering the entire C−H stretching region, the integrated absorbance decreases with increasing the percentage of E100.

Similarly, there is one sub-region that is also dominated either by petrol absorption peaks or by bioethanol peaks. The FTIR absorption peaks for only E100 appeared at 1275, 1325, 1420, and 1654 cm^{-1}. Besides, the peaks at 1454 and 1381 cm^{-1} are also appeared for E100 which are overlapped with the peaks of the pure petrol (E0) and the bioethanol blend (E15). The FTIR peak at about 1454-1455 cm^{-1} is found to be dominated by E0, but with a background peak of the E100. On the other hand, the FTIR peak at around 1380-1381 cm^{-1} is found to be slightly dominated by E100, but with a background peak of E0. These results obtained from the FTIR spectroscopic analysis are also agreeing with previous findings (Corsetti *et al*., 2016). Similarly, the stretching vibration of methylene functional group ($-CH_2$) of bioethanol occurs at 1420 which agrees with the results reported in previous works (Wawro *et al.*, 2019).

Table 3. FTIR band of the *Vitex negundo* and *Catharanthus roseus* extracts

Wavenumber (cm^{-1})		**Assignments**
V. negundo extract	*C. roseus* extract	
3320	3288	O-H stretching due to hydrogen bonding
3008	–	Aromatic (C-H) stretching
2926	2926	Methylene (C-H) asymmetrical stretching
2854	2850	Methyl (C-H) symmetrical stretching
2376; 2348; 2327	2376; 2348; 2327	C≡N stretching or P-H bonding
1692		C=O stretching (lower frequency observed may be due to conjugation with other groups)
1649	1649	-
1608; 1515		C-C ring stretching
	1572	C-C ring stretching
1448	1448	C-O-H in-plane bending
1370	1383	C-H bending
1268	1256	C-O bending
1165		P=O stretching
1028	1028	O-H bending
925	925	O-H bending
825	825	
816	816	C-H bending
779	779	
506		
418	418	

The FTIR spectra at about 728 cm^{-1} correspond to the vibrations of the CH bond of a long carbon chain of aliphatic hydrocarbon. The deformation vibrations of the CH bonds exhibiting a band with a peak at about 1455 cm^{-1} and 1380 cm^{-1} belong to the CH_2 and CH_3 groups, respectively, those are also the corresponding with the stretching vibrations of methylene (−CH_2−) and methyl (−CH_3) groups can be seen at frequencies of between 2972-2956 and 2885-2872 cm^{-1}, respectively (Larkin, 2011).

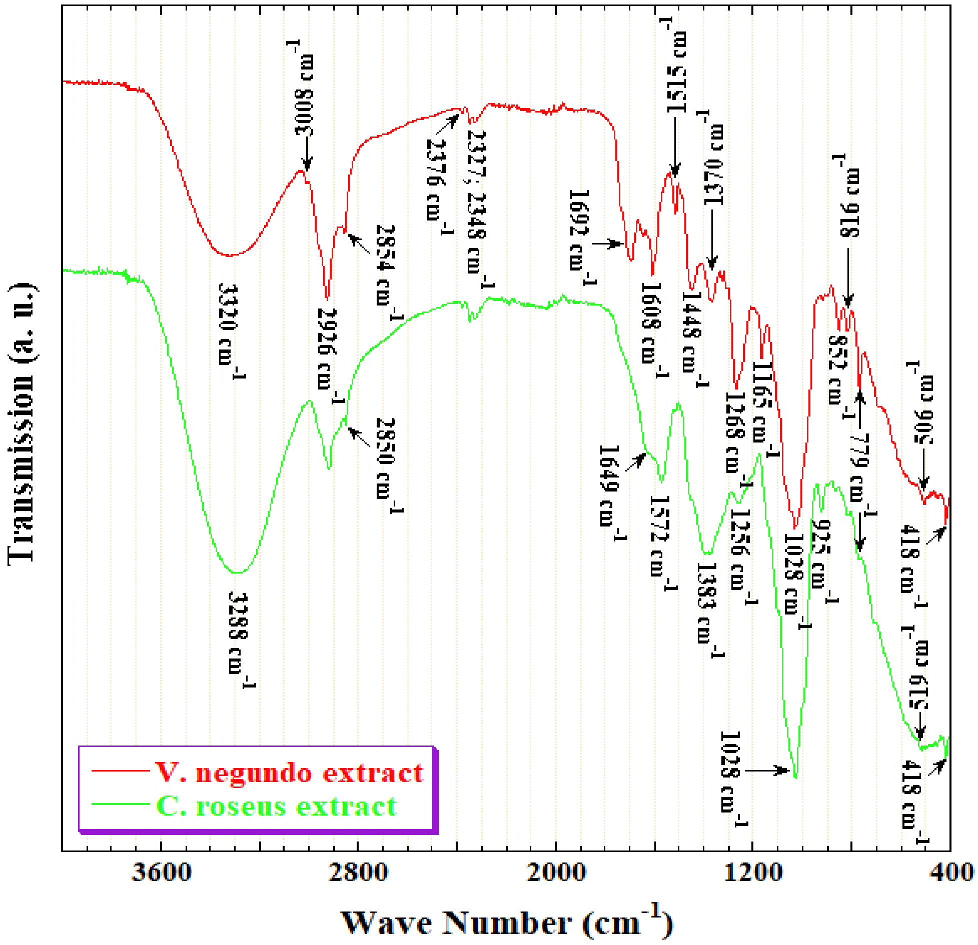


Figure 12: FTIR spectra of the methanol extracts of Vitex negundo and Catharanthus roseus leaves

Chapter– 4

CONCLUSIONS

The effectiveness of two green-based materials extracted from Nepali origin plant of *E. ganitrus* and *A. marmelos* leaves as a corrosion inhibitor was studied to increase the corrosion resistance property of the mild steel in E100 and E15 at 25 ± 2 ºC in airtight condition using immersion tests, corrosion inhibition efficacy and mechanism, and FTIR spectroscopic techniques. The following conclusions are point outs from the results and discussion:

1. The corrosion-resistant property of the mild steel in E0 is remarkably lower than in E100 and E15. Susceptibility to corrosion of the mild steel in E00 and E15 is found to be nearly one order of magnitude higher than in E0.

2. Both the plant extracts used in this study acted as a good green-based corrosion inhibitor to increase the corrosion resistance properties of the mild steel exposed for more than three months in bioethanol (E100) and its blend (E15) at room temperature in airtight conditions.

3. In particular, the corrosion-resistant behavior of the mild steel with separate addition of 1500-2000 ppm *Vitex negundo* extract in both E100 and E15 biofuels is found to be higher than in E0.

4. Langmuir and Temkin adsorption studies suggest that the phytochemical constitutes of each of both plants leaf extracts are physically adsorbed on the mild steel surface.

5. These plants extract showed the maximum inhibition efficiency as; $IE_{(E100+V.negundo)} = 89\ \% > IE_{(E15+V.negundo)} = 86\ \% > IE_{(E100+C.roseus)} = 75\ \% > IE_{(E15+C.roseus)} = 72\ \%$, indicates that the methanol extract of *V. negundo* leaf as comparison with the *C. roseus* plant extracts could be used as an efficient additive in both E100 and E15 biofuels to control their corrosive nature of the mild steel.

6. *V. negundo* and C. *roseus,* extracts have good anti-corrosion properties for mild steel in bioethanol and its blend fuels at room temperature in airtight conditions.

7. All the obtained results agreeing with the fact that both plant extracts could be promising for the formulation of effective, eco-friendly anti-corrosion biofuel-additives to retard their corrosion susceptibility on mild steel, especially in bioethanol and its 15 % blend.

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APPENDIXES

Appendix 1: Experimental procedures for phytochemical screening of plants (Bandiola, 2018; Thilagavathi *et al*., 2015)

a. Phenolic Compounds

- ***Lead Acetate Test:*** The plant extract was dissolved in distilled water and then added a few drops of 10 % lead acetate solution. A bulky white precipitate indicated the presence of phenolic compounds.

b. Alkaloids

- ***Dragendroff's test***: The extract was treated with Dragendroff's reagent (solution of potassium bismuth iodide). The formation of a red precipitate indicated the presence of alkaloids.

c. Carbohydrates

- ***Molish's Test:*** To 2 mL of extract, two drops of alcoholic solution of α-naphthol were added. The mixture was shaken well and a few drops of concentrated sulphuric acid was added slowly along the sides of the test tube. The appearance of a violet ring at the junction illustrated the presence of carbohydrates.

d. Terpenoids

- ***Salkowski's Test:*** Extract was treated with chloroform and then filtered and added with a few drops of concentrated sulphuric acid. It was then shaken and allowed to stand. The appearance of golden yellow color or red-brown color indicated the presence of terpenoids.

e. Steroids

- ***Libermann-Burchard's Test:*** Extract was added with chloroform. After filtration, it was treated with a few drops of acetic anhydride, boiled, and cooled. Then concentrated sulphuric acid was added. The formation of a brown ring at the junction indicated the presence of steroids.

f. Saponins

- ***Foam Test:*** Fifty (50) mg of the extract was diluted with distilled water and made up to 20 mL. The suspension was shaken in a graduated cylinder for 15 minutes. Saponins were detected by the formation of a two-cm layer of foam.

g. Tannins

- ***Ferric chloride Test:*** The extract (50 mg) was dissolved in 5 mL of distilled water. Few drops of neutral 5% ferric chloride solution were then added. The dark green color showed the detection of tannins.

h. Flavonoids

- ***Alkaline Reagent Test***: Extract was combined with a few drops of sodium hydroxide solution. The appearance of intense yellow color, which turned colorless on the addition of dilute acid, signified the presence of flavonoids.

i. Glycosides

- ***Legal's Test:*** 50 mg of the extract was dissolved in pyridine and then sodium nitroprusside solution was added. The solution was made alkaline using 10% NaOH. Glycosides were detected by the formation of a pink color solution.

PUBLICATION

ORIGINAL ARTICLE

European Journal of Advanced Chemistry Research
www.ej-chem.org

Assessment on the Effective Green-Based Nepal Origin Plants Extract as Corrosion Inhibitor for Mild Steel in Bioethanol and its Blend

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ABSTRACT

Effects of Nepal origin plant species of *Vitex negundo, Catharanthus roseu, Aegle marmelos* and *Elaeocarpus ganitrus* extracts on mild steel corrosion were explored in bioethanol (E100) and its blend (E15) in airtight condition at 25±2 °C using static immersion, inhibition efficiency and mechanism tests which were complemented with adsorption isotherms and potentiodynamic polarization studies. Corrosion resistance of the mild steel was increased with increasing 500-2000 ppm concentrations of each plant extract in E100 and E15 biofuels. Additions of *V. negundo* and *C. roseus* extract separately in both the biofuels seems to be more effective inhibition actions to prevent the mild steel corrosion than *A. marmelos* or *E. ganitrus* addition so as the corrosion rates of the mild steel in E100 and E15 are successfully lowered even than in commercial gasoline (E0). The results obtained from the corrosion rate revealed the order of the corrosion inhibition efficiency (IE) as *V. negundo* > *C. roseus* > *A. marmelos* > *E. ganitrus*. The maximum IE (IE_{max}) in *V. negundo* and *C. roseus* leaves was showed about 89-86% and 71-75%, respectively, at 2000 ppm concentration, in spite of the other two more plants leaf extract also used as the corrosion inhibitors for the mild steel in both E100 and E15 biofuels. The IE increased on increasing inhibitor concentration following the Langmuir and Temkin adsorption isotherms but decreased with immersion time which suggested that the corrosion inhibition mechanism is of physical type of adsorption of the leaves constituents on the mild steel surface. *A. marmelos* extract acted as an anodic type of inhibitor in E100 and E15, while *E. ganitrus* acted as mixed type inhibitor in E100 from the polarization and corrosion results.

ISSN: 2684-4478

DOI :10.24018/ejchem.2020.1.5.16

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Keywords: Anodic polarization, Biofuels, Corrosion test, Green inhibitor, Plant ingredients.

I. INTRODUCTION

The increasing industrialization and motorization of the world has led to a steep rise for the demand of petroleum-based fuels which are obtained from limited natural reserves. These finite reserves are highly concentrated in certain regions of the world. Therefore, those countries not having or limited these resources, Nepal for example, are necessary to look for alternative renewable biofuels, which can be produced from biomasses/wastages available within the country. In such circumstances, different types of biofuels might have been high possibility for a complete or partial replacement of the natural petroleum products in the future, because they have very close properties to that of the petroleum products and are environmentally ecofriendly [1], [2]. They provide an improvement of exhausts gas emissions from internal combustion engine of transport vehicles without any significant sacrifices in terms of energy conversion efficiency. An interesting finding of biofuel uses over the conventional fuel in aircraft is recently reported to minimize the emission of soot benefitting human health and the environment [3].

Among the biofuels, bioethanol, biodiesel and their blends are becoming one of the emerging renewable energy sources of many countries including in Nepal, because of its superior position over the non-renewable energy sources of petroleum products [4]. Major automotive companies in the most developed countries have been used flexible fuel vehicles (FFVs), whose fuel system and engine parts are designed to run at any bioethanol blends even up to almost 100 % bioethanol [5]. The components of the FFVs are made by those materials which are compatible even with the biofuels like flex bioethanol, biodiesel with petroleum products.

Bioethanol produced from different types of biomasses is becoming nowadays one of the promising renewable biofuels, unlike non-renewable petroleum-based fuels. Bioethanol blended fuel is generally used as a gasoline

PP43

INHIBITION EFFECT OF GREEN MATERIAL OF *VITEX NEGUNDO* LEAVES EXTRACT FOR CORROSION BEHAVIOR OF DIFFERENT METALLIC MATERIALS IN BIOFUELS AND THEIR BLENDS

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INTRODUCTION:

Nepal has prime policy to use renewable energy sources of biodiesel, bioethanol & their blends instead of non-renewable petroleum products recently.

However, biofuels & their blends are more corrosive than petroleum products to different metallic materials [1].

Therefore, it becomes important aspects for corrosion scientists to apply appropriate corrosion prevention methods in such biofuels.

Use of corrosion inhibitor is one of the most effective prevention methods against metallic corrosion even in different types of biofuels [2].

Many synthetic compounds were employed as corrosion inhibitors in the past, but most of them are quite toxic & do not fulfill environmental protection standards.

Therefore, it is urgent needs to develop new classes of natural green corrosion inhibitors, obtained from plant extracts to prevent the corrosivity of biodiesel & its blends towards different metallic materials.

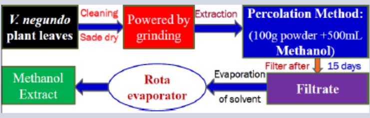
OBJECTIVE:

In this context, main objective of this work was to investigate the effects of different concentrations (i.e., 500-2000 ppm) of methanol extract of *Vitex negundo* plant leaf on the corrosion behavior of mild steel, aluminum & copper metals in pure biodiesel (B100), bioethanol (E100) and their blends, i.e., B10 & E15 with 90% petrodiesel (B0) and 85% petrol (E0), respectively, using immersion, inhibition efficiency & polarization tests at 25±2°C in airtight condition.

EXPERIMENTAL METHODS:

Sample Specimens: Mild steel, Pure Al & Cu metals having the size of (4 × 3 × 0.4) cm were mechanically polished using 200-1500 grit SiC paper in ethanol, rinsed with acetone & air-dried until the surface exhibited mirror like reflection in order to obtain reproducible results.

Preparation of Corrosion Inhibitor: Methanol extract of *V. negundo* [SIMALI in Nepali; Chaster tree in English] plant leaves were used as a green corrosion inhibitor.


V. negundo plant leaves → Cleaning, Sade dry → Powered by grinding → Extraction → Percolation Method: (100g powder +500mL Methanol) → Filter after 15 days → Filtrate → Evaporation of solvent → Rota evaporator → Methanol Extract

Average Corrosion Rate: weight loss method

$$\text{Corrosion Rate (mm/y)} = \frac{\Delta w\,(g) \times 87600}{d\,(g/cm^3) \times A\,(cm^2) \times t\,(hrs)}$$

Inhibition efficiency (IE%) &Surface coverage (θ):

$$IE_{CR,\%} = \frac{CR_{(o)} - CR_{(inh.)}}{CR_{(o)}} \times 100 \qquad \theta = \frac{CR_{(o)} - CR_{(inh.)}}{CR_{(o)}}$$

Inhibition Mechanism: Langmuir adsorption isotherm

$$\frac{C_{inh.}}{\theta} = \left(\frac{1}{K_{ads}}\right) + C_{inh.}$$

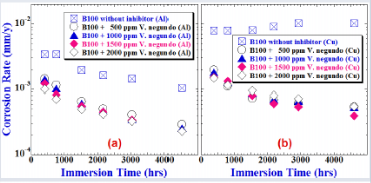
Where, $CR_{(o)}$ & $CR_{(inh.)}$ are corrosion rates with & without inhibitor, respectively; $C_{inh.}$ is concentration of inhibitor & K_{ads} is adsorptive equilibrium constant.

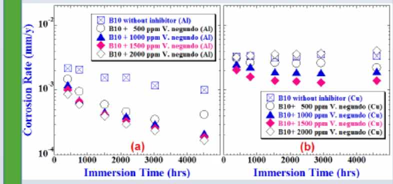
Anodic Polarization: carried out at scan rate of 30 mV/min. using a potentiostat/galvanostat (Hokuto Denki A-151 model)

RESULTS & DISCUSSION:

Corrosion Rate (CR):

- Corrosion rate (CR) of Al & Cu metals is decreased with increasing of *V. negundo extract* concentration in both B100 & B10 as shown below figures.

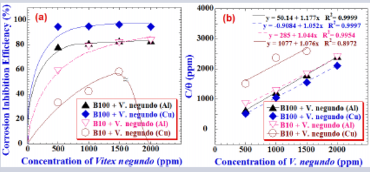




- CR of Al in B10 with 500-2000 ppm *V. negundo* is nearly one order of magnitude less than of Cu.

Corrosion Inhibition Efficiency (IE) & Mechanism:

- Inhibition efficiency (IE) is increased steeply with addition up to 500 ppm of the plant extract in B100 & B10 biofuels and maximum inhibition efficiency was obtained between 1000-2000 ppm in all cases except for copper in B10.
- Adsorption process was obeyed the Langmuir adsorption isotherm model to study the corrosion inhibition mechanism of Al & Cu metals by *V. negundo leaf* extract in both B100 & B10.



- % IE order of *V. negundo* plant extract in both B100 & B10 for Al & Cu metals are arranged as follows;

$$\%IE_{Cu\ in\ (B100+V.negundo)} = 96 > \%IE_{Al\ in\ (B100+V.negundo)} \geq \%IE_{Al\ in\ (B100+\ V.negundo)} = 83 > \%IE_{Cu\ in\ (B10+\ V.negundo)} = 58$$

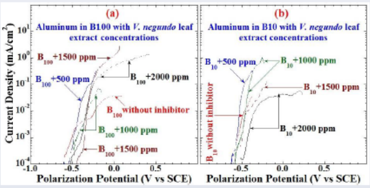
- It can be reasoned out from the above observed results of CR & %IE that the methanol fraction of the *T. cordifolia* plant leaves extract can be used as an additive in both biofuels of B100 and B10 for controlling of their corrosive nature towards aluminum and copper metals.

Potentiodynamic Polarization Curves:

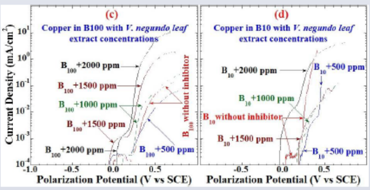
Anodic polarization measurement was carried out in both B100 & B10 in absence & presence of *V. negundo* leaf extract for a better understanding of passivity.

Anodic current density of Al is generally decreased with increasing of *V. negundo* extract concentrations in B100 as well corrosion potential is shifted to noble direction with increasing of extract concentrations [Figs (a) & (c)].

- Such results indicate that *V. negundo* leaf extract acts as an anodic type of corrosion inhibitor for aluminum metal in both B100 & B10 biofuels.



On the other hand, there is no regular trend of the change of the anodic current density & corrosion potential with concentration of the *V. negundo* extract additions in both B100 & B10 [Figs (b) & (d)], although corrosion rate is found to be decreased with increasing of plant extract concentrations as discussed above.



Results disclosed that the *V. negundo* plant extract acts as a mixed type of inhibitor for copper corrosion in both B100 & B10.

CONCLUSIONS:

- ✓ Estimated corrosion rate of Al & Cu metals in B100 & B10 is found higher than that of the corrosion rate of both metals in B0.
- ✓ In particular, the corrosion resistant properties of Cu in B100 & B10 is nearly one and half to two orders of magnitude higher than in B0 at 25±2°C in airtight condition.
- ✓ Trend of the inhibition activity of methanol extract of V. *negundo* for Al & Cu in B100 & B10 is in order of $\%IE_{(Cu\ in\ B100)} > \%IE_{(Al\ in\ B100)} > \%IE_{(Al\ in\ B10)} > \%IE_{(Cu\ in\ B10)}$.
- ✓ *V. negundo* leaves extract can be used as a good green corrosion inhibitor to increase the corrosion resistance properties of different vehicular metallic materials.
- ✓ *V. negundo* extract acts as anodic & mixed types of corrosion inhibitor for Al & Cu, respectively, in B100 & B10.

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The 8th Asian Conference on Colloid & Interface Science 2019 (ACCIS 2019), Sept 24-27, Kathmandu

*The 8th Asian Conference on Colloid & Interface Science (**ACCIS 2019**), Sept 24-27, 2019, **Abstract No. pp43** (pp. 173-174), Pulchowk Campus, Kathmandu, Nepal*