

Water-soluble chitosan from shrimp and mussel shells as corrosion inhibitor on tinplate in 2% NaCl

Harmami Harmami, Ita Ulfin, Arina Hidayatus Sakinah, and Yatim Lailun Ni'mah*

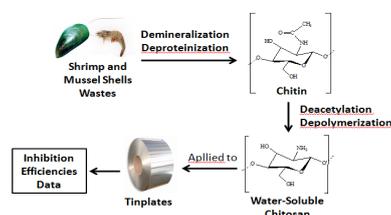
Department of Chemistry, Faculty of Sciences, Institut Teknologi Sepuluh Nopember (ITS), Kampus ITS Sukolilo, Surabaya 60111, Indonesia

* Corresponding author: yatimnikmah@gmail.com

Article history

Received 10 January 2018
 Revised 4 September 2018
 Accepted 11 October 2018
 Published Online 14 April 2019

Graphical abstract



Abstract

Water-Soluble Chitosan (WSC) was synthesized from shrimp and mussel shells and used as corrosion inhibitor on tinplate in NaCl 2%. Chitin was extracted from shrimp and mussel shells by demineralization and deproteinization reactions. Chitin was deacetylated to obtain crude chitosan. WSC was obtained by depolymerization reaction of the crude chitosan using H_2O_2 . WSC performance as corrosion inhibitor on tinplate in NaCl 2% was studied by weight loss and potentiodynamic polarization methods. WSC inhibition efficiency was studied in various concentrations in the range of 10-1500 mg/L. Maximum inhibition efficiencies of WSC from shrimp shells waste were 72.73% (weight loss method) and 91.41% (potentiodynamic polarization method), while maximum inhibition efficiency of WSC from mussel shells waste was 54.55% (weight loss method) with the addition of 1300 mg/L WSC concentration. Weight loss studies revealed that WSC acted as mixed type of inhibitor and obeyed Freundlich adsorption isotherm.

Keywords : Tinplate, corrosion inhibitor, water-soluble chitosan, weight loss, potentiodynamic polarization

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INTRODUCTION

Tinplate is low carbon steel coated on both sides with commercially pure tin. Tinplates are used in more than 80% of canning industry compared to the new alternative materials such as aluminium and chromated steel (Xia *et al.*, 2012). The tendency of tinplate to become thinner upon application can trigger the increment of corrosion probability (Huang *et al.*, 2014). On the other hand, the presence of Cl⁻ ions in seafood and cured food products can damage FeSn₂ layer on tinplate surface, which can also increase the corrosion probability (Xia *et al.*, 2012).

Corrosion is a metal destruction process which caused by the metal stability that has a tendency to its oxidation state than to reduction state. It happens because of the interaction between metal and environment (Trethewey & Chamberlain, 1991). Tinplate corrosion can damage the appearance of the product and affect the nutritional value and healthiness of the canned food (Catala *et al.*, 1998). Corrosion can cause high economic losses. According to study carried out by NACE (National Association of Corrosion Engineers) in 2011, total cost of corrosion in U.S was US \$2,2 trillion (Verma *et al.*, 2017). Among some corrosion prevention methods, corrosion inhibitor has several advantages such as economically-wise, efficient and found in various applications (Hamdani *et al.*, 2015).

Corrosion inhibitor is a compound which can be adsorbed on tinplate surface, occupied the active sites and decreased the corrosion rate. Some studies are reported to find an alternative for inorganic inhibitor because of its function as an oxidator at high concentration. Therefore, a green organic inhibitor is needed. Many non-toxic organic compounds such as amines, phosphonate acids, heterocyclic compounds and carboxylic acids are reported as corrosion inhibitors (Aghzzaf *et al.*, 2012). Biopolymer can be used as a corrosion inhibitor because it occupies on metal surface effectively and has high

chelate ability, big molecular size and multiple adsorption sites. One of biopolymers which can be used as corrosion inhibitor is chitosan and its derivatives (Sangeetha *et al.*, 2016).

Chitosan is a N-deacetylated product of chitin. Chitosan has a low toxicity, biodegradable characteristic and good adsorption ability (El-Haddad, 2013). Chitin and chitosan can be utilized in numerous industries including medicals, cosmetics, biotechnologies and food industries (Ghorbel-Bellaaj *et al.*, 2013). Chitosan can be synthesized from chitin. Chitin can be extracted from crab, mussel and shrimp shells wastes (Arancibia *et al.*, 2014). Chitosan can be used as corrosion inhibitor because of its high numbers of primary amine group which can bind on metal surface (Aghzzaf *et al.*, 2012). Some researches on chitosan and its derivatives are reported that it can be used as corrosion inhibitor on many kinds of metal such as chitosan on tinplate in 3% NaCl solution (Firdausi & Harmami, 2014), chitosan on SS 304 in 3% NaCl solution (Wardani & Harmami, 2014), chitosan on SS 304 in 3% NaCl solution (Riszi & Harmami, 2015), chitosan-doped-hybrid/TiO₂ nanocomposite on aluminium 3.5% NaCl solution (Balaji & Sethuraman, 2017) and water-soluble chitosan on mild steel in 1 M HCl (Saleh *et al.*, 2017). From the previous study, it was found that chitosan and its derivatives were insoluble in NaCl media (pH > 6) because of high molecular weight. This solubility problem makes chitosan has limiting application in aqueous solution application. In this research, water-soluble chitosan (WSC) from shrimp and mussel shells wastes would be synthesized as corrosion inhibitor on tinplate in 2% NaCl. WSC performances as corrosion inhibitor were evaluated by weight loss and potentiodynamic polarization methods. Isothermal adsorption and thermodynamic studies were studied to find the WSC corrosion inhibition mechanism on tinplate in 2% NaCl.

EXPERIMENTAL

Materials

The starting materials (shrimp shells waste) was collected from a local traditional market in Surabaya while mussel shells waste were pulverized in a mill and screened through a 40-mesh sieve. White tinplate (thickness = 0.1 cm, density = 7.625 g/cm³ and equivalent weight = 59.35 g/mol) was-in this study. White tinplate has tin layer with thickness of 30-50 μm in each side of carbon steel and the carbon steel itself has thickness of 0.094-0.09 cm.

Reagents

NaOH pellets (Merck, 99.99%), NaOH (SAP chemicals), HCl (SAP chemicals, 37%), aqua demineralization, acetone (Merck, 99.99%), ethanol (SAP chemicals, 96%), H₂O₂ (SAP chemicals, 30%), acetic acid (SAP chemicals, 30%), absolute ethanol (Merck, 99.99%) and NaCl *p.a* (Merck, 99.99%) were used in this study.

Solutions preparation

Required 1000 mL of 10% NaOH solution was made by dissolving 111 g of NaOH (SAP chemicals: density of 1.11 g/mL) with aqua demineralization in a 1000 mL volumetric flask. 100 mL of 50% NaOH (w/w) solution with density of 1.53 g/mL was made by dissolving 76.5 g of NaOH pellets (Merck, 99.99%) with aqua demineralization in a 100 mL volumetric flask. 100 mL of 2% CH₃COOH solution was made by diluting 6.67 mL of CH₃COOH (SAP chemicals, 30%) solution with aqua demineralization in a 100 mL volumetric flask. Required 1000 mL of 2% NaCl solution was made by dissolving 20 g NaCl *p.a* (Merck, 99.99%) with aqua demineralization in a 1000 mL volumetric flask.

Synthesis of water-soluble chitosan

Synthesis of water-soluble chitosan was carried out according to proposed method by Du *et al.* (2009). Shrimp and mussel shells powder of 50 g was soaked in 500 mL of HCl 7% and then filtered. The residue of shrimp and mussel powder was soaked in 500 mL of NaOH 10% and then filtered. The soaking process of the powder in HCl 7% and NaOH 10% was repeated 3 times. The residue (chitin) of shrimp and mussel powder was washed with 125 mL of ethanol 96% and then was dried. The crude chitosan from shrimp and mussel powder was obtained from 10 g of chitin by soaking it in 20 mL of NaOH 50% before being filtered and washed with hot aqua demineralization, and then was dried. Crude chitosan (from shrimp and mussel shells) of 1 g was soaked in 10 mL of acetic acid 2% and 4 mL of H₂O₂ 30%. The mixture was left to react using magnetic stirrer hotplate before being filtered in order to obtain the filtrate. Absolute ethanol was added into filtrate gradually and then incubated. The filtrate (from shrimp and mussel shells) was dried to obtain water-soluble chitosan. The percentages of chitin and water-soluble chitosan were calculated using Eq. (1).

$$\% \text{ Percentages} = \frac{\text{weight of chitin/WSC}}{\text{weight of sample}} \times 100\% \quad (1)$$

The chitin and water-soluble chitosan were characterized by Fourier-transform infrared (FTIR) spectrophotometer (Shimadzu FTIR-8400S). Deacetylation Degree (%DD) of WSC was measured by titrimetric method (Czechowska-Biskup *et al.*, 2012).

WSC inhibition analysis based on weight loss method

Tinplate surface (2 cm x 2 cm x 0.1 cm) was washed with water, followed by acetone. After that, tinplate was dried for 20 minutes at 60°C and then placed for 30 minutes at room temperature. The initial weight of tinplate (W') was measured. The corrosion media used in this research was NaCl 2% with and without WSC (from shrimp and mussel shells) at various concentrations (0, 10, 250, 200, 750, 1000, 1300 and 1500 mg/L). Tinplate 2x2 cm² was soaked in 15 mL of corrosion media for 72 hours, then lifted and washed with water and acetone. The tinplate was dried for 20 minutes at 60°C and then placed for 30 minutes at room temperature. The final weight of tinplate (W) was measured. Corrosion rates (mmpy), surface

coverages (θ) and inhibition efficiencies (%) of WSC were obtained from the initial and final weights of tinplate. The corrosion rates (CR), surface coverages (θ) and inhibition efficiencies (IE) were calculated using Eq. (2), (3) and (4), respectively.

$$CR \text{ (mmpy)} = \frac{0.000875 \times (W-W')}{\rho \times A \times t} \quad (2)$$

$$\theta = \frac{\Delta W - \Delta W_{inh}}{\Delta W} \quad (3)$$

$$IE \text{ (\%)} = \theta \times 100\% \quad (4)$$

W is weight of tinplate before being immersed in corrosion media (g), W' is weight of tinplate after being immersed in corrosion media (g), ρ is density of tinplate (g/cm³), "A" is the surface area of tinplate (cm²), t is the immersion time of tinplate in corrosion media, ΔW is weight differences of tinplate without the addition of water-soluble chitosan (g) and ΔW_{inh} is weight differences of tinplate with the addition of water-soluble chitosan (g).

WSC inhibition analysis based on potentiodynamic polarization method

Potentiodynamic polarization method was performed by Metrohm Autolab (PGSTAT302N) and processed by Nova 1.11 software. Potentiodynamic polarization method was performed by 3 electrodes cell with tinplate as working electrode, platinum wire as auxiliary electrode and Ag/AgCl (KCl 3 M) as reference electrode. This method was scanned at potential range of -150 to +150 mV and the scanning rate at 1 mV/s. Tinplate surface (4 cm x 1 cm x 0.1 cm) was washed with water and acetone. Tinplate was coated with commercial waterproof coating paint. The corrosion media was prepared using 2% NaCl with and without the addition of WSC from shrimp shells at various concentrations (0, 10, 250, 200, 750, 1000, 1300 and 1500 mg/L). Tinplate, auxiliary and reference electrodes were soaked in 25 mL of corrosion media for 20 minutes and then tested by potentiostat instrument. The data from this method was curve between potential and current density log function which called as Tafel plot. The Tafel plot was extrapolated. The Tafel plot would deliver some data such as corrosion potential (E_{corr}), corrosion current density (I_{corr}), cathodic Tafel slope (β_c), and anodic Tafel slope (β_a). The corrosion rates (CR) and inhibition efficiencies (IE) were calculated using Eq. (5) and (6), respectively.

$$CR \text{ (mmpy)} = \frac{0.00327 \times I_{corr} (EW)}{\rho} \quad (5)$$

$$IE \text{ (\%)} = \frac{I_{corr \text{ blank}} - I_{corr \text{ inh}}}{I_{corr \text{ blank}}} \times 100 \quad (6)$$

I_{corr} is the current density of tinplate, ρ is density of tinplate (g/cm³), EW is equivalent weight of tinplate (g/mol), I_{corr blank} is current density of tinplate without the addition of water-soluble chitosan and I_{corr inh} is current density of tinplate with the addition of water-soluble chitosan. The schematic diagram for preparation of water-soluble chitosan as corrosion inhibitor on tinplate in NaCl 2% was shown in Figure 1.

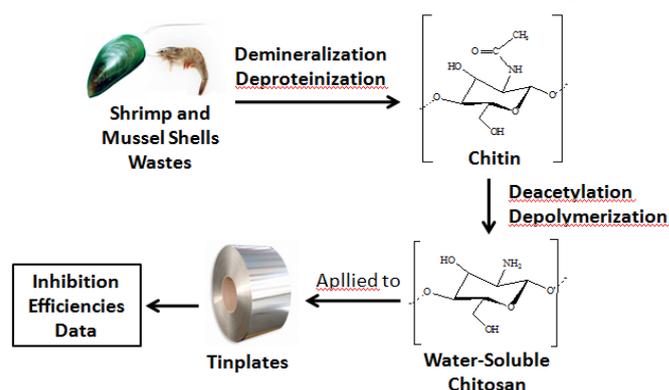


Figure 1. Schematic diagram for preparation of water-soluble chitosan as corrosion inhibitor on tinplate in NaCl 2%.

RESULTS AND DISCUSSION

Percentages of chitin and water-soluble chitosan

Water-soluble chitosan has been successfully synthesized in this research. WSC was used as corrosion inhibitor on tinplate in NaCl 2%. WSC was synthesized according to the research by Du *et al.* (2009). Shrimp and mussel shells powders were extracted from chitin by demineralization and deproteinization reactions. The demineralization process was carried out using HCl 7%. Deproteinization process was carried out using NaOH 10%. Chitin was deacetylated into crude chitosan using NaOH 50%. WSC was obtained by depolymerization of crude chitosan polymer chain using CH₃COOH 2% and H₂O₂ 30%. WSC from shrimp and mussel shells was hygroscopic white solid powder. WSC synthesis reaction from shrimp and mussel shells powders was shown in Figure 2.

Chitosan was insoluble in water and has poor solubility in neutral media which could limit its utilization (Du *et al.*, 2009). Therefore, to increase the chitosan utilization, chitosan was needed to be converted to water-soluble chitosan with lower molecular weights. Chitosan solubility was related to its deacetylation degree (DD). DD (%) of WSC in this research was 58.20%. DD of WSC was obtained by acid-base titration method using 0.1045 N HCl. It showed that 58.20% of amide groups has become primary amine groups. Chitin and WSC percentages were shown in Table 1. WSC percentages of shrimp shells have higher value than from mussel shells. The lower percentages of chitin content from mussel shells compared to shrimp shells waste might be related to the composition of their shell. Further study about the composition of mussel shells and shrimp shells might be required.

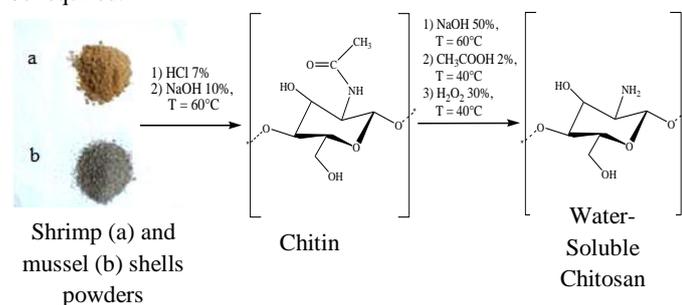


Figure 2 WSC synthesis reaction (Du *et al.*, 2009).

Table 1 Average percentage of chitin and WSC from shrimp and mussel shells wastes.

	Shrimp shells	Mussel shells
Chitin (%)	39.04	18.68
WSC (%)	27.03	3.24

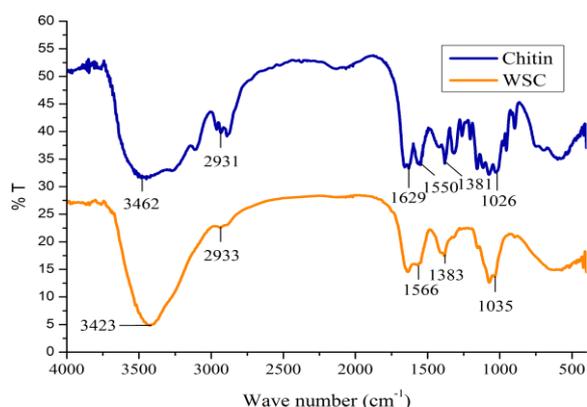


Figure 3 Chitin and WSC FTIR spectra derived from shrimp shells.

The FTIR spectra of chitin and WSC from shrimp shells were shown in Figure 3. Both FTIR spectra of chitin and chitosan have identical characteristics with that from literature (Kumari *et al.*, 2015).

In FTIR spectra of chitin, there were peaks at 3462.34 cm⁻¹ (O–H stretching vibration), 2931.90 cm⁻¹ (C–H sp³ vibration), 1629.90 cm⁻¹ (C=O amide stretching vibration), 1550.82 cm⁻¹ (–NH amide bending vibration), 1381.08 cm⁻¹ (C–N amide stretching vibration) and 1026.16 cm⁻¹ (–C–O–C stretching vibration). In FTIR spectra of WSC, there were peaks at 3423.76 cm⁻¹ (O–H stretching vibration), 2933.83 cm⁻¹ (C–H vibration), 1566.25 cm⁻¹ (N–H₂ bending vibration), 1383.01 cm⁻¹ (C–NH₂ stretching vibration) and 1031.95 cm⁻¹ (–C–O–C stretching vibration).

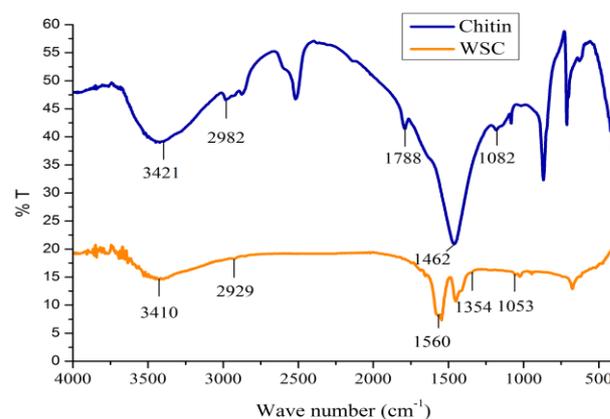


Figure 4 Chitin and WSC FTIR spectra derived from mussel shells.

The FTIR spectra of chitin and WSC from mussel shells were shown in Figure 4. Both FTIR spectra of chitin and chitosan have identical characteristics with that from literature (Ramasamy *et al.*, 2014). In FTIR spectra of chitin, there were peaks at 3421.83 cm⁻¹ (O–H stretching vibration), 2982.05 cm⁻¹ (C–H sp³ vibration), 1788.07 cm⁻¹ (C=O amide stretching vibration), 1462.09 cm⁻¹ (–NH amide bending vibration) and 1082.10 cm⁻¹ (–C–O–C stretching vibration). In FTIR spectra of WSC, there were peaks at 3410.26 cm⁻¹ (stretching vibration O–H), 2929.97 cm⁻¹ (C–H vibration), 1560.46 cm⁻¹ (N–H₂ bending vibration), 1354.07 cm⁻¹ (C–NH₂ stretching vibration) and 1053.17 cm⁻¹ (–C–O–C stretching vibration). Based on FTIR spectra in Figure 3 and 4, WSC were successfully synthesized from shrimp and mussel shells wastes. The FTIR spectra of chitosan and WSC were not significantly different. The functional groups of chitosan and WSC were similar but, the polymer chain length was different. The difference in the chain length would possibly influence solubility in water. Further study on chitosan and WSC solubility could be investigated in the next research.

Inhibition efficiencies of water-soluble chitosan based on weight loss method

Inhibition analysis by weight loss method was used to obtain corrosion rates (CR), surface coverages (θ) and inhibition efficiencies (IE) of WSC from shrimp and mussel shells wastes at various concentrations (10-1500 mg/L) in 2% NaCl. The average corrosion parameters of WSC from shrimp and mussel shells wastes were shown in Table 2 and 3, respectively. The curves of WSC concentrations derived from shrimp and mussel shells against inhibition efficiencies by weight loss method were shown in Figure 5.

Based on Figure 5 and corrosion parameters in Table 2 and 3, the inhibition efficiencies of WSC from shrimp and mussel shells by weight loss method have identical characteristics but have different values. The maximum inhibition efficiencies of WSC from shrimp and mussel shells were 72.73% and 54.55%, respectively, by the addition of 1300 mg/L WSC. Inhibition efficiency was increased as the WSC concentration was increased. The maximum inhibition efficiency was achieved by the addition of 1300 mg/L WSC. The presence of WSC (10-1300 mg/L) could block the corrosion sites, so metal dissolution process could be inhibited (Bhawsar *et al.*, 2015). WSC at higher concentration, > 1300 mg/L, was not adsorbed well to the metal surface, resulting in the increase of its diffusion to the solution and the decrease in the inhibition efficiency. Chitosan from mussel shells has a high mineral content even after demineralization

process. High mineral content in chitosan could form complex bonds with amino groups in chitosan molecule, inducing the chitosan obtained to be in a little amount and became less efficient to inhibit the corrosion (Pursetyo et al., 2017).

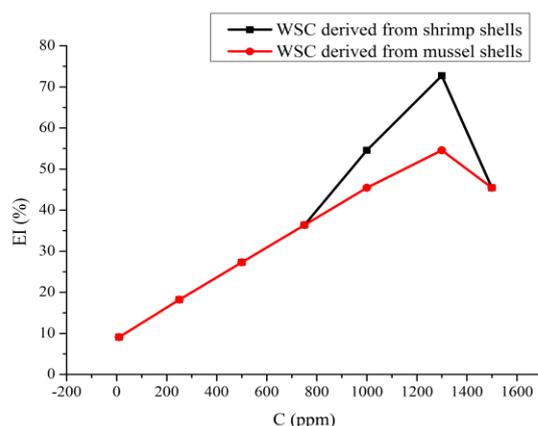


Figure 5 The curves of WSC concentration derived from shrimp and mussel shells against inhibition efficiency by weight loss method.

Table 2 Average corrosion parameters and inhibition efficiencies (IE) of shrimp shells WSC on tinplate in 2% NaCl by weight loss method.

WSC conc.(mg/L)	(W-W') (g)	CR (10 ⁻¹⁰ mmpy)	θ	IE (%)
0	0.0011	2.09	0.09	9.09
10	0.0010	1.90	0.18	18.18
250	0.0009	1.71	0.27	27.27
500	0.0008	1.52	0.36	36.36
750	0.0007	1.33	0.55	54.55
1000	0.0005	0.95	0.73	72.73
1300	0.0003	0.57	0.45	45.45
1500	0.0006	1.14		

Table 3 Average corrosion parameters and inhibition efficiencies (IE) of mussel shells WSC on tinplate in 2% NaCl by weight loss method.

WSC conc. (mg/L)	(W-W') (g)	CR (10 ⁻¹⁰ mmpy)	θ	IE (%)
0	0.0011	2.09	0.09	9.09
10	0.0010	1.90	0.18	18.18
250	0.0009	1.71	0.27	27.27
500	0.0008	1.52	0.36	36.36
750	0.0007	1.33	0.55	54.55
1000	0.0006	1.14	0.45	45.45
1300	0.0005	0.95	0.73	72.73
1500	0.0006	1.14	0.45	45.45

Inhibition efficiencies of water-soluble chitosan based on potentiodynamic polarization method

Corrosion inhibition analysis by potentiodynamic polarization method was used to obtain inhibition efficiencies (IE) and inhibition type from shrimp shells waste WSC at various concentrations (10-1500 mg/L) in 2% NaCl. Furthermore, WSC inhibition analysis was used to support the data from weight loss method. Tafel plots from potentiodynamic polarization analysis were shown in Figure 6. Tafel plots were extrapolated to obtain corrosion parameters such as I_{corr} and E_{corr} , and shown in Table 4. The curves of WSC concentration derived from shrimp shells against inhibition efficiency by weight loss and potentiodynamic polarization methods were shown in Figure 7. Based on Figure 7, it was found that the curves between WSC concentration of shrimp shells and its IE which obtained by weight loss and potentiodynamic polarization method have identical characteristics.

The addition of 10-1300 mg/L WSC could decrease I_{corr} . It was caused by the adsorption of WSC molecules on tinplate surface and thus, forms protective layer. So it could decrease the corrosion rates

(Pursetyo et al., 2017). Maximum inhibition efficiency of shrimp WSC by potentiodynamic method was 91.41% by the addition of 1300 mg/L WSC. The addition of 1500 mg/L WSC, resulted in the increase of I_{corr} . It was possibly caused by the desorption of protective layer into solution. Based on Table 4, the differences between E_{corr} of blank solution and E_{corr} of NaCl 2% by the addition of WSC were less than 85 mV. It could be concluded that WSC was a mixed type of inhibitor (anodic and cathodic) (Anshari & Quraishi, 2014). Anodic reaction was related to metal dissolution process, while cathodic reaction was related to H_2 formation.

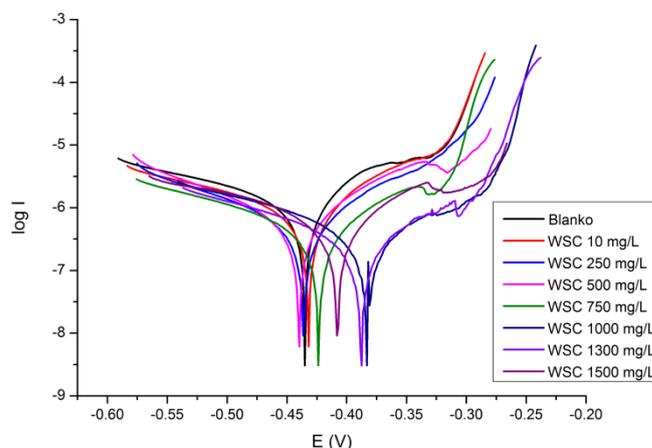


Figure 6 Tafel plots of tinplate in NaCl 2% by the addition of shrimp shells WSC.

Table 4 Average corrosion parameters and inhibition efficiencies (IE) of shrimp shells WSC on tinplate in NaCl 2% by potentiodynamic method.

WSC conc. (mg/L)	E_{corr} (mV)	β_a	β_c	I_{corr} ($\mu A/cm^2$)	CR (mmpy)	IE (%)
0	-434.23	389.59	99.07	1.74975	0.047	
10	-432.81	179.39	82.66	0.92066	0.025	47.38
250	-437.11	250.53	116.66	0.85460	0.022	51.16
500	-435.47	160.94	177.34	0.77062	0.021	55.96
750	-415.56	274.61	122.25	0.61461	0.016	64.87
1000	-389.99	109.85	74.98	0.31932	0.009	81.75
1300	-387.74	79.42	53.29	0.15030	0.004	91.41
1500	-421.53	193.87	141.73	0.65521	0.018	62.55

It was found that the inhibition efficiencies of WSC from shrimp shells tested by weight loss and potentiodynamic polarization methods have identical characteristics although at different values, as indicated from Figure 7 and Table 2 and 4.

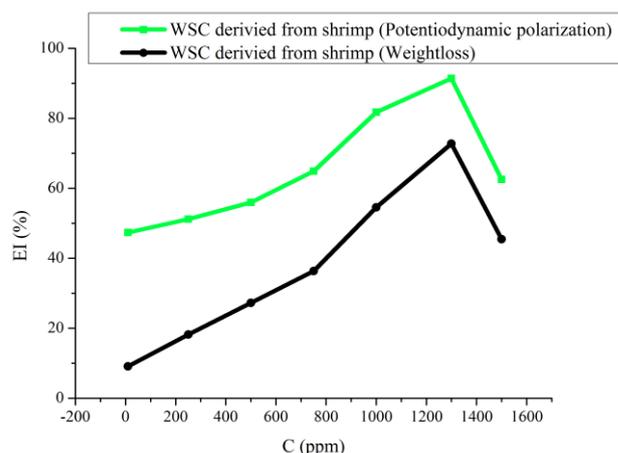


Figure 7 The curves of WSC concentration derived from shrimp shells against inhibition efficiency by weight loss and potentiodynamic polarization methods.

The maximum inhibition efficiency of WSC from shrimp shells by weight loss method was 72.73% and the maximum inhibition efficiency of WSC from shrimp shells by potentiodynamic polarization method was 91.41% by the addition of 1300 mg/L WSC. Inhibition efficiency was increased as WSC concentration was increased, with maximum inhibition efficiency at the addition of 1300 mg/L WSC.

Adsorption isotherm and corrosion thermodynamic studies

The corrosion inhibition mechanism could be studied by adsorption isotherm models of WSC on tinplate surface. There were a lot of adsorption isotherm models, such as Langmuir, Freundlich, Temkin, Frumkin and Flory-Huggins. Adsorption isotherm of WSC was obtained by plotting linear curve based on some equations of adsorption isotherm mentioned above (Sangeetha *et al.*, 2016). Adsorption isotherm curve of shrimp shells WSC was shown in Figure 8 (a) and adsorption isotherm curve of mussel shells WSC was shown in Figure 8 (b).

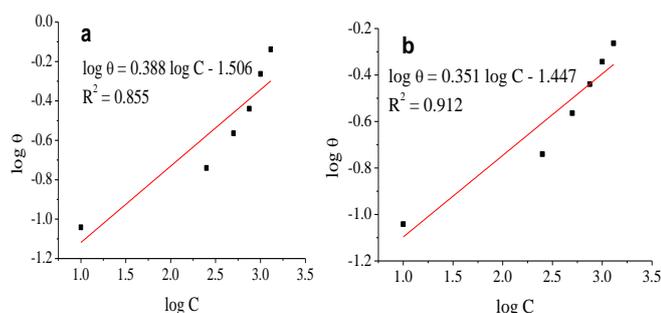


Figure 8 Freundlich adsorption isotherm of WSC from shrimp (a) and mussel (b) shells wastes.

WSC adsorption isotherm was obeyed Freundlich isotherm with correlation coefficients of 0.855 (WSC from shrimp shells) and 0.912 (WSC from mussel shells). The correlation coefficients of WSC from shrimp and mussel shells wastes were not linear, the tin plating (Sn) on both sides of tinplate was performed by hot dipping. Based on the Sn coating study, it was possible that the Sn layer formed has ununiform thickness. The FeSn₂ layer formed on the tinplate surface was served as protective layer that preventing steel corrosion (Martins, 2012). Different Sn coating thicknesses could cause WSC molecule adsorption on tinplate surface to be not uniform, making the regressions of WSC Freundlich adsorption isotherm from shrimp and mussel shells wastes were not linear.

Freundlich adsorption isotherm indicated that the interaction was not only between WSC molecule and tinplate, but also from interaction between WSC molecule and its solution, resulting in the decrease in the value of WSC inhibition efficiency on tinplate after the addition of maximum concentration. Based on Freundlich equation (Figure 8), the K_{ads} values (adsorption-desorption constant) of WSC were calculated from equation 7.

$$\log \theta = \log K_{ads} + n \log C \quad (7)$$

The K_{ads} values (adsorption-desorption constant) of WSC from shrimp and mussel shells wastes were 0.0312 and 0.0357, respectively. The ΔG°_{ads} (free Gibbs adsorption energy) values were calculated from equation 8.

$$k_{ads} = \frac{1}{1000} \exp \left[\frac{-\Delta G^{\circ}_{ads}}{RT} \right] \quad (8)$$

The ΔG°_{ads} values (free Gibbs adsorption energy) were -8.523 kJ/mol and -8.858 kJ/mol respectively. Negative value of ΔG°_{ads} showed that inhibitor adsorption process was spontaneous (Yaro *et al.*, 2013). ΔG°_{ads} values that higher than -20 kJ/mol indicated that the adsorption of WSC molecules on tinplate surface was physisorption.

CONCLUSION

Water-Soluble Chitosan (WSC) from shrimp and mussel shells wastes were good candidates for green corrosion inhibitors that acted efficiently on tinplate in NaCl 2%. Maximum inhibition efficiencies by weight loss method of WSC derived from shrimp shells and mussel shells wastes were 72.73% and 54.55%, respectively. The maximum inhibition efficiency was obtained by the addition of 1300 mg/L WSC. Weight loss studies revealed that WSC was acted as a mixed type of inhibitor and obeyed Freundlich adsorption isotherm. Inhibition efficiency of WSC derived from shrimp shells was higher than WSC derived from mussel shells. So, the inhibition efficiency of shrimp shells WSC by weight loss method was confirmed by potentiodynamic polarization method which was 91.41%.

ACKNOWLEDGEMENT

The financial supports from the Institute for research and community services (LPPM, Lembaga Penelitian dan Pengabdian Masyarakat) ITS (726/PKS/ITS/2017), and the facilities supports from Chemistry Department, Faculty of Mathematic and Natural Sciences, Institut Teknologi Sepuluh Nopember Surabaya (ITS) were acknowledged.

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