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Nano-Silicate from Paddy Waste as Natural Corrosion Inhibitor

Norinsan Kamil Othman, Denni Asra Awizar and Zulhusni Dasuki

Abstract

The highly advance usage of an agricultural waste of rice husk ash (RHA) from *Oryza sativa* L. was developed by extracting the nanosilicate contained in RHA as a corrosion inhibitor for carbon steel in 0.5 M NaCl media. The corrosion measurement was studied using weight loss, potentiodynamic polarization, electrochemical impedance spectroscopy (EIS), surface analysis, and adsorption isotherm study. The extracted nanosilicate powder from RHA was analyzed using Fourier Transform Infrared Spectroscopy (FTIR) to identify the presence of functional groups (SiO_2), whereas X-ray diffraction (XRD) to identify the phase of silica from RHA. The particle size of nanosilicate was confirmed by transmission electron microscopy (TEM) and Zetasizer analysis, and the results show particle size of nanosilicate in the range of 5–10 nm. The maximum inhibition efficiency (IE%) is up to 88% in NaCl media. On the other hand, the inhibitor adsorption properties follow Temkin isotherm with mixed type of inhibition properties. Surface analysis on specimen that was treated with nanosilicate was smoother with fewer pits and pores than untreated specimen. In future perspectives, nanosilicate from RHA has a promising advantages and imminent applications for industries revolving with composites, biomedicine, and many more.

Keywords: paddy rice husk, nanosilicate, corrosion inhibitor, sodium chloride

1. Introduction

Corrosion inhibitors are a favorable method to prevent corrosion; it can reduce the rate of metal corrosions from corrosive environments. Most of the processing industries, such as water heating system (boiler), seawater cooling system, and pipes, made use of corrosion inhibitor as protective

measurement against corrosion. This is because of corrosion inhibitor is a straightforward use and cost-effective. However, for more than a decade, inorganic and synthetic chemical-based corrosion inhibitor such as chromate and nitrate-based has been widely used in the industries and has led into a serious environmental deterioration and dreadful impact onto marine life as excessive usage of inhibitor has exposed into the environment [1].

These environmental issues regarding the use of the synthetic corrosion inhibitor have led into a rise in environmental warnings, by the authorities and NGOs, such as Environmental Protection Agency (EPA) and Food and Drug Administration (FDA), which has had issued some industrial guidance regarding the use of corrosion inhibitor in the industries. Since then, the urgency to develop environment-friendly corrosion inhibitor has greatly increased the researcher's interest especially in the development of corrosion inhibitor derived from natural sources, i.e. rice husk waste [2].

In general, corrosion inhibitors based on natural sources are environmentally acceptable, less toxic, inexpensive to process and abundant in nature compared to corrosion inhibitor based on synthetic chemical [3, 4]. In this study, corrosion inhibitor based on nanosilicate derived from rice husk waste would be the best candidate in replacing the synthetic corrosion inhibitor. As past study reported, silicate is naturally inorganic corrosion inhibitor that has been used in various applications, such as antifreeze in the engine, which helps prevent corrosion and as an engine coolant and lubricant [5]. Apart from its application as corrosion inhibitor, silicate extracted from rice husk can be manipulated into a lot of applications and fit into today's high technology advancement, for instance, fillers in high durability concrete and structures [6, 7], drug delivery and biomedical applications [8], and many more.

Asia has the largest rice production in tropical regions. By-products of the production of rice are rice husks and rice fingers. In 2007, statistics by the Ministry of Agriculture, Malaysia, has reported that more than 408,000 tons of rice (*Oryza sativa* L.) husks were produced in Malaysia every year. Rice husks contain a high percentage of silica, which is more than 90% [9].

In these times, the study in the field of nanotechnology is growing in parallel with the development of science and technology. Nanotechnology had been applied in various fields, such as biotechnology, medication, sensor, semiconductor, coating materials, and materials industrial uses [10]. Applications of nanotechnology attract interests due to the nanosized structure materials that contained unique properties compared to lump materials.

Based on past studies, commercial silicate corrosion inhibitor delivers good inhibition efficiency for metals and alloys. According to experts, silicate corrosion inhibitors are non-toxic and have been used many years in the industry. Moreover, silicate is a compound that has the ability to be adsorbed on the metal surface to form a thin layer of barrier on the metal surface and protects the metal from corroding [11].

Today, corrosion inhibitors' products in the market were more prone toward selecting corrosion inhibitors derived from natural plant in order to solve corrosion and its problem. Some researchers have been extracting organic and inorganic compounds containing distinctive

corrosion inhibition properties. The source materials of natural corrosion inhibitors are usually inexpensive, readily available and renewable. In other words, natural-based corrosion inhibitors can replace synthetic corrosion inhibitors that are highly toxic, have expensive processing cost, and may cause harm to the environment. In this recent study, the waste from the rice field which is the rice husk will be transformed into a new usable and advance compound which is the nanosilicate compound for the use of solving corrosion problems in heavy industrial usage operation. **Figure 1** shows the summary of what is this study all about.
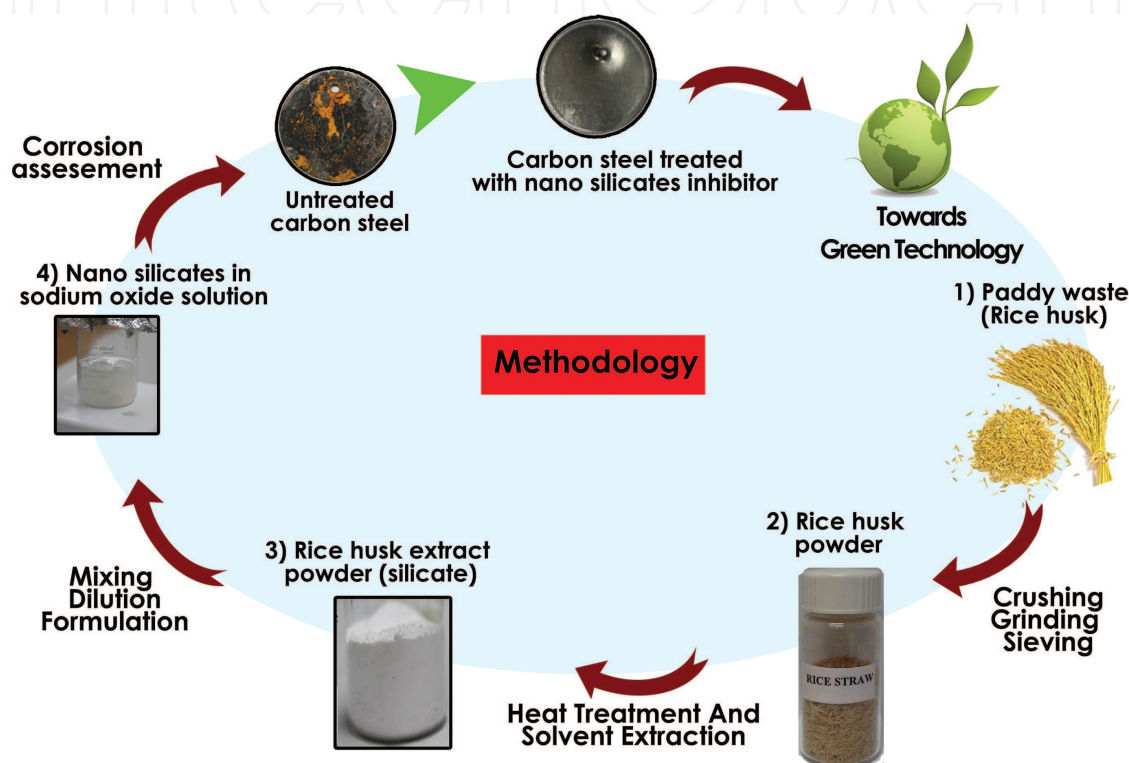
Figure 1. The development of nanosilicate from paddy waste as natural corrosion inhibitors.

As for the future prospect, the availability of abundant raw materials from natural sources can be the prime alternative to solve many industrial problems, i.e. corrosion. By utilizing the waste material and economic resources, such as the rice husk as corrosion inhibitor, the rice husk can produce efficient, harmless, and inexpensive nanosilica. Nanosilica can be extracted from rice husk ash (RHA) and formulated properly in order to act as corrosion inhibitor. Apart from that, the use of nanosilicate can be various and advance in the future. The three major objectives of this research work are the following:

i.   To formulate corrosion inhibitor based on nanosilicate from the extract of rice (*O. sativa* L.) husk ash.

ii. To determine the inhibition efficiency of the corrosion inhibitor based on nanosilicate in 0.5 M NaCl.

iii. To determine the surface morphology and type of adsorption isotherm for nanosilicate-based corrosion inhibitor on the surface of carbon steel samples.

2. Materials and methods

Rice (*O. sativa* L.) husk used in this study was obtained from Kedah, Malaysia. The chemicals used in this process were sodium hydroxide (NaOH), sulfuric acid (H$_2$SO$_4$), and hydrochloric acid (HCl) from Sigma-Aldrich.

2.1. Preparation and extraction method of nanosilicate from paddy waste for corrosion inhibitor

The collected rice husks were cleaned with distilled water to remove dirt and unwanted material before being dried. The cleaned rice husks were grounded using a blender and filtered with a 500 micron filter. Then, rice husks (50 g) were burnt in a furnace at a temperature of 600°C for 6 h according to the past methods [12, 13].

After a complete combustion, rice husk turned into white-gray ash. Then, 10 g of the ash was dissolved in 2.5 M NaOH (80 ml) to extract out the silica compound. This process carries out at a temperature of 90°C on a heating plate while the mixture was stirred with a magnetic stirrer for 3 h before it was filtered with filter paper. Then, a bright homogeneous and viscous gel of silica was obtained. Reactions that occurred over the rice husk ash containing silica and sodium hydroxide solution are as follows:

$$SiO_{2(s)} + 2NaOH_{(l)} \rightarrow Na_2SiO_{3(l)} + H_2O_{(l)} \qquad (1)$$
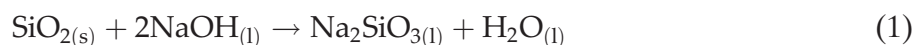
The next process was the process of neutralization whereby silica gel in alkaline condition was titrated with 2.5 M sulfuric acid until the pH reached to 2, before being stirred with a magnetic stirrer at a temperature of about 90°C. After 3 h of stirring, the agglomerated silica gel was rinsed with distilled water with a temperature of 60°C to remove the sulfuric acid, and the pH would become neutral at around 7.5–8. Lastly, the silica gel was dried in the oven at 70°C for 10 h to obtain a silica powder. This process can be determined using the following equation:

$$Na_2SiO_{3(gel)} + H_2SO_{4(l)} \rightarrow SiO_{2(s)} + H_2O_{(l)} \qquad (2)$$
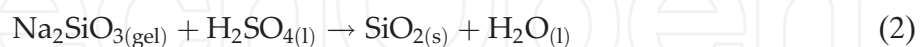
As for the preparation of nanosized silicate powder, reflux system method was followed. The apparatus used in this process is 250 ml round flask, condenser, and a magnetic stirrer system. Pure silica powder was filled in a round flask added with 80 ml of concentrated hydrochloric acid (6 M HCl). This process was carried out for 4 h at a temperature of 90°C. Then, the mixture was filtered using filter paper to obtain the silica gel. Later, 2.5 M NaOH (80 ml) is added in a vessel comprising the sample to dissolve silica and stirred for 10 h. Then the mixture was titrated with sulfuric acid (6 M H$_2$SO$_4$) to neutralize the pH of the solution to 7. The mixture was then precipitated, and the nanosilica was filtered with nano-filter paper. Once all the nanosized silica

is collected, it was dried in an oven for 48 h at a temperature of 50°C to obtain the nanosilicate powder. Then, as for preparing the nanosilicate powder for corrosion inhibitor, past method was followed in which the inhibition performance of nanosilicate is influenced by the molar ratio of SiO_2/Na_2O [14].

In this study, the best molar ratio of SiO_2/Na_2O has been determined as 3:1. Corrosion inhibitor based on nanosilicate with molar ratio (SiO_2/Na_2O) 3:1 was prepared by dissolving 6 g nanosilicate powder in a solution of 250 ml of 0.2 M NaOH. This solution was stirred with a magnetic stirrer until the solution appears clear and uniform. Equation was the reaction that occurs on nanosilicate powder and sodium hydroxide solution:

$$SiO_{2(s)} + 2NaOH_{(l)} \rightarrow Na_2SiO_{3(l)} + H_2O_{(l)} \tag{3}$$
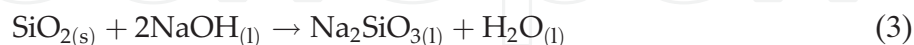
2.2. Corrosion test

ASTM G1-03 standard was followed for preparing corrosion test of carbon steel coupon in disc shaped with a diameter of 1.5 cm. Steel used in this study is the SAE 1045 carbon steel which consists of compositions Fe-bal; C, 0.4%; Mn, 0.75%; P, 0.004; and S, 0.5% in weight percentages.

All the carbon steel coupon samples were grinded from 400 to 800 grit using SiC sand paper with running tap water and were polished to produce carbon steel surface that has the same surface roughness. As for weight loss test, the coupon was weighed and its diameter and thickness were measured before and after undergoing weight loss immersion test for 7 days in 25 ml in 0.6 M NaCl solution. After 7 days of immersion, the coupons were removed from the solution and cleaned with distilled water and washed chemically and physically to remove the corrosion product according to the method ASTM G1-03. Based on these data, it can be calculated the lose weight (mg) by the following equation:

$$\Delta B = B_{before} - B_{after} \tag{4}$$

where ΔB is the loss of weight (mg) for the coupon, B_{before} is the weight of the coupon prior to immersion (mg) and B_{after} is the weight of the coupons after immersion (mg). The weight loss of data can also be calculated by surface coverage (θ), using the following equation:

$$\theta = \frac{B_{before} - B_{after}}{B_{after}} \tag{5}$$

The percentage of inhibition efficiency (IE%) as well as through the equation, from Ref. [15]:

$$IE\% = \frac{B_{before} - B_{after}}{B_{after}} \times 100 \tag{6}$$

To calculate the rate of corrosion (mg/cm^{2}h), follow the following equation (Ref. [13]):

$$CR = \frac{\Delta B}{LM} \tag{7}$$

where CR is the corrosion rate (mg/cm^{2}h), ΔB is the weight loss of carbon steel (mg) after immersion, L is the surface area (cm^2) and M is the time (hours).

2.3. Electrochemical test

Potentiodynamic polarization analysis was carried out using the potentiostat K47 Gamry. Potentiostat composed of three-cell electrode which are reference electrode (saturated calomel) with liquid KCl, the working electrode (sample), and the auxiliary electrode (carbon rod). The study was conducted at the potential range between –0.25 and 0.25 V at a scan rate of 1.0 mVs^{-1}. The surface area of the carbon steel corrosion in contact with the medium is 1.0 cm^2. Each experiment was repeated up to three times the reading. The percentage of inhibition efficiency, IE%, is calculated using the following equation:

$$IE\% = \frac{I_{corr(0)} - I_{corr(i)}}{I_{corr(0)}} \tag{8}$$

where $I_{corr(0)}$ = corrosion current density without the addition of inhibitors (mA cm^2) and $I_{corr(i)}$ = corrosion current density with the addition of inhibitors (mA cm^2).

Impedance studies were carried out using the potentiostat/galvanostat model high frequency response analyzer (FRA Solartron-1260). The initial frequency range used is 1000 kHz–100 Hz frequency end with 10 mV amplitude balance condition. Data were analyzed using the software ZView. Percentage of corrosion inhibition efficiency (IE%) was calculated using the following equation:

$$IE\% = \frac{R_{ct(i)} - R_{ct(0)}}{R_{ct(i)}} \tag{9}$$

where $R_{ct(0)}$ is the charge transfer resistance without the presence of the inhibitor (Ω cm^2) and $R_{ct(i)}$ is the charge transfer resistance in the presence of inhibitors (Ω cm^2).

2.4. Characterization of nanosilicate from rice husk

Few characterization tests had been performed on the nanosilicate, which are Fourier Transform Infrared Spectroscopy (FTIR), X-ray diffraction (XRD) and TEM. As for FTIR, the equipment used was Perkin Elmer Spectrum GX model. As for XRD, X-ray tube was operated at 60 kV maximum voltage and maximum current of 60 mA. Detection range is from 3 to 80°C. Transmission electron microscopy (TEM) is performed using Phillips CM12 model. The data obtained are in the form of an image or a two-dimensional image of the sample form. The surface of carbon steel coupons that have reacted with corrosive medium and inhibitor solution through weight loss test was scanned through a scanning electron microscope (SEM) ZEISS branded 55VP Supra model. In addition, Energy-dispersive X-ray (EDX) of INCA PENTA FETX3 was also performed on the surface of carbon steel corrosion with corrosion inhibitor and without inhibitors. EDX is used to determine the elements that are present on the surface of carbon steel samples.

3. Results and discussion

3.1. Nanosilicate extraction analysis

About 100 g of rice husk combustion in the furnace at a temperature of 600°C for 6 h resulted in 14.22 g rice husk ash (14–22%). Previous studies [16] have found that the percentage of rice husk ash is 12–20%. X-ray diffraction (XRD) was conducted to determine the phase that has formed from rice husk ash. Later, an analysis of X-ray test fluorescent (XRF) was conducted to determine the elemental composition contained in the rice husk ash.

Rice husk ash was burnt in a furnace at three different temperatures of 600, 700, and 900°C, respectively, for 6 h with a heating rate of 5°C furnace/min. Then, the rice husk ash was analyzed using X-ray diffraction to determine the silica phases formed in husks at three different firing temperatures, which is either amorphous or the crystalline phase. The method is carried out following the studies that have been done by Othman et al. [2].

Figure 2 shows the results of XRD diffraction peak for rice husk ash at different temperatures. Peak formed between the ranges of 22°–25° 2θ is the peak, which confirms the presence of silica [16, 20]. At the sintering temperature of 600°C, the XRD diffraction peak shows peaks formed are broad and wide. A second peak at 700°C has formed a sharp peak, whereas the third is the peak combustion temperature of 900°C that has formed a very sharp peak in the range of 22–25° 2θ. Through the analysis of the results of the XRD, diffraction peak formed demonstrated the formation of an amorphous phase. While the pointed summit has represented the formation of crystalline phases.
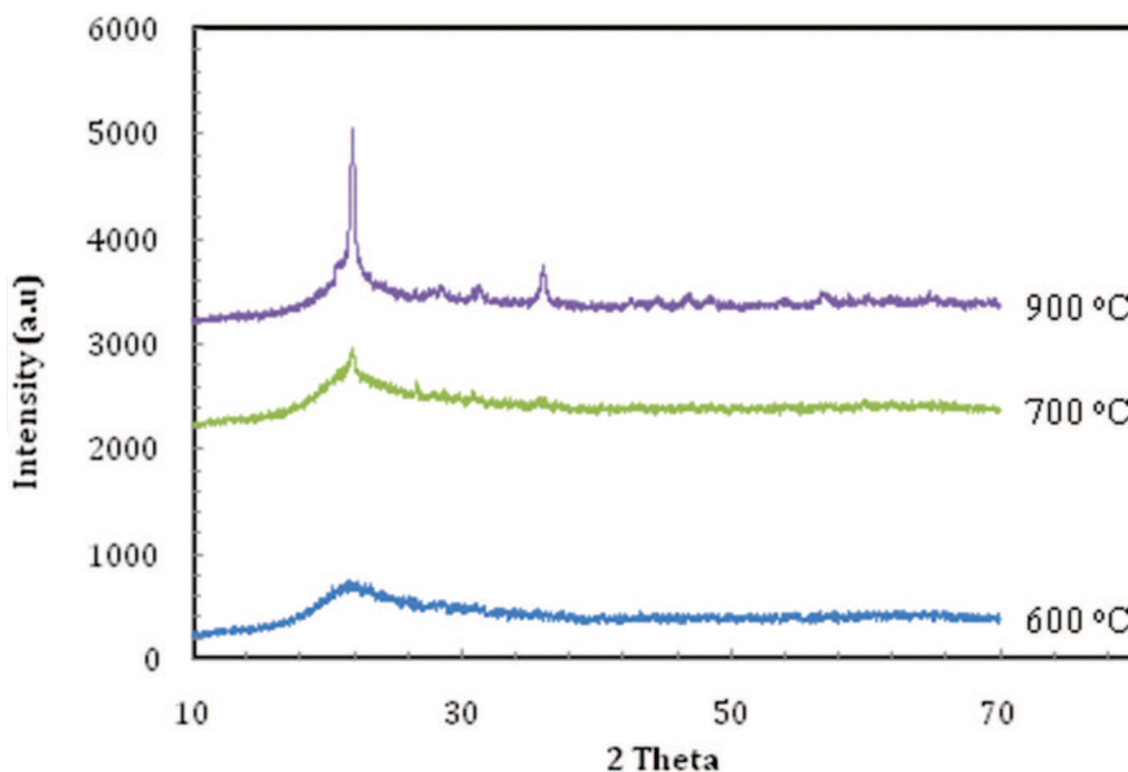
Figure 2. The results of XRD diffraction peak for rice husk ash at different temperatures.

According to previous studies, temperature and time during burning have affected the phases of the rice husk silica, in which combustion temperature below 700C formed an amorphous 3 phase, while temperatures above 700°C showed the formation of crystalline phase [19]. In this study, rice husk ash containing an amorphous phase has been selected as the main material for corrosion inhibitors. Silica particles with amorphous phases have some features that are suitable to act as corrosion inhibitors compared to crystalline phase, such attributes that helps in corrosion inhibition in amorphous silica are high surfaced area, small particle sizes, easily dissolved, irregular shapes, and high reactivity. Thus, the burning of rice husk at a temperature of 600°C is more suitable to be used to produce amorphous silica phases.

At a temperature of 700°C, rice husk ash was burnt, forming a semicrystalline phase and at a temperature of 900°C showed fully formed crystalline silica phases. Crystalline silica phases are unlikely suitable in this study, due to the insoluble crystalline phase [16]. Moreover, crystalline silica particles are harmful to human as it can caused silicosis, which is a respiratory disease caused by inhaling silica haze for long term as stated by the World Health Organization (WHO) in 1999.

The composition of the elements contained in rice husk ash was determined using X-ray instrumentation fluorescent (XRF) as shown in **Table 1**. The main element is oxygen (O) which is at 51.23% and silicon (Si) 42.44% (percentage by weight). In addition to the O and Si, there are also other elements, such as K, P, Mg, Ca, Fe, S, Na, Mn, Al, Zn, and Cl. These results show that rice husk ash contains the elements of O and Si, which represents the compounds of silica (SiO^2). Thus, rice husk ash has a high percentage of silica, which reached 93.67%. Some previous studies have also indicated that the elemental composition of the silica from rice husk ash up to 90% more [16].

Elements	Percentage (%)
Oxygen	51.23
Silica	42.4
Potassium	2.7
Phosphorous	1.0
Magnesium	0.6
Calcium	0.4
Iron	0.4
Sulfur	0.4
Sodium	0.18
Manganese	0.09
Aluminum	0.05

Table 1. The percentage breakdown of the elements contained in the rice husk ash.

Apart from that, the extraction nanosilicate from rice husk ash was analyzed using Infrared Spectroscopy (FTIR) to identify functional groups of the nanosilicate (SiO_2). Then particle size was determined using the transmission electron microscopy (TEM) and particle size instrumentation (Zetasizer) to determine the average size of the particles dispersed in solution.

Based on **Figure 3**, it shows that the spectrum produced two major peaks. A sharp peak and high intensity on adsorption band at 1055 cm^{-1} wave characterize the presence of siloxane groups of Si–O–Si asymmetric, whereas the peak at 791 cm^{-1} adsorption band characterizes the presence of Si–O–Si groups of symmetry at low intensity. The main peak shown in the spectrum is the peak that has been identified as a compound of silica (SiO$_2$) [13].
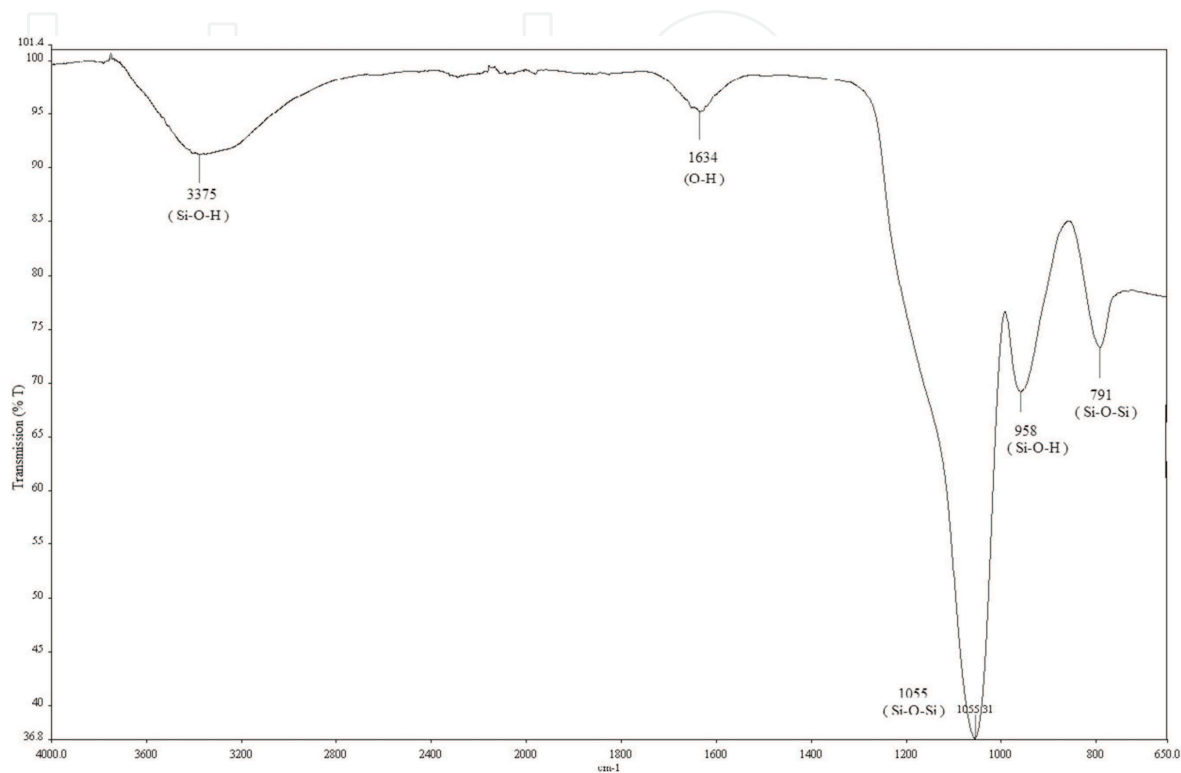

Figure 3. FTIR spectrums of nanosilicate powder.

Additionally, peaks of 3375 and 1634 cm^{-1} indicating the presence of silanol groups, which bind the 7 water group of (Si–O–H) due to the reaction between the silica with a solution of NaOH and 8 water during the extraction process silica from rice husk ash. The peak on the plane stretching vibration (plane) of 958 cm^{-1}, which further indicates silanol group [17].
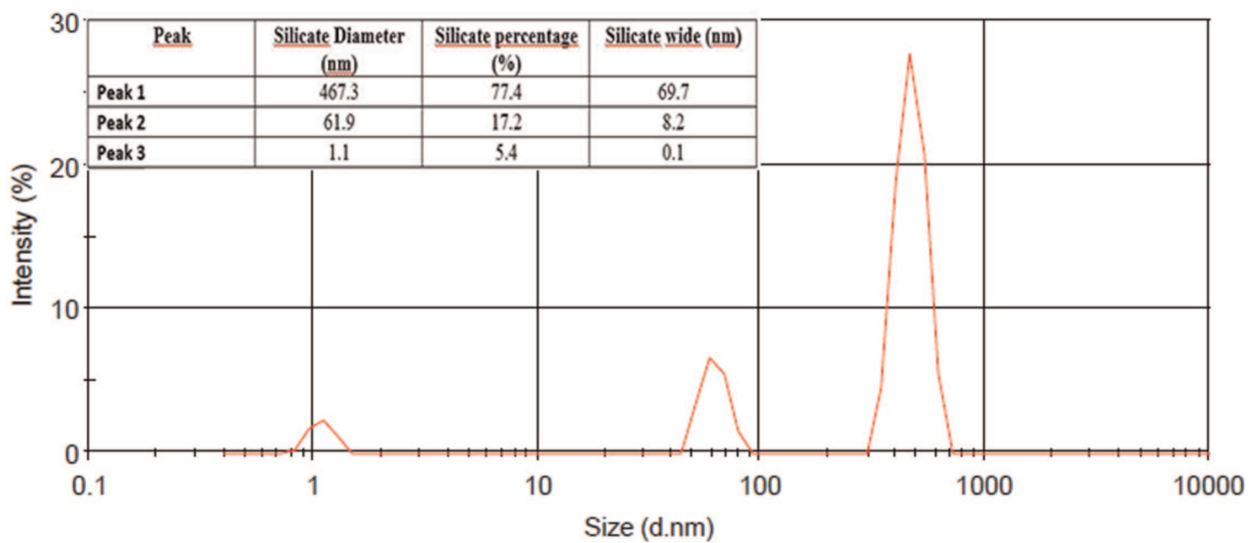
Other than that, the analysis of transmission electron microscopy (TEM) was used to identify the particle size of the silicate from the rice husk ash extraction. The results of TEM analysis have found that the size of the particles is nanosized silica powder. **Figure 4** represents nanosilicate micrograms of powder extract from rice husk ash. Silica was observed clotted with nanoscale size of approximately 5–10 nm. The silica has a spherical shape similar to previous studies [17].

The concentration of NaOH solution has affected the particle size nanosilicate formed. In the past study, it has been reported that nanosilicate powder particle measurement is influenced by the concentration of NaOH as solvent extraction, i.e. 2.0, 2.5, and 3.0 M NaOH [17]. The results obtained are nanosized silica with different measurements for each concentration of NaOH. NaOH solution with a concentration of 2.5 M produced silica particles having a particle size smaller than the concentration of 2 and 3 M NaOH, which is 5–10 nm.
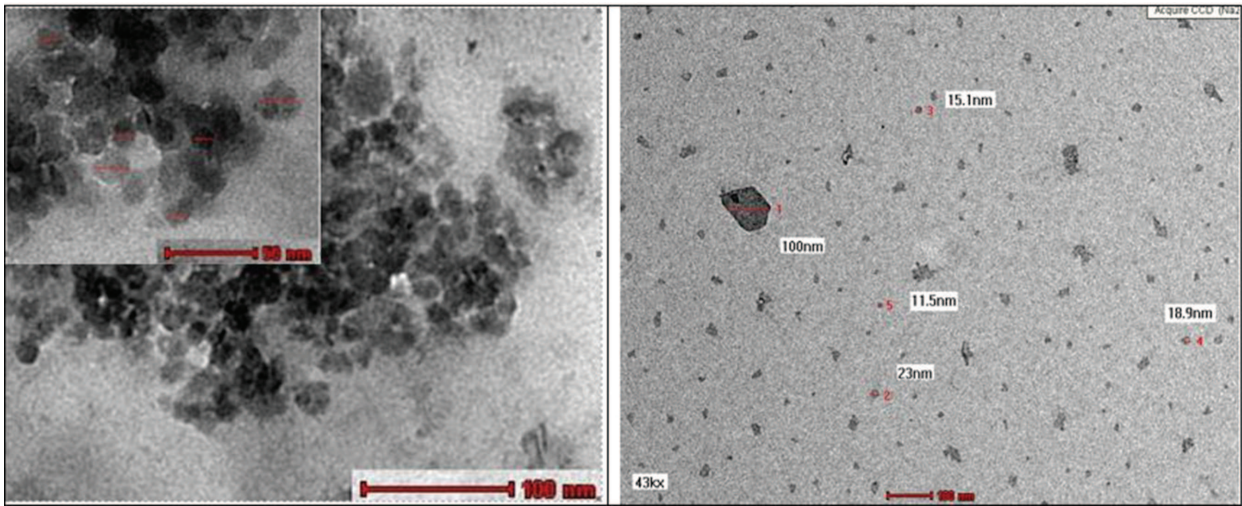
Figure 4. TEM image for nanosilicate powder from the extraction of rice husk and also TEM micrograph of nanosilicate corrosion inhibitor solution.

Figure 4 is a TEM micrograph of a solution of the formulated nanosilicate corrosion inhibitor. **Figure 4** has shown that the solution of the corrosion inhibitor has a fine particle sized of a nanosize between 10 and 100 nm. Characterization of particle size analysis was used to determine the average particle size of nanosilicate corrosion inhibitor. Results of the analysis states that there are three types of peaks indicate the average size of nanosilicate (**Figure 5**). It also shows the size distribution of the silica resulting from the analysis of zeta sizer. The average diameter size of the silica in the first peak is 1.1 nm, which has a share of 5.4%. Wide-sized silica that was featured by this peak was 0.14 nm, whereas the second peak that covers 17.2% indicates the presence of silica that has a diameter of 61.91 nm. The resulting width of silica of this peak is 8.2 nm. The third peak is the highest peak percentage and that is 77.4%.

Peak	Silicate Diameter (nm)	Silicate percentage (%)	Silicate wide (nm)
Peak 1	467.3	77.4	69.7
Peak 2	61.9	17.2	8.2
Peak 3	1.1	5.4	0.1

Figure 5. The graph zeta sizer analysis showed three types of particle size peak of nanosilicate.

Size diameter of silica is 467 nm with a width of 69.66 nm. Thus, from this discussion it concluded that the corrosion inhibitor solution of nanosilicate has a nanosized particle of silica.

3.2. Corrosion measurement analysis in 0.5 M NaCl as corrosive media

3.2.1. Inhibition effect through weight loss test

Table 2 shows the results of weight loss test after the addition of nanosilicate corrosion inhibitor in 0.5 M NaCl as corrosive media. The results of the weight loss for carbon steel samples without the presence of nanosilicate were recorded at the value of 4.3 mg. The effect of the inhibitor at concentration of 0.003 M nanosilicate has reduced the weight loss to 3.4 mg. The higher the addition of nanosilicate concentration, which is at 0.008, 0.016, and 0.03 M, the lower the weight loss of carbon steel. Based on these results, it has been found that the weight loss of carbon steel sample is proportional to the increase in the concentration of nanosilicate corrosion inhibitor.

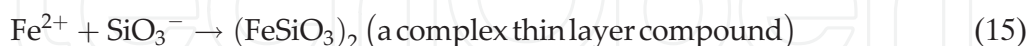| Inhibitor concentration (M)	Weight loss (mg)	Corrosion rate (mg/cm^{2}h)	Inhibition efficiencies (IE%)
0	4.3	0.556	0
0.003	3.4	0.440	20.9
0.008	1.4	0.181	67.4
0.016	1.0	0.129	76.7
0.030	0.5	0.065	88.4

Table 2. Weight loss, inhibition efficiencies %, and the corrosion rate of carbon steel in 0.5 M NaCl aqueous media without and with the presence of rice husk ash nanosilicate.

Table 2 also shows the corrosion rate of carbon steel and IE% in the presence of nanosilicate corrosion inhibitors. **Table 2** shows that the corrosion rate decreased after the addition of the nanosilicate corrosion inhibitor in NaCl media. According to the study of the past discussions which stated that the corrosion rate decreases with increasing concentrations of inhibitors, it has shown that the number of molecule inhibitors can reduce the corrosion reaction of carbon steel [18].

Not to mention, nanosilicate corrosion inhibitor also affects the IE% outcome of carbon steel sample. The highest efficiency percentage was demonstrated by the addition of 0.03 M nanosilicate at an efficiency up to 88.4%. The IE% continues to increase with increasing concentration of inhibitor [19]. This is due to the adsorption of nanosilicate corrosion inhibitor's molecules that managed to cover the surface of carbon steel [20], in which it makes a separation between the surface of carbon steel samples and the corrosive media. Apart from that, previous study has stated that the presence of cations Na$^+$ and Cl$^-$ ion also has encouraged the inhibition process for carbon steel samples [21].

Equation (10) until Eq. (14) is a reaction between carbon steel (Fe^{2+}) with NaCl as corrosive medium containing decomposing chloride ions. Then, the ions reacted with Fe^{2+} to produce FeCl$_2$:

$$NaCl \rightarrow Na^+ + Cl \tag{10}$$

$$Fe^{2+} + Cl^- \rightarrow FeCl_2 \tag{11}$$

$$Fe \rightarrow Fe^{2+} + 2e \, (\text{release of electrons}) \tag{12}$$

$$Fe^{2+} + 2e \rightarrow Fe \, (\text{accepts electrons}) \tag{13}$$

$$NaSiO_3 \rightarrow Na^+ + SiO_3{}^- \, (\text{nanosilicate}) \tag{14}$$

$$Fe^{2+} + SiO_3{}^- \rightarrow (FeSiO_3)_2 \, (\text{a complex thin layer compound}) \tag{15}$$

The presence of nanosilicate inhibitor molecules that have functional groups of SiO^{2-} plays an important role as inhibition agents. The reaction between Fe^{2+} with nanosilicate inhibitors has produced a complex compound which forms a thin layer (Eqs. (5) and (6)). In aqueous solution, the functional groups of nanosilicate SiO^{2-} will donate a pair of electrons on the surface of carbon steel whenever Fe^{2+} ions were released into the electrolyte solution. Furthermore, the inhibitor functional group, which is SiO^{2-}, is empty d-orbitals, which can form a thin layer and increase the adsorption and protection on the steel surface.

The thin layer on the surface of carbon steel that was formed is a compound that has high stability compared to Fe only [22]. Moreover, the carbon steel that has been added with nanosilicate corrosion inhibitors has more resistant toward corrosion as the nanosize of the silicate also contributes to the inhibition efficiency. Advantages of nanosilicate inhibitor is shown by the ability of nanosize silicate molecules that have a high surface area that can protect almost all of the active sites on the surface of carbon [12, 13]. Furthermore, the nanosize particle of nanosilicate forms a protective layer with good adhesion on the surface of carbon steel [23].

3.2.2. Potentiodynamic polarization analysis

Figure 6 shows the polarization curves for carbon steel in 0.5 M NaCl media with and without the presence of nanosilicate corrosion inhibitors. The E_{corr} values after the addition of nanosilicate shifted toward more positive for all concentrations than the sample without corrosion inhibitor solution. The apparent shift provides information that nanosilicate from rice husk ash is probably a mix type class of inhibitors. The decline in the value of the current density (I_{corr}) can be observed on the cathodic and anodic reaction after nanosilicate with various concentrations of inhibitor is added to 0.5 M NaCl. This proves that the addition of nanosilicate is able to inhibit both the anodic and cathodic reactions. I_{corr} devaluation that occurred in the anodic and cathodic reactions indicates the presence of molecular nanosilicate preventing current flow carried by ions in the electrolyte solution of NaCl. In the cathodic reaction, nanosilicate molecules adsorbed on the surface of carbon steel in turn can inhibit and prevent the cathodic reaction (decrease). Nanosilicate molecules that are present in a negative charge ($SiO_3{}^{2-}$) are engaged in the solution, which creates competition between the anion chloride (Cl^-) to approach the interface steel and bulk solution and then generates resistance to corrosion.
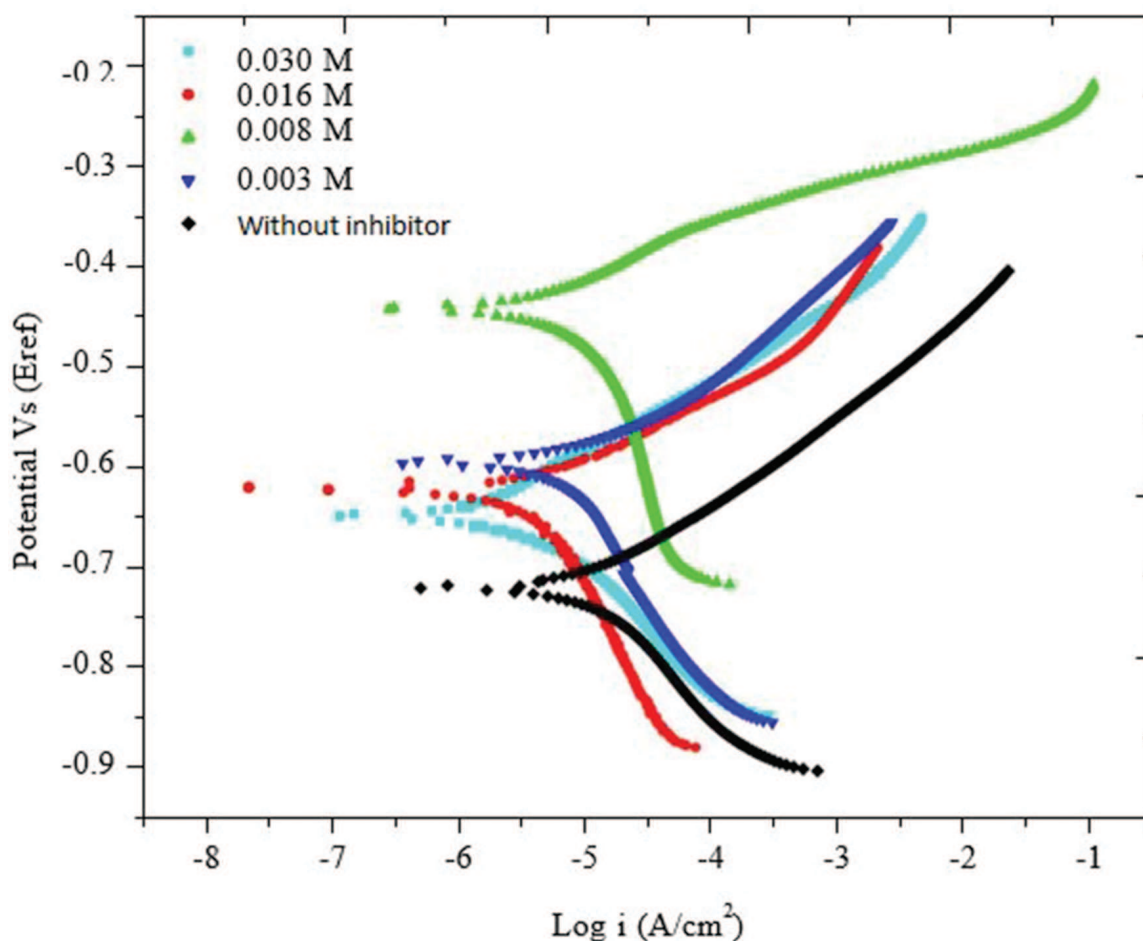
Figure 6. Polarization curves for carbon steel with various concentrations of nanosilicate inhibitor in 0.5 M NaCl as corrosive media.

Based on polarization curves and the data obtained, the inhibition behavior of nanosilicate inhibitor by potentiodynamic polarization test is in term with the results from weight loss analysis. Lower I_{corr} value of polarization curves shows an increase in the IE% for all concentrations of nanosilicate inhibitor, in which higher concentration of nanosilicate inhibitor causes the corrosion rate to decrease, which is from 0.174 to 0.026 millimeters per year (mmpy). These results indicate that nanosilicate molecules have been adsorbed on the surface of the carbon steel and reduced corrosion attack in NaCl medium.

Table 3 explains the changes in the apparent shift of E_{corr} for carbon steel samples with the presence and absence of nanosilicate inhibitor. Corrosion rate of corrosion inhibitors can be identified based on the maximum shift of E_{corr}. When the maximum displacement of E_{corr} value is <85 mV, then the inhibitor showed a mixed type inhibitor. Meanwhile, if the maximum value is E_{corr} > 85 mV, it can be classified as cathodic or anodic type of inhibitor. The results of the analysis showed that the nanosilicate inhibitor provides maximum displacement value of E_{corr} which is >85 mV. Thus, nanosilicate inhibitor for carbon steel in NaCl media can be categorized as cathodic or anodic type corrosion inhibitor.

The corrosion potential (E_{corr}) of carbon steel that has been treated with inhibitors has shifted toward more positive values than those untreated with inhibitor. Therefore, the corrosion potential of the reaction shows that the inhibition process is a mix type corrosion inhibitor but more prominently toward anodic type of inhibitor [19]. This is due to the inhibitor molecules that have been adsorbed on the steel surface to form a thin layer, which can prevent corrosion attacks of Cl ions. This is most likely due to the absorption and the formation of a protective film that has been formed between molecule inhibitors of nanosilicate and Fe atoms of carbon steel.

The results in **Table 3** show that the nanosilicate inhibitor has an average value of polarization resistance (R_p), which is more than 20 kΩ. Concentration of nanosilicate inhibitor of 0.030 M has the highest R_p value, which means it has lowest corrosion rate. Since higher R_p value decreases the corrosion rate, it causes IE% to be higher as well.

Concentration (M)	E_{corr} (mV)	I_{corr} (A/cm^2)	B_c (mV/Dec)	B_a (mV/Dec)	R_p (kΩcm^2)	Kadar Kakisan (mmpy)	IE (%)
0	−719.0	1.49×10^{-5}	154.1	95.1	1.714	0.174	0
0.003	−594.8	1.05×10^{-5}	269.2	93.7	2.868	0.123	29.5
0.008	−440.4	0.39×10^{-5}	204.3	53.4	4.697	0.046	73.8
0.016	−620.7	0.41×10^{-5}	241.3	81.2	6.426	0.048	72.5
0.030	−647.9	0.22×10^{-5}	102.4	84.3	8.953	0.026	85.2

Table 3. Results from potentiodynamic polarization analysis of carbon steel with various concentrations of nanosilicate inhibitor in NaCl 0.5 M.

3.2.3. Electrochemical impedance spectroscopy analysis

Figure 7 is a suppress semicircle graph of Nyquist plot showing the carbon steel that has been treated with and without nanosilicate inhibitor at concentrations of 0.003, 0.008, 0.016, and 0.03 M. According to the plot, the size of the overlapping semicircle of carbon steel increased with the development in silicate inhibitor concentration which causes an increase in the corrosion resistance of carbon steel [24]. Besides that, nanosilicate inhibitor that has been added at different concentrations has changed the corrosion mechanism of carbon steel in NaCl media [25].

From the impedance analysis (**Figures 7** and **8**), the IE% of 0.0016 M concentration has reached up to 21.65% only. Furthermore, past studies [26] state that for some situations, corrosion inhibitor effectiveness sometimes gives the declining or negative and inefficient result due to the concentration of the inhibitor, which is probably too low or too high during the impedance test.

In addition, the charge transfer resistance (R_{ct}) has been seen higher after the addition of nanosilicate inhibitor compared with the absence of inhibitor. This matter shows that there has been molecular adsorption of nanosilicate molecule on the surface of carbon steel that forms a protective layer. Without the presence of nanosilicate inhibitors, R_{ct} value is at 0.496 kΩcm^2. While after the addition of nanosilicate at concentration of 0.003, 0.008, 0.016,
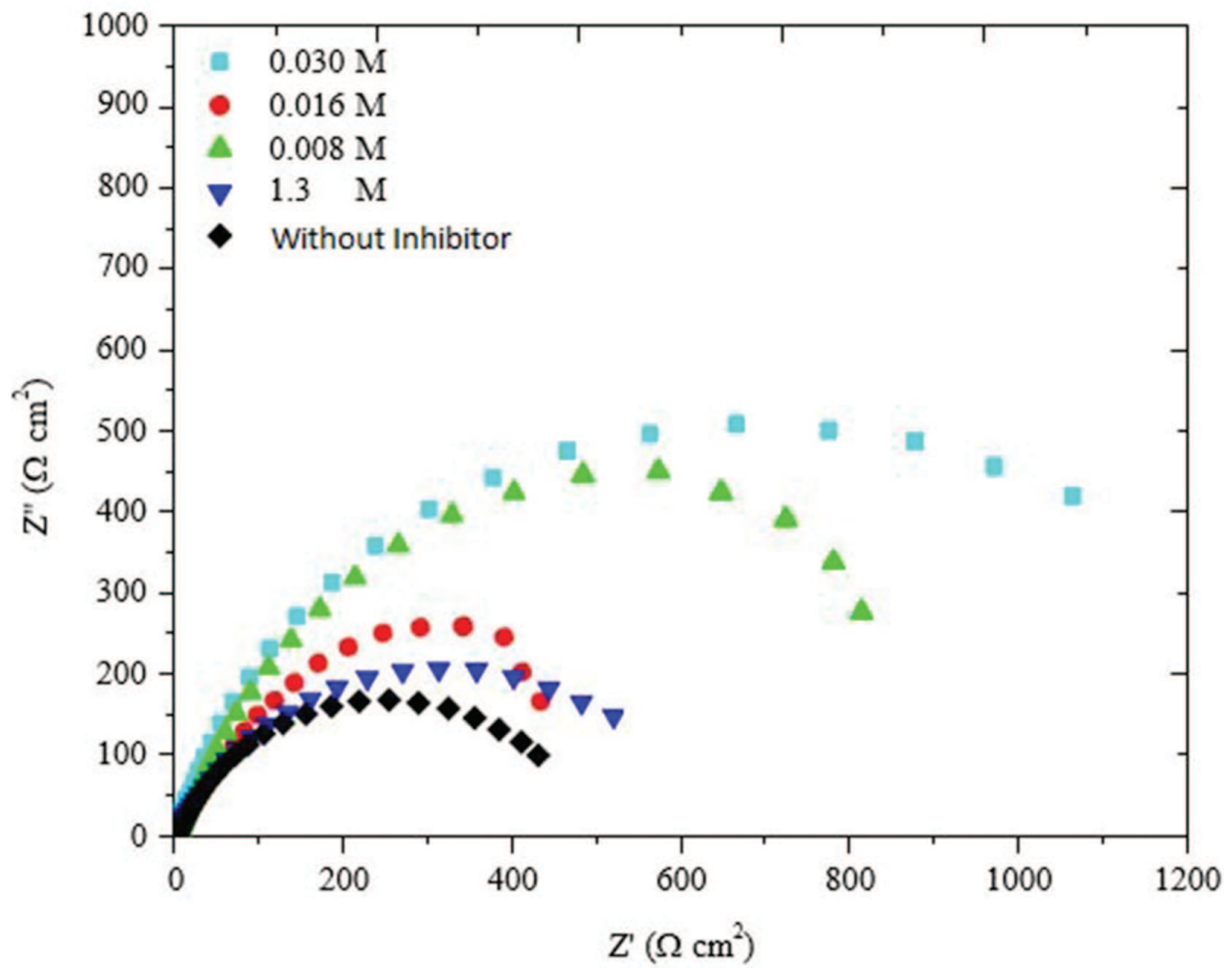
Figure 7. Nyquist plot for carbon steel with various concentrations of nanosilicate in 0.5 M NaCl.
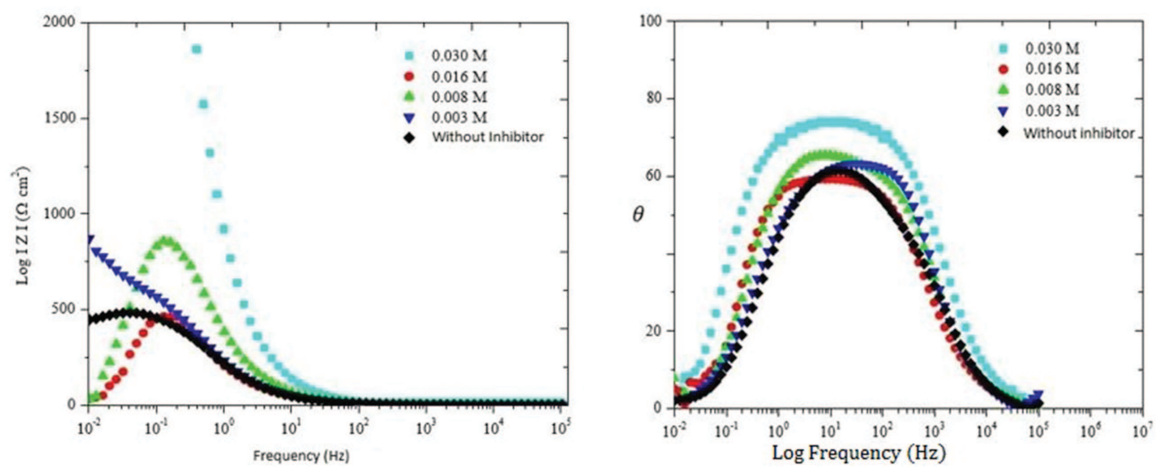

Figure 8. Bode plot for carbon steel with various concentrations of nanosilicate in 0.5 M NaCl.

and 0.03 M, it gave each values of R_{ct} at 0.630, 1.146, 0.634, and 5.426 cm^2 kΩ. Based on these results, it shows that with the addition of nanosilicate inhibitors, the values of IE% and R_{ct} have increased. The highest values of IE% and R_{ct} given are at the concentration of 0.03 M. Thus, it can be stated that the adsorption of molecules on the surface of carbon steel nanosilicate occurs well at a concentration of 0.03 M.

According to **Figure 8**, the overlapping semi-circular suppress can be seen at high frequencies, while the curve of induction is at low frequencies. There is only one time constant that was shown in the Bode plot of carbon steel in 0.5 M NaCl media at various concentrations of nanosilicate. **Figure 8** shows that the phase angle shifted to a higher value when the nanosilicate inhibitor reacts with various concentrations when added to the NaCl medium. This is due to the undergoing process of adsorption molecules on the surface of the metal [27]. Generally, the phase angle shift occurs with increasing concentrations of inhibitors that can further increase the inhibition efficiency percentage.

Moreover, the minimum phase angle is seen at low frequencies with values approaching to 80°. The highest phase shift angle approaching 90° explains good inhibition properties [28]. Other than that, Log Z value increased with the increasing of nanosilicate inhibitor concentration except at a concentration of 0.016 M. The maximum Z value was recorded at concentrations of 0.03 M. The curve of the graph was plotted horizontally at high frequencies for each nanosilicate concentration. According to past studies, it has stated that the formation of the oxide layer occurs at low frequencies, while the adsorption of molecules occurs at a high frequency of mid region with the gradient value of -1 which represents the capacitance value [28].

3.2.4. Surface morphology analysis

Morphology analysis of the carbon steel surface through light microscope with the presence and absence of nanosilicate in the 0.5 M NaCl medium was conducted. Preferred concentrations are 0.03 M. **Figure 9(a)** shows pitting corrosion that happens on the sample surface, while in **Figure 9(b)** there is no indication of pitting corrosion on the carbon steel surface that has been immersed in 0.5 M NaCl with 27 nanosilicate corrosion inhibitors. On the inhibitor-treated carbon steel, it was found to have less pitting corrosion. The surface appears to have more even surface than the surface of untreated carbon steel. These results correspond with the results of the weight loss test, potentiodynamic polarization and impedance. The percentage of inhibition efficiency (IE%) for carbon steel in 0.5 M NaCl medium only reached at 86% in 0.03 M nanosilicate inhibitor.

Based on **Figure 9(c)**, the images show that the surface of carbon steel without corrosion inhibitors appeared to be rough and porous. This is in accordance with a statement by Na and Pyun [29] that corrosion pits occur in a nearly neutral medium and in the presence of Cl$^-$ ion, whereas **Figure 9(d)** shows the carbon steel surface that has been treated with nanosilicate inhibitor, and it shows less pitting compared to **Figure 9(c)**. Thus, it is proven that the nanosilicate inhibitor has the potential as corrosion inhibitor for carbon steel in 0.5 M NaCl medium.

Figure 9(c) and **(d)** also represents the EDX analysis (to provide elemental identification and quantitative compositional information) on carbon steel surfaces that have been immersed in the 0.5 M NaCl medium with the presence and absence of nanosilicate inhibitor. The main

compositions on the surface of carbon steel that has been immersed in 0.5 M NaCl without being treated with nanosilicate inhibitor are Fe (91.34%), O (8.39%), and Cl (0.27%) (**Figure 9 (c)**). However, in **Figure 9(d)**, there are no chloride and oxygen detected. It shows that the corrosion has been retarded by nanosilicate inhibitor.
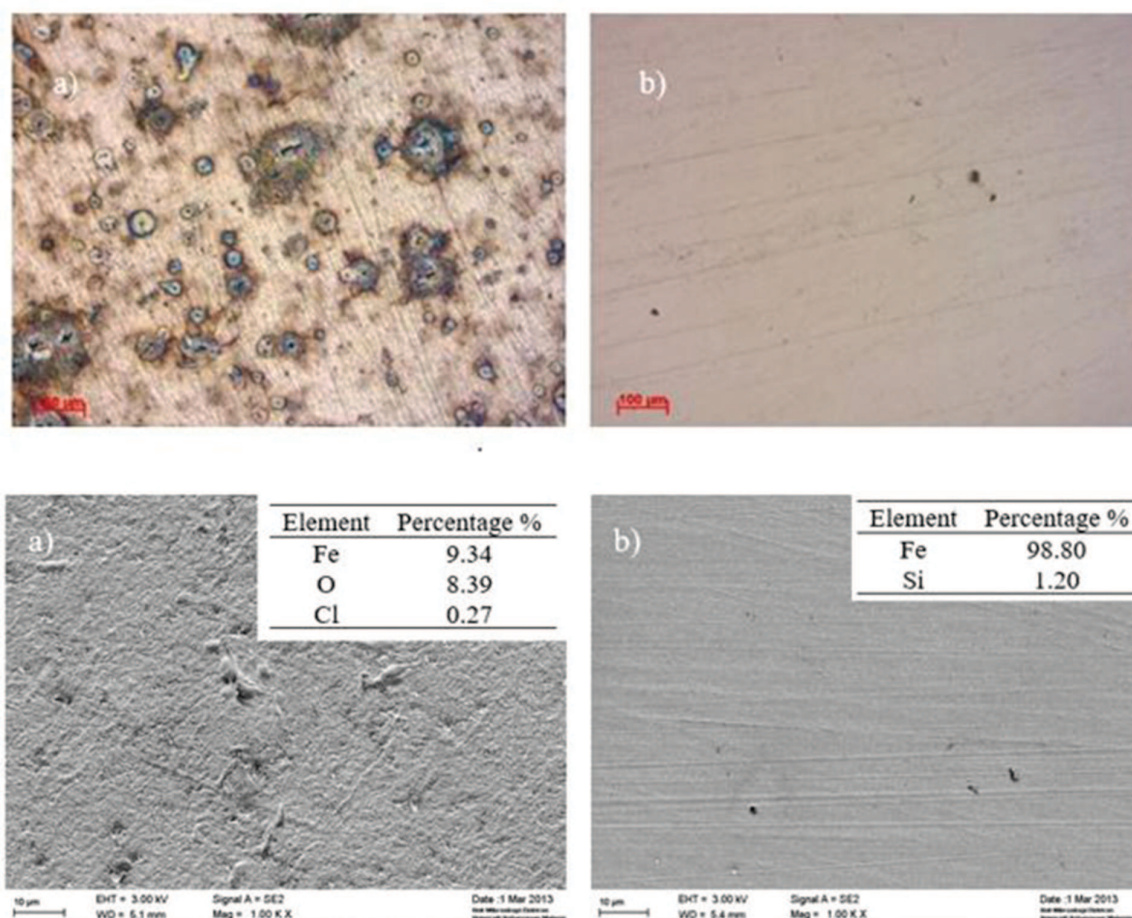
Figure 9. Light microscope and SEM image of carbon steel that has been treated in 0.5 M NaCl (a) without the presence of nanosilicate inhibitors, (b) in the presence of nanosilicate inhibitors and energy dispersive X-ray (EDX) analysis of immersed carbon steel (c) without the presence of nanosilicate inhibitors (d) in the presence of nanosilicate inhibitors.

3.2.5. Adsorption isotherm analysis

The relationship between corrosion inhibitor molecules and carbon steel surface can be explained by adsorption isotherms. To identify adsorption processes occurring in the study, the degree of surface coverage (θ) for each nanosilicate concentration inhibitor at different temperature of 40, 50, and 60°C (313, 323, and 333 K) was calculated. Data from the weight loss analysis of 0.5 NaCl medium were considered to explain the mechanism of adsorption by the adsorption isotherm plot [2]. Generally, the adsorption isotherm reported for the study of corrosion inhibitor is agreement to Langmuir isotherm. However, the type involved isotherm is dependent on many factors such as the type of inhibitor, the concentration of the inhibitor, corrosion medium use, temperature and methods of measurement carried out. Hence, the plot of the Langmuir, Freundlich, and Temkin isotherm is used as a comparison in this study.

In the Langmuir adsorption isotherm equation, Temkin, and Freundlich, respectively, exhibited linear graph with the regression line. The thermodynamic data for the Langmuir, Freundlich, and Temkin isotherm, respectively, are shown in **Table 4**. The results are obtained by comparing the regression (R^2) of the respective adsorption isotherms; it was found that the corresponding plot and regression value are close to 1 which is the Temkin isotherm. In the 0.5 M NaCl medium, the regression at 40°C, 50°C, and 60°C is close to 1, i.e. 0.9989, 0.9950, and 0.9535. This indicates that the temperature is suitable for the adsorption of nanosilicate on carbon steel through Temkin isotherm model [30].

Adsorption isotherm	Temperature (°C)	R^2
Langmuir	40	0.7686
	50	0.9910
	60	0.9389
Freundlich	40	0.9295
	50	0.9753
	60	0.8815
Temkin	40	0.9989
	50	0.9950
	60	0.9535

Table 4. Plots of Langmuir, Freundlich and Temkin adsorption isotherm for nanosilicate inhibitor in NaCl medium at 40, 50, and 60°C.

The results of thermodynamics for nanosilicate adsorption on the surface of carbon steel have produced a negative value for ΔG^o_{ads}. This shows that adsorption process has occurred spontaneously [31]. Huge value of K_{ads} characterizes the stability and strength of the interaction of the inhibitor molecules that has been adsorbed on the surface of metal/steel. Results of Temkin isotherm plots indicate the adsorption of nanosilicate molecule inhibitors occurred physically as R^2 regression is approaching to 1. It is clearly shown that the Temkin adsorption isotherm is suitable for nanosilicate corrosion inhibitors on the surface of carbon steel in 0.5 M NaCl medium.

Generally, if the ΔG^o_{ads} is about -20 kJ mol^{-1} or lower, it indicates the interaction between the electrostatic interactions of charged molecules and charged metal surface (**Table 5**). This condition is also called physical adsorption. Meanwhile if the ΔG^o_{ads} is -40 kJ mol^{-1} or more negative than -40 kJ mol^{-1}, it shows that the charge of the molecule inhibitors is moved to the metal surface to form a coordination bond called chemical adsorption [32]. In this study, the ΔG^o_{ads} is obtained between the range of -27 and -30 kJ/mol^{-1}. Therefore, it can be seen that the mechanism for nanosilicate adsorption on the surface of carbon steel is applicable for mixed adsorption (physical and chemical) [15]. Through physical adsorption, inhibition occurs as in electrostatic attraction between the charged molecules of nanosilicate inhibitors and carbon steel surface. Meanwhile, the chemical adsorption of charged nanosilicate inhibitor molecules and the surface of carbon steel molecules can cause better absorption by forming chemical bonds.

Corrosion media	Temperature (°C)	R^2	Ka_{ds} (M^{-1})	ΔGo_{ads} ($kJmol^{-1}$)
0.5 M NaCl	40	0.9989	520.06	−27
	50	0.9950	588.90	−28
	60	0.9535	795.33	−30

Table 5. Thermodynamic results through Temkin isotherm plots for the adsorption of the nanosilicate inhibitor on the surface of carbon steel.

4. Conclusions

Nanosilicate corrosion inhibitors from the rice husk ash have good inhibition properties to reduce the corrosion rate of carbon steel in 0.5 M NaCl. The effectiveness of amorphous nanosilicate corrosion inhibitor with nanosized SiO_2 functional groups with particle sized of 10–100 nm, as corrosion inhibitor, was proven through the weight loss test and electrochemical measurement test. The maximum IE% value reached up to 88.4% in 0.5 M NaCl media. This inhibitor can be classified into a mixed type of corrosion inhibitors. The presence of the protective layer has been contributing to the corrosion resistance reaction on the surface of carbon steel. Through morphology and microstructure analysis on the carbon steel samples, less corroded surface was seen on the samples treated with nanosilicate inhibitor. The adsorption isotherm tests showed that the nanosilicate inhibitor possess Temkin adsorption isotherm and ΔG^o_{ads} value obtained between the ranges of −27 and −30 kJ/mol^{-1}. The applications of silica derived from rice husk as corrosion inhibitor have proven its ability to retard corrosion in sodium chloride media. However the usage of rice husk plant waste would not stop on the extracts of nanosilicate only. Apart from nanosilicate, there were other compounds in the rice husk such as lignin and cellulose that would be a major interest for researchers in the future. As research trends nowadays that are more prone toward greener and environmental friendly approach, the waste of rice husk would be the best candidate for source of natural-based products with vast applications in advance.

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