Effectivity of Water-Soluble Chitosan from Rajungan Shell Waste as Corrosion Inhibitor on Iron in 1 M HCl

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Abstract. Corrosion is the process of metal oxidation in the presence of oxygen which causes losses in the industrial field. This study was conducted with the aim to determine the effectivity of water-soluble chitosan from crab shells as a corrosion inhibitor on iron in 1M HCl media. Crab shell waste was demineralized and deproteinated to obtain chitin. Chitin obtained was then deacetylated to obtain Water Soluble Chitosan (WSC). The inhibition efficiency of WSC on iron corrosion in HCL 1 M media was determined by the weight loss method. The results showed that the corrosion rate decreased with the increase of inhibitor concentrations of 0, 100, 300 and 500 ppm. However, the increase in temperatures (303, 313 and 323 K) also increased the corrosion rate. The inhibition efficiency increased as the inhibitor concentration increased. The optimum efficiency occurred at a temperature of 303 K and a concentration of 500 ppm which was equal to 98.94%. The corrosion rate decreased with the increase of pH values (3, 4 and 5). WSC adsorption from crab shell waste on the surface of iron in 1M HCl media follows the isothermal model of Freundlich adsorption. In the thermodynamic study, the values of Ea, ΔH, AS, and ΔG°Ads were used to determine the adsorption of iron inhibitors. The results of the study showed that the reaction is a physical reaction (physisorption), endothermic, and spontaneous.

Keywords: Water-Soluble Chitosan, Rajungan Shell, Corrosion Inhibitor

1. Introduction

Corrosion is defined as a reduction in the quality of a material (usually in the form of metal or a mixture of metals) as a result of gradual interactions with the environment that can occur due to physical and/or chemical interactions or the influence of living things (microorganisms). Corrosion is caused by several factors, one of which is the acidic environment. Strong acidic solutions, such as HCl, can also accelerate corrosion. HCl contains a very aggressive Cl-ions that can attract Fe when metal, ie iron or steel, is exposed to the solution, resulting in corrosion that causes the metal to be rusty [1]. Metal corrosion basically cannot be stopped, but it can be controlled or overcome in various ways, depending on the application of the metal.

Some methods to control and protect corrosion are by selecting materials, developing suitable metal alloys that are corrosion resistant, and coating metal surfaces with paint to separate them from the corrosive medium. However, the coating method has a disadvantage for there are possibilities the paint coating is scratched or exfoliated. This could lead to the occurrence of corrosion which can spread...
under the paint that is still intact. Based on various research results, using inhibitors remains as one of the most efficient and simplest methods for controlling corrosion, especially in acidic media [2,3]. Corrosion inhibitors are chemical compounds that can inhibit the rate of metal corrosion in their environment. The use of inhibitors to date is still the best solution to protect corrosion because it is easily applied at low cost. Corrosion inhibitors can be divided into two types namely organic and inorganic inhibitors. Inorganic inhibitors are quite effective in inhibiting corrosion rate but are toxic. Organic inhibitors, on the other hand, do not only inhibit the rate of corrosion, but also inexpensive, non-toxic, available in nature, easily renewed and do not damage the environment [4].

Most of the effective organic inhibitors that are widely used contain a heteroatom such as O, N, S and multiple bonds in their molecules through which they are adsorbed on the metal surface [5–9]. One of the organic inhibitors is a chitosan biopolymer which can be obtained from various types of marine animals. Chitosan can be synthesized from chitin found in crab shells, shellfish, shrimp and crabs. Among the marine animals, crab shell waste is a well-known problem that needs to be solved. There have been efforts to provide added value to the crab shell processing business as a means to overcome the environmental pollution problems it causes. One of the alternatives to overcome the waste is by synthesizing chitosan from crab shells. Chitosan is a product of N-deacetylation from chitin that has low toxicity and good adsorption ability [10]. Chitosan has a hydroxyl (OH) and amine groups (NH2) Which can bond with iron through electrostatic and covalent coordinate bonds. Corrosion control with water-soluble chitosan inhibitors in soft steel in HCl 1 M has a maximum inhibition efficiency of 73.5% [11]. Based on the high content of the primary amine group found in chitosan, chitosan can be used as a corrosion inhibitor. The reason is because the primary amine group can bind to the metal surface but in environments with a pH below 7, chitosan becomes water-insoluble. As a result, this limits its use as an inhibitor in runny media. Therefore, WSC can be synthesized from chitin crab shell extract. WSC have several well-liked properties, such as water-soluble, high gel formation capacity, and low toxicity, making its widely applicable [12]. Thermodynamic and isothermal adsorption studies evaluated the performance of WSC as a corrosion inhibitor. The variables studied included the concentration of chitosan inhibitors, the effect of temperature, immersion time, and pH of the corrosion medium on the corrosion rate after inhibitors were added.

2. Experimental

2.1. Material Preparation

The concrete frame iron was rectangular with a thickness of 0.5 cm and a width of 1 cm with a length (p) of 2.36 cm. The iron tip was drilled with a drill so that it could be hung on a corrosion medium to make the entire surface interact with the corrosion medium. Iron was cleaned using iron sandpaper and rinsed using distilled water. After that, the iron was rinsed using acetone and then dried in an oven with a temperature of 333 K for 15 minutes. The sample was cooled and weighed using an analytic balance. The weight obtained was recorded as the initial weight.

2.2. Water Soluble Chitosan Synthesis (WSC)

100 g of crab shell waste powder was mixed with HCl 1.5 M 1000 mL solution with a ratio of 1:10 (b/v). The crab shell powder was obtained from the results of demineralization. Crab shell was mixed with 3.5% NaOH solution with a ratio of 1:10 (b/v). The mixture was heated at a temperature of 333-343 K for 1 hour. Chitin from the demineralization and deproteinization was soaked in 60% NaOH solution (comparison of chitin weight: NaOH volume, 1: 10) at 373-383 K for 1 hour with stirring speed of 50 rpm. After that, the mixture was decanted or filtrated. The solid obtained was washed using distilled water to remove the remaining NaOH until the pH was neutral. The solid obtained was dried in an oven with a temperature of 333 K for 8 hours and then cooled in a desiccator. After that, the sample was weighed. The chitosan obtained was then characterized using FTIR.

2.3. Weight loss measurements

Iron was soaked in a test tube containing 10 mL of 1 M HCl solution with several WSC concentrations of 0, 100, 300, and 500 ppm. The 1 M HCl was used as a corrosion medium. The test tube was then
heated with temperature variations of 303, 313, and 323 K using a water bath for 3 hours. The reacted iron was cleaned and washed using distilled water, rinsed using acetone, and then dried and weighed [13]. Average weight loss, corrosion rate (Cr), inhibition efficiency (Ei), and the inhibited surface size were calculated using equations 1, 2 and 3 as follows [14,15].

\[ Cr = \frac{W}{A \cdot t} \]  
\[ Ei \% = (1 - \frac{Wa}{Wb}) \times 100 \]  
\[ \theta = 1 - \frac{Wa}{Wb} \]

W is weight loss (g), A is an area of the metal (cm\(^2\)) and t is the time of immersion (hours), Wa and Wb are weight loss with and without inhibition process.

2.4. Surface analysis
The scanning electron microscope or SEM was used to study the morphology and chemistry of the analyzed rusty iron surfaces.

3. Results and Discussion
3.1. Water Soluble Chitosan Synthesis (WSC)
The FTIR results of chitosan formation into WSC can be seen in Figure 1. The results of FTIR analysis shows that WSC compounds were successfully formed as showed by the appearance of several spectra which are hydroxyl groups (O-H) at 3442.82 cm\(^{-1}\), C=O bond at 1642.85 cm\(^{-1}\), N-H\(_2\) bond at 1561.72 cm\(^{-1}\), C-NH\(_2\) bond at 1414.46 cm\(^{-1}\), and C-O bond at 1046.02 cm\(^{-1}\). All of the WSC spectrum but the one appearing at 1414.46 cm\(^{-1}\), are the peak of the C-N vibration formation.

![WSC FTIR spectrum and chitosan from crab shells](image)

Figure 1. WSC FTIR spectrum and chitosan from crab shells

3.2. Effect of concentration and temperature
Based on Figure 2, it can be seen that the higher the concentration of WSC added, the lower the rate of corrosion. This means that the inhibitory ability of WSC increases with the increase of WSC concentration. The ability of inhibitors to inhibit the corrosion rate is due to the formation of a thin layer on the surface of the iron that blocks aggressive ions from acids and salts that can attack metals [16]. However, the corrosion rate will increase with the increase of temperature. This happens because the temperature is associated with the increase of molecular kinetic energy which causes an increase in the formation of hydrogen in acidic solutions making the rate of iron corrosion increases [17].
In this study, the most significant efficiency percentages were 98.94% at 303 K with a concentration of 500 ppm chitosan.

3.3. Adsorption isotherm

Table 1 presents a comparison of R² value of Freundlich, Langmuir and Temkin isotherms. In this study, the value of R² in Freundlich's isotherm is closer to 1 compared to R² in Langmuir and Temkin isotherms. This shows that the inhibitor has a heterogeneous surface and each molecule has different potential absorption and the assumption that adsorption occurs multilayer on the surface of the inhibitor.

| No. | Isotherm Adsorption Model | R² 303 K | R² 313 K | R² 323 K |
|-----|--------------------------|----------|----------|----------|
| 1   | Langmuir Isotherm        | 0.8051   | 0.8895   | 0.8912   |
| 2   | Freundlich Isotherm      | 0.9857   | 0.9618   | 0.9575   |
| 3   | Temkin Isotherm          | 0.9441   | 0.9009   | 0.8763   |

Furthermore, from the Freundlich equation, the K_ads value is determined. Based on Table 2, the adsorption constant value (K_ads) Freundlich increases with the increase in temperature because the adsorption rate also increases. However, at temperatures of 313 and 323 K, the constant value starts to decrease. This indicates that equilibrium has occurred at a temperature of 303 K. The constant adsorption value is used to determine the magnitude of free energy of adsorption.

| Temperature (K) | K_ads |
|----------------|-------|
| 303            | 0.68610 |
| 313            | 0.65780 |
| 323            | 0.51573 |

3.4. Thermodynamic studies

Thermodynamic studies are carried out by determining the activation energy, entropy, enthalpy, and free energy of adsorption. Determination of these parameters can be used to explain the inhibition reaction process that occurs.

| WSC concentration (ppm) | Ea (kJ/mol) | ΔH (kJ/mol) | ΔS (kJ/mol) |
|-------------------------|-------------|-------------|-------------|
| 100                     | 16,446      | 46,9        | 190,0       |
| 300                     | 34,826      | 103,3       | 375,5       |
| 500                     | 141,463     | 461,7       | 146,3       |

Data on Table 3 shows that the higher the concentration of WSC, the higher the activation energy. The increase of Ea value in the presence of WSC can be interpreted as physical adsorption of inhibitors that occur on the surface. Besides that, a high Ea value indicates a greater energy barrier that inhibits oxidation reactions, namely the corrosion process. The positive enthalpy values in Table 3 show that
the reaction is endotherms and the increase of ΔS value, causes the degree of regularity to increase, which slows down the corrosion process.

| Temperature (K) | Adsorption Free Energy (kJ/mol) |
|-----------------|---------------------------------|
| 303             | -9.2                            |
| 313             | -9.4                            |
| 323             | -9.0                            |

The ΔG° ads value obtained in table 4 is negative. This indicates that the adsorption inhibitor on the iron surface is a spontaneous reaction and the reaction that occurs is fisisorption because the value of ΔG is less than -20 kJ / mol.

3.5. Surface morphology analysis
Scanning Electron microscopy (SEM) is used to analyze iron surface morphology without and with WSC inhibitors.

Based on Figure 3 with an enlargement of 3000x, it can be seen that photos of iron surfaces in 1 M HCl solution without the addition of WSC inhibitors formed corrosion products and holes. The figure also shows that the addition of WSC inhibitors minimizes corrosion holes on the iron surface. This proves that water-soluble chitosan inhibitors can be adsorbed on the iron surface and form thin layers.

4. Conclusion
Iron corrosion rate decreases and inhibition efficiency increases with the increase of WSC concentration added to the corrosion medium. Meanwhile, when the temperature was increased, the rate of iron corrosion increases and the efficiency of inhibition decrease. The highest efficiency was detected at the temperature of 303 K and WSC concentration of 500 ppm. Thermodynamic corrosion study using the values of Ea, ΔH, ΔS, and ΔG° ads, shows that the corrosion inhibition process of WSC follows the physical adsorption process, endotherm, and occurs spontaneously. The study of Freundlich adsorption isotherm and SEM shows that the corrosion inhibition mechanism occurs through the adsorption process.

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