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Analysis of algal bloom species in eastern China and buoy-bead flotation used for treating microalgae

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ABSTRACT

Water eutrophication leads to the outbreak of algal bloom, polluting the environment and affecting the lives of residents. Sampling points were set at 23 locations in Huaihe River tributaries, Chaohu Lake and Taihu Lake to explore the dominant algae species causing blooms. Nine typical water samples were selected and harvested using low-density buoy-bead flotation method. The highest harvesting efficiency (94.1%) and highest enrichment ratio (12) were from the samples in the botanical port of Taihu Lake, Wuxi Province. The influencing factors were analyzed using the response surface method. The results showed that polyaluminium sulfate (PAS) concentration influenced the harvesting efficiency with sodium alginate microspheres (SAMs). The highest harvesting efficiency (94.3%) and the optimal enrichment ratio (5.5) were achieved from the botanical port with sodium silicate borate glass beads (SSBs). The results showed that, when SSBs were used, PAS concentration, buoy-bead concentration and dilution ratio were the significant factors. Fourier-transform infrared spectrometer showed that the hydroxyl groups on the surface of microalgae combined with carboxyl groups were the main reason for the adsorption of SAMs on microalgae. The optimal conditions for harvesting through SAMs were the PAS concentration of 50 mg/L, the pH of 10, the buoy-bead concentration of 1 ml/L, the flotation time of 6 min and the dilution ratio of 5. The optimal conditions for harvesting through SSBs were the PAS concentration of 100 mg/L, the pH of 6, the buoy-bead concentration of 1 mL, the flotation time of 12 min and the dilution ratio of 2. Based upon single factor analysis, the optimal concentration of PAS was 70 mg/L.

Keywords: Algal bloom; Microalgae; Response surface method; Buoy-bead flotation; Sodium alginate microspheres

1. Introduction

Due to the impacts of non-point and point source pollutants resulting from intensive agriculture and rapid urbanization, multiple lakes in Eastern China had suffered from varying degrees of eutrophication. The algal species causing water blooms are different because of the varieties of pollutants, meteorological conditions, and seasons. As the third largest freshwater lake in China, Taihu Lake once faced the problem of insufficient water supply due to the outbreak of large-scale *Microcystis Cyanobacteria* bloom [1–3]. In recent decades, the Huaihe River has widely been polluted, and many microalgae have erupted frequently with seasonal changes. In spring and autumn, Cryptoalgae and Naked Algae are dominant, whereas *Cyanobacteria* are dominant in summer [4]. The interdecadal gradient of water

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bloom coverage in Taihu Lake has been increasing in the past 20 y and *Cyanobacteria* are the dominant species. In Chaohu Lake, significant differences in water bloom outbreaks are observed during different time periods. However, the areas, frequency and duration of these outbreaks could not be ignored. Meteorological factors such as wind speed, temperature and nutritional factors such as total nitrogen and total phosphorus are the main reasons leading to the water bloom. However, the acting mechanism of meteorological factors still needs to be understood [5,6].

Although microalgae are the primary cause of blooms, they can bring satisfying economic benefits if harvested harmlessly. Microalgae are rich in lipids and proteins, which are considered as the most promising raw materials to produce biofuels, bio-based materials, and pharmaceutical products in the future [7,8]. Compared with fossil fuels, microalgal biodiesel is an important renewable energy resource with characteristics such as higher oil and biomass production [9,10]. Microalgae could also be used to realize the green treatment of various organic, inorganic sewage and landfill leachate [11–15]. At present, the common methods used for harvesting algae include precipitation, flocculation [16], filtration [17], centrifugation, magnetic bead separation, and air flotation. Since microalgae have small particle size and their density is close to that of water, these methods have limitations for treating algal blooms. For example, precipitation method needs long harvesting time and results in low harvesting efficiency [18]. The flocculants might threaten the environment and the high cost cannot be ignored [19]. The energy consumption of filtration method is high and the filter membrane also incurs large expense [20]. The centrifugal method is applicable for different kinds of microalgae with a convincing harvesting efficiency, but the overall energy consumption could be as high as 1.4 kWh/m^3 [21]. The air flotation method requires additional energy to obtain oscillating flow [22]. However, as compared to these traditional harvesting methods, buoy-bead flotation through low-density ballasted agents has recently emerged as an important method and is considered to be a time-saving and energy-efficient method to harvest microalgae [23]. The mechanism behind the buoy-bead flotation process is the attachment of algal cells onto the ballasted agents. Currently, sodium silicate borate has been used to make buoy-beads due to its non-poisonous and high-intensive characteristics [24,25]. Wen et al. [26] suggested that flocculants ($Al_2(SO_4)_3$) were added before the flotation and the achieved optimum harvesting efficiency could be up to 89.13%. However, most of the experiments were accomplished on pure microalgae species cultured in an incubator, whereas similar experiments focusing on species from natural lakes are still non-existent in literature.

In this study, the preponderant algae of Huaihe River, Chaohu Lake, and Taihu Lake were investigated. Based on the results, buoy-bead flotation with sodium alginate microspheres (SAMs) and sodium silicate borate glass beads (SSBs) was employed to curb the algal bloom. To determine the optimal harvesting efficiency of buoy-bead flotation process, the study used response surface method to evaluate the effect of various factors on the flotation process including polyaluminium sulfate (PAS) concentration, pH value, buoy-bead concentration, flotation time and dilution ratio. Finally, prominent factors affecting the harvesting efficiency were determined and a single analysis of the notable factor was made. Based upon algae's characteristics, a new kind of material, called SAMs, was developed to harvest microalgae depending on its characteristic [27]. These buoy-bead flotation method using SAMs was adopted to improve the harvesting efficiency as well as to inhibit the addition of the harmful chemicals, which is thus making it more environmentally friendly.

2. Materials and methods

2.1. Collection of the algal species

During the wet season (July 19–24, 2021), when the incidence of water bloom was high in southern China, multiple sampling points were set at the tributaries of Huaihe River, Chaohu Lake and Taihu Lake (as shown in Fig. 1). The samples were collected 10 cm below the surface of water and immediately incubated at 4°C until they were used for experiments.

In Fig. 1, the sampling points ①–⑦, the sampling points ①–⑦ of Qinglian Village in the tributaries of Huaihe River were located at the duck farm, the pig farm, the ordinary pond, the agricultural water lifting station, the Anfeng pond, the city moat, and the paddy field. The sampling points ⑧–⑬ of Chaohu Lake (b) were located at the sampling points 1–3 of Mushan Island in Zhongmiao Town, the Yangba Street in Xiyuan Square, the farmers' market in the Phoenix Mountain and the golden wharf. The sampling points ⑭–㉓ of Taihu Lake (c) were located at the Yangwan inlet, the Wuli Lake's intake gate, the botanical port, the Mingyue Bay, the Yali Bridge, the Yuantou Island, the Bogong Island, the Fishermen Island, the Nanchang Street and the Li Dike.

Polyethylene buckets with ropes or glass sampling bottles with pendants were immersed under the water surface to draw water samples. The sampling data were recorded, checked and supplied constantly. A central vertical line was set at each sampling point. There were 16 sampling points at the Chaohu and Taihu Lakes around 0.5 m below the water surface. Since the water depth of most sampling points in Qinglian Village was less than 0.5 m, the seven sampling points were set at 1/2 of the water depth. The sampling points were calibrated using the GPS (Global Positioning System) to ensure accuracy.

2.2. Preparation for SAMs and SSBs

SAMs were used to harvest the algae in nine typical water bodies. After the sample with the highest significance was selected, both the SAMs and SSBs were used on the single sample to analyze the results and undertake a comparison.

The preparation method of SAMs was as follows. (1) First, sodium alginate was dissolved in distilled water and mixed with calcium carbonate suspension. (2) Frying oil was added to the suspension and stirred until sodium alginate dispersed into smaller particles. (3) Acetic acid was added to the suspension to dissolve calcium carbonate on the surface of particles, which were solidified. (4) A certain concentration of calcium chloride solution was added to completely solidify the surface of particles. (5) Span-80 was used to clean

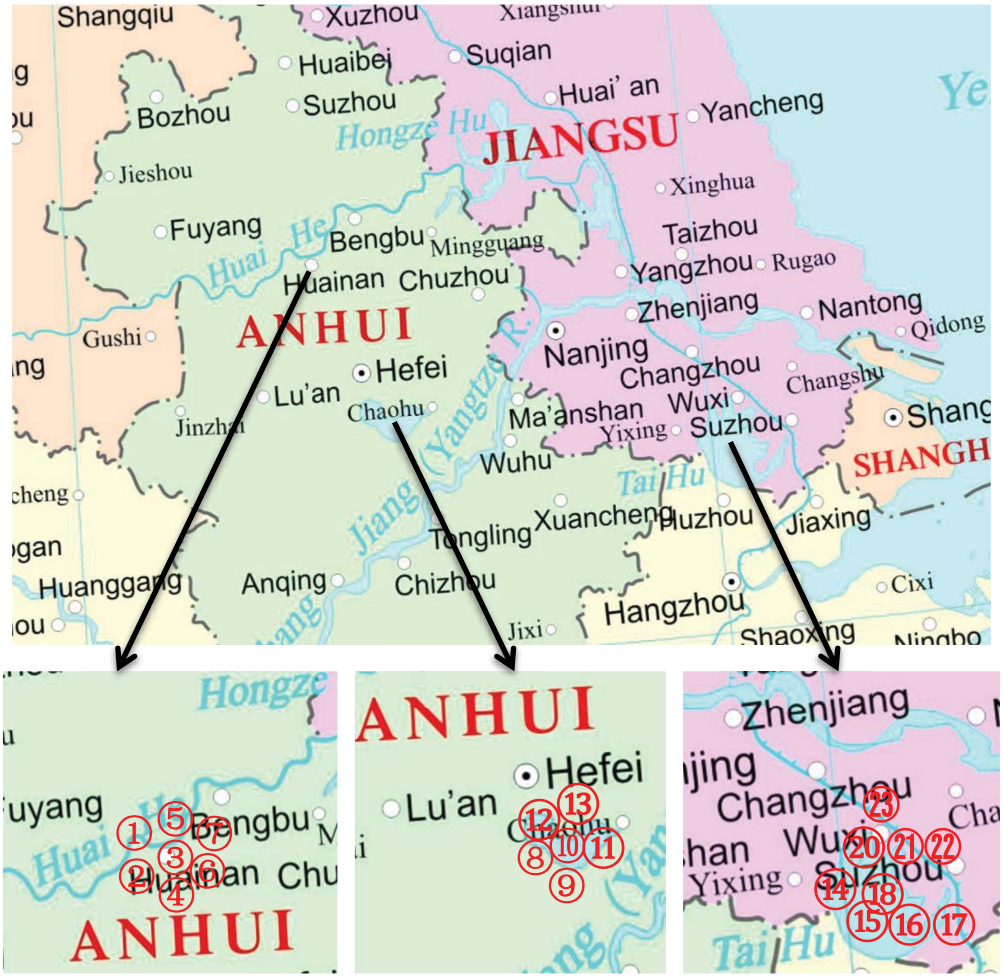


Fig. 1. Distribution areas of sampling points for algae analysis.

the re-frying oil on the surface of buoy-beads. (6) SAMs were washed with distilled water to make them neutral and then stored in distilled water for further use.

The preparation method of SSBs was as follows. (1) Sodium silicate borate glass beads were purchased from Aladdin website. (2) Hollow sodium silicate borate glass beads were added into the deionized water. (3) Stirring was undertaken as quickly as possible to homogenize the system, which was then stored in distilled water for further use.

2.3. Harvesting experiments

To achieve quality assurance, relevant standards and technical specifications were strictly implemented during the experiments. Out of the 23 locations including ①–③, ⑧, ⑭–⑱ as shown in Fig. 1, there were nine typical water samples with high concentration of algal liquid and research significance.

The flotation separation device is shown in Fig. 2. The flotation separation experiment was conducted as follows. (1) A certain amount of PAS was added to the 2 L flotation columns for pre-flocculation treatment. (2) The water samples were collected. (3) Stirring was conducted using the magnetic stirrer at the speed of 250 r/min for 1 min and the solution was let to stand for 15 min. (4) A peristaltic pump was used to inject the two buoy-bead dispersion systems into the flotation column, which were let to stand steadily after being stirred. (5) The combination system of buoy-beads and microalgae was filtered. (6) A peristaltic pump was used to extract the remaining suspended liquid 5 cm above the bottom of the flotation column. In total, around 10 mL liquid was collected. (7) The absorbance was measured before and after the harvest at 540 nm using DU 720 UV-Vis Spectrophotometer. The harvesting efficiency (Y) was calculated using Eq. (1).

$$Y = \frac{A_0 - A_1}{A_0} \times 100\% \tag{1}$$

where A_0 is the initial absorbance at 540 nm and A_1 represents the absorbance of microalgae obtained after flotation separation under the corresponding dilution ratio. Each experiment was repeated three times and the results were reported as the average values.

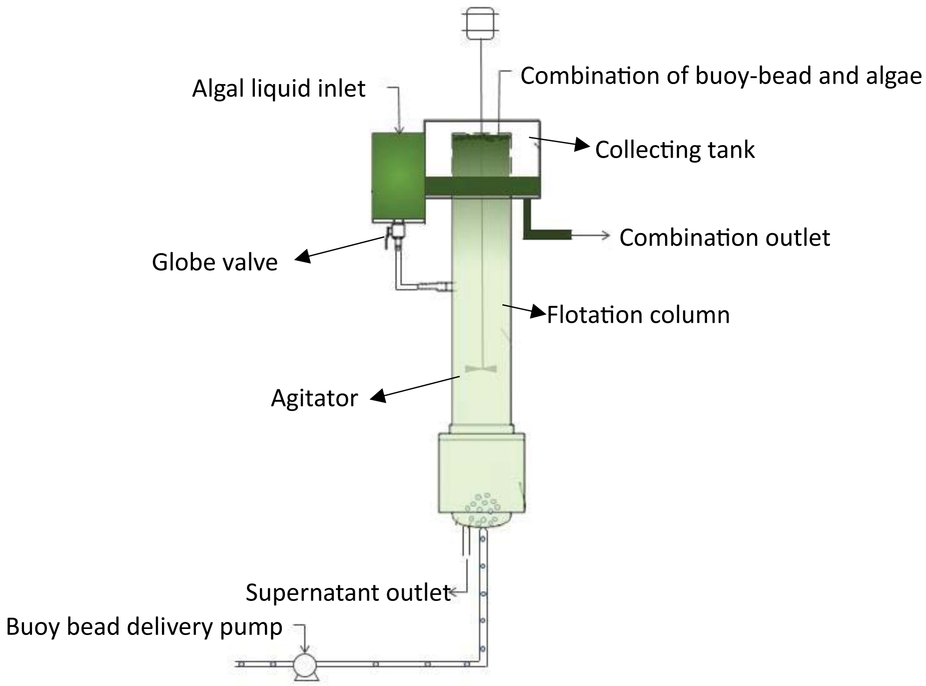


Fig. 2. Schematic of the buoy-bead flotation system.

A measuring cylinder was used to read the total volume of buoy-beads and algae liquid before flotation. The total volume of buoy-beads and collected microalgae after flotation was also obtained using the measuring cylinder. Each experiment was repeated three times and the results were reported as the average values. The enrichment ratio (*R*) was calculated using Eq. (2).

$$R = \frac{V_0}{V_1} \times 100\% \quad (2)$$

where V_0 is the total volume of both the buoy-beads and the collected microalgae after flotation and V_1 is the total volume of the buoy-beads and the algae liquid before flotation. For parallel experiments with the same concentration under the condition of normal absorbance, the greater the enrichment ratio, the better the harvesting efficiency.

2.4. Response surface optimization experiments

For the response surface analysis, the Design-Expert (Version 11.0.8, Stat-Ease, USA) software was used. Table 1 presents the design factors of Plackett–Burman design (PBD) experiments. There were 5 common physical influencing factors of flotation experiments, which include PAS concentration, pH value, buoy-bead concentration, flotation time and dilution ratio. Moreover, six virtual variables were added to carry out the PBD experiments. Each factor was designed with a low value (–1) and a high value (+1), and the range was as close to the growing environment of microalgae as possible. All values of 11 variables were randomly combined, and the harvesting efficiency under each random combination was obtained as response values.

Table 1
Values of various PBD experimental design factors

Variables	Degree of factors	
	–1	+1
PAS concentration, mg/L	50	100
pH	6	10
Buoy-beads concentration, ml/L	0.5	1
Flotation time, min	2	5
Dilution ratio	2	5

3. Results and discussion

3.1. Identification of the algal species

Microscopic examination was employed to determine the dominant algae species that caused the algal bloom by comparing with the algae collection [28].

The algae were classified, counted, and identified to genus or species, and the dominant algae species in each sampling point was determined. The pH meter was used to measure the pH values of natural water samples on-site. Table 2 lists the results of algae species in various samples.

In Table 2, the pH values of the samples in botanical port and the Yangwan inlet were measured after being diluted 10 times.

It can be seen from the results presented in Table 2 that the dominant algae species in Huaihe River were *Microcystis*, *Chlorella vulgaris* and Diatom. The dominant algae species in Chaohu Lake were *Coelomona*, *Microcystis* and *Chlorella vulgaris*. Furthermore, the dominant algae species in Taihu Lake were *Microcystis*. Among them, the algae species in Taihu Lake were the most abundant. Therefore, algae in fresh

Table 2
Summary of sampling points and the dominant algae species in them

Sampling areas	Number of sampling points/piece	Serial number	Sampling points	Microalgae species	pH
Huaihe tributary in Anhui Province	7	①	Duck farm	*Microcystis* sp., *Chlorella vulgaris*, Diatom	7.25
		②	Pig farm	*Euglena* sp., *Chlorella vulgaris*	7.74
		③	Ordinary pond	*Chlorella vulgaris*, *Microcystis* sp., *Peridinium*	6.97
		④	Agricultural water lifting station	*Microcystis* sp., *Chlorella vulgaris*, Diatom	7.09
		⑤	Anfeng pond	Diatom, *Microcystis* sp., *Chlorella vulgaris*	7.20
		⑥	City moat	Diatom, *Euglena* sp., *Chlorella vulgaris*	6.75
		⑦	Paddy field	Cryptoalgae, Diatom, *Microcystis* sp.	8.23
Chaohu Lake, Hefei City, Anhui Province	6	⑧	Sample 1 in Mushan Island	*Chlamydomonas*, *Chlorella vulgaris*, *Dactylococcopsis*	8.16
		⑨	Sample 2 in Mushan Island	*Coelomona*, *Microcystis* sp., *Chlorella vulgaris*	8.22
		⑩	Sample 3 in Mushan Island	Cruciform algae, *Coelomona*, *Chlorella vulgaris*	7.43
		⑪	Yangba Street in Xiyuan Square	*Coelomona*, *Microcystis* sp., *Chlorella vulgaris*	8.62
		⑫	Farmers' market in the Phoenix Mountain	*Aphanizomenon*, *Corynebacterium*, *Microcystis* sp.	7.49
		⑬	Golden wharf	Triangular algae, *Chlorella vulgaris*, *Dactylococcopsis*	8.89
Taihu Lake, Wuxi City, Jiangsu Province	10	⑭	Yangwan inlet	*Coelomona*, *Chlorella vulgaris*, *Microcystis* sp.	6.54
		⑮	Wuli Lake intake gate	*Microcystis* sp., *Dactylococcopsis*, *Coelomona*	7.64
		⑯	Botanical port	*Microcystis* sp., *Dactylococcopsis*, *Coelomona*	6.01
		⑰	Mingyue Bay	*Dactylococcopsis*, *Chlorella vulgaris*, *Microcystis* sp.	8.06
		⑱	Yali Bridge	*Coelosphaerium*, *Euglena ehrenbergii*	7.38
		⑲	Yuantou Island	*Prorocentrum*, *Chlorella vulgaris*, *Microcystis* sp.	7.59
		⑳	Bogong Island	*Coelomona*, *Chlorella vulgaris*, *Microcystis* sp.	8.02
		㉑	Fishermen Island	*Euglena* sp., *Dactylococcopsis*, *Microcystis* sp.	7.86
		㉒	Nanchang Street	*Dactylococcopsis*, *Coelomona*, *Microcystis* sp.	7.46
		㉓	Li Dike	*Microcystis* sp., *Euglena* sp.	8.42

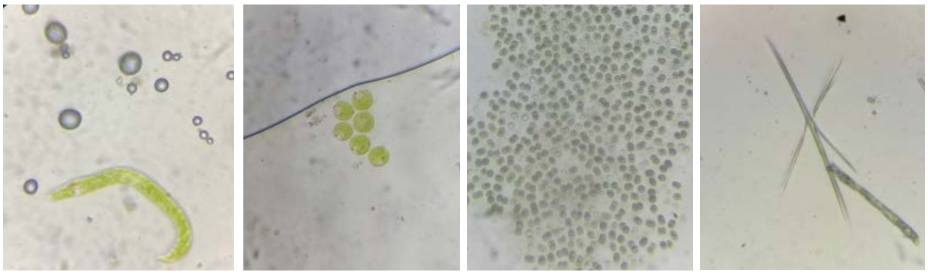

(a) (b) (c) (d)

Fig. 3. Display of microscopic examination results. (a) Cladophora in duck farm, (b) *Golenkinia longispicula* in Chaohu Lake, (c) *Microcystis* sp. in Taihu Lake, and (d) *Dactylococcopsis acicularis* in Taihu Lake.

water bodies were mostly *Cyanobacteria* and *Chlorophyta*. It was also known that pH values of these natural fresh water bodies were mostly within the range of 7–8. For some samples, the pH values lied within the range of 8–9, whereas the highest value was 8.89 in the golden wharf in Chaohu Lake. Only a handful of samples had pH values of less than 7, whereas the lowest value was 6.01 in the botanical port, Taihu Lake. Therefore, the environment suitable for the growth of algae was mostly neutral or weakly alkaline. However, some algae such as those in the botanical port and the Yangwan inlet could survive in much acidic water bodies, indicating that algae had good adaptability.

Five factors were randomly combined, which influenced the harvest of 9 typical water samples. Furthermore, 12 groups of repeated harvesting experiments were carried out with SAMs. The corresponding results are summarized in Fig. 4.

According to Fig. 4, all harvesting efficiencies were greater than 67.3%. It meant that the harvesting effect of SAMs was generally good. The typical water sample ⑯ at the botanical port yielded the highest harvesting efficiency and enrichment ratio. The harvesting efficiency was as high as 94.1%, whereas the enrichment ratio was as high as 12, indicating that the concentration of algae was high and the enrichment effect of SAMs was conspicuous. Meanwhile, the lowest harvesting efficiency, which was 67.3%, and the lowest enrichment ratio 0 occurred both for the typical water sample ⑰ at Mingyue Bay, indicating that the concentration of algae was low. The results presented in Table 2 show that the pH values behind those 9 samples ①–③, ⑧, ⑭–⑱ were 7.25, 7.74, 6.97, 8.16, 6.54, 7.64, 6.01, 8.06, and 7.38, respectively. It could be deduced that the pH values in natural water bodies were not closely linked to the highest harvesting efficiency because some were above 7, while others were not. In short, the typical water sample ⑯ at the botanical port was of great research significance.

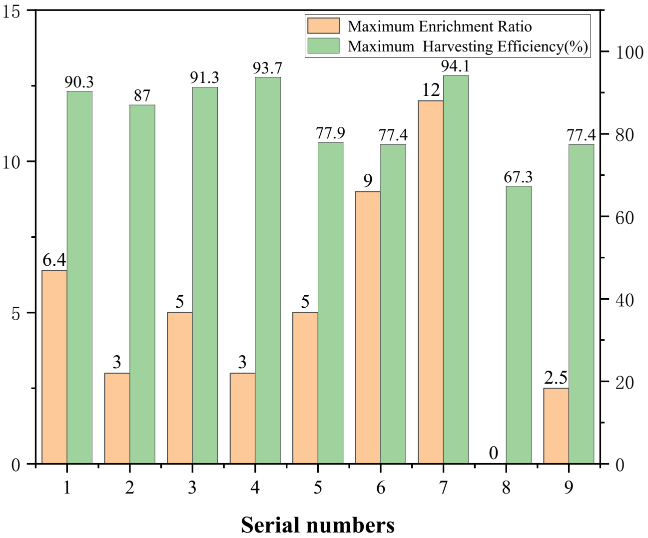


Fig. 4. Maximum enrichment ratio and harvesting efficiency (1–9 represented sampling points ①–③, ⑧, ⑭–⑱, respectively).

3.2. Screening of influencing factors of harvesting

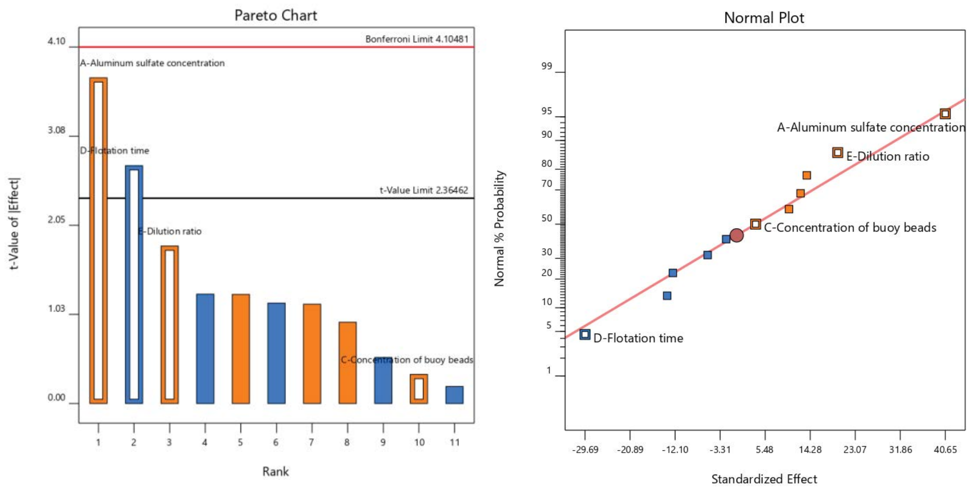
Pareto charts could show the degree of influence of various factors on the experimental results. When they were combined with normal plots, the factors that had the most significant influence on the experimental results could be selected. Figs. 5 and 6 are the Pareto charts. The influencing factors exceeding the horizontal black line are the most significant factors affecting the harvesting efficiency of buoy-bead flotation selected by the PBD experiments, representing that the level of influence was more than 90% on the experimental results. Figs. 5 and 6 are the normal plots, which were used to determine the size and direction of the influence of various factors on the experimental results. It is generally considered that the factors distributed around 0 had no significant influence on the harvesting efficiency. In these experiments, buoy-beads were used to replace microbubbles, and there was no effect of remaining time on the experimental results.

Using SAMs, the PBD experimental analyses of the influencing factors of the harvesting experiment were carried out for 9 water samples obtained from the sampling points of ①–③, ⑧, ⑭–⑱. The corresponding results are presented in Table 3.

The symbol "P" in Table 3 indicates that this factor had a relatively noteworthy impact on the results. The results showed that the concentration of PAS was the most common factor affecting the samples from 9 typical places. The second most important factor was the concentration of buoy-beads, that affected 5 places. The concentration of the buoy-beads was followed by the pH and flotation time, indicating that the pH and flotation time had a marginal influence on the harvesting efficiency. Furthermore, the dilution ratio basically had no influence on the results.

The water samples at the botanical port were selected to compare and analyze the two buoy-bead materials of SAMs and SSBs.

According to Fig. 5, when SAMs were used, the probability that PAS concentration became a significant influencing factor exceeded 90%. However, this would still be



(a) (b)

Fig. 5. Pareto chart (a) and normal plot (b) (SAMs).

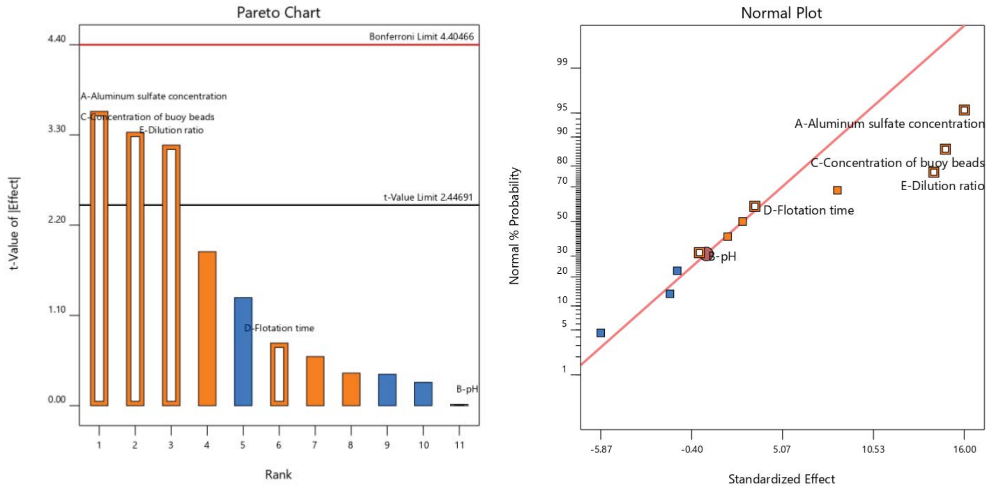


Fig. 6. Pareto chart (a) and normal plot (b) (SSBs).

Table 3
Summary of various influencing factors

Parameter	①	②	③	⑧	⑭	⑮	⑯	⑰	⑱
PAS concentration	P	P		P	P		P	P	
pH			P		P	P		P	
Buoy-beads concentration		P	P	P		P			P
Flotation time			P				P		P
Dilution ratio									

further discussed. According to Fig. 5, the pH and buoy-bead concentration had no significant influence on the harvesting efficiency, while PAS concentration and dilution ratio had remarkable effects.

According to Fig. 6, when SSBs were used, the probability that PAS concentration, buoy-bead concentration and dilution ratio became significant factors exceeded the value of 90%. However, its certainty would still be further discussed. From Fig. 6, it can be seen that the pH had no significant effect on the harvesting efficiency, while PAS concentration, buoy-bead concentration and dilution ratio had remarkable impacts.

As shown by the results presented in Table 4, '*A*' represented the flotation data of SAMs, while '*B*' represented the flotation data of SSBs. For *A* and *B*, the *p*-values of the models were both less than 0.05, whereas the *F*-values were close to each other and large in magnitude. The correlation coefficients (R^2) of the models were 0.78 and 0.85, respectively, which were both close to unity. The signal-to-noise ratios, namely the Adeq. Precision of the models, were 7.4265 and 8.8743, respectively, which were both higher than 4. Therefore, the models were prominent. When SAMs were used for harvesting the microalgae, the *p*-values of PAS concentration and flotation time were less than 0.05. Furthermore, the *F*-value of PAS concentration was larger, which was 14.07. The comprehensive results showed that PAS concentration had a significant impact on the harvesting of microalgae. When SSBs were used for harvesting microalgae, the *p*-values of PAS concentration, buoy-bead concentration and dilution ratio were less than 0.05, whereas the *F*-values were 12.89, 11.13 and 10.11, respectively, which were all high, indicating that they had a significant impact on the harvesting of microalgae.

The highest harvesting efficiency obtained was 94.3% and the enrichment ratio was 5.5 using SSBs. The highest harvesting efficiency was similar to that obtained using SAMs, while the enrichment effect was much lower than the SAMs.

Table 4
Parameters of different influencing factors of PBD experiments

Parameters	Sum of squares		Contribution rate (%)		*p*-value		*F*-value	
	A	*B*	*A*	*B*	*A*	*B*	*A*	*B*
Model	8,800.19	2,067.83			0.0183	0.0176	6.24	6.94
PAS concentration	4,958.08	768.00	44.0046	31.6666	0.0072	0.0115	14.07	12.89
pH		0.0133		0.000549768		0.9885		0.0002
Buoy-beads concentration	39.46	663.05	0.350204	27.3394	0.7477	0.0157	0.1120	11.13
Flotation time	2,643.89	34.68	23.4655	1.42995	0.0290	0.4744	7.50	0.5821
Dilution ratio	1,158.76	602.08	10.2844	24.8254	0.1127	0.0191	3.29	10.11

After analyzing the 12 groups of repeated experiments conducted by the samples from botanical port, the best harvesting conditions of the maximum harvesting efficiency at the botanical port were obtained as presented in Table 5.

The results presented in Table 5 show that, when SAMs were used, although the water sample was diluted 5 times, the PAS concentration required was still high, which was consistent with the results obtained from the response surface analyses. The concentration of SAMs buoy-beads was as high as 1 ml/L, which led to high collision probability and high capturing degree with algae. Additionally, the flotation time lasted 6 min, which was moderate among the set range. When using SSBs, the required PAS concentration and flotation time were both higher than the SAMs. The pH values of using SAMs and SSBs were 10 and 6, respectively, indicating that the dominant species of *Microcystis* could survive in acidic or alkaline environments and that the pH had an influence on harvesting efficiency.

Compared with the SAMs which were made up of natural materials, SSBs are inorganic hollow glass beads, requiring more PAS to overcome the electrostatic repulsion. When sodium silicate borate glass beads were used, hydrocyclone had to be used to separate the buoy-beads microalgae aggregates, increasing the harvesting cost. However, SAMs were made up of degradable biomaterials, which were rich in fats. Therefore, the buoy-beads microalgae aggregates could be used as raw materials to directly synthesize biodiesel. Theoretically, the harvesting of microalgae with SAMs could be up-scaled from laboratory scale to industrial scale.

3.3. Analysis of the mechanism

Fourier-transform infrared spectroscopy (FTIR) analyses of SAMs and SSBs are shown in Fig. 7.

Sodium alginate exhibited stretching vibrations of hydroxyl group (–OH) at 3,386.87 cm^{-1}, which deviated to the low band as compared with the stretching vibration of hydroxyl group (–OH) in the free water (3,500 cm^{-1}). This indicated that there was crystalline water in sodium alginate. Moreover, there may have been hydrogen bonding with other materials. In addition, the stretching vibration of ester bond (–C=O–), an organic functional group, appeared at 1,744.78 cm^{-1}, which could be combined with the hydroxyl to form carboxyl groups. Based on our previous work [9,26], the surface of microalgae contained hydroxyl groups, which could be combined with lipid bonds to form stable carboxyl groups. These groups could improve the harvesting efficiency of microalgae, reduce the use of flocculants and alleviate the secondary pollution to the environment.

Sodium silicate borate showed stretching vibrations of hydroxyl group (–OH) at 3,350.53 cm^{-1}, indicating that there was crystalline water in sodium silicate borate and that there may be hydrogen bonding with other materials. The stretching vibration of Si–O–Si appeared at 1,027.76 cm^{-1}, whereas the stretching vibration of Si–Si appeared at 771 cm^{-1}. Moreover, the bending vibration of O–Si–O appeared at 488 cm^{-1}, while the symmetrical stretching vibration of BO_3^{3-} appeared at 1,385 cm^{-1}, which indicated that sodium silicate borate was mainly composed of silicon dioxide, in which

Table 5
Optimum harvesting conditions of SAMs and SSBs

Conditions	PAS concentration (mg/L)	pH	Buoy-beads concentration (ml/L)	Flotation time (min)	Dilution ratio
SAMs	50	10	1	6	5
SSBs	100	6	1	12	2

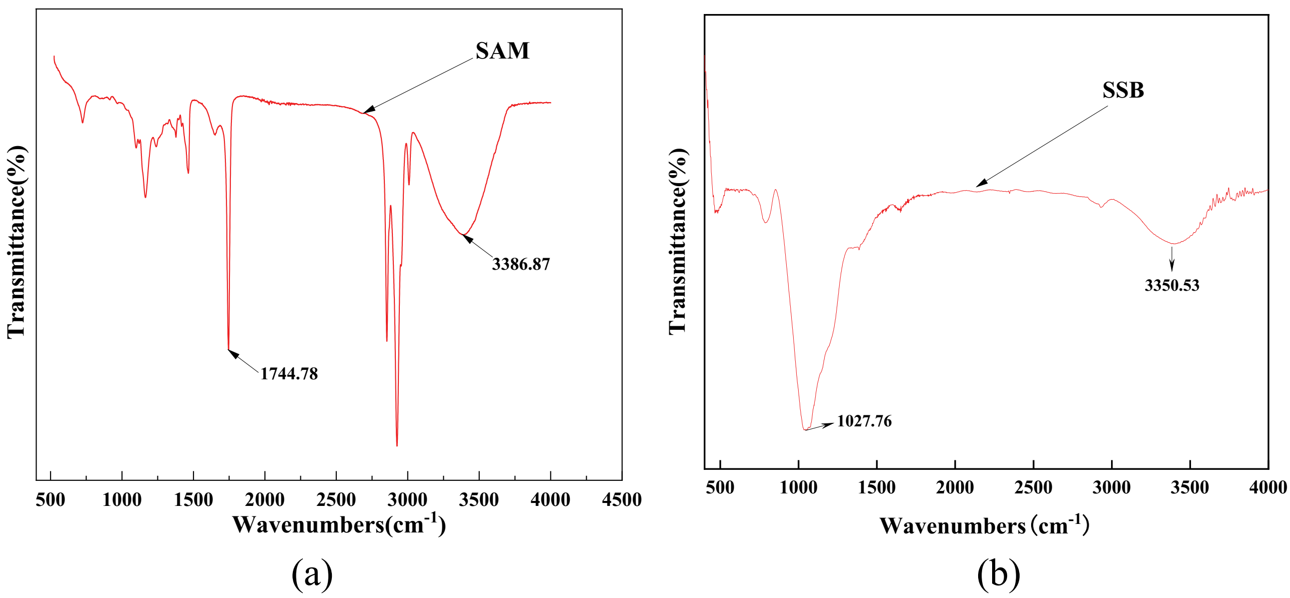


Fig. 7. FTIR of SAMs (a) and SSBs (b).

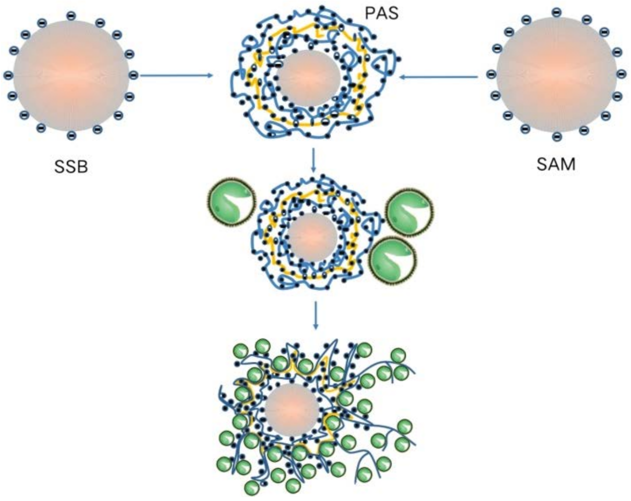


Fig. 8. Combination process of microalgae and buoy-beads.

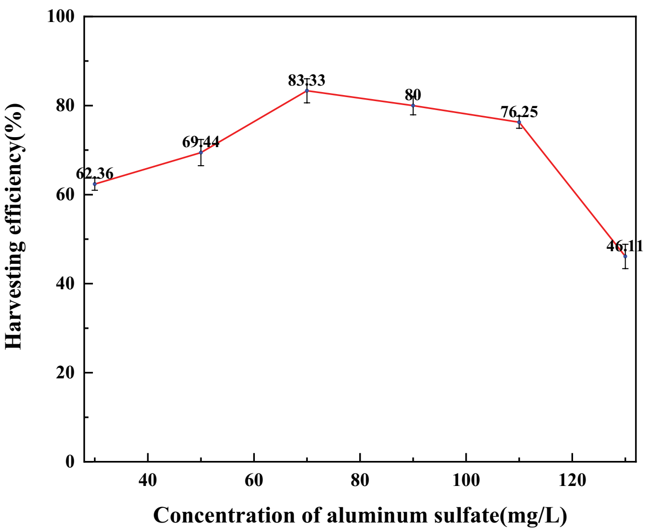


Fig. 9. Effect of different PAS concentrations on harvesting.

part of the silicon was replaced by boron atoms. Sodium silicate borate is an inorganic substance. When harvesting microalgae, only when more PAS was used, the electrostatic repulsion on the interface could be overcome. Therefore, compared with SAMs, SSBs cost more and could produce more secondary pollution because of the large usage of PAS.

The schematic of the buoy-bead flotation principle is shown in Fig. 8. Both the surfaces of buoy-beads and microalgae were negatively charged, which resulted in electrostatic repulsion. However, the Al^{3+} in the PAS was positively charged and played the role of neutralizing the negative charge and bridging the buoy-beads and the microalgae. Under the action of positive charge, flocs were formed between the microalgae, which could be adsorbed onto the buoy-beads in the process of their rising. Consequently, the harvesting efficiency was further improved.

The single-factor analysis of PAS concentration was carried out to obtain the variation curve of microalgae's harvesting efficiency with different PAS concentration when other factors used were the same as what has been shown by the results presented in Table 5.

As shown in Fig. 9, with the gradual increase of PAS concentration, the harvesting efficiency increased at first, and then, decreased. When the concentration increased to 70 mg/L, the harvesting efficiency reached the highest level at 83.33%. This was because the surfaces of different objects were generally negatively charged, and therefore, electrostatic repulsion was produced between the algae and the sodium alginate buoy-beads. However, the aluminum ion was positively charged and could neutralize the negative charge. With the continuous addition of PAS, more and more surface charges were neutralized and the repulsion energy decreased. The aggregation occurred which was caused by the mutual attraction among particles. Moreover, when the concentration of PAS continued to increase, the microalgae flocs and the weight increased. Then, the flocs sank with the decrease of both the enrichment ratio and the harvesting efficiency.

4. Conclusions

- The dominant algae species of Huaihe tributary were the *Microcystis*, *Chlorella vulgaris* and Diatom. The dominant algae species in Chaohu Lake were the *Coelomona*, *Microcystis* and *Chlorella vulgaris*. The dominant algae species in Taihu Lake were the *Microcystis*.
- The microalgae in nine typical water samples were harvested with SAMs. The highest harvesting efficiency was 94.1%, whereas the optimal enrichment ratio (12) was achieved from the botanical port. The lowest harvesting efficiency was 67.3%, whereas the lowest enrichment ratio (0) was achieved from the Mingyue Bay. The pH values in natural water bodies were not closely linked to the highest harvesting efficiency.
- To sample the botanical port, the optimal conditions using SAMs for harvesting were as follows: PAS concentration of 50 mg/L, pH of 10, buoy-bead concentration of 1 ml/L, flotation time of 6 min and dilution ratio of 5. The most significant factor affecting the harvesting efficiency was the PAS concentration. The highest harvesting efficiency (94.3%) and the optimal enrichment ratio (5.5) were achieved using SSBs. The optimal conditions for harvesting were as follows: PAS concentration of 100 mg/L, pH of 6, buoy-bead concentration of 1 ml/L, flotation time of 12 min and dilution ratio of 2. The significant factors affecting the harvesting efficiency were the PAS concentration, the buoy-bead concentration, and the dilution ratio. Generally speaking, the harvesting effect of SAMs was better than that of SSBs.
- The FTIR analyses showed that the surface of sodium alginate contained ester bonds, which could be combined with the hydroxyl groups on the surface of microalgae to produce stable carboxyl groups and natural adsorption. This function could reduce the influence of electrostatic repulsion, increase the flocculation, and decrease the secondary pollution of aluminum salt to the environment. The final aggregation of buoy-beads and microalgae was harmless to the environment. This not only saved the separation and recovery cost and time, but was also more convenient to use.

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