

Research Article

Modelling of Double-Layer Capacitance Based Sensor of The Growth of Marine Bio-Films of Metallic Alloys in Seawater

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SUMMARY

Experimental data of electrochemical impedance spectroscopy (EIS) were used for the first time to predict (model) the growth of the marine biofilm on the surface of two metallic alloys in seawater. The EIS data, i.e., double-layer capacitance (Cdl), of UNS 1020 carbon steel and stainless steel UNS S304 were used in this study. The Cdl values of the formed biofilm on the alloys were measured in seawater on a frequent basis. The total exposure of the alloys to the seawater was ranged between 90 days to 180 days. The carbon steel was found susceptible to microbiologically influenced (induced) corrosion (MIC). A mathematical model was derived to simulate a double-layer capacitance sensor to gradual predict the growth of the biofilm formation by correlating the obtained Cdl of the biofilm to the thickness of the biofilm formation. The mathematical correlation was based on taking into the account parameters such as; the dielectric constant of the formed biofilm, the dielectric constant of the seawater at two temperatures 18 °C and 33 °C, the volume fraction of the seawater in the biofilm, the dielectric constant of corrosion products, i.e., ferrous oxides; FeO, Fe₂O₃, magnetite; Fe₃O₄, iron oxide-hydroxide; FeOOH, Ferromanganese ;a mixture of MnO₂ and Fe₂O₃, Ferrous sulfate; Fe₂SO₄, Ferrochromium; FeCr, in the biofilm, and

the volume fraction of those corrosion products in the biofilm. The calculated thickness of the biofilms was in the range of a nanometer to a fraction of micrometer.

Keywords: *Microbiologically influenced corrosion (MIC); Electrochemical impedance spectroscopy (EIS); Mathematical correlation; Seawater; Double-layer capacitance (Cdl).*

Introduction

It has been widely known that marine biofouling of metal surfaces in contact with seawater is the main cause of several technical problems and economic loss in industry. Marine biofouling is defined as the community of organisms found growing on permanently submerged surfaces of objects in seawater. It has been reported that a total of 84 species of fouling organisms belonging to 69 genera, 49 families, and 10 phyla were recorded over the entire year dependent on the temperature of the seawater¹. The growth of this community usually interferes with the efficient use of the surfaces. For example, the organism is known to reduce the flowing of the fluids through the pipelines, to reduce the heat transfer in the heat exchanger systems, to reduce the ship's speed and encrusting of the support legs of oil rigs²⁻³. Marine micro fouling is defined as the growth of micro-organisms at metal–solution interfaces. Also, marine micro fouling can be even up to a few micrometers thick. It is known that marine micro fouling reduces heat transfer coefficient in heat exchange systems by as much as 40% besides causing what is known as microbiologically induced corrosion (MIC)⁴⁻⁵. Different types of bacteria cause corrosion by various mechanisms ranging from formation of differential aeration cells to production of aggressive environments through chemical changes⁶. It is expected that the seasonal changes in the Gulf seawater will have an effect on the MIC, due to the growth of the marine biofouling film at metal–solution interfaces. In other words, the growth of the marine biofouling film at metal–solution interfaces would control the corrosivity of the submerged metals in seawater.

In this study, modelling of the growth of the marine biofouling film at metal–solution interfaces will be carried out on the UNS 1020 carbon steel and stainless steel 304 samples. The growth of the marine biofouling film of both the alloys will be predicted by obtained experimental data of EIS measurements for a period of 6 months under a continuous flowing seawater condition. The prediction of the growth of the biofilm will take into the account parameters such as; the dielectric constant of the formed biofilm, the dielectric constant of the seawater at two temperatures 18 °C and 33 °C, the volume fraction of the seawater in the biofilm, the dielectric constant of corrosion products, i.e., FeO, Fe₂O₃, Fe₃O₄, FeOOH, Ferromanganese ;a mixture of MnO₂ and Fe₂O₃, Fe₂SO₄, and Ferrochromium FeCr in the biofilm, and the volume fraction of those corrosion products in the biofilm.

Theoretical Analysis

In literature, the relationship between the A.C. Impedance (Z) and the double layer capacitance (Cdl) of a developed film on a metal sample to the thickness of the formed film is given as the Following⁷⁻⁸ :

$$|Z| = 1 / Cdl = L / (\epsilon \epsilon_0 A) \quad (1)$$

Where:

Z is the A.C. impedance of the formed film, Ohm.cm².

Cdl is the Double layer capacitance of the formed biofilm, μ F.

ϵ_0 is the permittivity of the free space, 8.85 X 10⁻¹⁴ Farad/cm.

A is the area of the sample that exposed to the seawater, 1cm².

L is the thickness of the formed biofilm, nm, which can be obtained here by EIS, via Equ. (1).

ϵ is the static dielectric constant of the material under the investigation, of the biofilm.

In recent investigation of the author⁹, the dielectric constant of the biofilm has been extended to account for the volume fraction of the seawater in the film, as biological membrane¹⁰⁻¹¹. So;

$$\epsilon = (\epsilon_{bf} + v_{sw} \epsilon_{sw}), \text{ where} \quad (2)$$

ϵ_{bf} is the dielectric constant of the formed biofilm; $\epsilon_{bf} = 5$, when the pore fraction is equal to 0, an adhered thin layer¹⁰⁻¹¹.

ϵ_{sw} is the dielectric constant of the seawater, $\epsilon_{sw} = 70.2$ at 18°C ¹² and $\epsilon_{sw} = 67.4$, at 33°C ¹².

v_{sw} is the volume fraction of the seawater in the film. The value of $v_{sw} = 50\%$ and 75% will be considered in the film as the film grows outward of the surface of the alloys. The value of $\epsilon_{sw} = 70.2$ at 18°C ¹² will be considered at an exposure time of 0,1,5,10,20,30,60,90 days, from the November to February season. Furthermore, the value of $\epsilon_{sw} = 67.4$ at 33°C ¹² will be considered at an exposure time of 130,150,180 days, from the March to May season.

In the present work, the dielectric constant (ϵ) of the bio-film (Equ.2) has been further extended to account for not only the volume fraction of the seawater in the film, the dielectric constant of the seawater at two temperatures 18°C and 33°C , and the volume fraction of the seawater in the biofilm, but also to take into consideration the dielectric constant of corrosion products (ϵ_{cp}), i.e., FeO, Fe₂O₃, Fe₃O₄, FeOOH, Ferromanganese ; a mixture of MnO₂ and Fe₂O₃, Fe₂SO₄, and Ferrochromium FeCr, in the biofilm, and the volume fraction (v_{cp}) of those corrosion products in the biofilm. So Equ.2 becomes.

$$\epsilon = (\epsilon_{bf} + v_{sw} \epsilon_{sw} + \sum v_{cp} \epsilon_{cp}) \quad (3)$$

where,

$\sum v_{cp} \epsilon_{cp}$ is the summation of the number of the dielectric constant of the corrosion products (ϵ_{cp}) time the volume fraction of the corrosion products (v_{cp}). By substituting for the value of ϵ in Equ. 3 into Equ.1, and solving for the thickness of the biofilm (L), the value of L becomes:

$$L = \{(\epsilon_{bf} + v_{sw} \epsilon_{sw} + \sum v_{cp} \epsilon_{cp}) / (\epsilon_0 A)\} / Cdl \quad (4)$$

Therefore, It is expected that the corrosion products in the formed biofilm of the UNS 1020 carbon steel samples^{5-6,13} will be FeO, Fe₂O₃, Fe₃O₄, FeOOH, Ferromanganese; a mixture of MnO₂ and Fe₂O₃, and Fe₂SO₄ based on the composition of the steel samples; 0.18-0.23% C, 0.3-0.6% Mn, and balanced of Fe. Likewise, it is expected that the corrosion products in the formed biofilm of the UNS S304 stainless steel samples will be Ferromanganese (a mixture of MnO₂ & Fe₂O₃) and Ferrochromium; FeCr based on the composition of the stainless steel samples; 18-20% Cr, 8-12% Ni, 2% Mn, 1% Si, 0.08% C, and balance of Fe. The values of ϵ_{cp} of the corrosion products at room temperature can be obtained from the literature¹⁴: ϵ_{cp} of FeO=14.2; ϵ_{cp} of Fe₂O₃=14.2; ϵ_{cp} of Fe₃O₄=14.2; ϵ_{cp} of FeOOH=14.2; ϵ_{cp} of Fe₂SO₄=14.2; an average value of ϵ_{cp} of a mixture of the oxides MnO₂ and Fe₂O₃(Ferromanganese)= 5.1; and an average value of ϵ_{cp} of FeCr: Ferrochromium= 1.65.

In addition, the value of the volume fraction (v_{cp}) of corrosion products in the biofilm at UNS 1020 carbon steel samples is assumed around 3% and 5% for an accumulation of FeO, Fe₂O₃, Fe₃O₄, FeOOH and Fe₂SO₄ with respect to the volume fraction of seawater (v_{sw}) of 50% and 75%, respectively. In addition, the value of the volume fraction (v_{cp}) of corrosion products in the biofilm at UNS S304 stainless steel samples is assumed 1% and 3% for

each of Ferromanganese; a mixture of MnO₂ and Fe₂O, and FeCr with respect to the volume fraction of seawater (vsw) of 50% and 75%, respectively.

Consequently, Equ.4 describes the relationship between the double layer capacitance of the biofilm (from EIS) and the thickness of the biofilm which accounts for the volume fraction of the seawater in the film, the dielectric constant of the seawater at two temperatures 18oC and 33 oC, the volume fraction of the seawater in the biofilm, the dielectric constant of corrosion products (ecp), i.e., FeO, Fe₂O₃,Fe₃O₄, FeOOH, Ferromanganese ;a mixture of MnO₂ and Fe₂O₃, Fe₂SO₄ , and Ferrochromium FeCr, in the biofilm, and the volume fraction (vcf)of those corrosion products in the biofilm.

Mathematical Modelling

EIS data⁹ of metallic samples of UNS 1020 carbon steel (0.18-.23% C, 0.3-0.6% Mn, and balanced of Fe), and UNS S304 stainless steel (18-20% Cr, 8-12% Ni, 2% Mn,1% Si, 0.08% C, and balance of Fe) were used. Those two alloys have been selected in this study because of their common applications in seawater¹⁵. The output data of EIS were the Nyquist and Bode plots¹⁶⁻¹⁸. From these plots, values of double layer capacitance C_{dl} were obtained. A simple Randles circuit was used for interpreting the EIS data. The Randles semicircle was used for data fitting of the experimental results. The acquired electrochemical data (C_{dl}) were obtained from 11 tests in 180 days of exposure to seawater (0,1,5,10,20, 30,60,90,120, 150, and 180 days) for each alloy. The temperature of the seawater during the tests was varied from 18 °C in winter days to 33°C in the summer days. Also, the resistance of the seawater has an average value of 8 Ohms cm². Details on the experimental procedures can be obtained elsewhere⁹. The obtained data of the C_{dl} and the calculated of L of the biofilm, from Equ.(4), for the UNS 1020 carbon steel and stainless steel UNS S304, stainless steel are given in Table 1-3. The value of L was calculated as a function of the volume fraction of seawater in the biofilm, vsw =0,50,75%, and the dielectric constant of the seawater at different temperature, esw =70.2 at 18^oC (November to February) & esw =67.4 at 33oC (March to May). Tables 1, 2, and 3 contain the calculated L of the biofilm of both alloys in seawater, when vsw =0%, vsw =50%, vsw =75%, respectively. Table 1 contains the data of C_{dl} and L of the biofilm without corrosion products for both alloys. In contrast, Table 2 & and 3 contain the data of C_{dl} and L of the biofilm with corrosion products for both alloys.

Table 1: The EIS data of C_{dl} & calculated L of the biofilm of both alloys in seawater, vsw =0%.

Materials	Carbon Steel		Stainless Steel 304	
	C _{dl} (□F)	L (nm)	C _{dl} (□F)	L (nm)
Exposure Time (days)				
0	0.25	18	1.78	2.5
1	4.4	1	1.23	3.6
5	8.5	0.5	1.26	3.5
10	0.158	30	-	-
20	0.214	21	1.38	3.2
30	0.195	23	1.33	3.3
60	0.216	20	3.97	1.1

90	0.25	18	0.62	7.1
120	-	-	1.3	3.4
150	-	-	0.89	5
180	-	-	1.55	1

Table 2—The EIS data of C_{dl} & calculated L of the biofilm (ebf =5) of both alloys in seawater, v_{sw} =50% and e_{sw} =70.2 at 18°C (0,1,5,10,20,30,60,90 days) & e_{sw} =67.4 at 33°C (120,150,180 days), alongside v_{cp}=3% & e_{cp} =14.2 for the accumulation of FeO, Fe₂O₃, Fe₃O₄, FeOOH and Fe₂SO₄ in the biofilm at the steel samples & v_{cp}=1% & e_{cp} =5.1 for the accumulation of Ferromanganese ;a mixture of MnO₂ and Fe₂O, and v_{cp}=1% & e_{cp} =1.65 for the FeCr in the biofilm at the stainless steel samples.

Materials	Biofilm at carbon Steel with no corrosion products		Biofilm at stainless steel 304 with no corrosion products		Biofilm at carbon Steel with an accumulation of 3% corrosion products		Biofilm at stainless Steel with an accumulation of 1% of a mixture of MnO ₂ and Fe ₂ O, and 1% of FeCr		
	Exposure Time (days)	C _{dl} (□F)	L (nm)	C _{dl} (□F)	L (nm)	C _{dl} (□F)	L (nm)	C _{dl} (□F)	L (nm)
	0	0.25	142	1.78	19.9	0.25	143.5	1.78	20
	1	4.4	8	1.23	28.9	4.4	8.15	1.23	29
	5	8.5	4.1	1.26	28.2	8.5	4.22	1.26	28.2
	10	0.158	224.7	-	-	0.158	227	-	-
	20	0.214	165.9	1.38	25.7	0.214	167.6	1.38	25.8
	30	0.195	182	1.33	26.7	0.195	184	1.33	26.73
	60	0.216	164.3	3.97	8.9	0.216	166	3.97	8.95
	90	0.25	142	0.62	57.3	0.25	143.5	0.62	57.3
	120	-	-	1.3	25.7	-	-	1.3	26.4
	150	-	-	0.89	37.5	-	-	0.89	38.6
	180	-	-	1.55	21.5	-	-	1.55	22.4

Table 3—The EIS data of Cdl & calculated L of the biofilm of both alloys in seawater, vsw =75% and esw =70.2 at 18°C (0,1,5,10,20,30,60,90 days) & esw =67.4 at 33°C (120,150,180 days), alongside vcp=5% & ecp =14.2 for the accumulation of FeO, Fe2O3, Fe3O4, FeOOH and Fe2SO4 in the biofilm at the steel samples & vcp=3% & ecp =5.1 for the accumulation of Ferromanganese ;a mixture of MnO2 and Fe2O, and vcp=3% & ecp =1.65 for the FeCr in the biofilm at the stainless steel samples.

Materials	Biofilm at carbon Steel with no corrosion products		Biofilm at stainless steel 304 with no corrosion products		Biofilm at carbon Steel with an accumulation of 5% corrosion products		Biofilm at stainless Steel with an accumulation of 3% of a mixture of MnO ₂ and Fe ₂ O, and 3% of FeCr	
	C _{dl} (□F)	L (nm)	C _{dl} (□F)	L (nm)	C _{dl} (□F)	L (nm)	C _{dl} (□F)	L (nm)
Exposure Time (days)								
0	0.25	204.1	1.78	28.7	0.25	207	1.78	28.8
1	4.4	11.6	1.23	41.5	4.4	11.74	1.23	40.62
5	8.5	6	1.26	40.5	8.5	6.1	1.26	40.63
10	0.158	323	-	-	0.158	327	-	-
20	0.214	238.4	1.38	37	0.214	241.3	1.38	37.1
30	0.195	261.6	1.33	38.4	0.195	264.9	1.33	38.5
60	0.216	236.3	3.97	12.8	.216	239.1	3.97	12.9
90	0.25	204.1	0.62	82.3	0.25	207	0.62	82.6
120	-	-	1.3	37.8	-	-	1.3	37.95
150	-	-	0.89	43.7	-	-	0.89	55.44
180	-	-	1.55	31.7	-	-	1.55	31.83

Figures 1- 2 illustrate the growth of the biofilm (L) as a function of exposure time for the UNS 1020 carbon steel and UNS S304 stainless steel, respectively. The lines in Figs 1 and 2 represent vsw =0% (blue), vsw =50% (orange), and vsw =75%(gray) without corrosion products in the biofilm. In general, biofilms could be visually observed on the two alloys during the 0-180 days exposure¹³. On the contrary, the L value of the biofilms, which corresponds to the obtained values of Cdl, was calculated in the range of nanometer to fraction of micrometer, see Tables 1-3. In other words, the predicted L was calculated in an incubation period, much smaller than the visually one. Also, it is obvious from the Figs.1 and 2 that as the volume fraction of the seawater (vsw) was observed to increase in the biofilm, as a biological membrane, the L value of the biofilm increased as well, in the outward direction from the surface of alloys. This implies that the closer the biofilm layer to the surface of the alloys, the more adhered the biofilm to the surface in comparison to the outer layers of the biofilm. Consequently, the obtained Cdl corresponds to the adhered biofilm layer, blue line in Fig.1, rather than the loosely biofilm layers, orange & gray lines in Figs.1 and 2.

In contrast, Figs. 3 and 4 illustrate the growth of the biofilm (L) as a function of exposure time for the UNS 1020 carbon steel and UNS S304 stainless steel with corrosion products in the biofilm, respectively. The lines in Fig.3 represent $v_{sw} = 0\%$ (blue) with no corrosion products, $v_{sw} = 50\%$ (orange) with 3% of an accumulation of corrosion products, and $v_{sw} = 75\%$ (gray) with an accumulation of 5% of corrosion products in the biofilm at the carbon steel sample. In a similar fashion, the lines in Fig.4 represent $v_{sw} = 0\%$ (blue) with no corrosion products, $v_{sw} = 50\%$ (orange) with 1% corrosion products, and $v_{sw} = 75\%$ (gray) with 3% of corrosion products in the biofilm at the stainless-steel sample. Furthermore, it is obvious from the Figs.3 and 4 that as the volume fraction of the seawater (v_{sw}) and the volume fraction of the corrosion product (v_{cp}) were observed to increase in the biofilm, the L value of the biofilm increased as well, in the outward direction from the surface of alloys, as a biological membrane with corrosion products.

In addition, it seems that the growth of the adhered biofilms has maintained a constant stable thickness during the 180 days of exposure of the alloys to seawater, Figs.1-4. In fact, there is no particular feature that one can tell on the effect of the seasonal temperature on the growth of the adhered biofilm, blue line in Figs.1-4. In contrast, the growth of the loosely layer of the biofilms, orange ($v_{sw} = 50\%$) & gray ($v_{sw} = 75\%$) lines in Figs.1-4, had different feature than the adhered layer of the biofilm. For instance, in the case of the carbon steel sample, Fig.1, the layer (orange line, $v_{sw} = 50\%$) has initially increased from 224.7nm to 323 nm (gray line, $v_{sw} = 75\%$) in the first 10 days of exposure, without corrosion products. Then, the layer attained a thickness range between 150-250nm in the rest of the 90 days exposure time of the sample to seawater. Also, in the case of the carbon steel sample, Fig.3, the layer (orange line, $v_{sw} = 50\%$, $v_{cp} = 3\%$) has initially increased from 227nm to 327 nm (gray line, $v_{sw} = 75\%$, $v_{cp} = 5\%$) in the first 10 days of exposure, with an accumulation of corrosion products. Then, the layer attained a thickness range between 150-250nm in the rest of the 90 days exposure time of the sample to seawater. The test of the carbon steel samples was terminated after 90 days of exposure to the seawater due to the susceptibility of the samples to microbiological induced corrosion (MIC)13.

In the case of the UNS S304 stainless steel, Fig.2, the biofilm layer (orange line, $v_{sw} = 50\%$) has gradually increased from 57.3nm to 82.3 nm (gray line, $v_{sw} = 75\%$) in the first 90 days of exposure, without corrosion products. Then, the layer attained a thickness range between 21.5-43.7nm in the rest of the 90 days exposure time of the sample to seawater. However, in the case of the UNS S304 stainless steel sample, Fig.4, the layer (orange line, $v_{sw} = 50\%$, $v_{cp} = 1\%$) has initially increased from 57.3nm to 83.6 nm (gray line, $v_{sw} = 75\%$, $v_{cp} = 3\%$) in the first 90 days of exposure, with corrosion products. Then, the layer attained a thickness range between 22.4-55.4nm in the rest of the 90 days exposure time of the sample to seawater. On contrary to the model prediction of the growth of the biofilm at the UNS S304 stainless steel samples, there was no corrosion found on the samples 180 during the days of exposure to the sea water.

Figure 1: The growth of the biofilm as a function of exposure time of the carbon steel to seawater. The lines represent $v_{sw}=0\%$ (blue), $v_{sw}=50\%$ (orange), and $v_{sw}=75\%$ (gray) without corrosion products in the biofilm. The average temperature of the seawater was 18°C during the 90 days, November-February.

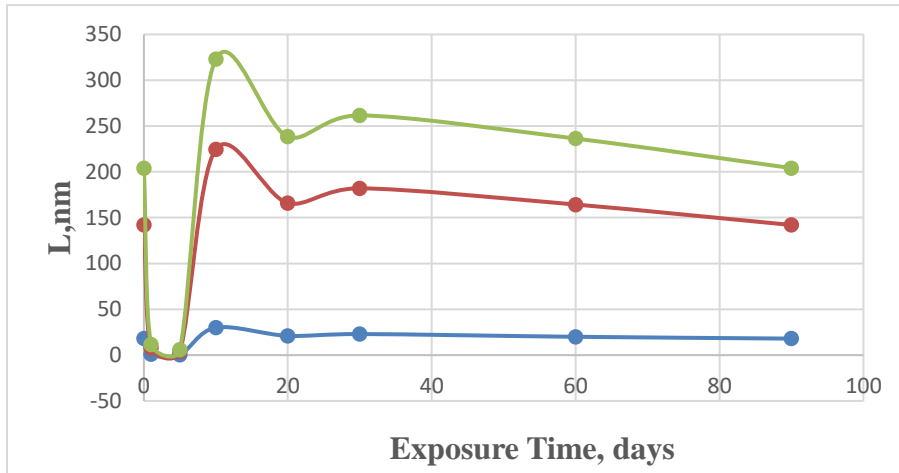


Figure 2: The growth of the biofilm as a function of exposure time of the stainless steel 304 to seawater. The lines represent $v_{sw}=0\%$ (blue), $v_{sw}=50\%$ (orange), and $v_{sw}=75\%$ (gray) without corrosion products in the biofilm. The average temperature of the seawater was 18°C during the 1st 90 days, November-February and was 33 °C during the 2nd 90 days March-May.

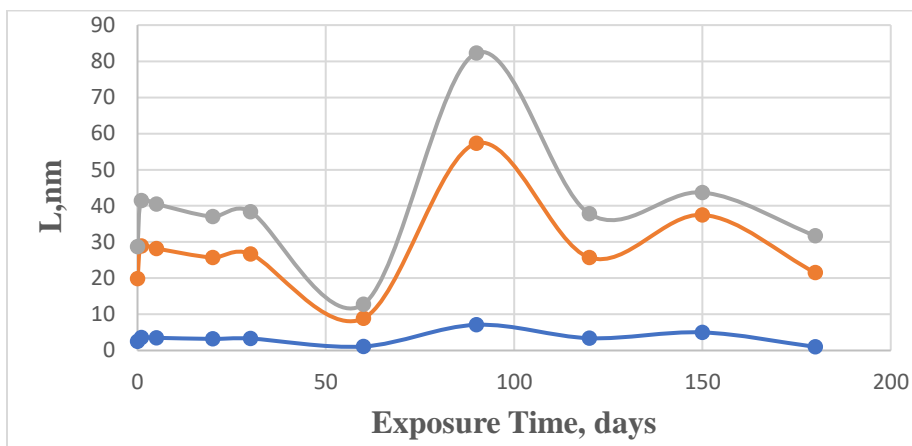


Figure 3: The growth of the biofilm as a function of exposure time of the carbon steel sample in seawater. The lines represent $v_{sw}=0\%$ (blue) with no corrosion products, $v_{sw}=50\%$ (orange) with 3% of an accumulation of corrosion

products, and $v_{sw} = 75\%$ (gray) with an accumulation of 5% of corrosion products in the biofilm. The average temperature of the seawater was 18°C during the 1st 90 days, November-February.

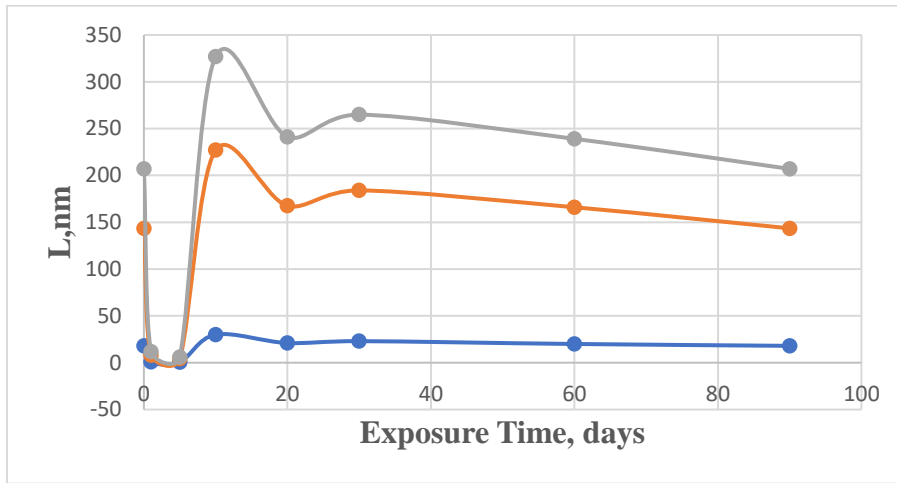
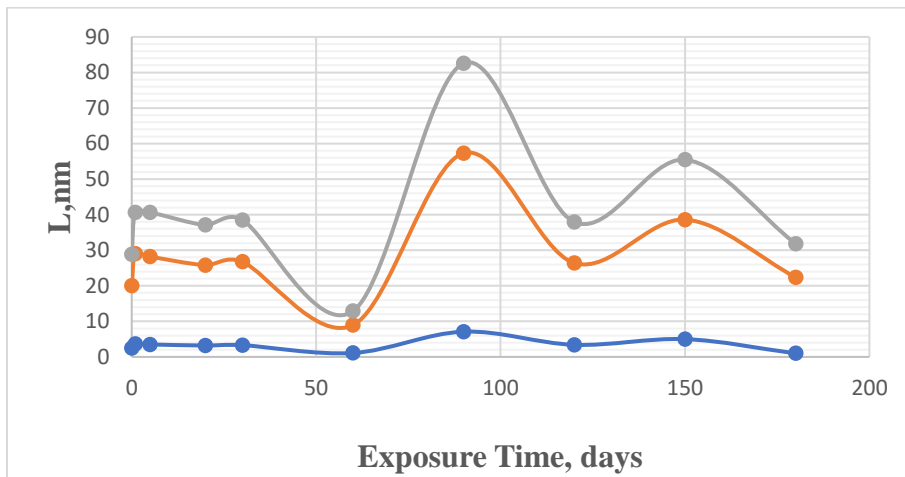


Figure 4: The growth of the biofilm as a function of exposure time of the stainless-steel sample in seawater. The lines represent $v_{sw} = 0\%$ (blue) with no corrosion products, $v_{sw} = 50\%$ (orange) with 1% corrosion products, and $v_{sw} = 75\%$ (gray) with 3% of corrosion products in the biofilm. The average temperature of the seawater was 18°C during the 1st 90 days, November-February and was 33°C during the 2nd 90 days March-May.



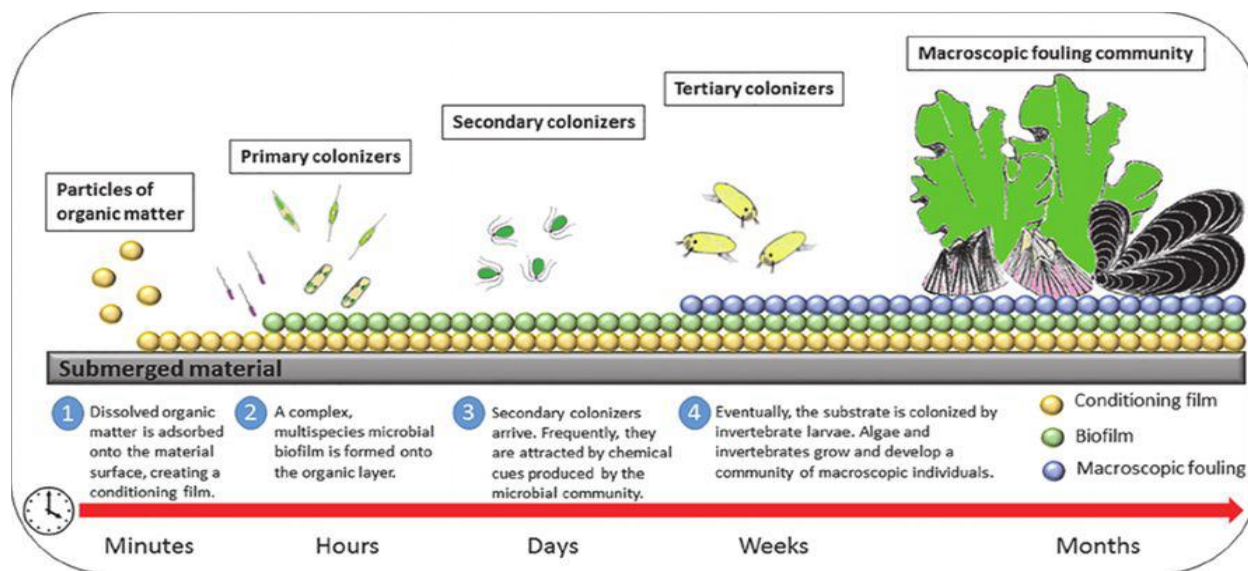
Interpretation of The Mathematical Modelling

The growth of marine bio-films on submerged samples of the carbon steel and stainless steel alloys, from the seawater, can only be possible to predict (Equ.4) from the interface region between the bio-films and the aqueous solution, For instance, see Figure 5 for the growth steps of the bio-film on a submerged material. On one hand, the formation of the adhered bio-film in Figs.1-4, blue lines without corrosion products($v_{cp}=0$), was predicted by mathematically correlating data of obtained double layer capacitance (Cdl) of the bio-film to the thickness of the biofilm formation (L) of the two metallic alloys in seawater during 6 months. On the other hand, the formation of

the loosely bio-film layers in Figs.1-4, orange and gray lines with assumed corrosion products ($v_{cp} > 0$), was predicted by mathematically correlating data of Cdl of the bio-film to L of the biofilm formation of the two metallic alloys in seawater for the same exposure period. In other words, the predicted adhered bio-film in, Figs.1-4, blue lines, can be depicted by step 2 in Fig.5, primary colonizers per se. In contrast, the predicted loosely bio-film layers in, Figs.1-4, orange and gray lines, can be illustrated by step 3-4 in Fig.5, secondary colonizers and its accumulations or its debris for the sake of illustration. So, it is expected that the adhered bio-film layer, i.e., primary colonizers, to maintain a constant thickness during the 90-180 days of exposure of the alloys to seawater, blue line in Figs.1-4 as depicted by step 2 in Fig.5. On the contrary, it is expected that the loosely bio-film layers, i.e., secondary colonizers and its accumulations or its debris, to initially increase or decrease then to maintain a certain thickness during the 90-180 days of exposure of the alloys to seawater with respect to the increase of the corrosion products, orange and gray lines in Figs.1-4 as depicted by step 3-4 in Fig.5.

Therefore, the accumulations or the debris of the loosely bio-film layers would be the main reason of the peculiar predictions of the growth of the loosely bio-film layers in comparison to the adhered bio-film layers

Figure 5. The growth steps of the of biofilm on a submerged material (NACE permission of reproducing the Figure).



Conclusions

The following conclusions have been drawn from the present investigation:

- 1- Mathematical modelling of the biofilm growth(L) of the UNS 1020 carbon steel and UNS S304 stainless steel alloys was carried out, implementing EIS data the Cdl of both alloys during 90-180 days exposure time in the seawater.

2- The L value of the biofilms, which corresponds to the obtained values of Cdl, (by EIS) was calculated in the range of a nanometer to a fraction of micrometer.

3-The L value was calculated as a function of the volume fraction of seawater in the biofilm, $v_{sw} = 0,50,75\%$, and the dielectric constant of the seawater at different temperature, $\epsilon_{sw} = 70.2$ at 18°C (November-February) & $\epsilon_{sw} = 67.4$ at 33°C (March to May), the dielectric constant of corrosion products (ϵ_{cp}) in the biofilm, and the volume fraction of those corrosion products (v_{cp}) in the biofilms.

4-The growth of the adhered bio-film layer was observed to maintain a constant thickness during the 90-180 days of exposure of the alloys to seawater, blue line in Figs.1-4. In contrast, the growth of the loosely layer of the biofilms, orange ($v_{sw} = 50\%$) & gray ($v_{sw} = 75\%$) lines in Figs.1-4, had different feature than the adhered layer of the biofilm.

5- The accumulations or the debris of the loosely bio-film layers would be the main reason of the peculiar predictions of the growth of the loosely bio-film layers in comparison to the adhered bio-film layers.

6- In the case of the carbon steel sample, Fig.1, the layer (orange line, $v_{sw} = 50\%$) has initially increased from 224.7nm to 323 nm (gray line, $v_{sw} = 75\%$) in the first 10 days of exposure, without corrosion products. Then, the layer attained a thickness range between 150-250nm in the rest of the 90 days exposure time of the sample to seawater.

7-Also, in the case of the carbon steel sample, Fig.3, the layer (orange line, $v_{sw} = 50\%$, $v_{cp} = 3\%$) has initially increased from 227nm to 327 nm (gray line, $v_{sw} = 75\%$, $v_{cp} = 5\%$) in the first 10 days of exposure, with an accumulation of corrosion products. Then, the layer attained a thickness range between 150-250nm in the rest of the 90 days exposure time of the sample to seawater.

8-In the case of the UNS S304 stainless steel, Fig.2, the biofilm layer (orange line, $v_{sw} = 50\%$) has gradually increased from 57.3nm to 82.3 nm (gray line, $v_{sw} = 75\%$) in the first 90 days of exposure, without corrosion products. Then, the layer attained a thickness range between 21.5-43.7nm in the rest of the 90 days exposure time of the sample to seawater.

9-However, in the case of the UNS S304 stainless steel sample, Fig.4, the layer (orange line, $v_{sw} = 50\%$, $v_{cp} = 1\%$) has initially increased from 57.3nm to 83.6 nm (gray line, $v_{sw} = 75\%$, $v_{cp} = 3\%$) in the first 90 days of exposure, with corrosion products. Then, the layer attained a thickness range between 22.4-55.4nm in the rest of the 90 days exposure time of the sample to seawater.

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