



Assessing removal efficiency of dissolved organic matter in wastewater treatment using fluorescence excitation emission matrices with parallel factor analysis and second derivative synchronous fluorescence



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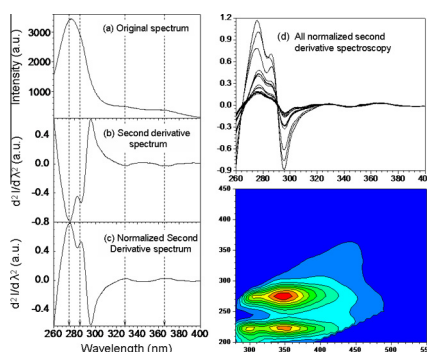
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HIGHLIGHTS

- Assess removal efficiency of DOM in WWTP by EEM with PARAFAC.
- Develop SDSF approach compared with EEM-PARAFAC to analyze DOM fractions.
- Verify availability of SDSF for DOM removal and optimize of sampling sites.

GRAPHICAL ABSTRACT



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ABSTRACT

To assess removal efficiency of dissolved organic matter (DOM) in the wastewater treatment plant (WWTP), fluorescence excitation emission matrices (EEM) with parallel factor analysis (PARAFAC) and second derivative synchronous fluorescence (SDSF) were used for the characterization of DOM in wastewater. In A²/O process, tryptophan-like and tyrosine-like materials were removed to the much greater extent than that of fulvic-like. The protein-like material might be mostly decomposed by anaerobic and aerobic bacteria in anaerobic/anoxic and oxic zones. C1, C2, I₂₇₆, I₂₈₆, AP₁ and AP₂ were much better in tracing variations of tryptophan-like and tyrosine-like materials than C3, I₃₂₉ and AF₁ in tracing fulvic-like. The number of sampling sites should be reduced, as concentration variations of DOM components were subtle among sampling sites in the oxic zone and secondary sedimentation tank. SDSF may be a useful tool as PARAFAC to monitor removal efficiency of DOM fractions from wastewater in the WWTP.

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1. Introduction

Reuse and recycling of treated wastewater effluent have played an increasingly prominent role in ensuring water quality, quantity, ecology and security during the last decades (Henderson et al., 2009; Ishii and Boyer, 2012). In wastewater treatment schemes,

ongoing successive managements, such as online monitoring, data processing, warning and emergency are essential to ensure efficiency and reliability of wastewater treatment performance. Although an online monitoring system has been applied to monitor water quality, the monitoring parameters are usually limited to total organic carbon, pH, conductivity, turbidity, color, dissolved oxygen, ammonia, nitrate and so on (Henderson et al., 2009).

Dissolved organic matter (DOM) is a heterogeneous mixture of aromatic, amino and aliphatic organic compound containing oxy-

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gen, nitrogen and sulfur functional groups (Chen et al., 2003). It is ubiquitous in natural and engineered aquatic systems, and has a multifunctional role in the aquatic environment (Murphy et al., 2011). DOM presents upcoming challenges in engineered systems due to its impact on all water treatment processes. Concentration and composition of DOM can dominate coagulation efficiency, membrane fouling, disinfection byproduct formation, oxidant demand, and microbial growth (Ishii and Boyer, 2012). Moreover the analysis and characterization of DOM in wastewater or treated wastewater have become important, for DOM can influence on the further treatment of wastewater and also on the fate and toxicity of organic or/and inorganic pollutants in receiving water.

Fluorescence spectroscopy has commonly been used to discriminate between DOM fractions (Hudson et al., 2008; Osburn et al., 2012). It has widely been applied in the water industry as a potential monitoring technique. Fluorescence monitoring is attractive as it is a rapid, inexpensive and reagentless technique that requires no sample preparation prior to analysis (Henderson et al., 2009). It can be utilized as an online monitoring tool for water quality assessment in natural water bodies and process control in water treatment, e.g., specific pollutants in industrial wastewater, oil in water and disinfection byproduct formation potentials in drinking water treatment (Liu et al., 2007; Borisover et al., 2009; Seredyńska-Sobecka et al., 2011). The most significant advance for fluorescence technique in recent years has been the ability to simultaneously scan excitation and emission wavelengths through a set light path length of aqueous sample to generate a fluorescence excitation-emission-matrix (EEM) (Baker et al., 2003). Chemometric techniques, including parallel factor analysis (PARAFAC), self-organizing map, principal filter analysis, partial least squares regression, etc., have been applied to interpret EEM.

PARAFAC can mathematically discriminate chemical independent but spectral overlapping fluorescence components and the maximum intensities (F_{max}) of these components are used to trace variability in DOM fluorescence in wastewater treatment plant (WWTP) (Henderson et al., 2009). Thus the online monitoring instruments may test the ability of the PARAFAC for monitoring WWTP performance through predictive algorithms in real-time. A new algorithm called EEMizer has been developed, which aims to automate the use of PARAFAC (Bro and Vidal, 2011). Synchronous fluorescence spectroscopy can provide a narrow, sharp and simple spectrum, compared with broad fluorescence emission/excitation spectra obtained in conventional fluorescence measurement

(Abdelal et al., 2009; Yu et al., 2012). However synchronous fluorescence spectroscopy has an extremely restricted scope of application in the analysis of DOM, because its selectivity is reduced by extensive spectral overlap (Mozo-Villaías, 2002). Derivatives can amplify narrow band and avoid broad band, for the amplitude of the derivative signal is inversely proportional to the band width of the original spectrum (Mozo-Villaías, 2002; Abdelal et al., 2009). The combination of synchronous fluorescence spectroscopy and derivatives is of great value to increasing sensitivity, which presents a further strategy for reduction of extensive spectroscopic overlap and rejection of matrix interference (Abdelal et al., 2009). Derivative synchronous fluorometric spectroscopy technique has been most widely utilized in the analysis of mixture of polycyclic aromatic hydrocarbons, rodenticides, inorganic ions and humic substances (Mozo-Villaías, 2002; Kumar et al., 2005; Abdelal et al., 2009; Yu et al., 2012). However, few studies have been carried out to assess removal efficiency of DOM fractions from wastewater in WWTP using this technique.

In this study, second derivative synchronous fluorescence (SDSF) approach compared with mature EEM-PARAFAC, is firstly developed to characterize DOM fluorescence properties of wastewater in WWTP. Multivariate statistics was used to verify the availability of SDSF for the assessment of DOM removal in wastewater treatment process and optimization of the sampling sites.

2. Methods

2.1. Sample collection

Gaobeidian WWTP is located in the southeastern Beijing City of China. It treats $1,000,000 \text{ m}^3 \text{ d}^{-1}$ wastewater from both domestic and industrial sources. A^2/O , a conventional active sludge process, is used in the WWTP for integrated removal of carbon, nitrogen and phosphorus, which incorporates anaerobic/anoxic and oxic zones in sequence (Wang et al., 2011, 2012). There are four rectangular aerated regions with six aeration tanks in each rectangular aerated region and three corridors in a given aeration tank. Each corridor has a length of 96 m, a width of 9.3 m and a depth of 6 m, and fifty percents of the first corridor is used as the anaerobic/anoxic zone (Fig. 1).

Water samples were collected at 22 sampling sites in Gaobeidian WWTP in 31 December 2011. Sites 1–3 are located in the primary sedimentation tank, sites 4–8 in the anaerobic/anoxic zone, sites 9–19 in the oxic zone and sites 20–22 in the secondary sedimentation tank.

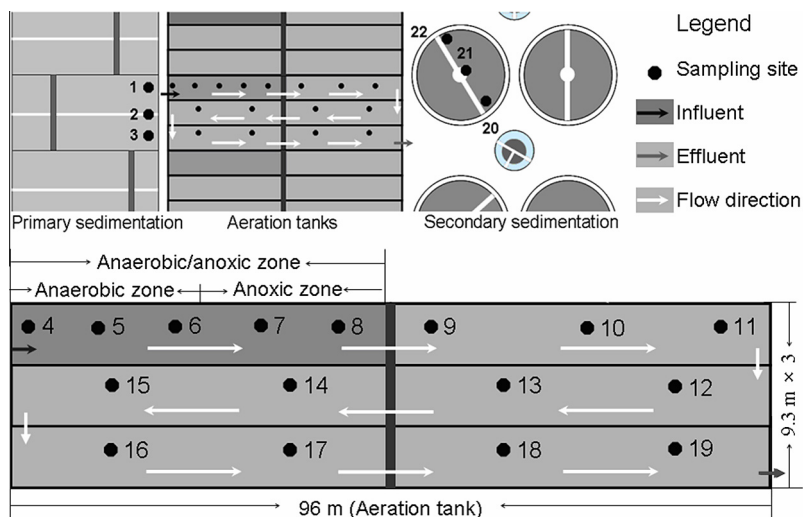


Fig. 1. Simplified wastewater treatment process diagram of an aerated region in Gaobeidian WWTP. Sites 1–3 in the primary sedimentation tank, sites 4–8 in the anaerobic/anoxic zone, sites 9–19 in the oxic zone and sites 20–22 in the secondary sedimentation tank.

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