Study the Microbiologically Influenced Corrosion of Carbon Steel

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Abstract

The main objective of this study was to evaluate the microbiologically influenced corrosion of carbon steel in water, samples of water taken from Al-Hilla rivers and distill water (control medium). Corrosion analyses by using (Liner polarization tafel test; weight loss method ; microstructure examination , surface roughness test and X-Ray diffraction analysis) and microbiological analyses by using (Isolation and identification by using appearance factors microscopic ,culturing factors and biochemical tests for biofilm of corrosion product) are used in this study.

The result of corrosion analyses shows the corrosion rates of carbon steel in rivers water are more than that in control water, the microstructure examination and surface roughness tests show increase in roughness of met.al. surfaces which are under the corrosion medium (rivers water) compared with control medium. The result of microbiological analyses shows the slides that made from the biofilm (product of corrosion) under microscopic appear small bacilli negative gram strain (G-ve) bacteria, where as culturing test shows small colonies with 2.5µm in diameter of bacteria have mucin appearance and green pigments as well as the result from biochemical tests; these facts indicate that *Pseudomonas aeruginosa* bacteria are correlated with the type of corrosion occurring in the carbon steel in the rivers water.

Keywords : Microbiologically Influenced corrosion , carbon steel, Corrosion , Bacteria, Biofilm, Microbiological analyses, MIC.

دراسة التآكل المتضمن الفعل الاحيائي للفولاذ الكربوني

الخلاصة

الهدف الاساسي من هذه الدراسة هو حساب التاكل المتضمن الفعل الحيوي للفولاذ الكربوني في الماء, عينات الماء تم اخذها من نهر الحلة كذلك الماء المقطر كوسط للسيطرة. تحليل التآكل باستخدام (الاستقطاب الخطي اختبار تافل , طريقة فقدان الوزن , الفحص المجهري , اختبار خشونة السطح و اختبار حيود الاشعة السينية) و تحليل مايكرو بايلوجي وباستخدام (العزل والتشخيص باستخدام العوامل المظهرية والمتضمنة الفحص تحت المجهر وعملية الزرع وكذلك الفحوصات التاكيدية باستخدام فحوصات البايو كيميائية للغشاء الحيوي لناتج التاكل) تم استخدامهما في هذه الدراسة.

نتائج تحليل التاكل اظهرت ان معدل التاكل للفولاذ الكربوني في ماء النهر يكون اكبر من حالة استخدام ماء المقارنة, اختبار الفحص المجهري وخشونة السطح اظهرت زيادة في خشونة السطح للمعادن التي تكون في وسط التاكل (ماء النهر) بالمقارنة مع ماء المقارنة. نتائج التحليل المايكرو بايلوجي اظهرت ان الشرائح التي تم تصنيعها من الغشاء الحيوي (نتائج التاكل) تحت المجهر اظهرت وجود بكتريا عصوية سالبة لصبغة كرام بينما اختبار الزرع اظهر مستعمرات صغيرة بكتيرية ذات قطر 2.5 مايكرومتر ذات مظهر مخاطي بالإضافة الى نتائج من فحوصات البايو كيميائية , كل هذه الحقائق اعطت دليل على وجود بكتريا من نوع (*Pseudomonas aeruginosa*) مرتبط بعملية التاكل الحاصلة للفولاذ الكربوني في ماء النهر.

الكلمات المرشدة: التاكل المتضمن الفعل الاحيائي, فولاذ كربوني,تاكل, بكتريا, الغشاء الحيوي,التحليل المايكروبايلوجي.

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Introduction

Microbial corrosion also called bacterial corrosion or microbially – induced corrosion (MIC), is corrosion caused or promoted by microorganisms , usually chemoautotroph's. It can apply to both metals and non – metallic materials, in both the presence and lack of oxygen[1]. Some bacteria directly oxidize iron to iron oxides and hydroxides , other bacteria oxidize sulfur and produce sulfuric acid causing biogenic sulfide corrosion[2,3].

Effect of carbonation on microbial corrosion of concretes had been studied by Nasir et.al. ,1993 [4] the result show the corrosion rates corresponded well with the carbonation rates .Microbiologically influenced corrosion in the fermilab main injector magnet low conductivity water system had been reported by P.G.Hurh et.al.,1999[5]. Microbial exopolysaccharides effect on corrosion and partial chemical characterization had been presented by Indraneel Majumdar et.al.,1999[6] ,the result showed that biofilm microorganisms produce EPS , which serve as corrosion inhibitor for mild steel , a number of bacteria isolated from the corrosion products showed potential for EPS production .In situ corrosion control in industrial water systems had been presented by J.F.Batista et.al.,2000[7] , the result show that the simultaneous use of a biocide and dispersant faild to control the corrosion in cooling tower of a met.al.lurgic industry system. Microbial corrosion induced by a new highly aggressive SRB strain had been reported by Hendrik Venzlaff et.al., 2005[8] . Microbiologically influenced corrosion in dairy effluent had been studied by B. Ramesh et.al.,2006[9], the result shows *Bacillus, Pseudomonas ,Micrococcus ,Niesseria ,Streptococcus,* and *Lactobacillus* wear found in dairy effluent and initiation of pitting coorosion of mild steel.Bacterial degradation and corrosion of naphtha in transporting pipeline had been presented by A.Rajasekar et.al.,2007[10], weight loss method are used in this study , the result shows the degraded organic compounds in naphtha encourages the growth of bacteriaand nhances the formation of corrosion products like ferric oxide and manganese oxide. Role of air microbes on atmospheric corrosion of mild steel had been studied by S. Maruthamuthu et.al. , 2008[11] , the result showed microorganisms enhance deterioration of materials of construction and steel structures and the deterioration is due to the presence of bacteria.Nicklin,2008[12], studies living with the threat of microbiologically influenced corrosion in submarine seawater system. Role of direct microbial electron transfer in corrosion of steels had been studied by Maha Mehanna et.al., 2009[13], the result showed G.sulfurreducens revealed here as a main player in electron transfer between 304L stainless steel and the surrounding medium and the corrosive/ protective action of G.sulfurreducens on steel surfaces depends strongly on the potential range and the age of the biofilm.Reza,2009[14] , studies a brief review of general patterns of MIC of carbon steel and biodegradation of concrete. Determining if Microbiologically Influenced Corrosion is responsible for the accelerated loss of port transportation

infrastructure had been presented by Randall et.al. ,2009[15], the results shows the roles of iron oxidizing and sulfate reducing bacteria in microbiologically influenced corrosion of steel structures in the Duluth – Superior harbor on Lake Superior in northern Minnesota. Characterization of corrosive bacterial consortia isolated from petroleum – product – transporting pipelines had been studies by Aruliah Rajasekar et.al., 2010[16] , the samples obtained from the diesel and naphtha - transporting pipelines showed the occurrence of 11 bacterial species , sulfate – reducing bacteria were not detected in samples from both pipelines.Comparative study of microbiologically influenced corrosion of stainless steels in reclaimed water in power plant had been studies by LI Jin et.al. , 2010[17] , the results show that this strain of SRB can survive in reclaimed water. Microbial communities in petroleum pipeline and its relationship with bio – corrosion had been presented by Aruliah et.al. , 2011[18], the results shows iron bacteria , acid producers , manganese oxidizing bacteria emolithotrophic bacteria was noticed in diesel pipeline .Inhibition and control of microbiologically influenced corrosion in oilfield materials had been studied by Akpabio,2011[19], the results shows that pre-characterization of the MIC-microorganisms assists the engineer and scientist in the effective control of microbiologically induced corrosion by helping to select an inhibitor which will act as a biocide and not a nutrient source.

The aim of this study was to evaluate the role of bacteria on the microbiologically Influenced corrosion of the carbon steel .

Experimental

Table 1 shows the chemical composition of the carbon steel . Disk samples (2mm thick and 15mm diameter) of carbon steel used in the linear polarization resistance and weight loss method for corrosion analyses .The samples are ground using paper grits as (180 , 400 ,600 , 800 ,1000 ,1200 and 2000) and polished with natural diamond size 0.1 micron with lubricating oil for lapping with diamond paste code PL0001 at room temperature by using polished instrument type (Hergon – mp 200V). After this state all samples were washed by distilled water and drying using electric drier.

Pickling

The purpose of pickling process is to remove rust and scales from the degreased surface, the composition of acid is used for the carbon steel samples is (3% HCl) by volume at room temperature for (2min.) after the pickling process all samples were washed by distilled water and alcohol and drying using electric drier .

The microbiologically induced corrosion test is done in river water and water control (distilled water).

Corrosion Analyses

Linear polarization Resistance

The tester consists of electrochemical corrosion test cell . The cell made from materials anti-corrosion as glass and the shape of the cell was semi- spherical with volume 1000 ml. The cell contains three electrodes are : Working electrode , Auxiliary electrode and reference electrode . In this study river water and water control (distilled water) solution was used. The polarization curve of anodic and

cathodic regions has been automatically control by computerized Potentionstat used the program Bank-Elechtionies. Potentistat type(Mlab 200 Banch Elektronik GMP, Germany ,2008 with SIC electrochemical sonfnat calculation) was used to test electrochemical corrosion as shown in Fig. 1.

Weight Loss Method

The samples were weighted before immersion in the water using ± 0.0001g accuracy electric balance , and after(15;30) days of immersion, the samples removed from the water and weighted. The corrosion rates of the metal are calculated in mils per year according to the following formula : the corrosion rate is calculated assuming uniform corrosion over the entire surface of the sample[19]

Corrosion rate = wk/AtD

Where:

W= Weight loss (g),K= 3450000 (corrosion rate in mils per year),t= time of exposure (h),A = Expanded surface area (cm^2),D= Density of metal sample (g cm^{-3}).

Microstructure Examination

Light optical microscope type (Union ME-3154) with fitted digital camera is used for imaging of specimen surfaces before and after corrosion tests.

Roughness Test

This test is applied to measure surface roughness of carbon steel and aluminum alloy before and after immersion for (15 and 30) days in reveries and control water by using surface roughness tester type (Hand-held Roughness Tester TR200 , by Time Group Inc.).

X-Ray Diffraction Analysis

The test carried out through scanning the specimen continuously within Bragg angle (2θ) range (10º-60º) using Cu target at voltage of 40 *kV* and 30 *mA* of current with continuous scan mode, range (10.000-60.000) degree. Sample of carbon steel after immersion in control water has been identified by X-ray diffraction technique in order to compare these diffraction patterns with sample of carbon steel after immersion in rivers water. The X-ray is generated by general electric diffraction type (Lab X,SHIMADZU,XRD-6000,X-RAY DIFFRACTOMETER) operating at scanning speed of 5.0000 deg/min.

Microbiological Analyses

Sampling (Collection of Samples)

Water was sampled in (1L) polyethylene containers and used in the experiments within 15 and 30 days , Samples of water (1L) were taken from Hilla river and control water for each sample of carbon steel . The river water samples were not prefiltered or sterilized before use in the experiments. Carbon steel immersion in (1L) of river water for 15 and 30 days and then swaps of biofilm taken and culturing on suitable medium.

Isolation and Identification

Bacteria isolated after culturing on nutrient agar (24hr.) and the diagnosing depending on the appearance factors (Microscopic and Culturing factors) and biochemical tests (Catalase production , Oxides production , Lipase production, Pyocyanin prod ,Geiatin liqufication, Starch test, Motility test, Indole test, Methyl red test, Voges proskauer test, Citrate utilization , Nitrate reduction).

Result and Discussion :

Corrosion Analyses :

Linear polarization Resistance :

Fig 2 and fig3 show the potentiostatic curves between potential and current density for carbon steel immersion in control water for 15 and 30 days respectively ; table 2 shows the corrosion current observed by using the tafel polarization method of the carbon steel immersion in control water after 15 and 30 days. Potentiostatic curves of carbon steel immersion in rivers water after 15 and 30 days shown in fig 4 and fig 5 ;table 3 shows the corrosion current observed by using the tafel polarization method of the carbon steel immersion in rivers water after 15 and 30 days. From the result of tables 2 and 3, the corrosion current of carbon steel in rivers water after 15 and 30 days 15.02µA ,18.48µA is much greater than for carbon steel in control water after 15 and 30 days 5.51µA,12.55µA.

Carbon steel is a relatively less resistant material to microbiological influenced corrosion so that when it is corrode the voluminous corrosion products thus produced can create areas of local low- and high –oxygen partial pressure so that areas with low partial pressure of oxygen become anodes and those having a relatively high partial pressure can form cathodes[14]. In this way, by establishment of differential aeration cells, the corrosion of the steel is initiated and/or accelerated.

Weight Loss Method

The corrosion rate of carbon steel in control water obtained from the weight loss study is shown in table 4 ,the corrosion rates of carbon steel were 1.632mpy , 1.958mpy at 360 h and 720 h respectively. Table 5 shows the corrosion rate of carbon steel in rivers water obtained from the weight loss study, the corrosion rates of carbon steel were 4.516 , 4.720 at 360 h and 720 h respectively.

Comparing the corrosion rates result in table 4 and table 5 it is noticed that the corrosion rate of carbon steel in rivers water is approximately (2.767) times more than that in control water for 360 h; furthermore the corrosion rate of carbon steel in the rivers water is approximately (2.41) times more than that in control water for 720 h.

In aerated environment areas of the met.al. surface between the columnar structures of the biofilm may be in contact with oxygenated electrolyte. These areas with relatively high oxygen concentrations within the biofilm are cathodic relative to areas with less oxygen. Beneath a microbial colony, oxygen is depleted as it is used by the organisms in their metabolism. Oxygen from the bulk electrolyte is unable to replenish those areas because of a combination of effects. First , oxygen migration through the film is slowed by the diffusion barrier effect, and second , oxygen that does penetrate the film is immediately used by the microbial metabolism, formation of such corrosion cell cause a pit to form at the anodic area under the bacterial colony[1]. Schematic of pit initiation and tubercle formation on the carbon steel under a biological deposit shown in fig (6)[1] . As the pit grows , iron dissolves according to the anodic reaction:

$$Fe \rightarrow Fe^{2+} + 2e$$

The cathodic reaction is reduction of dissolved oxygen out side the pit to form OH^- according to[1]

$$O_2 + 2H_2O + 4e^- \rightarrow OH$$

The insoluble ferrous hydroxide corrosion product forms by the reaction[1] :

$$3Fe^{2+} + 6OH^- \rightarrow 3Fe(OH)_2$$

Microstructure Examination

The microstructure of carbon steel that used in this study before corrosion shown in fig7 . Microstructure of carbon steel immersion in the control medium after 15 and 30 days shown in fig 8a,8b respectively ; microstructure of carbon steel immersion in the rivers water medium after 15 and 30 days shown in fig 9a,9b respectively .

Clearly from the results of the microstructure examination , the period and medium of immersion play important role in the degree of corrosion as shown in figures 8a,8b , and 9a,9b . Also the number ,size and diameter of cavity on the surface of the carbon steel that caused by corrosion differs from medium to another as well as to the time of immersion.

Roughness Test

Tables 6 and 7 show the results of surface roughness test of carbon steel before and after immersion for 15 and 30 day in control and rivers water respectively. Cleary from the results of the surface roughness test appears increased in the surface roughness of samples carbon steel immersion in river water compared with surface roughness number in control water , and this ensure the role of river water components in effect and causes of cavity and pits that result from the corrosion processes.

X-Ray Diffraction Analysis

X-ray diffraction patterns for carbon steel sample immersion in control and rivers water are shown in fig10 and fig 11 respectively; (FeO(OH), $Fe(OH)_2$,$Fe(OH)_3$) were noticed in the fig10 and fig11.The study of X-ray beaks indicate the presence of (FeO(OH) and $Fe(OH)_2$) on the surface of carbon steel and the large number of peaks due to iron hydroxide formed on the carbon steel samples after immersion in rivers water compared with in control water ; because the presence of bacteria in rivers water (source of biofilm) it is likely for the differential aeration cells to be established and contribute to the formation of anodic and cathodic sites. However, formation of differential aeration cells is not the only mechanism by which corrosion is enhanced. Normally in the system such as water contaminated with bacterial species , the biofilm formed ,more or less, resembles a poor coating where corrosion is enhanced by formation of differential concentration cells in addition to differential aeration cells[14].

Microbiological Analyses:

Biofilm Formation

The ability of an organism to survive on a surface and to influence corrosion is often related to associations between that organism and those of other species, the bacteria implicated in corrosion may begin their lives on a metal surface as a scatter of individual cells. Immersion of any solid surface in a natural environment , such as fresh water from rivers initiates a continuous and dynamic process, beginning with adsorption of nonliving, dissolved organic material and continuing through the formation of bacterial films. The process of colonization begins immediately on immersion with adsorption of a nonliving organic conditioning film. This conditioning film is nearly

complete within the first 2h of immersion, at which time the initially colonizing bacteria begin to attach in substantial numbers[1,20]. The bacterial film develops over a period of 24 to 72 h in must natural water as shown in fig 12b compared with fig 12a.Fig 13 shows the biofilm formed on carbon steel after immersion in rivers water after 30 days; from the figure the surface of carbon steel samples has covered with non-uniform structure of the biofilm it is likely for the differential aeration cells to be established and contribute to the formation of anodic and cathodic sites.

Microscoping Test

Small Bacilli negative gram strain(G-ve) bacteria appears under the microscope

Culturing Test

Growthing colonies on solid nutrient agar (24hr.,27°C) were small colonies with (2.5mm) in diameter, have mucin appearance and green pigments (pyocyanin production) as shown in fig 14.

Biochemical Test

Table 8 shows the result of the biochemical test of the culture (Catalase production , Oxidas production , Lipase production, Pyocyanin prod ,Geiatin liqufication, Starch test, Motility test, Indole test, Methyl red test, Voges proskauer test, Citrate utilization , Nitrate reduction). From the table, all the cultures produce *Pseudomonas aeruginosa* bacteria production was highest with culture , the culture (Oxides, Growthen Mac Conkey ager,Catalase,Pyocyanin ,Geiatin liguficution and Citrate Utilization) was positive , (Gram , strch ,Indole,Methyl red and Voges proskauer) was negative , (Nitrate Reduction and Lipase Production) was un stable and it was motile.

Based on these characteristics of the (Microscopic, Culture and Biochemical tests) was tentatively identified as *Pseudomonas aeruginosa* bacteria.

Conclusions

According to result of present study , the following can be concluded :

1- It is clear from this study that the corrosion rate of carbon steel in rivers water more higher than in control water.

2- Corrosion current of carbon steel in rivers water more than in control water.

3- *Pseudomonas aeruginosa* bacteria isolated from the corrosion product.

4- The activities of biofilm play important role in degree of corrosion.

5- Biofilm mediate interactions between met.al. surface and liquid environment leading to major modifications of met.al. – solution interface by drastically changing the concentration of ion and oxygen levels.

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Table (1) shown chemical composition of sample used.
Ref. State Company for Mechanical Industries.

Alloy	%C	%Cr	%Mn	%Si	% Fe
Carbon- steel	0.05	0.07	0.45	0.29	99.06

Table (2) Corrosion rate of samples by Linear polarization Resistance(Control water).

Alloy	Immersion period (days)	Slope1 (mv/Dec)	Slope 2 (mv/Dec)	$E_{Corr.}$ (mV)	$I_{Corr.}$ (µA)
Carbon-steel	15	39.60	-35.80	-511.50	5.51
Carbon-steel	30	80.30	-101.80	-601.20	12.55

Table (3) Corrosion rate of samples by Linear polarization Resistance(Rivers water).

Alloy	Immersion period (days)	Slope 1 (mv/Dec)	Slope 2 (mv/Dec)	$E_{Corr.}$(mV)	$I_{Corr.}$ (µA)
Carbon-steel	15	-65.40	65.20	-483.10	15.02
Carbon-steel	30	63.50	-151.20	-588.00	18.48

Table (4) Corrosion rate of samples by weight loss method (Control water) .

Alloy	Immersion period (h)	Density (g/cm^3)	Expended area (cm^2)	Weight loss (g)	Corrosion rate (mpy)
Carbon- steel	360	7.870	4.476	0.006	1.632
Carbon-steel	720	7.870	4.476	0.0144	1.958

Table (5) Corrosion rate of samples by weight loss method (Rivers water).

Alloy	Immersion period (h)	Density (g/cm^3)	Expended area (cm^2)	Weight loss (g)	Corrosion rate (mpy)
Carbon- steel	360	7.87	4.476	0.0166	4.516
Carbon- steel	720	7.87	4.476	0.0347	4.720

Table (6) Number of surface roughness of carbon steel before and after immersion in control water .

Solution	Immersion period (days)	No. of Roughness (µm)
--------	……..	0.002
Control Water	15	0.568
Control Water	30	0.964

Table (7) Number of surface roughness of carbon steel before and after immersion in rivers water .

Solution	Immersion period (days)	No. of Roughness (µm)
--------	……	0.002
Rivers Water	15	1.260
Rivers Water	30	2.521

Table (8) Biochemical tests results of the culture

Test	Result
Grams strain	G-ve-
Morphology	Bacilli
Growth Mac Conkey agar	+
Catalase production	+
Oxidase production	+
Lipase production	-/+
Pyocyanin production	+
Geiatin liqufication	+
Starch test	-
Motility test	+
Indole test	-
Methyl red test	-
Voges proskauer test	-
Citrate utilization	+
Nitrate reduction	-/+

Figure (1) Potentiostatic equipment

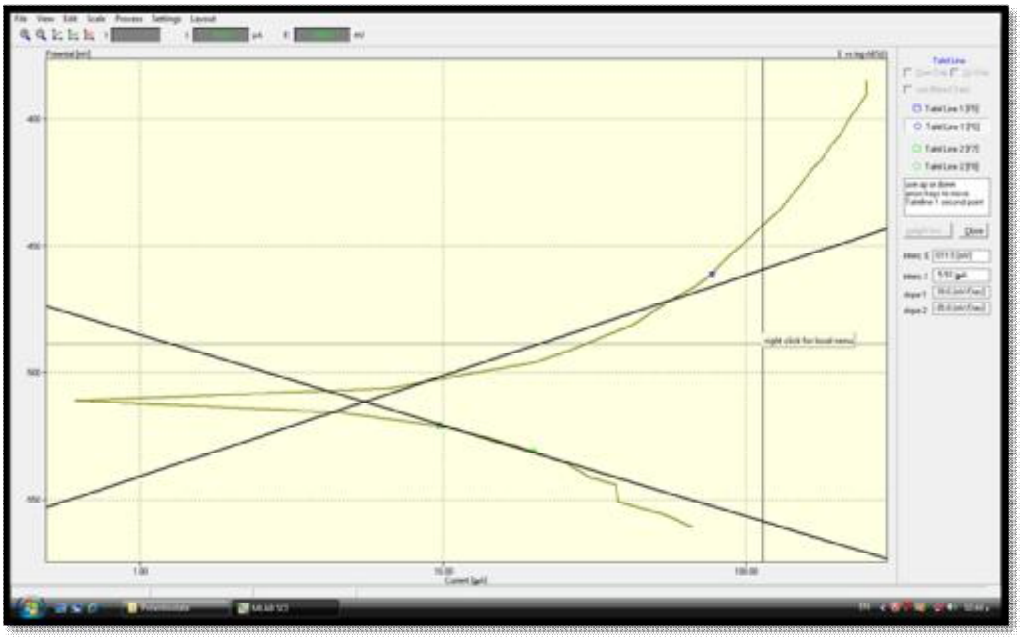


Figure (2) Polarization curve for carbon steel sample immerse in control media for 15 days.

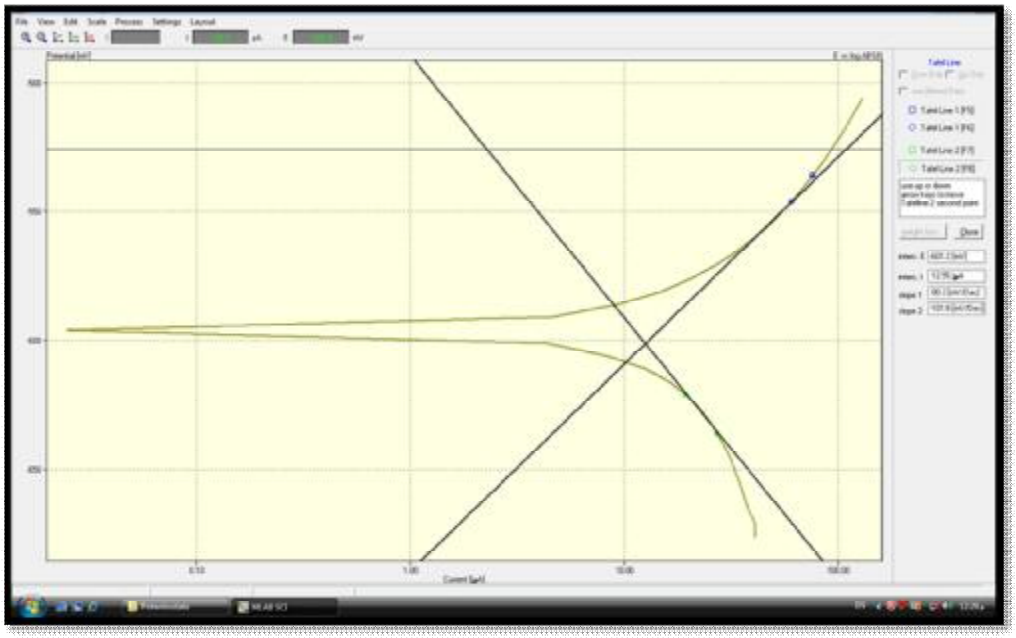


Figure (3) Polarization curve for carbon steel sample immerse in control media for 30 days.

Figure (4) Polarization curve for carbon steel sample immerse in rivers media for 15 days.

Figure (5)Polarization curve for carbon steel sample immerse in rivers media for 30 days.

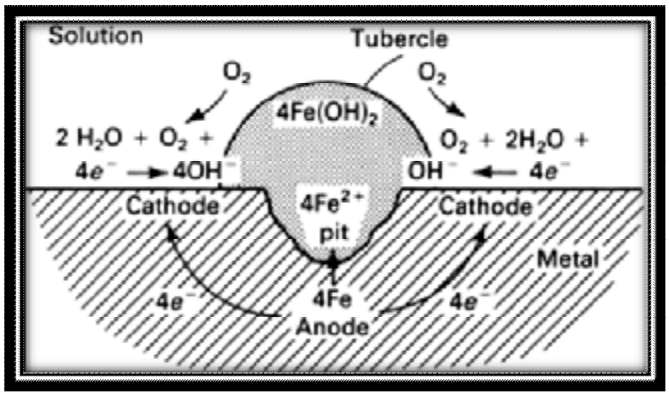


Figure (6) Schematic of pit initiation and tubercle formation under biological deposit[1].

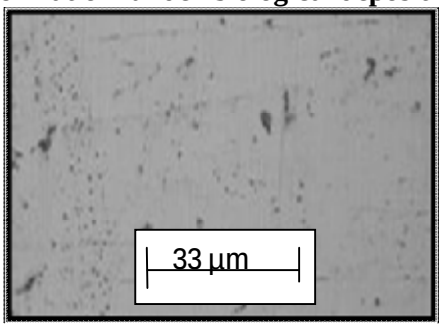
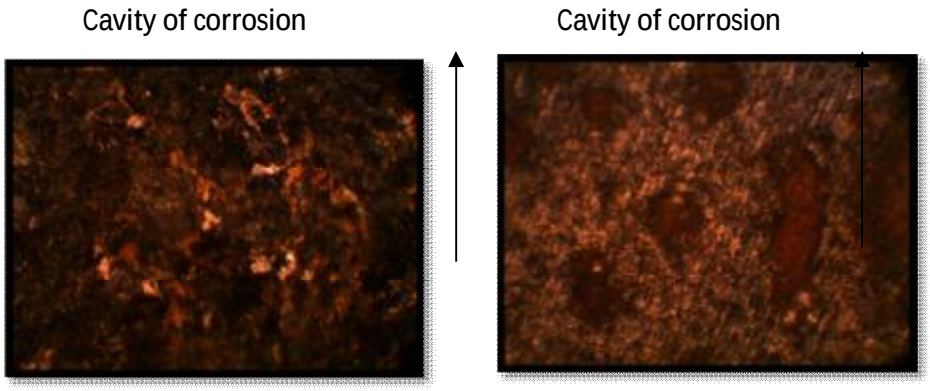
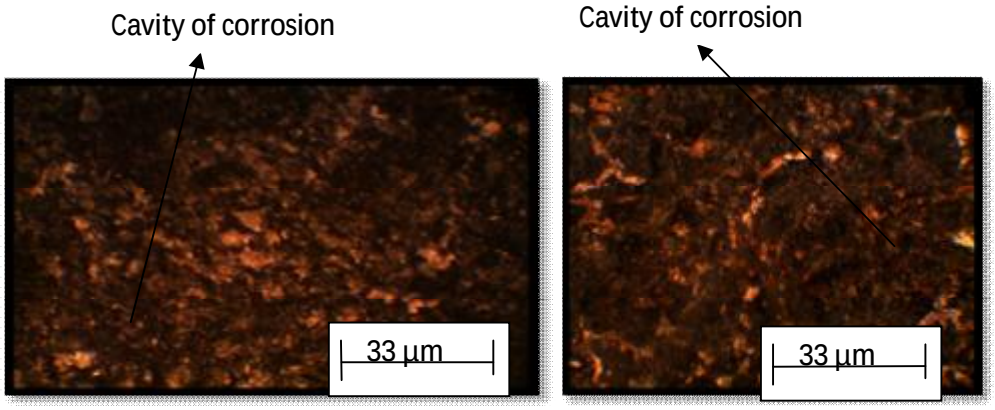


Figure (7) Surface of carbon steel before immersion in media.



-a- -b-

Figure (8) a Surface of carbon steel after immersion in control water for 15 days.
Figure(8) b Surface of carbon steel after immersion in rivers water for 15 days.



-a- -b-

Figure (9) a Surface of carbon steel after immersion in control water for 30 days.
Figure (9) b Surface of carbon steel after immersion in rivers water for 30 days.

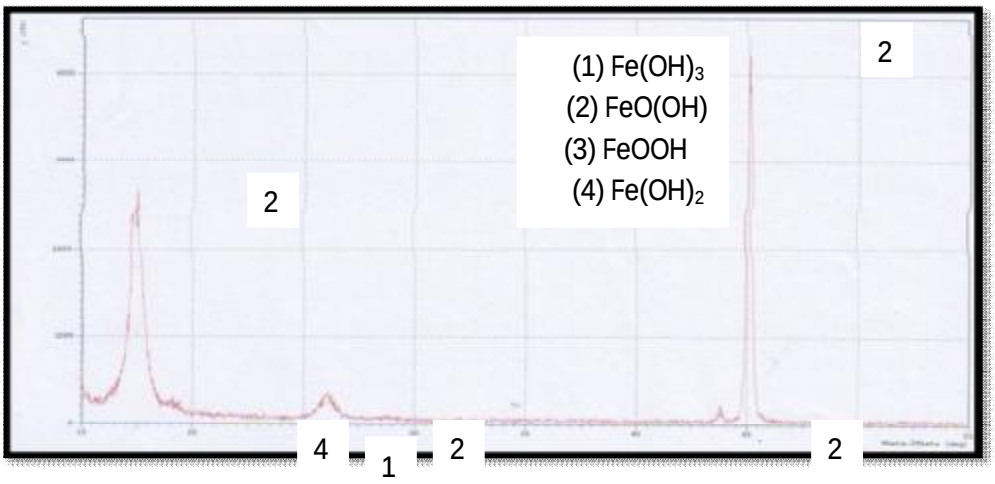


Figure (10) XRD patterns for carbon steel after immersion in control water.

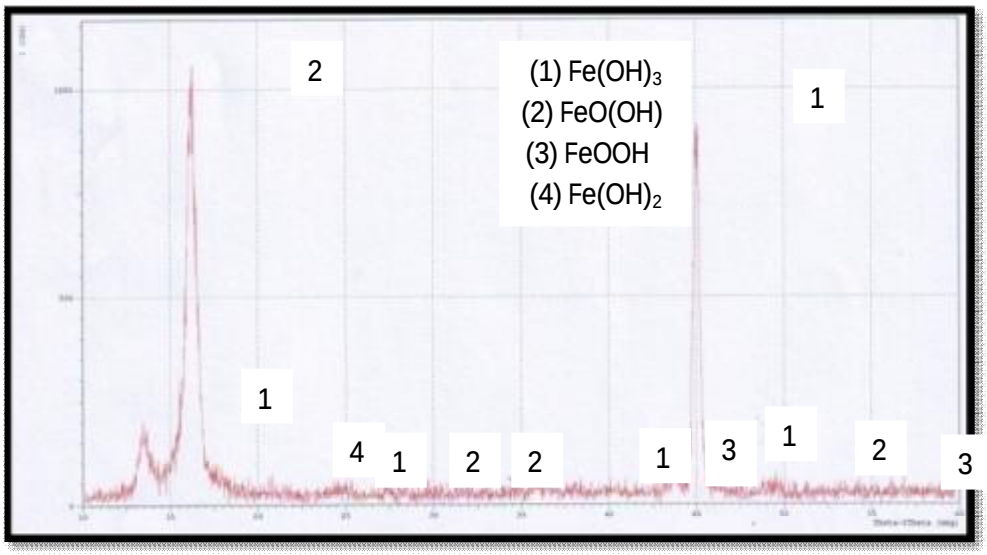
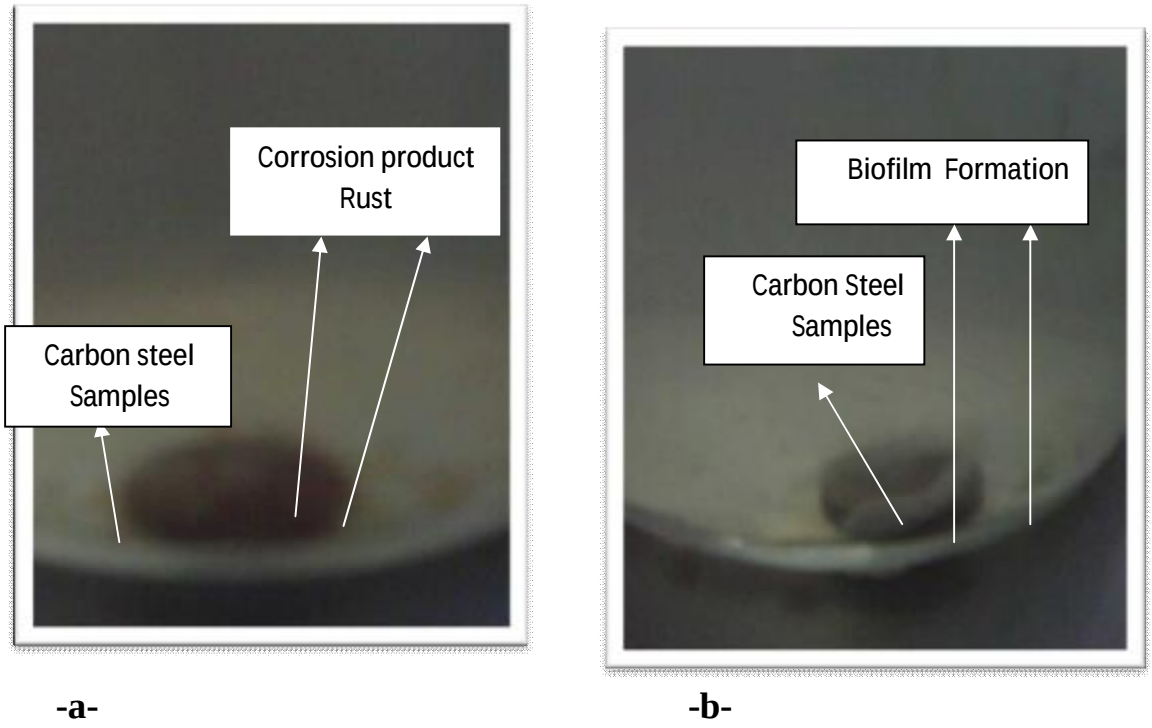


Figure (11) XRD patterns for carbon steel after immersion in rivers water .



-a- -b-

Figure (12) Samples of carbon steel after immersion in control media after 30 days

Figure (12) b Sample of carbon steel after immersion in rivers water after 30days.

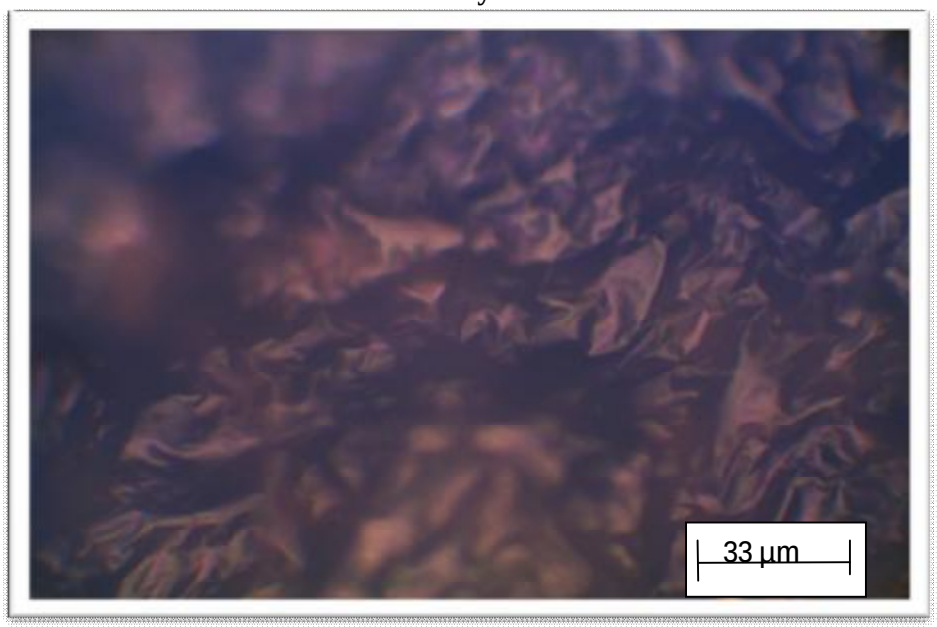


Figure (13) Biofilm formed on carbon steel after

immersion in rivers water after 30 days.

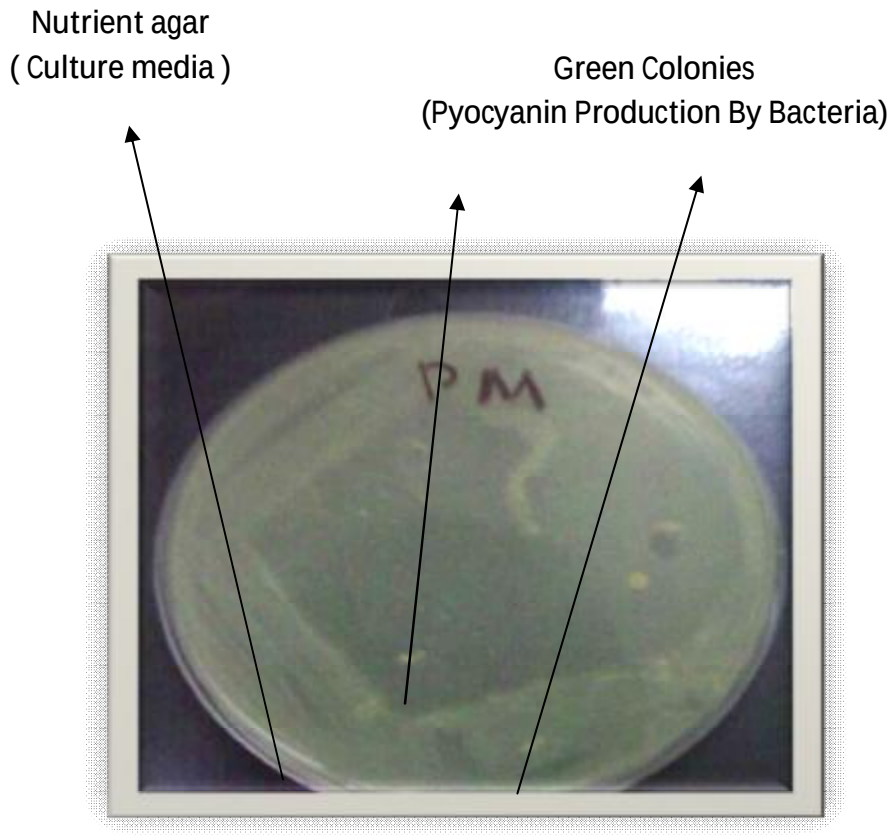


Figure (14) Pyocyanin production(Green Pigment) by bacteria on the culture in Petridish.