Treatment of petrochemical secondary effluent by an up-flow biological aerated filter (BAF)

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ABSTRACT

In this study, petrochemical secondary effluent was treated by a 55 cm diameter pilot-scale biological aerated filter (BAF) with a media depth of 220 cm. Volcanic rock grains were filled as the BAF media. Median removal efficiency of chemical oxygen demand (COD) and ammonia nitrogen (NH₃-N) was 29.35 and 57.98%, respectively. Moreover, the removal profile of the COD, NH₃-N, total nitrogen and total organic carbon demonstrated that the filter height of 140 cm made up to 90% of the total removal efficiency of the final effluent. By gas chromatography–mass spectrometry, removal efficiencies of 2-chloromethyl-1,3-dioxolane, and benzonitrile, indene and naphthalene were obtained, ranging from 30.12 to 63.01%. The biomass and microbial activity of the microorganisms on the filter media were in general reduced with increasing filter height, which is consistent with the removal profile of the contaminants. The detected genera Defluviicoccus, Betaproteobacteria_unclassified and the Blastocatella constituted 1.86–6.75% of the identified gene, enhancing the COD and nitrogen removal in BAF for treating petrochemical secondary effluent.

Key words | biological aerated filter, dehydrogenase, next-generation sequencing, organic compounds, petrochemical secondary effluent, specific oxygen uptake rate

INTRODUCTION

A large amount of petrochemical wastewater (WW) is generated in the petroleum refining industry and the manufacturing processes of numerous organic chemicals and raw materials. Petrochemical WW contains various refractory organics, including petroleum hydrocarbon, aniline, nitrobenzene, phenols and their homologs. These organics are highly toxic and inhibitory to microbial activity, and may result in a challenging issue treating petrochemical WW (Guo et al. 2009; Sponza & Oztekin 2010). In present-day China, more than 95% of the biological secondary effluent after treatments (e.g. conventional activated sludge process, anoxic-oxic (AO) process, anaerobic-anoxic-oxic (A²O), etc.) can meet the old integrated WW discharge standard GB 8978-1996 with chemical oxygen demand (COD) limit of 80 mg/L (Guo et al. 2009; Wu et al. 2015). However, for the strict requirements of environmental protection, a new and more strict emission standard of pollutants especially for the petroleum chemistry industry GB 31571-2015 began to be implemented from the year 2015 in which COD limit was 60 mg/L. Therefore, pollutants in petrochemical secondary effluent must be further reduced by advanced treatments.

Advanced treatments including biological activated carbon, membrane bioreactor, and advanced oxidation processes have become promising methods recently. However, there are clear limitations of these methods due to high expense of the activated carbon, chemical agents and membrane fouling problems, etc. (Wang et al. 2008b; Qiu et al. 2010; Cui et al. 2014). Biological aerated filters (BAFs) incorporate an inert medium to support biomass and filter out suspended solids (SS). They combine carbonaceous matter, ammonia and solids removal in a single unit. Therefore, BAFs have become a biological treatment option for advanced WW treatment and reuse in recent years (Wang et al. 2008b; Qiu et al. 2010). When microorganisms were immobilized on carriers, they showed significant advantages over those dissociated microbial communities. Therefore,
BAFs can maintain high hydraulic loading rates and retain a high biomass concentration to reduce environmental shock (Zhao et al. 2006). Moreover, the biomass and microbial activity can reflect the performance of the BAF. Techniques for the measurement of biomass activity, including adenosine triphosphate analysis, specific oxygen uptake rate (SOUR) and dehydrogenase (DHA) activity testing have been widely employed to monitor biological water and WW treatment processes (Lazarova & Manem 1995; Han et al. 2015). In addition, biodiversity and distribution of microbial communities are regarded as important indicators for functionality in WW treatment systems. Recently, next-generation sequencing (NGS) is superior and reliable at revealing the whole composition of microbial communities since this technology does not require subcloning or handling of individual clones (Margulies et al. 2005).

To date, interests in BAF have primarily been its application to low residual COD removal, stable performance and lower sensitivity to toxic shock loading in WW treatment. In previous studies, BAFs have been used in combination with other methods such as ozone treatment and membrane filtration (He et al. 2013), for the advanced treatment of oil field WW (Zhao et al. 2006) and textile washing WW (Wang et al. 2008a, 2008b). Meanwhile, research regarding the removal of recalcitrant chemicals has mainly concentrated on bench-scale experiments with synthetic WW. However, to our knowledge, extensive treatment research of actual petrochemical secondary effluent by pilot-scale BAF has rarely been performed. Meanwhile, the microbial diversity and community distribution at different height of filter media have not yet been clarified in the pilot-scale BAF for actual petrochemical secondary effluent. The main objectives of the present study were to: (1) operate a pilot-scale BAF and investigate its performance to simultaneously remove organic carbon and nitrogen; (2) quantify some characteristic organic matter in the influent and effluent; (3) analyze biomass, microbial activity, and diversity of the microbial communities on the filter media.

MATERIALS AND METHODS

Experiments were carried out using a pilot-scale BAF system built in a petrochemical wastewater treatment plant (PWWTP) in northeast China (Figure 1). The industrial WW came from about 70 sources involving ethylene glycol plant, oil refinery plant, resin factory, acrylonitrile butadiene styrene plants, etc. The up-flow BAF was a cylindrical reactor with 550 cm height and 50 cm inner diameter. Volcanic rock grains with size ranges of 3–5 mm were packed with a bed height of 220 cm. The influent was directly introduced from a secondary settling tank of the PWWTP. The BAF was periodically backwashed every 1–2 week(s) to remove the excess sludge (see Supplementary Material (SM) Page S2, available with the online version of this paper). The air–water ratio and the hydraulic retention time of the BAF treatment was controlled at 3:1 h and 3 h, respectively, based on our previous study (Wu et al. 2015). Therefore, the air flow rate was 700 L/h and the hydraulic loading rate was 1.20 m³/m²/h for the BAF. The characteristics of the WW are as follows: the COD content ranged from 60 to 120 mg/L with a mean value of 85 mg/L; the biological oxygen demand (BOD₅) ranged from 4.65 to 6.15 mg/L; ammonia nitrogen (NH₃-N) concentration was less than 2.0; the mean total nitrogen (TN) concentration was 13.6 mg/L; the pH value was 6.9–7.8. Water temperature was around 27 °C. Water and media samples were collected along different filter heights (Figure 1) and the water samples for gas chromatography–mass spectrometry (GC–MS) analysis were collected on the 57th day of the operation process.

The COD and NH₃-N of the samples were determined in accordance with the standard methods for the examination of water and wastewater (State Environmental Protection Administration of China 2002). The total organic carbon (TOC) and TN were determined by a TOC analyzer with a TN detector (TOC-CPH, Shimadzu, Japan). Considering complex composition of the petrochemical WW, eight kinds of organic pollutants with different types of chemical structure commonly detected previously were selected for the BAF treatment evaluation: 2-chloromethyl-1,3-dioxolane, and 2-pentanone, azabenzene, benzonitrile, indene, phenyl acetate, naphthalene and atrazine. The concentrations of these organic pollutants were analyzed by a GC–MS system with the selected ion monitor (SIM) mode (7890/5975,
Agilent, USA) (see SM Page S3). The biomass was determined by comparing the weight loss at 105 °C with the one at 600 °C. The microbial activity in the BAF was quantitatively determined by 2,3,5-triphenyl tetrazolium chloride (TTC)-DHA assay (Qi et al. 2012) with a little modification: triphenyl formazan (TTF) crystal extraction agent was changed into the absolute ethyl alcohol. The SOUR of the microorganisms on the filter media was analyzed according to ISO 8192 (2012). NGS (Illumina MiSeq sequencing) was conducted at Shanghai Majorbio Bio-Pharm Technology Co., Ltd (Shanghai, China) (see SM Page S4).

RESULTS AND DISCUSSION

Treatment performance

The collected influent and effluent samples were analyzed one or two times per day. As shown in Figure 2, at the start-up time of the BAF performance during 0–12 days, the COD and NH$_3$-N removal efficiencies fluctuated significantly. During the operation time, the COD volume loading was 0.43–1.78 kg/m$^3$/media/d with the median value of 0.76 kg/m$^3$/media/d; the effluent COD concentrations ranged from 13.38 to 86.82 mg/L with the median value of 52.26 mg/L; the median removal efficiency was 29.35%. At this stage, the mean volume loadings of the NH$_3$-N ranged from 0.01 to 0.33 kg/m$^3$/media/d with the median value of 0.024 kg/m$^3$/media/d. The effluent NH$_3$-N concentrations ranged from 0.53 to 14.94 mg/L with the median value of 0.57 mg/L and the median removal efficiency was 57.98%. Even though the influent COD load varied, the COD and NH$_3$-N removal efficiency could still be maintained at 20–50% and 40–100%, respectively (see SM Page S5, available with the online version of this paper). This demonstrated certain ability for the BAF to resist COD shock load treating petrochemical WW.

The removal profiles of COD, TOC, NH$_3$-N and TN at different BAF heights are presented in Figure 3. The removal efficiencies of the four parameters increased sharply from 0 to 30 cm of the bed height, and then smoothly from 85 to 140 cm. The petrochemical secondary effluent contained some biodegradable pollutants such as micromolecular and simple soluble compounds after the hydrolytic acidification-A-O biological treatment in the PWWTP (Yang et al. 2015). 95% of total removal rate of the effluent SS were filtered out below 140 cm of the media (See SM Page S6). COD mostly associated to SS concentration can be filtered out more easily than soluble fractions are degraded (Desbos et al. 1990). Additionally, dissolved oxygen (DO) and organic material concentration were abundant at the 30–140 cm height of the BAF. Aerobic environment with not more than 5 kg COD/m$^3$/d will be favorable for the nitrifiers (Desbos et al. 1990). Meanwhile, because of the competitive advantage of heterotrophic bacteria, the organic matter degradation area mainly formed in the inlet area (Qiu et al. 2010). Therefore, removal efficiencies of the organic carbon and nitrogen at the height of 140 cm made up to 90% of the total removal efficiencies of the final effluent in this study.

GC–MS analysis of semi-volatile organic compounds

Volatile organic compounds (VOC) are easily removed by good aeration in the PWWTP. Since semi-VOC (sVOC) are originated mainly from petroleum products, they are species that do not degrade easily and can remain attached to solid
particles for longer time (Ghanem 2005). The study of sVOC in petrochemical WW could reflect the BAF performance to some extent. In this study, quantitative results showed only four kinds of sVOC were detected: 2-chloromethyl-1,3-dioxolane, and benzonitrile, indene and naphthalene, with their removal efficiencies ranging from 30.12 to 63.01% (Table 1). In particular, organic pollutants not only appear in industrial effluents at high concentrations but also exhibit a high diversity with respect to their molecular structures (Botalova et al. 2009). 2-chloromethyl-1,3-dioxolane showed a high concentration of 20.17 μg/L in the influent. 2-chloromethyl-1,3-dioxolane was the raw material of the ethanediol and mainly discharged from the ethylene glycol plant from the industrial park (Haerens et al. 2009). Benzonitrile is a useful solvent and a versatile precursor to many derivatives. Indene and naphthalene are the common organics in petrochemical WW (Sponza & Oztekin 2014). Naphthalene is an important polycyclic aromatic hydrocarbon (PAH) and was included in the United States Environmental Protection Agency priority pollutant list for their persistence, bioaccumulation and toxic effects. Therefore, the concentrations of the organic compounds need to be controlled in treated WW effluents. The PAH value of the influent of the aeration unit from a PWWTP in Turkey was 1,380 μg/L. This value is much higher than the petrochemical secondary effluent in the present study. Sponza & Oztekin (2010) found that H₂O₂ sonication could provide 88–92% PAH removal and 100% acute toxicity of Daphnia magna removal can be reached. Therefore, the content of the heterocyclic compounds, carboxamides, and benzene compounds in the effluent decreased, indicating that the toxicity of the petrochemical secondary effluent might be reduced by BAF.

**Biomass and microbial activity**

A consortium of microorganisms was retained by the inert media of BAFs, either as surface-attached biofilm or in the interstitial pore spaces. As shown in Figure 4, biomass and microbial DHA on the media were gradually reduced from 20 to 125 cm, and then increased at 215 cm, the same with the study by Zhu et al. (2007). Microbial SOUR decreased along with the increase of the filter media. Since organic load and DO were high in the influent at the filter inlet, which was beneficial for the microbial growth, the biomass and bioactivity reached the highest value at 20 cm height (Tian et al. 2006). Therefore, the
majority of the organic carbon and nitrogen were degraded under the 140 cm height of the layer (see Figure 3). However, since DO in the water was lower than that in the filter inlet, the microbial respiration was inhibited to some extent and the SOUR was decreased at the 215 cm layer. Meanwhile, due to the organisms actively biodegrading leftover pollutants, the biomass and microbial DHA increased at 215 cm. This was closely related to the microbial community distribution on the filter media. Further, since the volcanic rock grain media did not present a passive adsorption after 24 h (see SM Page S7), the biomass actually contributed much to the pollutant removal in the BAF treatment (Figure 4).

**Microbial community analysis**

Illumina MiSeq sequencing was performed to reveal the microbial diversity and distribution in different heights of BAF media filter. The diversity estimators of Shannon index for samples are 5.73, 5.38, 5.31 and 5.39, respectively,
for 20, 75, 125, and 215 cm height of the BAF filter media. The diversity variance was in accordance with the biomass and microbial DHA variation along the filter media height (Figure 5). The bacterial community in the bottom of the BAF filter showed the maximum diversity. This confirmed that the COD, TOC NH3-N and TN were removed predominantly between 0 to 30 cm of the bed height (Figure 3).

As shown in Figure 5 and Table S2 (available with the online version of this paper), *Defluvicoccus*, *Betaproteobacteria_unclassified* and the *Blastocatella* constituted 1.28–6.75% of the identified gene. *Defluvicoccus* were capable of taking up a narrow range of substrates including acetate, propionate, pyruvate and glucose under anaerobic and aerobic conditions, and they also presented the denitrification capability (Burow et al. 2010; Wang et al. 2008a). In this study, the TN and NH3-N removal might be related to the *Defluvicoccus*. Some *Betaproteobacteria* can grow heterotrophically in defined media containing ethanol, toluene, benzene, ethylbenzene and dihydroxybenzoates as sole carbon sources (Nakatsu et al. 2006). *Blastocatella* showed aerobic chemooorganoheterotrophic growth on very few complex substrates (Foesel et al. 2013). As shown in Figure 5, the relative abundance of *Betaproteobacteria_unclassified* and *Blastocatella* first decreased at 50 cm of the filter media and then slightly increased. Their presence ensured the favorable COD removal. Further, the *Lactococcus* increased dramatically from 50 to 85 cm and then maintained stable and dominant at 140 and 230 cm. *Lactococcus* is a genus of amphotrobac attributed to the combined effects of the variety of bacteria existing in the BAF.

**CONCLUSIONS**

A pilot-scale BAF was used to treat petrochemical secondary effluent, showing the median removal efficiency of COD and NH3-N was 29.35 and 57.98%, respectively.
Removal profiles of the COD, TOC, NH$_3$-N and TN demonstrated that the filter height of 140 cm made up to 90% of the total removal efficiency of the final effluent. Four types of the sVOC: 2-chloromethyl-1,3-dioxolane, and benzonitrile, indene and naphthalene were removed by 30.12–63.01%. The biomass and microbial DHA were gradually reduced from 20 to 125 cm, and increased at 215 cm. This variation related to the diversity of bacterial community. The SOUR of the microorganisms of the filter media decreased with increasing filter height. The Defluviococcus, Betaproteobacteria unclassified and the Blastocatella which were presented along different height of the filter media enhanced the removal of organic carbon and nitrogen. The degradation of the organic pollutants of the petrochemical secondary effluent was attributed to the combined effects of the variety of bacteria existing in the BAF.

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REFERENCES


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