

Application of Electrotechnology for Removal and Prevention of
Reverse Osmosis Biofouling

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Fouling Mitigation in Membrane Separations

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ABSTRACT

One of the major factors limiting the use of membrane separation systems is membrane fouling (Cooper 1980). Membrane fouling places a large economic restriction on membrane systems operation; it can lead to reduced performance, higher energy consumption, and eventually, failure to meet the regulatory standards by the deterioration of the product stream.

Successful results from the application of electrotechnology have been obtained in removal and prevention of redevelopment of biofouling from operating reverse osmosis equipment (RO). Field observations are supported by Robbis device laboratory studies.

INTRODUCTION

A patented ceramic electrode (the Zeta Rod™) uses electrostatic dispersion of mineral and organic colloids to prevent scaling, biofouling, and corrosion in different HVAC equipment. The principles of operation of this capacitor based system are explained in detail in other publications (Pitts, 1995). The purpose of this study was to apply the same technology to RO membranes and see if the anti-scaling and anti-biofouling effects observed in the HVAC systems would have the same effect on RO membranes. This was done both in the field in a bottling plant, and in a controlled environment in a microbiology lab. The results of these studies provide the basis for a new technological approach to prevention of membrane fouling in membrane separation processes.

Membrane fouling can be classified in three main groups:

1. Crystalline fouling, or mineral scaling - results from to the deposition of minerals due to their high concentration in the solution stream.
2. Particle and colloid fouling- relates to the deposition of clay, silt, particulate humic substances, debris, and silica.
3. Microbiological fouling, or "biofouling"- refers to the adhesion and accumulation of microorganisms, forming biofilms (Geesey et al., 1994).

Current techniques to prevent or reduce the rate of membrane fouling involve a set of pre-treatment techniques (Zeman & Zydney, 1996, Geesey et al.,1994, Gutman, 1987, Kemmer, 1988, Stumm & Morgan, 1996) and complex processes varying from prefiltration units to water softeners in many different arrays and configurations. Other alternatives include the addition of chemical agents into the feed stream to act as dispersants to aid in the prevention of mineral scaling. Biocides are utilized in some applications to reduce the potential of biofouling.

All these techniques have proven to be inefficient, for it is still considered that periodic membrane cleaning is unavoidable for all membrane filtration equipment. Membrane cleaning requires the unit to be shut down for a chemical and/or a mechanical cleaning. Ironically, these procedures not only cause down time to the unit, and are labor intensive, in some instances they reduce the lifetime and efficiency of the membrane modules themselves due to their incompatibility with the chemical cleansers (Geesey et al., 1994).

TECHNICAL DISCUSSION

In order for biofouling to occur, there has to be an initial adhesion stage of the microorganisms and colloidal particles onto the membrane surface. Primary adhesion is a heterogeneous process, involving three chemical phases:

1. Semi solid phase: microorganisms; including variables such as species composition or microflora, nutrient status, hydrophobicity, surface charge, and extracellular polymeric substances.
2. Liquid phase: the fluid being filtered; with variables such as temperature, pH, dissolved organic and inorganic substances, viscosity, surface tension, and hydrodynamic parameters.
3. Solid phase: the membrane surface; influencing adhesion via chemical composition, surface charge, conditioning film, and biological affinity.

The surface charge is very likely to influence primary microbial adhesion. Most bacteria are slightly negatively charged in aqueous systems. The electrolyte concentration which also influences the electrostatic double layer, has been found to influence initial adhesion (Amjad, 1992). It is at this stage where biofouling should be controlled. By preventing bacteria and mineral deposits from forming or adhering onto the membrane surface, the initial stage of biofouling (which is prerequisite to the remainder of the process) will be eliminated.

Colloidal particles include mineral and biological particles found in all untreated water sources (Stumm & Morgan, 1996). Generally any particle with a radius smaller than 1.0 μm is considered a colloidal particle (Kemmer, 1988). Some organic and biological colloids which cause biofouling of membranes include different types of microorganisms, viruses, biocolloids, fibrils, humus colloids, and aggregates of exudates and macromolecular organic matter (Stumm & Morgan, 1996). It is this wide spectrum of biological materials that has made biofouling control by chemical additions such a difficult task. In part this is because of the tolerance of the different organisms to specific chemical compounds and because of the potential for damage to the membrane by chemical biocides and cleaning agents.

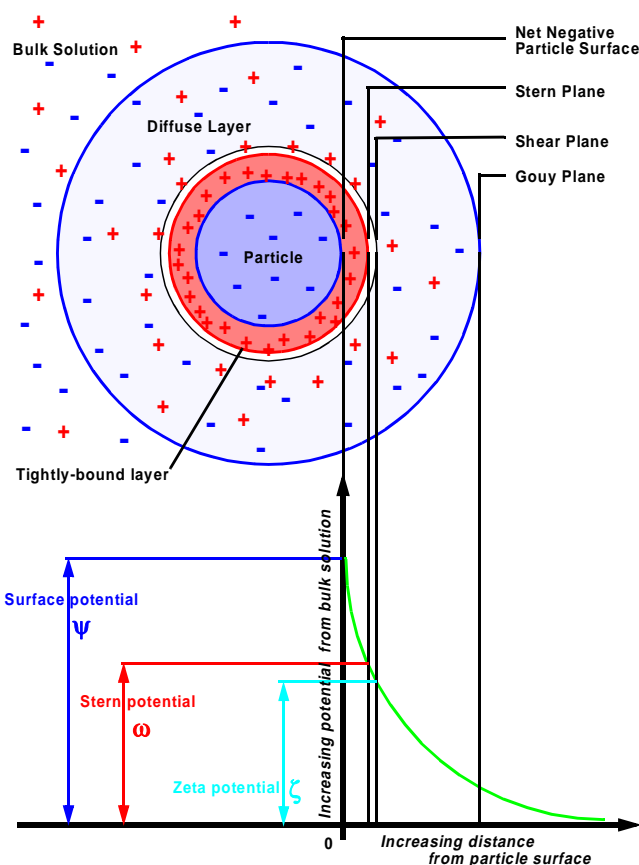


Figure 1: Double layer model of a particle suspended in water.

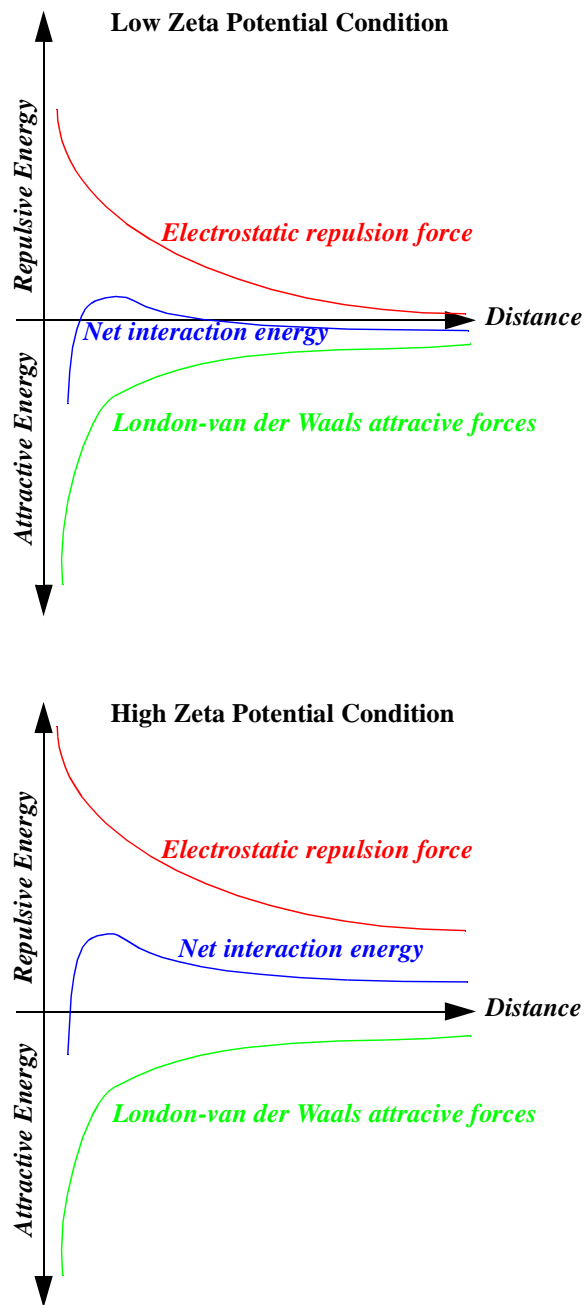


Figure 2: Net Interaction Energies at low and high Zeta Potential.

The fact that many organic and mineral colloidal particles possess a negative charge in aqueous environments causes them to repel one another, thus maintaining the stability of dispersion (Kemmer, 1988, Riddick, 1961). Electrochemical dispersion of colloidal particles has been studied for many years (Pitts, 1995, Riddick, 1961, Pitts, 1992, Elimelech et al., 1994). Several models such as the double layer theory, and the DLVO theory (named after Derjaguin, Landau, Verwey and Overbeek) attempt to explain the stability of colloids.

The double layer theory model (Figure 1) explains the repulsive forces between colloids. It is focused on the effect that the negatively charged colloids have over the positive ions in the bulk solution. The positive ions (also known as counter-ions) form a firmly attached layer around the surface of the colloid known as the Stern Layer. Additional positive ions attracted by the negatively charged colloidal particle face a repulsion force from the counter-ions attached on the Stern layer as well as by other counter-ions approaching the colloid. The density of this layer, known as the diffuse layer, gradually decreases with distance from the colloidal particle, until it reaches equilibrium with the rest of the ions in the solution. It is the diffuse layer surrounding the colloid that creates the most far-reaching repulsive force between colloidal particles; the higher the density of the diffuse layer, the greater the distance over which these repulsion forces are significant.

The primary function of the double layer is to neutralize the negatively charged colloid. This creates an electrokinetic potential between the surface of the colloid and any point in the bulk liquid. This potential (typically in the order of millivolts) is referred to as the surface potential.

The DLVO theory explains the stability of colloids by looking at two opposing forces acting upon colloidal particles. These two forces are the electrostatic repulsion explained by the double layer model and the Van der Waals forces which are weak attractive forces between particles.

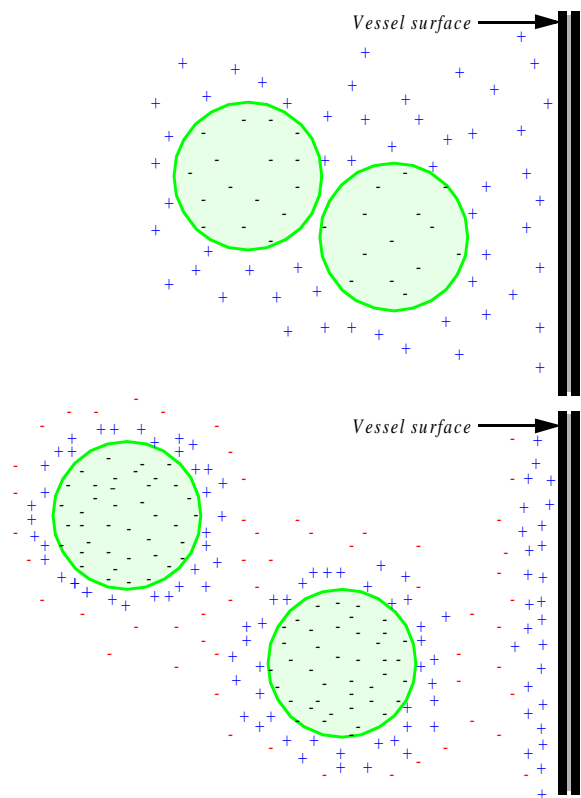


Figure 3: Simplified diagram of particle interaction at low and high Zeta Potential.

This theory explains the tendency of colloids to agglomerate or to remain in a stable state of dispersion by combining the two forces (Figure 2). The net interaction effect, shown in Figure 2 by the curve labeled "Overall interaction energy" is the result of the subtraction of the attraction force from the repulsion force. If the net value is positive a repulsion effect will be observed. In this figure it can be observed how, by increasing the natural ZP of the colloidal particles (lines 1), the overall interaction energy can be given a higher dispersion effect.

The natural ZP typically found in colloids in aqueous suspension ranges from -14 mV to -30 mV. At negative charge values higher than -30mV enough repulsion occurs to favor a stable dispersion. The more negative the charge value, the stronger the dispersion effect (Figure 3). For values ranging between -45 mV and -70 mV stable dispersions are assured.

As the ZP approaches zero, the repulsion effect is lost and agglomeration begins. For values ranging from -10 mV to -15 mV a threshold of agglomeration is observed, and from values between -5 mV to +5 mV strong agglomeration occurs (Riddick, 1961).

Pitts (1995) explains how the capacitive charge of particles can be significantly influenced by elevated voltage fields created by a capacitor system. This results in a sharp increase in the surface charge of wetted surfaces and a reduction of the surface tension of the bulk solution.

FIELD TESTS

Soft Drink Bottling Plant, Tucson , AZ.

An 18" ceramic electrode and a 30 kV DC power supply were installed in the pump suction of the reverse osmosis unit at soft drink bottling plant in Tucson, AZ. The objective of the installation was to study the effect of the high voltage electrostatic field created by the electrode on RO membranes as a means to keep them free of biological deposits (bio fouling).

The RO unit is described as follows:

Brand: OSMONICS

Model: OSMO 43CHF-PR216KY/DLX

Permeate Rate @77°F (25°C): 454 lt./min (120 gpm)

Concentrate Rate: 135 lt./min (35 gpm)

Pressure max / min: 2757 kPa (400 psi) (primary) / 1723 kPa (250 psi) final

The unit has a 3-2 series array, with each one of the vessels housing 5 FILMTEC membranes model: BW30-330.

The feed water to the unit is taken from the city of Tucson, AZ well system. It typically contains 300 parts per million (ppm) in total dissolved solids (TDS) (ranging from 250ppm to 500ppm). Pretreatment for the water involves sand filtration, carbon filtration and sodium softening.

Data Collection

The RO unit had been cleaned last during January 1997. The RO unit operates Monday through Thursday, each week, from 06:00 a.m. to 02:00p.m. Data was collected daily as normal quality control procedures for the facility.

The electrode and power supply were installed during the last week of March, 1997.

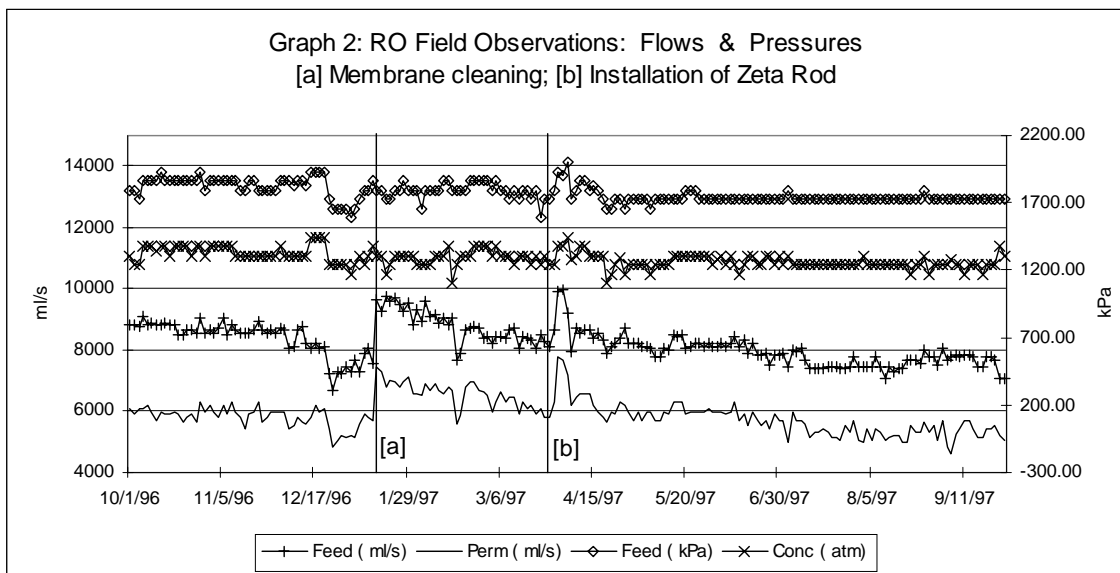
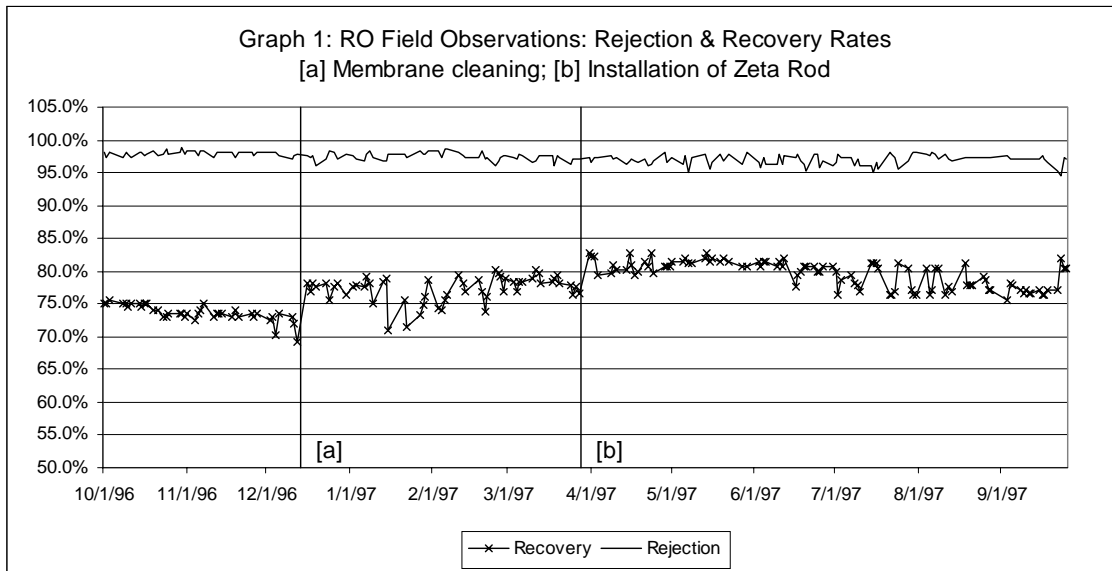
The data set utilized for the performance evaluation consisted of readings from October 1st 1996 through September 25th, 1997. There are, therefore, a total of 198 data points; 93 prior to the start of the treatment program, and, 104 points after.

Data Processing

For the performance evaluation the “raw data” was standardized to 25°C utilizing a normalization program (NORMPRO 2.0) from Fluid Systems.

Results

The most significant result of the study was the increase in the rate of permeate recovery. The recovery rate shows the amount of water produced as permeate as a percentage of feed water to the system. The figures for the recovery rate, salt rejection rate, and trans-membrane pressure drop (“dP” before the electrode installation averaged 77.26%, 97.5%, and 490 kPa respectively. After the installation, the values for those same parameters averaged 79.5%, 97.0%, and 474 kPa. This represents an increase in the recovery rate roughly of 3%. These results are shown in Graphs 1 - 2. Statistical data is shown in Table 1.



Facility management reported that historically membranes needed cleaning every 3 –4

Table 1: Field Observations - Statistical Data

Parameter	Flow (mL/s)		Recovery %	Rejection %	Trans-membrane dP	Temp. °C
	Feed	Permeate				
<i>Oct - Mar (93 observations)</i>						
Average	8642	6441	77.3	97.5	490	26.2
Std. Dev.	649	533	2.2	0.6	56	1.0
Minimum	7308	5670	71.0	96.1	345	25
Maximum	9765	7560	80.3	98.7	689	30
<i>Mar - Sept (104 observations)</i>						

Table 1: Field Observations - Statistical Data

Parameter	Flow (mL/s)		Recovery %	Rejection %	Trans-membrane dP	Temp. °C
	Feed	Permeate				
Average	7929	5705	79.5	97.0	475	28.4
Std. Dev.	499	531	2.0	0.8	37	1.1
Minimum	7056	4602	75.6	94.5	344	25
Maximum	9954	7796	82.8	98.2	551	34

months. On these occasions when the pressure vessels were opened, a heavy film of “slime” covered both the membranes and the interior walls of the vessels.

At the end of the testing period, one of the vessels was opened for a visual inspection. When the first membrane element was removed, the vessel wall showed a clean metal surface with no sign of biological deposits. The membrane body, like the vessel surface, was free of bio-film.

Two months after the initial test period ended, the membranes were cleaned, not because of a drop in performance, but as a preventive maintenance measure. Unlike previous cleaning experiences, the performance of the membranes was not enhanced, demonstrating that, the membranes had remained clean throughout the full nine month treatment period.

LABORATORY TESTS

In order to corroborate the results of the field study, laboratory tests were conducted in the microbiology laboratory of the University of Arizona in Tucson. Methods employed by the Bureau of Reclamation reverse osmosis research facility (Yuma, AZ) were followed. Robbins devices were fitted with reverse osmosis (RO) cellulose acetate membrane coupons. The purpose of the experiment was to establish if the electrostatic dispersion effect created by the capacitor system could inhibit biological growth and reduce biofouling of RO membranes in a nutrient rich environment.

Materials & Methods

Two Robbins device circuits were used for the experiment. A diagram of the circuits is illustrated in Figure 1. A control (treatment), and a treated unit. The treatment consisted of an electrode inserted into a metal reservoir. The electrode was powered by a 30 kV DC power supply.

In both cases, Tucson City water was used to make up the bulk solution. The water was amended with 0.1% glucose, 1 mg/L nitrate, and 0.1 mg/L orthophosphate to enhance the growth of indigenous bacteria in the tap water and to enable the tests to be completed over a short period of time.

The flow through each Robbins device circuit was circulated at a rate of 3-4 ml/min with a new amended tap water sample put in place every 48 hours to prevent the test population of bacteria from going into the death phase.

Viable plate counts were performed every 48 hours on the new tap water samples and on the old sample that was being removed.

Plugs with RO membrane coupons were removed after 24 hours, 48 hours, and 7 days of testing. At each of these times, coupons were tested in triplicate from the control and the test treatments. In addition at time 0, one coupon was tested for a background count. These tests consisted of viable plate counts performed by:

- 1) gently washing the membrane surface with sterile saline,
- 2) vigorously agitating the membrane coupon in 2 ml sterile saline with sterile glass beads, and
- 3) performing viable plate counts.

All plate counts were performed using the spread plate method on R2A agar and incubation at 27°C for 5 to 7 days. Bacteria were not identified.

Results

Results are shown in Table 2. The RO membrane coupons exposed to the treated circuit had significantly less biofilm on the surface than the control coupons at 24 hrs ($p = 0.05$). After 48 hours ($p = 0.24$) and after 7 days ($p = 0.93$), there was no significant difference between the control and the test coupons. In these later samples there were also no significant difference in the numbers of bacteria in the two reservoirs during this study ($p = 0.99$). The bacteria population had advanced after 48 hours to levels characteristic of sewage treatment population.

Table 2: RO Coupon Laboratory Test Results

Day/ Treatment	Temp °C	pH	Conductivity µS	CFU/mL		Coupons CFU/cm ²	P*
				48 hr water	fresh water		
Day 0 Control	23.6	8.12	360		2.9×10^2	$< 4.0 \times 10^1$	
Day 0 Test	23.6	8.12	360		2.9×10^2	$< 4.0 \times 10^1$	
Day 1 Control	23.0	7.83	380			1.7×10^6	
Day 1 Test	23.0	7.94	370			8.4×10^5	0.05
Day 2 Control	22.5	7.32	370	5.4×10^5	3.1×10^5	6.1×10^5	
Day 2 Test	23.0	7.74	370	3.1×10^5	1.3×10^5	1.1×10^6	0.24
Day 3 Control	24.0	7.59	370				
Day 3 Test	24.0	7.61	360				
Day 4 Control	23.5	7.46	370	5.3×10^6	2.9×10^6		
Day 4 Test	23.5	7.50	370	4.8×10^6	2.4×10^6		

Table 2: RO Coupon Laboratory Test Results

Day/ Treatment	Temp °C	pH	Conductivity μS	CFU/mL		Coupons CFU/cm ²	p*
				48 hr water	fresh water		
Day 5 Control	24.0	7.41	390				
Day 5 Test	24.0	7.45	400				
Day 6 Control	23.5	6.98	390	2.0 x 10 ⁷	1.4 x 10 ⁷		
Day 6 Test	23.5	7.27	400	3.6 x 10 ⁷	3.0 x 10 ⁷		
Day 7 Control	23.0	6.50	400			6.0 x 10 ⁶	
Day 7 Test	22.0	7.10	400			3.1 x 10 ⁶	0.93
* p represents the statistical probability of an error in the results. For the results in bacterial counts in the coupons for Day 1, the difference between Control and Test measurements is statistically significant, whereas the results obtained for Day 2 and Day 7 show no statistically significant difference.							

Results obtained in samples more representative of industrial water systems, even those very high in bacterial population (CFU/ml < 1 x 10⁵), show the electronic treatment to be effective as a control measure. The high-density electrostatic field was capable of reducing biofilm from formation on the membrane coupons.

The pH in the control reservoir was observed to drop more rapidly than in the test reservoir. This is likely the result of more acid production by larger populations of bacteria counted in the control, indicating a higher level of bacterial activity. The temperatures were maintained at comparable levels and the conductivity readings remained close by comparison in the two reservoirs.

The Robbins device circuits in the laboratory tests operated at laminar flow fluid velocities, a more severe test of fouling prevention than the turbulent flow common to commercial membrane designs.

Under laminar flow, a condition highly favorable for biofilm formation, a significant difference was established between the treated and the control coupons.

CONCLUSIONS

An electronic treatment technique that has been effective in dispersing colloidal particles contained in cooling water and process water has been shown effective as a means of preventing biofilm formation on reverse osmosis membranes.

The findings of this study are sufficiently promising to encourage an expectation of success in other applications. Further research we feel will likely extend benefits into online cleaning and prevention of fouling in other cross flow filtration systems such as ultrafiltration and ceramic filtration.

We hope that this preliminary work is sufficient to encourage further research that will more completely develop the full set of parameters controlling this new technology.

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