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Study on The Potential Application of Water Hyacinth as An Organic Corrosion Inhibitor

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ABSTRACT

Alloy and iron are examples of metals that commonly used as building materials and industrial purposes. Although they are strong materials, they are extremely corrosion prone. One of the methods for shielding metals from oxidation is the use of inhibitors. Although the synthetic corrosion inhibitors are highly efficient, due to their costs and dangerous environmental impacts, they cannot always be used for corrosion inhibition purposes. Therefore, in recent years, researchers based their works on green inhibitors of corrosion. This work was focused on the potential utilization of water hyacinth (WH) as a green corrosion inhibitor. The result of this work shows that the highest inhibition efficiency of WH extract is 65.3% in tap water and 47.1% in sodium chloride solution, when applied to SS400 metal. However, with the addition of an appropriate dose of gum Arabic (GA), the inhibition efficiency can be increased significantly. The highest inhibition efficiency of the WH and GA mixture is 71.08% in hydrochloric acid 32% solution after 3 days of immersion and 79.75% in sodium chloride 3.5% after 4 days of immersion.

CCS CONSEPTS

• Applied Computing ~ Physical science and engineering~ Chemistry

KEYWORDS

Water Hyacinth, Corrosion, Green Inhibitor, Corrosion Rate.

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1 Introduction

Alloy and iron are examples of metals that are commonly used as building materials and industrial purposes. Although they are strong materials, they are susceptible to corrosion. One of the most effective methods for shielding metals from oxidation is the use of inhibitors. Corrosion is described as an irreversible interfacial response of a material with the surroundings which destroys useful material properties by chemical or electrochemical processes. The use of inhibitors was widely accepted because of their ability to lower the corrosion level when incorporated into a corrosive environment. Most inorganic corrosion inhibitors have secondary effects in damaging the environment. Concerted efforts have been made over the years to replace these barriers with low-cost, eco-friendly, non-toxic and biodegradable green alternatives [1][2][3].

One of organic materials that can be potentially used as green inhibitor is water hyacinth (WH), for it has been proven by many researchers to show high antioxidant activity in its extract. Water hyacinth (Eichhornia *crassipes*) is a floating aquatic plant species. In some areas of Indonesian wetlands, such as many lakes or other basins, intense breeding led to water hyacinth developing into weeds. Because of its ability to quickly cover whole rivers, water hyacinth is considered the worst aquatic plant in the world. Within 6 months, the production of water hyacinth can exceed 125 tons of wet weight over 100 square meters [4]. Water hyacinth represents a vital percentage of an aquatic ecosystem. It has already been shown that water hyacinth is a very promising weed with many applications [5]. In accordance with the research conducted before, water hyacinth has proven to contain high phenolic content and antioxidant activity [6]. Hence, this work was aimed at studying the potential of using WH extract as green corrosion inhibitor on metals.

A study needs to also be performed to search for an enhancement of the potential utilization of WH extract as corrosion inhibitor through a combination with other substances. Gum arabic (GA), is a multiple scattered exudate obtained from Acacia trees mainly consist of amino acids linked to short arabinose side chain. Some researches also have been conducted regarding the use of gum arabic as a corrosion inhibitor. Therefore, the combination between WH extract and GA in inhibiting corrosion is also studied in this work, through the observation of corrosion rate and inhibition efficiency in different corrosive media. Visual observation on the surface of metal sample was also performed in this work.

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2 Research Method

2.1 Materials and Equipment

The main material, water hyacinth, was taken from Cipondoh Lake, Banten, Indonesia. To determine the total phenolic content (TPC) of water hyacinth analysis materials that were used were 96% ethanol, distilled water, gallic acid, sodium carbonate, and the reagent of Folin Ciocalciteau.

The sample used was steel SS400 which is commonly used for bridge construction materials with the size of 50 mm x 50 mm and 45 mm of thickness. Some amount of Acetone was used to clean the steel from fat. Gum Arabic was used as a material which supports the main active material water hyacinth to coat the sample, both materials react as inhibitor. Salt water and HCl were used as corrosive media where the metal samples immersed for a certain time in different concentration of inhibitor.

The equipment that were used in this experiment including oven, scales, centrifuge, sieve shaker, grinder, laboratory glassware, and spectrophotometer. Equipment that were used to determine the corrosion inhibitor analysis were weighing scale, driller, caliper, wires, sand paper, pH indicator, laboratory glassware, and camera.

2.2 Experimental Procedure

The experimental procedure was divided into two main parts, which were literature study and experiment on the sample. The literature study was focused more on comprising data from previous researches about the natural inhibitor, water hyacinth, gum arabic and corrosion rate. By comparing all the data from previous researches, some conclusions could be taken as reference for this study.

The experiment was divided into 4 different stages. After preliminary treatment of *Eichhornia crassipes*, the first stage was the extraction of water hyacinth with water and ethanol, the second step was total phenolic content analysis. The third stage was formulation of inhibitor solution by doing some literature reviews on how Gum Arabic can inhibit the corrosion and affect the water hyacinth extract. The last stage was the analysis of corrosion inhibitor by doing weight loss measurement and visual observation.

3 Results and Discussion

3.1 Literature Study

The literature study was focused on the usage of natural ingredients as a corrosion inhibitor. This part also points out the similarity between water hyacinth and the other natural ingredients which have been proven effective as a corrosion inhibitor.

3.1.1 Green Inhibitors from Natural Resources

The study of the use of inhibitors from organic materials, especially those derived from extracts of natural materials, has been a concern to researchers nowadays both in Indonesia and abroad, because these ingredients are harmless in their application and are environmentally friendly. Some of the studies that have been carried out are described below [3], [7]–[10].

Table 1. Several Types of Natural Ingredients with Its Inhibition Efficiency

Researcher	Natural Ingredients	Corrosive Media	Metals	Inhibitor Efficiency
Haryono et al	Pine Resin	Sea Water	Iron	87.22
Hermawan et al	Cocoa Leaves	Rain Water	Steel	93.06
Ali et al.	Guava Leaves	HCl	Iron	56.29
Singh et al.	Aloe Vera	HCl	Mild Steel	90
Vorobyova et al.	Grape Pomace	N/A	Mild Steel	92

From the Table 1, it can be seen several types of natural ingredients that previously has been examined and tested for its inhibiting effect on the metals. Although this data could not be a benchmark to each other since there might be differences in the corrosive media, corrosion rate method, inhibitor concentration, and types of metals, but it is clear enough to see that natural ingredients extracts have a potential to be applied on the metals as an inhibitor.

Bioactive compounds from the extraction of various plants have the ability to substitute conventional inhibitors which have high levels in toxicity. The exact mechanism of action of plant extract inhibitors depend on the composition of their active substances, and therefore many researchers also asserted many theories to explain their observations [11]. One idea seems to be that the bioactive components form onium ions in acid medium and then adsorbed on a cathodic surface of a metal and disrupt the cathodic reaction. The main components of natural inhibitors differ between one species of plants to another, but their functions are strongly related to their organic equivalents.

From the above discussion, it is quite obvious that natural plant extracts are effective green corrosion inhibitors against mild steel. In most of these extracts from several plants, the interaction of corrosion inhibitors could be subject to heterocyclic compounds such as flavonoids and alkaloids in it. Also, the presence of tannins, cellulose and polycyclic compounds typically improves on layer formation over the metal surface, thus contributing to inhibit the corrosion.

Table 2. Contents of Natural Ingredients Extract that Contribute to Inhibition Efficiency

Natural Ingredients	Extract Contents
Pine Resin	α-pinene
Cocoa Leaves	Alkaloid, flavonoid, terpenoid and saponins
Guava Leaves	Tannins.
Grape Pomace	Flavonoids, flavonol, flavanol and tannins.
Aloe Vera	Hemicellulose, tannins, vitamin E, and carotene

3.1.2 Inhibitory Effect of Water Hyacinth Extract

In accordance with the work done by Jimmy (2018), the phytochemical of water hyacinth has been observed with different tests to observe the presence of phytochemicals in different solvent. It was found that water hyacinth contains tannins, flavonoids, and saponins [12]. .

Apart from the total phenolic inside water hyacinth, the antioxidant activity also may be caused by natural phytochemicals contained in water hyacinth itself. Kurniawan *et al.* (2010) explained that the antioxidant activity of water hyacinth not only comes from phenolic contents, but also from vitamin C, carotene, and chlorophyll [13]. Monsod Jr (1981) also stated that vitamin E content in water hyacinth could act also as antioxidant [14].

Table 3. Natural Phytochemicals of Water Hyacinth

Natural Phytochemicals	Content in WH
Vitamin C	18.16 g/ 100 g WH
Carotene	0.86 mg / L
Chlorophyll	3.73 mg /L
Vitamin E	10.6 mg / g WH

3.1.3 Inhibitory Effect of Gum Arabic

Gum arabic (GA) is a dried, chunky exudate derived from various species of Acacia trees of the *Leguminosae* family. This is a water-soluble as well as complex combination of glycoproteins, polysaccharides, oligosaccharides and arabinogalactan. GA can be useful as hydrocolloid, emulsifier, texturizer, film former and stabilizer.

According to the work by previous researchers, with the addition of GA, the efficiency to inhibit metals from corrosion increases. The ability to inhibit was possibly caused by the adsorption of the inhibitor on the surface of the metal of oligosaccharides, polysaccharides, glycoproteins, and arabinogalactan constituents of GA on the metal surface which adsorbed on the surface of carbon steel to form a protective layer [15]. The adsorption behaviour of GA is due to its both hydrophilic and lipophilic properties as the polysaccharides content in GA are strongly water soluble, containing the hydroxyl functional group (– OH) and the carboxyl functional group (– COOH) which may be attracted onto the surface of metals to prevent it from corrosion [16].

3.1.4 Mixture of Water Hyacinth and Gum Arabic

In terms of formulating the inhibitor, some gum arabic was added by dissolving the gum arabic to the solution according to its weight percentage into the solution ranging from 0%, 5%, 10%, 15%, and 20%.

The WH extract used in this experiment was produced through extraction with water. Jimmy (2018) has conducted an experiment of water hyacinth extract in several types of solvent, one of them was water. As stated by Jimmy, the highest total phenolic content of WH extract in water coming from the extraction with ratio 1:75 which is 17.00 mg GAE/g WH [12]. Thus, the extraction process was carried out by 48 hours of maceration with water with the sample to solvent ratio of 1:75.

3.2 Anti-Corrosion Analysis

The greater the corrosion rate of a metal, the faster the material to be corroded. The quality of corrosion resistance of a material can be seen in Table 4. The weight loss method was used in this experiment to determine the corrosion rate.

Table 4. Corrosion Resistance Quality of a Material with Units

Relative corrosion resistance	mpy	Mm/yr	µm/y	pm/s
Outstanding	< 1	< 0.02	< 25	< 1
Excellent	1 – 5	0.02 – 0.1	25 – 100	1 – 5
Good	5 – 20	0.1 – 0.5	100 – 500	5 – 20
Fair	20 – 50	0.5 – 1	500 – 1000	20 – 50
Poor	50 – 200	1 – 5	1000 – 5000	50 – 200
Unacceptable	200 +	5 +	5000 +	200 +

3.2.1 Corrosion Rate Measurement

3.2.1.1 Effect of Each Inhibitor on Reducing the Corrosion Rate

The first batch of the immersion test was to observe the corrosion rate of the metals when the metals were immersed in a solution without inhibitor, with WH extract only, with GA solution only, and the combination of both. The solution that was used in the first batch was tap water which commonly known to have neutral pH around 7.

The use of this batch test was to determine the inhibiting effect of each inhibitor which later can be used for further formulation. The first solution used was tap water. The mineral content in tap water may also cause corrosion. The oxygen dissolved in tap water has bigger effect on forming the rust on the metals surface.

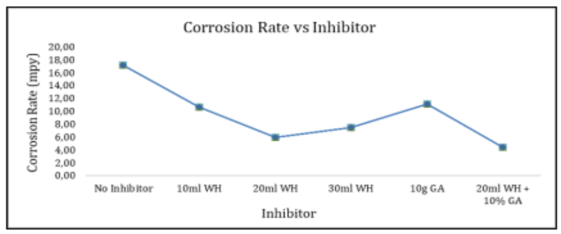

Figure 1. The Corrosion Rate in Water Media after 48 hours

The Figure 1 shows the correlation of corrosion rate in correlation with the amount of inhibitor dipped in the solution. The highest corrosion rate was recorded when the metal was immersed without any inhibitor in it, the corrosion rate was 17.17 mpy (mils per year). Whilst the lowest corrosion rate of 4.40 mpy was observed in the metal that was given 20ml water hyacinth extract plus 10% wt of gum arabic in the solution.

The metals were assumed to have the same dimension as each other although there might be a slight difference in initial weight due to the dissimilarity of the initial condition. Thus, the density of each metal was different.

The Figure 2 shows the comparison of inhibitors in different media which are sodium chloride and tap water. Based on the figure above, it is shown that all the samples immersed in WH extract encountered a reduction in corrosion rate. The metal immersed in 20 ml WH encountered the greatest reduction of corrosion rate. Water hyacinth extract could reduce greatly the corrosion rate due to lignin content in water hyacinth helps to delay corrosion. Lignin compounds have heterocyclic / aromatic structures that protect ferrous metals from reacting with oxygen.

Lignin compounds are organic compounds which have adsorption characteristic. In addition, lignin compounds react electrostatically between charged metals and charged molecules, reacting between charged electrons in pairs in the inhibitor molecule and the metal surface.

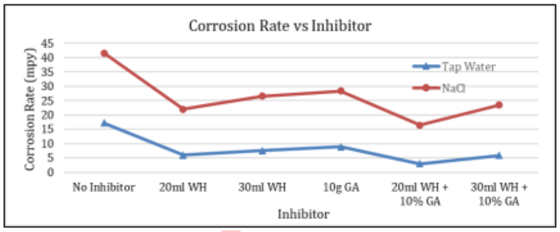

Figure 2. Comparison of Corrosion Rate in NaCl and Tap Water after 48 hours

In addition, the tannin content of water hyacinth also can inhibit corrosion because tannins can form iron + tannin complex compounds. Complex compounds formed by tannins will coat the metal and be useful to prevent corrosion. Iron is a transition metal, one of the characteristics of transition elements is that they have a tendency to form complex ions or complex compounds. The ions from iron have empty orbitals that can accept electron pairs from tannins. In accordance with Carey's theory (2007), that complex compounds can occur between ions of iron and ligands (EDTA, flavonoids, tannins), due to the coordination of iron bonds that have empty orbitals with ligands that have unpaired electrons [17].

Even though there was an inhibitor with more concentrated of 30 ml of WH extract, the corrosion rate reduction of metal in 30 ml WH extract was still less than the metal with 20 ml WH extract inhibitor. This was probably because the excessive concentrations of inhibitors could trigger the subsequent corrosion again due to the decomposition reaction of the inhibitor layer that has formed because it has passed the saturation in the inhibitor layer. This is in accordance with the work done by Malfinora (2014) that states the most optimal absorption of lignin is 10% v/v [18].

Inhibitor consist of 10% GA also proven to decrease the corrosion rate as it lowered the corrosion rate from 17.17 mpy without inhibitor to 11.10 mpy in Figure 1. This is the evidence that gum arabic itself has the ability to shield metals from corrosion. With the best formulation, the combination of water hyacinth extract and gum arabic can be utilized as a good source of inhibitor. The combination of 20 ml water hyacinth extract and 10% gum arabic showed an impressive result in reducing the corrosion rate to 4.40 mpy as shown in the Figure 1.

By comparing the ability of each inhibitor in different types of solution, both corrosion rate reductions in the Figure 2 displayed a similarity in pattern, but not quite in value. As can be seen from the pattern, the usage of 20 ml of water hyacinth extract has reduced the corrosion rate greater than the usage of 30 ml water hyacinth extract in both solutions. In addition, the combination of 20 ml WH extract and 10% arabic showed the most promising result. Therefore, for the next experiments, in order to achieve greater rate of reduction, the formulation would have a mixture of 20 ml WH extract in it.

3.2.1.2 Effect of Gum Arabic Addition on Inhibitor

As written in above discussion, the use of 20 ml water hyacinth extract could reduce the rate of corrosion more efficiently than 30 ml WH. In the next experiment, certain amount of gum arabic was added to improve the ability of WH extract in inhibiting the corrosion.

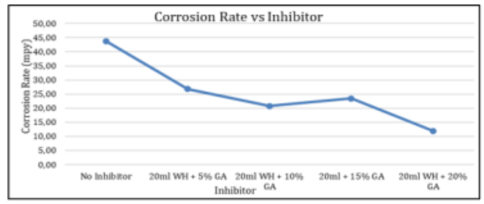

Figure 3. Corrosion Rate in NaCl Media after 24h

From Figure 3, it can be seen the correlation of corrosion rate in correlation with the amount of inhibitor dipped in the sodium chloride media for 24 hours. The presence of chloride in the solution causing the faster corrosion rate than in the Figure 1. The chloride ion content in the solution can attack the layers on the surface of the metals, which leading to the discharge of metal ions such as iron, nickel and chromium which are important ions of metals. In the present study, the concentration of sodium chloride was 3.5%. If the concentration of NaCl was higher, then the amount of chloride ions also higher which will generate the greater corrosion rate. This was due to the presence of chemical elements, especially the chloride ion Cl^- which is very aggressive, where these ions in addition to accelerating corrosion, can also take place without the supply of oxygen. In the process, the sodium chloride formed a strong electrolyte solution that causing corrosion of the metals. From the data obtained, it was found that the greater concentration of inhibitor consists of water hyacinth extract and gum arabic in sodium chloride solution 3.5%, then the rate of corrosion of metals were smaller and the efficiency of inhibition were even greater. This was caused by the increasing inhibitor mixture were absorbed in metal surface, so it can block the charge of corrosive ions on the steel surface.

The more concentrated gum arabic, the better the reduction rate. Although from the Figure 3, it can be perceived that there was a slight increase in corrosion rate at the concentration inhibitor of 20 ml WH + 15% GA, this could be happened due to the layer of Fe-inhibitor extract could not cover the entire surface of the steel, so that parts that were not covered by Fe could ionize and experience corrosion. In addition, there are impurities on the tannin extract attached to the surface of the steel also affect the corrosion rate. The addition of inhibitor in sodium chloride media could improve the quality resistance of the metals from fair to good as printed in the Table 4.

The metal samples that were immersed in hydrochloric solution suffered a great loss of weight which led to a big number of corrosion rate as can be seen in the Figure 4. This was probably caused by the over concentrated of the solution that made metals ion to be easily dissolved in the solution. The mass reduction occurred because the sample underwent an electrochemical process or can be called the process of corrosion in water. Electrochemistry occurs because the metal will dissolve into Fe^{2+} ions, these ions will diffuse into water which acts as a cathode and will form $Fe(OH)^2$ which will then be oxidized by O_2 in water and settles to form brownish Fe_2O_3.

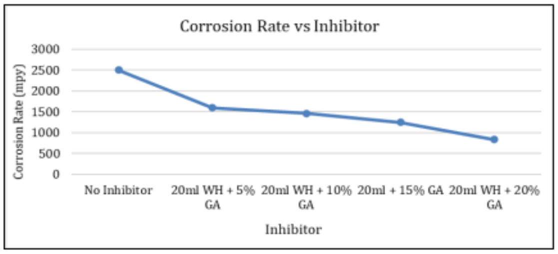

Figure 4. Corrosion Rate in HCl Media after 24h

Acid solutions, especially hydrochloric acid environments, are highly corrosive and causing steel metals to quickly corrode or damage at a rapid rate of corrosion in the presence of H^+ ion or low pH and the presence of chloride ions which are aggressive ions that can attack the passive layer (Fe_2O_3) or iron (III) hydroxide so that steel metals will experience pitting corrosion. Hydrochloric acid is a heavy reducing acid which turns it extremely corrosive when in interactions with certain metals. Hydrochloric acid is monoprotic, which implies that it has a strong degree of dissociation in liquids, resulting in an excessive amount of H+ ion concentration dissolved in the solution. The excessive amount of H+ ions implies that it has a very small pH point of 0-1. This indicates that it is a highly corrosive substance.

It is observable from the Figure 4 that the metal with no inhibitor in the solution encountered heavy reduction as the corrosion rate increased to 2500 mpy. However, even though the metal had a massive corrosion rate when immersed in a solution without inhibitor at all, the presence of inhibitor was again proven to decrease the rate of corrosion significantly. The addition of gum arabic in the solution gave rise to the results in accordance with the theory that the higher the concentration of the inhibitor, the higher the level of corrosion reduction.

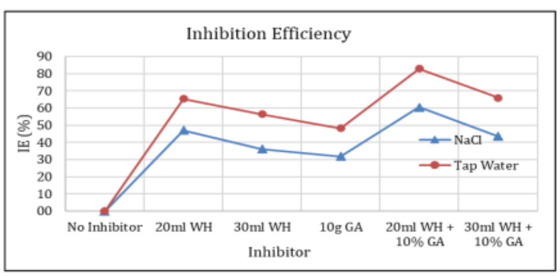

Figure 5. Inhibition Efficiency in Tap Water and NaCl media

3.2.2 Inhibition Efficiency

The efficiency of the inhibitor shows the percentage of corrosion rate reduction due to addition of inhibitors. The smaller the corrosion rate then the greater the efficiency of the inhibitor and the value of the efficiency of the inhibitor depends on the volume of the inhibitor given and the time of contact.

The Figure 5 shows the inhibition efficiency in accordance with the corrosion rate reduction in the Figure 2. It is shown that that the efficiency of water hyacinth extract was obtained at the highest 65.3% in tap water and 47.1% in sodium chloride solution.

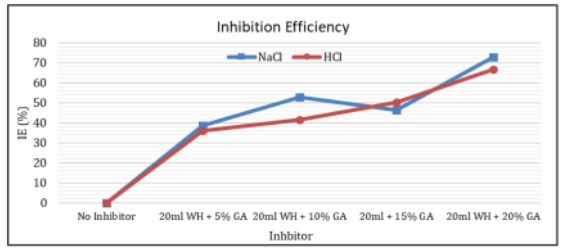

Figure 6. Comparison of Inhibition Efficiency in Corrosive Media after 24 hours

As can be seen from the figure above, the inhibition efficiency increased as the inhibitor was added. The highest efficiency of inhibitor was 72.77 % that was derived from the immersion of metal in sodium chloride with the addition of 20 ml water hyacinth extract mixed with 20% gum arabic which acted as inhibitor. Whilst in the HCl media, the highest efficiency was not slightly different as the IE could reach 66.68% with the same of inhibitor. The usage of mixture of 20 ml WH and 20% gum arabic was the foremost option among the other mixtures in 2 different medias as it showed the highest efficiency of inhibitor after the immersion of 24 hours.

From Figure 7, it can be seen the inhibition efficiency over time of immersion test in different media. The inhibitor used was the same which was a mixture of 20 ml WH extract and 20% w/w gum arabic that has the highest efficiency among the mixtures as displayed in the Figure 6.

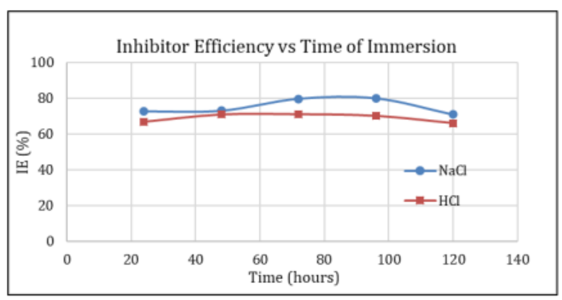

Figure 7. Inhibition Efficiency over Time of Immersion

Efficiency fluctuation of the inhibitor of the 20 ml WH extract plus 20% GA with the duration of immersion shown in the Figure 7. Inhibition efficiency of the inhibitors were observed to improve significantly by up to 24 hours and then after some time it continued to increase gradually until the fourth day in sodium chloride solution and the third day in hydrochloric acid media. showing the forming of persistent layer on the surface of metals were also fluctuating over time.

Samples with a certain amount of inhibitor added will be adsorbed onto the surface of the metal in a relatively short span of time. This caused a fairly lower corrosion rate. With the extended time of immersion as shown in the Figure 7 the inhibitor would be more adsorbed. This could cause an increase in the inhibition efficiency to a certain point where the adsorption has reached the saturation point, and then after that, the inhibition efficiency tends to be constant.

As can be seen from the Figure 7, the inhibition efficiency started to weaken at different point of time. This was caused by the different condition of the solution, the hydrochloric solution used in this study was almost ten times by concentration than the sodium chloride itself. The extremely concentrated hydrochloric acid which is known to be a highly corrosive substance could damage the layer formed by the addition of inhibitor. Moreover, over the time, according to the experiment done by Nugriani, the quality of the water hyacinth extract itself could reduce significantly especially the extract that was kept under the room temperature like in the present study [6]. The quality reduction means the reduction in terms of total phenolic contents in water hyacinth. As TPC could be the contributors to the corrosion inhibitor activity, when the TPC encountered a degradation then the inhibition efficiency also might be affected the same way.

Following the similar observation conducted before by using *Pluchea indica* leaves, *Psidium guajava* leaves, and Gum Arabic as an inhibitor, all these inhibitors followed the isotherm of Langmuir isotherm [19]–[21], which means that the inhibitor formed a monolayer on the metal surface to shield the metals from corrosion.

4 Conclusion

This study shows that the extract of water hyacinth can be used as a green corrosion inhibitor due to the content in it. The extract of water hyacinth by using water contains tannins and flavonoids that could inhibit the corrosion rate. Furthermore, high levels of lignin as well as vitamin E, carotene, and chlorophyll content in water hyacinth also may contribute to its inhibition efficiency. The highest inhibition efficiency of WH extract is 65.3% in tap water and 47.1% in sodium chloride solution. However, with the addition of an appropriate dose of gum arabic, the inhibition efficiency can be increased significantly. The highest inhibition efficiency of the WH and GA mixture is 71.08% in hydrochloric acid solution after 3 days of immersion and 79.75% in sodium chloride solution after 4 days of immersion.

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