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Composite biologically active filter (BAF) with zeolite, granular activated carbon, and suspended biological carrier for treating algae-laden raw water

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ABSTRACT

In this study, a composite biologically active filter (BAF) packed with suspended biological carrier (SBC), zeolite, and granular activated carbon (GAC) in order, was set to pretreat the algae-laden synthetic raw water. Over the long-term operation, stable and effective treatment was achieved under the algae concentration as high as 16.64 $\times 10^8$ cell/L, with average removal efficiencies of NH_4^+-N, Total Organic Carbon (TOC), and algae cells of 97.7%, 64.0%, and 78.6%, respectively. The pollutant removal of each filter were quantitatively assessed. The results revealed zeolite mainly contributed to the adsorption of NH_4^+-N (50.1%), GAC enriched the most functional microorganisms and contributed to nitrification (57.1%) and organics biodegradation (TOC: 63.9%, microcystin-LR (MC-LR): 96.8%). The addition of SBC filter enhanced the chemical and microbial removal ability of the BAF system. The structure and distribution of biofilm on each filter were different, GAC biofilm accumulated the most MCs degrading microbes, and the highest microbial community richness and diversity was observed in SBC biofilm. Overall, the composite BAF with zeolite-GAC-SBC is developed for algae-laden raw water pretreatment, enabling the application of BAF in drinking water pretreatment plants.

1. Introduction

Cyanobacterial (blue-green algae) blooms have emerged as a global issue, posing a pressing threat to water quality and human health [1]. Over 75% of natural and artificial lakes in China are impacted by algae blooms [2] and the majority of them also serve as drinking water sources. Due to the surface hydrophilicity and electrostatic repulsion, algae cells are stable in water without being removed easily [3]. Furthermore, algae cells and algae-derived organic matters (AOMs) release cyanotoxins [4] and precursor compounds that can form disinfection by-products (DBPs), respectively [5]. Microcystin-LR (MC-LR) is a cyanotoxin of increasing concern considering its toxicity and frequent detection in water and sediments [1,6,7].

In algae-impacted water, ammonia (NH_4^+-N) is commonly found as a concerning co-contaminant [8]. Excessive presence of ammonia (>1.5 mg/L) in water can cause a number of adverse effects, including eutrophication, oxygen depletion, and poisoning to aquaculture [9]. High concentrations of NH_4^+-N may also react with chlorine and form genotoxic and cytotoxic DBPs [10] during the chlorination disinfection [11]. Consequently, algae cells, AOM, and NH_4^+-N are primary contaminants in algae-laden water, underscoring the need to develop effective treatments, since conventional drinking water treatment processes (DWTPs) are inefficient for their removal [12].

Biological drinking water treatment (BioDWT) started in the early 1900s [13]. However, applications of BioDWT are scarce. Currently, several developed countries have applied BioDWT in drinking water production [14]. In comparison with conventional DWTPs, BioDWT is advantageous featuring zero chemical usage and minimal sludge production [15]. Thus, BioDWT is promoted as the future for DWTPs [14]. As reported, adding biological pretreatment in DWTPs can not only

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Table 1
Characteristics of influents of three BAF systems.

Influent	NH_4^+-N (mg/L)	NO_2^--N (mg/L)	NO_3^-N (mg/L)	TOC (mg/L)	Algae density (10^8 cell/L)
R1, R2	4.68±0.40	0.42±0.55	1.99±0.64	7.51±0.84	1.94±0.97
R3	4.68±0.40	0.42±0.55	1.99±0.64	7.51±0.84	16.64±0.32

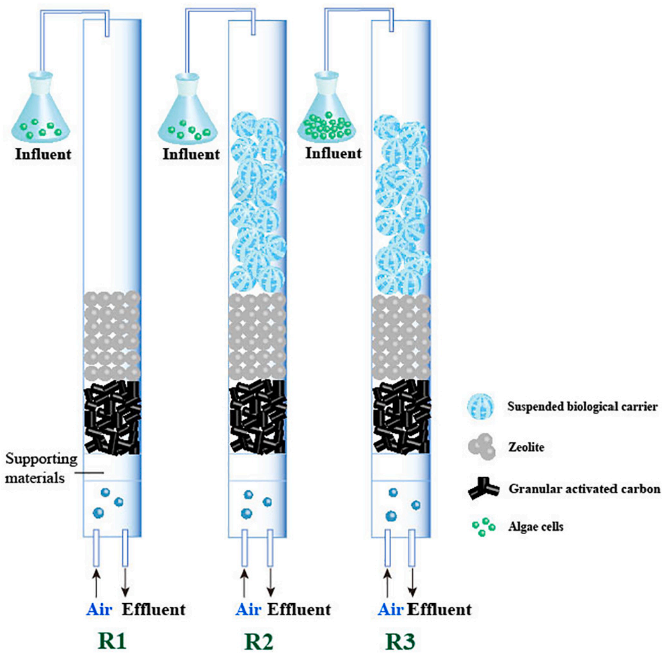

Fig. 1. Schematic diagram of three biologically active filters (BAFs).

decrease DBP formation potential [12], but also reduce microbial contamination to the subsequent distribution systems [11]. Thus, it is promising to utilize biological pretreatment for algae and NH_4^+-N removals to optimize the conventional DWTP operations. Nevertheless, investigations on biological pretreatment for drinking water production remain limited nowadays [11].

Biologically active filter (BAF) is widely acclaimed for wastewater treatment, but rarely applied in drinking water treatment. In the past few years, BAF progressively demonstrates its compatibility for micropollutant removal in drinking water sources and have been reported as an effective strategy for the pretreatments of DWTPs to remove ammonia at a high level [8,16]. Previous studies about BAF system for DWTPs mainly concentrated on the simultaneous removal of NH_4^+-N and COD [14], without specializing investigations of algal and associated chemical (cyanotoxin and AOMs) removal.

In BAF system, filter media are key components responsible for separating solid particles in the influent and enriching biofilm for pollutant removal [17,18]. Given the decisive role in the design and operation of BAF, it's of great practical value for the innovation of BAF media tailored for different treatment purposes [17]. For example, Yu et al. [18] demonstrated that the BAF with ceramsite had advantages in removing organic matter, turbidity and colourity. Feng et al. [19] and Chang et al. [20] found a pilot-scale BAF packed with zeolite was effective for the treatment of textile wastewater. Meanwhile, the BAF filled with gravel was more effective at TOC and formaldehyde elimination that the wetlands [21]. The carbonate BAF was suitable for wastewater treatment with lower pH or variable pH [17].

BAF media are divided into two types: submerged media (e.g., zeolite, granular activated carbon [GAC] [19], ceramsite) and floating media (e.g., polypropylene, polyethylene) [14]. Therein to, GAC is known for the adsorption of dissolved organic carbon (e.g. taste and odor compounds, micropollutants, halogenated hydrocarbons) in the drinking water treatment [22]. Moreover, Liu et al. [23] indicated that GAC can efficiently remove microcystins from natural water. Zeolite is a superior media in BAF system for pollutant (especially ammonia) adsorptions [19]. Notably, the combination of zeolite (upper layer) and GAC (bottom layer) was capable of efficient ammonia removals in BAF [24]. The floating media like plastic ball has an advantage in resisting the impact of low temperature and requires a low backwash rate [25]. Therefore, in response to the requirements for the removal of ammonia nitrogen and algae cells in this study, GAC, zeolite, and suspended polyethylene biological carrier (as floating media) were selected to set up a novel BAF system.

Recently, BAFs using a combination of different filter media have attracted increasing research interest [17,20]. Feng et al. [26] combined grain and slag as BAF media and investigated their characteristics in comparison with haydite media, results indicated that grain-slag BAF performed better in terms of chemical oxygen demand (COD) and ammonia removal. Liu et al. [27] selected ceramsite and GAC to set up two-layers-media BAF for tertiary treatment and its effluent satisfied the standard for domestic reuse in China. Syafalni et al. [24] found the BAF packed with the zeolite and GAC exhibited efficiency performance in the treatment of dye wastewater. Most of the previous studies were concentrated on the alteration of BAF operations for the improvement of pollutants removal. Fundamental understanding of specific removal contributions of the combined filters and their respective contributions to pollutant removal are still unstudied.

In this study, two submerged media, GAC and zeolite, and one floating media, suspended polyethylene biological carrier (SBC), were selected to construct composite BAFs. Three BAF systems (R1, R2 and R3) with different kinds of filters were built to pretreat algae-laden synthetic raw water. Pollutant removal effectiveness and DBP formation potential were monitored over a long-term operation for 225 days. In parallel, pollutant adsorption and biodegradation by SBC, GAC, and zeolite were assessed using batch experiments. Furthermore, surface morphology and microbial community of biofilm attached on the zeolite, GAC, and SBC were examined to reveal the underlying mechanisms of multi-filters in the novel BAF system and the role played by each filter media in the BAF operations, which will provide a new strategy for algae-laden raw water pretreatment and theoretical basis for filter media selection of BAF in the future.

2. Materials and methods

2.1. Synthetic raw water

Microcystin-producing *Microcystis aeruginosa* strain FACHB-1095 (Freshwater Algae Culture Collection at the Institute of Hydrobiology, FACHB) was used as archetypical toxic algae in this study [28]. FACHB-1095 was cultured with the BG11 medium under the following conditions: light intensity of 2000 lx, light-dark ratio of 14:10, and incubation temperature of 25 °C. As the influent for three reactors, synthetic raw water was prepared following the recipe shown in Table 1. Sodium acetate was added to mediate TOC in the synthetic water. R3 received the influent dosed with high concentration of algae cells (16.64 × 10^8 cell/L) to mimic heavy algae contamination.

2.2. Setup of BAF system

The schematic diagram of three BAF systems (named as R1, R2 and R3) was showed in Fig. 1. All BAF systems were built using transparent polyvinyl chloride (PVC) piping and the polyvinyl plastic column. The column was 750 mm in depth and 80 mm in diameter, and its effective working volume was 2.5 L.

Zeolite, granular activated carbon (GAC), and suspended biological carrier (SBC) were selected as three filter media. R1 was packed with zeolite and GAC, while R2 and R3 were packed with zeolite, GAC, and

Table 2
Characteristics of SBC, Zeolite, and GAC.

Media	Diameter	Specific surface area ($m^2 \cdot g^{-1}$)	Pore size	Packing density ($cm^3 \cdot g^{-1}$)
SBC	5.5 cm	8.5	/	0.98–0.99
Zeolite	2–4 mm	500–800	5–20 nm	/
GAC	2–4 mm	300–400	2–5 nm	0.45–0.55

Table 3
Major operating parameters for three BAF systems.

Stages	Time(d)	Ratio of gas to liquid	HRT(h)
Stage 1	0–65	10:1	8
Stage 2	66–149	10:1	4
Stage 3	150–225	4:1	4

SBC. SBC was manufactured by Zhejiang TianYu Environmental Protection Co., Ltd., China with a diameter of 5.5 cm, a density of 0.98–0.99 $g \cdot cm^{-3}$, and a specific surface area of 8.5 $cm^2 \cdot g^{-1}$, as well as many fins enabling better suspension in water. Zeolite (JinFeng Water Purification Materials Co., Ltd., China) was granular with a diameter of 2–4 mm, a particle pore size of 5–20 nm, a specific surface area of 500–800 $m^2 \cdot g^{-1}$, and a porosity of 40–50%. GAC (JinFeng Water Purification Materials Co., Ltd., China) were also granular with a diameter of 2.4 mm, a particle pore size of 2–5 nm, a packing density of 0.45–0.55 $cm^3 \cdot g^{-1}$, and a specific surface area of 300–400 $m^2 \cdot g^{-1}$. The filter medium height of SBC, zeolite, and GAC were 400, 50, and 50 mm, respectively. The gravel supporting layer under the filter media were 30 mm in depth (Table 2).

2.3. Operation conditions for BAFs

The influent TOC and NH_4^+-N concentrations for all three BAFs were maintained at 7.81 ± 1.62 mg/ L and 5.56 ± 0.93 mg/ L, respectively. Air was introduced from the bottom of the BAF using an aerator. BAFs were run through three operation stages by controlling hydraulic retention time (HRT) and aeration intensity as indicated in Table 3. All three BAFs were started up at a gas-to-liquid ratio of 10:1 and HRT of 8 h. After 65 days, HRT was reduced to 4 h without changing the gas-to-liquid ratio. After 150 days, the gas-to-liquid ratio was reduced to 4:1 and HRT was maintained at 4 h. To remove excess biomass, periodical backwash was conducted every 48 h.

2.4. Batch experiments

Three different filter media, including zeolite (5 g), GAC (5 g), and SBC (5 g), were collected from the running R3, and inoculated into 500-

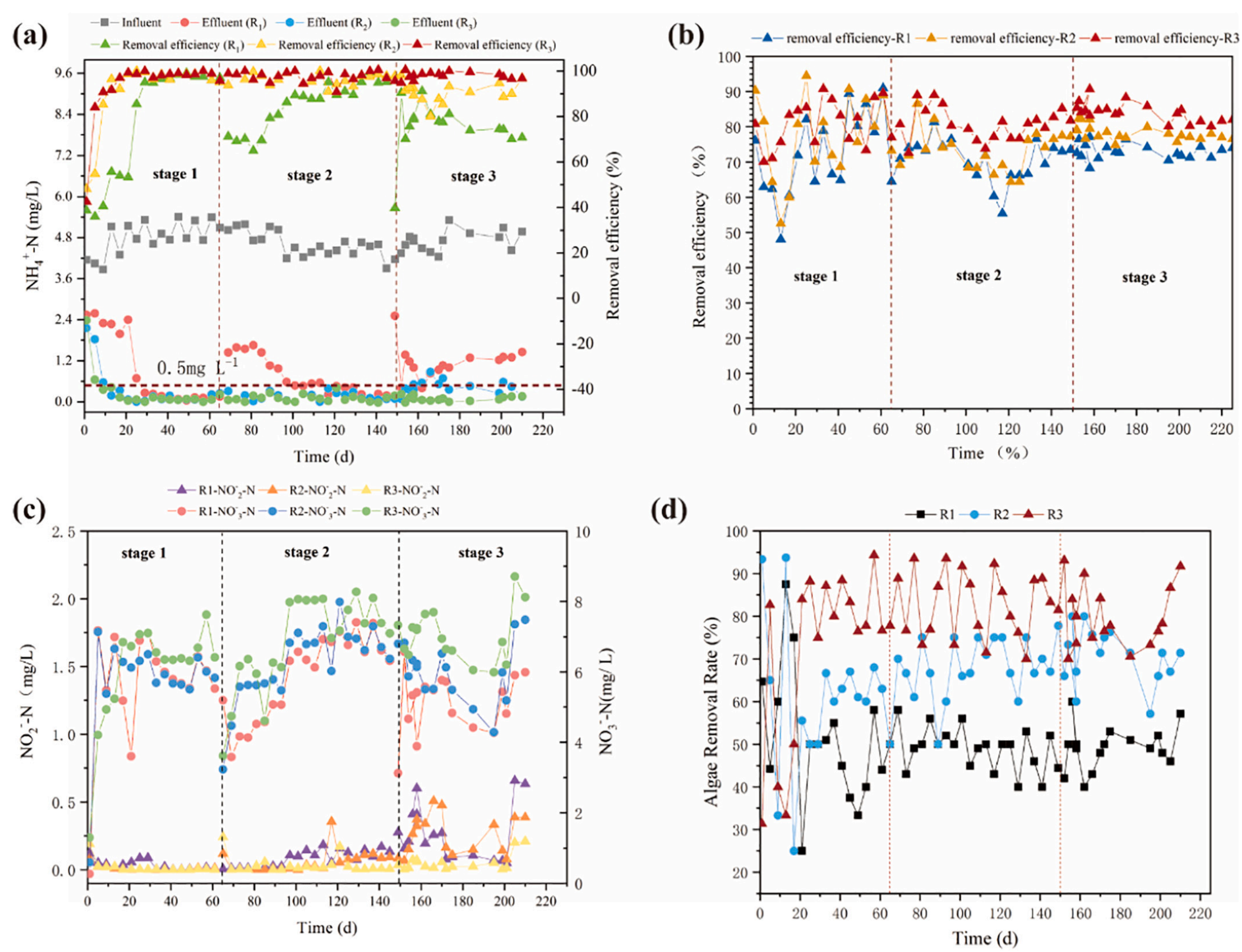

Fig. 2. Performance of three BAFs over three operation stages. (a) NH_4^+-N removal efficiency; (b) TOC removal efficiency; (c) effluent concentrations of NO_2^--N and NO_3^--N; (d) algae cells removal efficiency.

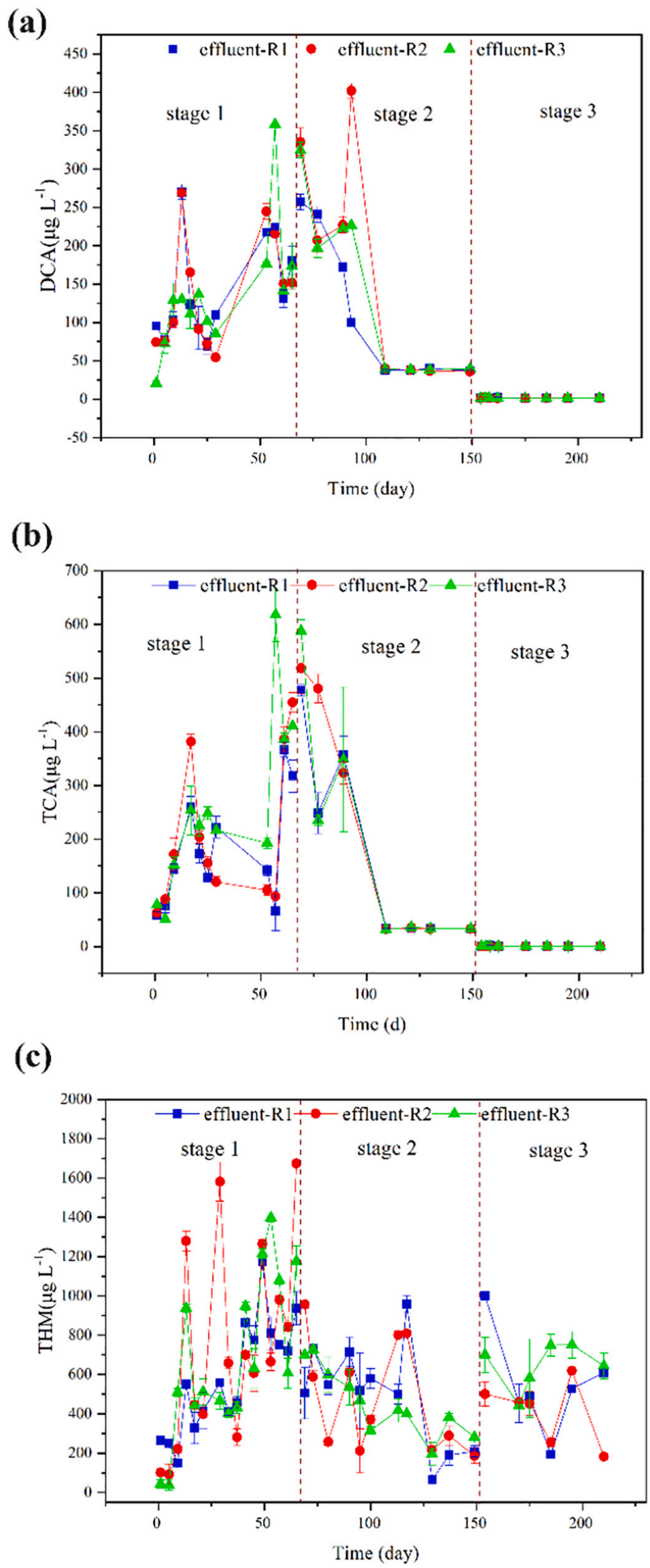

Fig. 3. DBP formation potential in effluents of three BAFs: (a) DCA; (b) TCA; (c) THMs.

mL amber glass flasks to investigate their effectiveness in removing pollutants via adsorption versus biodegradation. To investigate the adsorption extent, parallel treatments were prepared with 0.1% NaN_3 to fully prohibit the microbial activity, which thus excluded the contribution of biodegradation. All treatments were prepared in triplicate. Amber glass flasks were shaken at 150 rpm on an orbital shaker (Innova™ 2100, Platform Shaker, New Brunswick Scientific, USA) for 48 h at 25 °C. At select incubation intervals, 20 mL samples were taken and analyzed.

2.5. *Analytical methods*

Concentrations of TOC and NH_4^+-N were determined using TOC analyzer (TOC-VCPH, Shimadzu) and Nessler's reagent photometry, respectively, according to the Standard Methods issued by Chinese State Environment Protection Agency (SEPA) (Chinese SEPA, 2002). Algal cell density was estimated as follows: after fixation of algae with the Lugol's solution, samples were shaken and transferred to a blood cell counting plate for counting under a microscope (DEM, Leica-S8AP0, USA). Scanning electron microscopy (SEM, SU8010, Hitachi) was used to observe the surface morphology of biofilm formed on the SBC, GAC, and zeolite obtained from the R3. MC-LR was analyzed by high performance liquid chromatography mass spectrometry (LC-MS, Agilent-6460) after the solid phase extraction with Supelclean cartridge (6 cc, 500 mg). Trihalomethanes (THMs) were detected using gas chromatograph/mass spectrometry (GC/MS) (Agilent-6890, USA), and dichloroacetic acid (DCA) and trichloroacetic acid (TCA) were detected using gas chromatograph (GC) (Agilent-7890, USA), based on USEPA Method 524.2 [43].

2.6. *Analysis of microbial community in BAF*

Total genomic DNA was extracted from the biofilm samples on three different media using the EZNA soil DNA kit (OMEGA). DNA concentrations were determined by UV spectrophotometer (UV-2600, SHIMADZU, Japan). The primer set, 520F (5′-GCACCTAAYTGGGYDTAAAGNG-3′) and 802R (5′-TACNVGGGTATCTAATCC-3′), was used to amplify the V4 region of bacterial 16S rRNA genes. Amplicon-based sequencing was carried using Illumina MiSeq PE300 platform at Shanghai Personalbio Biotechnology Co. Ltd., China. Operational taxonomic units (OTUs) and species abundance were analyzed using QIIME (version 1.9.0). Biodiversity indexes and OTU venn were analyzed by Mothur (version 1.31.2). Principal components analysis (PCA) was conducted by R (VEGAN , ade4 , ggplot2). Microbial community structures were analyzed by MetaPhlAn (Metagenomic Phylogenetic Analysis, version 2.0).

3. Results and discussion

3.1. *TOC and nutrient removal of different BAF systems*

As shown in Fig. 2(a), NH_4^+-N removal efficiency in R1 (without SBC) noticeably decreased every time when the operation condition (e.g., HRT and gas-to-liquid ratio) was changed to the system. Contrastively, R2 and R3 showed stable NH_4^+-N removal efficiencies throughout the 225-day-long operation after the initial stabilization (~20 days). The average NH_4^+-N removal efficiencies of R1, R2, and R3 were 84.8%, 95.6%, and 97.7%, respectively. Thus, addition of SBC enhanced NH_4^+-N removal in BAFs and improved the system stability. TOC removal performances of R1, R2, and R3 through three different operation stages were showed in Fig. 2(b). The influent TOC concentrations of R1 and R2/R3 were 4.3 mg/L and 6.0 mg/L, respectively. Within the first 65 days, the TOC removal performance of R1, R2, and R3 were not stable. After 65 days, TOC average removal efficiencies of R1, R2, and R3 reached 43.4%, 51.3%, and 64.6%, respectively, indicating R3 exhibited the best performance in TOC removal.

As displayed in Fig. 2(c), relatively low NO_3^--N was detected in the effluents of three BAFs. Average concentrations of NO_3^--N in R1, R2, and R3 effluents were 5.57, 6.03, and 6.66 mg/L, respectively, meeting the Water Quality Standards of Drinking Water Sources (CJ3020–93) (<10

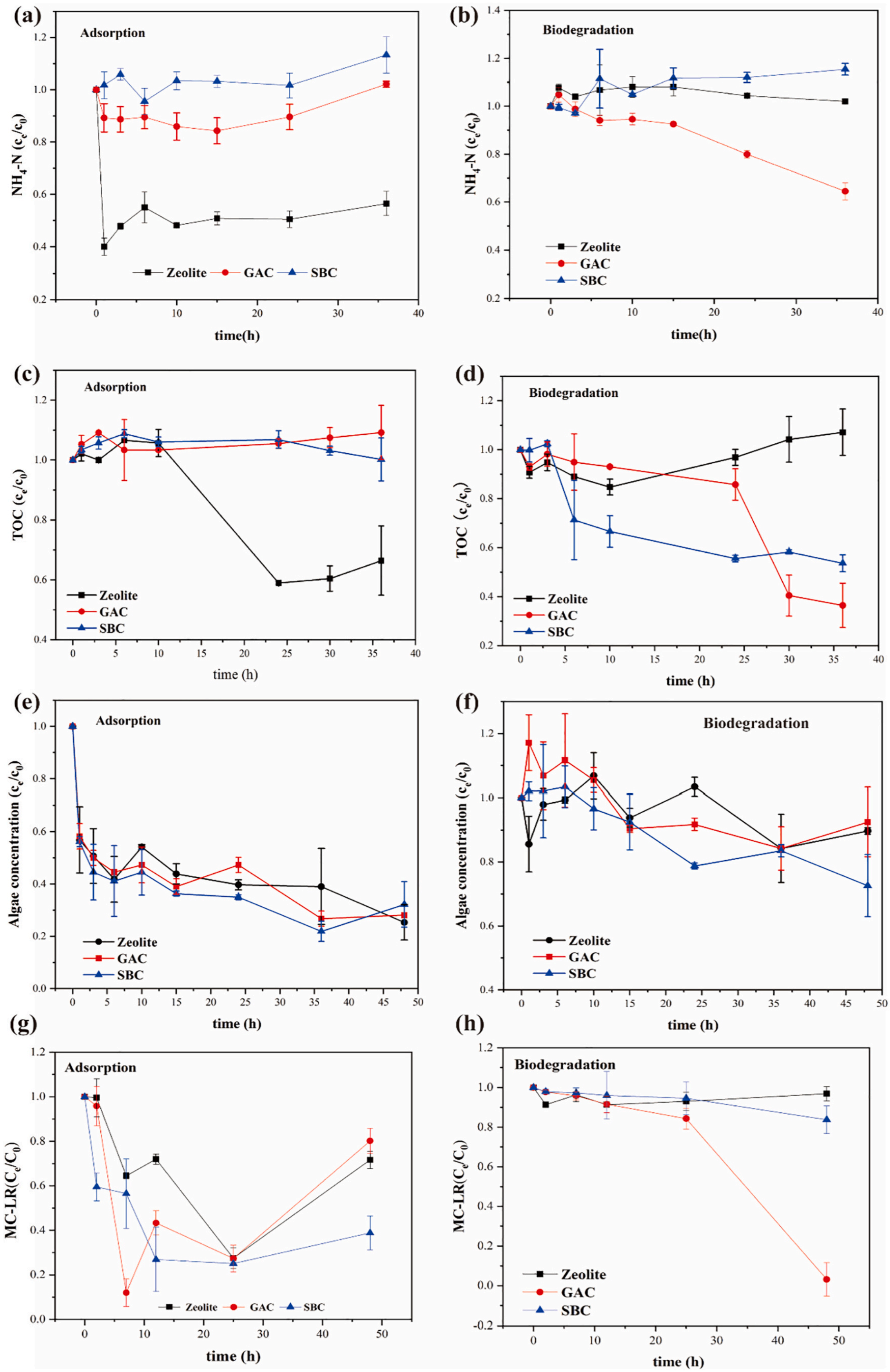

Fig. 4. Adsorption and biodegradation removals of contaminants of concern in different filter media: (a&b) NH_4^+-N; (c&d) TOC; (e&f) Algae cells; (g&h) MC-LR.

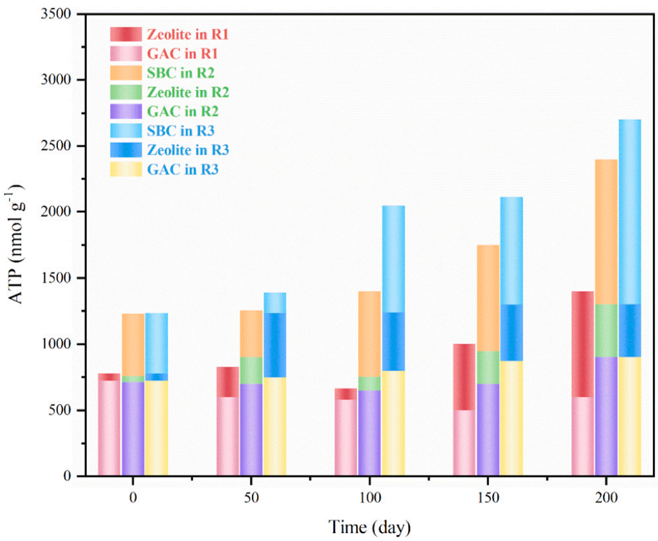

Fig. 5. ATP concentrations in different media filters of three BAF systems.

mg/L). NO_2^--N in R1, R2, and R3 effluents were minimal, with average concentrations of 0.13, 0.11, and 0.03 mg/L, respectively. These results indicated that ammonium in the influent can be efficiently transformed into nitrate during the BAF treatments without significant accumulation of nitrite. The nitrification activity of these three BAF systems was ranked as: R3 > R2 > R1.

Algae cell concentrations of R3 influent was $16.64 \pm 0.32 \times 10^8$ cell/L, which was about 8 times greater than that of R1/R2 ($1.94 \pm 0.97 \times 10^8$ cell/L). As shown in Fig. 2(d), average algae cell removal efficiencies of R1, R2, and R3 were 49.72%, 66.48%, and 78.63%, respectively. Compared to TOC and NH_4^+-N removal, algae removal showed fluctuations over the treatment for all three BAFs. R1 and R2 both received the low-algae influent and the higher algae removal efficiency of R2 could be attributed to the addition of SBC filter. R2 and R3 consisted of all three filter media and R3 performed better even under a high-level algae concentration in the long-term operations. Therefore, under a high-level algae concentration, no clogging issues was found in R3 during the long-term operations, and the algae removal performance of R3 was even enhanced by the combinations of SBC-GAC-Zeolite. This was an interesting finding and worthy of attention. Presumably, algae cells were intercepted by SBC first and thus less amount of algae entered into the GAC and zeolite filters, which reduced the clogging risk of BAF system and improved the algae removal ability. Our results demonstrated the possibility for applying BAF systems in the treatments of water that contains high concentrations of algae.

3.2. Disinfection by-product (DBP) formation potential of BAFs

Algae-laden water is prone to form DBPs due to its high content of organic matter (e.g. AOM, algae and NH_4^+-N) that may react with disinfectants in disinfection process, posing a major threat for drinking water safety. Therefore, removing corresponding precursors can effectively control DBP formations. To further assess DBP formation

Table 4
The richness and evenness indexes of SBC, GAC and zeolite biofilm communities in the R3 system.

Sample	Sequence	Chao1	ACE	Simpson	Shannon
SBC	38,886	5101.9	4950.9	0.9925	8.7658
Zeolite	19,405	2758.5	2830.4	0.9859	8.0573
GAC	26,873	3235.7	3208.7	0.9757	7.6912

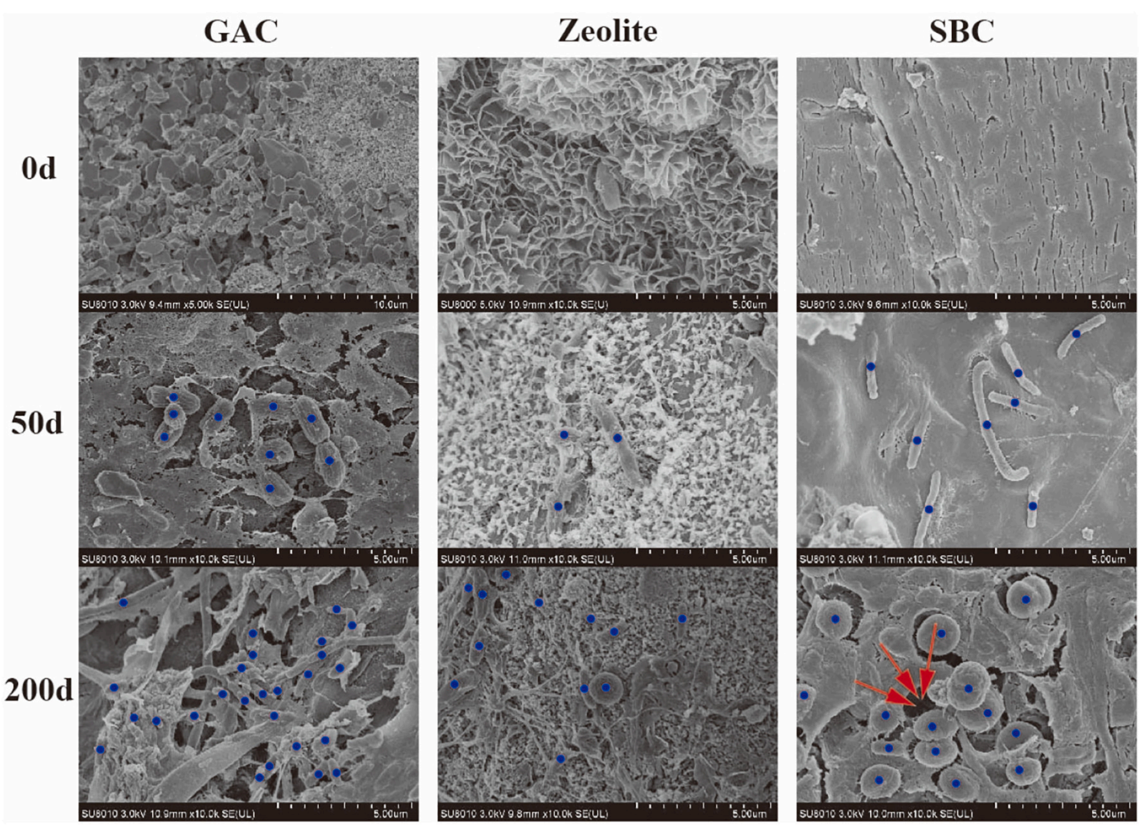

Fig. 6. SEM images of biofilms attached to the zeolite, GAC and SBC from the R3 system. (Red arrows: porous structures of SBC media; blue bots: microorganisms attached on different filter media).

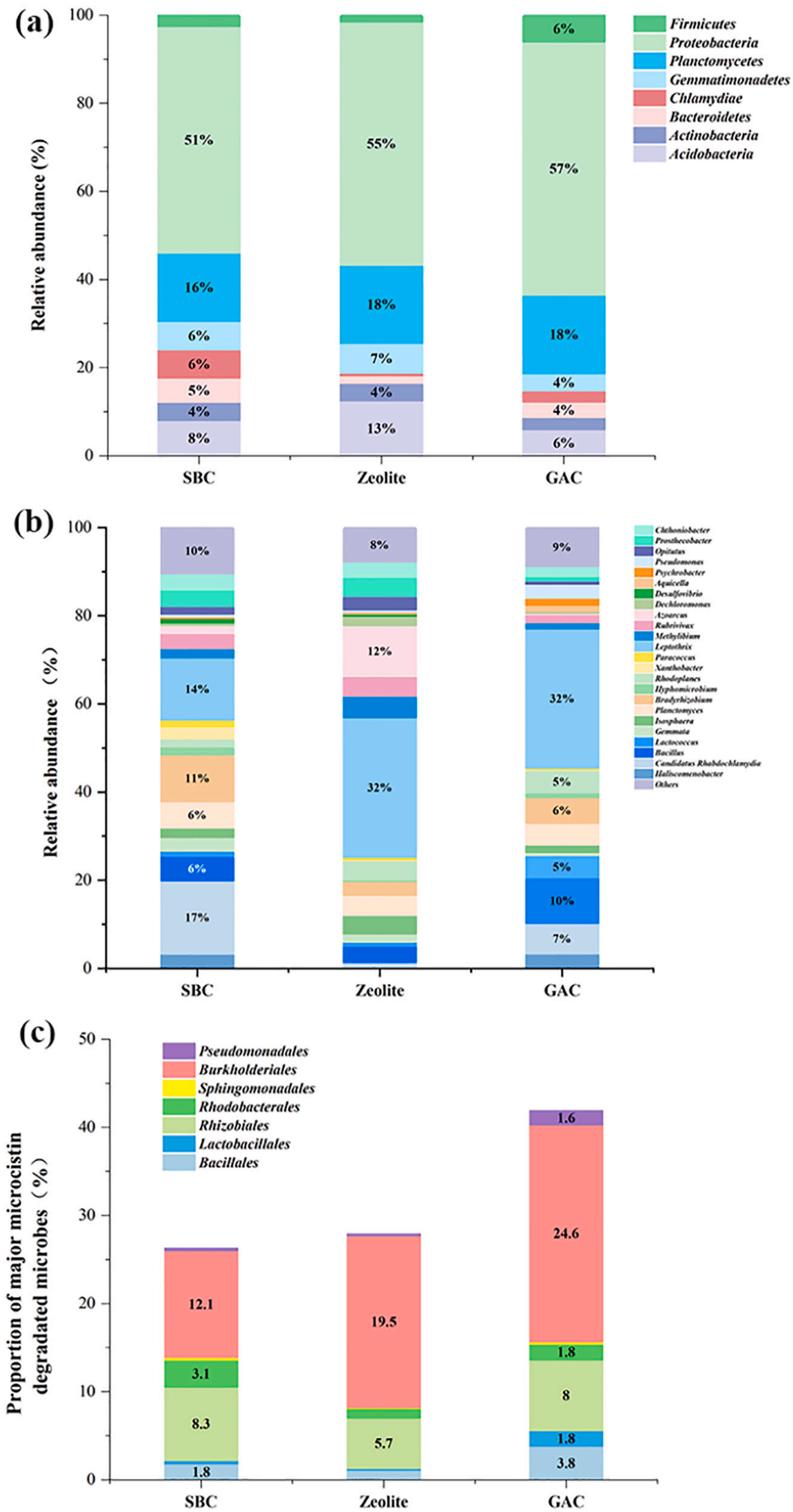

Fig. 7. The relative abundance of bacteria in the biofilms attached to SBC, GAC and zeolite from the R3 system: (a) at the phylum level; (b) at the genus level; (c) major MC degrading microorganisms at the order level.

potentials in the effluents of three BAFs, we primarily examined the formation potentials of trihalomethanes (THMs) and haloacetic acids (HAAs) (e.g. dichloroacetic acid (DCA) and trichloroacetic acid (TCA)).

As shown in Fig. 3(a) and (b), in the first two stages (ratio of gas to liquid: 10:1), the DCA and TCA formation potential in the three BAFs were high. It's probably because that high aeration intensity leads to high hydraulic shear, microbes fell off the surface of filters, and released more dissolve organic matter. After 110 days' operation, the formation of TCA and DCA decreased significantly below 50 μg/L in effluents from all three BAFs, even meeting the Standards for Drinking Water Quality

(GB5749–2006) (<700 μg/L). The concentrations of DCA in R1, R2, and R3 were 38.4, 37.9, and 39.1 μg/L, respectively. The concentrations of TCA in R1, R2 and R3 were 33.8, 33.4, and 33.8 μg/L, respectively. After 150 days, when the aeration intensity was reduced from a gas-to-liquid ratio of 10:1 to 4:1, accordant decrease in formation potentials of DCA and TCA was also observed. The average DCA concentrations were 1.71 μg/L in R1, 1.62 μg/L in R2, and 1.53 μg/L in R3, while the average TCA concentrations were 0.89 μg/L in R1, 0.72 μg/L in R2, and 0.74 μg/L in R3. Therefore, under the reduced aeration intensity, our BAF systems were effective in reducing DCA and TCA formation potentials, which could quite facilitates subsequent drinking water treatments.

As shown in Fig. 3(c), the formation potentials of THMs were higher than those observed for DCA and TCA in general. After 150 days, the average concentrations of THMs in R1, R2, and R3 were 545.3 μg/L, 411.1 μg/L, and 644.7 μg/L, respectively, which were much higher than the Standards for Drinking Water Quality (GB5749-2006) (<60 μg/L). It were probably attributed the increases of algogenic organic matter (AOM) released by dead *Microcystis aeruginosa*. As previous studies demonstrated, the DBP formation potentials by AOM at the death phase was 2.1–3.6 times than at the exponential growth phase (Park et al., 2021). Therefore, timely remove dead algae cells in the subsequent disinfections will be conducive to reduce the THM formation potentials. In addition, the reason why our BAF system was effective in reducing DCA and TCA formation potentials but had no positive effects on THM formation potentials controls should be further investigated.

In conclusion, BAF systems in this study had the pronounced positive effect on DBPs formation controls in long-term operations, especially for DCA and TCA, further highlighting the advantages of BAF applications in pretreatments of DWTPs. Although THM formation potentials showed a decreasing trend over the operation, their concentrations remained at a relatively high level, underscoring further investigation to address potential concern in the subsequent disinfections.

3.3. Biotic and abiotic removal by different filter media

As demonstrated above, R3 exhibited the best performance among the three BAFs and the filter media of SBC-GAC-Zeolite played a key role. To further investigate the specific contributions of SBC, GAC, and zeolite and their attached biofilms in the removal of NH_4^+-N, TOC, MC-LR, and algae cells, two batch experiments were prepared with individual filter media from R3 to assess their effectiveness in adsorption versus biodegradation.

As shown in Fig. 4(a), zeolite was the best in adsorbing NH_4^+-N with a removal efficiency of 50.1% at equilibrium. However, little or no contribution to nitrification was observed in biofilm-attached zeolite (Fig. 4(b)). Chang et al. [20] evaluated NH_4^+-N removal characteristics of zeolite (single media) in BAF in the treatment of textile wastewater, they estimated the adsorption contribution of in NH_4^+-N removal from zeolite (accounted for 59.8%) and also indicated a major role of adsorption, which was consistent with above results in this study. GAC adsorbed 15% NH_4^+-N and no significant NH_4^+-N adsorption was observed for SBC. Fig. 4(b) explained nitrification abilities of different filter media. Biofilm attached on GAC performed the best in nitrification among the three media and its NH_4^+-N removal efficiency was 57.1%. In the meanwhile, Lu et al. [29] in their previous studies also pointed out the importance of biodegradation in GAC media performance, besides, they found that bacterial metabolic activity of GAC biofilm could also renew the adsorption capacity of GAC. Therefore, the biodegradation played a major role in the pollutant removals of GAC filter, which also reached an agreement with this study. Overall, NH_4^+-N removals in R3 system were mainly contributed to the adsorption of zeolite and nitrification by the biofilm attached to GAC.

Fig. 4(c) showed that only zeolite showed significant adsorption of TOC with a removal efficiency of 41.01%. Meanwhile, no obvious TOC adsorptions presented in GAC, it seems to be inconsistent with the known perception of adsorption capacity of GAC. Probably, the GAC was taken from R3 (after 225 days), whose adsorption capacity decreased with the decreases/saturation of the available adsorption sites [30]. Fig. 4(d) showed that biofilms on GAC and SBC can both effectively degrade TOC with high removal efficiencies of 64.0% and 46.0%, respectively. Thus, TOC in R3 system was mainly removed by adsorption of zeolite and biodegradation of the biofilms on GAC and SBC.

Algae removal characteristics were showed in Fig. 4(e&f), there was no obvious difference in the contribution of each filter to the algae removals. Algae removal was dominated by adsorption in the three filters as compared to biodegradation. The algae cells average adsorption efficiency of the zeolite, GAC and SBC were 72.0%, 74.7% and 79.9%, respectively. Presence of algae in water is frequently accompanied with the release of microcystins. To further investigate performance of R3 system when responding high concentrations of microcystins, microcystins-LR (MC-LR) were chosen for batch experiments in this study. The initial concentration of MC-LR was dosed at 22.12 μg/L. GAC showed the highest MC-LR adsorption ability. The MC-LR concentration dropped to 2.65 μg/L after 7 h, showing a removal efficiency of 88.0%. However, the MC-LR concentration increased after 25 h, indicating its desorption from filter media. As shown in Fig. 4(h), GAC-attached biofilm had a long lag in MC-LR degradation. MC-LR was gradually biodegraded after 10 h and the removal reached 96.8% at 48 h. This indicated that the biofilm microorganisms attached on GAC had excellent ability in MC-LR biodegradation. Given the excellent adsorption and biodegradation of MC-LR by GAC, removal of MC-LR in the BAF system was probably achieved by a quick adsorption onto GAC and the subsequent biodegradation by the attached microorganisms.

Overall, different contaminants of concern were removed through the synergy of the biotic and abiotic processes contributed by three filter media and their attached biofilms. Defining removal characteristics of each filter provide scientific basis for filter material selections and facilitate future BAF filters optimizations.

3.4. Biofilm analysis

Adenosine triphosphate (ATP) is a direct energy source for all living cells. As previously reported, the active microbial biomass can be analyzed by the ATP assay since it is quick and accurate [31]. Therefore, ATP concentration was utilized to represent living microorganisms in biofilms attached on different filter media in R1, R2, and R3.

As the ATP concentration data shown in Fig. 5, gradual increase of active biomass was accumulated on the three BAF systems through the operations. The ATP concentrations of three BAFs at 200 days were: R3 > R2 > R1, indicating the R3 had the largest amounts of active biomass. The ATP increase amplitude of three filter media in R2 and R3 were: SBC > zeolite>GAC, which was consistent with the order of the three media in vertical direction. At the same time, no significant increase in active biomass on the GAC of R1 (without SBC) was observed along the operation. Therefore, the presence of SBC in BAF systems might also promote the growth of active microorganisms in GAC, accelerating the contaminant biodegradation.

In R3 system, in comparison with the pristine structure (0 day), formation of biofilms was visualized by SEM (Fig. 6) on the filters surface after 50 days. Many microorganisms were found rod-shaped and their abundance obviously increased with operations (200 days). The increase of biofilm was in good agreement with the ATP results described above. With operations, the SBC surface formed porous structures (red arrow part), which probably provide more space for pollutant adsorptions. In the meanwhile, these porous structure with vacancy intuitively proved that no obvious clogging issues presented in R3 system. Presumably, SBC formed porous structures on its surface during operations to intercept algae cells and reduce clogging issues. Zeolite presented schistose structure with the least attached microorganisms among the three filter media, suggesting the availability of adsorption sites that promote the adsorption removal as discussed above (Figs. 5 & 6).

3.5. Microbial community analysis of biofilm on different filters

High-throughput sequencing was used to analyze the microbial community structure of biofilms attached on the three media in the R3. A total of 38,886, 19,405, and 26,873 effective sequences were obtained for the biofilm samples on the SBC, zeolite, and GAC, respectively (Table 3), resulting in 2788, 1650, and 1923 operational taxonomic units (OTUs) (Supplementary information). As shown in Table 3, the indexes of Chao 1 and ACE indicated that the microbial community richness for the SBC biofilm was greater than those attached on GAC and zeolite. Simpson and Shannon indexes of biofilm on the SBC were also the highest, suggesting the high microbial diversity. Therefore, SBC enriched microorganisms with greater microbial community richness and diversity than the other two media. PC1 and PC2 explained 61.8% and 38.2% of the variance, respectively (Supplementary information). The variables of the SBC, GAC, and zeolite were distant from each other, indicating their surface microbial community structures were quite distinct from each other (Table 4).

As shown in Fig. 7(a), at the phylum level, *Proteobacteria* was the most dominant phylum in all the biofilms from three filter media, accounting for 51–57% of the total effective reads. The abundance of *Proteobacteria* and *Firmicutes* was higher in the GAC biofilm comparing with SBC and zeolite biofilms. *Proteobacteria* is widely distributed in drinking water, wastewater, soils, and sludge [6]. Many species in *Proteobacteria* are known for removing nitrogen in anaerobic, aerobic, and anoxic environments [5]. Moreover, the high abundance of *Proteobacteria* was reported to accelerate MC-LR biodegradation [32].

Three other dominant phylum included *Planctomycetes* (16–18%), *Acidobacteria* (6–13%), and *Gemmatimonadetes* (4–7%). The relative abundances of *Chlamydiae*, *Actinobacteria* and *Bacteroidetes* were higher in the SBC biofilm than those from the other two filter media. *Actinobacteria* are capable of degrading a wide span of organic and inorganic contaminants, and it plays a significant role in bioremediation [33]. As a phylum of gram-negative bacteria that are mainly distributed in anoxic environments, *Bacteroidetes* can participate in biological nitrification [34] and they are also involved in transformation of proteins and lipids [35]. Some bacteria that belong to *Planctomycetes* have the ability of denitrification and are involved in nitrogen cycle [36]. *Acidobacteria* showed a higher abundance in the zeolite biofilm than that the SBC and GAC biofilms. *Firmicutes* and *Proteobacteria* were most abundant in the GAC biofilm.

As shown in Fig. 7(b), at genus level, *Leptothrix* was the most dominant genera in the biofilms from zeolite and GAC, accounting for 32%, respectively. *Leptothrix* is a genus of sheathed filamentous bacteria that exist in different aquatic habitats as well as in wastewater treatment systems. They are capable of metal-oxidizing and accumulating iron and manganese ions into their sheaths, and therefore have been employed for iron and manganese removal in the groundwater [37]. *Azoarcus* took notably higher abundance in zeolite biofilms, as previous studies revealed, *Azoarcus* played an important role in COD removal under denitrifying conditions [38]. *Bradyrhizobium* and *Planctomyces* took higher abundance in SBC biofilm. *Bradyrhizobium* that isolated from activated sludge was capable of degrading ciprofloxacin [39]. *Planctomyces* is a kind of ANAMMOX bacteria, which can utilize NO_2^--N to oxidize NH_4^+-N and generate N_2 under hypoxic or anaerobic environment [40]. *Lactococcus* and *Bacillus* took notably higher abundance in GAC biofilms, *Lactococcus* is a genus of lactic acid bacteria, which is capable of glucose fermentation [41].

As demonstrated above, SBC and GAC were the two most microbiologically active filter media, and the microorganisms attached to them respectively played different roles in pollutant removals. GAC biofilms enriched dominant phylum that were capable of MC-LR degradations and nitrification, correspondingly played a major role in pollutant biodegradations in this study. Moreover, GAC also enriched genera of *Leptothrix* that were capable of metal-oxidizing, thus the metal removal capacity of GAC biofilm is supposed to further investigate. Compared with GAC, the microbial communities in the biofilms of SBC had different structures, SBC enriched dominant phylum that played a significant role in bioremediation and were capable of degrading a wide span of organic and inorganic contaminants. It also enriched dominant genera that were superior in degrading antibiotic. Thus SBC biofilms had the potential in multiple pollutant biodegradations, which are deserved looking forward to in the future.

As shown in Fig. 7(c), GAC accumulated the largest populations of putative microcystin degrading microorganisms, which together accounted for 41.9% (theoretical estimate). It was well aligned with the extraordinary MC-LR biodegradation by the GAC biofilm in our batch study. *Burkholderiales* (24.6%) and *Rhizobiales* (8.0%) were the two dominant orders that contain bacteria with MC degradation potentials [42]. Though previous studies reported *Sphingomonadales* can degrade MCs, such as MC-LR [32], the abundance of *Sphingomonadales* was relatively low (0.7%) in the biofilms in R3. Thus, the R3 system enriched a unique microbial community with capacity of MC biodegradation. MC removal capacity of *Burkholderiales* and *Rhizobiales* should be noticed and investigated further.

4. Conclusion

A biological aerated filter equipped with zeolite, GAC, and SBC was established for the efficient and stable pretreatment of algae-laden synthetic raw water, and NH_4^+-N, algae cells and MC-LR were effectively removed. The main contribution of zeolite was adsorption of NH_4^+-N and TOC, and GAC mainly worked in nitrification and organic biodegradation. The structure and distribution of biofilm on each media were different, SBC presented better in richness and diversity of microbial community, and GAC accumulated the most MCs degrading microbes such as *Burkholderiales* and *Rhizobiales*. Consequently, BAF with zeolite-GAC-SBC is an effective biological pretreatment process for performance stability of DWTPs.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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