Potential Use of ClO2 as a Disinfectant for Polyamide RO/NF Membranes

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Introduction

Biogrowth is a common problem in many membrane systems. Many effective practices have been developed to manage and cope with this problem. They include the use of pH swings, high temperature, non-oxidizing bicides (such as DBNPA, isothiazoline, and glutaraldehyde), elimination of food source and good practices to maintain a "clean" system. One of the more aggressive methods is the use of mild oxidants such as hydrogen peroxide or chloramines. As is well documented in literature, free chlorine can damage RO membranes in a very short time. The presence of transition metals will also greatly accelerate the oxidative degradation of the membrane. However, chloramines have been used successfully for many wastewater systems where ammonia is present in the feed stream and chlorine is added to obtain 1-2 ppm of chloramine. Chloramines have been used with sporadic success, and failure, for surface waters where both ammonia and chlorine need to be added to the water to generate the chloramine. Hydrogen peroxide can be used with peracetic acid as a disinfectant (See Hydranautics TSB 110), but the H_2O_2 concentration should not exceed 0.2% and temperature should not exceed 25C. However in the case of both chloramines and H2O2, special care should be taken that transition metals (Fe, Mn) are not present in the feedwater or deposited on the membrane, since these can accelerate oxidation reactions by 1-2 orders of magnitude.

Recently, ClO_2 has been considered as a potential disinfectant. ClO_2 is present as a dissolved gas in water. One advantage of ClO_2 is that it is a weaker oxidant than HOCl, HOBr and O_3. A weaker oxidant is less damaging to the membrane, and apparently the ClO_2 gas can penetrate the biofilm better and degrade the material. Because of the chemistry and reactivity differences between Cl_2 and ClO_2, it has been reported that approximately ¼ of the dose of ClO_2 is required to maintain an effective disinfectant concentration compared to Cl_2. Additionally, since it is gaseous, it will not be rejected by the membrane and will thus pass into the permeate at the same concentration as the feed. For these reasons, ClO_2 is gaining interest as a potential disinfectant which can be used with a membrane.

Reported Studies

There are a variety of studies that have been reported in literature on the use of ClO_2 with RO membranes. One of the first studies to characterize the effect of various oxidants on polyamide thin film composite membranes was by Glater (ACS Symposium Series No 153, Synthetic Membranes 1, 171 (1981)). This study showed that polyamide membranes were more sensitive to chlorine damage than were cellulose acetate membranes.

An article in Ultrapure Water Magazine (pp. 13-17, Sept 2004) reported the laboratory study where a polyamide RO membrane was exposed to as much as 100 ppm ClO_2 over six months. Testing showed that the membrane salt passage increased by about 50%, going from 1% up to about 1.5%. The article also reported on the exposure of a polyamide membranes in a RO unit that had 12 x 8" elements. The dosage varied between about 1 to 6 ppm, accumulating 12 ppm-hours of operation. The rejection did not change significantly. Finally, they did a field trial with a 300 gpm system. The ClO_2 concentration varied between 0.7 and 2.2 mg/L during a period of 105 min for a total exposure of 1.5 ppm hours. During this time, the salt passage did not change, but the bacterial counts decreased by 95%. In summary they showed that ClO_2 treatment could damage a polyamide membrane at high concentrations, but could potentially be used safely for sanitization at a relatively low dose.

In a separate study (private communication), trials were done where polyamide RO membranes were first tested with a 1% NaCl solution to determine flux and rejection. Then they were immersed in a closed tank of 200 ppm ClO_2 for 18 days. After soaking, the membrane samples were retested with 1% NaCl. The resulting flux decreased slightly, ranging from12-30% decline for the samples. The rejection decreased by 1-2% in two cases, but also increased by 1% in another case.

Studies by Adams (Desalination 78 (3), 439 (1990)) have shown that ClO_2 concentrations can be $1/4^{th}$ of the hypochlorite concentration to get the same biostatic properties. Additionally, ClO_2 concentrations of < 1.0 ppm were found to be much less damaging to the membrane than for Cl_2. Thus, it may be that low concentrations of ClO_2 are effective for biogrowth control, and less damaging to the membrane.

Finally, a trial reported by Averett et al (Southwest Chemistry Conference, Dallas TX, July 28-August 1, 2003) studied the performance of fouled polyamide RO elements which were treated with a <1.0 mg/L ClO_2 solution for 6 hrs per day for five days. This study showed that the bacterial counts were greatly reduced by the treatment and the membranes were cleaned to some degree. However, with the cleaning, there was an increase in salt passage (about 20%), likely due to the loss of the additional biofilm layer which plugged defects in the membrane.

Observations:

Extensive biofilm formation is damaging to RO membranes and can shorten membrane life. Efforts should be made to control biofilm growth and prevent excessive biofilm formation. If other conventional means of controlling biogrowth fail, ClO_2 can be used as an alternative to control biogrowth in polyamide RO membranes using short, low concentration dosages. Users should take care to ensure the system does not have transition metals (Fe, Mn) present in the water or on the membrane, as these can accelerate reactions between the membrane and the oxidant.

For sanitization, ClO_2 concentrations should be less than 1 mg/L and exposures of 1-4 hours being suitable to disinfect the system. If the oxidant demand due to organic materials is high, the ClO2 concentration may drop rapidly, thus requiring additional dosing to maintain an effective concentration. ClO_2 may be more effective than chloramines or peracetic acid, since ClO_2 is gaseous and can thus easily pass through the membrane and disinfect the permeate side of the sytstem.

Any time a chlorine containing oxidant is used with a polyamide membrane, it is essential that no free chlorine is present in the solution and the concentrations are measured accurately. ClO_2 concentration can be measured with UV-VIS spectrophotometry (AWWA Journal, pp. 81-87, Sept. 2004). The characteristic adsorption is at 360 nm, but other wavelengths can also be used. It is important to ensure that there is no interference caused by other species that adsorb in this range, which would confuse the actual ClO_2 measurement.

ClO_2 may have potential for being used as an occasional biogrowth control agent, even at concentrations < 1.0 mg/L. At this point further studies are needed to more fully characterize the effect on membrane performance. In particular Hydranautics is concerned with the effect of transition metals which are known to greatly accelerate the membrane oxidation for chlorine and chloramine attack. Since the reaction of ClO_2 is different than OCl^-, the interaction of ClO_2 with the membrane is not yet fully understood. Hydranautics does not fully endorse the use of ClO_2 for frequent cleaning or daily dosing until more extensive studies are done, especially with the presence of transition metals.

In some cases, biofouling in a system may be so extensive that membranes are being damaged and prematurely fail. In those cases, the user should consider all conventional methods to control biofouling. If those are not successful, they may elect to consider the use of ClO_2 as a last resort to extend the life of the membrane. In such cases, the customer may want to carry out their own trials to control biofouling with low dose ClO_2 prior to the extensive growth of a biofilm.