Chitosan Gel + Cu $^{2+}$ as the Corrosion Inhibitor on Mild Steel in the Peat Water Media

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ABSTRACT

The corrosion inhibition of mild steel by chitosan gel is investigated in peat water by using weight loss measurements. The results showed that the inhibition efficiency on static and dynamic system were 80.28% and 41.8% respectively. The spectrum analysis done by Fourier Transform Infrared Spectroscopy (FT-IR) from the corrosion product on steel surface showed that chitosan gel could obstruct the process of corrosion on mild steel in peat water media, because it formed Fe-chelating compounds. The characterization by Scanning Electron Microscopy (SEM) showed that chitosan gel forming a passivatable layer. To increase the corrosion inhibition efficiency in the dynamic system in this research done by modification with Cu^{2+} ions. The result of experiment showed that the increase of inhibition efficiency is reaching 60%.

Keywords: Chitosan gel, Corrosion inhibition, Mild steel, Peat water

ABSTRAK

Gel kitosan sebagai inhibitor korosi pada baja lunak diterapkan langsung dilapangan menggunakan metode pengukuran berat hilang (*WLM*). Hasil efisiensi inhibisi sistem statis dan dinamis berturut-turut adalah 80,28% dan 41,8 %. Hasil spektrum *FT-IR* dari hasil korosi (karat) pada permukaan baja menunjukkan gel kitosan dapat menghambat terjadinya korosi pada baja lunak dalam media air gambut karena membentuk senyawa Fe-khelat. Berdasarkan foto *SEM* memperlihatkan bahwa gel kitosan membentuk lapisan pasif pada permukaan baja. Untuk memperbaiki efisiensi inhibisi korosi pada sistem dinamis pada penelitian ini dilakukan modifikasi dengan ion Cu^{2+}. Hasil eksperimen menunjukkan terjadi kenaikan efisiensi inhibisi menjadi 60%.

Kata kunci: Air gambut, Baja lunak, Inhibitor korosi, Gel kitosan

INTRODUCTION

Indonesia is a tropical country that has a higher humidity and rainfall quantity. This condition may support the occurence of corrosion on metal. The process of corrosion is actually happen naturally, but it technically become one of the serious problems faced by modern people nowadays. It is estimated that our country had suffered billions of loss due to the corrosion per year. Therefore, it is urgently needed an useful technology that can protect metals from corrosion. One of the way to protect metals from corrosion that had successfully been implemented is by using the corrosion inhibitor. But, the problem is, many of the corrosion inhibitors used is relatively expensive and considered as poisonous substances.

In this research, chitosan is used as a substances that has a good effectivity and also ecology friendly. According to a research done by Erna (2009), it is showed that chitosan gel can be used to inhibit the corrosion happened on mild steel in peat water media, with the inhibition efficiency 93,32% in the laboratorium scale. Based on this research that showed a higher number of corrosion inhibition efficiency in chitosan gel, the researchers therefore did a research to study the inhibition characters of chitosan gel and its direct application in peat water statically and dinamically. To increase the number of its inhibition efficiency, the chitosan gel is combined with Cu^{2+}.

This research is really deserve to be done, due to the characteristics of chitosan gel which are biodegradable, bioactive, biocompatible, polycationic, non-toxic, renewable, and has a high number of molecule weight (Tang, *et.al*, 2007). And also due to the existence of peat water that is needed to be kept sustainable in our nature. Thus, this research is aimed to get the suitable inhibitor for mild steel in peat water. Based on the survey done in some areas in Riau, the production pipeline from a petroleum industry that through the peat areas has already been leading to the corrosion process. If it is not quickly solved, the pipeline can be thinning, and surely can harm the environment.

In this research, a sample of natural peat water is going to be used directly as the corrosive media and the corrosion rate of mild steel is also going to be calculated with or without inhibitor. The efficiency of chitosan gel is studied by using the Weight Loss method. Also, the characterization of steel surface is studied by using *Scanning Electron Microscope- Energy Dispersive X-ray* (*SEM-EDX*) and *FT-IR* spectroscope before and after using inhibitor.

MATERIALS AND METHODOLOGY

The materials used in this research are chitosan (R&M), Sodium Poliphosphate (Merck), $CuSO_4$ as the source of Cu^{2+}, ethanol, NaOH, HCl, mild steel plates 2x1 cm^2 with the code BJTP 24 (0,16 %C, 0,19% Si, 4,8% Mn, 0,16% P, 0,22% S and the rest is Fe), silicon carbide sand papers 100, 200 and 400-grit, acetic acid, NH_4OH, $CHCl_4$, acetone, detergent, peat water (from the area of Rimbo Panjang, Kampar - Riau) and aquades.

In addition to this, the equipments used in this research are oven, analytical scale, *Perkin Elmer System 2000 Fourier transform Infrared spectroscopy (FT-IR)*, *JEOL JED-2300 Scanning Electron Microscope (SEM-EDX)*, pH-meter and glass equipments.

The method used in making chitosan gel is a method reported by Tang *et.al*., (2007). The calculation of corrosion rate and corrosion inhibition efficiency done by the Weight Loss method, namely preparing the mild steel plate by cutting it down with size 1 x 2 cm^2 and cleaning its surface with silicon carbid sand paper 100, 200, and 400-grit, then wash it with the water, acetone, and ethanol. After that, dry it in the oven with temperature 40^{o}C in 15 minutes, and weighed it.

Then, the specimen of mild steel is immersed in peat water media for 3 days with static and dynamic system. After that, the specimen is washed with chloroform, acetone, and is brooched and cleaned with water. Then wash it again with ethanol, and dry it on the oven with temperature 60^{o}C. Next, weigh the specimen one again and calculate the corrosion rate of it, and also study the characterization of corrosion result by using *FT-IR* and morphology photos by using *SEM-EDX.*

The determination of modification inhibition effeciency with Cu^{2+} done by preparing the solution of $CuSO_4$ with concentration variation 100, 200, 300, 400 and 500 ppm.

RESULT AND DISCUSSION

The *FT-IR* spectrum from the corrosion product formed before and after using chitosan gel can be seen in Figure 1. The product of corrosion in mild steel surface which was immersed in peak water for 3 days without inhibitor showed that the corrosion product formed is the compound of γ–FeOOH (*lepidocrocite*) and Fe_3O_4 (*magnetite*) which is noticed with the appearance of peak 1636 and 574 cm^{-1} (Favre and Landolt, 1993). γ–FeOOH is formed because it is an oxide form of iron that is most rapidly occur in the water environment and easily changed to Fe_3O_4 (Perez, 2004).

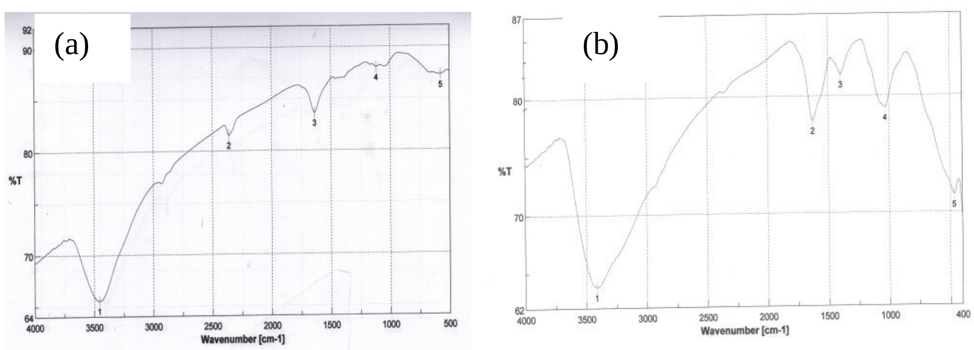

Figure 1. *FT-IR spectrum on mild steel surface*: (a) without, and (b) with chitosan gel in peak water

For the *FT-IR* spectrum that use inhibitor, the peak Fe-chelat can be seen in 1396 and 1031 cm^{-1} with smaller transmittance, this is because the ability of nano-chitosan to form aggregate or forming a wider continuous network structure to all existing volume, so that the film layer formed on the mild steel surface can be observed with the naked eyes. This is in accordance with the conclusion made by Abd El-Maksound (2008) that one of the working mechanism of inhibitor is the formation of sediment on the steel surface that can be observed with the naked eyes.

The analyzation result of *FT-IR* spectrum in this corrosion product proves that the mechanism of corrosion inhibition on mild steel in peak water happened through the process of adsorption in the mild steel surface, namely the formation of Fe (Fe-chelat) complex layer that can slowing down the corrosion rate.

The shape of mild steel specimen surface before and after immersed in peak water with and without inhibitor can be seen in the Figure 2. It is clearly seen that the surface of mild steel before being immersed in peak water is still smooth and the surface of mild steel after being immersed in peak water without inhibitor is forming a corrosion product that is noticed by the appearance of small holes due to the dissolution of Fe. This result of morphology photo by *SEM* proves that humic acid is the main component of peak water that cause the corrosion on the mild steel surface. This is in accordance with the conclusion reported by Dick dan Rodrigues (2006). The kind of corrosion in mild steel in peak water is the compund of pitting and evenly corrosion.

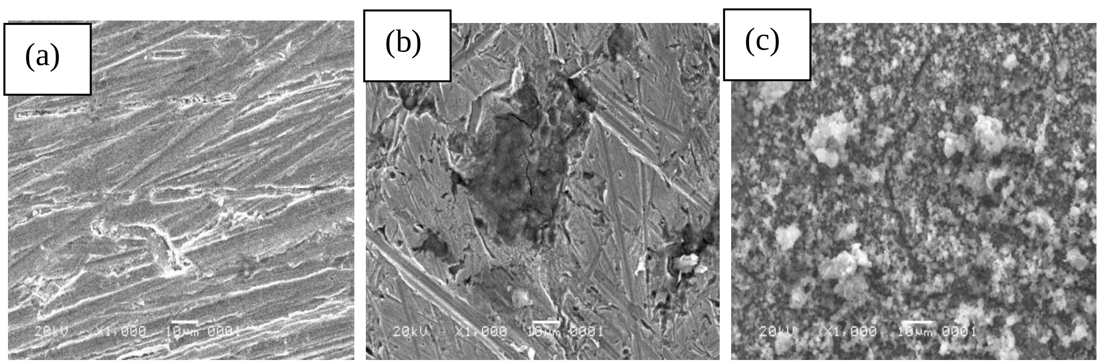

Figure 2. *SEM* morphology photo of the mild steel specimen: (a) before, (b) after being immersed in peak water without, and (c) with inhibitor chitosan gel for 3 days

The result of morphology photo by *SEM* proves that the use of chitosan gel forms a layer that is less evenly, but the size of surface pores seems smaller. This is because chitosan forms the aggregate on the steel surface.

The elements of mild steel surface was analyzed by using *SEM-EDX*. The result of spectrum from *EDX* on the mild steel surface in peak water with and without inhibitor can be seen in Figure 3.

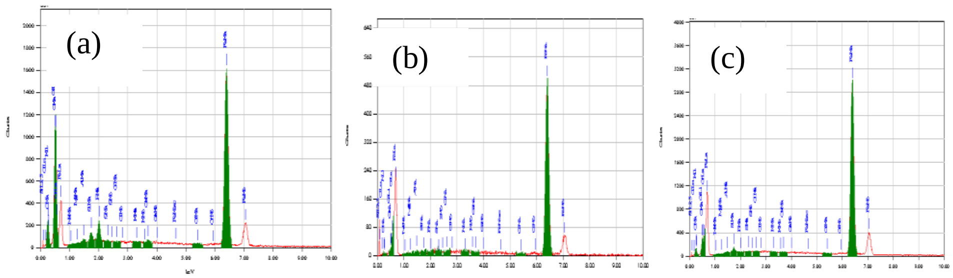

Figure 3. The *EDX* spectrum from the surface of mild steel specimen: (a) before being immersed, (b) after being immersed without, and (c) with inhibitor in peak water

The analyzation result of the elements on mild steel surface by using *SEM-EDX* can be seen in Table 1. It is surely can be seen that the atomic percentage of C element in steel specimen before being immersed in peak water is lower than the other specimen after being immersed. This is because the higher amount of C element in humic acid, that reaches 52,24% (Dick dan Rodrigues, 2006) in which half of them form a complex solution with Fe ion and another half attaches on the mild steel surface. At the same time, the one that using inhibitor showed the percentage increase of C atom. This is proved that the inhibitor molecules are absorbed on the mild steel surface and forming a layer.

Table 1. The analyzation result of C, Fe and O elements on the mild steel specimen which is immersed in peak water for 3 days.

% At	Mild steel surface		
	Sample	Without inhibitor	With chitosan gel
C	0,27	10,23	17,94
Fe	96,64	81,37	44,58
O	1,97	7,07	33,12

For the atomic percentage of Fe element, it is found that there is the decrease with the surface that use inhibitor. This is showed that Fe forms a complex compound with the inhibitor molecule, so that the percentage of Fe atom detected become smaller. At the same time, the O atom is detected on the mild steel surface by using inhibitor. This is because the passive layer is formed after the corrosion product occurs.

According to the spectrum analysis of *FT-IR*, the formed passive layer is the Fe-khelat which is hydrophobic. Passivation is a complex fenomena and can only be explained with the adsorption theory (Talbot, 1998). The process of adsorption in inhibitor on the steel surface is happened through the formation of intermediate Fe compound with the molocule of water. This is because the interaction energy of organic compound on metals surface is higher than the water molecule, so that the water molecule is adsorbed earlier (Abd El-Maksoud, 2008).

Table 2 is showing the the efficiency result of corrosion inhibition before and after chitosan gel is being modified with the Cu^{2+} ion and being applied in peak water. It is clearly seen from Table 2 that the corrosion inhibition on static system has already been improved, which is more than 80%. Meanwhile, in the dynamic system with the inhibitor which is modified with Cu^{2+} ion is found the increase of efficiency from 41,8% to 60% with the concentration of Cu^{2+} ion 500 ppm and chitosan gel is 400 ppm.

Table 2. The corrosion inhibition efficiency in some condition in the field

Inhibitor condition in field	Static system (chitosan gel)	Dynamic system (chitosan gel)	Dynamic system (chitosan gel + Cu^{2+})
Inhibition efficiency (%)	80,28	41,8	60

The increase in inhibition efficiency of chitosan gel can be proved by analyzing the morphology of steel surface before and after being modified with Cu^{2+} ion. The surface photo from *SEM* can be seen in Figure 4, where the molecules of Cu cover the steel surface with bigger pores in the steel surface which is immersed with peat water and Cu^{2+} ion without chitosan. But, after being modified with adding chitosan gel, it seems that the steel surface covered is more evenly, so that it can increase the number of inhibition efficiency if it is compared to the one without Cu^{2+} addition.

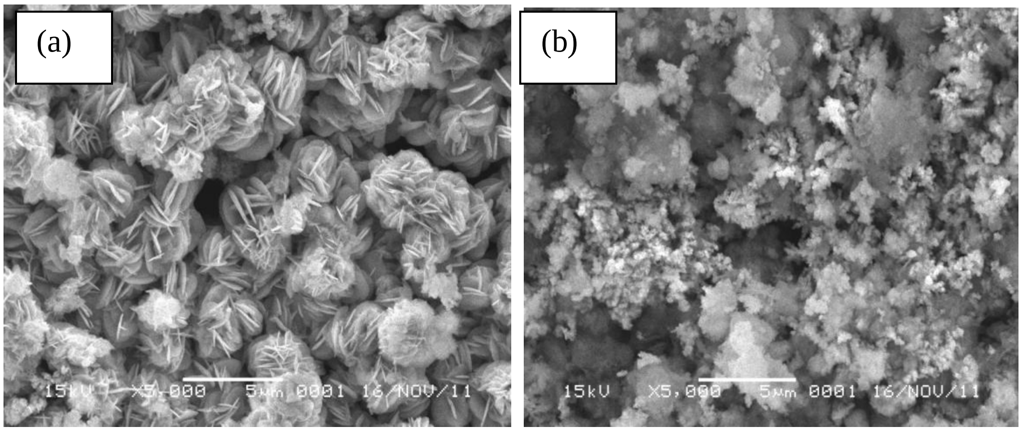

Figure 4. The morphology photo from *SEM* on the mild steel specimen: (a) immersed in peat water + Cu^{2+} , (b) immersed in peat water with nanoparticle of chitosan + Cu^{2+} for 3 days

CONCLUSION

The characterization of mild steel surface shows the corrosion inhibition mechanism of inhibitor on mild steel in peak water, that happened through the process of adsorption which is forming the passive layer (a complex compound of Fe-khelat). Chitosan gel is a good corrosion inhibitor to obstruct corrosion on mild steel in peat water in static system. Moreover, the existance of Cu^{2+} ion can increase the number of corrosion inhibition efficiency of chitosan gel in dynamic system from 41,8 % to 60%

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