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Cost-effectiveness Analysis on Magnetic Harvesting of Algal Cells

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Abstract

This study investigated the magnetic harvesting of algae via magnetic nanoparticles (MNPs). MNPs achieved high harvesting efficiency, over 95.0%, for various algal strains and could be effectively reactivated for low-cost algae separation. Comparing different harvesting efficiency, synthesis cost and reactivation methods, the present work evaluated the cost-effectiveness of different MNPs types and discussed the key factors affecting harvesting cost. Our results indicated a significant low cost and high harvesting effectiveness by naked MNPs and ultrasonic reactivation, though surface modified MNPs had higher harvesting capacity. Given the fact that algae harvesting is one of the most cost-consumption step in bioenergy production, we suggested magnetic algae harvesting with naked and reactivated MNPs as the most cost-effective technique for future industrial application.

Selection and Peer-review under responsibility of the Conference Committee Members of Functional Nanomaterials in Industrial Applications.

Keywords: magnetic nanoparticles (MNPs), algae harvest; reactivation; cost-effectiveness

1. Introduction

Algal biofuel is an important resource of sustainable energy [1]. During its production process, algae harvesting process had high energy consumption [2], such as filtration [3, 4], flocculation [5] and centrifugation [6]. Of all the new functional materials developed for cost- and energy-effective algae harvesting, magnetic nanoparticles (MNPs) have superparamagnetism and biological affinity, and can effectively capture various algal cells [7, 8]. Most recent studies addressed the surface functionalization for higher harvesting efficiency [9] or reactivation [10] for either

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cyanobacteria [10], microalgae [11, 12, 13] or algae [14], but there is limited study investigating the cost-effectiveness of applying various types of MNPs to evaluate their feasibility in engineering practice.

In this study, we synthesized different types of MNPs, and used both ultrasonic and alkaline reactivation methods on magnetic harvesting of various algal cells (*Synechocystis*, *Stigeoclonium*, *Nannochloropsis* and *Microcystis*). Further cost-effectiveness analysis provided deeper understanding on its feasibility in practical biomass harvesting and evaluated its potential in bioenergy industrial application.

2. Experimental Section

2.1. Magnetic nanoparticle synthesis

MNPs synthesis followed modified chemical decomposition method [15]. Precisely, A certain amount of $FeCl_2$ (1.0 M) and $FeCl_3$ (2.0 M) were mixed together for all the three types of MNPs (MNPs-A, 1-mL:1-mL; MNPs-B, 1-mL:2-mL; MNPs-C, 1-mL:4-mL). Subsequently, 25 mL NaOH (2.0 M) was added drop by drop, with constant vortex for 30 minutes. After magnetic separation by permanent magnet, the synthesized MNPs were further washed by deionized water until the pH was 7.0. From our previous work, the concentration of synthesized MNPs ranged from 8.0 to 14.5 g/L via gravimetric method [10]. The MNPs were then diluted to 5.0 g/L as stock solution for harvesting experiment.

2.2. Algal strains and cultivation

Four algal strains were used in this study including *Synechocystis*, *Stigeoclonium*, *Nannochloropsis* and *Microcystis*, and were purchased from Institute of Hydrobiology (Chinese Academy of Sciences). All the strains were cultivated in in BG-11 medium under the condition of 2000 lx light, 1:1 light/darkness and 25 ℃. The 1.0L BG-11 medium contained 1.5 g $NaNO_3$, 40 mg K_2HPO_4, 75 mg $MgSO_4•7H_2O$, 36 mg $CaCl_2•2H_2O$, 6 mg citric acid, 6 mg ferric ammonium citrate, 1 mg $EDTANa_2$, 20 mg Na_2CO_3, 2.86 mg H_3BO_3, 1.86 mg $MnCl_2•4H_2O$, 0.22 mg $ZnSO_4•7H_2O$, 0.39 mg $Na_2MoO_4•2H_2O$, 0.08 mg $CuSO_4•5H_2O$, and 0.05 mg $Co(NO_3)_2•6\ H_2O$. All the algal cells were collected after 15 days cultivation at the late exponential phase for harvesting experiment.

2.3. Algae harvesting and magnetic nanoparticles reactivation

For algae harvesting, 28 μL of MNPs stock solution was added into 972 μL algal suspension. Subsequently, the mixture was cultivated for 5 minutes at 150 rpm and the algae-MNPs complex was separated by permanent magnet for 5 minutes. The supernatant was analyzed for residual biomass to calculate the harvesting efficiency and the algae-MNPs pellets were reactivated for further algae harvesting. The reactivation of MNPs followed ultrasonic and alkaline methods, respectively. The ultrasonic reactivation applied chloroform:methanol (2:1, v/v) as the solvent [10]. The MNPs-algae pellets were added into 1.0 mL chloroform:methanol solvent and ultrasonically disrupted for 2 min (40 kHz and 75 W, KQ5200DA, Kun Shan Ultrasonic Instruments, China). The alkaline reactivation used NaOH solution (pH 11.0) and the MNPs-algae pellets were added into 5.0 mL NaOH solution and vortexed for 10 min. In both treatments, the reactivated MNPs were separated from reactivation suspension by magnet for 5 minutes and resuspended in deionized water for further algae harvest.

2.4. Chemical and data analysis

The amount of biomass was determined by gravimetric method as described before [10]. The 10.0 mL of each algal suspension was centrifuged at 10,000 rpm for 10 minutes and washed by deionized water three times. The cell pellet was then dried at 105 ℃ for 4 hours. The biomass concentration (dry cell weight per mL, DCW/mL) was calculated as the ratio of dry algal weight (mg) to the total volume (mL). The MNPs harvesting efficiency was calculated by the ratio of dry algal biomass in algae-MNPs pellets after separation to the total dry algal biomass. All the *algae* cultivation and MNPs harvesting were carried out with biological triplicates. The harvesting efficiencies were analyzed by one-way ANOVA with significance level <0.05.

2.5. Cost-effectiveness analysis

The cost-effectiveness analysis considered the cost of raw materials and reactivation precedure, evaluated by the cost per kg DCW. All the prices of raw materials for MNPs synthesis were from Sigma-Aldrich. The reactivation cost of ultrasonic treatment was evaluated by the electricity consumption of ultrasonic bath and the cost of solvent (methanol). The cost alkaline reactivation was calculated by the price of NaOH solution.

3. Results and Discussion

3.1. Impacts of magnetic nanoparticle synthesis on algae harvesting performance

The synthesized MNPs have strong capacity to adsorb algal cells and could be effectively separated by the permanent magnet. The algal suspension before magnetic harvesting was of yellow green (*Nannochloropsis*) or dark green (*Synechocystis*, *Stigeoclonium* and *Microcystis*) color. Mixed with MNPs, the algae-MNPs were formed in dark brown color and were easily separated by the magnetic field. Fig. 1 illustrated that the harvesting efficiency of *Microcystis* (averagely 98.71%) was the highest for all types of MNPs, followed by *Nannochloropsis* (98.10%), *Stigeoclonium* (94.89%) and *Synechocystis* (94.78%). The strong electrostatic attraction between MNPs and algal cells explained the mechanisms of magnetic harvesting. Though the harvesting efficiency was positively related to the harvesting time [9], such electrostatic attraction was so strong that the adsorption process required only less than 5 minutes for effective separation. It was therefore feasible in engineering application for high algae harvesting yield in a short time.

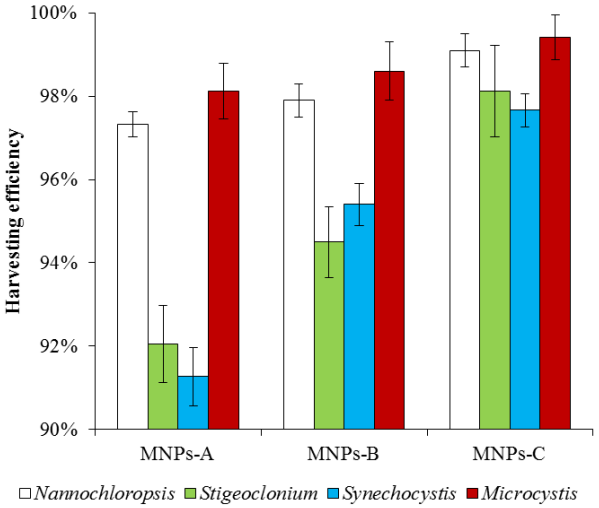

Fig. 1. Magnetic harvesting efficiency of different MNPs for various algal strains.

MNPs synthesis significantly affected algae harvesting efficiency, as illustrated in Fig. 1. MNPs-A had the lowest harvesting efficiency for all the four algal strains (91.27% to 98.12%) and the harvesting efficiency of MNPs-C was the highest (97.66% to 99.42%). The results indicated that the electrostatic attraction between algal cells and MNPs were dependent on the morphological structure and formation of MNPs. One explanation is the change of functional groups on MNPs. The three MNPs (MNPs-A, MNPs-B and MNPs-C) were consisted of different types of iron oxides attributing to the respective ratio of ferric to ferrous ions. In MNPs-A (Fe^{2+}/Fe^{3+}=1:2), and the nanocomposites were consisted of nano-scale round Fe_3O_4 nanoparticles (10-30 nm) and β-FeOOH nanorods (100-200 nm in length and 30-50 nm in diameter) [10]. MNPs-B had the Fe^{2+}/Fe^{3+} ratio of 1:1, indicating the perfect structure of round Fe_3O_4. The Fe^{2+}/Fe^{3+} ratio of MNPs-C was 2:1, containing Fe_3O_4 and excessive Fe_2O_4. Such different composition meant different functional and active sites on the surface of each MNPs, consequently

resulting in respective algal harvesting performance. The other reason explaining the change of harvesting efficiency of different MNPs was the zeta potential. The zeta potentials of each MNPs at pH 7.0 were different attributing to different protonated surfaces [13], and the difference in zeta potential between MNPs and algal cells determine the strength of electrostatic attraction. Besides, the zeta potential also determined the aggregation of MNPs at neutral pH [16], as found by Wang that bridging was the primary mechanisms of magnetic flocculation [9].

3.2. Magnetic nanoparticles reactivation efficiency

All the MNPs maintained high algae harvesting efficiency after five times reactivation, as shown in Fig. 2. Ultrasonic treatment effectively reactivated MNPs and maintained their algae harvesting capacity above 50% (Fig. 2a), though MNPs gradually lost the adsorption capacities and the harvesting efficiency decreased with the increasing reactivation times. After 5 times reactivation, the algae harvesting efficiency was 63.10%, 71.20%, 53.00% and 59.11% for *Nannochloropsis*, *Stigeoclonium*, *Synechocystis* and *Microcystis*, respectively. The algal cells were entirely disrupted after ultrasonic chloroform:methanol solvent reactivation [10], explaining the effective reactivation of MNPs. However numerous algal debris or residual extracellular molecules were captured by MNPs, causing less active functional sites on the surface and explaining the declining harvesting capacities. Some previous studies have shown that the zeta potential of MNPs decreased from -10 mV to -20 mV in ultrasonic treatment [10], as the evidence of algal debris adhesion on MNPs. In our previous work, ultrasonic time (2 to 10 minutes) did not affect harvesting efficiency recovery [10] and the results indicated ultrasonic treatment as an efficient reactivation approach for MNPs reuse.

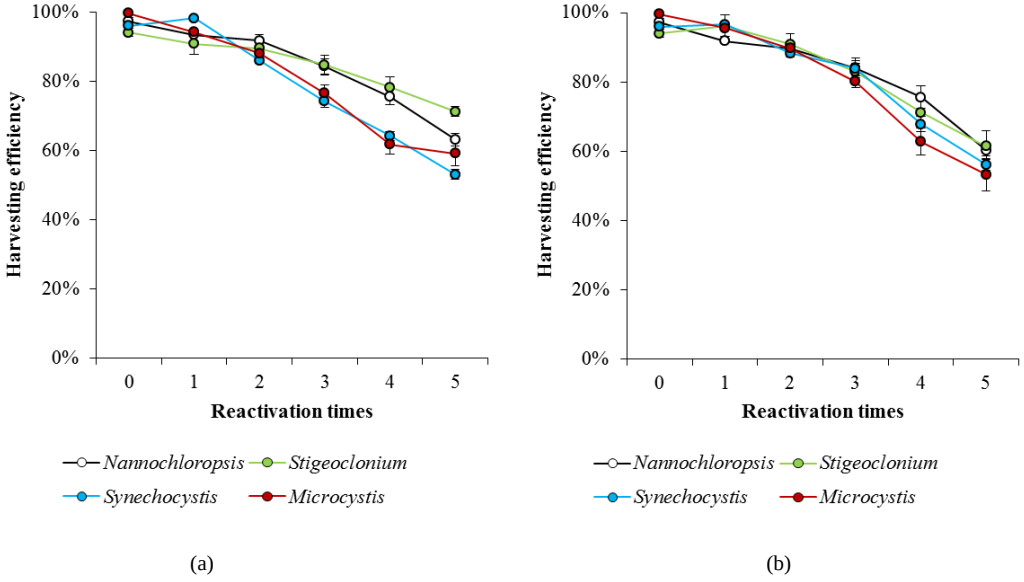

Fig. 2. Magnetic harvesting efficiency of reactivated MNPs for various algal strains. (a) for ultrasonic reactivation and (b) for alkaline reactivation.

Since pH value significantly changed the surface charge of MNPs and algal cells, the electrostatic attraction between MNPs and algae was broken due to the disruption of electrical double layer in alkaline solution [13, 17]. Some attempts therefore applied alkaline treatment to reactivate MNPs [18]. Fig. 2b showed that, similar to ultrasonic reactivation, the harvesting efficiency declined with the increasing reactivation times and it was 60.22%, 61.35%, 56.05% and 53.20% for *Nannochloropsis*, *Stigeoclonium*, *Synechocystis* and *Microcystis* respectively after 5 times reactivation. It was reported that the iron oxide nanoparticles behaved positively charged when pH was neutral or acidic and it therefore increased the electrostatic attraction between MNPs and the negatively charged algal cells [11, 18, 19]. At high pH value, both MNPs and algal cells were negatively charged and the formation of algae-MNPs was attributing to the electrostatic repulsion [13]. There was no significant difference between the harvesting

efficiencies of all the four algal strains in alkaline reactivation, indicating again that the mechanisms of alkaline reactivation was the disruption of electrostatic double layer and electrostatic repulsion, which was consistent for all the different algal cells.

Considering the different operation of ultrasonic and alkaline treatment, the ultrasonic chloroform:methanol solvent treatment was conducted at neutral pH (7.0) for only 60 seconds, whereas the alkaline reactivation took more than 600 seconds at alkaline pH (11.0). Though both methods could effectively reactivate MNPs, they were suitable in different situations. Ultrasonic treatment broke the algal cells and in the hydrophobic solvent, which was the routine biomass treatment and could be directly used for downstream industrial algal biomass production. Though alkaline treatment required longer reactivation time, it was able to be used in larger scale due to its easy operation by adding alkaline liquid. Meanwhile, the reactivation performance was comparable to previous reactivation for other algal strains via alkaline treatment [11, 20]. Compared to other magnetic harvesting with surface-modified MNPs, the reactivation operation maintained the harvesting efficiency of naked MNPs and significantly reduced the actual dosage of MNPs in algae harvesting, from about 0.08-3.1 kg DCW/kg MNPs to 0.24-15.50 kg DCW/kg MNPs. Thus, naked MNPs had great potential as low-cost and sustainable reagent in bioenergy industry.

3.3. Cost-effectiveness analysis on algae harvesting

Though many surface functionalization methods used micro- and macro-molecules to modify MNPs surface and improve the magnetic harvesting efficiency, the present study proved that naked MNPs also had good algae harvesting performance, and they were easier to be reactivated for further reduce the applicable cost. Thus, both naked and surface-modified MNPs had good performance in magnetic harvesting algae, but their cost-effectiveness in industrial application needed further analysis to evaluate their feasibility in practice.

The cost of ferric and ferrous salts ranged from £60 to £120 per kg MNPs for different synthesis methods, except that the MNPs were directly purchased from suppliers and the price was £340/kg MNPs [20]. The cost in synthesis procedure varied from £40 to £80 per kg MNPs, including microwave, heat or alkaline decomposition. During the reactivation process, ultrasonic treatment cost £1.0 to £2.0 for each 1 kg MNPs and the chloroform:methanol solvent was about £2.50 for 1 kg DCW. For alkaline reactivation, the NaOH concentration was 0.1 M and the estimated cost was £2.72 for 1 kg DCW.

Table 1. Economic analysis of algae magnetic harvesting with different magnetic materials.

MNPs	Algal strain	Surface modification	Capacity (g DCW/g)	Reactivation	Total cost (/kg DCW)	Reference
Iron oxide magnetic microparticles	*C. vulgaris*	-	0.4	Ultrasound[2]	£89.3	[18]
Fe_3O_4 and β-FeOOH nanorods	*M. aeruginosa*	-	3.74	Ultrasound[3]	£7.0	[10]
Fe_3O_4 powder (<5 μm)	*Chlorella sp. KR-1*	-	0.08	Alkaline/acid[4]	£4,250	[20]
Fe_3O_4		-	10.05	-	£13.0	[21]
Fe_3O_4	*B. braunii, C. ellipsoidea*	-	5.83-55.90	Solvent[3]	£0.5-4.3	[11]
Fe_3O_4	*B. braunii, C. ellipsoidea*	Polyacrylamide (CPAM)	21.40-114.80	-	£10.3-55.0	[9]
Fe_3O_4	*Chlorella sp.* KR-1	Chitosan	0.3-1.0	-	£8.9-185.7	[22]
Fe_3O_4	*Chlorella sp.*	Chitosan	~1.0	-	~44.8	[23]
Fe_3O_4, β-FeOOH and Fe_2O_4	*Synechocystis, Stigeoclonium, Nannochloropsis, Microcystis*	-	0.24-15.50	Ultrasound or alkaline[3]	£1.7-108.0	This study

[1]: Directly purchased from Sigma Aldrich; [2]: reactivation mentioned; [3]: 5 reactivations; [4]: 10 reactivations.

Table 1 listed the estimated cost of different magnetic harvesting materials and methods. This cost-effectiveness analysis revealed that the costs of all the surface modified MNPs ranged from £8.9 to £185.7 per kg DCW [9, 22, 23], which seemed expensive for engineering application. Besides, surface modification also led to the problems of low reactivation efficiency for reuse [24], causing large amount of MNPs wastes after algae harvesting. By applying naked MNPs harvesting, the total cost was significantly lower as about £3-500 per kg DCW. Further reactivated by ultrasonic/alkaline treatment, the harvesting cost could be further reduced to £0.5-108.0 per kg DCW [10, 11], much lower than surface modified MNPs with bright industrial potentials. However, considering the different heat content between crude oil ((45-47) $\times 10^6$J/kg) and algal biomass ((10-18) $\times 10^6$J/kg), the price of commercial crude oil is calculated as £3.7-16.3/10^9J (£20-90/barrel crude oil in the last ten years), which is equivalent to £0.037-0.293/kg DCW biomass and much lower than the current cost of magnetic harvesting in our cost-effective analysis. In the present study, all the costs were estimated based on the price list in Sigma Aldrich, which were much higher than the prices of used chemicals of commercial grades. The results indicated that the actual cost of applying MNPs in algae harvesting were overestimated but also hinted a significant gap between current magnetic algae harvesting and further application.

4. Conclusion

This research evaluated the impacts of MNPs synthesis and reactivation on algae harvesting, and applied cost-effectiveness analysis of magnetic algae harvesting. In our study, the naked MNPs achieved high algae harvesting capacity, ranging from 0.24 to 15.50 kg DCW/kg MNPs for different strains, similar to other MNPs in previous report. Different synthesis methods significantly affected harvesting efficiency, and higher ferric proportion contributed to higher algae harvesting performance. The cost-effectiveness analysis revealed that surface modified MNPs had high algae harvesting efficiency, but high unit harvesting cost due to the expensive polymers for surface modification. Either ultrasonic or alkaline treatment could effectively reactivate MNPs and they had similar reactivation cost. MNPs reactivation significantly reduced the materials consumption and the unit algae harvesting cost, proving itself as a promising method for industrial application. More research is suggested to keep on investigating cheaper methods for MNPs synthesis and possible cost-effective MNPs reactivation to further reduce algae harvesting cost and achieve sustainable algal biomass production for industrial purposes.

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References

[1] L. Christenson, R. Sims, *Biotechnol. Adv.*, 29 (2011) 686-702.
[2] E.M. Grima, E.H. Belarbi, F.G.A. Fernandez, A.R. Medina, Y. Chisti, *Biotechnol. Adv.*, 20 (2003) 491-515.
[3] N. Rossignol, L. Vandanjon, P. Jaouen, F. Quemeneur, *Aquac. Eng.*, 20 (1999) 191-208.
[4] X. Zhang, Q. Hu, M. Sommerfeld, E. Puruhito, Y. Chen, *Bioresour. Technol.*, 101 (2010) 5297-5304.
[5] J.A. Gerde, L. Yao, J. Lio, Z. Wen, T. Wang, *Algal Res.*, 3 (2014) 30-35.
[6] C.-Y. Chen, K.-L. Yeh, R. Aisyah, D.-J. Lee, J.-S. Chang, *Bioresour. Technol.*, 102 (2011) 71-81.
[7] R.F. Fakhrullin, L.V. Shlykova, A.I. Zamaleeva, D.K. Nurgaliev, Y.N. Osin, J. Garcia-Alonso, V.N. Paunov, *Macromol. Biosci.*, 10 (2010) 1257-1264.
[8] D. Zhang, J.P. Berry, D. Zhu, Y. Wang, Y. Chen, B. Jiang, S. Huang, H. Langford, G. Li, P.A. Davison, J. Xu, E. Aries, W.E. Huang, *ISME J.*, 9 (2015) 603-614.
[9] S.-K. Wang, F. Wang, Y.-R. Hu, A.R. Stiles, C. Guo, C.-Z. Liu, *ACS Appl. Mater. Interfaces*, 6 (2014) 109-115.
[10] Z. Lin, Y. Xu, Z. Zhen, Y. Fu, Y. Liu, W. Li, C. Luo, A. Ding, D. Zhang, *Bioresour. Technol.*, 190 (2015) 82-88.
[11] L. Xu, C. Guo, F. Wang, S. Zheng, C.-Z. Liu, *Bioresour. Technol.*, 102 (2011) 10047-10051.
[12] Y.-R. Hu, C. Guo, X. Ling, F. Wang, S.-K. Wang, Z. Hu, C.-Z. Liu, *Bioresour. Technol.*, 158 (2014) 388-391.
[13] Y.-R. Hu, C. Guo, F. Wang, S.-K. Wang, F. Pan, C.-Z. Liu, *Chem. Eng. J.*, 242 (2014) 341-347.
[14] M. Cerff, M. Morweiser, R. Dillschneider, A. Michel, K. Menzel, C. Posten, *Bioresour. Technol.*, 118 (2012) 289-295.
[15] D. Zhang, R.F. Fakhrullin, M. Özmen, H. Wang, J. Wang, V.N. Paunov, G. Li, W.E. Huang, *Microbial Biotech.*, 4 (2011) 89-97.
[16] M.J. Higgins, J.E. Sader, P. Mulvaney, R. Wetherbee, *J. Phycol.*, 39 (2003) 722-734.
[17] G. Prochazkova, N. Podolova, I. Safarik, V. Zachleder, T. Branyik, *Colloids and Surfaces B-Biointerfaces*, 112 (2013) 213-218.

[18] G. Prochazkova, I. Safarik, T. Branyik, *Bioresour. Technol.*, 130 (2013) 472-477.
[19] F. Qu, H. Liang, Z. Wang, H. Wang, H. Yu, G. Li, *Water Res.*, 46 (2012) 1490-1500.
[20] K. Lee, S.Y. Lee, R. Praveenkumar, B. Kim, J.Y. Seo, S.G. Jeon, J.-G. Na, J.-Y. Park, D.-M. Kim, Y.-K. Oh, *Bioresour. Technol.*, 167 (2014) 284-290.
[21] Y.-R. Hu, F. Wang, S.-K. Wang, C.-Z. Liu, C. Guo, *Bioresour. Technol.*, 138 (2013) 387-390.
[22] K. Lee, S.Y. Lee, J.-G. Na, S.G. Jeon, R. Praveenkumar, D.-M. Kim, W.-S. Chang, Y.-K. Oh, *Bioresour. Technol.*, 149 (2013) 575-578.
[23] P.Y. Toh, B.W. Ng, C.H. Chong, A.L. Ahmad, J.-W. Yang, C.J.C. Derek, J. Lim, *RSC Adv.*, 4 (2014) 4114-4121.
[24] S.-K. Wang, A.R. Stiles, C. Guo, C.-Z. Liu, *Algal Res.*, 9 (2015) 178-185.