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

ORIGINAL ARTICLE

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

Prakash Katuwal, Ramesh Regmi, Susan Joshi, and Jagadeesh Bhattarai

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.

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

Published Online: September 21, 2020

ISSN: 2684-4478

DOI :10.24018/ejchem.2020.1.5.16

Prakash Katuwal
Central Department of Chemistry, Tribhuvan University, Kirtipur, Nepal.
(e-mail: prakash.kc319@gmail.com)

Ramesh Regmi
Central Department of Chemistry, Tribhuvan University, Kirtipur, Nepal.
(e-mail: regmiramesh945@gmail.com)

Susan Joshi
Central Department of Chemistry, Tribhuvan University, Kirtipur, Nepal.
(e-mail: susanjoshi68@gmail.com)

Jagadeesh Bhattarai*
Central Department of Chemistry, Tribhuvan University, Kirtipur, Nepal.
(e-mail: bhattarai_05@yahoo.com)

**Corresponding Author*

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

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

additive in ordinary vehicles in most parts of the world, where the fuel system and engine parts are mostly composed by the metallic substances like iron, copper and aluminum, and their alloys so on [6]. The global bioethanol industry has witnessed high growth primarily because of the mandatory usage of bioethanol fuel blends, especially in transportation vehicles in many countries those are looking for an alternative fuel source with less 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 [7].

Bioethanol is mostly used in Brazil where about 20 % of cars burnt pure bioethanol (E100) and the rest of the car fleet has been adapted to use bioethanol-gasoline blends [8]. Also they want to achieve energy security by reducing their dependence on petroleum products [9]. It reported that bioethanol blends up to 20 % mixing with petrol could be used as biofuels without modifying of the existing vehicle engines [10]. It can run at a much higher exhaust gas recirculation rate and with higher compression ratios in spark ignition (SI) engines. Bioethanol blends serve as an oxygenation additive and help to increase the octane number of the fuel while simultaneously reduce the greenhouse gas emissions and other environmental pollutants [11] and hence the bioethanol and its blends are called good sources of the ecofriendly renewable energy.

Previous studies verified a good performance of vehicle engines when using hydrated bioethanol instead of gasoline for aluminum metal [12], as well as a decreased in the emission of greenhouse gases [13]. An important point to keep up in mind when selecting such renewable energy of the bioethanol fuels for the use and transport is their corrosion properties. These biofuels and their blends are reported to be more corrosive than the petroleum products to the vehicles engine and fuel storage parts made by such metallic substances [14]−[22]. Besides, various types of corrosion problems, such as pitting, crevice corrosion, and stress corrosion crack might be existed in ethanol production process and hence it is suggested the diamond like coating (DLC) on steel container which use for the ethanol production [23].

In general, presence of small amounts of water, methanol, sulfur, sulfate, chloride so on are some of the triggering factors for the bioethanol and its blends corrosion to various metallic materials. Even a small water droplet might be a primary corrosion provoking factors in bioethanol blends and it was reported in the literature that the critical water concentration for the corrosion of stainless steel depended on the ratio of bioethanol and commercial gasoline [24], [25]. Bioethanol-gasoline blends can easily absorb large amounts of water because of the presence of bioethanol. Hence it reported that the E60 blend showed the highest corrosion activity in most cases [26]. In contrast, it reported that 0.05 to 0.1 % of water contents in bioethanol was found to be sufficient for the formation of protective oxide film on the surface of aluminum metal and it inhibited further corrosion process [27]. Similarly, oxygen was reported to be a primary contributor for the occurrence of the stress corrosion cracking in ethanol [28].

There are insufficient numbers of literatures providing information on the corrosive nature of bioethanol and its blends to various metallic materials. A study showed localized type of pitting corrosion on aluminum alloy in bioethanol blend of E10 at 100 °C [29] 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 [30]. Similarly, it was reported that the increase in the bioethanol content from E10 to E20 or higher resulted non-linear corrosive effect on aluminum alloys [31] and in another study, pits and cracks were observed on the surface of AISI 4140 steel due to the decrease in oxidation stability of the bioethanol fuel [10]. The feasibility of bioethanol and biodiesel feed stocks, the compatibility of both bioethanol and biodiesels, and their blends to vehicle engines are recently reviewed [16]. Corrosion rate of metals in bioethanol blends with biodiesel and petro-diesel BDE was reported in the order: aluminum < mild steel < copper at both room and 60 °C temperatures [32]. In many instances, bioethanol is blended with gasoline in order to improve the chemical, physical as well as the corrosion resistance properties of the bioethanol fuel and to reduce the materials incompatibility and making it suitable for the automotive parts.

As such, uses of biocompatibility and eco-friendly plant extracts as green corrosion inhibitors in biofuels and their blends are currently becoming one of the subjects of research for metals protecting against their corrosion which are exposed in biofuels, because researchers proved that different plant extracts showed a synergistic effect for minimizing of metals/alloys corrosion in different aggressive environments except in biofuels [33]−[40]. Corrosion scientists feel that the uses of different phytoconstituents originated from plant parts could be an effective anticorrosion additive for biofuels to minimize/control their corrosive nature to metals/alloys, although a very few research works had reported the effects of some plant extracts as the corrosion-resistant additives in biodiesel [15], [41]−[45], bioethanol [46]−[48], and their respective blends.

Further studies on the effectiveness of different additives as green corrosion inhibitor, obtained from versatile plant parts such as; leaves of *Vitex negundo*, *Catharanthus roseu*, *Aegle marmelos* and *Elaeocarpus ganitrus* extracts are projected in this study to decrease the corrosiveness of bioethanol and its 15 % blend. The leaf, out of all parts of the plant, has the utmost preference for its abundance of phytochemicals (active components) produced through synthesis, which acts similarly to commercial inhibitors although extract of other parts of plants, i.e., root, stem, bark, seed etc have contributed to the inhibition efficiency.

Vitex negundo (English: Chaster tree & Nepali: SIMALI) belonging to 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 [49]. 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 [50]. Moreover, the methanol extracts of *V. negundo* leaves collected from different parts of the world had yielded polar organic phyto-constituents like phenols, alkaloids, steroids, glycosides, flavonoids and so on [51]−[53].

On the other hand, *Catharanthus roseus*, Periwinkle in English and SADABAHAR in Nepali belonging Apocynaceae family, is a 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 [54]. *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, lymphogranulomatosis and in solid infant tumors so on [55], [56]. It contains several functional entities such as fused heterocycles, hydroxyl and carbonyl groups which enhanced the corrosion inhibition action for mild steel in NaCl [57] and HCl [58] media.

Similarly, *Aegle marmelos* (BEAL in Nepali belonging to Rutaceae family), a moderate-sized, slender and aromatic tree growing in tropical to subtropical climates, is famous for its folk medicinal values in the most South Asian countries including Nepal. The methanol extract of *A. marmelos* leaf revealed the presence of more than three dozens of biologically active chemical constituents such as alkaloids, flavonoids, alcohols, aldehydes, aromatic compounds, fatty acid methyl esters, terpenoids, phenolics and steroids [59]−[63], whereas the potential pharmacological activities of the leaf extracts are reported to be hypoglycemic, anti-inflammatory, antimicrobial, anticancer, radioprotective, chemopreventive and anti-oxidative activity so on [64]−[67].

Besides, *Elaeocarpus* family has about 360 species worldwide and out of this, 26 species are reported in Nepal alone [68]. *E. ganitrus* is one among these 26 species of *Elaeocarpaceae* family plant which is evergreen broad-leaved tree [69], and found mostly in Eastern hilly districts of Nepal. Its fruits and leaves are known for various medicinal values and used in traditional Ayurveda for the treatment of various diseases. It was reported that seven *Elaeocarpus* species contained alkaloids, flavonoids and other phenolic constituents in their leaves [70]−[72]. It was also reported that 85 % of the antioxidant properties of the methanol/ethanol extract of *E. ganitrus* leaves was reported due to the contribution of phenolic and flavonoid components [73].

However, it has not yet reported one of the promising aspects of these four 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 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 [35], [74]−[76]. For examples, the corrosion inhibitive performance of *V. negundo* leaf extract in nitric acid for copper metal [37] and in alkaline solution for aluminum metal [74] was investigated. The phytochemicals of *C. roseus* extract were tested as good corrosion inhibitor for mild steel in aqueous 3.5 % NaCl [37], [57] and 1 M HCl [58] solutions.

Previous findings suggested that the compounds derived from *A. marmelos* fruit extracts are effective green corrosion inhibitors for carbon steel in HCl acid. In such circumstances, this research work aimed to carry out the assessment study on the effects of methanol extracts of *Vitex negundo, Catharanthus roseu, Aegle marmelos* and *Elaeocarpus ganitrus* plants on the mild steel corrosion in pure bioethanol (E100) and its 15 % blend (E15) with 85 % Euro-4 grade gasoline E100 using static corrosion rate, inhibition efficiency and electrochemical tests in airtight glass container at 25±2° C.

II. Materials and Methods

A. Preparation of Sample Coupon and Plant Extract

Mild steel sample specimens having the size of about 3 cm × 2 cm × 0.5 cm were prepared for static immersion, inhibition and electrochemical tests. Chemical components of the mild steel specimen are approximately as (wt %); C=0.17, P=0.05, Si=0.04, Mn=0.90, S=0.05 and balance by iron [37]. Surface of each specimen was mechanically polished using 200-1500 grit numbers SiC paper in ethanol, rinsed with acetone and air-dried until the surface exhibited mirror like reflection in order to obtain reproducible results.

Commercially available pure bioethanol (E100) and Euro-4 grade gasoline (E0), and their blend (E15) containing 15 % (v/v) bioethanol with gasoline were used as precursors for the preparation of electrolytes containing 500, 1000, 1500 and 2000 ppm of each four plants extract for electro-corrosion tests. The methanol extracts of the dried leaf powder of each plant of *V. negundo*, *C. roseu*, *A. marmelos* and *E. ganitrus* were obtained by Soxhlet extraction method and the extracts were added in E100 and E15 as green corrosion inhibitors.

B. Study of Corrosion Inhibition and Mechanism

Average uniform corrosion rate (millimeter/year) of the mild steel specimens in both E100 and E15 in absence and presence of 500, 1000, 1500 and 2000 ppm of each four plants extract was estimated at different exposure time durations using equation (1) [77], where Δw, d and A are the weight loss, density, area of the sample specimens, respectively, and t is immersion time. For comparison, the average corrosion rate of the mild steel in E0 was also estimated. The static immersion test for the determination of the average corrosion rate of the sample specimens was carried out in an airtight glass containers filled with each 100 mL electrolytic solution at temperature of 25±2 °C.

$$\text{Corrosion Rate (mm/y)} = \frac{\Delta w(g) \times 87600}{d(g/cm^3) \times A(cm^2) \times t(hr)} \quad (1)$$

Corrosion inhibition efficiency ($IE_{\%}$) and degree of surface coverage (θ) were obtained from corrosion data using equations (2) and (3), respectively [78], in absence

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

(CR_o) and presence (CR_{PE}) of different concentrations of each plant extract (PE). It is worthy to cite here that all the calculations of θ from the corrosion rates are based on the belief that the plant extract used as corrosion inhibitor totally prevents metal dissolution from the covered surfaces of the corroded metals [79]. The corrosion inhibition process was studied using both adsorption isotherms of Langmuir [80] and Temkin [81] relations, as equations (4) and (5), respectively.

$$IE_{\%} = \frac{CR_o - CR_{PE}}{CR_o} \times 100 \quad (2)$$

$$\theta = \frac{CR_o - CR_{PE}}{CR_o} \quad (3)$$

$$\frac{C_{PE}}{\theta} = \left(\frac{1}{K_{ads}}\right) + C_{PE} \quad (4)$$

$$\theta = \frac{(2.303 \times RT)}{b} \log K_T + \frac{2.303 \times RT}{b} \log C_{PE} \quad (5)$$

where, C_{PE} is the plant extract concentration and K_{ads} is the adsorptive equilibrium constant, K_T is Temkin isotherm constant, R is gas constant and T is absolute temperature, and b is Temkin constant which is related to the heat of adsorption. The plot of θ versus log C_{PE} gives a straight line that would confirm Temkin adsorption isotherm and this model takes into account the effect of indirect adsorbate-adsorbent interactions on the adsorption process. It is also assumed that heat of adsorption of all inhibitor molecules of plant extract in the layer decrease linearly as a result of θ increases [82].

C. *Polarization Measurement*

Polarization tests of the mild steel specimens was carried out in bioethanol and it 15 % blend in absence and presence of plant extract concentrations 25° C, open to air using a Hokuto Denki A-151 model potentiostat / galvanostat. The potentiodynamic polarization measurement was carried out at 30 mV/min sweep rate after 30 minutes immersion in the respective electrolytic solutions. The mechanically polished mild steel specimens, a saturated calomel electrode (SCE) and platinum mesh were used as working, reference and auxiliary electrodes, respectively, and thence the unit of all potential hereafter is expressed with reference to SCE.

III. Results and Discussion

A. *Effect of Plant Extract on Corrosion Inhibition and Mechanism*

Estimated average corrosion rate of the mild steel in E0 is remarkably lower than in E100 and E15 after exposure times up to 2330 hours at 25±2 °C in air tight condition, as depicted in Fig. 1. The corrosion resistance property of the mild steel is in the order: E100 < E15 < E0. With increasing the bioethanol concentration in gasoline the corrosion rate of mild steel is increased with increasing the bioethanol concentration in commercial petrol (gasoline). The result indicates that pure bioethanol has the greatest susceptibility to corrosion for 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, and the resulting biofuel becomes more corrosive [26].

Similar behavior of the corrosive degradation of metals in biodiesel-petrodiesel-bioethanol blends was reported lower than pure biodiesel, whereas higher than petrodiesel [83]. In another studies, the increase of water concentration in fuel-grade ethanol prompted the pitting corrosion loss of different types of steel [84]. Results showed that the water in the ethanol strongly influenced the surface film stability and interface electrochemistry in ethanolic environments. To minimize such type of high corrosivity of bioethanol and its blends and bring close to that of gasoline at the minimum or less, present work further study the effects of four different plants extract in both E100 and E15 to reduce their corrosivity rate for the mild steel. Hence, the effect of 500, 1000, 1500 and 2000 ppm of the methanol extract of each *V. negundo, C. roseu, A. marmelos* or *E. ganitrus* leaves in both E100 and E15 was studied to know the corrosion behavior of mild steel using immersion, inhibition efficiency and polarization tests.

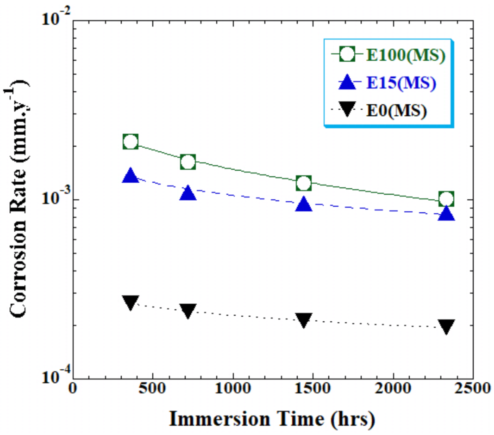

Fig. 1. Change in corrosion rate of the mild steel (MS) in E100, E15 and E0 at 25±2 °C in airtight condition, as a function of immersion time.

Corrosion rate of the mild steel is decreased to a large extent with increasing the amounts (i.e., 500, 1000, 1500 and 2000 ppm) of *V. negundo* extract in E100 at 25±2 °C in air tight condition which is also lower corrosion rate than in E100 and even lower than in E0, as shown in Fig. 2. Furthermore, the corrosion resistance property of the mild steel is increased with increasing the exposure time up to 2330 hours in all electrolytic solutions.

The similar synergistic effect of lower corrosion-resistant of the mild steel in E100 and E15 biofuels with additions 1000-2000 ppm *V. negundo* plant extract than in pure gasoline (E0) was observed from the estimated average corrosion rates at different immersion times, as summarized in Table I. However, the corrosion rate of the mild steel in E100 and E15 with additions of 500-2000 ppm of *C. roseus, A. marmelos* and *E. ganitrus* plant extracts did not lowered that in E0, although they enhanced remarkably the corrosion resistance property in both biofuels. These results revealed that leaf extract of each four plants act as a good green-based inhibitor to minimize/control the electrochemical corrosion of mild steel in E100 and E15 at room temperature.

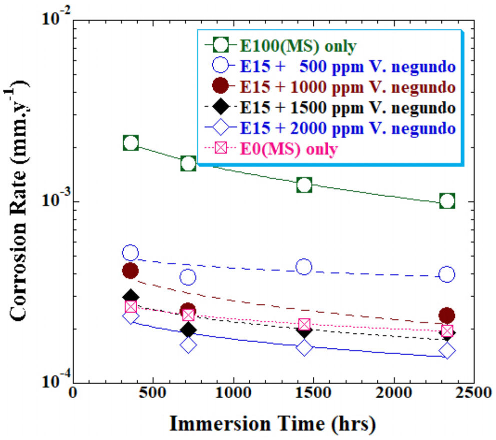

Fig. 2. Change in corrosion rate of the mild steel in E100 without and with different amounts of *V. negundo* extract at 25±2 °C in airtight condition, as a function of immersion time.

As a further matter, changes in the corrosion inhibition efficiency (IE) of each four green-based plants extract on the mild steel in E100 and E15 biofuels was studied and the results are depicted in Figs 3(a) and 3(b). In the addition up to 500 ppm of the plant extract in both biofuels, the IE is increased in most cases at a steep angle and it is found to be increased with further increase of the plant extract concentration up to 2000 ppm. Maximum IE in 2000 ppm addition of each *V. negundo*, *C. roseus*, *A. marmelos* and *E. ganitrus* extract in E100 for mild steel was found about 89%, 75%, 70 % and 51%, respectively, while it was about 86%, 72%, 57% and 40%, respectively, in E15 blend, as shown in Fig. 3(a) and 3(b).

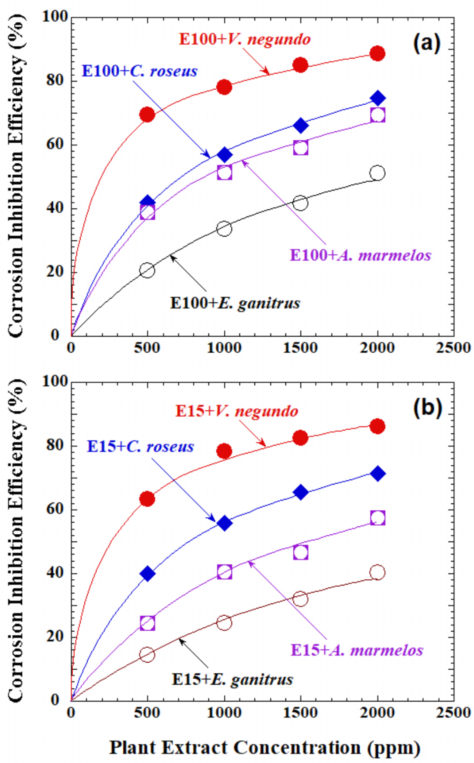

Fig. 3. Changes in the corrosion inhibition efficiency for mild steel after its exposure for 2330 hours in (a) E100 and (b) E15 at 25±2 °C, as a function of the concentration of four plants extract.

Consequently, the corrosion inhibition efficiency of the methanol extracts of these plant species in E100 and E15 for the mild steel is arranged in order as; $IE_{(E100+V.negundo)} \geq IE_{(E15+V.negundo)} > IE_{(E100+C.roseus)} \geq IE_{(E15+C.roseus)} > IE_{(E100+A.marmelos)} > IE_{(E15+A.marmelos)} > IE_{(E100+E.ganitrus)} > IE_{(E15+E.ganitrus)}$. 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 of their corrosive nature to mild steel, while *E. ganitrus* leaf extract assumed to be least effective corrosion inhibitor among the used four plants extract. These results are in agreement with the results of corrosion tests, as depicted above in Fig. 2 as well as summarized in Table I.

Furthermore, for *V. negundo* and *C. roseus* plants extract, the IE values in both E100 and E15 biofuels are comparable and almost same, even a very slightly lower in E15 than in E100, as shown in Fig. 4. This means both *V. negundo* and *C. roseus* plant extracts have almost the same degree of corrosion inhibition effect to increase the corrosion resistance properties of the mild steel in pure bioethanol and its 15 % blend at room temperature. However, to some extent, the remaining two plants (i.e., *A. marmelos* & *E. ganitrus*) extract has remarkably higher IE activities in E100 than in E15.

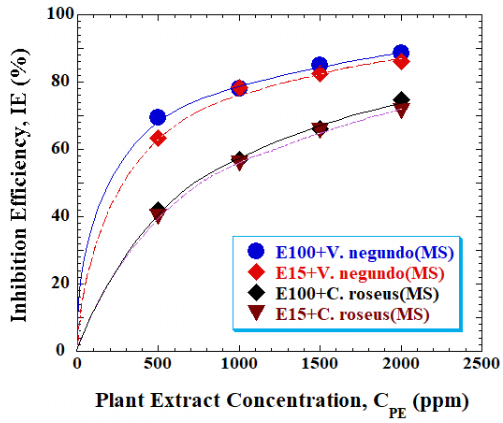

Fig. 4. Comparable corrosion inhibition efficiencies of *V. negundo* and *C. roseus* extracts in E100 and E0 biofuels for mild steel.

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 hetero atoms and aromatic ring compounds as the major phyto-constituents in these two plants comparison with the remaining *A. marmelos* and *E. ganitrus* plants. For example, abundant amounts of eight major ring compounds of flavonoids reported in methanol extract of Nepal origin *V. negundo* leaf in literature [50]. 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 [55].

TABLE I: ESTIMATED CORROSION RATE OF MILD STEEL IN BIOETHANOL AND ITS BLEND WITH AND WITHOUT FOUR PLANTS EXTRACT CONCENTRATION

Extract concentration, C_{PE} (ppm)	Time (hrs)	CR_{E100} (mm/y)	CR_{E15} (mm/y)	CR_{E0} (mm/y)						
0	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*			*A. marmelos*		*E. ganitrus*	
		CR_{E100} (mm/y)	CR_{E15} (mm/y)	CR_{E100} (mm/y)	CR_{E15} (mm/y)	Time (hrs)	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	360	0.00092	0.00079	0.00112	0.00098
	1008	0.00036	0.00038	0.00079	0.00051	720	0.00069	0.00067	0.00102	0.00089
	1344	0.00031	0.00043	0.00076	0.00053	1440	0.00062	0.00065	0.00087	0.00077
	1824	0.00031	0.00040	0.00074	0.00049	2330	0.00062	0.00064	0.00080	0.00072
	2330	0.00031	0.00031	0.00059	0.00051					
1000	336	0.00041	0.00042	0.00092	0.00060	360	0.00078	0.00074	0.00099	0.00088
	1008	0.00024	0.00025	0.00056	0.00042	720	0.00059	0.00061	0.00086	0.00077
	1344	0.00023	nd	0.00054	0.00035	1440	0.00054	0.00059	0.00074	0.00071
	1824	0.00022	0.00024	0.00049	0.00036	2330	0.00049	0.00051	0.00067	0.00064
	2330	0.00022	0.00018	0.00044	0.00037					
1500	336	0.00028	0.00030	0.00081	0.00059	360	0.00064	0.00057	0.00076	0.00069
	1008	0.00020	0.00020	0.00044	0.00040	720	0.00054	0.00050	0.00074	0.00067
	1344	**0.00019**	0.00020	0.00036	0.00032	1440	0.00050	0.00047	0.00064	0.00063
	1824	**0.00017**	**0.00019**	0.00037	0.00032	2330	0.00041	0.00045	0.00059	0.00058
	2330	**0.00015**	**0.00015**	0.00034	0.00029					
2000	336	0.00021	0.00024	0.00056	0.00056	360	0.00048	0.00042	0.00069	0.00064
	1008	**0.00015**	**0.00016**	0.00039	0.00032	720	0.00040	0.00038	0.00061	0.00056
	1344	**0.00015**	**0.00016**	0.00031	0.00031	1440	0.00038	0.00036	0.00056	0.00053
	1824	**0.00013**	**0.00015**	0.00029	0.00027	2330	0.00031	0.00036	0.00050	0.00051
	2330	**0.00012**	**0.00012**	0.00026	0.00024					

C_{PE}=Concentration of plants extract as inhibitor; nd=not determined; CR=corrosion rate; E100=bioethanol; E15=15% bioethanol blend

For the effectual use of corrosion inhibitors, it is important to know their action mechanism for the materials in the given environments. To choose an efficient inhibitor, it is necessary to consider several factors including environment properties, inhibitory properties, the potential presence of anticorrosion agents, and others. For such reasons, various adsorption isotherm equations are practically applied for better understanding of the corrosion inhibiting actions to metals by plant extracts in corrosive electrolytes [82], [85]. Langmuir and Temkin isotherms are some of the simplest adsorption models which describe the molecular interaction between the inhibitor molecules and the active surfaces of the corroded metallic materials based on the assumption that all adsorption sites are equivalent and the particle binding occurs independently from nearby sites being occupied or not [80], [81].

Specially, the Temkin isotherm model presumes as: the heat of adsorption of the surface molecules decreases linearly rather than logarithmically with coverage, the adsorption process is characterized by a uniform distribution of binding energies at the adsorbent surface and this model covers the adsorbate-adsorbent interaction [86], [87]. The liner forms of the Langmuir and the Temkin adsorption equations, as given above in equations (4) and (5), respectively, were applied to explain the inhibition mechanism of the plant extract for the mild steel corrosion control in both E100 and E15 biofuels.

Fig. 5(a) and 5(b) show the Langmuir adsorption plots for the mild steel in both E100 and E15 with 500-2000 ppm of each four plant extracts, respectively, which were obtained by plotting the ratio of the extract concentration (C_{PE}) to surface coverage (θ) and the C_{PE}. A linear correlation coefficient (R^2) is almost equal to unity in all cases which indicate that the adsorption process obeys Langmuir adsorption isotherm to study the corrosion controlling mechanism of the mild steel by the green-based plant extracts in both biofuels of E100 and E15 at 25±2 °C in airtight condition.

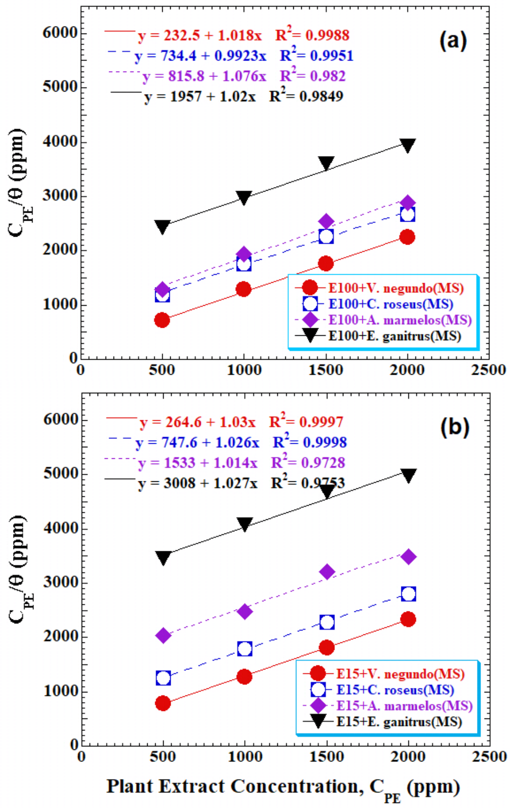

Fig. 5. Langmuir isotherm plots for the mild steel in (a) E100 and (b) E15 biofuels with different concentrations of plant extracts after immersion for 2330 hrs at 25±2 °C in airtight condition.

Furthermore, favorability of such adsorption process was confirmed from the calculation of a dimensionless

ORIGINAL ARTICLE

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

separation factor (R_L) [88], 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 the four plants extract can be explained by the formation of a stable and diffusion barrier metal-oxide layer formed on the surface the mild steel samples at 25±2 °C in airtight condition.

Similarly, plot of θ versus log C_{PE} gave a straight line which could confirm the Temkin adsorption isotherm for the adsorption of *V. negundo*, *C. roseus*, *A. marmelos* and *E. ganitrus* extracts as green-based inhibitors in E100 and E15 at 25±2 °C in airtight condition, as shown in Fig. 6(a) and 6(b), respectively. This implies that the adsorption behavior of such plant extracts on the surface of the mild steel is described by Temkin isotherm. In fact the applicability of Temkin adsorption isotherm verified a monolayer adsorption of the green inhibitors on the uniform surface of mild steel [35], [81]. 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 corrosion inhibitors of *V. negundo*, *C. roseus*, *A. marmelos* and *E. ganitrus* plant extracts in E100 and E15 biofuels.

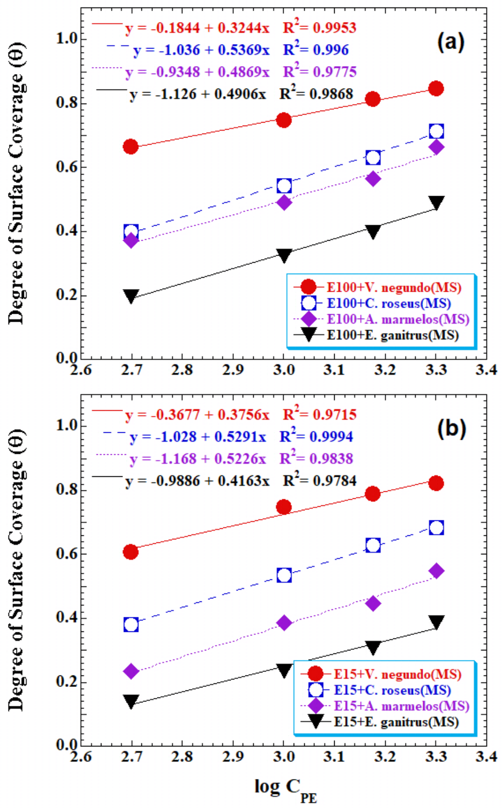

Fig. 6. Temkin isotherm plots for the mild steel in (a) E100 and (b) E15 biofuels with different concentrations of plant extracts after immersion for 2330 hrs at 25±2 °C in airtight condition.

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 from their corrosion by forming a barrier layers [89], 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 [90]. 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 [91].

B. Polarization Study

Dynamic test of the potentiodynamic polarization in additions of the static corrosion tests was also carried out in both E100 and E15 without and with the extract concentration for a comprehensive knowledge about the passivity of the mild steel. Fig. 7 shows the anodic polarization curves of the mild steel in E100 and E15 fuels at 25 °C. Corrosion potential (ϕ_{corr}) of the sample specimen in E100 is slightly noble direction than in E15. Anodic current density is lower in E100 than in E15 indicating a more stable anodic passive film formed on the surface of mild steel in pure bioethanol than its 15 % blend. However, the corrosion resistance property of the mild steel in E100 was slightly higher than in E15 blend as shown above in Fig. 1. These results indicated that the improvement of the corrosion resistance properties of the mild steel in E15 bioethanol blend is mostly controlled by the cathodic reactions. In previous works, similar behavior of mild steel degradation in bioethanol and it blends [26], and aluminum and copper metals in pure biodiesel and its 10 % blend [15] described.

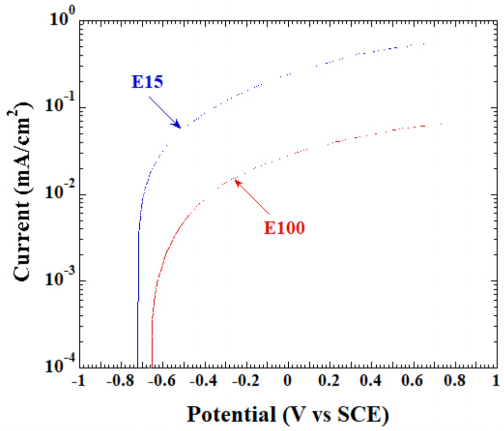

Fig. 7. Anodic polarization curves for mild steel specimen in E100 and E15 at 25 °C.

Influences of 500-2000 ppm of the green-based plant extracts in E100 and E15 on the anodic passivity of mild steel were studied at 25 °C, and the results are summarized in Fig. 8 and 9. Figures 8 (a) and 8(b) show the effect of the methanol extract of *A. marmelos* plant on the passivation of the mild steel in E100 and E15 biofuels, respectively. The ϕ_{corr} of the mild steel specimen shifted slightly to the noble direction with the addition of 500-2000 ppm *A. marmelos* extract in both biofuels of E100 and E15. Also, the anodic current density is decreased with increasing the *A. marmelos* concentrations in both E100 and E15 biofuels. The lowest current density observed for the mild steel in both biofuels with the additions of 1500 ppm and 2000 ppm of the plant extract. Consequently, it can be said that the anodic passivity of the mild steel is enhanced and a stable anodic passive film is formed on the surface of it in both E100 and

E15 biofuels with the additions of different concentrations of the green-based *V. negundo* extract as an effective corrosion inhibitor.

However, as shown in Fig. 8(b), the anodic passivity of the mild steel is significantly enhanced only to a certain anodic polarization beyond which trans-passive dissolution of the passive film formed on the surface of mild steel took place. Substantially, the results of corrosion potential shifting to noble direction, and decreases of the anodic current density as well the corrosion rate with the addition of 500-2000 ppm *A. marmelos* extract concentrations revealed that the plant extract acts as an anodic type of green-based inhibitor for mild steel corrosion in both biofuels of E100 and E15 at 25 °C.

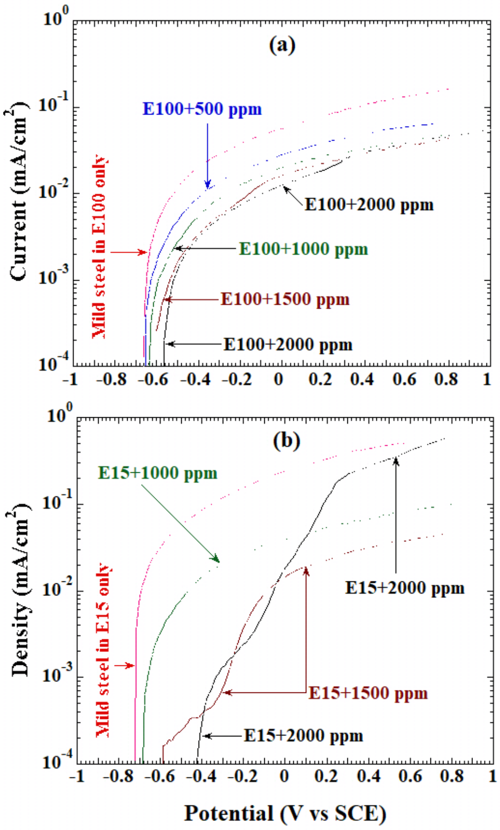

Fig. 8. Effects of *Vitex negundo* plant extract on the anodic passivation of the mild steel in (a) E100 and (b) E15 at 25 °C.

Similarly, the effects of 500, 1000, 1500 and 2000 ppm of *E. ganitrus* leaf extract on the anodic passivity of the mild steel in E100 at 25 °C was studied using potentiodynamic polarization measurements. The ϕ_{corr} of the mild steel is shifted to more positive direction and shows lowest current density with the addition of 500 ppm *E. ganitrus* extract in E100. Furthermore additions of 1000 ppm, 1500 ppm and 2000 ppm *E. ganitrus* extract in E100, the corrosion potential is slightly shifted to less noble ϕ_{corr} value and the current density is also slightly increased with increasing the extract concentrations than in 500 ppm. However, the ϕ_{corr} and the current density values are located between those in E100 without and with 500 ppm *E. ganitrus* extract concentration, as shown in Fig. 9. Consequently, it can be said that the anodic passivity of the mild steel is enhanced and a more stable anodic passive film is possible to form in E100 with 500 ppm *E. ganitrus* extract.

It is noticed from the static immersion tests as shown above in Fig. 4 that the corrosion rate of the mild steel increases with the additions of 500 to 2000 ppm of the plant extract in E100. These results revealed that the extract of *E. ganitrus* function as a mixed type inhibitor to control the mild steel corrosion in E100 at room temperature. Much alike behavior of the inhibitive effects of *Ficus carica* leaves extract in petroleum [92] and root extract of *Alkana tinctoria* plant in 0.5 M H_2SO_4 solution [93] on steel reported which showed the maximum corrosion inhibition efficiency of 70-80 % followed by Langmuir adsorption isotherm and acted as mixed type inhibitors.

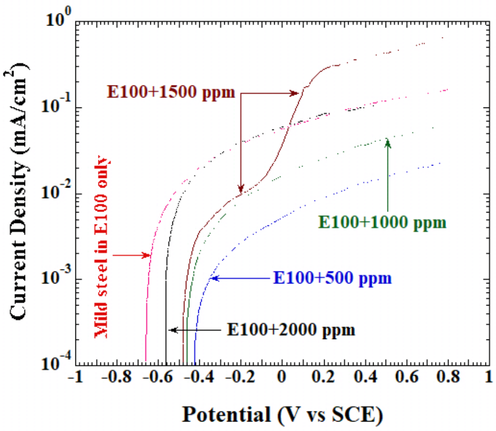

Fig. 9. Effects of the methanol fraction of *Elaeocarpus ganitrus* leaf extract on the passivity of the mild steel in E100 at 25 °C.

IV. Conclusion

Inhibition effect of the methanol extract of four Nepal origin plants (i.e., *Vitex negundo*, *Catharanthus roseus*, *Aegle marmelos* and *Elaeocarpus ganitrus*) on the corrosion susceptibility to mild steel was investigated in E100 and E15 biofuels at 25±2° C in airtight condition using static immersion, inhibition mechanism and anodic polarization test. Following outcomes of the present investigation are point wisely summarized as.

1. Corrosion-resistant property of the mild steel in pure gasoline (E0) is remarkably lower than in bioethanol and its blend with 85 % gasoline. 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. The leaf extracts of all four plants 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 and its blend at room temperature in airtight condition.
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 the four 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 % > $IE_{(E100+A.marmelos)}$=70% > $IE_{(E15+A.marmelos)}$=57 % >

IE$_{(E100+E.ganitrus)}$=51 % > IE$_{(E15+E.ganitrus)}$=40 %, indicates that the methanol extract of *V. negundo* leaf as comparson with other three plants extracts could be used as an efficient additive in both E100 and E15 biofuels to control their corrosive nature significantly to the mild steel.

6. *C. roseus*, *A. marmelos* and *E. ganitrus* extracts have also good anti-corrosion properties for mild steel in bioethanol and its blend fuels at room temperature in airtight condition.
7. The electrochemical corrosion and polarization studies suggested that extract of the *E. ganitrus* leaf acts as a mixed type of the green-based corrosion inhibitor in E100 at room temperature, while the *A. marmelos* extract acts as an anodic type inhibitor to control the mild steel corrosion in both E100 and E15 fuels at 25 °C.
8. All the obtained results agree that the four 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 with gasoline.
9. Future research needs to expand more for utilization of these plant extracts as biofuels additives are also envisioned.

Acknowledgment

The University Grants Commission-Nepal, Sanothimi, Bhaktapur is highly acknowledged for providing the UGC Master Research Support to RR (MRS-75-76-S&T-31) and PK (MRS-73-74-S&T-38) to carry out this research work in the Central Department of Chemistry, Tribhuvan University, Nepal.

References

[1] Haseeb, A. S. M. A., Fazal, M. A., Jahirul, M. I., and Masjuki, H. H. (2011). Compatibility of automotive materials in biodiesel: a review. *Fuel* 90(3):922-931. https://doi.org/10.1016/j.fuel.2010.10.042.

[2] Torsner, E. (2010). Solving corrosion problems in biofuels industry. *Energy Materials* 5(2):42-48. doi:10.1179/147842209X12579401586726.

[3] Kumal, R. R., Liu, J., Gharpure, A.,1, Vander Wal, R. L., Kinsey, J. S., Giannelli, B., Stevens, J., Cullen Leggett, C., Howard, R., Forde, M., Zelenyuk-Imre, A., Suski, K., Payne, G., Manin, J., Bachalo, W., Frazee, R., Onasch, T. B., Freedman, A., Kittelson, D. B., and Swanson, J. J. (2020). Impact of biofuel blends on black carbon emissions from a gas turbine engine. *Energy Fuels* 34(4):4958-4966. http://dx.doi.org/10.1021/acs.energyfuels.0c00094.

[4] Erdiwansyah, Mamat, R., Sani, M. S. M., Sudhakar, K., Kadarohman, A., and Sardjono, R. E. (2019). An overview of higher alcohol and biodiesel as alternative fuels in engines. *Energy Reports* 5:467-479. https://doi.org/10.1016/j.egyr.2019.04.009.

[5] Martini, G., Astorga, C., Adam, T., Farfaletti, A., Manfredi, U., Montero, L., Krasenbrink, A., Larsen, B., and De Santi, G. (2011). Effect of fuel ethanol content on exhaust emissions of a flexible fuel vehicle. JRC Report, European Commission Joint Research Centre Institute for Environment and Sustainability. https://doi.org/10.2788/39589.

[6] Nguyen, X. P., and Vu, H. N. (2019). Corrosion of the metal parts of diesel engines in biodiesel-based fuels. *International Journal of Renewable Energy Development* 8(2):119-132. https://doi.org/10.14710/ijred.8.2.119-132.

[7] Bisiga, C., Rothb, M., Müllerb, L., Comtec, P., Heebd, N., Mayere, A., Czerwinskic, J., Petri-Finka, A., and Rothen-Rutishausera, B. (2016). Hazard identification of exhausts from gasoline-ethanol fuel blends using a multi-cellular human lung model. *Environmental Research* 151:789-796. http://dx.doi.org/10.1016/j.envres.2016.09.010.

[8] Setting the ethanol limit in petrol (2002). An issue paper. Canberra, Australia: Environment Australia.

[9] Research & Markets (2020). Bioethanol market by feedstock (starch based, sugar based, cellulose based), end-up industry (transportation, pharmaceuticals, cosmetics, alcoholic beverages), fuel blend (E5, E10, E15 to E70, E75 and E85) and region-global forecast to 2025. https://www.researchandmarkets.com/r/9yor71.

[10] Cao, L., Frenkel, G. S., and Sridhar, N. (2013). Effect of oxygen on ethanol stress corrosion cracking susceptibility, Part 2: Dissolution-based cracking mechanism. Corrosion 69(9):851-862. https://doi.org/10.5006/0895.

[11] Anderson, J. E., DiCicco, D. M., Ginder, J. M., Kramer, U., Leone, T. G., Raney-Pablo, H. E., and Wallington, T. J. (2012). High octane number ethanol–gasoline blends: quantifying the potential benefits in the United States. *Fuel* 97:585-594. https://doi.org/10.1016/j.fuel.2012.03.017.

[12] Kramer, G. R., Méndez, C. M., and Ares, A. E. (2018). Evaluation of corrosion resistance of commercial aluminum alloys in ethanol solutions. *Materials Research* 21(6):e20170272 (pp. 12). https://dx.doi.org/10.1590/1980-5373-mr-2017-0272.

[13] Costa, R. C., and Sodre, J. R. (2010). Hydrous ethanol vs. gasoline-ethanol blend: Engine performance and emissions. *Fuel* 89(2):287-293. https://doi.org/10.1016/j.fuel.2009.06.017.

[14] Yesilyurt, M. K., Öner, I. V., and Yilmaz, E. C. (2019). Biodiesel induced corrosion and degradation: Review. *Pamukkale University Journal of Engineering Sciences* 25(1):60-70. http://dx.doi.org/10.5505/pajes.2018.01885.

[15] Subedi, B. N., Amgain, K., Joshi, S., and Bhattarai, J. (2019). Green approach to corrosion inhibition effect of *Vitex negundo* leaf extract on aluminum and copper metals in biodiesel and its blend. *International Journal of Corrosion and Scale Inhibitor* 8(3):744-759. http://dx.doi.org/10.17675/2305-6894-2019-8-3-21.

[16] Dharma, D., Ong, H. C, Masjuki, H. H., Sebayang, A. H., and Silitonga, A. S. (2016). An overview of engine durability and compatibility using biodiesel–bioethanol–diesel blends in compression-ignition engines. *Energy Conversion and Management* 128:66-81. https://doi.org/10.1016/j.enconman.2016.08.072.

[17] Sorate, K. A., and Bhale, P.V. (2015). Biodiesel properties and automotive system compatibility issues. *Renewable and Sustainable Energy Reviews* 41:777-798. https://doi.org/10.1016/j.rser.2014.08.079.

[18] Cao, L., Frankel, G., and Sridhar, N. (2013). Effect of chloride on stress corrosion cracking susceptibility of carbon steel in simulated fuel grade ethanol. *Electrochimica Acta* 104:255-266. https://doi.org/10.1016/j.electacta.2013.04.112.

[19] Haseeb, A.S.M.A., Masjuki, H.H., Ann, L.J., and Fazal, M.A. (2010). Corrosion characteristics of copper and leaded bronze in palm biodiesel. *Fuel Processing Technology* 91(3):329-334. https://doi.org/10.1016/j.fuproc.2009.11.004.

[20] Hu, E., Xu, Y., Hu, X., Pan, L., and Jiang, S. (2012). Corrosion behaviors of metals in biodiesel from rapeseed oil and methanol. *Renewable Energy* 37(1):371-378. https://doi.org/10.1016/j.renene.2011.07.010.

[21] Fazal, M.A., Haseeb, A.S.M.A., and Masjuki, H.H. (2013). Corrosion mechanism of copper in palm biodiesel. *Corrosion Science* 67:50-59. https://doi.org/10.1016/j.corsci.2012.10.006.

[22] Surisetty, V. R., Dalai, A. K., and Kozinski, J. (2011). Alcohols as alternative fuels: an overview. *Applied Catalysts A-General* 404(1-2): 1-11. https://doi.org/10.1016/j.apcata.2011.07.021.

[23] Radi, P. A., Vieira, A., Manfroi, L., de Nass, K. C. F., Ramos, M. A. R., Leite, P., Martins, G. V., Jofre, J. B. F., and Vieira, L. (2019). Tribocorrosion and corrosion behavior of stainless steel coated with DLC films in ethanol with different concentrations of water. *Ceramics International* 45(7)-B:9686-9693. https://doi.org/10.1016/j.ceramint.2019.02.103.

[24] Abel, J., and Virtanen, S. (2015). Corrosion of martensitic stainless steel in ethanol-containing gasoline: Influence of contamination by chloride, H_2O and acetic acid. *Corrosion Science* 98:318-326. https://doi.org/10.1016/j.corsci.2015.05.027.

[25] Thangavelu, S. K., and Ezhumalai, P. (2017). Corrosion behavior of low carbon steel in bioethanol fuel blends. *Solid State Phenomena* 263:115-119. https://doi.org/10.4028/www.scientific.net/SSP.263.115.

[26] Matejovsky, L., Macak, J., Pospisil, M., Baros, P., Stas, M., and Krausova, A. (2017). Study of corrosion of metallic materials in ethanol-gasoline blends: Application of electrochemical methods. *Energy Fuels* 31:10880-10889. https://doi.org/10.1021/acs.energyfuels.7b01682.

[27] Vargel, V. (2004). Corrosion of Aluminium (p. 648). Paris, France: Elsevier.

[28] Beavers, J, Sridhar, N., and Zamarin, C. (2009). Effects of steel microstructure and ethanol-gasoline blend ratio on SCC of ethanol pipelines, In: NACE Corrosion 2009 Conference & Expo, Paper No.: 09532. http://nace.confex.com/nace/2009/webprogram/Paper5465.html.

[29] Yoo, Y. H., Park, I. J., Kim, J. G., Kwak, D. H., and Ji, W. S. (2011). Corrosion characteristics of aluminum alloy in bioethanol blended gasoline fuel: Part 1. The corrosion properties of aluminum alloy in high temperature fuels. *Fuel* 90(3):1208-1214. https://doi.org/10.1016/j.fuel.2010.10.058.

[30] Aperador, W., Caballero-Gómez, J., and Delgado, A. (2013). Corrosion behavior of the AA2124 aluminium alloy exposed to ethanol mixtures. *International Journal of Electrochemical Science* 8(5):6154-6161.

[31] Jones, B., Mead, G., Steevens, P., and Timanus, M. (2008). The Effect of E20 on Metals Used in Automotive Fuel System Components. Report No.: 2-22-2008, St. Paul (MN), USA: Minnesota Department of Agriculture.

[32] Thangavelu, S. K., Ahmed, A. S., & Ani, F. N. (2016). Impact of metals on corrosive behavior of biodiesel-diesel-ethanol (BDE) alternative fuel. *Renewable Energy 94*:1-9. https://doi.org/10.1016/j.renene.2016.03.015.

[33] Bouazama, S., Costat, J., Desjobertb, J. M., Ben Ali, A., Guenbou, A., and Tabyaoui, M. (2019). Influence of *Lavandula dentata* essential oil on the corrosion inhibition of carbon steel in 1 M HCl solution. *International Journal of Corrosion and Scale Inhibition* 8(1):25-41. https://doi.org/10.17675/2305-6894-2019-8-1-3.

[34] Vorobyova, V. I., Skiba, M. I., Shakun, A. S., and Nahirniak, S. V. (2019). Relationship between the inhibition and antioxidant properties of the plant and biomass wastes extracts– A review. *International Journal of Corrosion and Scale Inhibition* 8(2): 150-178. https://doi.org/10.17675/2305-6894-2019-8-2-1.

[35] Rana, M., Joshi, S., and Bhattarai, J. (2017). Extract of different plants of Nepalese origin as green corrosion inhibitor for mild steel in 0.5 M NaCl solution. *Asian Journal of Chemistry* 29(5):1130-1134. https://doi.org/10.14233/ajchem.2017.20449.

[36] Akalezi, C. O., Ogukwe, C. E., Ejele, E. A., and Oguzie, E. E. (2016). Corrosion inhibition properties of *Gongronema latifollium* extract in acidic media. *International Journal of Corrosion and Scale Inhibition* 5(3):232-247. https://doi.org/10.17675/2305-6894-2016-5-3-4.

[37] Hussin, M. H., Kassim, M. J., Razali, N. N., Dahon, N. H., and Nasshorudin, D. (2016). The effect of *Tinospora crispa* extracts as a natural mild steel corrosion inhibitor in 1 M HCl solution. *Arabian Journal of Chemistry* 9(1):S616-S624. http://dx.doi.org/10.1016/j.arabjc.2011.07.002.

[38] Savita, Mourya, P., Chaubey, N., Singh, V. K., and Singh, M. M. (2016). Eco-friendly inhibitors for copper corrosion in nitric acid: Experimental and theoretical evaluation. *Metallurgical and Materials Transactions B* 47(1):47-57. https://doi.org/10.1007/s11663-015-0488-6.

[39] Verma, C., Ebenso, E. E., Bahadur, I., and Quraishi, M. A. (2018). An overview on plant extracts as environmental sustainable and green corrosion inhibitors for metals and alloys in aggressive corrosive media. *Journal of Molecular Liquids* 266:577-590. https://doi.org/10.1016/j.molliq.2018.06.110.

[40] Al-Turkustani, A. M., Arab, S. T., and Al-Dahiri, R. H. (2010). Aloe plant extract as environmentally friendly inhibitor on the corrosion of aluminum in hydrochloric acid in absence and presence of iodide ions. *Modern Applied Science* 4(5):105-124. https://doi.org/10.5539/mas.v4n5p105.

[41] Fazal, M. A., Haseeb, A. S. M. A., and Masjuki, H. H. (2011). Effect of different corrosion inhibitors on the corrosion of cast iron in palm biodiesel. *Fuel Processing Technology* 92(11):2154-2159. https://doi.org/10.1016/j.fuproc.2011.06.012.

[42] Amgain, K., Subedi, B. N., Joshi, S., and Bhattarai, J. (2018). Investigation on the effect of *Tinospora cordifolia* plant extract as a green corrosion inhibitor to aluminum and copper in biodiesel and its blend. In: *Proceedings of CORCON-2018*, Paper No.: PP19, NACE International-Gateway of India Section (NIGIS), Jaipur, India, pp. 1-11. http://dx.doi.org/10.13140/RG.2.2.16898.53448.

[43] Ashraful, A. M., Masjuki, H. H., Kalam, M. A., Rashedul, H. K., Sajjad, H., and Abedin, M. J. (2014). Influence of anti-corrosion additive on the performance, emission and engine component wear characteristics of an IDI diesel engine fueled with palm biodiesel. *Energy Conversion and Management*, *87*, 48–57. https://doi.org/10.1016/j.enconman.2014.06.093.

[44] Deyab, M. A. (2016). Corrosion inhibition of aluminum in biodiesel by ethanol extracts of Rosemary leaves. *Journal of the Taiwan Institute of Chemical Engineers* 58:536-541. https://doi.org/10.1016/j.jtice.2015.06.021.

[45] Priyatharesini, P. I., Kumar K. P. V., and Kumari, S. S. (2019) Studies of the anticorrosive nature of green Ricinus seed extract with neem biodiesel in copper metal. *Biofuels*. https://doi.org/10.1080/17597269.2018.1506634.

[46] Hoai Vu, N. S., Hien, P. V., Mathesh, M., Thu, V. T. H., and Nam, N. D. (2019). Improved corrosion resistance of steel in ethanol fuel blend by titania nanoparticles and *Aganonerion polymorphum* leaf extract. *ACS Omega* 4(1):146-158. https://doi.org/10.1021/acsomega.8b02084.

[47] Katuwal, P., Gaire, K. R., and Bhattarai, J. (2018). Study on the effects of ethylenediamine and plant extract as a corrosion inhibitor for mild steel passivation in bioethanol. In: *Proceedings of CORCON-2018,* Paper No.: MCI-35 (pp 9). NACE International-Gateway of India Section (NIGIS), Jaipur, India. https://www.researchgate.net/publication/328718532.

[48] Vu, N. S. H., Hien, P. V., Man, T. V., Hanh Thu, V. T., Tri, M. D., and Nam, N. D. (2018). A study on corrosion inhibitor for mild steel in ethanol fuel blend. *Materials* 11(1): Article No. 59 (pp. 11). https://doi.org/10.3390/ma11010059.

[49] Kunwar, R. M., Shrestha, K. P., and Bussmann, R. W. (2010). Traditional herbal medicine in Far-west Nepal: a pharmacological appraisal. *Journal of Ethnobiology and Ethnomedicine* 6(35):1-18. https://doi.org/10.1186/1746-4269-6-35.

[50] Gautam, L., Shrestha, S., Wagle, P., & Tamrakar, B. (2008). Chemical constituents from *Vitex negundo* (Linn) of Nepalese origin. *Scientific World* 6(6): 27-32. https://doi.org/10.3126/sw.v6i6.2630.

[51] Chen, J., Fan, C. L., Wang, Y., and Ye, W. C. (2014). A new triterpenoid glycoside from *Vitex negundo*. *Chinese Journal of Natural Medicines* 12(3):218-221. https://doi.org/10.1016/S1875-5364(14)60036-4.

[52] Patel, J. I., and Deshpande, S. S. (2013). Antieosinophilic activity of various subfractions of leaves of *Vitex negundo*. *International Journal of Nutrition, Pharmacology, Neurologic Diseases* 3(2):135-141. https://doi.org/10.4103/2231-0738.112839.

[53] Zheng, C. -J., Huang, B. -K., Wang, Y., Ye, Q., Han, T., Zhang, Q. -Y., Zhang, H., and Qin, L. P. (2010). Anti-inflammatory diterpenes from the seeds of *Vitex negundo*. *Bioorganic and Medicinal Chemistry* 18(1):175-181. https://doi.org/10.1016/j.bmc.2009.11.004.

[54] Moon, S. H., Pandurangan, M., Kim, D. H., Venkatesh, J., Patel, R. V., and Mistry, B. M. (2018). A rich source of potential bioactive compounds with anticancer activities by *Catharanthus roseus* cambium meristematic stem cell cultures. *Journal Ethnopharmacology* 217:107-117. https://doi.org/10.1016/j.jep.2018.02.021.

[55] Barrales-Cureño, H. J., Reyes, C. R., García, I. V., Valdez, L. G. L., De Jesús, A. G., Ruíz, J. A. C., Herrera, L. M. S., Caballero, M. C. C., Magallón, J. A. S., Perez, J. E., and Montoya, J. M. (2019). Alkaloids of pharmacological importance in *Catharanthus roseus*. London, UK: IntechOpen Ltd., pp. 18. http://dx.doi.org/10.5772/intechopen.82006.

[56] Ghozali, S. Z., Vuanghao, L., and Ahmad, N. H. (2015). Biosynthesis and characterization of silver nanoparticles using *Catharanthus roseus* leaf extract and its proliferative effects on cancer cell lines. *Journal of Nanomedicine and Nanotechnology* 6(4):1000305 (pp 6). http://dx.doi.org/10.4172/2157-7439.1000305.

[57] Palaniappan, N., Cole, I., Caballero-Briones, F., Manickam, S., Justin Thomas, K. R., and Santos, D. (2020). Experimental and DFT studies on the ultrasonic energy-assisted extraction of the phytochemicals of *Catharanthus roseus* as green corrosion inhibitors for mild steel in NaCl medium. *RSC Advances* 10:5399-5411. https://doi.org/10.1039/c9ra08971c.

[58] Shahba, R. M. A., Fouda, A. E. E., El-Shenawy, A. E., and Osman, A. S. M. (2016). Effect of *Catharanthus roseus* (*Vince rosea*) and turmeric (*Curcuma longa*) extracts as green corrosion inhibitors for mild steel in 1 M HCl. *Materials Sciences and Applications* 7:654-671. http://dx.doi.org/10.4236/msa.2016.710053.

[59] Kumar, K.N.S., and Hemalatha, S. (2013). Phytochemical evaluation of leaf extracts of *Aegle marmelos*. *International Journal of Development Research* 3(7):29-33.

[60] Mujeeb, F., Bajpai, P., and Pathak, N. (2014). Phytochemical Evaluation, Antimicrobial Activity and Determination of Bioactive Components from Leaves of *Aegle marmelos*. *BioMed Research International* 2014: Article ID 497606 (pp 11). http://dx.doi.org/10.1155/2014/497606.

[61] Das, P., Kar, P., Hasnu, S., Nath, S., and Tanti, B. (2017). Phytochemical screening and antioxidant activity of *Elaeocarpus serratus* L. of Assam. *Journal of Pharmacognosy and Phytochemistry* 6(4):866-869.

[62] Asaduzzaman, Md., Uddin, Md. J., Kader, M.A., Alam, A. H. M. K., Rahman, A. A., Rashid, M., Kato, K., Tanaka, T., Takeda, M., and Sadik, G. (2014). In vitro acetylcholinesterase inhibitory activity and the antioxidant properties of *Aegle marmelos* leaf extract: Implications for the treatment of Alzheimer's disease. *Psychogeriatrics* 14(1):1-10. https://doi.org/10.1111/psyg.12031.

[63] Begum Hussain, M. S., and Hiremath, M. B. (2020). Evaluation of in vitro antioxidant and anti-inflammatory activities of *Aegle marmelos* leaf extracts. *Asian Journal of Pharmaceutical and Clinical Research* 13(2):209-13. https://doi.org/10.22159/ajpcr.2020.v13i2.36870.

[64] Siddiqui, M. S., Sharma, G., and Sharma, A. (2020). Anti-diabetic and nephrotoxicity effect of Aegle marmelos leaf on alloxan-induced diabetic rat. *International Journal of Research in Pharmaceutical Sciences* 11(3):3966-3971. https://doi.org/10.26452/ijrps.v11i3.2588.

[65] Shenoy, A. M., Singh, R., Samuel, R. M., Yedle, R., and Shabraya, A. R. (2012). Evaluation of ulcer activity of Aegle marmelos leaves extract. *International Journal of Pharmaceutical Sciences and Research* 3(5):1498-1501. https://dx.doi.org/10.13040/IJPSR.0975-8232.3(5).1498-01.

[66] Baliga, M. S., Thilakchand, K. R., Rai, M. P., Rao, S., and Venkatesh, P. (2013). *Aegle marmelos* (L.) Correa (Bael) and its phytochemicals in the treatment and prevention of cancer. *Integrative Cancer Therapies* 12(3):187-196. https://doi.org/10.1177/1534735412451320.

[67] Dhankhar, S., Ruhil, S., Balhara, M., Dhankhar, S., and Chhillar, A. K. (2011). *Aegle marmelos* (Linn.) Correa: a potential source of phytomedicine. *Journal of Medicinal Plants Research* 5(9):1497-1507.

[68] Storrs, A., and Storrs, J. (1990). *Trees and Shrubs of Nepal and the Himalayas*. Kathmandu, Nepal: Pilgrims Book House, pp. 102-106.

[69] Bhatt, B., and Dahal, P. (2019). Antioxidant and antimicrobial efficacy of various solvent extracts of seed of Rudrakshya (*Elaeocarpus ganitrus*) from Ilam district of Nepal. *Journal of Nepal Chemical Society* 40:11-18. https://doi.org/10.3126/jncs.v40i0.27272.

[70] Okselni, T., Santoni, A., Dharma, A., and Efdi, M. (2018). Determination of antioxidant activity, total phenolic content and total flavonoid content of root, stem bark and leaves of *Elaeocarpus mastersii* King, *Rasayan Journal of Chemistry* 11(3):1211-1216. https://dx.doi.org/10.31788/RJC.2018.1133058.

[71] Chand, L., Dasgupta, S., Chattopadhyay, S. K., and Ray, A. B. (1977). Chemical investigation of some *Elaeocarpus* species. *Planta Medica* 32(2):197-199. https://doi.org/10.1055/s-0028-1097584.

[72] Ray, A. B., Chand, L., and Pandey, V. B. (1979). Rudrakine, a new alkaloid from *Elaeocarpus ganitrus*. *Phytochemistry* 18(4):700-701. https://doi.org/10.1016/S0031-9422(00)84309-5.

[73] Sathish Kumar, T., Shanmugam, S., Palvannan, T., and Bharathi Kumar, V. (2010). Evaluation of antioxidant properties of *Elaeocarpus ganitrus* Roxb leaves. *Iranian Journal of Pharmaceutical Research* 7(3):211-215. https://doi.org/10.22037/ijpr.2010.767.

[74] Sirajunnisa, S., Fazal Mohamed, M. I., and Subramania, A. (2014). *Vitex negundo* leaves extract as green inhibitor for the corrosion of aluminum 1 N NaOH solution. *Journal of Chemical and Pharmaceutical Research* 6:580-588.

[75] Bhardwaj, N., Prasad, D., and Haldhar, R. (2018). Study of the *Aegle marmelos* as a green corrosion inhibitor for mild steel in acidic medium: Experimental and theoretical approach. *Journal of Bio- and Tribo-Corrosion* 4:61 (pp 10). https://doi.org/10.1007/s40735-018-0178-4.

[76] Bhattarai, J., Rana, M., Bhattarai, M. R., Regmi, R., and Joshi, S. (2018). Effect of green corrosion inhibitor of Nepalese origin plants for corrosion control of mild steel in aggressive environments. In: *Proceedings of CORCON 2018*, Paper No. MCI-17, pp. 12, NIGIS/NACE Publication, Jaipur, India.

[77] Bhattarai, J., Akiyama, E., Habazaki, H., Kawashima, A., Asami, K., and Hashimoto, K. (1998). Electrochemical and XPS studies on the passivation behavior of sputter-deposited W-Cr alloys in 12 M HCl solution. *Corrosion Science* 40(2-3): 155-175. https://doi.org/10.1016/S0010-938X(97)00106-6.

[78] Subedi, D. B., Pokharel, D. B., and Bhattarai, J. (2020). Assessment on the effects of sodium salts of tungstate and nitrite as green inhibitor for the corrosion of Cr-5Ni-53W alloy in 0.5 M NaCl solution. *International Journal of Metallurgy and Alloys* 6(1):25-26

[79] Kuznetsov, Yu. I., Andreev, N. N., and Vesely, S. S. (2015). Why we reject papers with calculations of inhibitor adsorption based on data on protective effects? *International Journal of Corrosion and Scale Inhibitor* 4(2):108-196.

[80] Langmuir, I. (1916). The constitution and fundamental properties of solids and liquids, Part 1: Solids. *Journal of the American Chemical Society* 38(11):2221-2295. https://doi.org/10.1021/ja02268a002

[81] Tempkin, M. I., and Pyzhev, V. (1940). Kinetics of ammonia synthesis on promoted iron catalyst. *Acta Physicochimica USSR* 12:327-356.

[82] Ayawei, N., Augustus, A. N., and Wankasi, D. (2017). Modeling and interpretation of adsorption isotherms. *Journal of chemistry* 2017: Article ID3039817, pp 11. https://doi.org/10.1155/2017/3039817.

[83] Wan, Y., Sun, Y., Cai, D., Yin, L., Dai, N., Lei, L., Jiang, Y., and Li, J. (2020). Influence of ethanol on pitting corrosion behavior of stainless steel for bioethanol fermentation tanks. *Frontiers of Chemistry* 8:529 (pp 11). https://doi.org/10.3389/fchem.2020.00529.

[84] Lou, X., and Singh, P. M. (2010). Role of water, acetic acid and chloride on corrosion and pitting behavior of carbon steel in fuel-grade ethanol. *Corrosion Science* 52:2303-2315. doi:10.1016/j.corsci.2010.03.034.

[85] Vijayaraghavan, V., Padmesh, T. V. N., Palanivelu, K., and Velan, M. (2006). Biosorption of nickel (II) ions onto *Sargassum wightii*: Application of two-parameter and three-parameter isotherm models. *Journal of Hazardous Materials* B133:304-308. https://doi.org/10.1016/j.jhazmat.2005.10.016.

[86] Aharoni, C., and Ungarish, M. (1977). Kinetics of activated chemisorption: Part 2 Theoretical models. *Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases* 73:456-464. https://doi.org/10.1039/F19777300456.

[87] Amin, M. T., Alazba, A. A., and Shafiq, M. (2015). Adsorptive removal of reactive black 5 from wastewater using bentonite clay: Isotherms, kinetics and thermodynamics. *Sustainability* 7:15302-15318. https://doi.org/10.3390/su71115302.

[88] Dabrowski, A. (2001). Adsorption from theory to practice. *Advances in Colloid and Interface Science* 93(1-3):135-224. https://doi.org/10.1016/S0001-8686(00)00082-8.

[89] Popoola, L. (2019). Organic green corrosion inhibitors (OGCIs): A critical review. *Corrosion Reviews* 37(2):71-102. https://doi.org/10.1515/corrrev-2018-0058.

[90] Patni, N., Agarwal, S., and Shah, P. (2013). Greener approach towards corrosion inhibition. *Chinese Journal of Engineering* 2013: Article ID 784186 (pp 10). http://dx.doi.org/10.1155/2013/784186.

[91] Li, P., Lin, J. Y., Tan, K. L., and Lee, J. Y. (1997). Electrochemical impedance and X-ray photoelectron spectroscopic studies of the inhibition of mild steel corrosion in acids by cyclohexylamine. *Electrochimica Acta* 42(4):605-615. https://doi.org/10.1016/S0013-4686(96)00205-8.

[92] Anaee, R. A., Alzuhairi, M. H., and Abdullah, H. A. (2014). Corrosion inhibition of steel in petroleum medium by *Ficus carica* leaves extract. *Asian Journal of Engineering and Technology* 2(3):235-243.

[93] Haldhar, R., Prasad, D., Saxena, A., and Kaur, A. (2018). Corrosion resistance of mild steel in 0.5 M H_2SO_4 solution by plant extract of *Alkana tinctoria*: Experimental and theoretical studies. *The European Physical Journal Plus* 133(9): Article No.356. https://doi.org/10.1140/epjp/i2018-12165-0.

Prakash Katuwal had completed his MSc degree in Physical Chemistry doing dissertation works in the field of corrosion inhibition from Central department of Chemistry, Tribhuvan University, Nepal in 2018. He has been working as a Lecturer of Chemistry in colleges of Kathmandu, Nepal. He has published more than 10 articles in reputed journals.

Ramesh Regmi is an MSc dissertation student of the Central Department of Chemistry, Tribhuvan University, Nepal. He has been carried out his dissertation work in the field of biofuel corrosion inhibitor under the supervision of Prof. J. Bhattarai. He has awarded the Master Thesis Support by the University Grants Commission- Nepal.

Susan Joshi had completed her PhD in organic synthesis chemistry from Indian Institute of Technology, Delhi, India in 1998. She has been working more than thirty years as an Associate Professor of Chemistry in Central Department of Chemistry, Tribhuvan Univ., Nepal. She has published more than three dozens of articles.

Jagadeesh Bhattarai had completed his PhD degree in the field of corrosion sciences from Institute of Materials Research (IMR), Tohoku University, Japan in 1998. He has been working more than thirty two years as a full Professor of Chemistry in Central Department of Chemistry, Tribhuvan University. He had carried out research works at Tokyo Institute of Technology (1991-92) as an UNESCO-Research Fellow and Tohoku Institute of Technology (2007-08), as Visiting Researcher. He has published more than ten dozens of articles in reputed national and international journals. Now, he is the Chief Editorial of Journal of Institute of Science & Technology (JIST)-Institute of Science and Technology, Tribhuvan University, Nepal.