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Quantification and characterization of dissolved organic nitrogen in wastewater effluents by electrodialysis treatment followed by size-exclusion chromatography with nitrogen detection

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ABSTRACT

Dissolved organic nitrogen (DON) can act as a precursor of nitrogenous disinfection byproducts during oxidative water treatment. Quantification and characterization of DON are still challenging for waters with high concentrations of dissolved inorganic nitrogen (DIN, including ammonia, nitrate and nitrite) relative to total dissolved nitrogen (TDN) due to the cumulative analytical errors of independently measured nitrogen species (i.e., DON = TDN − NO_2^- − NO_3^- − NH_4^+/NH_3) and interference of DIN species to TDN quantification. In this study, a novel electrodialysis (ED)-based treatment for selective DIN removal was developed and optimized with respect to type of ion-exchange membrane, sample pH, and ED duration. The optimized ED method was then coupled with size-exclusion chromatography with organic carbon, UV, and nitrogen detection (SEC-OCD-ND) for advanced DON analysis in wastewater effluents. Among the tested ion-exchange membranes, the PC-AR anion- and CMT cation-exchange membranes showed the lowest DOC loss (1–7%) during ED treatment of a wastewater effluent at ambient pH (8.0). A good correlation was found between the decrease of the DIN/TDN ratio and conductivity. Therefore, conductivity has been adopted as a convenient way to determine the optimal duration of the ED treatment. In the pH range of 7.0–8.3, ED treatment of various wastewater effluents with the PC-AR/CMT membranes showed that the relative residual conductivity could be reduced to less than 0.50 (DIN removal >90%; DIN/TDN ratio ≤0.60) with lower DOC losses (6%) than the previous dialysis and nanofiltration methods (DOC loss >10%). In addition, the ED method is shorter (0.5 h) than the previous methods (>1–24 h). The relative residual conductivity was further reduced to ~0.20 (DIN removal >95%; DIN/TDN

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ratio ≤0.35) by increasing the ED duration to 0.7 h (DOC loss = 8%) for analysis by SEC-OCD-ND, which provided new information on distribution and ratio of organic carbon and nitrogen in different molecular weight fractions of effluent organic matter.

1. Introduction

Increasing dissolved organic nitrogen (DON) concentrations in the urban water cycle due to anthropogenic activities (e.g., wastewater discharge, agricultural runoff, etc.) have recently become a growing concern for drinking water treatment and/or municipal wastewater reclamation (Liu et al., 2012; Shah and Mitch, 2012; Westerhoff and Mash, 2002). Nevertheless, it has been difficult to assess the role of DON and often assumed that the behavior of DON is similar to that of dissolved organic matter (DOM) due to its small weight fraction in the DOM ([DON]/[DOM] <5% w/w) (Westerhoff and Mash, 2002). A high DON content may serve as a source of precursors for both halogenated (e.g., haloacetonitrile and halonitromethane) and non-halogenated (e.g., N-nitrosodimethylamine (NDMA)) nitrogenous disinfection byproducts (N-DBPs) formed during disinfection processes, such as chlorination and/or chloramination (Hu et al., 2010; Lee et al., 2007; Pehlivanoglu-Mantas and Sedlak, 2008; Shah and Mitch, 2012; Yang et al., 2010). Nitrogenous DBPs are potentially more mutagenic and carcinogenic than the regulated DBPs (i.e., trihalomethanes and haloacetic acids) (Plewa et al., 2004; Muellner et al., 2007; Richardson et al., 2007). The World Health Organization (WHO) has set a guideline value for NDMA of 100 ng/L in drinking water calculated by a health-based value of NDMA associated with a upper-bound excess lifetime cancer risk of 10^{-5} (WHO, 2006).

A quantification of DON concentrations may help to assess its role in drinking water and/or wastewater (e.g., precursor of DBPs). However, DON concentrations in water samples cannot be measured directly and have to be calculated by subtracting the sum of the concentrations of dissolved inorganic nitrogen (DIN) species (i.e., nitrite, nitrate, and ammonium/ammonia) from the concentration of the total dissolved nitrogen (TDN) (Westerhoff and Mash, 2002):

$$\mathrm{DON} = \mathrm{TDN} - \sum \mathrm{DIN} \quad (1)$$

The high-temperature combustion (HTC) method has been widely used to quantify TDN (Westerhoff and Mash, 2002; Vandenbruwane et al., 2007). Concentrations of DIN can be commonly measured by colorimetric or ion chromatographic methods (Westerhoff and Mash, 2002). However, the accuracy of DON measurements in samples with high DIN/TDN ratios is subject to incomplete oxidations of DIN species by the HTC method and cumulative analytical errors caused by the independent measurement of nitrogen species (Lee and Westerhoff, 2005; Vandenbruwane et al., 2007). It was proposed that the DIN/TDN ratio of samples should not exceed 0.60 to avoid an interference with DIN species for accurate DON measurements and reduce the cumulative analytical variance of DON measurements (Lee and Westerhoff, 2005).

Although a few methods, including nanofiltration, catalytic reduction, and dialysis treatment are available to reduce the DIN/TDN ratios to less than 0.60 for improving the accuracy of DON measurements in surface water and/or drinking water (Ambonguilat et al., 2006; Lee and Westerhoff, 2005; Vandenbruwane et al., 2007; Xu et al., 2010), some of them may not be useful for the practical DON measurements in real samples due to high DOC losses (DOC loss of nanofiltration = 19–24%; DOC loss of catalytic reduction = 30%). Among these, dialysis has been considered as the most attractive option to selectively remove DIN species for accurate DON measurements in drinking and/or surface waters (DIN removal >70%; DON loss <5%; DOC loss = 2%) (Lee and Westerhoff, 2005; Vandenbruwane et al., 2007). However, the dialysis method is problematic for the DON measurements in wastewater effluents since a significant fraction of DOC and DON is removed (DON loss >10%; DOC loss = 10–15%) (Lee and Westerhoff, 2005).

To get more information on DON, in terms of NDMA precursors and formation potential based on molecular weight (MW) fractions, Pehlivanoglu-Mantas and Sedlak (2008) have investigated the reactivity and fate of DON in wastewater effluents using fractionation by ultrafiltration (UF). This method is only applicable to fully nitrified and denitrified wastewater effluents with negligible DIN concentrations. An alternative approach to get comprehensive information on DON characteristics in wastewater effluents is size-exclusion chromatography equipped with organic carbon, UV, and nitrogen detection (SEC-OCD-ND). Unlike the conventional analytical methods (i.e., subtraction methods and UF fractionation), SEC-OCD-ND can not only quantify TDN concentrations but also provide qualitative information on DON fractions (i.e., MW distribution and molar ratio of organic nitrogen to organic carbon (N/C)) (Graeber et al., 2012; Huber et al., 2011). However, the current study found that removal of the DIN species is still necessary due to severe interferences of DIN species on the analysis of DON fractions in wastewater effluents using SEC-OCD-ND.

To overcome these problems, a novel treatment method capable of selectively removing DIN species from wastewater effluents is needed. Electrodialysis (ED) is a well-established method to remove inorganic ions from aqueous solutions (Strathmann, 2004). ED treatment has been applied to fresh water or seawater for DOM isolation (Vetter et al., 2007; Koprivnjak et al., 2006). ED treatment with pulsed electrical currents was also tested for enhanced DOM recovery from seawater (Gurtler et al., 2008). Nevertheless, the ED method has not been applied to wastewater effluent matrices for selective removal of DIN and recovery of effluent organic matter. Furthermore, membrane types, pH of sample and duration of ED operation, which are known as key parameters affecting the performance of ED processes (Kim et al., 2002; Van der Bruggen et al., 2004), should be optimized to enhance the removal efficiency of inorganic ions and minimize the loss of DON. Cation-exchange treatment has been used as a pre-softening step to replace magnesium and calcium with