SEBHA UNIVERSITY JOURNAL OF PURE & APPLIED SCIENCES VOL.21 NO. 1 2022
DOI: 10.51984/JOPAS.V21I1.1419

مجلة جامعة سبها للعلوم البحتة والتطبيقية
Sebha University Journal of Pure & Applied Sciences

Journal homepage: www.sebhau.edu.ly/journal/index.php/jopas

The Inhibition Effect of the Expired Esomeprazole on the Corrosion of Carbon Steel in Desalination Water

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Keywords:
Carbon Steel
Desalination Water
Expired Esomeprazole
Weight Loss Technique
Corrosion Rate
Efficiency
Lsi

ABSTRACT

A study has been carried out to evaluate the effect of expired Esomeprazole (S3O3N19H17C) (20mg) as Inhibitor on the corrosion behaviour of carbon steel in desalination water (Drinking water) by using weight loss technique at room temperature. The test solution used in this study was Desalination water (Drinking water) samples and expired Esomeprazole was used as Inhibitor. The Langelier Saturation Index (LSI) results and the potential pH diagram (Pourbaix diagram) gave an indication that Desalination water sample was a corrosive media. From the study results, it was found that all the weights of the tested specimens were decreased. Furthermore, the results of the carbon steel specimens that were tested in present of inhibitor showed that the weight loss and corrosion rate decreased as the weight of inhibitor increased. The maximum efficiency was found 52.08% when the weight of inhibitor was 2.0055g which was the maximum weight and the minimum corrosion rate was 0.0046cm/year. So, it was assumed that the expired Esomeprazole has good inhibition effect on the corrosion of carbon steel.

تأثير منع الايزومبرازول المنتهي الصلاحية على تآكل الصلب الكربوني في مياه التحلية

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الكلمات المفتاحية:
الفولاذ الكربوني
مياه التحلية
ايزوميبرازول منتهي الصلاحية
معدل التآكل
فقدان الوزن
الكفاءة
دليل لنجياير

الملخص

تم اجراء دراسة لتقييم تأثير إيزوميبرازول المنتهي الصلاحية(20مجم) كمثبط على سلوك تآكل الفولاذ الكربوني في مياه التحلية (مياه الشرب) في درجة حرارة الغرفة. محلول الاختبار المستخدم في هذه الدراسة كان عينات من مياه التحلية و الايزوميبرازول المنتهي الصلاحية استخدم كمثبط. من النتائج الدراسة, لقد وجد نقص في كل أوزان العينات المختبرة. علاوة على ذلك, أظهرت نتائج عينات الفولاذ الكربوني التي تم اختبارها بالمثبط أن فقدان الوزن و معدل التآكل ينخفض مع زيادة وزن المثبط. و كذلك كانت الكفاءة القصوى 52.08% عندما كان وزن المثبط 2.0055جم وهو اقصى وزن استخدم للمثبط و اقل معدل تآكل كان 0.0046سم/ سنة. لذلك, تم إفتراض أن الايزوميبرازول المنتهي الصلاحية له تأثير جيد على تآكل الفولاذ الكربوني. بالإضافة الى ذلك, أعطت نتائج دليل لنجيلير للتشبع و مخطط الأس الهيدروجيني و الجهد اشارة الى ان عينة مياه التحلية كانت وسط تآكل.

1- Introduction

Corrosion is the destructive attack of a metal by chemical or electrochemical reaction with its environment[1]. Also corrosion can be classified in to different ways: wet or dry, direct combination or electrochemical, and by corrosive media: atmospheric (gas corrosion), liquid (aqueous or non aqueous) and soil (underground)[2]. Water is corrosive media to most metals, consequently, Iron and steel corrode in water to form various compound depending upon the temperature and other environmental conditions[3]. Moreover, water ionizes to produce a hydrogen ion and a hydroxyl ion[3]:

$H_2O \leftrightarrow H^+ + OH^-$ ………………........(1)

Theoretically iron should react with water in the absence of air to form ferrous hydroxide[3]:

$Fe + 2H^2O$ or $2(H^+ + OH^-) \rightarrow Fe(OH)_2 + H_2$ …………..(2)

Steel is an iron-based alloy include carbon of less than about 2%. Carbon steels (sometimes named as plain carbon steels, ordinary steels, or straight carbon steels) are defined as steels that contain other elements than carbon, except those (like as silicon and aluminum) that can be added for deoxidation and those (like as manganese and cerium) also can be added to counteract certain

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Article History : Received 23 August 2021 - Received in revised form 19 May 2022 - Accepted 23 May 2022

deleterious effects of remaining sulfur[4].

Carbon steel is one of the most widely used materials in the industry. This material is used not only in many of the water- and steam-pressure-containing systems in power plants but also in the supports for these systems. Consequently, too many researchers have been studied corrosion of carbon steels, *Adan et al* (2014):[5] proved that the corrosion rates are higher in solutions with oxygen content in all solutions and the weight loss value and hardness reduced is directly proportionate to corrosion rate. Also *Al-Moubaraki et al*, (2008): [6] found that mild steel corrodes in HCl solutions with a first order reaction and the corrosion rate increases with the increase in acid concentration. To minimize corrosion rate or to increase the metals protection from corrosion, there are many methods can be used, one of these methods is to use Inhibitors. So Inhibitor can be defined as a chemical substance that, can be added in a small concentration to an environment to decreases the corrosion rate, also Inhibitors predominantly work by adsorbing themselves on the metal surface, by forming a film to protect the metal surface[7]. In general, the efficiency of an inhibitor increases with an increase in inhibitor concentration. According to the effect of Inhibitors, *Abdulmajed Alagta et al* (2008):[8] concluded that Hydroxamic acids successfully deposited and form protective self-assembled layers on the surfaces of carbon steel. Moreover, the electrochemical measurements gave an indication that the adsorption of hyrdoxamic acid molecules on the surfaces of carbon steel decrease the corrosion process. In addition, *ERGUN et al* (2006):[9] studied one component inhibitor on corrosion of carbon steel, the results showed that the best inhibitor effects were found % 93 when the solution containing 10 ppm chromate, % 95 when 50 ppm nitrite added to the solution and % 90 when the solution mixed with 50 ppm molybdate.

Figure (1)[10] illustrates the potential pH diagram (Pourbaix diagram) for iron exposed to water. The various regions indicate the compounds which are stable under those conditions. For example, at potential between -0.6 up to 0.8 volt and at pH values less than about 9, ferrous ion(Fe^{+2}) is the stable substance. This shows that iron can be corroded under the above conditions, yielding Fe^{+2} as shown in equation (4)

$Fe \rightarrow Fe^{+2} + 2e$ ………………….(3)

In other positions of this diagram, it is obvious that the corrosion of iron produces ferric ions(Fe^{+3}), ferric hydroxide($Fe(OH)_3$), ferrous hydroxide($Fe(OH)_2$), and at very high alkaline conditions, shows a complex iron ions. The large region in figure (1) labeled **Fe** indicates that iron can not be corroded under the above conditions of potential and pH[10]

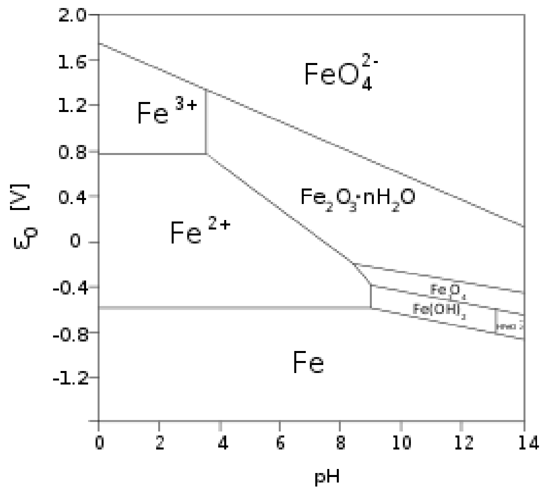

Figure 1: Simplified potential-pH diagram for the Fe-H_2O system (Pourbaix diagram)[10]

The tendencies of water to precipitate or dissolve calcium carbonate, can be predicted by using the Langelier Saturation Index (LSI) that was designed to measure calcite formation and used as a measure of corrosion. Also this index indicates the driving force for scale formation and growth in terms of pH as a master of variable. To calculate the LSI, it is important to know the actual pH, the temperature of water (º C), the alkalinity (mg/L, as $CaCO_3$, or calcite), the calcium hardness (mg/L Ca^{+2} as calcium carbonate), and the total dissolved solids (TDS) (mg/L TDS)[11].

Esomeprazole ($S_3O_3N_{19}H_{17}C$) (20mg) is sold under the trade name Nexium among others, and it is a medication which decreases stomach acid, also used to treat gastroesophageal reflux disease, peptic ulcer disease. The effectiveness of Nexium is the same as other proton pump inhibitors. It works by blocking H^+/K^+-ATPase in the partial cells of Stomach[12], so it is working as an inhibitor. For this reason the expired Esomeprazole was used in this study as inhibitor to study its effect on the carbon steel corrosion in desalination water (Drinking water) at room temperature.

2- Material and Method

2.1. Materials

The materials used in this study is carbon steel was purchased from the local market; this is according to the widely used in many constructions. The chemical composition of this material is due to the specifications of Musrata (Libya) steel factory is shown in Table 1. The specimens were cut from bar with cross-sectional area of 10mm×10mm and the length of each specimen is about 65mm as shown in Fig (2), and were cleaned well and polished by emery papers (400, and 1200).

Table 1: Chemical composition of carbon steel

Wt%C	Wt% Si	Wt%Mn	Wt%S	Wt%P	Wt% Fe
0.153	0.046	0.424	0.048	0.012	Balance

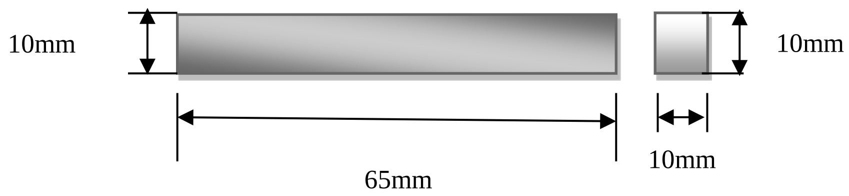

Figure 2: Dimensions of low carbon steel specimens.

2.2. Corrosion Tests

The test solution used in this study was Desalination water (Drinking water) samples, and a number of 600 ml beakers were used and filled by water, different weights from expired Esomeprazole inhibitor ($S_3O_3N_{19}H_{17}C$) were used and mixed with water in the beakers, and the specimens were completely immersed in the filled beakers. Each specimen was put in one beaker. The specimens were cleaned and weighed before and after the corrosion tests. Moreover, all the tests were carried out at room temperature and the period of all the corrosion tests was 37 days. Table 2 shows the chemical analysis of the used desalination water was done at the laboratories of the faculty of science, sebha university, Libya.

Table 2: Analysis of Desalination water

Parameter	Desalination water
Ph	8.77
Conductivity (μS/cm)	103.7
Salinity (ppt)	0.1
TDS (mg/L)	51
Total Alkalinity(mg/L)	25
Hardness Ca^{++} (mg/L)	22
Hardness Mg^{+2}(mg/L)	13
SO4 (mg/L)	0.5
K^+ (mg/L)	9.5
Na^+(mg/L)	25
Cl^- (mg/L)	3.9
Total Hardness (mg/L)	38

2.3. Langelier Saturation Index (LSI)

LSI is defined as the following equation[11]:

LSI = pH - pH_s ……………………..(4)

Where:

pH is the measured water pH.

pH_s is the pH at saturation in calcite or calcium carbonate and is defined as[11]:

pH_s = (9.3+A+B) – (C+D)…………..(5)

Where

$$A = [\log_{10}(TDS) - 1]/10$$
$$B = 13.12 \times Log_{10}(^oC + 273) + 34.55$$
$$C = Log_{10}[Ca^{++} as\ CaCO_3] - 0.4$$
$$D = Log_{10}[alkalinity\ as\ CaCO_3]$$

The LSI indicates three situations[11]:

The negative result of LSI indicates that no potential to form scale, the water will dissolve $CaCO_3$.

The positive result of LSI indicates that scale can form and $CaCO_3$ precipitation may occur.

LSI results is close to zero: Borderline scale potential.

The LSI index could be changed by the changes in temperature or water quality, or evaporation.

2.4. Corrosion rate calculations

Corrosion rate can be calculated by using the following relation[13]:

Corrosion rate $= (W \times 365)/(\rho \times A \times T)$ ………..(6)

Where:

W = weight loss (g)

365 = number of days per year (day/year)

A = the area of the specimen exposed to the solution (cm^2)

ρ = the metal (carbon steel) density ($7.8g/cm^3$)

T = exposure time of the specimens (37 days)

2.5. Efficiency calculations

The efficiency of an inhibitor can be expressed by a measure of this improvement[7]:

Inhibitor efficiency (%)

$= 100([CR_{uninhibited} - CR_{inhibited}]/CR_{uninhibited})$ ………(7)

Where :

$CR_{uninhibited}$ is corrosion rate of the uninhibited system

$CR_{inhibited}$ is corrosion rate of the inhibited system

3- Results and Discussion

It was seen that the color of the surfaces of all the specimens before the immersion in this study was as shown in Figure 3

Figure 3: photo of specimen before the immersion

According to the visual observations, it was observed that after two days from the immersion of all the specimens in presence and in absence of inhibitor , the color of the water was changed to red-brawn color, this color attributed to chemical reaction between Iron (Fe), Oxygen(O_2) and Water (H_2O) that produced Iron hydroxide ($Fe(OH)_3$. As the days progress until the end of the tests, only the color of the water in absence of inhibitor gradually changed and became more dark and in presence of inhibitor maintain its color, this indicates that the activity of the inhibitor played role in these processes. furthermore, the color of the specimens that immersed in the water in presence of inhibitor was changed to light brawn color and many spots appear on the surface, which attributed to pitting corrosion as shown in figure 4(a & b). While the color of the specimens surfaces that immersed in the water in absence of inhibitor was changed to light brawn color with large black areas and many spots appear on the surfaces of the specimens as shown in figure 5(a & b), these spots also were attributed to pitting corrosion and black areas were attributed to severe uniform corrosion, this means that the inhibitor has good effect on minimizing corrosion.

(a)

(b)

Figure 4: (a&b)photo of specimen immersed in water with inhibitor

(a)

(b)

Figure 5: (a & b) photo of specimen immersed in water without inhibitor

Table 3: The results of the corrosion tests for Carbon Steel specimens in Desalination water

No.	Weight before immersion (g)	Weight after immersion (g)	Weight loss (W) (g)	Area(Cm^2)	Corrosion rate cm/year	Weight of Inhibitor (g)	Efficiency of Inhibitor %
1	34.4200	34.2800	0.1400	19.9238	0.0088	0.2500	8.3
2	34.8095	34.6777	0.1318	20.1178	0.0082	0.500	14.6
3	34.8930	34.7650	0.1280	20.4232	0.0079	0.7509	17.7
4	34.9711	34.8462	0.1249	20.7368	0.0076	1.0077	20.8
5	34.7917	34.6894	0.1023	20.72	0.0062	1.2538	35.4
6	35.6666	35.5700	0.0966	21.24	0.0057	1.5000	40.6
7	34.7571	34.6682	0.0889	20.2664	0.0055	1.7541	42.7
8	34.6813	34.6062	0.0751	20.3448	0.0046	2.0055	52.8
9	35.2367	35.0789	0.1578	20.6192	0.0096	0	
10	34.3039	34.1618	0.1421	20.0704	0.0089	0	
11	33.9062	33.7603	0.1459	19.8744	0.0092	0	
12	34.3799	34.2279	0.1520	20.1488	0.0095	0	

Based on the results of the corrosion tests shown in Table 3, it can be seen that the weight loss and the corrosion rate of the specimens that were tested in water in presence of inhibitor are decreased gradually as increasing the weight of inhibitor from specimen No. 1 until specimen No. 8, while in the absence of inhibitor were found more than those tested in water in presence of inhibitor. Consequently, these results indicate that as increasing the weight of inhibitor the effect of the inhibitor increases. So that this inhibitor has a good inhibition effect on the corrosion process of carbon steel, this is due to the inhibition behaviour of Expired Esomeprazole ($S_3O_3N_{19}H_{17}C$) (20mg) that can be attributed to the presence of suitable Ione pair electrons electronegativity atoms, such as O, N, S for adsorption on carbon steel specimens surface to make protective film. In aqueous phase steel surface will attain the positively charged that can easily establish physically adsorbed film by electrostatic attraction with electronegativily functional groups through adsorption process. The same results obtained when Mingjun Cui and Xia Li [14] studied the corrosion inhibition performance of Nitrogen and Sulfur co-doped Carbon dots (N, S-CDs) for Q235 carbon steel in 1 M HCl solution and concluded that N, S-CDs could act as effective corrosion inhibitors to protect Q235 carbon steel from corrosion. Moreover, the inhibition efficiency increased with the increase in N, S-CD concentration.

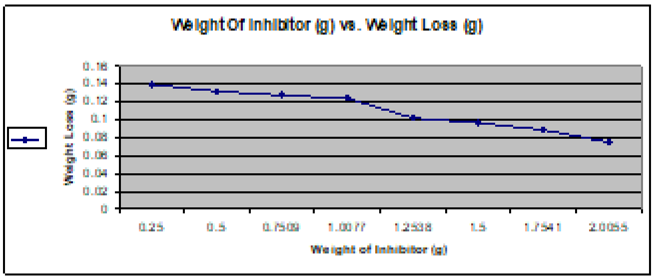

Figure 6: Plot of Weight of Inhibitor (g) versus Weight Loss (g)

Furthermore, the results shown n figure 6 for the plot of weight of Inhibitor versus weight loss, it is obvious that the curve show as increasing the weight of inhibitor, the weight loss decreasing.

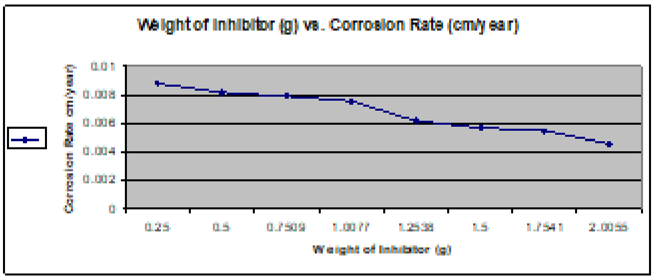

Figure 7: Plot of Weight of Inhibitor (g) versus Corrosion Rate (cm/year)

Moreover, the results shown in figure 7 for the plot of weight of Inhibitor versus corrosion rate, it is clear that the curve show as increasing the weight of inhibitor, the corrosion rate decreasing.

Referring to the results shown in Table 3, figure 6 and figure 7, the expired Esomeprazole has a good inhibition effect on the corrosion process of carbon steel.

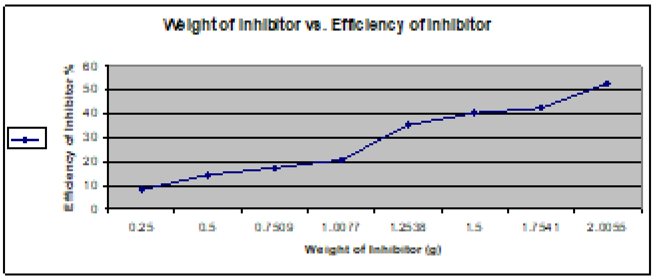

Figure 8: Plot of Weight of Inhibitor (g) versus Efficiency of Inhibitor%

According to the efficiency, it is apparent that the calculations show as the weight of inhibitor increase the efficiency increases as well as shown in figure 8. So, the maximum efficiency obtained is 52.08% this is when the weight of inhibitor is 2.0055g which is the maximum weight used in this study and corrosion rate is 0.0046 cm/year, this is for the specimen No. 8 and maximum corrosion rate of the specimen No 9 which is immersed in water in absence of inhibitor is 0.0096 cm/year as shown above. Based on the results explained above, the efficiency of the expired Esomeprazole inhibitor will be increased if the weight of this inhibitor increased more than what was used in this study.

Table 4: Result of The Langelier Saturation Index (LSI) of desalination water

Langelier Saturation Index (LSI) of desalination water	-0.349

According to the result obtained from the Langelier saturation index (LSI) shown in Table 4, it was found that the LSI of Desalination water samples are negative value this indicates that no chance to form scale, then water will dissolve $CaCO_3$. This result of LSI was calculated at room temperature (25°C). This result is compatible to the corrosion test results mentioned above in Table 3.

Referring to figure 1 that illustrates the potential pH diagram (Pourbaix diagram) for iron exposed to water and according to the standard Oxidation-Reduction (Redox) Potential at 25°C for iron which is -0.44 volts[10], and also regarding to the pH of the used Desalination water, it can be seen that at the potential of -0.44 volts and at the temperature of 25°C, the specimens of carbon steel will corrode in Desalination water (Drinking water) samples at pH of 8.77. Hence, depending on the results explained above, it is obvious that the Desalination water (Drinking water) is a corrosive media.

4. Conclusion

1. The colour of the water with and in absent of inhibitor was changed to red-brown colour
2. The colour of the water in absence of inhibitor gradually changed and became darker but in presence of inhibitor maintain its colour.

3. The colour of the specimens immersed in the water in presence of inhibitor was changed to light brown color, while the colour of the specimens surfaces immersed in the water in absence of inhibitor was changed to light brawn color with large black areas were attributed to severe uniform corrosion.
4. Pitting corrosion was seen on the most surfaces of the specimens.
5. The expired Esomeprazole as inhibitor has a good effect on the corrosion process of carbon steel.
6. The maximum efficiency obtained is 52.08%.
7. As increasing the weight of expired Esomeprazole, the weight loss and corrosion rate decreasing, whereas the efficiency increases.
8. The results of Langelier Saturation Index (LSI) and the potential pH diagram (Pourbaix diagram) gave an indication that Desalination water sample is a corrosive media.

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