Corrosion Inhibition of Carbon Steel Using Chitosan as an inhibitor in 3.5% NaCl Medium

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Abstract

Carbon steel is a metal that is widely used for the construction of industrial and marine applications. Hence, seawater is one of the corrosive mediums due to its Natrium Chloride (NaCl) content as a strong electrolyte. One method to control the corrosion rate is by adding the inhibitor. Chitosan has been chosen as inhibitor corrosion because of non-poisonous and green material. Corrosion inhibition of carbon steel in chitosan inhibitor presence in 3,5\% NaCl medium was studied using potentiodynamic polarization technique. This study aims to understand the effect of temperature and inhibitor concentration on carbon steel's corrosion behavior. This study also determined adsorption constant value ($k_{ads}$) of chitosan on the carbon steel surface. The corrosion rate has been analyzed by using potentiodynamic polarization. Firstly, carbon steel is prepared by cutting them in cuboid shape by dimensions 4cmx 1cm x 3mm. Secondly, a 3.5 \% sodium chloride solution is prepared by dilute NaCl crystal into demineralized water. The next step is inhibitor preparation by dissolve chitosan powder in the acid solution. The corrosion rate is analyzed in different temperatures, various from 30-70$^\circ$C, and chitosan concentration varied from 0 to 250mg/l. The results showed that chitosan is a promising corrosion inhibitor in sodium chloride medium. The inhibition efficiency at 30$^\circ$C reaches 84.92\% with a chitosan concentration of 250 mg/L.

Keywords: Chitosan, Corrosion, Inhibitor, potentiodynamic,

1. Introduction

Carbon steel has been widely used in the chemical industry, such as tanks and piping\cite{1}. In the desalination plants, Carbon steel is used in Multi-stage flash evaporation (MSF) tanks \cite{2}. During the evaporation process, the operation condition, such as temperature, pH, and chemical content, can cause corrosion on metal. Corrosion is the degradation of material properties due to interactions with their environments. Corrosion of most metals (and many materials for that matter) is inevitable. While primarily associated with metallic materials, all material types are susceptible to degradation\cite{3}.

Corrosion control has become very important in many industries. In this area, reducing the corrosion rate had been done by adding corrosion inhibitors into the corrosive solution. There are many types of corrosion inhibitors, inorganic, and organic. For such consumption purposes, such as desalination water or salt production, it may need to choose environmentally friendly and non-toxic inhibitors. Inhibitors from organic materials, such as amine, phosphonate acid, a heterocyclic compound, are non-toxic. They formed polymer film to protect metal in the corrosive medium \cite{4}.
Chitosan is a natural and linear polysaccharide made from chitin that is potentially applied as a corrosion inhibitor. It is produced by some chemical processes such as deproteinization, demineralization, decoloration, and deacetylation. Chitosan has fungicidal effects and elicitation on plant tissue defense mechanisms. It becomes useful and highly appreciated as a natural biodegradable, high molecular polymer compound, non-toxic and bioactive agent [5].

Chitosan is potentially used as metal protection due to its hydroxyl and Amina functional group. In an acid medium, Amina interacts with a metal ion to form a complex ion. In 2018, Mouaden et al. studied the chitosan polymer as a green corrosion inhibitor for copper in sulfide-containing synthetic seawater. They obtained that at a concentration of 800 ppm, chitosan exhibited a corrosion inhibition efficiency of 89% following physical adsorption. The influence of temperature and immersion time was studied in sulfide-contaminated synthetic seawater, and significant inhibition was observed even after 90 days [6]. Chitosan has been used as a green inhibitor corrosion in HCL 1M media and shows an inhibition efficiency of 73.5% [7]. In 2011, Erna et al. studied that chitosan effectively reduced the corrosion of mild steel in peat water, with the inhibition efficiency reached 93.32% [8]. Chitosan as a coating for aluminium alloy has been studied previously. Chitosan was modified with a synthetic polymer (poly(taconic acid), PTA) to promote the crosslinking between chitosan chains. It is obtained that chitosan protect metallic substrate either as components in multi-layer coatings systems or as free-standing film [9].

Besides chitosan, another organic inhibitor also has been studied for retarding the corrosion on carbon steel. Salleh and Abdullah (2018) studied corrosion inhibition of carbon steel using palm oil leaves extract in various temperatures and salinities concentration. Their result showed that the inhibition efficiency increased with the increase of inhibitor concentration but decreased with the temperature rise. The highest inhibitor efficiency reached 83.70%, with a corrosion rate of 0.44 mm/yr. This result was obtained at distilled water with inhibitor concentration 25% and temperature operation 303 K [10]. Although the inhibition efficiency quite high but the inhibitor concentration is used quite a lot.

In this research, chitosan was applied as a corrosion inhibitor for carbon steel in the 3.5% NaCl solution medium. The inhibition efficiency, temperature effect on corrosion behavior, and adsorption kinetics are studied in this present study. The benefit of this study is to evaluate whether chitosan can be applied as a corrosion inhibitor at the seawater evaporation process in salt production or desalinate water plants.

2. Material and Method

2.1. Material

In this experiment use material chitosan that purchased from Indramayu, West Java, in white powder form. Chitosan was originally extracted from the crab shell powder from a crab shell. Carbon steel specimens obtained from un-used construction plat, NaCl crystal, Acetic acid, and Aquadest obtained from chemical stores in Surabaya city.

2.2. Methods

2.2.1. Specimen Preparation

Specimens are prepared by cut the carbon steel to get thin samples with dimensions 4cm x 1cm x 3mm. Firstly, polished all of them with emery paper 120 grid first, then continued using 800 grade until smooth. Rinsed them with deionized water to remove the grinding residue. Carbon steel specimens will be applied as a working electrode in the electrochemical measurement.

2.2.2. Solution Preparation

The corrosive medium was prepared by diluting 17.5-grams sodium chloride (NaCl) crystal into 500 ml distilled water to get a 3.5% NaCl solution. Add the chitosan powder into 3.5% NaCl solution by concentration variation 25; 50; 75; 100 and 125 mg/L. Chitosan powder need to be diluted first using acetic acid before added into sodium chloride solution

2.2.3. Electrochemical methods

The electrochemical analysis was done by potentiodynamic polarization test using a potentiodynamic instrument. It is used to analyze the corrosion rate and inhibition efficiency. The electrochemical measurements were carried out using three-electrodes. The electrochemical
measurements were carried out using a three-electrode setup, comprised of the reference electrode (calomel electrode), a counter electrode (Pt), and a working electrode (carbon steel). The carbon steel specimen was covered by epoxy resin in the backside before applied as the working electrode. Potentiodynamic instrument connected with Autolab software Nova 1.1.1 to show the electrochemical behaviour. The scan rate was applied at 0.1mV/s for 120 seconds for each variable testing polarization.

2.2.4. Data Analysis

During the scanning process, the steel surface polarized positively (anodic) and negatively (cathodic)—potential polarization showing the polarization curve between Potential (E) dan log current (Log I). The polarization curve then extrapolated to find the intersection point between potential anodic and potential cathodic. From the intersection curve resulting ordinate corrosion current, I_{corr}, corrosion potential, E_{corr}, Tafel constant anodic (βa) and Tafel constant cathodic (βc). I_{corr} data were used to calculate the carbon steel surface that coverage by inhibitor molecules (θ) and inhibition efficiency (IE) by using the following equations

\[ \theta = \frac{I_{corr}^0 - I_{corr}}{I_{corr}^0} \]  

where I_{corr} is the corrosion current at a particular chitosan concentration in the solution, and I_{corr}^0 the corrosion current density in the absence of inhibitor.

\[ EI (%) = \frac{I_{corr}^0 - I_{corr}}{I_{corr}^0} \times 100 \]  

Adsorption-desorption constant value K_{ads} is obtained using the Langmuir model equation

\[ \frac{C}{\theta} = C + \frac{1}{K_{ads}} \]  

where C is inhibitor concentration.

The free energy adsorption ΔG_{ads} calculated from Langmuir interception chart according to the equation

\[ K_{ads} = \frac{1}{C} \exp \left( \frac{\Delta G_{ads}}{RT} \right) \]  

3. Results and Discussion

3.1. Potentiodynamic Polarization

Potentiodynamic polarization test is used to determine the corrosion rate of the specimen. It is also found out inhibition efficiency and protection characteristic of chitosan inhibitor on the surface of carbon steel in 3.5% NaCl solution medium. The polarization curve or Tafel curve shows the relation between corrosion potential

![Fig. 1. Tafel curve of carbon steel in 3.5% NaCl medium with various chitosan concentration at 40°C.](image)

(E_{corr}) and the current (I_{corr}). Potentiodynamic polarization of carbon steel in 3.5% NaCl solution in the absence and presence of the chitosan inhibitor with various concentration shown in figure 1.

Polarization curves shown in figure 1 explain that chitosan covers the carbon steel surface and slow down the corrosion process. From the data obtained, the average change of corrosion potential in 3.5% NaCl medium, both presence and the absence of chitosan inhibitor lower than 0.85mV, it shows protection type of inhibitor chitosan both anodic and cathodic [7]. Inhibitor Chitosan protonated in a 3.5% NaCl solution, and its molecule competed with hydrogen ion to be adsorbed in the cathodic site of the steel's surface. Extrapolation Tafel on the polarization curves has been done to obtain the parameter data such as βa, βc, potential corrosion, and current density. βa value related to dissolution iron metal (Fe) in the surface of carbon steel in anodic potential, and βc associated with the OH formation in the cathodic potential. Parameter

3.2. Corrosion Rate and Inhibition efficiency

The Corrosion rate of carbon steel in the NaCl medium evaluated by experiment at five different temperatures (30°C, 40°C, 50°C, 60°C, and 70°C). The corrosion rate as a function of inhibitor concentration in various temperatures is
shown in figure 2. From figure 2 can be explained that the higher temperature, the larger the corrosion rate. Temperature is one factor that can increase the corrosion rate of carbon steel[11]. The effect of adding the corrosion inhibitor to the solution decreases the corrosion rate in all temperature variables. The lowest corrosion rate was obtained at the addition of chitosan concentration 250mg/L, this result agree with the previous report showed that the corrosion rate decrease by increasing inhibitor concentration[12]. The decreasing corrosion rate is caused by the inhibition process of chitosan molecule on the carbon steel surface by physical adsorption[13]. The physical adsorption between inhibitor and carbon steel surface is weak bonding.

**Inhibitor efficiency**

Inhibition efficiency is calculated from the corrosion rate data by using equation 1. Inhibitor efficiency shows the ability of the inhibitor to decrease the corrosion rate. The relation between inhibitor concentration and inhibition efficiency can be shown in figure 3.

Figure 3 showed that the more quantity of inhibitor, the higher the inhibition efficiency. The best efficiency obtained at inhibitor concentration added 250 mg/L. There is an agreement with the previous study done by Laorouj et al. mention that increasing the amount of inhibitor increase its efficiency [14]. The report from Saleh et al. showed there is the tendency of inhibition efficiency by increasing the chitosan concentration diluted in the solution until 100ppm. But he also reported that when the inhibitor concentration more than 100ppm the efficiency decreasing [12].

### 3.3 Adsorption and thermodynamic characterization

Inhibition efficiency data are used to study the adsorption type of chitosan inhibitor on the carbon steel's surface. For evaluating the adsorption isotherm obeyed by this system, the graphic showing the relation between the inhibitor concentration C and C/θ need to be plotted, where θ is the degree of surface coverage. The degree of coverage implies how large the inhibitor molecule covers the steel surface on a certain area. Degree of surface coverage value obtained from (EI%)⁄100. The relation between C and C/θ is shown in figure 4.

From figure 4 we can see that at temperature 30-40°C, adsorption process quickly and at temperature 50-60°C reaction becomes slow. In figure 4, all line show the straight line (R² value 0.9559-0.99987). It indicated that the system follows Langmuir adsorption isotherm. From equation (3) the value adsorption constant, K_{ads} can be calculated from the intercept lines on the...
C/θ axis. Langmuir adsorption isotherm can be applied by assuming that the adsorption process only happened monolayer, localized, and the heat of adsorption not related to the surface’s temperature [15]. The value of $K_{ads}$ in equation 3 determine the adsorption-desorption constant. Equation 4 show the relationship between Gibbs free energy of adsorption $\Delta G^o_{ads}$ and the adsorption constant $K_{ads}$.

$$K_{ads} = \frac{1}{C} \exp\left(\frac{\Delta G^o_{ads}}{RT}\right)$$

Where $R$ is the constant gas value, and $T$ show the absolute temperature value. By the calculation using above equation, $\Delta G^o_{ads}$ obtained as listed in Tabel 1

Tabel 1 $K_{ads}$ and $\Delta G^o_{ads}$ value

| Temperature ($^\circ\text{C}$) | Adsorption constant, $K_{ads}$ (1/M) | Free Energy, $\Delta G^o_{ads}$ (kJ/mol) |
|-------------------------------|-----------------------------------|----------------------------------------|
| 30                            | 185825.2499                      | -40.7016                               |
| 40                            | 268983.5113                      | -43.0071                               |
| 50                            | 278233.7720                      | -44.4714                               |
| 60                            | 457686.8507                      | -47.2261                               |
| 70                            | 481208.7965                      | -48.7867                               |

The negative value of $\Delta G^o_{ads}$ indicate the stability of the adsorbed layer on the steel surface and spontaneity of the adsorption process. The value $\Delta G^o_{ads}$ decreased (become more negative) with increasing temperature, indicating the occurrence of endothermic[16]. The calculated values of $\Delta G^o_{ads}$ are between -40.7016 and -48.7867 kJ/mol. The adsorption of organic molecules on metal surfaces is considered as physisorption when the absolute value of $\Delta G^o_{ads}$ is 20 KJ/mol or lower and considered as chemisorption when the absolute value of $\Delta G^o_{ads}$ is 40 KJ/mol or higher. This process, involve charge sharing or transfer of electrons from the inhibitor molecules to the metal surface to form a coordinate type bond[14]. It can be predicted that the interaction of chitosan molecule with the carbon steel surface follow the chemisorptions.

4. Conclusions

The chitosan powder is a suitable corrosion inhibitor for carbon steel at 3.5% NaCl medium by showing good inhibition effectiveness even at higher temperature. The Inhibition efficiency increases with the rise of concentration and decreases with temperature. The best inhibition efficiency is 84.92% when the concentration of inhibitor 250mg/L and temperature 30°C. Adsorption of inhibitor tested follows Langmuir adsorption isotherm with the value of $K_{ads}$ increasing with the increase of temperature. The values of Gibbs free energy become more negative by increasing the temperature. The authors believe that the adsorption mechanism of chitosan molecules on the carbon steel surface may be a chemisorption process.

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References

[1] S. Winnik, Corrosion Under Insulation (CUI) Guidelines: Revised. Woodhead Publishing, 2015.
[2] I. Andijani dan S. Turgoose, "Studies on corrosion of carbon steel in deaerated saline solutions in presence of scale inhibitor," Desalination, vol. 123, no. 2–3, hal. 223–231, 1999.
[3] B. A. Shaw dan R. G. Kelly, "What is corrosion?," Interface-Electrochemical Soc., vol. 15, no. 1, hal. 24–27, 2006.
[4] A. A. Aghzzaf et al., "Corrosion inhibitors based on chitosan-heptanoate modified beidellite," Appl. Clay Sci., vol. 65–66, hal. 173–178, 2012, doi: 10.1016/j.clay.2012.04.025.
[5] S. Bautista-Baños et al., "Chitosan as a potential natural compound to control pre and postharvest diseases of horticultural commodities," Crop Prot., vol. 25, no. 2, hal. 108–118, 2006.
[6] K. El Mouaden et al., "Chitosan polymer as a green corrosion inhibitor for copper in sulfide-containing synthetic seawater," Int. J. Biol. Macromol., vol. 119, hal. 1311–1323, 2018.
[7] S. A. Al-Fozen dan A. U. Malik, "Effect of seawater level on corrosion behavior of different alloys," Desalination, vol. 228, no. 1–3, hal. 61–67, 2008, doi: 10.1016/j.desal.2007.08.007.
[8] M. Erna, S. Susilawati, R. Linda, H.
Herdini, Z. F. Auliyani, dan E. S. Dharma, “Efektifitas Kitosan Sebagai Pelapis (Coating) Korosi pada Logam Zn, Fe, Al dalam Media HCl Dan H2SO4,” *EduChemia (Jurnal Kim. dan Pendidikan)*, vol. 2, no. 2, hal. 119, 2017, doi: 10.30870/educhemia.v2i2.950.

[9] J. Carneiro, J. Tedim, dan M. G. S. Ferreira, "Chitosan as a smart coating for corrosion protection of aluminum alloy 2024: A review," *Prog. Org. Coatings*, vol. 89, hal. 348–356, 2015, doi: 10.1016/j.porgcoat.2015.03.008.

[10] N. I. H. Salleh dan A. Abdullah, "Corrosion Inhibition of Carbon Steel Using Palm Oil Leaves Extract," *Indones. J. Chem.*

[11] A. Zarrouk, B. Hammouti, H. Zarrok, S. S. Al-Deyab, dan M. Messali, "Temperature effect, activation energies and thermodynamic adsorption studies of L-Cysteine Methyl Ester Hydrochloride as copper corrosion inhibitor in nitric acid 2M," *Int. J. Electrochem. Sci.*, vol. 6, no. 12, hal. 6261–6274, 2011.

[12] C. W. Saleh, H. Harmami, dan I. Ulfin, “Pengendalian korosi menggunakan inhibitor kitosan larut air untuk baja lunak dalam media HCl 1M,” *J. Sains dan Seni ITS*, vol. 6, no. 1, hal. C1–C4, 2017.

[13] A. Hamdy dan N. S. El-Gendy, "Thermodynamic, adsorption and electrochemical studies for corrosion inhibition of carbon steel by henna extract in acid medium," *Egypt. J. Pet.*, vol. 22, no. 1, hal. 17–25, 2013, doi: 10.1016/j.ejpe.2012.06.002.

[14] M. Larouj *et al.*, "Thermodynamic study of corrosion inhibition of carbon steel in acidic solution by new pyrimidothiazine derivative," *J Mater Env. Sci.*, vol. 8, no. 11, hal. 3921–3931, 2017.

[15] C. Azmiyawati, “Kajian Kinetika Adsorpsi Mg (II) pada Silika Gel Termodifikasi Gugus Sulfonat,” *J. Kim. Sains dan Apl.*, vol. 9, no. 2, hal. 35–39, 2006.

[16] A. Peter dan P. J. de, "Atkin’s Physical Chemistry," Oxford University Press, 2002.