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A detailed dissolved organic matter characterization of starch processing wastewater treated by a sedimentation and biological hybrid system

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ABSTRACT

In this study, to investigate the evolution of dissolved organic matter (DOM) in starch processing wastewater (SPW) during the treatment of a sedimentation and biological hybrid system, the DOM was sampled at different treatment stage, and characterized by gel permeation chromatography (GPC), fluorescence excitation-emission matrix (EEM) and UV–Vis. The chromatograms demonstrated that the majority of molecules in the influent had a molecular weight (MW) of less than 0.5 kDa, while that of the oxic basin was mainly in the range of 0.5–2 kDa. The MW distribution became narrow along the treatment line. The proteinaceous matters with simple structure were more easily biodegraded during the treatment process. Most protein-like material could be effectively decomposed by the activities of anaerobic and aerobic bacteria. The microbial byproduct-like substances and humic acid-like materials were the main components of DOM in the effluent. The parameters obtained from the analysis were clustered into two groups, which represent the different treatment state of SPW.

1. Introduction

The starch processing industry requires intensive water consumption, and thus produces approximately 6–10 m^3 of wastewater for per ton starch [1]. The wastewater streams discharged from the starch processing industry are generally characterized by high-strength organic (COD 6000–12,000 mg/L), containing a large number of dissolved organic matter (DOM) [2]. The traditional treatment of starch wastewater typically focuses on anaerobic-aerobic process in practical full-scale application [3]. The bio-treated process could be also prone to producing DOM, such as soluble microbial products, which are released from the substrate metabolism and/or biomass decay [4].

DOM is a highly heterogeneous mixture, consisting of various molecular weight compounds [5]. It has been reported that the concentration and composition of DOM can dominate the wastewater treatment performance [6,7]. Moreover, the presence of DOM typically has an adverse effect on advanced treatment and wastewater reclamation systems, such as disinfection byproduct formation and membrane fouling [8]. How to effectively remove the DOM becomes the essential yet challenging task to meet the stringent governmental legislation, while also to improve the quality of the effluent for its possible reuse. However, the traditional monitoring parameters (e.g. COD, TN) are indirect indexes, and do not provide information regarding the composition and characterization of the DOM in the treating process [9]. Various techniques have been used to assess the characterization of DOM, including ^{13}C and ^{1}H nuclear magnetic resonance (NMR) spectroscopy, gel permeation chromatography (GPC), fluorescence excitation-emission matrix (EEM), ultraviolet–visible spectroscopy (UV–Vis), Fourier transform infrared (FTIR) spectroscopy, etc. [10,11]. At present, little information is available on the composition and transformation of DOM in SPW along the treatment system. In-depth information on DOM of SWP should be very useful in improving our understanding of the organic removal efficiency in wastewater treatment system, and for establishing a strategy for technology improvement and recycling system.

The objectives of this study are to obtain the characteristics of DOM for SPW, and to contribute to a better understanding the transformation and decomposition mechanism of organic matters during treatment. In this study, taking a typical corn starch processing factory as an example, the DOM fraction in SPW treated by the combination of sedimentation and bio-treated process was analyzed by means of GPC, EEM and UV–Vis.

2. Materials and methods

2.1. Treatment process

A corn starch processing corporation, located in Jilin Province, China, with a total production capacity of 600,000 t/a, was selected as the modeled system. The wastewater treatment system of the corporation

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consisted of a sedimentation tank, a hydrolysis acidification basin, an anaerobic basin and an oxic basin in series, of which the treatment capacity was 3500 m^3/d. The schematic diagram of wastewater treatment system was represented in Fig. 1. The respective hydraulic retention times of each unit were 3.75 h, 5 h, 5 h and 20 h. The mixed liquor suspended solids in the oxic stage was controlled at 3500–3700 mg/L.

2.2. Sample collection and preservation

Based on the relative study, concentration variations of DOM components were subtle among sampling sites in the oxic basin and secondary clarifier [12]. Therefore, the mixed liquor samples were taken from sedimentation tank, hydrolysis acidification tank, anaerobic basin and oxic basin under the full load operation. All of the water samples were centrifuged for 5 min at 10,000 rpm. Then the supernatant was withdrawn and filtered by a filter paper with a mean pore size of 0.45 μm for analysis.

2.3. Analytical methods

Prior to analysis, the dissolved organic carbon (DOC) of the samples were measured using a TOC-VCPH (Shimadzu, Japan) [13]. The molecular weight (MW) distributions of DOM in each of the samples were determined with a GPC analyzer (1206, Agilent, USA). The standard solutions of polyethylene glycols with MW of 400 Da, 1.05 kDa, 2.2 kDa, 5.25 kDa, 10.73 kDa and 30 kDa were used to calibrate the equipment. Then the elution was collected using an automatic fraction collector at different time intervals, and analyzed using the online detectors (organic carbon detector united with a UV spectroscope), to obtain the MW distribution.

EEM fluoresce measurements were carried out using a Hitachi F-7000 spectrofluorometer. The EEM spectra were recorded by scanning emission and excitation wavelengths from 200 to 500 nm. The excitation and emission bandwidths were set at 5 nm. The fluorometer was set at a speed of 1200 nm/min, and a PMT voltage of 700 V. All of the fluorescence spectra were regulated for first- and second-order Rayleigh and Raman scatter using interpolation [14]. Then the fluorescence regional integration (FRI) technique was adopted for analysis [15]. The percent fluorescence responses ($P_{i,n}$) were calculated by normalizing the cumulative excitation-emission area volumes to the relative regional areas.

UV–Vis spectroscopy was analyzed using a UV-1700 PC spectrophotometer (Shimadzu, Japan) in the wavelength range of 190–400 nm, with a 1 cm quartz cell.

Hierarchical cluster analysis (HCA) and principal component analysis (PCA) were conducted using SPSS version 16.0. The HCA was obtained based on all data for each of the treatment units with Ward's method, which uses the squared Euclidean distance as a similarity measure.

3. Results and discussion

3.1. MW distribution characteristics

DOM in the SPW is a mixture of various organic materials, including aromatic, amino and aliphatic organic compounds, etc. An in-depth understanding of the MW distribution of DOM is very critical for the estimation of the treatment process efficiency and design of the recycled wastewater treatment system. Fig. 2 shows the GPC chromatograms of DOM in the samples of the sedimentation tank, hydrolysis acidification basin, anaerobic basin and oxic basin. It has been reported that DOM species with shorter retention time are of higher apparent MW [4]. The GPC profiles in the sedimentation tank and hydrolysis acidification basin present similarities. The two main peaks were detectable with elution time of around 22.9 min and 25.1 min, and the peaks of the sedimentation tank showed a slightly broader distribution than those in the hydrolysis acidification basin, but had similar peak intensity. The GPC images of DOM in the anaerobic and oxic basin only had a low peak at the elution time of 21.2 min. It could be inferred that most of the organic materials were degraded by anaerobic and aerobic microorganisms. In comparison with the MW distribution of DOM in the sedimentation tank and hydrolysis acidification basin, the GPC images of DOM in the anaerobic and oxic basin demonstrated that the peaks appeared at the earlier elution time, and the DOM of the oxic basin had a relatively higher intensity than that of the anaerobic basin.

On the basis of the MW distribution obtained, the number-average molecular weight (M_n), weight-average molecular weight (M_w) and ratio of MW distribution in terms of M_w/M_n were calculated (Table 1). The lower value of M_w/M_n indicated the narrower range of MW distribution for organic matter. It can be seen that the M_w/M_n values of the units varied within the range of 1.62–1.10. Meanwhile, the MW distribution of DOM tended to be narrow following the wastewater treated in sequence from the sedimentation tank to the oxic basin. The MW distribution became overly concentrated. The results are in close agreement with the findings reported by Wang et al., which demonstrated that the types of DOM began to decline during the biological treatment [16]. This was due to the fact that low MW organic matter was preferentially removed during the treatment, while relative high-MW organic molecules were biologically recalcitrant.

The transformation of MW distribution during the treatment was illustrated in Fig. 2. The MW which were less than 0.2 kDa were absent in the DOM of the anaerobic and oxic basins, while they were present in the sedimentation tank and hydrolysis acidification basin. At the same

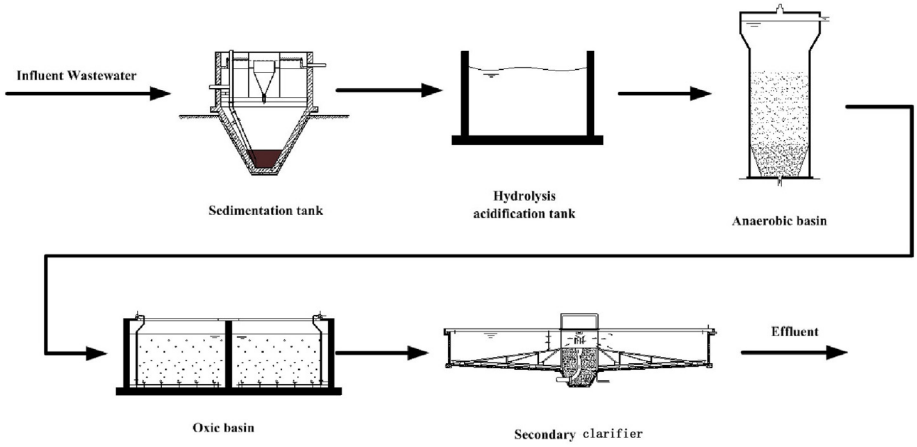

Fig. 1. Schematic diagram of the wastewater treatment system.