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Use of three-dimensional excitation and emission matrix fluorescence spectroscopy for predicting the disinfection by-product formation potential of reclaimed water

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ABSTRACT

This study was undertaken to demonstrate the feasibility of using three-dimensional excitation-emission matrix (3DEEM) fluorescence spectroscopy for the determination of chlorination disinfection by-product (DBP) precursors and the disinfection by-product formation potential (DBPFP) of reclaimed water samples. Two major DBP precursors were examined in this study, including humic acid (HA) and fulvic acid (FA). The 3DEEM fluorescence results obtained from various reclaimed water samples indicated that the reclaimed water samples were rich in fulvic acid-like substances that were associated with two main peaks (Ex/Em = 235–245/420–440 nm, and Ex/Em = 330–340/410–430 nm) in the fluorescence spectrum. The results also illustrated that the wavelength location of peak fluorescence intensity of a reclaimed water sample was independent of the influent water quality and the wastewater treatment process used in the reclamation plant. As a result, the peak fluorescence intensity and the wavelength location of the peak were used to identify the species of DBP precursors and their concentrations in the reclaimed water sample. Four regression models were then developed to relate the peak fluorescence intensity of the water sample to its DBPFP, including the formation potential of trihalomethane (THMFP) and the formation potential of haloacetic acid (HAAFP). The regression models were verified using the measured DBPFP results of a series of reclaimed water samples. It was found that the regression modeling results matched the measured DBPFP values well, with prediction errors below 10%. Therefore, the use of 3DEEM fluorescence spectroscopy together with the developed regression models in this study can provide a reliable and rapid tool for monitoring the quality of reclaimed water. Using this method, water quality could be monitored online, without utilizing the lengthy conventional DBPFP measurement.

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1. Introduction

Chlorination of both potable water and treated wastewater is widely used worldwide to effectively control most pathogens and provide residual disinfection capacity from the treatment site. In addition to its limited ability to control some specific pathogens like *Giardia* and *Cryptosporidium*, the main drawback of chlorination is that chlorine can react with natural organic matter (NOM) to generate various disinfection by-products (DBPs). Trihalomethane (THM) and haloacetic acid (HAA) are two of most prevalent groups of DBPs that are produced (Shon et al., 2006; Lu et al., 2009; Chen and Westerhoff, 2010). These DBPs are of serious human health and ecological concern due to their carcinogenic and mutagenic effects, and are therefore regulated by the US Environmental Protection Agency (USEPA), the World Health Organization (WHO), and many other regulatory agencies in the world (Rodriguez et al., 2007). For example, in the US, the maximum allowable levels of THM and HAA are set at 80 μg/L and 60 μg/L, respectively (Goslan et al., 2009). Many research studies have indicated that the level of DBPs produced during chlorination depends on the levels of precursors that are present. These precursors are defined as a mixture of organic and inorganic compounds that can form DBPs under disinfection conditions (Chen and Westerhoff, 2010). Particularly, high THM and HAA concentrations are found to be generally associated with high concentrations of humic and non-humic dissolved organic matter (DOM) (Bougeard et al., 2010). Humic substances are comprised of humic acids (HA) and fulvic acids (FA), and non-humic substances include hydrophilic acids, proteins, amino acids, and carbohydrates (Marhaba and Kochar, 2000). Among these, humic acid and fulvic acid have been identified as the most important DBP precursors (Zhang et al., 2008).

In order to better understand and control the formation of DBPs, the disinfection by-products formation potential (DBPFP) test has been widely used (Ates et al., 2007; Bougeard et al., 2010). DBPFP is the measurement of the extent to which the organic material in a water sample reacts with excess chlorine for a long contact time (i.e. 7 days) to form a suite of chlorinated products under controlled pH and temperature conditions. It was proposed by the American Public Health Association (APHA) as a standard analysis method (Sirivedhin and Gray, 2005). However, the DBPFP can be limiting since the measurement is very cumbersome. It requires large doses of chlorine, takes a long time to complete the reaction, and provides only a maximum value indicating the potential generation of DBPs. It does not allow for clear, specific, and quantitative classification of DBP precursors. These drawbacks have restricted its applications (Ates et al., 2007; Lu et al., 2009). A variety of surrogate parameters have thus been adopted to predict DBPFP, such as the ultraviolet absorbance at 254 nm (UVA254) and specific ultraviolet absorbance at 254 nm (SUVA254, defined as the UV absorbance of a water sample at 254 nm divided by the dissolved organic carbon concentration) (Domino et al., 2003; Weishaar et al., 2003; Chow et al., 2008). Generally, DBP precursors are organic compounds with unsaturated structures (such as benzene rings and double-bonds) which can absorb UV radiation in proportion to their concentrations, and many studies have reported good correlation between UVA254 (or SUVA254) and THM or HAA formation (Ates et al., 2007; Lu et al., 2009; Chen and Westerhoff, 2010). UVA254 (or SUVA254) has the advantage of requiring only simple water sample pre-treatment and a short measurement time. The result indicates the content of DOM which absorbs in the ultraviolet region, but the DBP precursors are only part of that DOM. As a result, the measurement provides only a non-specific index of DBP precursors.

Another alternative approach to investigate the formation of DBPs is the use of fluorescence-based techniques. These have recently received increasing research interest (Hudson et al., 2007; Hambly et al., 2010). As mentioned above, DOM contains large amounts of unsaturated and aromatic structures with different functional groups that have fluorescence characteristics. This allows for the utilization of fluorescence spectroscopy to extract information on the chemical structure, the functional groups, the spatial configurations, the intra-molecular and intermolecular kinetic characteristics, and the heterogeneity of components in DOM (Sheng and Yu, 2006). Thus, fluorescence spectroscopy has been used as a valuable water quality and pollution control monitoring tool, including the measurement of DBPFP (Henderson et al., 2009). In particular, DOM includes organic molecules with chromophoric (light absorbing) and fluorophoric (light emitting) moieties (Wang et al., 2009). Therefore, three-dimensional excitation-emission matrix (3DEEM) fluorescence spectroscopy has been widely used to detect detailed changes and transformations of organic matter in various environments (such as oceans, rivers, lakes, and soils) (Hudson et al., 2007; Wang et al., 2009; Peiris et al., 2010). This technique measures the fluorescence of water samples at various emission and excitation wavelengths. The excitation and emission wavelengths can range from short-wavelength UV (~200 nm) to visible blue-green light (~500 nm) (Spencer et al., 2007). By simultaneously determining three fluorescent parameters (excitation wavelength, emission wavelength, and the intensity of fluorescence), an excitation-emission matrix (EEM) can be established as a composite of emission scans for a sample at incremental excitation wavelengths (Yamashita and Tanoue, 2003). The results are arranged in a grid (excitation × emission × intensity). The specific excitation and emission wavelengths are characteristics of a particular molecular conformation (i.e. fluorophore) that can indicate the composition of organic compounds. Thus, the measured peak intensity is directly related to the concentration of the responsible fluorophore in the sample (Lakowicz, 1999; Henderson et al., 2009). When the concentration of a fluorescent substance in a sample is low, a positive linear correlation usually exists between the fluorescence intensity (FI) and the corresponding concentration (Wang et al., 2009). A large amount of data on the fluorescence characteristics can be collected for each sample through sequentially changing the excitation and emission wavelengths. This allows for a wide range of statistical analysis to obtain more theoretical and practical information on the study substances, such as the change of DOM compositions and concentrations (Spencer et al., 2007; Wang et al., 2009).