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Characterization of dissolved organic matter in the anoxic–oxic-settling-anaerobic sludge reduction process

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HIGHLIGHTS

- Fate of dissolved organic matters was studied in an oxic-settling-anaerobic process.
- The process showed good pollutants removal performance, and reduced sludge by 32%.
- Three fluorescent components were identified by parallel factor analysis.
- Molecular weight transformation proved sludge decay in anaerobic sludge holding tank.

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ABSTRACT

Three-dimensional excitation-emission matrix (EEM) fluorescence spectroscopy and gel permeation chromatography (GPC) analysis were employed to investigate the distribution and transformation of dissolved organic matter (DOM) in the anoxic–oxic-settling-anaerobic (A + OSA) process for sludge reduction. The A + OSA process showed a good performance in nitrogen and organic pollutants removal efficiency, and reduced sludge yield by 32% under a sludge retention time of 6 h in the anaerobic sludge holding tank (SHT). Parallel factor analysis was used to assess DOM composition from EEM spectra and three fluorescent components were identified: two humic-like components and one protein-like component. In the A + OSA process, the humic-like components were difficult to degraded, while the protein-like component was easily hydrolyzed and adsorbed under anoxic conditions. The fluorescence intensities of the humic-like and protein-like components were both strengthened in the SHT owing to sludge decay under the anaerobic condition. GPC analysis of the A + OSA system showed that the majority of molecules in the influent wastewater with molecular weight (MW) in the range of >250 and 30–50 kDa were mainly transformed into small molecules with MW in the range of 30–250 and <0.5 kDa in the effluent by microorganisms. The DOM in the SHT effluent demonstrated a broader MW distribution and higher intensity than that in the SHT influent, and the percentage of MW between 10 and 30 kDa in the SHT effluent were significantly increased owing to cell lysis and decay in the SHT.

1. Introduction

The activated sludge process is widely used for wastewater treatment; however, a huge amount of wastage activated sludge (WAS) generated during pollutants removal is difficult and expensive to handle and dispose of. According to statistics, the USA annually produces 8.2 million tons of dry sludge, and China is estimated to generate about 6.0 million tons in 2015 [1,2]. Sludge reduction in the wastewater treatment process has aroused much attention worldwide [3–8].

The oxic-settling-anaerobic (OSA) sludge reduction process by inserting an anaerobic sludge holding tank (SHT) in the sludge return line is considered as a promising way that can be employed in full-scale applications [1,5], and thus has been investigated by various researchers [6,7,9–12]. It was found that the OSA process could reduce WAS production by 14–58% [10,9], and improve pollutants removal efficiency and sludge settleability compared to the conventional activated sludge process [7,9]. A low oxidation–reduction potential (ORP) level [7,12], proper sludge retention time (SRT) of the SHT [9,11], and the presence of xenobiotic chemicals [6] are in favor of sludge reduction of the OSA process. The possible mechanisms of the OSA process consist of energy uncoupling,

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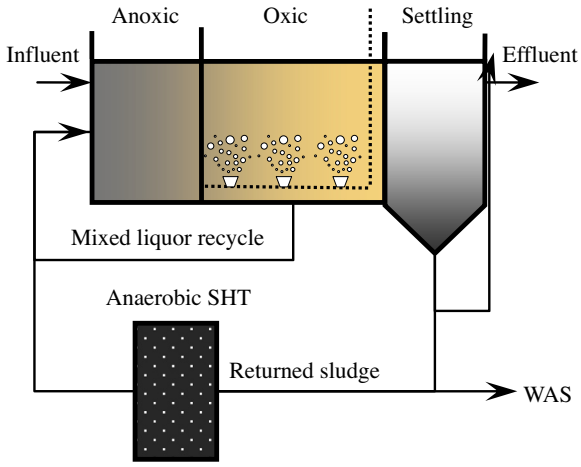

Fig. 1. Flow diagram of the A + OSA sludge reduction process.

domination of slow growers, sludge decay in the SHT and soluble microbial products (SMP) effect [7,9,11,12], but more supporting materials are required to substantiate the mechanism of sludge reduction. The distribution and transformation of dissolved organic matter (DOM), of which the majority is SMP originated from cell lysis and hydrolysis of particulate organic pollutants, will deepen the understanding of sludge reduction and SMP generation mechanisms in the OSA process.

DOM is a heterogeneous mixture composed of carbohydrates, proteins, lignins, organic acids, and biologically refractory components such as fulvic and humic substances [13]. In biological wastewater treatment, DOM affects both the kinetic activity and flocculating properties of activated sludge [14,15]. The DOM contains large quantities of aromatic and aliphatic organic compound [16], and its intrinsic spectrometric characteristics can provide information concerning the structure, functional groups, and heterogeneity of the components during sludge reduction [17]. However, to date, information on DOM in the OSA process could hardly be found in the literature, and researches regarding that should be very useful for understanding the sludge reduction mechanisms.

In this study, a modified OSA system (A + OSA) with an anoxic tank prior to oxic tank (Fig. 1) for nitrogen removal of municipal wastewater treatment was established and operated in order to verify the DOM distribution and transformation in the process. An anoxic/oxic (AO) system was also operated simultaneously under the same conditions for the estimation of sludge reduction. Detailed DOM characterization was carried out by three-dimensional excitation-emission matrix (EEM) fluorescence spectroscopy and gel permeation chromatography (GPC) technology. The parallel factor analysis (PARAFAC) was also adopted to decompose EEM into individual fluorescent components. The results obtained in this study are expected to provide an insight for DOM distribution and transformation of the OSA process.

2. Materials and methods

2.1. Experimental setup

Two pilot-scale systems, an A + OSA and a conventional AO, were both fed with wastewater of the Dongqu WWTP (Shanghai, China) with a constant flow rate of 50 L/d. The two systems were both operated for 3 months stably. In the A + OSA system, the effective volume of anoxic, oxic and SHT tank was 4.2, 12.5 and 12.5 L, respectively; the secondary settling tank was 17.7 L in volume and 0.45 m in depth. The effective volumes of treatment units in the AO system were the same as those in the A + OSA system. The dissolved oxygen (DO) in the oxic stage of the two systems was controlled at 3–4 mg/L. The ORP in the SHT tank was maintained at about −150 to −100 mV. Ratios of returned sludge and mixed liquor recycle were both set to 100% for the two systems. The SRT of the AO and A + OSA process was controlled at 20 and 60 d by WAS discharge, respectively.

2.2. Collection and pretreatment of samples

The mixed liquor samples were taken out from each reaction tank of the A + OSA system, and centrifuged for 5 min at 12,000 rpm. The extracted supernatant (represented DOM) was filtrated through an acetate cellulose membrane with mean pore size of 0.45 μm, and prepared for further analysis.

2.3. Analytical methods

2.3.1. Three-dimensional EEM fluorescence

The three-dimensional EEM fluorescence spectra were measured using a HORIBA MAX fluorospectrophotometer (HORIBA Scientific, France). The EEM spectra were collected with the scanning emission spectra from 220 to 550 nm at 5 nm increments by varying the excitation wavelengths from 220 to 550 nm at 5 nm sampling intervals. The excitation and emission slits were maintained at 10 nm and the scanning speed was set at 1200 nm/min for this study.

2.3.2. Parallel factor analysis (PARAFAC) analysis

PARAFAC is a valuable tool for characterizing and quantifying changes in DOM fluorescence enabling the tracing of different fractions in the natural environment [18,19]. The standard PARAFAC algorithm was based on interactive least squares algorithm, and minimized the sum of squared residuals. Determination of the optimum number of components was done by splitting half analysis and random initialization [20], as a part of the program. The PARAFAC analysis was done in MATLAB R2007a using the DOMFluor, which contains Nway toolbox ver 3.1.

The PARAFAC model returns relative intensities of derived components (scores). The intensity of component i in a given sample, I_i, was calculated as the fluorescence intensity at the peak excitation and emission maximum of component i using Eq. (1):

$$I_i = S_i \times Ex_i(\lambda_{max}) \times Em_i(\lambda_{max}) \quad (1)$$

where S_i is the relative intensity of component i; Ex_i (λ_{max}) and Em_i (λ_{max}) is the maximum of the excitation and emission loading of component i, respectively. The total fluorescence intensity of a given sample was calculated as the sum of the components present in the sample:

$$I_{TOT} = \sum_{i=1}^{n} I_i \quad (2)$$

2.3.3. Gel permeation chromatography

The molecular weight (MW) distribution of the DOM sample was measured by GPC analyzer (1206, Agilent, USA). Polyethylene glycols were used as standards for calibration. The elution at different time intervals was collected by an automatic fraction collector and automatically analyzed by using a UV spectroscope and a dissolved organic carbon analyzer to obtain a MW distribution.

2.3.4. Other item analysis

Chemical oxygen demand (COD), suspended solids (SS), ammonium nitrogen (NH_4-N), and total nitrogen (TN) in the influent and effluent were analyzed every two days according to Chinese standard methods [21]. Mixed liquor suspended solids (MLSS) and