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Corrosion of Aluminum Alloy in Chloride Medium Containing Pseudomonas aerginosa Bacteria.

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Abstract:

This paper reports the microbiologically induced corrosion (MIC) behavior of aluminum alloy in the chloride medium containing Pseudomonas aerinosa bacteria. MIC studies were performed at room temperature for 15 and 30 day in 2% NaCl electrolyte. System I consisted of 2% NaCl by weight (i.e.,uninoculated) as the control system; system II consists of system I inoculated with Pseudomonas aerinosa bacteria. Corrosion analyses by (Tafel polarization resistance and weight loss method); surface analysis (i.e Microstracture examination; Roughness test and X-Ray diffraction analysis) and microbiologically analyses (i.e Sampling; biofilm formation; isolation and identification) were used in this study. The result of Tafel polarization resistance and weight loss method showed that the bacteria caused increasing of corrosion current and increasing the rate of corrosion compared with system I. Surface analysis showed that the bacteria caused pitting corrosion and increasing the surface roughness compared with system I. The results of microbiologically analyses showed non-uniform and heterogeneous biofilm form on the surface of aluminum alloy after immersion in system II and show the role of Pseudomonas aerinosa bacteria in accelerating pitting corrosion of aluminum alloy in the chloride medium.

Keywords: Microbiologically induced corrosion, Chloride medium, Bacteria, Bioflim, Corrosion, Aluminum alloy. Microbiologically analyses.

Introduction:

Microbiologically influenced corrosion (MIC) is an electrochemical process where microorganisms initiate, facilitate, or accelerate a corrosion reaction on a metal. Surface. When present, microorganisms may produce diverse effects due to their interactions with the environment surrounding the metal. surface. MIC occurs in virtually all industries, including paper and pulp, sugar, dentistry, shipping, and gas and petroleum industries[1].MIC can be taken as a major cause of failures in industry for example it has been reported to be a primary mode of failure in power plant service water systems that accounts for at least 20% of all the damage caused by corrosion[2,3]. Many studies have indicated the importance of studying the microbiologically influenced corrosion of aluminum alloys.Anexnic aerobic biofilms inhibit corrosion of copper and aluminum have been studied by Jayaraman et al. 1999[4], this study is the first report of axenic aerobic biofilms inhibiting generalized corrosion of copper and aluminum. Pitting corrosion inhibition of aluminum 2024 by bacillus biofilms secreting polyaspartate had been presented by Ornek et al. 2002[5] ,pitting corrosion of aluminum 2024 in luria baertani medium was reduced by the secretion of anionic peptides by engineered and natural bacillus biofilms and was studied in continuous reactors using electrochemical impedance spectroscopy. Evaluation of microbiologically influenced corrosion inhibition (MICI) with EIS and ENA had been reported by Nagiub et al. 2002[6], MICI has been observed for Al 2024 ,mild steel and

cartridge brass when an artificial seawater solution containing growth medium was contaminated by bacteria. New evidences on the catalase mechanism of microbial corrosion had presented by Busalmen et al. 2002[7]. In this study changes on the oxygen reduction rate induced on aluminum brass by cell-free bacterial cultures of an isolated belonging to the genus pseudomonas were studied in relation to bacteria phase of growth and to the surface oxide layer composition after various electrochemical pre-treatments of the metal. samples. Biocorrosion and biofouling of metals and alloys of industrial usage present state of the art at the beginning of the new millennium had been reported by Videla 2003[8], in this study biocorrosion of aluminum and its alloys by fungal contaminants of jet fuels were studied. The importance of live biofilms in corrosion protection had been presented by Rongjun Zuo et al. 2005[9] .Al 2024 samples are used in this study , the results showed when antibiotics were added to the artificial seawater to kill the bacteria in the biofilm pitting occurred within a few hours as indicated by characteristic changes in the impedance. Filiform corrosion attack on pretreated aluminum alloy with tailored surface of epoxy coating had been studies by Liu 2007[10], in the study, on the basis of material analysis of 6016 aluminum alloy widely used in Europe automotive industry, the influenced of surface pretreatment on filiform corrosion and adhesion of epoxy coating/aluminum alloy interface were investigated and the effect of rolling direction and coating property on filiform corrosion was also examined. Investigations on reducing microbiologically – influenced corrosion of aluminum by using super-hydrophobic surfaces had been reported by T. Liu et al. 2010[11] the results showed that neither anodization nor chemical modification could decrease the bacterial adhesion and corrosion rate individually. Microbial corrosion of aluminum 2024 aeronautical alloy by hydrocarbon degrading bacteria bacillus cereus ACE4 and serratia marcescens ACE2 had been presented by Rajasekar et al. 2010[12], this paper reports the microbiologically induced corrosion and electrochemical behavior of aluminum alloy AA 2024 in the presence of hydrocarbon – degrading bacteria *Bacillus cereus* ACE4 aGram-positive bacteria and Serratia marcescens ACE2 aGram –negative bacteria. Inhibition of biocorrosion of aluminum 2024 aeronautical alloy by conductive ladder Polymer poly (o-phenylenediamine) had been studied by Rajasekar et al. 2011[13]. This study examines the role of conductive polymer poly (o-phenylenediamine) in corrosion inhibition and its antibacterial activity against bacterial biofilm on aluminum 2024 aeronautical alloy .The purpose of this study was to instigate the effect bacterial contaminant on the corrosion behavior of aluminum alloy in chloride medium , using a Gram-negative bacteria, Pseudomonas aeruginosa.

Expremental:

Microorganism:

The Pseudomnas aeruginosa bacteria that used in this study was diagnosed precisely in the Biology Department, College of Science, University of Babylon, and then added to the chloride medium to produce system II used in this study.

Samples Preparation:

Aluminum alloy has the following nominal composition (wt%):1.25%V, 1.68%Si, 8.6%Fe and the remaining is Al. Samples disk(15 mm diameter by 2mm thickness) were sequentially ground with a series of grit silicon carbide paper (grades 180,400,600,800,1000,1200 and 2000) to a smooth surface and were finally polished to a mirror finish surface using natural diamond size 0.1µm with lubricating oil for lapping with diamond paste code PL0001 at room temperature .The polished samples were rinsed with deionized water, and drying using electric drier, then the sample immersion in (3%HCl) by volume at room temperature for 2 min for pickling process; then sample were rinsed with deionized water, and surface sterilized by immersion in a 70% ethanol solution for 1 min and finally dried in a desiccator. The prepared samples were used for biocorrosion studies (i.e Tafel polarization

resistance and weight loss method); surface analysis (i.e Microstructure examination; Roughness test and X-Ray diffraction analysis) and microbiologically analised (i.e ,Sampling ; biofilm formation; isolation and identification).

Biocorrosion Studies:

Biocorrosion studies were performed at room temperature for 15 and 30 days in 2% NaCl by weight electrolyte. System I consisted of 2% NaCl as control. System II consisted of system I inoculated with 4 mL of Pseudomnas aeruginosa bacteria. All the experiments were conducted in a corrosion environment with 2% sodium chloride as the electrolyte.

Electrochemical Measurements

Polarization measurements were carried out using the potentiostat (Mlab 200 potentiostat banch elektronike gup germany, 2008 with SIC electrochemical software calculation). All experiments were performed in a three-electrode electrochemical cell, with a platinum electrode as the counter electrode, and a saturated calomel electrode as the reference electrode. After the biocorrosion experiments, the appropriate samples were removed and embedded in a sample holder of the corrosion cell, and they served as the working electrodes. The working electrode had an exposed surface area of 2 cm^2. 750 ml of the medium was transferred from each system into the electrochemical cell to serve as the electrolyte for the electrochemical analysis. Polarization measurements were made after steady-state open circuit potential; in order to estimate the open circuit potential (opc), the auxiliary electrode is closed(current=0)and estimate potential for 30 minute , corrosion potential (Ecorr) can be found where : Ecorr ≈ opc. Tafel plots were measured with a scan rate of 0.5 mVs^{-1} and were obtained by scanning from the open circuit potential Ecorr toward 200mV anodically and -200 mV cathodically.

Weight Loss Test:

Another vital method for estimating corrosion rate that is adopted in this work is using simple immersion test. This test has been implemented to estimate the corrosion rate for the aluminum alloy. This test is carried out in order to study the behavior of aluminum alloy in system I and system II as follows:-

Samples of aluminum alloy that were reviously prepared and kept with high attention are now re-washed with distilled water, rinsed with ethanol and dried. A precise weighing process is now carried out to record the initial weight of samples(W_1). The samples is weight by using ±0.0001g accuracy electric balance. Aluminum alloy samples are re-weighed (W_2) after 15and 30day (i.e.360 and 720 hrs.). The process of re-weighing is carried out under high attention by a perfect cleaning of samples by using distilled water and rinsing in ethanol with sufficient drying. The purpose of re-weighing process is to determine the weight loss as referred to by ($\Delta W=W_1-W_2$) in results and findings.The corrosion rates of the aluminum alloy wear calculated in mils per year according to the following formula;[14].

$$\text{Corrosion rate} = (W_1-W_2)\, k/AtD$$

Where:

W_1 and W_2 are weights in gram of aluminum alloy before and after immersion; k=3450000(corrosion rate cost in mils per year) ; t=time of exposure(h); A=Expanded surface area (cm^2); D=Density of alloy sample($g.cm^{-3}$).

Surface Analysis:

After the 15 and 30 day exposure the samples were examined; using light optical microscope type (Union ME-3154) with fitted digital camera is used for microstructure examination of specimen surface before and after corrosion test in system I and system II. Surface roughness tester type (Hand –held Roughness Tester TR200,by Time Group Inc.) using to measure surface roughness of aluminum alloy before and after immersion in system I and system II. General electric diffraction type (Lab X, SHIMADZU, XRD-6000, X-RAY DIFFRACTOMETER) using for X-Ray diffraction analysis. The test carried out through scanning the specimen continuously within bragg angle 2θ range

10°-60° using Cu target at voltage of 40 kV and 30mA of current with continuous scan mode range (10.000-60.000) degree. Aluminum alloy after immersion in system I has been identified by X-Ray diffraction technique in order to compare these diffraction pattern with aluminum alloy after immersion in system II.

Microbiologically analyses:

The aim from this analysis is to determine if Pseudomonas aeruginosa bacteria is responsible for accelerating the corrosion of aluminum alloy in the chloride medium. Subsamples of biofilm and corrosion product collected each 15 and 30 days from surface of aluminum alloy after immersion in the system II.

Bacteriological Diagnosis.

Subsamples of biofilm and corrosion product collected each 15 and 30 days from surface of aluminum alloy after immersion in the system II and culturing on nutrient agar 24hr. These cultures were characterized depending on their morphology (size, color and smile) of the colonies in the culture; shape, Gram strain of bacteria under light microscope, and the biochemical diagnosis, oxidase test, catalase test, indol test, methyl red test, voges-proskauer test, citrate utilization test, motility test, starch test, gelatin test, lipase test, nitrate reduction, glugose utilization test, trehalose utilization test and sucrose utilization test.

Results and discussion:

Biocorrosion Studies:

Electrochemical Measurements:

Fig 1 and fig 2 show the polarization curves for aluminum alloy in 2% NaCl solution in the absence and presence of Pseudomonas aeruginosa bacteria after 15 days immersion in system I and system II respectively. The corresponding data are presented in Table 1 and Table(2) for aluminum alloy in 2% NaCl solution in the absence and presence of Pseudomonas aeruginosa bacteria after 15 days immersion in system I and system II respectively. Fig 3 and Table 3 show the polarization curve and data for aluminum alloy in 2% NaCl solution in the absence of Pseudomonas aeruginosa bacteria after 30 days immersed in system I. Fig 4 and Table 4 show the polarization curve and data for aluminum alloy in 2% NaCl solution in the presence of Pseudomonas aeruginosa bacteria after 30 days immersion in system II.

The results showed that i_{corr} was high in presence of Pseudomonas aeruginosa bacteria when compared to control system I and bacterial system II. The presence of Pseudomonas aeruginosa bacteria significantly accelerated the corrosion current i_{corr} of aluminum alloy by 178.5% of magnitude (i.e., from 385.64 nA to 688.48 nA) after immersion in system I and system II for 15 days, furthermore the presence of Pseudomonas aeruginosa bacteria accelerated the corrosion current i_{corr} of aluminum alloy by 100.6% of its magnitude (i.e., from 877.24 nA to 882.89 nA) after immersion in system I and system II for 30days. The higher anodic current is due to pit formation on the aluminum alloy surface and the reduction in the cathodic current may be due to the consumption of oxygen by Pseudomonas aeruginosa bacteria [12], The localised activity of bacteria can substantially slow down the repassivation of the material due to higher rate of corrosion at local areas and limited oxygen availability under the biofilm[15]. The nature of the Tafel curves indicates that the anodic current was higher in the presence of Pseudomonas aeruginosa bacteria system II after immersion for 15 and 30 days compared with the control system I.

Weight Loss Test:

The corrosion rate of aluminum alloy obtained from the weight loss study in the system I and system II after 15 days of immersion is shown in Table 5. Table 6 shows the corrosion rate of aluminum alloy obtained from the weight loss study after 30 days of immersion in the system I and system II. The corrosion rate of aluminum alloy in system I were 0.292 mpy; 0.474 mpy , at 15 and 30 days (i.e.,360 and 720h); and the corrosion rate were 0.949 mpy, 0.876 after 15 and 30 days (i.e.; 360 and 720h) of immersion in the system II. Comparing the corrosion rate results in Table 5 ; it is noticed

that the corrosion rate of aluminum alloy in the system II is approximately 3.25 times more than that obtained for the alloy in the system I; furthermore the corrosion rate of alloy in the system II is approximately 1.84 time more than that in the system I when compared the results of the corrosion rate in Table 6 . Pitting is a highly localized type of corrosion in the presence of aggressive chloride ions. Pits are initiated by chloride attack at weak sites in the met al. oxide; the pits propagate according to the two following reaction [13]:

$$Al = Al^{3+} + 3e^- \quad (1)$$

$$Al^{+3} + 3H_2O = Al(OH)_3 + 3H^+ \quad (2)$$

While hydrogen evaluation and oxygen reduction are the important reduction processes at the intermet al.lic cathodes.

$$2H^+ + 2e^- \rightarrow H_2 \quad (3)$$

$$O_2 + 2H_2O + 4e^- \rightarrow 4\,OH^- \quad (4)$$

As a pit propagates, the environment within the pit (i.e., the anode) changes and the pH decrease (see reaction 2). The positive charge also cause the migration of chloride ions into the pit, resulting in HCl formation which further accelerates the pit propagation; the reduction reaction causes local alkalinization around the cathodic particles. Aluminum oxide is not stable in such an environment, and aluminum around the particles will dissolve the pits[13]. Furthermore the corrosion rate increasing in the system II caused by presence of Pseudomonas aeruginosa bacteria; pitting corrosion result of attack occurs under microbial deposits; the organisms grow in volcano- like turbercules with gas bubbling from the center as shown in Fig 5[16].

Surface Analysis:

Microstructure examination of specimen surface before immersion in the corrosion system shown in Figure 6 ; Figure 7: A;B show the microstructure of specimen surface after removing the corrosion products at 15 days of immersion in system I and system II respectively; furthermore the microstructure of specimen surface after removing the corrosion products at 30 days of immersion in system I and system II shown in Fig 7:C;D respectively. Pitting corrosion of the aluminum alloy occurred with Pseudomonas aeruginosa bacteria Fig 7B;D compared with system I without Pseudomonas aeruginosa bacteria Fig A;C ; the surface of aluminum alloy with Pseudomonas aeruginosa bacteria revealed a large quantity of corrosion products and more corrosion pits were evident in the presence of Pseudomonas aeruginosa bacteria. Surface roughness test results Table 7 and Table 8 revealed an increase in surface roughness of the aluminum alloy after immersion in system II compared with system I; pitting corrosion of aluminum alloy in the system II and it indicates that the ability of Pseudomnas aeruginosa bacteria to cause corrosion and form defects, cracking, pits and holes result from corrosion process which had covered the surface of aluminum alloy and caused the increasing in surface roughness compared with the results of surface roughness in the system I. Figure 8 and Figure 9 presents the details of XRD data corresponding to the phases present in the corrosion product samples of surface of aluminum alloy after immersion in the system I and II respectively. AlO(OH), $Al(OH)_3$, $(Al_2O_3)_4.H_2O$; were noticed in the system I and II; greater intensity of $Al(OH)_3$; $(Al_2O_3)_4H_2O$ peaks were observed in the system II when compared system I and II; Figure 8 and Figure 9; this indicates the role of Pseudomonas aeruginosa bacteria in accelerating the microbial corrosion of aluminum alloy in the chloride medium.

Microbiological Analyses:

Biofilm Formation:

Figure 10 show the microstructure of the surface of aluminum alloy after exposure to system II, without removal of biofilm and corrosion product, show the surface of alloy were covered with corrosion product, and shows the biofilm formed on the alloy surface, this biofilm is non-uniform and heterogeneous and caused differential aeration on aluminum alloy and caused increasing in corrosion rate. Non-uniform or patchy colonization by microbial biofilms results in the formation of differential cells,

where areas under respiring colonies are depleted of oxygen relative to surrounding non-colonized areas. These effects give rise to potential differences and consequently to corrosion rate, the areas under respiring colonies become anodic and there, metal. dissolution occurs [17].

Culturing Test; Microscopic Test & Biochemical Test:

Appernace shape of Pseudomonas aeruginosa bacteria in culturing medium of subsamples of biofilm and corrosion product collected from surface of aluminum alloy after immersion in system II shown in Figure11 ; from the figure a small bacilli negative gram strain (G-ve) bacteria; small colonies with 2.5mm in diameter have mucin appearance and green blue; pigments pyocyanin production growthing on solid nutrient agar 24h;27ºC, and the odor of the culture was like apple or grip molding. Table 9 shows the result of biochemical tests on the isolates; from the table, the ability of bacteria to motility, oxides, catalysis production, citritae utilization,unable to starch anylase and changing in the ability to lipose production. Also bacteria was utilization the glucose sugar, but it did not use trahalose sugar and unstable in suerose utilization. Bacteria has the ability in the gelatin liquida and this important character for bacteria diagnesing because this type of bacteria has effective role in the gelatinase production.Based on these characteristics of the culturing, microscope and biochemical test was tentatively identified as Pseudomnas aeruginosa isolated from corrosion product and its indicated the role of this bacteria in accelerating the corrosion rate of aluminum alloy in chloride medium.

Conclusion

1- The increasing of the pitting corrosion rates is caused by an increasing of the anodic dissolution rate of passive aluminum alloy due to biofilm formation.
2- Microbiologically influenced corrosion of aluminum alloy in the chloride Medium is a rather complex process (i.e., effected by chloride ions and bacteria effect).
3- The results show that the pitting attack of aluminum alloy was greatly increased in the presence of not protective biofilm.
4- This study shows the role of Pseudomonas aeruginosa bacteria in accelering pitting corrosion on aluminum alloy in the chloride medium.

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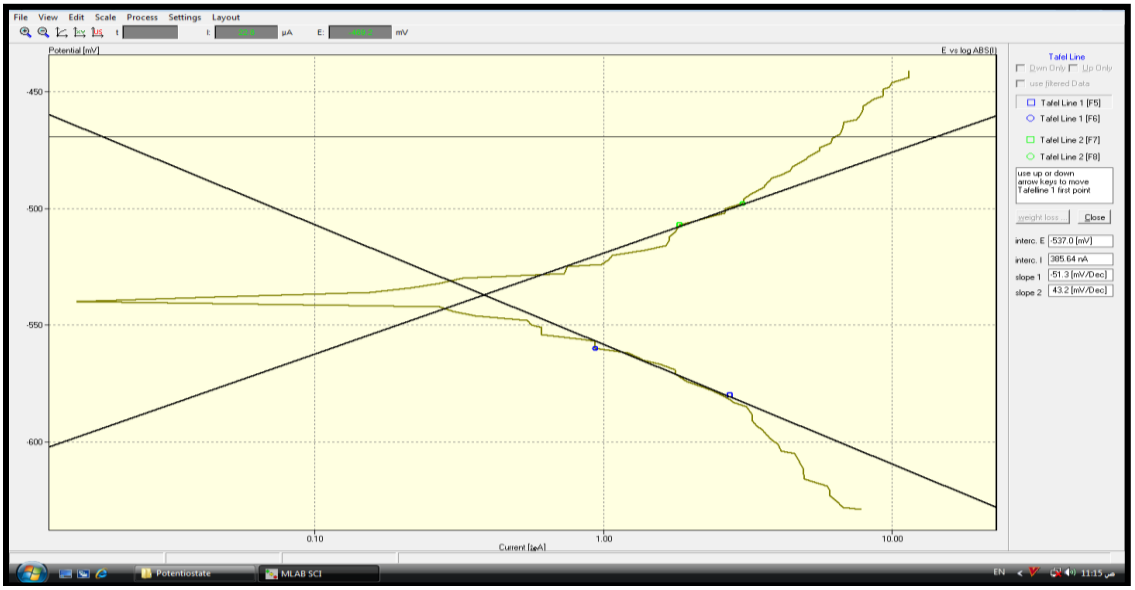

Figure 1. Tafel polarization curve of aluminum alloy after 15day of immersion in control medium system I.

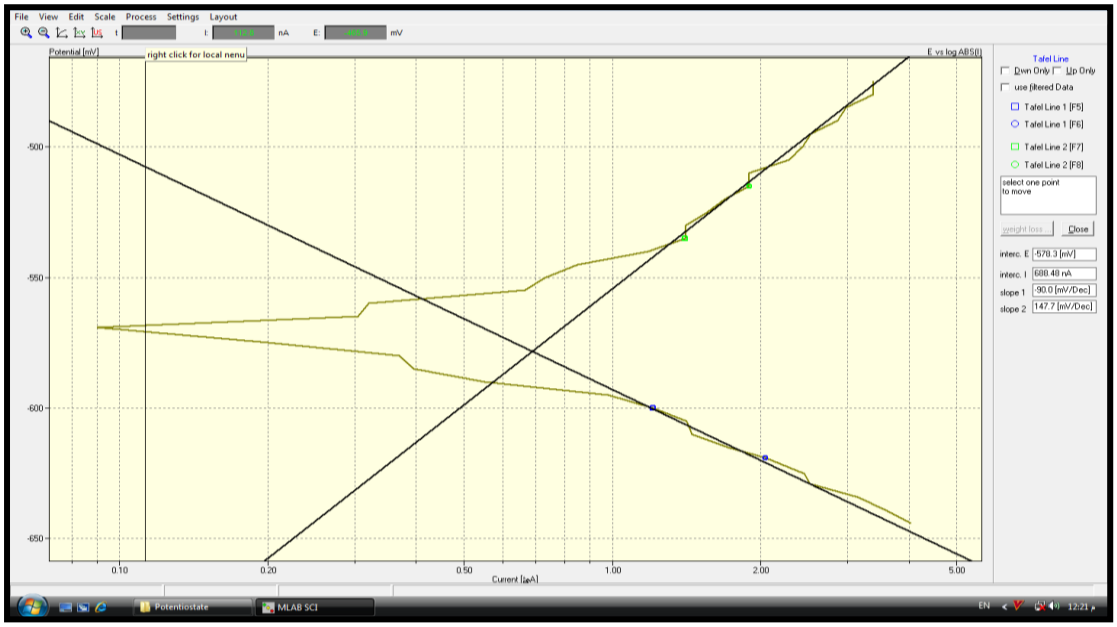

Figure 2. Tafel polarization curve of aluminum alloy after 15days of immersion in system II.

Table 1 Polarization Data for aluminum alloy after 15days of immersion in the system I

System	Immersion period (days)	Slope1 (mv/Dec)	Slope2 (mv/Dec)	$E_{Corr.}$ (mv)	$i_{corr.}$ (nA)
I	15	-51.3	43.2	-534	385.64

Table 2 Polarization Data for aluminum alloy after 15days of immersion in the system II.

System	Immersion period (days)	Slope1 (mv/Dec)	Slope2 (mv/Dec)	$E_{Corr.}$ (mv)	$i_{corr.}$ (nA)
II	15	-90.0	147.7	-578.3	688.48

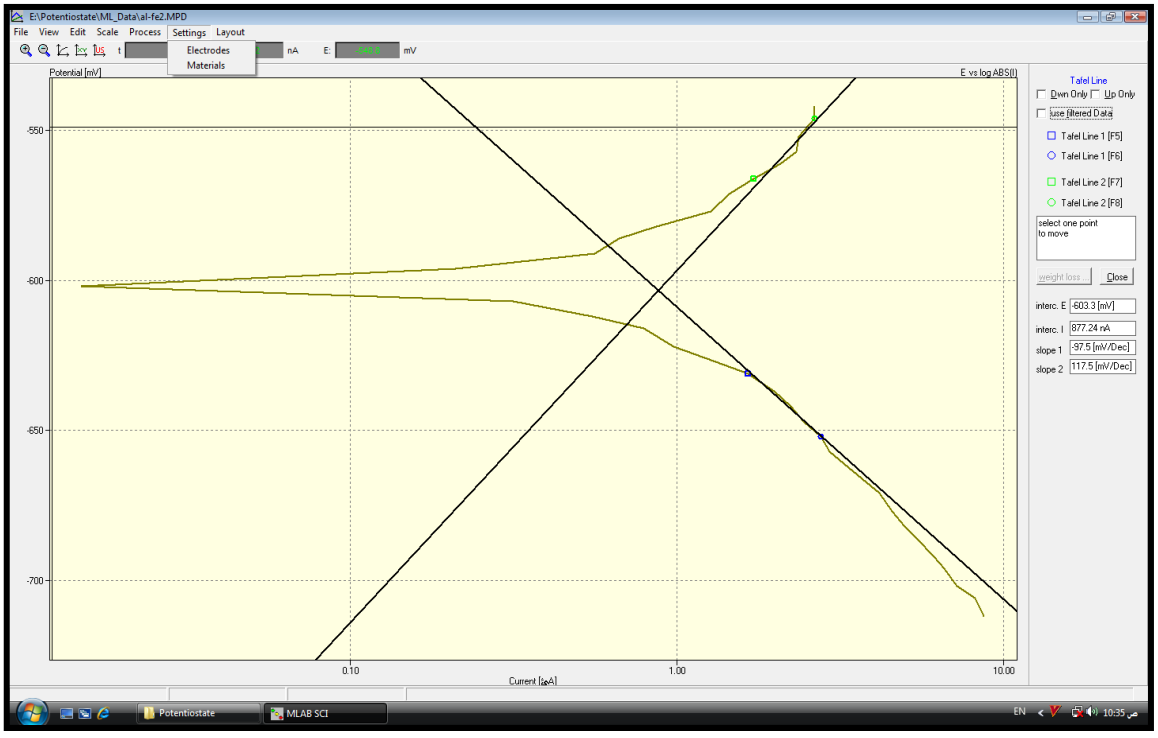

Table 3 Polarization Data for aluminum alloy after 30 days of immersion in the system I.

System	Immersion period (days)	Slope1 (mv/Dec)	Slope2 (mv/Dec)	$E_{Corr.}$ (mv)	$i_{corr.}$ (nA)
I	30	-97.5	117.5	-603.3	877.24

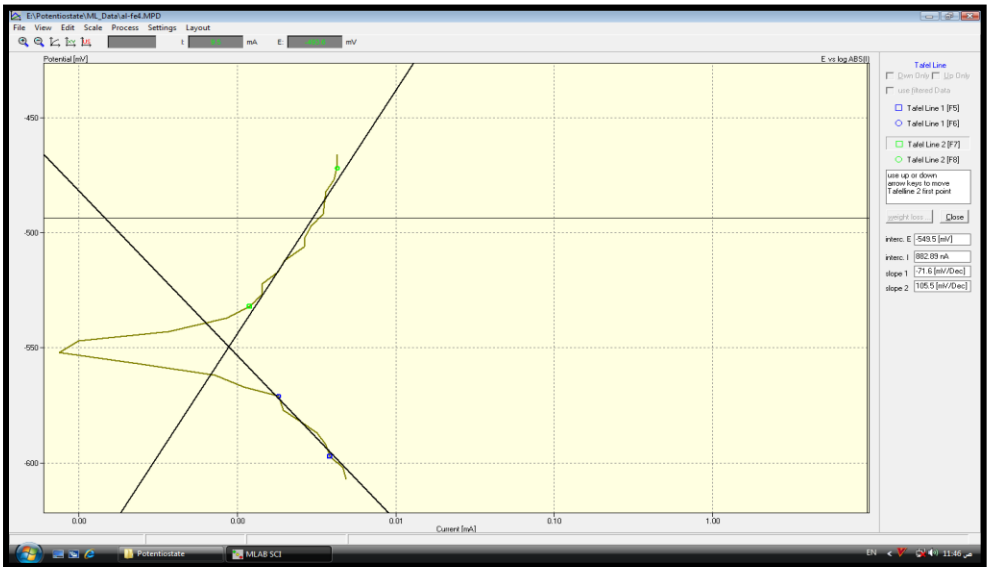

Figure 4. Tafel polarization curve of aluminum alloy after 30days of immersion system II.

Table 4 Polarization Data for aluminum alloy after 30days of immersion in the system II.

System	Immersion period (days)	Slope1 (mv/Dec)	Slope2 (mv/Dec)	$E_{Corr.}$ (mv)	$i_{corr.}$ (nA)
II	30	-71.6	105.5	-549.5	882.89

Table 5 Corrosion rate of aluminum alloy by weight loss in the system I and II.

System	Immersion	Density	Expended	Weight	Corrosion

	period (h)	(g/cm^3)	area (cm^2)	loss (g)	rate (mpy)
I	360	2.93	4.476	0.0004	0.292
II	360	2.93	4.476	0.0013	0.949

Table 6 Corrosion rate of aluminum alloy by weight loss in the system I and II.

System	Immersion period (h)	Density (g/cm^3)	Expended area (cm^2)	Weight loss (g)	Corrosion rate (mpy)
I	720	2.93	4.476	0.0013	0.474
II	720	2.93	4.476	0.0024	0.876

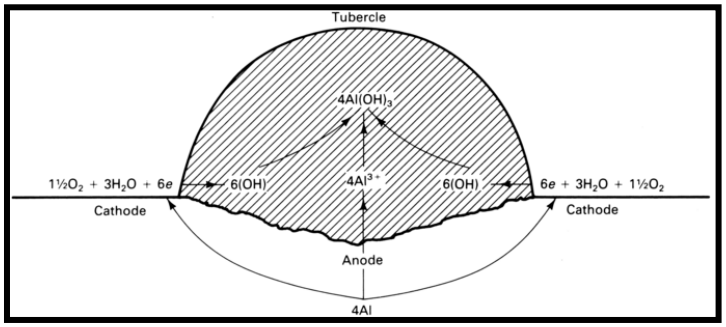

Figure 5 Schematic of tubercle formed by bacteria on an aluminum alloy(16).

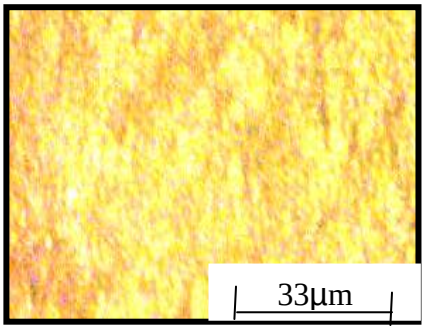

Figure 6 Surface of aluminum alloy before the immersion in system I and system II.

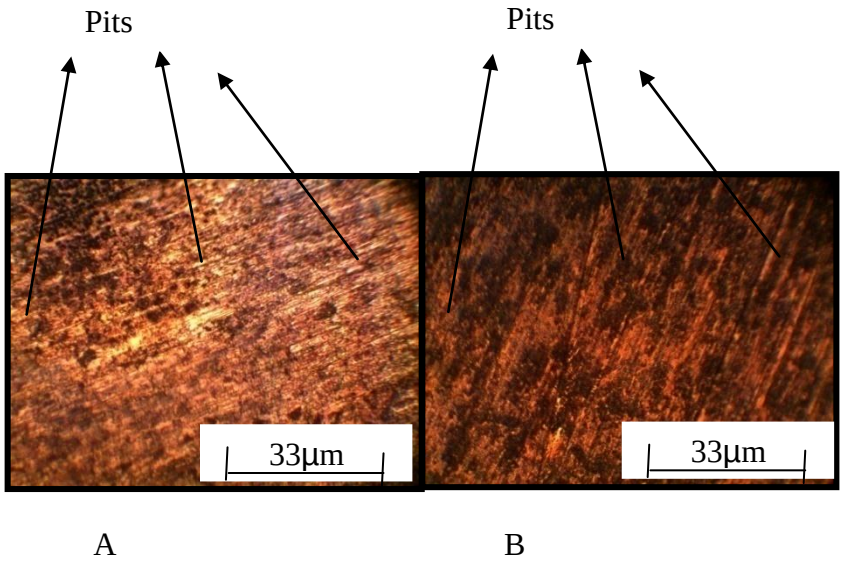

Figure 7 Surface of aluminum alloy after removing the corrosion products at 15 days of immersion in system: (A) I and (B) II .

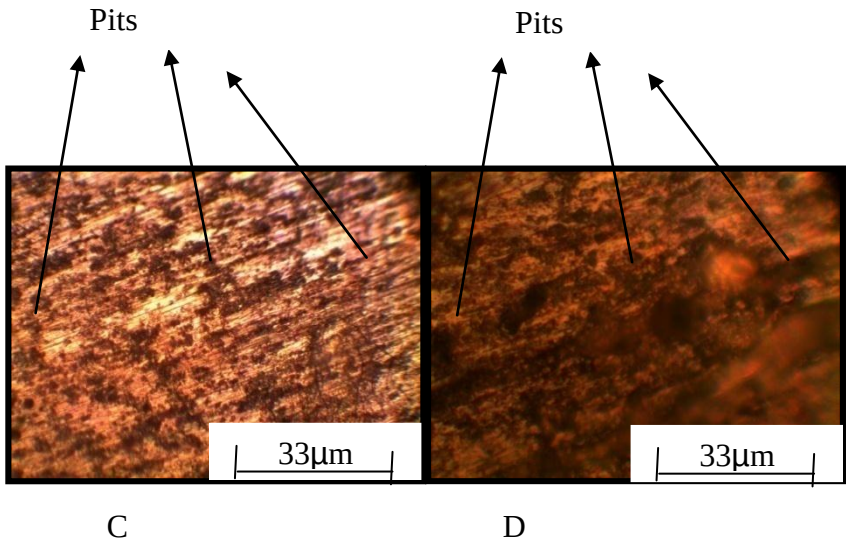

Figure 7 Surface of aluminum alloy after removing the corrosion products at 30 days of immersion in system: (C) I; (D) II.

Table 7 Number of surface roughness of aluminum alloy before and after immersion in system I.

Solution	Immersion period (days)	No. of Roughness (µm)
----------	----------	0.003
System I	15	0.032

System I	30	0.079

Table 8 Number of surface roughness of aluminum alloy before and after immersion in system II.

Solution	Immersion period (days)	No. of Roughness (μm)
----------	----------	0.003
System II	15	0.065
System II	30	0.099

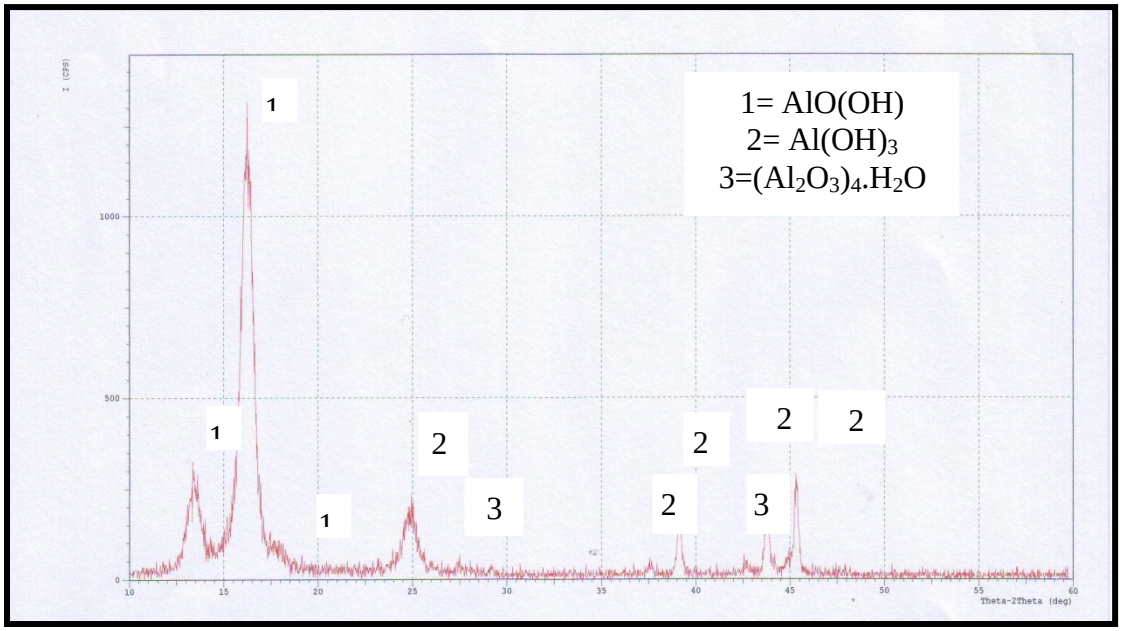

Figure (8) XRD Patterns for aluminum alloy after immersion in system I.

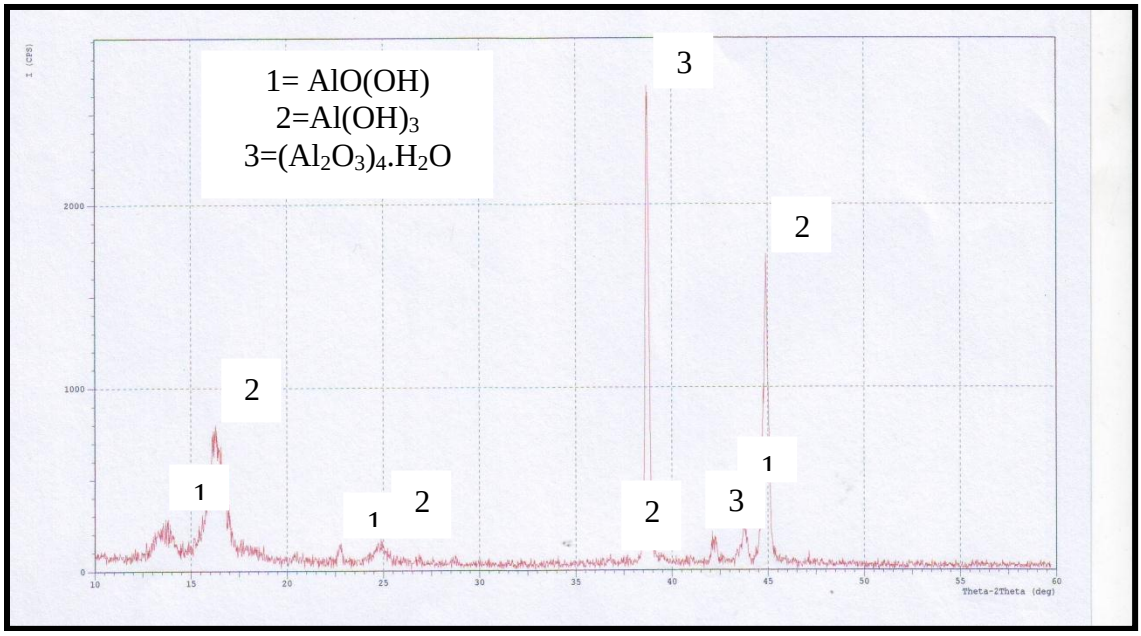

Figure (9) XRD Patterns for aluminum alloy after immersion in system II.

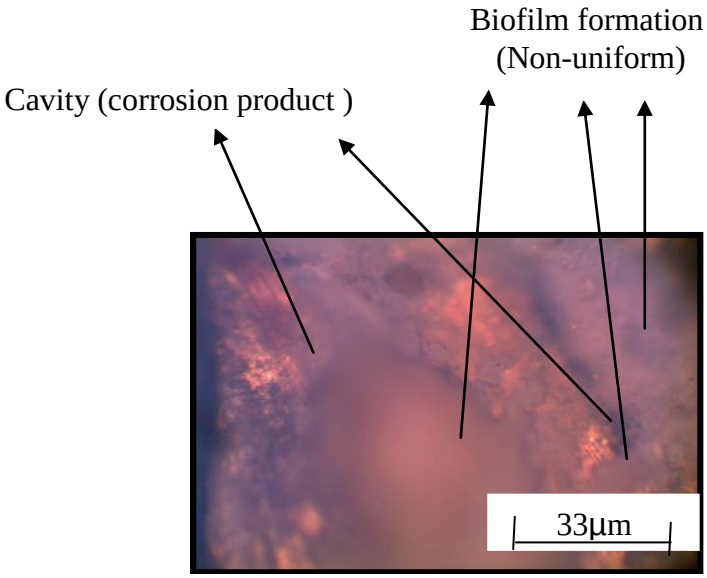

Figure10: Biofilm formation on the surface of aluminum alloy at 30 days of immersion in system II.

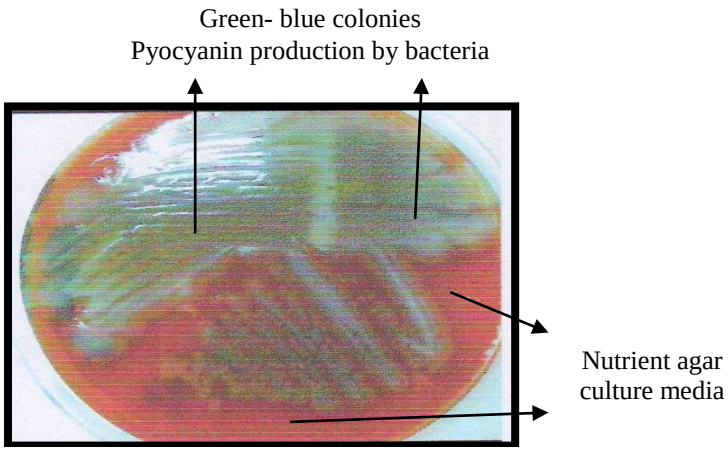

Figure11. Appearances shape of Pseudomonas aeruginosa bacteria in culturing medium of subsamples of biofilm and corrosion product collected from surface of aluminum alloy after immersion in system II.

Table 9 Biochemical characterization of isolates from surface of aluminum alloy after immersion in system II.

Characteristics	Results
Gram stain	**Negative**
Shape	**Rod**
Molility	+
Indol production test	-
Citrate utilization test	+
Voges proskauer test	-
Oxidase test	+
Methyl red test	-
Catalase test	+
Trehalose utilization test	-
Gelatin test	+
Starch test	-
Glucose utilization test	+
Surcrose utilization test	-/+
Nitrate reduction	-/+
Lipase test	-/+

تآكل سبيكة الالمنيوم في وسط كلورين

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الخلاصة:

هذا البحث يلخص سلوك التاكل المتضمن الفعل الحيوي لسبيكة الالمنيوم في وسط الكلورايد مع وجود بكتريا Pseudomnas aerinosa. التاكل المتضمن الفعل الحيوي انجز في درجة حرارة الغرفة ولمدة 15 و 30 يوم في 2%NaCl كمحلول الكتروليتي . نظام I يتكون من 2%NaCl أي بمعنى اخر لم يلقح بالبكتريا كوسط للمقارنة, نظام II يتكون من نظام I ملقح ببكتريا Pseudomnas aerinosa. تحليل التاكل باستخدام (استقطاب تافل و طريقة فقدان الوزن), تحليل السطح (الفحص المجهري, اختبار الخشونة وتحليل حيود الاشعة السينية) وتحليل مايكروبايلوجي (جمع العينات, تكون الغشاء الحيوي, العزل والتشخيص) تم استخدامها في هذه الدراسة. نتائج استقطاب تافل وطريقة فقدان الوزن أظهرت ان البكتريا تسبب زيادة في تيار التاكل وزيادة معدل التاكل بالمقارنة مع النظام I. تحليل السطح اظهر ان البكتريا سببت تاكل نقري وزيادة خشونة السطح بالمقارنة مع النظام I. نتائج التحليل المايكروبايلوجي اظهرت ان غشاء حيوي غير منتظم وغير متجانس يتكون على سطح السبيكة بعد الغمر في نظام II, واثبت دور Pseudomnas aerinosa بكتريا في زيادة التاكل النقري لسبيكة الالمنيوم في محلول الكلورايد.