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Water Recovery from Advanced Water Purification Facility Reverse Osmosis Concentrate by Photobiological Treatment Followed by Secondary Reverse Osmosis

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ABSTRACT

Reverse osmosis (RO)-based desalination and advanced water purification facilities have inherent challenges associated with concentrate management and disposal. Although enhanced permeate recovery and concentrate minimization are desired, membrane scaling due to inorganic constituents such as silica, calcium, phosphate, and iron hinders the process. To solve this problem, a new diatom-based photobiological process has been developed to remove these scaling constituents by biological uptake and precipitation. In this study, RO concentrate samples were collected from a full-scale advanced water reclamation facility in California and were treated in 3.8- and 57-L photobioreactors inoculated with a brackish water diatom *Pseudostaurosira trainorii* PEWL001 using light-emitting diode bulbs or natural sunlight as a light source. The photobiological treatment removed 95% of reactive silica and 64% of calcium and enabled additional water recovery using a secondary RO at a recovery rate up to 66%. This represents 95% overall recovery including 85% recovery in the primary RO unit. In addition to the scaling constituents, the photobiological treatment removed twelve pharmaceuticals and personal care products, as well as *N*-nitrosodimethylamine, from RO concentrate samples primarily via photolysis. This novel approach has a strong potential for application to brackish water desalination and advanced water purification in arid and semi-arid areas.

TOC/ABSTRACT ART

1. Introduction

According to the membrane water treatment facility database maintained by the American Membrane Technology Association, there are approximately 1000 reverse osmosis (RO)-based desalination and advanced water purification facilities (AWPFs) in the United States.¹ Although the RO technology has been proven very useful and reliable to produce very high quality, near drinkable permeate from non-potable water resources, such as brackish groundwater and recycled water,^{2,3} it generates a concentrate stream of 15 to 25% needing disposal. Concentrate generation and management has been one of the major challenges for utilities that own and operate RO-based water treatment facilities.^{3,4} The availability of economical methods for concentrate disposal is becoming a critical factor for successful RO-based water reclamation and groundwater desalination projects, especially in the inland areas where ocean discharge is not an option.

One way to reduce the concentrate volume at an RO facility is to increase permeate recovery. However, the solubility limits of inorganic constituents, such as calcium carbonate, calcium phosphate, silica, and calcium sulfate, are often exceeded in the RO concentrate when the permeate recovery rate is increased. This causes scaling on the membrane surface and a

reduction in permeate flux making higher recovery impractical. Several technologies have been proposed and tested to improve the permeate recovery, including use of antiscalants and secondary RO,^{2, 5} removal of scaling constituents by ion exchange or chemical softening,⁶ variation of the RO process with mechanical vibrations or precise control of concentrate discharge,^{7, 8} and non-RO based desalination processes, such as forward osmosis and electrodialysis reversal.⁹⁻¹² However, these technologies are highly chemical and/or energy intensive. In addition, the permeate quality in terms of dissolved constituent concentrations tends to decline at a higher recovery because more passage of dissolved constituents occurs as the reject stream becomes more concentrated unless a softening process is employed. Also, no trace organic removal could be expected by any of the existing methods.

Recently, a new photobiological process using brackish water diatoms has been developed to treat RO concentrate.^{13, 14} This unique process utilizes the natural biology of diatoms (Bacillariophyceae), which are a class of photosynthetic microalgae whose cells are enclosed by a rigid silicon dioxide (silica; SiO₂)-based structure called frustule.^{15, 16} Diatoms are capable of absorbing aqueous silica requiring the silicon for growth and cell division. It is also known that up to 70% of the dry weight of the cell is silica.¹⁷ Our previous studies demonstrated the rapid removal of aqueous silica from silica-rich agricultural drainage water RO concentrate from two AWWPs and one brackish groundwater desalination facility using a mixed culture¹⁴ or isolated diatom strains.¹³ In addition to aqueous silica and macronutrients, orthophosphate, ammonia, nitrate, calcium, bicarbonate, iron, and manganese were also effectively removed by the photobiological treatment. Since many of these constituents are known RO scalants/foulants, it was speculated that the photobiologically-treated RO concentrate could be desalinated further by a secondary RO to recover more water.¹⁴

The main objective of this study was to explore the feasibility of additional water recovery from AWPf RO concentrate by photobiological treatment followed by secondary RO. The photobiological treatment was conducted indoors with light-emitting diode (LED) bulbs or outdoors with natural sunlight. In addition to the laboratory-scale photobioreactors previously described,¹⁴ a new 57-L pilot-scale photobioreactor was designed, constructed, and used in this study. The removal of important trace wastewater contaminants, including pharmaceuticals and personal care products (PPCPs), as well as metals and *N*-nitrosodimethylamine (NDMA) by the photobiological process was also examined.

2. Experimental Section

Diatom Strain and RO Concentrate Samples

A brackish water diatom *Pseudostaurosira trainorii* E. Morales PEWL001 previously isolated from agricultural drainage water¹⁴ was used in this study. RO concentrate samples were obtained from the third stage of a full-scale RO unit at the Groundwater Replenishment System (GWRS) of the Orange County Water District (OCWD) in Fountain Valley, CA in January–May 2017. The RO concentrate samples were analyzed for water quality parameters upon arrival (Table 1) and refrigerated until use. The RO concentrate samples were typically used 4 to 5 days after the collection to ensure the absence of chloramine residual ($<0.02 \text{ mg} \cdot \text{L}^{-1}$ as Cl_2), which is toxic to diatoms.^{18, 19} Diatom stock cultures were maintained in 15- or 50-mL clear polypropylene centrifuge tubes (VWR International, Radnor, PA) containing 0.2- μm membrane filtered RO concentrate under continuous illumination with 9-W LED light bulbs (light temperature 5000 K, 800 lm each; Cree, Inc., Durham, NC) at $25 \pm 2 \text{ }^\circ\text{C}$.¹³

101

102 ***Photobiological Treatment Procedure***

103 Photobiological RO concentrate treatment experiments were carried out in two types of reactors,
104 namely white high-density polyethylene (HDPE) cylindrical containers (diameter: 230 mm) and
105 a rectangular pilot photobioreactor (dimensions: 610 mm × 914 mm × 154 mm) with two baffles.
106 The working volumes of the photobioreactors were 3.8 and 57 L, respectively. Water depths
107 were approximately 100 mm in the both reactors. The 3.8-L cylindrical reactors were covered
108 with a plastic food wrap and operated statically indoors or outdoors on a rooftop of a building in
109 Fountain Valley, CA (33°42'32"N 117°55'40"W), while the 57-L pilot reactor was operated
110 outdoors on the rooftop with a 6-mm thick clear corrugated polycarbonate panel cover with 80%
111 transparency based on photosynthetically active radiation (PAR) with continuous recirculation at
112 a flow rate of 3.8 L/min. The RO concentrate was filtered through 1.0- μ m glass fiber filters
113 (Whatman GF/B, GE Healthcare, Chicago, IL) prior to the experiment. A 9-W LED light bulb
114 was used as a light source for the indoor experiments, while natural sunlight was used as a light
115 source for the outdoor experiments. The PAR was measured at $4.1 \pm 0.3 \mu\text{E} \cdot \text{s}^{-1} \cdot \text{m}^{-2}$ for the
116 indoor experiments, while it ranged from 0 to 140 $\mu\text{E} \cdot \text{s}^{-1} \cdot \text{m}^{-2}$ for the outdoor experiments with a
117 cover depending on the weather and time of the day. To initiate the photobiological treatment,
118 pre-cultured diatom biomass ($\sim 0.3 \text{ g dry wt} \cdot \text{L}^{-1}$) was inoculated into RO concentrate. Samples
119 were periodically collected from the photobioreactors to measure pH, temperature, *in-vivo*
120 chlorophyll, phycocyanin, conductivity, residual reactive silica, and nutrient concentrations.
121 Several semi-batch cycles were conducted with both types of reactors by decanting supernatant
122 or using a pump after the completion of the previous cycle and then adding new RO concentrate.
123 The supernatant was filtered through 1.0- μ m glass fiber filters and kept in a refrigerator until use

in the subsequent secondary RO experiment. Aliquots of the supernatant samples were analyzed for various water quality parameters as described below.

Secondary RO Experiment

A bench-scale RO apparatus was constructed with a high-pressure pump, flow meters, pressure gauges, a housing with a residential RO membrane (M-T1812A36, diameter: 45.7 mm, length: 298.5 mm; Applied Membranes, Vista, CA), polyethylene tubing, fittings, and valves. A new RO membrane was used in each test, and conditioned with clean brackish water made with RO permeate and sodium chloride (total dissolved solids (TDS) = 8000 mg·L⁻¹, pH 7). A pilot-scale RO skid (Lifestream Water Systems, Huntington Beach, CA) with five 2.5-inch brackish water RO elements (4 × CSM RE2540-FE and 1 × CSM RE2540-TE, diameter: 61 mm, length: 1016 mm; TCK Membrane America, Anaheim, CA) was used in the pilot-scale secondary RO experiment. In both setups, permeate and concentrate flows were combined and returned to the feed water container to allow a continuous operation. The temperature of the feed water reservoir was maintained with a water bath at 20.5 ± 0.5 °C and 25 ± 1 °C for bench- and pilot-scale experiments, respectively. Flow rate and pressure were continuously monitored, and samples were periodically collected to measure temperature, TDS, pH, and other water quality parameters. Photobiologically-treated RO concentrate samples were filtered through 1.0-μm glass fiber filters prior to the RO experiment. Ammonia and sodium hypochlorite solutions were added to the filtered samples immediately before the secondary RO experiment to achieve ~2.5 mg·L⁻¹ of monochloramine as Cl₂ as a biostatic agent.²⁰

Analytical Methods

A Hach DR-2800 spectrophotometer and a Hach 2100N turbidimeter (Loveland, CO) were used for the colorimetric and turbidity analyses, respectively. A Hach ISENa38101 sodium ion selective electrode combined with an HQ40d portable meter was used for sodium analysis. Appropriate Hach methods were used for general chemical parameters including reactive silica, orthophosphate, ammonia-N, nitrate-N, chloride, sulfate, hardness, alkalinity, iron, manganese, color, and chemical oxygen demand (COD), as described earlier.^{13, 14} Analyses for boron, total organic carbon (TOC; Standard Methods 5310C), heavy metals (EPA Method 6010B) and NDMA (EPA Method 1625) were performed by TestAmerica (Irvine, CA). Forty-two different PPCPs were analyzed by liquid chromatography with tandem triple quadrupole mass spectrometry (LC-MS/MS) using previously developed analytical protocols.^{21, 22} The samples were diluted by 20 or 50 times prior to the PPCP analyses due to the large matrix effect. The PAR was measured by an International Light Technologies ILT 1400 portable radiometer with an attenuated PAR sensor (Peabody, MA). A Turner Designs AquaFluor® Handheld Fluorimeter (Model #: 8000-010, San Jose, CA) was used for phycocyanin and *in vivo* chlorophyll measurements.

3. Results and Discussion

3.1 Bench-Scale Semi-Batch Photobiological Treatment

3.1.1 Photobiological Treatment with LED

Figure 1 shows the result of a semi-batch experiment using two 3.8-L photobioreactors with one LED bulb per reactor as a light source. The duplicate reactors behaved very similar. In the first semi-batch cycle, reactive silica removal occurred within two days after initiation of the treatment, while the uptake of orthophosphate and ammonia started immediately. The nitrate concentration did not change significantly in the first eight days, which indicated that ammonia was the preferred nitrogen source for this diatom. Nitrate utilization started after ammonia was completely depleted. More than 90% of reactive silica was removed in ten days. In the second semi-batch cycle there was no lag period of reactive silica removal and more than 80% of reactive silica, as well as more than 95% of ammonia and orthophosphate, was removed within six days. This was significantly faster than the previous investigation of OCWD GWRS RO concentrate treatment using *Nitzschia communis* PEWL002 in a smaller 500-mL reactor.¹³ It was speculated that the purification of *P. trainorii* PEWL001 by removal of green algae cells improved the efficiency of the silica uptake of this strain. Also, the final biomass concentration was higher in this study (2.9 g dry wt·L⁻¹) than the previous study (2.1 g dry wt·L⁻¹),¹³ indicating that the growth conditions were more favorable in the present study.

In addition to the reactive silica and nutrients, calcium (45%), iron (80%), manganese (60%), and bicarbonate (50%) were removed by the photobiological treatment using an LED light source as shown in Table 1. This is consistent with our previous studies.^{13, 14} The concentration of COD decreased by 18% possibly due to biodegradation, while color increased by 31%. The pH of the treated RO concentrate samples was approximately one unit higher than that of the raw RO concentrate sample, which is due to photosynthesis and inorganic carbon utilization. The impact of photobiological treatment on trace RO constituents including metals, NDMA, and PPCPs are discussed in the latter section.

189

190 3.1.2 Photobiological Treatment with Sunlight

191 Since one of the most attractive advantages of this photobiological treatment process is the
192 potential use of natural sunlight as a light and energy source, a series of semi-batch experiments
193 were conducted outdoors using 3.8-L photobioreactors from April 12 to May 1, 2017. The
194 results are shown in Figure 2. After a 3-day lag period, reactive silica removal was initiated and
195 rapidly progressed. More than 90% of the reactive silica was removed within ten days in the first
196 semi-batch cycle. The silica uptake markedly accelerated in the following cycles. The apparent
197 silica uptake rates were calculated as 26, 37, and 39 $\text{mg}\cdot\text{L}^{-1}\cdot\text{day}^{-1}$ in the first, second, and third
198 semi-batch cycles, respectively. This is equivalent to the previous maximum uptake rate of 35
199 $\text{mg}\cdot\text{L}^{-1}\cdot\text{day}^{-1}$ for the treatment of an RO concentrate sample from another AWPf in Southern
200 California using the same diatom strain.¹³ Of note, for outdoor experiment, removal of reactive
201 silica was maintained throughout with only the available daylight. This is probably due to the
202 fact that silica uptake in diatoms is independent of the photosynthetic activities.¹⁶

203 Similar to the LED-based treatment, calcium, iron, manganese, and bicarbonate were removed
204 from the RO concentrate during the photobiological treatment using natural sunlight (Table 1).
205 Slightly better removal of calcium (64%) and bicarbonate (70%) was observed in this case,
206 which is probably due to higher pH (9.5) at the end of the photobiological treatment. The
207 removal of calcium and bicarbonate may be caused by biological calcification as well as
208 biologically induced precipitation of calcium carbonate by photosynthesis.²³ In addition to COD,
209 color was reduced by 23%, which was probably due to photobleaching by sunlight.²⁴ More
210 detailed characterization of dissolved organic matter (DOM) in raw and photobiologically-

treated RO concentrate is currently underway. Nevertheless, the apparent removal of organic matter in combination with significant removal of inorganic scalants such as reactive silica, calcium, phosphate, and bicarbonate, makes the secondary RO treatment of the photobiologically-treated concentrate more feasible.

3.2 Impact of Photobiological Treatment on Trace Constituents

The RO concentrate from an AWPf typically contains numerous wastewater-derived trace inorganic and organic contaminants including heavy metals, PPCPs, and disinfection by-products.^{25, 26} Therefore, the impact of photobiological treatment on these trace constituents are of special interest. Six trace metals, including a nonmetal (selenium), were detected in the OCWD GWRS RO concentrate as shown in Table 1. Other tested metals including antimony ($<0.010 \text{ mg}\cdot\text{L}^{-1}$), beryllium ($<0.002 \text{ mg}\cdot\text{L}^{-1}$), cadmium ($<0.005 \text{ mg}\cdot\text{L}^{-1}$), chromium ($<0.005 \text{ mg}\cdot\text{L}^{-1}$), cobalt ($<0.010 \text{ mg}\cdot\text{L}^{-1}$), lead ($<0.005 \text{ mg}\cdot\text{L}^{-1}$), vanadium ($<0.010 \text{ mg}\cdot\text{L}^{-1}$), and silver ($<0.010 \text{ mg}\cdot\text{L}^{-1}$) were not detected in any of the samples, while arsenic ($0.014 \text{ mg}\cdot\text{L}^{-1}$) and thallium ($0.012 \text{ mg}\cdot\text{L}^{-1}$) were detected in only one of the raw RO concentrate samples.

Therefore, those metals are not shown in Table 1. No marked removal of trace metals was observed in the photobiologically-treated RO concentrate samples, except for barium, which might have precipitated by mechanisms similar to calcium removal. A small concentration of boron was also present in the RO concentrate samples, which was virtually unchanged by the treatment.

As shown in Table 1, the majority of NDMA was removed by the photobiological treatment using LED (67%) or sunlight (80%), while sunlight photolysis alone could also remove NDMA.

It is well known that NDMA is directly photolyzed with UV irradiation.²⁷⁻²⁹ An additional study is needed to verify the degradation of NDMA by the photobiological treatment with non-UV emitting LED bulbs. Owing to the significant public health implications of NDMA³⁰ and the difficulty of its removal by RO,^{31,32} the demonstration of extensive removal of NDMA by photobiological treatment would reduce the concentration in the secondary RO permeate, which in turn would lessen the burden on the subsequent photolytic processes, such as UV and UV-based advanced oxidation in the AWWPs.

Among the 42 different PPCPs tested, 27 compounds were consistently detected in the RO concentrate samples tested in this study (Table S1), while fourteen PPCPs were not detected in any of the raw or treated samples (Table S2). Ibuprofen was not detected in any of the raw RO concentrate samples ($n = 16$) but was detected in a few treated samples (MDL = $\sim 1000 \text{ ng}\cdot\text{L}^{-1}$). It should be noted that the RO concentrate samples were diluted by 20 or 50 times prior to the PPCPs analysis due to the high salinity.

Twelve PPCPs were degraded by the photobiological treatment using LED and/or sunlight, while 15 compounds were not significantly degraded (Table 2). These results are generally consistent with previous reports. For example, UV photolysis of the nonsteroidal anti-inflammatory drug diclofenac is known³³, and the photobiological degradation of beta blockers such as atenolol and propranolol in a microcosm composed of a mixture of diatoms and bacteria has been reported elsewhere.³⁴ However, resistant of benzotriazole toward solar photolysis is contradictory to a previous report.³⁵ Also, significant photolysis/photobiodegradation of TCEP and PFOS under the test conditions was unlikely.³⁶⁻³⁸ More experiments are needed to confirm and verify the removal mechanisms of these PPCPs. PPCPs removal could be improved by combining pre-

oxidation such as ozonation or an advanced oxidation process³⁹⁻⁴¹ with the photobiological treatment.

3.3 Rooftop 57-L Pilot-Scale Photobioreactor Experiment

An additional outdoor semi-batch experiment was carried out in the 57-L photobioreactor on the rooftop from April 27 to May 15, 2017. As shown in Figure 3, the reactive silica and orthophosphate removal curves were very similar to those observed in LED- and sunlight-based photobiological treatment in static 3.8-L photobioreactors (Figures 1 and 2). The maximum reactive silica uptake rate of $46 \text{ mg} \cdot \text{L}^{-1} \cdot \text{day}^{-1}$ was observed in the third semi-batch cycle. However, the contamination of the photobioreactor with green algae (*Chlorella sorokiniana*) became so significant in the third cycle that the experiment was terminated. The presence of the green algae was detected by fluoroscopic *in vivo* chlorophyll measurements. At the end of the third cycle, the biomass concentration in the pilot-scale photobioreactor was estimated to be 10–15 g dry wt·L⁻¹, although this included a significant number of green algae cells.

As noted in the previous section, the reactive silica removal was not affected by the light-dark diurnal pattern in the photobiological treatment. In fact, the reactive silica uptake slowed down during the day (Figure 4). Small increases in the reactive silica concentration was observed during the first semi-batch cycle, which coincided with high water temperature (~40 °C). It is speculated that the higher temperature may have induced the release of silica from the intracellular pool of soluble silica, although it is not clear if the silica uptake and incorporation in

diatoms^{42, 43} is reversible. However, this clearly indicates that the reactive silica uptake in this photobiological process is independent of the photosynthesis of *P. trainorii* PEWL001 as speculated earlier.^{14, 16}

3.4 Secondary RO Experiment

Two experiments were conducted to test the feasibility of additional water recovery from the photobiologically-treated RO concentrate by secondary RO. In the first experiment, the treatability of raw (untreated) and photobiologically-treated RO concentrate samples were compared using a bench-scale RO apparatus (Figure 5a). While the RO membrane experienced a very rapid pressure build-up from 1.20 to 1.27 MPa within 25 min of operation and eventually failed, no pressure build-up was observed in the case with photobiologically-treated RO concentrate. The permeate and reject flow rates were kept very steady near 75 and 400 mL/min, respectively, for at least four hours in the latter case. Permeate recovery was about 15% in this experiment.

In the second experiment, a higher permeate recovery was attempted using a pilot-scale RO skid. Although the length of the test period was short, a maximum permeate recovery of 66% was achieved for up to one hour from 50 to 115 min without a significant increase in feed pressure (1.2 MPa) (Figure 5b). The permeate exhibited acceptable water quality (Table 3), except for pH (9.2) and nitrate-N ($19 \text{ mg} \cdot \text{L}^{-1}$), and could be used to mitigate seawater intrusion or for potable water reuse. The permeate from the primary RO unit can be used in a blend to lower these parameters below the regulated/recommended values (pH 8.5 and $10 \text{ mg} \cdot \text{L}^{-1}$, respectively). The concentration factor for the selected parameters ranged from 2.0 (nitrate-N) to 2.9 (magnesium)

as shown in Table 3. After two hours of the closed-loop run, the pilot RO experiment had to be terminated due to the limited volume (about 150 L) of photobiologically-treated RO concentrate from which samples were periodically withdrawn for analyses. Additional work is planned to obtain a larger volume of photobiologically-treated RO concentrate to perform a longer RO run and to investigate the signs of scaling and fouling in the RO elements.

This study demonstrated the feasibility of a previously proposed scheme¹⁴ of photobiological treatment followed by secondary RO desalination to recover more water at the advanced treatment facilities using bench- and pilot-scale photobioreactors and secondary RO units with RO concentrate samples. Since the permeate recovery of the RO process at the GWRS was 85%, the photobiological process and secondary RO would add another 10% of permeate that could be blended with permeate from the primary RO unit and used for beneficial reuse including potable reuse. The calculated overall permeate recovery was 95%. At the same time, the final concentrate flow was reduced by 10% of the initial RO feed, which represents a 66.7% reduction in the volumetric flow of liquid waste for disposal. This could be very attractive to inland utilities that currently face challenges related to the management and disposal of brine/concentrate from their AWWPs or brackish groundwater desalination facilities, while recovering more fresh water to offset the high cost of RO-based desalination systems. Removal of nutrients and some trace constituents, including NDMA, and little to no requirement of external chemicals or electrical power input for the scalant removal would be a great advantage over other approaches. Additional bench- and pilot-scale investigations are planned with some currently underway to study (1) the impact of DOM in the secondary RO process, (2) the removal of different trace organics in the RO, and (3) the integration and continuous flow operation of the photobiological treatment and secondary RO in a pilot-scale system.

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327 **Supporting Information**

328 Supporting tables referenced in this paper are provided in Supporting Information. This material

329 is available free of charge via the Internet at <https://pubs.acs.org>.

330

331 **Notes**

332 Pacific Advanced Civil Engineering, Inc. holds a U.S. patent (#9416036) relating to this

333 photobiological treatment technology. The authors declare that there is no other conflict of

334 interest.

335

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ABBREVIATIONS

AWPF, advanced water purification facility; COD, chemical oxygen demand; DOM, dissolved organic matter; GWRS, groundwater replenishment system; LC-MS-MS, liquid chromatography-tandem mass spectrometry; LED, light-emitting diode; NDMA, *N*-nitrosodimethylamine; NTU, nephelometric turbidity unit; OCWD, Orange County Water District; PAR, photosynthetically active radiation; PPCPs, pharmaceuticals and personal care products; PtCo, platinum-cobalt; RO, reverse osmosis; TDS, total dissolved solids; TOC, total organic carbon

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