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Organics and nitrogen removal from textile auxiliaries wastewater with A^2O-MBR in a pilot-scale

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HIGHLIGHTS

- A pilot-scale A^2O-MBR system treating textile auxiliaries wastewater was assessed.
- Organic matter and recycle ratio strongly affected the performance of the system.
- GC/MS analysis found some refractory organics in the MBR permeate.
- Combination of organic foulants and inorganic compounds caused membrane fouling.

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ABSTRACT

The removal of organic compounds and nitrogen in an anaerobic–anoxic–aerobic membrane bioreactor process (A^2O-MBR) for treatment of textile auxiliaries (TA) wastewater was investigated. The results show that the average effluent concentrations of chemical oxygen demand (COD), ammonium nitrogen (NH_4^+–N) and total nitrogen (TN) were about 119, 3 and 48 mg/L under an internal recycle ratio of 1.5. The average removal efficiency of COD, NH_4^+–N and TN were 87%, 96% and 55%, respectively. Gas chromatograph–mass spectrometer analysis indicated that, although as much as 121 different types of organic compounds were present in the TA wastewater, only 20 kinds of refractory organic compounds were found in the MBR effluent, which could be used as indicators of effluents from this kind of industrial wastewater. Scanning electron microscopy analysis revealed that bacterial foulants were significant contributors to membrane fouling. An examination of foulants components by wavelength dispersive X-ray fluorescence showed that the combination of organic foulants and inorganic compounds enhanced the formation of gel layer and thus caused membrane fouling. The results will provide valuable information for optimizing the design and operation of wastewater treatment system in the textile industry.

1. Introduction

As one of the largest industries in the world, the textile industry consumes large quantities of textile auxiliaries (TA), which include more than 100 kinds of specialty chemicals, such as softening agent, phosphates, polyamide resins, acrylic chelating agents, polyurethane coating agents and stiffening agents. In the TA production, considerable amounts of TA wastewater are generated. The TA wastewater is very chemical-intensive and known to contain high concentrations of organic matter, non-biodegradable matter, toxic substances and ammonia [1–3]. These compounds produce long-term environmental impacts, it is therefore important to remove these organics and ammonia from the TA wastewater for reducing their harm to the environment.

TA wastewater could be treated by physicochemical and biological methods or suitable combinations of them. Physicochemical methods involve adsorption, ion exchange, coagulation–flocculation, as well as advanced oxidation processes (such as Fenton oxidation, ozonation, photocatalytic oxidation and electrochemical oxidation) [4–6]. However, methods such as coagulation, ion exchange, and adsorption only transfer the organic pollutants from one phase to another. Advanced oxidation processes, such as Fenton oxidation, ozonation, photocatalytic oxidation and electrochemical oxidation, are very efficient and the fastest way for destruction of organic compounds, but they are expensive and could not be adopted commercially. Compared with physicochemical methods, biological treatment is often the most economical alternative for pollutant removal [7].

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Due to the low biodegradability and high toxicity of many textile chemicals, a conventional activated sludge system is inadequate in removing high concentrations of refractory organics and ammonia. In recent years, the membrane bioreactor (MBR), because of complete biomass retention, has been successfully integrated with an anaerobic–anoxic–aerobic (A^2/O) system for industrial wastewater treatment [8]. The combined system was efficient and cost-effective in removing refractory pollutants and ammonia, especially at high and varying loading rates [9]. The use of anaerobic process as a pretreatment process to partially convert refractory organics to intermediates that are more readily degradable, could be attractive for refractory wastewater treatment. The anoxic–aerobic process is a good option for achieving biological nitrogen removal via pre-denitrification and aerobic nitrification. MBR can keep a long sludge retention time (SRT), which allows the system to keep a sufficient amount of slow-growing bacteria, such as ammonia oxidizing bacteria and those specializing in degrading refractory compounds [10]. Therefore, the A^2O-MBR system is very attractive for chemical-intensive industrial wastewater treatment.

The efficiencies of organic compounds and nitrogen removal in the A^2O-MBR system are influenced by many factors, such as chemical characteristics of wastewater, internal recycle ratio, hydraulic retention time (HRT) and substrate loading rate. [11–13]. The chemical characteristics of TA wastewater determined the biodegrading capacity of the system. Internal recycle ratio was found to have an important role in nitrogen removal performance of the system. In addition, membrane fouling was inevitable in MBR systems. In the previous studies reported in the literature, there was little information on the nitrogen removal and behaviors of organic compounds in a A^2O-MBR system for TA wastewater treatment particularly at pilot-scale operation.

The objectives of the present research were: (1) to investigate the pollutant removal performance in a A^2O-MBR system, (2) to characterize in detail organic chemical composition in the raw wastewater and the effluents, (3) to compare the performance of two kinds of membrane modules and examine the membrane fouling behaviors.

2. Materials and methods

2.1. Experimental set-up and operating conditions

The pilot-scale experiments were carried out in a sequential system (in Fig. 1) of an anaerobic reactor (A1), an anoxic reactor (A2), followed by an aerobic membrane bioreactor (O-MBR). The working volumes of the three reactors were 3.8 m^3, 7.5 m^3 and 5.6 m^3, respectively. Reactor A1 was packed with bamboo carbon, which was generated at 600 °C under a slow pyrolysis process with a diameter of 3–5 mm. In the reactor A2, a mechanical stirrer was installed to agitate its content. The O-MBR could divide into buffer zone and reaction zone. An internal pump was installed in the buffer zone and mixed liquor from the bottom was continuously pumped to the reaction zone. Two different kinds of membrane modules were immersed and symmetrically placed in the reaction zone. One was a hollow fiber (HF) membrane module made of polyvinylidene fluoride (PVDF) with a nominal pore size of 0.1 μm and a total membrane surface area of 12.5 m^2 (SMM-1013, Memstar Technology Co. Ltd., Singapore). The other one was a flat-sheet (FS) membrane module with a nominal pore size of 0.1 μm and a total membrane surface area of 10.4 m^2 (DF80, Jiangsu Dafu Membrane Technology Co. Ltd., China). Air diffusers were installed underneath the membrane module to provide dissolved oxygen (DO) as well as to control membrane fouling and clogging. DO was maintained at 3–5 mg/L in the MBR during the experiments. Membrane filtration through a suction pump was carried out in an intermittent suction mode with 9 min of suction followed by a 2 min release. In situ membrane chemical cleaning was performed to reduce membrane fouling by 0.5% NaClO for 1 h when the trans-membrane pressure (TMP) increased to 20 kPa.

The sequential system was operated in a pre-denitrification mode, which consisted of three different steps. Firstly, TA wastewater was continuously pumped into reactor A1 for hydrolysis/acidification. Secondly, the water passed to reactor A2, where denitrification took place and a fraction of organic matter was degraded by heterotrophic bacteria. Thirdly, the water passed to the O-MBR where nitrification and degradation of remaining organic matter occurred, and the permeate water was separated by membrane modules while nitrate was recycled to A2 by partial recirculation. The inoculating sludge was drawn from the anaerobic sludge in a conventional TA wastewater treatment plant (Hangzhou, China). During the study, different internal mixed liquor recycle ratios from O-MBR to A2 were employed to assess chemical oxygen demand (COD) and nitrogen compounds removal of the system. Recycle ratios ranged from 0.5 to 2.5 of the influent flow rate. At the start-up period (Phase I), the influent flow rate was kept at 250 L/h, and the recycle ratio was controlled at about 0.5. The system was operated stably for 20 days. Afterwards, the recycle ratio was changed to about 1.5 and the system was then operated in this condition for 74 days (day 21–94, Phase II). From day 95 onward, the recycle ratio was maintained at 2.5 (Phase III) and methanol at a equivalent concentration of about 240 mg/L COD was supplemented as an organic source in the A1 effluent. Because the recycle ratio was high at all times, mixed liquor suspended solids (MLSS) concentrations in the reactors were similar. During the whole period of the study, no sludge was removed from the plant except for some incidents with accidental sludge loss. MLSS concentration in the O-MBR and the A2 fluctuated at 3500–5000 mg/L. The experiment was conducted under an ambient temperature of 20–25 °C. Furthermore, parameters such as temperature, level of the tanks, TMP, flow rates of partial recirculation and the permeate inside the O-MBR were measured automatically and registered continuously in a database with the aid of Realinfo software (Realinfo., China).

2.2. Characteristics of TA wastewater

TA wastewater was collected from Transfar Chemicals Co. Ltd., one of the largest TA manufacturing factories located in the southeast of China. It was firstly pumped into an intermediate tank before being continuously pumped into the bioreactor. A summary of the influent characteristics at different experimental phases are shown in Table 1. The raw wastewater had a highly variable composition. It can be seen that the average COD concentrations in the three phases were 657, 944 and 828 mg/L, while total nitrogen (TN) concentrations were 115, 106 and 121 mg/L, respectively.

Table 1
Characteristics of TA wastewater observed during the experiments.

Phase	pH	COD (mg/L)	NH_4^+–N (mg/L)	TN (mg/L)	COD/TN	Number of data points
I	7.29–9.37	657 ± 127	87 ± 5	115 ± 7	6.9 ± 1.8	10
II	7.42–8.71	944 ± 163	90 ± 19	106 ± 19	8.0 ± 2.0	35
III	7.50–8.74	828 ± 216	94 ± 21	121 ± 31	6.0 ± 1.3	23