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Pilot-scale integrated process for the treatment of dry-spun acrylic fiber manufacturing wastewater

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ABSTRACT

An integrated process of membrane bioreactor (MBR)—advanced ozonation (AO)—biological aerated filters (BAFs) was developed for the treatment of dry-spun acrylic fiber manufacturing wastewater in pilot scale. The results show that the removal efficiencies of chemical oxygen demand (COD) and ammonia nitrogen (NH_4^+-N) could exceed 90.0 and 95.0%, respectively. The COD concentration in the total effluent was maintained at 80.0–100 mg/L, and the NH_4^+-N concentration was below 10.0 mg/L. Both the MBR and BAFs could adapt to the influent of practical wastewater after a period of sludge acclimatization. The removal efficiencies of COD and NH_4^+-N in the MBR were maintained at 65.8–71.9 and 59.4–67.5%, respectively. Excitation–emission matrix spectroscopy confirmed that most of the easy degradable organics were removed in the MBR process. After the AO treatment, COD concentration in the wastewater was reduced by 106–157 mg/L and the biodegradability was enhanced. Simultaneous nitrification–denitrification was performed in the biofilm of BAFs, and the removal efficiency of total nitrogen was in the range of 58.2–71.6% after the entire integrated process.

Keywords: Dry-spun acrylic fiber manufacturing wastewater; Pilot scale; Integrated process; Pollutants removal; Excitation–emission matrix spectroscopy

1. Introduction

Over the past few decades, the acrylic fiber industry has rapidly progressed in many developing countries. China acquired the technology of dry-spun acrylic fiber (DAF) manufacturing from the American Dubos in the 1990s. The products of this technology are known for their high levels of quality and versatility. However, the effluents of DAF manufacturing contain organic and inorganic contaminants [1]. Some of these pollutants are toxic and biorefractory, which may have

serious environmental effects if discharged directly into receiving waters without appropriate treatment.

To improve its biodegradability, the DAF manufacturing wastewater was primarily mixed with domestic wastewater and then subjected to anaerobic, aerobic, and activated carbon (AC) biological treatments. However, highly toxic compounds are recalcitrant towards biodegradation, and high concentrations of inorganic salts (e.g. sulfates and sulfites) decrease the efficiency of anaerobic digestion [2]. High quantities of polymers and colloids in effluents are also difficult to biodegrade or precipitate naturally. Effluents of biological treatments still contain high concentrations of chemical oxygen demand (COD), ammonia nitrogen (NH_4^+-N), total nitrogen (TN), and toxic compounds. The biochemical process cannot efficiently remove organic pollutants to meet increasingly strict environmental standards. Thus, hybrid systems are often studied, particularly the combination of powerful ozone degradation, AC catalysis and membrane filtration [3], or AC with membrane bioreactor (MBR) [4] to remove biorefractory organics [5,6].

In this study, an integrated process is proposed for the treatment of DAF manufacturing wastewater generated from a petrochemical plant in China. It combines physical, chemical, and biological treatments, which include MBR, advanced ozonation (AO), and biological aerated filters (BAFs). The objective of this integrated process is firstly to remove biodegradable compounds with MBR, and then the ozonation successively decomposes the lower amount of pollutants that are mainly biorefractory. Finally, another biological treatment removes carbon compounds previously transformed into biodegradable compounds. In addition, an improvement of the denitrification is also expected. COD, NH_4^+-N, and TN removal efficiencies were analyzed to evaluate the pollutant treatment throughout the process. Excitation–emission matrix (EEM) spectroscopy was used to characterize the evolution of organics in the wastewater. To our knowledge, this is the first time that the treatment of real DAF manufacturing wastewater in pilot scale is studied.

2. Materials and methods

2.1. Pilot plant system

A schematic diagram of the pilot system for DAF manufacturing wastewater is presented in Fig. 1. All the pilot reactors were made of stainless steel, and the whole system consisted of three successive units which were MBR, AO, and BAFs, respectively. The DAF manufacturing wastewater was pumped through these three units in sequence and the influent flux

of the wastewater during overall operation was 4.8–6.7 m^3/d.

The effective volume of MBR was 3.0 m^3, and the available depth was 2.25 m and the hydraulic retention time (HRT) was 32.0 h. The MBR had a compact structure made up of six chambers. Firstly, the wastewater was pumped into the anaerobic chamber, and then flowed through five aerobic chambers in sequence. Hollow-fiber microfiltration membrane modules made of polyvinylidene fluoride were installed at the last aerobic chamber. The membrane had a total surface area of 12.0 m^2 and a nominal pore size of 0.22 μm (Tianjin Motian Membrane Engineering & Technology Co. Ltd, China). Effluent from the MBR was pumped into the AO unit. The sludge separated by the membrane flowed back into the anaerobic chamber at the reflux ratio of 50.0%.

The MBR was operated under the constant flux ranging from 16.7 to 23.3 L/h·m^2 throughout the study. Trans-membrane pressure (TMP) was monitored along operation with values under 15.0 kPa. Nevertheless, in order to prevent and control membrane fouling, once a week, manual cleaning of the membrane was carried out by rinsing fibers with tap water. No further chemical cleaning was needed. The TMP could be restored to below 5.0 kPa after membrane cleaning, the TMP then increased gradually to 12.6–14.2 kPa until the start of the next cleaning cycle.

The AO reactors were composed of an oxidation tower and a retention tank; their effective volumes were 0.9 and 1.0 m^3, respectively. Ozone was generated from pure dry oxygen using an ozonator (model 3S-OW-40, Tonglin Technology Co. Ltd, China) at concentrations of 50.0–80.0 mg/L. The ozone was fed into the reactor at a flow rate of 480 L/h through a micro-porous plate gas sparger located at the base of the oxidization tower. An ozone trap containing 4.0% potassium iodide solution was connected to the top of the reactors to collect all remaining ozone gas. Six ultrasonic vibrators (60 W each) were fixed in the oxidation tower to make the ozone sufficiently dispersed and dissolved in wastewater, thereby enhancing utilization efficiency of the ozone. Nine ultraviolet (UV) light lamps (120 W each) were set in the retention tank to catalyze the ozonation. The available depth of the retention tank was 2.6 m and the HRT was 6.8–9.5 h.

The BAFs were composed of two tanks in series. Effluent from the AO process was pumped into the bottom of the first tank (tank A) of the BAFs. Tank A was partially aerated and the volume ratio of anoxic/aerated zones was 1:2. The second tank (tank B) was completely aerated and the water flow was also upward. The dimension of each tank was 1.3 × 0.8 × 3.5 m, and

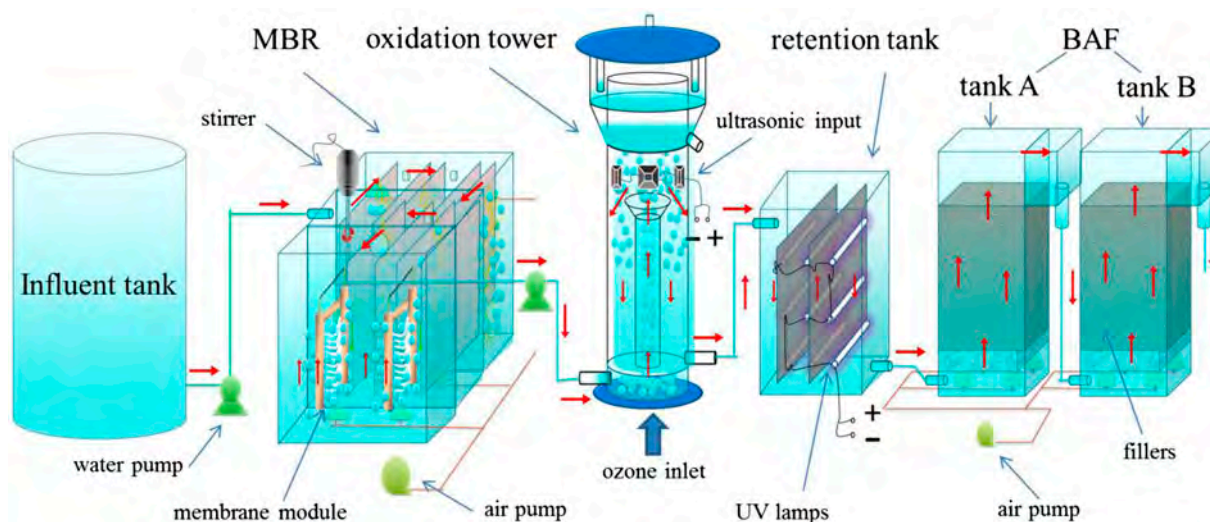Fig. 1. Schematic diagram of the pilot system.

Table 1
Wastewater quality of the influent

COD (mg/L)	BOD$_5$ (mg/L)	TOC (mg/L)	NH$_4^+$-N (mg/L)	TN (mg/L)	SS (mg/L)	pH	T (℃)
1,000–1,200	350–400	300–350	120–150	250–290	≤80	7.0–7.5	30–35

Table 2
Compositions of synthetic wastewater

Compounds	C$_6$H$_{12}$O$_6$	(NH$_4$)$_2$SO$_4$	KH$_2$PO$_4$	NaHCO$_3$	FeSO$_4$·2H$_2$O	MgSO$_4$·7H$_2$O	NaCl	Peptone
Concentration (mg/L)	550–800	320–460	150–220	120	12.0–14.0	18.0	50.0	30.0

the available depth was 3.2 m for each tank. Volcanic granular media with a diameter of 2.0–5.0 mm were packed into each tank with an available depth of 2.0 m, and the HRT for each tank was 10–15 h. The air-to-water flow rate ratio was controlled at 5:1, and the BAFs were backwashed every 15 d to remove excess biomass to avoid filter clogging.

2.2. Wastewater

The influent of the pilot experiment was the DAF manufacturing wastewater from an acrylic fiber factory in China. The wastewater quality is shown in Table 1. The inoculated sludge for the biological pilot reactors (MBR and BAFs) was excess sludge collected from the wastewater treatment plant in the acrylic fiber factory, and the mixed liquor suspended solid (MLSS) concentration was 3.0 g/L.

Both MBR and BAFs were started separately, and fed with synthetic wastewater for sludge acclimatization and biofilm growth. The composition of synthetic wastewater was listed in Table 2.

2.3. Analytical methods

SS, MLSS, COD, BOD$_5$, NH$_4^+$-N, TN, NO$_3^-$-N, and NO$_2^-$-N analyses were conducted according to standard methods [7] and pH was measured by a pH meter (Starter 3C, Ohaus, US). TOC was measured by a TOC analyzer (TOC-VCPN 5000A, Shimadzu, Japan). EEM spectroscopy was made using a fluorescence spectrophotometer (F-7000, Hitachi, Japan). Excitation and emission slit widths were set to 5 nm and PMT voltage to 700 V. The excitation wavelength was scanned from 200 to 400 nm and the corresponding emission wavelength was recorded from 260 to 550 nm. The scan speed was set at 1,200 nm/min and the blank scans were performed at intervals of 10 analysis using Milli-Q water.

3. Results and discussions

3.1. Sludge acclimatization in pilot MBR

After sludge inoculation, the MBR was fed with synthetic wastewater to start the experiment. The

influent COD concentration was 600–800 mg/L, and NH_4^+-N concentration was 60.0–70.0 mg/L. After 35 d of continuous operation, the effluent COD and NH_4^+-N concentrations were maintained below 50.0 and 1.0 mg/L, respectively. The MLSS concentration increased to 8.0 g/L with the sludge retention time maintained at 50 d. Thereafter, the MBR was fed with the mixture of DAF manufacturing wastewater and synthetic wastewater for sludge acclimatization. During the first 15 d, the proportion of synthetic wastewater gradually decreased until the influent was completely DAF manufacturing wastewater.

The evolutions of COD and NH_4^+-N concentrations during sludge acclimatization are described in Fig. 2. Influent concentrations of COD and NH_4^+-N increased until day 15 and remained nearly constant from days 16 to 28. Effluent COD concentration increased gradually even after day 15, and reached 330 mg/L on day 21. Thereafter, the effluent COD concentration was kept almost constant at 310–400 mg/L. The NH_4^+-N concentration in the effluent increased to 103.6 mg/L on day 14, which was almost as high as the concentration of the influent. It then decreased gradually and became stable in the range of 40.7–52.0 mg/L after day 24. The effluent COD and NH_4^+-N concentrations became stable since day 25 when sludge acclimatiza-

tion in the MBR was fully completed. The removal efficiencies of COD and NH_4^+-N were maintained at 65.8–71.9 and 59.4–67.5%, respectively. Due to the high MLSS concentration in the MBR, micro-organisms were abundant and active, which could tolerate higher toxicity and influent load than some other bioreactors such as sequencing batch reactor (SBR) [8–10]. Furthermore, long SRT in the MBR helped to enrich the ammonia oxidizing bacteria that had longer generation time for growth and multiplication than heterotrophic bacteria [11]. Thus, effluent NH_4^+-N concentration could be stabilized in a short time.

3.2. Start and operation of pilot BAFs

Pilot BAFs were started based on the same procedure as the pilot MBR. Synthetic wastewater was used as feed for 40 d until the biofilm was formed on the surface of media in the BAFs. After sludge acclimatization in MBR and biofilm formation in BAFs were completed, the entire pilot system operated continuously for the DAF manufacturing wastewater treatment. The effluent of AO mixed with synthetic wastewater was used as feed for the BAFs. During the first 20 d, the proportion of synthetic wastewater in the influent gradually decreased until the biofilm was
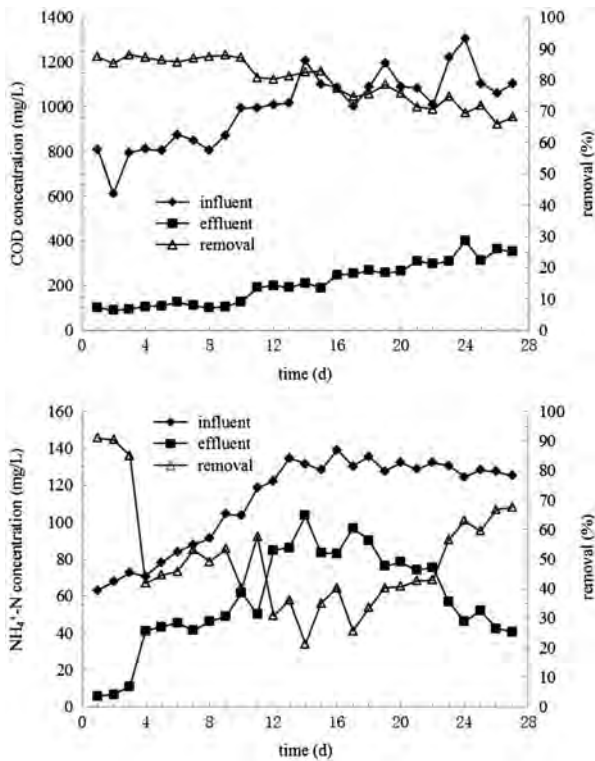
Fig. 2. Evolutions of COD and ammonia nitrogen removals during sludge acclimatization in MBR.
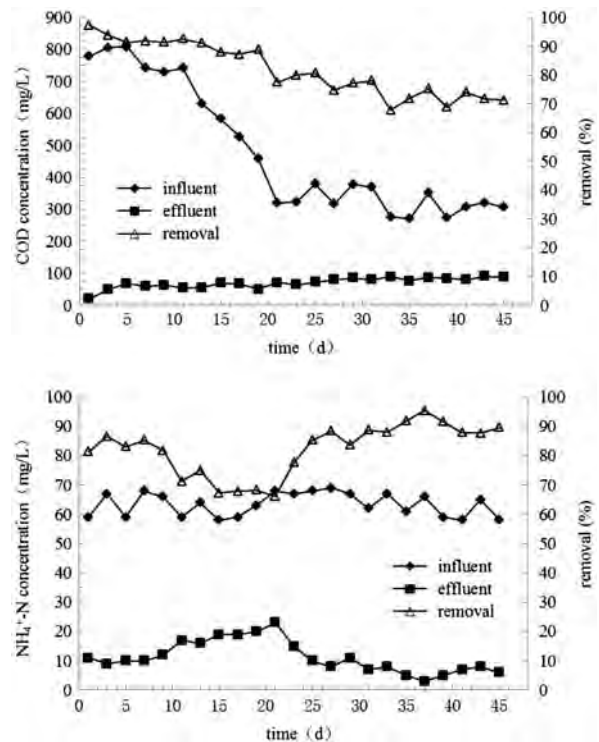
Fig. 3. Evolutions of COD and ammonia nitrogen removals during sludge acclimatization in BAFs.

completely acclimated to the practical wastewater. As shown in Fig. 3, due to the variation of influent during the first 20 d, influent COD concentration decreased from 800 to 270 mg/L, while influent concentration of NH_4^+-N was maintained in the range of 58.0–68.0 mg/L. Effluent COD concentration remained stable in the range of 65.0–91.0 mg/L after day 20, while effluent NH_4^+-N concentration increased gradually and fluctuated for 24 d. It then started to decrease and was maintained below 10.0 mg/L after 30 d of operation. Since day 37, white layer of biofilm had abundantly grown on the surface of the media, and the removal efficiencies of COD and NH_4^+-N had reached 75.3 and 95.5%, respectively. Because the BAFs provided high total porosity and large surface area for microbe inhabitance by the volcanic granular media, abundant biomass could attach to the surface of the media. Thus, the degradation of pollutants was active in the BAFs, which contributed to mitigating the loading shock [12]. These results would confirm that the BAFs had a strong adaptability to the influent of practical wastewater.

3.3. COD and NH_4^+-N removals during steady operation

Fig. 4 displays the evolutions of COD and ammonia nitrogen concentration when the whole system operated at steady state. During the 60 d of continuous operation, in spite of the fluctuation of water quality in the influent, the removal efficiencies of COD and NH_4^+-N could exceed 90.0 and 95.0%, respectively. The COD concentration in the total effluent was maintained at 80.0–100 mg/L and the NH_4^+-N concentration was below 10.0 mg/L. The BOD_5/COD ratio decreased from 0.3 to 0.1 after the MBR process, which indicated that the MBR had removed most of biodegradable organics from the DAF manufacturing wastewater, leaving the biorefractory substances transmitted into the AO unit. The COD concentration decreased by 106–157 mg/L after the AO process, whereas the BOD_5/COD ratio increased from 0.1 to 0.6, which demonstrated that the biodegradability of wastewater had been enhanced after the AO treatment.

The MBR, one of the biological processes used in variety of wastewater treatments, was adopted in this study as pretreatment process prior to the AO unit because of its economic advantages and strong resistance to impact load [13]. The DAF manufacturing wastewater still contained some biodegradable substrates, which could be utilized by micro-organisms during the MBR process. Thus, the MBR would reduce the ozone dosage for pollutants oxidation and cut down some running costs in the next AO unit.
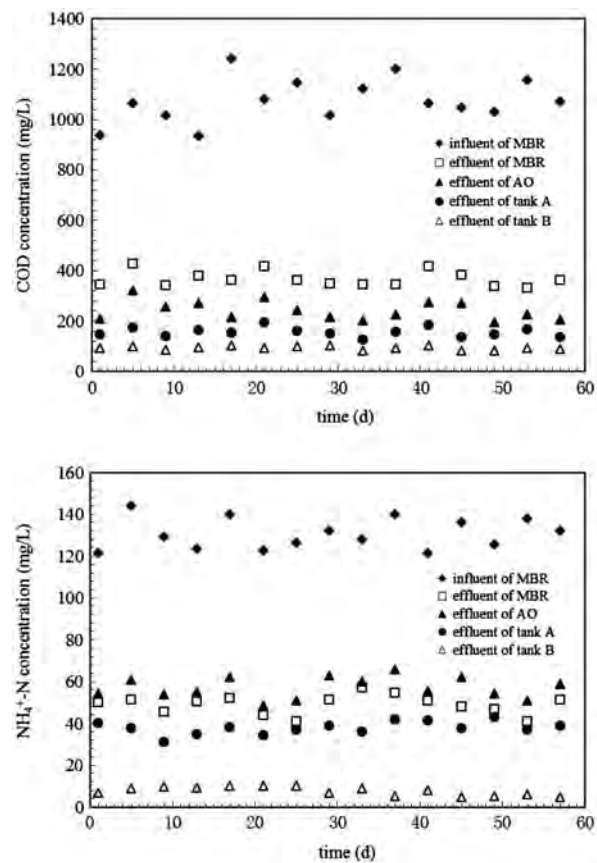

Fig. 4. Evolutions of COD and ammonia nitrogen concentrations during steady operation of the whole system.

Ozone is known as one of the most powerful oxidizing agents with a standard redox potential of 1.24 V in alkaline solutions [14]. In this study, the UV light catalyzed the ozone to form hydroxyl radicals that oxidized organic compounds at higher redox potential and reaction rate than ozone itself [15]. In addition, the ultrasonic made the ozone efficiently contact and react with target contaminants by enhancing the mass-transfer efficiency of the ozone between gas–liquid phases. Some organic contaminants were mineralized into carbon dioxide and water after the AO process, while the others were dissociated into small molecules, which therefore reduced the toxicity and improved wastewater biodegradability.

The NH_4^+-N concentration did not decrease as expected as it is well known that ozone does not react on ammonia. On the contrary, the effluent NH_4^+-N concentration of the AO process was even higher than that of the influent (Fig. 4). In addition, the pH value also decreased from 7.1 to 6.3 after the AO process. These results indicate that some of the amino groups were broken away from the organics and thus made

the NH_4^+-N concentration increased [16–18]. Meanwhile, some organic acids with small molecules might be formed after the AO treatment, which further contributed to the decrease in pH value.

The effluent COD concentration in tank A of the BAFs was in the range of 140–190 mg/L, and higher quantity of COD decreased in tank A than in tank B (Fig. 4). This is because that large number of organics were preferentially utilized as carbon source for the denitrification in the anoxic zone of tank A, which therefore decreased the COD concentration. Considering the evolution of NH_4^+-N concentration during the entire process, most of the ammonia nitrogen was removed in the MBR process and tank B of the BAFs. The effluent NH_4^+-N concentration in tank A was in the range of 31.1–42.8 mg/L and the removal efficiency of NH_4^+-N in tank B was 68.8–88.4%. During the BAFs process, tank A preferentially degraded the residual organics derived from the AO process, leaving the ammonia nitrogen flowing into tank B.

3.4. TN removal during steady operation

Fig. 5 shows the evolution of TN concentration during the steady operation of the entire system. It can be observed that the TN concentration in the total effluent was maintained in the range of 70.0–110 mg/L, corresponding to 58.2–71.6% in TN removal efficiency. The MBR could remove 19.8–31.3% of TN concentration from the influent, and the AO had no effect on TN removal. Tank A in the BAFs could decrease the TN concentration by 40.0–79.0 mg/L, possibly due to the denitrification process in the anoxic zone of tank A. However, tank B could also remove 23.7–59.4
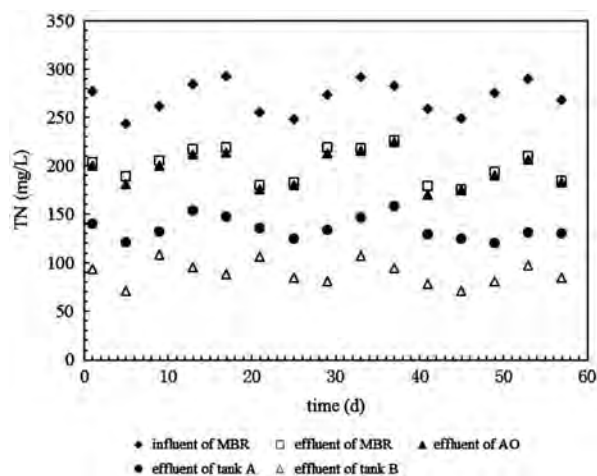

Fig. 5. Evolution of TN concentration during steady operation of the whole system.

mg/L of TN, in which the ammonia nitrogen was also removed. Table 3 shows the variation of NO_2^--N and NO_3^--N concentrations throughout the entire process when the system was in steady state. NO_2^--N concentration was stable in the range of 2.6–5.5 mg/L during the entire operation, and NO_3^--N concentration obviously increased to 52.1–60.7 mg/L after the MBR process, which was due to the effect of nitrification. Thereafter, the NO_3^--N concentration constantly decreased to 20.5–25.1 mg/L after the BAFs. Moreover, tank B decreased the NO_3^--N concentration by 14.7–19.8 mg/L, which was consistent with the decrease of TN concentration. This condition was probably caused by the partial denitrification that occurred in the internal part of the biofilm due to the lack of oxygen, thus it can be assumed that simultaneous nitrification–denitrification was performed in the biofilm of BAFs [19].

3.5. EEM analysis of the entire system

EEM spectra have been widely used for the characterization of organic compounds in water or wastewater [20–22]. In this study, when the pilot system was in stable operation, water samples were collected from the three treatment units for EEM analysis.

As shown in Fig. 6(a), two fluorescence peaks (B_1 and T_1) were observed in the EEM spectra of the raw wastewater. Peak B_1 was located at the Ex/Em wavelengths of 295/335 nm and was related to protein-like substances in the raw wastewater. Generally, this peak was induced by biodegradable substances that might be monocyclic or bicyclic aromatics, such as benzene, phenol, ethyl, benzene, and xylene [22]. In addition, peak T_1 was detected at the Ex/Em of 330/405 nm. This peak was due to fulvic-like compounds which probably contained three to five aromatic rings, such as phenanthrene, pyrene, and furan [23]. In the effluent of MBR (Fig. 6(b)), peak B_1 completely disappeared which indicated that monocyclic or bicyclic aromatic compounds were fully decomposed by the bioreaction of MBR. However, a new fulvic-like peak (T_2) was formed in the MBR effluent. This peak was probably related to the microbial by-products in the MBR [24]. The intensity of peaks T_1 and T_2 significantly decreased after AO treatment (Fig. 6(c)), confirming the efficiency of this process to remove these biorefractory compounds. After the BAF process, the intensity of these peaks further decreased (Fig. 6(d)), but in lower proportions.

These results indicate that most of the fluorescence compounds with complex structures could be decomposed and transformed during the ozonation

Table 3
NO_2^--N and NO_3^--N concentrations during the entire process

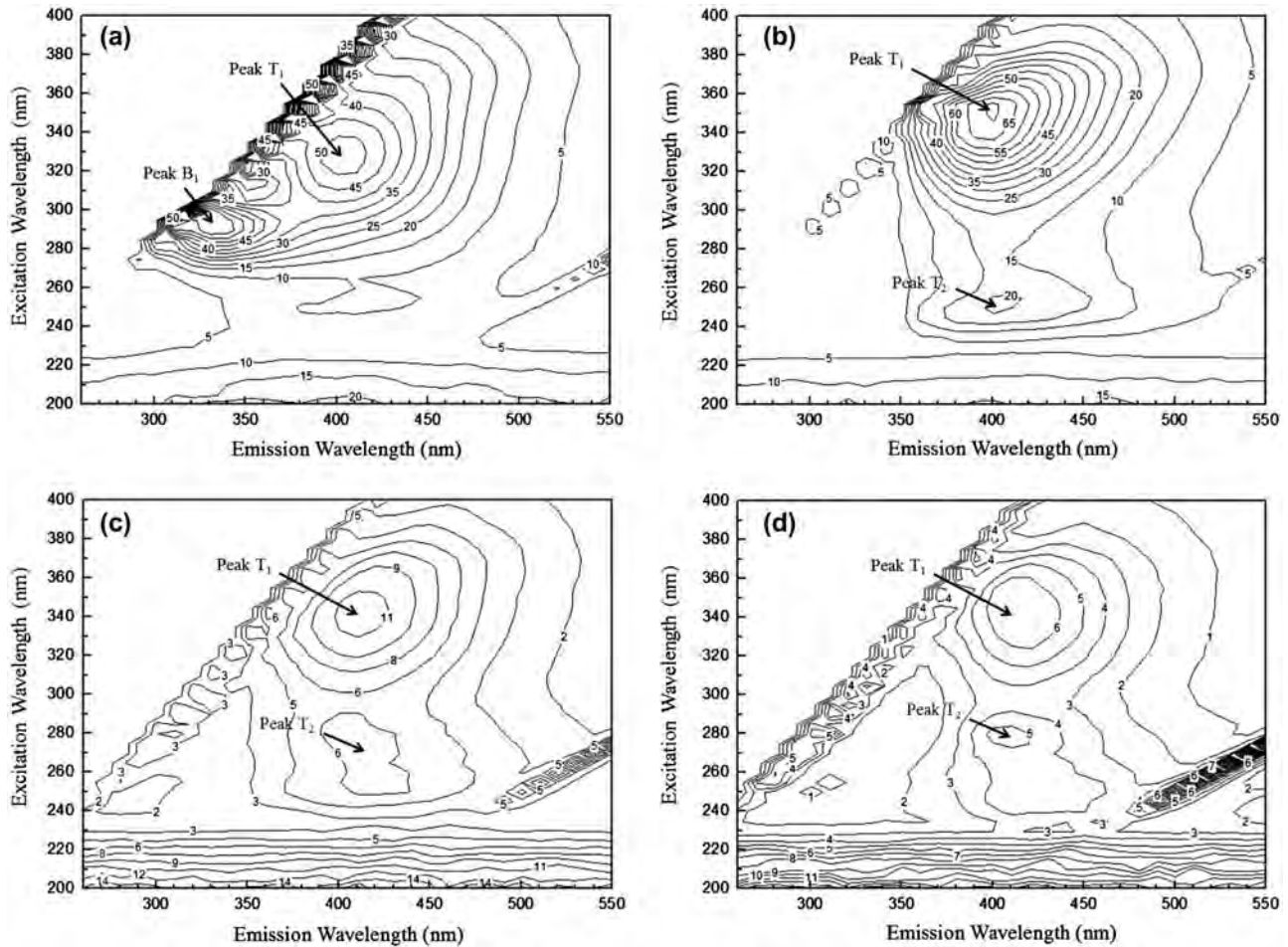|	Influent of MBR	Effluent of MBR	Influent of tank A	Effluent of tank A	Effluent of tank B
NO_2^--N (mg/L)	2.6–3.0	2.6–4.7	2.8–4.0	3.5–5.5	3.5–5.5
NO_3^--N (mg/L)	1.0–1.8	52.1–60.7	52.6–63.0	35.2–44.9	20.5–25.1

Fig. 6. EEM spectra of the samples collected after the different unit operations. (a) Raw wastewater; (b) after MBR; (c) after AO; and (d) after BAFs.

process. Furthermore, peaks T_1 and T_2 were red shifted in both excitation and emission wavelengths after the ozonation. From this result, it can be concluded that the complex aromatics were oxidized by the hydroxyl radical generated from the ozone, and the carbonyl and carboxyl groups were formed in the aromatic structure [25,26].

4. Conclusions

The real wastewater from DAF manufacturing was treated by an integrated process (MBR, AO, and BAFs) in pilot scale. Both of the MBR and BAFs could adapt to the influent of practical wastewater after a period of sludge acclimatization, and this integrated process had high COD and NH_4^+-N removal efficiencies. During the steady operation, the removal efficiencies of COD and NH_4^+-N could reach above 90.0 and 95.0%, respectively. The COD concentration in the effluent was maintained at 80.0–100 mg/L and NH_4^+-N concentration was below 10.0 mg/L. Most of the easy degradable organics were removed by the MBR; complex-structured organics were greatly decomposed and/or transformed into more biodegradable compounds by

the AO treatment. Most of the NH_4^+-N and TN were removed during the MBR and BAFs. Simultaneous nitrification–denitrification was performed in the biofilm of BAFs, and the TN removal efficiency reached 58.2–71.6% after the entire treatment.

Acknowledgements

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