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Review

Recent nanoparticle engineering advances in microalgal cultivation and harvesting processes of biodiesel production: A review

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HIGHLIGHTS

- Efficiency and cost of algal cultivation and harvest processes are key issues.
- Nanoparticle engineering has been extensively applied as a practical tool.
- Recent achievements using nanoparticle engineering are presented and discussed.

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ABSTRACT

Among the various steps entailed in the production of biodiesel from microalgae, the efficiency and cost-reduction of the cultivation and harvesting steps remain key obstacles to its practical commercialization. Recently, in order to overcome the technical bottlenecks and limitations with regard to both steps, nanoparticle engineering based on particles' unique physico-chemical and mechanical properties has been extensively applied as a powerful analytical and practical tool. These applications include the enhancement of cell growth and/or pigments by light back-scattering, the induction of intracellular lipid accumulation by nutritional competition and/or stress environment, the improvement of cell separation efficiency and processing time from culture broth, the multiple reuse of magnetic nanoparticle flocculant, and integrated one-pot harvesting/cell-disruption. This review presents and discusses the recent nanoparticle-engineering-based developments in the implementation of practical microalgal cultivation and harvesting processes.

1. Introduction

Microalgae-based biorefinement has received a tremendous amount of research attention as the principal cellular components, such as carbohydrate, protein, lipid, and pigment, have been effectively exploited for industrial applications (Kim et al., 2013a; Wijffels and Barbosa, 2010). Among the microalgal components, large-scale lipid (oil) utilization has been the primary focus recently in both the academic and industrial fields. Certainly, many engineers and scientists, in light of the rapid depletion of fossil-fuel reserves, rising energy demand and the greenhouse gas issue, consider microalgal lipid one of most desirable alternative biodiesel-production feedstocks (Scott et al., 2010; Praveenkumar et al., 2014a).

Microalgae have various advantages over conventional oil crops such as soybeans, rapeseed and sunflowers, based on high photosynthetic efficiency/productivity and high lipid content, tendency to grow irrespective of soil fertility, and ability to utilize wastewater nutrients and/or grow using non-potable water (Farooq et al., 2013a; Praveenkumar et al., 2014a; Rashid et al., 2014). Crucially, these microalgal properties allow for the utilization of untapped cultivation sites such as barren land, coastal areas, wastewater-treatment plant areas and others, and thereby ensure that there is no competition with agricultural crops for scarce existing lands. Such utilization, for example, avoids the ethical dilemmas that arise in the production of biodiesel from edible oils in poor countries (Pragya et al., 2013; Lee et al., 2013a).

Microalgal biodiesel production is a sequential process that consists of cultivation, harvesting, oil extraction, and biofuel conversion. Notwithstanding the extensive research of the last few decades, the efficiency and cost-reduction of microalgal biodiesel production remain as key obstacles to its optimal commercialization (price target: <USD \$2/kg of biodiesel) (Jones and Mayfield, 2012; Kim et al., 2013a). Among the four production steps, cultivation (>40% of total cost) is the single most expensive (Kim et al., 2013a). Industrial-scale cultivation that maintains a higher

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microalgal lipid productivity for native and/or genetically-engineered microalgae is difficult to achieve (Pattarkine and Pattarkine, 2012). What is problematic for the outdoor mass-cultivation of oleaginous microalgae, meanwhile, is the issue of contamination by foreign bacteria and fungi (Cho et al., 2013; Scott et al., 2010). As for microalgae harvesting, the cost is estimated to be high as 20–30% of the total biodiesel production cost, though it varies according to the type of harvesting method, the density of microalgal culture, and the microalgal species (Kim et al., 2013a; Mata et al., 2010; Rashid et al., 2014). No universal technology for economic harvesting of microalgal biomass for biodiesel production has yet been developed. With respect to each of these four steps, the common requirement is low-cost and low-energy technology that would render the entire microalgal biodiesel production process both efficient and sustainable. Recently, integrated approaches that overcome the technological-economic limitations of the current microalgal biodiesel production process, such as simultaneous harvesting/cell-disruption using nanoparticles (Lee et al., 2014b) and direct transesterification of microalgal oil to biodiesel (Hidalgo et al., 2013), have been reported.

Nanoparticle engineering is a concept covering the development and application of artificially synthesized and decorated nanoparticles on the nanometer scale (Lopez-Serrano et al., 2014). Nanoparticles offer, additionally to an extraordinarily larger surface area, unique physico-chemical and mechanical properties such as reactivity, tenacity, elasticity, strength and electricity, which differ from those of their bulk material (Zhang et al., 2013). Engineered nanoparticles therefore have been applied in a wide range of fields including crop production, cosmetics, drug delivery, photonic crystals, analysis, food, coatings, paints, bioremediation, catalysis, and materials science (Caruso, 2001; Husen and Siddiqi, 2014; Lopez-Serrano et al., 2014). Nanoparticle engineering, a relatively new field, provides very intriguing potential solutions to many of the challenges faced in each of the microalgal biodiesel production process steps. In order to improve, for example, biodiesel conversion yields and resultant fuel quality, various heterogeneous nanocatalysts have been extensively studied and covered in detail in recent review articles and book chapters (Pattarkine and Pattarkine, 2012; Pugh et al., 2011; Sani et al., 2013; Zhang et al., 2013). However, little in the way of review is available on the microalgal cultivation and harvesting processes involved in various nanoparticle engineering approaches such as light back-scattering (Eroglu et al., 2013), micronutrient supplementation (Kadar et al., 2012), lipid synthesis inducement (Kang et al., 2014), magnetic separation (Lee et al., 2014a), and natural and artificial nanoparticle flocculation (Farid et al., 2013; Lee et al., 2013c).

The purpose of this review was to update the recent developments on microalgal cultivation and harvesting processes from the nanoparticle engineering perspective. The major issues, as well as the efforts to deal with them via nanoparticle engineering approaches, are covered. We also discuss the future influences and implications of nanoparticle engineering with respect to the academic-research and industrial applications of microalgal biodiesel production.

2. Microalgal cultivation using nanoparticles

2.1. Background

Cultivation, among the four microalgal biodiesel production steps, is the most cost-burdensome (Kim et al., 2013a). The priorities to be addressed for this step are the increase of microalgal biomass productivity per ground area without competitive growth against foreign bacteria and fungi contaminations (Wijffels and Barbosa, 2010), the enhancement of intracellular oil accumulation in microalgae (Kang et al., 2014), and the maintenance of a stable microalgal culture in terms of the microbial community of microalgae and co-existing bacteria (Praveenkumar et al., 2014b). Isolation of novel microalgal species from their natural environments and their genetic engineering are options for improving the efficiency and yield of microalgal biodiesel production (Mata et al., 2010). Several closed photobioreactor and open-pond designs for cultivation of microalgae currently are being trialed, though these still suffer from one or more limitations in terms of gas transfer, mixing, light supply, and productivity (Pattarkine and Pattarkine, 2012; Wijffels and Barbosa, 2010). To enhance oil containment in cells, various approaches such as nitrogen deprivation (Farooq et al., 2013b), co-cultivation of antimicrobial agents (Kim et al., 2013b), and salt stress (Takagi et al., 2006) have been reported. Unique nanoparticles also have been applied in both indirect and direct modes in order to stimulate photosynthetic cell growth and/or induce intracellular accumulation of lipid under stressed conditions without killing cells (Table 1).

2.2. Indirect use of nanoparticles for photobioreactor cultivation

High nanoparticle concentrations in microalgal solutions can hinder the effective transfer of light into microalgal cells. In efforts to avoid this problem, indirect use of metal nanoparticles coupled to localized surface plasmon resonances (LSPR) placed outside of closed photobioreactors has been applied. Plasmons represent the collective oscillations of the free electrons at a metal-dielectric interface. Light adsorption and scattering at specific wavelengths can be amplified by resonant interactions between light (photons) and surface plasmons (Pattarkine and Pattarkine, 2012). Torkamani et al. (2010) reported significant increases (>30% versus control) of cell growth for *Chlamydomonas reinhardtii* and *Cyanothece* 51142 by strong backscattering of blue light from a suspension of silver nanoparticles. Eroglu et al. (2013) cultivated *Chlorella vulgaris* by placing spheroidal silver nanoparticles and gold nanorods alone or in combinations around photobioreactors; comparing this approach with the no-nanoparticle-positioning condition, they reported a significant increase in the accumulation of both chlorophyll and carotenoid pigments, which resulted in increased light uptake by microalgal cells. Furthermore, the nanoparticle suspensions could be effectively recycled for more than 5 cycles without any toxicological or contamination issues. Notably too, wavelength and light flux also can be controlled by the concentration and size of the nanoparticles, which can help to avoid photo-inhibition and stimulate specific microalgal species with different photopigments.

2.3. Direct use of nanoparticles as micronutrient supplement and lipid inducer

Nanoparticles have been added to culture media to supplement nutritional minerals (such as iron (Fe) and magnesium (Mg)) necessary for photosynthetic microalgal cells. Iron also has been reported to enhance lipid accumulation for marine microalga *C. vulgaris* (Liu et al., 2008). Kadar et al. (2012) compared conventional soluble iron (chelated with ethylenediaminetetraacetic acid (EDTA)) and synthetic nanoscale zero-valent iron (nZVI) nanoparticles for cultivation of three marine microalgae (*Pavlova lutheri*, *Isochrysis galbana* and *Tetraselmis suecica*). They reported normal growth at a standard growth rate for all three strains in the presence of nZVI. Interestingly, the lipid contents of *P. lutheri* and *T. suecica* were enhanced as compared with microalgae grown with Fe-EDTA. Iron nanoparticles such as nZVI can generate various reactive oxygen species (ROS, including singlet oxygen, superoxide, hydrogen peroxide, and hydroxyl radicals) via Fenton-type reactions that cause oxidative stress to microorganisms (Kadar