

## Anticorrosive Properties of Nano Silicate from Paddy Husk in Salt Medium (Sifat Antikakisan Nano Silikat daripada Sekam Padi dalam Medium Air Garam)

NORINSAN KAMIL OTHMAN\*, SOLHAN YAHYA & DENNI ASRA AWIZAR

### ABSTRACT

*Anticorrosive properties of nano silicate from paddy husk in salt medium was investigated via weight loss method, Tafel polarization and impedance techniques. Prior to the corrosion test, the silica powder was obtained from burning the rice husk and extended with a chemical treatment process. The size of silica powder was characterized via zeta sizer and showed the amount of micro silica particle appear more than the nano size particle. Nano silica powder was produced from the refluxing process of micro silica to enhance the good properties of silica particle. The corrosion inhibition efficiency of nano silicate showed good inhibition with increased in inhibitor concentrations. Weight loss test exhibits high inhibition as more than 80% even, immersed in the corrosive medium until 14 days. The nano silicate inhibitor affected the anodic reaction as showed by Tafel plot analysis. Impedance results also correlated with other test as shown by the large size of Nyquist semicircle which represents as high resistance of charge transfer. The surface morphology of inhibited specimen showed a smooth surface after nano silicate inhibitor applied in the NaCl medium as observed through scanning electron microscopy (SEM) and energy-dispersive x-ray spectroscopy (EDX).*

*Keywords: Carbon steel; corrosion inhibitor; impedans; nano silicate; SEM-EDX*

### ABSTRAK

*Sifat antikakisan bagi nano silikat daripada sekam padi dalam medium garam telah dikaji melalui kaedah ujian kehilangan berat, pengutuban Tafel dan impedans. Sebelum ujian kakisan dijalankan, serbuk silika diperolehi daripada pembakaran sekam padi dan dilanjutkan dengan proses rawatan kimia. Saiz serbuk silika dicirikan menerusi pengukur zeta dan keputusan mendedahkan bahawa jumlah zarah mikro silika adalah lebih banyak daripada zarah bersaiz nano. Serbuk nano silika dihasilkan daripada proses refluks serbuk mikro silika untuk meningkatkan sifat baik zarah silika. Perencatan kakisan oleh nano silikat menunjukkan keputusan kecekapan yang baik dengan peningkatan kepekatan nano silikat. Ujian kehilangan berat mempamerkan kecekapan setinggi lebih 80% walaupun direndam dalam medium mengakis sehingga 14 hari. Perencat nano silikat didapati memberi kesan terhadap tindak balas anodik seperti yang dinyatakan dalam analisis plot Tafel. Keputusan impedans memberikan korelasi yang sama dengan ujian lain seperti mana yang ditunjukkan oleh saiz separuh bulatan Nyquist yang besar yang mewakili kerintangan pemindahan cas yang tinggi. Morfologi permukaan spesimen yang direncat menunjukkan permukaan yang licin selepas nano silikat digunakan dalam medium NaCl sepertimana yang diperhatikan menerusi mikroskopi elektron imbasan (SEM) dan spektroskopi tenaga-serakan sinar-x (EDX).*

*Kata kunci: Keluli karbon; impedans; nano silikat; perencat kakisan; SEM-EDX*

### INTRODUCTION

The development of nanoparticle research has built a versatile facilities in advanced material technologies. With the rapid progress of nanoparticle approaches the used of nanosilica as a corrosion preventor tend to enhance the methods of controlling the metal degradation. The unique properties of nanosilica which have a higher surface area compared to microsize offer better inhibition in metal corrosion. Carbon steel, a general metal that susceptible to corrosion especially in marine environment need to be conserved in order to make it survived in any severe condition.

Nowadays, silicate's role as a corrosion inhibitor has received miscellaneous opinion. This is due to the general view stated that the use of inorganic corrosion

inhibitors provides poor impact to human, marine life and environment. However, all those negative impact could be avoided by complying regulations issued by Environmental Protection Agency (EPA), Food and Drug Administration (FDA) and an industrial guidance. In fact, the used of silica in corrosion inhibitor have a special dosage that has been certified by the regulation (Duke & Kubis 2009). Silica derived form natural sources such as rice husk, coconut fiber, bamboo, wheat husk, corn straw, sawdust has been widely studied in many areas. The properties of silica (Gao et al. 2011; Salasi et al. 2007) and nano silica (Conradi et al. 2014; Jiang et al. 2011; Phanasgaonkar & Raja 2009) on the anticorrosive performance have been successfully investigated in various aspects. A combination of silica nanoparticles into the organic-inorganic hybrid

nanocomposite coatings (Zandi-Zand et al. 2005) and commercial nano silica (Jiang et al. 2011; Shchukin et al. 2008) has been explored for corrosion protection.

The objective of this work was to study and evaluate the efficiency of nano silica extracted from husk of paddy as a green corrosion inhibitors.

## METHODS

Silica was extracted using a method adapting from previous studies (Amutha et al. 2010; Singh et al. 2008). The preparation of nano silica was initially done by the burning of rice husk at 600°C for 6 h. The rice husk ash obtained was dissolved in 2.5M NaOH in stirring condition at 90°C for 3 h. The solution was then repeatedly filtered by warm distill water and wet white powder was remained on filter paper. The yield of silica powder existed as a micro silica powder. The formation of nano silica was the extended process of as-received micro silica powder using refluxing process.

Nano silica powders was obtained by refluxing process of amorphous micro silica with 3 M HCl for 6 h at 90°C. The process was extended by filtration, titration and neutralization process with 2.5M NaOH and 2.5M H<sub>2</sub>SO<sub>4</sub>. The pure silica powder obtained after dried in oven at 50°C for 24 h. Zeta sizer and transmission electron microscopy (TEM) analysis was used to verify the size of the obtained silica powder in corrosion inhibitor solution. The nano silicate inhibitor solution was prepared by dissolving nano silica powder into 3M NaOH. The nano silicate concentrations were varied from 175, 325, 800 and 1500 ppm in 0.5 M NaCl solution.

Investigation of nano silicate as a corrosion inhibitor for carbon steel has been carried out in NaCl solution. A carbon steel used made up of 0.45% C, 0.75% Mn, 0.04% P, 0.05% S and remaining Fe. Weight loss method has been performed for 1, 7 and 14 days immersion in NaCl medium with and without nano silicate inhibitors. An

electrochemical techniques including Tafel polarization technique and impedance test were performed at the concentration of nano silicate inhibitors 175, 800 and 1500 ppm to evaluate the corrosion inhibition efficiency.

## RESULTS AND DISCUSSION

The obtained silica powder (before refluxing process) has been analysed via zeta sizer. The result from the analysis gives averages of 686.5 (d.nm) diameter sizes apparently for micro size particles. Micro silica powder showed the physical properties at the diameter larger than 100 nm. Nano silica particle exhibited the particle size in the diameter less than 100 nm however produced in a very small amount. In general, the extraction of nano particle from the micro particles materials will produce a little amount of yield. This signified that the production of silica from paddy husk would give more yield of nano silica if the volume of raw amorphous silica were increased at the early stage of nano silica extraction.

In our previous studies, the nano silica powders obtained has been deduced as an amorphous phase at 600°C burning process (Awizar et al. 2013). The results has confirmed by XRD analysis which showed a broad peak at 23°θ in XRD diffractogram as almost similar obtained by Amutha et al. (2010) and Thuadaj and Nuntiya (2008). This amorphous characters facilitate the process of dissolving nano silica powder. The amorphous silica which has a regular shape, high surface area and pores structure are easy to dissolve in NaOH (Della et al. 2002). Figure 1 shows the TEM micrograph of silica powders dissolved in 0.2M NaOH to produce a nano silicate corrosion inhibitor solution. The size of particle was in the range of 10-100 nm with nano size and homogeneous distribution in the solution. This nano silica powder was formulated in corrosion inhibitors solution for corrosion test.

Figure 2 shows the results of corrosion inhibition efficiency of carbon steel obtained from weight loss test

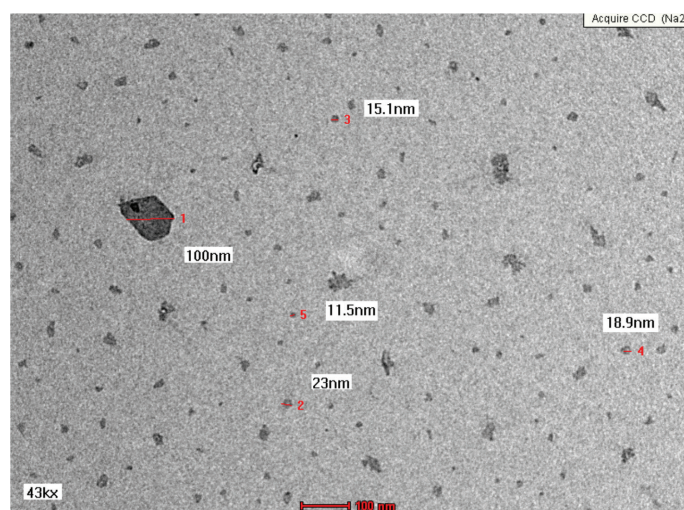


FIGURE 1. TEM micrograph of nano silicate corrosion inhibitor

for 1, 7 and 14 days. The efficiency was rapidly increased with the addition of nano silicate inhibitor from 175 to 325 ppm for all the three durations of immersion test. The efficiency was gradually increased up within 66 to 86% inhibition from 800 to 1500 ppm of inhibitor concentration. The inhibition efficiency for 1 day was lower than both 7 and 14 days immersion for all concentrations applied. The nano silicate inhibitor was believed to be able to form an almost perfect protective layer from 7 to 14 days immersion in the range of the concentration studied. The high concentration of inhibitors with the high surface area of nano silicate particles provides the large adsorption site on the carbon steel surface for the barrier from corrosion attack. As deduced by Gao et al. (2011) in the low concentration sodium silicate solutions, the silicate cannot form an integrated protective layer rapidly on the surface of the metal samples. This statements agreed with our result whereby at low inhibitors concentration, a very low efficiency were performed at 1 day immersion, meanwhile the efficiency was increased at prolonged immersion at the same inhibitors concentration.

Figure 3 shows the SEM-EDX micrograph of carbon steel corrosion immersed in NaCl with and without nano silicate inhibitor. The specimen without inhibitor (Figure 3(a)) shows a rough surface. A localize pits also likely to form throughout the uninhibited rough surface. The rough surface may contain high oxide components. This can be seen in the EDX spectrum with the appearance of O and Cl element with 8.39 and 0.27 wt. %, respectively. In contrast, the carbon steel in nano silicate inhibitors shows a very smooth surface (Figure 3(b)). The EDX analysis in

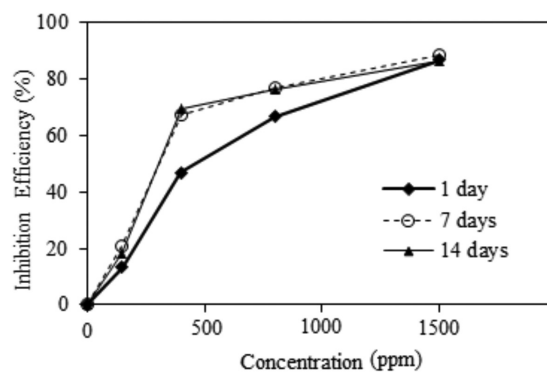


FIGURE 2. Corrosion inhibition efficiency of carbon steel in 0.5 M NaCl in the presence of nano silicate inhibitor calculated from the weight loss test

the area of the scanned surfaces showed the contents of Fe was higher than the uninhibited surface. The decrease in Fe element of uninhibited surface due to the dissolution of Fe in chloride solution. The element of O and Cl also was disappeared on the inhibited surface otherwise the Si element was presented. The Si element originated from nano silicate inhibitors. A protective film resulted from the adsorption of nano inhibitor on the metal surfaces could be the reason for the high resistance and greater corrosion inhibition efficiency. The deposition of thin silicate coatings on various metal has been reported extensively (Aramaki 2002; Gao et al. 2011; Phanasgaonkar & Raja 2009; Salasi et al. 2007). The thin layer as protective film may formed on the metal substrate even at low concentration as 15

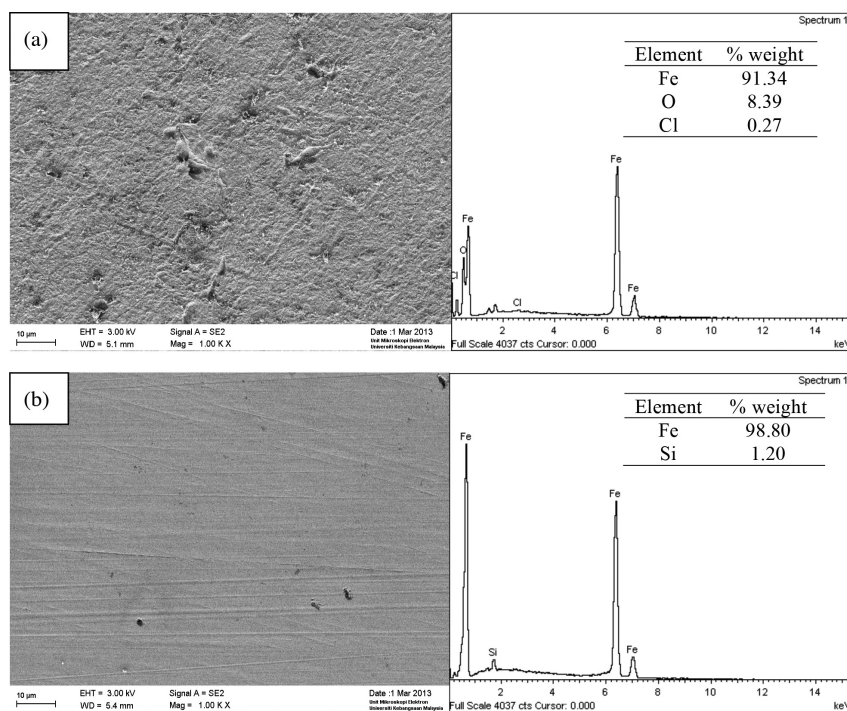


FIGURE 3. SEM-EDX micrograph of carbon steel corrosion immersed in (a) NaCl without nano silicate inhibitor (b) NaCl with nano silicate inhibitor

ppm (Salasi et al. 2007), 0.5 mmol/L (Gao et al. 2011) and 0.001M sodium silicate solution (Aramaki 2002).

Figure 4 shows the Tafel polarization plot of carbon steel in 0.5 M NaCl containing nano silicate inhibitors. The addition of inhibitors into the 0.5 M NaCl shifted the corrosion potential ( $E_{\text{corr}}$ ) value to the more positive potential. It can be seen that for all the systems containing nano silicate inhibitor, the value of corrosion current density ( $I_{\text{corr}}$ ) was reduced, consequently decreased the corrosion attack. Moreover the curve of anodic slope for each system containing inhibitor was lower than the anodic slope of the system without inhibitor, 0.5M NaCl. Therefore the corrosion rate was decreased and the corrosion of carbon steel may inhibited. The shift of  $E_{\text{corr}}$  value and reduction in  $I_{\text{corr}}$  at the anodic reaction may deduced that the nano silicate inhibitors inhibited the anodic reaction (Aramaki 2001). The nano silicate inhibitor affected the anodic reaction by forming the protective layer which provides a barrier for chloride attack. The nano silicate inhibitor is believed to adsorb on the carbon steel surface and prevent further corrosion.

The corrosion parameter obtained from the Tafel plot revealed the data of corrosion inhibition efficiency. The value of corrosion rate (CR) was decreased with increasing inhibitor concentration. The addition of inhibitor also decreased the  $I_{\text{corr}}$  and increased the polarisation resistance ( $R_p$ ). The increment of nano silicate inhibitors applied in the NaCl medium increased the inhibition efficiency (IE) from 29.5 to 85.2% at 175 to 1500 ppm. The increased in nano

silicate inhibitor concentration was increased the surface coverage of nano silicate inhibitor molecules on carbon steel. This situation enhanced the polarization resistance of carbon steel. The nano silicate compound acting by blocking the rapid transfer of electrons that served to dissolve the carbon steel. Moreover, the size of nano silicate particle provides a large surface area for the development of protective film. The formation of protective layer resulted from the interaction of nano particle of sodium silicate solution and Fe atom on the carbon steel surface.

Impedance technique has been applied in the corrosion test by analyzing the resistivity of nano silicate inhibitor towards steel corrosion in 0.5M NaCl. Figure 5(a) shows a Nyquist plot obtained from impedance measurement of carbon steel in nano silicate inhibitors. The Nyquist plot for 1500 ppm of nano silicate inhibitor shows the greatest size of semicircle. The size of the semicircle was reduced as the nano silicate inhibitor concentrations decreased. The smallest semicircle was shown by the system without nano silicate inhibitors indicating the less resistance to corrosion. The large semicircle size represents the greater resistance of charge transfer. As concentrations increased, the corrosion rate has reduced hence increased the inhibition efficiency. Sodium silicate inhibitor also enhance the charge transfer resistance and decreases the double layer capacitance (Salasi et al. 2007). The increase of charge transfer resistance by addition of nano silicate inhibitors up to 1500 ppm resulted in the decrease of metal dissolution reaction.

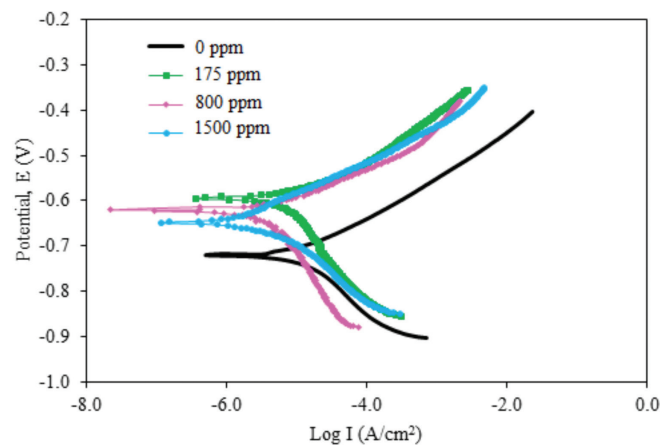


FIGURE 4. Tafel plot of carbon steel in 0.5 M NaCl in the presence of nano silicate inhibitor

TABLE 1. Tafel polarization parameters of the carbon steel in 0.5 M NaCl in the presence of different concentration of nano silicate inhibitor

Concentration inhibitor (ppm)	$E_{\text{corr}}$ (mV)	$I_{\text{corr}}$ ( $\text{A}/\text{cm}^2$ )	$R_p$ ( $\text{K}\Omega\text{cm}^2$ )	CR (mppy)	IE (%)
0	-719.0	$1.49 \times 10^{-5}$	1.714	0.174	0
175	-594.8	$1.05 \times 10^{-5}$	2.868	0.123	29.5
800	-620.7	$0.41 \times 10^{-5}$	6.426	0.048	72.5
1500	-647.9	$0.22 \times 10^{-5}$	8.953	0.026	85.2

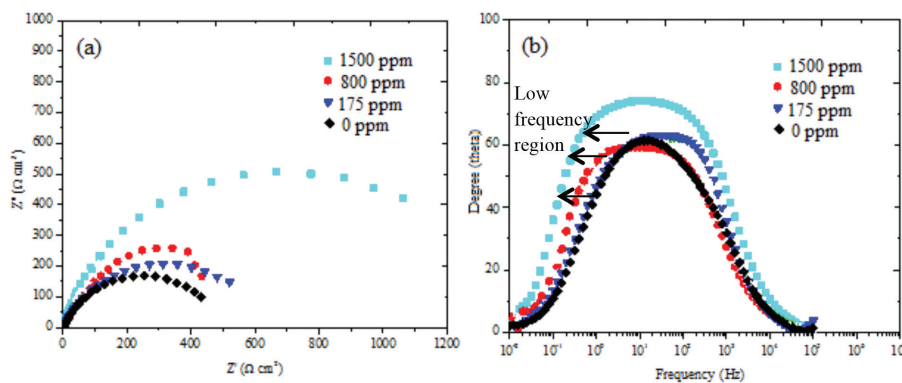


FIGURE 5. (a) Nyquist plot and (b) Bode phase plot for carbon steel with and without nano silicate in NaCl medium

The one time constant of Bode phase plot (Figure 5(b)) indicated that the corrosion process is mainly controlled by a charge transfer process (Solmaz 2014). The increase in the value of phase degree up to  $75^\circ$  signified that the adsorption of nano silicate inhibitors on the carbon steel surface may performed a better quality of the inhibitor monolayer (Mohammed et al. 2007). The low frequency phenomenon may be due to the water molecules and the active chloride ions, which penetrate through the defects of the protective layer (Gao et al. 2011). The middle frequency phase angle relates to the properties of the protective layer (Duan et al. 2006). A slight shift of phase curves for 1500 ppm inhibitor to the low frequency region may due to a little formation of an oxide layer on the carbon steel.

#### CONCLUSION

The anticorrosive properties of nano silicate derived from paddy husk show a bright potential as alternative materials in corrosion inhibitor. The corrosion test showed the high concentration of nano silicate gives better inhibition efficiency. Conventional weight loss method and more sophisticated techniques of electrochemical measurement has shown that the nano silicate inhibitor affected the anodic corrosion process and enhanced the resistance of charge transfer. The qualitative results also proved that the corrosion effect on carbon steel has reduced with the nano silicate application.

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School of Applied Physics  
Faculty of Science and Technology  
Universiti Kebangsaan Malaysia  
43600 Bangi, Selangor Darul Ehsan  
Malaysia

\*Corresponding author; email: insan@ukm.edu.my

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