Near real-time *N*-nitrosodimethylamine monitoring in potable water reuse via online high-performance liquid chromatography-photochemical reaction-chemiluminescence

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Takahiro Fujioka,[†,*] Taketo Tanisue,[‡] Shannon L. Roback,[§]
Megan H. Plumlee,[§] Kenneth P. Ishida,[§] Hitoshi Kodamatani,[‡]

[†]*Water and Environmental Engineering, Graduate School of Engineering, Nagasaki University, 1-14 Bunkyo-machi, Nagasaki 85 2-8521, Japan*

[‡]*Division of Earth and Environmental Science, Graduate School of Science and Engineering, Kagoshima University, Kagoshima 890-0065, Japan*

[§]*Orange County Water District, 18700 Ward Street, Fountain Valley, CA 92708, USA*

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* Corresponding author: Takahiro Fujioka, Email: tfujioka@nagasaki-u.ac.jp, Tel: +81 095 819 2695, Fax: +81 95 819 2620

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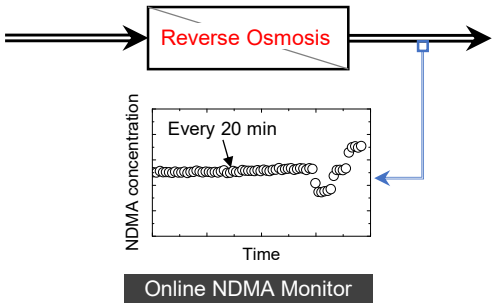


Near real-time monitoring of the concentration of *N*-nitrosodimethylamine (NDMA) in recycled wastewater was achieved by adapting a newly developed analytical technique—online high-performance liquid chromatography-photochemical reaction-chemiluminescence.

Abstract

Direct potable reuse requires stringent water quality assurance to protect public health. This study developed an online analytical technique—high-performance liquid chromatography followed by photochemical reaction and chemiluminescence detection (HPLC-PR-CL)—for determination of the concentration of *N*-nitrosodimethylamine (NDMA) and three other *N*-nitrosamines. Its feasibility for near real-time analysis was evaluated by analyzing an ultrafiltration (UF)-treated wastewater before and after a pilot-scale reverse osmosis (RO) treatment system. The online instrument with a method detection limit of 0.3–2.7 ng/L requires a direct injection (i.e., no sample pre-concentration) of only 20–200 μL sample volume for the determination of *N*-nitrosamine concentrations every 20 min. NDMA concentrations in UF-treated wastewater were successfully monitored in a range of 50–200 ng/L over the course of 24 h. Likewise, NDMA concentrations in RO permeate ranged from 25–80 ng/L over the course of 48 h. The online monitor was capable of recording variations in *N*-nitrosamine concentration in RO permeate that occurred following changes in feedwater concentration and temperature. This study demonstrates the potential for online water quality assurance that directly measures trace levels of organic contaminants, which is highly relevant to the implementation of potable reuse.

Water Impact Statement

Potable reuse requires robust water quality assurance for public safety. Particularly for direct reuse, there is a critical need for online monitoring. This work demonstrated an analytical technique to measure the probable human carcinogen *N*-nitrosodimethylamine (NDMA), adapting it for the first time to online use. NDMA concentration was measured automatically in ultrafiltration-filtered wastewater and reverse osmosis permeate every 20 min.

1 Introduction

Water reuse is critical for augmentation of potable water supplies in many regions.[1, 2] One major challenge in the use of highly treated wastewater for potable reuse is risk management and water quality assurance for trace organic chemicals (TOrCs). Most TOrCs including pharmaceuticals and endocrine disrupting compounds are well removed by reverse osmosis (RO). However, *N*-nitrosodimethylamine (NDMA, $C_2H_6N_2O$), a probable human carcinogen [3], readily permeates through an RO membrane[4-6] due to its small and uncharged nature.[7] A subsequent advanced oxidation process (AOP) comprised of ultraviolet (UV) light with an oxidant such as hydrogen peroxide can be used to reduce TOrCs to non-detectable levels[4, 8, 9] and is commonly employed in potable reuse to remove NDMA to below relevant limits such as the California regulatory notification level (NL)[10] and the Australian Guidelines of 10 ng/L.[11] As direct potable reuse (DPR) is being implemented, rigorous treatment and monitoring is essential for public safety. In DPR, water is reclaimed for potable use after advanced treatment *without* the use of an environmental buffer (e.g., aquifer storage) which can provide additional treatment, dilution, and response time.[12, 13] DPR serves the advanced treated water immediately upstream of a drinking water treatment plant ("raw water augmentation") or directly into the drinking water distribution system ("treated drinking water augmentation").

Online monitoring is expected to play a vital role in ensuring water quality and process integrity for DPR, with emphasis on the need for real-time or near real-time monitoring.[14] Online monitors for use in DPR scenarios are currently limited to bulk parameters such as total organic carbon (TOC), electrical conductivity, UV254, and fluorescence.[15] These surrogates are meant to indicate process performance and signal problems if out of range, rather than serve as a direct measure of specific compounds of concern.

The ability to monitor NDMA concentrations continuously (real-time) or with high frequency (near real-time) can improve the safety of water by providing an early warning of unforeseen spikes of NDMA and by indicating drift or failures in treatment processes (e.g., membrane defects). Current analytical methods for NDMA are incapable of online or frequent measurements. These methods require a pre-concentration step using solid or liquid-phase extraction to enable detection at trace concentrations, which is time consuming and labor intensive. This is typically followed by gas or liquid chromatography (GC or LC) and tandem mass spectrometry detection (MS/MS).[4, 16] The conventional methods require a large sample volume (200–1000 mL) for pre-concentration, increasing project complexity for monitoring programs and constraining research design. Moreover, the addition of isotope-labelled NDMA to samples is necessary to calculate the loss of NDMA during the sample preparation step. Due to the complexity of these analytical procedures, the analysis of NDMA at full-scale plants is performed with limited frequency (e.g., weekly, monthly). In contrast, a novel analytical method using automated high-performance liquid chromatography separation coupled with photochemical reaction (PR) and detection by chemiluminescence (CL)[17] allows for a direct injection of a small sample volume (20–200 μL) with no pre-concentration step for quantification of *N*-nitrosamines including NDMA. It requires only 15–20 min from the time of sample injection to the determination of *N*-nitrosamine concentrations and provides a similar or even lower detection limit than conventional methods.

HPLC-PR-CL for NDMA analysis has been validated in prior work including comparison with a conventional method (solid phase extraction followed by GC-MS/MS) and evaluation of interference by common process chemicals (monochloramine, hydrogen peroxide and hypochlorite) and organic compounds in treated wastewaters.[18] Among the process chemicals, only hypochlorite interfered with NDMA analysis but the interference was eliminated by dosing a reducing agent, which is a standard procedure for NDMA analysis to prevent

NDMA formation in the sample bottle prior to analysis. Interference from organic constituents in secondary and ultrafiltration (UF)-treated wastewaters was also avoided by reducing the sample injection volume, while no interference was identified with RO permeate.[18] In the prior work the analytical technique was developed for laboratory use with a manual or autosampler-assisted injection of manually collected samples using a bench top HPLC-PR-CL instrument.

The HPLC-PR-CL method has the potential to be adapted for online NDMA analysis due to its high speed, relative simplicity, and sensitivity. This study developed an online monitor using HPLC-PR-CL for automated determination of NDMA concentration and three other *N*-nitrosamines in near real-time. The online monitor was validated by continuously measuring the concentrations of *N*-nitrosamines in a pilot-scale UF-treated wastewater and RO permeate to track the variation in *N*-nitrosamine concentration as a function of changes in temperature and feed concentration. To our knowledge, in contrast to online monitors of water quality surrogates such as TOC and UV254, this system is the first online monitor for high frequency detection of a trace-level organic compound of public health concern in drinking water.

2 Methods

2.1 Chemicals

All chemicals used in this study were of analytical grade. Solutions containing *N*-nitrosamines – NDMA, *N*-nitrosomethylethylamine (NMEA), *N*-nitrosopyrrolidine (NPYR) or *N*-nitrosomorpholine (NMOR) **(Table S1)** – at 100 mg/L were purchased from Ultra Scientific (Kingstown, RI, USA). A stock solution of each *N*-nitrosamine was prepared at 1 mg/L in pure methanol. Luminol (5-amino-2,3-dihydro-1,4-phthalazinedione) was purchased from Wako Pure Chemical Industries (Tokyo, Japan). A luminol stock solution was prepared

at 20 mM in a 0.5 M carbonate buffer. UF-treated wastewater was prepared using a pilot-scale UF system by filtering an activated sludge treatment effluent collected at a municipal wastewater treatment plant in Japan. TOC, electrical conductivity and pH of the UF-treated wastewater were 16.1 mg/L, 1,290 μS/cm and 6.6, respectively.

2.2 Analytical techniques

The online monitor for *N*-nitrosamines used in this study was configured as an HPLC-PR-CL instrument[19] equipped with a six-port valve (**Fig. 1 and Fig. S2**). The target sample was fed to the six-port valve at a flow rate of 0.7–1 mL/min which resulted in <2 min travel time of the sample between the system sampling port and the online analyzer. At programmed intervals, the six-port valve injected a specific sample volume, 20 μL for UF-treated wastewater and 200 μL for RO permeate, into the HPLC-PR-CL. The injected sample first reached the HPLC where the separation of the *N*-nitrosamines occurred via an octadecylsilyl (ODS) column. Eluent solution (10 mM phosphate buffer with 5% methanol) was fed to the instrument in isocratic mode at a flow rate of 1.5 mL/min. Thereafter, each separated *N*-nitrosamine eluting from the column at different times was irradiated in the PR with UV light to produce nitric oxide which was transformed to peroxynitrite after reacting with superoxide anion radical, which was generated via the reaction of UV light with the eluent solution. Reaction details were previously specified in a study by Kodamatani et al.[17] A 0.05 mM luminol solution prepared with 0.5 M carbonate buffer (pH 10) was injected into the sample line at 0.5 mL/min. The reaction of peroxynitrite with luminol induced chemiluminescence and the concentrations of each *N*-nitrosamine were determined based on the intensity of the chemiluminescence. The method detection limit for NDMA (see Supporting Information S3) is 0.3 to 2.7 ng/L depending on the injection volume.

The online HPLC-PR-CL monitor was assembled with commercially available components: DGU-20A$_3$ degasser (Shimadzu), six-port valve (HV-2080-01, JASCO, Tokyo, Japan), valve controller (Nichiri Mfg. Co. Ltd., Chiba, Japan), CTO-20AC column oven (40 °C), InertSustain C18-AQ column (5 µm, 4.6 mm i.d., 250 mm GLsciences, Tokyo, Japan), CL-2027 chemiluminescence detector (JASCO, Tokyo, Japan), and Chromato-PRO data processor (Runtime Instruments, Kanagawa, Japan). In addition, a low-pressure mercury lamp (15 W, CL-15, Panasonic, Tokyo, Japan) was used to construct the photochemical reactor.

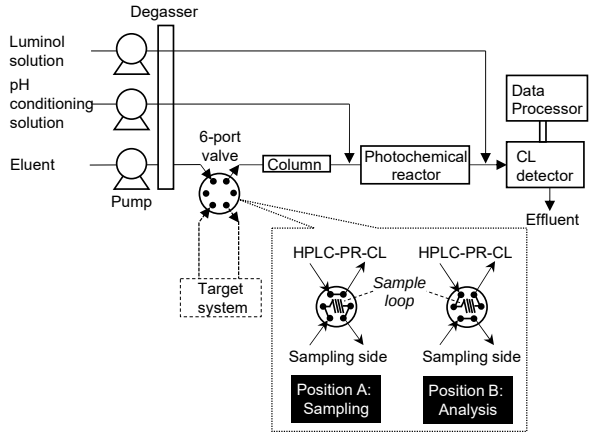


Fig. 1 – Schematic diagram of the online HPLC-PR-CL instrument with a 6-port valve.

2.3 Validation protocol

Prior studies have demonstrated the accuracy of the HPLC-PR-CL method for NDMA analysis in waters.[18, 19] In the present study, an online adaptation of the instrument was validated for UF-treated wastewater. The sampling system consisted of a 200 mL beaker holding UF-treated wastewater, a magnetic stirrer, a peristaltic pump and 6 mm i.d. PTFE tubing (**Fig. S4a**). The UF-treated wastewater was well mixed throughout the experiment.

The validation for RO permeate was performed using a pilot-scale cross-flow RO filtration system comprised of a 4 in. glass-fibre pressure vessel containing a 4-in. spiral wound RO

membrane element with a 7.43-m^2 membrane area (ESPA2-LD-4040, Hydranautics/ Nitto, Oceanside, CA, USA) (**Fig. S4b**). The filtration experiment was conducted with UF-treated wastewater spiked with 50–200 ng/L of NDMA. Permeation of the other three *N*-nitrosamines (NMEA, NPYR, and NMOR) through RO membranes is far less than NDMA due to their larger size in molecular dimension,[20] thus, the three *N*-nitrosamines were dosed at 500–2000 ng/L to attain a measurable concentration in the RO permeate. RO permeate and concentrate streams were recirculated into the feed reservoir and the sampling to the six-port valve was conducted after 2 h operation. Throughout the experiments, permeate flux was maintained constant at 20 L/m^2h with a constant recovery of 15%. Unless otherwise stated, feed solution temperature was maintained at 20 ± 0.5 °C in the reservoir using a titanium heat exchanging pipe connected to a chiller unit (CA-1116A, Tokyo Rikakikai Co. Ltd., Tokyo, Japan). The instrument was calibrated at the beginning of each experiment. Method calibration standards were prepared at 5–100 ng/L for NDMA and 50–1000 ng/L for the other *N*-nitrosamines. During continuous analysis, a standard *N*-nitrosamine solution was manually injected twice per day to ensure that the instrument response did not change.

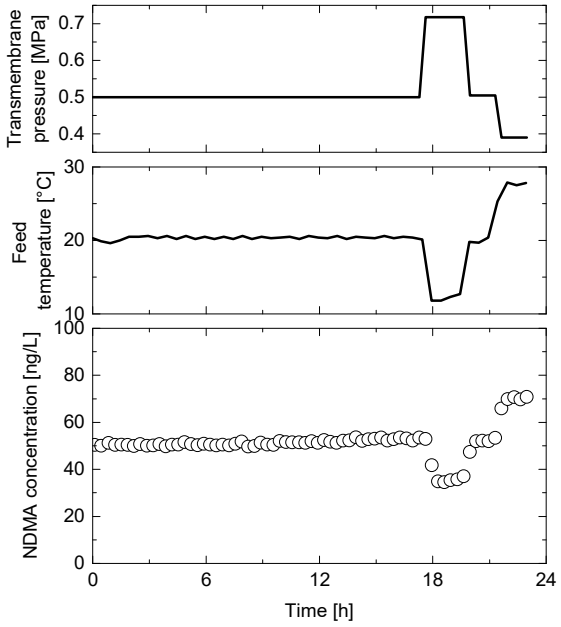
3 Results and discussion

3.1 Online analysis in UF-treated wastewater

Online analysis of NDMA was tested using a bench-scale wastewater recirculation system by spiking step-wise. Concentrations of NDMA and the other *N*-nitrosamines in the UF-treated wastewater were successfully monitored every 20 min for 24 h as shown in **Fig. S5**. A gradual decrease in *N*-nitrosamine concentration in the effluent was observed after 8 h, perhaps due to minor sorption of the *N*-nitrosamines to recirculating system components.

3.2 Online analysis in RO permeate

Online analysis for *N*-nitrosamines in RO permeate was performed by drawing samples from a pilot-scale RO system. NDMA concentrations in the RO permeate were successfully analyzed every 20 min over two days. The targeted (spiked) concentrations of NDMA and the other *N*-nitrosamines in the RO feed were 100 and 1000 ng/L, respectively. During the first 18 h when the feed temperature was maintained at 20 ± 0.5 °C, NDMA concentrations in the RO permeate remained constant at 50–52 ng/L **(Fig. 2)**. The impact of feed temperature on *N*-nitrosamine permeation was then evaluated between 18 – 23.5 h. When the RO feed temperature was increased from 12 to 28 °C, the NDMA concentration in the RO permeate increased considerably from 35 ng/L (67% rejection) to 70 ng/L (34% rejection). Similar changes in permeate concentrations were observed for NMEA, NPYR and NMOR **(Fig. S6)**. This is consistent with a previous study[20] where feed temperature was identified to be a critical factor governing the permeation of NDMA. The permeation of *N*-nitrosamines increased with an increase in solution temperature under conditions of constant permeate flux due to increased diffusivity of solutes through the RO membrane against a fixed water permeation rate.[20]



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199 **Fig. 2** – Online analysis of NDMA concentration in RO permeate (NDMA concentration in
200 RO feed = 106 ± 3 ng/L, permeate flux = 20 L/m^{2}h).

201 At 23.5 h, the concentration of NDMA in RO feed was reduced from 108 to 68 ng/L by
202 diluting the feed with UF-treated wastewater **(Fig. 3)**. At 44 h, the impact of *N*-nitrosamine
203 feedwater concentration was evaluated by a step-wise increase of NDMA from 68 to 204
204 ng/L **(Fig. 3)**. In response, the NDMA concentration in RO permeate increased from 26 to 81
205 ng/L, resulting in near constant rejection at 60–62%. A similar observation in solute
206 permeation was attained for NMEA, NPYR and NMOR **(Fig. S7)**. The results demonstrated
207 that the online monitor can be used as a tool to accurately identify changes in *N*-nitrosamine
208 concentration in RO permeate, improving data quality through more frequent sampling.

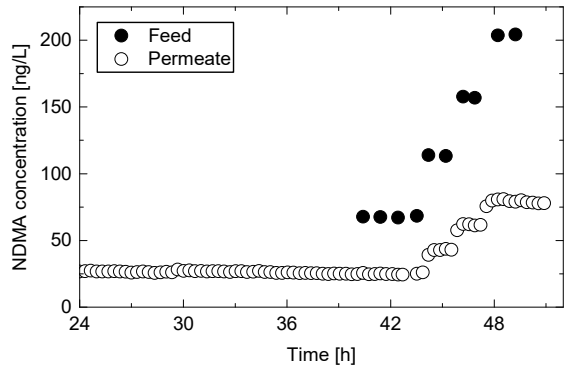

Fig. 3 – Online analysis of NDMA concentration in RO permeate (feed temperature = 20 °C, permeate flux = 20 L/m^{2}h, transmembrane pressure = 0.51 MPa). NDMA concentrations in the RO feed were determined based on manual samplings.

4 Conclusion

Online measurement of NDMA in near real-time was successfully demonstrated in this study. Because wastewaters contain a complex matrix of substances that could decrease the life of the separation column and influence the method accuracy, implementation at full scale will require a long-term investigation to identify any changes in separation performance and determine an appropriate replacement schedule. For example, periodic injection of matrix spike standards at known concentrations is recommended to confirm online monitor accuracy over time. Further validation of the HPLC-PR-CL method compared to conventional mass spectrometry-based methods[18] using treated wastewaters representing different potential facility installation locations (e.g. fully treated water after UV/AOP, ozone/biological activated carbon treated wastewaters) is also necessary to confirm the accuracy of the method in a host of different water matrices.

Use of this online monitor for NDMA/*N*-nitrosamine analysis in water reuse facilities could enhance the current portfolio of constituents monitored online continuously or near real-time to ensure the safety of potable reuse. There are several potential benefits:

- To our knowledge, online HPLC-PR-CL for NDMA/nitrosamines analysis is the only available (near) real-time monitor for direct measurement of a public health-relevant contaminant and TOrC in drinking water. Enhanced monitoring (higher frequency) ultimately provides more public health protection.

- Online data for NDMA in finished water from reclamation plants may improve compliance with permits and regulations. For example, early detection of process drift, a spike in the feedwater concentration, or membrane failure could prevent exceedance of NLs or other limits for NDMA. Similarly, other critical constituents may correlate with spikes or increases in NDMA.

- Online monitoring of NDMA in UV/AOP product water could be used to ensure removal of NDMA prior to delivery of treated water. UV/AOP is employed by many potable reuse plants to reduce NDMA to at-or-below the detection limit. The success of this process is essential to ensure confidence in the safety of the finished water. However, online NDMA monitoring would have to be justified given there are accepted, simpler methods for continuous performance documentation such as online monitoring of UVT and UV train power.

- Whether using HPLC-PR-CL as a bench top instrument or with online capability, staff time and sample volume required for NDMA/nitrosamine analysis is greatly reduced compared to conventional methods requiring sample pre-concentration and mass spectrometry for detection; for this reason, conventional methods are not suitable for online monitoring.

Acknowledgements

The authors acknowledge Hydranautics/Nitto for providing RO membrane elements.

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[1] *Water and Environmental Engineering, Graduate School of Engineering, Nagasaki University, 1-14 Bunkyo-machi, Nagasaki 85 2-8521, Japan*

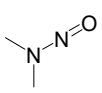
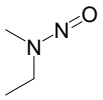
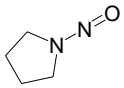
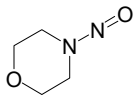
[2] *Division of Earth and Environmental Science, Graduate School of Science and Engineering, Kagoshima University, Kagoshima 890-0065, Japan*

[3] *Orange County Water District, 18700 Ward Street, Fountain Valley, CA 92708, USA*

Supporting Information

* Corresponding author: Takahiro Fujioka, Email: tfujioka@nagasaki-u.ac.jp, Ph +81 095 819 2695

Table S1 – Structure of the selected *N*-nitrosamines.

Compound	NDMA	NMEA	NPYR	NMOR
Structure				
Molecular Formula	$C_2H_6N_2O$	$C_3H_8N_2O$	$C_4H_8N_2O$	$C_4H_8N_2O_2$
Molecular Weight [g/mol]	74.05	88.06	100.06	116.06

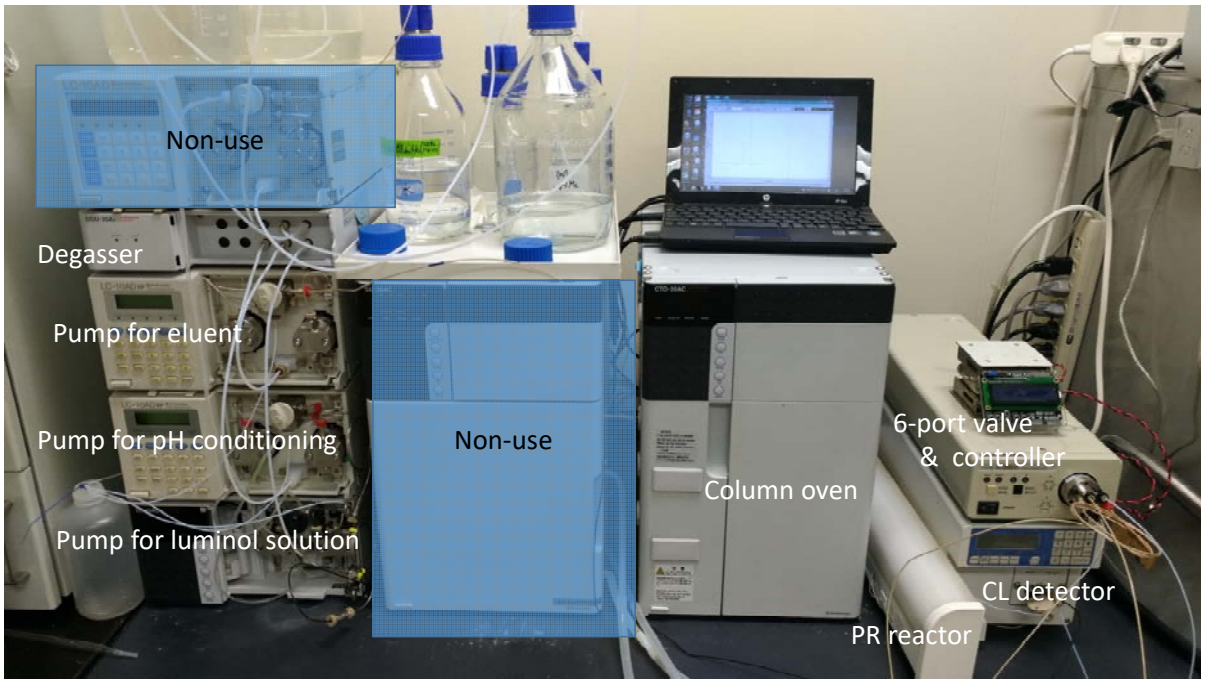


Fig. S2 – Photograph of the online HPLC-PR-CL instrument with a 6-port valve.

Supporting information S3 – Method detection limits:

The method detection limits (MDLs) were determined based on the Method Detection Limit Procedure of the U.S. Environmental Protection Agency (40CFR 136, Appendix B, revision 1.11). MDLs with a 200 µL injection volume for NDMA, NMEA, NPYR and NMOR were 0.3, 0.7, 1.4 and 0.8 ng/L, respectively. MDLs with a 20 µL injection volume for NDMA, NMEA, NPYR and NMOR were 2.7, 6.3, 7.7 and 11.8 ng/L, respectively.

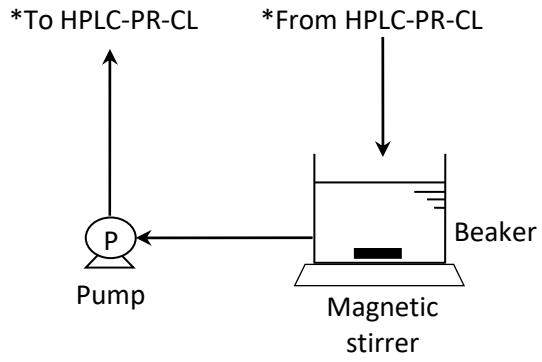


Fig. S4a – Schematic diagram of a wastewater recirculation system.

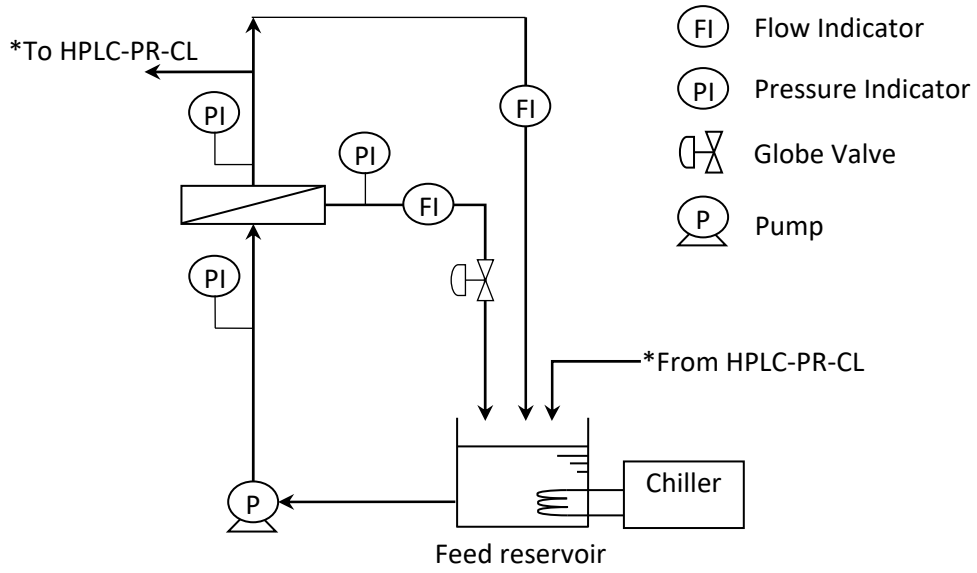


Fig. S4b – Schematic diagram of the RO treatment system. The system comprised of a 4-in. glass-fibre pressure vessel (ROPV, Nangang, China), 65-L stainless steel reservoir, a high-pressure pump (25NED15Z, Nikuni Co., Ltd., Kawasaki, Japan), digital flow meters (FDM, Keyence Co., Osaka, Japan), digital pressure indicators (GPM, Keyence Co., Osaka, Japan), a pressure gauge, stainless steel pipes in the feed stream and PVC pipes and PTFE tubing in the permeate stream). The membrane element was rinsed with pure water to eliminate residual preservatives on the RO element.

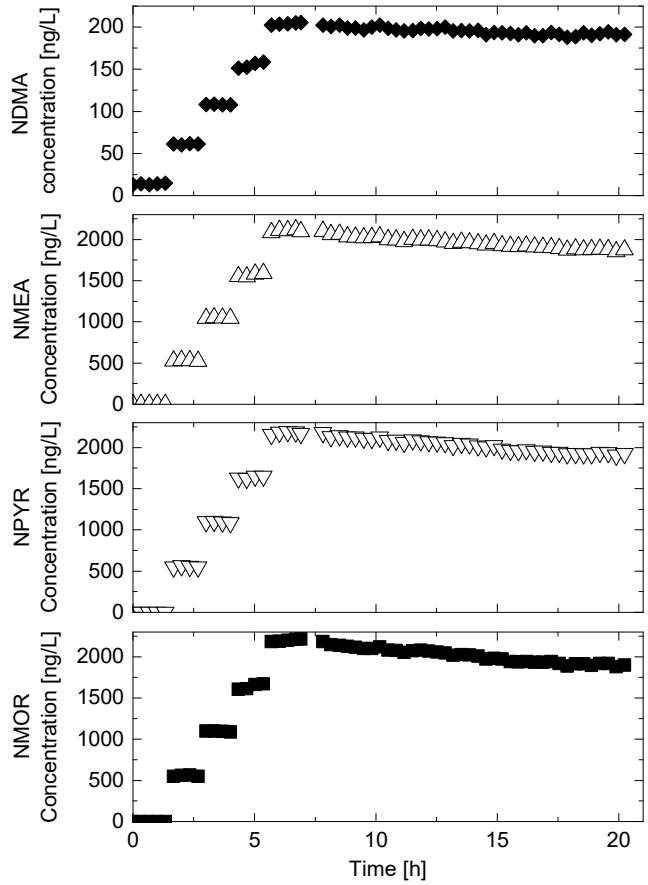


Fig. S5 – Online analysis of concentrations of *N*-nitrosamines in the UF-treated wastewater using the HPLC-PR-CL with a sample injection volume of 20 µL.

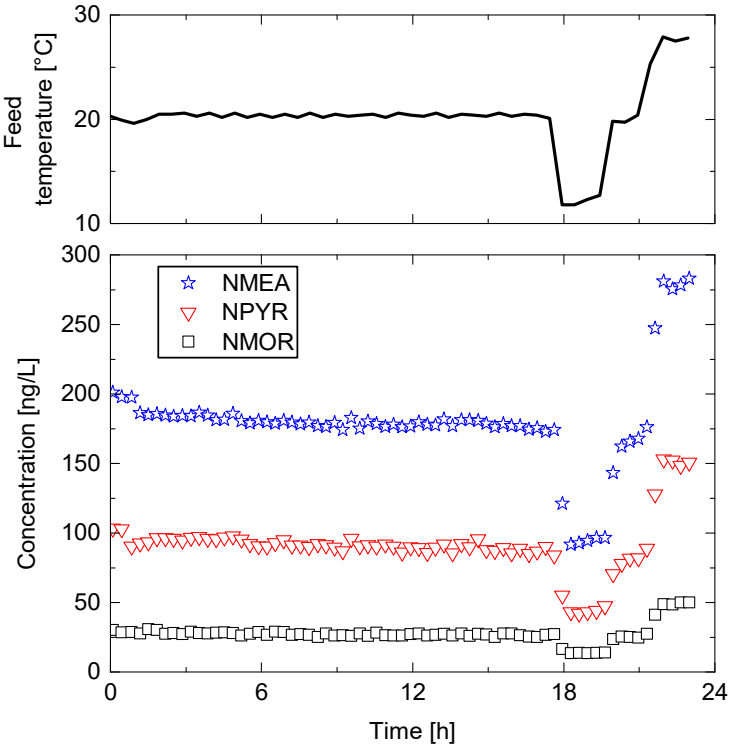


Fig. S6 – Online analysis of three *N*-nitrosamines (NMEA, NPYR and NMOR) in RO permeate (permeate flux = 20 L/m^{2}h, transmembrane pressure = 0.51 MPa). Concentrations of NMEA, NPYR, and NMOR in RO permeate were 900, 990, and 1,040 ng/L, respectively.

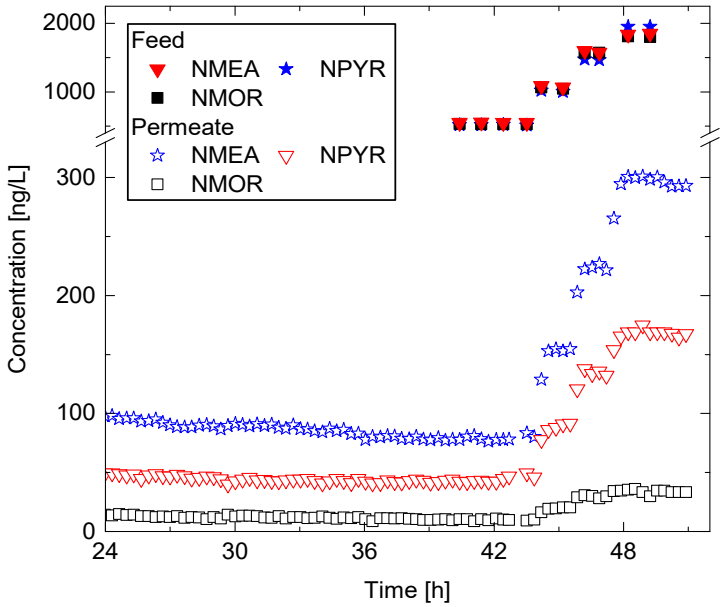


Fig. S7 – Online analysis of three *N*-nitrosamines (NMEA, NPYR and NMOR) in RO permeate (feed temperature = 20 °C, permeate flux = 20 L/m^{2}h, transmembrane pressure = 0.51 MPa). *N*-nitrosamine concentrations in the RO feed were determined based on manual samplings.