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Dimethyl Sulfoxide-Treated Starch of *Dioscorea hispida* as a Green Corrosion Inhibitor for Low Carbon Steel in Sodium Chloride Medium

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Additional information is available at the end of the chapter

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Abstract

This research was focused on discovering the utilization of *Dioscorea hispida* (*gadong* tuber) starch as a potential green corrosion inhibitor for SAE 1045 carbon steel in 0.6 M NaCl media. Raw starch from *gadong* tubers was obtained through the extraction and precipitation process prior to drying in producing fresh starch powder. The insoluble starch powder was then dissolved in 90% dimethyl sulfoxide (DMSO) solvent and was ready for corrosion inhibitor testing. The extraction of starch powder was analyzed using Fourier Transform Infrared Spectroscopy (FTIR) to identify the presence of functional groups that may contribute to the inhibition of the carbon steel sample. The inhibitive performance of *gadong* tuber starch (GTS) as a green corrosion inhibitor was studied by weight loss measurement and potentiodynamic polarization in a corrosive medium using 0.6 M sodium chloride (NaCl) solution. Effect of GTS concentration on corrosion behavior was investigated. Based on the findings, 1500 ppm of GTS demonstrated the highest corrosion inhibition performance as the corrosion rate of carbon steel immersed in plain 0.6 M NaCl was reduced from 0.131 to 0.018 mm/year, which is up to 86.3 IE% of inhibition efficiency in the presence of the green corrosion inhibitor. According to potentiodynamic polarization analysis, corrosion current density (I_{corr}) was also decreased from 1.13×10^{-5} to 1.55×10^{-6} mA/cm².

Keywords: green corrosion inhibitor, DMSO-treated starch, *gadong* tubers, sodium chloride, electrochemical

1. Introduction

Carbon steel is the most common form of steels and because of its low cost, it is the chief material of construction. Moreover, carbon steel is extensively used in many industries such as automotive, pipelines and chemical industries [1]. However, the metal corrodes when it comes in contact with the environment containing chlorides [2, 3], such as when the metals are exposed to seawater. Corrosion study of carbon steel is a fundamental academic and industrial concern that has acquired a considerable amount of interest [4]. Since carbon steel is one of the widely used alloys, with most heavy industries such as construction materials for pipe work in the oil and gas production and engineering materials in the ocean that use low-alloy steels for its piping system in order to transport corrosive media to the storage tank. Note that the corrosion potential of carbon steel in seawater is as low as -0.8 V [5], which means that carbon steel is vulnerable to corrosion attack when in contact with seawater due to the presence of aggressive chloride ions (Cl^-). Over a certain period of time, it attacks a wide range of scales [6].

The application of corrosion inhibitor is extensively known for its capability to prevent metal alloy structure from corrosion. Commonly, corrosion inhibitor is applied mostly in the oil and gas field, piping system and paint coating. [7, 8]. Basically, the ability of the corrosion inhibitor in retarding corrosion is due to the existence of one or more heteroatoms such as sulfur (S), nitrogen (N), oxygen (O) and phosphorus (P). These compounds usually manage to facilitate adsorption on the metal surface and are believed to form a protective thin film on the carbon steel surface. Normally, the efficiency factors for the adsorption properties are related to the nature and the state of substrate surfaces, the type of corrosive medium and chemical structure of the inhibitor [4].

By and large, there are two types of corrosion inhibitors: inorganic and organic corrosion inhibitors. Inorganic compounds such as chromate, dichromate, nitrite and nitrate are commonly used as corrosion inhibitors in several media and for different metals and alloys [5]. However, the biotoxicity of these products, especially chromate, is well documented [6], as well as their non-environmental-friendly characteristics [7], which limit their application. Currently, research in corrosion is oriented to the development of “green corrosion inhibitors”, compounds with good inhibition efficiency and low risk of environmental pollution and hazard [8].

Efforts have been paid in the pursuit to replace synthetic corrosion inhibitors with inhibitors obtained from eco-friendly substances. This interest has increased considerably due to the fact that naturally sourced corrosion inhibitor products contain mixtures of compounds having oxygen; sulfuric and nitrogen are eco-friendly, cheap, renewable and ecologically anti-corrosive substances, biodegradable and sourced from renewable materials [9, 10]. The successful uses of naturally occurring substances to inhibit the corrosion of metals in various environments have been reported by several researchers [11, 12, 13, 14].

The choice of optimal inhibitor should be based on its structure, ease of synthesis, cost of raw material and its toxicity in the environment must be negligible. The naturally eco-friendly corrosion inhibitors are indistinguishable due to several drawbacks such as: plant

extracts are rich valuable sources of natural compounds that could be extracted simply without economic cost and most of the natural products are easily biodegradable, have no toxicity and have continuous feed sources of materials [11, 13]. Many plant extracts have been used as effective corrosion inhibitors of low carbon steel in corrosive media [15]. Carbohydrate polymers, which represent a set of chemically stable, biodegradable and eco-friendly macromolecules, have been widely used as corrosion inhibitors [16]. The use of biopolymers is gaining ground as inhibitor formulations for various field applications. A number of green corrosion inhibitors of biopolymeric base have successfully been produced (Table 1).

Starch is one of the most abundant natural polymer which can be obtained at low cost as only a simple extraction process is involved [17]. It is regarded as an inexpensive, renewable and readily available alternative with essential and active ingredients responsible for the corrosion inhibition. Moreover, starch also falls under the biodegradable source which is a suitable candidate for developing environmentally friendly corrosion inhibitors [18]. This organic corrosion inhibitor would benefit several applications in industries involving seawater, such as for cooling purposes, ship cleaning and desalination plants. Apart from that, starch from *gadong* tuber (*Dioscorea hispida* sp.) hauls huge potential as an organic corrosion inhibitor replacing synthetic inorganic corrosion inhibitors in the market and is harmless to the environment and does not require enormous processing scale.

Corrosion inhibitor	Finding	Inhibition efficiency	Authors
<i>Xanthium strumarium</i> leaves (XSL)	Adsorption of XSL extracts obeyed Langmuir adsorption isotherm model which acted as a mixed mode of physical and chemical adsorption, as the free energy of adsorption was more than -20 kJ/mol.	94.82% at mL/L of XSL	Khadom et al. [11]
Gum <i>Arabic Acacia</i> (GA)	GA acted as a mixed-typed inhibitor which suppressed both the anodic and cathodic process by physical and chemical adsorption on the steel surface following Langmuir adsorption model.	97% at 1.0 gL ⁻¹ of GA	Azzaoui et al. [12]
Polysaccharide from <i>Plantago</i> (AX)	Inhibition efficiency increased with increasing AX concentration and solution's temperature, which indicated a major role of chemical adsorption. The adsorption of AX on carbon steel surface obeys Langmuir adsorption isotherm. The adsorption process is mixed adsorption and endothermic accompanied by a decrease in entropy.	93.54% at 1000 ppm AX	Mobin and Rizvi [13]
<i>Rollinia occidentalis</i> (RO) extract	RO extract might be considered a mixed-type inhibitor since it affected both the anodic and cathodic reactions. Moreover, this behavior can be understood in terms of an inhibition mode resulting from the geometric blocking of the metallic surface by the adsorbed inhibitive species.	85.7% at 1.0 gL ⁻¹	Patricia et al. [14]

Table 1. Comparative summary of various natural corrosion inhibitors used in corrosive media containing Cl⁻ on low carbon steel substrates.

Gadong tuber is a monocotile plant, which is an exotic tuber in our country, Malaysia (as shown in **Figure 1**). In previous years, it had been one of the sources of carbohydrates, but now the tubers are forgotten. Because it contains cyanide components in its alkaloid group, these tubers need to be soaked and cleaned first to remove the poison (*discorina*) before being eaten or used as a medicine. Interestingly, the extract from this tuber has been used as one of the ingredients in the production of poisons for the traditional Malay community in order to fish and control pests for rice cultivation.

There are about 1137 species of *Dioscorea* found throughout the world and scientific studies have begun since 1953 by scientists in the United States. The distribution of this species is wide-spread, from northern India encompassing South China to New Guinea. It grows extensively in areas such as secondary forests, bushes and sometimes planted in the yard and able to survive in various weather conditions and can survive for years and does not perish easily. There are several trade names for the *Dioscorea hispida* species around the world including *Mitsuda dokoro* (Japan), *Podava* (India) and *Sikapa* (Makassar). *Gadong* tubers grow in soil such as cassava and sweet potato. In the hole or base of trees, there are some round tubers that can grow up to several kilograms, hard skinned and with a fibrous root around them. Its skin is brownish yellow or slightly darker depending on the type of soil. When the *gadong* tuber has ripened in the soils, it turns greenish indicating that it contains high quantities of toxins. Planting methods usually use tubular cuttings and rarely use seed or stem cuttings. **Figure 2** shows the structure of the *Dioscorea hispida* sp. plant.

Since these tubers are no longer used as food source, our research group has exploited and modified the yields of these tubers to a more sophisticated material. In a series of *gadong* tuber studies, as an introduction, our research group introduces the benefits that can be derived from these toxic tubers. This chapter focuses on the development of green corrosion inhibitor from a natural source which is extracted from starch of *gadong* tuber (*Dioscorea hispida* sp.). the performance of starch from *gadong* tuber has been tested on a carbon steel sample in 0.6 M NaCl stimulating seawater. Corrosion evaluation was performed by weight loss measurement and electrochemical analysis. The experimental flow is shown in **Figure 3**.



Figure 1. (a) *Gadong* tuber plant and (b) *gadong* tuber.



Figure 2. Parts of *Dioscorea hispida* sp., 1. Stalks, 2. Tuber, 3. Stem, 4. Branch, 5. Male flowers and 6. Fruit (capsules).

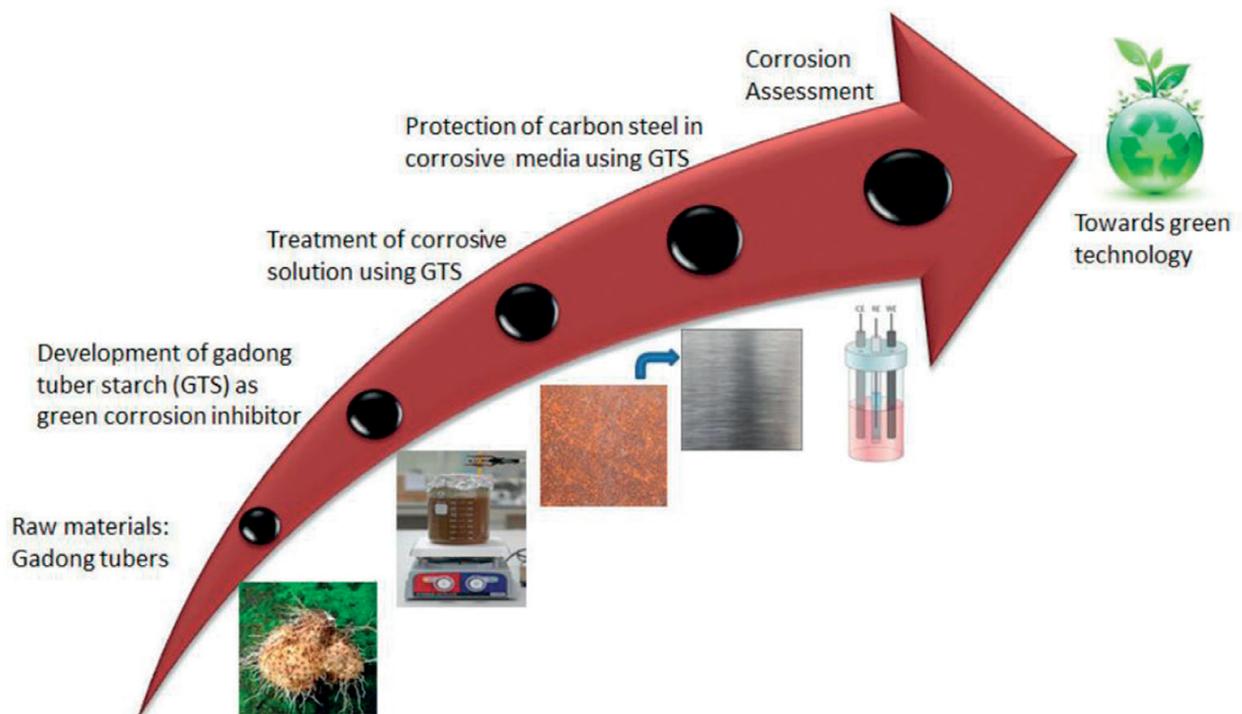


Figure 3. Development of starch from *gadong* tubers as a green corrosion inhibitor.

As for the future, the availability of abundant raw materials from natural sources can be the prime alternative to solve many industrial problems, especially corrosion. By consuming the naturally safe and economic resource, that is, *gadong* tubers, as corrosion inhibitors, the tubers can produce efficient, harmless and inexpensive functional starch. Apart from that, the uses of the starch can be numerous and advance in the future. The three major objectives of this research are the following:

1. To synthesize green corrosion inhibitor based on starch from the *gadong* tuber extract (*Dioscorea hispida* sp.).
2. To determine inhibition efficiency of the natural starch based on corrosion inhibitor in 0.6 M NaCl.
3. To investigate corrosion behavior and surface morphology of low carbon steel exposed in treated simulated seawater using *gadong* tuber extract.

2. Experimental procedure

2.1. Separation of starch

Starch separation method was conducted according to [19, 20] with a slight modification whereby, the freshly obtained tuber was washed with minimum distilled water, peeled and chopped into small pieces using a knife. Then, the chopped tuber was suspended in sufficient amount of distilled water prior to shattering using a blender (Panasonic MX-900) for 5 minutes. Then, the slurry suspension was filtered using a cheese cloth into a container before the filtrate was left for at least 5 hours for the starch to settle at the bottom of the container. The suspension was left to settle for 12 hours at normal room temperature in order to prevent the suspension from spoiling. Next, the supernatant was removed and the starch slurry was dried at 50°C for 2 days to remove all the water content. Finally, the starch powder was collected and stored for further usage. Subsequently, a method established by [21] was followed by dispersing 10% w/w of starch with 90% dimethyl sulfoxide (DMSO)-10% water. Then, the mixture was homogenized by a high-speed homogenizer for 15 minutes to achieve a homogenous brown-yellowish slurry before being diluted to the desired concentration.

2.2. Characterization of corrosion inhibitor

A mobile phase of the liquid chromatography was pumped through 0.5 mm filter into an injector fitted with a 100 ml injection loop to the chromatography column to a photometer with a helium-neon laser source ($\lambda = 632.8$ nm) and a K-5 flow cell. Meanwhile, the frit porosity and particle packing sizes for the column sets were 10 and 20 mm, respectively. The columns were placed in a column heater which was kept at 55°C. The mobile phase was 50 mM and the flow rate was 0.4 ml/min. The functional group of the treated and untreated starch with DMSO was identified by FTIR Spectrum, Perkin Elmer at a range of 400–1200 Hz. The untreated starch was characterized in powder form; meanwhile, the treated starch was in an aqueous form at 3000 ppm. Both the resultant spectra were obtained in order to compare the differences in the spectrum before and after being treated with DMSO.

2.3. Chemical composition of carbon steel used and sample preparation prior to corrosion measurement

The carbon steel used as a test sample was SAE 1045 with a composition of 98.63% Fe, 0.26% C, 0.47% Mn, 0.01% S, 0.01% P, 0.04% Cr, 0.43% Si, 0.02% Ni and 0.13% Al. Before performing morphological observation and corrosion measurement, the samples were ground by abrasive silicon carbide (SiC paper) from 120 to 1200 grit and polished using a lubricant and 1 μm diamond spray on polishing cloth.

2.4. Corrosion assessments

Gravimetric measurement was conducted according to ASTM G-31 Immersion Corrosion Testing of Metals standard. The corrosion behavior of carbon steel specimens with dimensions of 16.0 mm diameter and 3.0 mm thickness was weighed and measured, before being immersed in 240 ml solution containing 0.6 M NaCl. Different concentrations of the corrosion inhibitor ranging from 500 to 2500 ppm were studied during the 7 days of the immersion test. Then, the specimens were taken out and cleaned with cleaning solution as stated in ASTM G1-90 before being reweighed and measured to ascertain weight loss.

The electrochemical measurements were obtained using potentiostat-galvanostat GAMRY 3.2 which was connected to a computer with CMS 105 Gamry Framework Ver. 3.20 software. The three electrode cells were set up using a graphite rod as counter electrode (CE) and a saturated calomel electrode (SCE) as reference electrode. The working electrode (WE) was a carbon steel coupon with an exposed surface area of 2.01 cm^2 immersed in 150 ml of the respective solution. After the WE was immersed in the solution, open circuit potential was established for 30 minutes in order to achieve steady state potential before performing the electrochemical measurement. The current-potential Tafel slope were plotted by changing the electrode potential automatically from -0.25 to $+0.25$ V with the scanning rate of 0.1667 mV/s. The corrosion potential (E_{corr}) and corrosion density (I_{corr}) were assessed from the interception of the anodic and cathodic section of attained Tafel slopes.

2.5. Morphological study

The morphological study of the carbon steel sample surface was investigated using Ultra High Resolution field emission scanning electron microscopy (FESEM), Merlin. The sample surface was examined after immersion test in corrosive medium using 0.6 M NaCl solution and with the presence of corrosion inhibitor.

3. Results and discussion

3.1. FTIR analysis

Figure 4 shows the FTIR spectrum of extracted starch powder from the *gadong* tubers before and after treatment with DMSO. Through rough observations on the peak, (A) raw starch

powder and (B) raw starch powder treated with DMSO solvent, both spectra show similarities at the range of $3700\text{--}1500\text{ cm}^{-1}$ bands. They also possessed the same extremely broad bands at 3700 cm^{-1} . These spectra were typically referred to the mixture of two molecular identities of polysaccharides of starch [22].

On the other hand, the raw starch powder extracted from *gadong* tubers (A) showed a large number of adsorption bands in the region of $\sim 1200\text{ cm}^{-1}$, in which it was referring to the minor component of proteins and lipids in the GTS [23]. Moreover, at the fingerprint region of bands between 900 and 1500 cm^{-1} , bands at 997 , 1077 , 1149 and 1340 cm^{-1} were identified as -C-O-C- bonds in the anhydroglucose unit. The anhydroglucose unit is the most important chemical building block of polysaccharides of starch without containing water [24].

FTIR spectra of extracted GTS (A) before and after treatment with DMSO (B) displayed that both spectra exhibited a transmittance peak at 3288 cm^{-1} with broader band of spectrum B. This phenomenon was attributed to the complex vibrational stretches associated with free inter- and intra-molecular hydroxyl group (-R-OH). Spectrum B possessed a broader band of hydroxyl group as a result of a high amount of water content during dissolution process with DMSO [11]. Moreover, spectrum B had a base line slope at 1700 cm^{-1} and below which was due to DMSO water content during the dissolution of starch that made the starch granules swell, and almost all the semi-crystalline characteristics of the granules vanished. As the swelling enlarged, the starch granules burst releasing the starch into the solution and solubilizing the starch [25].

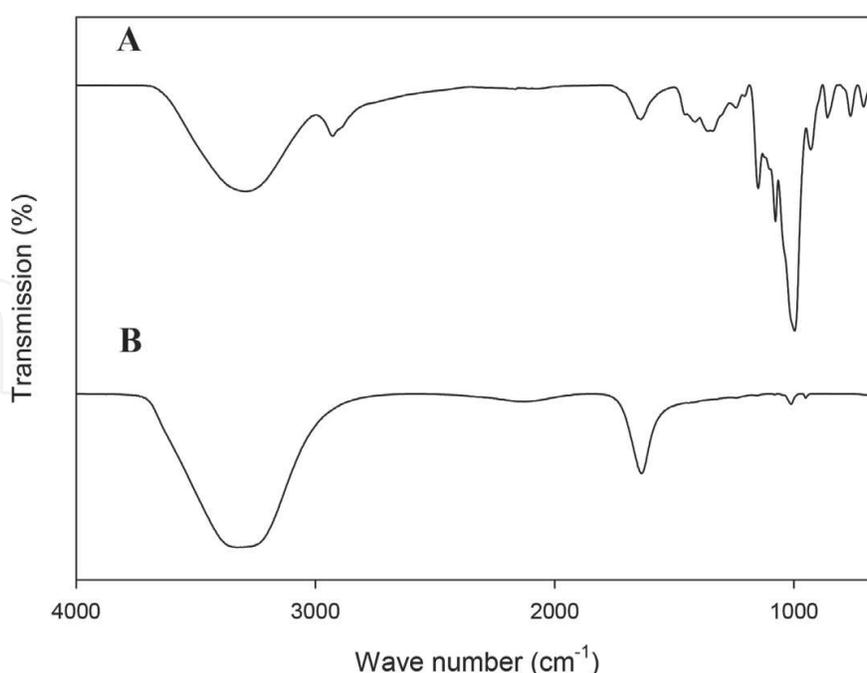


Figure 4. FTIR graph of extracted starch powder (A) before and after being treated with DMSO (B).

3.2. Corrosion measurement: gravimetric analysis

The corrosion behavior of SAE 1045 carbon steel in corrosive medium using 0.6 M NaCl was studied by the gravimetric method for 7 days of immersion, containing the concentrations of GTS ranging from 0 to 2500 ppm as a corrosion inhibitor. The calculated value of corrosion rate (mm/year) immersion test in NaCl medium is tabulated in **Table 2** and **Figure 5**. As displayed in **Figure 2**, corrosion rate of carbon steel in 0.6 M NaCl solution decreased with increasing concentrations of GTS up to 2000 ppm with lowest rate of corrosion at 0.048 mm/year. However, a further addition of GTS (using 2500 ppm) resulted in a slight increase in corrosion rate of 0.051 mm/year. This phenomenon indicated that the GTS might potentially act as corrosion inhibitor by enhancing the corrosion resistance of SAE 1045 carbon steel at a certain concentration of GTS.

Since inhibition efficiency is significantly dependent on the surface degree coverage of the GTS molecule on the surface of the carbon steel surface, the degree of the coverage can be calculated using the following formula [26]:

$$\theta = \frac{C_{R^0} - C_R}{C_{R^0}} \quad (1)$$

where C_{R^0} and C_R are the corrosion rates in the absence and presence of GTS as a corrosion inhibitor, respectively. **Table 2** shows the degree of the surface coverage (θ) that increased as a function of GTS concentration. The highest surface coverage of 0.59 was achieved by incorporating 2000 ppm of GTS. The phenomenon explained the improvement of corrosion protection by GTS which was due to the adsorption coverage of the corrosion inhibitor compound on the surface of the metal substrate. The adsorbed compound managed to impede the surface of the substrate from the surrounding corrosive media and thus stopped the corrosion process from taking place [22]. Moreover, the GTS molecules that adsorbed on the surface of the metal substrate interact between the lone pairs of electrons of the oxygen atom and the carbon steel surface, which supported the adsorption process. So, the presence of d π -vacant orbital of low energy in the iron atom also contributed to the adsorption process [27].

Concentration of GTS (ppm)	Corrosion rate (mm/year)	Coverage (θ)
0	0.116	0.00
500	0.108	0.06
1000	0.091	0.21
1500	0.050	0.57
2000	0.048	0.59
2500	0.051	0.56

Table 2. Calculated value of corrosion rate (mm/year), coverage area (θ) and inhibition efficiency (%) of carbon steel SAE 1045 after immersion in 0.6 M NaCl for 7 days.

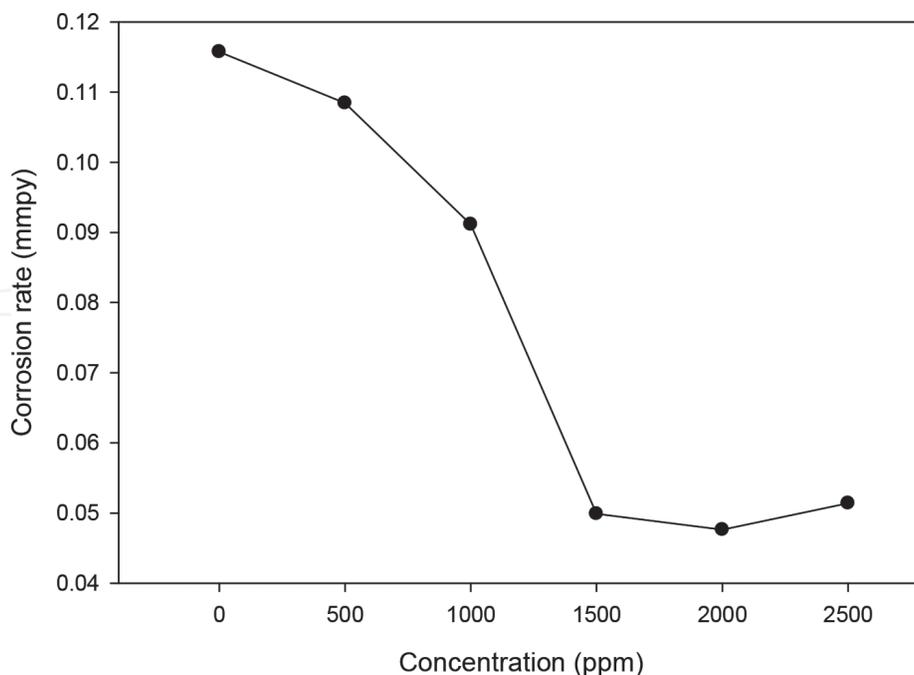


Figure 5. Gravimetric analysis of corrosion rate for various concentrations of *gadong* starch.

Due to the exposure to the aqueous solution, the inhibitor molecules which consisted of polymer compounds started to hydrolyze, inducing the bulk anions and cations in the media to increase and disturb the inhibition process. The hydrolysis of NaCl media caused the NaCl compounds to decompose into Na^+ cations and Cl^- anions. Some of these ions have reacted to water molecules and inhibitor molecules. The Na^+ ions that reacted with OH^- and Cl^- which combined with H^+ cations form a neutral solution or salt as corrosion products.

Apart from that, an increase in oxygen and carbon dioxide concentration in the inhibitor solution as the experiment was done in an open space for a 7-day period of immersion affected the inhibition and corrosion activity of the carbon steel samples. As reported by previous researchers, certain concentrations of inhibitors were affected by the concentration of oxygen and carbon dioxide contained in the inhibitor solution [28, 29]. In this current finding, the optimal concentration of the GTS was 2000 ppm for the 7 days of immersion testing. Further increasing of the starch to 2500 ppm was not significant in inhibiting corrosion activity as the corrosion rate increased to 0.051 mm/year.

3.3. Potentiodynamic polarization analysis

The potentiodynamic polarization measurement was used to capture the behavior of corrosion inhibition of GTS on the SAE 1045 carbon steel samples. The transition changes in Tafel slopes could be used to determine whether the GTS acts an anodic, cathodic or mixed type of inhibition process. The polarization curves of the carbon steel in 0.6 M NaCl corrosive medium with various concentrations of GTS are shown in **Figure 6**. According to the Tafel plot, corrosion potential (E_{corr}) of all concentrations of GTS added were mostly shifted towards

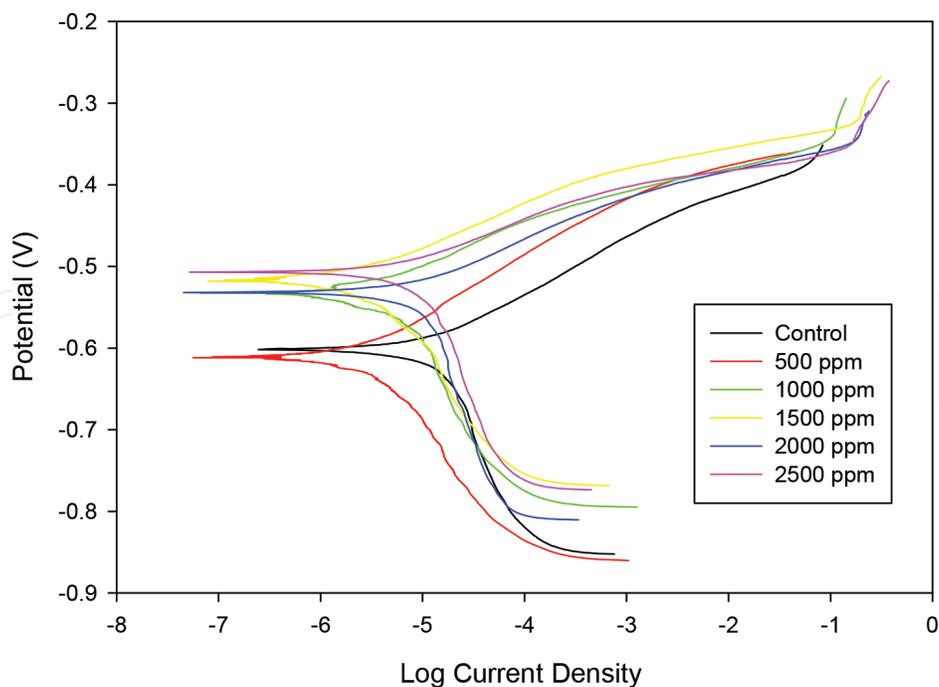


Figure 6. Potentiodynamic polarization curves of SAE 1045 carbon steel samples for various concentrations of GTS in 0.6 M NaCl solution.

a more positive position compared to the blank (control) sample. The E_{corr} shifting to a more positive position indicated that the GTS possessed a potential role in improving corrosion resistance of the carbon steel in treated NaCl solution by reducing the chemical reaction during immersion time [23, 28].

As shown in **Table 3**, E_{corr} of the immersed sample in plain 0.6 M NaCl was -601.4 mV. The E_{corr} was increased to -517.1 mV with an addition of 1500 ppm GTS. However, further increase of GTS to 2000 ppm decreased the E_{corr} which was -531.9 mV but then increased to 507.1 mV with an addition of and 2500 ppm. This fluctuating E_{corr} signified that the corrosion improvement was only achieved at a certain concentration of GTS. In general, maximum E_{corr} shift which is <85 mV demonstrated that the inhibitor is classified as a mixture inhibitor while for E_{corr} shift >85 mV, the inhibitor is a type of actual cathodic or anodic inhibitor [21]. From this finding, by incorporating the GTS into NaCl solution up to 2000 ppm provided maximum E_{corr} shift of 69.5 mV. Thus, it can be proposed that at these concentrations, the GTS is a type of mixture inhibitor as the maximum E_{corr} shift was less than 85 mV [19, 30].

Apparently, the incorporation of GTS offered an inclination to inhibit the corrosion activity by anode as the E_{corr} was shifted towards positive position. However, it was found that with addition of 2500 ppm GTS, this corrosion inhibitor potentially works as an actual anodic and cathodic type as the maximum E_{corr} is 94.3 mV, slightly larger than 85 mV. Due to the shifting plot towards positive position, the incorporation of GTS at this concentration was suggested to act as an anodic inhibitor where the corrosion activity was dominated by anodic reaction rather than cathodic reaction [20].

Concentration of GTS (ppm)	Corrosion potential, E_{corr} (mV)	Corrosion density, I_{corr} (mAcm^{-2})	β_a (mV)	β_c (mV)	Corrosion rate, (mm/year)	Inhibition efficiency (IE%)	Polarization resistance, R_p
0	-601.4	1.13×10^{-5}	66.9	232.2	0.131	0.00	1993
500	-612.0	2.52×10^{-6}	75.5	146.1	0.029	77.86	8587
1000	-532.8	2.24×10^{-6}	48.0	149.6	0.026	80.15	7036
1500	-517.1	1.55×10^{-6}	48.2	131.6	0.018	86.26	9912
2000	-531.9	6.66×10^{-6}	50.3	259.9	0.077	41.22	2750
2500	-507.1	5.93×10^{-6}	47.0	220.3	0.069	47.33	2836

Table 3. Electrochemical parameters obtained from potentiodynamic polarization analysis.

I_{corr} was reduced from 1.13×10^{-5} of plain 0.6 M NaCl to 1.55×10^{-6} mA/cm² in the presence of 1500 ppm GTS. This situation was in agreement with the corrosion rates of the tested materials, where the lowest corrosion rate (0.018 mm/year) was provided by treating the corrosive medium with 1500 ppm GTS. Increasing GTS concentration slightly increased the I_{corr} resulting in an increase in the corrosion rate. However, the I_{corr} of the samples immersed in GTS-treated NaCl was considerably lower than the sample immersed in non-treated solution. The reduction of I_{corr} shows that the corrosion inhibitor adsorbed on the surfaces expressively protects the surfaces from further corrosion attack; thus, the corrosion rate was potentially reduced.

In addition, there was no consistent change of β_a and β_c for the tested samples immersed in various concentrations of the incorporated GTS. This phenomenon signified that the corrosion inhibitor does not stop the corrosion activity but significantly retards the chemical reaction on the exposed surfaces. The inhibition reaction that occurred was due to a restriction mechanism towards active site of chemical reaction on the coupon's surface [24]. A maximum inhibition efficiency was achieved at 86.26 IE% with the addition of 1500 ppm GTS. This result proved that GTS significantly improved the corrosion resistance of SAE 1045 carbon steel in 0.6 M NaCl corrosive media.

Chemically, the carbon steel (Fe^{2+}) surrounded by the presence of NaCl begins to lose electrons, thus becoming a cation in solution:

Oxidation reaction: Fe is oxidized (loses electrons).



The lost electrons are now used to decrease the chlorides dissolved in the simulated seawater (the water will contain some Na^+ and Cl^- ions):



Reduction reaction: Cl is decreased (gains electrons).

The Fe²⁺ ions then chemically react and bond with the OH⁻ ions in water to create iron hydroxide, which eventually dries up to form rust:



The highest inhibition efficiency of 86.26 IE% was provided by incorporating 1500 ppm GTS into 0.6 M NaCl medium. This phenomenon is attributed to the optimum adsorption of natural starch corrosion inhibitor's molecules that managed to cover the surface of carbon steel, in which it makes a split-up between the surface of carbon steel samples and the corrosive media. In addition, the presence of Na⁺ cations and Cl⁻ anions also has fortified the corrosion inhibition mechanism of carbon steel samples in seawater [30, 31]. This scenario was supported by the formation of stable FeCl₂ salt as a corrosion product.

Figure 7 shows the SEM images and EDX characterization on carbon steel samples after immersion in 0.6 M NaCl for 7 days. The carbon steel immersed in plain NaCl shows a rough and thick layer of corrosion product. A thick deposition layer that covered most of the carbon steel surface was identified as ferrum (III) oxide (Fe₂O₃), which would easily fall off the surface, exposing a black layer (magnetite) underneath, which was due to corrosion process of steel [32]. This phenomenon was confirmed by EDX analysis that ferrum and oxygen elements were present on the surface of the carbon steel as a result of the reduction reaction of oxygen that originated from aqueous NaCl solution. The reduction reactions are as follows [33, 34]:



The Fe²⁺ ions then chemically react and bond with the OH⁻ ions in water to create iron hydroxide, which eventually dries up to form rust: (Iron (III) hydroxide).

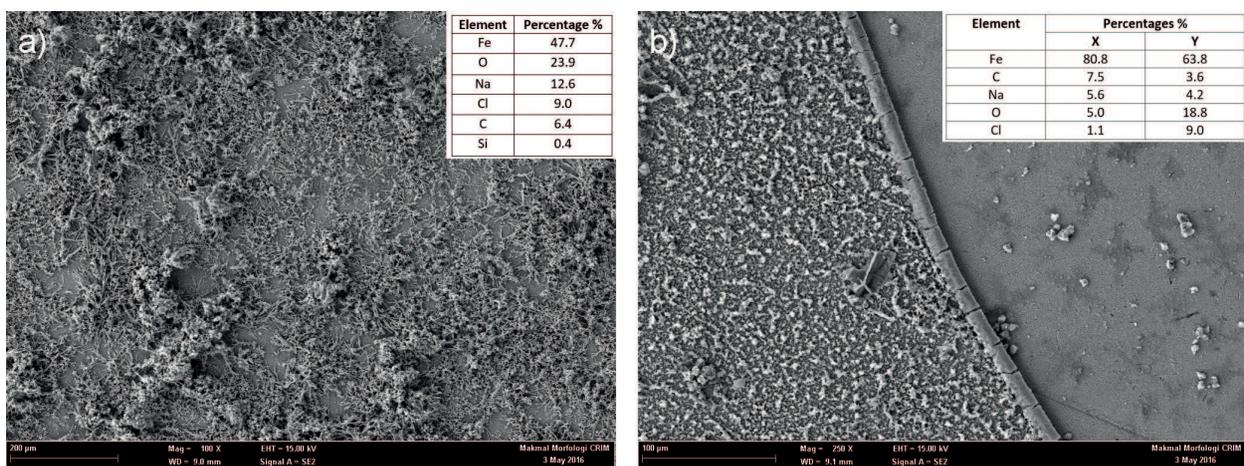


Figure 7. SEM images and EDX analysis of SAE 1045 carbon steels samples (a) without the presence of *gadong* starch (control) and (b) with the presence of 1500 ppm *gadong* starch as corrosion inhibitor after being immersed in 0.6 M NaCl after 7 days.

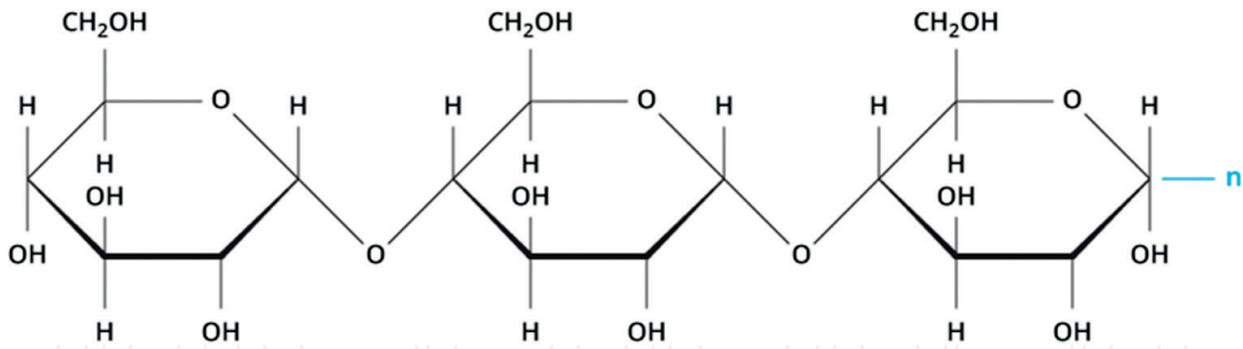
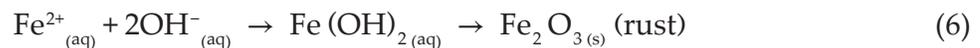


Figure 8. Basic chemical structure of polymeric starch.



The factors that will speed up the rate of corrosion include an increase in the amount of oxygen, temperature, chemical salts and humidity. However, as illustrated in **Figure 4(b)**, the carbon steel immersed in NaCl solution containing GTS as the corrosion inhibitor at 1500 ppm concentration shows most of the carbon steel surface with smooth terrain with small area of rough surface of corrosion product. This scenario signified that the corrosion resistance of carbon steel was remarkably enhanced with the presence of GTS as a corrosion inhibitor, with respect to its smoothness and less-corrosion product formed, indicating the reduction of corrosion rate.

The polysaccharides of starch were amylose, a long linear molecule, and amylopectin, a highly branched version of amylose molecule [13]. The basic chemical formula of the starch molecule is $(\text{C}_6\text{H}_{10}\text{O}_5)_n$. Starch is a polysaccharide comprising glucose monomers joined in α 1,4 linkages (**Figure 8**). The corrosion inhibition activity of GTS might be due to the presence of various organic compounds in its composition including anhydroglucose unit of polysaccharides ($-\text{C}-\text{O}-\text{C}-$ bonds) and hydroxyl group ($-\text{R}-\text{OH}$). These organic compounds contain the most important chemical building block of polysaccharides of starch and complex vibrational stretches associated with free inter- and intra-molecular hydroxyl groups which are the major adsorption centers [33]. Consequently, we suggest that the protective films may be formed on the metal surface through the adsorption process to inhibit the corrosion of mild carbon steel in artificial seawater [34].

The study showed that the inhibition of GTS molecules on the carbon steel surface in artificial seawater is a mixed inhibition, which might result either by electrostatic interaction of the polymer with positively charged carbon steel surface or through the lone pairs of electrons on oxygen atoms [21]. In the beginning, the protonated GTS molecules electrostatically interacted with the positively charged carbon steel. Then, the adsorbed GTS molecules began to participate with H^+ ions for electrons on the carbon steel surface [9]. This scenario resulted in the release of H_2 gas (due to aqueous state of NaCl solution) and GTS molecules returned to their neutral form. The carbon steel surface was reduced to be more negative which attributed to accumulation of electrons. Accordingly, an electron from the d-orbital of Fe might be transferred to a vacant π^* (anti-bonding) orbital of the GTS molecules to relieve the steel from extra negative charge and hence strengthen the corrosion inhibition of GTS via adsorption on the steel surface [28].

Natural products	Metal exposed	Test media	Concentration	IE%	References
Gadong tuber	SAE 1045 steel	0.6 M NaCl	1.5 g L ⁻¹	86.26	Current study
Saffron	Copper	Natural seawater	0.1 g L ⁻¹	67.00	[35]
Tobacco rob	Q235 steel	Artificial seawater	0.1 gL ⁻¹	83.90	[36]
<i>Santolina chamaecyparissus</i>	304 stainless steel	3.5% NaCl	1.0 gL ⁻¹	86.90	[37]
Lupine seed	Aluminum	2 M NaOH +0.5 M NaCl	0.16 gL ⁻¹	45.90	[38]
Burley tobacco	Steel/Al	3.5% NaCl	0.1 gL ⁻¹	~90.0	[39]
Tobacco	Aluminum	3.5% NaCl	1.0 wt%	96.60	[40]
Olive leaf	Copper	0.5 M NaCl	2.42 mmol L ⁻¹	90.0	[41]

Table 4. Comparison of the inhibition efficiency of GTS with other natural products extracts.

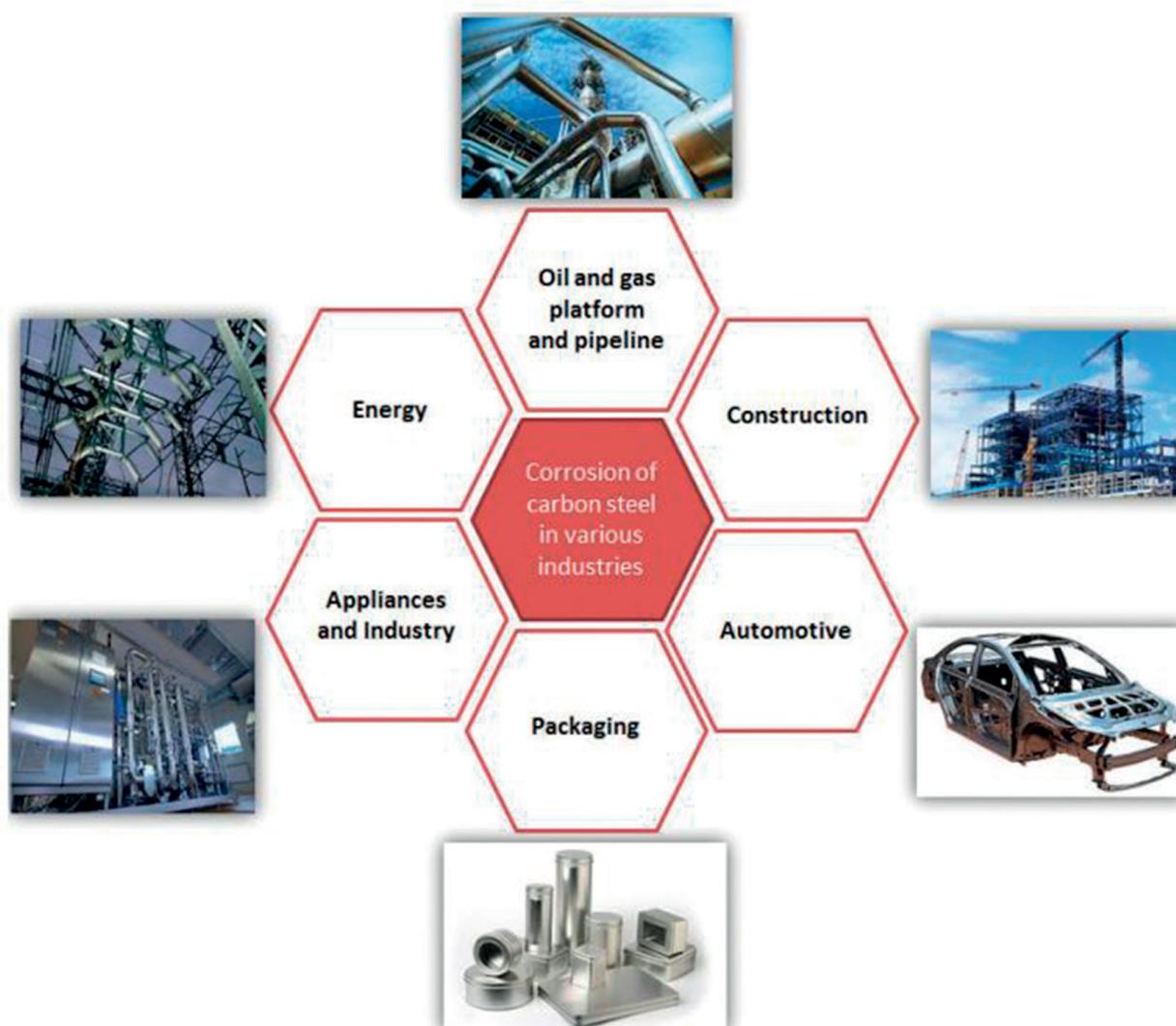


Figure 9. Schematic illustration of potential uses of green GTS in various industries.

Table 4 shows a comparison of the inhibition efficiency of currently produced GTS with other natural product extracts. The inhibition efficiency, IE% of GTS is 86.26 IE% by incorporating 1.5 g L^{-1} GTS on low carbon steel in artificial seawater was considerably comparable to other natural products. However, the inhibition efficiency of Saffron (0.10 g L^{-1}) was only 67.0% in natural seawater. The inhibition efficiency of Tobacco rob (0.1 g L^{-1}) on medium carbon steel, *Santolina chamaecyparissus* (1.0 g L^{-1}) on stainless steel, Lupine seed (0.16 g L^{-1}) on aluminum, Burley tobacco (0.1 g L^{-1}) on steel/Al, tobacco (1.0 wt%) on aluminum and olive leaf (2.42 mmol L^{-1}) on copper were 83.90, 86.90, 45.90, ~90.00, 96.60 and 90.0 IE%, respectively. A comparison of these data with the results of previous investigation indicated that GTS has good inhibition performance in artificial seawater. This finding proposed that the green GTS can be used in numerous industries suffering from corrosion attacks as shown in **Figure 9**.

4. Conclusion

Starch extracted from *Dioscorea hispida* sp. is an exceptional corrosion inhibitor for SAE 1045 carbon steel in 0.6 M NaCl solution. Through potentiodynamic polarization analysis, the GTS as corrosion inhibitor was identified as mixed type of corrosion inhibitor which was more prone towards anodic inhibition process. A maximum inhibition efficiency of 86.26 IE% was achieved with incorporation of 1500 ppm of GTS. Lower IE% at higher concentrations of GTS was due to excess amount of the starch molecules that failed to inhibit and alter the corrosive media from corroding the carbon steel sample. SEM images of the carbon steel samples upon immersion in NaCl media showed less-corrosion products formed on the steel surface upon the addition of the GTS.

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