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Optimization of Air Flotation and the Combination of Air Flotation and Membrane Filtration in Microalgae Harvesting

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Abstract: On account of its small size and poor sedimentation performance, microalgae harvesting is restricted from a wider application. Air flotation is an efficient and fast solid–liquid separation technology, which has the potential to overcome the impediments of microalgae harvesting. In this study, factors influencing microalgae harvesting by air flotation were investigated. The results illustrated that bound extracellular organic matter (bEOM) had a greater effect on microalgae harvesting by air flotation, compared with dissolved extracellular organic matter (dEOM). Microalgae harvesting by air flotation in different growth stages proceeded, and the effect of air flotation in the heterotrophic stage was better than the autotrophic stage. The molecular weight distributions demonstrated that after air flotation, the proportion of high MW substance increased, while the proportion of low MW substance decreased, regardless of whether dEOM or bEOM. Membrane filtration was carried out for the algal solutions before and after air flotation. The membrane of pre-flotation algal solution had a higher critical flux of 51 L/m^2·h than that of no-pre-flotation (24 L/m^2·h), and, thus, pre-flotation had an active effect on membrane filtration in microalgae harvesting. Moreover, the combination of air flotation and membrane filtration provided an efficient technology for microalgae harvesting.

Keywords: microalgae harvesting; air flotation; EOM; pre-flotation; membrane filtration

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1. Introduction

Traditional sewage treatment has many shortcomings such as a high cost and waste of energy. In recent years, more and more researchers are committed to the use of microalgae in sewage treatment [1,2]. Microalgae have a short growth period and a good absorption capacity for nitrogen and phosphorus in sewage. Microalgae can not only realize the sewage treatment but also produce many high value-added products [3]. The reduction in energy and costs associated with this process has the potential to make algal biofuels more economically competitive in the market [4].

In addition, greenhouse gas emissions, energy security and fossil fuel depletion, also have aroused people's attention. Microalgae can stabilize the CO_2 content in the atmosphere, and research on CO_2 sequestration by microalgae has attracted attention across the globe [1,5]. The biorefineries from microalgae can produce biodiesel, which is renewable and environmentally friendly, is expected to replace traditional fossil fuels and, thus, alleviate the energy crisis. Microalgal biorefineries could be effective for reducing the demand for fossil fuel and, thus, reduce greenhouse gas emissions, which mitigates the problems associated with global warming and climate changes [1,6]. However, microalgae are small and difficult to harvest, which becomes a major bottleneck and limits widespread use [7–9]. There are many technologies of microalgae harvesting, mainly including centrifugation, membrane filtration, coagulation and flocculation [10–15], however, most of these methods are of low efficiency and have high costs and high energy consumption. So, searching for new solutions is the next priority.

Air flotation has the advantages of fast operation speed, low space requirement, high flexibility and moderate operation cost, so it has the potential to overcome the obstacle

of microalgae biofuel production [16,17]. Air flotation is an efficient and fast solid–liquid separation technology, which was initially used mainly in beneficiation. Due to its simplicity and high efficiency, flotation is also used for oil sands separation, wastewater treatment and print links in paper recycling [18]. In the 1920s, air flotation technology began to appear in the field of water treatment. Flotation has also become one of the most popular techniques for algae harvesting from drinking water. At present, air flotation is extensively used in microalgae harvesting [17,19]. Air flotation can use gas bubbles to effectively capture particles up to 500 μm in water solution. It is an effective method for microalgae harvesting to utilize the low density and self-floating qualities of microalgae [20]. Microalgae are difficult to precipitate and have a certain hydrophobic effect, thus, it is easy to combine with microbubbles and float to the surface for harvesting. Therefore, air flotation is suitable for microalgae harvesting.

In this study, the effects of aerator pipe diameter, aeration rate, water depth, temperature, growth stage and the amount of air flotation on microalgae harvesting by air flotation were investigated, and comprehensive optimization was performed to determine the best operating conditions of the process. In order to verify the effects of dEOM and bEOM on microalgae harvesting by air flotation, 5 min air flotation experiments the raw were conducted with dEOM-extracted and bEOM-extracted solutions. dEOM and bEOM of microalgae solutions before and after air flotation were both detected. The combination of air flotation and membrane filtration was analyzed, which provided an efficient technology for microalgae harvesting. It is hoped that this study can offer a reference for microalgae harvesting by air flotation and a direction for membrane filtration.

2. Materials and Methods

2.1. Cultivation of Microalgae

Chlorella pyrenoidosa (*C. pyrenoidosa*, FACHB-9) was obtained from the Institute of Hydrobiology at the Chinese Academy of Sciences. Basal medium was compounded in sterile distilled water and used for *C. pyrenoidosa* cultivation. The microalgae were inoculated in glass flasks and placed in incubators [21]. The rest of the conditions were as follows: temperature was kept at 30 ± 0.5 °C; light intensity was 127 μmol/m^2 s; and light/dark was 14 h/10 h.

2.2. Experimental Setup

Laboratory-scale air flotation and filtration experiments proceeded in the device shown in Figure 1. The experimental device was homemade. Air flotation experiments were conducted in a flotation column, with an inner diameter of 4 cm and a height of 30 cm. Air was supplied using an aerator and the aeration rate was measured by a rotameter. The air from aerator pipe passed through sintered disc, which was installed on the bottom of the flotation column to release gas bubbles. In addition, manual collection was needed to gather the supper phase. Filtration experiments were proceeded in a filtration tank of 4 L to study the effect of pre-flotation on membrane filtration. To reduce membrane fouling, a micro-porous pipe was installed on the bottom of the membrane. In addition, 6 L/min was selected as the aeration flow rate. A hydrophilic PVDF membrane (Minglie, Shanghai, China) was used in the filtration, with a pore size of 0.1 μm and an effective filtration aera of 0.02 m^2. The filtrate was pumped using a peristaltic pump (BT100-LJ, Kejian, China). The volume and flow velocity of filtrate were recorded by an electronic balance connected to a computer. A vacuum meter was installed to measure the transmembrane pressure (TMP).

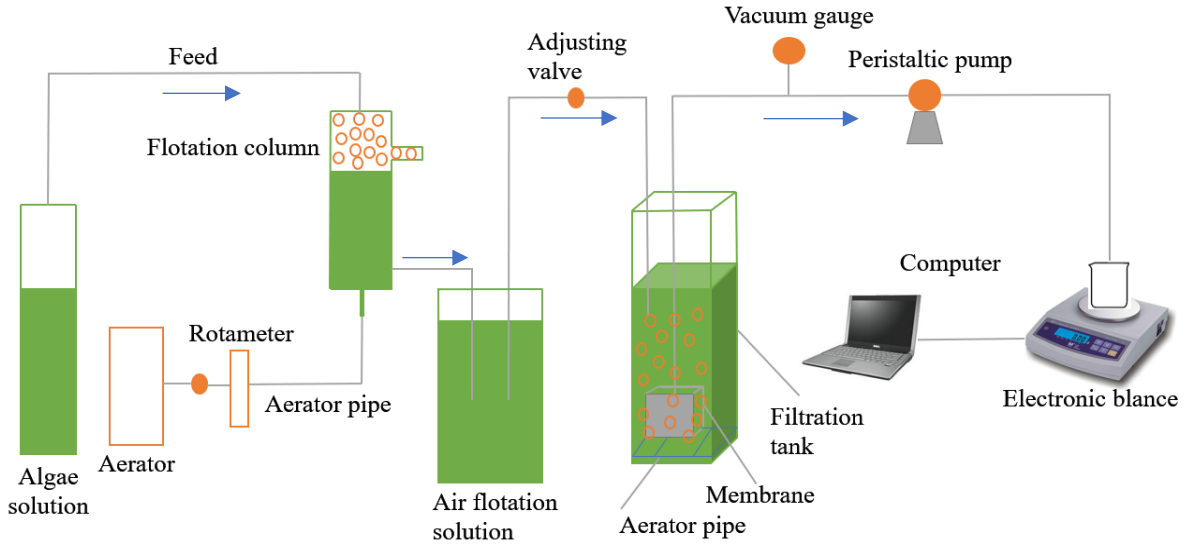

Figure 1. Schematic diagram of the experimental setup in the flotation and filtration experiments.

2.3. Optimization of Air Flotation Experiments

Effects of aerator pipe diameter, aeration rate, water depth and temperature on microalgae harvesting by air flotation were investigated, and the algae used in flotation was cultivated for 10 days. To detect the effect of aerator pipe diameter on air flotation, three aerator pipes were utilized in flotation experiment, and the conditions were as follows: aeration rate was 240 L/h, water depth was 16 cm, and temperature was 25 °C. Then, the impact of aeration rate on flotation was observed, and the conditions were as follows: aerator pipe diameter was 0.25 mm, water depth was 16 cm, and temperature was 25 °C. The influence of water depth on air flotation was also detected, and the conditions were as follows: aerator pipe diameter was 0.25 mm, aeration rate was 240 L/h, and temperature was 25 °C. The air flotation experiment proceeded in three different temperatures to observe the impact of temperature on flotation, and the conditions were as follows: aerator pipe diameter was 0.25 mm, aeration rate was 240 L/h, and water depth was 24 cm. Finally, effects of growth stage and the number of air flotation on microalgae harvesting by air flotation were conducted in the following conditions: aerator pipe diameter was 0.25 mm, aeration rate was 240 L/h, water depth was 24 cm, and temperature was 25 °C.

2.4. Filtration Experiments

Membrane filtration was carried out for the algal solutions before and after air flotation to investigate the effect of pre-flotation on membrane filtration in microalgae harvesting. The critical flux (J_C) was determined using an improved flux-step method (IFM) [22]. The initial flux, step height and step duration applied in critical flux tests were set as 15 L/m^2·h, 3 L/m^2·h and 15 min, respectively. In this research, an arbitrary minimum increase in the TMP ($\Delta P/\Delta t$) of 20 Pa/min was regarded as a reasonable estimate of critical flux. In the critical flux tests, there were two phases, which were called the ascending phase and the descending phase, respectively. In the ascending phase, critical flux was achieved when the membrane flux (J_H) increased; in the descending phase, J_H decreased stepwise and could achieve fouling condition. The continuous filtration was conducted for 24 h, and the initial flux was set as 24 L/m^2·h, which was the J_C of membrane in no-pre-flotation algal solution. When flux was kept constant at the initial flux, the membrane will be severely fouled in several hours during continuous filtration experiment, and filtration cannot be conducted for long periods. Thus, the peristaltic pump was kept at a constant speed in 24 h filtration experiments [23].

2.5. Analytical Methods

In this study, EOM was divided into dEOM and bEOM and extracted from algae solution by centrifugation method. Generally, EOM is extracted in two steps. First, two algae solutions (5 mL) were both centrifuged at 4000 rpm for 15 min in a high-speed centrifuge (CT15RT, Shanghai, China), and the supernatants were filtered through a 0.45 μm filter to obtain the dEOM. One dEOM was used to analyze its composition. Then, another dEOM was redissolved into the residual algae solution, and the solution, which achieved 5 mL by adding to basal medium, was centrifuged at 10,000 rpm for 15 min and subsequently filtered through a 0.45 μm filter to obtain the bEOM [24]. TOC, polysaccharides and proteins in dEOM were presented by d-TOC, d-polysaccharides and d-proteins, respectively; TOC, polysaccharides and proteins in bEOM were presented by b-TOC, b-polysaccharides and b-proteins, respectively.

TOC was measured using a total organic carbon analyzer (TOC-V_{CPH}, Shimadzu, Japan). The content of proteins was measured by the modified Lowry method, and the anthrone-sulfuric acid method was utilized to measure the concentration of polysaccharides. The concentration of *Chlorella pyrenoidosa* was measured using the OD_{680} method, and the concentration was in dry weight. The hydrophobic microalgae concentration was measured by using the modified adherence-to-hydrocarbon method [25]. The recovery rate (R) of microalgae was calculated by the following equation:

$$R = (c_{x0} - c_X)/c_{x0} \cdot 100\% \quad (1)$$

where c_{x0} (g/L) and c_X (g/L) represent the algae concentration before and after air flotation, respectively. The zeta potential of algae cells was determined using the dynamic light scattering (DLS) with a Malvern Zetasizer NANO ZS (Malvern Instruments Limited, Malvern, UK) at 25 °C. Fluorescence excitation–emission matrix (EEM) spectra was determined using a Fluorescence Spectrophotometer (F-4500, Hitachi, Tokyo, Japan) and before EEM analysis started, the pH of dEOM and bEOM solutions were regulated to about 7.0 ± 0.1 [26]. The molecular weight (MW) distribution of dEOM and bEOM were analyzed by high performance size exclusion chromatography (LC-10AD, Shimadzu, Kyoto, Japan) [27].

2.6. Statistical Analysis of Data

To verify the optimal conditions of microalgae harvesting by air flotation, the air flotation experiments under different conditions were each carried out once. The air flotation experiments under optimum conditions were conducted with three independent replicates. The values of algae concentration, microalgae recovery rate and EOM contents are all the mean of three replicates, and the averages were compared using the multiple range test at $p < 0.05$ to identify significant differences among the different treatments. The pH and zeta potential experiments were conducted with three independent replicates. The experiment with the best flotation effect of three replicates was selected for EEM spectra and MW distribution analysis. The filtration experiments were carried out once.

3. Results and Discussion

3.1. Optimization of Air Flotation Experiments

There are many factors affect air flotation and then influence the microalgae harvesting. In this study, aerator pipe diameter, aeration rate, water depth, temperature, growth stage and the number of air flotation were investigated and are shown in Figure 2. The diameter of aerator pipe can greatly affect the size of the air bubbles, and the larger the diameter is the larger the bubbles [28]. The size of the bubbles has an important impact on air flotation. As shown in Figure 2a, three different aerator pipe diameters were utilized in the air flotation experiments. After 90 min of flotation, the microalgae recovery rate of 0.25 mm was 32.61% (the algae concentration declined from 0.46 to 0.31 g/L), higher than that of 0.5 mm (23.91%, the algae concentration declined from 0.46 to 0.35 g/L) and 1 mm (19.57%, the algae concentration declined from 0.46 to 0.37 g/L). It was illustrated that a smaller

bubble size was more effective for microalgae harvesting compared with a larger bubble size. That was because a smaller bubble size may generate low buoyancy and create a small disturbance to the water, resulting in a long retention time in liquid and adequate contact between algae and bubbles [29].

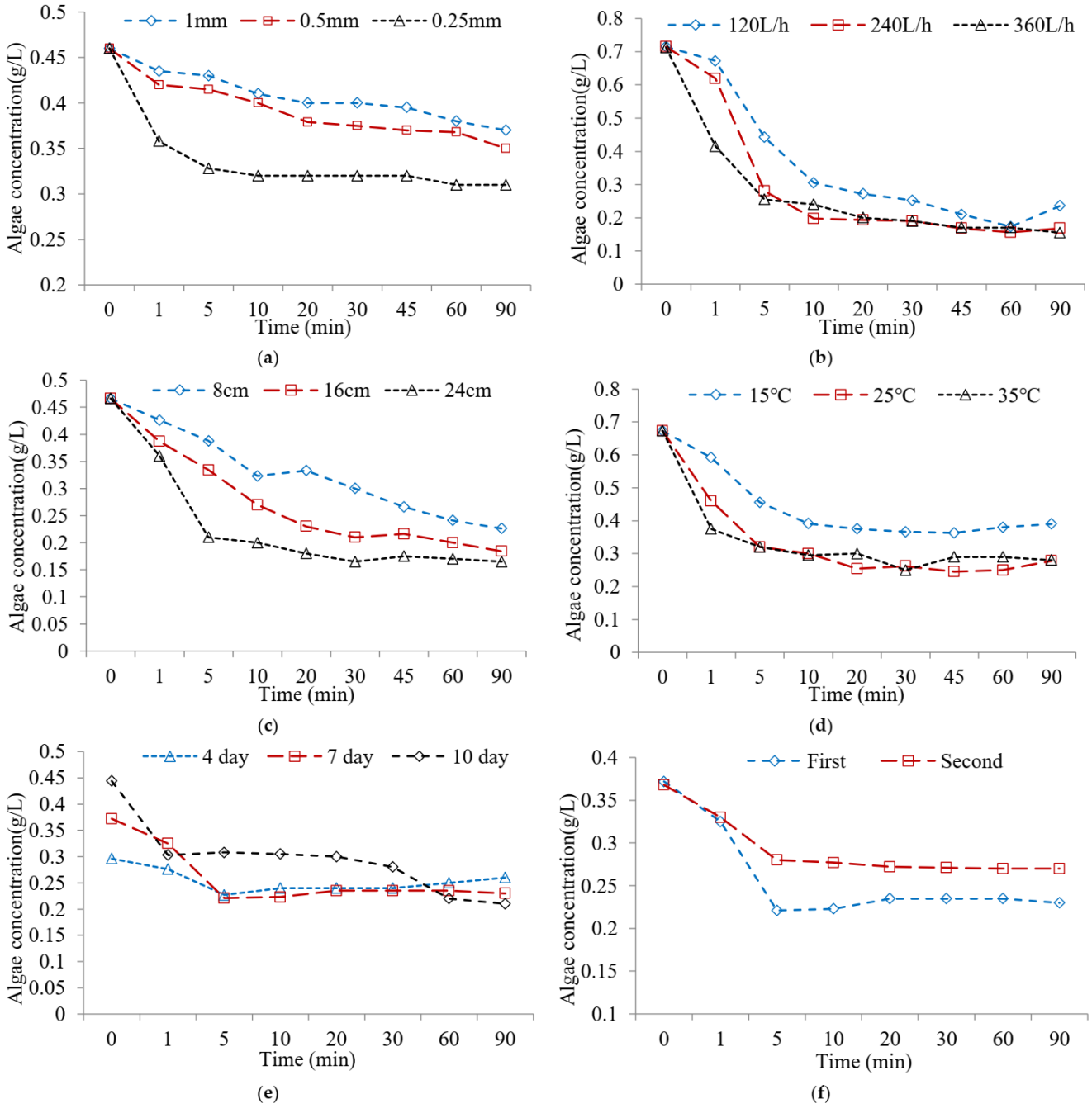

Figure 2. Factors influencing the algae concentration by air flotation: (**a**) aerator pipe diameter; (**b**) aeration rate; (**c**) water depth; (**d**) temperature; (**e**) growth stage; and (**f**) the number of air flotation.

As shown in Figure 2b, during the initial 5 min, the microalgae recovery rate of 360 L/h was 64.19% (the algae concentration declined from 0.712 to 0.255 g/L), higher than that of 120 L/h (37.92%, the algae concentration declined from 0.712 to 0.442 g/L) and 240 L/h (60.67%, the algae concentration declined from 0.712 to 0.28 g/L). The gas–liquid contact area extended as the aeration rate improved, which enhanced the collision and adhesion of the bubbles and algae. However, after 5 min, the algae concentration declined slowly,

and the curves of 240 and 360 L/h were almost the same, illustrating aeration rates of 240 and 360 L/h had a uniform impact on microalgae harvesting. That was because when the aeration rate was 360 L/h, the solution produced abundant bubbles and disturbances, which led to a large amount of gas being released to the air that could not be effectively utilized. Therefore, from an economic point of view, reducing the aeration rate can lessen energy consumption, and an aeration rate of 240 L/h was more appropriate for algae harvesting in comparison with 120 and 360 L/h. The greater the water depth is, the longer the gas–liquid contact time, which is conductive to the adhesion of the air bubbles and algae. As demonstrated in Figure 2c, the microalgae recovery rate increased with the water depth raised from 8 to 24 cm. After 5 min of air flotation, the microalgae recovery rate of 24 cm was 54.94% (the algae concentration declined from 0.466 to 0.21 g/L), much more than that of 8 cm (16.74%, the algae concentration declined from 0.466 to 0.388 g/L) and 16 cm (28.33%, the algae concentration declined from 0.466 to 0.334 g/L), illustrating that a water depth of 24 cm has the largest recovery rate for microalgae, compared with 8 and 16 cm.

The impact of temperature on air flotation is mainly reflected in three aspects: surface tension, interface adsorption and foam stability. Microalgae used in this experiment were cultivated at temperatures of 15, 25 and 35 °C, respectively. As shown in Figure 2d, after 30 min of air flotation, the microalgae recovery rate of 35 °C achieved the highest percentage (62.85%), and the concentration was 0.25 g/L. When the air flotation was conducted for 45 min, the microalgae recovery rates at 15 and 20 °C were 46.06% and 63.60%, so both achieved the highest, and the algae concentrations were 0.363 and 0.245 g/L, respectively. When the temperature was lower, the viscosity of water became larger and the floating rate of air bubbles became slower. While, as the temperature increased, the gas–liquid interface tension and foam stability increased and the adsorption rate of the interface accelerated, contributing to the efficiency of microalgae harvesting improving. However, the air bubbles were more likely to release into the atmosphere when the temperature increased. Thus, it was vital to select a suitable temperature for algae harvesting by air flotation. As demonstrated in Figure 2d, 25 °C was the optimal temperature compared with 15 and 30 °C.

Microalgae cultivated for 4, 7 and 10 days were used in this experiment, respectively. As shown in Figure 2e, the initial concentration of algae in different growth stages were distinct. After 5 min of flotation, for the growth of 4, 7 and 10 days, the microalgae recovery rates were 23.31% (the algae concentration declined from 0.296 to 0.227 g/L), 40.59% (the algae concentration declined from 0.372 to 0.221 g/L) and 30.63% (the algae concentration declined from 0.444 to 0.308 g/L), respectively. This was because the algae cultivated for 10 days had more hydrophobic algae compared with 4 and 7 days. With the flotation time extended, the algae concentration of 4 and 7 days both had a modest increase, illustrating that the water film layer between bubbles was likely to break due to the prolonged air flotation, and the algae desorbed from the bubbles and returned to the liquid. Microalgae harvested from air flotation were redissolved into the liquid, and then the second flotation of algae was conducted. From Figure 2f, it could be seen that the efficiency of microalgae harvesting by first air flotation was obviously higher than the second flotation. That was possibly ascribed to the surface properties of the algae changing after flotation [16] and becoming difficult to adhere to the bubble surface, which contributed to the recovery rate decreasing. In air flotation, if the microalgae are not collected in time, part of the microalgae will be dissolved into the algal liquid again, resulting in secondary floatation, thus reducing the efficiency of the floatation. Therefore, it is necessary to collect the microalgae immediately after they are lifted by the air, so as not to reintegrate the microalgae into the algae liquid and reduce the air flotation efficiency.

3.2. Effects of dEOM and bEOM on Microalgae Harvesting by Air Flotation

In order to verify the effects of dEOM and bEOM on microalgae harvesting by air flotation, a 5 min air flotation experiment was conducted on the raw dEOM-extracted

and bEOM-extracted solutions. As shown in Table 1, for the raw solutions, the recovery rate of microalgae by 5 min air flotation was 90.74%, higher than the dEOM-extracted solution (76.54%) and the bEOM-extracted solution (28.40%). It was illustrated that dEOM and bEOM both had an effect on air flotation; in addition, bEOM had a greater effect on microalgae harvesting by air flotation, compared with dEOM. That was because the main components of bEOM were proteins and polysaccharides [26], which affected the efficiency of air flotation.

Table 1. The recovery rates of microalgae for the raw dEOM-extracted and bEOM-extracted solutions. The values of algae concentration and recovery rate are both the mean of three replicates. Means values and standard deviations are presented.

	Algae Concentration (g/L)		Recovery Rate (%)
	Initial	Final	
Raw solution	0.81 ± 0.045	0.075 ± 0.004	90.74 ± 5.7
dEOM extracted	0.81 ± 0.045	0.19 ± 0.001	76.54 ± 5.1
bEOM extracted	0.81 ± 0.045	0.58 ± 0.037	28.40 ± 2.2

3.3. Microalgae Harvesting by Air Flotation in Different Growth Stages

Microalgae of different growth stages (autotrophic 30 and 100 days; heterotrophic 4; 7, 10 and 15 days) were harvested by air flotation. It can be seen from Figure 3 that the higher the proportion of hydrophobic microalgae is, the higher the recovery rate of microalgae. The reason is that hydrophobic microalgae provided a sufficient hydrophobic surface for the adhesion of the bubbles [30], contributing to the combination of bubbles and microalgae, hence, the recovery rate of microalgae was improved [31].

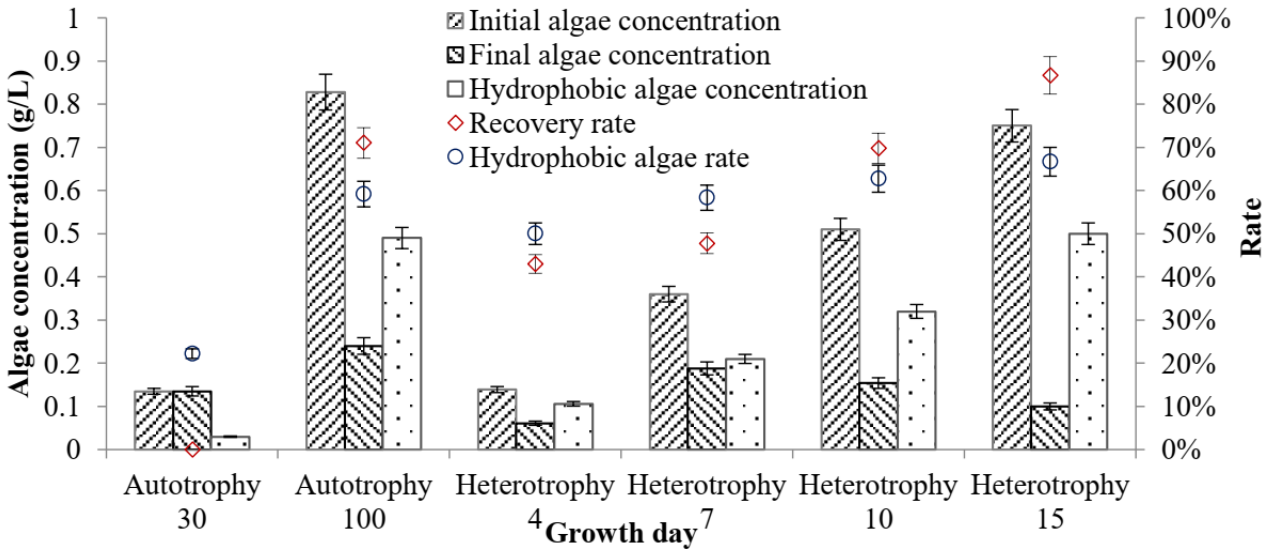

Figure 3. Recovery rates of microalgae in different growth stages.

On account of bEOM having a great effect on microalgae harvesting by air flotation, the composition of bEOM released by microalgae of different growth stages was analyzed. As demonstrated in Figure 4, the content of bEOM in autotrophic 30 days was obvious lower than the heterotrophic stage, illustrating the faster growth rate of microalgae in the heterotrophic stage [32]. The content of b-proteins was lower than b-polysaccharides in autotrophic 30 days, while the b-proteins was much higher than the b-polysaccharides in autotrophic 100 days and the heterotrophic stage. Most carbohydrates or polysaccharides are hydrophilic and most proteins are hydrophobic [4]. Once released by microalgae, the protein-like substances produced surface activity and combined with bubbles to change the bubble characteristics. The surface of the air bubbles that bound with proteins became

more and more hydrophilic, contributing to more hydrophilic algae cells that adhere to the bubbles. Therefore, the effect of microalgae harvesting by air flotation in the heterotrophic stage was better than the autotrophic stage.

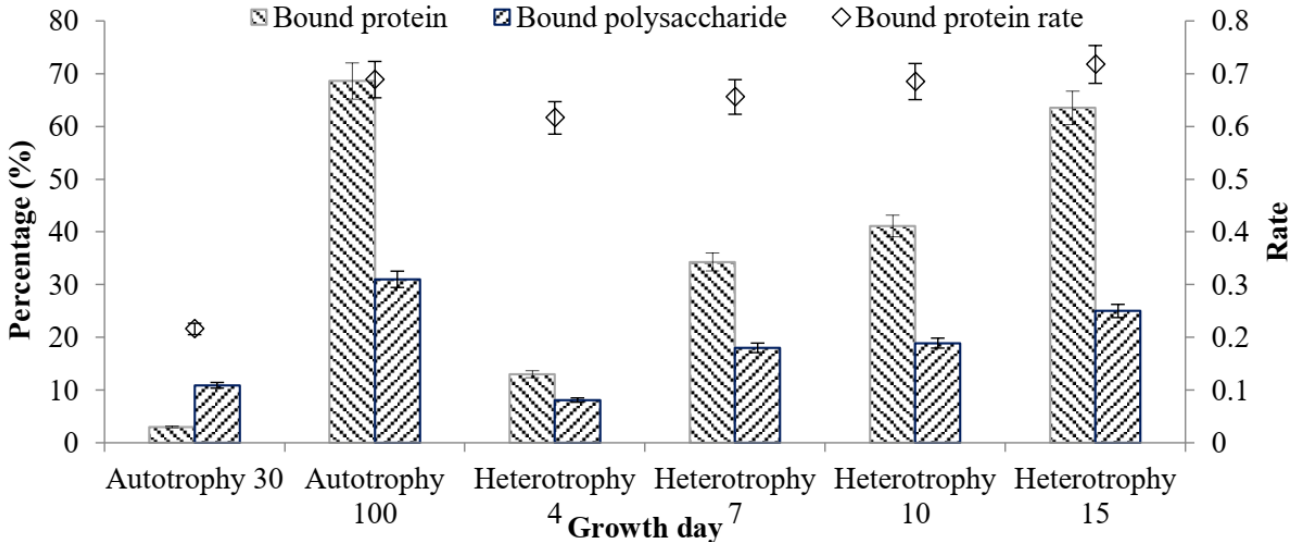

Figure 4. The contents of bEOM released by microalgae in different growth stages.

Zeta potential (ζ) is a vital element to characterize the surface properties of the particles (microalgae) in air flotation, since it is determined by the surface charge of the particles and by the adsorbed matter at the particle surface. Zeta potential reflects the interaction between particles, and a system with high zeta potential stays in a relatively stable condition. While the repulsive force between particles in a system with low zeta potential is small, the particles are prone to aggregation and sedimentation, which makes the microalgae easy to destabilize and adhere to microbubbles, contributing to the high recovery rate of microalgae in the air flotation experiment [33]. From Figure 5, the zeta potential of microalgae in different growth stages was investigated, and the higher the $|\zeta|$ is, the higher the recovery rate, so the result was inconsistent with this view. Therefore, it could be concluded that zeta potential was not an important factor affecting microalgae recovery rate.

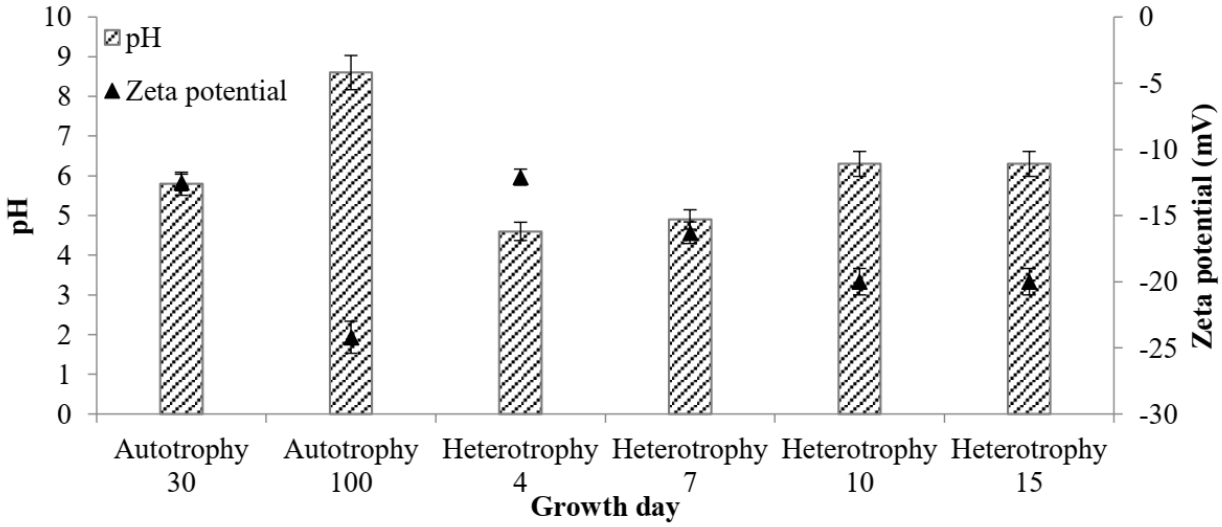

Figure 5. Zeta potential of microalgae in different growth stages.

3.4. Characterization of EOM

3.4.1. Contents of dEOM and bEOM

The contents of dEOM and bEOM in microalgae solutions before and after flotation are presented in Table 2. As shown in Table 2, the TOC, polysaccharides and proteins concentrations of dEOM were all higher than that of bEOM, whether before or after air flotation. After flotation, the reduction rate of b-TOC was 17.84% (from 52.9 to 43.46 mg/L), which is lower than d-TOC (20.27%, from 497.8 to 396.9 mg/L), while the reduction rates of the b-polysaccharides and b-proteins were 17.57% (from 19.18 to 15.81 mg/L) and 25.47% (from 24.22 to 18.05 mg/L), respectively, and those of the d-polysaccharides and d-proteins were 1.99% (from 78.85 to 77.28 mg/L) and 3.20% (from 96.54 to 93.45 mg/L), respectively. The reduction rates of the b-polysaccharides and b-proteins were both higher than the d-polysaccharides and d-proteins. It was illustrated that the reduction rate of bEOM was higher than dEOM, and, thus, the effect of bEOM on air flotation was larger than dEOM. In addition, the reduction rate of d-TOC was the highest compared with that of the d-polysaccharides and d-proteins, and the reduction rate of the b-proteins was the highest compared with that of b-TOC and b-polysaccharides.

Table 2. The contents of dEOM and bEOM in microalgae solutions before and after air flotation. The values of TOC, polysaccharides and proteins are all the mean of three replicates. Means values and standard deviations are presented.

		TOC (mg/L)	Polysaccharides (mg/L)	Proteins (mg/L)
Raw solution	dEOM	497.8 ± 28.9	78.85 ± 4.05	96.54 ± 5.56
	bEOM	52.9 ± 3.41	19.18 ± 1.23	24.22 ± 1.12
After flotation	dEOM	396.9 ± 22.37	77.28 ± 4.16	93.45 ± 4.77
	bEOM	43.46 ± 2.03	15.81 ± 0.77	18.05 ± 0.98

3.4.2. EEM Spectroscopies of dEOM and bEOM

On account of the high efficiency and convenience performance, EOM components have been widely characterized by EEM [34], however, it is difficult for EEM to detect polysaccharides [26]. As shown in Figure 6, Peak T_1 is relevant to protein-like (at an emission (Em) wavelength of 340–350 nm from excitation (Ex) of 220–275 nm); peak C and peak A are both relevant to humic-like (at Em wavelength of 420–450 nm from Ex of 230–260 and 320–350 nm) [35,36].

The fluorescence EEM spectra for dEOM and bEOM of the raw and flotation solutions are presented in Figure 6. For raw EOM, three peaks of dEOM were all more obvious than those of bEOM, illustrating that the contents of the d-proteins and d-humic-like were both higher than those of the b-proteins and b-humic-like. As shown in Figure 6, for flotation dEOM, the intensity of peak T_1 decreased but the intensities of peak A and C increased, demonstrating that d-proteins could be removed by air flotation. For flotation bEOM, the intensities of peak T_1, A and C all declined, illustrating bEOM could be effectively removed by air flotation, and the b-proteins had the optimal removal effect. The results were consistent with Table 2.

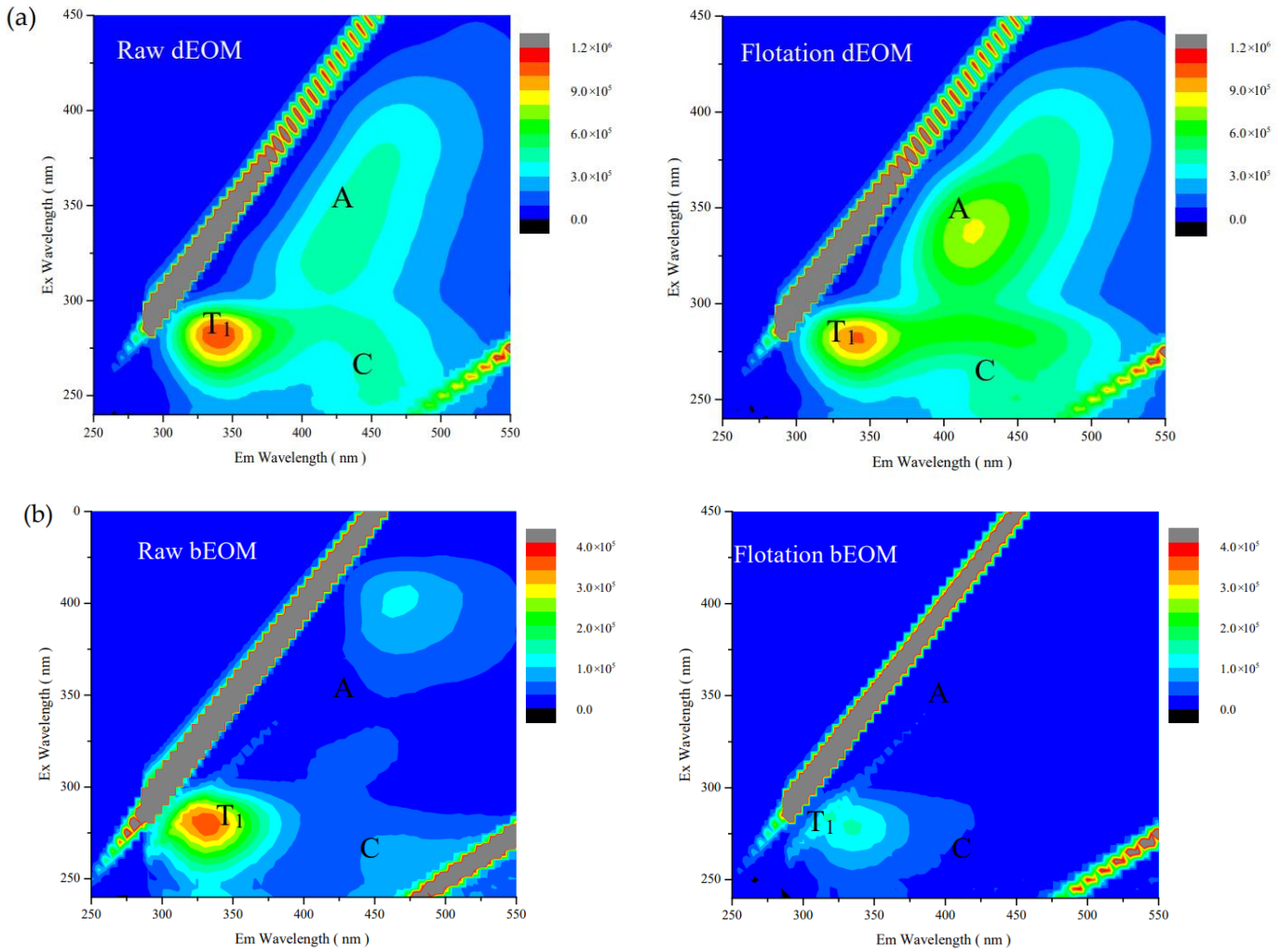

Figure 6. Fluorescence EEM spectra for (**a**) dEOM and (**b**) bEOM before and after air flotation.

3.4.3. Molecular Weight Distributions of dEOM and bEOM

MW distributions of dEOM and bEOM are presented in Figure 7a,b. It can be observed that MW distribution at 1–10 kDa was hardly detected, in accordance with a previous study that reported that EOM secreted by microalgae hardly contained MW distribution at 1–10 kDa [37]. For raw and flotation dEOM, there were three peaks (approximately 100 kDa, 25 kDa and 500 Da) of MW distribution. In addition, MW peak at 500 Da of flotation dEOM was lower than that of raw dEOM, demonstrating organic matters with an MW of 500 Da were easily removed by air flotation.

As shown in Figure 7b, MW of flotation dEOM and bEOM below 1 kDa accounted for 14.18% and 69.85%, respectively, both lower than that of raw dEOM (21.31%) and bEOM (71.67%). In addition, MW of flotation dEOM and bEOM above 100 kDa accounted for 22.52% and 30.05%, respectively, both higher than that of raw dEOM (19.53%) and bEOM (28.05%). After flotation, the proportion of high MW substance increased, while the low MW substance decreased. That was probably due to the low MW substance carrying more negative charge, which was easily rejected by electrostatic repulsion [38], while the high MW substance was easy to aggregate and form a bridge between microalgae, resulting in it being difficult to be removed by air flotation [35].

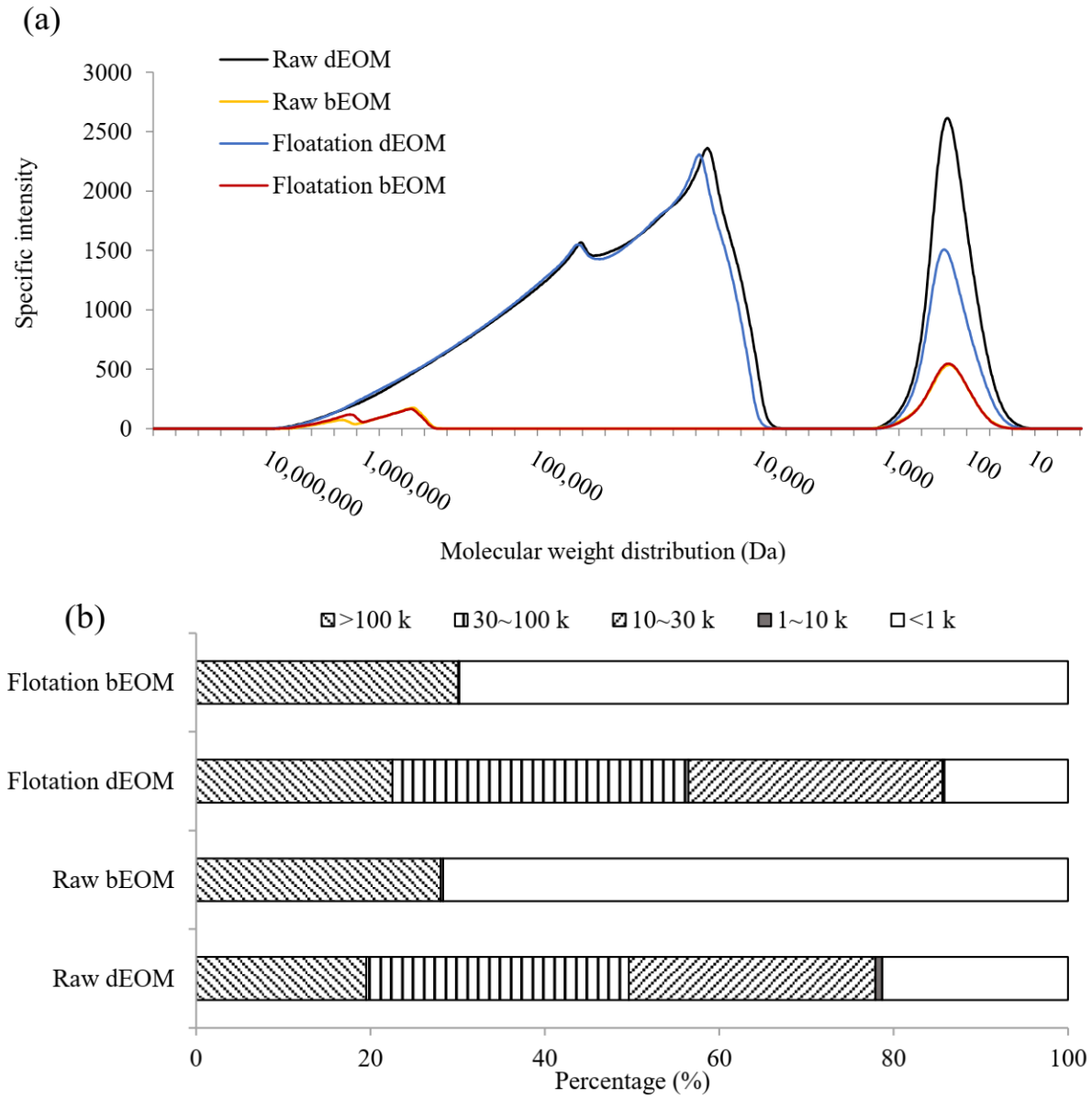

Figure 7. (**a**) MW distributions of dEOM and bEOM and (**b**) the percentage of MW distributions for dEOM and bEOM.

3.5. Effect of Pre-Flotation on Membrane Filtration in Microalgae Harvesting

Critical flux is a crucial parameter to conduct microalgae harvesting in membrane filtration [9]. As shown in Figure 8a, the membrane of pre-flotation algal solution had a higher J_C of 51 L/m^2·h than that of no-pre-flotation (24 L/m^2·h). When the flux reached the highest (54 L/m^2·h), the no-pre-TMP (16.7 kPa) was much higher than pre-TMP (0.65 kPa). In the descending phase, the no-pre-TMP was higher than the corresponding fluxes in the ascending phase, while the pre-TMP in the descending phase was almost the same as the ascending phase. Thus, the membrane filtration of no-pre-flotation algal solution could result in more severe membrane fouling, in comparison with pre-flotation algal solution.

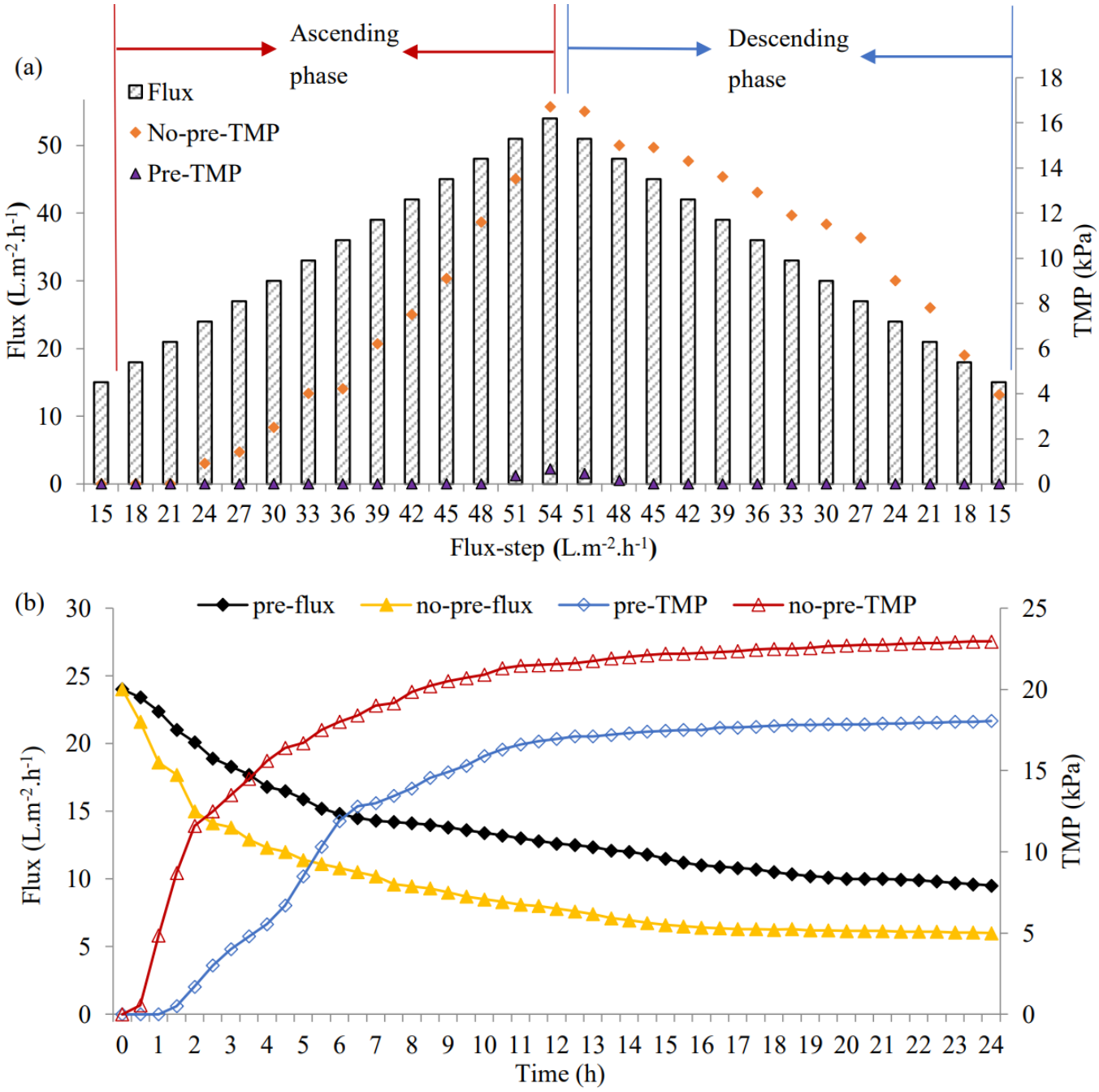

Figure 8. (**a**) Flux-TMP profiles of the improved flux-step method and (**b**) variations in flux and TMP during membrane filtration of pre-flotation and no-pre-flotation algal solutions.

The 24 h filtration experiments of pre-flotation and no-pre-flotation algal solutions proceeded, with detection of the effect of pre-flotation on membrane filtration. Then, 24 L/m^2·h was selected as the initial flux in the filtration, and the variations of flux and TMP are shown in Figure 8b. It could be observed from Figure 8b that during the initial 2 h of filtration, the no-pre-flux dropped sharply and the no-pre-TMP increased quickly, illustrating that the filtration of no-pre-flotation algal solution went through a rapidly declining stage at the beginning [9]. After 2 h of filtration, the pre-flux and no-pre-flux were 20.1 and 15 L/m^2·h, respectively, and the pre-TMP and no-pre-TMP were 1.7 and 11.6 kPa, respectively. When the filtration was conducted for 24 h, the pre-flux and no-pre-flux were 9.5 and 6 L/m^2·h, respectively, and the flux-attenuation rates of pre-flotation and no-pre-flotation algal solutions in the whole filtration experiment were 60.42% (from

24 to 9.5 L/m^2·h) and 75% (from 24 to 6 L/m^2·h), respectively. The results showed that pre-flotation had an active effect on membrane filtration in microalgae harvesting. That was possibly ascribed to the surface properties of algae changing after air flotation [16], hence, the algae had to be deposited on the membrane surface [39], thus alleviated membrane fouling and contributing to the filtration performance being enhanced.

4. Conclusions

There are many factors that affect air flotation then influence microalgae harvesting. In this study, aerator pipe diameter, aeration rate, water depth, temperature, growth stage and the number of air flotation were investigated. The size of the bubbles has an important impact on air flotation, and smaller bubble size was more effective for microalgae harvesting. With the increase in water depth, aeration rate and growth days, the recovery of microalgae showed an increasing trend, while 25 °C was the optimal temperature compared with 15 and 30 °C. The efficiency of microalgae harvesting during the first air flotation was obvious higher than the second flotation. The study illustrated bEOM had a greater effect on microalgae harvesting by air flotation compared with dEOM. Microalgae harvesting in different growth stages proceeded, and the effect of air flotation in the heterotrophic stage was better than in the autotrophic stage. In addition, the higher the proportion of hydrophobic microalgae is, the higher the recovery rate of microalgae. After air flotation, the proportion of high MW substance increased, while the proportion of low MW substance decreased. The membrane of pre-flotation algal solution had a higher J_C (51 L/m^2·h) than that of no-pre-flotation (24 L/m^2·h), and, thus, the pre-flotation had an active effect on membrane filtration in microalgae harvesting. In addition, the combination of air flotation and membrane filtration provided an efficient technology for microalgae harvesting.

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