Corrosion Inhibition Effect of *Diospyros blancoi* (Velvet Apple) Acid Leaf Extracts on Mild Steel in Acidic Medium

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Abstract
Mild steel has excellent applicability to structures that provide many benefits to man. On the other hand, exposure to chemical reactions including corrosion leads to their degradation. Thus, minimizing the effect of such phenomenon (corrosion) is needed (since it is a natural process). This study aimed to determine the corrosion inhibition of Diospyros blancoi (velvet apple) acid leaf extract on mild steel in an acidic medium. Further, it determines the concentration at which D. blancoi acid leaf extract (DbAE) performs best in corrosion inhibition parameters. Acidic environment immersion was done on mild steel sheets on treatments with different DbAE concentrations (5%, 10% and 15%).

Weight loss was the factor determined to determine the inhibition efficiency of the DbAE concentrations and the corrosion rate of the mild steels. Results showed that the inhibition efficiency is highest and the corrosion rate of mild steel is lowest at 15% DbAE concentration. It is recommended that sophisticated facility/ equipment be used to determine the effect of DbAE on the physical and chemical components of mild steel. Also, the production of D. blancoi must be done since the potential anticorrosion impact of this plant species has been determined.

Keywords: Corrosion inhibition, *Diospyros blancoi*, mild steel, hydrochloric acid.

Introduction

Metallic materials, including mild steel, have specific applicability in structures and other valuable materials including buildings, houses, equipment, household materials etc. due to inexpensive productivity and exhibition of some unique physical properties.[1,15] Despite the utility of these metals, their exposure to the environment brings about adversities such as chemical reactions from compounds of different sources lead to the deterioration or degradation of their components. One of the processes is corrosion which causes several economic-related consequences and environmental pollution.[2,10] Since corrosion is an environment-based phenomenon, its occurrence cannot be prevented. There is a need for metals to be protected from their damaging effect. There are various methods to avoid the corrosion of metals; however, corrosion inhibitors (CIs) applied to metal surfaces are notably one of the best but low-cost methods.[3,7] CIs come in organic and inorganic substances which are added in small concentrations to an environment to effectively reduce the corrosion rate of metal.[12,15]

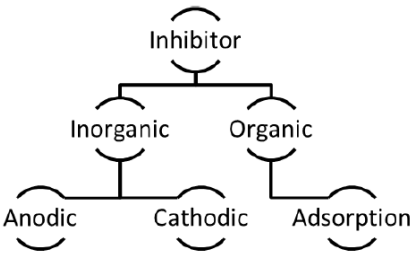


Figure 1: Classification of Inhibitors
(Source: INTECH©2014)

Mechanism of CIs generally includes the production of thin protective oxide film on the surface of the metal through chemisorption in aqueous media. In the case of inorganic CIs, anodic and cathodic actions are associated.[15] Anodic inhibition refers to the obstruction of the anode reaction which supports the polarization of the metal surface. In contrast, cathodic inhibition refers to the production of insoluble compounds that precipitate selectively on cathodic sites that control the diffusion of reducible species.[11] Meanwhile, organic CIs exhibit both anodic and cathodic actions.[15] These inhibitors build up a protective hydrophobic film that prevents the dissolution of the metal in the electrolyte.[3]

Because of the presence of pi (π) bonds, several inorganic, organic and polymeric compounds have demonstrated excellent corrosion inhibition activity.[15] However, worldwide health and environmental safety are compromised by challenges such as high toxicity levels for both humans and the environment.[11] The hunt for environmentally-friendly corrosion inhibitors (EFCIs), sometimes known as "green chemicals," has become increasingly popular as a result of this growing concern.[10]

EFCIs are found in plants that produce secondary metabolites, playing vital roles in corrosion exhibition. Phytochemical analyses of plant extracts show the presence of tannins, organic acids, alkaloids and lignin which are known to inhibit action.[1,15] Other plants have distinctive chemical components tested to be effective corrosion inhibitors. Metals exposed to different environments (i.e.

acidic aqueous and seawater) with plant extracts have been the mode of determining corrosion inhibition activities. Plant extracts from *Wrightia tinctoria, Chelodendrum phlomidis and Ipomoea triloba leaves,*[11] *Antigonon leptopus* leaves,[1] *Juniperus* plant,[2] *Chamaerops humilis* tannin extract[12] etc. have been tested for corrosion inhibition on steel and other metals in H_2SO_4 medium.

Corrosion inhibition of tobacco twig, stems, leaves, black pepper, acacia gum, castor seed, mango peel extract, *Hibiscus sabdariffa, Citrus aurantifolia*, grape pomace etc.[12] has been tested through HCl medium. In seawater medium, extracts of *Cuminum cyminum* plant,[5,15] *Asafoetida and Ginger*[12] etc. have been tested. *Lantana Camara* fruit and leaf extracts have been tested in both HCl and H_3PO_4 media.[8,12] Those extracts showed significant corrosion inhibition effects on various metallic materials.[11]

The Philippines is rich in plants since it is a tropical country. Biodiversity studies show various plant species that contain natural compounds with multiple significant uses in the different areas of human concerns. Among these biodiversities in the *Diospyros blancoi*, a plant that belongs to the *Ebanaceae* Family is locally known as *Mabolo* and velvet apple in the English language. It grows in areas with a monsoon climate from sea level to 800m elevation and almost any soil. This tree reaches a height of 14 meters with oblong to elliptic-shaped leaves. The mature tree has dulled green leaves with silvery undersides; emerging leaves are yellowish-green.

Traditionally, the juice of unripe fruit is used for wounds, oil from seeds is used for diarrhea and dysentery, infusion of fruit is used as a gargle in *Aphthous stomatitis*. This tree's bark and leaves can be used in snakebites, eyewash and in colds, heart problems, hypertension, spider bites, stomach aches, diabetes and eczema. The antioxidant property of this plant has been discovered in some countries and chemical analysis has been done by Howlader et al.[8]

In this study, the corrosion inhibition effect of *Diospyros blancoi* leaf extracts on mild steel shall be determined using three different media, namely sulphuric acid, hydrochloric acid and seawater, at different concentrations. Moreover, this research tends to determine which among the given media and under what specific concentration, the said plant extract is most effective in corrosion inhibition.[16]

Material and Methods

Collection and identification of Diospyros blancoi leaves: The leaves of the *Diospyros blancoi* were collected in Brgy. Gabut Norte, Badoc, Ilocos Norte. For proper taxonomic identification, sample leaves and parts of the plant species were brought to the Botanical Herbarium of the Museum of Natural History, University of the Philippines Los Baños, Laguna.[6] The leaves were washed thoroughly with tap water to remove the dirt and other impurities. The plant was then examined and classified belonging to order Ericales and family *Ebenaceae*. It is a plant of the genus *Diospyros*, identified species as *D. blancoi*, commonly known as *Kamagong*, *Mabolo*, *Tálang* in the Philippines.

D. blancoi is a medium-sized tree growing to a height of 20 meters. Leaves are leathery, oblong, up to 20 centimeters long, with a round base and acute tip. The blade is glossy green, smooth above and softly hairy below. Its edible fruit has a skin covered in a fine Velvet fur which is usually reddish-brown and soft, creamy, pink flesh, with a taste and aroma comparable to fruit cream cheese. The leaves were cut into small strips and shade-dried for 3-5 days. After shade drying, the leaves were subjected to ethanolic extraction through a rotary evaporator (Buchi).[8]

Phytochemical Analysis: This phase of the study was conducted at the Chemical Engineering Laboratory of the Adamson University, Manila. Proper protocols on securing permission to conduct laboratory testing were done. Fifty (50) mL of the ethanolic extracts was subjected to qualitative phytochemical analysis for the presence of the different constituents such as alkaloids, flavonoids, glycosides, saponins and tannins.[8,14] Procedures for the study were done based on the Organic Chemistry Laboratory Manual available at the said university. Extracts were placed on different test tubes and tested with various solutions. Observed changes on the extracts shall be recorded.[2]

Preparation of the Mild steel sheets: Mild steel sheet preparation was adapted from the procedures set with modifications.[4,5] The mild steel sheets were purchased from hardware in the City of Batac, Ilocos Norte and polished with emery paper (sandpaper) to obtain a mirror finish. Then, the polished sheets were washed with lukewarm distilled water with detergent, degreased with acetone, dried and put into desiccators to prevent moisture intrusion on the polished coupons.[5] Forty-eight polished mild steel sheets were used in the study. It was distributed in the following setups: three concentrations and negative control, one corrosive environment,[13] two replicates, three weight-loss observations and two trials (4x1x2x3x2=48).

Preparation of the Stock Solutions: About 170 mL of the ethanolic *Diospyros blancoi* (Db) extract was added with 2M hydrochloric acid (HCl) to form a 1000ml solution subjected to acidification via acid reflux set up for three hours, filtered and kept in a clean Florence flask overnight. This served as the *Diospyros blancoi acid extract* (DbAE) stock solution for the acidic medium.

Acid Environment Immersion: In this phase, three polished mild steel sheets were weighed using a digital balance (Mettler Toledo) before being soaked in three separate glass containers containing 100ml solutions with three concentrations (5%, 10% and 15%) the DbAE. The setups were prepared for three different immersion periods.[5] A setup was prepared for the three-hour immersion period, another setup for six-hour immersion and another setup for

the nine-hour immersion period respectively. After soaking, the sheets were washed, dried and weighed again to determine their final weight.

Inhibition Efficiency Percentage: The weight loss value, which was determined from the difference between the initial and final weight of the mild steel sheets, was used in computing the inhibition efficiency (IE) %:[1,11]
Inhibition Efficiency (%)

$$IE\ \% = \frac{W_u - W_i}{Wu} x100$$

where W_u is weight loss in the absence of inhibitor and W_i is weight loss in the presence of inhibitor.

Corrosion Rate Analysis: Once again, the mild steel sheets' computed weight loss values were used to calculate the corrosion rate. Together with the area, density and immersion time of the mild steel sheets, the values were entered in a free online corrosion calculator (http://www.corrosionsource.com). The computed value of the corrosion rate was expressed in millimeters per year (mm/year).[5]

The summary of the methods is illustrated in figure 2.

Results and Discussion

Inhibition Efficiency: Inhibition efficiency of the subjected material was based on its organic compounds, which turn as corrosion inhibitors established in the environment, the nature of the metal surface and the structure of the inhibitor itself .[3,15] The acid leaf extract of velvet apple (*Diospyros blancoi)* is tested as a mild steel sheet corrosion inhibitor in an acidic medium with varying concentrations. The inhibitive action of the extract is discussed, given the adsorption of *D. blancoi* molecules on the mild steel surface (Figure 3). The result implies that out of all the three concentrations, fifteen percent (15%) solution shows positive inhibition of the acid leaf extract established from different time duration of the analysis. The outcome was based on four trials with two replicas each to further analyze the adsorption of the acid leaf extract on the sample coupons.[11] The adsorption on the metal surface was related to the changes in impedance parameters to which the test subject was exposed in increasing time.[5,9] Furthermore, the result shows the one-way ANOVA on varying concentration vs. immersion time duration variance as shown in table 1.

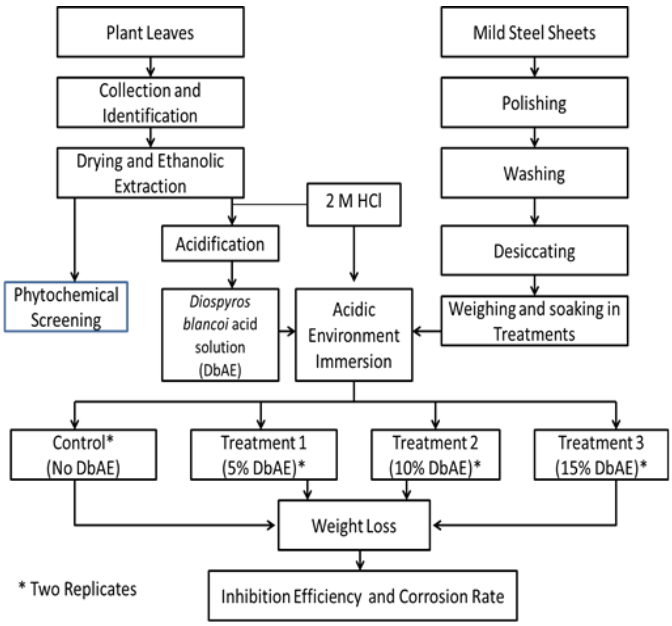


Figure 2: Flowchart of the course of study

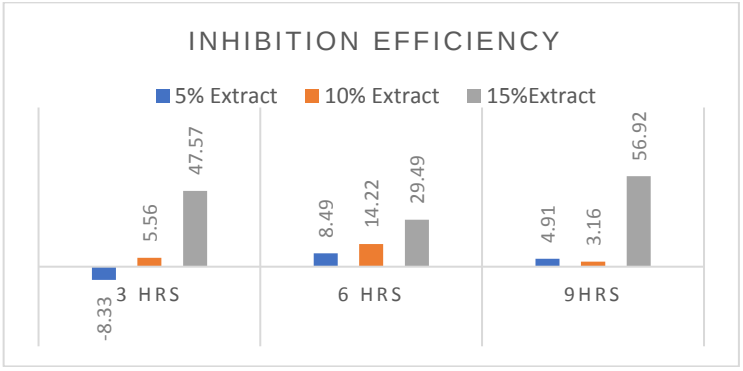


Figure 3: Inhibition Efficiency of *D. blancoi* acid leaf extract on mild steel sheets

Table 1
Analysis of variance between and within groups on inhibition efficiency.

ANOVA					
	Sum of Squares	**df**	**Mean Square**	**F**	**Sig.**
Immersion Time					
Between Groups	278.300	2	139.150	0.302	0.741
Within Groups	15182.756	33	460.084		
Total	15461.056	35			
Concentration					
Between Groups	13005.250	2	6502.625	87.379	0.000
Within Groups	2455.806	33	74.418		
Total	15461.056	35			

Table 2
Post Hoc tests on *D. blancoi* acid leaf extract inhibition efficiency on mild steel sheets.

Multiple Comparisons						
Dependent Variable: Concentration		**Mean Difference**	**Std. Error**	**Sig.**	**95% Confidence Interval**	
					Lower Bound	**Upper Bound**
5 Percent	10 Percent	-5.96167	3.52180	0.100	-13.1268	1.2035
5 Percent	15 Percent	-42.96833*	3.52180	0.000	-50.1335	-35.8032
10 Percent	15 Percent	-37.00667*	3.52180	0.000	-44.1718	-29.8415
*. The mean difference is significant at the 0.05 level.						

It can be gleaned in table 1 that there are no significant differences in the (Sig=0.741) inhibition efficiency of *D. blancoi* leaf extract on a mild steel sheet provided with three discrete immersion time limits. The findings imply that the immersion time does not affect the acid leaf extract's inhibition efficiency but its changing concentration. Furthermore, it was observed that the first three hours of the immersion time were the most crucial parts of the inhibition of the solution. Hence, succeeding immersion time does not show a huge gap from the other. The results suggest that the efficiency of an inhibitor increases with an increase in inhibitor concentration.[3,11]

As revealed in table 2, there is a significant difference (Sig= 0.000) in *D. blancoi* acid leaf extract concentration. Sophisticated corrosion inhibitor test methods, typically designed to reproduce the most extreme conditions in a system, have been employed to improve inhibitor capabilities.[4] Optimum inhibition concentration of 15% extract shows higher efficiency compared to 5% (MD=-42.96833) and 10% (MD=-37.00667) concentrations. Generally, the inhibitive effect of plant extract is attributed to the adsorption of organic substances on the metal surface blocking active sites or even forming a protective barrier.[4,15] However, laboratory and field performance correlation may be possible once key factors are considered involving inhibitor chemistry and corrosion theory.

Corrosion Rate: The corrosion rate is the speed at which metal deteriorates in a specific environment (corrosion potential, corrosion resistance). The rate of speed depends upon the environmental condition and the type and condition, of the metal.[9,17] Adsorption isotherm was investigated by weight-loss measurement estimating the influence of time on corrosion activities on metals which may differ depending on the caustic setting and duration of exposure.[7] Variation in corrosion rate can also occur due to changes in the concentration of corrosive agents in the environment.[1,13] The study uses a controlled environment to further analyze the corrosion activity on metals by mainly focusing on the corrosion inhibition of *D. blancoi* acid leaf extract for short and long-term exposures.[9]

Figure 4 shows the corrosion rate of mild steel sheets from the varying concentration of acid leaf extract observed under specific immersion time.

Findings show that the *D. blancoi* leaf extract under five percent (5%) and ten percent (10%) concentration poorly inhibits that mild steel sheet. On the other hand, it can be seen in figure 4 that fifteen (15%) concentration shows a lower corrosion rate (best described under 6 hours immersion time) than the different samples. This infers that the higher the inhibition efficiency on one concentration may lower the corrosion rate of the samples.[11,13] The result also implies that indicated immersion time (Table 3) does not affect the corrosion rate of mild steel sheets as the outcome shows matching results from different immersion times.[4]

The corrosion rates of those steels were measured by the weight-loss method after exposure for specific periods of time in various mediums. As seen in table 3, varying concentration shows a significant difference (Sig= 0.000) between and within groups.[4] However, the mild sheet metal

coupon corrosion rate under discrete immersion times was not significantly different (Sig= 0.200). Due to weight loss, the diameter of the mild steel coupons decreases as solution concentration increases remarkably (Figure 4). The result may suggest that higher concentration may yield a good result of corrosion inhibition (Table 4) as reflected in the study.[5]

The corrosion behavior of mild steel sheets under optimum 15% *D. blancoi* extract shows a lower corrosion rate than 5% (MD= 47.10833) and 10% (MD= 43.49083) extract. A protective oxide layer provided by higher concentrations of D. blancoi extract was seen as effective in lowering the corrosion rate of metals and uniform corrosion occurred on the mild steel sheet during the immersion test.[9]

Conclusion

Based on the study's findings, the effects of *D. blancoi* acid leaf extract were reported. The study used an acid-based extract from Velvet Apple as a corrosion inhibitor on mild steel sheet coupons. The active inhibition efficiency was shown at fifteen (15%) concentrations consistent in four trials under specified immersion time.

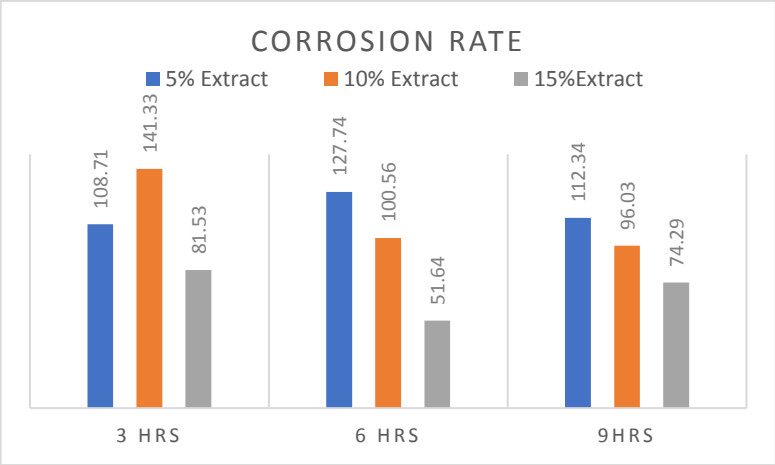


Figure 4: Corrosion Rate of Mild Steel Sheet exposed to acid leaf extract

Table 3
Analysis of variance between and within groups on corrosion rate.

ANOVA					
	Sum of Squares	**df**	**Mean Square**	**F**	**Sig.**
Immersion Time					
Between Groups	2251.871	2	1125.936	1.690	0.200
Within Groups	21986.311	33	666.252		
Total	24238.183	35			
Concentration					
Between Groups	16494.936	2	8247.468	35.149	0.000
Within Groups	7743.247	33	234.644		
Total	24238.183	35			

Table 4
Post Hoc tests on the corrosion rate of mild steel sheet exposed to acid leaf extract.

Multiple Comparisons						
Dependent Variable: Concentration		**Mean Difference**	**Std. Error**	**Sig.**	**95% Confidence Interval**	
					Lower Bound	**Upper Bound**
5 Percent	10 Percent	3.61750	6.25358	0.567	-9.1055	16.3405
5 Percent	15 Percent	47.10833*	6.25358	0.000	34.3853	59.8313
10 Percent	15 Percent	43.49083*	6.25358	0.000	30.7678	56.2138
* The mean difference is significant at the 0.05 level.						

The same results present a low corrosion rate on 15% concentration best described under 6 hours immersion time. As reflected from the increasing inhibition efficiency and decreasing corrosion rate, it is suggested for further studies to identify the components of the metal specimen and to use higher concentrations for yielding better results. Furthermore, considerations of using sophisticated equipment/facilities for determining the physical and chemical properties of the mild steel sheets, use of positive control for further comparison of results and the massive production of the plant species are also recommended.

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