FILMTEC Membranes

Biological Fouling Prevention

Introduction

All raw waters contain microorganisms: bacteria, algae, fungi, viruses and higher organisms. The typical size of bacteria is 1 to 3 µm. Microorganisms can be regarded as colloidal matter and removed by the pretreatment as discussed in separate information on Collodial Fouling Prevention. The difference from dead particles however, is their ability to reproduce and form a biofilm under favorable living conditions.

Microorganisms entering an RO system find a large membrane surface where the dissolved organic nutrients of the water are concentrated (due to concentration polarization): an ideal environment for the formation of a biofilm. Biological fouling of the membranes may seriously affect the performance of the RO system. The symptoms are an increase of the differential pressure from feed to concentrate, finally leading to telescoping and mechanical damage of the membrane elements and a membrane flux decline. Sometimes biofouling develops even on the permeate side, thus contaminating the product water.

A biofilm is difficult to remove, because it protects its microorganisms against the action of shear forces and disinfection chemicals. In addition, incompletely removed biofilms lead to a rapid regrowth.

Biological fouling prevention is therefore a major objective of the pretreatment process. The potential for biological fouling is higher with surface water than with well water. The assessment of this potential and the possible measures against biofouling are discussed in the following sections.

Assessment of Biological Fouling Potential

Culture Techniques

The concentration of bacteria in water is directly related to the water's biological fouling potential. The Total Bacteria Count (TBC) is a quantitative expression of the total number of viable microorganisms in a water sample. It is determined according to ASTM F60 by filtering a measured quantity of water through a membrane filter. Subsequently, the organisms thus retained on the filter surface are cultured on the proper nutrient medium to develop colonies, which are then observed and counted at low power magnification.

The main advantage of this method is that it can be easily performed without expensive equipment. The test results however, are only available after up to seven days, and the counted colonies may represent as little as 1-10 % of the actual number of living microorganisms. Nevertheless, culture techniques are still valuable as indicators of the level and the trend of the biological fouling potential. They can be applied to monitor the water quality from the intake through the subsequent treatment steps up to the concentrate stream and the permeate. An increase of the TBC in the concentrate stream is an indication of a biofilm development on the membranes.

Direct Bacteria Count

Direct count techniques employ filtration of the water sample and counting the retained microorganisms on the filter plate directly under a microscope. To make the microorganisms visible, they are stained with acridine orange and viewed with an epi-illuminated fluorescent microscope.

Thus an accurate count of total microorganisms is obtained immediately. The types of microorganisms can be assessed and differentiated from debris particles. Living and dead cells, however, cannot be differentiated. This can be accomplished by the INT technique, where the INT stain is reduced and accumulated only by living cells. Those can be readily distinguished from dead cells with phase microscopy.

Direct count methods should be preferred, because they are much faster and more accurate than culture techniques.

Biofilm Monitoring

The concentrations of microorganisms in raw water, in the feed stream and in the concentrate stream are important numbers to assess the biological fouling potential. However, other factors like the concentration and the kind of nutrients, and operating parameters can also determine the development of a biofilm. The formation of biofilms is being studied by several researchers, but not yet fully understood. The best method to detect

biofouling in its early stage is to observe a test surface in the feed stream. The “Robbin sampler” is a simple device to expose small test surfaces to a water stream (details: see). These surface samples can be removed and examined for attached bacteria on a regular basis. A careful and periodic inspection of the cartridge filters and the interior of the feed and brine piping is also helpful. The presence of slime or odor is an indication for biofouling.

Other Methods
The bacterial growth potential of a given water sample can be assessed with the Werner method. The sample is filter-sterilized, and an inorganic sterile nutrient salt solution is then added. Then, the sample is inoculated with a specific volume of a suspension of bacteria washed from the sterilizing filter. The growth rate of the bacteria can be quantified from a turbidity increase as measured by forward light scattering. Other techniques measure the assimilable organic carbon or the biodegradable organic carbon.

Chlorination
Chlorine (Cl_2) has been used for many years to treat municipal and industrial water and wastewaters as a disinfectant, because of its capacity to inactivate most pathogenic microorganisms quickly. The effectiveness of chlorine is dependent on the chlorine concentration, time of exposure and the pH of the water. Chlorine is used for the disinfection of potable water where a residual chlorine concentration near 0.5 mg/l is commonly used. In an industrial water treatment scheme, fouling of water intake lines, heat exchangers, sand filters, etc., may be prevented by maintaining a free residual chlorine concentration of 0.5-1.0 mg/l or higher, dependent on the organic content of the incoming water.

Chlorination as RO pretreatment is usually applied where biological fouling prevention is required, i.e. typically for surface waters. Chlorine is added at the intake, and a reaction time of 20-30 min. should be allowed. A free residual chlorine concentration of 0.5-1.0 mg/l should be maintained through the whole pretreatment line. Dechlorination upstream of the membranes is required however, to protect the membranes from oxidation (See subsequent section on Dechlorination).

Chlorination chemistry
Chlorine is most commonly available as chlorine gas and the hypochlorites of sodium and calcium. In water, they hydrolyze instantaneously to hypochlorous acid:

$$Cl_2 + H_2O \rightarrow HOCl + HCl \quad (1)$$
$$NaOCl + H_2O \rightarrow HOCl + NaOH \quad (2)$$
$$Ca(OCl)_2 + 2\,H_2O \rightarrow 2\,HOCl + Ca(OH)_2 \quad (3)$$

Hypochlorous acid dissociates in water to hydrogen ions and hypochlorite ions:

$$HOCl \leftrightarrow H^+ + OCl^- \quad (4)$$

The sum of Cl_2, NaOCl, $Ca(OCl)_2$, HOCl and OCl^- is referred to as free available chlorine (FAC) or free residual chlorine (FRC), given as mg/l Cl_2. As discussed later, chloramines are formed from the reaction of chlorine with ammonia compounds present in the water. These chlorine-ammonia compounds are referred to as combined available chlorine (CAC) or combined residual chlorine (CRC). The sum of free and combined available/residual chlorine is called the total residual chlorine (TRC).

$$TRC = FAC + CAC = FRC + CRC \quad (5)$$

The germicidal efficiency of free residual chlorine is directly related to the concentration of undissociated HOCl. Hypochlorous acid is 100 times more effective than the hypochlorite ion OCl^-. The fraction of undissociated HOCl increases with decreasing pH.

At pH = 7.5 (25°C, TDS = 40 mg/l), only 50% of free residual chlorine is present as HOCl, but 90% at pH = 6.5. The fraction of HOCl also increases with decreasing tem-perature. At 5°C, the HOCl mole fraction is 62% (pH = 7.5, TDS = 40 mg/l). In high salinity waters, less HOCl is present (30% at pH 7.5, 25°C, 40,000 mg/l TDS).

Chlorine demand
A part of the chlorine dosage reacts with ammonia nitrogen to combined available chlorine in a series of stepwise reactions:

$HOCl + NH_3 \leftrightarrow NH_2Cl$ (monochloramine) + H_2O (6)
$HOCl + NH_2Cl \leftrightarrow NHCl_2$ (dichloramine) + H_2O (7)
$HOCl + NHCl_2 \leftrightarrow NCl_3$ (trichloramine) + H_2O (8)

These reactions are governed primarily by pH and chlorine-to-nitrogen weight ratio. Chloramine also has a germicidal effect, albeit lower than that of chlorine. Another part of the chlorine is converted to nonavailable chlorine. This chlorine demand is caused by the reaction with reducing agents such as nitrite, cyanide, sulfide, ferrous iron and manganese. Chlorine is also consumed by the oxidation of orga-nic compounds present in the water.

To determine the optimum chlorine dosage, best point of injection, pH and contact time to prevent biofouling, the ASTM method D 1291, “Standard Practice for Determining Chlorine Requirement of Water”, should be applied on a representative water sample. For further details, the Handbook of Chlorination is recommended.

Sea water
The major difference of sea water chlorination chemistry in contrast to brackish water is the presence of bromide in sea water in concentrations of typically 65 mg/l. Bromide reacts rapidly with hypochlorous acid to hypobromous acid:

$Br^- + HOCl \rightarrow HOBr + Cl^-$ (9)

Thus, in chlorinated sea water the biocide is predominantly HOBr rather than HOCl. Hypobromous acid then dissociates to hypobromite ions as follows:
$HOBr \leftrightarrow OBr^- + H^+$ (10)

HOBr dissociation is less than HOCl dissociation. At pH 8, where only 28% of HOCl is undissociated, about 83% of HOBr is undissociated. In other words, effective disinfection can be performed at a higher pH than in brackish water, where no bromide is present. Both hypobromous acid and hypobromite ions interfere with free residual chlorine measurements and are included in the free residual chlorine value.

The reactions of HOBr with other compounds of the water are analogous to the reactions of HOCl. Bromamines and brominated compounds are the reaction products.

Dechlorination
When FILMTEC FT30 membrane is used in the reverse osmosis process, the RO feed must be dechlorinated to prevent oxidation of the membrane. FT30 membrane has some chlorine tolerance before noticeable loss of salt rejection is observed. Eventual degradation may occur after approximately 200-1,000 hours of exposure to one mg/l of free chlorine (200-1,000 ppm-h tolerance). The rate of chlorine attack depends on various feedwater characteristics. Under alkaline pH conditions, chlorine attack is faster than at neutral or acidic pH. An acidic pH is anyhow preferred for a better biocidal effect during chlorination. Chlorine attack is also faster at higher concentrations of heavy metals (e.g. iron), which catalyze membrane degradation, and at higher temperatures.

By comparison, some other polyamide RO membranes have essentially zero chlorine tolerance. The superior chlorine tolerance of the FT30 membrane can be attributed to the thicker barrier layer (about 2,000 Angstrom) and the fact that the polyamide is crosslinked. If dechlorination upsets occur in a FT30 RO system, and if corrected in a timely manner, membrane damage can be minimized.

For chloramine the tolerance of the FT30 membrane is 300,000 ppm-h, which implies that dechlorination is not required. However, since chloramines are formed by adding ammonia to chlorine, it is possible that free chlorine will be present. Since this free chlorine can be damaging to the membrane, dechlorination should still be considered.

Residual free chlorine can be reduced to harmless chlorides by activated carbon or chemical reducing agents. An **activated carbon** bed is very effective in dechlorination of RO feed water according to following reaction:

$$C + 2\ Cl_2 + 2\ H_2O \rightarrow 4\ HCl + CO_2 \qquad (11)$$

Sodium Metabisulfite (SMBS) is most common for removal of free chlorine and as a biostatic. Other chemical reducing agents exist, e.g. sulfur dioxide, but have not yet been proven cost-competitive with SMBS.

When dissolved in water, sodium bisulfite (SBS) is formed from SMBS:

$$Na_2S_2O_5 + H_2O \rightarrow 2\ NaHSO_3 \qquad (12)$$

SBS is then reducing hypochlorous acid according to:

$$NaHSO_3 + HOCl \rightarrow HCl + NaHSO_4 \qquad (13)$$

In theory, 1.34 mg of sodium metabisulfite will remove 1.0 mg of free chlorine. In practice however, 3.0 mg of sodium metabisulfite is normally used to remove 1.0 mg of chlorine.

Solid sodium metabisulfite has a usual shelf life of 4-6 months under cool, dry storage conditions. However, in aqueous solutions, sodium bisulfite can oxidize readily when exposed to air. A typical solution life can vary with concentration as follows:

Solution (wt.%)	Life (Maximum)
2	3 days
10	1 week
20	1 month
30	6 months

The SMBS should be of food grade quality and free of impurities. SMBS should not be cobalt-activated. Although the dechlorination itself is rapid, good mixing is required to ensure completion; static mixers are recommended. The injection point is preferably downstream of the cartridge filters in order to have these protected by chlorine. In this case, the SMBS solution should be filtered through a separate cartridge before being injected into the RO feed. Dechlorinated water must not be stored in tanks.

The absence of chlorine should be monitored using an oxidation-reduction potential (ORP) electrode downstream of the mixing line. The electrode signal shuts down the high pressure pump when chlorine is detected.

Shock Treatment
Shock treatment is the addition of a biocide into the feed stream during normal plant operation for a limited time period. Sodium bisulfite is the most commonly used biocide for this purpose. In a typical application, 500-1,000 mg/l $NaHSO_3$ are dosed for 30 minutes.

The sodium metabisulfite should be food grade, free of impurities and not cobalt-activated. The treatment can be carried out on a periodic basis, e.g. every 24 hours, or only when biogrowth is suspected. The efficiency of such treatment should be studied. The permeate produced during dosage will contain 1-4% of the bisulfite feed concentration. Depending on the permeate quality requirements, the permeate can be used or discarded during shock treatment. Bisulfite is more effective against aerobic bacteria than against an aerobic microorganisms. Therefore, the efficiency of the shock treatment should be carefully assessed using the techniques for assessing biological fouling potential preseiously describel.

Sanitization
Instead of continuously adding a biocide to the raw water, biofouling can be controlled by periodic sanitization of the system. This is usually practiced in medium risk applications. In high risk applications, sanitations may be an additional measure to a continuous biocide dosing.

Preventive sanitization are much more effective than corrective disinfections, because single attached bacteria are easier to kill and remove than a thick, aged biofilm.

Typical sanitization intervals are one per month, but they can be as short as one per day, depending on the feed water quality (e.g. waste water) or the permeate quality required (e.g. pharmaceutical grade water). The membrane life however, may be shortened by extensive sanitizations, depending on the type of chemical.

Other Methods
Microfiltration/Ultrafiltration offers advantages in that it can remove microorganisms and especially algae, which are sometimes very difficult to remove by standard techniques. The MF/UF membranes should be made from a chlorine-resistant material to withstand periodic sanitization.

Copper sulfate can also be used to control the biogrowth. Typically, copper sulfate is fed continuously at 0.1 to 0.5 mg/l concentrations. The generalized use of copper sulfate is however, not recommended due to the following:

- Commercial $CuSO_4$ may contain some impurities detrimental to the RO membranes.
- $CuCO_3$ and $Cu(OH)_2$ tend to precipitate outside of a given pH range of operation, causing fouling to RO devices, and making $CuSO_4$ ineffective.
- Copper ions can have negative effects on the environment.
- $CuSO_4$ only works properly against a limited range of microorganisms (e.g. some algae) but has only a marginal effect on most bacteria.
- Environmental protection standards of several countries limit the discharge amount of Cu salts, making it difficult to change dosage of this chemical if the biolife situation of a given plant requires it.

Ozone is an even stronger oxidizing agent than chlorine. However, it decomposes readily. A certain ozone level must be maintained to kill all microorganisms. The resistance of the materials of construction against ozone has to be considered. Usually, stainless steel is employed. De-ozonation must be performed carefully to protect the membranes. Ultraviolet irradiation has been used successfully for this purpose.

Ultraviolet irradiation at 254 nm is known to have a germicidal effect. Its application has come into use especially for small scale plants. No chemicals are added, and the equipment needs little attention other than periodic cleanings or replacement of the mercury vapor lamps. UV treatment is limited however, to relatively clean waters, because colloids and organic matter reduce the penetration of the radiation.

Sodium bisulfite concentrations in the range of up to 50 mg/l in the feed stream of sea water RO plants have proven effective to control biological fouling. Colloidal fouling has also been reduced by this method. As a side benefit, no acid is required for calcium carbonate control because of the acidic reaction of bisulfite:

$$HSO_3^- \rightarrow H^+ + SO_3^{--} \qquad (14)$$

Granular activated carbon (GAC) filtration as pretreatment method is known to be a risk of releasing bacteria which might cause biofouling of the membranes. The high inner surface of the carbon pores together with adsorbed organic nutrients promote biological activity in the filter. However, when such filters are operated at sufficiently low filter velocities (2-10 m/h) and with sufficiently high beds (2-3 m), all the biolife activity takes place in the upper region of the filter bed, and the filtered water is almost free of bacteria and nutrients. This technique is widely used in public water works, where the biological activity of the carbon filter is further enhanced by ozonation of the feed.

The strategy of promoting bioogical growth in a restricted place where it is of no harm to the membranes, rather than trying to kill all microorganisms, might be a good approach to control biofouling of the membranes. However, there is little practical experience to date.

To prevent biological fouling of the membranes, the entire system from the raw water intake up to the membranes has to be kept clean and in a sanitary state. Please refer to separate information on Control of Microbiological Activity, for more details.

The technical information contained here is extracted from the **FILMTEC Membranes - Technical Manual.** References to other sections of the manual have been replaced with short references to additional but separate information available from our web site. The information in these extracts has been updated and supercedes that contained in the full manual.

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