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The kinetics of the polyacrylic superabsorbent polymers swelling in microalgae suspension to concentrate cells density

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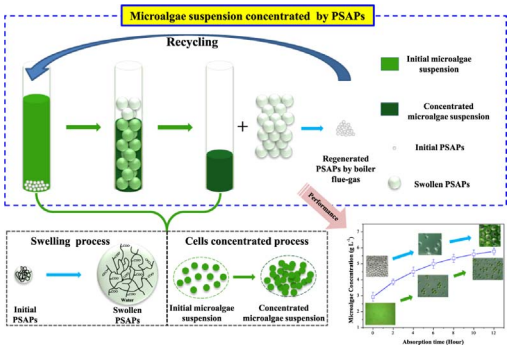
GRAPHICAL ABSTRACT



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ABSTRACT

Different from current harvesting methods, the aim of this study was to concentrate microalgae by removing the medium with polyacrylic superabsorbent polymers (PSAPs). This method can concentrate freshwater microalgae *Chlorella* sp. at a relatively high biomass concentration of 90.23 g L^{-1}. Without further dewatering, the concentrated microalgae can be directly used to produce biofuels by oil extraction or fermentation. The kinetic characteristics of PSAPs swelling in different solutions were investigated. The results indicate that the negative influence on absorbency caused by ionic strength was greater than microalgae concentration. Compared with the diffusion part, water absorbed by the relaxation of PSAPs was dominant and accounted for over 97%. Equilibrium absorbed water equations under different microalgae concentration were fitted and could provide guide to quantifiably concentrate microalgae. Increasing temperature decreased the absorbency of PSAPs, while, the absorption and desorption rate were increased. Moreover, the absorbency remained at 91.45% after recycling three times.

1. Introduction

Microalgae biomass is known as one of the greatest potential feedstocks of biofuels due to microalgae cells' high lipid content, short growth period and strong growth ability (Chang et al., 2016; Chen et al., 2015; Huang et al., 2016). Due to the high CO_2 fixation efficiency, microalgae can also release the chronic high levels of greenhouse gas CO_2 which has serious impacts on the global environment. In addition, during growth, microalgae can accumulate various valuable products, such as polyunsaturated fatty acids, antibiotics, antioxidants for food supplements and pigments (Chen et al., 2015; Chiu et al., 2015; Milano et al., 2016). Generally, the main methods of large-

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scale microalgae cultivation are outdoor open raceway ponds and closed photobioreactors (PBRs). Nevertheless, the microalgae characteristics of the dilute nature (usually less than 0.5 g L^{-1}), small size (diameter range from 2 μm to 20 μm), density close to water (1070–1140 kg m^{-3}) and electronegative surface charge (from −10 mV for *Chlorella* to −35 mV for *Scenedesmus*) at a wide pH range (Henderson et al., 2008; Nyomi Uduman, 2010; Ozkan & Berberoglu, 2013; Wang et al., 2015) cause the harvesting process to consume approximately 20–30% of the total cost of the biomass production (Kumar et al., 2017; Luo et al., 2017). Moreover, microalgae harvesting has already become the main bottleneck of the microalgae commercialization process (Soh et al., 2014; Wang et al., 2015).

Current microalgae harvesting methods include centrifugation, filtration, flotation, flocculation or a combination of these methods. Both centrifugation and filtration can avoid the addition of chemicals and gain relatively high total suspended solids (TSS) of 12–22% and 18%, respectively (Grima et al., 2003). However, it is unfeasible to apply these methods at a large scale because the energy consumption is too high (Coward et al., 2013; Nyomi Uduman, 2010). Moreover, filtration requires relatively high operating and maintenance costs due to the continuous fouling/clogging and subsequent replacement of the membranes (Bilad et al., 2014). Flocculation has been proven to be a relatively low-cost method for concentrating microalgae at large scale (Vandamme et al., 2013). However, the additives (e.g., flocculants) are difficult to remove and might be harmful to microalgae cells. For example, the use of ferric salts has been shown to lead to a brown-yellow coloration of the microalgae, and cell lysis was observed (10–25%) when using aluminum salts (Papazi et al., 2009). Flotation is commonly preceded by flocculation and is more effective than flocculation. However, the energy requirements and equipment costs remain too high for sustainable large-scale application at the time (Barros et al., 2015; Wiley et al., 2009). Hence, the ideal method for microalgae harvesting should be low-cost, no use of poison and easy separation with microalgae cells. Super-absorbent polymer gels (SAPs) are hydrogels with the capacity of absorbing considerable amounts of water without dissolving. Xie et al. (2016) used SAPs to concentrate pathogens (*Escherichia coli* and bacteriophage MS2) in water samples; meanwhile, no poison and easy separation was achieved as the diameter of the SAPs was much larger than the pathogens' after absorbing water.

The ability of SAPs to absorb water is caused by hydrophilic functional groups attached to the polymeric backbone, whereas their resistance to dissolution arises from cross-links between network chains (Kozicki et al., 2016; Makuuchi, 2010). SAPs can also show dramatic volume transition in response to a variety of external environment stimulations including temperature, pressure, sound, pH, ionic strength and molecular species. Additionally, SAPs have a wide application in agriculture, medicine, biology and environmental treatments (Ahmed, 2015). When absorbing water, some ions can get into the structure of the polymer as the Donnan effect (Dhara et al., 1999). According to this feature, Martín del Campo and Patiño (2013) used PSAPs to concentrate *Chlamydomonas reinhardtii* and removed part of the sulfur that was harmful to generate hydrogen (H_2) under anoxic conditions. Therefore, this is an ideal method for microalgae harvesting, and it can not only concentrate microalgae but also reduce the ions that are harmful for microalgae to utilize in the later period. In addition, the absorbency of PSAPs is related to the microalgae species, culture medium and ion content in the culture suspension, which makes a great difference between the PSAPs swelling in the microalgae suspension and the swelling process in water. Additionally, the swelling process of PSAPs is important to the design of the recovery process and large-scale application. Nevertheless, there are few studies on PSAPs concentrating microalgae and no mention of the kinetic characteristics of PSAPs swelling in microalgae suspension.

Herein, the present study aims to concentrate microalgae by PSAPs that absorb the water of the culture suspension. To fulfill this purpose, the absorbing characteristics of PSAPs were studied and different kinds of culture media were used to determine the feasibility of this method, which has rarely been investigated. Moreover, the effects of microalgae concentration, harvesting temperature, and the reusability of PSAPs were also studied.

2. Materials and methods

2.1. Experimental approach

2.1.1. Microalgae strain and cultivation conditions

The microalgae strains used in this study were freshwater microalgae *Chlorella* sp. FACHB-31 and marine microalgae *Chlorella* sp. SSCCC-8 obtained from the Institute of Hydrobiology and the Institute of Oceanology, Chinese Academy of Sciences, respectively. The freshwater *Chlorella* sp. were grown in BG11-Modified (BG11-M) medium (Sun et al., 2016) and SE medium, and the marine *Chlorella* sp. were cultured in f/2 medium (Lananan et al., 2013). All of the experiments of microalgae cultivation were performed in cylindrical PBRs (serum bottles with an external diameter of 80 mm, an inner diameter of 74 mm, and a height of 150 mm) containing 500 mL of autoclaved medium with continuous illumination of 90 μmol·m^{-2}·s^{-1}. Balanced with nitrogen, 5% CO_2 (v/v) gas was aerated into the PBRs at a rate of 0.1 vvm (volume of gas per volume of broth per min).

2.1.2. Experimental setup and operation

The microalgae harvesting was conducted by adding transparent PSAP spherical particles (2.0–3.0 mm, Shenyang Shuanglong Co. Ltd., China) with a diameter in the range of 2.0–3.0 mm to the microalgae suspension. Microalgae biomass concentration was measured gravimetrically by sampling 10 mL of microalgae suspension from the PBRs when cultivated for 7 days. The sampled suspension was centrifuged (GL-21 M, Xiangyi Centrifuge Instrument Co. Ltd., China) at 8000 rpm for 10 min and then washed twice with de-ionized water before drying at 85 °C to a constant weight. Different concentrations of microalgae were achieved by quantifiably removing the superfluous supernatant of the centrifuged microalgae suspension according to the measured microalgae concentration and then resuspending the solution. The harvesting temperature was maintained by using a thermostatic bath (DFY 10L/20, YIKE Instrument, Shanghai, China).

In this study, 10 spherical PSAP particles were taken as a group and duplicated twice to eliminate the individual influences. Additionally, all of the experiment data shown are reported as mean values and standard deviations (in the figures) or standard errors (in the tables). During the absorption period, the mass of the PSAPs was measured on an analytical balance (BP114, Sartorius, Germany) at regular intervals of 30 min in the first 2 h and 60 min in the following 10 h, and the excess liquid was removed with a paper towel before being weighed. Additionally, the diameter of the PSAPs was examined with a metric vernier caliper.

To regenerate PSAPs, the swollen PSAPs were dewatered in an electrical convection oven (BGZ-70, Shanghai Boxun Co. Ltd., China). After the first cycle of absorption/desorption, the PSAPs were reused for two more cycles.

2.2. Determination of the PSAPs swelling model

The diffusion-relaxation theory proposed by Berens et al. (Fátima Rosa, 2002) was used to fit the evolution of the absorbed mass by PSAPs. The absorption process in the diffusion-relaxation model is composed of the liquid diffusion in the polymer and relaxation of the chains caused by the expansion of the structure. The absorbed mass of the liquid in the diffusion process, $M_{t,F}$, and relaxation process, $M_{t,R}$, per unit mass of the polymer at time t is expressed as Eqs. (1) and (2):

$$M_{t,F} = M_{\infty,F}\left[1-\frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}exp(-n^2k_F t)\right] \quad (1)$$

$$M_{t,R} = M_{\infty,R}[1-exp(-k_R t)] \quad (2)$$

where $M_{\infty,F}$ is the final equilibrium adsorption mass in the diffusion process, $k_F = 4\pi^2 D/d^2$ is the diffusion rate constant for a diameter d (an equivalent diameter, to weight with some non-sphericity), $M_{\infty,R}$ is the final equilibrium adsorption mass in the relaxation process and k_R is the relaxation rate constant. The total absorbed mass, M_t, absorbed per unit mass of the polymer at time t will be expressed as $M_t = M_{t,F} + M_{t,R}$. Dividing by M_∞, the final equilibrium adsorption mass, the equation becomes:

$$\frac{M_t}{M_\infty} = x\left[1-\frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}exp(-n^2k_F t)\right] + (1-x)[1-exp(-k_R t)] \quad (3)$$

where $x = \frac{M_{\infty,F}}{M_\infty}$ and $1-x = \frac{M_{\infty,R}}{M_\infty}$ represent the weights of the diffusion and relaxation contributions, respectively.

2.3. Analytical methods

2.3.1. Determination of the absorbency of PSAPs

The absorbed mass of water per gram of PSAPs at time t, denoted by Q(t), is calculated as:

$$Q(t) = \frac{M(t)-M_0}{M_0} \quad (4)$$

where M(t) and M_0 are the mass of the PSAPs at time t and the mass of PSAPs in the dry state, respectively. When the mass of PSAPs in the solution no longer changes with time, it is said to be the equilibrium value. Furthermore, it is denoted by Q(e) and calculated as:

$$Q(e) = \frac{M_{max}-M_0}{M_0} \quad (5)$$

where M_{max} is the mass of PSAPs when it is in equilibrium with the solution in contact.

The harvesting and desorption ratio F is expressed as Eq. (6):

$$F = \frac{M_t}{M_0} \quad (6)$$

2.3.2. Determination of the nutrient concentration

To analyze the nutrient concentration, 5 mL of the microalgae culture medium was centrifuged and then washed once more with de-ionized water. Two kinds of supernatant were collected and mixed together. The samples were diluted to ensure that the highest ion concentration was lower than 20 mg L^{-1}. Then the diluted samples were injected into an ion chromatograph (ICS-5000, ThermoFisher, USA) equipped with an anion analytical column (4 × 250 mm, AS11-HC) and a self-regenerating suppressor (4 mm, ASRS 300) to determine the nutrient concentration.

3. Results and discussion

3.1. Performance of the microalgae harvesting with PSAPs

To determine the performance of PSAPs, 0.456 g of PSAPs (24 particles) was dipped in suspension with a microalgae concentration of 2.93 g L^{-1}. The experimental data displayed in Fig. 1 show that the microalgae concentration increased from 2.93 g L^{-1} to 5.78 g L^{-1} in 12 h and the diameter of PSAPs increased accordingly from 2.91 mm to 14.25 mm. During the first 2 h, the microalgae concentration increased to 0.94 g L^{-1}, whereas the increment diminished gradually and was only 0.18 g L^{-1} in the last 2 h. This was mainly because of the weakened concentration gradient between the inside of the PSAPs and the swollen solution as more and more water was absorbed into the PSAPs.

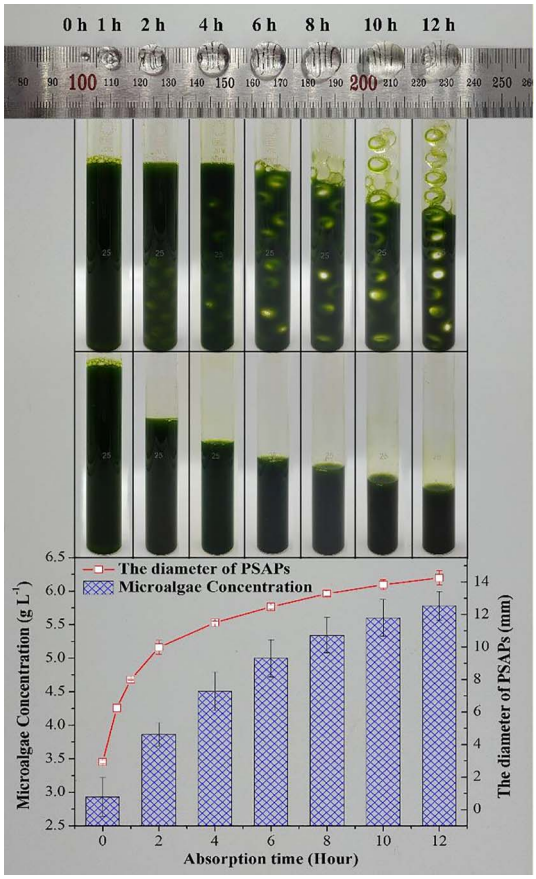

Fig. 1. The concentration of microalgae and diameter of PSAPs with 0.456 g of PSAPs dipped in microalgae culture suspension.

To understand the absorption process, it is necessary to research the kinetic characteristics of PSAPs swelling process and the influencing factors' effect on the absorbency.

3.2. Kinetic characteristics of PSAPs swelling in microalgae suspension

As shown in Fig. 2a, the absorbed mass of the liquid in de-ionized water was 131.49 g per g PSAPs (g g^{-1}) after 12 h, whereas 66.72 g g^{-1} was obtained for the solution of 1 g L^{-1} NaCl. Then, it absorbed 33.28 g g^{-1}, 21.61 g g^{-1}, 17.65 g g^{-1} and 17.02 g g^{-1} with the concentration of NaCl solution at 5 g L^{-1}, 15 g L^{-1}, 25 g L^{-1} and 35 g L^{-1}, respectively. This indicated that the ionic strength of the swollen solution had a dramatically negative influence on the absorbency of the PSAPs. This can be understood in that the great ionic strength reduced the concentration gradient between the inside of PSAPs and the swollen solution, which was one of the driving forces of the relaxation process.

In this study, the model for the swelling kinetic originates from the diffusion-relaxation theory (Fátima Rosa, 2002). The experimental data of PSAPs absorbing the NaCl solution with different concentrations (Fig. 2a) was fitted with Eq. (3) to determine the parameters k_F, k_R and x for each experimental group (Table 1). The results show that the higher the concentration of the solution was, the greater the diffusion proportion accounted for. This might be caused by the ions (Na^+ and Cl^-) of the solution that could also diffuse into the polymer during the swelling process. Hence, Na^+ would be adsorbed into the network chains of the polymer due to the fixed and negatively charged groups (Dhara et al., 1999; Chen, 2003). Moreover, the electrostatic repulsion resulted from the fact that the presence of these fixed charges on the polymer chains would be weakened, which would further affect the relaxation process. In particular, the diffusion proportion increased from 0% to 2.25% as the NaCl concentration increased from 0 to

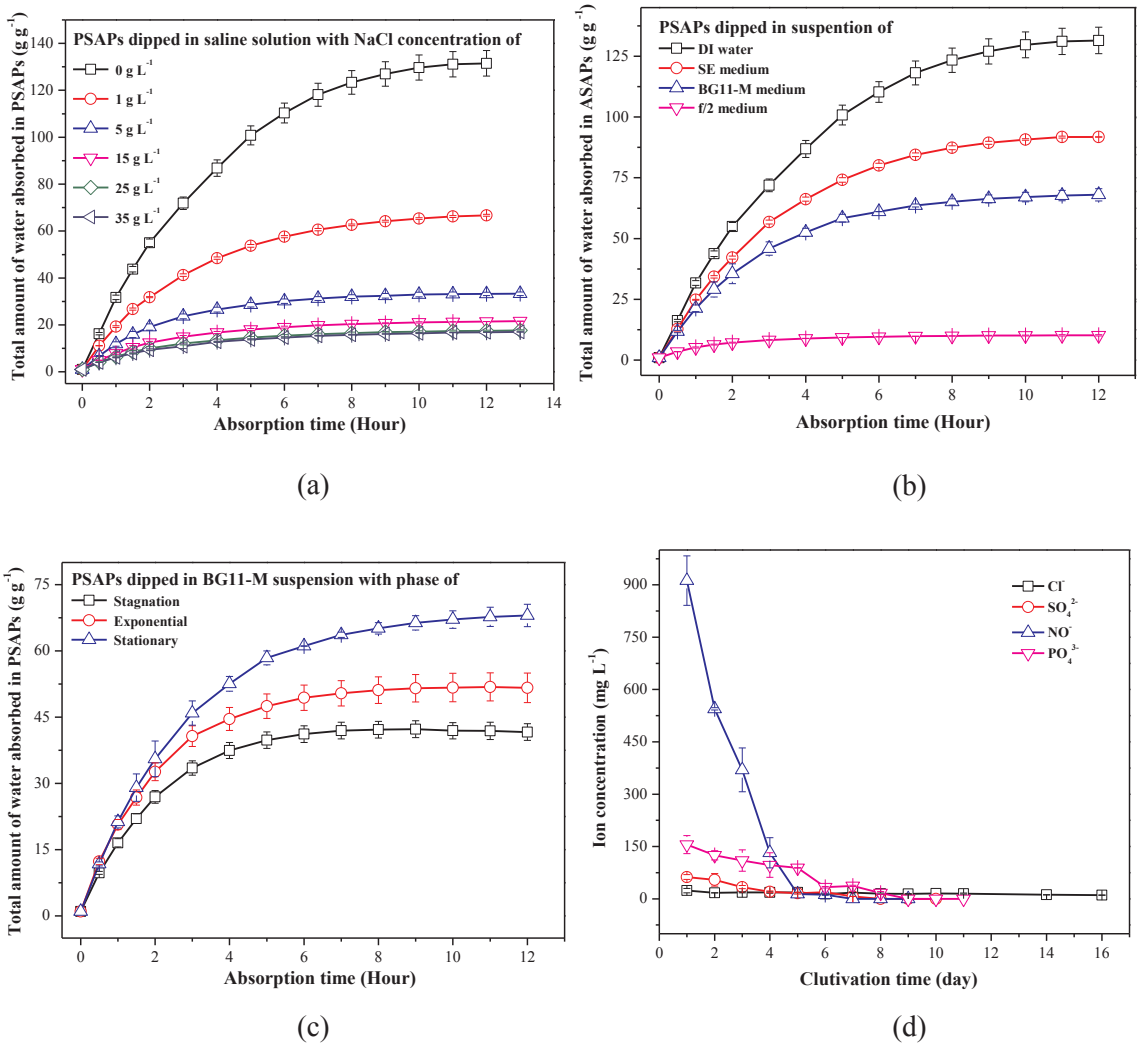

Fig. 2. The total amount of water absorbed in PSAPs dipped in different solutions. (a) Effect of NaCl concentration; (b) effect of the medium; and (c) effect of growth periods on absorption characteristics of PSAPs. (d) Comparisons of ion concentration in BG11-M culture during microalgae growth.

Table 1
Fitting coefficients for kinetics parameters in different NaCl concentration solutions.

NaCl concentration ($g\,L^{-1}$)	x %	1 − x %	k_F s^{-1}	k_R s^{-1}	R^2
0	0	100	0	0.2915	0.9963
1	1.25×10^{-14}	100	7.4134×10^{-25}	0.3336	0.9989
5	0.28	99.72	6.6382×10^{-25}	0.4214	0.9991
15	1.91	98.09	9.6977×10^{-24}	0.4259	0.9965
25	2.19	97.81	2.8594×10^{-21}	0.4174	0.9950
35	2.25	97.75	5.8018×10^{-20}	0.3966	0.9936

x: The diffusion proportion of the absorbed water by PSAPs.
1 − x: The relaxation proportion of the absorbed water by PSAPs.
k_F: Diffusion rate constant.
k_R: Relaxation rate constant.
R^2: Determination coefficients.

35 $g\,L^{-1}$ and as the high concentration of ions decreased the relaxation capacity of PSAPs. Moreover, the proportion of the relaxation part was much greater than the diffusion part. Therefore, the absorbency of PSAPs in NaCl solution was much lower than the absorbency in deionized water and the fitted equations of 0 $g\,L^{-1}$ and 35 $g\,L^{-1}$ are shown as Eqs. (7) and (8), respectively.

$$\frac{M_{t,0}}{M_\infty} = [1-exp(-0.2915t)] \quad (R^2 = 0.9963) \tag{7}$$

$$\frac{M_{t,35}}{M_\infty} = 0.0225\left[1-\frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}exp(-n^2 5.8018\times10^{-20}t)\right] + 0.9775[1-exp(-0.3966t)] \quad (R2 = 0.9936) \tag{8}$$

For a better evaluation of the performance of the PSAPs on the microalgae harvesting, a comparison of the absorbency between the freshwater medium (SE and BG11-M) and the seawater medium (f/2 medium) was conducted (Fig. 2b). The experimental data indicate that this method was more suitable for freshwater medium as the absorbency of the freshwater medium SE and BG11-M was 91.79 $g\,g^{-1}$ and 68.20 $g\,g^{-1}$, whereas it was 10.23 $g\,g^{-1}$ for the seawater medium f/2. In addition, it also reflects that the ionic strength of the BG11-M medium was greater than the SE medium. However, considering the common use of BG11 medium especially for large-scale cultivation (Bennion et al., 2015; Rodolfi et al., 2009), BG11-M medium was chosen as the main swollen solution during further research.

Research on the absorbency and the four main ion concentrations (NO_3^-, SO_4^{2-}, PO_4^{3-} and Cl^-) of BG11-M medium (Fig. 2c and d) in different periods (delay, logarithmic and stable) was also conducted to better understand the harvesting process. The ion concentrations of NO_3^-, SO_4^{2-} and PO_4^{3-} decreased from 912.1120 mg L^{-1}, 62.5920 mg L^{-1} and 188.3220 mg L^{-1} to 020 mg L^{-1} using 7, 8 and 9 days, respectively. However, Cl^- dropped more than half from 23.6520 mg L^{-1} to 10.6720 mg L^{-1} in 16 days. As the ion concentration

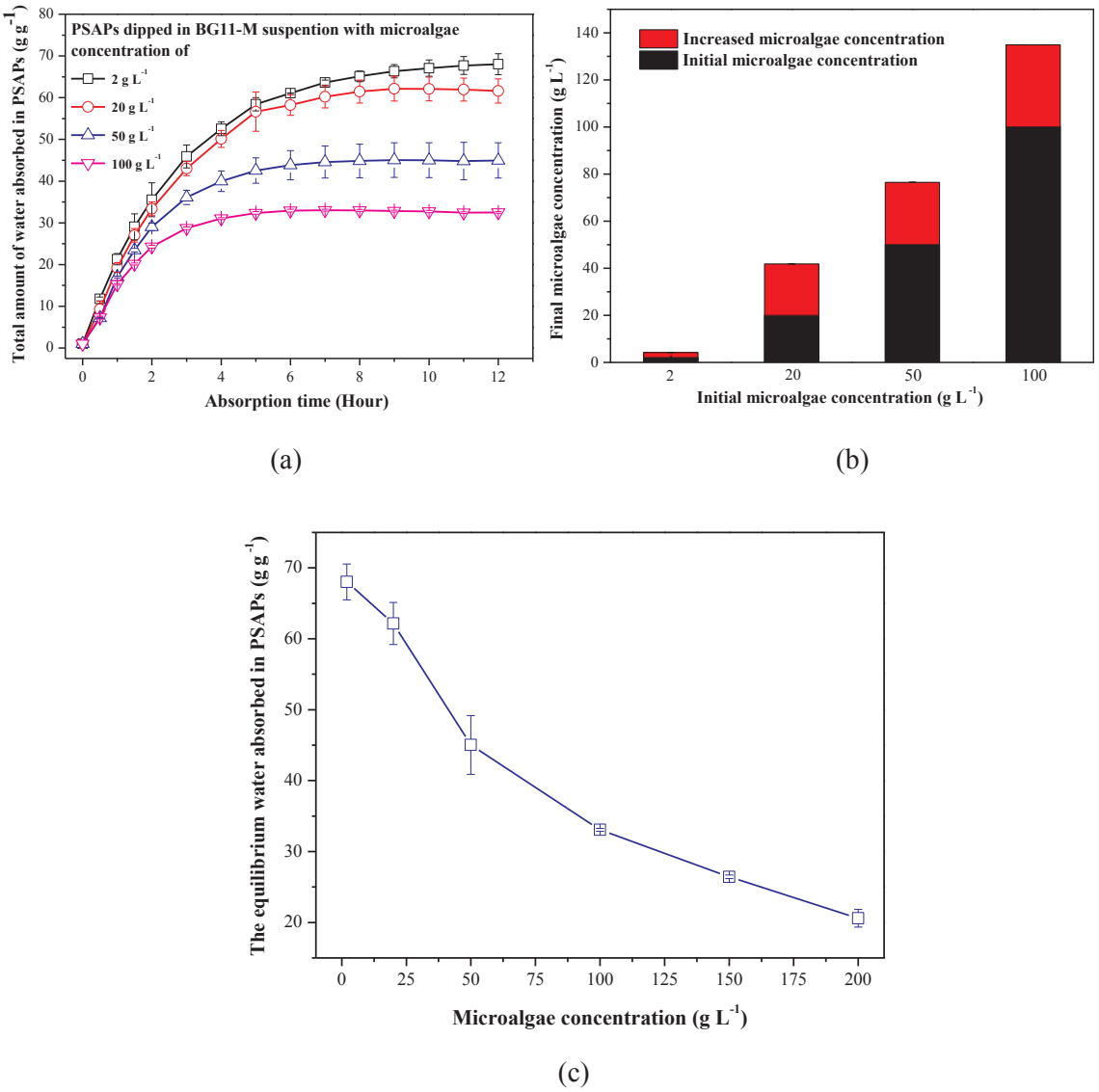

Fig. 3. Effect of microalgae concentration on absorbency (a) and the equilibrium absorbed mass of water (c); (b) initial and increased microalgae concentration during the harvesting of PSAPs.

of the medium decreased over time, the absorbency of PSAPs increased from the delay period (41.63 g g^{-1}) to the logarithmic period (51.64 g g^{-1}) and then to the stable period (68.02 g g^{-1}). The results demonstrate that the stable period was the most suitable time to concentrate microalgae as the concentration of microalgae cells was high and the absorbency of PSAPs was great.

3.3. Effects of microalgae biomass concentration and temperature on the absorbency of PSAPs

3.3.1. Effects of the initial microalgae biomass concentration

Because the biomass concentration of microalgae increases during the whole harvesting period with PSAPs, it is necessary to investigate the effect of microalgae biomass concentration on the absorbency of PSAPs (Fig. 3a and b). It is indicated that the absorbency of PSAPs dropped with an increasing microalgae concentration. The absorbency decreased from 68.02 g g^{-1} to 33.05 g g^{-1} with the initial microalgae concentration increased from 2 g L^{-1} to 100 g L^{-1} and the microalgae suspension was concentrated to 4.18 g L^{-1} and 134.89 g L^{-1}, respectively. As the ion concentration of these microalgae suspensions remained the same, the distinction of the absorbency should be mainly caused by the different concentrations of microalgae cells. Moreover, compared with ion strength, the influence of microalgae concentration was obviously weak as the absorbency of the 5 g L^{-1} NaCl solution was 33.28 g L^{-1} which was almost the same of the 100 g L^{-1} microalgae suspension (33.05 g L^{-1}). The experimental data of absorbency with different microalgae concentrations (Fig. 3c) were used to fit the equilibrium absorbed mass of water. According to the experimental curve of Fig. 3c, the selected fitting model is experiment decline model of Eq. (9), and the fitted equation is shown as Eq. (10).

$$Q_e = a + b\exp(-x/c) \tag{9}$$

$$Q_e = 14.977 + 55.493\exp(-x/90.150) \quad (R^2 = 0.9928) \tag{10}$$

Hence, the needed amount of PSAPs could be calculated by the integral method according to Eq. (10). Furthermore, to better understand the swelling kinetics of the absorption process, the diffusion-relaxation model mentioned above was applied to the experiment (Table 2) and the fitted equation of 2 g L^{-1} microalgae was shown as Eq. (11). As shown in Table 2 and different from the NaCl solution, the diffusion proportion of PSAPs in the microalgae suspension remained 0 consistently. This was possibly due to the fact that the microalgae cells mainly set back the diffusion process, as the PSAPs were surrounded by too many small microalgae cells. The surrounded small cells could

Table 2
Fitting coefficients for kinetics parameters in different microalgae concentration solutions.

Microalgae concentration ($g\,L^{-1}$)	x %	1 − x %	k_F s^{-1}	k_R s^{-1}	R^2
2	0	1	0	0.3780	0.9995
20	0	1	0	0.4140	0.9966
50	0	1	0	0.5109	0.9963
100	0	1	0	0.6632	0.9953

x: The diffusion proportion of the absorbed water by PSAPs.
1 − x: The relaxation proportion of the absorbed water by PSAPs.
k_F: Diffusion rate constant.
k_R: Relaxation rate constant.
R^2: Determination coefficients.

further restrict the movement of water into the network structure of the polymer as the diameter of *Chlorella* sp. was only about 5–10 μm (Illman et al., 2000).

$$\frac{M_t}{M_\infty} = [1-exp(-0.378t)] \quad (R^2 = 0.9995) \tag{11}$$

Since the microalgae biomass concentration negatively influenced the PSAP performance, an experiment was conducted to investigate the microalgae harvesting limit of the PSAP method as shown in Table 3. A total of 4.32 g of PSAPs was used to concentrate 200 mL of microalgae suspension with a dry weight of 1.42 $g\,L^{-1}$ biomass (cultivated with BG11-M medium for 7 days). Approximately 4 h later, there was only 2.7 of ml microalgae suspension left with a microalgae concentration of 40.71 $g\,L^{-1}$, and some microalgae cells adhered to the particles and the container. The microalgae concentration of 40.71 $g\,L^{-1}$ was not the harvesting limit of the PSAP method. To explore the limit, 0.18 g PSAPs was used to concentrate 6 ml of microalgae suspension with a dry weight of 40.71 $g\,L^{-1}$. After 4 h, the concentration was increased to 90.23 $g\,L^{-1}$. With the development of wet biomass conversion technology, the requirements of biomass conversion on the microalgae concentration were no longer high. A microalgae concentration of 50–100 $g\,L^{-1}$ was suitable for oil extraction and biogas fermentation (Cheng et al., 2012; Kanda and Li, 2011). In addition, the concentrated microalgae suspension could directly be used to extract oil or for fermentation with no additional harvesting.

3.3.2. Effects of temperature on the absorbency of PSAPs

As mentioned above, the current large-scale cultivation of microalgae mainly occurs in outdoor open raceway ponds and closed PBRs. Because it is difficult to control the temperature of the environment, it is necessary to study the impact of the harvesting temperature on the PSAPs absorbing characteristic. As shown in Fig. 4, PSPAs were used to concentrate microalgae with various temperatures (5–35 °C). When the suspension temperature increased, the absorption rate of water increased as the higher temperature enhanced the thermal motion of the polymer. That is, the absorption process was accelerated and the absorption time was shortened. At 35 °C, it took only 9 h for the PSAPs to concentrate the microalgae suspension, whereas it took at least 12 h at 4 °C. In addition, the summer season would benefit the harvesting process as the temperature in summer is higher than other seasons.

Table 3
Microalgae suspension concentrated by PSAPs.

Initial microalgae concentration ($g\,L^{-1}$)	Initial volume of microalgae suspension (mL)	PSAP dosage (g)	Harvesting ratio	Final microalgae concentration ($g\,L^{-1}$)
1.42	200	4.32	28.66	40.71
40.71	6	0.18	2.22	90.23

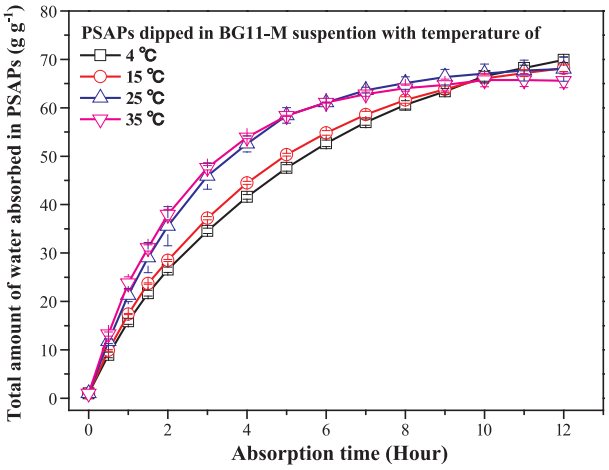

Fig. 4. Effect of temperature on the absorption characteristics of PSAPs in BG11-M medium.

This also indicates that the absorbency dropped gradually with rising temperature. The absorbency at 35 °C (65.58 $g\,g^{-1}$) was approximately 93.80% of that at 4 °C (69.91 $g\,g^{-1}$). This was possibly due to the enhanced polymer thermal motion, which had the potential to produce elastic shrinkage as the polymer had absorbed a considerable amount of medium and the polymer network had already fully expanded.

3.4. Regeneration and reusability of PSAPs

Experiments with different desorption temperatures (60–90 °C) were conducted to verify the suitable desorption temperature of PSAPs (Fig. 5a). When the heating temperature increased, the polymer desorption rate increased as the higher temperature enhanced the thermal motion of the polymer. This could lead to the improvement in evaporation of the outer layer water in PSAPs, which heightened the ion concentration of the outer layer and in turn absorbed the water of the inner layer. At 60 °C, it took 10 h to regenerate the PSAPs to the initial weight and 6 h at 70 °C. In addition, it took almost 3 h at 80 °C and 90 °C. Thus, we could make a conclusion that it was more suitable to regenerate the PSAPs at 80 °C. Additionally, the input energy would be reduced if we used the discharged high temperature boiler flue-gas to regenerate the PSAPs.

The reusability process of PSAPs was performed with the condition of swelling in BG11-M medium at 25 °C and dewatering in a convection electrical oven at 80 °C. After one cycle, the regenerated PSAPs were reused in fresh BG11-M medium to eliminate the influence of the microalgae concentration. As shown in Fig. 5, the absorbency of PSAPs remained at 95.81% of the original after one cycle, and still remained at 91.45% after two cycles. In addition, there was a phenomenon in that the color of the PSAPs changed from transparent to light yellow after regeneration. This might also be due to the Donnan effect (Dhara et al., 1999) as the ions and some microalgae residues would get into the network structure of the polymer.

4. Conclusions

PSAPs can be used to concentrate freshwater microalgae *Chlorella* sp. with a TSS of 9.02%, and the concentrated microalgae suspension can directly be used to extract oil with no additional harvesting. PSAPs can regenerate and be reused at least three times with the absorbency remaining at 91.45% of the original. To further evolve this method, future work will focus on the development of systems to concentrate the microalgae suspension at a large scale. Nonetheless, this study demonstrates a promising microalgae harvesting method for freshwater

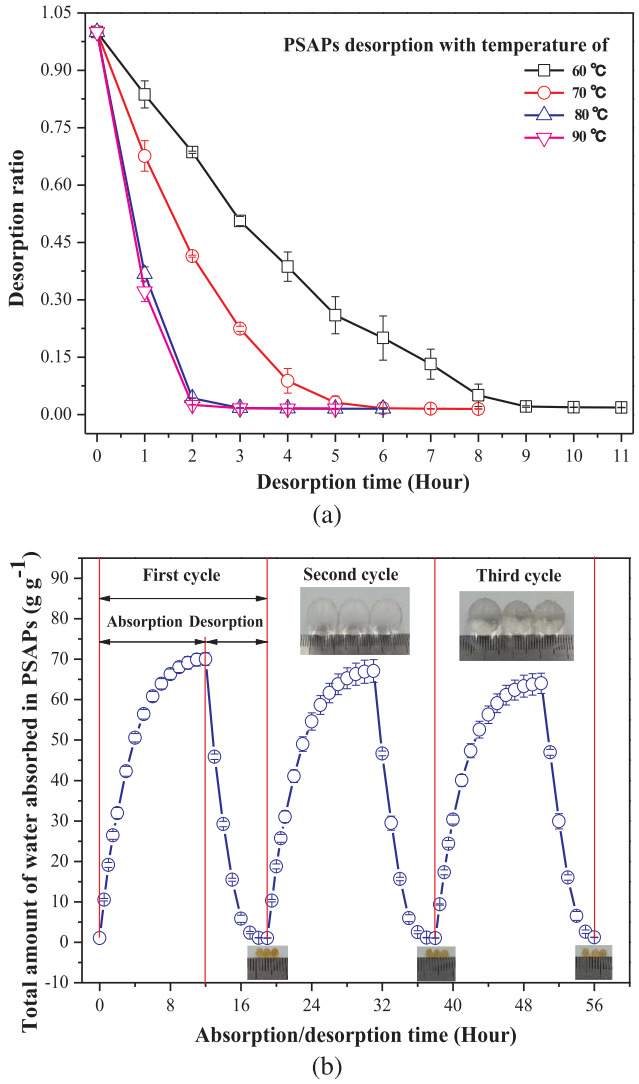

Fig. 5. (a) Effect of temperature on the desorption characteristics in a convection electrical oven. (b) Absorption/desorption cycles of PSAPs performed at 25 °C/80 °C in BG11-M medium.

microalgae with a relatively high concentration.

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References

Ahmed, E.M., 2015. Hydrogel: preparation, characterization, and applications: a review. J. Adv. Res. 6 (2), 105–121.
Barros, A.I., Gonçalves, A.L., Simões, M., Pires, J.C.M., 2015. Harvesting techniques applied to microalgae: a review. Renew. Sustain. Energy Rev. 41, 1489–1500.
Bennion, E.P., Ginosar, D.M., Moses, J., Agblevor, F., Quinn, J.C., 2015. Lifecycle assessment of microalgae to biofuel: comparison of thermochemical processing pathways. Appl. Energy 154, 1062–1071.
Bilad, M.R., Arafat, H.A., Vankelecom, I.F.J., 2014. Membrane technology in microalgae cultivation and harvesting: a review. Biotechnol. Adv. 32, 1283–1300.
Chang, H.X., Huang, Y., Fu, Q., Liao, Q., Zhu, X., 2016. Kinetic characteristics and modeling of microalgae *Chlorella vulgaris* growth and CO_2 biofixation considering the coupled effects of light intensity and dissolved inorganic carbon. Bioresour. Technol. 206, 231–238.
Chen, G., Zhao, L., Qi, Y., 2015. Enhancing the productivity of microalgae cultivated in wastewater toward biofuel production: a critical review. Appl. Energy 137, 282–291.
Cheng, J., Xia, A., Liu, Y., Lin, R., Zhou, J., Cen, K., 2012. Combination of dark- and photo-fermentation to improve hydrogen production from Arthrospira platensis wet biomass with ammonium removal by zeolite. Int. J. Hydrogen Energy 37 (18), 13330–13337.
Chiu, S.Y., Kao, C.Y., Chen, T.Y., Chang, Y.B., Kuo, C.M., Lin, C.S., 2015. Cultivation of microalgal Chlorella for biomass and lipid production using wastewater as nutrient resource. Bioresour. Technol. 184, 179–189.
Coward, T., Lee, J.G.M., Caldwell, G.S., 2013. Development of a foam flotation system for harvesting microalgae biomass. Algal Res. 2 (2), 135–144.
Dhara, D., Nisha, C.K., Chatterji, P.R., 1999. Super absorbent hydrogels: interpenetrating networks of poly (acrylamide-co-acrylic acid) and poly (vinyl alcohol): swelling behavior and structural parameters. J. Macromol. Sci. A 36 (2), 197–210.
Fátima Rosa, J.B., Casquilho, Miguel, 2002. Kinetics of water absorbency in AA/AMPS copolymers: applications of a diffusion-relaxation model. Polymer 43 (1), 63–70.
Grima, E.M., Belarbi, E.-H., Fernández, F.G.A.N., Medina, A.R., Chisti, Y., 2003. Recovery of microalgal biomass and metabolites: process options and economics. Biotechnol. Adv. 20, 491–515.
Henderson, R., Parsons, S.A., Jefferson, B., 2008. The impact of algal properties and pre-oxidation on solid-liquid separation of algae. Water Res. 42 (8–9), 1827–1845.
Huang, Y., Sun, Y., Liao, Q., Fu, Q., Xia, A., Zhu, X., 2016. Improvement on light penetrability and microalgae biomass production by periodically pre-harvesting *Chlorella vulgaris* cells with culture medium recycling. Bioresour. Technol. 216, 669–676.
Illman, A.M., Scragg, A.H., Shales, S.W., 2000. Increase in Chlorella strains calorific values when grown in low nitrogen medium. Enzyme Microb. Technol. 27, 631–635.
Kanda, H., Li, P., 2011. Simple extraction method of green crude from natural blue-green microalgae by dimethyl ether. Fuel 90 (3), 1264–1266.
Kozicki, M., Kolodziejczyk, M., Szynkowska, M., Pawlaczyk, A., Lesniewska, E., Matusiak, A., Adamus, A., Karolczak, A., 2016. Hydrogels made from chitosan and silver nitrate. Carbohyd. Polym. 140, 74–87.
Kumar, V., Nanda, M., Verma, M., 2017. Application of agar liquid-gel transition in cultivation and harvesting of microalgae for biodiesel production. Bioresour. Technol. 243, 163–168.
Lananan, F., Jusoh, A., Ali, N., Lam, S.S., Endut, A., 2013. Effect of conway medium and f/2 medium on the growth of six genera of South China Sea marine microalgae. Bioresour. Technol. 141, 75–82.
Luo, S., Griffith, R., Li, W., Peng, P., Cheng, Y., Chen, P., Addy, M.M., Liu, Y., Ruan, R., 2017. A continuous flocculants-free electrolytic flotation system for microalgae harvesting. Bioresour. Technol. 238, 439–449.
Makuuchi, K., 2010. Critical review of radiation processing of hydrogel and polysaccharide. Radiat. Phys. Chem. 79 (3), 267–271.
Martín del Campo, J.S., Patiño, R., 2013. Harvesting microalgae cultures with superabsorbent polymers: desulfurization of *Chlamydomonas reinhardtii* for hydrogen production. Biotechnol. Bioeng. 110 (12), 3227–3234.
Milano, J., Ong, H.C., Masjuki, H.H., Chong, W.T., Lam, M.K., Loh, P.K., Vellayan, V., 2016. Microalgae biofuels as an alternative to fossil fuel for power generation. Renew. Sustain. Energy Rev. 58, 180–197.
Nyomi Uduman, Y.Q., Danquah, Michael K., Forde, Gareth M., Hoadley, Andrew, 2010. Dewatering of microalgal cultures a major bottleneck to algae-based fuels. J. Renew. Sustain. Energy. 2 (1), 23–571.
Ozkan, A., Berberoglu, H., 2013. Physico-chemical surface properties of microalgae. Colloid Surf. B 112, 287–293.
Papazi, A., Makridis, P., Divanach, P., 2009. Harvesting *Chlorella minutissima* using cell coagulants. J. Appl. Phycol. 22 (3), 349–355.
Rodolfi, L., Chini Zittelli, G., Bassi, N., Padovani, G., Biondi, N., Bonini, G., Tredici, M.R., 2009. Microalgae for oil: strain selection, induction of lipid synthesis and outdoor mass cultivation in a low-cost photobioreactor. Biotechnol. Bioeng. 102 (1), 100–112.
Soh, L., Montazeri, M., Haznedaroglu, B.Z., Kelly, C., Peccia, J., Eckelman, M.J., Zimmerman, J.B., 2014. Evaluating microalgal integrated biorefinery schemes: empirical controlled growth studies and life cycle assessment. Bioresour. Technol. 151, 19–27.
Sun, Y., Liao, Q., Huang, Y., Xia, A., Fu, Q., Zhu, X., Zheng, Y., 2016. Integrating planar waveguides doped with light scattering nanoparticles into a flat-plate photobioreactor to improve light distribution and microalgae growth. Bioresour. Technol. 220, 215–224.
Vandamme, D., Foubert, I., Muylaert, K., 2013. Flocculation as a low-cost method for harvesting microalgae for bulk biomass production. Trends Biotechnol. 31 (4), 233–239.
Wang, S.-K., Stiles, A.R., Guo, C., Liu, C.-Z., 2015. Harvesting microalgae by magnetic separation: a review. Algal Res. 9, 178–185.
Wiley, P.E., Brenneman, K.J., Jacobson, A.E., 2009. Improved algal harvesting using suspended air flotation. Water Environ. Res. 81 (7), 702–708.
Xie, X., Bahnemann, J., Wang, S., Yang, Y., Hoffmann, M.R., 2016. Nanofiltration enabled by super-absorbent polymer beads for concentrating microorganisms in water Samples. Sci. Rep. 6, 20516.
Xue-ping Chen, G.-R.S., Huang, Jian, Huang, Zhi-ming, Weng, Zhi-xue, 2003. Synthesis and properties of acrylic-based superabsorbent. J. Appl. Polym. Sci. 92, 619–624.