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Impact of Water Hardness on Corrosion Rates of Carbon Steel

A Study on Lime Scale Formation

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Abstract

This project focuses on the experimental study to establish the relationship between the hardness of different types of water that forms lime scales on metal surfaces and the corrosion rates of carbon steel, expressed in penetration rates per unit time. 48 square metal samples were cut from carbon steel sheets with known metallurgical composition fabricated by Libyan Iron and Steel Company in Misurata and supplied by Brega Company. Four groups of aerated water were used to immerse all samples groundwater from North-Ajdabiya region and diluted seawater with distilled water in different ratios (50%, 25%, and 12.5%) respectively. Each group was separately warmed and controlled at 100 C°, after which the 12 samples were immersed in each of the four types of water described above for four periods. The chemical analysis of every kind of water was conducted in the laboratory at Hawari GMMR headquarters in Benghazi. In the top of the list was diluted seawater with (12.5%) distilled water which has a total hardness (17415.6 mg/l); followed by diluted seawater (25%) with a total hardness of (11009.9 mg/l); in third place was diluted seawater (50%) with total hardness (5404.8 mg/l); while groundwater had a lowest value of hardness (1601.4 mg/l). For more than 40 days, all samples were subjected to water aerated by a pumped stream of air. Corrosion rates (in mpy)

were determined as weight loss of metal as result of corrosion. Although the groundwater has a lower value of CaCO_3 , the result showed that samples immersed in heated groundwater and then exposed to the same type of water has the lowest corrosion rate. In contrast, the lowest rates of corrosion were in diluted seawater (12.5% and 25%) respectively due to the high concentration of CaCO_3 . Therefore, the highest rate of corrosion was noted in diluted seawater (50%) because of a decrease in CaCO_3 content.

Keywords: Corrosion rates, groundwater, diluted seawater, hardness of water.

تأثير عسرة المياه على معدلات تآكل الفولاذ الكربوني: دراسة حول تكوين

القشور الجيرية

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الملخص

تركز هذه الدراسة على البحث التجريبي لدراسة العلاقة بين عسر أنواع مختلفة من المياه التي تشكل ترسبات الجير على سطوح المعادن ومعدلات التآكل للفولاذ الكربوني، المعبر عنه بمعدلات الاختراق لكل وحدة زمن. تم قص 48 عينة معدنية مربعة من أوراق الفولاذ الكربوني بتركيبية معدنية معروفة، التي تم تصنيعها من قبل شركة الحديد والصلب الليبية في مصراثة والتي تم توريدها عن طريق شركة البريقة. تم استخدام أربع مجموعات من المياه المهواة لغمر جميع العينات على التوالي: مياه الجوف من منطقة شمال اجدابيا ومياه البحر المخففة بالماء المقطر بنسب مختلفة (50%، و25%، و12.5%) على التوالي. تم تسخين كل مجموعة على حدة والتحكم بها عند 100 درجة مئوية، بعد ذلك تم غمر العينات الـ 12 في كل نوع من أربعة أنواع من المياه المذكورة أعلاه لأربع فترات زمنية. تم إجراء تحليل كيميائي لكل نوع من أنواع المياه في المختبر في مقر هوارى جمر في بنغازي. كانت أعلى قيمة لصلابة المياه في المرتبة الأولى لمياه البحر المخففة بنسبة (12.5%) من الماء المقطر التي تبلغ صلابتها الإجمالية (17415.6 ملغ/ل)؛ تليها

مياه البحر المخففة بنسبة (25%) بصلاية إجمالية (11009.9 ملغ/ل)؛ و في المرتبة الثالثة كانت مياه البحر المخففة بنسبة (50%) بصلاية إجمالية (5404.8 ملغ/ل)؛ بينما كانت لمياه الجوف أقل قيمة للصلاية (1601.4 ملغ/ل). لأكثر من 40 يوماً، تمت تعريض جميع العينات لمياه مهواة بتيار هوائي مضخم. تم تحديد معدلات التآكل (بوحدة mpy) ك فقدان الوزن للمعدن نتيجة للتآكل. على الرغم من أن مياه الجوف لديها قيمة أقل لـ $CaCO_3$ ، إلا أن النتيجة أظهرت أن العينات التي غمرت في مياه الجوف المُسخنة ثم تعرضت لنفس نوع الماء كانت لديها أدنى معدل للتآكل. على النقيض، كانت أدنى معدلات التآكل في مياه البحر المخففة (12.5% و 25%) على التوالي بسبب التركيز العالي لـ $CaCO_3$. لذلك؛ لوحظ أن أعلى معدل للتآكل كان في مياه البحر المخففة بنسبة (50%) بسبب انخفاض محتوى $CaCO_3$.
الكلمات الرئيسية: معدلات التآكل، مياه الجوف، صلاية المياه، مياه البحر المخففة.

1. Introduction

Corrosion is a natural phenomenon resulting from a joint physico-chemical interaction between the metal and the surrounding environment (air, water, soil) which leads to changes and damage to the metal and it cannot be completely controlled but we can work to limit its spread. There is another definition of corrosion, which was defined by the scientist - Evans as a thermodynamic process generated by the activity of electrons and the ability of metals and non-metals to form electrochemical cells that lead and cause the transfer of electrons and ions between the anode and cathode through the metal and the outer environment, causing the destruction of the crystal structure of the alloy and its melting in its surroundings [1]. One of its basic concepts is that it is partial or complete damage that occurs to the metal or alloy in terms of appearance or performance due to the interaction that occurs between the metal or alloy with the surrounding atmosphere. Many chemical and physical factors affect corrosion rates such as salt concentration, dissolved gases, temperature, and others [2].

Corrosion is one of the important problems that occur in engineering and industrial facilities, especially to some parts of machines and equipment after their manufacture and when used as a result of exposure to corrosive media [3]. Corrosion is also one of the problems faced and suffered by many petroleum facilities, such as oil and gas lines and tanks, and the corrosion of pipes buried in the

soil, distillation towers, food cans, plates and steel sections. Corrosion also occurs in many other important sectors such as the sectors of industry, shipping, equipment and military facilities, which results in severe damage to the facilities and huge costs represented in the loss of production and replacement costs and the application of anti-corrosion methods. These costs include direct costs and indirect costs [4].

Carbon steel is one of the most important metals facing this problem, especially mild steel, as it is widely used in industrial and engineering applications, and mild steel is known to be highly corrosive in humid environment [5].

The research that was conducted to study the effect of river water salinity on the resistance to electrochemical corrosion of low carbon steels showed that river water samples were collected from four different regions. The results showed that, The highest rate of corrosion was in the environment that contains chlorides and high amounts of oxygen, while other regions showed similar corrosion rates [6].

The corrosion behavior of carbon steel in natural water media of different salinity are drinking water, sea water, and a mixture of drinking water and sea water. Where this study was under three temperatures (20 C°, 30 C° and 40 C°) in a period of (1- 4 hours). That all media corroded iron in varying degrees, and the rate of corrosion in sea water was the highest. The results also indicated that the rate of corrosion for all iron models increases at a temperature of 30 degrees Celsius. These rates were calculated using the weight loss method [7].

The medium carbon steel was immersion in the corrosion media used in another study which is rain water, drinking water and sea water. The exposure time to water media was determined (30, 60, 90, 120 days) it was observed that the corrosion rate in salt water is higher than it is in drinking water and rain water, and also the longer the exposure time to the corrosion media was. The rate of wear is lower and the weight loss continues to increase [8].

As for groundwater in the city of Ajdabiya, A hydro-chemical study was conducted for some groundwater wells in the city of Ajdabiya_Libya. Several tests and analyzes were conducted to reveal the nature of this water in terms of its chemical and biological composition, as well as to detect the percentage of pollution. Random sites were chosen to conduct the study, where samples were taken from 16 subterranean wells divided across the city, it was clear

from the results that the samples were completely free of color and odor, with the exception of one sample that had an odor, as well as some samples that had an unpalatable taste, most of the electrical conductivity samples were within the Libyan standard specifications. As for the dissolved solids, pH, total hardness of water, chloride, sulfate, sodium and potassium ions, they fell within the permissible limits according to the Libyan standard specifications, and The concentrations of heavy metals Pb, Zn, Cu, Ni Cr, Cd, and Hg were studied. It was also found that the concentrations of these metals were within the permissible limits according to the Libyan standard specifications, and the percentage of phosphates was completely non-existent. in some wells as a result of pollution with sewage water, Radioactive contamination was also measured, as the area was completely free of pollution. Through the obtained results, a rise in the ground water level was observed, and that the water from the studied wells was not suitable for drinking and can be used for irrigation. It was recommended to conduct periodic analyzes of the water in the study area [9].

In (2021), Corrosion behavior of mild steel in Distilled water diluted with seawater and Great Man Made River (GMMR) for Ajdabiya city [10]. Corrosion rates increased with the reduction of total water hardness for all three types of diluted seawater. However, the lowest corrosion rates were observed in samples submerged in GMMR water. The corrosion rate also decreased after immersion in heated diluted seawater for more than 30 minutes.

The aim of this study was to determine how adhered scales caused by natural hardness of groundwater and seawater mixed with distilled water will affect corrosion rate in relation to temperature and immersion time.

In general, this method, sometimes called (the gravimetric method), is widely used to determine corrosion rates, especially those that cause significant loss of weight. However, local corrosion rates are difficult to calculate using this method because they are difficult to sense with little or no loss of weight (Mohamed, no date); therefore, the following relationship is used to determine the rate.

$$MPY = \frac{K * W}{p * A * t} \quad (1)$$

Where:

MPY: The unit of corrosion rate (mils per year).

K: A constant value equal to 354 so that the result is (mpy).

W: The amount of weight loss measured in milligrams (mg).

p: Density, measured in (g/cm³).

A: The surface area exposed to the corrosion media is measured in (in²).

t: The test period measured in hours (hr).

1.2 Problem statement

1. Effect of water hardness on mild steel in aerated water.
2. Investigation corrosion rate in different types of water.

1.3 Objectives

1. The objective of this study was to investigate the effect of mill scales due to natural hardness of water on corrosion rate.
2. Examine the influence of temperature on corrosion rates.
3. The effect of immersion time on corrosion rates.

2. Experimental section

2.1 Materials and apparatuses

The experimental procedure used in this study was 48 squared cross-sectional areas of (ASTM A285 Grade C), plate samples (2.5 cm x 2.5 cm) with identical small thicknesses (Figure 1a). The chemical composition of the steel alloy can be found in a technical data sheet provided by “Sirte-Al-Buraiqah Company” Table (1). The sample identification code number was attached to each sample by drilling a small hole in one corner, as illustrated in (Figure 1). This study included the use of simple tools, such as a water heater, a mercury thermometer, four glass containers, a sensitive electric balance, an electric dryer, and emery papers (P400, P600, P800, and P1200), and oxygen pump.

Four different aerated water baths with various compositions and temperatures were used for the steel samples to investigate the effect of their hardness on low carbon steel corrosion rate, Ajdabiya groundwater and a mixture of seawater and distilled water were selected and analyzed.

Table 1. Chemical composition (Wt%) of low steel used.

Elements	C	Si	Mn	P	S	Al	Cr	Cu	N	Mo	Nb	Ti	V
Wt%	0.2	0.4	0.4 – 1.2	0	0	0	0	0.3	0	0.1	0	0	0

2.2 Tests and experimental procedures

1. According to NACE standard; the steel sheet was cut into (48) squared samples (2.5 cm* 2.5 cm* 2 mm). A small hole was

- drilled at one of the four corners of each coupon with diameter (3 mm) to facilitate the attachment of thin fishing line thread with holds at the end of it a small tag with a code number for the sample.
2. Each sample was individually cleaned using different numbers of emery papers (P400, P600, P800 and P1200), and then polished until a bright metal surface was obtained for all sides.
 3. Wash the samples with distilled water and then with dilute acetone solution, which was used as a solvent (to remove impurities). Then dry the samples using an electric dryer.
 4. The length, width and thickness of each sample were accurately measured to the nearest millimeter such that total surface area of all sides.
 5. The weight of each sample was determined to the nearest milligrams. An electric balance available at the Chemistry Laboratory at Ajdabiya University was used to weigh all samples.
 6. Two types of water were chosen in this study which is (Groundwater: Obtained from one of the wells in the North-Ajdabiya region and a mixture of sea water mixed with distilled water with a different concentration).
 7. Physical and chemical analyses were performed on a one-liter sample Selected water. In addition, microbial analysis was performed on polluted water (groundwater). This analysis was carried out and approved by a quality lab in the (GMRP) main head quarter in Hawari; Benghazi (Table 2)
 8. Four glass containers were filled with four types of water it was stirred and its temperature periodically by a flow of air that is pumped and bubbles in each container in an attempt to maintain a stable dissolved oxygen concentration at all times during the experiment.
 9. It was planned in advance to specify 12 pre-identified samples for each type of water, 3 for direct exposure to water, 3 for each period of three periods of immersion in preheated water (100 C°) before exposure to water.
 10. Each set of these samples was immersed in each type of water selected in this work heated and sustained at 100°C in the water bath using pre-identified specially prepared wooden hangers. Three samples were withdrawn from the bath at the end of each consecutive 15 minutes' period of continuous exposure last.

11. The previous step was repeated with the use of the remaining water.
12. After 40 days of immersion for each type of water, the samples were withdrawn from each container making sure that the date, hour and minute of the moment of samples withdrawal were recorded.
13. All samples were subjected to cleaning with use of rubber stoppers and soft emery paper avoiding the use of any metallic materials. The cleaning process of the corrosion product continued until the shiny metal surface appeared again.
14. After cleaning, each sample was weighed again. We calculated the weight difference between the initial and final measurements for each sample. This difference provided a clear representation of the total weight loss attributed to corrosion from exposure to the various water types used in this study.



Figure 1 . Pictures showing the samples used and the attached identification code number

Table 2. The chemical analysis of one liter samples of each water type.

Condition	T (°C)	PH	EC (µs/cm)	TDS (mg/l)	T.H (mg/l)	Ca.H (mg/l)	Mg.H (mg/l)
Guideline		6.5 - 9	1800	1200	500	150	350
Groundwater	16.1	8.13	5990	3900	1601.4	700.6	900.8
1/2 Distilled Water, 1/2 Sea Water	16.5	8.38	30600	24480	5404.8	600.5	4804.3
1/4 Distilled Water, 3/4 Sea Water	16.2	8.36	41800	33440	11010	2702	8307.5
1/8 Distilled Water, 7/8 Sea Water	15.8	8.38	47000	37600	17416	1201	16215

3. Results

Tables (3) to (6) summarize the experimental weight loss in milligrams of known metallurgical mild steel evaluated in this study as a result of corrosion in four different types of water selected in this study. The tables also include calculated corrosion rates represented as mils of penetration per year based on the average measured weight losses of all 48 samples.

Table 3. Summary of experimental measurements of all samples in water of groundwater

NO	I.T	W1	W2	ΔW	T	A	D	Mpy	mpy average
A11	0	15790	15600	190	962	5.7	7.85	2.357	2.662
A12	0	15743	15300	443	962	5.7	7.85	5.495	
A13	0	15511	15500	11	962	5.7	7.85	0.136	
A21	15	15773	15600	173	962	5.7	7.85	1.831	1.831
A22	15	15648	15500	148	962	5.7	7.85	2.146	
A23	15	15522	15400	122	962	5.7	7.85	1.836	
A31	30	15636	15500	136	962	5.7	7.85	1.926	1.926
A32	30	15764	15600	164	962	5.7	7.85	1.687	
A33	30	15766	15600	166	962	5.7	7.85	2.034	
A41	45	15829	15700	129	962	5.7	7.85	2.183	2.183
A42	45	15793	15600	218	962	5.7	7.85	1.600	
A43	45	15781	15600	181	962	5.7	7.85	2.704	

Symbols explanation:

- **NO:** Sample ID Number - A unique identifier for each sample.

- **I.T:** Immersion Time (min) - The duration for which the sample was immersed in the testing environment.
- **W1:** Initial Weight (mg) - The weight of the sample before immersion.
- **W2:** Final Weight (mg) - The weight of the sample after immersion.
- **ΔW :** Weight Loss (mg) - The difference between the initial and final weight, indicating material loss due to corrosion.
- **T:** Exposure Time (hr) - The total time the sample was exposed to the corrosive environment.
- **A:** Sample Total Area (inch²) - The surface area of the sample exposed to the environment.
- **D:** Density (g/cc) - The density of the material of the sample.
- **Mpy:** Corrosion Rate (mpy) - The rate of corrosion measured in mils per year.
- **mpy average:** Average Corrosion Rate (mpy) - The average corrosion rate for a set of samples under the same conditions.

Table 4. Summary of experimental measurements of all samples in (50% distilled water, 50% seawater)

NO	I.T	W1	W2	ΔW	T	A	D	Mpy	mpy average
B11	0	15565	15400	165	962	5.7	7.85	2.046	2.836
B12	0	15756	15500	256	962	5.7	7.85	3.175	
B13	0	15565	15300	265	962	5.7	7.85	3.287	
B21	15	15837	15700	137	962	5.7	7.85	1.699	2.455
B22	15	15786	15600	186	962	5.7	7.85	2.307	
B23	15	15771	15500	271	962	5.7	7.85	3.361	
B31	30	15750	15600	150	962	5.7	7.85	1.860	4.585
B32	30	15744	15500	244	962	5.7	7.85	3.026	
B33	30	15815	15100	715	962	5.7	7.85	8.870	
B41	45	15604	15400	204	962	5.7	7.85	2.530	2.761
B42	45	15821	15600	221	962	5.7	7.85	2.741	
B43	45	15743	15500	243	962	5.7	7.85	3.014	

Table 5: summary of experimental measurements of all samples in (25% distilled water, 75% seawater)

NO	I.T	W1	W2	ΔW	T	A	D	Mpy	mpy average
C11	0	15699	15500	199	962	5.7	7.85	2.468	2.501
C12	0	15533	15300	233	962	5.7	7.85	2.890	
C13	0	15373	15200	173	962	5.7	7.85	2.146	
C21	15	15472	15300	172	962	5.7	7.85	2.133	2.493
C22	15	15922	15700	222	962	5.7	7.85	2.754	
C23	15	16509	16300	209	962	5.7	7.85	2.592	
C31	30	15633	15500	133	962	5.7	7.85	1.649	2.212
C32	30	15620	15400	220	962	5.7	7.85	2.729	
C33	30	15982	15800	182	962	5.7	7.85	2.257	
C41	45	15698	15500	198	962	5.7	7.85	2.456	2.389
C42	45	16018	15800	218	962	5.7	7.85	2.704	
C43	45	15762	15600	162	962	5.7	7.85	2.009	

Table 6: summary of experimental measurements of all samples in (12.5% distilled water, 87.5% seawater)

NO	I.T	W1	W2	ΔW	T	A	D	Mpy	mpy average
D11	0	15612	15400	212	962	5.7	7.85	2.630	2.109
D12	0	15662	15500	162	962	5.7	7.85	2.009	
D13	0	15736	15600	136	962	5.7	7.85	1.687	
D21	15	15764	15600	164	962	5.7	7.85	2.034	2.079
D22	15	15700	15500	200	962	5.7	7.85	2.481	
D23	15	15739	15600	139	962	5.7	7.85	1.724	
D31	30	15669	15500	169	962	5.7	7.85	2.096	2.005
D32	30	15595	15400	195	962	5.7	7.85	2.419	
D33	30	15521	15400	121	962	5.7	7.85	1.501	
D41	45	15581	15400	181	962	5.7	7.85	2.245	2.398
D42	45	15559	15500	59	962	5.7	7.85	0.731	
D43	45	15740	15400	340	962	5.7	7.85	4.217	

Figure (2) shows how the corrosion rate values were graphically represented as a function of immersion time for each set of samples heated at certain intervals at 100°C for the four water types

identified in this study, namely, groundwater and mixed seawater with different proportions distilled water.

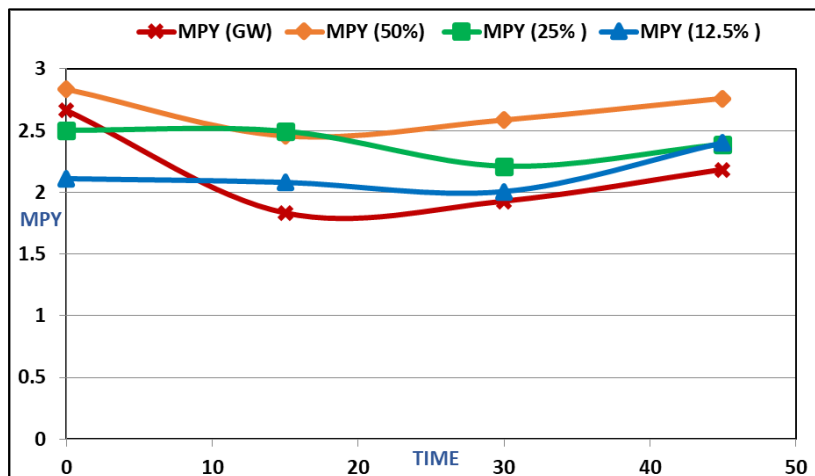


Figure (2) Corrosion Rate vs. Immersion Time for Different Water Types.

4. Discussion

1. General Trends in Corrosion Rates: Groundwater and 50% diluted seawater initially exhibited the highest corrosion rates due to the direct exposure to oxygen and high temperatures. However, these rates significantly declined after 15 minutes of immersion as lime scales formed on the metal surface. Following this reduction, the corrosion rates showed an upward trend, indicating a breakdown of passive films.
2. Role of Lime Scale Formation: The samples immersed in 50% diluted seawater and groundwater developed coherent lime scales that acted as a barrier, reducing oxygen penetration. This protective effect resulted in a substantial decrease in corrosion rates during the initial immersion period.
3. Microbial Contribution in Groundwater: The high initial corrosion rates in groundwater samples at zero time are attributed to the presence of microorganisms. These microorganisms likely enhanced initial surface activity. Over time, the increase in water temperature caused microbial activity to decrease, reducing the corrosion rate significantly.
4. Behavior in High-Hardness Water (25% and 12.5% Diluted Seawater): The samples immersed in 25% and 12.5% diluted seawater (with CaCO_3 concentrations of 11,009.9 mg/l and

17,415.6 mg/l, respectively) exhibited relatively constant corrosion rates during the first 15 minutes. This stability can be attributed to the consistent concentration of dissolved minerals that slowed the rate of lime scale formation.

5. Effect of Hardness and Immersion Time: The gradual decrease in CaCO₃ concentration in the diluted seawater types (25% and 12.5%) resulted in slower lime scale deposition. However, as immersion time increased, the corrosion rates stabilized due to the formation of a less coherent protective scale.
6. Reversal of Trends After 30 Minutes: A significant reversal in corrosion rate trends was observed at 30 minutes of immersion for all water types. This phenomenon is likely due to the breakdown of passive films on the metal surfaces, which exposed the underlying metal to the corrosive media, leading to resurgence in corrosion activity.

5. CONCLUSION

Water hardness has a positive effect on immersion samples in regard to corrosion rates, especially diluted seawater (50%) and groundwater which consists of limestone and the micro-organisms. When the water is heated these elements will build up and make a coherent scale on the metal surface to reduce the corrosion rate. Regards to the other two types of diluted seawater (25% - 12.5%) have similar behavior in depositing lime scale but to a lesser degree. The stability of the formed scale is affected negatively if heat transfer is involved also, extended time periods of immersion (over 30 minutes) thus, the rate of corrosion increases with the percentage of dissolved oxygen added from distilled water. Steel corrosion resistance improved as the exposure time in hot water due to a decrease in dissolved oxygen content. Therefore; a pump air was used to create bubbling air to keep constant oxygen concentration close to sample surfaces.

REFERENCES

- [1] Al-qahtany, (1995). Corrosion as a Thermodynamic Process: Interaction between Metal and Environment.
- [2] Materials Science (2009). Introduction to Corrosion and Its Effects. P. 112.
- [3] Ferry, et al. (2013). Corrosion in Engineering and Industrial Facilities.

- [4] Chemistry, (no date). The Economic Impact of Corrosion in Industry.
- [5] Sabih, (1995). Corrosion of Mild Steel in Humid Environments.
- [6] Ibrahim, et al. (2013). Effect of River Water Salinity on Corrosion Resistance of Low Carbon Steels.
- [7] El-Sherif, et al. (2016). Corrosion Behavior of Carbon Steel in Natural Water Media.
- [8] Yahya, et al. (2019). Effect of Salt Water on Corrosion of Carbon Steel.
- [9] Emhanna, et al. (2016). Hydro-Chemical Study of Groundwater in Ajdabiya, Libya.
- [10] Hwwili, et al. (2021). Corrosion Behavior of Mild Steel in Distilled Water and Mixed Water from Seawater and Great Man-Made River in Ajdabiya, Libya.