



Corrosion Inhibition of Aluminum Alloy (R408, R613) in Sodium Hydroxide Alkali Medium by Expired Drug of Ketoprofen

Ahmed N. Abd and Noor I. Khaleel

Department of Chemistry – College of Science – University of Diyala

noorismaeel91noor@gmail.com

Received: 5 June 2022

Accepted: 4 October 2022

DOI: <https://doi.org/10.24237/ASJ.01.04.658B>

Abstract

The deterrent effect of medication molecules that have expired, ketoprofen, on aluminum alloy (R408, R613) corrosion in 0.2 M NaOH solution was investigated using the weight loss approach at (20, 30, 40, and 50 °C). When the inhibitor concentration is increased (25,75,125,175,225,275 ppm), the efficiency of inhibition improves. Adsorption is governed by the Langmuir isotherm model. As a result, the effectiveness of inhibition is dependent. Whether the inhibitor is present or not, the strongest inhibitor had an inhibition efficiency of 84 percent. maximum temperature and concentration.

Keywords: Aluminum, Alkali solution, Corrosion, Expired Drug, Ketoprofen, Inhibitor.

تنشيط تآكل سبائك (R408 ، R613) في وسط هيدروكسيد الصوديوم الاساسي بواسطة عقار الكيتوبروفين المنتهي الصلاحية
الألومنيوم

احمد نجم عبد ونور اسماعيل خليل

جامعة ديالى – كلية العلوم – قسم علوم الكيمياء



الخلاصة

تم فحص التأثير الرادع لجزيئات الدواء التي انتهت صلاحيتها ، كيتوبروفين ، على تآكل سبائك الألومنيوم (R408) ، (R613) تم فحص التأثير الرادع لجزيئات الدواء التي انتهت صلاحيتها ، كيتوبروفين ، على تآكل سبائك الألومنيوم في محلول هيدروكسيد الصوديوم 0.2 مولار باستخدام نهج فقدان الوزن (20 ، 30 ، 40 ، 50 درجة مئوية). عندما يزداد تركيز المانع ، تحسّن كفاءة التثبيط . يخضع الامتزاز لنموذج متساوي الحرارة لاكمير. سواء كان المانع موجودًا أم لا ، فإن أقوى مثبت له كفاءة تثبيط تبلغ 84 بالمائة. درجة الحرارة القصوى والتركيز.

الكلمات المفتاحية: الألومنيوم، النوبان الأساسي، التآكل، عقار منتهي الصلاحية، كيتوبروفين، مثبت.

Introduction

A material dissolves and is consumed as a result of corrosion, which is an irreversible interfacial a material's and its environment's reaction. The substance in question frequently suffers detrimental effects from corrosion [1]. Good indicators of where the reaction usually starts on a metal surface include the metal's weight or changes in its chemical or physical properties over time [2]. When metals and their transient unstable forms, like ores or natural minerals, exhibit a strong urge to transfer to a more thermodynamically stable state, corrosion as a natural process will take place. Metals can take on a variety of forms due to their environment, including oxides, hydroxides, and other forms [3]. A high strength-to-density ratio makes aluminum and its alloys one of the most economical and long-lasting metals in the market today. Only a few examples are hang glider frames, inline skating frames, inline skate frames, two-wheelers, hiking equipment, and transportation [4]. The nonferrous metal utilized the most is aluminum. It is crucial that this metal resists corrosion. An effective way to avoid corrosion is by using corrosion inhibitors [5]. A chemical is an inhibitor compound or combination of chemicals that successfully inhibits or decreases corrosion in environments that are corrosive without significantly altering the reactivity of the environment's constituents. Human health and safety concerns are now the primary focus of corrosion inhibition research. The focus of the research has been on compounds that are safe for the environment, such as plant extracts. Numerous chemical substances are employed for this [6].



Alkaloids, tannins, pigments, and amino acids are a few examples of natural substitutes of non poisonous and non detrimental substances. Due to their biodegradability, environmental friendliness, low cost, and widespread availability, Instead of some common plants and plant products have been explored as corrosion inhibitors for different metals and alloys in a range of conditions. [7]. It was a surprising that expired medications discovered to be appropriate and economical rather than leftover medicinal components or corrosion inhibitors [8]. This distinctive property encourages worldwide research into the potential of medicines as corrosion inhibitors. Environmental criteria are better met by drugs that are non-toxic and ecologically friendly rather than risky inhibitors. As a result, both new and old drugs have been used in research trials as corrosion inhibitors [9].

Some of the most essential qualities that inhibitors must have been listed below: It must provide efficient corrosion protection even at low inhibitor concentrations.

On all exposed components, corrosion prevention is a must.

- It must be capable to function well in difficult conditions (higher temperatures and velocity).
- The corrosion rate shouldn't substantially increase if the inhibitor dosage is too low or too high; instead, it should suppress both uniform and localized corrosion. It must continue to work well over time.

Experimental part

Extraction of Expired Drugs

Expired medicines with a higher water solubility were used to create today's corrosion inhibitors. Figure 1 depicts the molecular structure of ketoprofen. In addition, Table (1) shows the chemical characteristics of ketoprofen. The active substance of the green inhibitors, which include ketoprofen, was extracted from an expired medicine. The medication is crushed with a pestle, combined with distilled water, allowed to stand for 24 hours, then filtered for 1-2 hours before being dried for 4 hours each day in an oven set to 80 degrees Celsius [10].



Inspections and tests were conducted to recover materials from expired medications. High performance liquid chromatography (HPLC) was used to quantify the amount of active ingredient in the extract, and fourier transform infrared spectroscopy (FTIR) was used to confirm the presence of useful aggregates in the extract.

Sample Preparation

Aluminum Alloy (R408, R613) was used to study the corrosion test (weight loss).

First, specimens were created. Getting a uniform surface after cutting the specimen is crucial for determining corrosion resistance. Square specimens (3 cm, 3 cm, and 1 mm) were cut using an electrical saw before being molded into a final specimen with a hole drilled on one side, enabling straightforward suspension in the corroding solution. To create a smooth and scratch-free surface, the specimens were then grounded and polished using different papers in a series of (220, 400, 600, 800, 1000, 1500, and 2000). The items were polished, utilizing Silver suspension The samples were then rinsed with distilled water. The polished samples were shrunk with acetone before being dried and stored in a plastic container. A four-digit electronic scale was used to weigh the samples, and an electronic vernier was utilized to determine their size [11].

Table 1: Chemical properties of ketoprofen

Color	White yellow
Formula Molecular	$C_{16}H_{14}O_3$
Weight in Molecules	254.281 g/mol
Company	Sanofi
Country of origin	France



Figure 1: Appearance and chemical structure of ketoprofen

Creating a Corrosion Medium

In this investigation, corrosion media, comprising a 0.2M NaOH solution, were employed. 500 mL flasks with different drug concentrations were filled with this medium, which was produced with distilled water.

Fourier Transform Infrared Spectrum (FTIR)

The FTIR technique is used to identify the active groups in medicines following extraction by combining a sample of the extract with KBr and capturing the spectra. Perkin Elmer's spectrum as depicted (65).

Atomic Force Microscopy (AFM)

AFM was used to gauge the surface's roughness, and the topography of the surface was displayed.

Scanning Electron Microscope (SEM)

After the requisite study, SEM was used to examine the surface morphology of Aluminum Alloy (R408 , R613)



Result and Discussion

Weight Loss Measurement

Aluminum Alloy (R408 , R613) specimens were utilized to determine how much weight had been removed. After being cleaned and dried, 200 mL of 0.2M NaOH were used to completely submerge the specimens.

For three hours, a solution with and without an inhibitor (ketoprofen) was evaluated. The materials were cleaned, Dried with electric dryer then weighed using an analytical balance .

Weight loss was assessed using varied inhibitor concentrations (25, 75, 125, 175, 225, 275) and temperatures (20, 30, 40, and 50 ⁰c) in trials (k).

The following expression was used to compute the corrosion rate (CR corr). [12]

In this formula, (CR) stands for corrosion rate, (W) for weight loss (measured in grams), (A) for sample area (measured in t), and (m2) for the number of days the object will be submerged. Every day, the rate of corrosion is reported in grams per square meter (gmd). The equation below can be used to calculate the efficiency ratio given the corrosion rate: [13]. Under various implemented conditions, such as temperature and concentration, we looked into damping's speed and power. Table 2 presents the results. In Table 2, the findings from an investigation into the rate and potency of damping under varied implementation conditions, temperature, and concentration are summarized. Where the corrosion rates in the absence and presence of various inhibitory concentrations, respectively, are (CR uninhibit) and (CR inhibit). It explains why corrosion speeds up as the temperature rises and slows down when the inhibitor concentration rises. Inhibition efficiency increases along with the temperature and inhibitor concentration.

The Impact of Inhibitory Concentration on Aluminum Alloy Corrosion (R408 , R613)

The addition of ketoprofen medication extracts significantly reduces the corrosion rate, as shown in Table 2, and the corrosion rate of Aluminum Alloy (R408 , R613) generally increases with temperature. The higher the concentration, the lower the rate of ketoprofen corrosion

(0.2M NaOH). As a result, ketoprofen delayed aluminum corrosion in (0.2M NaOH), indicating that it could be used in the future. Figures 2 and 3 as a corrosion inhibitor for that metal [14].

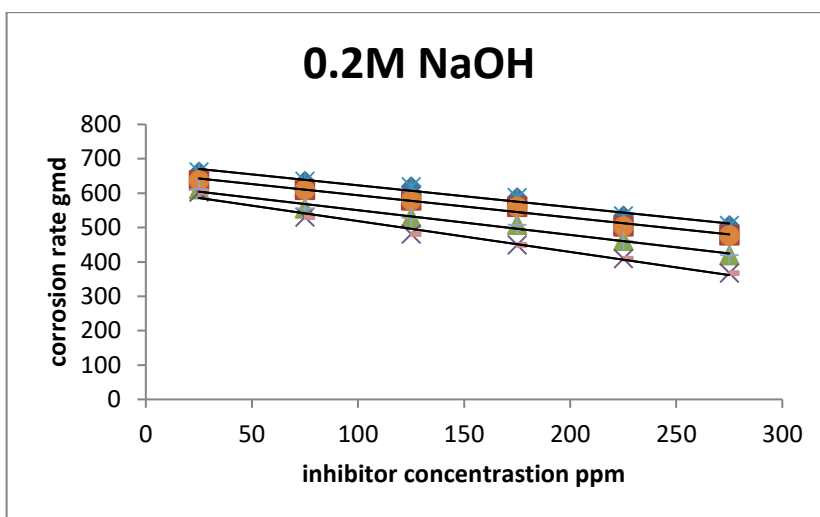


Figure 2: Inhibitor concentration effects (ketoprofen extract) on the corrosion rate of aluminum alloy (R408, R613) 0.2 NaOH.

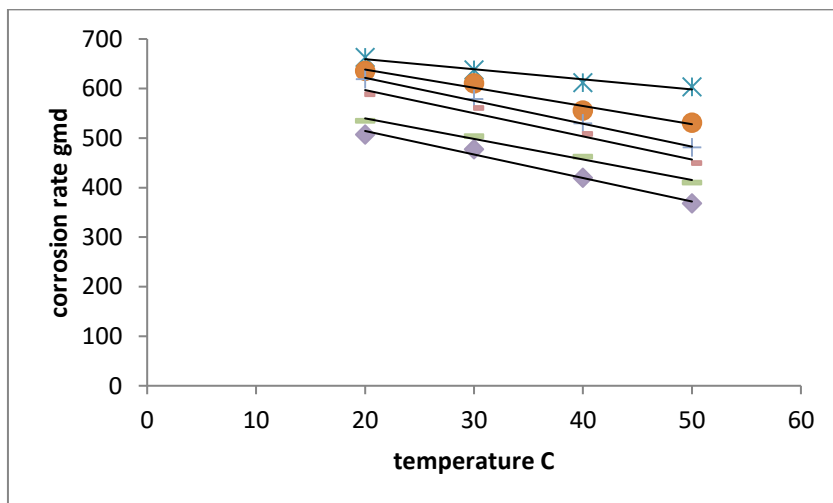


Figure 3: Effect of temperature on the rate corrosion of aluminum alloy(R408 , R613) in (0.2M NaOH) at various inhibitor concentration(ketoprofen extract).



Table 2: The effect of temperature on the corrosion rate, inhibition efficiency and surface coverage of aluminum alloy (R408 , R613)in (0.2M NaOH) in absence and presence of Ketoprofen extract.

Run	C _{inh} (ppm)	Time (3h)					
		T (°C)	A . T	Δ W . T	CR (gmd)	Θ (surface coverage)	IE%
1	Blank	20	0.8181	87.5400	2242.90	0	0
2		30	0.8075	85.7556	2259.91	0	0
3		40	0.8118	85.1766	2287.38	0	0
4		50	0.8119	84.3552	2309.94	0	0
5	25	20	0.2463	89.2422	662.37	0.7	70
6		30	0.2282	85.9110	637.49	0.717	71.7
7		40	0.2192	86.0322	611.49	0.732	73.2
8		50	0.2119	84.2940	603.31	0.738	73.8
9	75	20	0.2341	88.4202	635.42	0.716	71.6
10		30	0.2166	85.2096	610.07	0.73	73
11		40	0.1967	84.9792	555.52	0.757	75.7
12		50	0.1818	82.1928	530.84	0.77	77
13	125	20	0.2161	83.802	618.88	0.724	72.4
14		30	0.1979	82.0488	578.87	0.743	74.3
15		40	0.1794	81.369	529.14	0.768	76.8
16		50	0.1629	81.265	481.09	0.79	79
17	175	20	0.2120	86.5218	588.05	0.73	73
18		30	0.1958	83.8218	560.61	0.75	75
19		40	0.1760	83.1300	508.11	0.777	77.7
20		50	0.1505	80.3382	449.59	0.805	80.5
21	225	20	0.1828	82.0794	534.50	0.76	76
22		30	0.1666	79.4322	503.37	0.777	77.7
23		40	0.1525	79.2090	462.06	0.797	79.7
24		50	0.1315	76.998	409.88	0.822	82.2
25	275	20	0.1805	85.4610	506.89	0.773	77.3
26		30	0.1627	83.8218	465.84	0.793	79.3
27		40	0.1448	82.7802	420.06	0.816	81.6
28		50	0.1171	76.429	367.92	0.84	84

Inhibitor Performance and Adsorption Studies

The corrosion rate can be significantly reduced by increasing the inhibitor concentration from 25 to 275 ppm. The corrosion rate decreases to its lowest level with a low inhibitor concentration (275 ppm). This could be as a result of the inhibitor concentration being so high (275 ppm), as it covers the metal surface at all three temperatures (20, 30, and 40 °C). The surface coverage information is highly important for studying adsorption characteristics. The surface coverage of an inhibitor at a given concentration is calculated using equation (1). The information on corrosion rate can be used to investigate the adsorption mechanism.



$$\theta = \frac{IE}{100} \dots\dots\dots (1)$$

Where Θ surface coverage

IE inhibition efficiency

Langmuir Adsorption Isotherm

It is calculated using the formula (2). Inhibitors of the ketoprofen extract in 0.2M NaOH are shown in Figure 6 as graphs of (C_i/Θ) vs (C_i) at (293, 303, 313, and 323) k, Because the data fits on straight lines, inhibitors are adsorbed in accordance with the Langmuir adsorption isotherm. It could also explain the increase in inhibitor efficacy caused by an increase in the number of solvent molecules that are adsorbed on the aluminium surface, protecting active sites from acid attacks and preventing corrosion at the same time. [15]

$$\frac{C_i}{\theta} = \frac{1}{K_L} + C_i \dots\dots\dots (2)$$

The degree of surface covering (Θ), the concentration inhibitor (C), the adsorptive static equilibrium (K_{ads}), and the molecular interaction parameters are all included.

Table 3: Show the (K_{ads}), (ΔG°_{ads}), and (R^2) for Langmuir type adsorption isotherm of (ketoprofen extract) for aluminum alloy (R408, R613) corrosion in 0.2 M NaOH at different temperatures.

Temperature(K)	K_L (L/mg)	ΔG° (KJ/mol)	R^2
293	0.115	- 4.5152	0.9984
303	0.118	- 4.7342	0.9991
313	0.124	- 5.0195	0.9988
323	0.127	- 5.2441	0.9989

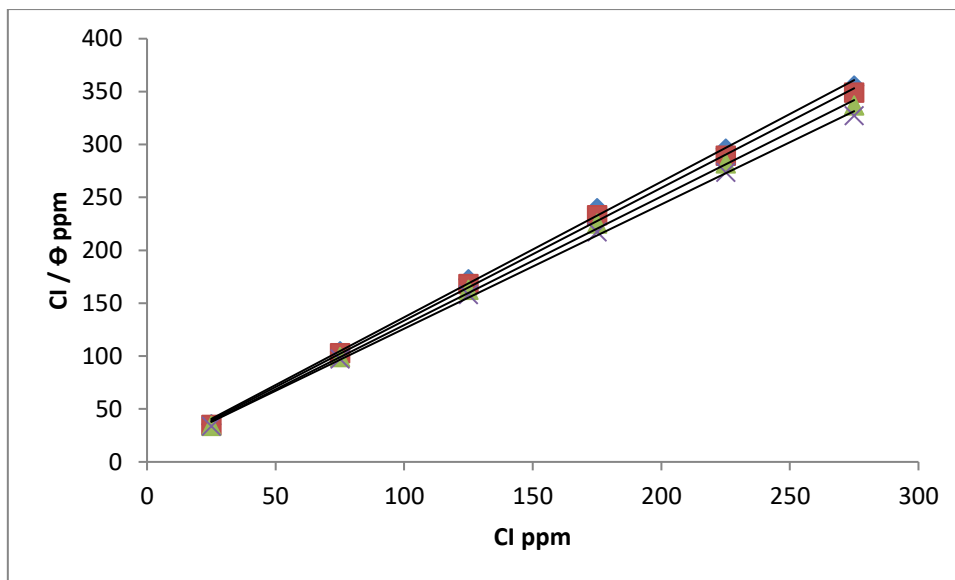


Figure 4: Langmuir adsorption isotherm of (ketoprofen extract) for aluminum alloy (R408, R613) corrosion in (0.2M NaOH).

Freundlich Adsorption Isotherm

It is calculated using an equation (3). The values of (n and (KF)) are obtained by plotting ($\ln\theta$) versus ($\ln C_i$) with slope and intercept, respectively. Given the poor correlation coefficient readings, Freundlich does not appear to be a good fit for the system. The Langmuir isotherm, however, is applicable since the correlation coefficient values are high and the adsorption isotherm system provides a superior fit [16].

$$\ln\theta = \ln Kf + n \ln C_i \dots\dots\dots (3)$$

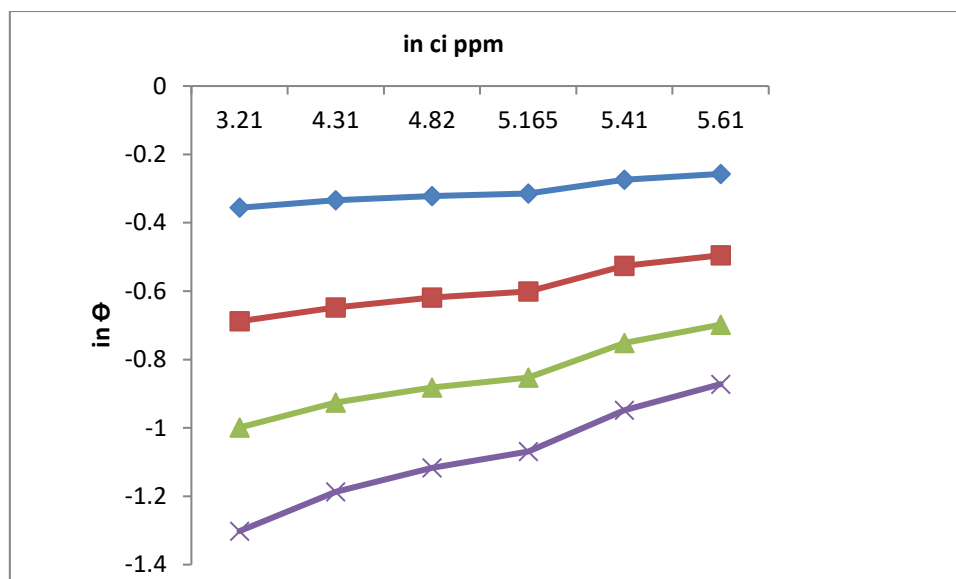


Figure 5: Isotherm Freundlich adsorption of (ketoprofen extract) for aluminum alloy (R408, R613) corrosion in (0.2M NaOH).

Table 4: Show the (K_F), slope (n), and (R^2) for Freundlich type adsorption isotherm of (ketoprofen extract) for aluminum alloy (R408, R613) corrosion in (0.2M NaOH).

Temperature(K)	K_F (L/mg)	n	R^2
293	1.6313	0.0378	0.8064
303	1.5896	0.0372	0.8365
313	1.5695	0.0411	0.9078
323	1.6099	0.0516	0.9659

Timken Adsorption Isotherm

The calculated equation (4) was used to provide an explanation for the extracts' adsorption on the aluminum metal surface. Figure (6) plots the surface coverage (Θ) versus ($\ln C_i$), with the slope and intercept resulting in the values (a) and (KT), respectively. It is clear that the Timken isotherm not possible to be applied because the correlation coefficient values are low.

The Langmuir adsorption isotherm is the best in this arrangement due to the strong correlation coefficient values (17).



$$\theta = \frac{1}{-2a} \ln KT - \frac{1}{2a} \ln Ci \dots\dots\dots (4)$$

Surface coverage (Θ) vs. ($\ln Ci$) can be used to depict the (L/gm) equation (6), whereas slope and intercept result in values of a and KT, respectively. [17]

The tables 3, 4, and 5 display the kinematic information. They demonstrate the corrosion-inhibiting substances operate near the metal's surface show that the inhibition as being closer would resemble the Langmuir adsorption isotherm description than the Freundlich or even the Timken adsorption isotherm.

The monolayer generation in accordance with adsorption utilizing the Langmuir isotherm produced the highest correlation coefficient (R2) in this case. The type of adsorption is physical because Gads have negative values and are less than 20 kJ.mol-1.

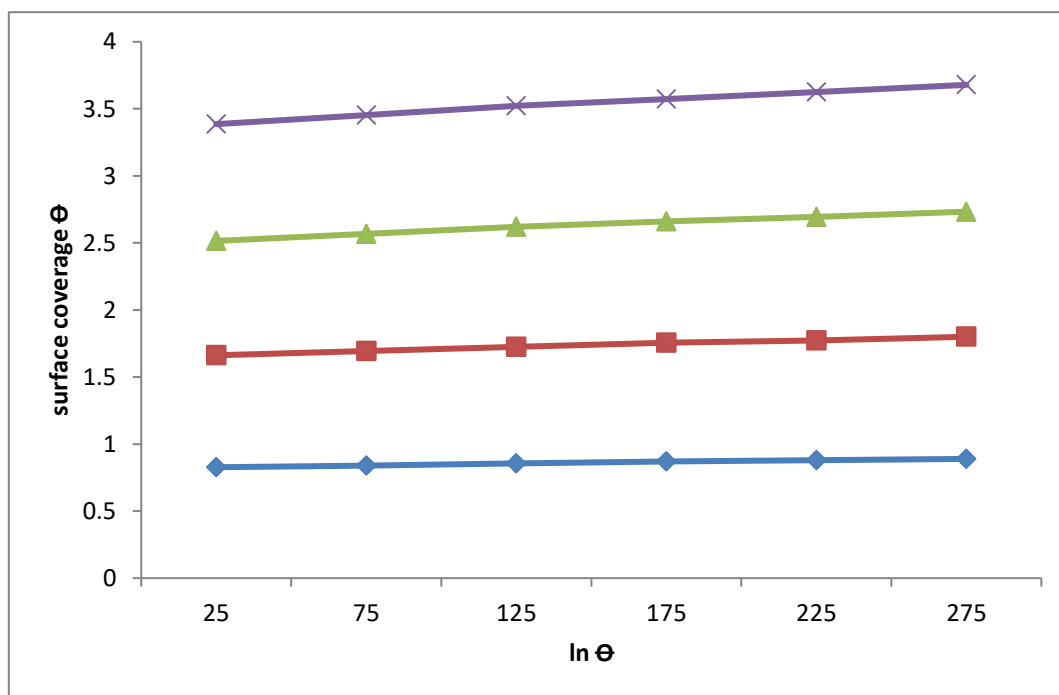


Figure 6: Timken adsorption isotherm of (ketoprofen extract) for aluminum alloy (R408, R613) corrosion in (0.2M NaOH).

Table 5: Show the (K_T), slope (a), and (R^2) for Timken type adsorption isotherm of (ketoprofen extract) for aluminum alloy (R408, R613) corrosion in (0.2M NaOH).

Temperature K	A	K_T	R^2
293	0.0003	1.9951	0.953
303	0.0003	2.0293	0.9751
313	0.0003	2.0696	0.9809
323	0.0004	2.0871	0.9817

FTIR Studies

Figure 7 shows that the peak at 3413.9 cm⁻¹ was attributed to (O-H) stretching, whereas the peaks at 3057.4 cm⁻¹ and 2930.7 cm⁻¹ were attributed to (C-H)AR stretching and (C-H)Alph. stretching, respectively. For (C=C), the stretching maxima were found at 1653.5 1 and 1653.5 cm⁻¹, respectively. The stretching peaks for (C=O) were found at 1079.2 cm⁻¹, and (C-O) was given credit for the peak at 2930.7 cm⁻¹.

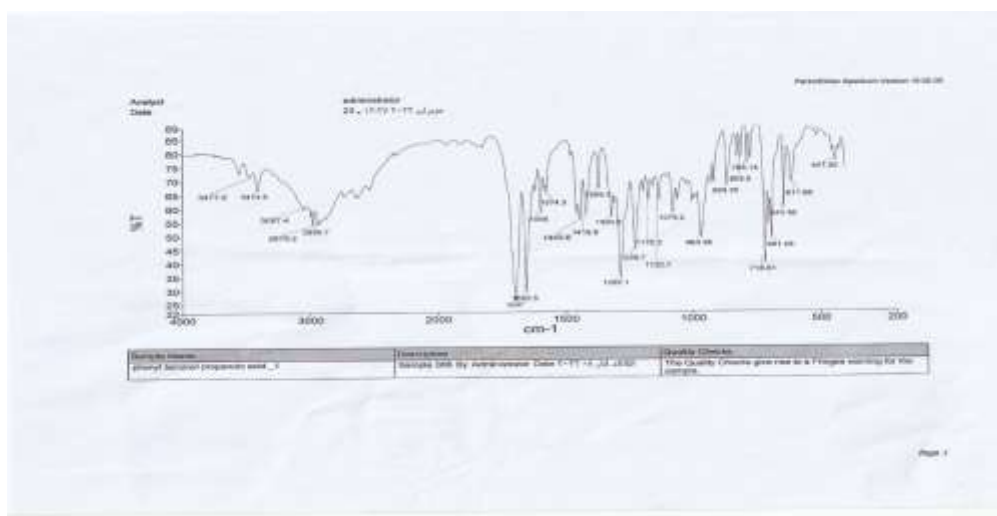


Figure 7: FTIR spectra of ketoprofen extract

Atomic Force Microscope Studies

Using AFM technology, the surface morphology of aluminum alloy (R408, R613) was analyzed in the absence and presence of ketoprofen extract. When the extract was stronger, inhibition was also stronger [18]. The measurements of rate roughness Ra produced by microscopic

research of the atomic force (AFM) include the root-mean-squared roughness (R_q), mean height measured, and length of valuation measured from the average line for distractions taken into account (Figures 8–10) [19].

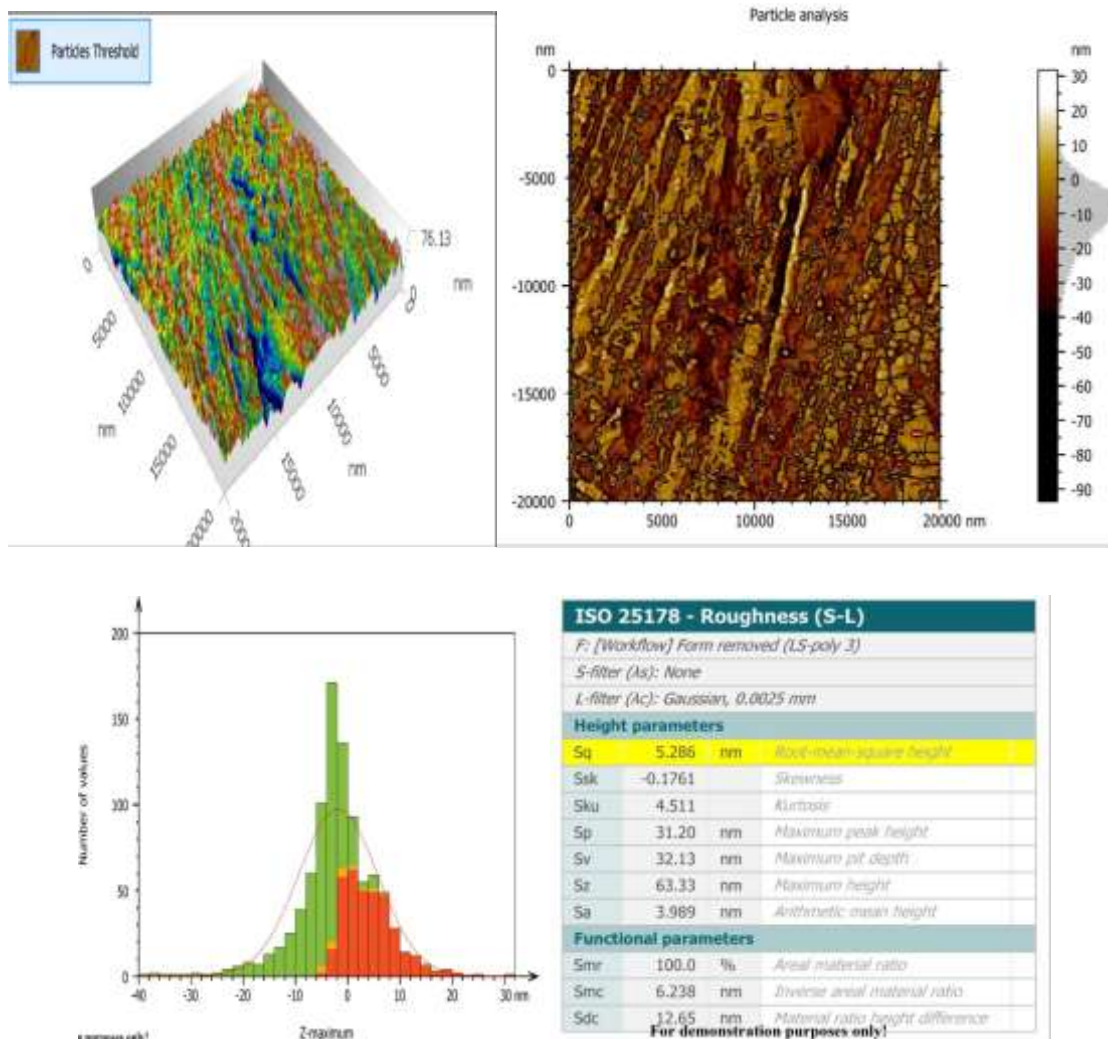


Figure 8: Images of AFM for polished aluminum alloy (R408, R613) surface.

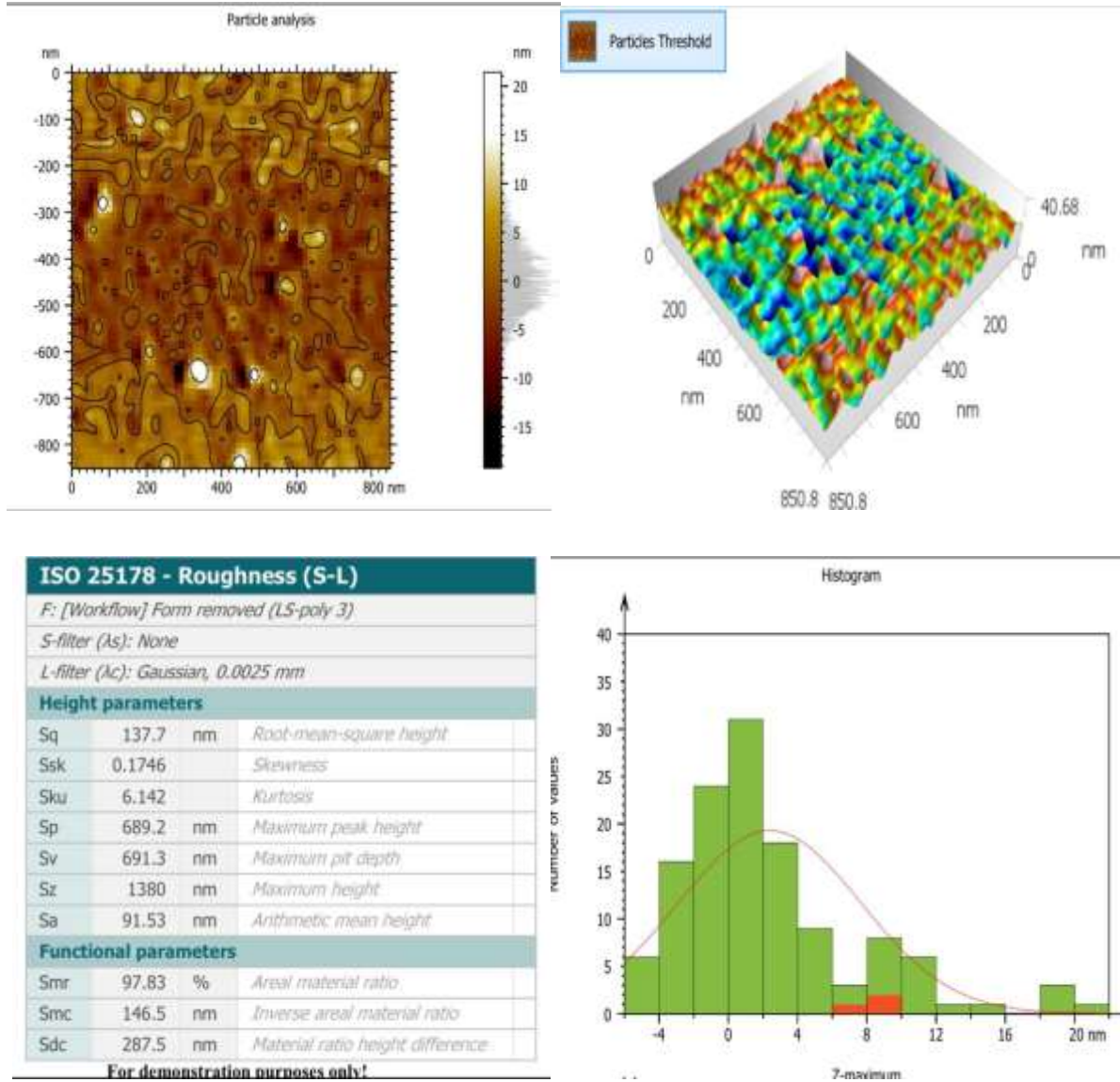


Figure 9: Images of AFM aluminum alloy (R408, R613) surface immersed in (0.2M NaOH).

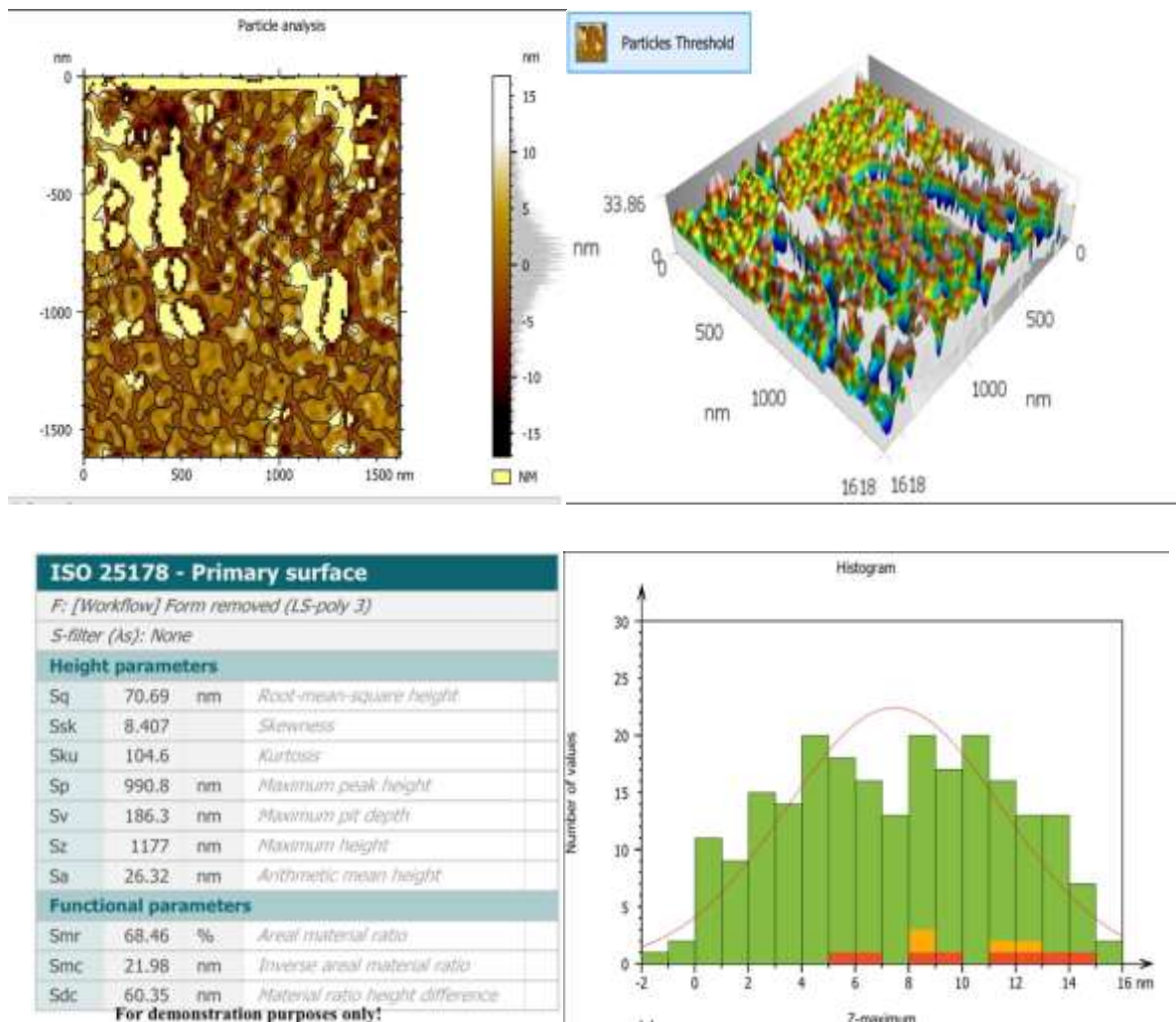


Figure 10: Images of AFM aluminum alloy (R408, R613) surface immersed in (0.2M NaOH) presence (275 ppm) of ketoprofen

Acknowledgement

The authors express their sincere thanks and gratitude to the Department of Chemistry, College of Science, University of Diyala, Iraq for providing the facilities for all laboratory tests.



References

1. WH. Ailor, Handbook on corrosion testing and evaluation. Symposium on the state of the art in corrosion testing, (Toronto, Canada, John Wiley and Sons, Inc., New York), June 21-26(1971)
2. V. Cicek, Cathodic protection: Industrial solutions for protecting against corrosion, (John Wiley & Sons), (2013)
3. PR. Roberge, Corrosion engineering, (McGraw-Hill Education), (2008)
4. P. Su, L. Li, W. Li, C. Huang, X. Wang, Y. Liu, A. Singh, Int. J. Electrochem. Sci.,15,1412-25(2020)
5. M. Sangeetha, Portugaliae Electrochimica Acta, 31(1),44-45(2013)
6. VL. Delinder, (Corrosion Inhibitors Basics: An Introduction. Houston, Texas, USA: NACE International), (1984)
7. SK, Sharma, A. Mudhoo, E. Khamis, Adsorption Studies, Modeling, and Use of Green Inhibitors in Corrosion Inhibition: An Overview of Recent Research. Green Corrosion Chemistry and Engineering: Opportunities and Challenges, 319-37(2011)
8. I. Ahamad, MA. Quraishi, Corrosion science, 52(2),651-656(2010)
9. A. Ahmed, E. Nazeer, R. Fouda, Intermed, (39),921(2013)
10. A. A. Rana, Using Some Expired Drugs as Corrosion Inhibitors for Low Carbon Steel, University of Technology Materials Engineering Department, (2018)
11. W. A. Isa, Z. W. Ahmed, Ibn AL-Haitham Journal For Pure and Applied Science, 28(3), (2017)
12. A. Kalla, International Journal of Industrial Chemistry, 7(4),419-429(2016)
13. A. Preetha, F. Selvarani, Int. J. Adv. Res, 5,1457-1467(2017)
14. E. Okon Nnabuk, F. Awe, Portugaliae Electrochimica Acta, 36(4),231-247(2018)
15. R. Beda, Advances in Chemistry, 6975248(2017)
16. A. Fouda, Arabian Journal of Chemistry, 5(3),297-307(2012)
17. P. Ejikeme, International Journal of Materials and Chemistry, 5(1),14-23(2015)
18. A. Asan, A Study in Protection of Corrosion by Using Nanoparticles (TiO₂, SiO₂) for Some Metals and Alloys., College of Science for Women University of Baghdad,(2012)
19. CM. Anbarasi, S. Rajendran, International Scholarly Research Notices, (2014)