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Corrosion Control of Metal Alloy Using Inhibitor Synergy: Phospate – Carbohydrazide

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ABSTRACT

Stainless steel is a kind of metal alloy that is widely used in industrial equipment. The problem faced by all metals that come into contact with corrosive medium is corrosion. Corrosion or metal deterioration can not be avoided since it is a spontaneous reaction between the metal with its environment. One method to control the corrosion of metal alloy is by adding the inhibitor into the medium. The addition of inhibitors in synergy is discussed. The addition of a phosphate inhibitor as a film-forming role on the metal surface is assisted by the addition of carbohydrazide components in controlling dissolved oxygen levels in seawater. The addition of inhibitors in synergy is expected to increase the efficiency of the inhibitor's performance in a single work. This research aims to determine the best composition for phosphate and carbohydrazide inhibitors due to the effect of synergy in controlling the corrosion rate of metal alloys in seawater. The synthetic seawater medium was the 3.5% NaCl dilution prepared by diluting the NaCl crystal into the demineralized water. The phosphate inhibitor was added into the medium with various compositions (100, 200, 300, 400, and 500 ppm). Then, the carbohydrazide was added into the medium with the multiple compositions 5, 7.5, 10 and 15. The corrosion rate measurement was done by using Electrochemical Impedance Spectroscopy Instrument. The Stainless steel sample was prepared by cutting the stainless steel plate with a size 1cm x 1 cm and a thickness of around 2- 3 mm. The measurement process was done by putting the specimen in the working electrode and dipping into the medium with and without the inhibitors. The results show that the addition of inhibitor effectively decreases the corrosion rate. The best result is obtained when the ratio between phosphate and carbohydrazide is 100:10 ppm, which reduces the corrosion rate from 0.40128 mpy to 0.008 mpy

Keywords: Carbohydrazide, corrosion, inhibitor, metal alloy, phospate

Introduction

Metal alloys such as stainless steel are widely used as industrial equipment due to their corrosion resistance. On the other hand, metal alloy deterioration still occurs due to the interaction with its environment. Corrosion is a problem for all industrial equipment from metal, especially when the equipment comes in contact with a corrosive medium such as acid, base, or seawater (Umoren et al., 2013). Some factors affecting the corrosion rate are the solution concentration, pH, flow rate, and temperature (Pramudita et al., 2019). Corrosion in metal alloy causes an increase in maintenance cost. Therefore, some effort need to do to protect the metal alloy so that corrosion can be minimized.

Adding a so-called substance inhibitor to the medium is one way to prevent or obstruct the corrosion rate. The inhibitor prevents the metal's corrosion by treating the metal surface in contact with the medium (Kesavan et al., 2012). Adding inhibitor corrosion is relatively effective

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on reducing the corrosion rate (Araoyinbo et al., 2018). Many substances were applied for inhibitor corrosion. According to their basic ingredients, Corrosion inhibitors can be divided into organic and inorganic compounds. Organic inhibitors generally come from extracts of natural materials containing N, O, P, and S atoms, the atoms having lone pairs of electron. Inorganic inhibitors currently commonly used are sodium nitrite, crystalline, phosphate, and zinc salt.

An organic compound such as chitosan is widely used to obstruct corrosion in seawater medium (El Mouaden et al., 2018). Adenine was studied as an effective inhibitor in an acid medium (Scendo & Trela, 2013). The essential oil extracted from diverse plants also became promising as a corrosion inhibitor (Hossain et al., 2020). Besides the organic compound, the inorganic compound is also widely used as an inhibitor of corrosion. Phosphate is one good alternative for corrosion inhibitors due to its low cost and toxicity (Yohai et al., 2013).

The previous study showed that phosphates inhibitors are effective in the presence of oxygen (anodic inhibition) (Simões et al., 2009). Other studies suggest phosphate acts as a cathodic inhibitor (Shi & Sun, 2014). The adding phosphate showed 80% effectiveness in decreasing the corrosion rate.

Sodium phosphate (Na_3PO_4) and sodium tripolyphosphate ($Na_5P_3O_{10}$) are inhibitors that are often used to prevent pitting corrosion in steel. Regarding safety, phosphate and polyphosphate compounds are relatively safer than other inorganic inhibitors, such as nitrate, sulfate, and molybdate. Phosphate and polyphosphate inhibitors are suitable for protecting steel from an environment rich in chloride. Chloride ions in seawater very easy to attack thin steel surfaces. This can cause corrosion which, if left too long, can cause damage to the equipment (Lata & Chaudhary, 2008).

Carbohydrazide is a volatile type of inorganic inhibitor that reacts readily with oxygen at low temperatures and pressures. A carbohydrazide compound is known as an oxygen scavenger. It is a substance that can decrease dissolved oxygen levels in a liquid without adversely affecting the chemical cycle (Rahman et al., 2018). Carbohydrazide compound has the chemical formula $(N_2H_3)_2CO$. It is stable up to a temperature of 135 C. However, carbohydrazide could be toxic to aquatic organisms but not to humans. The use of carbohydrazide as a corrosion inhibitor has been investigated. The results showed that adding carbohydrazide could decrease the corrosion rate. Even though carbohydrazide decomposed, the decomposition product of carbohydrazide, i.e. hydrazine, is known to inhibit corrosion (Fytianos et al., 2016).

The mixture of two substances was applied as a corrosion inhibitor to increase the inhibition efficiency. The synergistic effect of an organic inhibitor has been studied. The authors investigated indium and gallium inhibitors' synergistic effect in an aqueous chloride solution in the aluminum alloy. The proposed mechanism was that indium enters the surface oxide film as trivalent ions and creates additional cation vacancies. Gallium ions occupied these other vacancies resulting in the improvement of the surface activation, which is proof of the synergistic inhibition activity (Mathiyarasu et al., 2001). Potassium chromate inhibitors and sodium nitrite inhibitors with various concentrations have been reported as corrosion inhibitors in 3.5M sodium chloride and 0.3M sodium sulfide media. The results showed that potassium chromate inhibitor performed better inhibition than sodium nitrite in both sodium chloride and sodium sulfide media. However, the combination of potassium chromate and sodium nitrite as inhibitors showed increased inhibition on the mild steel in two media (Afolabi, 2007).

This research aims to determine the inhibition performance of the combination of phosphate-carbohydrazide inhibitors for stainless steel in a seawater medium. The best composition between phosphate and carbohydrazid was also investigated.

Material and Methods

The materials used in this study were Sodium Triphosphate ($Na_5P_3O_{10}$) and Carbohydrazide compounds (CH_6N_4O), Distilled water, and NaCl crystals obtained from a chemical store in Tidar, Surabaya, East Java. The alloy metal specimen was obtained from an unused stainless steel pipe.

Corrosive medium preparation

The corrosive medium used in this study was synthetic seawater prepared by adding Sodium Chloride crystal (NaCl) into distilled water to get a 3.5% NaCl concentration.

Carbohydrazide and Sodium triphosphate inhibitor solution preparation

Inhibitors solution was prepared by adding the carbohydrazide in various concentrations of 5; 7.5; 10, and 15 (ppm) and sodium triphosphate with different concentrations (0, 100, 200, 300, 400, 500) into the 100 ml 3.5% NaCl media.

Specimen material preparation

Stainless steel specimen prepared by cutting stainless steel plate with size ± 1 cm x 1 cm x 0.15 cm. The next step, perforate the side of the specimen equal to the diameter of the glass tube, then connect the glass tube with an electric cable. The specimen was designed as a working electrode in the instrument.

Corrosion rate measurement

Electrochemical measurement was used to determine the corrosion rate of stainless steel in seawater medium before and after adding the inhibitor. The electrochemical measurements were done using electrochemical impedance spectroscopy. The working electrode was attached to the electrochemical cell opposite the Pt auxiliary electrode and the calomel electrode. The Working electrode (carbon steel specimen) surface area was prepared as described in the specimen material preparation section.

Results and Discussion

The Corrosion rate of metal alloy (stainless steel) was measured by using Electrochemical Impedance spectroscopy. The Corrosion rate of stainless steel in various concentrations of Phospate and Carbohydrazide inhibitors is shown in figure 1. The corrosion rate decreased significantly when the phosphate and carbohydrazide inhibitors were added. The best result was obtained at a combination of carbohydrazide concentration of 10 ppm and phosphate of 100 ppm with a corrosion rate of 0.0088 mm/year. However, when the amount of phosphate increases, there is an increase in the corrosion rate. the best condition obtained phosphate ratio of 100 - 300 ppm with carbohydrazide of 7.5 - 10 ppm. This is because the phosphate inhibitor requires the appropriate dissolved oxygen level to work optimally in coating the 304 stainless steel test metal.

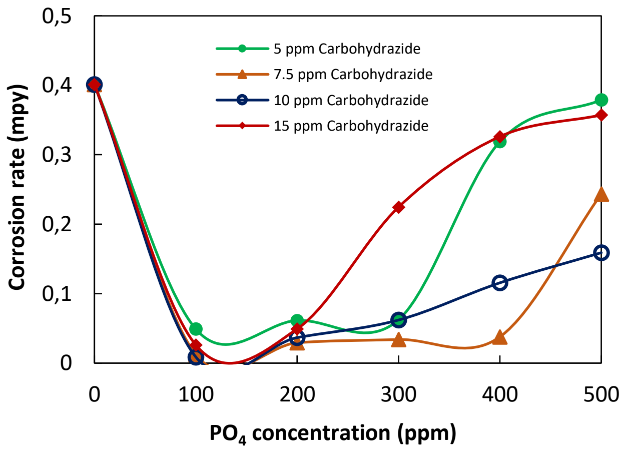

Figure 1. Effect of the PO_4 inhibitor and Carbohydrazide on Corrosion Rate of mild steel in seawater media

If the dissolved oxygen level is too small, the phosphate inhibitor cannot form a thin layer covering all the test metals. If the dissolved oxygen content is too large, it will create a thick layer. This thick layer is easily broken. In addition, it can increase the scope of dissolved carbon dioxide, which can initiate pitting corrosion. The reaction between oxygen and sodium triphosphate is as follows:

$$4Na_3PO_4 + 3O_2 \rightarrow 6Na_2O + 4PO_4 \text{ ....(1)}$$

Also, the carbohydrazide reaction with oxygen is as follows:

$$H_6N_4CO + 2O_2 \rightarrow CO_2 + 2N_2 + 3H_2O \text{......(2)}$$

From this reaction, it can be seen carbohydrazide acts as a substance to regulate dissolved oxygen levels. The best conditions were obtained from the study results, namely the combination of carbohydrate side concentration of 10 ppm and phosphate of 100 ppm. Another parameter to see the effectiveness of inhibitor is the inhibiton efficiency. The inhibiton efficienecy of combination between phospate and carbohydaride in various composition is shown in figure 2.

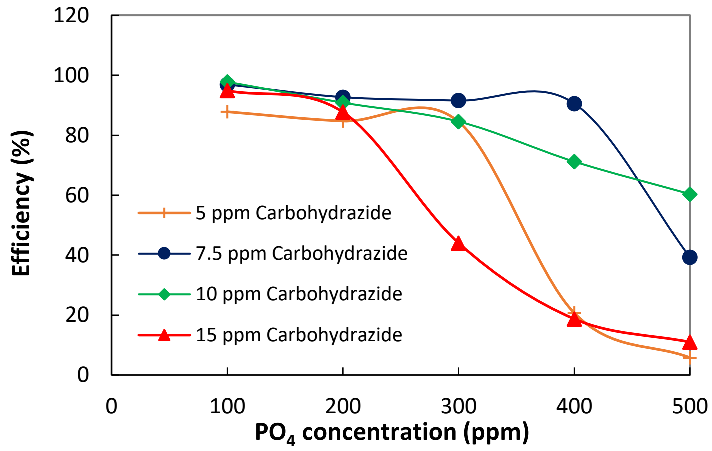

Figure 2. The inhibition efficiency (%) of mild steel at various concentrations of PO4 and Carbohydrazide 3.5% NaCl medium

Figure 2 shows that the efficiency of the inhibitor decreases with the addition of the inhibitor phosphate and carbohydrazide. The highest efficiency of inhibitor was obtained in the ratio of carbohydrazide inhibitor and phosphate 10: 100, which was 97.9751%, and the lowest efficiency was in the proportion of carbohydrazide inhibitor and phosphate 5: 500, which was 5.7885 %. The highest concentration of phosphate shows a lower efficiency. It means that the concentration of the inhibitors added should be proper.

Conclusion

The ratio of the concentration of Carboyhydrazide with the best phosphate concentration in reducing the corrosion rate is 10: 100 ppm by obtaining a decrease in the corrosion rate from 0.401 mpy to 0.0088 mpy with an inhibitory effect of 97.7951%. The addition of carbohydrazide compounds must be appropriate so that the phosphate inhibitor can work optimally in forming a film layer on the surface of 304 stainless steel.

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