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Short Communication

Online monitoring of *N*-nitrosodimethylamine rejection as a performance indicator of trace organic chemical removal by reverse osmosis

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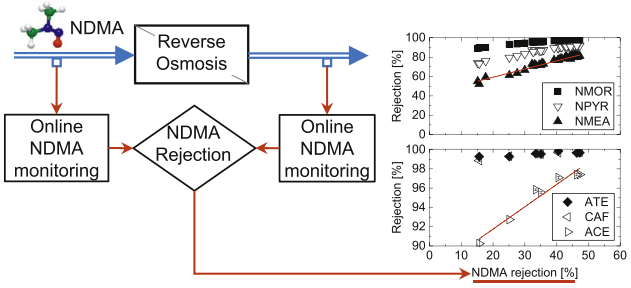
HIGHLIGHTS

- Online NDMA analyzers enabled to track variations in NDMA rejection by RO.
- Linear correlation between NDMA rejection and six TOrC rejection was observed.
- NDMA rejection can be a conservative surrogate indicator for TOrC removal by RO.

GRAPHICAL ABSTRACT



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ABSTRACT

The security of recycled water quality in potable reuse can be enhanced by improving the credibility of reverse osmosis (RO) treatment for the removal of trace organic chemicals (TOrCs). This study evaluated the potential of online monitoring of *N*-nitrosodimethylamine (NDMA) before and after RO treatment as a surrogate indicator for TOrC removal by RO. This pilot-scale study monitored NDMA concentrations in RO feedwater (ultrafiltration-treated wastewater) and RO permeate every 22 min using novel online NDMA analyzers—high-performance liquid chromatography followed by photochemical reaction and chemiluminescence detection. NDMA rejection by RO varied considerably in response to changes in operating conditions (permeate flux and feedwater temperature). A high linear correlation between NDMA rejection and the rejection of six other TOrCs was observed. The linear correlation was also identified for an RO membrane damaged with chlorine. The correlation between another potential surrogate indicator (conductivity rejection) and TOrC rejection was relatively low. NDMA, which is the smallest compound among regulated TOrCs, revealed rejections lower than the other TOrCs, indicating that NDMA rejection can be a conservative surrogate indicator capable of predicting changes in TOrC removal.

1. Introduction

Potable water reuse (PR) has been increasingly important in

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many parts of the world as an attractive strategy to augment drinking water supplies. PR is typically performed by replenishing the drinking water sources (e.g. dams and aquifers) with recycled water that exceeds drinking water standards. This approach is referred as indirect PR. Direct PR, which transfers recycled water directly to a drinking water treatment plant, is also being considered as a feasible option, but it requires more stringent monitoring of water quality (Leverenz et al., 2011; Arnold et al., 2012; CSWRCB, 2016). In particular, pathogens and trace organic chemicals (TOrCs) (e.g. pharmaceuticals, personal care products, steroid hormones, pesticides, and disinfection by-products) that are ubiquitously present in wastewater are of great importance due to their adverse consequences for human health.

In typical PR, the removal of TOrCs below their regulated limits is achieved through an advanced water treatment process typically comprised of reverse osmosis (RO) treatment and an advanced oxidation process (AOP) such as ultraviolet (UV) irradiation with hydrogen peroxide (H_2O_2) (Poussade et al., 2009; Drewes and Khan, 2011). Although RO treatment can sufficiently remove most TOrCs, some low molecular weight TOrCs such as *N*-nitrosodimethylamine (NDMA, disinfection by-product) (USEPA, 1993) are not well rejected. Since there is no tool or technology capable of ensuring membrane integrity for the removal of TOrCs by RO, most of recent PR schemes in the USA and Australia essentially rely on AOP-based post treatment for their removal. In contrast to RO, treatment performance of AOP for TOrC removal can be ensured through the online monitoring of UV power input, UV transmittance, and H_2O_2 dose (Plumlee et al., 2008). This indicates that only a single reliable barrier for TOrC removal is in place in PR.

A provision for the credible removal of TOrC by RO treatment can enhance the security of recycled water quality. The analysis of TOrCs requires laboratory testing with labor intensive pretreatment such as solid or liquid phase extraction and sophisticated analytical instrument (e.g. gas chromatography and mass spectrometry) (Munch and Bassett, 2004). More importantly, their occurrence could be site specific and they could often be detected at very low concentrations in RO feed. In contrast, NDMA is commonly identified at concentrations higher than 10–30 ng/L in RO feed due to its ubiquitous presence in raw wastewater (Fujioka et al., 2012a). NDMA is also formed through the chloramination process intended for mitigation of RO biofouling, increasing NDMA concentration prior to any RO process (Krauss et al., 2009; Farré et al., 2011; Shah and Mitch, 2012; Krasner et al., 2013). Thus, NDMA removal by RO could potentially be used as a surrogate indicator for TOrC removal.

A recent work by the authors (Fujioka et al., 2017) demonstrated the ability of online monitoring of NDMA in RO permeate using a newly developed NDMA analyzer—high-performance liquid chromatography followed by photochemical reaction and chemiluminescence detection (HPLC-PR-CL). Monitoring NDMA concentrations in RO permeate online allows for improved early warning of NDMA spikes, which could exceed regulatory limits (e.g. 10 ng/L California regulatory notification level) in the final product water (CDPH, 2015). In addition, the adaptation of this technique to both RO feedwater and RO permeate can provide an online rejection data, which can be utilized as a surrogate indicator for TOrC removal.

The primary objective of this study was to examine the applicability of online-monitored NDMA rejection as a surrogate indicator of TOrC removal by RO treatment at the pilot scale. Correlation of rejection between NDMA and representative TOrCs was evaluated through monitoring NDMA concentrations every 22 min before and after RO treatment using untreated and chlorine-treated RO membrane elements.

2. Materials and methods

2.1. Chemicals

All chemicals used in this study (Table 1) were of analytical grade. Four *N*-nitrosamines—NDMA, *N*-nitrosomethylethylamine (NMEA), *N*-nitrosopyrrolidine (NPYR), *N*-nitrosomorpholine (NMOR)—were purchased from Ultra Scientific (Kingstown, RI, USA). A stock solution of *N*-nitrosamines was prepared at 1 mg/L in pure methanol. The other chemicals selected as TOrCs were purchased from Wako Pure Chemical Industries (Osaka, Japan). A stock solution with a concentration of 1 mg/L of each chemical was prepared in pure methanol. TOrCs were categorized as neutral (ionised by $\leq$ 50%) and charged (ionised by >50%) (Table S1). All chemicals used here can be classified as hydrophilic TOrCs (Log*D* = <2.0) (Bellona et al., 2004; Van der Bruggen et al., 2006) except for carbamazepine; thus, the impact of adsorption on the rejection of most of the TOrCs was expected to be negligible. Ultrafiltration (UF)-treated wastewater was obtained by filtering an activated sludge effluent from a municipal treatment plant in Japan. Total organic carbon (TOC), electrical conductivity, and pH of the UF-treated wastewater were 6.5 mg/L, 895 μS/cm, and 7.0, respectively.

2.2. Pilot-plant validation test protocol

The validation test was performed using a pilot-scale cross-flow RO treatment system (Fig. S2). The pilot system held a 4-in. spiral wound ESPA2 RO membrane element with a 7.43 m^2 effective membrane area (Hydranautics, Oceanside, CA, USA). RO treatment was performed using untreated or chlorine (Cl_2)-treated ESPA2 RO membrane element. The Cl_2-treated ESPA2 RO membrane was prepared by feeding the element a 20 mg/L NaOCl solution at a recovery of 25% and feedwater temperature of 15–20 °C for 28 days. RO treatment was conducted after spiking *N*-nitrosamines and TOrCs in the UF-treated wastewater at 170–550 ng/L and 45 μg/L for each chemical, respectively. Rejection of NMEA, NPYR, and NMOR by RO membranes is typically higher than NDMA due to their larger size in molecular dimension; thus, the three *N*-nitrosamines were dosed at high target concentrations (550 and 200 ng/L for the untreated and Cl_2-treated RO membranes, respectively) to identify a measurable concentration in the RO permeate. Unless otherwise stated, the RO system was operated under standard conditions (permeate flux = 20 L/m^2h, feed solution temperature = 15 °C and system recovery = 20%) for 21 h. *N*-nitrosamine concentrations in RO feedwater and permeate were monitored by drawing samples from the pilot system into the online NDMA analyzers. The analysis of the TOrCs was conducted by collecting 250 mL grab samples from the RO feedwater and 500 mL from the RO permeate.

2.3. Analytical techniques

Concentrations of *N*-nitrosamines in RO feedwater and permeate were determined by high-performance liquid chromatography-photochemical reaction-chemiluminescence (HPLC-PR-CL) analyzers (Fujioka et al., 2016; Kodamatani et al., 2016) equipped with a six-port valve (Fig. S3) (Fujioka et al., 2017). Sample volumes of 20 μL (RO feedwater) and 200 μL (RO permeate) were injected into the HPLC-PR-CL every 22 min. Conductivity and temperature of RO feedwater and permeate were also monitored using conductivity meters (Orion Star™ A325, Thermo Fisher Scientific, MA, USA). Concentrations of TOrCs in RO feedwater and permeate were determined using an ultra-performance