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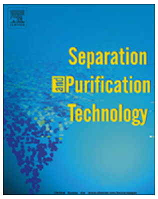

Fractionation of nitrogen-enriched dissolved organic matter in water

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ABSTRACT

Dissolved organic nitrogen (DON) in water is associated with disinfection by-products (DBPs) formation especially for nitrogenous DBPs (N-DBPs), which possess stronger adverse health effects than traditional carbonaceous DBPs (C-DBPs). DON characteristics affect not only the amount but also the speciation of DBPs formation. To characterize DON constituents in water, this study modified and validated a DON fractionation method using DAX-8, XAD-4, and MSC-1H resins. The method was then used to investigate the characterization and composition of DON constituents in treated wastewater effluents and raw waters. From validation tests using nitrogenous surrogate solutions, recoveries of each pretreatment step as well as selected eluents and flow rates were acceptable for fractionation of aqueous DON. The absence of any statistically significant difference in DON compositions between duplicate treated effluents also validated the applicability of the modified fractionation method for field water. The proposed method will be useful for characterizing and evaluating the properties, amounts, and compositions of DON-enriched materials in water and help address the current lack of information on DON profiles in water sources.

1. Introduction

Organic matter in water is composed of natural organic matter (NOM) and anthropogenic organic substances. NOM originating from humification is considered the one of the principal precursors of disinfection by-products (DBPs) in water treatment. NOM molecules smaller than 0.45 μm in diameter are considered dissolved organic matter (DOM), which consists of ~50% hydrophobic humic substances and ~30% hydrophilic acids, as well as carbohydrates, amino acids, and hydrocarbons [1].

In recent decades, dissolved organic nitrogen (DON) such as aromatic proteins and some enriched nitrogen contents [2] as parts of DOM have gained attention as potential DBPs precursors, owing to increases in disinfectant consumption and possible membrane fouling [3,4]. Although DON substances are only present at low levels in natural water, a minute concentration in water sources is easily sufficient to boost levels of nitrogenous DBPs (N-DBPs) (e.g. nitrosamines, nitromethanes, haloacetonitriles). These N-DBPs are recognized as more significant carcinogens and toxicants than the traditional carbonaceous DBPs (C-DBPs) [5].

Several studies have suggested that DON substances with specific characteristics significantly affect the amount and speciation of DBPs formation after treatment with various disinfectants [6–8]. The hydrophobic fraction was found to be more reactive to form trihalomethanes than the transphilic and truly hydrophilic fractions [9,10]. Hydrophilic and low-molecular weight fractions (passing through a 1 kDa ultrafilter) contained most precursors of *N*-nitrosodimethylamine (NDMA) [11]. Dotson et al. [12] showed that nitrogen-enriched DOM isolates treated with free chlorine had greater halogenous DBP formation potentials (DBPFPs) (mostly trichloromethane [TCM], dichloroacetonitrile [DCAN], and trichloronitromethane [TCNM]) than those treated with chloramine. Only certain selected nitrogen-enriched isolates could form NDMA, especially in the hydrophilic bases (HPIB) fraction. Characterizing and quantifying DON matter is thus of great importance for controlling and removing DBPs in drinking water.

Several studies have adopted filtration and resin adsorption to fractionate DON materials in water to identify the relationships between DON characteristics and DBPs formation [13–16] besides widely used and traditional surrogates such as dissolved organic carbon (DOC), DON, or specific UV absorbance (SUVA). However, only a few studies dealing with DON fractionation are available; compared to NOM contents, DON is present at lower concentrations (with a median value of ~0.3 mg/L in surface waters) and in lesser proportions (<10%). Consequently, analytical limitations arise [17].

For filtration approaches of DON fractionation, DON substances were fractionated based on their physical sizes. However, DON materials with different physiochemical characteristics behave dif-

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ferently to their environment and show different reactivities to form DBPs. DON contents after fractionation via filtration may also be underestimated due to the fouling of filtration devices [3,4]. Therefore, resin adsorption of DON fractionation may offer a better approach to identifying the relationships between DON characteristics and DBP formation. Chen and Valentine [14] used XAD-8, AG-MP-50, and A-7 resins to determine how various NOM fractions contributed to NDMA formation and found that the hydrophilic and basic fractions tended to form more NDMA than the hydrophobic and acid fractions. A study of sixteen NOM isolates separated by XAD-8 and XAD-4 resins was performed to identify NOM properties and DBP formation during chloramination [16]. Leenheer et al. [18], focusing on organic nitrogen, adopted a dialysis method to optimize a preparative DON fractionation method and then concentrate the isolated fractions for the study of N-DBPs formation. They used XAD-1, XAD-4, and MSC-1H resins in a modified NOM fractionation method to fractionate DON materials into seven fractions according to size, polarity, and acid/alkaline/neutral characteristics [19,20]. This DON fractionation scheme required large water volumes to obtain sufficient amounts of isolates; unavailability of commercial XAD-1 resin is at present a further limitation of this method. Furthermore, Leenheer et al. [18] emphasized its applicability to the analysis of field samples rather than to method modification and validation. Although column recoveries (95–115%) and overall recoveries (81%) of DOC were reported, the fundamental recoveries of each pre-treatment and the selection of flow rates and eluent solutions were not documented [19,20].

In order to characterize the DON constituents in water samples taken in the field, this study modified and evaluated a DON fractionation method according to the scheme proposed by Leenheer et al. [18]. First, urea and histamine solutions were used to verify the recovery and efficiency of each of several pre-treatments. Second, prepared surrogate solutions were used to optimize flow rates and eluent solutions for the fractionation processes. Finally, two duplicated samples of treated effluents were used to validate the modified DON fractionation method.

2. Experimental materials and methods

2.1. DON sources and sample collection

Water samples (52–132 L) were collected from the treated effluents of Neihu Municipal Wastewater Treatment Plant (WWTP) in Taipei City (TN) and the raw waters of Tai Lake Water Treatment Plant (WTP) in Kinmen (KT) during April 2009 to April 2010. The unchlorinated TN effluents had been treated with grit chambers, primary sedimentation basin, biological aeration, and secondary precipitation. The untreated KT source waters were polluted by animal husbandry wastewater and domestic sewage and had severe eutrophication problems [21]. Since both treated wastewater effluents and algal activities have been observed to increase DON concentrations in drinking water supplies [22], both the TN and KT samples were suitable for validation of the DON fractionation method.

Samples were prefiltered by a 1 μm ceramic cartridge filter and a 0.45 μm glass fiber cartridge filter (Advantec, Japan), then concentrated to ~10 L using a reverse osmosis (RO) system (R/O-180, Gentech, Taiwan) with a Dow Filmtec RO element (Molecular Weight Cut Off [MWCO] = 100 Da) (TW30-1812-50, Dow, USA). This RO element was composed of aromatic polyamide with free amine and carboxylate end groups and used to increase recoveries of DOM (recoveries >96.4%) [23–25]. A 100 Da MWCO membrane enabled us to physically isolate DON and achieve >95% recovery of DON substances [26]. After RO concentration, concentrates were adjusted to pH 1 with HCl solution to facilitate disruption of NOM/metal aggregates for further DON fractionation [27].

2.2. Water quality parameters

An ASI 5000 TOC analyzer (Shimadzu, Japan) was used for non-purgeable dissolved organic carbon (NPDOC) determination. UV absorbance at 254 nm (UV_{254}) was measured with a UV 160A UV/visible spectrophotometer (Shimadzu, Japan). Total dissolved nitrogen (TDN) was measured following Bronk et al. [28]. Merck Ammonium Cell Test kits (Merck, Germany) were used for ammonia measurements. Concentrations of nitrite and nitrate were determined using a DX-120 ion chromatograph (Dionex, USA) equipped with an AS9 column. DON concentrations were obtained by subtracting dissolved inorganic nitrogen (nitrite, nitrate, and ammonia) (DIN) from TDN.

2.3. DON fractionation scheme

The preparative fractionation scheme for DON-enriched matters was modified from the method proposed by Leenheer et al. [18] using XAD-1, XAD-4, and MSC-1H resins. In this study, DAX-8 (a substitute for XAD-1), XAD-4, and MSC-1H resins with different chemical affinities were used to divide DON substances into seven fractions: hydrophobic acids (HPOA), hydrophobic bases/neutrals (HPOB/N), amphiphilic acids (AMPA), amphiphilic bases/neutrals (AMPB/N), hydrophilic acids/neutrals (HPIA/N), HPIB, and amino acids (AA) (Figs. 1 and 2).

2.3.1. Reagents and equipment

Supelite DAX-8 and Amberlite XAD-4 resins were obtained from Supelco (USA), and MSC-1H resin was purchased from Sigma–Aldrich (Germany). Since both XAD-1 and XAD-8 (another widely used substitute for XAD-1) are no longer available, Supelite

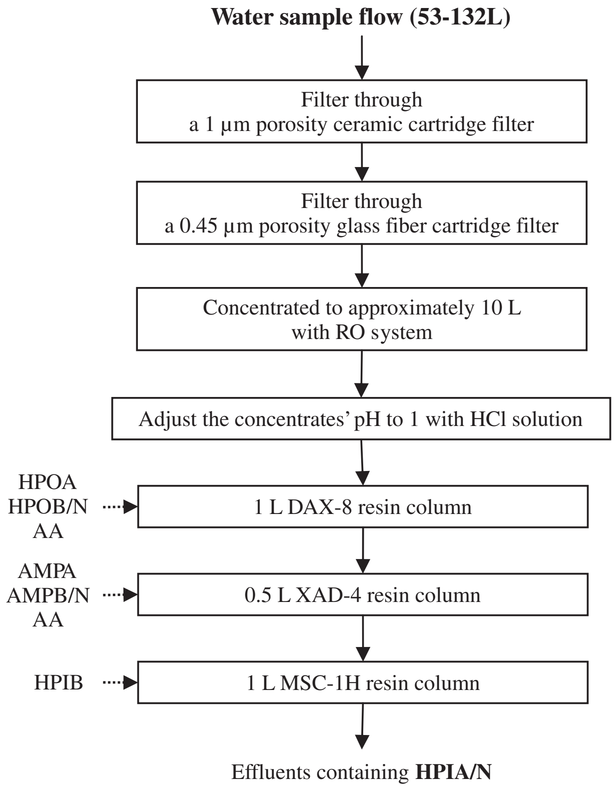

Fig. 1. The adsorption scheme of DON fractionation.