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Selective elimination of chromophoric and fluorescent dissolved organic matter in a full-scale municipal wastewater treatment plant

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ABSTRACT

Effluent organic matter (EfOM) from municipal wastewater treatment plants potentially has a detrimental effect on both aquatic organisms and humans. This study evaluated the removal and transformation of chromophoric dissolved organic matter (CDOM) and fluorescent dissolved organic matter (FDOM) in a full-scale wastewater treatment plant under different seasons. The results showed that bio-treatment was found to be more efficient in removing bulk DOM (in terms of dissolved organic carbon, DOC) than CDOM and FDOM, which was contrary to the disinfection process. CDOM and FDOM were selectively removed at various stages during the treatment. Typically, the low molecular weight (MW) fractions of CDOM and protein-like FDOM were more efficiently removed during bio-treatment process, whereas the humic-like FDOM exhibited comparable decreases in both bio-treatment and disinfection processes. Overall, the performance of the WWTP was weak in terms of CDOM and FDOM removal, resulting in enrichment of CDOM and FDOM in effluent. Moreover, the total removal of the bulk DOM ($P < 0.05$) and the protein-like FDOM ($P < 0.05$) displayed a significant seasonal variation, with higher removal efficiencies in summer, whereas removal of CDOM and the humic-like FDOM showed little differences between summer and winter. In all, the results provide useful information for understanding the fate and transformation of DOM, illustrating that sub-fractions of DOM could be selectively removed depending on treatment processes and seasonality.

Introduction

Urban water scarcity has been receiving greater than ever attention due to the increasing human population, which exacerbates the urbanization and/or degradation of water resources. In recent years, treated wastewater has been considered as an alternative resource to alleviate water shortages (Hoffbuhr, 2007). However, the presence of large amount of organic matter in wastewater presents a huge challenge to treatment processes (*e.g.*, biological/chemical / physical) and/or technologies (*e.g.*, membrane filtration) (Ishii and Boyer, 2012; Shon et al., 2006). Meanwhile, a large amount of the treated wastewater is discharged into receiving waters, thus effluent organic matter (EfOM) is increasingly having an

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adverse impact on water quality and aquatic ecosystems (Vaquer-Sunyer et al., 2015), and a potential influence on current drinking water supplies (Nam et al., 2008; Oulton et al., 2010). Hence, it is crucial that the fate of dissolved organic matter (DOM) throughout wastewater treatment plants (WWTPs) should be examined to control the quantity and chemical characteristics of EfOM.

In municipal WWTPs, bio-treatment is a common approach for the elimination of nutrients (Mayor et al., 2004) and DOM (Shon et al., 2006; Park et al., 2010), whereas disinfection process is employed to inactivate pathogens before the bio-treated wastewater is discharged into aquatic ecosystems and is reclaimed (Han et al., 2015). The removal of DOM is primarily assessed by chemical parameters (*i.e.*, dissolved organic carbon (DOC), chemical oxygen demand (COD) and biochemical oxygen demand (BOD)), which are influenced by the origins of DOM in raw wastewater, the variability of treatment processes (*i.e.*, membrane bioreactors and nanofiltration) and other factors (*i.e.*, environmental and instrument-related variability) (Park et al., 2010; Wei et al., 2012; Henderson et al., 2009). Seasonal variability (*e.g.*, rainfall and temperature), for example, is known to have a strong influence on DOC and BOD/COD (Zhao et al., 2013). Quantification of DOC and BOD/COD provides only basic information about the chemical compositions and properties of DOM. More crucially, the design and optimization of WWTPs should focus not only on water-quality improvement but also on the toxicity of the treated water. For instance, antiestrogenic activity in biologically treated wastewater has been shown to significant increase following chlorination, probably caused by formation of antiestrogenic disinfection by-products (DBPs) (Wu et al., 2009). Therefore, more specific and sensitive analytical approaches are required to evaluate DOM removal as a function of treatment processes.

The optical methods have been widely applied in characterizing the DOM, particularly UV–vis spectroscopy and fluorescence excitation emission matrix spectroscopy (EEMs) with parallel factor (PARAFAC) analysis. UV–vis spectroscopy has been used to trace the source, composition and reaction of chromophoric dissolved organic matter (CDOM) in natural water (Helms et al., 2008; Yan et al., 2013a; Yan et al., 2014a). The absorption spectral slopes ($S_{275–295}$) or slope ratios (S_R) have been linked to the molecular weight of CDOM (Helms et al., 2008). The log-transformed absorbance spectra have been employed to quantify DOM-metal interactions and generation of DBPs after chlorination (Yan et al., 2013a; Yan et al., 2014a). Meanwhile, combined EEMs with PARAFAC could shed light on the fingerprint of fluorescent dissolve organic matter (FDOM) and sources of DOM (Ishii and Boyer, 2012; Henderson et al., 2009; Maqbool et al., 2016; Murphy et al., 2011). A specific fluorescent component, as such a tryptophan-like component, could be used as an effective surrogate for monitoring DOM transformation in wastewater treatment (Yu et al., 2013). Similarly, UV–vis spectroscopy and fluorescence spectroscopy have been increasingly used for on-line monitoring of DOM in wastewater treatment as they do not require pretreatment and are non-destructive (Henderson et al., 2009; Carstea et al., 2016). Also, a range of studies were conducted to investigate the fate of DOM along the treatment lines in multiple WWTPs during extended periods of time using UV–vis spectroscopy and EEMs with PARAFAC (Murphy et al., 2011; Cohen et al., 2014; Lourenco et al., 2006). The prediction capability of on-line monitoring is based on the strong correlation between spectroscopic proprieties (*e.g.*, intensity of either certain fluorescent components or absorbance at certain wavelengths) and the water quality parameters (*e.g.*, BOD, COD and DOC) (Shutova et al., 2016). However, a majority of these studies mainly focused on the application of UV–vis spectroscopy or fluorescence spectroscopy in detecting the change of wastewater quality, while there are few studies performed using combined fluorescence and UV–visible absorbance. UV–vis absorbance measurement can provide as a complementary method for fluorescence measurement, because FDOM is a small fraction of CDOM. On the other hand, fluorescence measurement is more sensitive and selective relative to UV–vis absorbance (Henderson et al., 2009), so it is essential to examine simultaneously the fate and transformation of CDOM and FDOM to ensure reliability of treated wastewater (Louvet et al., 2013). Moreover, the effect of seasonal variation on DOM removal was rarely taken into consideration, although some studies were performed with a long-term examination.

In this study, we applied differential log-transformed UV–vis absorbance spectra with Gaussian fit and differential EEMs in conjunction with PARAFAC analysis to identify the temporal variability of DOM in a full-scale WWTP; CDOM and FDOM were targeted to trace DOM transformation throughout the lifecycle of the processing in summer and winter. Sampling was designed to permit the examination of the effects of both seasonal variation (summer and winter) and treatment processes (sedimentation, bio-treatment and disinfection) on the selective removal of CDOM and FDOM from wastewater.

1. Materials and methods

1.1. Sampling

All samples were collected from a WWTP located in Guangzhou City, China. Approximately 300,000 m^3 of wastewater from domestic sources is treated in the WWTP daily, with solid retention time of 20 days. An anaerobic–anoxic–aerobic (A2/O) process is employed for wastewater treatment and chlorine dioxide (ClO_2) is used as disinfectant. Primary sedimentation is performed to remove particular matter in primary clarifier, while activated sludge is separated from treated wastewater by gravitation in secondary clarifier. Details of the processing and sampling points are presented in Fig. 1. In addition, pH values were relatively stable, ranging from 6.93 to 6.78 in the whole treatment process. A 200 mL sample was collected at each sampling site using polyethylene terephthalate bottles. Wastewater samples were collected once in every two weeks from May 2013 to January 2014 and classified broadly into two parts: wastewater taken in summer (from June to Aug 2013) and wastewater sampled in winter (from November 2013 through January 2014). All samples were transported to the laboratory immediately, then filtered through 0.45 μm nitrocellulose membrane filters. The filtered samples were stored at 2–4°C under dark conditions and analyzed within 48 hr. Prior to spectral analysis, BOD, COD, ammonia nitrogen (NH_4^+-N), total nitrogen

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