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Combined MBR with Photocatalysis/Ozonation for Bromoamine Acid Removal

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Abstract A combined biological (augmented membrane bioreactor (MBR)) and photochemical (photocatalysis and ozonation) treatment has been proposed for bromoamine acid (BAA) removal in dyeing wastewater. It was demonstrated that the color and chemical oxygen demand removal in the sequential augmented MBR was about 90% and 50%, respectively. By ribosomal intergenic spacer analysis, it was found that the introduced strain QYY was maintained as the predominant species and the diversity of the system was relatively low throughout the operation. Photocatalysis and ozonation processes were efficient to treat the effluents from MBR with high color and total organic carbon removal more than 90% within 120 min. Therefore, the hybrid treatment system is a possible way to achieve the complete mineralization of BAA.

Keywords Membrane bioreactor · Bioaugmentation · Bromoamine acid · Ribosomal intergenic spacer · Photocatalysis and ozonation

Introduction

Dyeing industry effluents constitute one of the most problematic wastewaters to be treated not only for their high chemical and biological oxygen demands but also for color, which is the first contaminant to be recognized by human eyes [1, 2]. Because of their commercial importance, the impact and toxicity of dyes that are released in the environment have been extensively studied [3]. 1-amino-4-bromoanthraquinone-2-sulfonic acid (bromoamine acid,

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BAA), an important intermediate, is widely used in synthesis of anthraquinone dyes. It is water-soluble and makes water bodies red resulting in serious environment pollution [4]. Therefore, proper treatment, recycling, and disposal practices for such wastewater are necessary to prevent environmental pollution and foster an approach towards sustainable development.

A variety of physical, chemical, and biological processes have been developed to treat BAA contaminated wastewater, including bioaugmentation and TiO_2-assisted photocatalysis and ozonation etc. [5–8]. However, any method has its effectiveness and limitations as a single treatment process. In order to overcome the economical drawback and considering that biological treatment is the most desirable method, a two-stage process is being currently proposed by many researchers [9–11]. Such interesting coupled systems have been applied to successfully treat different kinds of industrial wastewater such as effluents from textile industry, olive mill, polyester resin production and so on [9]. The coupled processes of photocatalysis and biological treatment (usually preferred to activated sludge) have been studied in previous reports [3, 10–11]. However, little has been referred about the process combined augmented membrane bioreactor (MBR) with photocatalysis and ozonation.

In our lab, photocatalysis/ozonation and biodegradation have proved to be capable of removing BAA significantly as separate treatment process previously [6, 8]. However, with regard to photocatalysis/ozonation process, the following points were taken into account: the toxicity of some intermediates from the chemical reaction, the expenses associated to reagents, and energy consumption. For microbial treatment, there were also some limits of BAA removal such as relatively low chemical oxygen demand (COD) removal, etc. Also, when the influent concentration was increased, the system could not remove BAA adequately and the effluent maintained yellow. Therefore, it is essential to design a plausible technique to make BAA completely mineralized in dyeing wastewater. The main aim of this study is to investigate the performance of a coupled method which combined augmented MBR with photocatalysis/ozonation processes for BAA wastewater treatment.

Materials and Methods

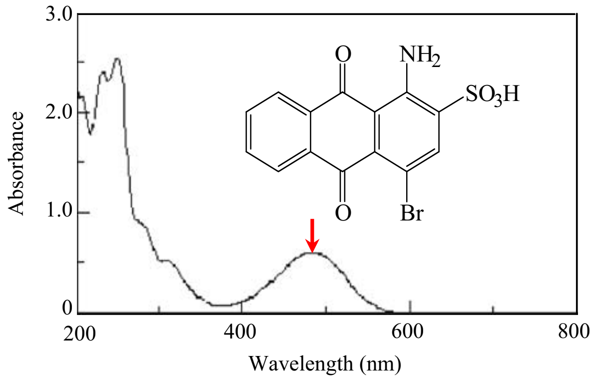
Chemicals

1-amino-4-bromoanthraquinone-2-sulfonic acid, BAA, was kindly presented by Dye Synthesis Laboratory of Dalian University of Technology and used without prior purification. The characteristic wavelength of BAA is 485 nm and its molecular mass is 382.19. The exact chemical structure and UV-visible absorption spectrum of BAA is illustrated in Fig. 1. All other chemicals were of analytical grade.

Coupled Biological and Photochemical Reactors

A schematic diagram of the laboratory-scale MBR combined with photocatalysis/ozonation is shown in Fig. 2. The augmented MBR was shown on the left hand side of Fig. 2. The membrane module was composed of hollow fiber membrane with the pore size of 0.2 μm, which directly submerged with working volume of approximately 10 L. The membrane flux of the MBR system was operated on an 11-h cycle and each cycle consisted of 30 min fill, 7 h react, 3 h settle, and 30 min decant. The influent BAA was about 50 to 350 mg L^{-1}, the dissolved oxygen was kept at 4–5 mg L^{-1} and hydraulic retention time (HRT) was 17 h.

Fig. 1 UV-visible absorption spectra (100 mg L^{-1}) and chemical structure of BAA



Activated sludge taken from Dalian Chunliuhe Wastewater Treatment Plant was seeded to the MBR as the indigenous populations at an initial concentration of approximately 3.0 g L^{-1}. Synthetic BAA wastewater (COD/N/P=100:5:1) was used as the influent for the MBR system containing BAA, $(NH_4)_2SO_4$, Na_2HPO_4, KH_2PO_4, and some trace elements, pH 7.0. After the culture reached the mid-exponential growth phase, cells of strain QYY were harvested by centrifugation (4 °C, 8000 r min^{-1} for 10 min), washed twice with sterile water and then used as inoculums.

The effluents of MBR system were subjected to photocatalytic reactor (2 L), which was on the right hand side of Fig. 2. The reactor comprised a TiO_2 thin film supported on a glass surface and a coaxial UV source (a 39W UV lamp with a characteristic wavelength of 254 nm). For ozonation, the TiO_2 film was removed and pure oxygen was used to generate

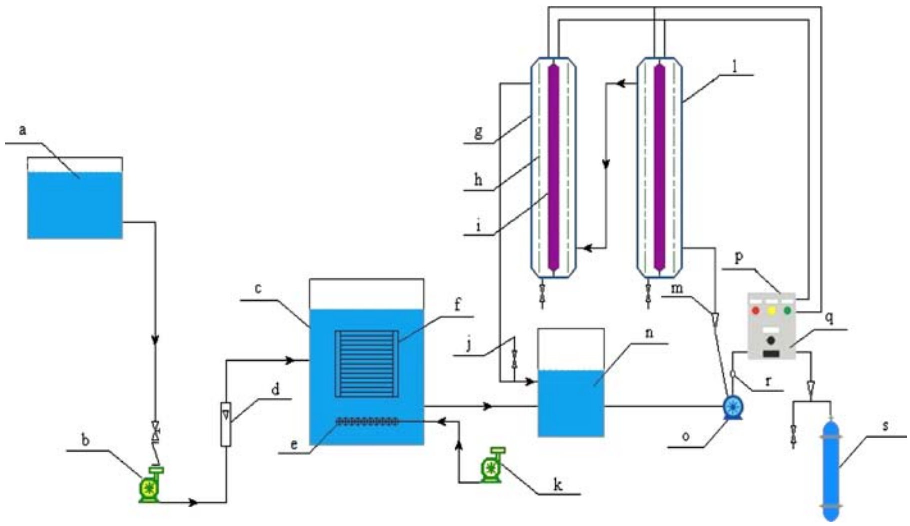


Fig. 2 Schematic diagram of augmented MBR combined with photocatalysis and ozonation processes: (*a*) feed tank, (*b*) feed pump, (*c*) membrane bioreactor, (*d*) flow meter, (*e*) aeration pipe, (*f*) membrane module, (*g*) and (*l*) photocatalytic reactors, (*h*) photocatalytic film, (*i*) UV lamp, (*j*) sampling valve, (*k*) aeration pump, (*m*) flow meter, (*n*) storage tank, (*o*) gas–liquid mixing pump, (*p*) control box, (*q*) ozonizer, (*r*) inverted valve, (*s*) O_2 supply

ozone in the ozonizer. The ozone dose was 7 mg min^{-1} with O_2 flow rate 100 mL min^{-1}. And the HRT was about 30 min. All experiments were performed at 25±1 °C.

Microorganism, Culture Conditions

Strain QYY was isolated from sludge samples in our previous study and has been identified as *Sphingomonas xenophaga* according to the 16S rRNA sequence analysis [5]. And strain QYY has been deposited in the China General Microorganism Culture Center as a patent strain with the number 1172.

The media used in this study were BAA–Luria-Bertani medium (BLB), which contained (g L^{-1}): 10 Bactotryptone, 5 Bactoyeastextract, 10 NaCl, 0.1 BAA, pH 7.0. Strain QYY was grown in the BLB medium at 30 °C, 150 r min^{-1}.

Sampling, DNA Extraction, and PCR Amplification

A mixed liquor sample (5 mL) was collected from the MBR and centrifuged for 10 min at 8,000 r min^{-1}. The supernatant was decanted and the pellets were stored at −20 °C for DNA extraction. Genomic DNA was extracted from the sludge samples by the method described previously [12]. The ITS region between bacterial 16S rRNA and 23S rRNA gene was obtained as reported previously [7]. PCR amplified fragments were separated on native polyacrylamide (6%) gels, which were stained with ethidium bromide and photographed for RIS analysis. The cluster analysis of RISA was generated using UVI-Band-Map soft.

Analytical Methods

Cell concentration was measured spectrophotometrically at 660 nm. The BAA concentration was estimated from the standard curve of dye concentration versus optical density at its characteristic absorbance wavelength (485 nm) using a UV-visible spectrophotometer (UV-560, Jasco, Japan). Standard method was used to measure COD concentration [13]. Total organic carbon (TOC) was measured using a total organic carbon analyzer (Shimadzu, Japan). Before the measurements of COD and TOC, samples were prepared by filtering through a 0.45 μm membrane filter.

Results and Discussion

BAA Removal in the Sequential MBR System

In our previous studies, we examined the augmented MBR for BAA removal in a continuous flow mode. The results showed that the effluent contained some yellow products and the COD removal efficiency was less than 50%. In the continuous flow mode, the products were easy to be polymerized. Therefore, in order to overcome the inconveniences of the continuous MBR, the sequential MBR (SMBR) was applied in this study. And for further mineralization of the effluents from MBR, the combined methods were proposed as shown in Fig. 2. The process was performed as follows: first, BAA containing wastewater was applied on the MBR augmented by *S.* xenophaga QYY, which was operated in a sequential flow mode. And then the effluents from MBR system were as influents of photocatalytic reactor.

The results showed that the SMBR could be started up rapidly and operated in a relatively stable status. As shown in Fig. 3a, when the BAA concentration was up to 350 mg L^{-1}, the decolorization efficiency of supernatant and effluent were both more than 90% and no yellow products were formed. And the corresponding COD removal efficiencies were 52% and 62%, respectively (Fig. 3b). The settle and flocculation ability were becoming better throughout the operation. The dehydrogenase activity was declined and kept relatively stable and the concentrations of protein and carbohydrate in EPS were increased (data not shown).

Population Dynamics in the Sequential MBR

With the rapid development of modern molecular ecological methods, it is possible to detect and monitor the complex systems. In this study, RISA technique was used to analyze

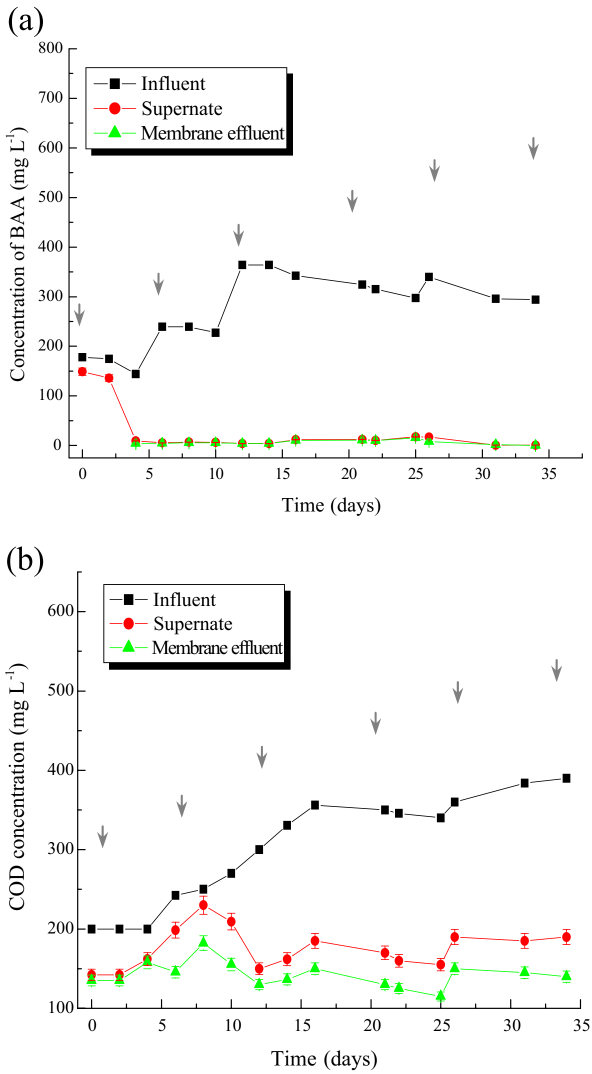


Fig. 3 BAA removal in the sequential augmented MBR system: **a** color removal, **b** COD removal. Sample points were indicated by the *arrows* in the graph. *Filled square* influent, *filled circle* supernate, *filled triangle* membrane effluent

the microbial community dynamics and predominant species, etc. The samples taken from the system were indicated by the arrows in Fig. 3a, b. The RISA profiles showed that there were substantial changes in the microbial community and the genetic diversity of the activated sludge community was dramatically declined after 30 days' operation (Fig. 4a). It was obvious that the inoculated strain QYY was predominant, which was indicated by the bands near 1.5 kb. And it was also suggested that the community structure in the SMBR system was as simple as that in the continuous MBR system.

Although the performance of the SMBR system was kept well with high color removal performance, the microbial community changed substantially. Degrees of similarity between populations were summarized by a dendrogram constructed using UPGMA (Fig. 4b). In the samples of day 0 and day 4, the population structure was different from that of other samples. After 10 days' operation, the structure of microbial community was similar (Fig. 4b). Populations in the SMBR system fell into three separate groups with relatively low similarity. As shown in Fig. 4b, the similarity between populations on day 18/day 34 and day 12/day 26 clustered within one group, respectively. Therefore, it was concluded that the SMBR possessed the proper community structure for BAA removal.

Further Treatment of Effluents from the SMBR by Photocatalysis/Ozonation Process

It was observed that the effluents of SMBR seemed not to polymerize the products within 30 days' operation. However, the effluents became yellow when the SMBR system was operated for a long time. Therefore, it is necessary to treat the effluents for complete decolorization or degradation. In this study, the effluents were feed as influents to the photocatalysis/ozonation process.

The UV-visible spectra of the MBR-effluents during the photocatalysis/ozonation process were given in Fig. 5, and the initial concentration of TOC was about 140 mg L^{-1}. In Fig. 5,

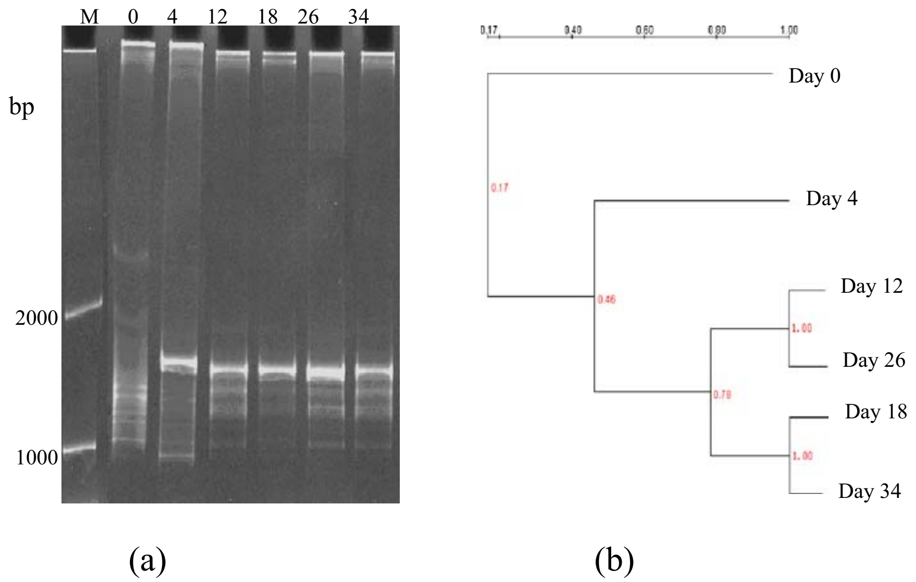
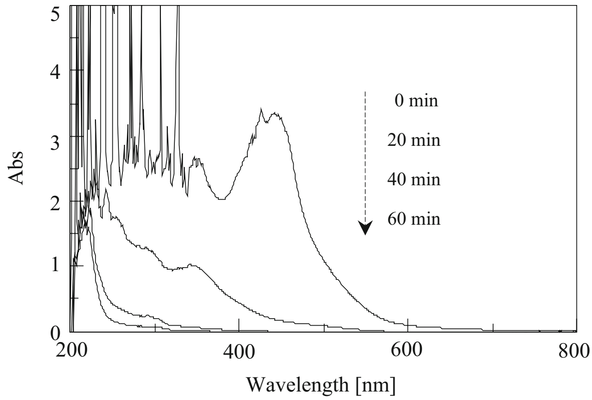


Fig. 4 **a** RISA fingerprints of microbial populations in the sequential augmented MBR system, **b** cluster analysis. *M* DL 2000 marker, *numbers* shown above each lane represent the time of sample collection (days)

Fig. 5 UV-visible spectra of the MBR-effluent treatment during photocatalysis and ozonation processes

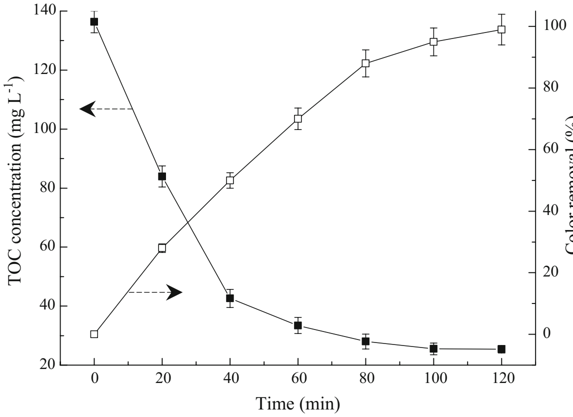


the maximum absorbance peaks (around 447 nm) which were attributed to the presence of the byproducts produced from the SMBR decreased with irradiation time increase and finally disappeared (Fig. 5). Complete discolorization of the effluents was observed after 60 min treatment. It was obvious that there were so many peaks in the ultraviolet region at 0 min, which indicated that the products were polycyclic aromatic like compounds [14]. This should be explained that the COD could only be partially removed by the SMBR system.

The color and TOC removal performance of the MBR-effluents by photocatalysis/ozonation was shown in Fig. 6. It was suggested that the high removal efficiency could be obtained as 90%. Therefore, it could be concluded that BAA was mineralized by the proposed couple methods. And there seemed no toxicity compounds with high molecular mass formed by this treatment process. In our previous study, photocatalysis/ozonation has been used as the pre-treatment for further aerobic treatment of BAA, which was found that such combined process was not a cost-effective strategy [8]. It was proved that only 40% TOC of BAA (300 mg L^{-1}) was removed within 120 min. However, if the photochemical process was selected as a post-treatment, the treatment time would become shorter and efficiency was significantly improved.

There have been some reports on the integration of biological and photochemical processes for wastewater treatment [9, 15–17]. Usually, there are two conditions for the

Fig. 6 Time course of TOC and color removal of the MBR-effluent by photocatalysis and ozonation processes. *Filled square* TOC removal, *unfilled square* color removal



combined treatment: (1) biological treatment should be placed before the chemical oxidation and (2) chemical treatment would be followed by the biological treatment. As reported previously, if the pre-treatment time is too short, the intermediates present in the solution are still structurally close to the initial bio-recalcitrant compounds and the efficiency of both the biological and the whole coupled process were dramatically diminished [9]. In our study, it is advisable to design the cheaper treatment (MBR) remove the major part of the pollutant and to make the more expensive one (photocatalysis/ozonation) perform the final polish.

Conclusions

In conclusion, the proposed treatment combined augmented MBR and photocatalysis/ozonation for pollutants removal can serve as an attractive solution, particularly when the high efficient microbial organism could be successfully used for bioaugmentation. Photocatalysis and ozonation processes are efficient to treat high colored effluent from MBR and to remove TOC more than 90% within 120 min. Further research is being carried out to optimize the conditions for this new combined process for field application.

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