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Characterization of soluble microbial products as precursors of disinfection byproducts in drinking water supply

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HIGHLIGHTS

- Soluble microbial products (SMPs) are produced by biodegradation in polluted water.
- SMPs can be important disinfection byproduct (DBP) precursors in water supply.
- Proteins and humic substances in SMPs are the main wastewater-derived DBP precursors.
- Small organic molecules (<1 kDa) account for most SMPs and their DBP formation.

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ABSTRACT

Water pollution by wastewater discharge can cause the problem of disinfection byproducts (DBPs) in drinking water supply. In this study, DBP formation characteristics of soluble microbial products (SMPs) as the main products of wastewater organic biodegradation were investigated. The results show that SMPs can act as DBP precursors in simulated wastewater biodegradation process. Under the experimental conditions, stabilized SMPs had DBPFP (DBP formation potential) yield of around 5.6 μmol mmol^{-1}-DOC (dissolved organic carbon) and DBP speciation profile different from that of the conventional precursor, natural organic matter (NOM). SMPs contained polysaccharides, proteins, and humic-like substances, and the latter two groups can act as reactive DBP precursors. SMP fraction with molecular weight of <1 kDa accounted for 85% of the organic carbon and 65% of the DBP formation. As small SMP molecules are more difficult to remove by conventional water treatment processes, more efforts are needed to control wastewater-derived DBP problem in water resource management.

1. Introduction

The formation of disinfection byproducts (DBPs) in drinking water has been a major problem of drinking water quality with its considerable public health concerns. The main organic DBP groups formed by chlorination include trihalomethanes (THMs) and haloacetic acids (HAAs). It has been found that THMs, many HAA species such as dichloroacetic acid (DCAA), and certain other halogenated DBPs are carcinogenic, mutagenic, or teratogenic (Legay et al., 2010). Natural organic matter (NOM), which is mainly composed of humic substances, is known to be the major DBP precursor in surface water (Chang et al., 2001; Hua and Reckhow, 2007). Numerous studies have been conducted on NOM to determine its characteristics and DBP yield during water disinfection (Xie, 2003).

The presence of DBP precursors in source water can also be attributed to water pollution caused by human activities. Water pollution is becoming one of the most serious global environmental issues, especially in developing countries that are experiencing rapid population and economic growth. Many surface water bodies, such as rivers and lakes, are used for both wastewater disposal and fresh water withdrawal for municipal use. Upper reaches of many water sources have been polluted by wastewater discharge (Zheng et al., 2007). Such pollution of the raw water source can greatly affect the drinking water quality. Researchers have found that wastewater organic pollutants increase DBP precursors in the receiving water, resulting in more DBP formation in the finished drinking water (Chen et al., 2009; Chu et al., 2002; Krasner et al., 2009). There is thus a need to address the problem of wastewater-derived DBPs in water supply.

Wastewater organics are mainly composed of biodegradable compounds that would undergo biodegradation after being discharged into the upstream of receiving water sources (Dignac et al., 2001; Dignac et al., 2000). Soluble microbial products (SMPs) are an important result of the biological degradation process (Aquino and Stuckey, 2002; Liu and Li, 2010). SMPs are organic compounds that are released by microorganisms into the solution from substrate metabolism and microbial cell decay. SMPs can be grouped into two categories based on the microbial growth phases: utilization-associated products (UAPs),

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which are SMPs that are associated with substrate metabolism and biomass growth, and biomass-associated products (BAPs), which are SMPs resulted from the biomass decay (Barker and Stuckey, 1999). The exact chemical compositions for UAP- and BAP-based SMPs remain to be determined. However, conceptually, UAPs are produced in the early phase of organic biodegradation and BAPs are released in the later phase of biodegradation when the substrates have been exhausted. According to Aquino and Stuckey (2004a), UAPs have both biodegradable and non-biodegradable fractions, while BAPs mainly contain non-biodegradable compounds.

It has been suggested that SMPs can increase the DBP formation in chlorinated water (Chen et al., 2008; Cheng and Chi, 2003; Dotson et al., 2009). The influence of SMPs on the formation of DBPs in the wastewater effluent after wastewater disinfection has been reported (Wei et al., 2011; Zhang et al., 2009). However, there are few studies on the characteristics of SMPs as DBP precursors in the surface water supply. Moreover, the UAPs and BAPs may behave differently in DBP formation owing to their different chemical features (Boero et al., 1996). This laboratory study was conducted to investigate the properties of SMPs as DBP precursors derived from wastewater organic biodegradation in a polluted raw water source, including the dynamics of SMP production and DBP formation in biodegradation process, DBP-forming organic components, and molecular size-based DBP yield and speciation.

2. Materials and methods

2.1. The dynamics of organic degradation, SMP production, and its DBP formation potential

Laboratory experiments were conducted to simulate the biodegradation of wastewater organics and the production of SMPs in natural water. The biodegradation experiments were carried out on glucose-based synthetic wastewater in 10-L bioreactors placed in a temperature-controlled biochemical oxygen demand (BOD) incubator at 20 °C. Glucose was selected to represent biodegradable wastewater organics, as it can be biodegraded completely leaving only SMPs as the remaining organics in the solution. Glucose (Unichem) was dissolved in Milli-Q water (Millipore) at 200 mg L^{-1}, giving a dissolved organic carbon (DOC) concentration of 80 mg L^{-1}. Activated sludge was dosed as the seed biomass at a suspended solid (SS) concentration of 2 mg L^{-1} into the bioreactors to initiate biodegradation. NH_4Cl, $FeCl_3$, $CaCl_2$, and $MgSO_4$ were added as nutrients according to the guidelines for running BOD tests (Velp Scientifica, 2004). The water pH was maintained at around 7 with a phosphate buffer solution. The solution was aerated by an air pump with an air flow rate of 4 L min^{-1} to provide oxygen to the solution. The biodegradation experiment was conducted for 15 days to study the dynamics of SMP production and DBP formation. Water samples were collected in triplicates from the incubated bioreactor every 12 h for the first 5 days and every 24 h for the next 10 days for subsequent organic analysis and DBP formation tests. The samples were filtered through a 0.45-μm membrane (Millipore) to remove all of the bacteria and suspended solids. The filtered water, or the SMP solution, was then chlorinated to determine the DBP formation potential (DBPFP) of the dissolved organic matter in the solution after various incubation periods. The filtered water samples were also analyzed for their DOC content and UV absorbance value at 254 nm (UV_{254}).

2.2. Organic components of SMPs in relation to DBP formation

For further characterization of SMPs as DBP precursors, including the organic components and molecular weight distribution of SMPs, a more concentrated glucose solution was used for incubation to produce a sufficient amount of SMPs. The initial glucose concentration was 2000 mg L^{-1}, and the seed activated sludge concentration was 20 mg L^{-1} accordingly in the bioreactor. As described in Section 2.1, nutrients were added, the water pH was buffered at about 7, and the organic solution was aerated in the bioreactor. The aerobic incubation was carried out at 20 °C for 5 days, and the water solution was sampled every day. Samples were taken from the suspension in triplicates and filtered through a 0.45-μm membrane immediately after sampling.

The filtered samples were analyzed for their SMP contents, including carbohydrates or polysaccharides, proteins, and humic-like substances. Proteins and humic-like substances were analyzed based on the colorimetric absorbance measurement with a UV/VIS spectrophotometer (UV/VIS Lambda 25, Perkin Elmer) at 750 nm following the modified Lowry method (Li and Yang, 2007) using bovine serum albumin (Sigma) and humic acid (Fluka) respectively as the standards. The carbohydrates were measured with the UV/VIS spectrophotometer at 620 nm following the phenol-sulfuric acid method (Li and Yang, 2007), with glucose as the standard.

A fluorescence spectrophotometer (Hitachi F-7000) was used to analyze the soluble organic compounds in the water samples after different degradation periods, and the results were described with fluorescence excitation–emission matrix (FEEM) (Chen et al., 2003). The spectrophotometer used a xenon excitation source, and the slits were set to 2.5 nm for both excitation and emission. To obtain the FEEMs, the excitation wavelength was increased from 220 to 400 nm in 5-nm steps. For each excitation wavelength, the emission was detected from 300 to 550 nm in 2-nm steps. Spectral subtraction was applied to the FEEM measurement to eliminate the blank spectra resulting from pure water (Her et al., 2003), and the instrumental correction was made internally following the procedure (Hitachi F-7000 Instruction Manual) recommended by the manufacturer.

2.3. Molecular weight distribution of SMPs in relation to DBP formation

The SMP samples obtained through the procedure in Section 2.2 after 5 days of biodegradation were further separated by ultrafiltration (UF) into different fractions based on molecular weight cutoffs. Ultrafiltration was carried out using a pressurized UF unit (Amicon, Millipore) as described by Aiken (1984). For the UF-based fractionation, 500 mL of the filtered water sample was passed through four membranes (Amicon, Millipore) with different cutoffs in the following sequence: 100, 30, 10, and 1 kDa. The staged filtration resulted in 5 solutions of the same volume (100 mL) with apparent organic sizes of <0.45 μm, <100 kDa, <30 kDa, <10 kDa, and <1 kDa. After the UF separation, the solutions were analyzed for their organic contents and tested for DBPFPs. Accordingly, the DOC, UV_{254}, and DBPFP of the SMP fractions within the apparent molecular weight ranges of >100 kDa, 30–100 kDa, 10–30 kDa, 1–10 kDa, and <1 kDa were determined.

2.4. DBPFP determination

DBPFP tests were conducted to evaluate the quantity and reactivity of the organic DBP precursors in the water samples. The DBP formation tests were carried out by chlorinating the filtered water samples in accordance with the Standard Methods (APHA, 2005). For each DBPFP test, a 100-mL water sample was chlorinated with NaOCl (Unichem), and the resulting solution was incubated in dark for 7 days at pH 7.0 ± 0.2 with a 0.5 N phosphate buffer. To ensure the presence of free chlorine residue after 7 days of incubation, chlorine demand tests were conducted, i.e., the water samples were dosed with 100 mg L^{-1} Cl_2, incubated for 12 h, and the free chlorine residue was measured. The NaOCl dose for the DBPFP test that would result in a free chlorine residue of between 3 and 5 mg L^{-1} was then determined. The actual free chlorine residue in the chlorinated water after 7 days of incubation was also measured, and only the samples that had residual free chlorine concentrations of 3–5 mg L^{-1} were used. Immediately after the incubation, the excess chlorine in the water samples was quenched with NH_4Cl