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Biofouling of Revrse Osmosis Membranes in a Petrochemical Complex: Possibility of Anti-microbial Coating Based on Initial Experimental Results

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Abstract

In this root cause analysis, the biofouling of membranes in the reverse osmosis (RO) unit of a petrochemical complex is studied. The overall cause of biofouling was found to be inappropriate water treatment of pre-RO systems. More specifically, undertreatment of water by sand filters, pressure-srised filters, and cartridges caused an increase in microbial contamination on RO membranes, therefore leading to biofouling. Biodegradation of polymers is a mechanism by which the act of microorganisms will cause a loss of mechanical integrity in such materials. It is important to understand the mechanism and look for ways in which it can be controlled. The following were advised to control biofouling in the RO system of this petrochemical complex: 1. Chemical washing of sand filters as pressurized filters as well as RO membranes. 2: Application of UV, or alternatively, removal of chemical chlorination and installation of non-oxidizing biocides after chlorination. 3: Replacement of phosphorus-containing anticalins instead of non-phosphorus sealants. 4: Application of superhydrophobic anti-microbial coatings on membranes.

Key words: Biodeterioration, Biofouling, Reverse Osmosis (RO), Antimicrobial Coating,Biofilm, Temenos.

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Introduction

Reverse Osmosis (RO) is a method by which the water needed by industrial units is refined. By applying pressure to the water to pass it through semi-permeable spiral-shaped membranes, about 99% of the salts in the water are physically separated from it. RO is a routine process applied in industry, and some of its advantages are low energy consumption, high efficiency, and a high rate of recycling purified water from contaminated waters. On the other hand, however, one of their serious drawbacks is that they are very suitable environments to allow "Fouling." Four main types of fouling common in RO systems are:

1.Organic debris fouling
2.Non-organic debris fouling (trap of colloids and other particles)
3.Crystal fouling (slits)
4.Biofouling

A case of biofouling of RO membranes in a petrochemical complex has been analyzed for root causes. More RO systems are composed of two phases:

•**Phase 1**: (Pre-treatment): In this phase, via filtration and goacoliation of the feed water, solid and sustained particles in the feed water are separated. As a common practice, multi-media filters are used to pick up particles between 5 and 20 microns. Cartridge filters, on the other hand, separate more than 10 microns of colloids and microorganisms. Chemical treatment (such as chlorination or the application of biocides) is also done at this phase.

•**Phase 2:** The focus in this phase is the RO's semi-permeable membranes. In this phase, the water is passed through the membranes at high pressure. Each bundle contains about 30 polyamide spiral membrane folios. Each folio is made up of two membranes with a permeable space in between. To make a unit of RO membrane, membranes with a feed spacer in between are wrapped around each other. Upon purification, the feed water enters via feed canals and leaves as brine (10–20% of the feed water leaves the system as brine).

The cardinal elements of the water purification circuit can be shown in Figure 1. However, it is important to understand the biofilm formation mechanism (in a water-containing environment) and, even more importantly, why biofilm is the wrong name for a correct concept and what can be suggested instead.

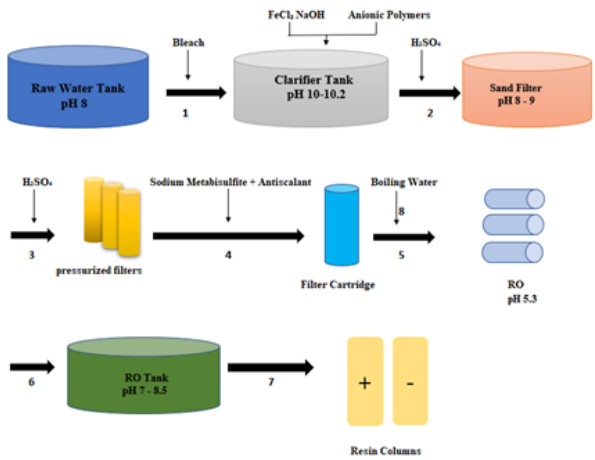

Figure 1. Main elements of the water purification circuit, including filters and RO units and their roles in the whole circuit.

Biofouling happens when biofilm is formed on the memberanes. The biofilm thus formed can have many adverse effects, perhaps the most important of which will be reducing the feasibility of the treatment. Figure 2 shows examples of biofilms formed on the memberanes:

Figure 2. (clockwise) Example of the biofilm formed on the memberanes from different angles.

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Biofilm Formation dynamism

Biofilm is actually a process of continuous construction and deconstruction that continues until an external factor (chemical, such as the application of biocides; mechanical, such as scrubbing or pigging) destroys its survival. One very important point here is that "biofilm" is the wrong name for the right mechanism because a biofilm is neither completely made up of biological material nor has a film structure. The best alternative term we have proposed is "temenos" (Javaherdashti, 2020). In this paper, from now on, instead of the technically wrong term "biofilm,", we will be using the term "temenos.". Figure 3 shows various steps involved in temenos formation:

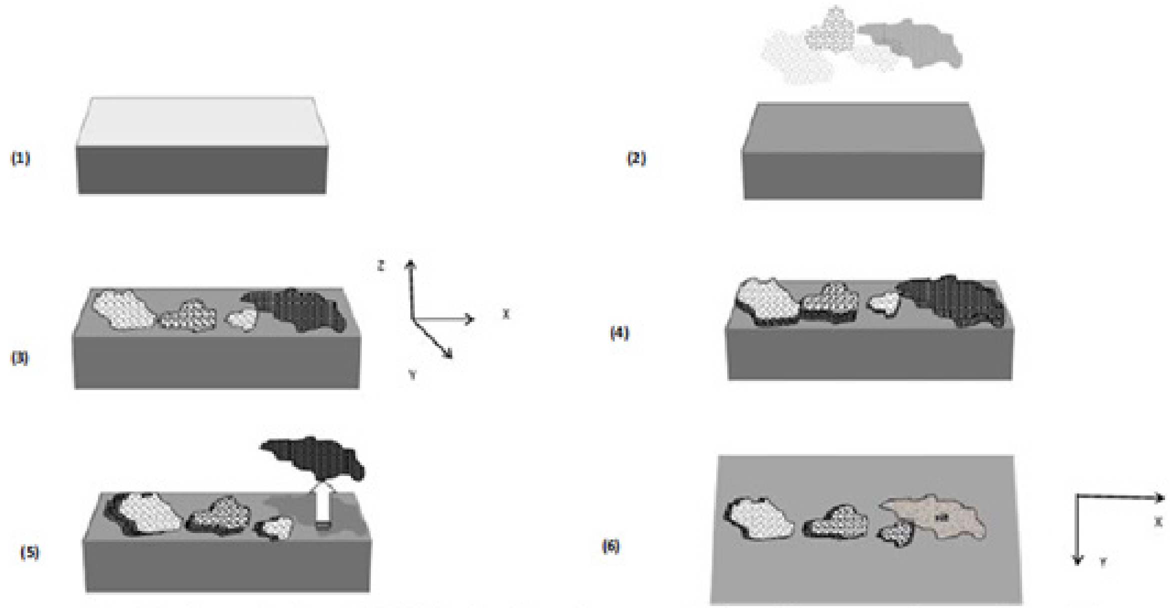

Figure 3. Six steps involved in biofilm formation (Javaherdashti, 2015).

Temenos can lead to pitting, most probably by creating electrochemical cells such as, but not limited to, differential aeration cells via the mechanisms shown in Figure 4:

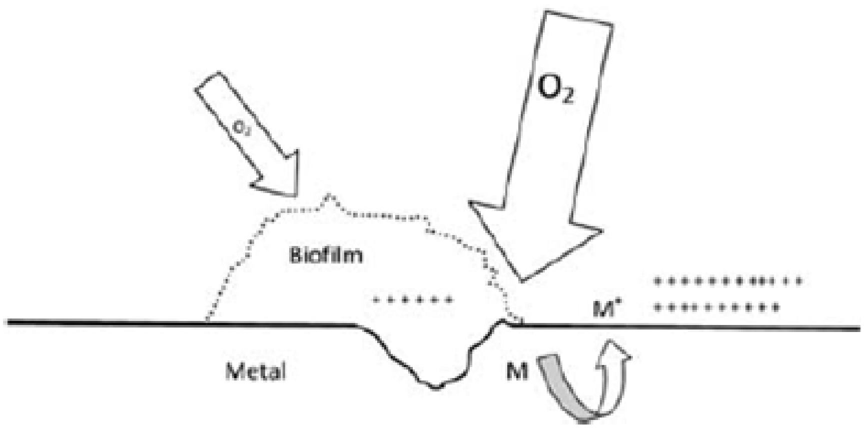

Figure 4. Schematic presentation of establishing differential aeration cells and differential concentration cells leading into pitting approximately Temenos (Javaherdashti, 2017).

These corrosion mechanisms may act as "series" or "parallel" corrosion process geometries, details of which have been discussed in detail elsewhere (Javaherdashti, R., & Akvan, 2017; 2019).

MIC prevention and control methods

Out of five main measures by which MIC can be addressed and rectified, that is to say, physical measures (e.g., coating), chemical measures

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(biocides), electrical measures (cathodic protection), mechanical measures (pigging), and materials selection and design measures, the two important methods applicable to surfaces on which Temenos is highly likely to occur, such as Ro memberanes, are:

a.Chemical treatment by using biocides

b.Application of an antimicrobial coating

The classification of biocides and the pros and cons of each class have been addressed elsewhere (Javaherdashti et al., 2013).

Anti-microbial Coating

The main mechanism by which microbial corrosion is facilitated is the formation of biofilms (more correctly, Temenos), because these structures constitute diffusion barriers beneath which electrochemical cells are stablished. These cells, such as but not limited to differential aeration cells, serve to create spots with different local oxygen partial pressures, leading to anode and cathode formation and thus pitting corrosion. While there are various methods to treat biofilms, such as the use of biocides that are applicable to already - formed biofilms, the antimicrobial coating formulated by Eninco Engineering BV Group prevents biofilm formation in the first place.

MIC is a serious issue in many industries, such as ship hulls, ballast tanks, piers and jetties, pipelines, water and wastewater facilities, power plant equipment, and assets such as condensers, hot - box and boiler-fit pumps, as well as wet-type cooling towers, upstream and downstream, oil and gas, offshore and onshore industries, and under-ground metallic fire water systems. Therefore, the coating can be applied to all metallic parts made of carbon steel and therefore reduce MIC very efficiently.

There are five methods by which MIC can be controlled: material selection, cathodic protection, use of biocides, use of coatings, and mechanical removal of biofilms (e.g., by applying PIGs). The main disadvantages of the above methods are:

•Material selection is always too costly.

•Cathodic protection is not effective all the time.

•The use of biocides, even so-called "green biocides," is introducing synthetic compounds into nature.

•Currently, coatings in use do not apply smart technology as we have proposed and therefore may not be reliable.

•Mechanical removal does not always remove all the biofilms; thus, re-growth may occur.

This coating is formulated based on nanosilver phosphate, nanosilica, and copper II oxide in the resin network and co-reactant. The nanoparticles are touch- and heat-sensitive agents. The method that is used to keep nanoparticles in the film coating is the encapsulation of active ingredients. By using this method, the incompatibility between different particles will be prevented. For producing microcapsules, the interfacial cross-linking method will be used by adding an active ingredient to an aqueous solution of the cross-linkable polymer. Based on our experiments, we have confirmed that there are some important properties of this coating, such as:

•Long-term durability (no water uptake) happened after> 10,000 hours (ten thousand hours).

•Needs a very thin layer of film coating (less than 200 microns).

•It is not toxic (very low VOC%).

•easy method of application (applicable by conventional methods such as brushes, rollers, and spraying)

•biofilm prevention efficiency up to 99.99%

•cost-effective (compared with conventional prevention methods)

•protecting the environment (due to not using biocidal chemicals and very low VOC%)

•The adhesion of the coating to the interface is extremely high (5 B, ASTM D 3359).

•The surface is completely hydrophobic.

•This coating has a total resistance to mechanical and chemical defects.

•Transparent film layer

•Fast drying time (less than 30 min.)

•Polyaspartic-acrylic-based solvent

A theoretical study on the possibility of using self-healing principles in creating structures containing corrosion inhibitors and biofilm prevention agents was started in 2010 by Dr. R. Javaherdashti as a possible way to control and prevent corrosion. However, in 2019, Dr. A. Assarian became successful in taking the first experimental and practical steps to complete the laboratory phase of anti-microbial coatings based on in-situ interfacial polymerization.

Nanocoating creates a compatible network of molecules on a surface. Nanocoatings are nanoscale thin films that are applied to surfaces to provide higher corrosion protection, better antifouling and anti-microbial properties, excel-

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lent thermal shock, heat and radiation resistance, self-cleaning or self-healing, water resistance, and improvement properties. Figure 5 schematically represents the model used in manufacturing this antimicrobial coating:

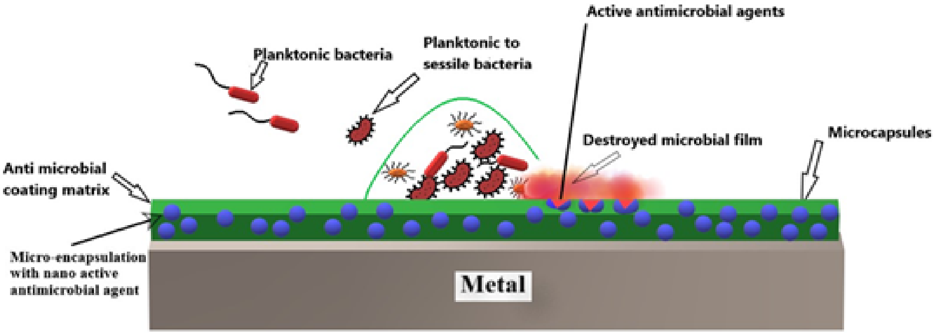

Figure 5. Schematic Summary of the Mechanisms by Which Anti-Microbial Coating Works

The following are some of the top applications of nanocoatings, which are mostly used:

- •Anti-corrosive coatings
- •Waterproof and non-stick coatings
- •Anti-microbial coatings
- •Thermal barrier coatings
- •Anti-abrasion coatings
- •Self-healing coatings
- •Anti-reflection coatings
- •Anti-graffiti coatings

Non-stick coatings have the same properties as waterproof coatings, but they are able to repel oil, dirt, water, and almost any liquid. It is a magnificent subject in the food packaging industry because they have many problems designing packages for some food products, for example, mayonnaise and ketchup sauce. Because these products stuck on the package and could not come out smoothly, the last portion of these products remains in the bottles, and the customer has to throw away the remaining portions (Nuraje et al., 2013; Rivero et al., 2018).

Anti-microbial coatings prevent and reduce the growth of microorganisms on surfaces. Application of these coatings is so important in public places, healthcare industries, and public transport, as well as in kitchens, air conditioning, sanitary facilities, food packaging, and pharmaceutical industries, for reducing the risk of infectious diseases (Cloutier et al., 2015). On the other hand, nano-silica is an excellent additive that can alter the functionality of other particles or fillers, increase hydrophobic or oleophobic coating characteristics, modify rheology and thixotropy, and increase adhesion.

The method used to produce nanocapsules is interfacial cross-linking, as schematically shown in Figure 7.

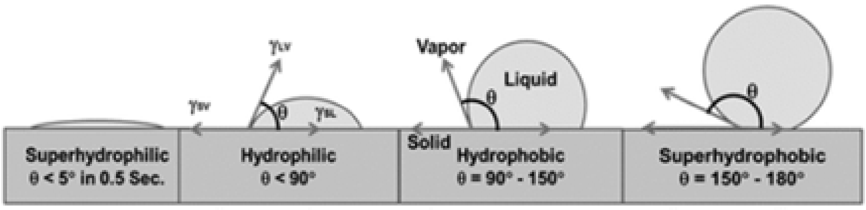

Figure 6. Hydrophobic contact angle in comparison with hydrophilic (Nuraje et al., 2013)

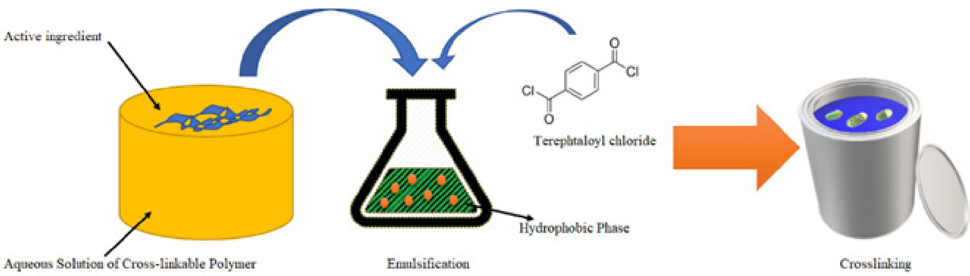

Figure 7. Mechanism of microcapsule formation by interfacial cross-linking (Munin & Edwards-Lévy, 2011)

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Fouling RO memberanes include not only Temenos formation but also the so-called "protobiofilms." The following describes this issue very briefly; more details have been given elsewhere (Rivero et al., 2018; Nuraje et al., 2013); there are also transparent exopolymer particles (TEP) that act as a hub for floating bacterial colonies to which, on average, 5–20% of floating bacteria in the water are attached. TEPs with a higher percentage of attached bacteria are referred to as "proto-biofilms.". While temenoses are established bacterial colonies, prot-biofilms are floating bacterial colonies.

Temenos, which are mainly made up of extracellular polymeric substances (EPS), along with TEP, can have several adverse effects on the RO members, mainly:

1.Interuption by EPS and TEP with salts disposal from water, thus increasing hydraulic resistance and decreasing the efficacy of the RO memberane,

2.Increased need for chemical washing of membranes.

3.Decrease in the useful life of the assets and increased need for replacement of intensively fouled membranes.

4.Decrease in production of water due to long out-of-service periods that are also caused by chemical treartment of memberanes and downtime imposed by memberanes replacement.

It is a known practice that while it is almost impossible to prevent Temenos formation on meberanes due to continuous contact between membranes and water, by carrying out a root cause analysis and applying suitable MIC management, Temenos formation can be controlled to a high extent. The ways in which biofouling is handled in this pterochemical complex are as follows:

1.Adding sodium hypochlorite as a biocide,

2.Addition of ferric chloride as a coagulant

3.Adding anionic polymers for foloculation

4.Adding sodium hydroxide and sulfuric acid to regulate pH

5.Adding an anti-scalant (Flocon 260®) that contains derivatives of phenolic acid and carboxylic acid.

6.To dichlorinate, add sodium metabisulfite.

7.Addition of hot water to the RO system to regulate temperature.

In this paper, we briefly discuss our approach to the biofouling issue at a Petrochemical Complex and the solutions we made that, based on the client's report, worked well for them.

Methodology

Using a strile spatula, a thin layer of microbial film developed on an out-of-service fouled memberane was taken and sent to the laboratory to extract the DNA using MMM (Molecular Microbiology Methods). Based on the stages shown in Figure 1, the characterization of the bacteria studied at each stage is shown in Table 1. The results of MMM are shown in Figure 2. As shown in the figure, both microbial order and microbial classes are shown. Having such information is a must to allow us to characterize the microorganisms involved and the chemical way they must be treated.

As it appears from Table 1, by adding bleach to the water coming from the raw water tank (Figure 1), at all stages involving sand filters, pressurized filters, cartridge filters, and mebranes, instead of decreasing the planktonic bacteria numbers, it shows an increase. This is an indication of poor MIC corrosion management. In addition, while water samples from exit waters from raw water tanks and clarifier tanks contain facultative anaerobic bacteria, the samples from sand filters contain both facultative anaerobic and strict aerobic bacteria. Bacteria observed in waters from both pressurized filters and filkter cartridges contain strict aerobic bacteria. All these indicate that the possible source of the problem is sand filters because they not only show no effect on decreasing the risk level but also act as a food source for the bacteria. However, from a health point of view, the most significant issue is the appearance of Legionella in the Temenos. These bacteria have very dangerous impacts on human health (that can lead to death) and are mostly developed in the Temenos, which are developed in cooling towers.

Advised countermeasures

The solutions were proposed as per the important elements of the process circuit as follows:

3.1. Sand filters and pressurized filters

To rectify the MIC issue in these filters, it was advised to backwash them with highly oxygenated water, acid, or high dosages of ozone. To make sure the advised solutions are working as expected, it is necessary to carry out bacterial counts using suitable kits.

3.2. Chlorination issues

What we recommended instead of adding metabisulphite or even active carbon were the three following alternatives:

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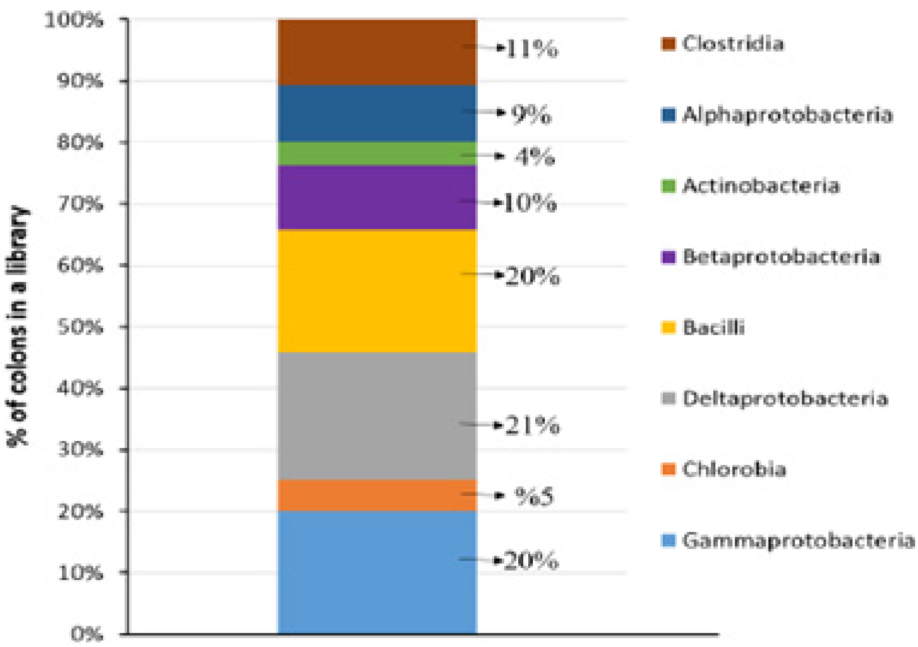
Table 1. Microbial Characterization Table at Each Process Stage Shown in Figure 1

Stage	Bacteria Count (cfu/ml)* 10^5	Type of bacteria	Contamination assessment
1	150	Anaerobic (Facultative)	Dangrous
2	0.24	Anaerobic (Facultative)	Mean
3	11	Anaerobic (Facultative & strict)	Dangerous
4	75	Strict Aerobic	Dangerous
5	43	Strict Aerobic	Dangerous
6	93	Strict Aerobic	Dangerous
7	0.46	Facultative Anaerobic	Mean
8	0	-	Safe
Cooling Towers	460	Stric Aerobic	Dangerous
Tank A	210	Facultative Anaerobic	Dangerous
Tank B	0	-	Safe
Tanks C	93	Facultative Anaerobic	Dangerous



Microbial classes' composition detected in Biofilm sample

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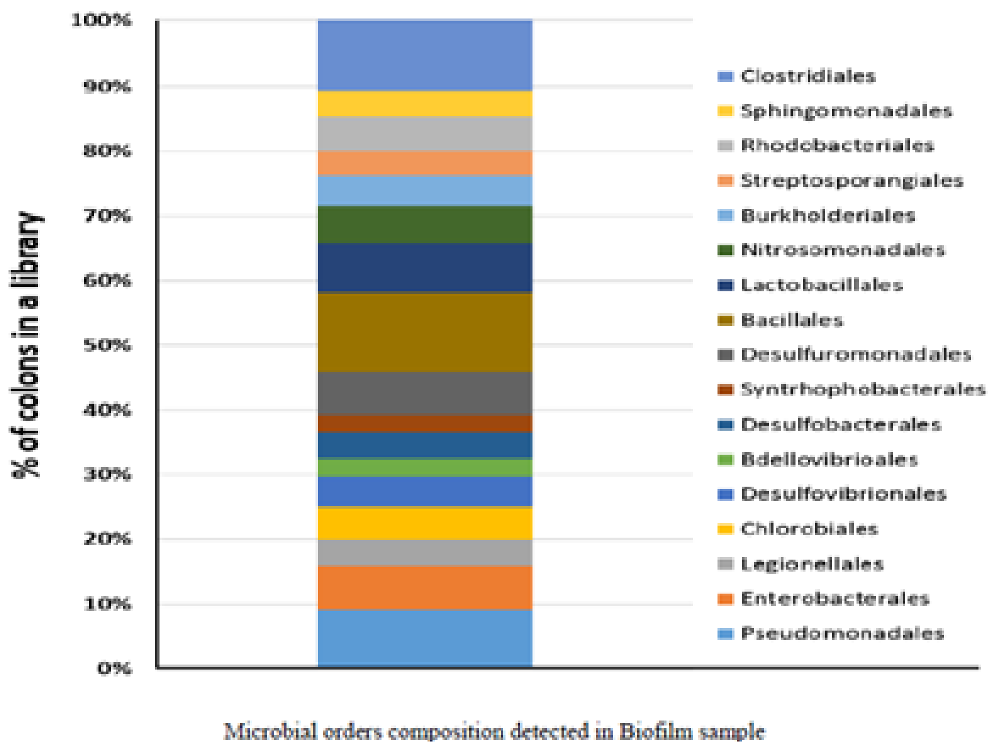

Figure 2. Distribution of microbial species in the Temenos sample taken from an out-of-order memberane due to extensive biofouling (up) as per microbial class and (below) as per microbial orders.

3.2.1. Application of UV (ultraviolet radioation). UV has an efficiency of 99.999% in reducing viable bacterial numbers (Nuraje et al., 2013).

3.2.2. Installation of nanofilters before RO membranes. While nanofilters are very efficient in the physical reduction of bacteria, a serious drawback of them is their very high amount and rate of biofouling.

3.2.3. Addition of non-oxidizing biocides such as DBNPA (2,2-dibromo-3-nitrilopropionamide) after cartridge filters. These biocides have no destructive effects on the structure of the RO membranes.

3.3. Antiscalant issues

The antiscalant added after chlorination contains phsopahte derivatives. Phosphate is a necessary nutrient for bacteria. It was recommended to replace non-phosphate antiscallants instead of currently in-use antiscallant chemicals.

3.4. membrane backwash regime

The results obtained for the Temenos characterization and bacterial scattering patterns showed that they are mainly made up of proteins and lipids. To address the formed Temenos on these membranes, it was advised to wash them using a basic solution containing a surfactant (1% sodium hydroxide and 0.03% sodium dodecile sulfate (SDS) with a pH of 11.5 at a temperature equal to 30 oC) that can absorb both lipids and proteins. The pH and temperature must be highly observed to be within the recommended range. Recycling of the materials was advised for 1 hour.

In addition to the above, it is also possible to use and apply anti-microbial coatings. These coatings do not allow temenos to be formed on the surfaces, including RO membranes.

Conclusions

A case study in a petrochemical complex was studied. This Petrochemical Complex is one of the biggest complexes in the region, and the problems encountered are typical of almost all such industrial complexes.

The case studied proved that it was microbial contamination of the RO components (the memberanes), with a high likelihood and tendency to lead to microbial corrosion or deterioration.

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Some suggestions that worked for the problem were:

Chemical washing of sand filters as pressurized filters as well as RO membranes,

Application of UV, or alternatively, removal of chemical chlorination and installation of non-oxidizing biocides after chlorination,

Replacement of phosphorus-containing anticalins instead of non-phosphorus sealants

In addition to the above, as the use of coatings is also a proven way to address corrosion, particularly MIC/MID, we also propose the application of superhydrophobic anti-microbial coatings on membranes. These new generations of smart coatings can be used in any case that would lead to creating conditions favorable for biodiarity and microbial corrosion.

Authors Disclaimres:

These authors express their consent to making it open for all to access and download.

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