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Review

Current progress and future prospect of microalgal biomass harvest using various flocculation technologies

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HIGHLIGHTS

- Approaches of various bio-based flocculation methods are comprehensively summarized.
- Possible underlying mechanisms of bio-based flocculation are discussed.
- Prospect of genetic engineering of microalgae for self-flocculation is proposed.

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ABSTRACT

Microalgae have been extensively studied for the production of various valuable products. Application of microalgae for the production of renewable energy has also received increasing attention in recent years. However, high cost of microalgal biomass harvesting is one of the bottlenecks for commercialization of microalgae-based industrial processes. Considering harvesting efficiency, operation economics and technological feasibility, flocculation is a superior method to harvest microalgae from mass culture. In this article, the latest progress of various microalgal cell harvesting methods via flocculation is reviewed with the emphasis on the current progress and prospect in environmentally friendly bio-based flocculation. Harvesting microalgae through bio-based flocculation is a promising component of the low-cost microalgal biomass production technology.

1. Introduction

Development of alternative fuels and clean energy is becoming imperative with the concern of dwindling reserve of fossil fuels, the increasing global demand of energy, and the chronically high levels of greenhouse gas (especially CO_2) emissions which have serious impacts on global environment. Biofuels from microalgae biomass have been extensively studied recently (Georgianna and Mayfield, 2012), and the capability of microalgae to grow in wastewater or seawater leads to a significant reduction of usage of arable land and freshwater. In addition, photoautotrophic microalgae can grow 10–50 times faster than terrestrial plants, and thus can achieve a higher carbon dioxide fixation rate (Chisti, 2007; Wijffels and Barbosa, 2010). On the other hand, microalgal biomass has also been identified as competent feedstock for the extraction of various valuable products including triacylglycerol (TAG), bioalcohols (e.g., ethanol and butanol), polyunsaturated fatty acids (e.g., eicosapentaenoic acid, EPA, and docosahexaenoic acid, DHA), and pigments (e.g., lutein and chlorophyll). The biosynthesis potential of microalgae has enabled the production of biofuels, food additives, fine chemicals and nutrient supplements through biorefinery (Harun et al., 2010).

One of the bottlenecks for commercialization of microalgae-based industrial processes is the high energy input for the production and recovery of microalgal biomass. The difficulty in microalgae biomass harvesting lies in the highly dilute culture with a cell density of lower than 1.0 g L^{-1} in cost-effective open pond cultivation systems (Huerlimann et al., 2010). As a result, a huge volume

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of water has to be removed during microalgae harvesting process. Furthermore, the small size of microalgal cells at 2–20 μm and their colloidal stability of suspension in culture medium make harvesting process more difficult. High cost involved in harvesting process accounts for about 20–30% or even higher total production cost (Grima et al., 2003). Consequently, effective microalgae cell harvesting with minimal instrument investment and energy consumption is of great significance to reduce the overall production cost in microalgae industry (Grima et al., 2003; Milledge and Heaven, 2012; Schlesinger et al., 2012).

Nowadays, various technologies have been developed for microalgae harvesting, including centrifugation, filtration, flotation, and flocculation (Chen et al., 2011; Uduman et al., 2010). Although centrifugation is used for harvesting microalgae to yield high-value products, it is far more expensive and energy intensive in harvesting microalgae for the production of bulk products such as biofuels (Uduman et al., 2010). From the viewpoint of engineering, filtration is cost-effective, but its productivity is too low to separate microalgal cells from the bulk culture (Chen et al., 2011). Bubble flotation that was developed initially in chemical and metallurgical industries for extracting chemicals or minerals from slurry is notoriously instable and not efficient when applied for microalgae biomass recovery (Uduman et al., 2010).

Cell flocculation has been widely employed as a simple and cheap method to harvest yeast biomass from the fermentation broth (Bauer et al., 2010). The genetic basis of yeast flocculation and its control have been extensively studied (Zhao et al., 2012; Li et al., 2012). Using cell flocculation technology to recover microalgal biomass has also been of great interest (Alam et al., 2014; Guo et al., 2013b; Salim et al., 2014; Wan et al., 2013). A variety of flocculation strategies, such as physical, chemical and biological methods, have been developed for microalgae harvesting as summarized in a recent review by Vandamme et al. (2013). It was estimated that the energy and cost involved in microalgae harvesting can be reduced significantly when flocculation is applied for the pre-concentration of microalgal biomass (Brentner et al., 2011). For instance, more than 95% of the energy required for harvesting microalgae by centrifugation can be saved by employing chitosan-based flocculation as a pre-concentration step (Xu et al., 2013), while energy consumption in harvesting target microalgae can change from 13.8 MJ kg^{-1} dry cell weight (DCW) when using centrifugation to 13.4 MJ kg^{-1} DCW if bioflocculation is applied before centrifugation (Salim et al., 2012). Moreover, due to the capacity for treating a large amount of microalgal biomass, flocculation with aggregation of microalgal cells for easily separation from medium by gravity sedimentation has been considered to be a better method for microalgae harvesting when compared with other conventional methods (e.g., centrifugation and filtration) (Milledge and Heaven, 2012; Uduman et al., 2010). Flocculation can also be used to combine with other harvesting methods to concentrate a large volume of dilute microalgae culture.

Flocculation has been studied as a promising method to harvest microalgae with low cost, and various novel flocculation technologies have been developed. However, there are still a lot of challenges in microalgae biomass harvesting using efficient and cost-effective flocculating technologies. In this article, the recent advances in flocculation technology are reviewed with especial emphasis on the application of bio-based flocculation for cost-effective harvesting of microalgae biomass.

2. Flocculation methods for microalgae harvesting

Flocculation for microalgae harvesting was mainly performed using chemical flocculation, physical flocculation and bio-based flocculation. Flocculation can also occur spontaneously when pH in the solution is increased to a certain high level (Brady et al., 2014), which is termed as autoflocculation. Similarly, flocculation can be achieved by adjusting pH in the culture medium, which is discussed in the section of chemical flocculation. This article provides a comprehensive review on various flocculation technologies with critical discussions on their advantages and drawbacks.

2.1. Chemical flocculation

In general, chemical flocculation in microalgae can be induced by three main types of flocculants, namely, inorganic flocculants (including metal salts, ammonia, etc.), inorganic polymers, and organic polymers. Literature shows examples of successful applications of using chemical flocculation in harvesting the cells of various microalgae species, such as *Scenedesmus* sp. (Chen et al., 2013), *Chlorella* sp. (Papazi et al., 2009), *Nannochloropsis* sp. (Rwehumbiza et al., 2012), *Neochloris* sp. (Beach et al., 2012), and *Phaeodactylum* sp. (Zheng et al., 2012). The overview of various chemical flocculants in recent years with their advantages and disadvantages is presented in Table 1.

The remarkable high flocculation efficiency and technological convenience in microalgae harvesting have made chemical flocculants feasible for bulk microalgae biomass production. Nevertheless, the persistence of inorganic or organic pollutants resulting from the addition of chemical flocculants could cause secondary pollution, and the residual chemical flocculants (e.g., aluminum) in microalgal biomass may interfere with the use of biomass in food and animal feed. The residual aluminum affects composition of fatty acids methyl esters (FAMEs), and it also exists in the lipids extracted from the harvested microalgae (Rwehumbiza et al., 2012). Aluminum salts (e.g., $AlCl_3$ and $Al_2(SO_4)_3$) could cause cell damage, whereas ferric salts (e.g., $FeCl_3$ and $Fe_2(SO_4)_3$) influenced the quality of pigments in microalgae, especially chlorophyll (Papazi et al., 2009). Polyaluminum chloride (PAC) presented in the harvested microalgal biomass could significantly inhibit the enzymatic and chemical transesterification (Tran et al., 2013). In contrast, harvesting microalgae via aqueous ammonia rarely affected the distribution of algae metabolite contents, such as chlorophyll, protein, and lipid (Chen et al., 2012). Chitosan could benefit downstream dewatering processes (e.g., centrifugation and filtration) by saving time and cost (Xu et al., 2013). Little influence on the biodiesel conversion was observed using chitosan (Tran et al., 2013). In addition, despite the characteristics of organic flocculants in being safe and biodegradable, the application of several chemical flocculants like chitosan, and cationic starch for microalgae harvesting is restricted due to their pH dependence (Farid et al., 2013; Letelier-Gordo et al., 2014). Moreover, high ionic strengths demanded in the flocculating process may make seed flour and γ-PGA suboptimal in marine microalgae harvesting. In addition, it should be noted that addition of organic polymers is more expensive when compared with inorganic flocculants. Therefore, flocculation induced by pH adjustment using prevalent alkaline or acid has lightened and expanded the microalgae harvesting methods.

The fact that microalgal cells are capable of forming stable suspension due to the negative charged surface has made the flocculation via pH adjustment feasible, since changed H^+/OH^- ratio and Mg^{2+} presented in the medium can disrupt the electrostatic interactions between anionic algae (Brady et al., 2014). Moreover, the absence of chemical flocculants during flocculating process can strongly eliminate the risk of chemical contamination and secondary pollution. Recently, many microalgae species were successfully harvested via pH-induced flocculation without adding any chemical flocculants. More specifically, 95% cells flocculation efficiency was achieved when the culture medium of *Nannochloropsis* sp. (10^7 cells mL^{-1}) in late exponential phase was adjusted to pH