

SYNERGISTIC EFFECT OF HYDROQUINONE ON THE INHIBITION EFFICIENCY OF PYRROLE AND PYRIDINE ON CARBON STEEL IN STATIC ENVIRONMENT

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ABSTRACT

The secondary effect of hydroquinone as oxygen scavenger on the corrosion inhibition behaviour of pyrrole and pyridine in static 3.5 wt% NaCl solution was investigated using Linear Polarization Resistance Method (LPRM). Experimental results found that the inhibition effect of pyrrole and pyridine increased with the increase of hydroquinone concentration. The inhibition efficiency was found to be improved by about 70% after addition of hydroquinone into saline solution containing 100 ppm each of pyrrole and pyridine. The addition of hydroquinone eliminated dissolved oxygen molecules which took part in cathodic reaction and hence reducing the corrosion rate of steel when immersed in the salt water.

Keywords: Corrosion inhibition; inhibition efficiency; oxygen scavengers; dissolved oxygen; Linear Polarization Resistance Measurement (LPRM)

INTRODUCTION

Carbon steel is often used as the material of construction for transmission pipelines in the oil and gas production sector and also in various other chemical processing industries [1]. However, they are susceptible to corrosion especially when exposed to chloride containing environment, resulting in economic losses and giving rise to many potential safety problems [2]. Corrosion inhibitor is often considered as the most effective and practical method of corrosion prevention for internal surfaces protection and protection of difficult to reach surfaces [3]. Inhibitors extracted or formulated from organic compounds containing oxygen, sulphur, nitrogen and phosphorus work as effective inhibitors against corrosion of carbon steels [4]. They function at the interface between the steel surface and aqueous corrosive solution through adsorption mechanism which formed protective films on the steel surface [5]. The adsorption of organic inhibitor molecules through physical adsorption or chemical adsorption can change the corrosion resistance properties of the substrate metals [6].

Studies have found that the synergistic inhibition effect is an effective method, through addition of a secondary compound into the solution containing the inhibitor for improving inhibition efficiency [7]. Also, it has been proven to decrease the amount of organic inhibitor consumption and to expand the application of organic inhibitor in a particular media [8].

Previously, pyrrole and pyridine had been proven as effective corrosion inhibitors for carbon steel when immersed in an aqueous media [9]. These inhibitors have electron lonepairs on the nitrogen atom which promotes surface adsorption of the inhibition molecules on to the steel surface, and enhances corrosion inhibition. However, there were few reports on the synergistic effect on pyrrole and pyridine with other secondary compounds. This research focuses on the inhibition effect of pyrrole and pyridine which could be further improved by introducing oxygen scavenger, for example hydroquinone. Presently, hydroquinone is example of an organic compound used in the water treatment for boiler feeds. This study was conducted using linear polarization resistance method (LPRM).

EXPERIMENTAL

Specimen and test solution

A commercial grade carbon steel specimen of dimension 1cm x 1cm x 0.5cm was soldered to nichrome wire which was then embedded in a cold mounting polymer. The nichrome wire was then placed in a PTFE tubing to prevent direct contact with the sodium chloride solution. The chemical composition of specimen was analyzed using Inductively Couple Plasma (ICP) and CHNS analyzer before proceed the next experiment. The result of this analysis is as shown in Table 1. The specimens was prepared by grinding with different grades of SiC papers which ended up with 1000 grades. A 3.5 wt% sodium chloride solution was used as the aqueous solution. The pyrrole, pyridine and hydroquinone were then added in sequence in performing the tests.

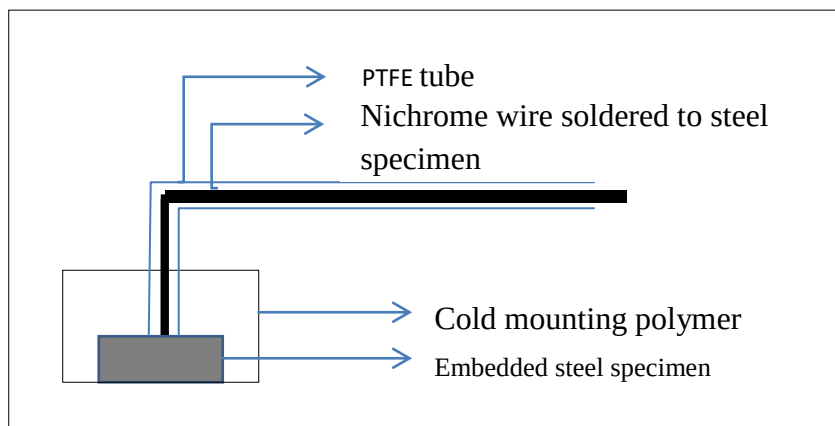


Figure1: Schematic diagram of steel specimen for corrosion inhibition testing

Linear polarization resistance measurement and surface morphology analysis

In the Linear Polarization Resistance measurement, R_p values obtained were measured by using a VoltaLab, Model PGP 201 operating in the potentiostat mode. Three electrodes system was immersed in test solution in a static condition and at room temperature, (25°C). The NaCl solution in a 500 ml of beaker was injected with each, 100 ppm of pyrrole and pyridine with an arbitrarily chosen concentrations (50,100,150,200 ppm) of hydroquinone. The R_p values were chosen to indicate the corrosion rates which vary with time since R_p is inversely proportional to corrosion rate base on principle of Faraday's Law. According to Stern-Geary equation [10],

$$R_p = \frac{b_a b_c}{2.3 I_{corr} (b_a + b_c)} \quad (1)$$

Rearrange above equation;

$$I_{corr} = \frac{b_a b_c}{2.3 (b_a + b_c) R_p} \quad (2)$$

Where b_a and b_c are Tafel constant for anodic and cathodic respectively. Tafel constant for both anodic and cathodic reaction of carbon steel are constants. Corrosion rate (milli-inches per year) can be calculated from the following equation [11];

$$Corrosion\ rate\ (mpy) = \frac{0.13 I_{corr} (E.W)}{Ad} \quad (3)$$

E.W stands for equivalent weight. A (cm^2) represents the area uniformly where the corrosion take place and d is the density (g/cm^3) of the steel specimen. The value 0.13 is the metric and time conversion factor. By substituting equation (2) into (3), the equation will be;

$$Corrosion\ rate\ (mpy) = 0.057 \frac{b_a b_c}{Ad (b_a + b_c) R_p} (E.W), \text{ where } C = 0.057 \frac{b_a b_c}{Ad (b_a + b_c)} (E.W) \quad (4)$$

$$Corrosion\ rate\ (mpy) = C \frac{1}{R_p} \quad (5)$$

According Equation 5, it can be simplified that corrosion rate of specimen is inversely proportional to the polarization resistance, R_p [12]. The higher the value of R_p , the lower the value of corrosion rate. The inhibition efficiencies were evaluated from the measured value of R_p according to Eq.6;

$$IE\% = \frac{R_p - R_{p0}}{R_p} \times 100\% \quad (6)$$

Where R_p and R_{p0} are the polarization resistance value with and without addition of HQ. After the experiment was done, the specimen was stored in desiccator immediately

to avoid any contact with surrounding. Then, the surface morphology of carbon steel was examined using Field Emission Scanning Electron Microscope, FESEM (DSM 982 Gemini Supra 40 VP) and Atomic Force Microscope, AFM (XE-100, Park System).

RESULT AND DISCUSSION

Table 1: Typical chemical composition of a commercial grade carbon steel specimen, analyzed by ICP and CHNS analyzer

Elements	Weight percent (%)
Carbon	0.060
Aluminium	0.092
Manganese	0.550
Nickel	0.056
Copper	0.350
Zinc	0.025
Lead	0.070
Chromium	0.064
Iron	Balance

Figure 2 and Figure 3 show the value polarization resistance variation with time when immersed in 3.5 wt% NaCl solution containing 100 ppm of pyrrole and later with pyridine. Arbitrarily selected concentrations of HQ, for example were (50, 100, 150 and 200 ppm). Both of figures show the value of R_p increasing steadily with time at higher concentration of pyrrole and pyridine.

Figure 2 shows small variation of polarization resistance, R_p with time when 100 ppm pyrrole was injected into 3.5 wt% NaCl solution. At the highest concentration of 200 ppm of HQ addition, a drastic increase in R_p values was observed from 2.788 kohm.cm² to 4.346 kohm.cm². Figure 3 shows small increment in R_p value was observed after addition of HQ. However, the R_p values were increased slightly 2.305 kohm.cm² at 200 ppm of hydroquinone before started to decrease after 20 minutes immersion. It was found that polarization resistance, R_p in both inhibitors increase with an increased in concentration of HQ. With the increase in concentration of HQ, more oxygen molecules will react to HQ, enhancing more uniform surface coverage, which decreases the cathodic reaction rate of the hydrogen reduction [13].

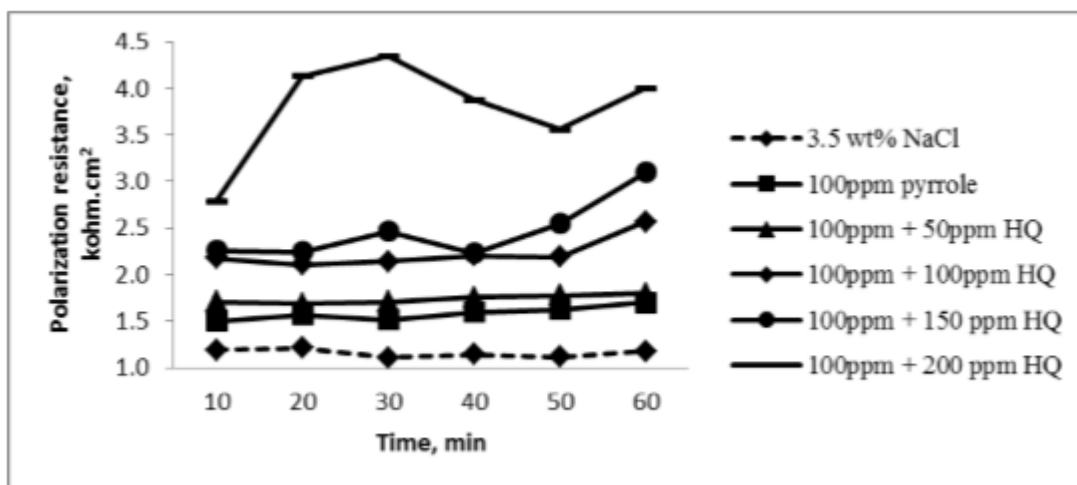


Figure 2: Variation of R_p values with immersion time in pyrrole-inhibited 3.5 wt% NaCl solution and different HQ addition

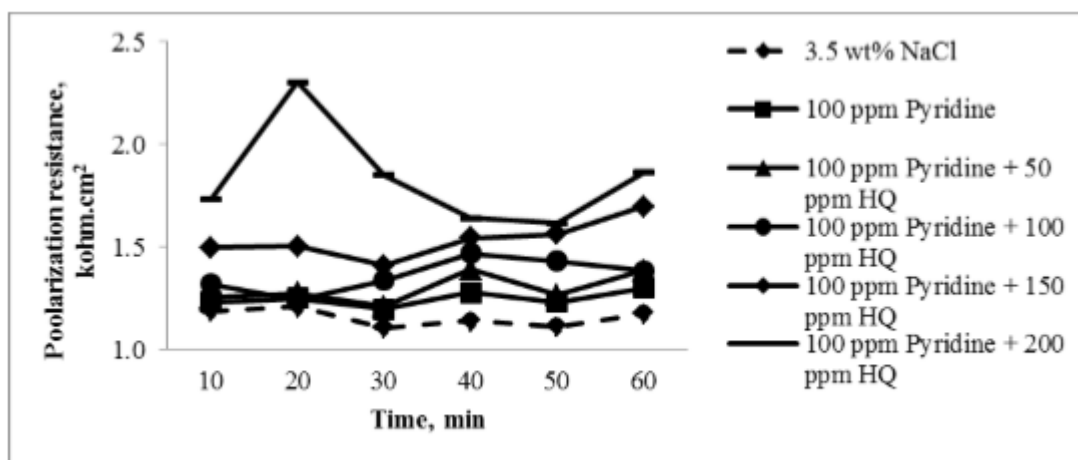


Figure 3: Variation of R_p values with immersion time in pyridine-inhibited 3.5wt% NaCl solution and different HQ addition

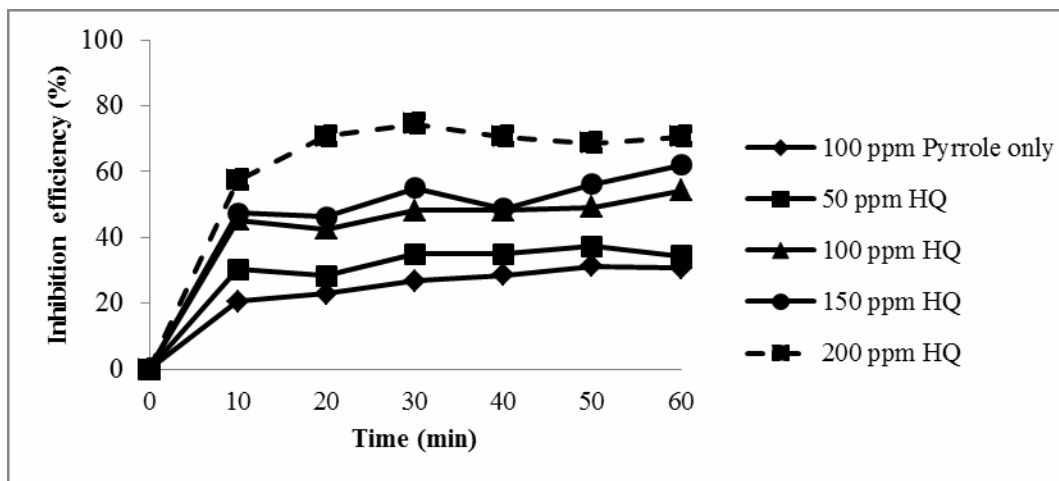


Figure 4: Variation of percentage inhibition efficiency with time in pyrrole-inhibited 3.5 wt% NaCl solution and different concentration of HQ

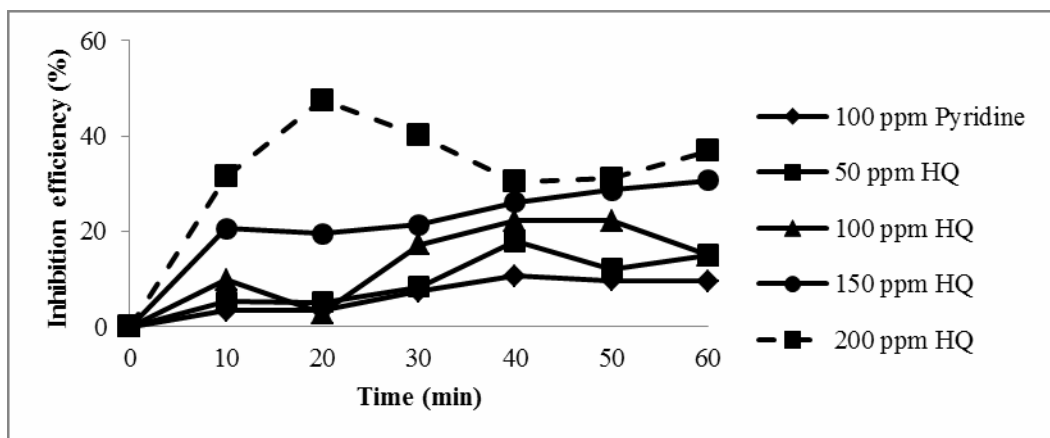


Figure 5: Variation of percentage inhibition efficiency with time in pyridine-inhibited 3.5 wt% NaCl solution and different concentration of HQ

Figure 4 and Figure 5 show the effect of HQ addition on the inhibition efficiency that contained 100 ppm of pyrrole and pyridine. There were relatively small effects on inhibition efficiency observed after adding these inhibitors. However, after addition of 50 ppm, 100 ppm, 150 ppm and 200 ppm of HQ in the inhibited solution, the inhibition efficiency increased. Figure 4 shows that the inhibition efficiency of pyrrole reached about 70% at the highest concentration of 200 ppm HQ compared to inhibition efficiency of pyridine which was recorded about 47%.

Oxygen scavenger was added to deplete the maximum possible amount of dissolved oxygen in solution in order to enhance the inhibition efficiency [10]. HQ is widely used in the industry initially as catalyst to enhance compounds like hydrazine as oxygen

scavenger. Over the time it is found that HQ itself is effective as oxygen scavengers and it is proven to have lowered the amount of dissolved oxygen to the 1-2 ppb range [14]. Besides that, HQ also performed greater reactivity with oxygen at room temperature and less toxic as compared to hydrazine [15]. According to Buecker [16], HQ is an oxygen scavenger which will react with the dissolved oxygen to form benzoquinone and water.

The reaction of HQ with dissolve oxygen is known to occur as shown below,



During oxidation of HQ, it is possible effect on the reaction solution because the benzoquinone is very much dependent upon pH especially under alkaline [17]. By acting as oxygen scavenger, amount of dissolved oxygen molecules available become depleted and the corresponding the involved cathodic reaction will be decreased correspondingly. As more concentration of HQ was added into solution, more oxygen molecules reacted with HQ hence reducing the anodic reaction correspondingly, that is, anodic dissolution is decreased.

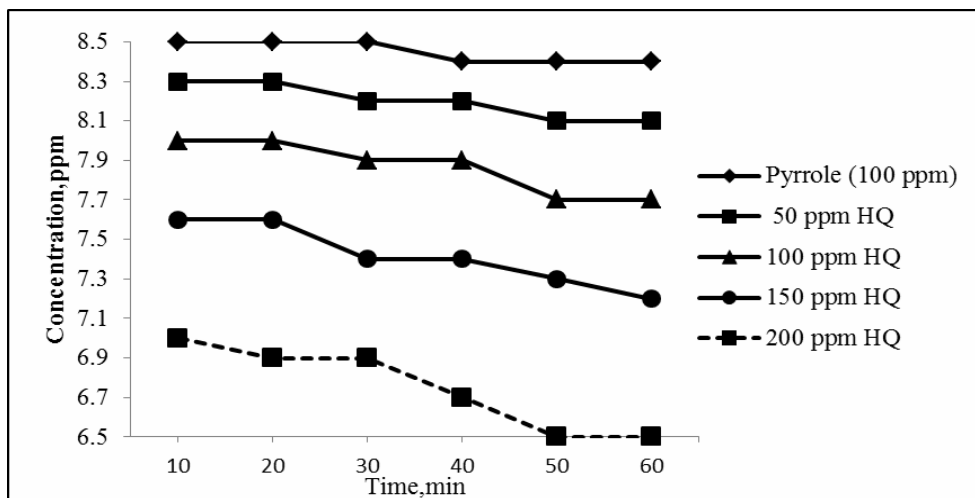


Figure 6: Variation of dissolved oxygen with time in 3.5 wt% NaCl solution at room temperature (25°C)

Figure 6 shows the variation dissolved oxygen (ppm) upon addition of different concentration of HQ within period of 60 minutes at room temperature (25°C). The dissolved oxygen was measured using Dissolved Oxygen meter (Model YSI 5000). The initial dissolved oxygen in 3.5 wt% NaCl was 8.5 ppm and after addition of 50 ppm, 100 ppm, 150 ppm of HQ, the dissolved oxygen was observed to decrease rapidly. At concentration of 200 ppm, the dissolved oxygen decreased to 6.5 ppm and then reaching plateau after 60 minutes. This is because most of dissolved oxygen in the solution had reacted with HQ and therefore will affect the cathodic reaction. This demonstrates further addition of hydroquinone promote depletion of dissolved oxygen in the 3.5 wt% sodium chloride solution.

Surface morphology

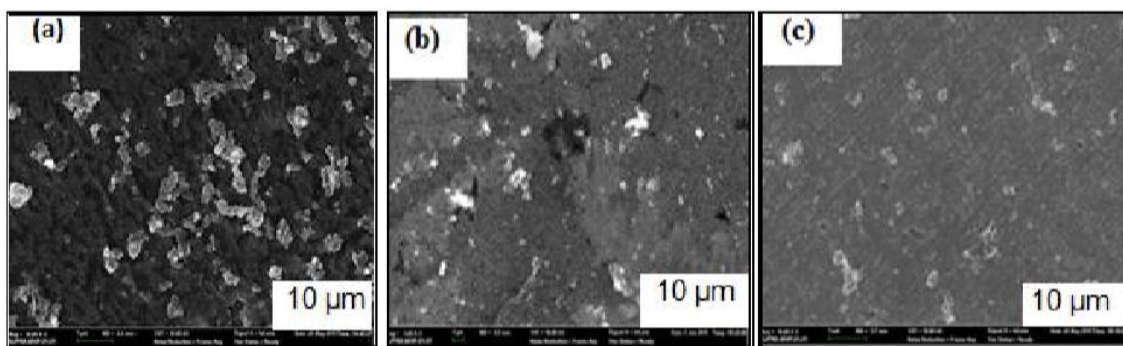


Figure 7: FESEM micrographs samples in (a) 3.5 wt% NaCl b) 100 ppm pyrrole c) 100 ppm pyrrole + 200 ppm HQ

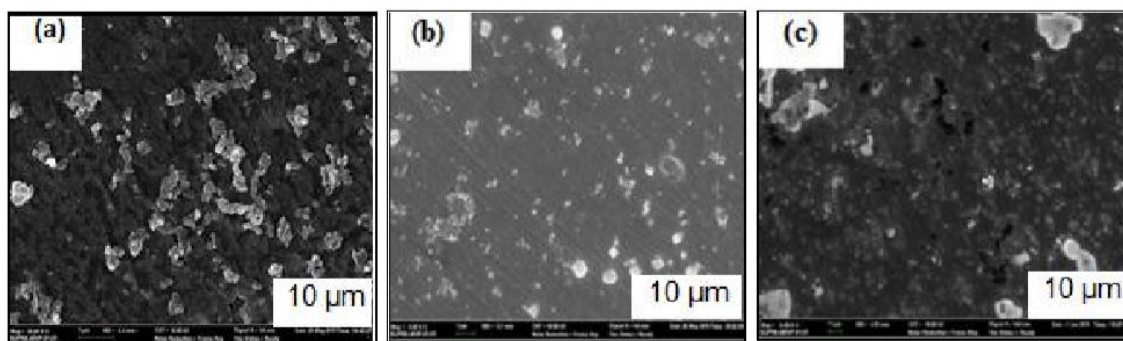


Figure 8: FESEM micrographs sample in (a) 3.5wt% NaCl b) 100 ppm pyridine c) 100 ppm pyridine + 200 ppm HQ

The FESEM images of carbon steel specimen after 60 minutes immersion in 3.5 wt% of NaCl solution in the absence and presence of HQ at static condition and room temperature (25°C) were presented in Figure 7 and Figure 8. The magnification of image specimen is 500x.

In Figure 7(a) and 8(a), in the absence of inhibitors, the surface specimen was affected by aggressive medium. The surfaces were corroded and pores were seen clearly. In Figure 7(b), the smoother surface was observed than in Figure 7(a) after adding of pyrrole in solution. In the presence of HQ, the surface is protected further. It is clear that, the pyrrole inhibited corrosion of carbon steel in the solution by forming protective adsorbed film on surface of specimen and addition of HQ reacted to dissolved oxygen which further reduces the corrosion rate.

In figure 8(b), in the presence of pyridine, the corrosion products were observed still over the surface specimen. However, the smoother surface was observed and less corrosion deposit were seen in figure 8(c) after adding HQ. It is indicated combination

of both inhibitors and HQ, increase the inhibiting effect of pyrrole and pyridine.

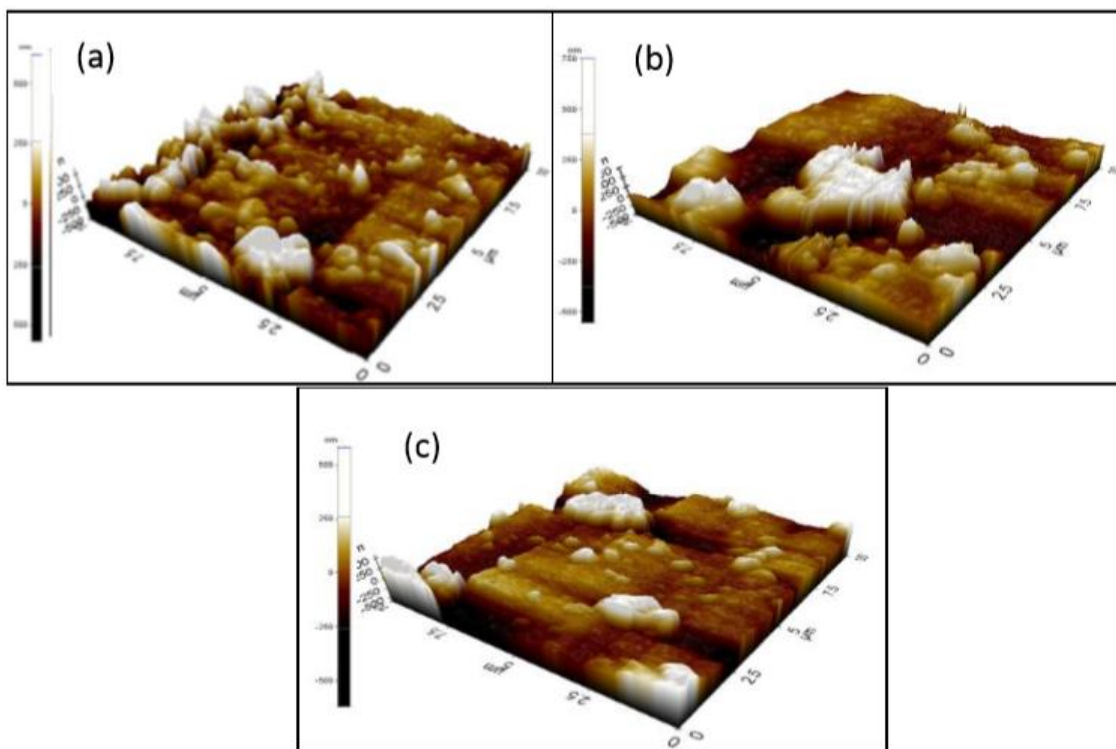


Figure 9: AFM images after 60 minutes immersion in (a) 3.5wt% NaCl b) 100 ppm pyrrole c) 100 ppm pyrrole + 200 ppm HQ

The surface roughness of specimen was analyzed by AFM. In AFM analysis, the average Ra value was indicated the corrosion product that formed in metal surface not to adsorb layer [18]. The three dimensional AFM images of carbon steel specimen after 60 minutes immersion in inhibited solution in the absence and presence of HQ at static condition and room temperature are as shown in Figure 9 and Figure 10.

Figure 9(a) and Figure 10(a) show surface morphology of the specimen immersed in 3.5 wt% NaCl solution indicating a lot of surface irregularities. It can be clearly observed that in the absence of inhibitor, the steel surface was seriously corroded with areas of uniform corrosion. In the presence of pyrrole, smoother surface was obtained and the Ra value decreased from 97 nm to 1.441 nm. as a consequence of low corrosion damage and the protective formation of an inhibitor layer on steel surface [19]. However after addition of 200 ppm of HQ to the inhibited solution as shown in Figure 9(c), the surface roughness covers a large portion of surface area and the Ra value was 0.094 nm.

In the presence of pyrdine Figure 10(b) clearly show less of bulges and more uniform surface compared to Figure 10(a) with average Ra value of 1.430 nm. This is due to the

involvement of inhibitor molecules in the interaction with the reaction sites of steel surface, resulting in a decrease in the contact between iron and the aggressive medium and sequentially exhibited excellent inhibition effect. At Figure 10(c), the surface roughness more smoothter and plateau after addition of 200 ppm HQ containing 100 ppm of pyridine and the Ra value was 0.134 nm. From the Ra result obtained, it is observed that a synergistic effect HQ on pyrrole and pyridine enchances inhibition effect of pyrrole and pyridine.

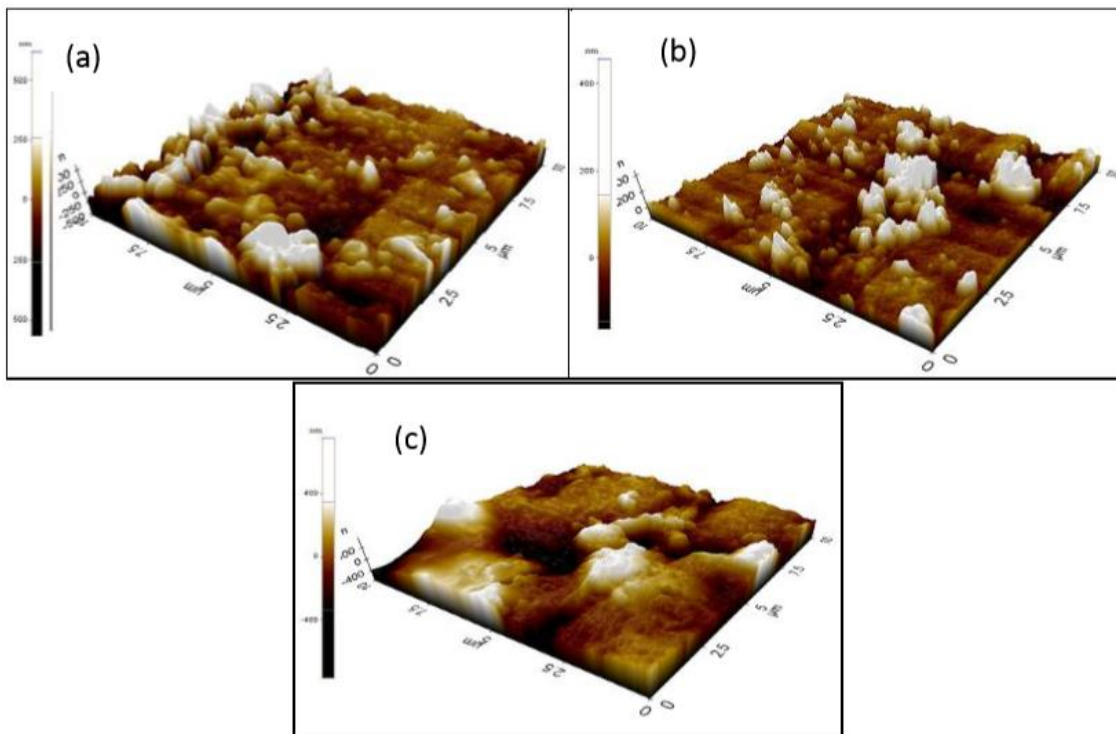


Figure 10: AFM images after 60 minutes immersion in (a) 3.5 wt% NaCl b) 100 ppm pyridine c) 100 ppm pyridine + 200 ppm HQ

CONCLUSION

It has been demonstrated that the addition of HQ as an oxygen scavenger improves the inhibition efficiency of pyrrole and pyridine in 3.5 wt% NaCl solution at static and room temperature. The R_p value of pyrrole and pyridine was increased after addition HQ indicates the corrosion rate become decreased. The effect was observed to be greater with pyrrole inhibited 3.5 wt% NaCl solution than with pyridine due to presence N-H groups which promotes effective surface adsorption leading to the formation of an insoluble protective surface film [20].

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