

Functional magnetic nanoparticles for microalgal biomass harvesting

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ABSTRACT

Magnetic harvesting of *Chlorella pyrenoidosa* was attempted using several magnetic particles with a magnetic separation system. Compared with other particles, CPAM-Fe₃O₄ particles were more efficient for the harvesting of *C. pyrenoidosa* and a high recovery efficiency of more than 93% was obtained at a dosage of 1500 mg/L. Using a magnetic separator, more than 90% of the *C. pyrenoidosa* cells can be separated at a feed rate of 100 mL/min. In addition, the protein content and amino acid composition of the algal cells were not influenced by the magnetic separation and detachment process. The efficient and reliable magnetic separation procedure provides a great potential for microalgal harvesting in practice.

Keywords: Microalgal Harvesting, Magnetic nanoparticles

1 INTRODUCTION

Microalgae has been considered as promising candidates for biofuel production over the past few years due to its uncomparable advantages such as a high lipid content and growth rate, utilization of non-arable land (Christi, 2007). In addition, it can accumulate various naturally-produced compounds used in pharmaceutical industries, as food supplements and animal feed (Mata, Martins, Caetano, 2010). *Chlorella pyrenoidosa* is a green alga commonly used as human and animal nutrition supplement due to its ability to accumulate various high-value compounds such as fatty acids, carotenoids, pigments, xanthophylls, especially rich in protein (as high as 50–65% of its dry weight) (Su; Zhang; Zhang; Zhou; Li, 2011).

Due to the small size of algal cells and the dilute nature of microalgal cultures, the harvesting process usually costly and energy-consuming and was regarded as a bottleneck for the industrialization of microalgae-based products. Traditional microalgae harvesting methods including

centrifugation, filtration, flocculation, sedimentation, and flotation have various disadvantages. In recent years, a few attempts on harvesting microalgal cells using magnetic particles have been made (Wang; Sterile; Guo; Liu, 2015). Those naked and surface functionalized magnetic particles showed good potential for the recovery of algal cells. In addition, an effective magnetic separation system was developed and achieved high recovery efficiencies using either naked Fe₃O₄ or surface functionalized magnetic particles (Hu, Guo, Wang, Wang, Pan, Liu, 2014; Hu, Wang, Wang, Liu, Guo, 2013).

In current study, the magnetic harvesting of *C. pyrenoidosa* cultivated in outdoor raceway pond was investigated using several magnetic particles with a magnetic separation system. In addition, effect of magnetic particles and the detachment process on the protein content and amino acid composition of *C. pyrenoidosa* cells was also studied.

2 EXPERIMENTAL

The *C. pyrenoidosa* (FACHB 9) were cultivated in the BG-11 medium. A raceway pond with a working volume and depth of 45 L and 14 cm, respectively, was applied for the outdoor cultivation of the microalgae. CO₂-enriched air (2%, v/v) was bubbled into the culture using four plastic pipes placed at the bottom of the pond with holes at a flow rate of 0.5 v/v/m. *C. pyrenoidosa* grew from an inoculum of 0.3 g/L to 1.1 g/L after 4 days. The pH of the final broth was around 7.0.

Three kinds of magnetic particles were investigated for the harvesting of *C. pyrenoidosa*, include naked Fe₃O₄, polyethylenimine/Fe₃O₄ nanocomposites (PEI-Fe₃O₄), and cationic acrylamide (CPAM) surface functionalized Fe₃O₄ particles (CPAM-Fe₃O₄). The preparation of those particles was according to the methods reported by Xu et al., Hu et al., and Wang et al., respectively. 6, 11, 12 Algal harvesting was firstly tested in Erlenmeyer flasks by mixing

a certain dosage of magnetic particles with algal broth on a rotary shaker at 150 rpm for 2 min, 2 min, and 10 min for Fe₃O₄, PEI- Fe₃O₄, and CPAM- Fe₃O₄, respectively. Then placed the flasks on a permanent magnet for 2 min and the cell concentration of the decanted supernatant was measured. The magnetic separator used in this study has been reported by Hu et al.¹³ The separation process was conducted in continuous mode as the procedures reported by Wang et al.¹⁴ The detachment of the collected particle-cell aggregates was operated according to the method for *C. ellipsoidea* reported by Xu et al. ⁶

The recovery efficiency was calculated based on Wang et al.¹² The collected cells after detachment was lyophilized using a lyophilizer (ALPHA1–2, CHRIST, Germany) and analyzed its protein content and amino acid composition based on the methods reported by Wang et al. ¹⁵ and compared them with that from centrifugation collected cells.

3 RESULTS AND DISCUSSION

Recovery efficiencies of naked Fe₃O₄, PEI- Fe₃O₄, and CPAM- Fe₃O₄ on the harvesting of *C. pyrenoidosa* cells were illustrated in Figure 1. The results indicated that CPAM- Fe₃O₄ particles showed more effective for the harvesting of *C. pyrenoidosa* than other two kinds of magnetic particles. This was mainly due to the high flocculation capacity of CPAM. It can effectively flocculate algal cells into large flocs and the flocs can be easily separated based on the magnetic character of Fe₃O₄ under an external magnetic field. Compared with CPAM- Fe₃O₄ particles, the harvesting capacities for *C. pyrenoidosa* of naked Fe₃O₄ and PEI- Fe₃O₄ particles was much lower. At a CPAM- Fe₃O₄ dosage of 1500 mg/L, the recovery efficiency can reached more than 93%.

As shown in Figure 2, the magnetic separation process of *C. pyrenoidosa* by CPAM- Fe₃O₄ particles was rapid and can be effectively separated within 2 min. Using CPAM- Fe₃O₄ particles, the continuous separation of *C. pyrenoidosa* was operated on the magnetic separation system.¹³ At a particle dosage and feed rate of 1500 mg/L and 100 mL/min, respectively, a recovery efficiency of more than 90% can be achieved in this separation process.

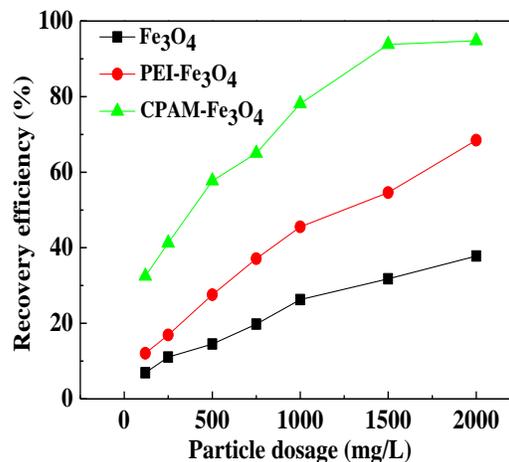


Figure 1 Recovery efficiency of *C. pyrenoidosa* using different magnetic particles on various dosage.



Figure 2 Photographs for the time-lapse magnetic separation process of *C. pyrenoidosa* using CPAM-Fe₃O₄ particles. From left to right: 0 s; 30 s; 60 s; 120 s.

The target product in the cultivation of *C. pyrenoidosa* was usually protein due to its high protein content. Therefore, it is significant to investigate the influence of the harvesting method on the protein content and composition. As shown in Table 1, the protein content and amino acid composition of *C. pyrenoidosa* after harvesting by CPAM- Fe₃O₄ particles and detachment by acid were similar with that obtained by centrifugation. The results indicated that this separation procedure has no obvious effects on the quality of the protein produced by *C. pyrenoidosa*. The magnetic harvesting method in this study was effective and reliable for the harvesting of *C. pyrenoidosa*.

TABLE 1 Amino acid and protein of the algal cells collected by magnetic separation and centrifugation.

Amino acid	Content (% of DW)	
	Magnetic	Centrifugation

		separation	
Essential amino acids	Phe	2.11	2.08
	Thr	1.76	1.95
	Met	0.36	0.38
	Val	2.62	2.50
	Ile	1.59	1.53
	Leu	4.13	3.96
	Trp	0.11	0.14
	Lys	2.71	2.77
	Total	15.39	15.31
Non-essential amino acids	Ala	3.60	3.77
	Gly	2.33	2.61
	Tyr	1.34	1.40
	Ser	1.48	1.69
	His	0.82	0.84
	Arg	3.20	3.22
	Glu	5.24	5.64
	Asp	3.72	3.93
	Pro	1.88	1.99
	Cys	0.30	0.39
	Total	23.91	25.48
Total amino acid (% of DW)		39.30	40.79
Total protein (% of DW)		47.00	51.40

A magnetic separator was built for continuous harvesting of microalgal (Figure 3). The separator is composed of permanent magnet drum, Scraper blade and Separation chamber. Magnetic nanoparticles can adsorb on microalgal cells, then they will attach on magnet drum, and are scraped by scraper blade.

A typical magnetic microalgal harvesting system is shown in Figure 4. At the end of microalgal culture,

magnetic nanoparticles are added in the algal cultural solution. The solution then is pumped to the chamber of magnetic separator. Along with the rotate of magnet drum, magnetic particles coated cells are adsorbed on to the drum. The remained clear water then goes to the collecting tank. The separated cells with coated particles are harvested by scraping from the magnet drum.

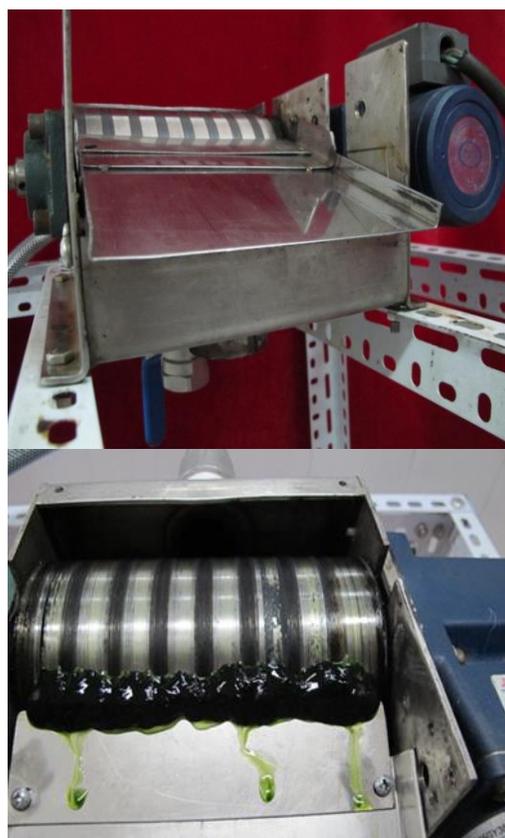


Figure 3 Photograph of magnetic separator

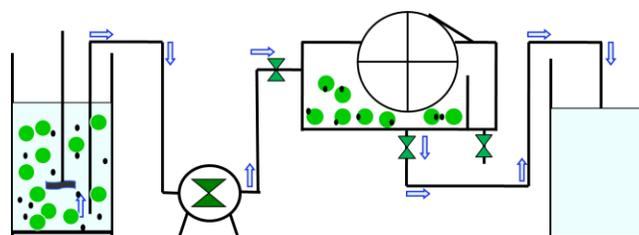


Figure 4 The schematic illustration how the magnetic separator works. From left to right: mixing tank, peristaltic pump, magnetic separator, and collecting tank

4 CONCLUSION

In order to recovery of microalgal, magnetic nanoparticles are applied to microalgal harvesting process. Three kinds of magnetic nanoparticles are compared for separating *Chlorella pyrenoidosa*. Among the three nanoparticles investigated, CPAM- Fe₃O₄ particles were more efficient for the harvesting of *C. pyrenoidosa* than other two kinds of magnetic particles. This may be the electrostatic interaction between cation acrylamide and microalgal cells with negative charge. A recovery efficiency of more than 93% can be reached at a dosage of 1500 mg/L. Integrated the magnetic particles with a magnetic separator, the *C. pyrenoidosa* cells can be effectively separated at a feed rate of 100 mL/min under continuous mode. The magnetic separation procedure has no negative influence on the production of the protein in *C. pyrenoidosa* cells and showed great potential for the efficient harvesting of microalgal cells.

REFERENCES

- Y.Chisti, *Biotechnol. Adv.* 25, 294, 2007
- T. M. Mata, A. A. Martins, and N. S. Caetano, *Renew. Sustain. Energy Rev.* 14, 217, 2010
- H. Y. Su, Y. L. Zhang, C. M. Zhang, X. F. Zhou, and J. P. Li, *Bioresour. Technol.* 102, 9884, 2011
- S.K. Wang, A.R. Stiles, C. Guo, C.Z. Liu, *Algal Research* 9,178, 2015
- Y.R. Hu, C. Guo, F. Wang, S.K. Wang, F. Pan, C.Z. Liu, *Chemical Engineering Journal*, 242, 341, 2014
- Y.R. Hu, F. Wang, S.K. Wang, C.Z. Liu, C. Guo, *Bioresource Technology*, 138, 387, 2013