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Phosphate limitation in reverse osmosis: An option to control biofouling?

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ABSTRACT

The focus of this study was to develop and evaluate a method to measure phosphate down to a level of 1 μg P/L or lower, and to make an inventory of the concentration of phosphate in reverse osmosis (RO) feed water. In addition, the phosphate concentration was measured before and after various pre-treatment steps in three integrated membrane systems (IMS), and the pre-treatment steps were evaluated and compared in terms of their ability to remove phosphate. An existing method was modified to allow phosphate to be measured to levels below 1 μg P/L. After modification, the limit of detection was approximately 0.2 μg P/L. The phosphate concentration was monitored in three IMS. The feed water to all four systems was surface water, and the pre-treatment scheme comprised the following steps: (in-line) coagulation, UF/MF followed by antiscalant and/or acid addition prior to the RO units. The level of phosphate in the feed water (surface water) varied from 7–115 μg P/L. In pre-treatment systems without in-line coagulation, no phosphate removal was observed. The combination of in-line coagulation and UF reduced the phosphate level by 75–98%, to 0.2–2.8 μg P/L. However, after the addition of phosphonate antiscalant and/or acid, the phosphate concentration increased by 48 to 680% to 0.6–1.4 μg P/L in three IMS.

Keywords: Phosphate limitation; Integrated membrane systems; Bio-fouling; Antiscalants

1. Introduction

Biological fouling has been called "the Achilles heel of membrane processes" [1]. Biofouling is a known problem in membrane systems, and the efficiency of many membrane systems is limited by fouling. The growth of bacteria on a membrane spacer or surface is known as biofilm formation. The accumulation of biofilm and biomass that lead to clogging (decrease in permeability) of the membrane is known as biological fouling, or biofouling [2]. This clogging increases the hydraulic resistance of the membrane, which leads to an increase in pressure drop along the elements. According to Al-Ahmad [2], the negative effects of biofouling are flux decline, increased differential pressure and increased feed pressure, membrane biodegradation and increased salt passage. Each of these factors will lead to an increase in operational and maintenance costs for any given plant due to increases in elements needed for required production, energy consumption, chemical and labor costs (for cleaning), lower quality water (hence more post-treatment), and element replacement rate.

Biofouling is typically only identified once an element has been compromised. Therefore, both prediction and

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prevention have been the focus of research. Vrouwenvelder and van der Kooij [3] measured biomass in feed water by monitoring adenosinetriphosphate (ATP), total direct cell counts (TDC), and assimilable organic carbon (AOC). In 2003, Vrouwenvelder et al. [4], compiled a set of tools that can identify the likelihood of fouling. Some of these tools determine biofouling potential, while other focus on scaling. Most of these tools measured the feed water quality (AOC, MFI–UF), while others were destructive (membrane autopsy). Thus, to date most research on biofouling has been focused on establishing a correlating between the carbon concentration in the RO feedwater and the biofouling potential in an RO plant. In addition, Vrouwenvelder et al. [5] tested 14 antiscalants that were either polyacrylic acid, phosphonate, or both. The AOC of each was measured and found to correlate with the biomass production potential (BPP). They found that high levels of AOC increased growth and that antiscalants with higher phosphate, but lower levels of AOC, had a much lower BPP. While there are many methods to pretreat feed water to prevent biofouling, such as biocides [2], enhanced coagulation [6], and biological filters [7], there is little information on the potential causes of biofouling. Only Vrouwenvelder considers low levels of nutrients to be an influence, and this he prescribes to the choice of antiscalants [5].

In 1997, Flemming stated that even if there is a four log removal of microorganisms during pre-treatment, they, unlike other fouling causes, increase via reproduction using biodegradable substances [1]. Though biofouling can marginally enhance nutrient removal of dissolved substances, it is a phenomenon that needs to be prevented to ensure longevity of membrane systems. Microorganisms need a minimum quantity of nutrients for biological growth. Phosphate (PO_4^{3-}) is considered to be a limiting nutrient, for the growth rate of the microorganisms may be dependant on the phosphate concentration. Therefore, it is theorized that in order to reduce biofouling, a reduction in phosphate is necessary. However, the levels of phosphate required may be so low that it is undetectable by current standard laboratory procedure.

Phosphate can be classified into three types: orthophosphates ($H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-}); condensed phosphates (pyro-, meta-, and other polyphosphates); and organic phosphates [8]. The focus of this study is orthophosphate, which is the form, "...in which phosphorus is most readily available for biological utilization" [8]. Orthophosphate shall be referred to as phosphate throughout the study. Phosphate is present in both seawater and surface water. During pretreatment, phosphate is removed by either physicochemical or biological means. In chemical precipitation, the addition of a metal salt (e.g., $FeCl_3$, $AlCl_3$) to the water instigates a reaction that creates insoluble metal phosphates (e.g., $FePO_4$, $AlPO_4$) that precipitate out of solution [9], and, according to Morse, the most suitable metals are iron and aluminium, added as chlorides or sulphates [9]. Both examples noted above remove the phosphate from solution before retaining it during flocculation and physical removal during sedimentation. Phosphate can also be removed by biological processes. Since phosphorus is a necessary and often limiting nutrient for cell growth, bacteria can be cultured for maximum removal efficiency. This treatment is common in wastewater treatment plants where an anaerobic or anoxic phase precedes an aerobic environment. However, this may require an additional carbon source and results in a large quantity of sludge [9]. In Western Europe, typical wastewater influent comprises 7 mg P/L, which can be reduced to below 1 mg P/L in the effluent.

Typical seawater has less than 33 μg P/L of phosphate [10] with an average of 20 μg P/L [11]. The European Environmental Agency shows 2004 data that along the coast of the Netherlands the concentration of phosphate in seawater is greater than 30 μg P/L, while in adjacent marine waters it is reduced to approximately 20 μg P/L [12]. Data from the European Environmental Agency EEA show the average concentration of orthophosphate in almost 1,000 EU rivers in eight countries was about 45 μg P/L in 2003. This is relatively stable, following a steady decrease over the previous decade. In 171 EU lakes in 14 countries, the concentration in 2003 was about 13 μg P/L and had been constant over the previous decade.

The focus of this study was to develop and evaluate a method to measure phosphate down to a level of 1 μg P/L or lower, and to make an inventory of the concentration of phosphate in reverse osmosis (RO) feed water. In addition, the phosphate concentration was measured before and after various pre-treatment steps in three integrated membrane systems (IMS), and the pre-treatment steps were evaluated and compared in terms of their ability to remove phosphate. Finally, the relationship between the phosphate level in RO feedwater and the extent of biofouling in the three IMS systems is discussed.

2. Methods and materials

The procedure used in this study was a modification of the ascorbic acid method. For concentrations below 20 μg/L it is necessary to extract the molybdenum blue via hexanol and measure the extracted concentrate on a spectrophotometer at 680 nm.

2.1. Reagents

All chemicals used had a minimum assay of 95%, though an assay of 99% is preferable. No phosphate impurities were noted. All reagents were mixed with

water filtered by the Millipore Milli-Q Advantage A10 ultrapure water purification system.

Reagent 1: H_2SO_4 2.5 M. 70 mL concentrated H_2SO_4 was added to 420 mL H_2O and stored in a 500 mL glass stoppered bottle.

Reagent 2: Potassium antimonyl tartrate. 1.3715 g $K(SbO)C_4H_4O_6.½H_2O$ was dissolved in 400 mL H_2O and diluted to 500 mL in a volumetric flask, then stored in a 500 mL glass stoppered bottle.

Reagent 3: Ammonium heptamolybdate. 20 g $(NH_4)_6Mo_7O_{24}.4H_2O$ was dissolved in 500 mL H_2O and stored in a 500 mL glass stoppered bottle.

Reagent 4: Ascorbic acid 0.1 M. 1.76 g ascorbic acid was dissolved in 100 mL H_2O. This solution is stable for about 1 week at 4°C. However, it was prepared daily.

Combined reagent: The above reagents were mixed in the following order: 125 mL Reagent 1 + 12.5 mL Reagent 2 + 37.5 mL Reagent 3 + 75 mL Reagent 4. The mixture was stored in a 250 mL glass stoppered bottle.

Stock P solution: 439.0 mg KH_2PO_4 (dried at 105°C for a few hours) was dissolved in 1000 mL. 1 mL = 100 μg PO43-P and stored in a 1 L glass stoppered bottle.

Standard P solution: 5.00 mL Stock P solution was diluted to 1000 mL. 1 mL = 0.05 μg P. This solution was stored in a 1 L glass stoppered bottle.

All glassware and plastic bottles were soaked in an acid wash consisting of one part HCl (32%) and four parts MilliQ (MQ) water for 1 h, then rinsed using 20–30 mL MQ water and shaking for 5 s, at least three times.

2.2. Calibration

To create a calibration line, 0, 1.00, 2.00, 3.00, and 4.00 mL of Standard P solution (0–0.2 μg P) was added to five 250 mL bottles. MQ water was added until the end volume was 200 mL (0–1 μg P/L). Then, 20 mL of combined reagent was added to each bottle and shaken vigorously for 10 s, then allowed to stand for 10 min. Thereafter, 15.0 mL n-hexanol was added and the mixture was shaken vigorously for 15 min. The mixtures were then transferred into separation funnels, and after 15 min, the aqueous layer was rejected. Subsequently, 1 mL isopropanol was added and swirled gently in the funnel to clear water mist, and then the aqueous layer was further rejected. The solvent layer was collected in a centrifuge tube and centrifuged for about 1 min at 5000 rpm. The absorbance was measured at 680 nm in a 5 cm cuvette against n-hexanol and plotted against μg P/L. From this graph, a mathematical expression of the calibration line was determined in the form of

$$y=mx+b$$

where y is the absorbance, x the phosphate concentration (μg P/L) = μg P in sample*1000 mL/mL sample; b is the intercept and m is the slope = absorbance/(μg P/L).

2.3. Procedure

A sample not exceeding 200 mL and containing between 0.00 and 10 μg P was placed into a 250 mL bottle. A blank (sample with 0.00 μg P added) was also always carried out. The same procedure was followed as in the calibration. The μg P/L was calculated from the equation

$$\mu g\ P/L = (A - B)/m$$

where A is the absorbance of sample, B the absorbance of the blank and m is the absorbance/(μg P/L).

3. Results and discussion

3.1. Calibration

A calibration line was constructed for every batch of samples measured. From the results of these measurements, calibration lines were determined. This was done for both glass and PE measurement bottles, using 1 cm and 5 cm cuvettes for glass, but only 5 cm cuvettes for PE (Table 1). The results from 1 cm cuvettes were multiplied by 5. The original result is also shown in parenthesis. Only calibration lines with an R^2>0.97 were used in calculating the average and standard deviation; the units of both are absorbance/(μg P/L).

The averages from all the different types of calibration lines were similar: PE had an average of 0.390 absorbance/(μg P/L), while glass gave 0.0363 absorbance/(μg P/L) and 0.0407 absorbance/(μg P/L) with the different size cuvettes. If the two glass measurements were combined, the n = 15 samples would have an average of 0.0383 absorbance/(μg P/L) and a standard deviation of 0.0038 absorbance/(μg P/L). PE bottles gave a higher standard deviation, 0.0077 absorbance/(μg P/L). The PE calibration was verified because the combined glass average showed no significant difference between the averages of glass and PE. Therefore, a conversion of 0.0390 absorbance/(μg P/L) was used for all results.

Table 1
Average calibration lines for different materials and cuvette sizes

Material	Glass	Glass	PE
Cuvette, cm	1	5	5
n	8	7	8
Average	0.0363 (0.0074)	0.0407	0.0390
Standard deviation	0.0030 (0.0006)	0.0034	0.0077

3.2. Limit of detection

The LOD was determined using polyethylene sample bottles. The calibration used is noted in Section 3.1. For five different attempts at measuring the LOD, the results are given in Table 2.

The LOD is defined as the average of at least 10 sample blanks plus three times the standard deviation. This absorbance is then transformed into μg P/L by the calibration line. An example of the determination of the LOD is shown below. Please note that absorbance is unitless.

$$Average+3*(sd)=\mathrm{LOD}$$

$$0.0020+3*(0.0009)=0.0046$$

Using 0.0390 units of absorbance/(μg P/L),

$$\mathrm{LOD}=\frac{0.0046}{0.0390}=0.12\,\mu\mathrm{g\,P/L}$$

The average LOD for the $n = 5$ measurements was *0.194 μg* P/L. Therefore, the LOD was set at 0.20 μg P/L. Any reading on the spectrophotometer that correlated with a concentration that was lower than 0.20 μg P/L was noted as <0.20 μg P/L.

3.3. Storage equipment

The preferred material to store and measure phosphate is polyethylene (PE) since absorption of phosphate to and from the container is less than with glass. However, the majority of the lab analysis was performed in glassware, due to the limited availability of PE containers. This material may give results that are different from the glass since the hexanol used coated PE and sticks to the surface. Not only does it make the PE bottles more difficult to clean, but it also reduces the volume of concentrated sample to be analyzed in the spectrophotometer. Nevertheless, PE containers were used in the analysis because the LOD is lower than the LOD for glass.

Table 2
Limit of detection data

Average absorbance	Standard deviation	*n*	LOD, μg/L
0.0020	0.0009	12	0.12
0.0043	0.0017	12	0.24
0.0027	0.0017	12	0.20
0.0048	0.0014	10	0.23
0.0031	0.0015	12	0.19

3.4. Fate of phosphate in four EU treatment plants

Three treatment plants (referred to as Plants A through C) were sampled (in duplicate and averaged) in order to make an inventory of the concentration of phosphate in RO feed water. In addition, the phosphate concentration was measured before and after various pre-treatment steps in four IMS, and the pre-treatment steps were evaluated and compared in terms of their ability to remove phosphate. Finally, the relationship between the phosphate level in RO feed water and the extent of biofouling in the three IMS is discussed.

3.4.1. Plant A

Plant A (Fig. 1) has a production capacity of 1200 m^3/h of high quality industrial water from surface water. This treatment plant was sampled twice, once in the middle of the spring (A1) and again in early summer (A2). The first batch of samples was collected in the middle of spring, and again in early summer.

Canal water was pretreated with 8 mL/L of PAC followed by rapid sand filtration. The PAC dose is dependant on the turbidity, with more added when the turbidity is higher (computer controlled), to reduce fouling in the pipeline (3 km) to the treatment plant. The water is filtered through 150 μm filters. Ferric chloride is added, ranging from 2–5 mg/L (computer controlled), with a typical dose of about 3 mg/L. Thereafter, the water is fed to a 100 kDa UF membrane. These are dead-end UF filters which are backwashed approximately every 15 min. After UF, an antiscalant is added, as well as sodium bisulphite if chemical (chlorine) residuals are present. The RO elements are replaced ca. every 5 years. The recovery of the RO is 85%, and it is cleaned once every 2 months in non-summer months and once every 2 weeks in summer, with acid followed by base. The average number of cleanings is 12 per year.

Fig. 2 and Table 3 show the change in phosphate concentration throughout the during treatment process.

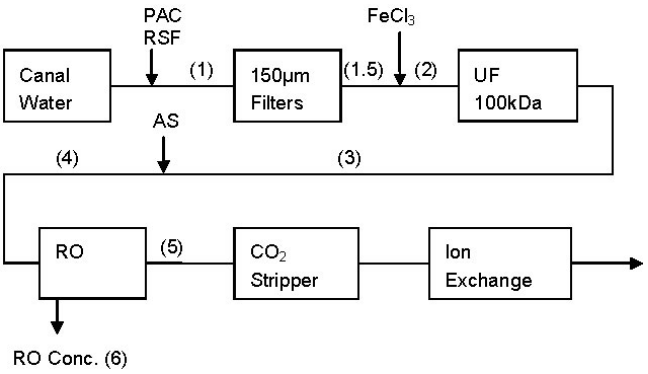

Fig. 1. Treatment scheme of Plant A. Numbers in parenthesis represent sampling points.

Table 3
Phosphate concentration and removal over various treatment steps at Plant A

Sample	Spring		Summer		Notes
	μg P/L	% change	μg P/L	% change	P conc. interpolated/extrapolated from calibration
1	41.13		114.71		Raw water
1.5	34.15	−17	111.97	2	Before coagulation
2	12.51	−63	120.12	0.07	After coagulation (UF feed)
3	<0.20	−98	2.04	−98	UF permeate
4	1.56	6.82	3.02	0.48	UF permeate + AS+ acid (RO feed)
5	<0.20	−87	<0.20	−93	RO permeate

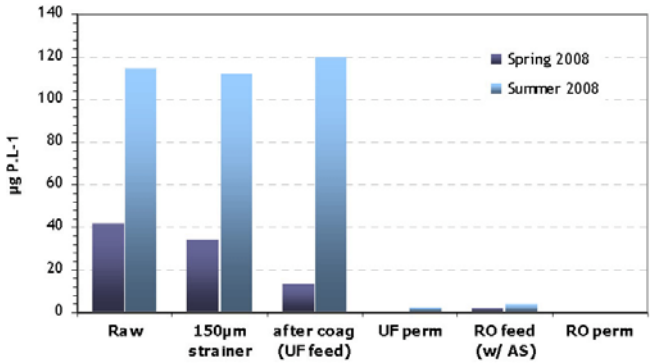

Fig. 2. Phosphate level over various treatment steps for Plant A in mid-spring and early summer.

The feed water differed between the two samples, from 41 to 114.7 μgP/L in the spring and summer, respectively (Table 3). This can be attributed to the time of year (temperature) that the samples were taken and dose of PAC added. Since the coagulant addition is dependent on raw water quality, it is likely that the concentrations added were not the same during both samplings. However, the ferric chloride coagulation removed almost 70% of the phosphate in the earlier sample but added 5% more phosphate to the latter sample. Since the raw water, pre-coagulation, and post-coagulation samples were all diluted 1:1 with MQ water, this 5% difference can be due to dilution error and the phosphate concentration during these three steps may not have changed. The pH of the water may vary by season (e.g., due to fertilizer run-off), which is known to affect the solubility of $FePO_4$, which is at its minimum pH = 5. Also, the different water temperatures have an effect on coagulation, but the coagulation efficiency is better at higher temperatures, which does not explain why there is no phosphate removal during the summer coagulation step.

In the case of both samples, UF removed 98% of the phosphate (Table 3), but the mid-spring sample was below the limit of detection, noted as <0.20 μg P/L, while the early summer sample was just over 2 μg P/L.

Table 4
Cleaning frequency and phosphate concentration for Plant A

Recovery, %	85
Cleaning frequency	
Total, y	12
Non-summer, months	0.5
Summer, months	2
RO feed, μg P/L	
Spring	1.56
Summer	3.02

The addition of (phosphonate) antiscalant and acid increased the concentration in both cases by an additional 1–1.5 μg P/L to 1.56 μg P/L in mid-spring and 3.02 μg P/L in the early summer. These were the levels of the RO feed. The RO permeate was below the LOD.

Chemical cleaning of the RO units was much less frequent in the non-summer months when the phosphate concentration was half of what it is during the summer. However, in this plant, when the phosphate concentration increases by a factor of two, the cleaning frequency increases by a factor of four. This increase in cleaning frequency can be due to the increase in temperature, as well as the increase in phosphate concentration, since the growth rate of bacteria is greater at higher temperatures.

3.4.2. Plant B

This plant treated river water for use in industry (Fig. 3). It currently produces 63 m^3/h. The samples were collected in winter and early summer. The raw river water passed through a heat exchanger before being dosed with up to 6 mg/L $FeCl_3$ and sent to the continuous sand filter. After that, the water is fed to UF membranes (MWCO = 150–200 kDa). The UF was backwashed with permeate water every 15 min, and chemically enhanced backwashed with NaOCl every 6 h. Every 3 or 4 weeks the UF was cleaned in place with acid. After UF, 3.8–4.0 mg/L of phosphonate antiscalant was added, as well as HCl to adjust the pH to 7.5. The

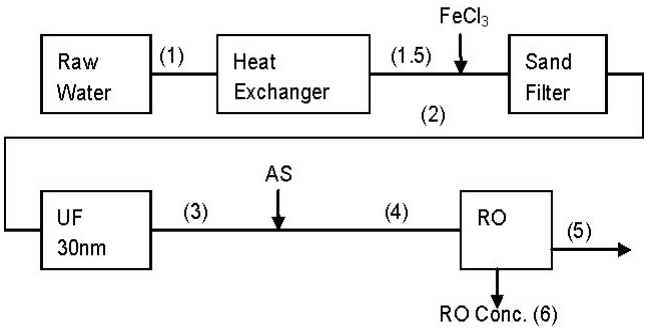

Fig. 3. Treatment scheme of Plant B. Numbers in parenthesis represent sampling points.

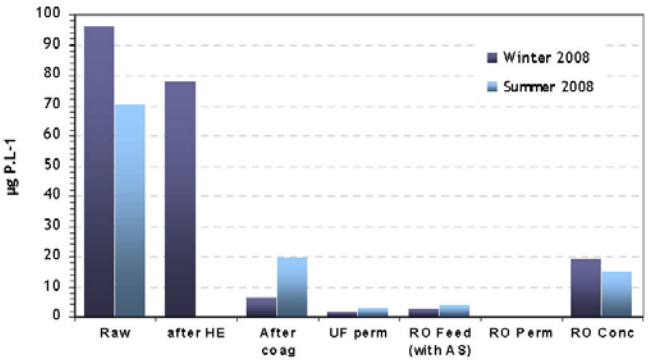

Fig. 4. Phosphate level over various treatment steps for Plant B in winter and early summer.

Table 5
Phosphate concentration and removal over various treatment steps of Plant B

Sample	Winter		Summer		Notes
	µg P/L	% change	µgP/L	% change	P conc. interpolated/extrapolated from calibration
1	96.47		70.18		Raw water
1.5	77.56	−20	—		Before coagulation (after heat exchanger)
2	6.09	−92	19.67	−72	After coagulation (UF feed)
3	1.54	−75	2.80	−86	UF permeate
4	2.44	0.58	3.95	0.41	UF permeate + AS+ acid (RO feed)
5	<0.20	−92	<0.20	−95	RO permeate
6	18.91		14.72		RO concentrate

recovery of the RO is 75%. The RO units were cleaned once per month in winter and two or three times a month in summer with firstly caustic soda, then citric acid with 0.1% HCl, and finally commercial cleaning agents.

Fig. 4 shows the change in phosphate throughout the treatment process. Table 5 contains the averaged phosphate concentration in samples collected in the treatment plant. The feed water differed between the two samples from ca. 96 µg P/L in the winter to 70 µg P/L in the summer (Table 5). However, the phosphate level in the feed water was 25% lower in the summer sample compared to the winter sample. This is unusual, considering the weather was considerably warmer in the summer. However, precipitation may have diluted the sample since the source is surface water. The pretreatment to the UF feed water, coagulation, removed almost 94% of the phosphate in the winter (to about 6 µg P/L) and 72% of the phosphate in the summer, to almost *20 µg* P/L (Table 5). There was no pH control in the coagulation step. $FeCl_3$ appeared to be less effective in warmer weather, possibly due to variation in pH, even though the increase in temperature should cause it to be more effective.

The raw water passed through a heat exchanger prior to the addition of coagulant. The UF removed 75% of the phosphate in the winter, to about 1.5 µg P/L and 86% of the phosphate in the summer, to 2.8 µg P/L (Table 5). The addition of phosphonate antiscalant (3.8–4 mg/L) and acid increased the concentration in both cases by ca. 1 µg P/L to 2.44 µg P/L in the winter and 3.95 µg P/L in the early summer. These were the levels of the RO feed. The RO permeate was below the LOD.

The chemical cleaning frequency of the RO units was three times more frequent in the summer than it was during the rest of the year, even though the phosphate concentration only increased by 50% (Table 6). The RO concentrate was analyzed for this plant. By knowing the recovery (R) of the plant, it is possible to calculate the concentration factor (CF) of the RO concentrate compared to the feed (Table 7). The concentration factor can be calculated as

$$\frac{1}{1-R}=CF$$

The recovery at this plant is 75%; therefore,

$$\frac{1}{1-0.75}=4$$

assuming that salt rejection is 100%.

Table 6
Cleaning frequency and phosphate concentration for Plant B

Recovery, %	75
Cleaning frequency	
Total/y	20
Non-summer, months	1
Summer, months	3
RO feed, μg P/L	
Winter	2.44
Summer	3.95

Table 7
Concentration factor and relationship to RO feed and RO concentrate

	B1	B2
Recovery, %	75	75
CF	4.00	4.00
RO feed, μg P/L:		
Actual	2.44	3.95
Theoretical (calculated)	4.73	3.68
RO concentration, μg P/L:		
Actual	18.91	14.72
Theoretical (calculated)	9.74	15.82

Since the concentration factor was 4, the RO concentrate should be about four times greater than the difference between the RO permeate, which is assumed to be zero due to 100% rejection and RO feed. Therefore, from the actual RO feed it is possible to calculate what the RO concentrate should be based on the *CF*. Conversely, from actual RO concentrate it is possible to calculate what the RO feed should be.

During winter, the actual concentrate is twice as high as the theoretical concentrate. Some of this difference may be due to measurement error. Some of this also may be due to degradation of the phosphonate antiscalant or release of phosphate by bacteria. For the summer period, the actual concentrate was the same as the theoretical concentrate. The actual concentrate was about 7% lower than the calculated. This could signify the consumption of some phosphate by bacteria within the RO unit, i.e. the presence of a biofilm. Since this unit is cleaned 2–3 months in the summer, it is very likely that there is a biofouling problem.

3.4.3. Plant C

This plant treats canal water for use in industry, and has a capacity of 100 m^3/h (Fig. 5). The samples were collected in early summer. The feed water is surface water, which is fed by a river and a canal. Some of this water is used as cooling water; therefore, the intake water is always above 10°C, typically 15–25°C. No

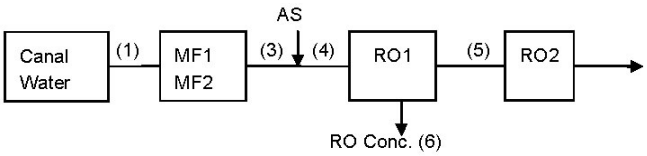

Fig. 5. Treatment scheme for Plant C. Numbers in parenthesis represent sampling points.

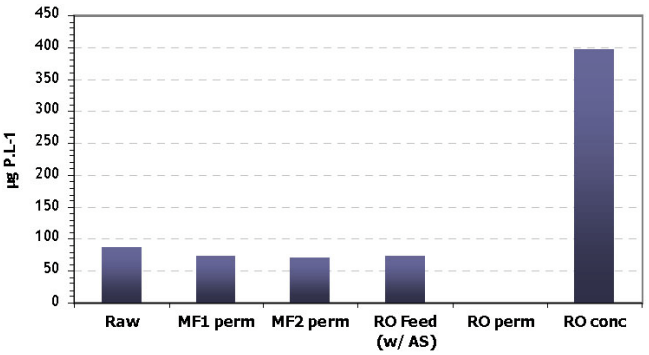

Fig. 6. Phosphate level over various treatment steps for Plant C in early summer.

coagulant is added prior to the MF membranes, but the water does pass through a 300 μm screen. After microfiltration, a double pass RO is used to produce high-grade water for high pressure boilers. A phosphonate antiscalant (4.5 mg/L) is dosed before the first RO pass. However, the cooling water is chlorinated nightly for 30–40 min at 20° with a peak of 50 mg/L Cl_2. When this occurs the MF permeate does not enter the RO as feed water.

The MF units are cleaned by air scour a few times per day, as well as regular backwashes with water. Also daily there is enhanced flux maintenance with NaOCl and caustic at pH 10. Finally, the MF is cleaned in place once per year. The cleaning frequency of RO1 is once per year. Cleaning occurs when there is a 15% increase in net driving pressure or loss of the mass transfer coefficient for water.

Fig. 6 shows the change in phosphate throughout the treatment process, and Table 8 shows phosphate concentration in samples collected in the treatment plant. These are averaged and converted into phosphate concentration.

The concentration of phosphate in the feed water (ca. 85 μg P/L) of plant C (Table 8) was similar to Plant B (78–96 μg P/L). However, the treatment process and RO cleaning frequency are quite different. Even though the phosphate concentration in the RO feed water is high, a 15% increase in net driving pressure or loss of mass transfer coefficient was not observed in the RO units. This could be because of the nightly chlorination of the MF feed water. Even though the MF permeate is diverted from the RO (since chlorine may damage the

Table 8
Phosphate concentration and removal over various treatment steps of Plant C

Sample	Summer		Notes
	μg P/L	% change	P conc. interpolated/extrapolated from calibration
1	85.14		Raw water
3.1	72.47		MF1 permeate
3.2	70.97	−16	MF2 permeate
4	71.40	0.006	MF permeate + AS (RO feed)
5	<0.20	1	RO permeate
6	397.95		RO concentrate

Table 9
Concentration factor and relationship to FO feed and RO concentrate

Recovery, %	80
CF	5.00
RO feed, μg P/L:	
Actual	71.40
Theoretical (calculated)	79.59
RO concentration, μg P/L:	
Actual	397.95
Theoretical (calculated)	356.99

Table 10
Cleaning frequency and phosphate concentration for Plant C

Recovery, %	80
Cleaning frequency	
Total/y	1
Non-summer, y	1
Summer, y	1
RO feed, μg P/L	
Non-summer	Not tested
Summer	71.40

RO membrane), it still is effective at sterilizing the MF unit and reducing the number of bacteria present in the MF permeate. In addition, since the bacterial cell wall is a semi-permeable membrane, a change in salinity, for example, from saline to fresh water, may cause some bacteria to absorb more water, thus explode and die. This osmotic shock may occur when the RO feed water (TDS = 7000 mg/L), which is saline MF permeate, is replaced with RO permeate (TDS <100 mg/L) during chlorination of the cooling towers. Since this occurs nightly, any biofils formed may be effectively removed before they result in biofouling.

The concentrate of this plant was measured and compared to the theoretical amount of phosphate that should be in the RO concentrate (Table 9). The theoretical RO concentrate is about 10% less than what is actually measured. This means that either some phosphate leaves the RO unit because of release by bacteria, or the difference may just be due to measurement error. There is no evidence of fouling at this plant, as the RO units are only cleaned once per year. Even though the levels of phosphate in the RO feed water are very high (ca. 85 μg P/L), the difference in theoretical and actual phosphate may be due to dilution error during measurement.

3.4.4. All plants

The addition of antiscalant can affect the concentration of phosphate in the RO feed. All plants used a phosphonate antiscalant and in all cases except for Plant C, the addition of an antiscalant increased the concentration of phosphate in the RO feed. This increase was between 0.9 and 1.4 μg P/L. However, since all of antiscalants are proprietary, the percentage of phosphonate in each antiscalant is unknown. Also, it is not known if there are other chemicals present in the antiscalant that may cause it to degrade. In the two IMS analyzed in this study, the antiscalant addition increased the phosphate concentration by 48–680%.

Phosphate removal data (Tables 3 and 5) show that in-line coagulation was effective in terms of phosphate removal (63–92%). However, when inline coagulation was combined with UF, the removal increased to 75–98%. The cleaning frequency and antiscalant doses are shown in Table 11, and show that antiscalants add between 0.9 and 1.4 μg P/L to the UF in Plants A and B. This increase is equivalent to a 50% to 680% increase in phosphate (Table 11). Since such a large increase occurs, the optimization of pretreatment loses its effectiveness, if whatever phosphate is removed is going to be added again via antiscalants. In conjunction with optimizing in-line coagulation for phosphate removal, it is also necessary to optimize antiscalant addition with respect to phosphate. While Plants A and B follow similar patterns, an increase in phosphate in the RO feed in warmer months and more frequent RO cleaning, Plants C shows different results.

Table 11
Cleaning frequency and antiscalant doses for all plants

Plant	RO recovery, %	Cleaning frequency		RO treatment, AS dose, mg/L	MF/UF permeate, μg P/L	RO feed	% change
		Non-summer	Summer				
A1	85	0.5/month	2/month	1–1.5	<0.20	1.56	7.28
A2					2.04	3.02	
B1	75	1/month	3/month	3.8–4	1.54	2.44	1.1
B2					2.80	3.95	
C	80	1/y	1/y	4.5	71.72	71.40	−0.4

In Plant C, coagulant was not added prior to the MF units, and thus the phosphate level in the RO feed water was over 70 μg P/L. However, there no evidence of biofouling in this plant as the increase in mass transfer coefficient for water or head loss across the pressure vessel was negligible. As stated earlier, this could be because of the osmotic shock that occurs when RO permeate was recirculated over the RO units while the cooling towers were chlorinated.

4. Conclusions

- An existing method [13] was modified to allow phosphate to be measured to levels below 1 μg P/L. The LOD determined was approximately 0.2 μg P/L.
- In one integrated membrane system where no coagulant was added during pre-treatment prior to MF, no removal of phosphate was observed. The phosphate level in the RO feed water was the same as in the raw water (70 μg P/L).
- In two IMS where in-line coagulation was combined with UF, the level of phosphate in the feed water (surface water) was reduced from 41–115 μg P/L by 96–99%, to <0.2–2.8 μg P/L.
- In the three IMS analyzed in this study, the antiscalant addition increased the phosphate concentration by 48–680% in RO feed water.
- Care has to be taken that phosphate is not reintroduced via the addition of phosphonate antiscalant and/or acid prior treatment in the RO units.
- The optimization of pretreatment (inline coagulation) loses its effectiveness if whatever phosphate is removed during coagulation is added again via antiscalants.

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