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Measurements of dissolved organic nitrogen (DON) in water samples with nanofiltration pretreatment

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ABSTRACT

Dissolved organic nitrogen (DON) measurements for water samples with a high dissolved inorganic nitrogen (DIN, including nitrite, nitrate and ammonia) to total dissolved nitrogen (TDN) ratio using traditional methods are inaccurate due to the cumulative analytical errors of independently measured nitrogen species (TDN and DIN). In this study, we present a nanofiltration (NF) pretreatment to increase the accuracy and precision of DON measurements by selectively concentrating DON while passing through DIN species in water samples to reduce the DIN/TDN ratio. Three commercial NF membranes (NF90, NF270 and HL) were tested. The rejection efficiency of finished water from the Yangshupu drinking water treatment plant (YDWTP) is 12%, 31%, 8% of nitrate, 26%, 28%, 23% of ammonia, 77%, 78%, 82% of DOC (dissolved organic carbon), and 83%, 87% 88% of UV_{254} for HL, NF90 and NF270, respectively. NF270 showed the best performance due to its high DIN permeability and DON retention (~80%). NF270 can lower the DIN/TDN ratio from around 1 to less than 0.6 mg N/mg N, and satisfactory DOC recoveries as well as DON measurements in synthetic water samples were obtained using optimized operating parameters. Compared to the available dialysis pretreatment method, the NF pretreatment method shows a similar improved performance for DON measurement for aqueous samples and can save at least 20 h of operating time and a large volume of deionized water, which is beneficial for laboratories involved in DON analysis. DON concentration in the effluent of different treatment processes at the YDWTP and the SDWTP (Shijiuyang DWTP) in China were investigated with and without NF pretreatment; the results showed that DON with NF pretreatment and DOC both gradually decreased after each water treatment process at both treatment plants. The advanced water treatment line, including biological pretreatment, clarification, sand filtration, ozone-BAC processes at the SDWTP showed greater efficiency of DON removal from 0.37 to 0.11 mg N L^{-1} than that at the YDWTP, including pre-ozonation, clarification and sand filtration processes from 0.18 to 0.11 mg N L^{-1}.

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1. Introduction

Natural waters contain significant levels of dissolved inorganic nitrogen (DIN, including nitrate, ammonium, and nitrite) as well as dissolved organic nitrogen (DON). Typical DON concentrations in surface waters vary, ranging from less than 0.1 to larger than 10 mg N L^{-1}, with a median value of approximately 0.3 mg N L^{-1} (Westerhoff and Mash, 2002). Because DON comprises a relatively small portion of the dissolved organic matter (DOM), researchers tend to ignore DON and assume that dissolved organic carbon (DOC), nitrate and ammonium play a more important role in water treatment processes (Westerhoff and Mash, 2002). However, there are increasing concerns regarding DON in water treatment processes recently due to its preferential reaction with oxidants/disinfectants (e.g., chlorine, chloramines, ozone (O_3) and potassium permanganate) to form nitrogenous disinfection by-products (N-DBPs) (e.g., nitrosamines including N-nitrosodimethylamine [NDMA], halonitromethanes, and haloacetonitriles) (Westerhoff and Mash, 2002; Richardson, 2003; Mitch et al., 2003). Toxicity results indicate that N-DBPs show much stronger carcinogenicity or mutagenicity than that of the regulated DBPs, such as trihalomethanes (THMs) and haloacetic acids (HAAs) (Richardson et al., 2007; Plewa et al., 2004; Lee et al., 2007). The presence of DON also contributes to membrane fouling in water treatment processes (Her et al., 2000). Despite considerable information detailing DOC characteristics (such as structures and specific functional groups) and fate during water treatment processes (Bruggen and Vandecasteele, 2003; Her et al., 2000; Lin et al., 2007; Richardson et al., 2007; Solinger et al., 2001), little is known about DON.

It is important to use available analytical methods for DON determination to investigate its fate, properties and reactivity in waters and water treatment processes. The DON concentration in water samples cannot be quantified directly but must be determined by subtracting the sum of DIN species from the total dissolved nitrogen (TDN). Because DON only contributes a relatively small portion of the total mass of TDN in human-impacted surface waters (Perakis and Hedin, 2002), and DON is the residual concentration after subtracting a much larger concentration (DIN species) from the measured TDN (see Eq. (1)), the accuracy of DON measurements is subject to significant cumulative analytical errors of each independently measured nitrogen species (TDN, nitrite, nitrate and ammonia).

$$DON = TDN - DIN = TDN - (NO_3^- + NO_2^- + NH_3/NH_4^+) \quad (1)$$

Negative DON concentrations were reported in practical measurements in the case of high DIN/TDN ratios (Vandenbruwane et al., 2007; Solinger et al., 2001; Lee and Westerhoff, 2005). Lowering the DIN/TDN ratio in water samples is necessary to improve the accuracy of DON measurements. Lee and Westerhoff (2005) reported a dialysis-based pretreatment to reduce DIN species in bulk water. They found that 70% of DIN was removed, and more than 95% of DON recoveries were obtained for surface and finished water after 24 h dialysis using a cellulose ester dialysis tube. Although dialysis pretreatment leads to a more accurate DON determination for surface and drinking waters, the method may not be applicable for wide use because it is not time and cost effective. Catalytic reduction of nitrate is another way to lower the DIN/TDN ratio (Ambonguilat et al., 2006). However, DON and DOC can be adsorbed onto the catalyst and will likely compete with nitrate for active catalytic sites. Extensive testing has indicated that catalytic reduction of nitrate is not suitable for DON determination (Ambonguilat et al., 2006).

Another possible method for reducing the DIN/TDN ratio is to increase the DON concentration in combination with complete or partial DIN removal by means of membrane separation. Reverse osmosis (RO) is a popular technology for DOM concentration and isolation in surface waters, with overall DOC retention close to 100% (Croué, 2004). However, a lower DIN/TDN ratio cannot be achieved because DIN concentrates along with the organics and remains in the concentrated solution. Therefore, it is more practical to find a suitable separation process that allows DIN pass through freely and still retains most organics, including DON.

A nanofiltration (NF) membrane has properties that lie somewhere between ultrafiltration (UF) and RO. NF has been shown to be effective for removing DOC and DBPs precursors and controlling salt passage with a different membrane (Teixeira and Rosa, 2006; Bruggen and Vandecasteele, 2003; Lin et al., 2006). The permeate flux of an NF membrane is based on the applied transmembrane pressure, membrane resistance, feed water temperature, and the composition of feed water. The selectivity of a membrane is due to the combined factors of membrane characteristics, solution properties, and operating conditions (Ahn et al., 1999; Nghiem et al., 2005; Garba et al., 2000; Lin et al., 2007). The major rejection mechanisms for NF membranes include molecular sieve effects and electrostatic effects. Although the molecular weight cutoff (MWCO) of commercial NF membranes is around 200 Da (Ahn et al., 1999; Nghiem et al., 2005; Garba et al., 2000; Lin et al., 2007), molecules below the MWCO of a membrane may also be rejected by the electrical attraction or repulsion of charged species onto a charged membrane surface.

The assumption of this study is that NF pretreatment will retain most of the DON in the concentrate while allowing DIN species (nitrate, nitrite and ammonia) to pass through into the permeate. As a result of increasing DON concentration and decreasing the DIN/TDN ratio, a more accurate DON measurement in water samples with high DIN/TDN ratios can be obtained (Lee and Westerhoff, 2005). Because NF separation performance is significantly affected by membrane characteristics (such as MWCO, pore size distribution, charge and hydrophobicity), solution properties (such as solution composition, ionic strength and pH), and operating parameters (such as applied pressure and permeate flux), factors such as membrane type, solution pH, and the initial ratio of sample volume to NF surface area (*R*) were studied to determine the critical parameters needed to optimize NF pretreatment performance. The objectives of this study were: (1) to investigate the feasibility of NF pretreatment for DON measurement using different commercial NF membranes; (2) to optimize the operating parameters for the NF pretreatment system; and (3) to measure the DON concentration in raw water and the effluent of different treatment processes in two